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PHOSPHINE SUBSTITUTION IN $\eta^5$-CYCLOPENTADIENYL-BIS-TRIPHENYLPHOSPHINECOBALT(I): EVIDENCE FOR A DISSOCIATIVE MECHANISM

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Abstract: The substitution of trimethylphosphine for triphenylphosphine in $\eta^5$-cyclopentadienyl-bis-triphenylphosphinecobalt(I), 1, to form $\eta^5$-cyclopentadienyltrimethylphosphinetriphenylphosphinecobalt(I) was studied at -60°C in an NMR spectrometer. Kinetic measurements show the process to be first order in 1 and zero order in PMe$_3$; added PPh$_3$ strongly inhibits the reaction rate. This information indicates the reaction proceeds by rapid reversible phosphine dissociation through the unsaturated CpCo(PPh$_3$) intermediate. The rate for generation of that intermediate, $k_1$, is $1.15 \times 10^{-3}$ sec$^{-1}$ while the ratio of rate constants $k_2$ (for conversion of intermediate to products) to $k_1$ (return to starting materials) is 4 at -60°C. Possible structures for CpCo(L) are discussed in light of recent indications that the linear structure has an open-shell electronic configuration.
Introduction

It has been known for almost 20 years that rapid CO exchange in CpCo(CO)₂ and CpRh(CO)₂ occurs by an associative (SN₂) mechanism¹,² rather than by dissociation of a carbonyl group to give a (possibly linear) CpMCO intermediate. Although there was some indication initially³ that CpCo(CO) could be produced on photolysis of CpCo(CO)₂, recent evidence indicates⁴ that the products of this irradiation are CpCo(CO)N₂ and η³-CpCo(CO)₃.

It seems possible⁵ that the apparent difficulty of generating d⁸ complexes having CpML structures (especially in thermal reactions) might be due to the fact that such complexes are forced by symmetry⁶ to have open-shell electronic configurations (a similar problem exists with d² Cp₂ML complexes⁷). If this is so, the CpCo(CO)₂ displacement discussed above may not be an isolated example, and other CpML₂ complexes should also find ways to avoid dissociative mechanisms for ligand replacement. We decided to test this hypothesis by examining the mechanism of ligand replacement in CpCo(PPh₃)₂(1), a material quite closely related to CpCo(CO)₂. In contrast to results obtained on the latter complex, we have found there is apparently no energetic problem with dissociative ligand replacement in the bis-phosphine 1.

Results and Discussion

Complex 1 reacts cleanly with trimethylphosphine in toluene-δ₈ to form the mixed complex 2 and PPh₃ (Scheme 1). The reaction is so rapid that it is necessary to cool the reaction
vessel to -60°C in order to follow the conversion of starting material to products using conventional NMR techniques. A second-order plot of ln([PMe₃]/[1]) vs. time shows significant curvature, but a first-order plot of ln[1] vs. time is nicely linear (Fig. 1), indicating that the reaction is first order in [1] and zero-order in [PMe₃]. As shown in Fig. 2 and Table 1, the reaction rate is also strongly inhibited by added triphenylphosphine.

Three classic mechanisms, two associative and one dissociative, are shown in Scheme 1. Mechanism (a) should exhibit bimolecular kinetics under all conditions, and therefore cannot be operating. Mechanism (b) would give a rate law which could, under some conditions, be first order in [1] and zero order in [PMe₃]. However, if this mechanism were operative, inhibition by PPh₃ could be produced only by buildup of significant quantities of a complex such as C (L = PPh₃). No evidence for this complex was detected during the course of our NMR experiments.

The simple dissociative mechanism outlined as path (c) in Scheme 1 gives the rate law shown in eq. (1). At low [PPh₃] this

\[
R = \frac{k_1k_2[1][PMe₃]}{k_1[PPh₃] + k_2[PMe₃]} \quad (1)
\]

should reduce to a first order rate law; as addition of PPh₃ increases the importance of the initial term in the denominator, inhibition should set in, as is observed. The form of the rate decrease can be modeled easily. Scheme 2 shows the \( k_{obs} \) vs.
[PPh₃] data obtained, and the best-fit curve calculated using eq. (1). The fit illustrated is obtained with $k_1 = 1.15 \times 10^{-3}$ sec⁻¹ and $(k_2/k_1) = 4$. This value for $k_1$ corresponds to an activation free energy ($\Delta G^\ddagger$) of 15.2 kcal/mole at -60°C, in agreement with calculations which suggest an activation energy of 12-13 kcal/mole⁹. Because this step is dissociative, $\Delta S^\ddagger$ is certainly greater than 0, and this $\Delta G^\ddagger$ value therefore provides a maximum estimate of $\Delta H^\ddagger$.

The intermediate involved in these substitutions undoubtedly has the empirical formula CpCo(PPh₃). However, the precise structure of this intermediate is not yet clear. The symmetry and d-orbital configuration of CpCo(PPh₃) is such that the lowest singlet state of the simple linear complex has an open shell structure⁶. The presence of an open-shell electronic structure in the transition state of a concerted pericyclic organic reaction indicates that a level crossing is encountered in the MO correlation diagram for the process; this normally is manifested in a high activation energy barrier¹⁰. Whether such correlations necessarily exist in organotransition metal reactions, where filled and unfilled d-orbitals normally lie much closer together in energy, is not clear. What is clear from our data is that substitution is an especially facile process in CpCo(PPh₃)₂. Therefore, either (a) linear (probably singlet) CpCo(PPh₃) is an intermediate in the reaction, and the fact that this singlet has an open-shell electronic structure does not destabilize it appreciably, or (b) the substitution reaction avoids the linear intermediate by some means, for example by
remaining in a bent configuration. Further (and more ingenious) experiments will be required to distinguish between these possibilities.

Experimental Section

General. All manipulations of oxygen or water sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of N₂ in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

\[ \text{CpCo(PPh}_3\text{)}_2^{11}, \text{CpCo(PPh}_3\text{)(PMe}_3\text{)}^{12}, \text{PMe}_3^{13}, \text{and PPh}_3\text{–d}_{15}^{14} \]

were all prepared by previously published methods. Toluene-\(d_8\) was vacuum transferred from a purple sodium/benzophenone/tetraglyme ketyl solution.

NMR Experiments. \(^1\text{H}\) nuclear magnetic resonance (NMR) spectra were recorded on a high field (180.09 MHz) instrument equipped with a Bruker magnet, Nicolet Technology Corp. model 1180 data system, and electronics assembled by Mr. Rudi Nunlist (U. C. Berkeley). Spectra were recorded at -60°C, the probe being maintained at that temperature by a precooled nitrogen stream.

NMR experiments were carried out as follows: Various amounts of \(\text{PPh}_3\text{–d}_{15}\) (see Table 1) were weighed into standard 5 mm NMR tubes fused to 14/20 ground glass joints. The sample tubes were taken into the dry box and each prepared in the following manner. A standard solution of \(\text{CpCo(PPh}_3\text{)}_2\) was prepared by dissolving 0.052 g (0.080 mmoles) of that compound in 2.00 ml toluene-\(d_8\); 0.250 ml of that solution was transferred into each NMR tube by syringe. Toluene-\(d_8\) was added to the tubes to bring
the total volume of the solution in the each tube to 0.50 ml. In turn, each tube was capped with a teflon needle valve, taken out of the dry box and placed on a vacuum line. The samples were degassed by three freeze-pump-thaw cycles on the vacuum line and charged with PMe₃ while frozen at -196°C. The phosphine was added by expansion into a 25.85 ml known volume bulb (above the sample tube) to a pressure of 4.79 torr (as measured using an MKS Baratron capacitance manometer) followed by vacuum transfer of the contents of the bulb into the NMR tube. The tube was sealed with a flame and stored at -196°C until ready for use. At that time, the tubes were thawed at -78°C and shaken at that temperature before being dropped into the pre-cooled NMR probe. Spectra were taken under computer control until completion of each reaction.

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References and Notes.

4) Chrichton, O.; Rest, A. J.; Taylor, D. J. J. Chem. Soc.,

5) We are grateful to Prof. J. Collman for bringing this prediction to our attention; cf. (a) Collman, J. P. and Hegedus, L. S., "Principles and Applications of Organotransition Metal Chemistry", University Books, Inc., to be published; (b) Berg, J. and Collman, J. P. manuscript in preparation.


8) If the concentration of C were to build up, but C was in rapid equilibrium with I on the NMR time scale, one would expect a dramatic change in the chemical shifts of the resonances due to I; no such change is observed.

9) We are grateful to Dr. R. McKinney for sharing the results of his calculations with us prior to publication. For related work, see McKinney, R. J.; Pensak, D. A. Inorg. Chem., 1979, 18, 3413.


Table 1

Observed Rate Constants for the reaction of PMe₃ with CpCo(PPPh₃)₂ in the Presence of Added PPh₃

<table>
<thead>
<tr>
<th>[1]ᵃ</th>
<th>[PMe₃]ᵃ</th>
<th>[PPPh₃]ᵇ</th>
<th>k_{obs} (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.012</td>
<td>0.000</td>
<td>1.12 x 10⁻³</td>
</tr>
<tr>
<td>0.02</td>
<td>0.013</td>
<td>0.025</td>
<td>1.12 x 10⁻³</td>
</tr>
<tr>
<td>0.02</td>
<td>0.012</td>
<td>0.076</td>
<td>1.14 x 10⁻³</td>
</tr>
<tr>
<td>0.02</td>
<td>0.012</td>
<td>0.307</td>
<td>2.06 x 10⁻⁴</td>
</tr>
<tr>
<td>0.02</td>
<td>0.013</td>
<td>0.757</td>
<td>1.65 x 10⁻⁵</td>
</tr>
</tbody>
</table>

ᵃ) In moles/liter ᵇ) Concentration of d₁₅-triphenylphosphine in moles/liter. Deuterated material used to avoid swamping the NMR receiver by the triphenylphosphine proton signals.
Scheme 1

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{+ \text{PMe}_3} \text{CpCo} - \text{PPh}_3 + \text{PPh}_3 \]

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{+ \text{PMe}_3} \text{CpCo} - \text{PMe}_3 - \text{PPh}_3 \]

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{+ \text{L}} \text{LCo} - \text{PPh}_3 \]

\[ \text{PPh}_3 + \text{CpCoPPh}_3 \xrightarrow{k_2 + \text{PMe}_3} 2 \]

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{k_1 \text{ or } k_{-1}} \text{CpCo} - \text{PPh}_3 \]

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{+ \text{PMe}_3} \text{CpCo} - \text{PMe}_3 - \text{PPh}_3 \]

\[ \text{CpCo} - \text{PPh}_3 \xrightarrow{+ \text{L}} \text{LCo} - \text{PPh}_3 \]

\[ \text{PPh}_3 + \text{CpCoPPh}_3 \xrightarrow{k_2 + \text{PMe}_3} 2 \]
Figure 2. A plot of $\ln(k_{\text{obs}})$ vs $[\text{PPh}_3]$ where $k_1 = 1.15 \times 10^{-3}$ sec$^{-1}$ and $k_2/k_1 = 4$. 