*Organometallics* **1991**, *10*, 419–423

# Reaction of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ with a Chelating Phosphine Ligand: Generation of Stable 17- and 19-Electron Complexes. Dynamic Equilibrium of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ and $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$

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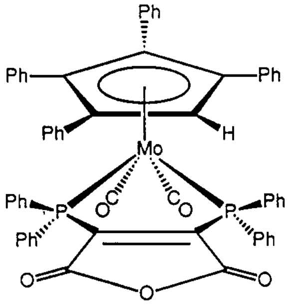
*Received February 1, 1990*

The synthesis of the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex is described. In solution, the dimer is in equilibrium with 2 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ monomers. The equilibrium constant for the dimer–monomer equilibrium, as determined by electronic absorption spectroscopy, is 8.7 (±5.1) × $10^{-5}$ at 23 °C. (A 1 × $10^{-4}$ M solution of the dimer is thus 40% ± 15% dissociated.) $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ reacts with $L_2$ ($L_2$ is the chelating phosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride) to form the 19-electron ("18 + $\delta$") $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ and the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complexes. ($L_2$-P,P′ indicates two P atoms are coordinated, and $L_2$-P indicates one P atom is coordinated.) Variable-temperature electron spin resonance (ESR) showed a dynamic equilibrium between these 19- and 17-electron complexes with lower temperature favoring the 19-electron complex, and higher temperature the 17-electron complex. The $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex has two magnetically equivalent P atoms, and the room-temperature ESR spectrum is a 1:2:1 triplet. This spectrum and its temperature-dependent behavior is compared and contrasted with the spectrum of the analogous $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex. Infrared, ESR, and electronic spectroscopic data are reported for all of the complexes generated in this study.

## Introduction

Ligands with low-energy, conjugated $\pi^*$ orbitals are frequently capable of stabilizing 19-electron organometallic complexes.[1] The stability of 19-electron complexes containing these ligands is attributed to the fact that the unpaired ("19th") electron preferentially occupies the ligand $\pi^*$ orbital rather than a higher-energy metal–ligand antibonding orbital.[1] Nineteen-electron complexes of this type have been dubbed "18 + $\delta$" complexes to emphasize that the unpaired electron is primarily ligand localized.[2] We recently reported the synthesis, characterization, and dynamic ESR properties of the 18 + $\delta$ $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex.[34]



($L_2$ is the chelating phosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride; $L_2$-P,P′ indicates two phosphorus atoms of the chelate are coordinated; $L_2$-P indicates only one phosphorus atom is coordinated.)

The ESR spectrum of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex is temperature dependent because cyclopentadienyl ring rotation is slow on the ESR time scale at room temperature but fast at higher temperatures.[3] Thus, the spectrum is a doublet of doublets at *room temperature* but a 1:2:1 triplet at 185 °C. (The two phosphorus atoms ($I_p = {}^1/_2$) are magnetically inequivalent at room temperature because of the orientation of the $C_5Ph_4H$ ring.[3a] See the picture above.) Crucial to our analysis and interpretation of the dynamic ESR spectra was our observation that the room-temperature spectrum of the related $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex is a 1:2:1 triplet. Note that the $C_5$ ring is completely substituted in this complex so the two phosphorus atoms are magnetically equivalent, even when ring rotation is slow.

The $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex was synthesized by reacting $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ with the $L_2$ ligand:

$$(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6 + 2L_2 \rightarrow 2(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P') + 2CO \quad (1)$$

Other paramagnetic species also form in reaction 1, and in this paper, we report the complete details of the reaction between $(\eta^5\text{-}C_5Ph_5)_2Mo_2((CO)_6$ and $L_2$. In addition, we report on the synthesis and characterization of the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ dimer and its solution equilibrium with two $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ radicals.

## Experimental Section

All operations were performed under a nitrogen atmosphere by using standard Schlenk techniques or a Vacuum Atmospheres Co. glovebox.

**Materials and Supplies.** Benzene and toluene were distilled over sodium metal, and tetrahydrofuran (THF) was distilled from potassium metal. Dichloromaleic anhydride (Aldrich) was used as received. $Ph_2PSiMe_3$ was synthesized as previously described.[6]

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(1) For a review, see: Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215–245.

(2) The term "18 + $\delta$ complex" is used to describe those 19-electron adducts that are essentially 18-electron complexes with reduced ligands.[3] The term 18 + $\delta$ is preferred when the term "19-electron adduct" might lead to confusion about the electronic structure of the adduct. Examples of 18 + $\delta$ complexes are increasingly numerous; see: (a) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504–505. (b) Creber, K. A. M.; Wan, J. K. S. *Trans. Met. Chem.* **1983**, *8*, 253–254. (c) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 2101–2102. (d) Alberti, A., Hudson, A. *J. Organomet. Chem.* **1983**, *241*, 313–319. (e) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144–4151. (f) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442–3448. (g) Kaim, W. *J. Oganomet. Chem.* **1984**, *262*, 171–178. (h) Kaim, W. *Inorg. Chim. Acta* **1981**, *53*, L151–L153. (i) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365–3368. (j) Alegria, A. E.; Lozada, O.; Rivera, H.; Sanchez, J. *J. Organomet. Chem.* **1985**, *281*, 229–236.

(3) (a) Mao, F.; Philbin, C. E.; Weakley, T.; Tyler, D. R. *Organometallics*, in press. (b) Mao, F.; Sur, S. K.; Tyler, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 7627–7628.

(4) Previous work by Fenske[5] and us[3,6] showed that the unpaired electron is localized on the $L_2$ ligand in 18 + $\delta$ complexes containing this ligand.

(5) Fenske, D. *Chem. Ber.* **1979**, *112*, 363–375.

**Table I. Infrared Data**

| complex | $\nu(C\equiv O)$, cm$^{-1}$ | $\nu(C=O)$, cm$^{-1}$ | solvent | ref |
|---|---|---|---|---|
| $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$ | 2010 w, 1953 vs, 1910 s | | THF | 3a |
| $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$ | 2007 s, 1950 vs, 1925 s, 1901 m | | THF | 3a |
| $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ | 2013 m, 1943 s, 1917 s, 1886 m | | Nujol | this work |
| | 2015 m, 1942 vs, 1916 s, 1887 m | | benzene | this work |
| | 2013 w, 1942 vs, 1918 s, 1889 w | | THF | this work |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ | 1996 s, 1907 s, 1897 s | | benzene | this work |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ | 2009 s, 1915 s, 1908 s | | Co matrices at 12 K | 17 |
| $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3(L_2\text{-}P)$ | 2049 s, 1981 s, 1958 s | 1737 m, 1653 s | THF | 3a |
| $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ | 1958 s, 1886 s | 1741 s, 1673 s | THF | 3a |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ | 1960 s, 1885 s | 1742 m, 1672 s | THF | this work |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ | 2013 s, 1939 s | 1796 m, 1721 m | THF | this work |
| $L_2$ | | 1838 m, 1816 w, 1763 s | THF | 3a |

**Instrumentation.** Electronic absorption spectra were recorded on a Beckman DU7 or Perkin-Elmer Lambda 6 spectrophotometer. Infrared spectra were recorded by using a Nicolet 5 DXB FT-IR spectrometer and $CaF_2$ cells (solution) or NaCl plates (Nujol mull). ESR spectra were recorded on a Varian E-line spectrometer and referenced to a solid sample of DPPH (diphenylpicrylhydrazyl).

**Synthesis of 2,3-Bis(diphenylphosphino)maleic Anhydride ($L_2$).** Due to typographical errors, the synthesis of $L_2$ was reported incorrectly in our previous paper.[3b] Here we present the corrected version. Dichloromaleic anhydride (8 g, 0.05 mol) in 160 mL of absolute ethyl ether at 0 °C was added dropwise to $Ph_2PSiMe_3$ (7.5 g, 0.1 mol) over 1 h. A reddish solution and yellow precipitate formed. The mixture was cooled to −80 °C for 20 h, and the precipitate was then filtered under $N_2$ and dried under vacuum for 12 h to remove the $Me_3SiCl$ that had formed. Pure yellow crystals of the product were obtained by recrystallization from $Et_2O$ (93% yield). It is very important to completely remove all of the $Me_3SiCl$ prior to recrystallization of the product; recrystallization of a product mixture containing $Me_3SiCl$ turned the product into an unidentified black substance.

**Synthesis of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6\cdot 3H_2O$.** The standard method developed by Birdwhistle et al.[7] for the synthesis of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ was not successful for the synthesis of this dimer. Therefore, we modified the method as follows. Pentaphenylcyclopentadiene[8] (860 mg, 1.92 mmol) and 75 mg (1.9 mmol) of potassium were mixed in 30 mL of diglyme. The mixture was refluxed for $^1/_2$ h and then cooled to room temperature, resulting in a yellow suspension. $Mo(CO)_6$ powder (1.0 g, 3.8 mmol) was degassed and added to the suspension. The mixture was then refluxed for another 2 h, during which time the color of the solution changed from red brown to dark brown. $Fe(NO_3)_3\cdot 9H_2O$ (3.0 g, 7.4 mmol), in a mixture of 2 mL of glacial acetic acid and 20 mL of $H_2O$, was added dropwise to the dark brown solution in an ice bath. A purple precipitate of the dimer formed immediately. The mixture was stirred at 0 °C for another 2 h and then filtered at 0 °C. The precipitate was washed with ice cold water, ether, and pentane and then dried under high vacuum. Yield: 1.1 g, 90%. Anal. Calcd for $C_{76}H_{50}Mo_2O\cdot 3H_2O_6$: C, 69.94; H, 4.33. Found: C, 69.83; H, 4.55. (Attempts to remove the water by drying the sample under high vacuum for periods of up to a week were unsuccessful. Three elemental analyses on three samples prepared independently gave the same results as reported here. The lattice water shows up as a peak at 3400 cm$^{-1}$ (br) in the infrared spectrum of the product.) The dimer was identified by comparison of its IR spectrum with that of the analogous compound $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$.[3] A clean IR analysis of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ could be obtained in a Nujol mull (Table I). However, solution spectra of the dimer always showed the presence of the radical monomer $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ (1966, 1907, and 1897 cm$^{-1}$ in benzene). The dimer is extremely air-sensitive in solution and moderately air-sensitive in the solid state. Once the reaction of the dimer formation above is completed, solutions containing the dimer should be filtered immediately in order to avoid decomposition, especially when both diglyme and water are present. The $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex is only slightly soluble ($\leq 10^{-4}$ M) in common organic solvents, and for that reason, we found it impossible to recrystallize in significant amounts. As synthesized above, the dimer is pure by infrared spectroscopy, but ESR spectroscopy showed the presence of trace amounts of uncoordinated $C_5Ph_5^\bullet$ radical (see below).

The ESR spectrum of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ monomer cannot be observed at room temperature. (Note also that no room-temperature ESR spectrum is observed for the analogous $CpCr(CO)_3$ complex or for $V(CO)_6$.[9]) However, solutions of the dimer (in benzene, toluene, THF, or cyclohexane) showed a well-resolved 33-line ESR signal ($g = 2.0031 \pm 0.0002$) at room temperature. The spectrum of the dimer in KBr powder also showed a broad ESR signal at room temperature. The ESR signal in both cases is attributed to the $C_5Ph_5^\bullet$ free radical, generated in the preparation of the dimer.[10]

**Determination of the Equilibrium Constant and Extinction Coefficient.** Based on the equilibrium in eq 2, the following equation can be derived:

$$A = \epsilon\{C - [K_{eq} + (K_{eq}^2 + 4K_{eq}C)^{1/2}]/8\}$$

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(6) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130–134.

(7) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

(8) Ziegler, K.; Schnell, B. *Justus* Liebigs *Ann. Chem.* **1925**, *445*, 266–281.

(9) (a) Krusic, P. J.; McLain, Morton, J. R.; Preston, K. F.; Page, Y. L. *J. Magn. Reson.* **1987**, *74*, 72–81. (b) Morton, J. R.; Preston, K. F.; Cooley, N. A.; Baird, M. C.; Krusic, P. J.; McLain, S. J. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83* (12), 3535–3540. (c) Pratt, D. W.; Myers, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 6470–6472. (d) Rubinson, K. A. *J. Am. Chem. Soc.* **1976**, *98*, 5188–5191. (e) Ammeter, J. H.; Zoller, L.; Bachmann, J.; Balzer, P.; Gap, E.; Bucher, R.; Deiss, E. *Helv. Chim. Acta* **1981**, *64*, 1063–1082. (f) Boyer, P.; Lepage, L.; Morton, J. R.; Preston, K. F.; Vuolle, M. *Can. J. Spectrosc.* **1981**, *26*, 181–185. (g) Bratt, S. W.; Kassyk, A.; Perutz, R. N.; Symons, M. C. R. *J. Am. Chem. Soc.* **1982**, *104*, 490–494. (h) Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2074–2076.

(10) We sugest that when $C_5Ph_5^-$ is reacted with $Mo(CO)_6$ to form $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3^-$, a small amount of unreacted $C_5Ph_5^-$ is oxidized to $C_5Ph_5^\bullet$ by $Fe(NO_3)_3$ in the subsequent step. To check this hypothesis, we synthesized the $C_5Ph_5^\bullet$ radical from $K^+[C_5Ph_5]^-$ by electrochemical oxidation[11a] and by a chemical oxidation with $Fe(NO_3)_3$.[11b] The ESR spectrum of the solution containing $C_5Ph_5^\bullet$ was identical with the spectrum of the solutions containing $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$. In a related experiment, we showed that the 17-electron $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3$ radical (in equilibrium with the $(\eta^5\text{-}C_5Ph_5)_2Cr_2(CO)_6$ dimer), obtained via electrochemical oxidation of $K^+[(\eta^5\text{-}C_5Ph_5)Cr(CO)_3]^-$, also showed the same ESR spectrum. Again, we attribute the spectrum to the $C_5Ph_5^\bullet$ radical.[13]

(11) Synthesis of $C_5Ph_5^\bullet$ via: (a) **Electrochemical oxidation.** The bulk electrolysis was carried out by using a Princeton Applied Research Electrochemistry Station. A Pt gauze basket, a Pt gauze strip, and a silver wire were used as the working, auxiliary, and reference electrodes, respectively. $K^+[C_5Ph_5]^-$ (10 mg, $2.1 \times 10^{-2}$ mmol) in 50 mL of 0.1 M TBAP/THF was oxidized at −0.31 V vs SCE. After the electrolysis, the color of the solution changed from red orange to violet, the color of $C_5Ph_5^\bullet$ in solution.[8] The solution was used directly for ESR without the separation of the electrolyte. The ESR spectrum showed 33 lines as reported by Reitz.[12] (b) **Chemical oxidation.** Ziegler and Schnell obtained the radical via the reaction of $C_5Ph_5Br$ and Ag.[8] We synthesized the radical under the same conditions as used in the synthesis of the dimer. $K^+[C_5Ph_5]^-$ (50 mg, 0.1 mmol) was dissolved in 10 mL of diglyme and cooled in an ice bath. With stirring, $Fe(NO_3)_3\cdot H_2O$ (40 mg, 0.1 mmol) in 1 mL of $H_2O$ was added to the above solution at 0 °C. The ice bath was removed, and degassed benzene (30 mL) was immediately added to the mixture. After stirring or shaking, the top benzene layer turned violet. The benzene solution was separated from the aqueous layer and used for the ESR experiments.

(12) Reitz, D. C. *J. Chem. Phys.* **1961**, *34*, 701–702.

(13) Mao, F.; Tyler, D. R. Unpublished results.

**Table II. Electronic Spectra of Various Molybdenum Dimers**[a,19]

| complex | $\lambda_{\sigma\rightarrow\sigma^*}$, nm | $\lambda_{d\pi\rightarrow\sigma^*}$, nm |
|---|---|---|
| $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$ | 394 | 510 |
| $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_6$ | 410 | 496 |
| $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$ | 433 | 524 |
| $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ | 443 | 552 |

[a] All measurements were made in toluene at 25 °C.

where $A$ is the absorbance of the dimer at 562 nm, $\epsilon$ is the extinction coefficient of the dimer at 562 nm,[14] $C$ is the initial concentration of the dimer, and $K_{eq}$ is the equilibrium constant. To determine $K_{eq}$, the absorbance of a series of dimer solutions was measured at $\lambda$ = 562 nm. The absorbances at different concentrations were fit to the equation above by using a VMS/SAS-ETS computer program on a VAX-8800 computer.[15] The iterative program uses the SYSLIN procedure, and it combines an iterated ordinary least-squares (ITOLS) estimation method with the Gauss–Newton minimization method to perform the iterative calculations until convergence is achieved.

## Results and Discussion

**Dimer–Monomer Equilibrium.** Infrared spectroscopy showed that the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex was in equilibrium with the 17-electron monomer in solution:

$$(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6 \overset{K_{eq}}{\rightleftharpoons} 2(\eta^5\text{-}C_5Ph_5)Mo(CO)_3 \tag{2}$$

The following evidence for the equilibrium is presented for the case of benzene solvent, but similar results were obtained in toluene. A solution of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ in benzene showed bands at 2015 (m), 1942 (vs), 1916 (s), and 1887 (m) cm$^{-1}$, attributed to the dimer, and additional bands at 1996 (s), 1907 (s), and 1897 (s) cm$^{-1}$.[16] Assignment of the latter set of bands to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ radical is suggested by comparison to the frequencies reported for the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radical, generated in CO matrices, at 12 K (2009, 1915, 1908 cm$^{-1}$).[17] Consistent with the solution equilibrium in eq 2, the bands we attribute to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ radical were not seen in the solid-state infrared spectrum of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$. The infrared data are summarized in Table I. Included in the table are infrared data for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$, $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$, and other related dimer complexes. Note the close similarity of the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ spectrum to the spectra of these complexes.

The electronic spectrum of the dimer is typical for a metal–metal bonded complex.[18] There is a band maximum at 443 nm (toluene) that is assigned to the $\sigma \rightarrow \sigma^*$ transition and a weaker band at 562 nm (toluene) assigned to a $d\pi \rightarrow \sigma^*$ transition. The electronic spectra (and assignments) of related $Cp_2Mo_2(CO)_6$ complexes are reported in Table II for comparison to the spectrum of the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex.

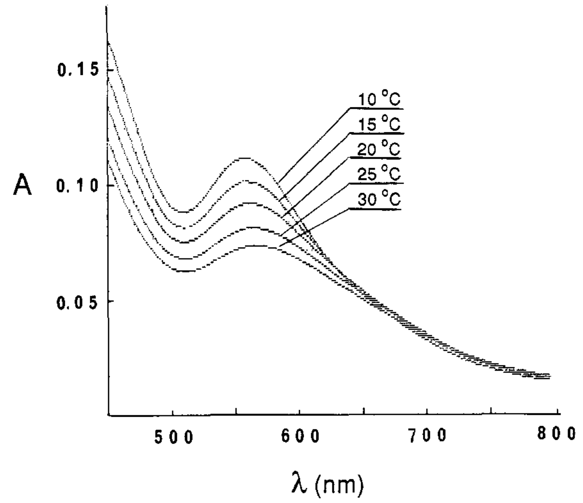

**Figure 1.** Electronic spectrum of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ ($1 \times 10^{-4}$ M) in toluene at various temperatures. The spectra were corrected for solvent volume changes with temperature.

A dilute solution of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ (in toluene) is brownish yellow at room temperature and purple at −30 °C. Consistent with the dimer–monomer equilibrium in eq 2, we found that the intensities of the dimer $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ absorption bands decreased (reversibly) as the temperature of the solution increased (Figure 1).[14,20] As expected, higher temperatures favor dissociation of the Mo–Mo bond. (An isosbestic point is maintained at 625 nm (Figure 1) at temperatures below 20 °C. As the temperature is increased, however, the isosbestic point shifts to lower energy. We attribute the shift of the isosbestic point to a temperature-dependent equilibrium between the anti and gauche rotational isomers.[21])

The absorbance data at $\lambda$ = 562 nm (25 °C) for different concentrations of starting material were used to calculate the equilibrium constant for eq 2. The following values of the dimer extinction coefficient and equilibrium constant at 25 °C were obtained: $\epsilon_{562} = 1640 \pm 240$; $K_{eq} = 8.7\ (\pm 5.1) \times 10^{-5}$. Thus, for a typical concentration of the dimer, say $1 \times 10^{-4}$ M, the dimer is 40% ± 15% dissociated. [For comparison, the $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ complex is about 10% dissociated at 25 °C,[21] and $(\eta^5\text{-}C_5Me_5)Cr_2(CO)_6$ is "extensively dissociated".[9h]]

Because there is no significant monomer–dimer equilibrium for the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ dimer at room temperature in solution, the equilibrium in the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex is logically attributed to the steric bulkiness of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ monomers and the resulting weak Mo–Mo bond. A similar explanation was proposed to account for the more extensive dissociation of the $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_6$ complex compared to $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$.[9h]

**Reaction of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ with $L_2$.** The thermal reaction of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ ($1 \times 10^{-4}$ M) with $L_2$ ($5 \times 10^{-3}$ M) in THF was monitored by infrared and ESR spectroscopy. Infrared spectroscopy showed the disappearance of the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ bands at 1942, 1918, and 1889 cm$^{-1}$ and the appearence of new bands in the $\nu(C{\equiv}O)$ region at 2013, 1960, 1939, and 1885 cm$^{-1}$. The bands at 1960 and 1885 cm$^{-1}$ are assigned to the $(\eta^5\text{-}$

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[14] The monomer is yellow and does not absorb at 562 nm.

[15] *SAT/ETS User's Guide*, Version 5; SAS Institute Inc.: Cary, NC, 1988; p 505.

[16] As expected, the infrared spectrum of the monomer is most easily seen in dilute solutions. As the concentraton of the solution is increased, several of the monomer peaks are obscured by the overlapping, more intense, dimer peaks.

[17] Mahmoud, K. A.; Rest, A. J. *J. Am. Chem. Soc.* **1983**, *246*, C37–C41.

[18] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187–218.

[19] In contrast to $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$ and $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_6$, both $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$ and $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ showed two bands in the $\sigma \rightarrow \sigma^*$ transition region [$(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$: 399 and 433 nm; $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$: 371 and 433 nm]. We tentatively assign the lower energy band to the $\sigma \rightarrow \sigma^*$ transition for the following reason. As the dimer becomes more stereically bulky, the Mo–Mo bond becomes weaker, and thus, the energy of the $\sigma \rightarrow \sigma^*$ transition will decrease. Note in Table II that the $d\pi \rightarrow \sigma^*$ transitions also decrease in energy as the dimer becomes more sterically bulky.

[20] By analogy to the $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ radical, the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ radical is not expected to absorb in the visible region. See ref 16 and: Hughey, J. L., IV; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440–4441.

[21] McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643–644.

**Table III. ESR Data**

| complex | formal no. of valence electrons | $a_{P_1}$ | $a_{P_2}$ | $a_{Mo}$ | $g^a$ |
|---|---|---|---|---|---|
| $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3(L_2\text{-}P)^b$ | 19 | 2.45 | 9.02 | 0.52 | 2.004 |
| $(\eta^5\text{-}C_5H_4Me)Mo(CO)_2(L_2\text{-}P,P')^b$ | 19 | 8.26 | 8.26 | 0.68 | 2.005 |
| $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)^c$ | 19 | 3.46 | 8.86 | not obsd | 2.004 |
| $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')^d$ | 19 | 9.06 | 10.07 | 0.85 | 2.006 |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')^e$ | 19 | 10.38 | 10.38 | 0.75 | 2.006 |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)^e$ | 17 | 2.30 | 5.61 | 0.49 | 2.003 |
| $(\eta^5\text{-}C_5Ph_5)Mo(CO)(L_2\text{-}P,P')^e$ | 17 | 12.01 | 12.01 | too weak to observe | 2.004 |

[a] ±0.001. [b] $CH_2Cl_2$ at 25 °C. [c] THF, at -20 °C.[2a] [d] -14 °C, in THF. [e] THF, at 25 °C.

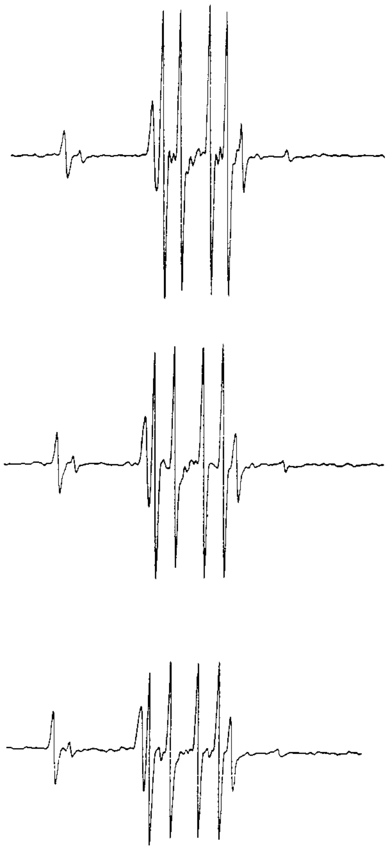
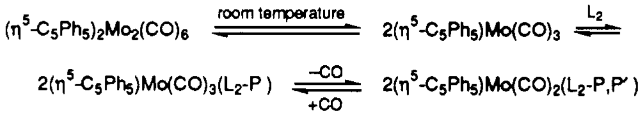


**Figure 2.** ESR spectra of a THF solution containing $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ and $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ at various temperatures: (a) 45 °C; (b) 23 °C; (c) 11 °C. These species were generated by reaction of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ ($1 \times 10^{-4}$ M) with $L_2$ ($5 \times 10^{-3}$ M).

**Scheme I**



$C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex by comparison to the spectrum of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex (1958 and 1886 cm$^{-1}$; Table I). Recall that the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex is synthesized by reaction of photogenerated $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3$ radicals with $L_2$.[3] Because the $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ complex is in equilibrium with $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ radicals in solution, it is reasonable that an analogous reaction to form $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ should occur when $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ is reacted with $L_2$. The product giving rise to the bands at 2013 and 1939 cm$^{-1}$ could only be identified after consideration of its ESR spectrum. The ESR results are discussed next.

Two major sets of signals were observed in the ESR spectrum of the solution from the reaction of $(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$ with $L_2$: a 1:2:1 triplet and a 1:1:1:1 quartet (Figure 2a). The triplet ESR signal is assigned to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex by consideration of the likely structure of this complex. Once again, it is convenient to refer to the related $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex. This complex has a "four-legged piano stool" structure, as shown in the picture in the Introduction. Note that the two phosphorus atoms in this complex are magnetically inequivalent because of the orientation of the $C_5Ph_4H$ ring. It is likely that the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex has the same structure as its $C_5Ph_4H$ analogue. In the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex, however, the two phosphorus atoms will be magnetically equivalent because the Cp ring is completely substituted. Consequently, the ESR spectrum is a 1:2:1 triplet, as shown in Figure 2a. (Recall that the unpaired electron in complexes containing the $L_2$ ligand is localized on the $L_2$ ligand.[3,5,6])

As Figure 2 shows, the peak heights of the triplet are no longer in the ratio 1:2:1 when the temperature of the sample is lowered from 45 to 23 °C or below (Figure 2b,c); in particular, the middle line of the triplet becomes increasingly broad and decreases in height as the temperature is lowered. We attribute this feature to the magnetic inequivalence of the two phosphorus atoms, caused by slower Cp ring rotation, at the lower temperatures. (Although the Cp ring in $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P)$ is symmetrically substituted, there are conformations in which the two phosphorus atoms are magnetically inequivalent.) Consequently, the triplet signal begins to split into a quartet signal.

The structural difference between $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2\text{-}(L_2\text{-}P,P')$ and $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ is reflected by the dynamic ESR spectra of the two complexes: the two phosphorus atoms of the former complex become equivalent at a much lower temperature (i.e., 45 °C, Figure 2a) than those of the latter complex (185 °C).[3b]

Several complexes might give rise to the four-line ESR spectrum in Figure 2a. One possibility is the $(\eta^5\text{-}C_5Ph_5)\text{-}Mo(CO)_3(L_2\text{-}P)$ complex, formed prior to $(\eta^5\text{-}C_5Ph_5)Mo\text{-}(CO)_2(L_2\text{-}P,P')$ in the reaction of $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3$ with $L_2$ (Scheme I). The phosphorus atoms are inequivalent in the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ molecule, and a doublet of doublets pattern is therefore expected. Previous work of ours with the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)$ complex, however, suggests that the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex would not be stable at room temperature.[3a] We generated $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)$ at -20 °C from $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$ and $L_2$ and showed that, even at this temperature, the molecule converted quickly to the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex. At room temperature, the conversion was so fast that $(\eta^5\text{-}C_5Ph_4H)\text{-}Mo(CO)_3(L_2\text{-}P)$ was not observed by infrared or ESR spectroscopy in the reaction of $(\eta^5\text{-}C_5Ph_4H)_2Mo_2(CO)_6$ with $L_2$. The fast conversion of $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)$ to $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ was attributed to steric crowding in the complex.[3a] Dissociative substitution reactions (as the substitution reactions of 19-electron complexes are known to be[6]) are facilitated by increased steric crowding.[22] The $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex is even more sterically crowded than its $C_5Ph_4H$ analogue, and the reaction to give $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ should therefore be even more facile. Hence, it is unlikely that the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex will be long-lived enough to be spectroscopically observable, and therefore, the quartet ESR spectrum cannot be assigned to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex.

We suggest assignment of the quartet spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex. This species has two inequivalent phosphorus atoms, and therefore, a quartet spectrum is predicted. The variable-temperature ESR spectra in Figure 2, which show a reversible conversion between the triplet and quartet signals, are consistent with this proposed assignment. The conversion between the two was cycled numerous times by raising and lowering the temperature, and the conversion is completely reversible. Assignment of the quartet spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex is logical because of the simple equilibrium that can be written between the two species:

$$\underset{19e^-}{(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')} \overset{K_{eq}}{\rightleftharpoons} \underset{17e^-}{(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)} \quad (3)$$

Note that the temperature dependence of the proposed equilibrium is correct: higher temperature will favor the dissociation of the Mo–P bond, giving rise to more of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ complex (the quartet).[23] Assignment of the infrared bands at 2013 and 1939 $cm^{-1}$ to this 17-electron species is suggested.

The behavior of the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex in solution is different from that of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ complex. We found no evidence for dissociation of a Mo-P bond in the latter complex.[3] The lack of dissociation is probably attributable to the fact that the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$ molecule is less sterically crowded than the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ molecule.

The ESR data lend further support to the proposed assignment of the 4-line spectrum to the 17-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ species rather than to the 19-electrn $(\eta^5\text{-}C_5Ph_5)Mo(CO)_3(L_2\text{-}P)$ complex. The phosphorus coupling constants of this latter complex would be similar to the coupling constants of the related 19-electron $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_3(L_2\text{-}P)$ and $(\eta^5\text{-}C_5H_4Me)Mo(CO)_3(L_2\text{-}P)$ complexes. Note, however, that while the $a_{P_2}$ values of these two 19-electron complexes are similar to each other, they are quite different from the $a_{P_2}$ value of the complex we assign as $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P)$ (Table III).

**Acknowledgment** is made to the National Science Foundation for support of this research. D.R.T. acknowledges the Alfred P. Sloan Foundation for a fellowship.

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(23) Also observed in Figure 2 is a weak 1:2:1 triplet. We assign this weak triplet to the $(\eta^5\text{-}C_5Ph_5)Mo(CO)(L_2\text{-}P,P')$ 17-electron radical, formed by CO loss from the $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2(L_2\text{-}P,P')$ complex.

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# Synthesis and Chemistry of Novel 2,2′-Binaphthyl-Substituted Organotin Lewis Acids

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*Received June 7, 1990*

The synthesis and chemistry of novel Lewis acids containing neutral tin-centered Lewis acidic groups at the 2- and 2′-positions of 1,1′-binaphthyl are described. (±)-2,2′-Dibromo-1,1′-binaphthyl (**3**) was converted to the dilithio derivative, which was treated with trimethyltin chloride to yield 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl (**4**) in excellent yield. Compound **4** then underwent highly selective methyl–Sn cleavage in the redistribution reactions with methyltin trichloride and tin tetrachloride to afford 2,2′-bis(monochlorodimethylstannyl)- and 2,2′-bis(dichloromethylstannyl)-1,1′-binaphthyl, **2a** and **2b**, respectively. The chlorotins were then converted into the organotin triflates, **2c** and **2d**, by metathetic reactions with silver triflate. Interaction of the bis(dichlorotin) **2b** and DMSO afforded a mono-DMSO (**12**) whose X-ray crystal structure revealed that coordination of DMSO occurred to one tin center and a chloride ligand from this tin had bridging interaction with the other tin moiety. An estimation of the equilibrium constant for the formation of **12** was obtained by $^{119}Sn$ NMR spectroscopy.

## Introduction

Chiral ligands containing the 2,2′-disubstituted binaphthyl group have achieved remarkable success in the areas of chiral recognition of host molecules[1-3] and in certain asymmetric syntheses, such as the rhodium-catalyzed hydrogenation of aminoacrylic acid derivatives[4,5] and the alkylation and arylation of aldehydes.[6] On the other hand, very little is known about Lewis acids containing the 1,1′-binaphthyl group,[7] and we are not aware of any report of a Lewis acid, chiral or achiral, in which the Lewis acidic center is *directly* attached to the 1,1′-binaphthyl group in

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