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Dynamic ESR Study of the 19-Electron (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$ Complex (L_2 = 2,3-Bis(diphenylphosphino)maleic Anhydride). Measurement of the Barrier to Ring Rotation

Fei Mao, Sandip K. Sur, and David R. Tyler*

Department of Chemistry, University of Oregon
Eugene, Oregon 97403

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Fluxional processes in transition-metal organometallic complexes are typically studied by NMR spectroscopy.[1] Stable paramagnetic organometallic complexes are becoming increasingly common,[2] however, and NMR methods cannot, in general, be used for studies of these molecules. ESR spectroscopy has been used to study stereochemical nonrigidity in organic radicals,[3] but there are a few instances of it being used to study fluxional behavior in paramagnetic organometallic complexes.[4] In this communication we report the results of a variable-temperature ESR study of the 19-electron[5] (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$ radical complex (L_2 = the chelating phosphine ligand 2,3-bis(diphenylphosphino)maleic anhydride).[7] From an analysis of the spectra, we were able to determine the activation parameters for rotation of the C_5Ph_4H ring about the bonding axis.

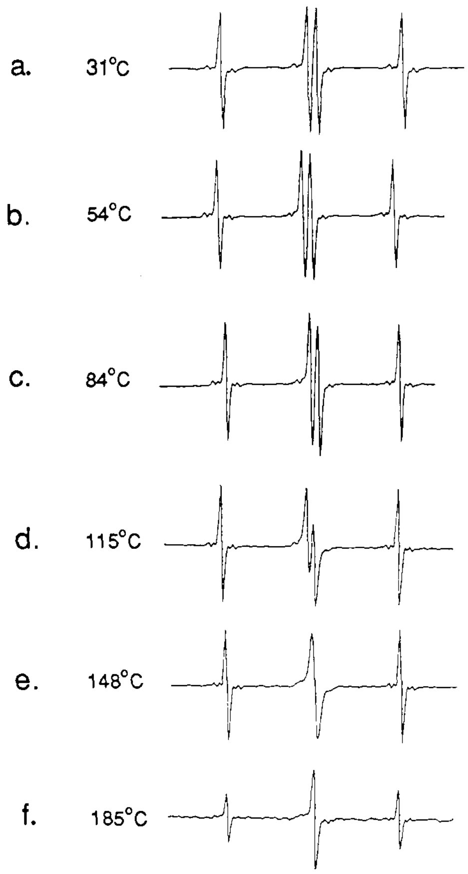

Figure 1. ESR spectra of (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$ (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride) in *o*-dichlorobenzene at various temperatures.

Figure 1 shows the ESR spectrum[8] of the (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$ complex in *o*-dichlorobenzene at various temperatures. At 31 °C (Figure 1a) the two phosphorus atoms are magnetically inequivalent because the spectrum shows four well-resolved lines ($g_{iso} = 2.0058$; $a_{P_1} = 9.01$ G, $a_{P_2} = 9.94$ G). As the temperature increased, the two middle lines began to overlap (Figure 1b,c,d) and eventually (at 148 °C) broadened into a single line (Figure 1e). When the temperature was increased further, this broad middle line began to sharpen and eventually the spectrum became a 1:2:1 triplet ($a_P = 8.92$ G),[9] indicative of magnetically equivalent

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(7) Synthesis of (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$. [(η^5-C_5Ph_4H)Mo(CO)$_3$]$_2$ (1.0 × 10^2 mg; 9.1 × 10^{-2} mmol) and L_2 (85 mg; 1.8 × 10^{-1} mmol) were added to 30 mL of THF. The solution was stirred and irradiated ($\lambda > 520$ nm; high pressure Hg arc lamp from the Oriel Corp.) for ~24 h. (The undissolved [(η^5-C_5Ph_4H)Mo(CO)$_3$]$_2$ did not affect the reaction because it dissolved as the reaction proceeded.) During the irradiation, a stream of N_2 was passed through the reaction vessel so that any CO formed in the reaction was swept out. As the reaction proceeded, the color of the solution turned from red to purple and eventually to green. The green solution was then concentrated to about 10 mL by pumping off the solvent, followed by the addition of pentane or hexane to precipitate the green product (η^5-C_5Ph_4H)Mo(CO)$_2$L$_2$; yield: 75%. The product was recrystallized from THF/hexane. ν(CO) (THF) 1958 (s), 1887 (s), 1741 (s), 1673 (s). Anal. Calcd for $C_{59}H_{41}MoO_5P_2 \cdot C_4H_8O$: C, 71.39; H, 4.66; P, 5.84. Found: C, 71.29; H, 4.38; P, 5.89.

(8) All ESR spectra were measured on a Varian E-109 spectrometer operating at X-band frequency with 100 kHz magnetic field modulation and equipped with Varian E-272B field/frequency lock assembly. The temperature at the sample was controlled by a Varian E-4557-9 variable-temperature accessory, and DPPH was used as *g*-marker and for magnetic field calibration.

(9) Ideally, the ^{31}P coupling constant in the fast-exchange limit (8.92 G) should be the average of the two coupling constants in the slow-exchange limit (9.01 and 9.94 G). We attribute the nonideal behavior observed with this molecule to a decrease in the electron-withdrawing ability of the η^5-C_5Ph_4H ligand as the temperature is increased. We suggest that, as the temperature is increased, the electron-withdrawing ability decreases because rapid dynamic rotation of the phenyl rings destroys the extensive conjugation in the ligand. The decreased electron-withdrawing ability of the η^5-C_5Ph_4H ligand will polarize the unpaired electron toward the oxygen atoms of the L_2 ligand. Consequently, there will be less unpaired electron spin density on the two phosphorus atoms at higher temperature, and the ^{31}P coupling constants will be smaller than at lower temperatures. (The $^{95,97}Mo$ coupling constant should also decrease with increasing temperature. However, this coupling constant is so small that we were unable to measure a decrease within experimental error; $a_{Mo,-14°C} = 0.85 \pm 0.02$ G; $a_{Mo,185°C} = 0.81 \pm 0.02$ G.) In support of this explanation, we note that our previous study of the 19-electron Co(CO)$_3$L$_2$ complex and its substituted derivatives (Co(CO)$_2$L′L$_2$) showed that the phosphorus coupling constants decreased as the electron-donating ability of the substituting ligands increased.[6b] In addition, NMR spectroscopic results on diamagnetic complexes containing the η^5-C_5Ph_4H ligand are consistent with the proposal that phenyl ring rotation increases with increasing temperature. Thus, Castellani and Trogler[10] showed that the proton signal in the η^5-C_5Ph_4H ligand shifted upfield as the temperature increased. The upfield shift was attributed to phenyl ring rotation; the rotation caused the loss of deshielding from the ring currents of adjacent coplanar phenyl rings.

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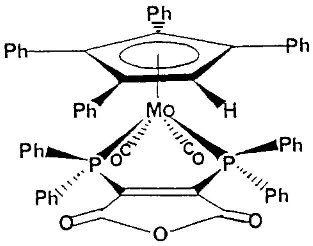
phosphorus atoms (185 °C, Figure 1f). Upon cooling, the spectral changes reversed.[11]

A crystal structure of the complex showed that it has a "four-legged piano stool" structure as shown schematically below.[12]



Because the C_5Ph_4H ring is unsymmetrically substituted, the phosphorus atoms are inequivalent, as shown. Rotation of the ring will "exchange" the phosphorus atoms, and fast rotation of the ring will make the two phosphorus atoms magnetically equivalent. Therefore, we attribute the dynamic ESR spectrum to rotation of the C_5Ph_4H ring. By approximating the effect of the ring rotation as a "two-site exchange" case,[13] we were able to calculate the rate constants for the ring rotation. (Table I in the Supplementary Material lists the rate constants at various temperatures.) A plot of $\ln(k/T)$ vs $1/T$ yielded the following activation parameters: $\Delta H^{\ddagger} = 2.2 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22.9 \pm 0.3$ cal K^{-1} mol^{-1}.

To confirm our assumption that ring rotation caused the dynamic ESR spectrum of the $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ complex, we synthesized the 19-electron $(\eta^5\text{-}C_5Ph_5)Mo(CO)_2L_2$ complex (note the symmetrically substituted C_5 ring).[14] The ESR spectrum of this complex was a 1:2:1 triplet, consistent with a structure in which the two phosphorus atoms are magnetically equivalent because the ring is symmetrically substituted.

The rotation of cyclopentadienyl and other rings in organometallic complexes has been widely reported.[15] In general, the energy barrier to ring rotation is very small. That barrier which does exist is generally attributed to intermolecular forces. In contrast, the activation barrier observed for C_5Ph_4H ring rotation in $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2L_2$ is largely due to unfavorable intramolecular steric interactions. Molecular models of the complex showed that the major barrier comes from the interaction between the phenyl rings on the C_5 ring and the phenyl rings bonded to the phosphorus atoms. For the C_5 ring to rotate freely, the phenyl groups on the C_5 ring and on the phosphorus atoms must rotate cooperatively in a "gearing" fashion.[16] Such a dynamic process would require a transition state of highly organized structure, resulting in a large negative activation entropy. The molecular models also showed that the alternative phosphorus-exchange pathway involving a trigonal-bipyramidal transition state was unlikely because of unfavorable steric interactions between the phenyl groups on the C_5 ring and the phenyl groups on the phosphorus atoms. The large negative activation entropy can also rule out a phosphorus-exchange mechanism that takes place via the dissociation of one end of the chelate ligand; this type of dissociative mechanism would result in a positive, rather than a negative, activation entropy.

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Supplementary Material Available: A listing of the calculated rate constants at various temperatures, a table of coupling constants at various temperatures, and a plot of ln (k/T) vs $1/T$ (3 pages). Ordering information is given on any current masthead page.

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Conversion of Epoxides to Rhodium Enolates: Direct Evidence for a Mechanism Involving Initial C–H Activation

Jianxin Wu and Robert G. Bergman*

Department of Chemistry, University of California and
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

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We wish to report the reaction of a low-valent metal complex with ethylene oxide that is phenomenologically related to metal-induced oxirane reactions reported earlier.[1-10] However, in the present case direct detection of an intermediate demonstrates that the reaction takes place by initial C–H activation, rather than by attack at a ring C–O bond, leading to a metalated oxirane. In addition, we have found that conversion of the metalated intermediate to the final reaction product, a C-bond rhodium enolate, involves predominant 1,2-rearrangement of hydrogen rather than rhodium.

In analogy to the photochemical reaction of $Cp^*(L)RhH_2$ (**1**, $Cp^* = (\eta^5\text{-}C_5Me_5)$; L = PMe_3) with alkanes,[11] irradiation of **1** in ethylene oxide at −60 °C also leads to products too sensitive to survive warming to 25 °C, and these materials have therefore been characterized by low-temperature spectroscopy. Thus, when **1** was irradiated for 3 h in excess ethylene oxide (**2a**) in a sealed NMR tube held at temperatures below −60 °C, and the tube transferred into a spectrometer probe precooled to this temperature, we observed the clean formation of the two disastereomeric (both the rhodium center and α-carbon atom are stereocenters) metalated epoxides $Cp^*(L)Rh(H)(CHCH_2O)$, **3a**, in over 95%

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