

Synthetic Routes to 3-Fold Symmetric Tridentate Oxygen Donor Ligands

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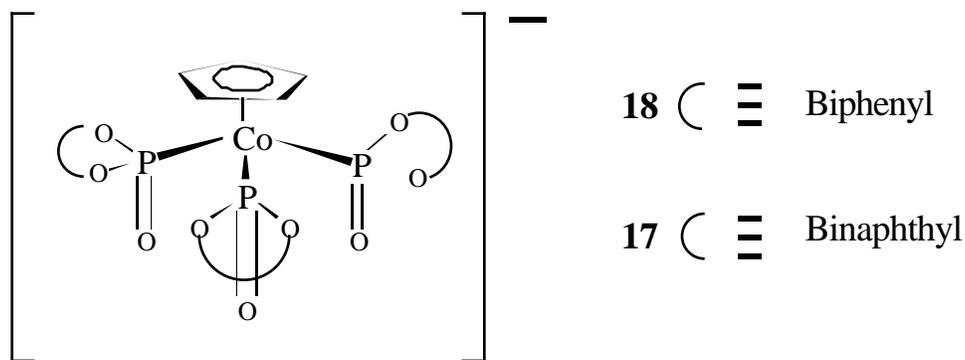
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ABSTRACT

The class of ligands represented by $[\text{CpCo}(\text{P}(\text{O})(\text{OR})_2)_3]^-$, \mathbf{L}^- , were first synthesized by W. Kläui in 1977. These ligands have been found to coordinate to a variety of low and high oxidation state metals through the use of its three P=O oxygen atoms as donors. The ligands act as mono-anionic six electron donors which make them similar to the more widely known cyclopentadienyl ligands, $(\text{C}_5\text{H}_{5-x}\text{R}_x)^-$, but have electronic properties like those of fluoride or oxide. Also, it has been found that the coordination chemistry of \mathbf{L}^- resembles the unsubstituted tris(pyrzazolyl)hydroborato six electron ligand, $(\text{RB}(\text{pz})_3)^-$. All three of these ligands can be modified by changing the substituent R. The Kläui ligand offers a good opportunity to synthesize a chiral derivative.

In the process to obtain the chiral version, (cyclopentadienyl)tris(biphenylphosphito-P)cobaltate(1-), **18**, was synthesized from 2,2'-biphenol. This was characterized through NMR, mass spectroscopy, and XPS. Next, a racemic version, (cyclopentadienyl)tris(biphenylphosphito-P)cobaltate(1-), **17**, was synthesized from (\pm) 1,1'-bi-2-naphthol. A one-pot synthesis for the rac-binaphthyl phosphite derivative was developed with an increased yield from the previously published synthesis. The racemic version of the ligand was characterized by NMR and mass spectroscopy. The chiral version has not yet been synthesized, however, by following the developed procedure for the non-chiral version, the ligand could be synthesized from optically active 1,1'-bi-2-naphthol.



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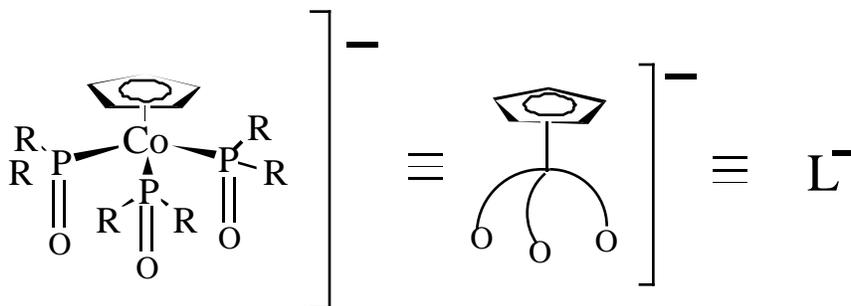
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Chapter 1: Background

1.1 INTRODUCTION

The class of ligands represented by $[(C_5H_5)Co\{P(O)R_2\}_3]^-$, L^- , were first synthesized in 1977 by Wolfgang Kläui.¹ These anionic cyclopentadienyl complexes prove to be excellent tridentate oxygen donor ligands because of the three P=O functions. The ligands dissolve without decomposition in aqueous sulfuric acid, and are not oxidized by atmospheric oxygen or nitric acid.² The extremely robust character of these ligands and their unique electronic properties allows them to coordinate to a variety of low and high oxidation state metals. They are also known to stabilize a variety of organometallic fragments that have not been previously stabilized by oxygen donor ligands. In general, the Kläui ligand offers a wide range of possibilities as a versatile oxygen donor ligand. In the following sections, the synthesis, chemistry, and coordination of L^- will be discussed in depth.



1.2 SYNTHESIS

When a 1:2 mixture of cobaltocene and diesters of phosphorous acid or secondary phosphine oxides is heated without solvent to 100-140°C, a black viscous slurry results. From this slurry, air-stable orange crystals of the cobalt(II) complexes CoL_2 , **1**, separate.^{1,3} The free ligand, L^- , can be cleaved from the complex by further reacting CoL_2 with sodium cyanide in the presence of atmospheric oxygen.⁴ The substituent R is easily varied and the synthesis can be carried out as a one-pot reaction allowing easy access to a variety of L^- type ligands. (Scheme 1.1)

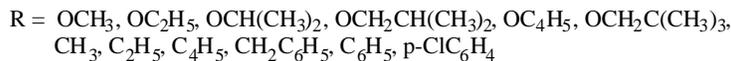
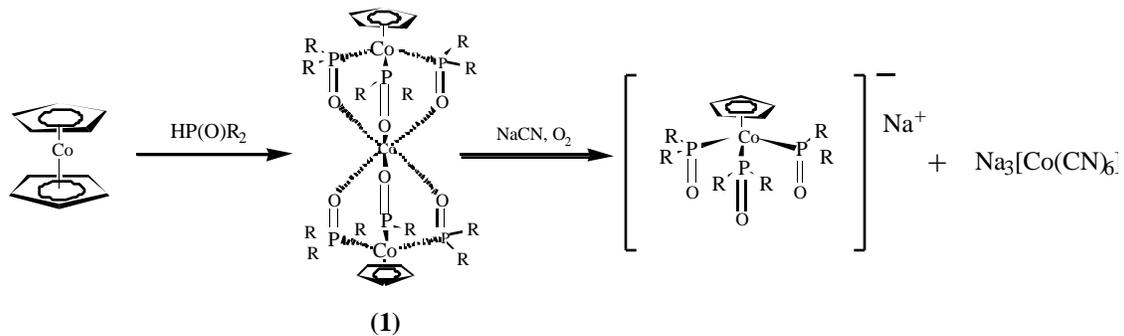
¹ W. Kläui, H. Neukomm, H. Werner, and G. Huttner, *Chem. Ber.*, 110 (1977) 2283

² N. El Murr, A. Chaloyard, and W. Kläui, *Inorg. Chem.*, 18 (1979) 2629

³ W. Kläui, W. Eberspach, and R. Schwarz, *J. Organomet. Chem.*, 252 (1983) 347

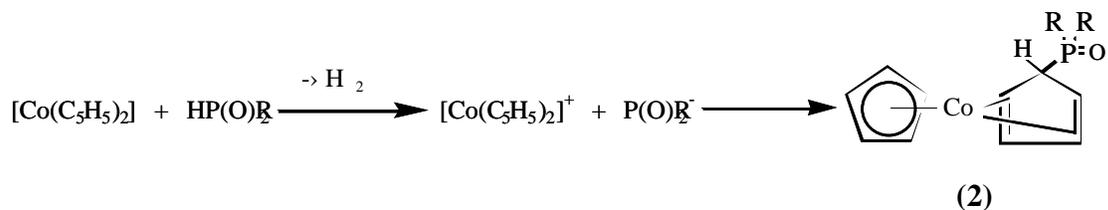
⁴ W. Kläui, *Z. Naturforsch.*, 34b (1979) 1403

Scheme 1.1:



The mechanism for the first step of the reaction, formation of the trinuclear compound **1**, is only partly understood. The reaction proceeds via a thermally labile cobalt(I) cyclopentadiene complex [(C₅H₅)Co(1-*exo*-P(O)R₂-C₅H₅)], **2**. A proposed pathway to **2** is through protonation of cobaltocene by the secondary phosphine oxide followed by formation of a cobaltocenium ion and elimination of dihydrogen.⁵ (Scheme 1.2) How the intermediate further reacts to form **1** is still not understood. The second step, cleavage of **L** from **1**, is a simple ligand substitution, which is followed by oxidation and further reaction of the intermediate ion [Co(CH)₅]³⁻ to give the stable Co(III) complex [Co(CN)₆]³⁻.⁶

Scheme 1.2:

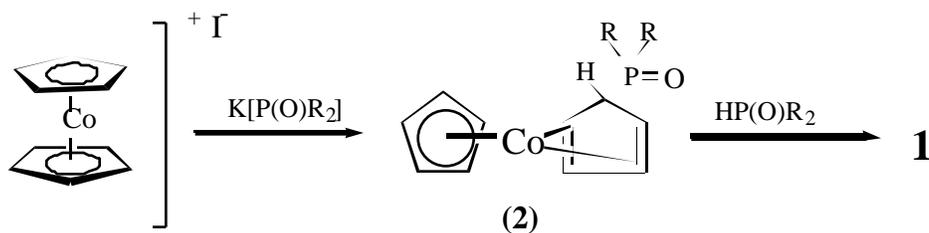


After the isolation of the cobaltocenium intermediate, it was proposed that **2** could be directly synthesized from cobaltocenium iodide and the potassium salts K[P(O)R₂] (R = *n*-C₄H₉, *i*-C₄H₉).⁵ From **2**, the sandwich complex and eventually **L** could be synthesized. This proved to be an interesting alternative since it avoids the air-sensitive cobaltocene. (Scheme 1.3)

⁵ W. Kläui, *Z. Naturforsch.*, 34b (1979) 1403

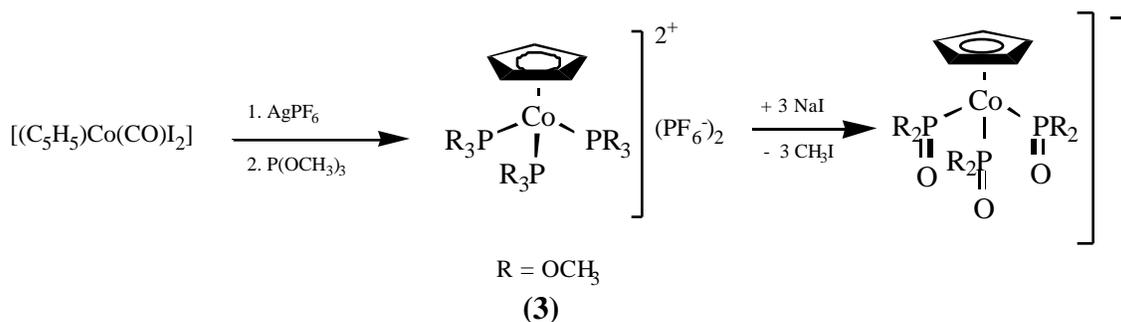
⁶ W. Kläui, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 627

Scheme 1.3:



In 1982, a completely different synthesis for **L**⁻ was introduced. The carbon monoxide and iodo-ligands in [(C₅H₅)Co(CO)I₂] were replaced by trimethylphosphite to make compound **3**. Then, through the use of the Michaelis-Arbusov reaction⁷, the trimethylphosphite ligands were converted successfully into dimethylphosphito ligands.⁸ (Scheme 1.4) An interesting feature of this synthesis is the ability to modify **3** and make the analogous rhodium ligands containing a C₅Me₅ (Cp*) fragment.

Scheme 1.4:



1.3 SYMMETRY

These ligands are sometimes referred to as tripod ligands because of their C_{3v} symmetry. The center axis through the cobalt atom is a 3-fold rotation axis assuming the symmetry of the Cp ring is ignored. Also, there is a vertical reflection plane along the C₃ axis. (Figure 1.1)

⁷ A. K. Bhatlacharya, and G. Thyagarajan, *Chem. Rev.*, 81 (1981) 415

⁸ W. Kläui, H. Otto, W. Eberspach, and E. Buchholz, *Chem. Ber.*, 115 (1982) 1922

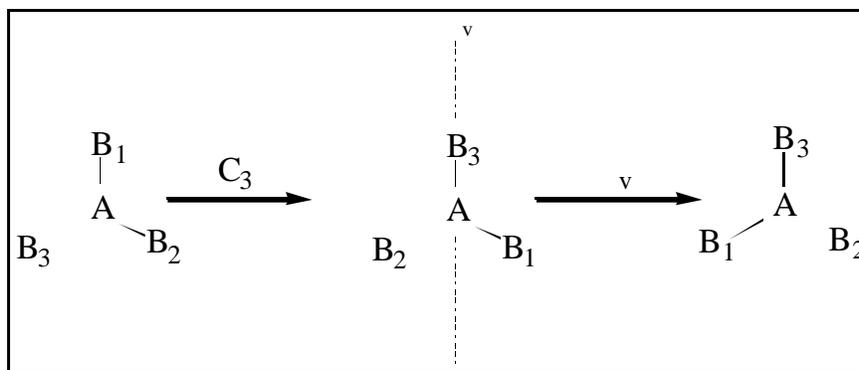


Figure 1.1 Representation of the symmetry elements present in L^- . If $B_1=B_2=B_3$, and they are symmetric, then the point group is C_{3v} .

A chiral version of the ligand can be obtained by varying the R groups on L^- . When the 2 groups R' and R'' differ, the three phosphorous atoms of the tripod ligand become stereogenic centers, thus, eliminating the reflection plane. If the substituents R' and R'' are small, then all of the 16 stereoisomeric complexes $[CoL_2]$ are formed. However, if R' and R'' differ in size, cleavage with cyanide leads to a uniform ligand L^- consisting of the (R,R,R)- and (S,S,S)- enantiomers.⁹ (Figure 1.2)

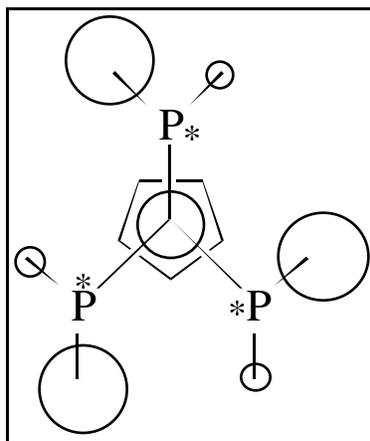


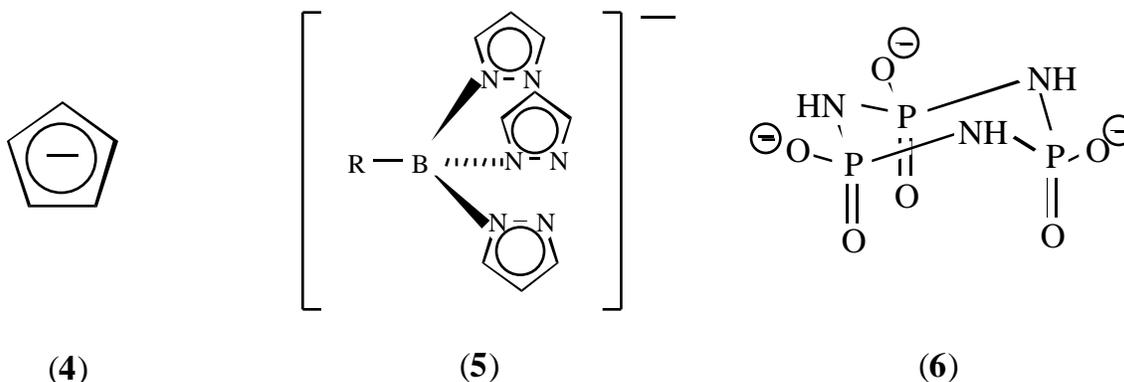
Figure 1.2: Newman projection along the three-fold axis of a chiral ligand L^- with the (S,S,S)- configuration

1.4 COORDINATION CHEMISTRY

The tridentate donor ligands are monoanionic, facially coordinating, six electron

⁹ E. M. Holt, W. Kläui, and J. J. Zuckerman, *J. Organomet. Chem.*, 335 (1987) 29

ligands resembling the formally equivalent cyclopentadienyl, **4**, and tris(pyrazolyl)borate, **5**, anions.¹⁰ With a cone angle of 160°, **L**⁻ is comparable with that of C₅Me₅⁻ (146°) and HB(pz)₃⁻ (180°).¹¹ However, the electronic properties of **L**⁻ are like that of oxide or fluoride (see Section 1.5), making its coordination different from its analogs.



The isoelectronic trimetaphosphimate **6**, with three P=O functional groups available for coordination, appears to represent a simple model for **L**⁻. However, in the Cu(II) complex [Cu(H₂O)₂{P₃O₆(NH)₃}₂] ligand **6** acts as a bidentate P=O ligand distorting the six-membered ring by placing the third coordination site away from the Cu(II) ion.¹² Whereas, **L**⁻ functions as a tridentate P=O ligand, and the Jahn-Teller distortion of the CuO₆ octahedron is small.¹³ Therefore, although **6** appears to be a good model for coordination, it displays much weaker chelate formation than **L**⁻ due to the flexibility of its six-membered ring.¹²

The oxygen tridentate ligand forms coordination complexes with a large number of monovalent, divalent, and trivalent metals.^(4, 13,14,15,16,17,18) (Figure 1.3) These stable 2:1 complexes with the general formula [ML₂] are formed at room temperature from aqueous solutions of **L**⁻ Na⁺ and the corresponding metal ions in quantitative yields.¹⁹ The ligand, **L**⁻, provides tridentate coordination to the metals via ligation of the three phosphonyl oxygen atoms.⁹ X-ray spectroscopy shows [ML₂] to be a sandwich-like compound with a

¹⁰ W. Kläui, W. Eberspach, and P. Gütlich, *Inorg. Chem.*, 26 (1987) 3977

¹¹ D. Baudry, M. Ephritikhine, W. Kläui, M. Lance, M. Nierlich, and J. Vigner, *Inorg. Chem.*, 30 (1991) 2333

¹² V. I. Sokol, L. Ya. Medvedeva, L. A. Butman, and I. A. Rozanov, *Sov. J. Coord. Chem. Engl. Transl.*, 2 (1976) 434

¹³ E. Dubler, L. Linowsky, and W. Kläui, *Transition Met. Chem.*, 4 (1979) 191

¹⁴ R. Cotton, and W. Kläui, *Inorg. Chim. Acta*, 211 (1993) 235

¹⁵ E. Dubler, L. Linowsky, and W. Kläui, *Transition Met. Chem.*, 4 (1979) 191

¹⁶ W. Kläui, *Helvetica Chimica Acta*, 60 (1977) 1296

¹⁷ W. Kläui, *J. Organomet. Chem.*, 184 (1980) 49

¹⁸ W. Kläui, K. Dehnicke, *Chem. Ber.*, 111 (1978) 451

¹⁹ O. Krampe, C. Song, and W. Kläui, *Organometallics*, 12 (1993) 4949

linear arrangement of the octahedrally surrounded metal ion and the 2 cobalt atoms.²⁰ Also, 1:1 complexes of \mathbf{L}^- can be formed with BF_3 or BPh_4^- , producing the cations $[\text{LBF}]^+$ and $[\text{LBPh}]^+$. This makes \mathbf{L}^- one of the few ligands to form both metal and nonmetal derivatives.^{6, 18}

H																			He
Li	Be											B	C	N	O	F		Ne	
Na	Mg											Al	Si	P	S	Cl		Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn	
Fr	Ra	Ac	Unq	Unp	Unh	Uns													

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.3: All the elements shaded in gray are known to form complexes with the ligands \mathbf{L}^- .

The oxygen—oxygen distance in metal complexes of \mathbf{L}^- varies from 3 to 3.28 Å, allowing the facially coordinating oxygen tripod ligand to adjust to the steric demands of a metal ion.¹⁹ Because \mathbf{L}^- has an ideal geometry for the formation of facial metal complexes, there is little loss of internal rotational entropy upon coordination.²¹ In fact, this favorable entropy term causes these complexes to be very thermodynamically stable.¹⁴ (Figure 1.4)

²⁰ W. Kläui, and H. Werner, *Angew. Chem. Int. Ed. Engl.*, 15 (1976) 172

²¹ W. Kläui, and A. Müller, *J. Organomet. Chem.*, 253 (1983) 45

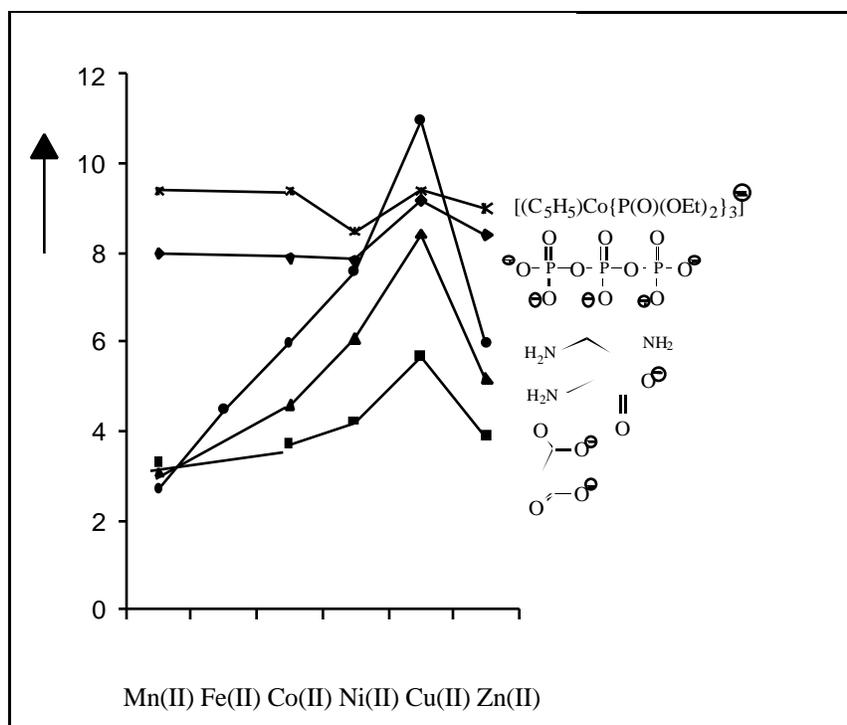
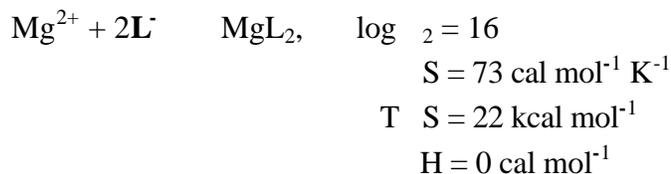


Figure 1.4: Graphic representation of the complex stability constants $\log K_1$ of L^- and several typical chelating ligands with the metal ions Mn^{2+} Zn^{2+} .

For both L^- and tripolyphosphate, all the complex stability constants are high, and they are essentially independent of the nature of the metal ion.⁶ In the case of ethylenediamine, glycinate, malonate, and many other ligands, the complex stability constants increase along the Irving-Williams series from Manganese through iron, cobalt, and nickel up to copper, decreasing again with zinc.²² The large K_1 values for L^- and tripolyphosphate are a consequence of a high entropy of complexation, whereas the other ligands have an exothermic complex formation.⁶ Thermodynamic data confirms that the large formation constant in complexation is completely due to the entropy term. (Scheme 1.5) Also, the large value for S suggests that L^- induces a considerable amount of structure in water, and this structure disappears upon complexation.⁶

Scheme 1.5:



²² B. Lenders, W. Kläui, M. IrmLer, and G. Meyer, *J. Chem. Soc. Dalton Trans.*, 7 (1990) 2069

1.5 Electronic Properties

Whether a ligand is strong or weak in terms of ligand field theory, cannot be determined by the stability of its metal complexes. The electronic spectra of $[ML_2]$ complexes where $M = Ti^{3+}$, Co^{2+} , Ni^{2+} , and Cu^{2+} , represents a summation of the (d-d) spectra and internal-ligand transitions for the MO_6 fragment.^{8,10} From these (d-d) band transitions, L^- can be placed accordingly in the spectrochemical and nephelauxetic series.^{8,23,24} (Figure 1.5)

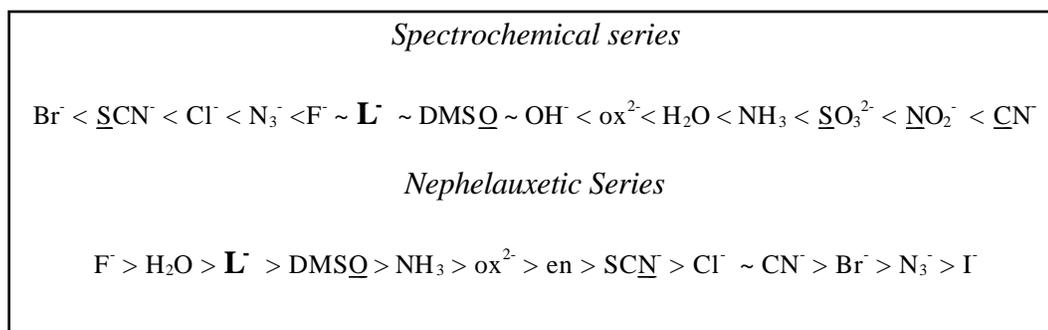


Figure 1.5: Positions of L^- in the spectrochemical and Nephelauxetic series. Elements that are directly bound to the central atom of the complex are underlined.

The Fajans-Tsuchida spectrochemical series^{25,26} places the ligands in ascending order of the crystal field splitting (Δ_0) which they produce when complexed to a given metal ion. However, the order of the ligands are independent of the metal ion, with very few exceptions. The oxygen tripod ligands are equivalent to fluoride, making them weaker than water. In fact, L^- are among the weakest of the oxygen ligands.¹²

The nephelauxetic or “cloud expanding” series is a list of ligands in order of decreasing B (interelectron repulsion parameter). Like the spectrochemical series, it is also independent of the metal ion. A low value of B indicates a small amount of d-d electron repulsion. The decreased electron-electron repulsion may be caused from an increased distance between electrons or an increased size of the bonding orbitals.²⁷ Since the CpCo fragment of the tripod ligand is unable to delocalize the electron density from the metal ions coordinated through the P=O bridges, (see Section 1.7) it is placed early on

²³ C. K. Jørgensen: *Modern Aspects of Ligand Field Theory*, North-Holland Amsterdam (1971)

²⁴ C. K. Jørgensen, *Prog. Inorg. Chem.*, 4 (1962) 73

²⁵ K. Fajans, *Naturwissenschaften*, 11 (1923) 165

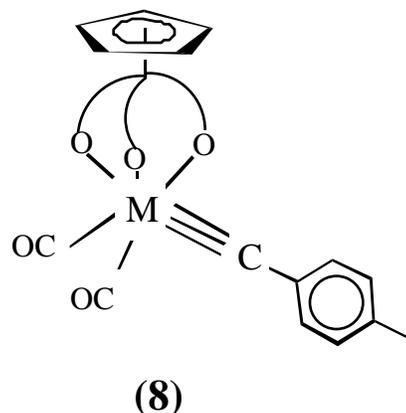
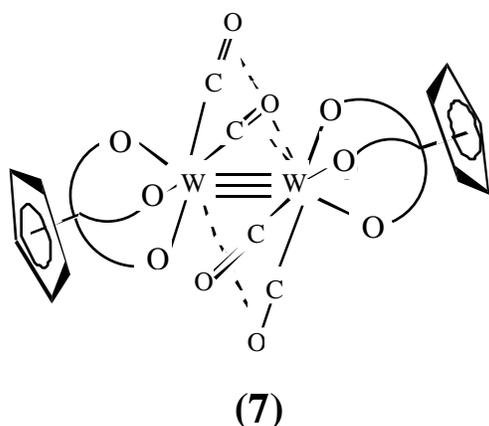
²⁶ R. Tsuchida, *Bull. Chem. Soc. Japan*, 13 (1938) 388, 436, 471

²⁷ N. N. Greenwood and A. Earnshaw: *Chemistry of the Elements*, Pergamon Press, (1984) 1096-1099

the series labeling the ligand as “hard.” Therefore, L^- has a decreased tendency to form covalent bonds with metal ions.

1.6 ORGANOMETALLIC CHEMISTRY

The placement of L^- in the spectrochemical and nephelauxetic series, characterizes it as being a very hard and weak ligand, similar to oxo and fluoride ligands. As a result, L^- should be able to stabilize metal ions in their medium to high oxidation states. In fact L^- forms stable 2:1 complexes with titanium (II, III, or IV), vanadium (II, III, or IV), and 1:1 complexes with molybdenum (V) and tungsten (VI).²⁸ Therefore, it is interesting that L^- can also form very stable metal carbonyl and nitrosyl complexes of the type $[LM(CO)_2(NO)]$ ($M = Cr, Mo, W$).²¹ Normally, oxygen and other strongly electronegative ligands (e.g. fluoride) form only labile and thermally unstable Group VI metal carbonyl derivatives.²⁹ Yet, L^- forms stable organometallic complexes such as $[L_2W_2(CO)_4]$, **7**, containing a W—W triple bond³⁰, and $[L(CO)_2M-CAr]$ ($M = Mo$ or W), **8**, containing a metal carbyne fragment.³¹



Through the use of IR spectroscopy, the metal carbonyl complexes made it possible to study the effects of varying the alkoxy or alkyl group on L^- , by measuring the C=O stretching frequencies. A series of $[LCuCO]$ complexes were synthesized in which the R group was altered to obtain various steric requirements ($R = OMe, OEt, O-i-Pr, OBU$, etc.).³² From this study it was discovered that variations of L^- mainly influence the basicity and not the oxygen—oxygen distance of the ligands. Also, the size of R has no

²⁸ W. Kläui, A. Müller, W. Eberspach, R. Boese, and I. Goldberg, *J. Am. Chem. Soc.*, 109 (1987) 164

²⁹ J. F. White, and M. F. Farona, *J. Organomet. Chem.*, 37 (1972) 119

³⁰ W. Kläui, A. Müller, R. Herbst, and E. Egert, *Organometallics*, 6 (1987) 1824

³¹ W. Kläui, H. Hamers, M. Pfeffer, and A. de Cian, J. Fischer, *J. Organomet. Chem.*, 394 (1990) 213

³² W. Kläui, B. Lenders, B. Hessner, and K. Evertz, *Organometallics*, 7 (1988) 1357

influence on the electronic properties of the CuCO complexes. However, a similar study of a copper-olefin fragment found that the size of R does affect the rate of exchange of the ethylene ligand in [LCu(C₂H₄)] complexes.³² These results demonstrate not only the effect of the R group on coordination, but also the importance of organometallic complexes and their usefulness in studying complexation.

As mentioned previously, both the oxygen tripod ligand and cyclopentadienyl (Cp) formally represent facially coordinating, monoanionic six electron ligands. (see Section 1.3) This similarity allows comparison between the organometallic complexes of these two ligands. In fact, Cp and L⁻ are the only ligands known to stabilize the W₂(CO)₄ unit. From the comparison of these tungsten compounds, L⁻ was found to induce more back bonding than (C₅H₅)⁻ and (C₅Me₅)⁻ due to its strong electron donating ability.³⁰ In the Rh(I) carbonyl complexes of L⁻ and Cp, the oxygen tripod ligand undergoes CO substitution much faster than its Cp analogue. An explanation for this increased rate is that the intermediary transition from tridentate to bidentate coordination is energetically more favorable than the “slipping reaction” of ⁵-Cp/ ³-Cp.³³ Another interesting correlation is that L⁻ is only weakly basic relative to Cp, therefore, many tripod complexes of carbonyl-metal fragments can be prepared and reacted in aqueous medium.²¹ In terms of reaction chemistry, isoprene can be inserted into the metal-hydrogen bond of the hydrido complex **9** (M = Mo, W; R = OC₂H₅), leading to the allylic complexes **10**.²⁸ (Scheme 1.6) On the other hand, the analogous cyclopentadienyl compounds **11** react with conjugated dienes to give hydrogenation of the olefin and formation of the binuclear complexes [{(C₅H₅)M(CO)₃}₂].³⁴

³³ W. Kläui, M. Scotti, M. Valderrana, S. Rojas, G. M. Sheldrick, P. G. Jones, and T. Schroeder, *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 683

³⁴ A. Miyake, and H. Kondo, *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 631, 880

has one negative charge.³⁵ The lower wave numbers indicate an increase in electron density at the metal center. These strong electron donating properties contrasts with the early position of L^- in the spectrochemical series.²¹ Also, the classification of “hard” would suggest that L^- is best suited to stabilize metals in higher oxidation states. Yet, the oxygen tripod ligands form a variety of very stable organometallic compounds. How can this be? These contradictions can be explained if L^- is considered as a strong π -donor.

The π -donor ability of the oxygen tripod ligand can be further explained through the use of molecular orbital (MO) diagrams. Both σ - and π -interactions between the metal and ligands affect the ligand field splitting in an octahedral complex. The extent to which they become important depends entirely on the ligand. For this purpose, only the π -interactions will be considered. The metal has both t_{1u} (4p) and t_{2g} (3d) orbitals available for π -bonding. However, only the t_{2g} orbitals readily π -bond with the ligand because the t_{1u} orbitals are used to form strong σ -bonds. Therefore, assuming there are appropriate t_{2g} orbitals on the ligand, π -bonding between a metal and ligand is possible.⁴¹

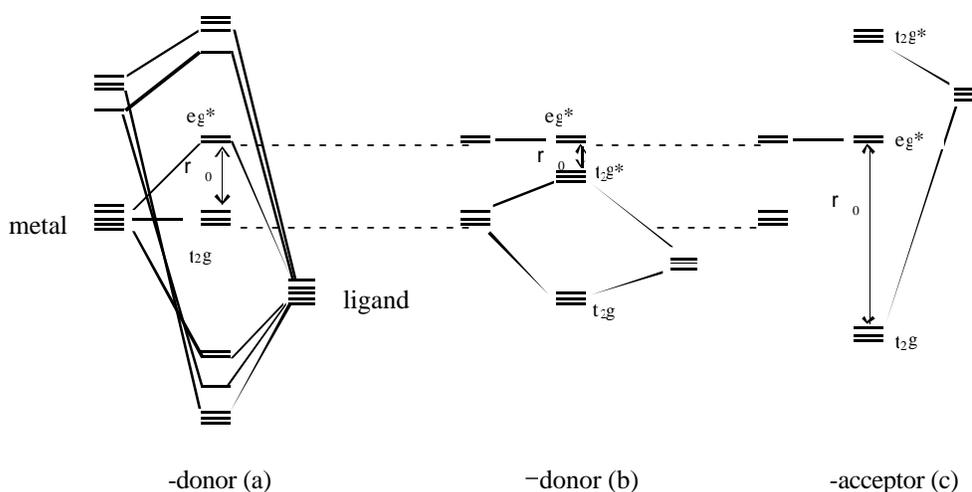


Figure 1.6: Energy level diagrams of an octahedral complex for (a) π -donor ligands only, (b) π -donor ligands such as F or L^- and (c) π -acceptor ligands such as CO , P , S .

Figure 1.6 demonstrates the two types of π -bonding interactions that the ligand can initiate, π -donor and π -acceptor. In the case of a π -donor interaction (b), the ligand's 2p orbitals are more electronegative than the metal 3d orbitals, therefore they are placed lower on the MO diagram. These filled orbitals cause the metal t_{2g} orbitals to split into bonding and antibonding orbitals with the t_{2g} bonding orbitals closely resembling the ligand orbitals (similar in energy). As a result, the filled 2p orbitals of the ligand will place its electrons into the t_{2g} bonding orbitals and the metal 3d electrons will enter the t_{2g}^* orbital. Since the level of the e_g^* is unaffected by π -bonding, Δ_0 ($e_g^* - t_{2g}^*$ or $e_g^* - t_{2g}$) will be reduced compared to a σ -only bonding interaction. Therefore, the ligand *donates*

electron density to the metal through the π -bond.⁴¹

Example (c), shows the MO diagram for a π -accepting interaction. In this case, the ligand has empty 3d orbitals which are available for bonding, unlike the filled 2p orbitals of the π -donor. These orbitals are less electronegative than the metal 3d orbitals, and are raised in energy. Now, the t_{2g} bonding orbitals resemble the metal orbitals, and are appropriately filled with the metal 3d electrons. Thus, ν_{CO} is increased due to the lowered energy of the t_{2g} orbital and the empty orbitals of the ligand are available to *accept* electron density from the metal, also known as back bonding.⁴¹

The effect this π -interaction has on metal carbonyl complexes of the type $[LM(CO)_3]$ can be measured by the C–O stretching frequencies. Normally, the greater the positive charge on the metal, the more difficult it is for the metal to back bond electrons into the t_{2g}^* orbitals of the CO ligands.⁴¹ However, L^- is a good π -donor, therefore, it donates electron density to the metal which allows the metal to form a strong π -bond with the CO ligand lengthening the existing C–O triple bond. In fact, it induces more extensive M–CO back bonding than is observed with other monoanionic six electron ligands. For example, the wave numbers of the CO vibrations in the Molybdenum and Tungsten complexes $[(6e^- \text{ ligand})M(\text{CR})(CO)_2]$ decline by 25-50 cm^{-1} through the sequence $C_5H_5^- > C_5Me_5^- > B(pz)_4^- > HB(pz)_3^- > L^-$.⁴² This supports the idea that L^- is a good π -donor.

1.8 APPLICATIONS

1.8.1 Catalysis

For catalytic applications, the metal ion coordinated to L^- should remain in a high oxidation state throughout the catalytic cycle. This would indicate that the stability of the complex is a function of the chelate effect and electrostatic interaction instead of the synergistic effects between opposing π -donor and π -acceptor ligands. This type of stability is beneficial for oxygen-transfer reactions.⁶ A good example is the peracetic acid oxidation of 1-octene to heptanoic acid catalyzed by the ruthenium tripod complex $[L_{OEt}Ru(CO)_2Cl]$. (Figure 1.7) The yield of heptanoic acid with the catalyst (1:4000) was 75% compared to the 4% yield without it.⁴³

⁴¹ J. E. Huheey: *Inorganic Chemistry*, 3rd edition; Harper Collins Publishers, (1983) 430-434

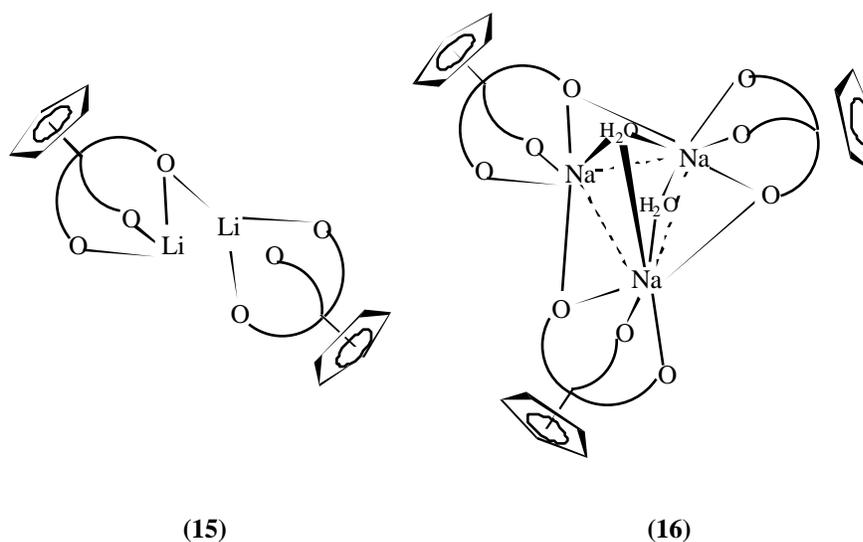
⁴² W. Kläui, and H. Hamers, *J. Organomet. Chem.*, 345 (1988) 287

⁴³ S. Warwel, M. R. Klaas, and M. Sojka, *Ber.-Dtsch. Wiss. Ges. Erdoel, Erdgas Kohle, Tagungsber.*, 9204 (1992) 161

The oxygen tripod ligand allows for electronic and steric control of the catalyst, thereby producing a high percentage of ortho-quinone and only a small amount of muconic acid anhydride. Other oxovanadium (IV) catalysts concentrate on the cleavage of the catechol ring instead of the oxidation into ortho-quinone. Oxo, peroxy, and dioxy complexes of the tripod ligand are also under investigation.⁴⁴

1.8.2 Lithium Chemistry

Ionophores selective to Li^+ ions have received special interest in view of the importance of Li^+ in the treatment of manic depressive patients. The organometallic ligand **L** was reported as being an active species in the transport of Li^+ and Na^+ ions through phospholipid membranes.⁴⁵ Results indicated that the rate of transport of Li^+ is inversely proportional to Li^+ concentration and increases in H^+ concentration, suggesting a LiL-HL exchange as a possible mechanism. Through competition experiments, the selectivity of Li^+ over Na^+ ions was found to exceed a factor of 40 making the oxygen tripod ligand comparable with other Li^+ ionophores.⁴⁵ The reason for the preferential transport of Li^+ ions may be the fact that the lithium salts LiL exists as the dimer **15** in lipophilic medium⁴⁶ whereas NaL forms trimers, **16**, of the type $[\text{Na}_3\text{L}_3(\text{H}_2\text{O})_2]$.²⁸



Besides being used as an ionophore for the transport of Li^+ , **L** was also used to extract Li^+ from brines.⁴⁷ Extraction solvents such as alcohols, crown ethers, or 4-acyl-5-pyrazolones are commonly used for the liquid-liquid extraction of lithium,^{48, 49, 50, 51, 52, 53,}

⁴⁵ H. Shiner, G. Navon, and W. Kläui, *J. Am. Chem. Soc.*, 108 (1986) 5005

⁴⁶ I. Goldberg, H. Shinar, G. Navon, and W. Kläui, *J. Inclusion Phenom.*, 5 (1987) 181

⁴⁷ H. Bukowsky, E. Uhlemann, and W. Kläui, *Anal. Chim. Acta*, 319 (1996) 271

⁴⁸ I. A. Epstein, E. Feist, I. Zmora, and Y. Marcus, *Hydrometallurgy*, 6 (1981) 269

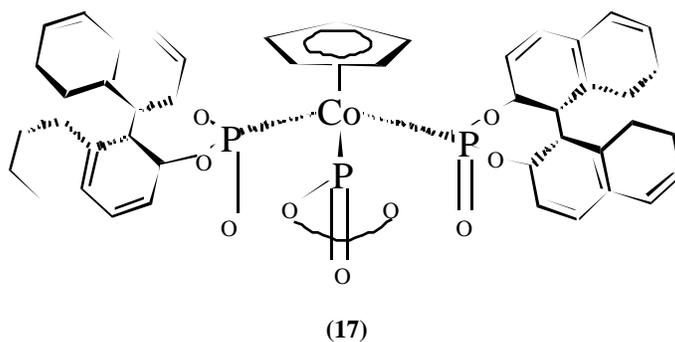
⁴⁹ H. Bukowsky, E. Uhlemann, and D. Steinborn, *Hydrometallurgy*, 27 (1991) 317

⁵⁰ G. G. Gabra, and A. E. Torma, *Hydrometallurgy*, 3 (1978) 23

⁵⁴ however, certain amounts of magnesium and calcium are coextracted with the Li^+ ion. Therefore, due to its unique chemical properties and stable complexes with the smaller alkali and alkaline earth metal ions⁵⁵, the oxygen tripod ligand was investigated. From solutions of alkali metal chlorides, lithium was specifically extracted up to 98%. However, when Li^+ extraction was studied in comparison to magnesium and calcium salts, the difference in extraction rates were small, making a simple extraction of Li^+ from Mg^{2+} and Ca^{2+} difficult. An alternative method using the sodium salt of L^- was found to be very effective. If the Ca^{2+} and Mg^{2+} ions were precipitated with an aqueous solution of NaL , **16**, before extraction then Li^+ ions could be extracted up to 98% by a chloroform solution of the same reagent. It was suggested that the aggregation behavior of **16** influences the selectivity of Li^+ ions in the extraction process.⁵⁵

1.9 RESEARCH OBJECTIVES

As mentioned previously, by varying the R groups on L^- it is possible to synthesize a chiral version of the oxygen tripod ligand.(see Section 1.3) Prior to this research, all of the R groups on L^- have been alkoxy or alkyl chains of varying steric requirements. Therefore, by using a chelating R group such as rac-binaphthyl or biphenyl, a new type of ligand can be made.



The objective of this research is to design a synthetic route to the optically active ligand, $[(\text{C}_5\text{H}_5)\text{Co}\{\text{P}(\text{O})\text{R}_2\}_3]^-$, **17**, where R = + 1,1'-bi-2-naphthyl.

In the process to obtain this chiral ligand, the biphenyl version of the tripod ligand, **18**, will be synthesized and characterized first. This will determine the feasibility of a chelated R group on L^- . However, in order to synthesize the biphenyl version,

⁵¹ H. Bukowsky, and E. Uhlemann, *Sep. Sci. Technol.*, 28 (1993) 1357

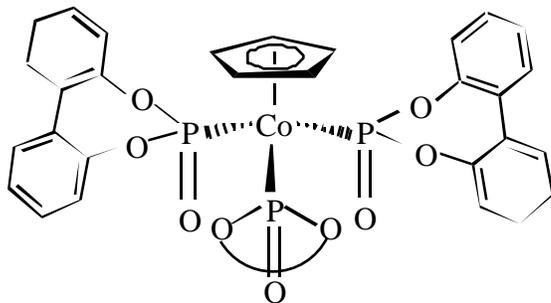
⁵² M. J. Pugia, G. Ndip, H. K. Lee, I. W. Yang, and R. A. Bartsch, *Anal. Chem.*, 58 (1986) 2723

⁵³ S. Umetani, K. Maeda, S. Kihara, and M. Matsui, *Talanta*, 34 (1987) 779

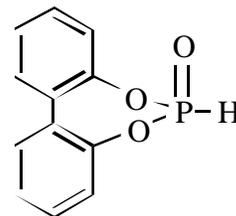
⁵⁴ H. Bukowsky, E. Uhlemann, K. Gloe, and P. Mühl, *Anal. Chim. Acta.*, 257 (1992) 105

⁵⁵ W. Kläui, and G. Anderegg, *Z. Naturforsch.*, 36b (1981) 949

2,2'-biphenyl phosphite, **19**, will need to be made. From **19** and cobaltocene, the biphenyl ligand can then be synthesized. (see Section 1.2) Afterwards, when **18** is synthesized, a racemic version of **17** will be attempted. If successful, then a route to the optically active ligand will be available.



(18)



(19)

Chapter 2: Experimental

2.1 Experimental Conditions

All manipulations and reactions were performed under an atmosphere of purified nitrogen or argon using standard schlenk techniques. Organic solvents were dried by activated alumina and degassed by passing through a supported-copper oxygen scavenger (Q-5) obtained from Engelhardt. Hexamethylphosphorous triamide, 2,2'-biphenol, and 1,1'-bi-2-naphthol were obtained from Aldrich and used without further purification. Cobaltocene was synthesized according to the literature⁵⁶ and stored in sealed ampoules.

NMR measurements were performed on a Bruker WP200 at 200.133 MHz for ¹H, 50.323 MHz for ¹³C, and 81.015 MHz for ³¹P. Higher resolution ¹H, ¹³C, and ³¹P NMR spectra were obtained on a Bruker WP360 at 360.13, 90.56, and 145.78 MHz respectively and on a Varian RU400 NMR spectrometer at 399.052, 100.577, and 161.903 MHz respectively. All chemical shifts for ³¹P spectra are reported relative to 85% H₃PO₄ and ¹³C, ¹H are reported relative to tetramethylsilane (TMS). Key to NMR data: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; m, multiplet; br, broad; asterisk, pseudo.

FAB Mass Spectra were recorded on a VG 7070E-HF spectrometer. Elemental analyses were performed by Atlantic Microlab.

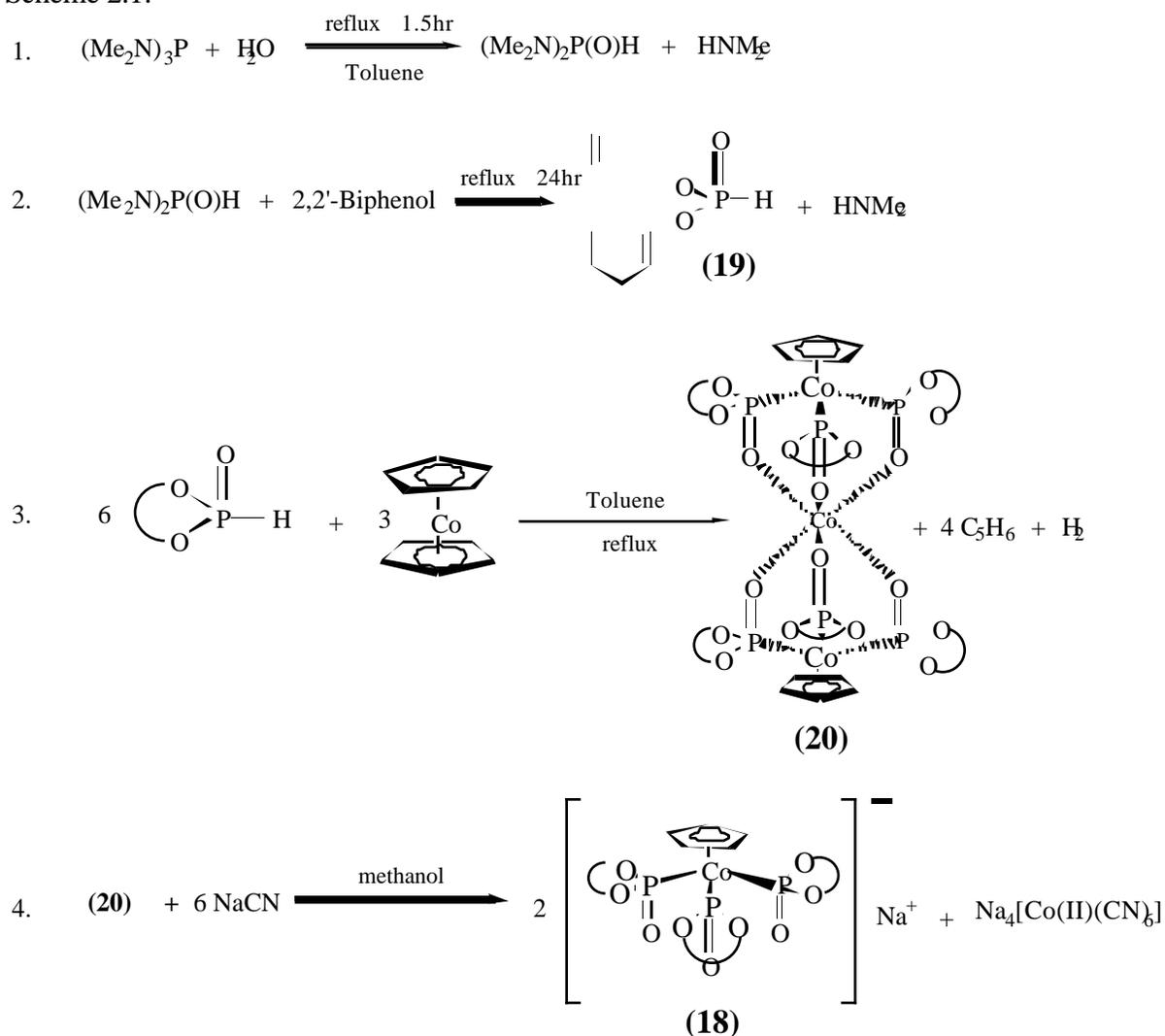
2.2 Preparation of (Cyclopentadienyl)tris(biphenylphosphito-*P*)cobaltate (18)

A four step synthesis was used to synthesize the biphenyl version of the tridentate oxygen donor ligand. (Scheme 2.1) The biphenyl phosphite, **19**, has been previously synthesized by three different methods. The synthesis developed by Page et. al.⁵⁷ was found to be the fastest and highest yielding reaction. Steps 3 and 4 are a modification of the Kläui synthesis developed in 1979.⁴ In step 3, the reactants are refluxed in toluene instead of heated neat. In step 4, the isolation of product involved immediate filtration because of the insolubility of (**18**) in methanol.

⁵⁶ *Handbook for Inorganic Chemistry Laboratory*, Virginia Polytechnic Institute and State University

⁵⁷ P. Page, M. Mazières, J. Bellan, and M. Sanchez, *Phosphorous, Sulfur, and Silicon*, 70 (1992) 205

Scheme 2.1:



2.2.1 Synthesis of 5,7-dioxa-6-phospha-dibenzo(a,c)cycloheptene 6-oxide (19)

Water (1.0mL, 0.055mol) was added to a solution of hexamethylphosphorous triamide (10mL, 0.055mol) and toluene (120mL) in a 500mL flask with stirring and refluxed under a nitrogen atmosphere for 1.5 hour until a clear yellow solution was formed. The solution was cooled to room temperature, then 2,2'-biphenol (10.2g, 0.055mol) was added, and the sides of the flask were rinsed with a small aliquot of toluene. The mixture was heated to reflux for approximately 24 hours. The ^{31}P NMR spectrum of the solution was checked at intervals until only a single peak at ~13ppm was present. At that time heating was discontinued and the reaction was allowed to cool to room temperature. The solution was filtered to remove unwanted solid impurities and then cooled in a refrigerator (~ 8°C) for 6 hours. After cooling, an oily solid was present and the solution was filtered again to obtain a clear solution. The toluene was removed

under reduced pressure and the resulting white solid was washed three times with 25mL of hexane and dried under nitrogen for 2 days to yield 10.7g (84%) of product.

Analytical data for 5,7-dioxa-6-phospha-dibenzo(a,c)cycloheptene 6-oxide (19)

White solid, mp. 109-110°C; Literature value for mp.= 109-110°C⁵⁸

Spectral Data:

¹H NMR (200Hz, in CDCl₃): 7.3 [d, J_{P-H} = 733 Hz, 1H], 7.3-7.6 [m, 8H, aromatic protons]

³¹P NMR (81.02Hz, in CDCl₃): 13.4 [s]

2.2.2 Synthesis of bis[(cyclopentadienyl)tris(biphenylphosphito-P)cobalt-O, O', O'']cobalt(II) (20)

In a dry box, cobaltocene (1.0g, 0.0053mol) and 5,7-dioxa-6-phospha-dibenzo(a,c)cycloheptene 6-oxide (2.5g, 0.011mol) were added together in a 150mL flask. Toluene (35mL) was added to dissolve both solids and the solution was refluxed under nitrogen for 24 hours with constant stirring. The resulting yellow precipitate was filtered and washed three times with 20mL of toluene and then dried under reduced pressure for 18 hours. The final yield was 6.6g (74%).

Analytical data for bis[(cyclopentadienyl)tris(biphenylphosphito-P)cobalt-O, O', O'']cobalt(II) (20)

Yellow solid, mp. decomposes at 252°C

Spectral Data:

¹H NMR (200Hz, in CDCl₃): 4.9 [s br., 5H], 6.7-8.0 [m br., 24H, aromatic protons]

³¹P NMR (81.02Hz, in CDCl₃): 120 [s br]

Elemental Analysis:

Anal. Calc'd. for C₈₂H₅₈O₁₈P₆Co₃ (MW = 1694g/mol): C, 58.14%; H, 3.451%

Found: C, 59.69%; H, 4.19% (submitted)

Mass Spectrum: [M+] at 1694 by F.A.B.

2.2.3 Synthesis of sodium(cyclopentadienyl)tris(biphenylphosphito-P)cobaltate(III) (18)

Bis[(cyclopentadienyl)tris(biphenylphosphito-P)cobalt(III)-O, O', O'']cobalt(II)

⁵⁸ V. V. Ovchinnikov, O. A. Cherkasova, and L. V. Verizhnikov, *J. Gen. Chem. USSR*, 52 (1982) 615

(1.5g, 0.89mmol) and sodium cyanide (0.36g, 7.4mmol) were placed in a 100mL flask with 45mL of methanol and stirred in air for 24 hours. Methylene chloride (5mL) was added to facilitate the solubility of the sandwich complex **20**; the solution was then stirred continuously for an additional 48 hours. The yellow precipitate present was filtered and washed three times with methanol. The solid was dried under reduced pressure for 48 hours. The final yield of the air stable ligand was 1.1g (74%)

Analytical data for (cyclopentadienyl)tris(biphenylphosphito-*P*)cobaltate(III) (**18**)

Yellow solid, mp. decomposes at 346°C

Spectral Data:

¹H NMR (200MHz, in CDCl₃): 4.7 [s, 5H], 7.2-7.7 [m, 24H aromatic protons]

¹³C NMR (100.6MHz, in CDCl₃): 87.2 [s], 122.8 [s], 124.8 [s], 129.2 [s], 129.8 [s], 130.8 [s], 151.1 [s]

³¹P NMR (161.9MHz, in CDCl₃): 122 [s]

Elemental Analysis:

Element	Found	Trihydrate	Anhydrous
C (%)	54.45	55.05	58.89
H (%)	3.72	3.94	3.48

Mass Spectrum: [MH⁺] at 841 by F.A.B.

XPS Data:

Element	Atomic Concentration	
	Experimental(%)	Theoretical(%)
Carbon	74.63	74.50
Oxygen	17.82	16.36
Phosphorus	4.23	5.45
Sodium	1.97	1.89
Cobalt	1.35	1.89

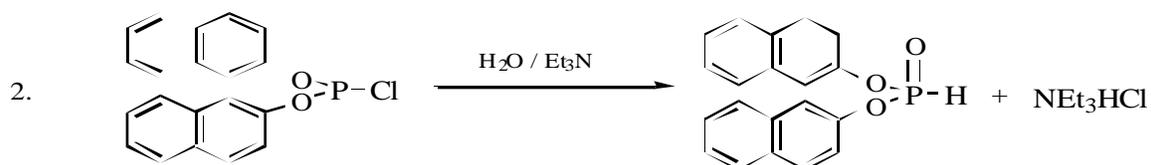
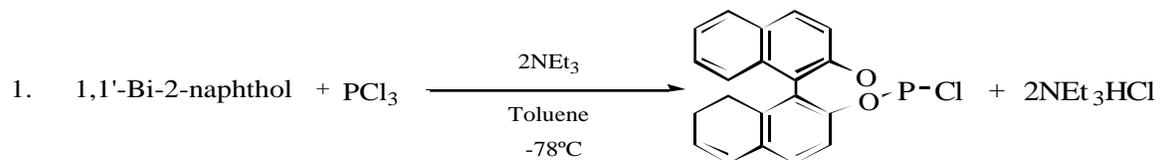
2.3 Preparation of sodium(cyclopentadienyl)tris(rac-binaphthylphosphito-*P*)cobaltate(III)

Two different syntheses were used for the rac-binaphthyl phosphite, **21**. Scheme 2.2a describes a synthesis previously reported in the literature.⁵⁹ However, because the

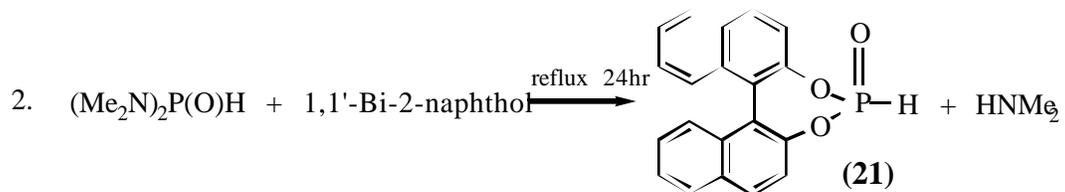
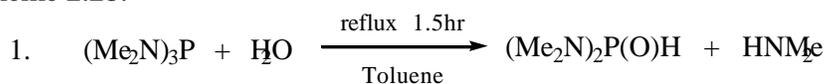
⁵⁹ N. Greene and T. Kee, *Syn. Commun.*, 23 (1993) 1651

synthesis used for the biphenyl phosphite was less air-sensitive than the PCl_3 reaction, it was modified to be used for the rac-binaphthyl phosphite as well. (Scheme 2.2b)

Scheme 2.2a:

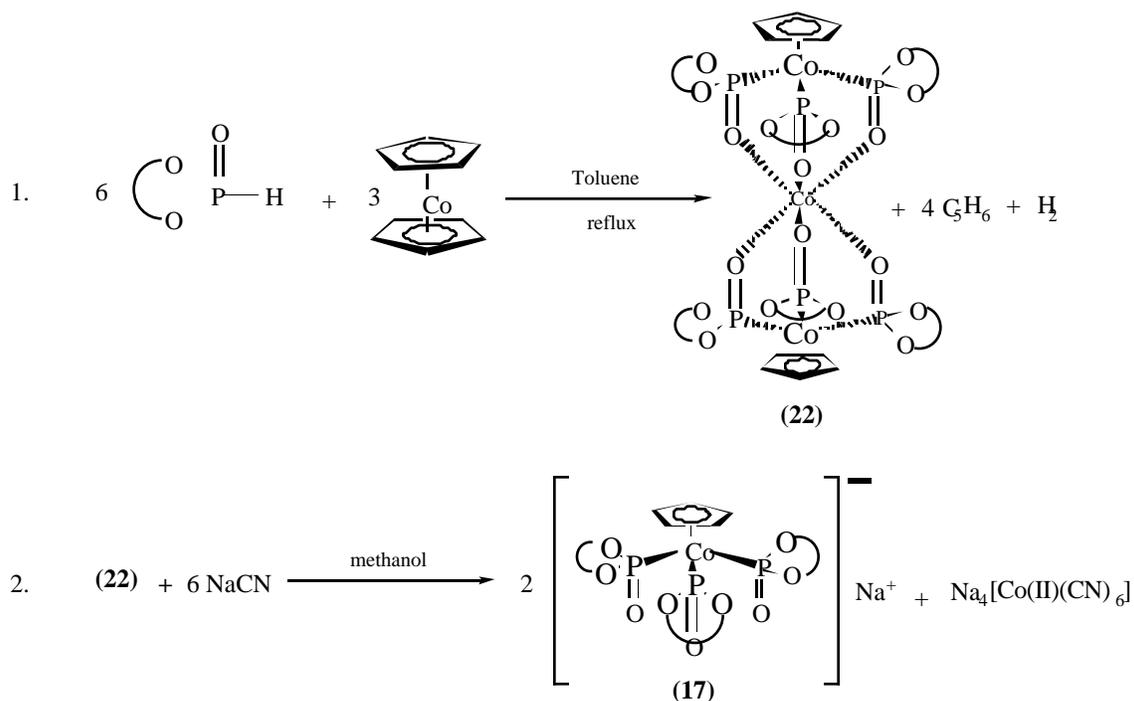


Scheme 2.2b:



The reaction sequence for the rac-binaphthyl version of the tridentate oxygen donor ligand is also a modification of the Kläui synthesis that was initially developed for alkoxy phosphites. (Scheme 2.3)

Scheme 2.3:



2.3.1a Synthesis of 3,5-dioxa-4-phospha-cyclohepta(2,1-a; 3,4-a')dinaphthalene 4-oxide via (Me₂N)₃P (21)

Water (0.32mL, 0.018mol) was added to a solution of hexamethylphosphorous triamide (3.2mL, .018mol) and toluene (38mL, 0.35mol) in a 250mL flask with stirring and refluxed under a nitrogen atmosphere for 1.5 hours until a clear yellow solution was formed. When the solution was cooled to room temperature, \pm 1,1'-bi-2-naphthol (5.0g, 0.018mol) was added to the solution as a suspension in 30mL of toluene. The mixture was heated to reflux for approximately 48 hours. The ³¹P NMR of the mixture was checked intermittently until only a single peak at ~14ppm was present, after which the reaction was discontinued and allowed to cool to room temperature. The mixture was then filtered to remove unwanted solid impurities and cooled in a refrigerator (~8°C) for 6 hours. After cooling, a small amount of white solid byproduct was present; the mixture was filtered again to remove the solid and obtain a clear solution. The toluene was removed under reduced pressure until a small amount of solid was present in the mixture. 60mL of pentane was then added to the mixture with stirring. The resulting white precipitate was filtered and then dried under nitrogen for 2 days to yield 4.7g (80%) of product.

2.3.1b Synthesis of 3,5-dioxa-4-phospha-cyclohepta(2,1-a; 3,4-a')dinaphthalene 4-oxide (21) via PCl₃

In a 250mL 3-necked flask under nitrogen, PCl₃ (1.6mL, 0.018mol) and triethylamine (5.0mL, 0.036mol) were dissolved in 10mL of toluene and cooled to -78°C. A suspension of ±1,1'-bi-2-naphthol (5.9g, 0.018mol) in 100mL of toluene was added through a dropping funnel over a period of 2 hours. The mixture was then slowly warmed to room temperature for 16 hours resulting in a pale yellow viscous mixture with NEt₃HCl as a precipitate. The ³¹P NMR spectrum was checked and a singlet was present at 176.6ppm. Without filtering, water (0.32mL, 0.018mol) and NEt₃ (2.5mL, 0.018mol) were added to the mixture resulting in more NEt₃HCl precipitate. The mixture was stirred for 20 hours with occasional recording of the ³¹P NMR spectrum. When a singlet at 13.7ppm was the only peak, the mixture was filtered to remove the NEt₃HCl. The ammonium salt was washed two times with 20mL of toluene to remove any product and the filtrate was combined with the original solution. The toluene was then removed by reduced pressure resulting in an off-white solid. The solid was recrystallized in 45mL of toluene to yield 3.2g (53%) of the final compound.

Analytical data for 3,5-dioxa-4-phospha-cyclohepta(2,1-a; 3,4-a')dinaphthalene 4-oxide (21)

White solid, mp. 186-188°C; Literature mp. = 185-187°C ⁵⁸

Spectral Data:

¹H NMR (400MHz, in CDCl₃): 7.3 [d, J_{P-H} = 731Hz, 1H], 7.3-8.1 [m, 12H, aromatic protons]

¹³C NMR (81.02MHz, in CDCl₃): 120.2 [s], 120.9 [s], 126.1 [d, J_{P-C} = 5.79Hz], 127.0 [s], 127.2 [d, J_{P-C} = 6.09Hz], 128.6 [s], 131.4 [d, J_{P-C} = 7.10Hz], 131.9 [s], 132.4 [d, J_{P-C} = 12.4Hz], 145.3 [d, J_{P-C} = 42.3Hz]

³¹P NMR (161.9MHz, in CDCl₃): 13.70 [s]

2.3.2 Synthesis of bis[(cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobalt(III)-O, O', O'']cobalt(II) (22)

In a dry box, cobaltocene (0.69g, 0.0036mol) and 3,5-dioxa-4-phospha-cyclohepta(2,1-a; 3,4-a')dinaphthalene 4-oxide (2.7g, 0.0073mol) were added together in a 100mL flask. Toluene (40mL) was added to dissolve both solids and the solution was refluxed under nitrogen for 24 hours with constant stirring. The resulting yellow precipitate was filtered and washed three times with 20mL of toluene and then dried

under reduced pressure for 18 hours. The final yield was 2.2g (79%).

Analytical data for bis[(cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobalt-O, O', O'']cobalt(II) (22)

Yellow solid, mp. decomposes at 259°C

Spectral Data:

¹H NMR (200Hz, in CDCl₃): 4.59 [s br., 5H], 7.18-8.40 [m br., 24H, aromatic protons]

³¹P NMR (81.02Hz, in CDCl₃): 116.44 [s br]

Elemental Analysis:

Anal. Calc'd. for C₁₃₀H₈₂O₁₈P₆Co₃ (MW = 2295 g/mol): C, 68.05%; H, 3.602%

Found: C, 65.47%; H, 4.62% (submitted)

2.3.3 Synthesis of sodium(Cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobaltate(III) (17)

Bis[(cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobalt-O, O', O'']cobalt(II) (1.2g, 0.50mmol) and sodium cyanide (0.29g, 6.0mmol) were placed in a 100mL flask with 50mL of methanol and stirred in air for 60 hours. The yellow precipitate present was filtered and washed three times with 50mL of methanol. The solid was dried under reduced pressure for 48 hours. A 25mL solvent mixture (CCl₄: CHCl₃: MeOH = 10:10:1) was added to dissolve the yellow solid and the undissolved byproducts were filtered out. The solvent was then removed under reduced pressure for 18 hours and the final yield of the air stable ligand was 0.85g (75%).

Analytical data for sodium(cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobaltate(III) (17)

Yellow solid, mp. decomposes at 364°C

Spectral Data:

¹H NMR (400MHz, in THF): 4.55 [s, 5H], 7.29-8.13 [m, 36H aromatic protons]

¹³C NMR (100.6MHz, in CDCl₃): 86.108 [s], 122.4 [s], 122.6 [s], 123.7 [d, JP-C = 6.94Hz], 124.9 [d, JP-C = 20.5Hz], 126.085 [d, JP-C = 44.25Hz], 127.405 [s], 128.6 [d, JP-C = 7.644Hz], 130.2 [d, JP-C = 51.90Hz], 132.1 [d, JP-C = 25.95Hz], 150.36 [s br]

³¹P NMR (161.9MHz, in THF): 120.5 [s]

Elemental Analysis:

Element	Found	Trihydrate	Anhydrous
C (%)	64.39	65.34	68.43
H (%)	4.03	3.96	3.63

Mass Spectrum:

[M+] at 1141 by F.A.B.

[MNa+] at 1164 by F.A.B.

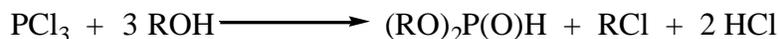
Chapter 3 : Results and Discussion

3.1 2,2'-BIPHENYL PHOSPHITE

3.1.1 Synthetic Routes

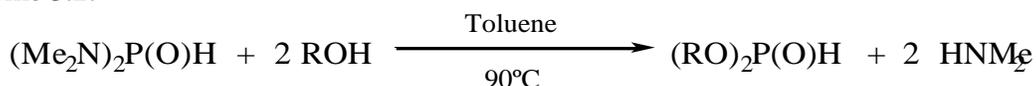
The general method of synthesis for phosphites of the type $(RO)_2P(O)H$ is an esterification of phosphorus trichloride.⁶⁰ (Scheme 3.1)

Scheme 3.1:



Although the esterification is a successful synthesis, it is very air-sensitive and gives low yields. Therefore, the synthesis developed by Page et. al.,⁵⁷ was used for the synthesis of 2,2'-biphenyl phosphite. This synthesis involved the alcoholysis of bis(dimethylamino) phosphonate. (Scheme 3.2)

Scheme 3.2:



According to the literature, tris(dimethylamino) phosphonate is first refluxed with water in toluene to make bis(dimethylamino) phosphonate. To this solution, an equal amount of 2,2'-biphenol is added and the mixture is heated to 90°C for 8 hours. The 2,2'-biphenyl phosphite was identified by its ³¹P NMR spectrum in solution. Then the solution was further reacted with sodium hydride and used in the Michaelis-Becker-Nylen⁶¹ synthesis to prepare 2-phosphonomethyl pyridines. Since the 2,2'-biphenyl phosphite was used previously in situ, a method was needed to isolate and purify the compound.

The first step was filtration. After the reaction was completed, a solid brown byproduct was present. This byproduct, although not identified, did not contain any phosphorous signals and, therefore, did not contain any product. However, further analysis showed that when the solid was dissolved in water, addition of NaOH produced an unidentified gas while the brown solution went clear. It was also found that when the gas was efficiently purged from the system the amount of byproduct was reduced.

At this point, two different methods were attempted to isolate the 2,2'-biphenyl phosphite. The first method involved the immediate removal of the solvent, toluene at reduced pressure, leaving behind a viscous oil. The ³¹P NMR spectrum showed a singlet at 14.3ppm, consistent with the phosphite. However, the ¹H NMR spectrum contained an unidentified singlet at 5.18ppm and the integrated intensity of the biphenyl protons is too high compared to the phosphite proton. Therefore, the oil was washed with diethyl

⁶⁰ L. Beslier, M. Sanchez, D. Houalla, and R. Wolf, *Bull. Soc. Chim. Fr.*, (1971) 2563

⁶¹ Y. S. Michaelis, *Liebigs Ann. Chem.*, 38 (1896) 293, 193

ether. The mixing of the ether with the oil removed the sticky impurity resulting in a white solid. After sitting in the refrigerator for 8 hours, the solid was filtered and washed three times with cold ether. The precipitate was then identified by spectroscopy to be the 2,2'-biphenyl phosphite. Unfortunately, this work-up was not reproducible. In later experiments, a white solid was also formed along with the oil. The ^{31}P NMR spectrum identified two singlets at -1.24ppm and -3.51ppm. This solid was also insoluble in diethyl ether, and precipitated out with the final product making a separation very difficult and possible in only low yields.

The second method attempted avoided the immediate removal of solvent. Instead, the filtered solution was placed in the refrigerator ($\sim 8^\circ\text{C}$) for 8 hours. This cold temperature caused the oil and solid white byproduct to precipitate. The cold toluene containing the dissolved product was then decanted to remove the unwanted impurities. Next, the toluene was removed under reduced pressure resulting in pure 2,2'-biphenyl phosphite in 84% yield. The phosphite was recrystallized by a methylene chloride/hexane solution. Overall, the second method proved to be the most efficient and reproducible with consistent high yields.

3.1.2 Analytical Data Interpretation

Since 2-2'-biphenyl phosphite has already been synthesized, the literature characterization of the compound was used as a reference. However, the only spectral data available was a ^{31}P NMR identification⁵⁷ which reports a singlet at 11.8ppm with $J_{\text{P-H}} = 730\text{Hz}$. The ^{31}P NMR obtained through these experimental procedures shows a singlet with a chemical shift of 13.4ppm with $J_{\text{P-H}} = 733\text{Hz}$. A ^1H and ^{13}C NMR were not available for comparison. A computer simulation of the spectrum is consistent with the chemical shifts obtained. The ^1H NMR spectrum provides evidence of the phosphite proton being coupled by the phosphorus atom and correctly places the aromatic protons in the accepted region of $\sim 7.2\text{-}7.6\text{ppm}$.

Further identification by Ovchinnikov⁵⁸ reports the melting point as $109\text{-}110^\circ\text{C}$, the experimental melting point was also $109\text{-}110^\circ\text{C}$. The final data available for comparison reports the compound as a viscous oil,⁶² and lists the results from an elemental analysis study. As is mentioned in Section 2.2.1, the 2,2'-biphenyl phosphite was isolated as a white solid. However, it is observed that the white solid reacts with water to form an oily substance. The oil has a ^{13}C NMR spectrum that can only be explained if 2,2'-biphenyl phosphite ester is partially hydrolyzed. Also, the ^1H NMR spectrum exhibits an extra singlet at a chemical shift of 6.52ppm, which may correspond to the O-H proton, and a wider range of chemical shifts for the aromatic region, consistent with two different ring systems. However, the ^{31}P NMR spectrum is similar to the one for the unhydrolyzed product with only a slight upfield shift. Therefore, because Natchev does not report any spectral data, it is possible that his reported compound is actually a mixture of the phosphite and hydrolyzed phosphite. It can be further

⁶² I. A. Natchev, *Phosphorous and Sulfur*, 37 (1988) 149

demonstrated by comparing Natchev's elemental analysis data with the calculated data of the hydrolyzed phosphite. (Table 3.1) A mixture of products would explain the lower than calculated value for %C found and the higher than calculated value for %H found.

Table 3.1: A = 2,2'-biphenyl phosphite; B = hydrolyzed 2,2'-biphenyl phosphite

ELEMENT	FOUND [62]	Calc'd for cmpd. A	Calc'd for cmpd. B
Carbon	61.77 %	62.08 %	56.61 %
Hydrogen	4.11 %	3.91 %	4.43 %

In conclusion due to the similar ^{31}P NMR spectra, the clean ^1H NMR spectra, and the similar melting points it appears that 2,2'-biphenyl phosphite was experimentally synthesized. Furthermore, the phosphite is characterized as a white solid instead of an oil.

3.2 SYNTHESIS OF THE BIPHENYL COBALT SANDWICH COMPLEX

3.2.1 Synthetic Routes

The synthesis for making bis[(cyclopentadienyl)tris(biphenylphosphito-*P*)cobalt(III)-O, O', O'']cobalt(II) was based on the synthesis developed by Kläui in 1977.¹ However, all of Kläui's syntheses were run neat using a liquid phosphite. Since 2,2'-biphenyl phosphite is a solid, it was dissolved in toluene and reacted with cobaltocene in a 4:1 ratio. The solution was refluxed for 24 hours resulting in a yellow solution with a small amount of yellow precipitate. Toluene was then removed under reduced pressure and the remaining solid was redissolved in methylene chloride. The final compound is believed to be paramagnetic since it contains an octahedral Co(II). This makes the use of NMR spectroscopy to characterize the compound and identify impurities very difficult. Therefore, TLC with methylene chloride as the solvent was used to determine the presence of impurities in the sample. The results showed that the impurities present were much less polar than the sandwich complex and could be easily removed through a column. Methanol was used as the final solvent to remove the desired sandwich complex off the column. The final product, a yellow solid, was identified by FAB MS as the desired biphenyl cobalt sandwich complex. However, due to the large amount of separated impurities, including unreacted 2,2'-biphenyl phosphite, the yield was only 10%.

The reaction was tried a second time, with a ratio of 1:2, thereby reducing the amount of initial 2,2'-biphenyl. After 24 hours of refluxing, a large amount of yellow precipitate was formed and the reaction was stopped. The precipitate was filtered under nitrogen and identified as bis[(cyclopentadienyl)tris(biphenylphosphito-*P*)cobalt(III)-O, O', O'']cobalt(II) with an overall yield of 80%.

3.2.2 Analytical Data Interpretation

Bis[(cyclopentadienyl)tris(biphenylphosphito-*P*)cobalt-O, O', O'']cobalt(II) is believed to be paramagnetic since the spectral analysis of the biphenyl cobalt sandwich complex produced very broad peaks. However, it was possible to get an approximation of the proton and the phosphorous chemical shifts. The ^1H NMR data gives a reasonable integration for the sandwich complex with 5 protons assigned to the cyclopentadienyl ring and 24 protons assigned to the biphenyl rings. The ^{31}P NMR spectrum resulted in a very broad singlet at $\sim 119\text{ppm}$. This chemical shift is reasonable considering that the phosphorous atom is bound to a cobalt atom and three oxygen atoms. Analysis by FAB MS gives $[\text{M}^+] = 1694$ amu indicating that there was no loss or addition of protons.

3.3 SODIUM(CYCLOPENTADIENYL)TRIS(BIPHENYLPHOSPHITO-*P*)COBALTATE(III) (18)

3.3.1 Synthetic Routes

The synthesis used was a modification of Kläui's synthesis.⁴ The literature suggests a ratio of 1:6 for the sandwich complex versus the sodium cyanide. However, it was found that a 1:12 ratio yielded better results. Also, the biphenyl cobalt sandwich complex was insoluble in methanol, therefore a small amount of CH_2Cl_2 was added to the mixture until a clear solution was formed. After stirring for 2 days, a yellow precipitate identified as the final ligand, appeared and was filtered. The alkoxy analogs to this compound are soluble in methanol and do not precipitate out; therefore their isolation entails many different steps to remove $\text{Na}_4[\text{Co}(\text{II})(\text{CN})_6]$. The easy isolation of the ligand allowed for a pure product with a good yield of 74%.

3.3.2 Analytical Data Interpretation

The spectral data was found to be consistent for this compound. The ^1H NMR showed a singlet with a chemical shift of 4.74ppm which is comparable to the literature value of 4.84ppm.⁵⁶ Also the integration for the cyclopentadienyl protons relative to the biphenyl protons was within one proton of the expected value. The ^{13}C NMR had seven singlets, six corresponding to the biphenyl carbons and one singlet for the equivalent cyclopentadienyl carbons. However, none of the expected splitting of the biphenyl carbons by the phosphorous atom is seen in the spectrum. This could be a result of the ring system going planar due to the steric hindrance of the compound, thereby causing the bond overlapping in the system to be altered.

The XPS study on the ligand verified the relative mole percentages of the elements present at the surface. This was a good qualitative analysis to determine the purity of the ligand.

In conclusion, the ability to synthesize this ligand and characterize it demonstrated the feasibility of having chelated groups on the phosphite. The methods

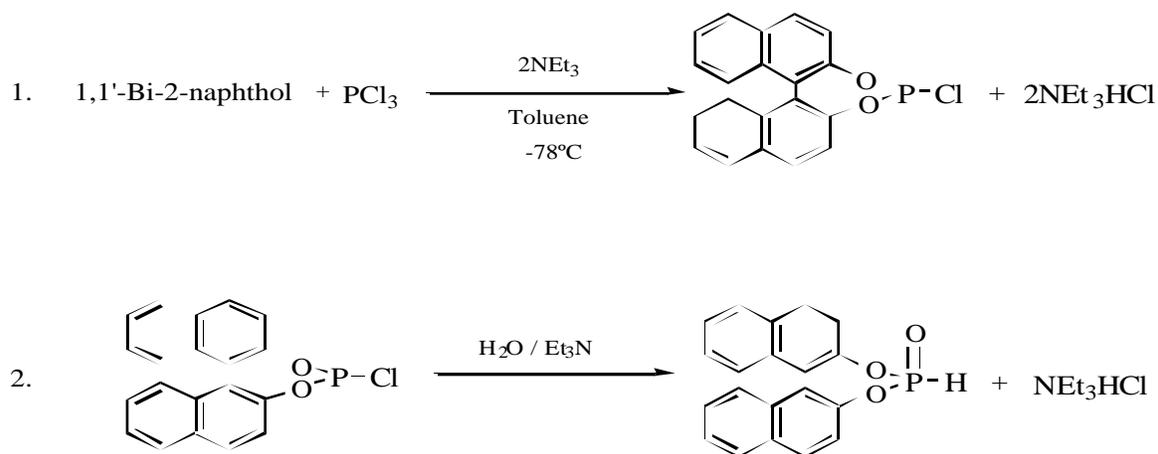
used for this synthesis have made possible the synthetic pathway for the more desired compound, (cyclopentadienyl)tris(rac-binaphthylphosphito-*P*)cobaltate(1-).

3.4 1,1'-BI-2-NAPHTHYL PHOSPHITE

3.4.1 Synthetic Routes

The currently accepted synthesis for \pm 1,1'-bi-2-naphthyl phosphite is the reaction of phosphorous trichloride and triethylamine in the presence of \pm 1,1'-binaphthol to produce (rac-O,O-binaphtholato)PCl. The hydrolysis of (rac-O,O-binaphtholato)PCl in the subsequent step leads to the desired phosphite.⁵⁹ (Scheme 3.3)

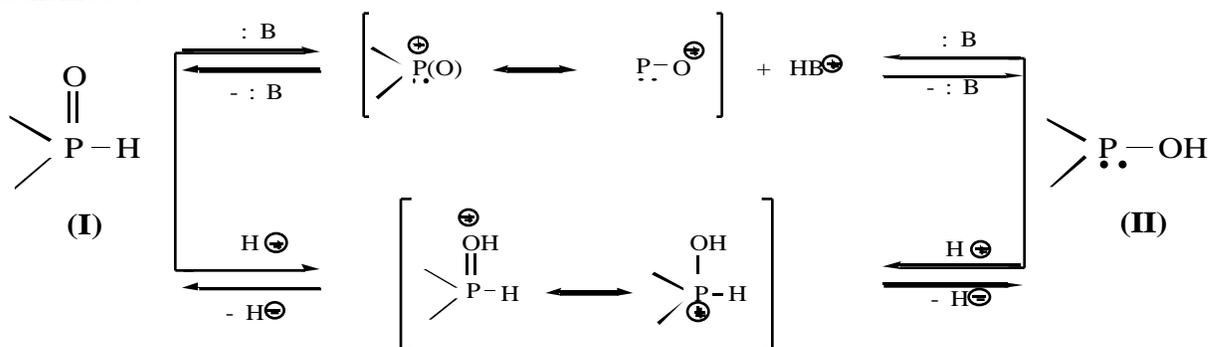
Scheme 3.3:



The literature reports step two of the synthesis as taking only one hour for completion. Experimentally, the same step took five days for 75% completion. The reason for the increased reaction time was due to a tautomeric relation within the phosphite. This problem is not new to organophosphorous chemistry, and has been extensively studied in the case of dialkyl phosphites.⁶³ (Scheme 3.4)

⁶³ E. E. Nifant'ev, *Russ. Chem. Rev.*, 47 (1978) 835

Scheme 3.4:



The tautomerism is catalyzed by acids and bases. At equilibrium they exist almost exclusively in form **I**, however, phosphinylidene compounds containing substituents more electronegative than alkoxy will contain more appreciable concentrations of form **II**.⁶³ In the case of $\pm 1,1'$ -bi-2-naphthyl phosphite the initial form of the phosphite appears to be mostly **II**, however, over time the structure converts to form **I**.

Since the conversion of **II** to **I** is catalyzed by acids, the presence of NEt_3HCl in solution should aid in the conversion. Therefore, instead of filtering the salt before the water addition, like the procedure suggests, it was left in solution to act as a catalyst. The result was a decreased reaction time from 5 days to 20 hours. However, the yield obtained for the reaction was only 53%, whereas the reported literature yield was 73%.⁵⁹

Therefore, the method developed by Page et. al.⁵⁷ for the synthesis of 2,2'-biphenyl phosphite was modified in order to produce the desired $\pm 1,1'$ -bi-2-naphthyl phosphite. The starting material $\pm 1,1'$ -bi-2-naphthol was added to the bis(dimethylamino) phosphonate as a suspension in toluene due to its insolubility in the solvent. This aided in the absorption of the reactant into the solution. Also, instead of the 24 hour reaction time at 90°C which was used for the 2,2'-biphenyl phosphite, the $\pm 1,1'$ -bi-2-naphthyl phosphite required a 48 hour reaction time period at 112°C . The need for longer time is most likely due to the previously mentioned tautomerism. The isolation of the final compound was slightly different from the analog. Instead of completely removing the solvent before drying, the $\pm 1,1'$ -bi-2-naphthyl phosphite was precipitated out of the toluene solution with pentane, then dried under nitrogen. The final yield for this synthesis was 80%, making this the highest yielding synthesis for this compound thus far.

3.4.2 Analytical Data Interpretation

The literature reports $\pm 1,1'$ -bi-2-naphthyl phosphite as having a melting point of $185\text{-}187^\circ\text{C}$.⁵⁸ The experimentally obtained compound exhibited a melting point of $186\text{-}187^\circ\text{C}$, well within the reported range. Spectrally, ^1H NMR and ^{31}P NMR data were available in the literature. Kee et. al.⁵⁸ reported a doublet at 7.5ppm with a $J_{\text{P-H}} = 724\text{Hz}$

and a multiplet at 8.3-7.4ppm for the ^1H NMR, and a singlet at 14.0ppm for the ^{31}P NMR. The ^1H NMR and ^{31}P NMR recorded in this work are within $\pm 0.3\text{ppm}$ of the reported values. Further spectral analysis is presented by a ^{13}C NMR spectrum. The coupling from the phosphorous atom to the carbon atoms can be seen up to four bonds away, after which there is no noticeable coupling.

In summary, the $\pm 1,1'$ -bi-2-naphthyl phosphite was synthesized successfully by a new method that avoided the air-sensitive phosphorous trichloride and allowed for higher yields of product with an overall shorter reaction time. The analytical data presented gives an excellent indication that the correct compound was synthesized.

3.5 RAC-BINAPHTHYL COBALT SANDWICH COMPLEX

3.5.1 Synthetic Routes

The synthetic pathway for bis(cyclopentadienyl)tris(rac-binaphthylphosphito-*P*)cobalt-O, O', O'')cobalt(II) was based on the method developed for the biphenyl version of the sandwich complex. The isolation of the final compound was achieved by filtration due to its insolubility in toluene. The overall yield of the reaction, 79%, was comparable to the yields obtained for the alkoxy analogs.⁴

3.5.2 Analytical Data Interpretation

Similar to the biphenyl version, bis(cyclopentadienyl)tris(rac-binaphthylphosphito-*P*)cobalt-O, O', O'')cobalt(II) is a yellow solid that decomposes above 259°C. Both the ^1H NMR and ^{31}P NMR data are consistent with the structure. However, there is slightly less broadening in the rac-binaphthyl version than was seen in the biphenyl version, indicating that the ring system may have some control over the magnetic moment of the complex.

3.6 SODIUM(CYCLOPENTADIENYL)TRIS(RAC-BINAPHTHYLPHOSPHITO-*P*)COBALTATE(III)

3.6.1 Synthetic Routes

Although the same synthetic pathway for the biphenyl version of the tridentate ligand was used, a slight modification in the isolation step was necessary for the purification of the compound. The addition of methylene chloride to the methanol mixture resulted in low yields, leaving the majority of the ligand still in the methanol solution. Therefore, instead of adding methylene chloride to the methanol mixture, as was done in the biphenyl version, the mixture was permitted to stir continuously for 3 days.

Afterward, the precipitate was filtered and dissolved in a solvent mixture of 10mL CCl₄, 10mL CHCl₃, and 1mL of MeOH. This solvent system dissolved the ligand, but not the unwanted byproduct, Na₃[Co(III)(CN)₆]. The final yield for the ligand was 79%.

3.6.2 Analytical Data Interpretation

The air stable, yellow solid decomposes at a temperature above 364°C, suggesting the extreme stability of this ligand. The spectral analysis is similar to the data collected for the biphenyl version of the ligand. ¹H NMR spectrum shows the cyclopentadienyl singlet at 4.5ppm and the aromatic chemical shift region is from 7.3ppm- 8.1ppm. The phosphorous signal is at a chemical shift of 121ppm, slightly upfield from the biphenyl version's singlet at 122ppm. An interesting comparison of this ligand versus the biphenyl version is in the ¹³C NMR spectrum. The rac-binaphthyl ligand exhibits coupling of the carbon atom by the phosphorous atom, whereas in the biphenyl version there was no coupling seen.

This further supports the idea that the coordination to the cobalt atom by the phosphorous and the increased steric hindrance from the ligand structure causes the ring system to change in its spatial arrangement. In fact, the coupling seen in the rac-binaphthyl ligand displays a larger coupling from the phosphorous than is seen in the free phosphite.

The overall reaction yield for the synthesis of (cyclopentadienyl)tris (rac-binaphthylphosphito-P)cobaltate(1-) from the starting alcohol is ~50%. Since the optically pure +1,1'-bi-2-naphthol is expensive, this method creates a plausible and economical route for the synthesis of the chiral version of this ligand.

3.7 Concluding Remarks

The most difficult and time consuming step of the overall synthesis of the tridentate ligand is the synthesis of the starting phosphites. Although both of the phosphites used have been previously synthesized, the lack of complete characterization available in the literature have made the identification of these compounds challenging. Also, due to the eventual goal of an optically active ligand, the yields obtained in these syntheses should be the highest achievable. The reported yields for ±1,1'-bi-2-naphthyl phosphite were not very desirable and a new synthesis was needed. The modification of the biphenyl phosphite synthesis to make ±1,1'-bi-2-naphthyl phosphite proved to be worthwhile for both time considerations and economical factors achieving a yield of 80%

The synthesis of sodium(cyclopentadienyl)tris(rac-binaphthylphosphito-P)cobaltate(III) has also opened the door to a new type of tridentate oxygen donor ligands. Once the rac-binaphthyl group is changed to the optically active binaphthyl group, it will be possible to obtain chiral ligands with C₃ symmetry. Previously, the chiral version of L⁻ was only obtained by coordinating two different alkoxy groups to the phosphite functionality. Now chiral and non-chiral ligands with chelating groups can be economically and efficiently synthesized by the methods described in this thesis.

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