## The Synthesis, Characterization, and Reactivity of Some Ir(III) Dicationic Complexes

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Dissertation submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

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October, 1998 Blacksburg, Virginia

# The Synthesis, Characterization, and Reactivity of some Ir(III) Dicationic Complexes

By

Marion A. Franks Joseph S. Merola, Committee Chairman Department of Chemistry (ABSTRACT)

The complex [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl was prepared by the reaction between [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl and HCl gas in methylene chloride. The product precipitated from the solution and is soluble in polar solvents such as water, acetonitrile, and acetone. [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl undergoes reaction in water to form fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. Also, other [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][X]<sub>2</sub> salts were prepared with X being PF<sub>6</sub>, OTF, or BF<sub>4</sub>. It was determined that each salt retained a certain amount of excess acids and [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][OTF]•HOTf was the most stable in the solvent acetonitrile while [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> showed signs of reaction in acetonitrile after 4 hours. The dicationic salts were also reductively deprotonated by DMSO to form the Ir(I) starting material. Finally a slow equilibrium was noted for [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> in water by the observation of the reductive deprotonation product.

The grignard reaction was employed to synthesize  $Ir(CH_3)_3(PMe_3)_3$ . IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> reacts with methyl grignard in THF/Benzene to form fac-Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. Only the facial isomer of this reaction was observed and the product was soluble in nonpolar solvents. Acidolysis was utilized to synthesize facIrCH<sub>3</sub>Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>.3</sub> from the reaction between Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> and 2 equivalents of HCl. Ir(III) methyl dications have also been synthesized by the reaction of 2 equivalents triflic acids with fac-Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. The product of the reaction, mer-IrCH<sub>3</sub>(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was used to study the insertion of alkynes into the Iridium methyl bond.

IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was synthesized by the careful acidolysis of IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub> using 1 equivalent of HCl. IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was also synthesized by the metathesis of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> with 2.04 equivalents of silver triflate. The product of that reaction, IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>, has been used to form dimers and trimers of styrene via catalysis and to isomerize alkene alcohols to aldehydes. IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was also used as a polymerization initiator for vinyl and allyl ethers.

This dissertation is dedicated to my mother for all of the love, encouragement, and support that she has shown me even though it wasn't always easy. To my brother Maceo for always encouraging me and being there for me, whatever the circumstance. Most importantly to my Lord and Savior Jesus Christ for loving, forgiving, and saving me when no one else could.

### Acknowledgments

I would like to thank Dr. Joe Merola for all of his efforts, patience, and understanding. I am thankful that he took me in at a time when I was "green" and he gave me the chance to experience organometallic chemistry. I would also like to thank the other members of my committee for their support. I am especially thankful to Dr. Brewer for giving me the opportunity to try my synthetic "hand" with other metals besides iridium. I would like to thank Dr. Tanko and Dr. Anderson for their permanent open doors and invitations to play softball and the annual NCAA pool. I would like to thank Dr. Deck and Dr. Hanson for "dropping the hammer" in divisional meetings and for always being available and willing to help me at all times. I would also like to especially thank Dr. Calter for pinch-hitting in my dissertation defense. I would like to thank Dr. McGrath, Dr. Ward, and the NSF Center of Va Tech who were responsible for my being here in the first place.

I would like to thank each Merola group member that has helped me along the way. I would like to thank Rob "the Pharaoh" Pafford, Robert "Otis" Clark, and Art Grieb for showing me the ins and outs of working with iridium. I would like to thank Dr. Chris Roy for telling me how to get the synthetic "hands". I would like to thank Lisa Huff for teaching me about those things you just can't learn in lab. I would like to especially thank Paul "Baby Doc" Chirik and Shannon "Mama Duck". Rice for being superfriends in and out of the lab. I also want to thank Tina Peace for reminding me of me sometimes. Special thanks to Jeff Clark and Woody Jackson for stopping by and reminding me that there is more than organometallic chemistry under the sun. Finally I would like to acknowledge the great help I received from Bill, Geno, and Tom of Analytical Services.

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### **New Complexes**





(1)

(2)







(5)







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(7)

(8)





(10)





(11)

(12)





(13)



(15)

(16)









(21)







(23)





(24b)



(25)



(26)



(27)



## Chapter 1. Literature Review: Aqueous Organometallic Chemistry

#### 1.1 Water: The Abundant Solvent.

Water is by far the most important and useful compound known to man. Water makes up about 75% of the earth's surface and about 65% of the human body .<sup>1</sup> Therefore, for millions of years, water has been the solvent of life. It has been essential in many biochemical processes and it turns out that water is crucial to man's everyday existence. Even though water has been so instrumental in everyday life, the development of organic chemistry, especially organometallic chemistry has avoided water as a solvent.

Water has some intriguing chemical properties. Water is not flammable and it has a high boiling point (100 °C) compared to other compounds with hydroxy functionality. The boiling point is important because as a solvent, water can reach higher temperature than other hydroxy compounds. If used in a reactor, the heat produced can be transferred from that reaction to other parts of the chemical plant. Water also has the highest value of specific heat of all substances.<sup>1</sup> Therefore, rapid changes in ambient temperature result in slow changes in water temperature. This property would be useful for controlling the temperature in endo and exothermic reactions when water is the solvent. Water is also polar, which may be useful in the solvation of many compounds. Water's polarity coupled with its high dielectric constant (80.20 @ 20°C) make it an excellent choice as a solvent.

Another interesting property of water is its ability to undergo ionic selfdissociation.

 $2 H_2 O = H_3 O^+ + OH$ 

Figure 1.1 Autoionization of Water

According to Bronsted theory of acids and bases, water could act as both an acid or a base. According to Lewis theory, water acts as a Lewis base. It is possible for water to donate its lone pair of electrons to various Lewis Acids to form a Lewis acid base pair.

Water has several different properties as a ligand in transition metal complexes. Due to the fact that water usually binds to transition metals through the lone pair of its oxygen atoms, water has been described as a "hard" ligand. In many of the late metal systems, water has been used as a weakly coordinating ligand, while in the early metals, water tends to bind more strongly. Water is a good -donor ligand with an insignificant tendency toward back bonding. Therefore, high-valence metals tend to form more stable complexes with water.

#### **1.1.2** The use of water in organic synthesis.

There is an increasing interest in the using of water as a solvent in organic reactions. For Instance, water has shown interesting results when used as the solvent for Diels-Alder chemistry.<sup>2</sup>,<sup>3</sup>,<sup>4</sup> For example, Breslow found that the reaction between cyclopentadiene and methyl vinyl ketone was about 700 times faster when used with water as opposed to isooctane.<sup>4</sup> This acceleration of the Diels-Alder reaction was defined as a "hydrophobic effect". <sup>5</sup>,<sup>6</sup> The effect states that hydrophobic interactions brought together two nonpolar groups in the transition state and caused the reaction to be accelerated as compared to instances when nonpolar solvents were used.<sup>5</sup>,<sup>4</sup> A hydrophobic interaction is defined as the association of a relatively nonpolar molecular group in water with other nonpolar molecules.<sup>1</sup>. Furthermore, the interaction is not due to the attraction of the nonpolar groups but is due to the large cohesive energy density of water. The large cohesive energy density causes the polar water molecule surrounding the nonpolar compounds to associate with each other.<sup>1</sup>



Figure 1.2 Diels-Alder Reaction between Cyclopentadiene and 3-Butenone

Solvent	$k_2 X 10^5 (M^{-1} s^{-1})$
Isooctane	$5.94 \pm 0.3$
MeOH	75.5
H <sub>2</sub> O	$4{,}400\pm70$
H <sub>2</sub> O/LiCl (4.86 M)	10,800
$H_2O/C(NH_2)_3^+Cl^-$ (4.86 M)	4,300
H <sub>2</sub> O/ -Cycldextrin (10mM)	10,900
H <sub>2</sub> O/ -Cyclodextrin (10mM)	2,610

#### **Table 1.1**<sup>4</sup>

Rate Constants for Cyclopentadiene Reaction with 3-Butenone in Selected Solvents

The data from Table 1.1 shows that water enhances the rate of the Diels-Alder reaction shown in Figure 1.2. LiCl (4.86 M) also helps to enhance the rate of reaction. Daily has described these acceleration using LiCl as being catalyzed by the Lewis acid present in solution and not via an increase in pressure i.e. the cohensive energy density theory.<sup>6a</sup> In this particular case, the Lewis acid is the Li cation. The results of these water accelerated Diels-Alder reaction suggests that there is validity in the hydrophobic effect.

The Diels-Alder reaction is typically selective for endo addition of the diene to the dienophile. Water has an affect on the stereoselectivity of some Diels-Alder reaction.<sup>7</sup>,<sup>8</sup>

The reaction between cyclopentadiene and butenone gave a 21: 4 ratio of endo/exo product. This ratio was over 5 times more than the same reaction done neat.



Figure 1.4 Reaction between Cyclopentadiene and Butenone Showing the Endo and Exo Products

The stereochemical change was explained by the need to minimize the transition-state surface area in water solution, which favors the more compact endo stereochemistry.<sup>1</sup>

#### **1.2 Water Soluble Complexes with Water Soluble Ligands.**

The majority of literature dealing with water-soluble complexes involves watersoluble phosphine ligands that contain  $SO_3^-$ , COOH, OH, or NH<sub>2</sub> as a moiety of an aromatic or aliphatic functional groups. Much of this research focused on  $SO_3^-$  as the functionality, probably because of its solubility and stability at different pH's. The carboxy and amino substituted phosphines are only soluble in basic and acidic media, respectively. <sup>9</sup>

#### 1.2.1 Biphasic Homogeneous Catalysis Using Water Soluble Phosphines

Biphasic homogeneous catalysis has its beginnings with Manassen's statement:<sup>10</sup> ".... the use of two immiscible liquid phases, one containing the catalyst and the other containing the substrate, must be considered. The two phases can be separated by conventional means and high degrees of dispersion can be obtained through emulsification."

From that statement, a new form of catalysis was born. There have been many different projects that have come about from Mannassen's idea. The most prevalent embodiment of Manassen's concept is the water-soluble phosphine derived catalyst.

One of the most successful water-soluble phosphines used as an ancillary ligand is  $P(m-C_6H_4SO_3[Na])_3$  which is usually called TPPTS. TPPTS is similar to triphenylphosphine, but it has an electron-withdrawing  $SO_3^-$  group on each phenyl ring that decreases the basicity of the phosphorus atom.<sup>11</sup>



Figure 1.5 Structure of TPPTS

#### **1.2.2 Water Soluble Hydroformylation Catalysts.**

Rhone-Poluenc/Ruhrchemie uses TPPTS as the phosphine ligand in a commercial biphasic hydroformylation process.<sup>13</sup> Hydroformylation, also called the oxo process, is the most important commercial process for the production of aldehydes. This process is responsible for the production of 4 million tons of aldehyde each year.<sup>12</sup> It is also responsible for the coproduction of many alcohols, carboxylic acids, and propylene. In the oxo process, an alkene can be converted into an aldehyde by the addition of  $H_2$  and

CO in the presence of a catalyst. The term "hydroformylation" derives its name from the addition of a formyl group and a hydrogen across an olefin.



**Figure 1.6** Basic Scheme Depicting the Hydroformylation of Olefins.

During the process, two isomers are formed as products, the branched product ( or the iso product) and the straight chained product ( or the normal product). Presently, the normal isomer ( or n isomer) is the desired isomer in commercial hydroformylation. As a result, chemoselectivity and regioselectivity are major factors in process development research. Today, there are two major catalysts for large-scale hydroformylation. The first employs a binuclear catalyst precursor  $Co_2(CO)_8$  and the other uses the more popular Wilkinson type RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> system.

In the Rhone-Poulenc/Ruhrchemie process, the reaction reactants are soluble in the aqueous/organic phases whereas, the products are insoluble in the aqueous phase. This process uses the sulfonated analog of Wilkinson's catalyst, RhH(CO)(TPPTS)<sub>3</sub>, to convert propene to butyraldehyde. The Ruhrchemie plant reacts propene with "syn gas" to afford n-butyraldehyde and only 4% yields of isobutyraldehyde. The process is responsible for the production of over 330,000 tons/year of butyraldehyde.<sup>9</sup>



Synthesis of TPPTS

The synthesis of TPPTS is shown in Figure 1.7. Triphenylphosphine is treated with oleum ( 20% solution of  $SO_3$  in  $H_2SO_4$ ) to form the sulfonic acid intermediate. Neutralization with NaOH affords TPPTS. Phosphine oxide byproducts are removed by extraction.<sup>13</sup>

There are other related sulfonated phosphines that have been used extensively.



**Figure 1.8** Other Sulfonated Phosphine Ligands

These complexes are synthesized under conditions similar to those used to make TPPTS.

#### **1.2.3 Water Soluble Hydrogenation Complexes**

Hydrogenation has also been extensively investigated using water-soluble phosphine ligands. Hydrogenation is the process of adding  $H_2$  across multiple bonds such as olefins.

Cat.,  $H_2$ 

Figure 1.9 Catalytic Hydrogenation of Olefins

Manassen reported the biphasic homogeneous hydrogenation of olefins using TPPMS-substituted Rh and Ru catalysts. <sup>14</sup> Manassen added TPPMS to RhCl<sub>3</sub>•3H<sub>2</sub>O intending to obtain a complex analogous to RhCl(PPh<sub>3</sub>)<sub>3</sub>. The complex was dissolved into aqueous solution and was stirred into a cyclohexane solution of cyclohexene in a hydrogen atmosphere.



Figure 1.10 Biphasic Hydrogenation of Cyclohexene

Very little product was obtained from the cyclohexane layer. When the reaction was completed again with the addition of a water-soluble cosolvent (i.e. methanol, ethanol) the reaction rates increased considerably. Manassen concluded that the rate of the hydrogenation is dependent on the solubility of the olefin and also that the reaction does not occur at the water-cyclohexane interface. Wilkinson also used Rh(TPPMS)<sub>3</sub>Cl to hydrogenate 1-hexene and cis and trans 2-hexene. Rh(TPPMS)<sub>3</sub>Cl hydrogenated 1-

hexene in 73% yield at 25 °C. Olefin isomerization products made up 22% of the product. Rh(TPPMS)<sub>3</sub>Cl was more efficient as a catalyst for the hydrogenation of terminal olefins as opposed to internal olefins.

Darensbourg used 1, 3, 5-Triaza-7-phophaadamantane (better know as "PTA") as a water-soluble ligand.<sup>15</sup>



**Figure 1.11** The Structure of 1, 3, 5-Triaza-7-Phosphaadamantane (PTA)

Structurally, PTA is much different from the triphenylphosphine analogs that have already been described. The cone angle for PTA is  $102^{\circ}$ , which is similar to PMe<sub>3</sub>.<sup>16</sup> PTA is also basic, water-soluble, and air stable like PMe<sub>3</sub><sup>17</sup>. The PTA ligand is more likely to bind to transition metals through the phosphine rather than the amines based on reaction of molybdenum complexes with its nitrogen analog tetraazaadamantane.<sup>18</sup> For example, Tyler observed that tetraazaadamantane did not react with  $[(CpCH_2CH_2NH_3^+)Mo(CO)_6][NO_3]_2$  whereas the PTA ligand did.

In an attempt to synthesize an analog of Wilkinson's catalyst, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl, Darensbourg prepared Rh(PTA)<sub>3</sub>Cl as shown below.

RhCl<sub>3</sub> + PTA → RhCl(PTA)<sub>3</sub>

**Figure 1.12** Reaction between PTA and RhCl<sub>3</sub> The complex was used as a catalyst for hydrogenation and for the reduction of aldehydes to alcohols. As a hydrogenation catalyst, Rh(PTA)<sub>3</sub>Cl hydrogenated transcinnamaldehyde to hydrocinnamaldehyde as the major product in 93.9% conversion. Although Rh(PTA)<sub>3</sub>Cl is structurally similar to Wilkinson's catalyst, it did not readily decarbonylate aldehydes. In the hydrogenation of allybenzene the major products formed are the isomerization products (primarily trans-propenylbenzene).



**Figure 1.13** Rh(PTA)<sub>3</sub>Cl catalyzed Hydrogenation of trans-cimmamaldehyde

Darensbourg also isolated  $RuCl_2(PTA)_4$  and  $RuCl_2(PTA)_4 \bullet 2HCl$ . These complexes were are hydrogenation catalysts in the hydrogenation of aldehydes, olefins, and unsaturated aldehydes. <sup>9</sup>, <sup>15</sup>





**Figure 1.14** Structure of Ru-PTA Complexes.

 $RuCl_2(PTA)_4$ •2HCl was synthesized by the addition of hydrochloric acid to  $RuCl_2(PTA)_4$ . The amines of PTA were protonated creating an ammonium salt. The ammonium salt is more water-soluble than the free base and thus served as a catalyst more readily than the  $RuCl_2(PTA)_4$  complex.

One problem with the PTA system is the formation of the corresponding oxide, PTAO. Although there has not been any direct evidence, a mechanism was postulated for the formation of the oxide.



[RhH(PTA)<sub>2</sub>]<sup>+</sup> + PTAO + HCI

Figure 1.15 Proposed Synthesis of PTAO

Figure 1.15 shows the proposed mechanism for the formation of PTAO. The Rh(I) species  $RhCl(PTA)_3$  undergoes a reversible oxidative addition of H<sub>2</sub>O which forms a hexacoordinate Rh(III) complex. The Rh(III) complexes then losses a PTA ligand as PTAO in a reductive fashion along with the reductive elimination of HCl.

Baird used the amphos ligand, shown in 1.16, in the preparation of rhodium complexes. The ligand gains its water solubility from the cationic ammonium group. Baird prepared a water-soluble hydrogenation catalyst, by the reaction of  $[Rh(NBD)Cl]_2$  and 4 equivalents of amphos (NBD=norbornadiene).<sup>19</sup> The reactivity of this catalyst is on the same order as that of the  $[Rh(NBD)(PPh_3)_2]^+$  analog which was first synthesized by Osborn and Shrock.



Figure 1.16 Structure of Amphos

Aqueous solutions of  $[Rh(NBD)(amphos)_2]^+$  catalyze the hydrogenation of water-soluble olefins in single phase systems (water & methanol), and the hydrogenation and hydroformylation of water insoluble olefins in organic solvents.

The amphos complex gave higher reaction rates in methanol than in water. The explanation for this trend is attributed to either higher solubility of hydrogen in methanol or lower stability of the intermediate,  $[RhH_2(amphos)_2(H_2O)_2]^+$ . Although water is a weakly bound ligand, the fact that this particular intermediate can be observed suggests that it may inhibit the catalytic activity of the system. The active catalytic species in the reaction should be  $[RhH_2(amphos)]^+$  which is coordinatively unsaturated. Thus, water could impede incoming substrate and thereby decrease the rate of reactivity. Hanson also investigated hydroformylation with Rh complexes containing amphos as the ligand. <sup>20</sup>

#### 1.2.4 Asymmetric Catalysis Using Water Soluble Complexes

Asymmetric catalysis is an area of vigorous investigation. The chemistry of asymmetric catalysis has not eluded the world of water-soluble catalysis. Sinou prepared asymmetric water-soluble diphosphine complexes of the type  $[Rh(COD)(P-P)]^+ClO_4^-$ .<sup>21</sup> The focus of this research is the ligand 2-[(Diphenylphosphinomethyl]-4-

(Diphenylphosphino)Pyrrolidine. (Figure 1.16) Sinou used this compound to complete the asymmetric hydrogenation of olefins.



Figure 1.16

Structure of 2-[(Diphenylphosphinomethyl]-4-(Diphenylphosphino)Pyrrolidine

Bakos described the asymmetric catalytic hydrogenation of imines in a two phase system using a water-soluble catalyst to give secondary amines with high enantionselectively. <sup>22</sup> Using sulfonate BDPP, he successfully hydrogenated several imines.



X= H, 4-OMe, 3-OMe, 2-OMe

Catalyst=Rh(COD)(BDPP-s)

**Figure 1.17** Asymmetric Hydrogenation of Immines to Secondary Amines.

Using oleum to directly sulfonate BDPP, similar to the TPPTS synthesis, Bakos created a water-soluble asymmetric ligand.



Structure of BDPP

The catalyst [Rh(COD)(BDPP-s)]<sup>+</sup> was quite chemoselective, and it only produced small amounts of primary amines and ketones. Bakos also noted that the catalyst showed highest enantioselectivity in water-ethyl acetate where it gave a 96% yield of the secondary amine with 96% e.e.

#### **1.3** Water Soluble Complexes with Water as a Ligand.

Another class of water-soluble transition metals are those whose water solubility is derived from the fact that there is a direct metal to water interaction. These complexes are called intrinsically water-soluble. Water has been proposed as the coordinating ligand in many mechanisms that describe these solvento complexes as intermediates. Crabtree described a class of complexes with the structure  $[IrH_2(PPh_3)_2(H_2O)_2]^+$ .<sup>23</sup> These complexes react with olefins at low temperatures to produce olefin bound iridium hydride intermediates. These complexes were used to study the mechanism of Crabtree's olefin hydrogenation catalyst. Furthermore,  $[IrH_2(PPh_3)_2(H_2O)_2]^+$  is the catalytic precursor to the active intermediate  $[IrCOD(PPh_3)_2]^+$  which undergoes oxidative addition with H<sub>2</sub>.

Clark synthesized  $[RuH(H_2O)(CO)(PPh_3)_3]BF_4$  from the reaction of  $RuH_2(CO)(PPh_3)_3$  with 1 equivalent of tetrafluoroboric acid in water. This acidolysis yielded a weakly coordinating  $BF_4$  ligand that was easily replaced by water and later by other substrates. Even though this product was not water-soluble, it is an example of a

complex with weakly coordinating ligands that could be replaced by water which is a topic that will be covered later.



Figure 1.19 Water Bound Ru(II) Chemistry

Grubbs observed another intrinsically water-soluble ruthenium complex.  $[Ru(H_2O)_6](tos)_2$  (tos=tosylate) is a complex that was synthesized and is an active ROMP catalyst. <sup>24</sup>, <sup>25</sup>

$$\begin{bmatrix} OH_{2} \\ H_{2}O \\ H_{2}O \\ OH_{2} \end{bmatrix} \begin{bmatrix} H_{3}C \\ H_{3}C \\ OH_{2} \end{bmatrix}_{2}$$

#### Figure 1.20

Structure of Hexaaquoruthenium (II) Tosylate

Grubbs determined that hexaaquoruthenium(II) catalyzes olefin isomerization with allylic alcohols and allylic ethers. (Figure 1.21)



Figure 1.21 Isomerization of Allyl Alcohol using  $[Ru(H_2O)_6]^{2+}$ 

Grubbs observed that allyl alcohol was easily isomerized to propionaldehyde in water at room temperature and that secondary allyl alcohols were converted to ketones. (Figure 1.22)



Figure 1.22 Isomerization of 2 cyclohexenol using [Ru(H<sub>2</sub>O)<sub>6</sub>](tos)<sub>2</sub>

Grubbs elucidated a mechanism for these isomerizations. The mechanism is reversible and it shows the metal complex "walking" the olefin down the chain until it reaches the hydroxy group. At that point, the olefin tautomerizes into the unreactive aldehyde or ketone.

Benyei also examined  $[Ru(H_2O)_6](tos)_2$  as a catalyst for the hydrogenation of olefins and carbonyl compounds.<sup>26</sup> The mechanism of the catalyst action was described

as hydrogen transfer. He described the reaction between  $[Ru(H_2O)_6](TOS)_2$  and several heterocyclic nitrogen donors.



The reaction shown in Figure 1.23 was carried out using several different amines and phosphines and the corresponding catalytic activity of each was measured. The catalytic activity of the  $[Ru(H_2O)_2(sparteine)_2](Tos)_2$  is higher than that of  $[Ru(H_2O)_2(PTA)_3](tos)_2$  but less than that of  $Ru(H_2O)_2(TPPMS)_2(Tos)_2$  for the reduction of benzaldehyde. The results suggests that the presence of added ligands helps to increase the catalytic activity of these systems.



Figure 1.24 Hydrogen Transfer Reduction of Acetophenone

Benyei showed that the hydrogen transfer reduction of acetophenone can be completed using  $[Ru(H_2O)_6](Tos)_2$  in the presence of sparteine and isopropanol.(Figure 1.24) The reactions produced yields up to 72% of the observed product. As expected these reactions are pH dependent and at more basic pH's, the ruthenium complex was reduced to metallic ruthenium. Grubbs also investigated water-soluble ROMP catalysts. <sup>24</sup> From the reaction between  $RuCl_2(PCy_3)_4$  and diphenylcyclopropene, Grubbs synthesized a simple, water-soluble, carbene catalyst.



**Figure 1.25** Grubbs' ROMP Catalyst

Grubbs found that this complex is an active olefin metastasis catalyst and is also an active catalyst for living ROMP.



**Figure 1.26** ROMP of Norbornene using Grubbs' ROMP Catalyst

Espenson described an aqueous catalyst for the Diels-Alder reaction. <sup>27</sup> Methylrhenium trioxide is prepared by the reaction between dirhenium heptoxide and tetramethyl tin. Methylrhenium trioxide (MTO) in 1% catalytic excess produced greater than 99:1 endo to exo product ratio in the reaction of methyl vinyl ketone, and cyclopentadiene.



Figure 1.27 Diels-Alder Reaction of Methylvinylketone and Cyclopentadiene

Just as in the purely organic reactions, water helped increase the endo/exo ratio of the Diels-Alder reaction. Table 1.2 shows that when the reaction is done under aqueous conditions, the endo/exo ratio is 20: 1. Table 1.28 also shows that when 1% MTO is used in the absence of aqueous solution, the endo/exo ratio is 15.4. These results suggests that there is a synergistic effect when using aqueous solution and 1% MTO.

Conditions	endo/exo	t <sub>50</sub> /min
neat	3.15: 1	45
1% MTO	15.4: 1	20
aqueous	20: 1	25
aqueous, 1% MTO	>99: 1	14

#### **Table 1.28**

Endo/Exo Ratios of Catalyzed Diels-Alder reaction

Herrmann has shown that there is a reaction that takes place between MTO and water which could help explain the synergistic effect. <sup>28</sup>, <sup>29</sup>


Figure 1.29 Reaction of MTO and Water

Fish described the structure and reactivity of the water-soluble complex  $[Cp*Rh(H_2O)_3]^{2+}$ . The complex is pH dependent and at higher pH's, the water ligands can be deprotonated.



**Figure 1.29** Fish's Rhodium Complex.

Jensen described  $[PtH(H_2O)(PR_3)_2]^+$  from the reaction of  $PtHCl(PR_3)_2$  (R=Me, Et) and NaOH in a 1:1 acetonitrile/water solution. The complex is part of a catalytic reaction in which actonitrile is hydrolyzed to acetamide.  $[PtH(H_2O)(PR_3)_2]^+$  is believed to be the catalytically active species and the reaction is believed to proceed as shown below. The mechanism shows the formation of the catalyst precursor by the reaction of PtHCl(PR\_3)\_2 with NaOH. The result of this reaction is the substitution of the chloride ligand for a hydroxy ligand. In water, the hydroxy ligand is displaced by water or protonated by water forming the active catalyst. This active catalyst hydrolyzes acetonitrile at a rate of 178 mol/(mol of catalyst•hr). The reaction also has a turnover number greater than 6000 at 80 °C.



### Figure 1.30

Catalytic Hydrolysis of Acetontrile to Acetaminde

Deeming prepared an Ir(III) complex with water bound to the metal center. <sup>30</sup>

Deeming created the water bound species by the addition of silver perchlorate to

 $IrCl_3(PMe_2Ph)_3$  in wet acetone.



# Figure 1.31 Synthesis of [IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>(H<sub>2</sub>O)][ClO<sub>4</sub>]

Deeming observed that the water binds more preferentially than acetone in  $[IrCl_2(PMe_2Ph)_3(H_2O)][ClO_4]$ . He attributed this feature to a strong trans influence of PMe\_2Ph on H<sub>2</sub>O. At the same time, he noted that water is a good leaving group in the presence of donor atoms such as P, N, S, and O. Deeming substituted H<sub>2</sub>O by SH<sub>2</sub>, NH<sub>3</sub>, and PH<sub>3</sub>.



Where L=PH<sub>3</sub>, SH<sub>2</sub>, NH<sub>3</sub>

### Figure 1.32

Substitution of  $H_2O$  Ligand on Ir(III) Complex by Groups with Strong Donor Atoms

## **1.4 Platinum Metal Complexes with Weakly Coordinating Anions.**

The chemistry of weakly coordinating anions is becoming more important in transition metal catalysis. <sup>31</sup>, <sup>32</sup>, <sup>33</sup>, <sup>34</sup>. The use of these anions has been prevalent in the catalytic polymerization of olefins <sup>35</sup>, <sup>36</sup>, <sup>37</sup> the catalytic formation of carbon-carbon bonds, <sup>38</sup> and the activation of R-H bonds. More specifically, weakly coordinating anions have been used to create active open sites on metal centers. Although used often in early metal Ziegler Natta catalyst, there have been some instances where late metals have required the use of weakly coordinating anions to boost the reactivity of a catalytic system.<sup>39</sup>

The assumption that can be made about the action of these anions is based on Hard-Soft-Acids-Bases theory (HSAB). <sup>40</sup> HSAB, just like in organic chemistry, helps define the polarizability of atoms and molecules. In the theory, acids are defined as acceptor atoms and bases are defined as donor atoms. The theory also defines hard as atoms having low polarizability and high electronegativity. Soft is a term that has been defined those atoms which are highly polarizable with low electronegativity. According to the theory, there is one rule which states that hard acids prefer to bond to hard bases and soft acids prefer to bond to soft bases. The transition metals have been classified. By definition third row metals and some second row metals are classified as soft while those early (electropositive) metals in high oxidation states are generally hard. Thus, atoms such as nitrogen, oxygen, and fluorine (which are considered hard) bind more readily to early metals but less favorably with the late metals. Hence, some researcher use weakly coordinating anions with hard atoms to take advantage of the softness of late transition metals. In the case of platinum metals the use of  $ClO_4^-$ ,  $PF_6^-$ ,  $BF_4^-$ , and  $OTf^-$  as anions, which are considered hard and weakly coordinating, have been examined and reported. In this section, we hope to report some of these examples and the chemistry which followed.

. Bergman reported a new transition metal complex of the structure  $Cp*Ir(CH_3)$  (SOCF<sub>3</sub>)(PMe<sub>3</sub>).<sup>41</sup> This complex has been used to activate carbon-hydrogen bonds in alkanes.



### Figure 1.33

C-H activation of Benzene using Cp\*Ir(CH<sub>3</sub>)(OTf)(PMe<sub>3</sub>)

The reaction shown in Figure 1.33 was completed in 100 % yield at room temperature. The proposed mechanism for this chemistry is that the benzene group is oxidatively added to the metal species followed by the rapid reductive elimination of methane from the metal center. Bergman found that by using anions that coordinate even more weakly than triflate, he can increase the rate of the reaction.

Caulton found that Ir(III) alkyls can be protonated to form unsaturated metal cations. <sup>42</sup>



Where  $X=CH_3$  or H; S=MeOH,  $CH_3CN$ , or  $C_3H_6O$ 

### Figure 1.34 Acid Cleavage of Ir(III) Alkyls

Acidolysis causes the loss of a neutral alkane from the metal center. Caulton described the mechanism as the protonation of the metal center followed by the reductive elimination of the alkane. The process produces an open site of unsaturation which can be filled by solvents, substrates, or other Lewis basic materials. Caulton used tetrafluoroboric acid for the bulk of his studies. He found that  $BF_4^-$  is a weakly coordinating anion. This may be true because it is believed and have been observed that  $BF_4^-$  binds through the hard flouride atoms. Weakly coordinating anions are important in cases where an open site is manufactured because they are able to act as spectators during reactions. Other anions may interfere and inhibit the reaction via their desire to bind tightly to the metal center. HSAB theory dictates that weakly coordinating anions not have the urgency to bind to the metal center.

Flood used acidolysis to create unsaturations in Rh (III) compounds.<sup>43</sup>, <sup>44</sup> Using the Cn ligand (Cn = 1,4,7-trimethyl-1,4,7-triazacyclonone), Flood reported the acidolysis of one and two methyl ligands. He isolated the chloride, triflate, and tetrafluoroborate products of both the RhMe<sub>2</sub>XCn and RhMeX<sub>2</sub>Cn complexes.



Where X = CI, OTf, or BF<sub>4</sub>.

# Figure 1.35

Acidolysis of RhCnMe<sub>3</sub> using Various Acids.

Flood also observed the reactivity of RhMe<sub>2</sub>XCn and RhMeX<sub>2</sub>Cn with olefin substrates and found that the triflate analogs are the most reactive. He found that the triflate complexes take up CO rapidly and form RhMe<sub>2</sub>(CO)Cn and RhMe(CO)<sub>2</sub>Cn quantitatively.



**Figure 1.36** CO Substitution in RhMe<sub>2</sub>(OTf)Cn

Flood has also shown that solvents such as acetone, acetonitrile, water, and THF can be used to substitute for triflate in RhMe<sub>2</sub>(OTf)Cn and RhMe(OTF)<sub>2</sub>Cn.

Flood claimed that RhMe<sub>2</sub>(OTf)Cn shows better reactivity with olefins than the PMe<sub>2</sub>Ph analogs prepared by Caulton.<sup>45</sup> Flood attributed the better reactivity to the steric and electronic properties of the Cn ligand. More specifically, the sigma donor ability of the nitrogen atoms vs that of the phosphorus atom tends to give the Cn ligand an advantage over the PMe<sub>2</sub>Ph ligand as far as binding of substrate and insertion into the metal Rh bond. Caulton found that the PMe<sub>2</sub>Ph analog is more likely to undergo

reductive elimination of ethane instead of insertion of the olefin in the methyl rhodium bond.

Brookhart used a cobalt catalyst to complete the polymerization of ethylene.<sup>46</sup> Using the Co(III) complex  $[Cp*Co(P(OMe)_3)CH_2CH_2-\mu-H^+]^+$ , shown in Figure 1.37, he proposed that ethylene can undergo a polymerization that does not follow the normal Cossee-Arlman mechanism but was produced by an agostic interaction between the olefin and the metal center.



**Figure 1.37** Brookhart's Co(III) Polymerization Catalyst

Brookhart also synthesized a Rh(III) analog of this compound which catalyzes the dimerization of styrene and the tail to tail dimerization of methyl acrylate.<sup>47</sup>



**Figure 1.38** Brookhart's Dimerization of Methyl Acrylate using a Rh(III) Catalyst

Eisenberg synthesized the Ir(III) complex  $[Ir(CH_3)(CO)(OTf)_2(dppe)]$ . In his synthesis, he has shown that iodine can be easily substituted by triflate while using silver triflate as a metathesizing agent.



Figure 1.39 Synthesis of [Ir(CH<sub>3</sub>)(CO)(OTf)<sub>2</sub>(dppe)]

The triflates in this complex were expected to act as weakly coordinating ligands toward any incoming substrates. An intriguing reaction takes place between  $[Ir(CH_3)(CO)(OTf)_2(dppe)]$  and  $H_2$ . Eisenberg has shown that the analogous hydride structure can be synthesized as shown in Figure 1.40.



Figure 1.40 Reaction of [Ir(CH<sub>3</sub>)(CO)(OTf)<sub>2</sub>(dppe)] and H<sub>2</sub>

While no direct evidence was obtained to verify the mechanism of the reaction, Eisenberg postulated that the binding of dihydrogen to the metal center (displacing triflate) followed by the protonation and elimination of the methyl group. Eisenberg also reported the hydrogenation of olefins using this complex. (Figure 1.41)



Where  $R = H, C_4 H_9$ 

# Figure 1.41

Hydrogenation of Olefins using [IrH(CO)(OTf)<sub>2</sub>(dppe)]

Eisenberg noted that the catalyst showed relatively low turnover frequencies for the hydrogenation of ethylene and 1-hexene (120 hr<sup>-1</sup> and 52 hr<sup>-1</sup> respectively). He also determined that [IrH(CO)(OTf)<sub>2</sub>(dppe)] tended to produce 1-hexene isomerization products in the attempted hydrogenation of 1-hexene This suggests that the complex can undergo insertion followed by rapid -hydride elimination.

Crabtree synthesized a series of complexes having the form  $[Ir(COD)(PPh_3)L]A^-$ , where A<sup>-</sup> represents the weakly coordinating anions  $PF_6^-$  or  $BF_4^-$ , to hydrogenate hindered olefins in the presence of hydrogen gas. <sup>48</sup>



Figure 1.42

Crabtree's Catalyst for Hindered Olefin Hydrogenation

Crabtree found that by using weakly coordinating anions that acted as spectator ligands (i.e.  $PF_6^-$  and  $SbF_5^-$ ) he could increase the rate of reaction in these systems over those which used  $BF_4^-$  and  $ClO_4^-$ . This suggests that there is a correlation between the binding affinity of an anion and the rate of hydrogenation in this system. Thus, it may be

possible for this same correlation to be superimposed in other areas of transition metal catalysis.

The remainder of this dissertation presents the synthesis, characterization and reactivity of Ir(III) dications which use weakly coordinating ligands to stabilize open sites for reaction with olefin and acetylene substrates. Our objective was to show that by using weakly coordinating ligands, it may possible to observe an increase in the rate of oligomerization for our dicationic complexes when compared to monocationic or neutral complexes. This dissertation also will examine the chemistry of these complexes in water.

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# Chapter 2: The Protonation of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl

### **2.1 Introduction**

The protonation of metal complexes is a viable method of preparing late transition metal hydrides.<sup>1</sup>, <sup>2</sup> Protonation of a metal complex usually occurs when the basicity of the metal center is enhanced due to all the low-lying orbitals being filled as a result of interactions with donor ligands.<sup>3</sup> Vaska has reported the protonation of IrH(CO)(PPh<sub>3</sub>)<sub>3</sub> with HCl gives the cis-dihydride cation.<sup>4</sup> (Figure 2.1)



**Figure 2.1** Protonation of Vaska's Complex Using HCl

Vaska's complex,  $IrHCO(PPh_3)_3$ , with its large electron density on the metal center acts in a basic fashion to complete a formal oxidative addition of HCl. The formal oxidative addition serves to change the oxidition state of the Ir(I) complex to an Ir(III) complex, thus changing the proton to a hydride when bound to the electropositive metal center.

Bullock showed that a transition metal complex can be successfully protonated.<sup>5</sup>



Figure 2.2 Protonation of OsCp\*H(CO)<sub>2</sub> using Triflic Acid

In an attempt to make the dihydrogen complex  $[Cp*Os(h^2-H_2)(CO)_2]OTf$ , Bullock and others protonated  $Cp*OsH(CO)_2$  using triflic acid.<sup>5</sup> (Figure 2.2) The reaction gave an 87:13 ratio of  $[Cp*Os(H)_2(CO)_2]OTf$  to the desired product. Each of the protonated complexes are extremely acidic and were used as catalysts for the hydrogenation of olefins. The dihydrogen complex's acidity is greater than that of the dihydride. Therefore, it can be deduced that there is a fine balance between the acidic dihydrogen and a electronegative hydride tautomers. That balance can be controlled by the donor ligands bound to the metal and by the metal itself.

Metal hydrido complexes are key intermediates in a number of catalytic processes including hydrogenation, hydroformylation, hydrosilation, hydrocyanation, isomerization, and polymerization.<sup>6</sup> Merola showed that [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl is a good starting material for the production of hydrides. Previously, he used

[Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl as a source of iridium(I) in the oxidative addition of H-H bonds <sup>7</sup>, B-H bonds <sup>8</sup>,C-H bonds <sup>9</sup>, <sup>10</sup> N-H bonds <sup>11</sup>, O-H bonds <sup>12</sup>, and C-S bonds <sup>13</sup>.



Where E=H, C, B, N, or O

**Figure 2.3** Oxidative Addition using [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl

Merola showed that reactions of [Ir(COD)-(PMe<sub>3</sub>)<sub>3</sub>]Cl and E-H substrates produced iridium hydride complexes as shown in Figure 2.3. Some of these complexes are water-soluble catalysts for the hydrogenation of alkynes and alkenes. Based on previous results, we wanted to discover what chemistry can evolve from the oxidative addition of binary acids to this Ir(I) precursor. Although the substrates were different, our hopes were that our chemistry would be similar to that of Vaska's mentioned above. We also believed that the product born out of these reactions would be good precursors to watersoluble catalysts. Therefore, this chapter will describe the protonation of complex (1) using various binary acids.

### 2.2 Results and Discussions

# 2.2.1 Protonation of Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>Cl by HCl

We were interested in exploring the protonation complex (1) using various acids.  $[Ir(COD)(PMe_3)_3]Cl$  reacts with HCl, in methylene chloride, to form an Ir(III) monohydride. (Figure 2.4) The product is white and insoluble in most common solvents with the exception of acetone, DMSO, and acetonitrile. This polar solubility behavior suggests that the product is a salt. It was also noted that the product is water-soluble and there are a variety of reactions that take place depending on the solvent in which the product is dissolved. Through elemental analysis, NMR spectroscopy, and aqueous titration with base, we were able to determine that the reaction proceeded as shown in Figure 2.4. We believe that [IrHCOD(PMe\_3)\_3][Cl]\_2 retains 2 equivalents of hydrogen chloride as an adduct.



**Figure 2.4** Protonation of [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl in CH<sub>2</sub>Cl<sub>2</sub> using HCl.

In general, we believe that there are two factors involved in this protonation that determine whether or not the complex will become a dicationic hydride of the nature  $[IrH(COD)(PMe_3)_3][Cl][X]$  or one which retains an extra equivalents of acid in the outer sphere. One of the factors may be the hydrogen bonding capability of the counterion and the solvent. The second may be the polarity of the solvent used. In aprotic solvents, like methylene chloride, two extra equivalents of HCl are retained and we speculate that they are hydrogen-bonded to the chloride ions in the solid lattice. In short, we believe that the reaction with HCl in no aqueous media forms the bichloride anion. We determined this phenomenon by using aqueous titration and elemental analysis.

Previous work showed that [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl develops an equilibrium with pyridinium chloride as shown in Figure 2.12.<sup>14</sup> Pyridinium chloride has a pKa of about 5.2 in water<sup>15</sup>. Therefore, the pka of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl should be about the same. Titration of 0.2 mmol of the [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>[HCl]<sub>2</sub> with .01N NaOH shows a strong acid to strong base relationship and determination of the equivalence point of the curve showed that equivalence occured after the addition of 0.53 mmols of NaOH. We determined that an excess of 3 mmols of base was required to neutralize the complex. We reasoned that those 3 extra equivalents of base need to neutralize the acid corresponds to the neutralization of two excess equivalents of HCl and another equilavent of HCl from the metal center via a reductive elimination or a depronation pathway. Thus, we suggest that some strong bases are exceedingly more basic than the hydride from the metal center and in effect are strong enough to treat the hydride as a proton.

The calculation for the pKa using the Henderson-Hasselbalch equation affords a pKa of 2.34 for this species. As compared to the expected 5.2 pKa from the equilibrium reaction of  $[IrCOD(PMe_3)_3]$ Cl and pyridinium chloride. We find that the acidic 2.34 pKa is almost 3 orders of magnitude more acidic than what is expected from pyridinium chloride.

Data from "Ircodp3H2+HCI2CL2 .2mmol"



**Figure 2.5** Titration Curve of 0.2 mmol of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub>•2HCl with 0.01M NaOH in H<sub>2</sub>O

### 2.2.2 Removal of Extra Equivalents of HCl

The reaction between [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl and 2 equivalents of KOH in H<sub>2</sub>O afforded a product which was deficient of hydrides. The product was a complex mixture of unknown COD-containing species. KOH was too strong a base and attacked the hydride attached to the metal center. The gentler base NaHCO<sub>3</sub> was used but with no better results. We also have attempted to induce the [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl to react with 2 equivalents of the starting material in order to complete the reaction shown in Figure 2.6.



Figure 2.6 Proposed Reaction between [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl and 2 Equivalents of [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl

The major products of this complicated reaction were identified as  $IrCl_3(PMe_3)_3$ , IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>, and unreacted [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl. We speculate that the loss of the extra equivalents of HCl produces a "naked" chloride anion, in non aqueous solvent, which can immediately attack the iridium center and displace a COD ligand and form the IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>. Further reaction of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> with HCl can form IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> via acidolysis of the hydride.

#### 2.2.3 Protonation of Ir(COD)(PMe<sub>3</sub>)<sub>3</sub> Using Other Acids

The chloride anion is considered somewhat hard and binds tightly to the Ir(III). Hence, we were interested in using counterions that were bulkier and more dispersed anionic charge than the chloride anion. We believed that by using bulky counterions that are weaker nucleophiles and have greater charge dispersal than the chloride ions, there would be less occasion for the products to retain excess acis as shown in Figure 2.4.



# **Figure 2.7** Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl and HBF<sub>4</sub>•Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>

Tetrafluoroboric acid protonated  $[Ir(COD)(PMe_3)]Cl$  as shown in Figure 2.7. Based on the elemental analysis of the product, we determined that the complex retains one extra equivalent of tetrafluoroboric acid. We observe that by using the bulkier, less anionic  $BF_4^-$  counterion, there is only one equivalent of binary acid that hydrogen bonds to presumably the chloride in the crystal lattice. We believe that this implicates the presence of chlorine for the unusual hydrogen bonding found in this metal complex.

When triflic acid was used to protonate the  $[Ir(COD)(PMe_3)_3]OTf$  the resulting  $[IrH(COD)(PMe_3)_3][OTf]_2$  complex also retains just one equivalent of triflic acid. (Figure 2.8) The structure of the complex was determined by X-ray crystallography and the emperical formula verified by elemental analysis.



**Figure 2.8** Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]OTf and Triflic Acid in CH<sub>2</sub>Cl<sub>2</sub>



**Figure 2.9** ORTEP Drawing of the structure of [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][OTf]<sub>2</sub>•HOTf

Metric data for (6) indicated an elongated Ir-P(3) bond (2.444 Å) which highlights the trans influence of the hydride. The average Ir-P bond length of other PMe<sub>3</sub> was 2.336 Å. The difference of more than 0.1Å is significant, it suggests that there is a great trans influence between the hydride and the trans phosphine. We believe that this strong trans influence rationalizes some of the reactions described below.

We have also found that a complex without a nucleophillic counter ion will exhibit no hydrogen bonding in methylene chloride solution. Based on this information, we feel that the nucleophilicity of the counter ion plays a role in the hydrogen bonding effect seen in the protonation of the  $[Ir(COD)(PMe_3)_3]Cl$ .



**Figure 2.10** Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl and HBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>

 $[IrHCOD(PMe_3)_3][BF_4]_2$  is different from most of the other Ir(III) dications because it does not retain extra equivalents of acid. The reason for this is because the  $BF_4^-$  anion is bigger and has a smaller charge to size ratio than the other cations that were used in this study. There was another difference noted in the nature of this species. In water, acetone, and acetonitrile, we observe the equilibrium shown in Figure 2.11 for complex (8). The equilibrium was determined in the <sup>1</sup>H and <sup>31</sup>P NMR. We believe that the equilibrium may suggest that there is a certain stability that is obtained from the presence of the excess acid in the Ir(III) dications that were described previously.



Figure 2.11 Equilibrium between  $[IrHCOD(PMe_3)_3][BF_4]_2$  and  $[IrCOD(PMe_3)_3]BF_4$  in Solution

It is also possible to protonate the  $[Ir(COD)(PMe_3)_3]Cl$  using pyridinium chloride. The reaction has different pathways depending on which type of solvents and concentrations are used. In H<sub>2</sub>O, the monohydride product is formed and is in equilibrium with the reactants. This is similar to the complex (8) which also undergo equilibrium in H<sub>2</sub>O. (Figure 2.11)



**Figure 2.12** Equilibrium of Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl and Pyridinium Chloride

The reaction, in  $CH_2Cl_2$ , produced many different products which were not in equilibrium with the reactants but may have been the result of a lack of excess acid to stabilize the hydride.



(9)

### Figure 2.13

Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl and Pyridinium Chloride in CHCl<sub>3</sub> The first product noted was that shown in Figure 2.13. It is expected that 2 equivalents of the pyridinium chloride is needed for this reaction to go to completion. The driving forces that we believe are responsible for the ejection of the phosphine is the relief of the trans influence caused by the hydride trans to the phosphine and the production of the phosphonium chloride which precipitates from solution. The trans influence of a ligand has been defined as the extent to which that ligand weakens the bond trans to itself. <sup>6</sup> Having a hydride trans to a phosphine results in an interaction in which , the phosphine metal bond is weakened and lengthened.

The <sup>1</sup>H NMR spectroscopy clearly shows two signals in the hydride region which we have described as a triplet and a doublet of triplets. The doublet of triplet at -11.25 ppm is indicative of a hydride which is coupled to two cis phosphines and has a larger coupling to a trans phosphine. The splitting pattern is indicative of a complex with a facial arrangement of phosphines. The triplet at about -16.5 ppm is indicative of a hydride which is coupled to two cis phosphines and trans to either a chlorine or nitrogen atom. Based on the data received in the normal region of the <sup>1</sup>H NMR spectrum as well as the <sup>13</sup>C and <sup>31</sup>P NMR spectra, both complexes had COD ligands bound to the metal center and complex (9) existed with the pyridine ligand bound trans to the hydride.



### Figure 2.14

<sup>1</sup>H NMR Spectroscopy (Hydride Region) of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub> and [IrH(COD)(PMe<sub>3</sub>)<sub>2</sub>(Pyr)][Cl]<sub>2</sub>

In the reaction of one equivalent of pyridinium chloride and of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl, there are other products after 48 hours which included [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>, IrH(2-pyr)(PMe<sub>3</sub>)<sub>3</sub>Cl and [IrH(2-pyr)(pyr)(PMe<sub>3</sub>)<sub>3</sub>]Cl. The presence of [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub> suggests that the pathway shown in Figure 2.12 was followed. The latter two complexes are a result of the oxidative addition of pyridine to the iridium center.( Figure 2.15)



**Figure 2.15** Oxidative Addition of Pyridine

The presence of pyridine is mandatory for the oxidative addition of pyridine to  $[IrCOD(PMe_3)_3]Cl$ . This would suggest that the pyridine was again produced from the pathway shown in Figure 2.12. The third product can be prepared simply by the substitution of the chloride on the metal with excess pyridine as shown in Figure 2.16.



**Figure 2.16** Substitution of Chloride by pyridine in IrH( <sup>2</sup>-Pyr)(PMe<sub>3</sub>)<sub>3</sub>Cl

The last of the iridium (III) hydride dicationc salts containing COD that will be discussed in this manuscript is  $[IrHCOD(PMe_3)_3][PF_6]_2$ , which was synthesized by reaction of  $[IrHCOD(PMe_3)_3]Cl_2$  with an excess KPF<sub>6</sub>. in H<sub>2</sub>O. (Figure 2.17).



Figure 2.17 Synthesis of [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

This dicationic salt is engaging because it did not retain extra equivalents of excess acid and it remained soluble in organic solvent. This solubility allowed us to observe the hydride for these complexes spectroscopically. Although we deduced the presence of a hydride from the <sup>31</sup>P NMR and X-ray crystallography of the complex, we were limited to the use of  $D_2O$  as a NMR spectroscopy solvent for the other dicationic salts which

retained excess acid. In  $D_2O$ , these hydride complexes undergo rapid deuterium-hydride exchange which makes the hydride unobservable in <sup>1</sup>H NMR spectroscopy.

# 2.2.4 NMR Spectroscopy of Iridium Hydride Dicationic Salts

The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra for these complexes indicate a facial arrangement of the phosphines. The <sup>1</sup>H NMR spectrum (D<sub>2</sub>O) of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>] [PF<sub>6</sub>]<sub>2</sub>, shown in Figure 2.18, clearly shows a doublet at 1.9 ppm (J<sub>P-H</sub>=6.9Hz) which have been assigned to two equivalent PMe<sub>3</sub> ligands which are trans to the olefins of the bound (COD) ligand. There is also a second doublet at 2.0 ppm (J<sub>P-H</sub>=8.8Hz) which have been assigned to the third PMe<sub>3</sub> ligand which is trans to the hydride.



**Figure 2.18** <sup>1</sup>H NMR Spectrum of [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> Complex



<sup>1</sup>H NMR spectrum (Hydride Region) of [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

The hydride region of the <sup>1</sup>H NMR clearly shows a doublet of triplets at -10.5ppm ( $J_{H-Ptrans}=95.1Hz$ ,  $J_{H-Pcis}=16.2Hz$ ) as shown in Figure 2.19. This splitting pattern is representative of a hydride which is cis to two phosphines and it gave a small coupling constant J=16.2Hz and a triplet splitting pattern. Also, the hydride is trans to another phosphine which gave a much larger coupling constant of J= 95.1Hz and splits the triplets into a doublet of triplets. Due to the fact that there are only three phosphines on the metal center, it can be reasoned that the complex is facial with respect to the alignment of the phosphines.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (CH<sub>3</sub>CN), for complex (12), clearly shows a doublet at -46.1 ppm ( $J_{P-P}=21.2Hz$ ) for the two equivalent phosphine ligands that are cis to an inequivalent phosphine ligand and a triplet at -62.4 ppm for the inequivalent phosphine ligand that is cis to the two equivalent phosphine ligands.



Figure 2.20 <sup>31</sup>P NMR Spectrum for [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

Compounds	<sup>1</sup> H-P (PMe <sub>3</sub> ) trans COD	<sup>1</sup> H-P (PMe <sub>3</sub> ) trans H	<sup>31</sup> P trans COD	<sup>31</sup> P trans H
[IrH(COD)(PMe <sub>3</sub> ) <sub>3</sub> ][Cl] <sub>2</sub> •2HCl	1.9ppm	2.0 ppm	-46.1 p	-62.4 p
( <b>D</b> <sub>2</sub> <b>O</b> )	(6.9 Hz)	(8.8 HZ)	(21.2 Hz)	
IrH(COD)(PMe <sub>3</sub> ) <sub>3</sub> ][BF <sub>4</sub> ][Cl]•HBF <sub>4</sub>	1.9ppm	2.0 ppm	-43.1 p	-59.7
( $\mathbf{D}_2\mathbf{O}$ )	(7.9Hz)	(8.7 HZ)	(25.1Hz)	

Table 2.1<sup>1</sup>H and <sup>31</sup>P Resonances for Dicationic Ir(III) Salts

$[IrH(COD)(PMe_3)_3][BF_4]_2$	1.9ppm	2.0 ppm	-42.6 p	-59.7
( <b>D</b> <sub>2</sub> <b>O</b> )	(9.7 Hz)	(9.0HZ)	(25 Hz)	
[IrH(COD)(PMe <sub>3</sub> ) <sub>3</sub> ][Cl] <sub>2</sub>	1.9ppm	2.0 ppm	-42.9 p	-59.1
( <b>D</b> <sub>2</sub> <b>O</b> )	(10.1Hz)	(8.4HZ)	(22.7Hz)	
[IrH(COD)(PMe <sub>3</sub> ) <sub>3</sub> ][OTf] <sub>2</sub>	1.8ppm	1.9 ppm	-42.4 p	-58.2
(CD <sub>3</sub> CN)	(9.8Hz)	(8.8 HZ)	(19.5 Hz)	
$[IrH(COD)(PMe_3)_3][PF_6]_2$	1.8ppm	1.9 ppm	-39.9 p	-55.5
(CD <sub>3</sub> CN)	(10Hz)	(9.2 HZ)	(24.5 Hz)	

Table 2.1 shows the Chemical shifts and some coupling constants from the <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy for the various dicationic salts that were synthesized. There are no major differences in the base structure of all these salts, therefore it would be expected that the <sup>1</sup>H and <sup>31</sup>P NMR would be the same. For the most part that is the case, however there are a few differences that could help us to understand the nature of these hydrides. The <sup>31</sup>P NMR spectra show a resonance that corresponds to a PMe<sub>3</sub> group which is trans to a hydride. In the spectrum of the [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>] [Cl]<sub>2</sub>•2HCl complex there is a chemical shift of -62.4 ppm for the PMe<sub>3</sub> ligand trans to the hydride and a chemical -46.1 ppm for the other two PMe<sub>3</sub> ligands that are trans to the COD ligand. shift of These chemical shifts become interesting when compared to those of the other complexes under the conditions.  $[IrHCOD(PMe_3)_3][C1][BF_4] \bullet HBF_4$  has chemical shifts for the analogous PMe<sub>3</sub> resonances at -59.1 ppm and -43.1 ppm respectively.  $[IrHCOD(PMe_3)_3][BF_4]_2$  has the analogous chemical shifts at -59.7 ppm and -42.6 ppm. Therefore, if there were any spectroscopic trend that could support the fact that there is acid stabilization of these dications it could be the tendency for the <sup>31</sup>P NMR resonance to appear more upfield than those that do not have acid stabilization.

#### 2.2.4 Protonation In Aqueous Solvent

In these protonation reactions there are solvation effects. While using aprotic solvents, like methylene chloride, we have seen the effects noted above but when using a more protic solvent like water, we do not see direct evidence of the hydrogen bonding shown above.



**Figure 2.21** Reaction between [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]Cl and HCl(aq) in Water.

In protic solvent such as water, we believe that the hydrogen bonding of the HCl to the chloride anion is diluted because of the presence of many hydrogen bonding  $H_2O$  molecules. Therefore, because of the diluting effect of the hydrogen bonding solvent, the hydride is stabilized by the water and less binary acid is necessary.

#### **Experimental Section**

**General Procedures**. All reactions were carried out under an atmosphere of purified nitrogen. Toluene, ether, pentane were purchased from Fisher Scientific. Toluene was distilled from potassium benzophenone; methylene chloride was distilled from  $P_2O_5$ ; ether and pentane were distilled over Na/K alloy. Water was deionized and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Hydoiridic acid was purchased from PGN Chemicals and was used as received. [Ir(COD)Cl]<sub>2</sub> was prepared using a method analogous to the literature

procedure.<sup>16</sup> [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl (1) and [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> (7) were prepared as described previously.<sup>17</sup> The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WP200 SY spectrometer operating at 200.132 MHz for protons, 81.015 MHz for phosphorus, 67.925MHz for carbon, and Bruker WP360 SY spectrometer operating at 360.134 MHz for protons, 145.785 MHz for phoshorus, and 90.556 MHz for carbon. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia. Single crystal X-ray diffraction experiments were performed on a Siemens R3m/V diffractometer with SHELXTL-PLUS software as supplied by Siemens Corporation.

Synthesis of  $[IrH(COD)(PMe_3)_3][Cl]_2 \cdot 2HCl MAF.220. (2)$  A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line.  $[Ir(COD)(PMe_3)_3]Cl$ , (2 g, 3.55 mmol), was added to the flask and dissolved in methylene chloride (35 mL). Anhydrous HCl gas was passed over the solution and a white precipitate was formed. The reaction was stirred for an additional 3 hours and the precipitate was filtered using a cannula filter. The precipitate was washed with copious amounts of methylene chloride followed by pentane and then dried under vacuum to yield 2.04 g (85.3%) of a white solid identified as  $[IrH(COD)(PMe_3)_3][Cl]_2 \cdot 2HCl$  on the basis of the following : Elemental analysis for  $C_{17}H_{42}Ir_1P_3Cl_4$ : Anal. Calcd for: C, 30.35% H, 6.30% Cl, 20.81%. Found C, 30.54% H, 6.48% and Cl, 17.82%.

<sup>1</sup>H<u>NMR</u> (D<sub>2</sub>O): 1.9 (d, 18H,  $J_{P-H} = 6.9$ Hz, PCH<sub>3</sub> trans to COD), 2.0 (d, 9H,  $J_{P-H} = 8.8$ Hz, PCH<sub>3</sub> trans to D), 2.6-2.8 (m, 8H, COD aliphatic), 4.6 (br m, 2H, olefinic COD), 4.2 (br m, 2H, olefinic COD) ppm. (The hydride exchanges immediately with D<sub>2</sub>O and is not observed in the protonNMR.)

<sup>31</sup>P<u>NMR</u> (D<sub>2</sub>O): -46.1 (d, 2P,  $J_{P-P} = 21.2Hz$ , P trans COD), -62.4 (m, 1P, P trans D) ppm.

Synthesis of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>-MAF.212. (3) A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line. [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl, (2 g, 3.6 mmol), was dissolved in water (20 mL). Aqueous HCl (0.1N), (39 mLs, 3.9 mmol), was added to the mixture while stirring for 10 minutes and allowed to stir for 20 minutes after the addition. The product was concentrated to dryness under vacuum. The product was reprecipitated with methylene chloride and penatane and washed several times using pentane. The washed product was dried under vacuum to yield (1.73) 81.3% of white powder identified as [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub> based on the following information:. Elemental analysis of  $C_{17}H_{40}Ir_1P_3Cl_2$ : Anal. Calcd for: C. 34.00% H, 6.71% and Cl, 11.81 %. Found: C, 30.27% H, 6.35% and Cl, 11.75%.

<sup>1</sup>H<u>NMR</u> (D<sub>2</sub>O): 1.9 (d, 18H, J<sub>P-H</sub> =10.1Hz, PCH<sub>3</sub> trans to COD), 2.1 (d, 9H, J<sub>P-H</sub> =8.4 Hz, PCH<sub>3</sub> trans to <sup>2</sup>H), 2.7-2.9 (m, 8H, aliphatic COD), 4.6 (m, 2H, olefinic COD), 5.178 (m, 2H, olefinic COD) ppm.

<sup>31</sup>P<u>NMR</u> (D<sub>2</sub>O): -42.9 (d , 2P,  $J_{P-P} = 22.7$ Hz, P trans to COD), -59.1 (m , 1P, P trans <sup>2</sup>H) ppm .

Synthesis of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>][Cl]•HBF<sub>4</sub> MAF.058. (4) A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line equipped with nitrogen. [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl, (1 g, 1.80 mmol), was dissolved in methylene chloride (20 mL). H BF<sub>4</sub>•E<sub>t2</sub>O, (0.379 mL, 2.57 mmol), was slowly added to the stirring solution and a white precipitate immediately formed. The solution was stirred for an additional 24 hours under a nitrogen atmosphere and then was filtered using a cannula filter. The precipitate was washed with methylene chloride and pentane and then dried under vacuum to yield (702 mg) 64.1% yield of a white powder identified as [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>][Cl]•HBF<sub>4</sub> on the basis of the following information:

Elemental analysis for  $C_{17}H_{41}Ir_1P_3Cl_1B_2F_8$  Calcd: C, 27.60% H, 5.59% and Cl, 4.79%. Found: C, 28.31% H, 5.81% and Cl, 4.42%.

<sup>1</sup>H<u>NMR</u> (D<sub>2</sub>O): 1.9 (d, 18H,  $J_{P-H} = 7.9$ Hz, PCH<sub>3</sub> trans to COD), 2.0(d, 9H  $J_{P-H} = 8.7$ Hz, PCH<sub>3</sub> trans to D), 2.7-3.1 (m, 8H, aliphatic COD), 4.7 (br m, 2H, olefinic COD), 5.2 (br m, 2H, olefinic COD) ppm. <sup>31</sup>P<u>NMR</u> (D<sub>2</sub>O): -43.1 (d, 2P,  $J_{P-P} = 25.1$ Hz, P trans COD), -59.7(m, 1P, P

trans <sup>2</sup>H) ppm.

The Synthesis of  $[Ir(COD)(PMe_3)_3][OTf]$  - MAF.301. (5) A flask was equipped with a magnetic stirring bar and connect to a Schlenk line charge with argon gas.  $[IrCOD(PMe_3)_3]Cl$ , (4.3 g, 7.62 mmol), was dissolved in degassed, distilled water (40 mL). A solution of NH<sub>4</sub>CF<sub>3</sub>SO<sub>3</sub> (0.422 M, 20 mL) was added to the stirring mixture and a white precipitate was formed. The reaction was stirred for 20 hours to ensure that the reaction was complete. The white precipitate was collected by filtration and washed with cold water. The complex was dried using a vacuum and a yield of (2.92g) 52% of white powder identified as  $[Ir(COD)(PMe_3)_3][OTf]$  on the following information: Elemental analysis of C<sub>19</sub>H<sub>39</sub>Ir<sub>1</sub>P<sub>3</sub>F<sub>3</sub>S<sub>1</sub>O<sub>3</sub>: Anal. Calcd for: C. 31.90% and H, 5.80%. Found: C, 30.52% and H, 5.52%.

<sup>1</sup>H<u>NMR</u> (CD<sub>3</sub>CN): 1.6(br m, 27H, PCH<sub>3</sub> five cordinate fluxional), 2.2-2.5 (m, 8H, aliphatic COD), 3.2-3.5 (m, 4H, olefinic COD) ppm.

 $^{31}P$ <u>NMR</u> (CD<sub>3</sub>CN): -54.5 (s , 3P, P fluxional) ppm .

<sup>13</sup>C <u>NMR</u> (CD<sub>3</sub>CN): 19.9 (m, 9C, fluxional PMe<sub>3</sub>), 34.7 (s, 4C, aliphatic COD C),
69.2 (s, 4C, olefenic COD C).

## The Synthesis of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][OTf]<sub>2</sub>•HOTf -MAF.400. (6)

A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line charged with argon gas. [IrCOD(PMe<sub>3</sub>)<sub>3</sub>]OTf, (1.25 g, 1.901 mmol) was dissolved into methylene chloride (15 mL). The solution was cooled to -78 °C and triflic acid in diethyl ether (0.189 mL, 2.093 mmol) was added dropwise to the stirring solution. The stirring solution produced a white precipitate and the reaction was allowed to proceed for 20 minutes to 0 °C. Afterwards the product was filtered using a sintered glass filter and washed several times using diethylether. The compound was dried overnight under vacuum to yield (1.49 g ) 97.1% of a white powder identified as [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][OTf]<sub>2</sub>•HOTf on the basis of the following information: Elemental analysis of C<sub>19</sub>H<sub>40</sub>Ir<sub>1</sub>P<sub>3</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: Anal. Calcd for: C, 24.57% and H, 4.23%.

Found: C, 24.81% and H, 4.45%

- <sup>1</sup>H<u>NMR</u> (CD<sub>3</sub>CN): 1.8 (d, 18H,  $J_{P-H} = 9.8Hz$ , PCH<sub>3</sub> trans to COD), 1.9 (d, 9H,  $J_{P-H} = 8.8Hz$ , PCH<sub>3</sub> trans to H) 2.5-2.6 (m, 6H, aliphatic COD), 2.8 (m, 2H, aliphatic COD), 4.5 (m, 2H, olefinic COD), 5.0 (m, 2H, olefinic COD) ppm.
- <sup>31</sup>P<u>NMR</u> (CD<sub>3</sub>CN): -42.4 (d, 2P,  $J_{P-P} = 19.5$ Hz, P trans to COD), -58.2 (t, 1P,  $J_{P-P} = 20.1$ Hz, P trans H) ppm.
- <sup>13</sup>CNMR (CD<sub>3</sub>CN): 18.14 (d, 1C,  $J_{C-P}=33.5Hz$ , C on cis PMe3), 19.21 (t, 6C,  $J_{C-P}=20.8Hz$ , C on trans PMe3), 30.62 (s, 2C, aliphatic COD C close to the metal), 33.58 (s, 2C, aliphatic COD C away from metal), 90.34 (s, 2C, olefinic COD C close to metal), 98.55 (s, 2C, olefinic COD C away from metal).

Synthesis of  $[IrH(COD)(PMe_3)_3][BF_4]_2$  (8). A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line.  $[Ir(COD)(PMe_3)_3]BF_4$ ,(656 mg, 1.10 mmol), was dissolved in methylene chloride (40 mL) and stirred for 20 minutes.
HBF<sub>4</sub>•Et<sub>2</sub>O, (0.142 mL, 0.96 mmol) was slowly added to the homogenous solution and a white precipitate immediately formed. The mixture was stirred for an additional 24 hours. The precipitated was filtered using a cannula filter and was washed with methylene chloride and pentane. The washed product was dried under vacuum and collected to yield (0.671g) 89.3% of product identified as [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> on the basis of the following information:

Elemental analysis of  $C_{17}H_{40}P_3Ir_1B_2F_8$ : Anal. Calcd for: C, 29.03% and H, 5.73%. Found: C, 28.99% and H, 5.66%.

<sup>1</sup>H<u>NMR</u> (D<sub>2</sub>O): d 1.9 (d, 18H J<sub>P-H</sub> =9.7Hz, PCH<sub>3</sub> trans to COD), 2.0 (d, 9H, J<sub>P-H</sub> =9.0Hz, PCH<sub>3</sub> trans to <sup>2</sup>H), 2.6-3.0 (br m, 8H, aliphatic COD), 4.5 (br m, 2H, olefinic COD), 5.5 (br m, 2H, olefinic COD) ppm

<sup>31</sup>PNMR (D<sub>2</sub>O): d -42.6 (d , 2P, 
$$J_{P-P} = 25.0Hz$$
, P trans to COD), -59.7 (m  
, 1P, P trans to <sup>2</sup>H) ppm.

**The Synthesis of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> MAF.392. (12)** A side armed flask was equipped with a magnetic stir bar and connected to a Schlenk line charged with argon gas. [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][Cl], (1.73 g, 2.88 mmol) was dissolved into 30 mL of distilled, degassed water. A white precipitated was produced by adding an aqueous solution of KPF<sub>6</sub> (0.576 M, 20 ml) to the stirring solution of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>. The reaction was stirred for 30 minutes before being filtered using a sintered glass filter. The product was washed several times using a copious amount of distilled, degassed water. The complex was dried under vacuum to yield (1.73g) 73.3% of a white powder identified as [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>. based on the following information: Elemental analysis of  $C_{17}H_{40}Ir_1P_5F_{12}$ : Anal. Calcd for: C. 24.91% and H, 4.92%. Found: C, 24.67% and H, 4.82%.

<sup>1</sup>H<u>NMR</u> (CD<sub>3</sub>CN): d 1.8 (d, 18H,  $J_{P-H} = 10.0$ Hz, PCH<sub>3</sub> trans to COD), 1.9 (d, 9H,  $J_{P-H} = 9.2$ Hz, PCH<sub>3</sub> trans to H) 2.5-2.6 (m, 4H, aliphatic COD),

2.8-2.9(m, 4H, aliphatic COD), 4.4 (m, 2H, olefinic COD), 5.0( m, 2H, olefinic COD) -10.5 (dt, 1H,  $J_{H-Ptrans}=95.1Hz$ , hydride trans to P  $J_{H-Pcis}=16.2Hz$ , hydride cis to two P) ppm.

- <sup>31</sup>P<u>NMR</u> (CD<sub>3</sub>CN): -39.9 (d, 2P,  $J_{P-P} = 24.5Hz$ , P trans to COD), -55.5 (t, 1P,  $J_{P-P} = 24.6Hz$ , P trans H) ppm.
- <sup>13</sup>C<u>NMR</u> (CD<sub>3</sub>CN): 18.12 (d, 1C,  $J_{C-P}$ =33.5Hz, C on cis PMe<sub>3</sub>), 19.17 (t, 6C,  $J_{C-P}$ =21.7Hz, C on trans PMe<sub>3</sub>), 30.59 (s, 2C, aliphatic COD C close to the metal), 33.56 (s, 2C, aliphatic COD C away from metal), 90.38 (s, 2C, olefinic COD C close to metal), 98.62 (s, 2C, olefinic COD C away from metal).

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# Chapter 3: The Reactivity of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl

## **3.1 Introduction**

The aqueous chemistry of organometallic catalysts has been a topic of interest for the past few years.<sup>1,2</sup> There is an emphasis being placed on the use of less harmful solvents in the chemical industry and this impetus led many researchers to the use of water as a replacement for more common solvents.<sup>3,4,5,6</sup> Being oxophillic, many early metal compounds decompose in water.<sup>7</sup> Therefore, late metal complexes are better suited for the study of transition metal complexes in water. Previously, Merola and Matthews noted some interesting chloride dissociation chemistry using  $Ir(H)_2Cl(PMe_3)_3$ .<sup>8</sup> Unlike many other water-soluble complexes, the Ir complexes studied by Merola do not gain their ability to become water-soluble from the use of its ancillary ligands but from the ability of the metal itself. He showed that in H<sub>2</sub>O, the Cl<sup>-</sup> dissociates from the metal center and is replaced by the harder water ligand as shown in Figure 3.1. The aquo ligand binds weakly to the metal center and therefore can be replaced by an activated olefin or acetylene. He used  $Ir(H)_2Cl(PMe_3)_3$  to examine the hydrogenation of different olefin substrates in water.<sup>8</sup>



**Figure 3.1** Substitution of Cl<sup>-</sup> with Water in IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub>

# 3.2 Results and Discussions

# 3.2.1 Reactivity of [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl in Aqueous Solvent

Previously, we noted that when  $[Ir(COD)(PMe_3)_3]Cl$  is protonated using strong acids, it retains an extra equivalents of acid as an adduct. We were interested in exploring the chemistry of these complexes in aqueous solution. One strong factor which makes water an ideal medium is that most of these dicationic complexes are not soluble in non polar or slightly polar solvents. In water, complex (2) produces the fac- $[IrCl_3(PMe_3)_3]$ complex as shown in Figure 3.2. We have not determined the mechanism of this reaction, but it yielded high percentages of pure products.

This facial trichlorotris(trimethylphosphine)iridium complex was first synthesized by Shaw and coworkers as a by product in the synthesis of the meridional isomer <sup>9</sup> and secondly as the product of a photochemical isomerization. <sup>10</sup>



Figure 3.2 Synthesis of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> from [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl

Using water as our solvent, we have been able to prepare this complex in high yields, in the absence of light, with no evidence of the meridional product. There is an unusual stability for this facial product in water that was not observed previously.



**Figure 3.3** ORTEP drawing of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>

Figure 3.3 shows the ORTEP drawing based on the X-ray crystallography data that was obtained from the single crystal of the fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> complex. The structure clearly shows a facial arrangement of the chlorides and phosphines. On the average, the P-Ir-P bond angles were observed as 96° while the Cl-Ir-Cl bond angles were observed as 86°. These bond angles suggest that the facial arangement forces the bulkier PMe<sub>3</sub> to repel one another out of the ideal 90° angle. These PMe<sub>3</sub> ligands also forces the Cl to fit more closely angles which are smaller than the ideal 90° arrangement.

# 3.2.2 NMR spectroscopy of IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> in D<sub>2</sub>O

In both the meridonal and the facial isomers of the  $IrCl_3(PMe_3)_3$  complexes, we have found that Cl<sup>-</sup> is lost when dissolved in D<sub>2</sub>O. The <sup>1</sup>H NMR spectrum of the facial product shows a deceptive doublet. This doublet is believed to overlap another doublet which arises from the coupling of CH<sub>3</sub> protons to their adjacent phosphorus atoms which are trans to two bound D<sub>2</sub>O ligands. The other doublet arises from the coupling between the CH<sub>3</sub> protons and their adjacent phosphorus atom which is trans to a bound Cl. Attempts to separate the doublets by going to higher fields or lower temperatures proved unsuccessful in D<sub>2</sub>O.



<sup>1</sup>H NMR Spectrum of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> in  $D_2O$ 

The <sup>31</sup>P NMR spectrum for this species clearly show a doublet, a triplet , and a broad singlet. The doublet arises from two equivalent phosphorus atoms (trans to  $D_2O$ ) coupling one unequivalent phosphorus atom (trans toCl). The triplet arises from one phosphorus atom (trans to Cl) coupling two other phosphorus atoms (trans to  $D_2O$ ).

The broad singlet arise from  $[Ir(D_2O)_3(PMe_3)_3][Cl]_3$  where all phosphorus atom are equivalent.



The meridional complex in  $D_2O$  gave a different more straight forward spectra. In the <sup>1</sup>H NMR spectrum, there is an overlapping doublet and triplet. The doublet is assigned to CH<sub>3</sub> protons of PMe<sub>3</sub> coupling to their adjacent phosphorus atom which is trans to Cl. The triplet (virtual) arises from the CH<sub>3</sub> protons of PMe<sub>3</sub> coupling to their adjacent phosphorus atom and its trans phosphorus atom.



The <sup>31</sup>P NMR spectra shows a doublet, doublet of doublets, and singlet. The coupling assignments for these three are the same as for the facial isomer. The only difference is the chemical shifts for the various resonances.



# 3.2.3 Thermal Isomerization of mer-[IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>]

Mer-[IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>] isomerizes when heated in water. In the presence of NaCl this intermediate forms the facial product Figure 3.9 and 3.10 depict the <sup>1</sup>H NMR spectra which shows the isomerization of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> to fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. The spectra shows two doublets growing in at 1.61 ppm and 1.83 ppm. The two doublets have been assigned to the protons of one PMe<sub>3</sub> that is trans to a chloro ligand and the protons of two PMe<sub>3</sub> ligands that are trans to two aquo ligands. Therefore after two weeks, the proton NMR shows only the two doublets in a 2 to 1 ratio. This suggests that the structure for this species is fac-Ir(D<sub>2</sub>O)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub>.

This conversion is possible in the absence of light and is only observed when using aqueous hydrogen bonding solvents. We believe that the reaction is possible because the bound aquo ligands are labile and can produce five-coordinate transition states. The aquo ligand leaves the metal center and produces a five-coordinate transition state that has an equilibrium between two isomers: the square pyramidal and the trigonal bipyrimadal isomers. It is predicted that there is a small energy difference between these two five-coordinate transition states, therefore the equilibrium between the two isomers is rapid. In the course of the ligand substitution it may be possible that the constant shifting between the square pyramidal and the trigonal bipyramidal isomers can cause the formation of many different ligand substitution products.



Top to Bottom - <sup>1</sup>H NMR Spectrum of the Thermal Isomerization of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> to fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> top=1 Hour Heating Bottom=24 Hours Heating



**Figure 3.10** Top to Bottom - <sup>1</sup>H NMR Spectrum of the Thermal Isomerization of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> to fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> top=40 Hours Heating Bottom=2 weeks Heating

We have also noticed that the facial isomer does not form the meridonal isomer by heating in  $H_2O$ . We are actively involved in studying this transformation in order to obtain more insight on the aqueous chemistry of chloroiridic compounds. These results as well as results from other systems would suggest that there is an affinity for PMe<sub>3</sub> to be trans to aquo ligands. This argument supports the mechanism and would help explain why the facial complex does not undergo the same thermal isomerization.



### **Figure 3.11** Thermal Isomerization Pathway of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>

We also have entertained the idea that the facial product is the kinetic product of this reaction and its ability to easily crystallize out of aqueous medium produces the high yields of facial products that we have observed.

We have also modeled these complexes using the CACHE Molecular Modeling Package. The molecular mechanics optimization data reports that the facial isomer has a relative energy of 45.7 kcal/mol while the meridional isomer has a relative energy of 40.9 kcal/mol. This result was expected because of the steric effects that the facial isomer would produce by having three phosphines along the same face of the metal. We must take into consideration that the molecular mechanics optimization does not account for the trans influence or the ability for these complexes to undergo ligand loss. However, these relative values may be acceptable for steric considerations. Once again, our results show that the facial isomer can be easily obtained. This is probably due to the lack of steric energy difference that a five-coordinate transition state would produce for the water coordinated species.

# 3.2.3 Aqueous Chemistry of other [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>]<sup>2+</sup> Salts

In our attempts to understand the aqueous chemistry involved in the synthesis of the fac- $[IrCl_3(PMe_3)_3]$  we decided to use similar conditions to crystallize our  $[IrH(COD)(PMe_3)_3][BF_4][Cl]$ •HBF<sub>4</sub> complex. Using water as the solvent once again, we were able to isolate a single crystal from the reaction of water with complex (4).



Figure 3.12 Iridium Dimer Formation

Although the mechanisms of these reactions remain unknown, there are many observations that have been made. We have noticed that the cyclooctadiene is displaced in both cases. Attempts to identify the fate of the cyclooctadiene by analyzing the by

products of the reaction were unsuccessful but we believe that water may have help to catalyze its dissociation. Secondly, in the complex  $[IrH(COD)(PMe_3)_3][BF_4]_2$ •HCl, we have noted that the lack of chlorine contributes to the development of the facial product.

We believe that this bridged binuclear complex is formed and stable in water because of the lack of excess chloride anions. It is our opinion that the chloride anions act in a nucleophilic capacity to attack the iridium center and form the mononuclear complexes as seen in [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][Cl]<sub>2</sub>•2HCl . A lack of chlorines may cause these hydride salts to form the binuclear product in the presence of water. The low yields observed in these reactions in contrast to the previous reactions shows more evidence that the chlorines may have a role in the formation of complex (15). Therefore, It is predicted that three molecules [IrH(COD)(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>][Cl]•HBF<sub>4</sub> are needed in order to complete the reaction in Figure 3.6 and on the average, we have received yields of 20-30% for this reaction. Attempts to characterize the by-products of the reaction shown in Figure 3.6 have been unsuccessful.



Figure 3.13 ORTEP Drawing of Iridium Dimer Complex

# 3.2.5 Reaction Between Dicationic Salts and Lewis bases

Our attempts to crystallize  $[IrH(COD)(PMe_3)_3][BF_4]_2$  have proven unsuccessful. We noticed that by heating the complex in Lewis basic solution, we displace the COD ligand and can obtain the six-coordinate cyclooctadiene dissociation product with bonding to the Lewis basic solvents like acetonitrile, water, and methanol. We have also done the analogous reaction using  $[IrH(COD)(PMe_3)_3][BF_4][C1]$ •HBF<sub>4</sub> and have observed the same results.



Figure 3.14 Reaction of Dication Salts with Lewis Bases

We have also noticed that without a Lewis basic solvent there is no reaction when heated over extended periods. Therefore, it is believed that the solvent also plays an important part in the dissociation of the cyclooctadiene moiety in these complexes.

The <sup>1</sup>H NMR spectrum for complex (17) shows no signs of the COD ligand and in the hydride region, a doublet of triplet which arises from the coupling between the hydride and a meridional assemblage of PMe<sub>3</sub> ligands around the metal center.



Figure 3.15  $^{1}$ H NMR (Hydride Region) of [IrH(CH<sub>3</sub>CN)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> (17)

The triplet is a result of two equivalent cis phosphorus atoms coupling to the hydride and these triplets are again split into a doublet of triplets by the third inequivalent cis phosphorus atom coupling to the hydride.

The <sup>31</sup>P NMR spectrocopy for complex (17) shows a doublet and a triplet which is indicative of a meridional arrangement of the PMe<sub>3</sub> ligands around the metal center. The doublet arises from the coupling of two equivalent phosphorus atoms to one inequivalent phosphorus atom and the triplet is a result of the one inequivalent phosphorus atom being split by two equivalent phosphurus atoms . The products of these reactions, may prove useful in aqueous organometallic catalysis as well as the synthetic method used to make them.



Even though the COD moiety was not characterized after the reaction, it is possible that the olefin was more susceptible to nucleophillic attack because of its association with the more electrophillic metal center. Clark and Jones suggested that Ir(III) olefins are more susceptible to nucleophillic attack due to the donation of olefin p electons into metal orbitals.<sup>11</sup> Therefore, it is possible for the olefin to then be attacked by solvent and also substituted by solvent due to the weakening of its bonds. Over the course of the reaction, the COD ligand is expelled from the metal center and forms a coordinatively unsaturated complex which is attacked by the Lewis basic solvent.



Possible Mechanism for Lewis Base Attack on  $[IrHCOD(PMe_3)_3]X_2$ 

We have also noticed other atypical reactions when observing these protonated complexes. In DMSO, we have noticed that the complexes undergo rapid deprotonation. This can be attributed to the DMSO's ability to act as a base in the presence of the protonated metal complex.



Figure 3.18 Reductive Deprotonation of Ir(III) Dicationic Salt Using DMSO

# 3.2.6 Reactions of Iridium (III) Dications With Acetonitrile and Acetone

The reactivity of the complex (12) in solvents that are more Lewis basic are also complicated. Complex (12) undergoes reaction in acetonitrile as well as in acetone, whereby the trimethylphosphine ligand trans to the hydride dissociates from the metal center. The free trimethylphosphine ligand then reacts further to give several different products. One driving force for the initial dissociation of trimethylphosphine could be trans-labelizing effect that exists between the hydride and the trans phosphine.



**Figure 3.19** Major Product of Reaction Between [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> and Acetonitrile

X-ray crystallography data shows a bond lengthening of the Ir-P bond which is trans to the hydride. Once again, this bond length is about 0.1 Å longer than other Ir-P bonds that we have observed. Another factor could be an incoming solvent effect whereby these are intermediates structures that are trapped by good Lewis bases. Figure 3.19, 3.24, and 3.26 describe the formation of three major products caused by the dissociation of trimethylphosphine from the metal center.



<sup>1</sup>H NMR Spectrum of IrH(COE-4PMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN) (Complex 19) -Phosphine Region

A single crystal of complex (19) was harvested from the reaction mixture and was analyzed by NMR spectroscopy. Figure 3.20 clearly shows three doublets in the phosphine region of the <sup>1</sup>H NMR spectrum. These three doublets have been defined as the protons of the two PMe<sub>3</sub> groups coordinated to the metal at 1.69 ( $J_{H-P}=10.8Hz$ ) and d 1.73 ( $J_{H-P}=10.8Hz$ ) ppm. The two phosphines are inequivalent due to the s bonded COE ligand which was attacked by PMe<sub>3</sub> and changed it bonding from an <sup>2</sup> bound olefin to an <sup>1</sup> bound alkyl group. The third doublet at 1.38 ( $J_{H-P}=7.2Hz$ ) is due to the trimethyl phosphonium group bound to the COD ring. The assignments were made based on the chemical shift of the resonances. It is known that phosphines bound to transition metals tend to resonate more down field than free phosphines. In this case, we have two resonances which are downfield of a third resonance. We deduced that the third resonance was the trimethylphosphonium-cyclooctenyl protons and not one of the other PMe<sub>3</sub> protons.



Figure 3.21 shows the <sup>31</sup>P NMR spectrum of the same crystal. Again we have observed the presence of three doublets. Each inequivalent PMe<sub>3</sub> is represented by a doublet and the third phosphonium is also represented by a doublet. The splitting pattern for this species is quite complex. It was not expected that the phosphonium would couple with either of the PMe<sub>3</sub> ligands but seemingly there is a small coupling to one of the PMe<sub>3</sub> ligands possibly the PMe<sub>3</sub> (A) ligand trans to the s bound carbon of the COE ligand

shown in Figure 3.22. The  $PMe_3$  (A) coupling to the phosphonium may be incindentally overlapping with  $PMe_3$  (A) coupling to  $PMe_3$  (B). While the three phosphines have different chemical shifts, due to the variability of <sup>31</sup>P NMR spectroscopy, no assignments of these resonances were made.



Figure 3.22 Structure of IrH(COE-4PMe<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)

We first observed complexes (18), (19), and (20) via <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy 5 hours after dissolving complex (12) into acetonitrile. We also observed a similar reaction in acetone. The products from the acetone reaction however, evolved much more slowly than those from acetonitrile reaction. This is in agreement with what is expected from the Lewis base activities of these two solvents. It is expected that the acetonitrile would act as a better Lewis base than the acetone and therefore be able to trap more of the reaction intermediates by coordinating onto the metal center and inhibiting the metal center from undergoing further reactions

X-ray crystallographic data also shows that the phosphine is bound exo to the cyclooctenyl with respect to iridium. This suggests that the product is formed by an exo attack of the phosphine on the coordinated double bond of COD. If the PMe<sub>3</sub> were

bonded endo to the cycloctyenyl, it would have suggest that the phosphine underwent an endo attack (probably insertion into the metal olefin bond, which is endo, because of the need for a cis coplanar arrangement).



Figure 3.23

ORTEP Representation of data obtained from the X-ray Crystallography of a Single Crystal of Complex 19, the PMe<sub>3</sub> attacked Cyclooctadiene complex.

The evolution of complex (19) shown in Figure 3.22 is formed by the attack of  $[IrHCOD(PMe_3)_2(CH_3CN)][PF_6]_2$  (complex (20)) with free PMe<sub>3</sub>. Complex (20) was first observed in the NMR spectroscopy of the reaction 2 hours after dissolving complex (12) into acetonitrile. At this time, in the <sup>1</sup>H NMR spectrum, a triplet at -17.06 ppm was observed. This triplet was indicative of a hydride being cis to two PMe<sub>3</sub> Ligands and trans to a bound acetonitrile group. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, this complex gave rise to a singlet at -28.68 ppm. The singlet is consistent with a pair of chemically equivalent PMe<sub>3</sub> ligands.



### Figure 3.24

Postulated First step in the Formation of PMe<sub>3</sub> Attacked Cyclooctadiene Complex (19)

The inference can be made that Figure 3.24 depicts the first step of the overall reaction. The basis for this inference is that the X Ray crystallography suggests that the PMe<sub>3</sub> ligand attacks the COD from outside of the coordination sphere and not as an insertion. Eisenstein describe the nucleophilic attack on <sup>2</sup> alkene-metal complexes as a slippage pathway.<sup>12</sup> The slippage occurs changing the <sup>2</sup> alkene to a <sup>1</sup> complex which then undergo attack from the incoming nucleophile. In our case, the COD may have become more electropositive due to the initial loss of the basic PMe<sub>3</sub> ligand from the coordination sphere. This loss of a basic bonding ligand caused the metal to lose electron density and subsequent donation of electron density from the olefin caused the olefin to become more electrophilic. The olefin is then subject to attack from incoming nucleophiles. Roy showed that the COD ligand of the [Ir(COD)(DMPE)]Cl complex experiences a bond rearrangement while undergoing reaction with amino acids in water.<sup>13</sup> Roy's complex suggests that bisphosphine systems may react more readily toward bound olefins than trisphosphine systems. Hence, it stand to reason that if the first step in the reaction to form complex 19 is the formation of the bisphosphine

complex 20, then it is more likely that complex 20 can rearrange and accommodate the attack of PMe<sub>3</sub> more easily than a trisphosphine system.



Figure 3.25 Roy's COD Rearrangement Using [Ir(COD)(DMPE)]Cl

Indeed we have noted the same allyl rearrangement when dissolving  $[IrH(COD)(PMe_3)_3][OTf]_2$  in H<sub>2</sub>O. We were able to observe the formation of the complex 18, as shown in Figure 3.26, by X-ray crystallography.



**Figure 3.26** Formation of Complex (18) from (6).



ORTEP Drawing of Complex (18)

Although we have not proposed a mechanism for this species, it is evident that a  $PMe_3$  ligand is dissociated from complex (8) (possibly by the trans influence of the hydride) which makes the metal center less electron rich. Thus it is possible that an electron sink forms which forces the olefin of the COD ligand to rearrange and form the allyl complex.. In complex (18), we observe that  $PMe_3$  does not attack the cod as in the other cases.

A third product observed in the reaction between  $[IrHCOD(PMe_3)_3][PF_6]_2$  and acetonitrile was identified as  $[IrCOD(PMe_3)_3][PF_6]$ . Figure 3.28 depicts the possible equilibrium which leads to the formation of complex 19.



**Figure 3.28** Observed Product of Reaction Between PMe<sub>3</sub> and [IrHCOD(PMe<sub>3</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

Even though the reaction shown in Figure 3.28 produces a phosphonium cation, the equilibrium is completely dependent on the amount of PMe<sub>3</sub> that is produced in the reaction from Figure 3.24. The addition of excess trimethylphosphine to complex (12) as shown in Figure 3.28 caused the formation of the two products,  $[IrCOD(PMe_3)_3][PF_6]$  and HPMe<sub>3</sub>PF<sub>6</sub>. It was also determined that the addition of excess acid (HPF<sub>6</sub>) to the same reaction seemed to stabilize the reaction and inhibit the formation of  $[IrCOD(PMe_3)_3][PF_6]$  and HPMe<sub>3</sub>PF<sub>6</sub>.

While warming the reaction mixture shown in Figure 3.24 to 50 °C, we observe the formation of the  $IrH(PMe_3)_3(CH_3CN)_2$  complex. After further heating, the  $IrH(PMe_3)_3$  ( $CH_3CN)_2$  was the sole product of the reaction. As described in the previous section, this type of product is expected from the reaction with Lewis basic solvents. Once again no attempt to characterize the cyclooctenyl ligand was persued but it is believed that the ligand underwent reaction with the Lewis Basic solvent in order to facilitate its thermal ligation.

# **Experimental Section**

**General Procedures**. All reaction were carried out under an atmosphere of purified nitrogen. Toluene, ether, pentane were purchased from Fisher Scientific. Toluene was distilled from potassium benzophenone; methylene chloride was distilled from P<sub>2</sub>O<sub>5</sub>; ether and pentane were distilled over Na/K alloy. Water was deionized and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Hydoiridic acid was purchased from PGN Chemicals and was used as received. [Ir(COD)Cl]<sub>2</sub> was prepared using a method analogous to the literature procedure<sup>14.</sup> [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl (1) and [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> (7) was prepared as described previously.<sup>15</sup> Also, mer- IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> was prepared as described previously.

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WP200 SY spectrometer operating at 200.132 MHz for protons, 81.015 MHz for phosphorus, 67.925MHz for carbon, and Bruker WP360 SY spectrometer operating at 360.134 MHz for protons, 145.785 MHz for phoshorus, and 90.556 MHz for carbon. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia. Single crystal X-ray diffraction experiments were performed on a Siemens R3m/V diffractometer with SHELXTL-PLUS software as supplied by Siemens Corporation.

Synthesis of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> (15). Compound (2), (50 mg, 0.074 mmol) was placed into a 2 dram vial and dissolved into water (2.5 mL). The vial was allowed to sit in open air covered by a tissue while slowly evaporating . After 32 days, many crystals had formed. The crystals were then gently washed using acetone, dried , and stored in a 2 dram vial, charged with nitrogen gas. The product was characterized by <sup>1</sup>H and <sup>31</sup>P NMR and a suitable crystal was obtained and examined by single crystal X-ray diffraction. Elemental Analysis for C<sub>9</sub>H<sub>27</sub>Ir<sub>1</sub>P<sub>3</sub>C<sub>13</sub>: Anal. Calcd for: C, 20.52% H, 5.17% Cl, 20.19%. Found: C, 19.87% H, 5.32% and Cl, 19.43%.

<sup>1</sup>H <u>NMR</u> (D<sub>2</sub>O): 1.84( d,  $J_{H-P} = 10.0$ Hz, 27H, 3 PCH<sub>3</sub>).

<sup>31</sup>PNMR (D<sub>2</sub>O): -35.5 (d, 2P, 
$$J_{P-P} = 20.3$$
Hz, P trans Cl), -40.26 (s, 0.3P, P trans Cl in fac- IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>), -41.9 (dd, 1P,  $J_{P-} = 20.3$ Hz, P trans H<sub>2</sub>O).

The Thermal Isomerazation of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. A NMR tube was charge with (25 mg, 0.047 mmol) of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> and D<sub>2</sub>O (0.6mL). The tube was heated to 90 °C using a preheated oil bath. The reaction was followed by <sup>1</sup>H and <sup>31</sup>P NMR for many days. NaCl (100 mg) was added to the solution to help identify some of the water coordinated intermediates produced by the reaction.

# **0Hrs:**

<sup>1</sup>H NMR (D<sub>2</sub>O): 1.59 (vt, 12H, 
$$J_{H-P} = 3.5Hz$$
, PCH<sub>3</sub> trans to PCH<sub>3</sub>), 1.67 (dt, 9H,  
 $J_{H-P} = 10.8Hz$ , PCH<sub>3</sub> trans D<sub>2</sub>O), 1.80 (d, 12H,  $J_{H-P} = 10.8Hz$ ,  
CH<sub>3</sub>P trans Cl).

<sup>31</sup>PNMR (D<sub>2</sub>O): -29.5 (d, 2P, 
$$J_{P-P} = 16.0$$
Hz, P trans D<sub>2</sub>O), -32.6 (d, 1P,  $J_{P-P} = 16.04$ , P trans Cl), -36.22 (s, .2P, P trans Cl in mer- IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>, -38.9 (t, .5P  $J_{P-P} = 18.9$ Hz, P trans Cl ) -43.5 (dd , 1P,  $J_{P-P} = 17.9$ Hz,  $J_{P-P} = 21.8$ Hz, P trans D<sub>2</sub>O).

24Hrs:

 $D_2O$  in meridional complex)

# 3 Weeks:

<sup>1</sup>H<u>NMR</u> (D<sub>2</sub>O): 1.69 (d, 18H,  $J_{H-P}$ =10.0Hz, PCH<sub>3</sub> trans to D<sub>2</sub>O in facial complex), 1.89 (d,  $J_{H-P}$ , 1H, 10.0Hz, CH<sub>3</sub>P trans to Cl in facial complex).

<sup>31</sup>P<u>NMR</u> (D<sub>2</sub>O): -32.34 (d, 0.4P,  $J_{P-P} = 20.3$ Hz, P trans P), -35.44 (d, 2P,  $J_{P-P} = 19.4$ Hz, P trans to P in facial complex), -39.09 (s, 1.0P, P trans D<sub>2</sub>O in facial complex), -40.33 (s, 0.3P, P trans to Cl in facial complex), -41.74 (t, .1P,  $J_{P-P} = 17.8$ Hz, P trans D<sub>2</sub>O in meridional complex).

The Thermal Isomerazation of fac-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. A NMR tube was charge with Compound (15) (25 mg , 0.047 mmol) in D<sub>2</sub>O (0.6mL). The tube was heated to 90 °C using a preheated oil bath and the reaction was followed by <sup>1</sup>H and <sup>31</sup>P NMR. Over the period of 3 weeks, no observable change took place.

# 0 Hrs:

<sup>1</sup> H <u>NMR</u> (D <sub>2</sub> O):	d 1.84( d, J <sub>H-P</sub> =10.0Hz, 27H, 3 PCH <sub>3</sub> ).
<sup>31</sup> P <u>NMR</u> (D <sub>2</sub> O):	d -35.5 ( d , 2P, J <sub>P-P</sub> =20.3Hz, P trans Cl), -40.26 (s, 0.3P, P
	trans Cl in fac- $IrCl_3(PMe_3)_3$ , -41.9 (dd , 1P, $J_{P-P} = 20.3Hz$ , P
	trans H <sub>2</sub> O).

The Heating of  $[IrH(COD)(PMe_3)_3][BF_4]_2$  in CD<sub>3</sub>CN. Synthesis of Complex (17) A NMR tube was charged with complex (8) (25 mg, 0.035 mmol and CD<sub>3</sub>CN (0.75mL). The NMR tube was placed into an oil bath preset at 80 °C for 4 hours before being removed and observed by <sup>1</sup>H and <sup>31</sup>P NMR.

<sup>1</sup>H <u>NMR</u> (CD<sub>3</sub>CN): 1.72 (t, J<sub>H-P</sub>=7.2Hz, PCH<sub>3</sub> trans P), 1.75 (d, J<sub>H-P</sub> =14.4Hz, PCH<sub>3</sub> trans CD<sub>3</sub>CN), 1.94 (bs, 2H,aliphatic protons (uncoordinated COD)), 2.34 (bs, 4H, (uncoordinated COD) aliphatic), 5.54 (bs, 2H, olefinic protons (uncoordinated COD)).

# <sup>31</sup>P<u>NMR</u> (CD<sub>3</sub>CN): -37.5 (d, 2P, $J_{P-P}=25.9$ Hz, P trans P), -43.4 (t, 1P, $J_{P-P}=20.3$ Hz, P trans CD<sub>3</sub>CN).

The Heating of  $[IrH(COD)(PMe_3)_3][BF_4][Cl] \cdot HBF_4$  in CD<sub>3</sub>CN. A NMR tube was charged with  $[IrH(COD)(PMe_3)_3][BF_4][Cl] \cdot HBF_4$  (25 mg, 0.034 mmol). The white powder was dissolved into 0.75 mLs of d-CH<sub>3</sub>CN. The NMR tube was placed into an oil bath preset at 80 °C. The tube was allowed to sit for 4 hours before being removed and observed by <sup>1</sup>H and <sup>31</sup>P NMR.

<sup>1</sup>H NMR (CD<sub>3</sub>CN): 1.72 (t, 
$$J_{H-P}=7.2Hz$$
, PCH<sub>3</sub> trans P), 1.75 (d,  $J_{H-P}=14.4Hz$ ,  
PCH<sub>3</sub> trans CD<sub>3</sub>CN), 1.94 (bs, 2H,aliphatic protons  
(uncoordinated COD)), 2.34 (bs, 4H, (uncoordinated COD)  
aliphatic), 5.54 (bs, 2H, olefinic protons (uncoordinated COD)).  
<sup>31</sup>P NMR (CD<sub>3</sub>CN): -35.20 (d, 2P,  $J_{P-P}=21.9Hz$ , P trans P), -40.66 (t, 1P,  $J_{P-P}=21.9Hz$ , P trans CD<sub>3</sub>CN).

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# Chapter 4: The Synthesis and Characterization of Ir (III) Complexes for use as Polymerization Catalysts

# 4.1 Introduction

An important application of organometallic complexes is as catalysts in organic reactions. Though there are two types of transition metal catalysts, i.e. homogeneous and heterogeneous, heterogeneous catalysts have historically been the dominant type of catalyst used in the chemical industry. Homogeneous catalysts are an important part of many industrial processes. Homogeneous catalysts are typically organotransition metal complexes. Therefore, it is easy to modify these complexes in order to increase their selectivity, reactivity, and as we shall see, their active sites.

An important feature of homogeneous catalysis is that they have a well defined active site. In many cases these active sites are occupied by ligands which inhibit the reactivity of the catalysts. There are many ways to create and control open active sites on homogeneous catalysts. Caulton showed that it possible to create unsaturations in Os, Ir, and Rh complexes that allow these complexes to coordinate substrates and undergo further reactivity. <sup>1</sup>

As shown in Figure 4.1, Caulton proposed and demonstrated that acidolysis can be used to cleave donor ligands from a metal center and create reactive, unsaturated metal monocations that can be trapped by Lewis bases. <sup>2</sup> In his proposed mechanism, he describes a protonation of Ir(III) by a binary acid which forms an Ir(V) complex in the transition state. The Ir(V) complex undergoes a reductive elimination of HX to form an Ir(III) complex with that is coordinatively unsaturated. This complex can be trapped using a Lewis base to yield the [IrX<sub>2</sub>BP<sub>3</sub>] complex.

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Figure 4.1 Caulton's Acidolysis Proposal for Ir Complexes

Previously, Merola synthesized and characterized  $IrH_2Cl(PMe_3)_3$  and used it as a hydrogenation catalyst. In nonaqueous solvent, the complex is neutral and reacts slowly with olefins and acetylenes. In water, he found that the complex coordinates water and creates and open site which makes the complex far more reactive. This open site exists because the soft iridium metal center is bound to a hard oxygen atom-containing ligand. According to the hard and soft acids and bases rule, this mixture of a hard ligand with a soft metal will cause the ligand to be weakly coordinated.

We felt that it could be possible to create metal complexes with two open sites for coordination of substrates. We hoped that the extra open site could possibly enhance the activity of oligomerization and polymerization for these catalysts. Our plan was to synthesize complexes with weakly coordinating ligands and to exploit the water solubility of these Ir(III) complexes. There are many benefits to using the more environmentally friendly solvent, which include ease of separation of the products from the catalytic mixture, the ease of handling of the solvent, and the abundance of the solvent.

### 4.2 Results and Discussions

# **4.2.1 Iridium Methyl Complexes**

Ir(Me)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> is easily synthesized via Grignard reaction with Methyl Grignard Reagent.



Synthesis of fac-Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>

As shown in Figure 4.2, IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> is so stable that it can be treated under the same conditions as organic substrates. The reaction was worked up with water as a weak acid because stronger acids tended to cause the liberation of methane from the metal center which resulted in the formation of the undesired Ir(III) trication. Also, the reaction worked better using a toluene/THF mixture than using THF or toluene alone. When either solvent was used alone in this synthesis, low yields were observed. The reaction requires higher temperatures and better solubility in order to get an optimum yield.
$Ir(CH_3)_3(PMe_3)_3$ , complex (21), is a white powder that crystallizes easily upon evaporation in ether or pentane.



Figure 4.3 <sup>1</sup>H NMR Spectrum of Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>

In the <sup>1</sup>H NMR spectrum, a doublet at about 1.1 ppm ( $J_{H-P}=6.9$ Hz) and a multiplet at about 0.4 ppm(J<sub>H-Ptrans</sub>=10.8Hz, J<sub>H-Pcis</sub>=3.5Hz) are observed. The doublet is a result of the methyl's of three equivalent facial phosphines being coupled to the phosphine. The multiplet was a result of the protons on the methyl ligands being coupled to the phosphine trans to it as well as the two phosphines cis to it.



In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this compound, a singlet at -59.37 ppm is observed. This suggests that all three of the cis phosphines are chemically equivalent in the complex. Finally, in the <sup>13</sup>C spectrum of the complex, a multiplet at 16.82 ppm (J<sub>C</sub>. <sub>Pcis</sub>=12.4Hz, J<sub>C</sub>-Ptrans=118Hz) and a pair of doublet of doublets at -7.09ppm and -8.02ppm (J<sub>C</sub>-Pcis =28.0Hz, J<sub>C</sub>-Ptrans=372.0Hz) were observed. The doublet of doublet suggests that while the phosphines were chemically equivalent the methyls of the PMe<sub>3</sub> groups are not magnetically equivalent.



**Figure 4.4a** ORTEP Drawing for fac-Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> (21)

Figure 4.4a shows the X-ray crystal structure of the complex (21). The structure does not reveal any anomalies in the structure.

### 4.2.2 Synthesis of the Monomethyl Complexes

In order to create a complex with weakly coordinating ligands bound to the Iridium center, it became necessary to cleave two of the methyl groups away from the center using binary acids. The first acid that was tried was hydrochloric acid.



**Figure 4.5** Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> reaction with 2.1 Equivalents of HCl

As shown in Figure 4.5, the addition of 2 Equivalents of hydrochloric acid leads to the formation of the fac-IrCH<sub>3</sub>Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>. This compound was water-soluble. Based on similar chemistry with other complexes, it is believed that the water solubility of this complex arise from its ability to undergo ligand substitution between the chloro and aquo ligands. We have also noted that upon sitting in D<sub>2</sub>O for longer than 16 hours, complex (22) tended to lose its methyl resonance in the <sup>1</sup>H NMR spectrum. One explanation for this signal lose could be the formation of d<sub>1</sub>-Methanol and re-oxidative addition of D<sub>2</sub>O forming a deuteride complex in basic conditions. There were no observations made that would justify this argument because the methyl peaks in D<sub>2</sub>O tended to be broad even at 0 hours.



**Figure 4.6** Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> Reaction with 2.1 Equivalents of Triflic Acid

Using triflic acid to cleave two of the Methyl groups, we have been able to synthesize the  $IrCH_3(OTf)_2(PMe_3)_3$  complex as shown in (4).

The reaction produced the meridional isomer of the ditriflate complex. The fact that the ditriflate complex is meridional and the dichloro complex is facial in methylene chloride may suggest that the binding ability of ligand plays a role in the overall mechanism of the reaction. It may be possible that the triflate ligand is so weakly binding that it allows the trimethyl phosphine ancillary ligands to move about the iridium center, during the reaction, until the more stable product is formed. The opposite could be said about the cholride ligand, whereby it binds so strongly, that the facial complex alone is produced. The <sup>1</sup>H NMR spectroscopy of complex (23) shows



<sup>1</sup>H NMR Spectrum of IrCH<sub>3</sub>(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>



#### 4.2.3 Attempted Synthesis of the Dimethyl Complexes

Using the same methodology as in the monomethyl case, we have tried to make the dimethyl complexes with only one unsaturation on the metal center. These reactions were not successful. We have found that these reactions produced a great number of products including the ditriflate complexes and other unidentified complexes. This result may be due to the fact that trimethyl phosphine is the ancillary ligand involved.



(24b)

**Figure 4.9** Proposed Synthesis of [Ir(CH<sub>3</sub>)<sub>2</sub>(OTf)(PMe<sub>3</sub>)<sub>3</sub>]

Caulton and his group made and characterized  $[Ir(CH_3)_2(PMe_2Ph)_3(CH_3CN)]BF_4$  using  $Ir(CH_3)_3(PMe_2Ph)_3$  and  $HBF_4$ •Et<sub>2</sub>O in acetonitrile at low temperatures. They found it difficult to synthesize the monomethyl complexes using the same methodology. It is striking that we could not complete the same dimethyl reaction while using an analogous complex.



Figure 4.10 Caulton's Synthesis of [Ir(CH<sub>3</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (CH<sub>3</sub>CN)]BF<sub>4</sub>

In another case, Matthews and Merola showed that when using  $IrH_2Cl(PMe_3)_3$ , it is difficult to substitute the Cl ligand and exchange it for a more weakly coordinating ligand without the presence of H<sub>2</sub>O to act as an intermediary ligand. Matthew's attempts to complete the reaction of  $IrH_2Cl(PMe_3)_3$  with AgPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> may have produced the following structure.



Figure 4.11 Matthew's Iridium Chloro Dimer Complex.

The  $IrH_2Cl(PMe_3)_3$  complex is isolobal to the  $Ir(CH_3)_2Cl(PMe_3)_3$  complex, therefore, it could be possible that once the chloride ligand is exchanged for a triflate ligand, products similar to that of the chloro-dimer shown above can evolve. This could explain why it is so difficult to synthesize the  $[Ir(CH_3)_2(OTf)(PMe_3)_3]$  complex cleanly. This could also suggest that there is a difference in the reactivity of the trimethylphosphine complex versus the dimethylphenylphosphine complexes, although the reaction was not done in acetonitrile.

## 4.3 Iridium Hydride Complexes 4.3.1 Iridiumdihydridochloro Complex Synthesis

Previously, the Merola group described the synthesis and characterization of  $IrH_2Cl(PMe_3)_3$ . The complex was synthesized by the oxidative addition of dihydrogen gas using [IrCOD(PMe\_3)\_3]Cl.



<sup>1</sup>H NMR Spectraof IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub> - Hydride Region Hydride A (top) Hydride B (Bottom).

The complex is a Wilkinson's catalyst-like analogue with iridium as the central metal and trimethyl phosphine as the ancillary ligand. Figure 4.11 shows the hydride region of the <sup>1</sup>H NMR spectrum for the IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub> complex. As can be seen in Figure 4.12, the signals for the IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub> complex are found at -22.46 ppm ( $J_{H-P}$ =11HZ,  $J_{H-P}$ 

$$_{\rm H}$$
=5.6Hz) and -11.2 ppm (J<sub>H-Ptrans</sub> =135Hz, J<sub>H-P</sub>=22.2Hz, and J<sub>H-H</sub>=5.6Hz)

respectively. The splitting pattern for the resonance at -11.2 ppm (hydride A) show a doublet of triplets of doublets. The large doublet splitting is assigned to that of the trans phosphine coupling to the hydride. This large coupling (135Hz) is expected because of the trans influence of the phosphine on the hydride. There are also two other couplings, the coupling to the other cis phosphines to the hydride (22.2Hz) which give the triplet splitting pattern and the coupling to the other hydrideB to hydrideA (5.6Hz) giving a smaller doublet splitting pattern. There is also a resonance at -24.1 ppm (hydride B) which is assigned to the hydride which is trans to a chloride. This hydride shows a multiplet and the splitting pattern is due to coupling to the three cis phosphines to hydride B (11Hz) and also coupling of the cis hydride A to hydride B (5.6Hz). The NMR spectroscopy of this complex shows how essential the <sup>1</sup>H NMR spectrum can be in the determination of the structure of these iridium hydride complexes.

#### 4.3.2 The Synthesis and Characterization of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

We have also prepared the  $IrH(OTf)_2(PMe_3)_3$  using the same method-ology. Starting from the  $IrH_2Cl(PMe_3)_3$  complex. We have used hydrochloric acid to cleave the hydride from the metal center and produce  $IrHCl_2(PMe_3)_3$  as shown in Figure 4.13.



**Figure 4.13** Synthesis of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> via Acidolysis Using HCl and IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub>.

The complex has properties that are similar to those of the  $IrH_2Cl(PMe_3)_3$  complex. At low temperatures the reaction shown in Figure 4.10 proceeds cleanly. The dichloride complex NMR spectroscopy is similar to that of the dihydride complex. The <sup>1</sup>H NMR clearly shows a doublet and a triplet at 1.73 (J<sub>H-P</sub>=4.0) and 1.71 (J<sub>H-P</sub>=3.6Hz) respectively. The splitting is assigned to the PMe<sub>3</sub> protons that are cis to two other PMe<sub>3</sub> groups. The methyl protons are coupled to the adjacent phosphines which split the signal into a doublet. While the triplet splitting pattern is assigned to the PMe<sub>3</sub> ligand are coupled to the adjacent phosphine. This double coupling casues the formation of what is called a virtual triplet. The triplet is a result of the incidental overlap of the two doublets formed from the two separate couplings of equivalent phosphines.

There's a multiplet that is found at -22.46 ppm ( $J_{H-P}=14.0Hz$ ). The multiplet splitting pattern arise from the hydride which is trans to a chloride being coupled to three cis phosphines.



**Figure 4.14** <sup>1</sup>H NMR Spectrum of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> - Hydride Region.



Figure 4.15 <sup>31</sup>P NMR Spectrum of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

The <sup>31</sup>P{H} NMR spectrum for this complex shows a doublet at -41.14 ppm ( $J_{P-P}=21.1Hz$ ) and a triplet at -44.93ppm ( $J_{P-P}=20.3Hz$ ) integrated into a 2 to 1 ratio respectively. The doublet-triplet splitting pattern is indicative of a meridional complex. The doublet is a result of two equivalent trans phosphines being coupled to one phosphine cis to them. The triplet is the result of one phosphine being coupled to two cis phosphines.

We are also interested in the nature of this complex in water. Before carrying out these studies, we made a few predictions. The first prediction is that the reaction of this complex with water would be similar to  $IrH_2Cl(PMe_3)_3$  reaction with water. Therefore, we expect that chlorine would be substituted by water in this complex. The second prediction is that the complex is only water-soluble when a water molecule is bound to the metal center. Even with our predictions it is difficult to determine exactly what happened so we used the "salt effect" to help us better understand the chemistry involved. Our method was to dissolve complex (25) in D<sub>2</sub>O and observe it by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and then to add NaCl to the sample and observe the NMR spectroscopy again. If the first prediction is true, there should be an equilibrium between the water complex and the chloride complex which is based on the chloride concentration of the reaction. There are three logical equilibria that can be postulated for this reaction as shown below.



**Figure 4.16** Proposed Equilibria Based on the Salt Effect of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> in Water.



**Figure 4.17** <sup>1</sup>H NMR Spectra Showing the Effect of the Additionof NaCl to IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>. The Top Picture Shows the Hydride Region Before Salt Addition, the Bottom is After the Salt Addition.

Figure 4.17 show the hydride region of the <sup>1</sup>H NMR of the  $IrHCl_2(PMe_3)_3$  in D<sub>2</sub>O before and after the addition of NaCl. Though there are only two resonances at -22.7 ppm and -24.1ppm, it is expected that one resonance represents a hydride trans to oxygen and the other resonance represents a hydride trans to chloride. After the addition of NaCl, there is an abundance of the resonance at -24.1. Therefore it can be assumed that the NaCl added product (hydride trans to chloride) is indeed represented by the peak at -24.1ppm. Based on our knowledge of Ir(III) hydrides, it is indicative of the hydride trans to a chloride to have a chemical shift more upfield than a hydride trans to an oxygen in the <sup>1</sup>H NMR spectrum.

More dramatic is the difference in the <sup>31</sup>P NMR spectra observed during the "salt effect" reaction. The <sup>31</sup>P NMR spectrum clearly shows two sets of doublet triplet pairs which represent each complex. The first pair has a doublet at -30.8 ppm and a triplet at -44.0 ppm. The second pair has a doublet at -38.4 ppm and a triplet at -41.3 ppm. The before spectra shows the expected aqua complex as having its doublet at -30.8 ppm while the chloride complex having its doublet at -38.4 ppm. As expected the addition of salt increases the amount of the chloride complex in the solution. Upon addition, a precipitate is also noted which may be the insoluble dichloride complex.

Based on the second prediction, the complex should have an aqua group attached to the metal center in order to be soluble in  $D_2O$ . The fact that there are only two species observed in the NMR spectrum suggests that equilibrium #2 can be ruled out as a possible mechanism of this species. The second prediction, having been validated by the formation of a precipitate upon the addition of NaCl suggests that the equilibrium #3 can be eliminated as well. Equilibrium #1 is the more likely mechanism because it has only two species possible that are NMR observable.



Figure 4.18

<sup>31</sup>P NMR Spectra Showing the "Salt Sffect" by Adding NaCl to IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> in D<sub>2</sub>O. Top Picture is the Spectrum Before NaCl Addition and the Bottom is the Spectrum After the Additonof NaCl.

#### 4.3.3 Iridiumhydridoditriflate Complex Synthesis

Upon addition of silver triflate to the  $IrHCl_2(PMe_3)_3$ , we were able to obtain  $IrH(OTf)_2(PMe_3)_3$  by extraction with methylene chloride.



Synthesis of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> via Metastasis with AgOTf

Complex (26) was observed and characterized by NMR spectroscopy and chemical analysis. The <sup>1</sup>H NMR shows a doublet and a triplet in a 2: 1 ratio in the phosphine region. The doublet at  $1.82 (J_{H-P}=7.2Hz)$  ppm Is indicative of one PMe<sub>3</sub> ligands being cis to two equivalent PMe<sub>3</sub> ligands. The splitting pattern arises from the coupling between the PMe<sub>3</sub> protons coupling to the phosphine of PMe<sub>3</sub> ligand. The triplet at  $1.68 (J_{H-P}=4.2Hz)$  ppm is indicative of two equivalent PMe<sub>3</sub> ligands that are cis to another PMe<sub>3</sub> ligand. The splitting pattern arises from the coupling between the PMe<sub>3</sub> protons and the trimethyl phosphine, there is also a virtual coupling with the phosphorus trans to these protons. This coupling creates a virtual triplet.

The hydride region show a doublet of triplets at 29.28 ( $J_{H-P}=12.6Hz$ ) ppm. The splitting pattern arises from the hydride being coupled to two equivalent phosphines and one inequivalent phosphine. The chemical shift of the hydride suggests that the hydride is trans to an oxygen. We believe that the oxygen is that of the triflate anion. An

impurity resonance exists in the hydride region of the <sup>1</sup>H NMR at about -28 ppm. It is evident that the impurity is a hydride species whose resonance suggests that the hydride is trans to an oxygen also.



<sup>1</sup>H NMR spectrum for IrH(OTF)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

We believe that this species may be an acetone bound complex which came about from the workup of the triflate complex. We have made no attempt to fully characterize the impurity because we expect that it would have the same function as the catalyst i.e. it would act as a weakly coordinating anion and produce an open site for substrate coordination.



Figure 4.21 <sup>1</sup>H NMR Spectrum of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

The <sup>31</sup>P NMR spectrum shows a doublet and a triplet in a two to one ratio at - 25.31 ( $J_{H-P}$ =20.25) and -44.62 ( $J_{H-P}$ =20.25) ppm respectively. The doublet splitting pattern arises from two equivalent phosphines coupling to one inequivalent phosphine and the triplet splitting pattern arises from one inequivalent phosphine coupling to two equivalent phosphines. The <sup>31</sup>P NMR spectrum is indicative of a meridional arrangement of phosphines around the metal center.



<sup>31</sup>P NMR spectrum of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

The advantages that the ditriflate complex should hold over the dichloride complex is the ability of the triflate to act as a weakly coordinating ligand and more easily dissociate from the metal center. We believe that this weak ligand would provide a site that is open and active toward substrate coordination with no competition from other moieties. This also suggests that the ditriflate complex can be used in noncoordinating solvent such as methylene chloride whereby it would be substituted by incoming substrates exclusively. While the chloride complex is able to bind water, the presence of water and chloride anion in solution may act as inhibitors in the substrate coordination process. This phenomenon would tend to decrease the overall reactivity of the catalyst and subsequently yield to the formation of hydride elimination products. We were able to obtain a single crystal suitable for X-ray crystallography from the reaction. We have determined that even under anhydrous conditions, the crystal gathered water from either the solvent or the air. This suggests that the triflate ligands are weakly coordinated and that the open sites are reactive.



Figure 4.23 ORTEP Drawing of [IrH(D<sub>2</sub>O)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>][OTf]<sub>2</sub>

### 4.3.4 Iridium tristriflate Complex Synthesis

Another complex that we serendipitously prepared was  $Ir(OTf)_3(PMe_3)_3$ . We stumbled across this complex first while unsuccessfully trying to carefully add 2 equivalents of triflic acid to 1 equivalent of  $Ir(CH_3)_3(PMe_3)_3$ . We noted that the acidolysis could continue on to the tristriflate product if there were an excess of 3 equivalents of acid used in the reaction with  $Ir(CH_3)_3(PMe_3)_3$  as shown in Figure 4.24.



Figure 4.24

Synthesis of Ir(OTf)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> Using Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> and Triflic Acid.

We have since found that complex 27 can be synthesized easier by reacting three equivalents of silver triflate with mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> in acetone as shown in 4.25.



**Figure 4.25** Synthesis of Ir(OTf)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> Using Ir(Cl<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> and Silver Triflate.

We have observed that the tritriflate complex is only soluble in Lewis basic, polar solvents such as  $H_2O$ ,  $CH_3CN$ , acetone, and DMSO. The complex readily bound  $D_2O$  and we were able to observe it by <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR spectroscopy. The <sup>1</sup>H NMR spectrum shows a doublet at 1.93 ( $J_{H-P}=10.01$ ) ppm.



The doublet splitting pattern is assigned to of three PMe<sub>3</sub> ligands that are equivalent and cis to one another. This would also mean that the phosphines are in a facial arrangement around the metal center. Figure 4.27 shows the  ${}^{31}$ P NMR spectrum for Ir(OTf)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>. The <sup>31</sup>P NMR spectrum shows a singlet at 35.48 ppm. Again, this singlet is assigned to three PMe<sub>3</sub> phosphines that are equivalent along the same face of the metal.



## 4.3.5 Other IridiumHydrido Synthesis



 Table 4.1

 <sup>1</sup>H and <sup>31</sup>P NMR Spectroscopy Data for Synthesized Monohydride Ir(III) Complexes in Various Solvents

Ir(III) MonoHydrides	$^{1}\mathrm{H}$	<sup>31</sup> P trans	<sup>31</sup> P trans
Compounds	Hydride	Р	Х
IrH(PMe <sub>3</sub> ) <sub>3</sub> (Cl) <sub>2</sub>	-22.4 (dt)	-41.0p(d)	-44.9 p (t)
(CDCl <sub>3</sub> )			
$IrH(PMe_3)_3 (OTf)_2$	-29.1 (dt)	-24.8p (d)	-35.5p (q)
(CDCl <sub>3</sub> )			
$IrH(PMe_3)_3 (Cl)_2$	-22.4 (dt)	-39.4p (d)	-43.1p (t)
$(CD_2Cl_2)$			
$IrH(PMe_3)_3 (OTf)_2$	-29.3 (p)	-25.4p (d)	-44.6p (t)
$(CD_2Cl_2)$			
IrH(PMe <sub>3</sub> ) <sub>3</sub> (Allyl al)	not observed	-25.3(d)	-44.5(p)
$(CD_2Cl_2)$		-26.3(d)	
IrH(PMe <sub>3</sub> ) <sub>3</sub> (4-Pentenol)		-24.3 (d)	-41.5 (t)
$(CD_2Cl_2)$	-23.5 (q)	-25.4 (d)	-39.3 (?)
IrH(PMe <sub>3</sub> ) <sub>3</sub> (3-Butenol)	-10.4 (q)	-38.1p (dd)	-43.5(t)
$(CD_2Cl_2)$			
IrH(PMe <sub>3</sub> ) <sub>4</sub> OTf	-11.5(dq)	-41.3(t)	-58.3(d)
$(CD_2Cl_2)$	-23(dt)	-47.0(t)	-54.4(d)
		-46.8(s)	
IrH(PMe <sub>3</sub> ) <sub>3</sub> (Cl) <sub>2</sub>	-22.5(m)	-30.7(d)	-44.2(t)
( <b>D</b> <sub>2</sub> <b>O</b> )	-24.0 (m)	-38.5(d)	-41.5(t)

$IrH(PMe_3)_3 (OTf)_2$	-27.5 (m)	-26.7(d)	-44.4(t)
( <b>D</b> <sub>2</sub> <b>O</b> )			

Table 4.1 clearly shows that a trend develops in the <sup>1</sup>H NMR according which relates the chemical shift of the hydride with the sigma bonding capability of the ligand trans to it. This trans influence through the d-orbital of the metal and its effect on the chemical shift of the hydride is well established in our group using these type of complexes.

#### **Experimental Section**

**General Procedures**. All reaction were carried out under an atmosphere of purified nitrogen. Toluene, ether, pentane were purchased from Fisher Scientific. Toluene was distilled from potassium benzophenone; methylene chloride was distilled from  $P_2O_5$ ; ether and pentane were distilled over Na/K alloy. Water was deionized and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Hydoiridic acid was purchased from PGN Chemicals and was used as received. [Ir(COD)Cl]<sub>2</sub> was prepared using a method analogous to the literature procedure.

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WP200 SY spectrometer operating at 200.132 MHz for protons, 81.015 MHZ for phosphorus, 67.925MHz for carbon, and Bruker WP360 SY spectrometer operating at 360.134 MHz for protons, 145.785 MHz for phosphorus, and 90.556 MHz for carbon. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia. Single crystal X-ray diffraction experiments were performed on a Siemens R3m/V diffractometer with SHELXTL-PLUS software as supplied by Siemens Corporation.

#### Synthesis of IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub> (13)

A 50.0 mL three-necked flask equipped with a magnetic stir bar and a septum was charged with 2.00 g of  $[Ir(COD)(PMe_3)_3]$ Cl in a dry box. The flask was connected to a double manifold (vacuum/nitrogen) Schlenk line and 20.0 mL of mesitylene was added by syringe. The flask was fitted with a reflux column equipped with a nitrogen inlet and connected to the Schlenk line. Hydrogen gas was bubbled through the mixture at a slow rate and the suspension was stirred by magnetic stirrer and heated to about 100°C. Upon heating, the white solids dissolved and after 3 hours of heating, a light yellow color solution was observed. The solvent was removed under reduced pressure, and the resulting solids were washed three times with pentane to give white solids. The white solids were dried in vacuo to yield 2.13 g of (2) (4.65 mmol, 94.3 % yield).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -24.1 (m, 
$$J_{H-P} = 11Hz$$
,  $J_{H-H} = 5.6Hz$ , 1H), -11.2 (dtd,  $J_{H-Ptrans} = 135Hz$ ,  $J_{H-Pcis} = 22.2Hz$ ,  $J_{H-H} = 5.6Hz$ , 1H), 1.63 (t,  $J_{H-P} = 4.8$   
Hz, 18H of trans PMe<sub>3</sub>), 1.55 (d,  $J_{H-P} = 11.1Hz$ , 9Hz of cis PMe<sub>3</sub>).

$$\frac{{}^{31}\text{PNMR}}{(\text{CD}_2\text{Cl}_2)}: -40.72 \text{ (d, } J_{\text{P-P}} = 21.6\text{Hz}, 2\text{P of trans PMe}_3\text{), } -46.51 \text{ (t, } J_{\text{P-P}} = 21.6\text{Hz}, 1\text{P of cis PMe}_3\text{).}$$

 $\frac{^{13}\text{CNMR}}{^{13}\text{CNMR}} (\text{CD}_2\text{Cl}_2): \qquad 22.48 \text{ (t, J}_{C-P} = 66.3\text{Hz, 6C of trans PMe}_3\text{), 20.09 (d, J}_{C-P} = 104.2\text{Hz, 3C of cis PMe}_3\text{).}$ 

#### Preparation of fac-Ir(CH<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> (21). MAF.286

A 100 mL round Bottom side arm flask was charged with 1.5 g (2.85 mmol) of mer-IrCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> which was dissolved into 40 mL of benzene. A three molar methyl magnesiumbromide solution, 8.5 mL (25.6 mmol), was added to the flask and the mixture was refluxed for 3 hours. During this time, the color of the solution changed from yellow to white. The reaction was stopped and cooled in a 0 °C ice bath. The solution was hydrolyzed using a copious amount of distilled degassed water. The final product was extracted from benzene using a separatory funnel. The benzene layer was separated and dried using a vacuum. The reaction yielded 794 mg (60%) of product. The white product was collected and found to be  $Ir(CH_3)_3(PMe_3)_3$  based on the following observations:

<sup>1</sup>H NMR (
$$C_6D_6$$
): 1.1 (d, 27H,  $J_{H-P} = 6.9$ Hz, 3 cis PMe<sub>3</sub>), 0.4(m, 9H,  $J_{H-Ptrans} = 10.83$   
HZ,  $J_{H-Pcis} = 3.51$ Hz cis trimethyl phosphines).

<sup>31</sup>P NMR ( $C_6D_6$ ): -59.37(s, 3 equivalent cis P). <sup>13</sup>CNMR( $C_6D_6$ ): 16.82(m, 9C,  $J_{C-Pcis}=12.4Hz$ ,  $J_{C-Padj}=118Hz$ , 3 CH<sub>3</sub>P not magnetically equivalent), 7.56 (dd, 3C,  $J_{C-Pcis}=28Hz$ ,  $J_{C-Ptis}=372Hz$ , 3CH<sub>3</sub> trans to PMe<sub>3</sub> not magnetically equivalent).

#### Preparation of fac-IrCH<sub>3</sub>Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (22). MAF.324.

A 50 mL round bottom side arm flask was charged with 40.5 mg (0.087 mmol) of  $Ir(CH_3)_3(PMe_3)_3$  and dissolved in methylene chloride (20mL). The flask was equipped with a stirring bar and the solution was cooled to -78° C. A 37% solution of hydrochloric acid (15mL) was added to the flask and the reaction was allowed to continue for 16 hours. The color of the solution changed from a clear solution to a red solution. The solution was concentrated to dryness using a vacuum and the product was washed using diethyl ether (30 mL). The product was again dried and collected in 67% yield. The product was identified as fac-IrCH<sub>3</sub>Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> based on the following information:

$$\frac{{}^{1}\text{H NMR}}{^{1}\text{H NMR}} (\text{CD}_{2}\text{Cl}_{2}): 1.56 \text{ (d, 18H, J}_{\text{H-P}}=9.0\text{Hz, 1 cis PMe}_{3}\text{), 1.52(d, 9H, J}_{\text{H-P}}\text{, P}=7.3\text{Hz}\text{), 0.52(t, 3H, J}_{\text{H-P}}=5.6\text{Hz, methyl trans to OTf}\text{).}$$

$$\frac{{}^{31}\text{P NMR}}{^{31}\text{P NMR}} (\text{CD}_{2}\text{Cl}_{2}): -42.12 \text{ (d, 1P, J}_{\text{P-P}}=30.0\text{Hz, PMe}_{3}\text{ trans to CH}_{3}\text{), -42.41 (d, 2P, J}_{\text{P-P}}=17.0\text{Hz, 2 PMe}_{3}\text{ trans Cl}\text{).}$$

Preparation of mer-IrCH<sub>3</sub>(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (23). MAF.317

A 100 mL round bottom side arm flask was charged with 650 mg (1.396 mmol) of  $IrCH_3(PMe_3)_3$ . The white crystals were dissolved into 10 mL of  $CH_2Cl_2$  and the flask was equipped with a PEV funnel and a magnetic stirring bar. The solution was cooled to -78 °C using a dry ice-acetone bath while 255.90 ml (2.89 mmol) of triflic acid was dissolved into 40 mL of diethylether in the funnel. The triflic acid solution was dropwise added to the methylene chloride solution while the reaction was allowed to slowly increase in temperature. The reaction began to produce a precipitate while stirring. The reaction was stopped when the temperature equilibrated to room temperature and the precipitate was collected by filtration. The precipitate was washed using benzene and dried using a vacuum. The product was collected and identified as  $IrCH_3(OTF)_2(PMe_3)_3$  based on the following observations:

<u><sup>1</sup>H NMR</u> (CD <sub>2</sub> Cl <sub>2</sub> ):	1.56 (d, 9H, $J_{H-P}$ =11.6Hz, 1 cis PMe <sub>3</sub> ), 1.52(t, 18H, $J_{H-P}$
	$_{P}$ =4.0Hz), 0.52(t, 3H, J <sub>H-P</sub> =5.6Hz, methyl trans to OTf).
$3^{1}P$ NMR (CD <sub>2</sub> Cl <sub>2</sub> ):	-25.40 (d, 2P, J <sub>P-P</sub> =20.3Hz, equivalent trans PMe <sub>3</sub> ), 41.82 (t,
	1P, J <sub>P-P</sub> =14.6Hz, 1 cis PMe <sub>3</sub> ).
$\frac{13}{\text{CNMR}}$ (CD <sub>2</sub> Cl <sub>2</sub> ):	17.76(d, 3C, $J_{C-p}$ =43.5Hz, CH <sub>3</sub> P trans to OTf), 14.79 (t, 6C,
	J <sub>C-p</sub> =19.7Hz, 2 trans CH <sub>3</sub> P) 14.11 (t, 1C, J <sub>C-P</sub> =16.3Hz, CH <sub>3</sub> cis
	to 3 $PMe_3$ ).

#### Preparation of IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (25). MAF.420

A 100 ml round bottom side armed flask was charged with 540 mg (1.18 mmol) of  $IrH_2Cl(PMe_3)_3$ . The powder dissolved into dry methylene chloride and cooled to -78 °C using a dry ice-acetone bath. The solution was the treated with 1.24 ml (1.24 mmol) of HCl 1M in 30 ml of ether. The reaction was stopped after 1 hour of continuos stirring. The reaction produced a brown precipitate which was discarded by filtration. The

solution was dried using a vacuum and collected in the drybox. The reaction yielded 345 mgs (60%) of an off white product. The <sup>1</sup>H & <sup>31</sup>P NMR spectroscopy of the product was obtained and the identity of the product was determined to be mer-IrHCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> based on the following observations:

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -22.46 (dt, 
$$J_{H-p} = 14.0Hz$$
,  $J_{H-P}=20.0Hz$ , 1H, Hydride), 1.71 (t,  
 $J_{H-P} = 3.6Hz$ , 18H of trans PMe<sub>3</sub>), 1.73 (d,  $J_{H-P} = 4Hz$ , 9Hz of cis PMe<sub>3</sub>).

- $\frac{{}^{31}\text{PNMR}}{(\text{CD}_2\text{Cl}_2)}: -41.14 \text{ (d, } J_{\text{P-P}} = 21.1\text{Hz}, 2\text{P of trans PMe}_3\text{)}, -44.93 \text{ (t, } J_{\text{P-P}} = 20.3\text{Hz}, 1\text{P of cis PMe}_3\text{)}.$
- $\frac{^{13}\text{CNMR}}{^{13}\text{CNMR}} (\text{CD}_2\text{Cl}_2): 22.60 \text{ (d, } J_{\text{C-P}} = 41.7\text{Hz}, 3\text{C of cis PMe}_3\text{)}, 18.23 \text{ (t, } J_{\text{C-P}} = 19.9 \text{Hz}, 6\text{C of trans PMe}_3\text{)}.$

#### Preparation of IrH(OTF)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (26). MAF.365

A 25 mL round bottom side armed flask was charged with 787 mg (1.60 mmol) of  $IrHCl_2(PMe_3)_3$  and 904mg (3.52 mmol) of silver triflate. The mixture was dissolved in 15 mL of acetone and stirred using a stirring bar. After 2 hours, the reaction was stopped and the product was dried using a vaccuum. The solid product was extracted using  $CH_2Cl_2$  and filtered through dry Celite. The filtered solution was dried again using a vacuum and reprecipitated using  $CH_2Cl_2$  and diethylether. The precipitate was collected by filtration and dried using a vacuum. The reaction yielded 478 mg (41%) of product. The off white powder was observed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and found to be  $IrH(OTf)_2(PMe_3)_3$  based on the following observations:

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.82 (d, 9H, 
$$J_{H-P} = 7.2$$
Hz, cis P(CH<sub>3</sub>)<sub>3</sub>), 1.68 (t, 18H,  $J_{H-P} = 4.2$ Hz, trans P(CH<sub>3</sub>)<sub>3</sub>), -29.28 (dt, 1H,  $J_{H-P} = 12.6$ Hz, Hydride trans to OTf).

$$\frac{{}^{31}\text{P NMR}}{^{13}\text{C }\text{D}_2\text{Cl}_2):} = -25.31 \text{ (d, 2P, } J_{\text{P-P}} = 20.3\text{Hz, trans PMe}_3\text{), } -44.62 \text{ (t, 1P, } J_{\text{P-P}} = 20.3\text{Hz cis PMe}_3\text{).} = 20.3\text{Hz cis PMe}_3\text{).} = 20.3\text{Hz cis PMe}_3\text{).} = 17.28 \text{ (t, 6C, } J_{\text{C-P}} = 17.21\text{, trans Me}_3\text{P}\text{), } 21.44 \text{ (d, 3C, } J_{\text{C-P}} = 44.37\text{,} \text{cis Me}_3\text{P}\text{)}$$

#### Preparation of fac-Ir(OTf)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> MAF.234

A 50 mL round bottom flask equipped with a magnetic stirring bar was charged with  $Ir(CH_3)_3(PMe_3)_3$ , (0.227g, 0.49 mmol). The powder was dissolved in methylene chloride (25mL). The solution was cooled to -78 °C. Triflic acid (0.187 mL, 2.11 mmol) was added to the solution The solution began to bubble releasing CH<sub>4</sub> gas. The reaction color changed from colorless to a brown red solution. The reaction was allowed to continue for 16 hours. Afterwhich, the reaction was stopped and the complex was concentrated to dryness using a vacuum. The product was washed with  $Et_2O$  (40 mL) and dried again. The washed product was a white crystalline species. The complex was observed by <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR and was characterized as  $Ir(OTF)_3(PMe_3)_3$  based on the following data:

<u><sup>1</sup>H NMR</u> (D <sub>2</sub> O):	1.24 (d, 9H, $J_{H-P}$ =11.6Hz, 1 cis PMe <sub>3</sub> ), 1.19(t, 18H, $J_{H-}$
	$_{P}$ =4.0Hz), 0.52(t, 3H, J <sub>H-P</sub> =5.6Hz, Methyl trans to OTf).
<sup>31</sup> P NMR (D <sub>2</sub> O):	-59.37(s, 3 equivalent cis P).
$\frac{19}{\text{FNMR}}$ (D <sub>2</sub> O):	165(s, triflate anions not bound to metal)

#### Preparation of IrH(OTf)(PMe<sub>3</sub>)<sub>4</sub> (30). MAF.488

A NMR tube was placed into an argon filled drybox and charged with 33 mg (0.046 mmol) of  $IrH(OTf)_2(PMe_3)_3$ . The tube was taken out of the drybox and the solid was dissolved into 0.80 mL of CD<sub>2</sub>Cl<sub>2</sub>. 4.91 mL (0. 047 mmol) of PMe<sub>3</sub> was added to the tube. The reaction was observed by <sup>1</sup>H and <sup>31</sup>P NMR.

- $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (\text{CD}_{2}\text{Cl}_{2}): 1.91 \text{ (t, 18H, J}_{\text{H-P}} = 18.0\text{Hz, trans P(CH_{3})_{3}), 1.80 (s, 40.5 \text{ H,}} (CH_{3})_{3}\text{P equivalent}, 1.61 (d, 9\text{H, J}_{\text{H-P}} = 10.0\text{Hz, P(CH_{3})_{3} trans to} OTf), -12.54 (dq, J_{\text{H-Ptrans}} = 154.1\text{Hz, J}_{\text{H-Pcis}} = 14.0\text{Hz, Hydride} trans to PMe_{3}), -29.28 (dt, 1\text{H, J}_{\text{H-P}} = 14.0\text{Hz, Hydride trans to} OTf).$
- $\frac{{}^{31}\text{P NMR}}{(\text{CD}_2\text{Cl}_2):} = -25.31 \text{ (d, 2P, J}_{\text{P-P}} = 20.3\text{Hz, trans PMe}_3\text{), } -44.62 \text{ (t, 1P, J}_{\text{P-P}} = 20.3\text{Hz cis PMe}_3\text{).}$

## References

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# Chapter 5: The Reactivity of Some Ir(III) Monohydrides with Olefin Substrates

#### **5.1 Introduction**

For some time, the chemistry of the platinum metals have been centered around different modes of E-H activiation as well as the design of catalysts for use in hydrogenation, hydrosilation, and hydroformylation. Recently, some attention was focused on the use of cationic late metals and their reactivity to advance these different forms of catalysis. By using noncoordination solvents, Crabtree and coworkers are able to enhance the catalytic activity of the complex  $[M(Cod)L(py)]PF_6$ -(where M=Rh,Ir) toward alkene hydrogenation.<sup>1</sup>



Figure 5.1 Crabtree's Catalyst used to hydrogenate hindered olefins

Crabtree found that his complex catalyzed the hydrogenation of hindered olefins much better than did Rh analogs and Rh hydrogenation catalyst of that time. This suggests that the increased electron density of Ir, as compared to Rh, may have aided in those hydrogenations.

Beta elimation occurs more readily in late metals with more electron desity, hence, the catalytic chemistry of olefin polymerization and oligo-merization have been used primarily with early metals. Recently, Brookhart and coworkers have used cationic Pd(II) complexes to efficiently polymerize a multitude of olefin substrates.<sup>2, 3</sup>. Brookhart showed that it is possible to mimic the catalytic activity of Ziegler Natta Polymerization by using "coordinative polymerization" in his Pd system. Figure 5.2 shows Brookharts synthesis of a Pd species labelled (1). This complex (1) derives its activity from the fact that the Et<sub>2</sub>O group is a liabile ligand that easily undergoes substitution with incoming substrates to allow reaction to occur at the active site on the metal. This process is not reductive but instead leads to an insertion of an olefin or alpha olefin into the metal methyl bond to form oligomers and polymers.



**Figure 5.2** Brookhart's Pd PolymerizationCatalyst
Brookhart's group showed that its also possible to observe the same reactivity in Ni systems using MAO as a cocatalyst.



Figure 5.3 Brookhart's Nickel Catalyzed Polymerization

Figure 5.3 shows that the Nickel complex with a chelating diamine can undergo some of the same type of reaction as early Ziegler Natta catalysts with similar activity and steric control.

Others have examined group 9  $d^6$  cationic complexes having aryldialkylphosphine and macrocyclic amine ligands for use in oligomerization, but these have been found to have low activity.<sup>4, 5</sup>

The compounds  $IrHX_2(PMe_3)_3$  and  $IrCH_3X_2(PMe_3)_3$  have been synthesized and characterized. We have also used these complexes in reactions with Olefins, Acetylenes, and Solvents to determine if these complexes could be active as olefin polymerization catalysts.

# 5.2 Results and Discussion

#### 5.2.1 Transition Metal Catalyzed Olefin Polymerization Mechanisms.

The Cosee mechanism of transition metal catalyzed olefin polymerization is proposed for many transition metal catalyzed polymerization reactions including many Ziegler-Natta systems. The essential features of the mechanism are the formation of a metal alkyl complex followed by the rapid insertion of an olefin substrate into the metal alkyl bond. After the insertion, the process is repeated creating longer and longer polymer chains until chain termination occurs.



Process continues, then chain terminates.

# Figure 5.4

Mechanism for Cossee-Arlman Polymerization

In many cases the mechanism is dependent on the ability of the olefin to undergo insertion into the metal alkyl bond. Crabtree describes the process of olefin insertion catalysis using transition matals as being dependent on the ability of the olefin to coordinate to the metal center. <sup>6</sup> In late metal polymerization, where the coordination and

insertion of the olefin into the metal hydride bond is in competition with – hydride elimination, the ability of the metal to coordinate another equivalent of olefin substrate rapidly is important. -Hydride elimination (the opposite of insertion) is the process of creating a metal hydride and an olefin from a metal alkyl complex. The metal alkyl's – hydrogen must be coplanar with the metal and the metal must have an open site in order for the process to be completed. The process is the oppopsite of an alkene undergoing a 1, 2 insertion into a metal hydride bond.

There are a few ways to increase the ability of the metal to coordinate olefin substrates. Some of these ways involve the manipulation of the metal to accomodate the olefin substrates. Therefore, many researchers have used early metals in order to compete favorably with – hydride elimination. It is well known that early metals are oxophillic due to their hard nature and lack of electoron density. This translates into the fact that most early metals cannot be used in conjunction with olefins having Lewis Basic functionalities such as -OR, NR<sub>2</sub>, SR<sub>2</sub>, etc... In order to have use of olefins with these functionalities, it may be possible to use late metals for this purpose.

One way to reduce the propensity of a compound to undergo -hydride elimination is to make a metal complex which is coordinatively saturated upon formation of the metal alkyl. -hydride elimination will not occur if there are no open sites present on the metal center. Another way to bypass -hydride elimination is by changing the functionality of the incoming substrate so as to activate the olefin and make it more reactive. Again, Crabtree noted that olefins that are activated will bind more easily to metal centers. <sup>6</sup> An activated olefin is an olefin which has a group attached to it which causes the olefin to become more polar. The way that we hope to integrate these postulates into our chemistry is by using olefins that are so activated that they immediately bind to the metal center and insert into the metal hydride bond faster than - hydride elimination can occur.

## 5.2.2 Reaction between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and Allyl Alcohol

A brief look at the structure of allyl alcohol shows that it is an olefin which is activated by the inductive effects of the polar hydroxy group.



Figure 5.5 Structure of allyl alcohol

The electron density of the substrate is polarized toward the more electronegative oxygen atom and this imbalance cause a slight charge separation across the olefin. For this reason, we believed that a good starting point for our reactivity studies would be with allyl alcohol. Another characteristic that this substrate possesses is its water solubility. We are interested not only in developing late metal polymerization catalysts but also those which work with water as a solvent or cosolvent.

The reaction below was completed and the product was characterized as the aldehyde. The reaction was done in an air tight screw capped NMR tube and followed by NMR spectroscopy.



**Figure 5.6** Reaction between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and allyl alcohol

Subsequently, the above reaction, Figure 5.6, was also completed in a 2000: 1 substrate to catalyst ratio with water as the solvent in a high pressure tube heating to 85 °C. After distillation of the volatile low boiling products and seperation of all the different extracts, only a few products remained. The results, aside from the formation of more aldol condensation products, were the same. Its obvious that the aldehyde product was the result of the isomerization and eventual tautomerization of allyl alcohol. It is believed that once the aldehyde is formed, it can no longer react with the metal center.



## Figure 5.7

<sup>1</sup>H NMR spectra of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> reaction with 2000 equivalents of allyl alcohol at 0 hours (top), 24 hours (middle,) and 72 hours (bottom) at room temperature in d-CH<sub>2</sub>Cl<sub>2</sub>

The <sup>1</sup>H NMR spectra for the reaction clearly shows that the olefinic resonances from about 3.8 ppm to 6.8 ppm were decreasing in size while new aliphatic like peaks (triplet and quartet) grew into the spectra at about 0.75 - 2.5 ppm. The triplet at d 0.75 ppm is assigned to the CH<sub>3</sub> protons of acetaldehyde. The quartet at 2.25 ppm is assigned to the CH<sub>2</sub> protons of acetaldehyde. While the singlet at 9.51 ppm is assigned to the OCH proton of acetaldehyde. The B.P. and GC/MS data supports the structure that is assigned as the product for this reaction. We have used the data that we have collected from this reaction to propose the following mechanism.



**Figure 5.8** Proposed Mechanism of Allyl Alcohol isomerization using IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

As can be seen in the proposed mechanism, it is believed that the olefin coordinates to the metal center and immediately undergoes 1, 2-migratory insertion forming a metal alkyl complex. Afterwhich, the metal alkyl is subjected to – hydride elimination. All the steps of the mechanism are considered reversible until the decoordination step after the –hydride elimination. The isomerized alkene then undergoes tautamerization to form the unreactive aldehyde. The reformed metal hydride then repeats the process thus catalytically forming the aldehyde. The fact that the olefin coordinated preferentially in the presence of water suggests that the olefin was activated. The main problem was that the second olefin was unable to coordinate and insert faster than the process of –hydride eliemination upon the formation of the metal alkyl.

The reaction was also attempted in the presence of CO.



**Figure 5.9** Carbon Monoxide poisoning of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> in allyl alcohol

In the presence of CO, nothing happened. Unlike the reaction with water as the solvent, CO seems to bind more preferentially to metal center than the olefin. Therefore, because the olefin could not bind to the metal center, no reaction occured. The results suggests that the lack of open sites on the metal is responsible for the lack of reactivity. Therefore, it is believed that the reaction is not catalyzed by heterogenous particles in solution nor is it catalyzed by the presence of a charged species, but it can be reasoned that the reaction follows the given mechanism.

## 5.2.3 Reaction between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and other Alkene-ols.

IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was reacted with longer chained alkene-ols and the reactivity of these compounds are similar to that of allyl alcohol. Our hope was that the longer chain would help to inhibit the isomerization. It was reasoned that a longer chain would lower the inductive effects of the hydroxy group on the olefin. Although this would expectedly reduce the activity and thus the binding of olefin to the metal center, we also hoped that it would slow the "olefin walk" towards the hydroxy group. In one of the longer chained cases, 4-pentenol, the product was isomerized into the corresponding aldehyde.



Figure 5.10 Catalytic Isomerization of 4-Pentenol

After 16 hours or reaction, as shown in Figure 5.10, 4-pentenol started its "olefin walk". The "olefin walk" produced 3-pentenol, 2-pentenol, pentanal, and the aldol condenation product in a 1.0: 1.2: 4.3: 6.4 ratio, respectively, after 16 hours. This means

that after 16 hours, roughly 83% of 4-pentenol was isomerized to pentanal, while there was only 9 % and 8% of the 2-pentenol and 3-pentenol present respectively. The aldol condensation is expected because water tends to catalyze the reaction. The reaction was also completed in methylene chloride and it was showed that the reaction was faster in the noncoordinating solvent than in coordinating solvent. Therefore, it is believed that the reaction proceeded through the binding of the substrate into a catalyst open site. This suggests that the reaction followed the same mechanism as the allyl alcohol case.



<sup>1</sup>H NMR Spectroscopy of 4-Pentenol Reaction with IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub> After 24 Hours

The <sup>1</sup>H NMR spectroscopy for the reaction clearly shows the presence of more than one olefinic species in the region from d 4.0 to 6.0 ppm. The proton NMR also shows the existence of aldehyde products in small amounts.



 $^{13}\text{C}$  NMR of 4-Pentenol Reaction with IrH(OTf)\_2(PMe\_3)\_3 After 24 hours of Heating in CD\_2Cl\_2

The <sup>13</sup>C NMR spectrum also shows the emergence of two different olefin species as well as the presence of an aldehyde. The products were identified using the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and a percentage of the different isomers were quantified using the integration of the <sup>1</sup>H NMR spectra. Also GC/MS was completed using these mixtures.



Figure 5.13 GC/MS Data of 3-Pentenol



**Figure 5.14** GC/MS of the Products of Reaction Between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and 4-Pentenol (top) and NIST standard GC/MS for 4-Pentenol (bottom).

The GC/MS shows that the reaction product is no longer 4-pentenol but that it has similar MW. The GC/MS also shows the inclusion of higher MW products which could be due to the olefin dimerization or aldol condensation products present in the mixture. Using a simple distillation we were able to separate out three isomers from the mother liquor and examine those by <sup>1</sup>H and <sup>13</sup>C NMR. Based on the B.P. data for these compexes, we have confirmed the presence of these "olefin walk" products.

5-Hexenol was also used in an analogous reaction and similar results were noted. In this particular case, the use of water was a hindrance on the reaction because of the phase separation that was observed at the beginning of the reaction. Upon heating, the olefin became more soluble in water but it is expected that the rate of reaction was limited by the solubility of the olefin. As in the other examples, this reaction also underwent isomerization to hexanal.



Figure 5.15 Catalytic Isomerization of 5-Hexenol

After 16 Hours, there was roughly 40% 5-hexanal that was isomerized from 5hexenol. Compared with 4-pentenol after 16 hours, its obvious that the rate of reaction was much slower than that of allyl alcohol.



Figure 5.16 , shows the  ${}^{1}H$  NMR spectra of the reaction between 5 hexanol and  $IrH(OTf)_2(PMe_3)_3$  at 0 hours and 16 hours. Its clear that after 16 hours of reaction, there

are many products formed and all of the starting material was consumed. Just as in the 4-Pentenol case, there is a change in the olefinic region of the <sup>1</sup>H NMR spectrum. There is also the formation of new aliphatic protons as well as aldehyde formation. Those new resonances have been assigned to the isomerization and aldol condensation products.

There are two factors which could inhibit the isomerization. The first, the two phases, has already been discussed. The second was the decrease of the inductive effect of the hydroxy group. This decrease in the inductive would serve to lower the activity of the olefin and thus lessen the instance of binding to the metal center. In either case, these factors should help lead us to the conclusion that the reaction is definitely taking place at the metal center and not in a heterogenous or cationic fashion. This also leads us to the conclusion that one mechanism can be postulated for all of the alkenol case.



Figure 5.17

Generic Postulated Mechanism of the Isomerization of Alkene-ols using IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

The rates for the reaction of alkene-ol can have been roughly calculated using the relative integration of the products from <sup>1</sup>H NMR spectro-scopy over standard times.

Substrate Used	Turnover Rate •h <sup>-1</sup> of isomerization
Allyl Alcohol	4.3
3-Butenol	0.24
4-Pentenol	1.6
5-Hexenol	0.75

Table 5.1

Relative Rates of Isomerization of Alkene-ol s Using IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

From Table 5.1, we explain the data with various arguments about solubility and inductive effects. Once again another case of sterics vs electronics. However, there is one outlying point which we have neglected thus far. The reaction of  $IrH(OTf)_2(PMe_3)_3$  and butenol produced a rate that was impeded with respect to the other rates.

## 5.2.4 Reaction Between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and 3-Butenol.

As shown in the previous section, 3-butenol isomerization rate in the presence of  $IrH(OTf)_2(PMe_3)_3$  is not in line with those alkene-ols whose chain is longer and shorter than it. The reaction between  $IrH(OTf)_2(PMe_3)_3$  and 3-butenol was studied and we found that the reaction was

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# b **ited b** y the formation of a

а

ble product.

#### Figure 5.18

Reaction Between IrH(OTf)2(PMe3)3 and 3-Butenol

Figure 5.18 shows  $[IrH(^{2}CH_{2}CH(CH_{2})_{2}h^{1}O)(PMe_{3})_{3}]$  as the product of the reaction between  $IrH(OTf)_{2}(PMe_{3})_{3}$  with 3-butenol. It is believed that this product has a stability which may be due to the fact that it forms a 5 to 6 memberered ring. The strain energy of cyclopropane, cyclobutane, cyclopentane, and cyclohexane are 27.6, 26.4, 6.5, and 1.7 kcal/mol respectively.<sup>7</sup> This strain energies may help us to understand the unusal stability of complex (28). The ORTEP drawing of the complex shows that a 5 to 6 membered ring exists with a <sup>2</sup> bound olefin and the <sup>1</sup> bound O of the hydroxy portion of 3 butenol. Interestingly, the bond lengths of the bound 3-butenol complex do not show much difference than those of the free 3-butenol. Also, C(3) and C(4) on the ring structure has a more pronounced eliptical shape. We believe that this difference in size may be due to those carbon swaying back and fourth in a "swing like" fashion. Therefore it helps to prove that the molecule is indeed bound to the metal center.



Figure 5.19 ORTEP Drawing of [IrH( <sup>2</sup>CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>2</sub> <sup>1</sup>O)(PMe<sub>3</sub>)<sub>3</sub>] (Complex 28)

If we were to exclude the bonding from the d-orbitals of the metal, we could deduce that  $[IrH( {}^{2}CH_{2}CH(CH_{2})_{2} {}^{1}O)(PMe_{3})_{3}]$  derives its stability from the 5 to 6 membered ring that is formed. This would be similar to the cycloalkane case wereby the 5 and the 6 member rings would be considered more stable.

Another convient possibility for the stability of the [IrH( <sup>2</sup>CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>2</sub>

 $^{1}$ O)(PMe<sub>3</sub>)<sub>3</sub>] complex is hydrogen bonding between the hydroxy proton and the iridium hydride. Crabtree showed that hydrogen bonding can exist between hydrides and N-H and O-H groups. <sup>8</sup>



**Figure 5.20** Crabtree's Example of Hydrogen Bonding in Transition Metal Hydride Complexes

Crabtree prepared a series of complexes analogus to the one shown in Figure 5.20. He showed that these complexes have a H---H distance about 1.8 Angstroms. He also found that the J coupling from the NMR spectrum was between 2 and 4Hz. From the NMR data, he determined that the H-bond strength was about 4.3 +/- 0.8 kcal/mol.



 $\label{eq:Figure 5.21} Figure 5.21 \\ Hydride of [IrH( \ ^2CH_2CH(CH_2)_2 \ ^1O)(PMe_3)_3] from the ^1H \ NMR \ Spectrum$ 

We believe that we can rule out hydrogen bonding stabilization from the hydride to the O-H bond. In the <sup>1</sup>H NMR spectrum the J coupling is much greater than 2 to 4Hz. This would suggest that the hydride is not hydrogen bonding to another proton.

In the <sup>1</sup>H NMR spectrum of the reaction shown in Figure 5.21, we did observe a quartet at -10.39 ppm ( $J_{H-P}$ =18.0Hz). The quartet represented a hydride trans to an olefin and cis to three PMe<sub>3</sub> ligands. There was also a multiplet at 6.14ppm, a doublet at 5.34ppm, a triplet at 3.75ppm, a quartet at 2.36ppm, and a singlet at 1.95ppm. The multiplet at 6.14ppm represents the internal proton of the bound olefin and the doublet at 5.34 ppm represents the two external protons on the bound olefin. The triplet at 3.75 ppm represents the protons adjacent to the hydroxy group, the quartet at 2.36 ppm represents the protons adjacent to the olefin and the singlet at 1.95 ppm represents the proton of the bound of the singlet at 1.95 ppm represents the proton of the hydroxy group.



**Figure 5.22** Reaction between Complex 28 and 3-Butenol while heating at 64 °C: Synthesis of complex 29

We have also noted that by heating complex 28 in the presence of 3 butenol that another product evolves. We have postulated based on the chemical shift of the hydride that

there is an oxygen trans to it. In fact, we believe that the reaction follows the pathway shown in Figure 5.22.

We believe heating the solution causes the olefin to become more labile. So, 3-butenol is able to substitue for the olefin because of the Lewis basic lone pair on the oxygen atoms of 3 butenol. We also believe that the longer chain alkene alcohols go through this same binding pathway whereby the oxygen of the alcohol binds directly to the metal center. In fact, for the 4-pentenol case, we have observed a similar trans oxygen hydride at the beggining of the reaction. This is opposite from the allyl alcohol case whereby the olefin was bound directly to the metal center. These clues would suggest that for the alkene alcohols, as the olefin becomes further and further separated from the alcohol, the olefin becomes less and less activated. Consequently, two types of bonding exists for the alkene alcohols to the metal center and 3-butenol represents the intermediary case. The data also suggest that these reactions can be manipulated and controlled thermally. Thus the trend that these reactions should follow is that the higher the heat, the faster the reaction takes place.

### 5.2.5 IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> reaction with Styrene.

The use of styrene as a substrate is appealing for many reasons. Styrene is an olefin which is bound to a phenyl ring. The phenyl ring makes the olefin more activated thru resonance and inductive effects. The main drawback to the use of styrene is the lack of water solubility of the substrate.



Figure 5.23 Structure of Styrene

In the reaction between  $IrH(OTf)_2(PMe_3)_3$  and styrene, we have observed the formation of 1, 3 diphenylbutene. NMR Spectroscopy and GC/MS were used to determine the structure of this species.



Figure 5. 24 Reaction Between Styrene and (26) Producing 1,3-Diphenylbutene

Although the product was unexpected, its structure gave us clues about the mechanism through which the compound was made. Due to the fact that polymer was not made, we can rule out the formation of this complex through radical methods. Also, we have been able to make this compound thermally in the absence of light. The radical reaction would have produced polystyrene as shown below.



Figure 5.25 Radical initiation of styrene polymerization

From the structure that was obtained, we believed that the reaction was catalyzed by the metal and that the reaction took place on the metal center. We have proposed a mechanism for the oligomerization of styrene based on these facts. In the proposed mechanism, we believe that the first step is the coordination of the olefin onto the metal center via substitution of the weakly coordinated triflate anion. We are not sure weather or not two styrene substrates bind to the metal center at this time. We have proposed that the styrene cis to the hydride undergoes insertion into the metal hydride bond forming the 2- ethylbenzene bound product. The complex having a second bound styrene ligand then undergoes another insertion forming the 1,2 addition product. The 1,2 addition product can undergo -hydride elimination and form the styrene dimer which we have assigned as being the product of this reaction. Upon – hydride elimination the original ditriflate catalyst is reformed and



Figure 5.26 Proposed mechanism for the dimerization of Styrene

available to undergo reaction with more substrate following this reversible mechanism.



<sup>1</sup>H NMR Spectroscopy for the reaction between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and excess styrene a 0 hours (top), 8 hours (middle), and 32 hours (bottom).

From the <sup>1</sup>H NMR spectra shown in Figure 5.27, it is easy to see the slow dimerization of styrene to 1,3-diphenyl-butene. After 32 hours there is hardly any styrene olefin resonances to be found in the <sup>1</sup>H NMR while the doublet of the methyl group at 1.48 ppm is a great indicator for the presence of 1,3-diphenyl-butene.



# Figure 5.29

GC/MS of Reaction Between  $IrH(OTf)_2(PMe_3)_3$  and Styrene. The Top Spectrum Shows the NIST Standard for 1,3-Diphenyl-butene While the Bottom Spectrum Shows the Product of the Reaction.

From the GC/MS data, we have determined that the major product is 1,3diphenyl-butene. Figure 5.29 shows a comparison of the NIST standard of the 1, 3diphenylbutene vs the GC/MS data from the major component of our reaction. The comparison shows that the two spectra are almost identical.



GC/MS of a Minor Product of the Reaction Between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and Styrene

We have speculated the existence of some trimer species based on the GC/MS of some of the minor products of the reaction between  $IrH(OTf)_2(PMe_3)_3$  and styrene. The presence of the peak at 312, as shown in Figure 5.30, on a few of the major MS spectra convinced us that some trimer may exist. Although we have not proposed a structure for the trimer, it is possible that with longer reaction times and higher temperatures, the dimer structure could duplicate the same reaction pattern as the monomer did.

## 5.2.6 Reaction Between IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and Other Olefins

In an attempt to polymerize an olefin substrate, we turned our attention to acylamide and acrylic acid.





Acrylamide

Acrylic Acid

Figure 5.31 Structure of Acrylimide and Acrylic Acid

Our hope was that the olefins would be activated by the adjacent amide or carboxyllic acid and their electron withdrawing abilities. We also hoped that the reaction could be done in water because of the good solubility that both of these substrates possess. We used the catalyst in 1:200 and 1:2000 molar ratio with each olefin substrate. As shown in Figure 5.32, we believe that we formed a polymer.



Where R=NH<sub>2</sub> or OH

## Figure 5.32

Polymer Catalysis Using IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and Acrylic Substrates

We do not have any characterization of the polymer due to the fact that it crosslinks and forms a very viscous gel which has water trapped in the lattice. Upon removal of the water by thermal dehydration a solid crosslinked polymer is formed and we have yet to find a solvent or solvent system in which these polymers are soluble. We have attempted the reaction in the absence of catalyst to find that no reaction took place. Thus, we believe that  $IrH(OTf)_2(PMe_3)_3$  and  $IrHCl_2(PMe_3)_3$  were responsible for the polymerization of these substrates.

We have also studied the reaction between  $IrH(OTf)_2(PMe_3)_3$  and allyl ethers. Once again, we were interested in the allyl ethers because of their good water solubility. We were also motivated to use allyl ethers because unlike many other olefin substrates, are not susceptible to cationic/anionic polymerization. We felt that it was important to determine if these polymerizations took place on the metal center or if they were a result of a charged species being in the presence of olefins that undego cationic/anionic polymerization.



Where R=phenyl or ethyl

Figure 5.33 Polymerization of AllylEthers

The reactions between  $IrH(OTf)_2(PMe_3)_3$  and the allyl ethers were rapid relative to other catalysis we have attempted using  $IrH(OTf)_2(PMe_3)_3$ . We determined that the reaction produced many aliphatic species and loss all of it olefinc species over the period of minutes.



## Figure 5.34

<sup>1</sup>H NMR Spectroscopy of Polymerization of Allylphenyl Ether: 0 Hour (Top) and 72 Hours (Bottom)

The proton NMR shows that the olefinic region of the proton NMR disappears and an aliphatic region of the NMR produces many different resonances. The same trend is noted in the <sup>13</sup>C NMR spectra for this reaction. Although no conclusive proof of polymerization or polymer structure was ascertained from this reaction due to the messy spectra, the fact that the olefin resonances disappeared and the aliphatic peaks reappeared and the favorable mass spectometry data suggest that at the least oligomerization of the olefins took place.

We determined that in the absence of catalyst, no reaction took place. Finally, we completed the reaction in the presence of hydroquinone in order to determine if the polymerization was a radical initiated process. In the presence of hydroquinone, we observed that the reaction was sluggish. We concluded that either the Ir(III) system is a radical initiator or that the hydroquinone competed with the substrate and was able to bind to the metal center.

We also used vinyl acetate in the reaction with  $IrH(OTF)_2(PMe_3)_3$  as shown in Figure 5.35.



**Figure 5.35** Vinyl Acetate Reaction with IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

This reaction produced no product and over a period of serveral days, no change took place. We believe that it may be possible that the resonance contributions, shown in Figure 5.36, may have thwarted our efforts.



Figure 5.36 Resonance Contributions of Vinyl Acetate

It is possible that the resonance contribution from the charge separation products could help make the oxygen atom of vinyl acetate more Lewis basic. A strongly Lewis basic oxygen could then proceed to bind to the metal center and inhibit any reaction that might take place.

Finally, we used ethylvinylether in reaction with  $IrH(OTf)_2(PMe_3)_3$  as shown in Figure 5.37



**Figure 5.37** Ir H(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> Catalyzed Polymerization of Ethylvinyl Ether

Unlike the allyl ethers, the vinylethers are not expected to undergo radical initiation. Upon addition of the ethylvinylether to a catalyst solution, we observed rapid reaction. The NMR spectroscopy for this reaction clearly shows that the olefinicproton resonances dissappeared and followed by the emergence of aliphatic proton resonances. Just as in the allyl ether, there is the possibility of the reaction taking a different pathway but we don't have enough evidence to support or deny our claim in this particular area.

We carried out an analogous reaction in water only to find the hydrolysis products as shown in Figure 5.38.



**Figure 5.38** Hydrolysis of Vinylethylether in the Presence of IrH(OTf)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

The results suggests that polymerization in water may not be viable for these systems due to the competetion and reactivity that water provides.

# **Experimental Section**

**General Procedures**. All reaction were carried out under an atmosphere of purified nitrogen. Toluene, ether, pentane were purchased from Fisher Scientific. Toluene was distilled from potassium benzophenone; methylene chloride was distilled from P<sub>2</sub>O<sub>5</sub>; ether and pentane were distilled over Na/K alloy. Water was deionized and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Allylethylether, allylphenylether, vinylethylether, vinyl acetate, styrene, 3-butenol, 4-pentenol, 5-hexenol, and allyl alcohol were purchased from Aldrich Chemical Company and used as recieved. The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WP200 SY spectrometer operating at 200.132 MHz for protons, 81.015 MHZ for phosphorus, 67.925MHz for carbon, and Bruker WP360 SY spectrometer operating at 360.134 MHz for protons, 145.785 MHz for phoshorus, and 90.556 MHz for carbon. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia. Single crystal X-ray diffraction experiments were performed on a Siemens R3m/V diffractometer with SHELXTL-PLUS software as supplied by Siemens Corporation.

#### **Reaction between Complex 26 and Allyl Alcohol in H<sub>2</sub>O.**

A thick walled reaction tube was charged with 52 mgs (0.069 mmol) of complex 26 and dissolved in water (4 mL). Allyl alcohol (4.3mL, 88.77 mmol) was added to the tube. The reaction was heated to 64 °C. After 3 days, the reaction produced two seperate layers, an aqueous layer and an organic layer. The organic layer was seperated using a seperatory funnel and distillation seperated the products. The products were observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy using d-chloroform and the mother liquor was

compared to the distilate. Our finding were that in both cases, the product was the same. Chloroform was used to seperate any organic product from the water and the results yielded the catalyst and byproducts thereof. We have described the complex as acetaldehyde based on the following information.

 $^{1}$ HNMR (CD<sub>2</sub>Cl<sub>2</sub>):9.40 (s, 1H, aldehydic proton adjacent to carbonyl), 1.96 (q, 2H,<br/>J<sub>H-H</sub>=7.2Hz CH<sub>2</sub> adjacent to CH<sub>3</sub>), 0.59 (t, 3H, J<sub>H-H</sub>=7.2Hz<br/>CH<sub>3</sub> adjacent to CH<sub>2</sub>).

## Reaction between Complex 26 and Allyl Alcohol in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 26 mgs (0.033 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). Allyl alcohol (0.070ml, 1.02 mmol) was added to the tube. The reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

<sup>1</sup><u>H NMR</u> (CD<sub>2</sub>Cl<sub>2</sub>): 9.28 (s, 5H, aldehydic proton adjacent to carbonyl), 1.96 (q, 2H, J<sub>H-H</sub>=7.2Hz CH<sub>2</sub> adjacent to CH<sub>3</sub>), 1.20 (bm, 3.6H, Iridium catalyst), 0.59 (t, 3H, J<sub>H-H</sub>=7.2Hz CH<sub>3</sub> adjacent to CH<sub>2</sub>), 0.446 (bm, 2.4H, iridium catalyst).

 $\frac{^{13}\text{CNMR}}{^{10}\text{CNMR}} (\text{CD}_2\text{Cl}_2): \quad \text{d} \ 105.98 \text{ (s)}, \ 62.84 \text{ (s)}, \ 59.75 \text{ (s)}, \ 28.56 \text{ (s)}, \ 20.07 \text{ (s)}, \ 16.98 \text{ (s)}, \ 10.58 \text{ (s)}.$ 

## Reaction between Complex 26 and 3-Butenol in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 27 mgs (0.036 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). 3-Butenol (0.092ml, 1.08 mmol) was added to the tube. The reaction was observed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy over a period of several days and the following observations were made:

$^{1}$ <u>H NMR</u> (CD <sub>2</sub> Cl <sub>2</sub> ):	1.87 (q, 1H, $J_{H-P}$ = 2Hz, 18H, PMe <sub>3</sub> trans to PMe <sub>3</sub> ), 1.69 (d, 9H,
	$J_{H-P}=10HzHz$ , PMe <sub>3</sub> cis to two equivalent phosphines), 1.49 (m,
	2H,), -10.36 (q, 1H, $J_{H-P}$ =18.6Hz, hydride cis to 3 phosphines),
$\frac{^{31}\text{PNMR}}{(\text{CD}_2\text{Cl}_2)}$ :	-38.96 (dd, 2P, $J_{P-P}$ =59.9Hz, $J_{P-P}$ =13.8Hz, PMe <sub>3</sub> trans to
	PMe <sub>3</sub> ), -44.02 (t, J <sub>P-P</sub> =13.8, PMe <sub>3</sub> cis to 2PMe <sub>3</sub> ).

## Reaction between Complex 26 and 4-Pentenol in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 28 mgs (0.039 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). Allylethylether (0.040ml, 0.39 mmol) was added to the tube and a vigorous reaction took place. The reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

<sup>1</sup> HNMR (CD <sub>2</sub> Cl <sub>2</sub> ):	4.36 (t, 1H, $J_{H-H}$ =3.6Hz), 3.63 (q, 8H, $J_{H-H}$ =7.2Hz), .58 (q,
	6H, J <sub>H-H</sub> =7.2Hz), 3.46 (q, 4H, J <sub>H-H</sub> =7.2Hz), 3.43 (q, J <sub>H-</sub>
	$_{\rm H}$ =7.2Hz), 2.16 (s, 6H), 1.16 (q, 39H, J $_{\rm H-H}$ =10.8Hz, CH <sub>2</sub>
	adjacent to $CH_3$ and O), 0.88 (t, 54H, $J_{H-H}$ =10.8Hz, $CH_3$ adjacent
	to $CH_2$ ).
$\frac{13}{\text{CNMR}}$ (CD <sub>2</sub> Cl <sub>2</sub> ):	105.98 (s), 62.84 (s), 59.75 (s), 28.56 (s), 20.07 (s), 16.98 (s),
	10.58 (s).

## Reaction between Complex 26 and Allylethylether in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 31 mgs (0.043 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). Allylethylether (0.122ml, 1.077 mmol) was added to the tube and a vigorous reaction took place. The reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

# 10.58 (s).

## Reaction between Complex 26 and Allylphenylether in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 31 mgs (0.043 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). Allylphenylether (0.148ml, 0.1077 mmol) was added to the tube and a vigorous reaction took place. The reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

$$\begin{array}{ll} \underline{^{1}\text{H NMR}} \ (\text{CD}_{2}\text{Cl}_{2}): & 7.26 \ (\text{t}, \ 10\text{H}, \ \text{J}_{\text{H-H}} = 7.2\text{Hz} \ \text{meta protons}), \ 6.95 \ (\text{t}, \ 5\text{H}, \ \text{J}_{\text{H-}} \\ & \\ & \\ & \\ & \\ H = 7.2\text{Hz}, \ \text{para protons}), \ 6.88 \ (\text{d}, \ 10\text{H}, \ \text{J}_{\text{H-H}} = 7.2\text{Hz}, \ \text{ortho} \\ & \\ & \\ & \\ & \\ protons), \ 5.8 \ (\text{s}, \ 6\text{H}), \ 1.86\text{-}1.62 \ (\text{m}, \ 20\text{H}), \ 1.16\text{-}0.94 \ (\text{m}, \ 24\text{H}). \\ \hline \\ & \\ \underline{^{13}\text{CNMR}} \ (\text{CD}_{2}\text{Cl}_{2}): \ \ \text{d} \ \ 157.75 \ (\text{s}, \ \text{ipso carbon}), \ 131.56 \ (\text{s}, \ \text{phenyl carbon}), \ 122.43 \ (\text{s}, \ \text{phenyl carbon}), \ 117.22 \ (\text{s}, \ \text{phenyl carbon}), \ 40\text{-}15 \ (\text{m}, \ \text{aliphatic carbons}). \end{array}$$

## Reaction between Complex 26 and Ethylvinylether in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 31 mgs (0.043 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). EthylVinylether (0.106ml, 1.077 mmol) was added to the tube and a vigorous reaction took place and the color of the reaction changed from clear to dark brown within seconds. The reaction was observed by <sup>1</sup>H and
<sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

 $^{1}$ H NMR (CD<sub>2</sub>Cl<sub>2</sub>):3.493 (bm, 20H), 1.57 (bm, 7H), 1.18 (bm, 20.9H). $^{13}$ CNMR (CD<sub>2</sub>Cl<sub>2</sub>):74.16 (s), 64.37 (q, J<sub>C-C</sub>=20.88), 41.59 (m), 40.14 (m), 15.94 (d, J<sub>C-C</sub>=30.79).

#### Reaction between Complex 26 and Ethylvinylether in D<sub>2</sub>O.

A screw capped NMR tube was charged with 31 mgs (0.043 mmol) of complex 26 and dissolved in d-H<sub>2</sub>O (0.5mL). Ethylvinylether (1.3ml, 11.02 mmol) was added to the tube. Ethylvinylether showed slight solubility at the beginning of the reaction so the tube was heated to 84 °C. As the reaction continued the aqueous and the organic layers began to dissappear. The reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of several days and the following observations were made:

 1 + NMR (CD<sub>2</sub>Cl<sub>2</sub>):
 9.61 (s, aldehyde proton), 3.56 (q, 2H, J<sub>H-H</sub>=7.2Hz, CH<sub>2</sub>

 adjacent to CH<sub>3</sub>), 1.23 (t, 3H, J<sub>H-H</sub>=7.2Hz, CH<sub>3</sub> adjacent to CH<sub>2</sub>).

  $1^{3}CNMR$  (CD<sub>2</sub>Cl<sub>2</sub>):
 220 (s, aldehyde CO), 59.81 (s, CH<sub>2</sub> adjacent to CH<sub>3</sub>), 18.76 (s, CH<sub>3</sub> adjacent to CH<sub>2</sub>).

#### Reaction between Complex 26 and Vinyl Acetate in CD<sub>2</sub>Cl<sub>2</sub>.

A screw capped NMR tube was charged with 31 mgs (0.043 mmol) of complex 26 and dissolved in d-methylene chloride (0.75mL). Vinyl acetate (0.102ml, 1.077 mmol) was added to the tube and no reaction took place. The tube was heated to 64 °C and the reaction was observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy over a period of three weeks The color of the solution and the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy did not change during the course of the reaction.

# $\frac{^{1}\text{HNMR}}{^{1}\text{HNMR}} (\text{CD}_{2}\text{Cl}_{2}): \qquad 6.38 \text{ (d, 2H, J}_{\text{H-H}}=7.2\text{Hz}), 6.13 \text{ (d, 1H, J}_{\text{H-H}}=3.6\text{Hz}), 6.09 \text{ (d,} \\ 1\text{H, J}_{\text{H-H}}=3.6\text{Hz}), 5.81 \text{ (d, 2H, J}_{\text{H-H}}=7.2\text{Hz}), 3.73 \text{ (s, 6H)} \\ \frac{^{13}\text{CNMR}}{^{13}\text{CNMR}} (\text{CD}_{2}\text{Cl}_{2}): \qquad 168.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 132.2 \text{ (s, internal olefin protons)}, 130.1 \text{ (s,} \\ 180.3 \text{ (s, Carbonyl)}, 180.3 \text{ (s, Carbonyl)$

external olefin protons), 53.29 (s, OCH<sub>3</sub>).

**Reaction between Complex 26 and Acrylamide in H<sub>2</sub>O.** A thick walled reaction tube was charged with 28 mgs (0.039 mmol) of complex 26 and dissolved in distilled, degassed water (8.0 mL). Acrylimide (5.52 g, 77.66 mmol) was added to the tube and the tube was fitted with a teflon screw top equipped with an O-ring. The tube was heated to 84 °C for 24 hours. After 24 hours, the tube was open and a viscous gel was removed from the tube. The product was examined by <sup>1</sup>H and <sup>13</sup>C NMR but it was determined that water was trapped in the lattice and it created a large peak which drowned out all of the signals present. An attempt to removed the water using a drying oven was successful but it produced a solid (hard crosslinked polymer) that was insoluble in all of the common solvents available.

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### **Chapter 6: Conclusions and Future Work**

The studies carried out in this dissertation were aimed at developing active dicationic catalyst for use in oligomerization and polymerization. We set out to develop a Ir(III) complex with sites of unsaturation that could be used to coordinate olefins which could undergo further reactive on the metal center. We used different weakly coordinating ligands in an effort to determine if the reaction would proceed more readily with these ligands than with ligands that were bound more strongly.

In this dissertation, it was shown that dicationic salts can be made from the protonation of  $[Ir(COD)(PMe_3)_3]Cl(1)$ . We showed that there is hydrogen bonding that takes place in these salts whereby, the number of excess acid that is retained is dependent on the nature counterion of the salt as well as the solvent used to make the salt. We observed that these salts were not easily neutralized by commonly used bases but in the presence of DMSO, the salts were deprotonated very easily. We also observed that while using acetonitrile and acetone as a solvent,  $[IrH(COD)(PMe_3)_3][PF_6]_2$  underwent dissociation of PMe<sub>3</sub> to create other products. We noted that when the same reaction was attempted in the presence of excess HPF<sub>6</sub>, no dissociation occured. We believe that there is a acid stability for these complexes which arises out of the ability for an acid to form a hydrogen bond with the hydride of the salt and thus weaken the trans influence of the hydride on the PMe<sub>3</sub>.

We showed that it is possible to sythesize  $Ir(CH_3)_3(PMe_3)_3$  (21) via the reaction between  $IrCl_3(PMe_3)_3$  (15) and an excess of methylmagnesiumbromide. Using (21) it is also possible to make  $IrCH_3(OTf)_2(PMe_3)_3$  (23) by careful acidolysis using triflic acid. Complex (23) has been used to study the insertion of acetylenes into the iridium methyl bond. We also used acidolysis to cleave one hydride of  $IrH_2Cl(PMe_3)_3$  (13) to cleanly prepare  $IrHCl_2(PMe_3)_3$  (25) in high yields. We synthesized  $IrH(OTf)_2(PMe_3)_3$  (26) by the metathesis reaction between (25) and silver triflate. We observed the reaction of different olefins with (26) and have determined that it can be used for the dimerization of styrene and the oligomerization of different allyl ethers and vinyl ethers. We showed that (26) can also be used to isomerize allyl alcohols to their aldehyde isomers.

A brief survey of the results of the catalytic reactions of the complexes synthesized in this dissertation reveal that these catalyst are similar to other monohydridic complexes with respect to the isomerization of allyl alcohols. However, our system reveals that the chemistry indeeds place on the metal center and that there is the possiblity for the use of water as a solvent in these systems.

#### 6.2 Future Work

The immediate goal of this chemistry should be to reexamine the insertion chemistry of acetylenes into the iridium methyl bond of (**23**). Also a series of competition experiments should be done to determine clearly which site of unsaturation is more active towards the coordination of olefins and acetylenes. The products of those reactions should help to understand the role of both sites unsaturation and weather or not that second site is contributing to the insertion chemistry. It is possible that the site cis to the hydride coordinates an olefin or acetylene and inserts the olefin or acetylene into the metal hydide bond. It is also possible that this coordination insertion chemistry is continued from the cis open site alone because of geometric or electronic reasons. By determining which site is more reactive towards coordination, we can began to rule out some of the electronic effects.

The future goal for this chemistry is to continue this chemistry using other ancillary ligands like, PMe<sub>2</sub>Ph, DEPE, DMPE, PEt<sub>3</sub>, amino acids, diamines and amines. It has been shown that using weaker donors result in better insertion chemistry on select late metals. It is reasonable to conclude that the use of ancillary ligands other than PMe<sub>3</sub> may result in Ir(III) dications which are able to undergo insertion before -hydride elimination occurs. The result would be less occasion of isomerization and more of oligomerization and polymerization. It should also be possible to select these ancillary ligands with steric properties that could help enhance the regiodevelopment of the oligomers and polymers being formed.

Along the same lines, an ancillary ligand that would allow the hydride to position itself along the same face as the sites of unsaturation may also increase the chances of polymerization or oligomerization taking place.

# Appendi x

Table 6.1 Crystal data and structure refinement for Complex (6)

Identification code  $[IrH(COD) (PMe_3)_3] [OTf]_2$ Empirical formula  $C_{22}H_{46}F_6Ir0_7P_3S_2$ 885.82 Formula weight Temperature 298(2) K 0.71073 A Wavel ength Tri clini c Crystal system P-1 Space group Unit cell dimensions a=13. 820(2) A al pha =91. 394(6) deg. b = 13.977(2) A beta = 92.420(9) deg. c = 20.170(3) A gamma = 117.985(3) deg. 3433. 2(9) A<sup>3</sup>, Volume, Z 4 1.714 Mg/m<sup>3</sup> Density (calculated) Absorption coefficient 4. 219 mm<sup>-1</sup> F(000) 1768 0.3 x 0.4 x 0.6 mm Crystal size 1.89 to 25.00 deg. Theta range for data collection Limiting indices  $-1 \le h \le 15$ ,  $-16 \le k \le 15$ ,  $-23 \le l \le 23$ 13584 Reflections collected Independent reflections 11963 [R(int) = 0.0459]Absorption correction Semi-empirical from psi-scans Max. and min. transmission 0.9656 and 0.6683 Full-matrix least-squares on  $F^2$ Refinement method Data / restraints / parameters 11874 / 0 / 748 Goodness-of-fit on F^2 1.117 Final R indices [I > 2sigma(I)]R1 = 0.0437, wR2 = 0.0946R1 = 0.0707, wR2 = 0.1384R indices (all data) Extinction coefficient 0.00199(13)Largest diff. peak and hole 1.068 and -1.214 e. A<sup>-3</sup>

	x	у	Z	U(eq)
 Ir(1)	3580(1)	3504(1)	3766(1)	25(1)
$\Gamma(1)$	3383(1) 4531(7)	-304(1)	3700(1) 3094(4)	23(1)
C(1)	331(7)	-4003(7)	3054(4)	32(2)
C(2)	3457(8)	-4037(7)	3034(4) 3373(5)	40(2) 51(2)
C(3)	3000(3) 2708(8)	-5940(7)	3373(3)	51(2)
C(4)	2780(7)	-3900(7)	4073(3)	31(3)
C(3)	3209(7)	-4001(7)	4459(4)	39(2)
C(0)	4369(7)	-4200(8)	4409(4)	40(2)
C(7)	5169(6) 5442(7)	-4317(6)	4104(3) 2477(4)	43(2)
$\mathbf{U}(\mathbf{\delta})$	3443(7) 9719(9)	-4101(8)	3477(4)	41(2) 22(1)
$\Gamma(1)$	2002(2)	-3003(2)	4300(1)	33(1)
P(2)	3003(2)	-2803(2)	2091(1)	33(1)
P(3)	3331(2)	-1838(2)	3930(1)	33(1) 59(2)
C(1A)	33/8(8)	-2743(9)	3383(4)	32(3)
C(1B)	1349(8)	-4070(8)	4680(5)	48(2)
$\mathcal{L}(1\mathcal{L})$	2457(8)	- 1856(8)	4482(5)	50(2)
C(2A)	1528(7)	- 3463(9)	2773(5)	54(3)
C(2B)	3392(9)	- 1381(8)	2896(5)	51(3)
C(2C)	3402(8)	- 2991(8)	2077(4)	46(2)
C(3A)	6122(8)	-1365(8)	3205(5)	49(2)
C(3B)	5327(8)	- 656(7)	4268(5)	50(2)
U(3U)	6389(8)	- 1846(9)	4524(5)	56(3)
r(2)	62/4(1)	2909(1)	11330(1)	30(1)
C(9)	5523(8)	1529(7)	10538(5)	46(2)
C(10)	5079(8)	1111(7)	11137(5)	50(2)
C(11)	5363(11)	354(9)	11520(7)	72(4)
C(12)	6263(10)	956(9)	12055(6)	69(3)
C(13)	7130(9)	2070(8)	11884(5)	50(2)
C(14)	7573(8)	2308(8)	11272(5)	45(2)
C(15)	7333(9)	1489(9)	10710(5)	54(3)
C(16)	6367(9)	1273(9)	10235(6)	59(3)
P(4)	4801(2)	3298(2)	11249(1)	37(1)
P(5)	7274(2)	4315(2)	12121(1)	41(1)
P(6)	7186(2)	3984(2)	10388(1)	36(1)
C(4A)	3574(9)	2280(11)	10796(7)	81(4)
C(4B)	4296(9)	3399(10)	12029(5)	63(3)

Table 6.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters ( $A^2\ x\ 10^3)$  for 6. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(4C)	4917(10)	4467(10)	10850(6)	70(4)
C(5A)	8746(9)	4810(10)	12141(5)	63(3)
C(5B)	7204(10)	5579(8)	12127(5)	65(3)
C(5C)	6927(9)	3901(9)	12963(5)	61(3)
C(6A)	7697(9)	5429(8)	10480(5)	58(3)
C(6B)	8400(9)	3968(10)	10112(6)	64(3)
C(6C)	6350(9)	3664(9)	9619(5)	56(3)
S(1)	3942(2)	1454(2)	3515(1)	46(1)
0(1A)	4204(7)	1260(7)	2861(4)	72(2)
0(1B)	4363(6)	2576(5)	3720(4)	67(2)
0(1C)	4057(6	796(6)	4007(4)	61(2)
C(17)	2468(9)	955(9)	3431(6)	57(3)
F(17A)	2102(6)	1140(8)	3990(5)	115(3)
F(17B)	2193(6)	1440(6)	2976(5)	100(3)
F(17C)	1952(6)	-84(5)	3288(4)	88(2)
S(2)	6483(2)	-2166(2)	1221(2)	61(1)
0(2A)	5998(9)	-2680(10)	1798(5)	121(4)
0(2B)	6113(10)	-1492(9)	935(7)	133(5)
0(2C)	6591(9)	-2887(7)	68(5)	100(3)
C(18)	7890(13)	- 1233(13)	1504(10)	100(5)
F(18A)	8472(9)	-706(9)	1059(8)	178(6)
F(18B)	8353(8)	- 1748(10)	1787(8)	189(7)
F(18C)	7914(9)	- 486(9)	1952(6)	147(4)
S(3)	1121(2)	3743(2)	11490(1)	56(1)
0(3A)	939(9)	3986(8)	12133(5)	107(3)
0(3B)	464(8)	3893(8)	10994(5)	105(4)
0(3C)	2252(7)	4156(8)	11378(5)	91(3)
C(19)	615(11)	2301(11)	11483(8)	81(4)
F(19A)	685(13)	1927(10)	10910(7)	187(6)
F(19B)	1140(8)	2022(8)	11892(7)	150(5)
F(19C)	- 434(7)	1812(7)	11619(7)	147(5)
S(4)	1081(2)	3360(3)	5839(2)	60(1)
0(4A)	540(9)	3579(11)	6356(5)	124(4)
0(4B)	2236(7)	3938(9)	5864(6)	113(4)
0(4C)	589(8)	3312(9)	5197(4)	94(3)
C(20)	766(16)	1999(20)	5938(14)	147(10)
F(20A)	1237(17)	1867(17)	6450(11)	272(11)
F(20B)	- 230(11)	1359(10)	5903(11)	245(10)
F(20C)	1184(11)	1670(10)	5445(10)	199(8)
C(102)	8882(12)	1899(14)	3622(8)	94(5)
0(101)	7908(10)	1526(13)	3657(8)	180(7)
C(103)	9512(12)	3100(17)	3568(7)	117(7)
C(101)	9441(18)	1277(20)	3634(16)	208(14)
C(105)	1387(19)	- 1372(26)	11178(12)	160(11)
0(102)	2148(15)	- 1447(18)	11152(8)	198(8)
C(106)	649(29)	- 1684(57)	10776(20)	621(71)
C(104)	1241(30)	- 701(35)	11622(25)	384(35)

Ir(1) - C(2)	2.278(8)
Ir(1) - C(1)	2.279(8)
Ir(1) - C(6)	2.293(8)
Ir(1) - C(5)	2.293(8)
Ir(1) - P(2)	2.331(2)
Ir(1) - P(1)	2.341(2)
Ir(1) - P(3)	2.444(2)
C(1) - C(2)	1.370(12)
C(1) - C(8)	1.513(12)
C(2) - C(3)	1.518(12)
C(3) - C(4)	1.513(14)
C(4) - C(5)	1.508(13)
C(5) - C(6)	1.360(13)
C(6) - C(7)	1.512(12)
C(7) - C(8)	1.521(12)
P(1) - C(1A)	1.796(9)
P(1) - C(1B)	1,799(9)
P(1) - C(1C)	1,809(9)
P(2) - C(2B)	1,801(9)
P(2) - C(2A)	1.802(9)
P(2) - C(2C)	1.805(9)
P(3) - C(3B)	1.808(9)
P(3) - C(3A)	1.810(9)
P(3) - C(3C)	1.816(10)
Ir(2) - C(9)	2.276(9)
Ir(2) - C(10)	2.279(9)
Ir(2) - C(13)	2.297(9)
Ir(2) - C(14)	2. 318(9)
Ir(2) - P(5)	2.332(2)
Ir(2) - P(4)	2.340(2)
Ir(2) - P(6)	2.452(2)
C(9) - C(10)	1.392(13)
C(9) - C(16)	1.518(13)
C(10) - C(11)	1.508(14)
C(11) - C(12)	1.51(2)
C(12) - C(13)	1.51(2)
C(13) - C(14)	1. 378(13)
C(14) - C(15)	1.500(14)
C(15) - C(16)	1.51(2)
P(4) - C(4B)	1.776(9)
	- ( - )

P(4) - C(4C)	1.781(10)
P(4) - C(4A)	1.811(12)
P(5) - C(5B)	1.813(11)
P(5) - C(5A)	1.814(11)
P(5) - C(5C)	1.818(10)
P(6) - C(6B)	1.800(10)
P(6) - C(6A)	1.802(10)
P(6) - C(6C)	1.809(10)
S(1) - O(1C)	1.423(7)
S(1) - O(1A)	1.435(8)
S(1) - O(1B)	1.436(7)
S(1)-C(17)	1.816(11)
C(17) - F(17B)	1.300(13)
C(17) - F(17C)	1.300(12)
C(17) - F(17A)	1.322(13)
S(2) - O(2B)	1.391(10)
S(2) - O(2A)	1.405(10)
S(2) - O(2C)	1.408(9)
S(2) - C(18)	1.82(2)
C(18) - F(18A)	1.24(2)
C(18) - F(18B)	1.29(2)
C(18) - F(18C)	1.35(2)
S(3) - O(3A)	1.397(9)
S(3) - O(3B)	1.406(9)
S(3) - O(3C)	1.420(8)
S(3) - C(19)	1.796(14)
C(19) - F(19B)	1.26(2)
C(19) - F(19A)	1.28(2)
C(19) - F(19C)	1.33(2)
S(4) - O(4B)	1.409(9)
S(4) - O(4A)	1.416(9)
S(4) - O(4C)	1. 421(9)
S(4) - C(20)	1.76(2)
C(20) - F(20B)	1.24(2)
C(20) - F(20A)	1.26(3)
C(20) - F(20C)	1.34(3)
C(102) = O(101)	1.20(2)
C(102) - C(101)	1.41(2)
C(102) - C(103)	1.49(2)
C(105) - O(102)	1.11(2)
C(105) - C(106)	1.18(3)
C(105) - C(104)	1.37(4)
C(2) - Ir(1) - C(1)	35.0(3)
C(2) - Ir(1) - C(6)	83.8(3)
C(1) - Ir(1) - C(6)	76.6(3)
C(2) - Ir(1) - C(5)	77.2(3)

C(1) - Ir(1) - C(5)	90.5(3)
C(6) - Ir(1) - C(5)	34.5(3)
C(2) - Ir(1) - P(2)	89.0(2)
C(1) - Ir(1) - P(2)	92.9(2)
C(6) - Ir(1) - P(2)	169. 2(2)
C(5) - Ir(1) - P(2)	150.5(2)
C(2) - Ir(1) - P(1)	145.6(2)
C(1) - Ir(1) - P(1)	172.7(2)
C(6) - Ir(1) - P(1)	96.1(2)
C(5) - Ir(1) - P(1)	83. 4(2)
P(2) - Ir(1) - P(1)	94.38(8)
C(2) - Ir(1) - P(3)	118.8(2)
C(1) - Ir(1) - P(3)	83.8(2)
C(6) - Ir(1) - P(3)	83.6(2)
C(5) - Ir(1) - P(3)	116.6(2)
P(2) - Ir(1) - P(3)	92.89(8)
P(1) - Ir(1) - P(3)	95.26(8)
C(2) - C(1) - C(8)	123.6(8)
C(2) - C(1) - Ir(1)	72.5(5)
C(8) - C(1) - Ir(1)	111.9(5)
C(1) - C(2) - C(3)	123.7(8)
C(1) - C(2) - Ir(1)	72.5(5)
C(3) - C(2) - Ir(1)	113.4(6)
C(4) - C(3) - C(2)	114.9(7)
C(5) - C(4) - C(3)	114.2(8)
C(6) - C(5) - C(4)	125.4(8)
C(6) - C(5) - Ir(1)	72.8(5)
C(4) - C(5) - Ir(1)	110.0(6)
C(5) - C(6) - C(7)	122.6(9)
C(5) - C(6) - Ir(1)	72.8(5)
C(7) - C(6) - Ir(1)	114.7(6)
C(6) - C(7) - C(8)	113.8(7)
C(1) - C(8) - C(7)	114.3(7)
C(1A) - P(1) - C(1B)	103.6(5)
C(1A) - P(1) - C(1C)	102.3(5)
C(1B) - P(1) - C(1C)	100.9(5)
C(1A) - P(1) - Ir(1)	113.7(3)
C(1B) - P(1) - Ir(1)	111.9(3)
C(1C) - P(1) - Ir(1)	122.1(3)
C(2B) - P(2) - C(2A)	103.8(5)
C(2B) - P(2) - C(2C)	100.1(5)
C(2A) - P(2) - C(2C)	102.1(5)
$U(\Delta D) - \Gamma(\Delta) - \Gamma(1)$	120.4(3)
$U(\Delta A) - \Gamma(\Delta) - \Gamma(1)$ $C(2C) = D(2) = I_{m}(1)$	111.9(3) 116.9(3)
$C(2\mathbf{R}) = \mathbf{P}(2) = C(2\mathbf{A})$	110. 2(3) 102. 0(5)
$C(3\mathbf{D}) = \mathbf{\Gamma}(3) = C(3\mathbf{A})$	102.0(3)
U(3D) - F(3) - U(3U)	97.0(3)

C(3A) - P(3) - C(3C)	101.6(5)
C(3B) - P(3) - Ir(1)	117.1(3)
C(3A) - P(3) - Ir(1)	116.2(3)
C(3C) - P(3) - Ir(1)	119.1(4)
C(9) - Ir(2) - C(10)	35.6(3)
C(9) - Ir(2) - C(13)	91.3(4)
C(10) - Ir(2) - C(13)	76.8(4)
C(9) - Ir(2) - C(14)	76.4(4)
C(10) - Ir(2) - C(14)	82.8(4)
C(13) - Ir(2) - C(14)	34.7(3)
C(9) - Ir(2) - P(5)	171.9(3)
C(10) - Ir(2) - P(5)	146.7(3)
C(13) - Ir(2) - P(5)	83.2(3)
C(14) - Ir(2) - P(5)	95.8(3)
C(9) - Ir(2) - P(4)	94.2(3)
C(10) - Ir(2) - P(4)	89.7(3)
C(13) - Ir(2) - P(4)	148.1(2)
C(14) - Ir(2) - P(4)	170.6(3)
P(5) - Ir(2) - P(4)	93.63(9)
C(9) - Ir(2) - P(6)	83.1(2)
C(10) - Ir(2) - P(6)	118.7(3)
C(13) - Ir(2) - P(6)	117.4(2)
C(14) - Ir(2) - P(6)	84.3(2)
P(5) - Ir(2) - P(6)	94. 15(8)
P(4) - Ir(2) - P(6)	94. 49(8)
C(10) - C(9) - C(16)	121.4(10)
C(10) - C(9) - Ir(2)	72.4(5)
C(16) - C(9) - Ir(2)	113.0(6)
C(9) - C(10) - C(11)	123. 4(9)
C(9) - C(10) - Ir(2)	72.1(5)
C(11) - C(10) - Ir(2)	115.0(8)
C(10) - C(11) - C(12)	111.8(9)
C(11) - C(12) - C(13)	115.3(10)
C(14) - C(13) - C(12)	123. 9(10)
C(14) - C(13) - Ir(2)	73.5(5)
C(12) - C(13) - Ir(2)	108.2(7)
C(13) - C(14) - C(15)	124.9(9)
C(13) - C(14) - Ir(2)	71.8(5)
C(15) - C(14) - Ir(2)	113.5(6)
C(14) - C(15) - C(16)	116.1(8)
C(15) - C(16) - C(9)	113.6(8)
C(4B) - P(4) - C(4C)	103.1(5)
U(4B) - P(4) - U(4A)	101.9(6)
U(4U) - P(4) - U(4A)	98.9(6)
U(4B) - F(4) - IF(Z)	113.0(4)
U(4U) - F(4) - IF(2)	$1 \ge 1 \cdot \ge 2(4)$
U(4A) - P(4) - Ir(2)	115.4(4)

C(5B) - P(5) - C(5A)	101.1(6)
C(5B) - P(5) - C(5C)	101.4(5)
C(5A) - P(5) - C(5C)	103.6(5)
C(5B) - P(5) - Ir(2)	122.0(4)
C(5A) - P(5) - Ir(2)	114.3(4)
C(5C) - P(5) - Ir(2)	112.2(4)
C(6B) - P(6) - C(6A)	99. 1(5)
C(6B) - P(6) - C(6C)	101.5(5)
C(6A) - P(6) - C(6C)	101.1(5)
C(6B) - P(6) - Ir(2)	119.2(4)
C(6A) - P(6) - Ir(2)	117.2(3)
C(6C) - P(6) - Ir(2)	115.7(3)
0(1C) - S(1) - 0(1A)	114.8(5)
0(1C) - S(1) - 0(1B)	114.9(5)
0(1A) - S(1) - 0(1B)	115.0(5)
0(1C) - S(1) - C(17)	102.9(5)
0(1A) - S(1) - C(17)	103.3(5)
0(1B) - S(1) - C(17)	103.4(5)
F(17B) - C(17) - F(17C)	108.6(10)
F(17B) - C(17) - F(17A)	106.1(10)
F(17C) - C(17) - F(17A)	107.9(10)
F(17B) - C(17) - S(1)	112.0(8)
F(17C) - C(17) - S(1)	111.1(8)
F(17A) - C(17) - S(1)	110. 9(8)
0(2B) - S(2) - O(2A)	117.7(8)
0(2B) - S(2) - 0(2C)	114.6(7)
0(2A) - S(2) - 0(2C)	111.5(7)
O(2B) - S(2) - C(18)	103.2(7)
O(2A) - S(2) - C(18)	104.0(8)
0(2C) - S(2) - C(18)	103.7(8)
F(18A) - C(18) - F(18B)	108(2)
F(18A) - C(18) - F(18C)	105. 4(14)
F(18B) - C(18) - F(18C)	108(2)
F(18A) - C(18) - S(2)	114(2)
F(18B) - C(18) - S(2)	110. 5(11)
F(18C) - C(18) - S(2)	110. 3(11)
0(3A) - S(3) - 0(3B)	113.6(7)
0(3A) - S(3) - 0(3C)	113.0(7)
0(3B) - S(3) - 0(3C)	117.1(6)
O(3A) - S(3) - C(19)	102.7(7)
O(3B) - S(3) - C(19)	104.8(6)
0(3C) - S(3) - C(19)	103.6(6)
F(19B) - C(19) - F(19A)	106.3(14)
F(19B) - C(19) - F(19C)	108.6(13)
F(19A) - U(19) - F(19U)	107.5(13)
F(19B) - U(19) - S(3)	113.2(10)
F(19A) - C(19) - S(3)	111.1(12)

F(19C) - C(19) - S(3)	110.0(10)
0(4B) - S(4) - 0(4A)	117.7(7)
0(4B) - S(4) - 0(4C)	113.0(7)
0(4A) - S(4) - 0(4C)	113.0(6)
0(4B) - S(4) - C(20)	105.1(8)
0(4A) - S(4) - C(20)	103. 5(10)
0(4C) - S(4) - C(20)	102. 4(11)
F(20B) - C(20) - F(20A)	111(2)
F(20B) - C(20) - F(20C)	106(3)
F(20A) - C(20) - F(20C)	103(2)
F(20B) - C(20) - S(4)	114.0(13)
F(20A) - C(20) - S(4)	113(2)
F(20C) - C(20) - S(4)	109. 2(14)
0(101) - C(102) - C(101)	124(2)
0(101) - C(102) - C(103)	116(2)
C(101) - C(102) - C(103)	120(2)
0(102) - C(105) - C(106)	127(3)
0(102) - C(105) - C(104)	125(3)
C(106) - C(105) - C(104)	107(3)

Symmetry transformations used to generate equivalent atoms:

Table 6.4 Anisotropic displacement parameters ( $A^2 \times 10^3$ ) for 6. The anisotropic displacement factor exponent takes the form: -2 pi<sup>2</sup> [  $h^2 a^{*2} U11 + \ldots + 2 h k a^* b^* U12$  ]

	U11	U22	U33	U23	U13	U12
 Ir(1)	27(1)	28(1)	25(1)	3(1)	3(1)	16(1)
C(1)	39(5)	40(5)	23(4)	-2(3)	-1(3)	24(4)
C(2)	57(6)	37(5)	33(5)	5(4)	3(4)	29(5)
C(3)	60(6)	28(5)	67(7)	-2(4)	8(5)	24(5)
C(4)	53(6)	35(5)	70(7)	10(5)	10(5)	23(5)
C(5)	48(5)	47(5)	33(5)	13(4)	15(4)	31(5)
C(6)	46(5)	59(6)	31(4)	13(4)	8(4)	36(5)
C(7)	47(5)	54(6)	48(5)	9(4)	2(4)	37(5)
C(8)	40(5)	49(5)	43(5)	-1(4)	11(4)	29(4)
P(1)	34(1)	38(1)	34(1)	4(1)	10(1)	23(1)
P(2)	37(1)	36(1)	30(1)	4(1)	0(1)	21(1)
P(3)	33(1)	37(1)	32(1)	-3(1)	4(1)	14(1)
1 (0)	00(1)	57(1)	<b>5</b> ~(1)	0(1)	.(1)	-

C(1A)	53(6)	79(7)	30(5)	0(5)	4(4)	37(6)
C(1B)	45(6)	51(6)	53(6)	9(5)	20(5)	27(5)
C(1C)	53(6)	55(6)	55(6)	-3(5)	10(5)	37(5)
C(2A)	35(5)	68(7)	63(7)	9(5)	- 12(5)	27(5)
C(2B)	78(7)	45(6)	47(6)	14(4)	7(5)	41(6)
C(2C)	65(6)	61(6)	25(4)	3(4)	-7(4)	41(5)
C(3A)	41(5)	54(6)	40(5)	4(4)	12(4)	12(5)
C(3B)	47(6)	40(5)	58(6)	-8(4)	3(5)	17(5)
C(3C)	41(6)	62(7)	54(6)	- 10(5)	-11(5)	17(5)
Ir(2)	33(1)	31(1)	30(1)	6(1)	5(1)	18(1)
C(9)	43(5)	29(5)	54(6)	- 11(4)	2(4)	8(4)
C(10)	45(6)	28(5)	71(7)	0(4)	9(5)	11(4)
C(11)	91(9)	44(6)	92(9)	29(6)	28(8)	37(7)
C(12)	90(9)	59(7)	89(9)	30(6)	23(7)	58(7)
C(13)	60(6)	54(6)	56(6)	16(5)	12(5)	42(5)
C(14)	35(5)	47(5)	59(6)	11(5)	8(4)	24(4)
C(15)	66(7)	57(6)	57(6)	16(5)	21(5)	42(6)
C(16)	69(7)	46(6)	63(7)	- 14(5)	9(6)	28(6)
P(4)	40(1)	45(1)	37(1)	10(1)	7(1)	28(1)
P(5)	41(1)	45(1)	34(1)	0(1)	0(1)	19(1)
P(6)	40(1)	40(1)	32(1)	9(1)	10(1)	21(1)
C(4A)	49(7)	93(10)	105(10)	-6(8)	- 19(7)	40(7)
C(4B)	67(7)	102(9)	47(6)	24(6)	23(5)	60(7)
C(4C)	84(8)	80(8)	80(8)	42(7)	31(7)	61(7)
C(5A)	56(7)	74(8)	46(6)	- 3(5)	-5(5)	21(6)
C(5B)	81(8)	50(6)	54(7)	- 11(5)	11(6)	23(6)
C(5C)	68(7)	61(7)	47(6)	2(5)	7(5)	23(6)
C(6A)	67(7)	38(5)	63(7)	16(5)	25(6)	18(5)
C(6B)	61(7)	75(8)	70(7)	24(6)	28(6)	39(6)
C(6C)	68(7)	59(6)	36(5)	9(5)	7(5)	25(6)
S(1)	46(1)	35(1)	61(2)	7(1)	4(1)	23(1)
0(1A)	87(6)	80(6)	63(5)	15(4)	26(4)	48(5)
0(1B)	56(5)	34(4)	109(6)	-4(4)	-7(4)	22(3)
0(1C)	77(5)	47(4)	69(5)	11(3)	- 15(4)	38(4)
C(17)	55(7)	47(6)	71(7)	-6(5)	- 13(6)	27(5)
F(17A)	69(5)	149(8)	126(7)	-24(6)	21(5)	52(5)
F(1/B)	85(5)	85(5)	133(7)	1(5)	-41(5)	48(5)
F(1/C)	60(4)	53(4)	135(7)	-3(4)	-10(4)	16(3)
S(2)	60(2)	56(2)	70(2)	-10(1)	6(1)	31(1)
U(2A)	98(8)	148(10)	86(7)	1(7)	39(6)	29(7)
U(2B)	121(9)	85(7)	213(13)	- 35(8)	- 66(9)	/5(/)
0(20)	154(10)	70(6)	88(7)	-6(5)	26(6)	b1(b)
U(10) E(10A)	74(1U) 192(0)	73(1U) 110(0)	104(10) 969(10)	SU(11) 69(10)	29(10) 00(10)	33(8) 94(7)
Г(10A) Г(10D)	123(9)	196(0)	203(10) 246(10)	00(10) 52(11)	99(10) 55(0)	29(C)
F(19C)	115(9)	105(9)	340(19) 176(11)	-51(7)	-33(9)	30(U) 21(R)
S(3)	113(0)	54(9)	64(9)	-31(7) 1/(1)	-13(7)	29(1)
5(5)	40(2)	J4(2)	04(2)	14(1)	5(1)	~~(I)

0(3A)	127(9)	101(8)	82(7)	- 15(6)	28(6)	44(7)
0(3B)	76(6)	111(8)	119(8)	52(7)	- 18(6)	37(6)
0(3C)	48(5)	98(7)	113(7)	36(6)	23(5)	21(5)
C(19)	69(9)	66(8)	97(10)	-9(8)	-27(8)	27(7)
F(19A)	232(15)	139(10)	182(12)	-92(9)	- 42(11)	90(10)
F(19B)	122(8)	98(7)	242(13)	71(8)	- 31(8)	62(6)
F(19C)	59(5)	67(5)	285(15)	39(7)	- 14(7)	5(4)
S(4)	44(2)	76(2)	64(2)	4(1)	9(1)	32(1)
0(4A)	106(8)	216(14)	69(6)	-24(7)	6(6)	92(9)
0(4B)	51(5)	109(8)	159(10)	-2(7)	27(6)	19(5)
0(4C)	112(8)	139(9)	57(5)	8(5)	-7(5)	82(7)
C(20)	83(13)	169(20)	232(26)	112(20)	61(15)	87(14)
F(20A)	299(23)	316(23)	303(23)	207(20)	59(18)	218(20)
F(20B)	111(9)	103(9)	508(31)	110(13)	116(15)	27(7)
F(20C)	118(9)	110(9)	391(25)	- 35(12)	- 7(12)	76(8)
C(102)	55(8)	107(12)	105(12)	-27(9)	11(8)	25(9)
0(101)	69(8)	193(15)	224(17)	- 78(12)	36(9)	19(8)
C(103)	68(10)	207(21)	65(9)	13(11)	14(7)	55(12)
C(101)	116(18)	166(23)	370(44)	- 23(25)	12(22)	90(18)
C(105)	101(16)	271(32)	129(17)	- 70(18)	- 18(13)	112(19)
0(102)	173(16)	350(27)	148(14)	- 13(14)	13(12)	186(18)
C(106)	226(36)	1374(181)	333(50)	- 555(85)	- 201(37)	481(74)
C(104)	276(45)	433(67)	546(82)	-251(61)	- 193(50)	282(50)

	X	У	Z	U(eq)
H(1)	2539(49)	- 4457(49)	3792(30)	7(15)
H(1A)	4761(7)	- 3657(7)	2691(4)	38
H(2A)	3068(8)	- 4903(7)	2628(4)	48
H(3A)	2445(9)	-6486(7)	3099(5)	61
H(3B)	3644(9)	-6140(7)	3376(5)	61
H(4A)	1924(8)	- 6203(7)	4057(5)	62
H(4B)	2841(8)	-6486(7)	4313(5)	62
H(5A)	2935(7)	- 4849(7)	4864(4)	47
H(6A)	4671(7)	- 3781(8)	4911(4)	48
H(7A)	4889(8)	- 5299(8)	4184(5)	53
H(7B)	5869(8)	- 4196(8)	4459(5)	53
H(8A)	6100(7)	- 3465(8)	3493(4)	49
H(8B)	5598(7)	- 4679(8)	3238(4)	49
H(1AA)	4122(8)	-2179(9)	5374(4)	77
H(1AB)	3377(8)	-3394(9)	5533(4)	77
H(1AC)	2992(8)	-2524(9)	5687(4)	77
H(1BA)	927(8)	- 4264(8)	4262(5)	72
H(1BB)	1004(8)	- 3822(8)	4995(5)	72
H(1BC)	1389(8)	-4692(8)	4842(5)	72
H(1CA)	2096(8)	- 1912(8)	4055(5)	74
H(1CB)	3141(8)	- 1197(8)	4522(5)	74
H(1CC)	1998(8)	- 1849(8)	4824(5)	74
H(2AA)	1247(7)	-4235(9)	2764(5)	81
H(2AB)	1321(7)	-3260(9)	2360(5)	81
H(2AC)	1230(7)	- 3243(9)	3132(5)	81
H(2BA)	4176(9)	-964(8)	2957(5)	77
H(2BB)	3059(9)	- 1202(8)	3253(5)	77
H(2BC)	3149(9)	- 1219(8)	2481(5)	77
H(2CA)	3238(8)	- 3734(8)	2002(4)	69
H(2CB)	4175(8)	- 2529(8)	2049(4)	69
H(2CC)	3005(8)	- 2808(8)	1746(4)	69
H(3AA)	6189(8)	- 1945(8)	2983(5)	74
H(3AB)	6840(8)	- 786(8)	3334(5)	74
H(3AC)	5746(8)	- 1103(8)	2910(5)	74
H(3BA)	4931(8)	-822(7)	4665(5)	75
H(3RR)	4972(8)	-412(7)	3945(5)	75

Table 6.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters  $(A^2\ x\ 10^3)$  for 6.

H(3BC)	6065(8)	-95(7)	4369(5)	75
H(3CA)	6514(8)	-2451(9)	4420(5)	84
H(3CB)	6143(8)	-1896(9)	4965(5)	84
H(3CC)	7060(8)	- 1183(9)	4497(5)	84
H(2)	5450(73)	2338(72)	12065(45)	52(27)
H(9A)	5006(8)	1585(7)	10214(5)	55
H(10A)	4308(8)	942(7)	11155(5)	60
H(11A)	5597(11)	-35(9)	11216(7)	87
H(11B)	4714(11)	- 175(9)	11722(7)	87
H(12A)	6620(10)	519(9)	12158(6)	83
H(12B)	5930(10)	1032(9)	12453(6)	83
H(13A)	7632(9)	2504(8)	12259(5)	60
H(14A)	8329(8)	2899(8)	11295(5)	54
H(15A)	7203(9)	809(9)	10897(5)	65
H(15B)	7983(9)	1733(9)	10458(5)	65
H(16A)	6012(9)	515(9)	10082(6)	71
H(16B)	6637(9)	1705(9)	9851(6)	71
H(4AA)	3749(9)	2155(11)	10358(7)	121
H(4AB)	3034(9)	2528(11)	10765(7)	121
H(4AC)	3287(9)	1617(11)	11025(7)	121
H(4BA)	4205(9)	2795(10)	12285(5)	94
H(4BB)	3602(9)	3393(10)	11959(5)	94
H(4BC)	4809(9)	4063(10)	12264(5)	94
H(4CA)	5189(10)	4486(10)	10418(6)	106
H(4CB)	5417(10)	5108(10)	11111(6)	106
H(4CC)	4209(10)	4438(10)	10806(6)	106
H(5AA)	8898(9)	4206(10)	12139(5)	94
H(5AB)	9084(9)	5263(10)	12536(5)	94
H(5AC)	9036(9)	5223(10)	11758(5)	94
H(5BA)	6450(10)	5427(8)	12118(5)	97
H(5BB)	7539(10)	5969(8)	11744(5)	97
H(5BC)	7587(10)	6010(8)	12523(5)	97
H(5CA)	6936(9)	3227(9)	13024(5)	92
H(5CB)	6208(9)	3812(9)	13036(5)	92
H(5CC)	7454(9)	4447(9)	13274(5)	92
H(6AA)	7128(9)	5578(8)	10629(5)	87
H(6AB)	7922(9)	5745(8)	10059(5)	87
H(6AC)	8313(9)	5736(8)	10799(5)	87
H(6BA)	8257(9)	3231(10)	10039(6)	96
H(6BB)	8990(9)	4327(10)	10445(6)	96
H(6BC)	8599(9)	4337(10)	9705(6)	96
H(6CA)	5664(9)	3648(9)	9703(5)	84
H(6CB)	6215(9)	2967(9)	9438(5)	84
H(6CC)	6727(9)	4207(9)	9308(5)	84
H(10B)	9016(12)	3402(17)	3566(7)	175
H(10C)	9888(12)	3257(17)	3163(7)	175
H(10D)	10038(12)	3411(17)	3940(7)	175

H(10E)	8923(18)	526(20)	3669(16)	313
H(10F)	9965(18)	1517(20)	4008(16)	313
H(10G)	9815(18)	1363(20)	3232(16)	313
H(10H)	719(29)	- 2160(57)	10453(20)	931
H(10I)	655(29)	- 1076(57)	10560(20)	931
H(10J)	- 30(29)	- 2069(57)	10987(20)	931
H(10K)	1828(30)	- 427(35)	11961(25)	576
H(10L)	553(30)	- 1099(35)	11821(25)	576
H(10M)	1239(30)	- 107(35)	11394(25)	576

Table 15.1 Crystal data and structure refinement for 15.

Identification code	fac-IrCl3(PMe3)3*2DMS0 (15)
Empirical formula	$C_{17} H_{40} C_{16} F_8 Ir O_2 P_3 S_6$
Formula weight	1118.66
Temperature	298(2) K
Wavelength	0. 71073 A
Crystal system	Tri clini c
Space group	P1
Unit cell dimensions	a = 8.891(2) A al pha = 60.107(14)
deg.	
	b = 9.215(2) A beta = 78.975(10)
deg.	
	c = 9.236(2) A gamma = 81.307(7)
deg.	
Volume, Z	642. 6(2) $A^3$ , 1
Density (calculated)	2.891 Mg/m <sup>3</sup>
Absorption coefficient	6. 581 mm <sup>-1</sup>
F(000)	550
Crystal size	0.4 x 0.4 x 0.8 mm
Theta range for data collection	2.34 to 24.99 deg.
Limiting indices	$-1 \le h \le 10$ , $-9 \le k \le 9$ , $-10 \le l \le 10$
Reflections collected	2587
Independent reflections	2587 [R(int) = 0.0000]
Absorption correction	None
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2582 / 3 / 218
Goodness-of-fit on $F^2$	0. 798
Final R indices [I>2sigma(I)]	R1 = 0.0326, WR2 = 0.0813
R indices (all data)	R1 = 0.0469, WR2 = 0.1438
Absolute structure parameter	0.005(7)
Extinction coefficient	0.050(3)
Largest diff. peak and hole	1.858 and -1.879 e. $A^{-3}$

	x	У	Z	V(eq)
 Ir(1)	4413	7280	8057	27(1)
Cl (1)	2191(6)	5642(6)	8938(6)	53(1)
Cl (2)	2591(7)	9692(6)	7025(6)	49(1)
Cl (3)	3775(6)	7214(6)	10773(5)	50(1)
P(1)	6177(5)	9228(5)	7098(5)	35(1)
P(2)	6020(6)	4985(5)	9383(5)	34(1)
P(3)	4630(5)	7092(5)	5657(5)	36(1)
C(11)	6067(22)	10186(17)	8418(18)	59(4)
C(12)	8207(16)	8680(17)	6836(18)	54(3)
C(13)	5994(21)	11044(16)	5039(15)	58(4)
C(21)	7632(18)	4481(16)	8178(17)	53(3)
C(22)	6979(21)	5029(17)	10928(17)	59(4)
C(23)	5095(19)	3074(16)	10540(19)	62(4)
C(31)	3160(23)	8338(23)	4359(20)	77(5)
C(32)	4425(21)	5020(17)	5979(18)	59(3)
C(33)	6342(21)	7641(20)	4153(18)	65(4)
S(1)	10033(5)	- 191(5)	11616(5)	58(1)
0(101)	11373(23)	1185(22)	10154(27)	123(6)
C(101)	9650(22)	- 1117(28)	10514(29)	91(6)
C(102)	8577(20)	932(19)	11715(22)	58(4)
S(2)	9583(7)	4070(8)	4027(9)	90(2)
0(201)	11048(29)	4400(36)	4819(31)	183(11)
C(201)	8420(18)	3288(30)	5318(29)	94(8)
C(202)	10552(21)	2737(21)	3320(18)	70(5)

Table 15.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters ( $A^2\ x\ 10^3)$  for 15. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 15.3 Bond lengths [A] and angles [deg] for 15.

Ir(1) - P(2)	2.278(5)
Ir(1) - P(3)	2.278(4)
Ir(1)-P(1)	2.281(4)
Ir(1)-Cl(2)	2.422(5)

Ir(1)-Cl(1)	2.430(5)
Ir(1)-Cl(3)	2.436(4)
P(1) - C(12)	1.80(2)
P(1) - C(11)	1.810(13)
P(1) - C(13)	1.818(12)
P(2) - C(23)	1.774(14)
P(2) - C(21)	1.793(14)
P(2) - C(22)	1.817(13)
P(3) - C(33)	1.80(2)
P(3) - C(31)	1.80(2)
P(3) - C(32)	1.813(14)
S(1) - C(102)	1.548(14)
S(1)-C(101)	1.72(2)
S(1)-0(101)	1.73(2)
S(2) - C(201)	1.38(2)
S(2) - C(202)	1.72(2)
S(2) - 0(201)	1.74(3)
P(2) - Ir(1) - P(3)	95.5(2)
P(2) - Ir(1) - P(1)	96.6(2)
P(3) - Ir(1) - P(1)	97.06(14)
P(2) - Ir(1) - Cl(2)	172.1(2)
P(3) - Ir(1) - Cl(2)	92.1(2)
P(1) - Ir(1) - Cl(2)	84.4(2)
P(2) - Ir(1) - Cl(1)	93.6(2)
P(3) - Ir(1) - Cl(1)	84.3(2)
P(1) - Ir(1) - Cl(1)	169. 49(13)
Cl(2) - Ir(1) - Cl(1)	85.1(2)
P(2) - Ir(1) - Cl(3)	85.5(2)
P(3) - Ir(1) - Cl(3)	169. 93(14)
P(1) - Ir(1) - Cl(3)	92.8(2)
Cl(2) - Ir(1) - Cl(3)	86.6(2)
Cl(1) - Ir(1) - Cl(3)	85.6(2)
C(12) - P(1) - C(11)	101.6(8)
C(12) - P(1) - C(13)	100. 2(8)
C(11) - P(1) - C(13)	102.2(7)
C(12) - P(1) - Ir(1)	121.3(5)
C(11) - P(1) - Ir(1)	113.1(5)
C(13) - P(1) - Ir(1)	115.8(5)
C(23) - P(2) - C(21)	102.3(7)
C(23) - P(2) - C(22)	103.7(8)
C(21) - P(2) - C(22)	100. 2(8)
U(23) - P(2) - Ir(1)	113.9(6)
U(21) - P(2) - Ir(1)	119.8(5)
U(22) - P(2) - Ir(1)	114.7(5)
U(33) - P(3) - U(31)	102.1(9)
C(33) - P(3) - C(32)	100.2(8)

C(31) - P(3) - C(32)	102.2(8)
C(33) - P(3) - Ir(1)	121.3(6)
C(31) - P(3) - Ir(1)	113.2(5)
C(32) - P(3) - Ir(1)	115.2(5)
C(102) - S(1) - C(101)	106.1(9)
C(102) - S(1) - O(101)	105.1(10)
C(101) - S(1) - O(101)	100.5(10)
C(201) - S(2) - C(202)	111.2(11)
C(201) - S(2) - O(201)	109.7(13)
C(202) - S(2) - O(201)	100.0(12)

Symmetry transformations used to generate equivalent atoms:

	U11	U22	U33	U23	U13	U12
Ir(1)	27(1)	27(1)	26(1)	- 11(1)	0(1)	-2(1)
Cl (1)	36(3)	54(2)	64(2)	-24(2)	4(2)	- 18(2)
Cl (2)	49(3)	46(2)	46(2)	- 20(2)	-9(2)	15(2)
Cl (3)	56(3)	58(2)	32(2)	- 23(2)	2(2)	2(2)
P(1)	36(3)	32(2)	35(1)	- 16(1)	1(2)	-9(2)
P(2)	36(2)	30(2)	31(2)	- 10(1)	-5(2)	-1(2)
P(3)	42(2)	38(2)	31(2)	- 19(1)	-6(2)	-4(2)
C(11)	78(10)	55(7)	58(7)	- 34(6)	0(7)	- 25(8)
C(12)	38(7)	52(7)	61(7)	- 18(6)	-2(6)	- 14(6)
C(13)	78(10)	44(6)	41(6)	-6(5)	-8(7)	-27(7)
C(21)	50(8)	46(6)	57(7)	-26(6)	4(6)	4(6)
C(22)	79(11)	53(7)	51(7)	-22(6)	- 39(7)	10(7)
C(23)	55(9)	37(6)	62(8)	- 3(6)	-2(7)	0(6)
C(31)	84(12)	103(12)	64(8)	- 57(9)	- 41(9)	36(11)
C(32)	69(10)	53(7)	60(8)	-29(6)	- 11(7)	-7(7)
C(33)	69(10)	73(9)	51(7)	- 36(7)	19(7)	- 15(8)
S(1)	53(2)	58(2)	56(2)	-24(2)	-7(2)	0(2)
0(101)	91(12)	116(12)	160(17)	- 73(12)	31(12)	- 37(11)
C(101)	48(9)	136(18)	134(17)	- 106(16)	3(10)	0(11)
C(102)	36(8)	66(8)	104(11)	-64(8)	- 38(8)	34(7)
S(2)	57(3)	112(4)	143(5)	-96(4)	3(3)	-12(3)
0(201)	100(17)	296(33)	158(19)	- 115(22)	19(16)	-58(22)
C(201)	30(7)	158(20)	140(17)	- 117(17)	54(10)	- 52(10)
C(202)	69(10)	92(11)	51(7)	- 43(8)	-9(7)	23(9)

Table 15.4 Anisotropic displacement parameters  $(A^2 \times 10^3)$  for 15. The anisotropic displacement factor exponent takes the form: -2 <sup>2</sup> [  $h^2 a^{*2}$  U11 + ... + 2 h k a\* b\* U12 ]

	х	У	Z	U(eq)
Ш(11А)	5018(22)	10528(17)	9650(19)	20
П(11А) Ц(11Р)	3018(22)	10538(17) 11141(17)	8030(18) 7847(18)	89
П(11D) Ц(11C)	6079(22)	11141(17) 0296(17)	7047(10) 0459(19)	09 80
П(11С) Ц(19А)	0443(22)	9360(17)	9430(10)	09
П(12A) Ц(12P)	0414(10) 9527(16)	0101(17) 7022(17)	0143(10) 7010(18)	01 81
П(12D) Н(12C)	8761(16)	7922(17) 0676(17)	7919(18) 6308(18)	01 81
$\Pi(120)$ $\Pi(121)$	4042(21)	9070(17) 11480(16)	4005(15)	01 97
H(13R)	4342(21) 6313(21)	10718(16)	4333(13) 4182(15)	87
H(13C)	6620(21)	10710(10) 11801(16)	4102(15) 4853(15)	87
H(130)	8226(18)	5445(16)	7/01(17)	80
H(21R)	7275(18)	4157(16)	7431(17) 7470(17)	80
H(21C)	8260(18)	3572(16)	8928(17)	80
H(22A)	7517(21)	6035(17)	10406(17)	89
H(22B)	7695(21)	4070(17)	11358(17)	89
H(22C)	6230(21)	5006(17)	11838(17)	89
H(23A)	4197(19)	3202(16)	11243(19)	94
H(23B)	5786(19)	2200(16)	11232(19)	94
H(23C)	4800(19)	2785(16)	9773(19)	94
H(31A)	2175(23)	8143(23)	5044(20)	115
H(31B)	3175(23)	8033(23)	3503(20)	115
H(31C)	3347(23)	9504(23)	3839(20)	115
H(32A)	3531(21)	4560(17)	6777(18)	89
H(32B)	5318(21)	4305(17)	6404(18)	89
H(32C)	4318(21)	5098(17)	4928(18)	89
H(33A)	7219(21)	7038(20)	4715(18)	97
H(33B)	6447(21)	8825(20)	3638(18)	97
H(33C)	6276(21)	7354(20)	3302(18)	97
H(10B)	10520(22)	- 1837(28)	10423(29)	136
H(10C)	9450(22)	- 264(28)	9407(29)	136
H(10D)	8768(22)	- 1765(28)	11098(29)	136
H(10E)	8732(20)	1481(19)	12321(22)	88
H(10F)	7714(20)	252(19)	12288(22)	88
H(10G)	8384(20)	1759(19)	10596(22)	88
H(20B)	7896(18)	4060(30)	5688(29)	140
H(20C)	8849(18)	2333(30)	6241(29)	140
H(20D)	7707(18)	2925(30)	4922(29)	140

Table 15.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters  $(A^2\ x\ 10^3)$  for 15.

H(20E)	11352(21)	3311(21)	2425(18)	105
H(20F)	9852(21)	2374(21)	2910(18)	105
H(20G)	10996(21)	1780(21)	4229(18)	105

Table 18.1 Crystal data and structure refinement for 18.

Identification code	$IrH(4-COAlllyl)(PMe_3)_2(H_20)$
Empirical formula	$C_{15}$ $H_{30}$ $F_3$ Ir $O_4$ $P_2$ S
Formula weight	617.59
Temperature	298(2) K
Wavelength	0. 71073 A
Crystal system	Tri clini c
Space group	P-1
Unit cell dimensions	a = 8.449(2) A al pha = 76.515(13)
deg.	
	1.801 Mg/m <sup>3</sup>
Absorption coefficient	6. 135 $mm^{-1}$
F(000	604
Crystal size	0.3 x 0.4 x 0.6 mm
Theta range for data collection	1.83 to 27.51 deg.
Limiting indices	- 1<=h<=10, - 14<=k<=14, - 15<=l<=15
Reflections collected	6244
Independent reflections	5187 [R(int) = 0.0287]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	1.0000 and 0.4015
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4997 / 0 / 236
Goodness-of-fit on $F^2$	1. 037
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0890
R indices (all data)	R1 = 0.0479, wR2 = 0.1097
Extinction coefficient	0.0103(7)
Largest diff. peak and hole	1. 496 and -1. 147 e. $A^{-3}$

	x	У	Z	U(eq)
Ir(1)	6999(1)	7408(1)	7520(1)	38(1)
C(1)	6695(9)	8868(6)	6166(6)	62(2)
C(2)	8049(10)	8664(8)	5219(6)	80(2)
C(3)	9695(10)	8195(9)	5667(8)	85(3)
C(4)	9601(7)	7305(7)	6793(6)	61(2)
C(5)	9326(8)	7659(8)	7862(6)	66(2)
C(6)	8227(9)	8648(7)	8104(6)	61(2)
C(7)	7958(12)	9893(7)	7333(8)	81(2)
C(8)	6652(10)	10023(6)	6590(8)	76(2)
0(1)	7336(5)	5852(4)	9044(3)	51(1)
P(1)	4442(2)	7935(1)	8379(1)	48(1)
P(2)	6400(2)	6093(2)	6564(1)	52(1)
C(1A)	4329(12)	8805(10)	9444(8)	101(3)
C(1B)	3448(10)	6702(7)	9157(8)	83(3)
C(1C)	2883(8)	8817(7)	7522(7)	68(2)
C(2A)	4764(13)	6589(9)	5681(9)	101(3)
C(2B)	5905(13)	4689(7)	7432(8)	84(3)
C(2C)	8040(12)	5469(10)	5623(8)	90(3)
S(1)	8608(2)	6337(2)	11674(2)	66(1)
0(2)	8138(10)	5659(8)	12741(6)	121(3)
0(3)	10145(9)	5927(8)	11159(8)	132(3)
0(4)	7360(9)	6667(7)	10942(5)	101(2)
C(9)	8892(19)	7711(11)	11913(11)	114(4)
F(1)	9274(17)	8458(8)	11015(8)	205(5)
F(2)	7487(18)	8187(10)	12448(10)	232(6)
F(3)	9930(14)	7567(9)	12649(8)	177(4)

Table 18.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters (A $^2\ x\ 10^3)$  for 18. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Ir(1) - C(1)	2.083(6)	
Ir(1) - C(5)	2.157(6)	
Ir(1) - C(6)	2.224(6)	
Ir(1) - C(4)	2.237(6)	
Ir(1) - O(1)	2.283(4)	
Ir(1) - P(1)	2.291(2)	
Ir(1) - P(2)	2.296(2)	
C(1) - C(2)	1.529(11)	
C(1) - C(8)	1.538(11)	
C(2) - C(3)	1.524(12)	
C(3) - C(4)	1.520(10)	
C(4) - C(5)	1.436(11)	
C(5) - C(6)	1.387(11)	
C(6) - C(7)	1.526(10)	
C(7) - C(8)	1.497(12)	
P(1) - C(1B)	1.804(7)	
P(1) - C(1A)	1.808(8)	
P(1) - C(1C)	1.809(7)	
P(2) - C(2A)	1.806(8)	
P(2) - C(2B)	1.812(8)	
P(2) - C(2C)	1.813(8)	
S(1)-0(3)	1.401(7)	
S(1) - O(2)	1.404(7)	
S(1)-0(4)	1.425(6)	
S(1) - C(9)	1.752(12)	
C(9) - F(1)	1.27(2)	
C(9) - F(3)	1.313(14)	
C(9) - F(2)	1.35(2)	
C(1) - Ir(1) - C(5)	96.7(3)	
C(1) - Ir(1) - C(6)	81.4(3)	
C(5) - Ir(1) - C(6)	36.9(3)	
C(1) - Ir(1) - C(4)	82.2(3)	
C(5) - Ir(1) - C(4)	38.1(3)	
C(6) - Ir(1) - C(4)	<b>68.</b> 2(3)	
C(1) - Ir(1) - O(1)	178.0(2)	
C(5) - Ir(1) - O(1)	82.3(2)	
C(6) - Ir(1) - O(1)	96.8(2)	
C(4) - Ir(1) - O(1)	97.9(2)	
C(1) - Ir(1) - P(1)	92.7(2)	
C(5) - Ir(1) - P(1)	130. 5(2)	
C(6) - Ir(1) - P(1)	98.0(2)	
C(4) - Ir(1) - P(1)	165.8(2)	

Table 18.3 Bond lengths [A] and angles [deg] for 18.

0(1) - Ir(1) - P(1)	86.65(13)
C(1) - Ir(1) - P(2)	93.6(2)
C(5) - Ir(1) - P(2)	129. 5(2)
C(6) - Ir(1) - P(2)	163. 5(2)
C(4) - Ir(1) - P(2)	95.6(2)
0(1) - Ir(1) - P(2)	88. 38(13)
P(1) - Ir(1) - P(2)	98.00(7)
C(2) - C(1) - C(8)	114.0(6)
C(2) - C(1) - Ir(1)	108.6(5)
C(8) - C(1) - Ir(1)	108.4(5)
C(3) - C(2) - C(1)	111.7(6)
C(4) - C(3) - C(2)	113.2(6)
C(5) - C(4) - C(3)	123. 2(8)
C(5) - C(4) - Ir(1)	<b>68</b> . 0(4)
C(3) - C(4) - Ir(1)	108.5(5)
C(6) - C(5) - C(4)	124.7(7)
C(6) - C(5) - Ir(1)	74.2(4)
C(4) - C(5) - Ir(1)	73.9(4)
C(5) - C(6) - C(7)	125.9(8)
C(5) - C(6) - Ir(1)	<b>68</b> . 9(4)
C(7) - C(6) - Ir(1)	109.8(5)
C(8) - C(7) - C(6)	112.1(6)
C(7) - C(8) - C(1)	112.1(7)
C(1B) - P(1) - C(1A)	101.4(5)
C(1B) - P(1) - C(1C)	101.2(4)
C(1A) - P(1) - C(1C)	101.9(4)
C(1B) - P(1) - Ir(1)	115.7(3)
C(1A) - P(1) - Ir(1)	115.0(3)
C(1C) - P(1) - Ir(1)	119.0(3)
C(2A) - P(2) - C(2B)	102.6(5)
C(2A) - P(2) - C(2C)	102. 2(5)
C(2B) - P(2) - C(2C)	98.0(5)
C(2A) - P(2) - Ir(1)	118.8(3)
C(2B) - P(2) - Ir(1)	115.5(3)
C(2C) - P(2) - Ir(1)	110.0(4)
0(3) - S(1) - 0(2)	110.1(0) 114.2(5)
0(3) - S(1) - 0(4)	114.3(3) 112.4(5)
O(2) - S(1) - O(4) O(3) - S(1) - O(4)	113.4(3) 101.2(6)
O(3) - S(1) - C(9)	101.3(0) 105.7(6)
O(A) = S(1) = C(3)	103.7(0) 103.9(6)
F(1) - C(9) - F(3)	110.7(14)
F(1) - C(9) - F(2)	109.5(12)
F(3) - C(9) - F(2)	102.8(11)
F(1) - C(9) - S(1)	113.9(9)
F(3) - C(9) - S(1)	112.2(9)
F(2) - C(9) - S(1)	107.1(12)

Symmetry transformations used to generate equivalent atoms:

Table 18. 4 Anisotropic displacement parameters  $(A^2 \times 10^3)$  for 18. The anisotropic displacement factor exponent takes the form: -2 <sup>2</sup> [  $h^2 a^{*2}$  U11 + ... + 2 h k a\* b\* U12 ]

	U11	U22	U33	U23	U13	U12
lr(1)	36(1)	36(1)	39(1)	3(1)	- 12(1)	- 11(1)
C(1)	62(4)	53(4)	61(4)	26(3)	- 25(3)	- 19(3)
C(2)	81(5)	95(6)	51(4)	19(4)	-8(4)	- 29(5)
C(3)	60(5)	99(7)	83(5)	11(5)	1(4)	- 25(5)
C(4)	33(3)	69(4)	73(4)	11(3)	-7(3)	- 16(3)
C(5)	50(4)	85(5)	68(4)	1(4)	- 25(3)	- 31(4)
C(6)	63(4)	62(4)	68(4)	-9(3)	- 24(3)	- 30(3)
C(7)	93(6)	57(4)	103(6)	-4(4)	- 25(5)	- 37(4)
C(8)	80(5)	39(3)	104(6)	12(4)	- 18(4)	- 24(4)
0(1)	56(2)	45(2)	47(2)	10(2)	- 17(2)	- 10(2)
P(1)	44(1)	43(1)	55(1)	-5(1)	-8(1)	-3(1)
P(2)	54(1)	54(1)	51(1)	- 14(1)	- 12(1)	-9(1)
C(1A)	83(6)	140(9)	95(6)	- 72(7)	-27(5)	17(6)
C(1B)	60(4)	69(5)	95(6)	12(4)	23(4)	-9(4)
C(1C)	49(4)	55(4)	96(5)	-5(4)	- 25(4)	4(3)
C(2A)	113(7)	91(7)	119(7)	- 45(6)	- 73(7)	6(6)
C(2B)	102(7)	55(4)	106(6)	-21(4)	-8(5)	- 34(4)
C(2C)	90(6)	107(7)	74(5)	- 36(5)	0(5)	-2(5)
S(1)	66(1)	65(1)	62(1)	-9(1)	- 16(1)	3(1)
0(2)	131(6)	131(7)	87(4)	26(4)	- 30(4)	- 36(5)
0(3)	88(5)	117(6)	182(8)	-64(6)	5(5)	27(4)
0(4)	99(5)	131(6)	74(4)	-17(4)	- 35(3)	- 4(4)
C(9)	156(11)	82(7)	111(8)	-39(7)	- 45(9)	12(8)
F(1)	355(16)	116(6)	165(8)	21(6)	- 83(10)	- 111(9)
F(2)	298(15)	160(9)	238(12)	- 133(9)	- 48(11)	88(10)
F(3)	233(11)	167(8)	171(8)	- 45(6)	- 83(8)	- 69(8)

	x	У	Z	U(eq)
H(1A)	5651(9)	8908(6)	5892(6)	74
H(2A)	7802(10)	8089(8)	4834(6)	95
H(2B)	8100(10)	9415(8)	4675(6)	95
H(3A)	10424(10)	7809(9)	5118(8)	102
H(3B)	10150(10)	8870(9)	5753(8)	102
H(4A)	10208(7)	6493(7)	6792(6)	74
H(5A)	9819(8)	7094(8)	8496(6)	79
H(6A)	7979(9)	8650(7)	8911(6)	73
H(7A)	7664(12)	10497(7)	7790(8)	98
H(7B)	8964(12)	10033(7)	6865(8)	98
H(8A)	6781(10)	10680(6)	5947(8)	91
H(8B)	5602(10)	10223(6)	7008(8)	91
H(1AA)	4829(12)	9502(10)	9127(8)	152
H(1AB)	4886(12)	8322(10)	10066(8)	152
H(1AC)	3212(12)	9052(10)	9705(8)	152
H(1BA)	3430(10)	6164(7)	8672(8)	125
H(1BB)	2355(10)	7008(7)	9426(8)	125
H(1BC)	4029(10)	6277(7)	9787(8)	125
H(1CA)	3271(8)	9516(7)	7057(7)	103
H(1CB)	1929(8)	9062(7)	8002(7)	103
H(1CC)	2621(8)	8341(7)	7050(7)	103
H(2AA)	4911(13)	7340(9)	5179(9)	151
H(2AB)	3747(13)	6693(9)	6146(9)	151
H(2AC)	4763(13)	5998(9)	5248(9)	151
H(2BA)	6713(13)	4344(7)	7941(8)	127
H(2BB)	5877(13)	4142(7)	6958(8)	127
H(2BC)	4862(13)	4838(7)	7856(8)	127
H(2CA)	8992(12)	5171(10)	6011(8)	136
H(2CB)	8270(12)	6083(10)	4974(8)	136
H(2CC)	7725(12)	4821(10)	5386(8)	136

Table 18.5. Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters ( $A^2\ x\ 10^3)$  for 18.

Table 19.1 Crystal data and structure refinement for 19.

Identification code Empirical formula Formula weight Temperature Wavel ength Crystal system Space group Unit cell dimensions deg. deg. deg. Volume, Z Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected Independent reflections Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I > 2sigma(I)]R indices (all data) Extinction coefficient

Largest diff. peak and hole

 $IrH(COE-PMe_3) (PMe_3)_2(CH_3CN]$ (19) $C_{21}H_{46}F_{12}IrN_2P_5$ 901.65 298(2) K 0.71073 A Tri clini c P-1 a = 11.106(2) A al pha = 77.227(8)b = 12.718(2) A beta = 68.31(2)c = 13.832(2) A gamma = 76.815(9)1747. 2(5)  $A^3$ , 2 1.714 Mg/m<sup>3</sup> 4. 130 mm<sup>-1</sup> 892 0.2 x 0.4 x 0.8 mm 2.00 to 25.00 deg.  $-1 \le h \le 10$ ,  $-14 \le k \le 14$ ,  $-15 \le l \le 16$ 6750 5714 [R(int) = 0.0655]Semi-empirical from psi-scans 1.0000 and 0.8196 Full-matrix least-squares on  $F^2$ 5498 / 0 / 375 1.013 R1 = 0.0379, wR2 = 0.0926R1 = 0.0540, wR2 = 0.12100.0033(4)0.850 and -0.810 e. A<sup>-3</sup>

	Х	У	Z	V(eq)
 In(1)	11702(1)	2004(1)	9202(1)	27(1)
P(1)	11752(1) 13056(2)	-3004(1)	-2303(1)	57(1)
P(2)	13030(2) 19778(9)	-2200(2)	-3607(1)	52(1)
$\Gamma(\mathcal{L})$	10753(6)	-4000(2) -1453(5)	-1846(5)	32(1) 39(1)
C(2)	9474(7)	-1400(5)	-2095(5)	44(2)
C(2)	8382(7)	-1747(5)	-1392(6)	49(2)
C(3)	8684(7)	-2967(5)	-1451(6)	52(2)
C(5)	9910(7)	-3623(5)	-1271(5)	$\frac{32(2)}{44(2)}$
C(6)	10523(6)	-3478(5)	-632(5)	42(2)
C(0)	10020(0) 10160(7)	-2559(6)	-3(5)	50(2)
C(8)	10100(7) 10550(7)	-1489(5)	-686(5)	45(2)
N(1)	13152(6)	-2959(4)	-1583(4)	49(1)
C(9)	13952(8)	-2908(6)	-1255(6)	56(2)
C(10)	14956(8)	-2805(8)	-855(8)	78(3)
P(3)	8813(2)	355(1)	-2078(1)	48(1)
C(1A)	14711(9)	-2166(9)	-4035(8)	90(3)
C(1B)	13158(10)	-2782(7)	- 5001(6)	76(3)
C(1C)	12502(9)	- 774(6)	-4327(6)	73(3)
C(2A)	12067(12)	- 5443(9)	- 3261(11)	110(4)
C(2B)	12727(10)	- 5735(6)	- 1407(7)	84(3)
C(2C)	14507(8)	-5095(7)	-3335(7)	73(2)
C(3A)	8124(10)	826(7)	-3102(7)	73(2)
C(3B)	10046(8)	1143(6)	-2328(7)	64(2)
C(3C)	7549(8)	661(7)	- 884(7)	70(2)
P(4)	7513(3)	4373(2)	-2135(3)	95(1)
F(4A)	8924(10)	4247(18)	-2547(12)	308(10)
F(4B)	7499(11)	4048(13)	- 3091(11)	257(8)
F(4C)	5997(9)	4380(11)	- 1604(8)	198(5)
F(4D)	7524(12)	4761(7)	- 1114(8)	177(4)
F(4E)	7196(14)	5539(7)	- 2572(8)	202(5)
F(4F)	7678(13)	3205(6)	- 1456(12)	221(6)
P(5)	5977(2)	-776(2)	2282(2)	67(1)
F(5A)	7126(9)	- 1270(7)	1419(7)	180(4)
F(5B)	6644(9)	229(7)	2015(8)	164(4)
F(5C)	4792(8)	- 324(8)	3184(7)	175(4)

Table 19.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters (A²  $x\ 10^3)$  for 19. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

5298(9)	- 1783(6)	2576(8)	173(4)
5242(10)	- 177(9)	1533(8)	191(5)
6693(11)	- 1305(11)	3074(9)	233(6)
9056(15)	7659(14)	- 4699(10)	124(5)
8806(26)	6751(18)	- 5056(15)	224(11)
9304(16)	8334(11)	- 4472(10)	151(5)
	$5298(9) \\5242(10) \\6693(11) \\9056(15) \\8806(26) \\9304(16)$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

Table 19.4	Bond lengths	[A]	and	$\operatorname{angl} \operatorname{es}$	[deg]	for	19.
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Ir(1)-N(1)	2.112(7)
Ir(1) - C(1)	2.143(6)
Ir(1) - C(6)	2.248(6)
Ir(1) - C(5)	2.253(6)
Ir(1) - P(1)	2.291(2)
Ir(1) - P(2)	2.357(2)
P(1) - C(1A)	1. 786(9)
P(1) - C(1B)	1. 796(8)
P(1) - C(1C)	1.818(8)
P(2) - C(2B)	1.795(8)
P(2) - C(2C)	1.804(8)
P(2) - C(2A)	1.808(10)
C(1) - C(8)	1. 528(8)
C(1) - C(2)	1.530(10)
C(2) - C(3)	1. 525(10)
C(2) - P(3)	1.829(6)
C(3) - C(4)	1.525(9)
C(4) - C(5)	1. 501(10)
C(5) - C(6)	1.361(9)
C(6) - C(7)	1.503(9)
C(7) - C(8)	1.527(9)
N(1) - C(9)	1.156(9)
C(9) - C(10)	1.456(12)
P(3) - C(3B)	1.767(8)
P(3) - C(3A)	1.779(8)
P(3) - C(3C)	1. 781(8)
P(4) - F(4A)	1. 439(10)
P(4) - F(4B)	1.476(10)
P(4) - F(4E)	1. 487(8)
P(4) - F(4C)	1.567(10)
P(4) - F(4F)	1.584(10)
P(4) - F(4D)	1.601(9)
P(5) - F(5A)	1.512(7)
P(5) - F(5E)	1. 520(8)
P(5) - F(5B)	1.531(7)
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P(5) - F(5D)	1.535(7)
P(5) - F(5F)	1.536(9)
P(5) - F(5C)	1.542(8)
C(11) - N(2)	1.10(2)
C(11) - C(12)	1.47(2)
N(1) - Ir(1) - C(1)	89.5(2)
N(1) - Ir(1) - C(6)	82.9(2)
C(1) - Ir(1) - C(6)	77.6(2)
N(1) - Ir(1) - C(5)	117.6(2)
C(1) - Ir(1) - C(5)	84.7(2)
C(6) - Ir(1) - C(5)	35.2(2)
N(1) - Ir(1) - P(1)	91.9(2)
C(1) - Ir(1) - P(1)	92.1(2)
C(6) - Ir(1) - P(1)	168.5(2)
C(5) - Ir(1) - P(1)	150. 2(2)
N(1) - Ir(1) - P(2)	89.9(2)
C(1) - Ir(1) - P(2)	173.0(2)
C(6) - Ir(1) - P(2)	95.3(2)
C(5) - Ir(1) - P(2)	89.3(2)
P(1) - Ir(1) - P(2)	94.90(7)
C(1A) - P(1) - C(1B)	105.7(5)
C(1A) - P(1) - C(1C)	101.2(5)
C(1B) - P(1) - C(1C)	99.6(4)
C(1A) - P(1) - Ir(1)	116.5(3)
C(1B) - P(1) - Ir(1)	114.2(3)
C(1C) - P(1) - Ir(1)	117.4(3)
C(2B) - P(2) - C(2C)	99.6(4)
C(2B) - P(2) - C(2A)	104.3(5)
C(2C) - P(2) - C(2A)	101.9(5)
C(2B) - P(2) - Ir(1)	113.0(3)
C(2C) - P(2) - Ir(1)	119.8(3)
C(2A) - P(2) - Ir(1)	115.9(4)
C(8) - C(1) - C(2)	112.9(5)
C(8) - C(1) - Ir(1)	108.8(4)
C(2) - C(1) - Ir(1)	113.0(4)
C(3) - C(2) - C(1)	114.3(5)
C(3) - C(2) - P(3)	108.1(5)
C(1) - C(2) - P(3)	114.0(5)
C(4) - C(3) - C(2)	115.4(6)
C(5) - C(4) - C(3)	118.8(6)
C(6) - C(5) - C(4)	128.7(6)
C(6) - C(5) - Ir(1)	72.2(4)
C(4) - C(5) - Ir(1)	115.6(4)
C(5) - C(6) - C(7)	126.8(6)
C(5) - C(6) - Ir(1)	72.6(4)

C(7) - C(6) - Ir(1)	111.5(4)
C(6) - C(7) - C(8)	112.6(5)
C(1) - C(8) - C(7)	113.3(5)
C(9) - N(1) - Ir(1)	175. 3(6)
N(1) - C(9) - C(10)	178.1(8)
C(3B) - P(3) - C(3A)	107.1(4)
C(3B) - P(3) - C(3C)	107.6(4)
C(3A) - P(3) - C(3C)	107.0(4)
C(3B) - P(3) - C(2)	112. 2(3)
C(3A) - P(3) - C(2)	108. 2(4)
C(3C) - P(3) - C(2)	114. 5(3)
F(4A) - P(4) - F(4B)	90. 4(8)
F(4A) - P(4) - F(4E)	99. 2(10)
F(4B) - P(4) - F(4E)	89. 5(8)
F(4A) - P(4) - F(4C)	173. 4(10)
F(4B) - P(4) - F(4C)	91.1(7)
F(4E) - P(4) - F(4C)	87. 3(7)
F(4A) - P(4) - F(4F)	87. 2(9)
F(4B) - P(4) - F(4F)	99.6(8)
F(4E) - P(4) - F(4F)	168.8(7)
F(4C) - P(4) - F(4F)	86. 2(7)
F(4A) - P(4) - F(4D)	89.7(8)
F(4B) - P(4) - F(4D)	178.3(8)
F(4E) - P(4) - F(4D)	88.8(5)
F(4C) - P(4) - F(4D)	89.1(6)
F(4F) - P(4) - F(4D)	82.0(6)
F(5A) - P(5) - F(5E)	93. 3(7)
F(5A) - P(5) - F(5B)	88. 4(5)
F(5E) - P(5) - F(5B)	87.1(6)
F(5A) - P(5) - F(5D)	92.6(5)
F(5E) - P(5) - F(5D)	93.6(6)
F(5B) - P(5) - F(5D)	178.7(6)
F(5A) - P(5) - F(5F)	89.7(7)
F(5E) - P(5) - F(5F)	175.8(8)
F(5B) - P(5) - F(5F)	90.0(6)
F(5D) - P(5) - F(5F)	89.2(6)
F(5A) - P(5) - F(5C)	177. 5(6)
F(5E) - P(5) - F(5C)	87.8(7)
F(5B) - P(5) - F(5C)	93. 9(5)
F(5D) - P(5) - F(5C)	85.1(5)
F(5F) - P(5) - F(5C)	89. 3(7)
N(2) - C(11) - C(12)	176(2)

Symmetry transformations used to generate equivalent atoms:

	U11	U22	U33	U23	U13	U12
Ir(1)	38(1)	36(1)	34(1)	-9(1)	- 10(1)	- 1(1)
P(1)	49(1)	56(1)	36(1)	-6(1)	-3(1)	0(1)
P(2)	49(1)	44(1)	60(1)	-20(1)	- 14(1)	6(1)
C(1)	37(4)	40(3)	37(3)	-4(3)	-9(3)	- 11(3)
C(2)	54(4)	40(3)	36(3)	- 11(3)	- 13(3)	-1(3)
C(3)	43(4)	44(4)	64(4)	-12(3)	-23(3)	0(3)
C(4)	40(4)	49(4)	64(4)	- 14(3)	- 11(3)	-8(3)
C(5)	41(4)	37(3)	50(4)	-7(3)	-8(3)	- 10(3)
C(6)	43(4)	34(3)	39(3)	-1(3)	-8(3)	- 4(3)
C(7)	51(4)	56(4)	40(4)	- 11(3)	- 12(3)	- 5(3)
C(8)	47(4)	43(3)	48(4)	- 18(3)	- 18(3)	2(3)
N(1)	49(4)	44(3)	49(3)	-7(2)	- 15(3)	2(3)
C(9)	52(5)	54(4)	59(4)	- 15(3)	-21(4)	6(4)
C(10)	43(5)	102(7)	109(7)	- 46(6)	- 39(5)	2(5)
P(3)	49(1)	42(1)	47(1)	-7(1)	- 17(1)	3(1)
C(1A)	58(6)	122(8)	70(6)	4(5)	- 5(5)	- 26(6)
C(1B)	99(7)	67(5)	45(4)	- 14(4)	- 12(4)	6(5)
C(1C)	87(6)	57(5)	52(4)	4(4)	-4(4)	- 10(4)
C(2A)	121(10)	84(7)	164(12)	- 60(7)	-81(9)	2(7)
C(2B)	106(8)	42(4)	72(6)	-6(4)	- 5(5)	8(4)
C(2C)	63(5)	69(5)	67(5)	- 20(4)	- 12(4)	23(4)
C(3A)	85(7)	66(5)	70(5)	3(4)	- 45(5)	7(5)
C(3B)	65(5)	42(4)	83(6)	-9(4)	-24(4)	-7(4)
C(3C)	64(5)	58(5)	71(5)	-22(4)	-7(4)	10(4)
P(4)	81(2)	59(1)	166(3)	- 30(2)	-69(2)	8(1)
F(4A)	75(6)	600(32)	244(15)	- 89(17)	- 35(8)	- 54(12)
F(4B)	180(10)	357(17)	327(16)	-271(15)	- 116(11)	44(10)
F(4C)	121(7)	301(14)	170(9)	15(9)	-69(7)	- 45(8)
F(4D)	272(12)	125(6)	196(9)	-27(6)	- 152(10)	-26(7)
F(4E)	351(16)	101(6)	156(8)	16(5)	- 117(10)	- 18(8)
F(4F)	248(13)	78(5)	386(18)	- 37(7)	- 181(14)	12(6)
P(5)	59(1)	67(1)	63(1)	-8(1)	-2(1)	- 20(1)
F(5A)	153(7)	157(7)	151(7)	- 71(6)	50(6)	0(6)
F(5B)	153(7)	135(6)	206(9)	- 18(6)	- 22(6)	-98(6)
F(5C)	131(7)	195(9)	153(7)	-85(6)	51(6)	- 49(6)

Table 19.4 Anisotropic displacement parameters  $(A^2\ x\ 10^3)$  for 19. The anisotropic displacement factor exponent takes the form: -2  $^2$  [  $h^2\ a^{*2}$  U11 + ... + 2 h k a\* b\* U12 ]

F(5D)	171(8)	102(5)	211(9)	- 20(5)	7(7)	-82(5)
F(5E)	166(9)	238(11)	179(9)	71(8)	- 107(8)	-68(8)
F(5F)	169(9)	336(16)	167(9)	108(10)	- 90(8)	- 74(10)
C(11)	135(12)	166(14)	70(7)	- 22(8)	- 15(7)	- 50(11)
C(12)	337(30)	216(20)	150(16)	- 74(14)	- 22(17)	- 160(21)
N(2)	209(15)	154(12)	125(10)	- 38(8)	- 86(10)	- 30(10)

Table 19.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters (A²  $x\ 10^3)$  for 19.

H(1) 11155(75) - 2936(59) - 2907(59)   H(1A) 11322(6) - 909(5) - 2253(5)   H(2A) 9678(7) - 1231(5) - 2815(5)   H(3A) 8183(7) - 1654(5) - 669(6)   H(2P) 7600(7) 1428(5) 1578(6)	
H(1A) $11322(6)$ $-909(5)$ $-2253(5)$ $H(2A)$ $9678(7)$ $-1231(5)$ $-2815(5)$ $H(3A)$ $8183(7)$ $-1654(5)$ $-669(6)$ $H(2P)$ $7600(7)$ $1428(5)$ $1578(6)$	64(22)
H(2A)9678(7) $-1231(5)$ $-2815(5)$ $H(3A)$ $8183(7)$ $-1654(5)$ $-669(6)$ $H(2P)$ $7600(7)$ $1428(5)$ $1578(6)$	47
H(3A) 8183(7) $-1654(5)$ $-669(6)$ H(2P) 7600(7) 1428(5) 1578(6)	53
H(2D) = 7600(7) = 1429(5) = 1579(6)	59
$\Pi(3D)$ (000(7) -1438(3) -1578(6)	59
H(4A) 7946(7) - 3294(5) - 941(6)	62
H(4B) 8721(7) - 3053(5) - 2142(6)	62
H(5A) 9972(7) -4400(5) -1289(5)	52
H(6A) 10896(6) -4168(5) -291(5)	50
H(7A) 10590(7) -2760(6) 523(5)	60
H(7B) 9220(7) -2451(6) 362(5)	60
H(8A) 9871(7) -889(5) -422(5)	54
H(8B) 11356(7) -1384(5) -626(5)	54
H(1AA) 14718(9) -1860(9) -3462(8)	134
H(1AB) 15110(9) -1725(9) -4689(8)	134
H(1AC) 15196(9) - 2895(9) - 4028(8)	134
H(1BA) 12290(10) - 2822(7) - 4967(6)	115
H(1BB) 13664(10) - 3502(7) - 4983(6)	115
H(1BC) 13574(10) - 2332(7) - 5643(6)	115
H(1CA) 11605(9) -680(6) -4291(6)	110
H(1CB) 13040(9) - 560(6) - 5039(6)	110
H(1CC) 12569(9) - 328(6) - 3879(6)	110
H(2AA) 12059(12) - 4990(9) - 3914(11)	165
H(2AB) 11185(12) - 5531(9) - 2822(11)	165
H(2AC) 12581(12) -6145(9) -3397(11)	165
H(2BA) 11843(10) - 5675(6) - 922(7)	127
H(2BB) 13288(10) - 5559(6) - 1098(7)	127
H(2BC) 13024(10) - 6469(6) - 1562(7)	127
H(2CA) 14693(8) -4646(7) -4013(7)	109
H(2CB) 14741(8) -5851(7) -3424(7)	109

H(2CC)	15006(8)	- 4943(7)	- 2960(7)	109
H(3AA)	7448(10)	415(7)	-2992(7)	110
H(3AB)	8797(10)	732(7)	- 3768(7)	110
H(3AC)	7756(10)	1586(7)	- 3097(7)	110
H(3BA)	10442(8)	910(6)	- 1790(7)	96
H(3BB)	9662(8)	1900(6)	-2329(7)	96
H(3BC)	10703(8)	1047(6)	- 3001(7)	96
H(3CA)	6862(8)	244(7)	- 728(7)	105
H(3CB)	7199(8)	1426(7)	-959(7)	105
H(3CC)	7904(8)	478(7)	- 321(7)	105

Table 21.1 Crystal data and structure refinement for 21.

Identification code Empirical formula Formula weigh Temperature Wavelength Crystal system Space group Unit cell dimensions

deg.

Volume, Z Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected Independent reflections Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on  $F^2$ Final R indices [I > 2sigma(I)]R indices (all data) Extinction coefficient Largest diff. peak and hole

 $fac-Ir(CH_3)_3(PMe_3)_3$  (21)  $C_{12}$  H<sub>36</sub> Ir P<sub>3</sub> 465.52 298(2) K 0.71073 A Monocl i ni c P2(1)/na = 9.3643(13) A al pha = 90 deg.beta = 93.843(2)b = 13.638(3) A gamma = 90 deg. c = 15.290(2) A 1948. 3(5)  $A^3$ , 4 1.587 Mg/m<sup>3</sup> 7.081 mm<sup>^</sup>-1 920 0.2 x 0.4 x 0.6 mm 2.00 to 22.49 deg. - 1<=h<=10, - 1<=k<=14, - 16<=l<=16 3396 2537 [R(int) = 0.0700]Semi-empirical from psi-scans 1.0000 and 0.2643 Full-matrix least-squares on  $F^2$ 2346 / 0 / 146 1.029 R1 = 0.0506, wR2 = 0.1198R1 = 0.0734, wR2 = 0.13860.0015(3)2. 205 and -1. 043 e.  $A^{\text{-3}}$ 

	x	у	Z	U(eq)
 I(1)	670(1)	2270(1)	2214(1)	52(1)
$\Gamma(1)$	0/0(1)	2379(1)	3214(1)	33(1)
$\mathcal{L}(1)$	1498(20)	968(11)	3564(13)	122(7)
C(2)	- 927(20)	1606(12)	2420(13)	127(8)
C(3)	1896(24)	2207(14)	2095(14)	133(8)
P(1)	- 396(4)	3780(3)	2637(3)	65(1)
P(2)	2642(4)	3136(3)	3889(3)	77(1)
P(3)	-619(4)	2241(3)	4429(3)	72(1)
C(1A)	45(20)	4137(14)	1547(11)	116(6)
C(1B)	-2347(16)	3747(15)	2494(14)	130(8)
C(1C)	- 190(17)	4969(10)	3163(12)	103(6)
C(2A)	3679(21)	3918(18)	3192(16)	186(12)
C(2B)	4091(23)	2363(14)	4354(18)	144(10)
C(2C)	2507(19)	3940(15)	4842(14)	152(9)
C(3A)	296(23)	1725(19)	5393(14)	164(10)
C(3B)	-2153(17)	1397(13)	4363(14)	122(7)
C(3C)	-1549(20)	3292(15)	4878(12)	126(7)

Table 21.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters (A<sup>2</sup>  $x\ 10^3$ ) for 21. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 21.3	Bond	lengths	[A]	and	angl es	[deg]	] for	21
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$\mathbf{T}$ (1) $\mathbf{C}$ (1)	0 10(0)
1r(1) - C(1)	2.13(2)
Ir(1) - C(3)	2.14(2)
Ir(1) - C(2)	2.139(14)
Ir(1) - P(3)	2.290(4)
Ir(1) - P(2)	2.299(4)
Ir(1) - P(1)	2.305(4)
P(1)-C(1C)	1.81(2)
P(1) - C(1A)	1.81(2)
P(1) - C(1B)	1.83(2)
P(2) - C(2B)	1.82(2)
P(2) - C(2A)	1.83(2)
P(2) - C(2C)	1.83(2)
P(3) - C(3A)	1.80(2)

P(3) - C(3C)	1.83(2)
P(3) - C(3B)	1.84(2)
C(1) - Ir(1) - C(3)	84.1(8)
C(1) - Ir(1) - C(2)	85.8(7)
C(3) - Ir(1) - C(2)	83.4(8)
C(1) - Ir(1) - P(3)	85.7(5)
C(3) - Ir(1) - P(3)	169.0(5)
C(2) - Ir(1) - P(3)	91.9(6)
C(1) - Ir(1) - P(2)	91.5(6)
C(3) - Ir(1) - P(2)	87.1(7)
C(2) - Ir(1) - P(2)	170.3(6)
P(3) - Ir(1) - P(2)	97.1(2)
C(1) - Ir(1) - P(1)	170.7(6)
C(3) - Ir(1) - P(1)	91.5(6)
C(2) - Ir(1) - P(1)	85.6(5)
P(3) - Ir(1) - P(1)	98.03(14)
P(2) - Ir(1) - P(1)	96. 51(13)
C(1C) - P(1) - C(1A)	98.3(8)
C(1C) - P(1) - C(1B)	98.7(8)
C(1A) - P(1) - C(1B)	100.6(8)
C(1C) - P(1) - Ir(1)	122.8(5)
C(1A) - P(1) - Ir(1)	117.1(6)
C(1B) - P(1) - Ir(1)	115.5(6)
C(2B) - P(2) - C(2A)	98.8(11)
C(2B) - P(2) - C(2C)	97.1(11)
C(2A) - P(2) - C(2C)	100. 5(12)
C(2B) - P(2) - Ir(1)	118.0(7)
C(2A) - P(2) - Ir(1)	116.3(8)
C(2C) - P(2) - Ir(1)	121.9(6)
C(3A) - P(3) - C(3C)	102.2(11)
C(3A) - P(3) - C(3B)	97.3(10)
C(3C) - P(3) - C(3B)	97.0(9)
C(3A) - P(3) - Ir(1)	116.6(8)
C(3C) - P(3) - Ir(1)	122.0(6)
C(3B) - P(3) - Ir(1)	117.3(7)

Symmetry	transformations	used	to	generate	equi val ent	atoms:

	U11	U22	U33	U23	U13	U12
 In(1)	69(1)	49(1)	51(1)	7(1)	12(1)	7(1)
C(1)	$\frac{02(1)}{160(17)}$	40(1) 64(10)	1/3(10)	-7(1) -2(11)	13(1) 28(14)	7(1) 30(11)
C(1)	189(19)	65(11)	143(19) 119(18)	-30(11)	-51(14)	-30(11)
C(3)	160(19)	139(17)	110(18)	-12(14)	92(15)	30(14)
P(1)	72(2)	67(2)	54(3)	4(2)	-9(2)	4(2)
P(2)	42(2)	90(3)	99(4)	13(2)	-2(2)	3(2)
P(3)	75(2)	67(2)	77(3)	7(2)	25(2)	-3(2)
C(1A)	162(17)	111(14)	74(14)	19(11)	0(12)	8(13)
C(1B)	90(12)	122(16)	173(22)	29(15)	-25(12)	5(11)
C(1C)	112(12)	58(9)	136(17)	2(10)	-24(11)	17(9)
C(2A)	120(16)	218(27)	217(28)	127(23)	- 11(16)	-67(16)
C(2B)	111(16)	163(22)	155(24)	29(16)	-21(15)	35(13)
C(2C)	123(15)	158(19)	167(23)	-74(18)	- 42(15)	-29(14)
C(3A)	166(20)	216(28)	106(19)	73(19)	- 13(15)	- 33(19)
C(3B)	106(13)	96(13)	171(21)	-4(13)	54(13)	- 30(10)
C(3C)	169(18)	124(16)	95(16)	- 3(13)	79(14)	18(14)

Table 21.4 Anisotropic displacement parameters ( $A^2 \times 10^3$ ) for 21. The anisotropic displacement factor exponent takes the form: -2 p<sup>2</sup> [ h<sup>2</sup> a\*^2 U11 + ... + 2 h k a\* b\* U12 ]

Table 21.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters  $(A^2\ x\ 10^3)$  for 21.

	х	У	Z	U(eq)
 H(1A)	1136(20)	766(11)	4109(13)	
H(1B)	2524(20)	997(11)	3627(13)	182
H(1C)	1207(20)	505(11)	3114(13)	182
H(2A)	- 1569(20)	2067(12)	2128(13)	191
H(2B)	- 1453(20)	1183(12)	2784(13)	191

H(2C)	- 474(20)	1219(12)	1993(13)	191
H(3A)	1780(24)	2777(14)	1728(14)	199
H(3B)	1570(24)	1638(14)	1770(14)	199
H(3C)	2889(24)	2130(14)	2283(14)	199
H(1AA)	- 13(20)	3574(14)	1168(11)	174
H(1AB)	1000(20)	4397(14)	1571(11)	174
H(1AC)	- 617(20)	4628(14)	1323(11)	174
H(1BA)	- 2645(16)	3144(15)	2214(14)	195
H(1BB)	- 2680(16)	4290(15)	2136(14)	195
H(1BC)	- 2742(16)	3790(15)	3056(14)	195
H(1CA)	- 392(17)	4912(10)	3768(12)	155
H(1CB)	- 843(17)	5427(10)	2875(12)	155
H(1CC)	773(17)	5196(10)	3123(12)	155
H(2AA)	3053(21)	4382(18)	2890(16)	279
H(2AB)	4130(21)	3519(18)	2773(16)	279
H(2AC)	4398(21)	4262(18)	3549(16)	279
H(2BA)	3714(23)	1896(14)	4748(18)	216
H(2BB)	4795(23)	2764(14)	4668(18)	216
H(2BC)	4526(23)	2022(14)	3891(18)	216
H(2CA)	1769(19)	4418(15)	4716(14)	227
H(2CB)	3404(19)	4268(15)	4969(14)	227
H(2CC)	2277(19)	3555(15)	5339(14)	227
H(3AA)	829(23)	1159(19)	5233(14)	245
H(3AB)	- 391(23)	1537(19)	5800(14)	245
H(3AC)	938(23)	2204(19)	5660(14)	245
H(3BA)	- 2788(17)	1566(13)	3866(14)	183
H(3BB)	- 2654(17)	1447(13)	4888(14)	183
H(3BC)	- 1818(17)	737(13)	4299(14)	183
H(3CA)	- 2084(20)	3629(15)	4413(12)	189
H(3CB)	- 860(20)	3732(15)	5158(12)	189
H(3CC)	- 2189(20)	3066(15)	5300(12)	189

Table 26.1 Crystal data and structure refinement for 26.

Identification code	$[IrH(H_20)_2(PMe_3)_3][0Tf]_2$ (26)
Empirical formula	$C_{11}$ $H_{32}$ $F_6$ Ir $O_8$ $P_3$ $S_2$
Formula weight	755. 60
Temperature	298(2) K
Wavelength	0. 71073 A
Crystal system	Tri clini c
Space group	P-1
Unit cell dimensions	a = 10.316(2) A al pha = 105.168(7)
deg.	
	b = 10.7653(11) A beta =
104. 728(9) deg.	
	c = 14.195(2) A gamma = 107.021(8)
deg.	
Volume, Z	1358. 2(3) $A^3$ , 2
Density (calculated)	1.848 Mg/m <sup>3</sup>
Absorption coefficient	5. 317 $\text{mm}^{-1}$
F(000)	740
Crystal size	0.3 x 0.4 x 0.6 mm
Theta range for data collection	2.12 to 24.99 deg.
Limiting indices	$-1 \le h \le 12$ , $-11 \le k \le 11$ , $-16 \le l \le 16$
Reflections collected	4881
Independent reflections	$4121 \ [R(int) = 0.0260]$
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	1.0000 and 0.3005
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4030 / 0 / 297
Goodness-of-fit on $F^2$	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1031
R indices (all data	R1 = 0.0501, $wR2 = 0.1358$
Extinction coefficient	0.0071(7)
Largest diff. peak and hole	2. 078 and -1. 710 e. $A^{-3}$

	х	у	Z	U(eq)
 Ir(1)	5060(1)	- 2412(1)	- 2336(1)	31(1)
0(1)	5766(7)	-4125(6)	-2974(5)	45(1)
0(2)	3102(6)	-4124(7)	-2583(5)	45(1)
P(1)	3622(2)	-2695(2)	-4018(2)	45(1)
P(2)	7047(2)	-792(2)	-2284(2)	48(1)
P(3)	5902(2)	-2241(2)	-595(2)	41(1)
C(1A)	4077(14)	- 1495(16)	-4666(12)	106(5)
C(1B)	3274(20)	- 4319(15)	- 4956(10)	116(6)
C(1C)	1891(13)	- 2660(19)	-4037(12)	112(6)
C(2A)	6983(14)	885(12)	-2183(14)	103(5)
C(2B)	8749(9)	- 292(10)	- 1245(9)	67(3)
C(2C)	7549(12)	-1392(12)	-3412(10)	73(3)
C(3A)	7083(12)	-3122(12)	-240(9)	68(3)
C(3B)	6779(14)	- 502(11)	421(9)	74(3)
C(3C)	4397(10)	- 3028(11)	-213(8)	62(2)
S(1)	3557(2)	-7405(2)	-2905(2)	53(1)
0(3)	3973(10)	- 8390(8)	- 2559(8)	102(3)
0(4)	4210(10)	- 6918(8)	-3586(7)	92(3)
0(5)	3528(9)	-6287(7)	-2105(6)	71(2)
C(1)	1693(14)	- 8363(12)	- 3729(12)	86(4)
F(1)	1108(10)	- 7624(11)	- 4107(10)	159(5)
F(2)	943(11)	-8847(15)	- 3210(13)	183(6)
F(3)	1572(11)	-9452(9)	- 4504(8)	136(4)
S(2)	- 46(2)	- 3637(3)	- 1720(2)	60(1)
0(6)	471(13)	-2803(9)	-616(8)	125(4)
0(7)	1027(10)	- 3429(12)	- 2141(10)	113(4)
0(8)	- 1355(7)	- 3601(8)	-2295(7)	77(2)
C(2)	- 468(20)	- 5324(15)	- 1702(14)	103(5)
F(4)	- 1024(18)	-6224(11)	-2744(11)	196(7)
F(5)	- 1503(14)	- 5663(11)	- 1300(13)	174(6)
F(6)	600(13)	- 5576(11)	- 1230(10)	150(4)

Table 26.2 Atomic coordinates (  $x\ 10^4)$  and equivalent isotropic displacement parameters (A<sup>2</sup>  $x\ 10^3$ ) for 26. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Ir(1) - O(2)	2.173(5)
Ir(1) - P(2)	2.238(2)
Ir(1) - O(1)	2.236(5)
Ir(1) - P(3)	2.340(2)
Ir(1) - P(1)	2.355(2)
P(1) - C(1B)	1.769(13)
P(1) - C(1C)	1.791(11)
P(1) - C(1A)	1.795(10)
P(2) - C(2A)	1.796(11)
P(2) - C(2B)	1.806(10)
P(2) - C(2C)	1.823(12)
P(3) - C(3A)	1.803(9)
P(3) - C(3C)	1.823(9)
P(3) - C(3B)	1.827(10)
S(1)-0(3)	1.408(8)
S(1)-0(5)	1.436(8)
S(1)-O(4)	1.432(9)
S(1) - C(1)	1.788(12)
C(1) - F(1)	1.27(2)
C(1) - F(2)	1.29(2)
C(1) - F(3)	1.33(2)
S(2) - O(7)	1.377(8)
S(2) - O(8)	1.407(7)
S(2) - O(6)	1.450(10)
S(2) - C(2)	1.748(14)
C(2) - F(6)	1.28(2)
C(2) - F(5)	1.34(2)
C(2) - F(4)	1.40(2)
D(9) In(1) D(9)	179 0(9)
0(2) - 11(1) - 1(2) 0(2) - 1n(1) - 0(1)	172.9(2) 83.6(2)
P(2) - Ir(1) - O(1)	91 7(2)
0(2) - Ir(1) - O(1)	31.7(2)
P(2) - Ir(1) - P(3)	97 74(8)
$\Omega(1) - Ir(1) - P(3)$	97.74(8) 95.9(2)
O(2) - Ir(1) - P(1)	30.0(2)
P(2) - Ir(1) - P(1)	94, 80(9)
0(1) - Ir(1) - P(1)	$92 \ A(2)$
P(3) - Ir(1) - P(1)	164, 76(8)
C(1B) - P(1) - C(1C)	104.70(0) 106.6(9)
C(1B) - P(1) - C(1A)	103.1(8)
C(1C) - P(1) - C(1A)	98.8(7)
C(1B) - P(1) - Ir(1)	111.6(5)
C(1C) - P(1) - Ir(1)	110.6(5)

Table 26.3 Bond lengths [A] and angles [deg] for 26.

\_

C(1A) - P(1) - Ir(1)	124.3(5)
C(2A) - P(2) - C(2B)	100.8(6)
C(2A) - P(2) - C(2C)	107.4(7)
C(2B) - P(2) - C(2C)	99.7(5)
C(2A) - P(2) - Ir(1)	116.6(4)
C(2B) - P(2) - Ir(1)	118.7(4)
C(2C) - P(2) - Ir(1)	111.7(4)
C(3A) - P(3) - C(3C)	101.7(5)
C(3A) - P(3) - C(3B)	104.3(6)
C(3C) - P(3) - C(3B)	101.0(5)
C(3A) - P(3) - Ir(1)	118.6(4)
C(3C) - P(3) - Ir(1)	110.8(3)
C(3B) - P(3) - Ir(1)	117.9(4)
0(3) - S(1) - 0(5)	114.9(5)
0(3) - S(1) - 0(4)	116.9(6)
0(5) - S(1) - 0(4)	112.1(5)
0(3) - S(1) - C(1)	103.7(6)
0(5) - S(1) - C(1)	104.0(6)
0(4) - S(1) - C(1)	103.1(7)
F(1) - C(1) - F(2)	106.8(14)
F(1) - C(1) - F(3)	109. 5(14)
F(2) - C(1) - F(3)	107.1(12)
F(1) - C(1) - S(1)	113.0(9)
F(2) - C(1) - S(1)	110. 4(12)
F(3) - C(1) - S(1)	109.8(10)
0(7) - S(2) - 0(8)	115.8(6)
0(7) - S(2) - 0(6)	113.1(8)
0(8) - S(2) - 0(6)	112.8(6)
0(7) - S(2) - C(2)	105.6(7)
0(8) - S(2) - C(2)	106. 2(7)
0(6) - S(2) - C(2)	101.8(7)
F(6) - C(2) - F(5)	108. 2(14)
F(6) - C(2) - F(4)	106.8(14)
F(5) - C(2) - F(4)	107(2)
F(6) - C(2) - S(2)	115.7(13)
F(5) - C(2) - S(2)	111.9(12)
F(4) - C(2) - S(2)	106. 4(12)

Symmetry transformations used to generate equivalent atoms:

	U11	U22	U33	U23	U13	U12
Ir(1)	28(1)	32(1)	31(1)	10(1)	10(1)	12(1)
0(1)	34(3)	42(3)	58(4)	10(3)	17(3)	19(3)
0(2)	26(3)	47(3)	59(4)	20(3)	15(3)	10(2)
P(1)	45(1)	58(1)	37(1)	21(1)	11(1)	24(1)
P(2)	38(1)	38(1)	58(2)	18(1)	13(1)	7(1)
P(3)	37(1)	51(1)	34(1)	13(1)	10(1)	19(1)
C(1A)	76(8)	150(13)	108(12)	102(11)	14(8)	33(8)
C(1B)	164(16)	107(10)	39(7)	-3(7)	- 11(8)	67(11)
C(1C)	58(7)	224(18)	101(11)	96(12)	34(8)	82(10)
C(2A)	82(9)	54(6)	175(17)	53(8)	41(10)	24(6)
C(2B)	33(5)	68(6)	70(7)	8(5)	8(5)	3(4)
C(2C)	55(6)	88(7)	75(8)	37(6)	33(6)	13(5)
C(3A)	77(7)	95(8)	55(6)	38(6)	25(6)	54(6)
C(3B)	85(8)	69(6)	49(6)	4(5)	19(6)	25(6)
C(3C)	52(5)	91(7)	43(5)	27(5)	24(5)	20(5)
S(1)	49(1)	46(1)	49(1)	13(1)	5(1)	12(1)
0(3)	118(8)	75(5)	100(7)	28(5)	6(6)	52(5)
0(4)	93(6)	69(5)	89(7)	10(4)	45(5)	3(4)
0(5)	95(5)	56(4)	58(5)	19(3)	20(4)	33(4)
C(1)	64(7)	62(7)	98(10)	19(7)	6(7)	7(6)
F(1)	91(6)	134(7)	188(12)	45(8)	- 41(7)	45(6)
F(2)	83(7)	202(12)	229(16)	84(12)	72(9)	- 11(7)
F(3)	110(7)	88(5)	113(8)	- 19(5)	- 10(6)	-1(5)
S(2)	37(1)	67(1)	87(2)	39(1)	26(1)	24(1)
0(6)	137(9)	82(6)	77(7)	- 18(5)	-6(7)	14(6)
0(7)	89(6)	172(9)	184(11)	130(9)	102(7)	93(7)
0(8)	38(4)	86(5)	102(7)	33(5)	11(4)	31(3)
C(2)	125(13)	83(9)	114(13)	43(9)	55(11)	40(9)
F(4)	277(16)	98(7)	139(11)	- 17(7)	7(11)	80(9)
F(5)	175(11)	104(7)	288(18)	110(9)	142(12)	30(7)
$\mathbf{F}(6)$	181(10)	199(9)	200(12)	105(9)	CT( <b>0</b> )	100(0)

Table 26.4 Anisotropic displacement parameters  $(A^2 \ x \ 10^3)$  for 26. The anisotropic displacement factor exponent takes the form: -2 p^2 [ h^2 a^\*2 U11 + ... + 2 h k a^\* b^\* U12 ]

	x	У	Z	U(eq)
H(1AA)	4288(14)	- 569(16)	- 4213(12)	159
H(1AB)	3273(14)	- 1753(16)	- 5295(12)	159
H(1AC)	4913(14)	- 1523(16)	- 4837(12)	159
H(1BA)	4176(20)	- 4384(15)	- 4973(10)	174
H(1BB)	2699(20)	- 4395(15)	- 5632(10)	174
H(1BC)	2756(20)	- 5060(15)	- 4771(10)	174
H(1CA)	2028(13)	- 1792(19)	- 3536(12)	167
H(1CB)	1386(13)	- 3418(19)	- 3862(12)	167
H(1CC)	1330(13)	- 2751(19)	- 4722(12)	167
H(2AA)	6108(14)	768(12)	- 2703(14)	154
H(2AB)	7809(14)	1438(12)	- 2291(14)	154
H(2AC)	6998(14)	1346(12)	- 1500(14)	154
H(2BA)	8924(9)	- 1111(10)	- 1215(9)	101
H(2BB)	8705(9)	199(10)	- 591(9)	101
H(2BC)	9522(9)	303(10)	- 1377(9)	101
H(2CA)	7592(12)	- 2290(12)	- 3487(10)	109
H(2CB)	8482(12)	- 739(12)	- 3311(10)	109
H(2CC)	6836(12)	- 1462(12)	- 4030(10)	109
H(3AA)	7932(12)	- 2790(12)	- 410(9)	102
H(3AB)	6580(12)	- 4108(12)	-619(9)	102
H(3AC)	7366(12)	- 2938(12)	497(9)	102
H(3BA)	6209(14)	39(11)	287(9)	110
H(3BB)	7731(14)	- 52(11)	420(9)	110
H(3BC)	6857(14)	- 578(11)	1090(9)	110
H(3CA)	3681(10)	-2635(11)	- 368(8)	93
H(3CB)	4749(10)	-2847(11)	524(8)	93
H(3CC)	3968(10)	- 4016(11)	- 592(8)	93
H(2B)	2449(132)	- 3794(115)	-2279(98)	85(37
H(2A)	3311(117)	- 4588(112)	- 2296(93)	74(36
H(1B)	5022(135)	- 4966(125)	- 3389(104)	88(38
H(1A)	6605(128)	- 4066(106)	-2753(93)	69(34

Table 26.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters  $(A^2\ x\ 10^3)$  for 26.

Table 28.1 Crystal data and structure refinement for 28.

Identification code Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

deg.

Volume. Z Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected Independent reflections Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on  $F^2$ Final R indices [I > 2sigma(I)]R indices (all data) Extinction coefficient Largest diff. peak and hole

 $IrH(h^2-3-butenol)(PMe_3)_3$ (28) $C_{15}H_{35}F_{6}Ir0_{7}P_{3}S_{2}$ 790.66 298(2) K 0.71073 A Monocl i ni c P2(1)/na = 14.861(2) A al pha = 90 deg.b = 16.469(2) A beta = 94.009(7)c = 23.732(3) A gamma = 90 deg.5794. 5(12)  $A^3$ , 8 1.813 Mg/m<sup>3</sup> 4.988 mm<sup>-1</sup> 3112 0.3 x 0.4 x 0.6 mm 1.85 to 25.00 deg.  $-1 \le h \le 15$ ,  $-1 \le k \le 19$ ,  $-28 \le l \le 28$ 11920 9872 [R(int) = 0.1325]Semi-empirical from psi-scans 0.9681 and 0.3373 Full-matrix least-squares on  $F^2$ 8971 / 12 / 613 0.926 R1 = 0.0529, wR2 = 0.1236R1 = 0.0982, wR2 = 0.14490.00049(6)1. 504 and -1. 106 e. A<sup>-3</sup>

	x	У	Z	U(eq)
 Ir(1)	7571(1)	8664(1)	927(1)	48(1)
C(1)	8041(11)	9948(7)	1153(7)	101(5)
C(2)	7215(12)	9874(7)	1334(7)	88(4)
C(3)	7195(16)	9717(11)	1967(8)	159(9)
C(4)	7866(14)	9149(12)	2176(6)	148(8)
0(1)	7790(6)	8417(5)	1822(3)	78(2)
P(1)	9100(2)	8386(2)	845(2)	66(1)
P(2)	7354(2)	8957(2)	- 3(1)	64(1)
P(3)	6044(2)	8326(2)	1002(2)	72(1)
C(1A)	9916(8)	9197(7)	744(8)	106(5)
C(1B)	9572(9)	7920(8)	1499(6)	97(5)
C(1C)	9341(8)	7667(7)	305(6)	83(4)
C(2A)	8238(10)	9541(8)	- 306(6)	96(4)
C(2B)	6408(9)	9581(9)	- 206(6)	103(5)
C(2C)	7223(10)	8083(7)	- 457(5)	85(4)
C(3A)	5197(9)	9107(8)	995(8)	116(6)
C(3B)	5928(12)	7809(11)	1650(8)	136(7)
C(3C)	5603(9)	7628(8)	489(7)	102(5)
Ir(2)	7453(1)	5037(1)	- 1752(1)	63(1)
C(5)	7569(12)	6233(7)	-2170(6)	101(5)
C(6)	6993(14)	6393(12)	- 1945(9)	130(7)
C(7)	6056(12)	6265(11)	-2317(9)	141(7)
C(8)	6100(12)	5606(10)	-2742(7)	126(7)
0(2)	6411(7)	4891(6)	-2435(4)	103(3)
P(4)	6239(3)	4966(2)	- 1160(2)	94(1)
P(5)	8514(3)	5232(2)	- 1061(2)	104(1)
P(6)	8485(2)	4519(2)	-2358(2)	80(1)
C(4A)	5838(14)	5827(10)	- 793(8)	154(8)
C(4B)	6393(14)	4286(11)	- 558(9)	166(9)
C(4C)	5234(13)	4519(16)	- 1551(9)	198(12)
C(5A)	9549(12)	5613(12)	- 1251(9)	165(9)
C(5B)	8198(15)	5975(11)	- 562(8)	157(8)
C(5C)	8822(11)	4348(8)	-640(6)	119(6)
C(6A)	9185(11)	3713(9)	-2075(7)	114(5)
C(6B)	7934(12)	4071(16)	- 2959(8)	184(11)

Table 28.2 Atomic coordinates (  $x \ 10^4$ ) and equivalent isotropic displacement parameters ( $A^2 \ x \ 10^3$ ) for 28. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(6C) S(1) O(1A) O(1B) O(1C) C(9) F(9A) F(9B)	$9221(19) \\12603(2) \\13382(8) \\12701(9) \\11824(7) \\12474(13) \\13144(10) \\12443(9)$	5178(12) 8053(2) 7585(8) 8903(6) 7661(8) 8047(9) 8383(8)	-2710(12) 1096(2) 1228(6) 1228(5) 1244(6) 342(9)	$245(17) \\ 85(1) \\ 145(4) \\ 137(4) \\ 144(5) \\ 115(6)$
S(1) 0(1A) 0(1B) 0(1C) C(9) F(9A) F(9B)	$12603(2) \\13382(8) \\12701(9) \\11824(7) \\12474(13) \\13144(10) \\12443(9)$	8053(2) 7585(8) 8903(6) 7661(8) 8047(9) 8383(8)	$1096(2) \\1228(6) \\1228(5) \\1244(6) \\342(9)$	$85(1) \\ 145(4) \\ 137(4) \\ 144(5) \\ 115(6)$
0(1A) 0(1B) 0(1C) C(9) F(9A) F(9B)	$13382(8) \\ 12701(9) \\ 11824(7) \\ 12474(13) \\ 13144(10) \\ 12443(9)$	7585(8) 8903(6) 7661(8) 8047(9) 8383(8)	1228(6) 1228(5) 1244(6) 342(9)	$145(4) \\ 137(4) \\ 144(5) \\ 115(6)$
0(1B) 0(1C) C(9) F(9A) F(9B)	$12701(9) \\11824(7) \\12474(13) \\13144(10) \\12443(9)$	8903(6) 7661(8) 8047(9) 8383(8)	1228(5) 1244(6) 342(9)	137(4) 144(5) 115(6)
0(1C) C(9) F(9A) F(9B)	11824(7) 12474(13) 13144(10) 12443(9)	7661(8) 8047(9) 8383(8)	1244(6) 342(9)	144(5) 115(6)
C(9) F(9A) F(9B)	12474(13) 13144(10) 12443(9)	8047(9) 8383(8)	342(9)	115(6)
F(9A) F(9B)	13144(10) 12443(9)	8383(8)		110(0)
F(9B)	12443(9)		115(6)	187(5)
1(00)		7325(6)	118(5)	154(4)
F(9C)	11794(9)	8434(7)	134(5)	175(5)
S(2)	10392(3)	3259(3)	-3612(2)	106(1)
0(2A)	10521(11)	3786(7)	-4152(6)	189(7)
0(2B)	9560(7)	2894(7)	-3588(6)	133(4)
0(2C)	10793(8)	3615(6)	- 3113(5)	127(4)
C(10)	11142(12)	2543(12)	-3835(7)	113(5)
F(10A)	11138(11)	1946(7)	-3377(6)	207(6)
F(10B)	11930(6)	2779(8)	- 3844(5)	166(5)
F(10C)	10882(6)	2143(5)	- 4273(4)	119(3)
S(3)	9579(3)	8351(3)	- 1540(3)	118(2)
0(3A)	9341(17)	8597(13)	-2103(11)	295(13)
0(3B)	9847(14)	8995(11)	- 1207(13)	338(18)
0(3C)	9039(9)	7786(7)	- 1294(6)	151(5)
C(11)	10653(15)	7840(18)	- 1606(13)	156(8)
F(11A)	11000(12)	7712(19)	- 1154(9)	342(16)
F(11B)	11152(11)	8365(10)	- 1870(10)	271(11)
F(11C)	10594(12)	7275(9)	- 1926(7)	222(7)
S(4)	7694(5)	5723(4)	1025(3)	149(2)
0(4A)	7097(15)	5868(12)	560(7)	271(11)
0(4B)	8481(12)	5789(12)	986(13)	335(18)
0(4C)	7180(13)	5901(16)	1509(11)	292(13)
C(12)	7640(19)	4682(14)	1173(11)	144(6)
F(12A)	6894(12)	4465(12)	1155(14)	355(16)
F(12B)	8030(17)	4355(11)	735(9)	290(11)
F(12C)	8191(12)	4436(9)	1550(6)	222(7)
0(3)	7938(9)	7038(7)	2280(5)	142(5)
0(3)	7938(9)	7038(7)	2280(5)	142(

Table 28.3	Bond lengths	[A] and	angl es	[deg]	for	28.

Ir(1) - O(1)	2.163(7)
Ir(1) - P(2)	2.259(3)
Ir(1) - C(1)	2.279(11)
Ir(1) - C(2)	2.291(13)
Ir(1) - P(1)	2.340(3)
Ir(1) - P(3)	2.355(3)

C(1) - C(2)	1.33(2)
C(2) - C(3)	1.53(2)
C(3) - C(4)	1.43(2)
C(4) - O(1)	1.47(2)
P(1) - C(1C)	1.800(13)
P(1) - C(1B)	1.829(13)
P(1) - C(1A)	1.831(12)
P(2) - C(2B)	1.781(12)
P(2) - C(2C)	1.801(12)
P(2) - C(2A)	1.818(14)
P(3) - C(3C)	1.767(13)
P(3) - C(3B)	1.78(2)
P(3) - C(3A)	1.800(12)
Ir(2) - O(2)	2.174(9)
Ir(2) - C(5)	2.218(11)
Ir(2) - P(5)	2.219(4)
Ir(2) - P(6)	2.336(4)
Ir(2) - P(4)	2.366(4)
Ir(2) - C(6)	2.37(2)
C(5) - C(6)	1.07(2)
C(6) - C(7)	1.61(2)
C(7) - C(8)	1.49(2)
C(8) - O(2)	1.44(2)
P(4) - C(4A)	1.79(2)
P(4) - C(4B)	1.82(2)
P(4) - C(4C)	1.85(2)
P(5) - C(5A)	1.75(2)
P(5) - C(5B)	1.79(2)
P(5) - C(5C)	1.807(13)
P(6) - C(6B)	1.76(2)
P(6) - C(6A)	1.788(13)
P(6) - C(6C)	1.79(2)
S(1) - O(1C)	1.392(10)
S(1) - O(1A)	1.408(11)
S(1) - O(1B)	1.440(11)
S(1) - C(9)	1.79(2)
C(9) - F(9C)	1.27(2)
C(9) - F(9A)	1.29(2)
C(9) - F(9B)	1.30(2)
S(2) - O(2B)	1. 380(10)
S(2) - O(2C)	1.415(11)
S(2) - U(2A)	1.569(13)
S(2) - U(10)	1.73(2)
C(10) - F(10B)	1.24(2)
U(10) - F(100)	1.27(2)
U(10) - F(10A)	1.47(2)
S(3)-U(3B)	1.37(2)

S(3) - 0(3C)	1.384(12)
S(3) - O(3A)	1.42(2)
S(3) - C(11)	1.82(2)
C(11) - F(11A)	1.18(3)
C(11) - F(11C)	1.20(2)
C(11) - F(11B)	1.33(3)
S(4) - O(4B)	1.18(2)
S(4) - O(4A)	1.39(2)
S(4) - O(4C)	1.45(2)
S(4) - C(12)	1.75(2)
C(12) - F(12A)	1.16(3)
C(12) - F(12C)	1.24(2)
C(12) - F(12B)	1.34(3)
0(1)-Ir(1)-P(2)	178.5(2)
0(1) - Ir(1) - C(1)	85.5(5)
P(2) - Ir(1) - C(1)	93.0(5)
0(1) - Ir(1) - C(2)	76.9(5)
P(2) - Ir(1) - C(2)	101.8(4)
C(1) - Ir(1) - C(2)	33.9(5)
0(1) - Ir(1) - P(1)	88.0(2)
P(2) - Ir(1) - P(1)	91.89(12)
C(1) - Ir(1) - P(1)	85.3(4)
C(2) - Ir(1) - P(1)	117.3(4)
0(1) - Ir(1) - P(3)	87.8(3)
P(2) - Ir(1) - P(3)	92.95(12)
C(1) - Ir(1) - P(3)	118.9(4)
C(2) - Ir(1) - P(3)	85.6(4)
P(1) - Ir(1) - P(3)	155.01(11)
C(2) - C(1) - Ir(1)	73.5(8)
C(1) - C(2) - C(3)	115(2)
C(1) - C(2) - Ir(1)	72.5(8)
C(3) - C(2) - Ir(1)	106.8(9)
C(4) - C(3) - C(2)	113(2)
C(3) - C(4) - O(1)	108.4(12)
C(4) - O(1) - Ir(1)	114.0(8)
C(1C) - P(1) - C(1B)	104.2(6)
C(1C) - P(1) - C(1A)	102.7(7)
C(1B) - P(1) - C(1A)	101.5(7)
C(1C) - P(1) - Ir(1)	115.6(4)
C(1B) - P(1) - Ir(1)	109.2(5)
C(1A) - P(1) - Ir(1)	121.6(4)
U(2B) - P(2) - C(2C)	104.4(7)
U(2B) - P(2) - U(2A)	99.5(7)
U(2U) - P(2) - C(2A)	103.7(7)
U(2B) - P(2) - Ir(1)	116.4(5)
C(2C) - P(2) - Ir(1)	114.6(4)

C(2A) - P(2) - Ir(1)	116.2(5)
C(3C) - P(3) - C(3B)	103.3(8)
C(3C) - P(3) - C(3A)	103.5(7)
C(3B) - P(3) - C(3A)	103.9(8)
C(3C) - P(3) - Ir(1)	114.5(5)
C(3B) - P(3) - Ir(1)	109.3(6)
C(3A) - P(3) - Ir(1)	120.5(5)
0(2) - Ir(2) - C(5)	80.7(5)
0(2) - Ir(2) - P(5)	178.0(3)
C(5) - Ir(2) - P(5)	97.3(5)
0(2) - Ir(2) - P(6)	88.0(3)
C(5) - Ir(2) - P(6)	88.5(4)
P(5) - Ir(2) - P(6)	92.5(2)
0(2) - Ir(2) - P(4)	84.6(3)
C(5) - Ir(2) - P(4)	113.3(4)
P(5) - Ir(2) - P(4)	95.7(2)
P(6) - Ir(2) - P(4)	155. 31(13)
0(2) - Ir(2) - C(6)	77.3(5)
C(5) - Ir(2) - C(6)	26.8(5)
P(5) - Ir(2) - C(6)	100.7(5)
P(6) - Ir(2) - C(6)	114.7(5)
P(4) - Ir(2) - C(6)	86.6(5)
C(6) - C(5) - Ir(2)	84.6(14)
C(5) - C(6) - C(7)	113(2)
C(5) - C(6) - Ir(2)	68.6(13)
C(7) - C(6) - Ir(2)	102.1(11)
U(8) - U(7) - U(6)	113(2)
U(2) - U(8) - U(7)	106.3(12)
C(8) - U(2) - Ir(2)	118.3(8)
C(4A) - P(4) - C(4B)	97.7(9)
C(4A) - P(4) - C(4C)	100.0(10) 101.6(11)
C(4D) - F(4) - C(4C) C(4A) = D(4) = Im(2)	101.0(11) 192.0(6)
C(4A) - F(4) - FF(2) C(AB) P(A) Fr(2)	123.0(0) 116.0(6)
C(AC) = P(A) = Ir(2)	110.0(0) 110.0(6)
C(5A) = P(5) = C(5B)	101 6(10)
C(5A) - P(5) - C(5C)	101.0(10) 103.8(9)
C(5B) - P(5) - C(5C)	100.0(0) 104.6(8)
C(5A) - P(5) - Ir(2)	101.0(0) 117.0(7)
C(5B) - P(5) - Ir(2)	112.5(7)
C(5C) - P(5) - Ir(2)	115.6(5)
C(6B) - P(6) - C(6A)	102.7(9)
C(6B) - P(6) - C(6C)	98.1(13)
C(6A) - P(6) - C(6C)	105. 5(9)
C(6B) - P(6) - Ir(2)	111.3(6)
C(6A) - P(6) - Ir(2)	115.5(5)
C(6C) - P(6) - Ir(2)	121.0(7)

0(1C) - S(1) - 0(1A)	112.1(8)
0(1C) - S(1) - O(1B)	118.0(8)
0(1A) - S(1) - O(1B)	114.5(8)
0(1C) - S(1) - C(9)	102.5(8)
0(1A) - S(1) - C(9)	104.4(8)
0(1B) - S(1) - C(9)	103.1(7)
F(9C) - C(9) - F(9A)	104(2)
F(9C) - C(9) - F(9B)	107(2)
F(9A) - C(9) - F(9B)	103(2)
F(9C) - C(9) - S(1)	115(2)
F(9A) - C(9) - S(1)	113(2)
F(9B) - C(9) - S(1)	114.3(12)
0(2B) - S(2) - 0(2C)	118.2(8)
0(2B) - S(2) - O(2A)	115.8(8)
0(2C) - S(2) - O(2A)	112.7(8)
0(2B) - S(2) - C(10)	108.3(8)
0(2C) - S(2) - C(10)	107.2(7)
0(2A) - S(2) - C(10)	90.6(9)
F(10B) - C(10) - F(10C)	113(2)
F(10B) - C(10) - F(10A)	106(2)
F(10C) - C(10) - F(10A)	104(2)
F(10B) - C(10) - S(2)	115.0(14)
F(10C) - C(10) - S(2)	116.0(13)
F(10A) - C(10) - S(2)	101.2(12)
0(3B) - S(3) - 0(3C)	115.7(13)
0(3B) - S(3) - O(3A)	112(2)
0(3C) - S(3) - O(3A)	118. 4(13)
0(3B) - S(3) - C(11)	100.8(13)
0(3C) - S(3) - C(11)	105.2(12)
0(3A) - S(3) - C(11)	102.3(14)
F(11A) - C(11) - F(11C)	117(4)
F(11A) - C(11) - F(11B)	109(3)
F(11C) - C(11) - F(11B)	103(3)
F(11A) - C(11) - S(3)	110(2)
F(11C) - C(11) - S(3)	113(2)
F(11B) - C(11) - S(3)	105(2)
0(4B) - S(4) - 0(4A)	120(2)
0(4B) - S(4) - 0(4C)	128(2)
0(4A) - S(4) - 0(4C)	104. 5(14)
0(4B) - S(4) - C(12)	99. 4(14)
0(4A) - S(4) - C(12)	107.0(13)
0(4C) - S(4) - C(12)	90(2)
F(12A) - C(12) - F(12C)	120(3)
F(12A) - C(12) - F(12B)	108(3)
F(12C) - C(12) - F(12B)	97(3)
F(12A) - C(12) - S(4)	111(2)
F(12C) - C(12) - S(4)	115(2)

Symmetry transformations used to generate equivalent atoms:

Table 28.4 Anisotropic displacement parameters  $(A^2 \times 10^3)$  for 28. The anisotropic displacement factor exponent takes the form: -2 <sup>2</sup> [  $h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12$  ]

	U11	U22	U33	U23	U13	U12
	41(1)	49(1)	50(1)	1(1)	1(1)	4(1)
$\Gamma(1)$	41(1)	42(1)	59(1)	-1(1)	-1(1)	4(1)
$\mathcal{L}(1)$	113(13)	32(6)	158(15)	-48(8)	2(11)	3(7)
$\mathcal{L}(\mathcal{Z})$	109(12)	48(7)	111(12)	-4(7)	25(10)	6(8)
C(3)	255(27)	110(13)	111(15)	- 26(12)	3(16)	74(16)
C(4)	214(21)	153(16)	68(10)	- 41(11)	- 52(12)	78(16)
0(1)	102(7)	92(6)	39(4)	- 10(4)	-2(4)	12(5)
P(1)	46(2)	50(2)	101(3)	0(2)	3(2)	1(1)
P(2)	70(2)	58(2)	65(2)	10(2)	1(2)	7(2)
P(3)	50(2)	71(2)	96(3)	8(2)	14(2)	3(2)
C(1A)	59(8)	60(8)	199(17)	2(9)	4(9)	-9(7)
C(1B)	74(9)	93(10)	118(12)	23(9)	- 30(8)	8(8)
C(1C)	61(8)	70(8)	119(11)	- 5(8)	25(7)	3(7)
C(2A)	111(11)	87(9)	94(10)	32(8)	35(9)	18(9)
C(2B)	102(11)	108(11)	93(10)	29(9)	-28(9)	22(9)
C(2C)	112(11)	81(9)	62(8)	-4(7)	7(7)	10(8)
C(3A)	67(9)	86(10)	197(18)	-4(11)	27(10)	28(8)
C(3B)	112(13)	142(15)	159(17)	30(13)	51(12)	30(12)
C(3C)	68(9)	87(9)	151(14)	-23(9)	-3(9)	- 25(8)
Ir(2)	75(1)	45(1)	71(1)	4(1)	15(1)	12(1)
C(5)	183(16)	53(7)	70(8)	39(6)	42(10)	65(9)
C(7)	115(15)	130(15)	174(19)	28(15)	- 10(13)	33(12)
C(8)	161(17)	111(13)	98(12)	- 14(10)	- 55(11)	49(12)
0(2)	98(7)	95(7)	112(8)	-9(6)	- 18(6)	13(6)
P(4)	107(3)	71(2)	109(3)	5(2)	46(2)	19(2)
P(5)	138(4)	77(2)	93(3)	-1(2)	-23(3)	1(3)
P(6)	82(2)	85(2)	74(2)	12(2)	17(2)	23(2)
C(4A)	234(23)	92(11)	149(16)	- 10(11)	102(16)	44(13)
C(4B)	191(20)	134(16)	183(19)	67(15)	97(17)	48(15)

C(4C)	124(16)	305(32)	174(20)	- 89(22)	73(15)	- 71(20)
C(5A)	137(17)	140(17)	207(22)	-17(16)	- 52(16)	- 29(14)
C(5B)	229(23)	102(13)	137(16)	- 32(12)	- 17(16)	22(14)
C(5C)	164(16)	88(10)	97(11)	-1(9)	- 45(11)	33(10)
C(6A)	135(14)	96(10)	116(12)	14(9)	33(10)	57(10)
C(6B)	123(15)	313(30)	116(14)	-87(18)	2(12)	98(18)
C(6C)	334(36)	134(17)	297(32)	101(20)	239(30)	94(20)
S(1)	70(2)	67(2)	121(3)	12(2)	21(2)	-1(2)
0(1A)	111(9)	161(11)	160(11)	36(9)	- 12(8)	23(8)
O(1B)	214(14)	87(7)	113(8)	- 16(6)	30(8)	1(8)
0(1C)	97(8)	170(11)	170(11)	40(9)	46(8)	- 44(8)
C(9)	109(11)	60(8)	179(20)	15(9)	23(11)	5(8)
F(9A)	204(13)	188(12)	179(11)	-1(9)	85(10)	- 53(10)
F(9B)	238(12)	84(6)	141(9)	-7(6)	12(8)	- 18(7)
F(9C)	206(12)	154(9)	162(10)	39(8)	-14(9)	68(9)
S(2)	67(2)	105(3)	142(4)	- 40(3)	- 5(3)	15(2)
0(2A)	243(17)	117(9)	191(13)	93(9)	- 86(12)	- 22(9)
0(2B)	78(7)	133(9)	192(12)	- 30(8)	40(7)	- 21(7)
0(2C)	140(10)	115(8)	124(9)	- 50(7)	4(7)	26(7)
C(10)	93(9)	148(14)	96(10)	-25(7)	5(10)	- 19(11)
F(10A)	284(17)	141(10)	187(12)	39(8)	- 49(12)	48(10)
F(10B)	62(5)	228(12)	209(11)	- 93(10)	13(6)	3(7)
F(10C)	134(7)	111(6)	113(7)	-44(5)	14(6)	-7(5)
S(3)	91(3)	115(3)	150(4)	14(3)	24(3)	6(3)
0(3A)	310(28)	251(23)	320(29)	152(22)	- 14(22)	85(19)
0(3B)	272(23)	193(16)	580(45)	-242(25)	244(28)	- 115(17)
0(3C)	138(10)	123(9)	198(13)	23(9)	58(9)	- 31(8)
C(11)	102(16)	202(23)	169(19)	- 56(14)	34(13)	- 21(15)
F(11A)	139(13)	634(45)	241(20)	-65(26)	- 71(14)	94(20)
F(11B)	171(13)	213(15)	450(32)	-84(17)	176(17)	- 73(12)
F(11C)	295(19)	160(12)	219(16)	- 56(10)	80(14)	22(12)
0(4A)	368(28)	252(20)	178(16)	34(14)	-96(17)	143(19)
0(4B)	130(14)	207(18)	676(52)	243(26)	88(21)	40(13)
0(4C)	169(17)	358(31)	346(30)	- 119(25)	- 10(18)	85(19)
C(12)	154(16)	125(17)	153(18)	31(13)	6(13)	- 28(14)
F(12A)	182(16)	211(18)	679(47)	67(24)	69(24)	- 83(15)
F(12B)	432(33)	193(16)	248(20)	-64(15)	47(19)	76(18)
F(12C)	302(20)	185(13)	178(13)	78(11)	10(12)	86(13)
0(3)	212(13)	109(8)	97(8)	27(6)	- 42(8)	- 24(8)

	х	У	Z	U(eq)
H(1A)	8532(11)	9994(7)	1443(7)	122
H(1B)	8100(11)	10316(7)	838(7)	122
H(2A)	6729(12)	10199(7)	1148(7)	106
H(3A)	7287(16)	10226(11)	2168(8)	191
H(3B)	6604(16)	9512(11)	2045(8)	191
H(4A)	7774(14)	9011(12)	2565(6)	177
H(4B)	8462(14)	9385(12)	2162(6)	177
H(1AA)	9843(8)	9619(7)	1017(8)	159
H(1AB)	9816(8)	9416(7)	370(8)	159
H(1AC)	10516(8)	8982(7)	794(8)	159
H(1BA)	9470(9)	8270(8)	1812(6)	145
H(1BB)	10208(9)	7840(8)	1478(6)	145
H(1BC)	9285(9)	7406(8)	1552(6)	145
H(1CA)	9112(8)	7869(7)	- 57(6)	124
H(1CB)	9058(8)	7158(7)	378(6)	124
H(1CC)	9981(8)	7591(7)	304(6)	124
H(2AA)	8808(10)	9274(8)	-229(6)	144
H(2AB)	8264(10)	10074(8)	- 142(6)	144
H(2AC)	8110(10)	9585(8)	- 707(6)	144
H(2BA)	6430(9)	10065(9)	20(6)	154
H(2BB)	5862(9)	9290(9)	- 151(6)	154
H(2BC)	6424(9)	9725(9)	- 597(6)	154
H(2CA)	7713(10)	7713(7)	- 372(5)	127
H(2CB)	7225(10)	8252(7)	-844(5)	127
H(2CC)	6663(10)	7818(7)	- 397(5)	127
H(3AA)	5381(9)	9520(8)	1264(8)	174
H(3AB)	4635(9)	8876(8)	1091(8)	174
H(3AC)	5123(9)	9343(8)	624(8)	174
H(3BA)	6154(12)	8145(11)	1958(8)	204
H(3BB)	6265(12)	7311(11)	1653(8)	204
H(3BC)	5303(12)	7690(11)	1688(8)	204
H(3CA)	5638(9)	7857(8)	119(7)	153
H(3CB)	4985(9)	7513(8)	552(7)	153
H(3CC)	5947(9)	7134(8)	516(7)	153
H(5A)	8114(12)	6532(7)	- 2056(6)	121
H(5B)	7458(12)	6222(7)	-2578(6)	121

Table 28.5 Hydrogen coordinates (  $x\ 10^4)$  and isotropic displacement parameters  $(A^2\ x\ 10^3)$  for 28.

H(6A)	7044(14)	6805(12)	- 1647(9)	156
H(7A)	5586(12)	6139(11)	-2067(9)	169
H(7B)	5893(12)	6769(11)	- 2510(9)	169
H(8A)	5509(12)	5511(10)	- 2931(7)	151
H(8B)	6514(12)	5749(10)	- 3024(7)	151
H(4AA)	5716(14)	6264(10)	- 1055(8)	231
H(4AB)	6289(14)	5995(10)	- 507(8)	231
H(4AC)	5296(14)	5685(10)	-619(8)	231
H(4BA)	6615(14)	3773(11)	- 680(9)	248
H(4BB)	5826(14)	4208(11)	- 395(9)	248
H(4BC)	6820(14)	4519(11)	- 281(9)	248
H(4CA)	5412(13)	4051(16)	- 1757(9)	297
H(4CB)	4967(13)	4913(16)	- 1809(9)	297
H(4CC)	4803(13)	4361(16)	- 1288(9)	297
H(5AA)	9791(12)	5258(12)	- 1523(9)	247
H(5AB)	9962(12)	5646(12)	-922(9)	247
H(5AC)	9462(12)	6144(12)	-1412(9)	247
H(5BA)	7628(15)	5830(11)	- 424(8)	236
H(5BB)	8150(15)	6497(11)	- 742(8)	236
H(5BC)	8648(15)	5998(11)	- 252(8)	236
H(5CA)	8288(11)	4097(8)	- 516(6)	178
H(5CB)	9207(11)	4509(8)	- 317(6)	178
H(5CC)	9136(11)	3969(8)	- 863(6)	178
H(6AA)	9522(11)	3897(9)	- 1739(7)	172
H(6AB)	9594(11)	3549(9)	-2349(7)	172
H(6AC)	8815(11)	3260(9)	- 1984(7)	172
H(6BA)	7534(12)	4460(16)	- 3146(8)	276
H(6BB)	7594(12)	3610(16)	- 2848(8)	276
H(6BC)	8373(12)	3900(16)	- 3213(8)	276
H(6CA)	9586(19)	5482(12)	- 2435(12)	368
H(6CB)	8868(19)	5545(12)	- 2950(12)	368
H(6CC)	9603(19)	4860(12)	- 2935(12)	368

Vita

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