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Reversible Metal-to-Metal Methyl Transfer in η^5-Cyclopentadienyl(triphenylphosphine)dimethylcobalt(III)

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Abstract: Labeling techniques have been used to demonstrate that η^5-cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (**1**) undergoes intermolecular cobalt-to-cobalt methyl group exchange. The reaction follows second-order kinetics; rate constants for methyl exchange between complexes **1** and its methylcyclopentadienyl analogue **4** show decreasing magnitude with increasing bulk of cyclopentadienyl substituents. Studies of the reaction with excess triphenylphosphine and complexes labeled with the nondissociating trimethylphosphine ligand indicate the reaction requires dissociation of phosphine from one of the two partners in the exchange before scrambling can take place. Further studies with other complexes (e.g., $Cp_2Zr(CH_3)_2$) suggest that alkyl exchange between two transition-metal centers may be a more general reaction than has heretofore been suspected.

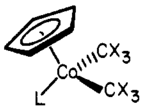
Introduction

One of the easiest ways in which carbon–metal bonds may be formed and broken is by transfer of alkyl groups from one metal to another. Alkyl transfers from main-group to transition-metal atoms have been known for many years, and there are now several examples of alkyl transfer between transition-metal atoms.

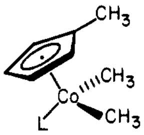
Normally the characteristics of these transfer reactions can be easily classified as to their electronic character. For example, transfers of alkyl groups from main-group alkyl reagents to metal halides,[2] or vitamin B_{12}–analogue cobalt alkyls to higher oxidation-state metals,[3] can be thought of as involving transfer of an essentially nucleophilic alkyl to an electrophilic metal center. Alkyl transfers from Co(II) species to other metals are normally considered to be radicaloid substitution reactions.[4] Certain types of alkyl-transfer reactions, however, are more difficult to classify. Among the most interesting of these are transfer of alkyl groups between similar (or identical) metal centers. Often these reactions (e.g., the interconversion of alkylplatinum halides with dialkyl- and dihaloplatinum complexes,[5] alkyl exchange involving zirconium and aluminum complexes[6]) involve situations in which the transfer of an alkyl group to the (electrophilic?) metal center is assisted by the simultaneous reverse transfer of halogen or other (nucleophilic?) ligand in the opposite direction.

However, a few stable symmetrically bridging dimeric organotransition-metal complexes, in which alkyls bridge two metals without assistance of a nucleophilic ligand, are now known.[7] This suggests bridging alkyls might be accessible as transition states or short-lived intermediates from many other stable *unbridged* metal alkyls. We have now found that this is apparently true in η^5-cyclopentadienyl(triphenylphosphine)dimethylcobalt, a complex known for almost 15 years,[8] where degenerate methyl transfer occurs easily at 60 °C. In this paper we report the results of a mechanistic study of this symmetrical alkyl-transfer reaction. Our results indicate that an unsaturated site on *one* of the two participating centers is required, and we have collected information about the effect of phosphine and cyclopentadiene substituents on the reaction rate.

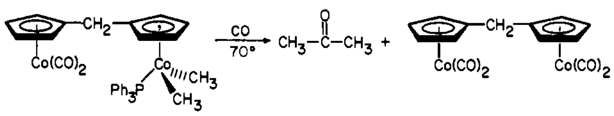
Results



1, L = PPh$_3$, X = H
1-d$_6$, L = PPh$_3$, X = D
3, L = PMe$_3$, X = H
3-d$_6$, L = PMe$_3$, X = D



2, L = PPh$_3$
4, L = PMe$_3$



5

Alkyl exchange involving the $RCpCo(L)Me_2$ moiety was first implicated during a control experiment designed to investigate the molecularity of the carbonylation of binuclear complex **5**.[9] When a mixture of **5**-d_0 and **5**-d_6 (labeled methyl groups) was carbonylated at high (0.25 M) concentrations at 70 °C with 5 atm of CO, the acetone produced was partly (ca. 30%) d_3 in addition to the expected acetone-d_6 and -d_0. Carbonylation of mixtures of **1** and **1**-d_6 at higher concentrations (0.25 M) showed alkyl crossover similar to that seen with **5**. As reported elsewhere[10], carbonylation of **1** and **1**-d_6 at moderate concentrations (0.05 M) yields only acetone-d_6 and -d_0. Heating a 0.25 M

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(1) Hertz Foundation Fellow, 1977 to present.

(2) For leading references regarding the extensive body of literature dealing with alkylation reactions see: (a) Heck, R. F. "Organotransition Metal Chemistry", Academic Press: New York, 1974; Chapter 2. (b) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Chapman & Hall: London, 1968; Vol. 2, Chapter 7. (c) Sinn, H.; Opermann, G. *Agnew. Chem.* **1966**, *78*, 986.

(3) See, for example: (a) Dodd, D.; Johnson, M. D. *Chem. Commun.* 1971, 1371. (b) Costa, G.; Mestroni, G.; Cocevar, C. *Ibid.* **1971**, 1869. (c) Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Dalton Trans.* **1972**, 1519. (d) Halpern, J. *Ann N.Y. Acad. Sci.* **1974**, *239*, 2. (e) Andeson, S. N.; Balard, D. H.; Chrzastowski, J. Z.; Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1972**, 685. (f) Dodd, D., Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664.

(4) See for example: ref 2d or (a) Van den Bergen, A.; West, B. O. *Chem. Commun.* **1971**, 52. (b) Van den Bergen, A.; West, B. O. *J. Organomet. Chem.* **1974**, *64*, 125. (c) Espenson, J. H.; Sellers, T. D., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 94. (d) Espenson, J. H.; Leslie, J. P., II *Ibid.* **1974**, *96*, 1954. (e) Espenson, J. H.; Shveima, J. S. *Ibid.* **1973**, *95*, 468.

(5) For examples of alkyl transfer between transition metals which is assisted by a potentially bivalent bridging group (e.g., halogen, CH_2) see: (a) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 480. (b) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1810. (c) Thompson, P. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1975**, 841, (d) Dodd, D.; Johnson, M. D. *Chem. Commun.* **1971**, 1371. (e) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. (f) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *Ibid.* **1979**, 54. (g) Puddephatt, R. J.; Thompson, P. J. *Ibid.* **1977**, 1219 (h) Dodd, D.; Johnson, M. D.; Tockman, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 3664. (i) Fanchiang, Y. T.; Ridley, W. P.; Wood, J. M. *Ibid.* **1979**, *101*, 1442.

(6) Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303. (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 638. (c) Schwartz, J.; Labinger, J. A. *Angew. Chem.* **1976**, *88*, 402, (d) Carr, D. B.; Yoshifuji, M., Shoer, L. I.; Gell, K. I.; Schwartz, J. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 127. (e) Labinger, J. A.; Hart, D. W.; Siebert, W. E., III; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

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Scheme I

$$\mathrm{CpCo(L_1)(CH_3)_2} + \mathrm{CpCo(L_1)(CD_3)_2} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} 2\ \mathrm{CpCo(L_1)(CH_3)(CD_3)} \tag{1}$$

$$\mathrm{CpCo(L_1)(CH_3)_2} + \mathrm{MeCpCo(L_2)(CH_3)(CD_3)} \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{CpCo(L_1)(CD_3)(CH_3)} + \mathrm{MeCpCo(L_2)(CH_3)_2} \tag{2}$$

$$\mathrm{CpCo(L_1)(CH_3)_2} + \mathrm{MeCpCo(L_2)(CD_3)_2} \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{CpCo(L_1)(CD_3)(CH_3)} + \mathrm{MeCpCo(L_2)(CD_3)(CH_3)} \tag{3}$$

$$\mathrm{CpCo(L_1)(CH_3)(CD_3)} + \mathrm{MeCpCo(L_2)(CD_3)_2} \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{CpCo(L_1)(CD_3)_2} + \mathrm{MeCpCo(L_2)(CH_3)(CD_3)} \tag{4}$$

$$\mathrm{CpCo(L_1)(CD_3)_2} + \mathrm{MeCpCo(L_2)(CH_3)_2} \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{CpCo(L_1)(CD_3)(CH_3)} + \mathrm{MeCpCo(L_2)(CD_3)(CH_3)} \tag{5}$$

$$\mathrm{MeCpCo(L_2)(CH_3)_2} + \mathrm{MeCpCo(L_2)(CD_3)_2} \underset{k_3}{\overset{k_3}{\rightleftharpoons}} 2\ \mathrm{MeCpCo(L_2)(CH_3)(CD_3)} \tag{6}$$

mixture of **1** and **1**-d_6 at 60 °C for 40 h without CO, followed by dilution to 0.05 M and treatment with CO under conditions previously established to preclude crossover during carbonylation, gave a *statistical* ratio of acetone-d_6, -d_3, and -d_0. Clearly the scrambling reaction was taking place in a prior process unconnected with the carbonylation.

In order to study the alkyl transfer directly by ^{1}H NMR, we prepared the methylcyclopentadienyl analogue **2**; preliminary measurements demonstrated that the cobalt-bound methyl resonances of **1** and **2** could be resolved cleanly. When equal amounts of **1**-d_6 and **2** were dissolved in THF-d_8 and heated in a sealed NMR tube at 61.7 °C, a new methyl doublet, corresponding to the resonance observed for **1**, was seen growing into the NMR spectrum at the expense of the original methyl doublet of **2**. Addition of excess triphenylphosphine was found to reduce the rate of scrambling. In order to further study the role of phosphine in this exchange, we prepared the trimethylphosphine analogues **3** and **4**. In contrast to PPh$_3$, the rate of dissociation of PMe$_3$ from the cobalt center in these complexes is known[10] to be negligible at temperatures near 60 °C. The reaction of **1**-d_6 with **4** was found to again exchange methyl groups at 62 °C, but the rate was reduced to somewhat less than half that associated with interchange involving **1** and **2** at that temperature. Heating **3**-d_6 in the presence of **4** at 62 °C showed no evidence of scrambling. These results clearly indicate that dissociation of phosphine from *one* metal center is both necessary and sufficient for exchange to take place.

Because there are a large number of (in principle) chemically distinguishable species involved in these exchange processes (see Scheme I) and each step is reversible, the kinetics required to describe them are complex. Assuming for the moment that we may ignore secondary isotope effects, we characterized each system [(a), (b), and (c) in Table I] by six different exchange equilibria (Scheme I) but only three different phenomenological rate constants. The fact that no exchange is observed in system c requires that k_3 in systems c and b (which is the same rate constant as k_3 in system c) be effectively zero under our reaction conditions. Similarly, k_1 is associated with the same process in systems a and b. Using this type of reasoning, one may reduce the set of nine rate constants in Table I to four which are essentially zero and five which need to be determined; two of the five are identical. An additional complication arises from the fact that our NMR analysis does not measure the concentrations of the individual complexes but rather the total "concentration" of methyl groups bound, for example, to CpCo, and separately the "concentration" of methyl groups bound to MeCpCo. The ratio "*R*" plotted against time in Figures 1, 2, and 3 is simply the former "concentration" (methyl groups bound to CpCo) divided by the total "concentration" of all metal-bound groups.

Table I. Rate Constants for Methyl-Exchange Reactions Shown in Scheme I (Solvent: THF-d_8)

system	ligands	rate constants,[a] M^{-1} s^{-1}		
		k_1[b]	k_2[c]	k_3[b]
a	L$_1$ = L$_2$ = PPh$_3$	3.6 × 10^{-3}	2.2 × 10^{-4}	8.3 × 10^{-6}
b	L$_1$ = PPh$_3$, L$_2$ = PMe$_3$	3.6 × 10^{-3}	8.6 × 10^{-5}	0
c	L$_1$ = L$_2$ = PMe$_3$	0	0	0

[a] Starting concentrations of cobalt complexes in each case are 0.175 M. [b] Value ±10%. [c] Value ±0.5%.

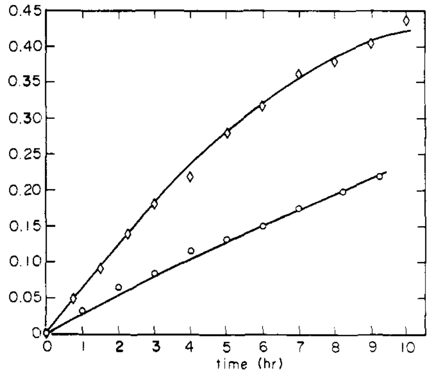

Figure 1. Computer simulation of the rate of methyl exchange in the reaction between **1**-d_6 and **2** (◇) and between **1**-d_6 and **4** (○). Diamonds (◇) and circles (○) are experimental data; solid lines are calculated by using the rate constants shown in Table I. The function *R* plotted on the abcissa is the ratio of integrated metal-bound methyl absorption in the Cp-substituted complex in each reaction divided by the total CH$_3$ integration (metal-bound methyls in Cp-substituted plus MeCp-substituted complexes).

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(7) Krueger, C.; Sekutowski, J. C.; Berke, H.; Hoffmann, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1110–5. (b) Hursthouse, M. B.; Jones, R. A.; Abdul-Malik, K. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. (c) Calvert, R. B.; Shapley, J. R. *Ibid.* **1978**, *100*, 6544. (d) Masters, A. F.; Mertis, K.; Gibson, J. F.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 389. (e) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 480. (f) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(8) (a) King, R. B. *Inorg. Chem.* **1966**, *5*, 82. (b) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.

(9) Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4766.

(10) The thermal decomposition of **1** as well as the reactions of **1** with PhCCPh, C$_2$H$_4$, and CO all demonstrate an inverse dependence of reaction rate upon phosphine concentration. See for example: (a) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 3237. (b) Evitt, E. R.; Bergman, R. G. *Ibid.* **1979**, *101*, 3973. (c) Evitt, E. R.; Bergman, R. G. *Ibid.*, submitted for publication.

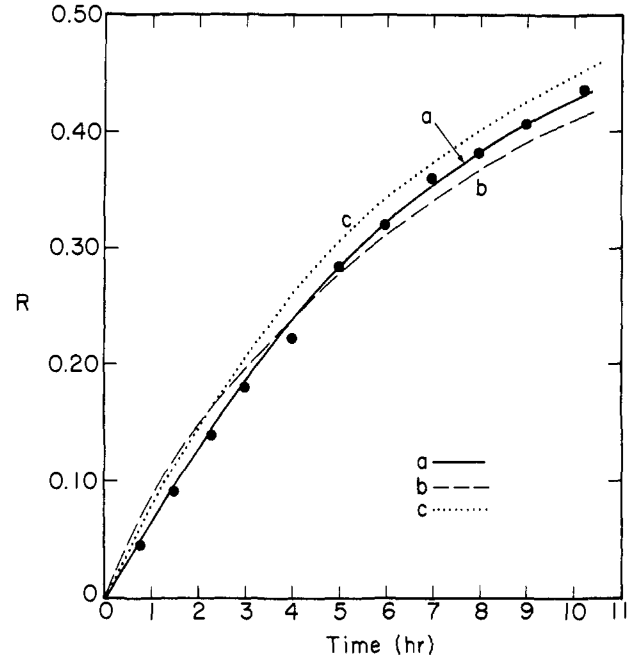


Figure 2. Effects of variations in k values on fit of data for case a of Table I. Line a shows best fit line for the data points (●). Line b shows result of variation of 2% in k_2 (k_1 and k_3 unchanged). Line c shows change in line caused by 20% variation in k_1 (k_2 and k_3 unchanged).

We were able to satisfactorily model the variations in "R" vs. time (Figure 1) by use of an interactive mechanism simulation computer program.[11] This program takes rate constants and reaction steps as input material and, through probability calculations based on concentrations, rate constants and frequency of a given step, simulates the series of reactions, and calculates the concentrations of individual species with time. For the case of system a, the ratio "R" is

$$R = \frac{[\mathbf{1}\text{-}d_3] + 2[\mathbf{1}\text{-}d_0]}{[\mathbf{1}\text{-}d_3] + 2[\mathbf{1}\text{-}d_0] + [\mathbf{2}\text{-}d_3] + 2[\mathbf{2}\text{-}d_0]}$$

This, given all the individual concentrations, is calculated and plotted against time. The rate constants are then varied until the fit is optimized. To save time, initial rate constants are estimated by assuming that at short reaction times reaction 5 in Scheme I is the only important step (due to insignificant concentrations of other species initially) and calculating the second-order rate constant for that step from the data. Reactions involving k_1 or k_3 are less frequent than those involving k_2 because of concentrations of species involved as well as the sheer number of steps involving k_2 in the mechanism outlined in Scheme I. Therefore, k_1 and k_3 affect the overall fit less than k_2 and that latter rate constant was optimized first followed by the optimization of k_1 and k_3. An obvious consequence of this method is that k_1 and k_3 are known with less accuracy than k_2. The rate constants thus calculated can be found in Table I while sample fits are illustrated in Figure 1. The satisfactory nature of the fit indicates that the reaction follows second-order kinetics and that our initial assumption, that secondary isotope effects are negligible within our experimental error, is valid. The effects of varying the rate constants on the fit can be seen in Figure 2.

Discussion

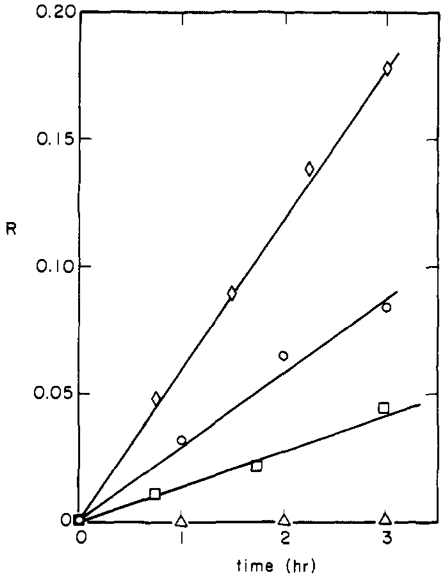
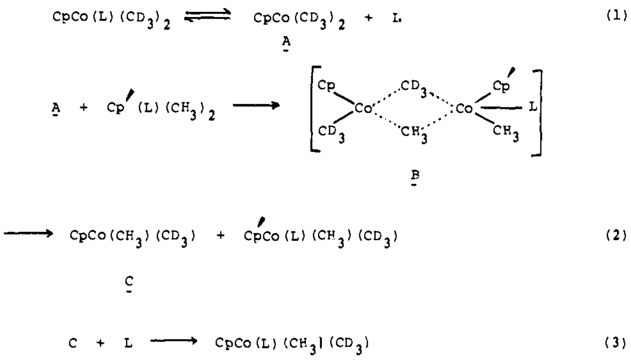


Figure 3. Plots of the ratio R (see Figure 1 for definition of this ratio) vs. time for the following reactions: ◊, **1**-d_6 with **2**; O, **1**-d_6 with **4**; □ **1**-d_6 with **2** containing excess (1.75 M) PPh_3; △, **3**-d_6 + **4**.

Scheme II



With these rate constants in hand, we can draw some preliminary conclusions about the mechanism of the exchange reaction. The effect of changing PPh_3 concentrations on the exchange rate, the fact that two PMe_3 complexes react so slowly, and mechanistic studies of other reactions[10] of dialkyl **1** indicate that the exchange requires initial dissociation of phosphine. The fact that the PMe_3 complex will transfer methyl groups to a PPh_3 complex, but not to a second PMe_3 complex, indicates each exchange step takes place between one complex which has lost a phosphine and a second complex which has not. The decrease in magnitude in going from k_1 to k_2 to k_3, the decrease in rate with increased phosphine concentration, and dissociation rates in other systems[10] all suggest that phosphine is lost in a rapid preequilibrium step, followed by rate-determining combination of the second complex with the unsaturated intermediate so generated, as shown in Scheme II. It seems reasonable that the binuclear transition state involved in this second step is destabilized by steric repulsions between methyl groups on the cyclopentadienyl rings. Any intermediate or transition state must account for the reversible methyl exchange observed in order to interconvert states A and C. By cleavage in either of two possible ways, a transition state or intermediate having structure B fulfills these requirements. Precedent for B in nontransition-metal alkyl exchanges and particularly the known stable transition-metal complexes with bridging alkyl groups[7] make it the attractive intermediate. Whatever the transition state actually is, clearly this exchange is significantly different in nature from both exchanges involving anionic supernucleophile Co^{I} and Rh^{I} porphyrins, and the radicaloid alkyl exchanges of Co^{II} systems. Both of those exchange mechanisms involve only one alkyl group per pair of metal complexes, and the net effect is never alkyl scrambling among thermodynamically equivalent species. Rather, this exchange shows striking similarities to many substitution reactions involving other (halogen, hydride, and mixed alkyl/halo) ligands and to main-group/transition-metal alkyl exchanges. Its dependence upon the

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(11) Program MSIM4 developed by D. L. Bunker and F. Houle, University of California, Irvine, CA, and available from the Quantum Chemistry Program Exchange (Program No. 293).

unsaturated (and perhaps electrophilic) character of one partner may prove more general as further mechanistic information becomes available.

The facile exchange of alkyl groups in otherwise stable metal alkyls bodes caution for crossover experiments designed to probe the important mechanistic question of molecularity during reactions of those species. In extensions of the results outlined above, we have obtained preliminary evidence that alkyl exchange between transition-metal centers may be a more general process than has heretofore been suggested. Thus, although **1**-d_6 and Cp_2MoMe_2 do not exchange methyls, we *do* observe such exchange between **1**-d_6 and Cp_2ZrMe_2. Further research will be required to define more precisely the scope of these reactions, the factors which control their efficiency, and the nature of the exchange transition state.

Experimental Section

General. All manipulations of oxygen- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or by using standard Schlenk or vacuum line techniques.

Tetrahydrofuran (THF) and diethyl ether were distilled from purple sodium/benzophenone ketyl solutions. Benzene and hexanes were degassed and used as supplied from J. T. Baker ("Analyzed Reagent" grade). PPh_3 (MCB) was recrystallized twice from hexanes and dried overnight under high vacuum. Methylcyclopentadiene was freshly distilled at atmospheric pressure from the commercially available (Aldrich) dimer and stored at −78 °C until used.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283 grating spectrophotometer using solutions of samples in sodium chloride cells (0.10-mm path length).

Elemental analyses were conducted by the University of California, Berkeley analytical facility.

NMR Experiments. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 spectrometer. Spectra are reported in units of ppm downfield from tetramethylsilane but were most often measured relative to residual ^1H absorption in deuterated solvent: benzene-d_6 (δ 7.15), THF-d_8 (δ 1.73), and acetone-d_6 (δ 2.04). Deuterated THF and benzene were vacuum transferred from ketyl solutions while acetone-d_6 was transferred from Linde 4A° molecular sieves and degassed with three freeze-pump-thaw cycles on a vacuum line.

NMR experiments were carried out as follows: a standard NMR tube fused to a 14/20 ground-glass joint was loaded with the desired compounds in the drybox, capped with a Teflon needle valve, placed on a vacuum line, and evacuated. The tube was charged with the desired amount of solvent by vacuum transfer from a graduated tube of solvent. The tube was then sealed and carefully thawed before being heated in a refluxing $CHCl_3$ bath. Spectra were recorded by removing the tube from the bath after the desired elapsed time, plunging it into ice water (none of the reactions proceeded at measurable rates below 55 °C), and placing it in the NMR probe when dry. The spectrum was recorded and the tube replaced in the constant temperature bath.

Syntheses. $CpCo(PPh_3)(CH_3)_2$, $CpCo(PPh_3)(CD_3)_2$, and $CpCo(P(CH_3)_3)(CD_3)_2$ were prepared by previously published methods.[6c] Methylcyclopentadienyl analogues were prepared by the same methods used to prepare the unsubstituted cyclopentadienyl complexes. Structures of previously known compounds were established by comparison of spectral data with those reported earlier; new compounds were characterized by standard spectral and analytical techniques. Data for new compounds follow: $(C_5H_4CH_3)Co(CO)I_2$: NMR ($CDCl_3/Me_4Si$) δ 5.42 (s, 4 H), 2.50 (s, 3 H); IR (Et_2O) 2065 cm^{-1}. Anal. Calcd for $C_7H_7CoI_2O$: C 20.02; H, 1.68; Co, 14.04; I, 60.45. Found: C, 20.22; H, 1.78; Co, 13.1; I, 60.48. $(C_5H_4CH_3)Co(PPh_3)I_2$: NMR ($CDCl_3/Me_4Si$) δ 7.2–7.9 (m, 15 H), 5.05 (m, AA′, 2 H), 4.15 (m, BB′, 2 H), 2.54 (d, J = 2.5 Hz, 3 H). Anal. Calcd for $C_{24}H_{22}CoI_2P$: C, 44.07; H, 3.39; Co, 9.01; I, 38.80; P, 4.73. Found: C, 43.85; H, 3.49; Co, 8.64; I, 39.02; P, 4.90. $(C_2H_4CH_3)Co(PPh_3)(CH_3)_2$: NMR (THF-$d_8$) δ 7.2–7.6 (m, 15 H), 5.1 (m, AA′BB′, 4 H), 1.58 (d, J = 3 Hz, 3 H), −0.05 (d, J = 5.5 Hz, 6 H). Anal. Calcd for $C_{26}H_{28}CoP$: C, 72.55; H, 6.56; Co, 13.69; P, 7.20. Found: C, 72.60; H, 6.55; Co, 14.0; P, 7.04. $(C_5H_4CH_3)Co(P(CH_3)_3)(CH_3)_2$: NMR (THF-$d_8$) δ 5.05, 5.30 (m, AA′BB′, 4 H), 2.35 (s, 3 H), 2.25 (d, J = 9 Hz, 9 H), 0.30 (d, J = 6 Hz, 6 H). High resolution MS: parent ion *m/e* calcd for $C_{11}H_{22}CoP$: 244.0799. Found: 244.0795.

Acknowledgments. We are grateful to Dr. F. A. Houle for assistance with the computer simulation, and we acknowledge financial support from the Division of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-48.

Tautomeric Catecholate–Semiquinone Interconversion via Metal–Ligand Electron Transfer. Structural, Spectral, and Magnetic Properties of (3,5-Di-*tert*-butylcatecholato)(3,5-di-*tert*-butylsemiquinone)(bipyridyl)cobalt(III), a Complex Containing Mixed-Valence Organic Ligands

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Abstract: The bipyridyl adduct of tetrameric $[Co(3,5\text{-}DBSQ)_2]_4$ has been formed by treating the parent Co(II) complex with bipyridine in toluene solution. Structural features within the inner coordination sphere are consistent with a Co(III) metal center. One of the independent quinone ligands is coordinated as a semiquinone and the other as a catecholate. In toluene solution the results of magnetic, EPR, NMR, and spectral experiments suggest an equilibrium between a Co(II) species $Co(3,5\text{-}DBSQ)_2(bpy)$ and the Co(III) form found in the solid state, Co(3,5-DBCat)(3,5-DBSQ)(bpy). These two forms of the complex are related by the transfer of an electron between the metal ion and one of the quinone ligands.

Introduction

Mechanistic details of inner-sphere metal–ligand electron transfer, induced either thermally or photochemically, are of fundamental chemical importance but remain poorly understood.[1] Specific questions concern the nature of the ligand-radical species which is often the initial product of an outer-sphere electron-transfer process and the kinetics of the inner-sphere electron-transfer step.

Our studies on the coordination properties of orthoquinone ligands have shown that they are capable of chelating to metals as unreduced *o*-benzoquinones, as partially reduced *o*-semiquinones

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(1) Tabue, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970.

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