

and the metalloprotein rubredoxin (Rb) (Table IV).<sup>25</sup> All the indications are therefore that both  $\text{Mo}_4\text{S}_4^{5+}$  reactions are outer sphere.

From the Marcus equations,<sup>26</sup> using the rate constant for the reaction of  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  with  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  ( $0.01 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>27</sup> the self-exchange rate constant for  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+/4+}$  is  $760 \text{ M}^{-1} \text{ s}^{-1}$ . No corrections have been made for work terms, which may be significant in view of the high charge product of the reactants.<sup>28</sup> The rate constant obtained indicates a favorable electron-transfer process.<sup>13</sup>

Finally we draw attention to the quite remarkable stability of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  over a wide  $[\text{H}^+]$  range, 0.01–4.0 M. If stored  $\text{O}_2$ -free in 2 M HPTS the cluster is stable for weeks. It is oxidized

only slowly in air,  $t_{1/2} \sim 4$  days at  $50^\circ\text{C}$ . This behavior contrasts with that of the biologically relevant  $\text{Fe}_4\text{S}_4$  cube, which in aqueous solution as tetrahedrally ligated  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  has only limited stability.<sup>29-31</sup>

**Acknowledgment.** We thank the Climax Molybdenum Co. Ltd., and the U.K. Science and Engineering Research Council for a CASE/SERC studentship (to C.S.) and the University of Newcastle upon Tyne for a Ridley Fellowship (B.-L.O.).

**Registry No.**  $\text{Mo}_4\text{S}_4^{5+}$ , 99145-05-8;  $\text{Mo}_3\text{S}_4^{4+}$ , 101660-28-0;  $\text{Mo}_4\text{S}_4^{4+}$ , 104843-16-5;  $\text{Mo}_4\text{S}_4^{6+}$ , 117626-49-0;  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{O})_6]^{2+}$ , 52700-51-3;  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  (M = Cr), 20574-26-9;  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  (M = V), 15696-18-1;  $\text{V}(\text{O})_2^+$ , 18252-79-4;  $[\text{Mo}_4\text{S}_4(\text{NCS})_{12}]^{6-}$ , 103731-75-5; NCS<sup>-</sup>, 302-04-5.

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## Mechanism of the Substitution Reactions of the Nineteen-Electron $\text{Co}(\text{CO})_3\text{L}_2$ Complex [ $\text{L}_2 = 2,3\text{-Bis}(\text{diphenylphosphino})\text{maleic Anhydride}$ ]

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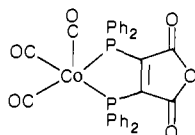
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Received January 11, 1988

**Abstract:** The substitution reactions of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex [ $\text{L}_2 = 2,3\text{-bis}(\text{diphenylphosphino})\text{maleic anhydride}$ ] with phosphines, phosphites, and iodide were studied. This 19-electron complex (perhaps better described as an 18-electron complex with a reduced ligand) was chosen as a model to study the substitution reactions of more reactive 19-electron complexes. Although a dissociatively activated substitution pathway seemed likely, the molecule has a square-pyramidal geometry and the possibility of associatively activated reactions was also anticipated. The complex reacted with entering ligands at room temperature in  $\text{CH}_2\text{Cl}_2$  to form  $\text{Co}(\text{CO})_2\text{L}_2\text{L}'$  [ $\text{L}' = \text{PR}_3, \text{P}(\text{OR})_3, \text{I}^-$ ]. The derivative with  $\text{L}' = \text{PPh}_3$  was structurally characterized by a single-crystal X-ray analysis. The substitution reactions followed first-order kinetics, and the rates were independent of the entering ligand concentration and the nature of the entering ligand. A dissociatively activated pathway involving loss of CO (not chelate dissociation) is proposed. Rate constants as a function of temperature yielded the following activation parameters:  $\Delta H^\ddagger = 23.8 \pm 0.6 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 11.1 \pm 2.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ . For comparison purposes, the substitution reactions of the 18-electron  $\text{Co}(\text{CO})_3\text{L}_2^+$  complex were studied. No substitution reactions of this complex took place under the same conditions used for  $\text{Co}(\text{CO})_3\text{L}_2$ . Thus, the lability of the latter complex can be attributed to the extra electron. ESR studies of  $\text{Co}(\text{CO})_3\text{L}_2$  showed a slight delocalization of the extra electron into  $^{13}\text{CO}$  orbitals (orbitals that are likely Co–CO antibonding); electronic occupation of these orbitals will weaken the Co–CO bond, and we propose this is the origin of the lability.

Reactions of 17-electron organometallic radicals with 2-electron donor ligands yield 19-electron adducts.<sup>1</sup> Because 19-electron adducts represent a new class of organometallic complexes and because these molecules are expected to be important intermediates whenever metal radicals are formed,<sup>2</sup> we have begun a systematic study of their reactivity.<sup>3</sup>

In this paper, we report the results of our study on the substitution reactions of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex [ $\text{L}_2 = 2,3\text{-bis}(\text{diphenylphosphino})\text{maleic anhydride}$ ].<sup>4</sup> This 19-electron complex



(perhaps better described as an 18-electron complex with a reduced ligand) was chosen for our initial substitution study for two reasons:

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(2) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 89–94.

(3) In previous work, we showed that many 19-electron complexes are powerful reductants,<sup>4</sup> and we showed that this property made them key intermediates in the photochemical disproportionation reactions<sup>5</sup> of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ ,  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ , and  $\text{Mn}_2(\text{CO})_{10}$  dimers.<sup>6,7</sup> In addition, we demonstrated that the 19-electron complexes could be used to reduce a wide variety of organic, inorganic, and organometallic complexes; even complexes with reduction potentials more negative than  $-1.5 \text{ V}$  (vs SCE) are reduced with ease.<sup>4</sup>

(4) Stiegman, A. E.; Goldman, A. S.; Leslie, D. B.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1984**, 632–633.

(5) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–240.

(6) (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037. (b) Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434–4436. (c) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–258.

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<sup>†</sup> Oregon State University.

(1) it is relatively stable,<sup>9</sup> and thus the reactions occur on a measurable time scale, and (2) it has a square-pyramidal coordination geometry.<sup>8</sup> Because of the square-pyramidal geometry, the molecule has a vacant coordination site and may therefore react by an interesting associatively activated mechanism rather than the predicted dissociatively activated pathway.<sup>1</sup>

The  $\text{Co}(\text{CO})_3\text{L}_2$  complex was first synthesized from  $\text{Co}_2(\text{CO})_8$  and  $\text{L}_2$  by Fenske, who showed that the odd electron is delocalized over the Co atom and the  $\pi^*$  system of the  $\text{L}_2$  ligand.<sup>8</sup> The relative stability of the complex can be attributed to the ability of the  $\text{L}_2$  ligand to delocalize the extra electron. In order to determine the effect of the extra electron on the substitution reactions of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex, we also investigated the substitution reactions of the 18-electron  $\text{Co}(\text{CO})_3\text{L}_2^+$  complex.

### Experimental Section

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

**Materials and Supplies.** Dichloromaleic anhydride (Aldrich) was recrystallized from diethyl ether. (*n*-Bu)<sub>2</sub>O and  $\text{Me}_3\text{SiCl}$  (Aldrich) were distilled over sodium pyridine, respectively.  $\text{Ph}_2\text{PCl}$  (Alfa) was purified by distillation. THF, diethyl ether, and benzene were distilled over sodium.  $\text{CH}_2\text{ClCH}_2\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were distilled over  $\text{CaH}_2$ . Phosphines and phosphites were obtained commercially and used as received.  $\text{Na}^+\text{PPh}_2^-$ ,<sup>14</sup>  $\text{Me}_3\text{Si-PPh}_2$ ,<sup>14</sup> and  $\text{Co}(\text{CO})_3\text{L}_2$ <sup>8</sup> [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride] were synthesized according to procedures described in the literature.

**2,3-Bis(diphenylphosphino)maleic Anhydride.** Attempts by us to prepare this ligand according to the reported procedure<sup>15</sup> gave small yields (40%). Therefore, the procedure was modified as follows. Dichloromaleic anhydride (8 g, 0.5 mol) in 80 mL of absolute ethyl ether at 0 °C was added dropwise to  $\text{Ph}_2\text{PSiMe}_3$  (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  $\text{N}_2$  and dried under vacuum for 12 h to remove the  $\text{Me}_3\text{SiCl}$  that had formed. Pure yellow crystals of the product were obtained by recrystallization from  $\text{Et}_2\text{O}$  (93% yield). It is very important to completely remove all of the  $\text{Me}_3\text{SiCl}$  prior to recrystallization of the ligand; recrystallization of a product mixture containing  $\text{Me}_3\text{SiCl}$  turned the product into an unidentified black substance.

**$\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ .** A solution of 440 mg (1.65 mmol) of  $\text{PPh}_3$  in 1 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise to a solution of 200 mg (0.33 mmol) of  $\text{Co}(\text{CO})_3\text{L}_2$  in 2 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was stirred for 6 h in a glovebox. After the reaction was completed (as monitored by ESR and infrared spectroscopy), hexane was added and light green crystals of  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  formed which were washed with hexane five times to remove excess  $\text{PPh}_3$ . Elemental analysis was performed by Mikroanalytisches Labor Pascher, Germany. Anal. Calcd for  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3 \cdot 1/2\text{H}_2\text{O}$ : C, 67.61; H, 4.26; P, 10.90. Found: C, 67.09; H, 4.61; P, 10.1. The color of the crystals depends on the solvents in which they are formed; crystals formed from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  are dark green.

(7) (a) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527-529. (b) Stiegman, A. E.; Goldman, A. S.; Philbin, C. E.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2976-2979.

(8) Fenske, D. *Chem. Ber.* **1979**, *112*, 363-375.

(9) With regard to the relative stability of the complex, it is conceptually useful to define three limiting classes of 19-electron complexes. Class I:  $\sigma^*$  complexes; the 19th electron is in an M-L antibonding orbital, e.g.,  $\text{Mn}(\text{C-O})_3\text{Br}^-$ ,<sup>10</sup>  $\text{CpMo}(\text{CO})_3\text{I}^-$ .<sup>11</sup> Class II: complexes that have a metal valence electron count lower than 19 due to a geometry change such as a slipped Cp ring, bent CO ligand, or a "five-coordinate" phosphoranyl radical structure.<sup>1</sup> Class III:  $\pi^*$  complexes; complexes where the 19th electron is primarily in a low-energy ligand orbital (generally a  $\pi^*$  orbital), e.g.,  $\text{Mo}(\text{CO})_4(\text{bpy})^-$ ,<sup>12</sup>  $\text{CpMo}(\text{CO})_2(\text{c-hex-DAB})$ <sup>13</sup> (c-hex-DAB =  $\text{c-C}_6\text{H}_{11}\text{N}=\text{CHCH}=\text{N-c-C}_6\text{H}_{11}$ ). The class III adducts can be thought of as 18-electron complexes with reduced ligands. For this reason they are generally more stable than the adducts in class I or II.<sup>1</sup>

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(14) Kuchen, W.; Buchwald, H. *Chem. Ber.* **1959**, *92*, 227-231.

(15) Fenske, D.; Becher, H. *J. Chem. Ber.* **1974**, *107*, 117-122.

Table I. Infrared Spectroscopic Data in  $\text{CH}_2\text{Cl}_2$

complex <sup>a</sup>	$\nu(\text{C}\equiv\text{O})$ , $\text{cm}^{-1}$	$\nu(\text{C}=\text{O})$ , $\text{cm}^{-1}$
$\text{Co}(\text{CO})_3\text{L}_2$	2080 (s), 2031 (s), 2009 (s)	1742 (s), 1670 (s)
$\text{Co}({}^{13}\text{CO})_3\text{L}_2$	2029 (s), 1980 (s), 1960 (s)	1748 (s), 1679 (s)
$\text{Co}(\text{CO})_2\text{L}_2\text{P}(\text{Bu})_3$	2002 (m), 1944 (s)	1733 (s), 1656 (s)
$\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$	2009 (m), 1954 (s)	1735 (s), 1657 (s)
$\text{Co}(\text{CO})_2\text{L}_2\text{P}(\text{OMe})_3$	2020 (m), 1983 (s)	1735 (s), 1658 (s)
$\text{Co}(\text{CO})_2\text{L}_2\text{P}(\text{OPh})_3$	2026 (m), 1969 (s)	1737 (s), 1660 (s)
$[\text{NBu}_4^+][\text{Co}(\text{CO})_2\text{L}_2\text{I}^-]$ $\text{L}_2$	1993 (m), 1936 (s)	1727 (s), 1649 (s), 1838 (m), 1816 (w), 1763 (s)
$[\text{Co}(\text{CO})_3\text{L}_2^+]\text{I}^-$	2040 (w), 2017 (m), 1966 (s)	1845 (w), 1780 (s)
$[\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3^+][\text{FeCl}_4^-]$	2029 (m), 1979 (s)	1850 (w), 1783 (s)

<sup>a</sup>  $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride.

**Synthesis of  $[\text{Co}(\text{CO})_3\text{L}_2^+]\text{I}^-$ .** A reaction vessel with two compartments separated by a porous glass frit was used in the synthesis. In a drybox, 200 mg (0.16 mmol) of  $\text{Co}(\text{CO})_3\text{L}_2$  was dissolved in 8 mL of THF and then loaded in one of the compartments of the vessel. In the other compartment was loaded 43 mg (0.17 mmol) of iodine dissolved in 3.5 mL of hexane. After the reaction vessel was cooled to 0 °C in an ice bath the vessel was tilted so that the  $\text{Co}(\text{CO})_3\text{L}_2$  solution dripped slowly into the iodine solution through the frit. About 20 min after all the  $\text{Co}(\text{CO})_3\text{L}_2$  had been added to the iodine solution, the vessel was removed from the ice bath, and the solvent was pumped off. The solid left in the vessel was dried in vacuo overnight, during which time all of the solvent and the excess iodine were removed.  $[\text{Co}(\text{CO})_3\text{L}_2^+]\text{I}^-$  was obtained as a green powder. Infrared frequencies are reported in Table I.

**$^{13}\text{CO}$  Exchange.** Ten milligrams of  $\text{Co}(\text{CO})_3\text{L}_2$  dissolved in 8 mL of THF was loaded in a break-seal flask containing 100 mL of  $^{13}\text{CO}$  at room temperature and 1 atm. After the seal was broken the system was stirred for 3 days. Infrared frequencies are reported in Table I.

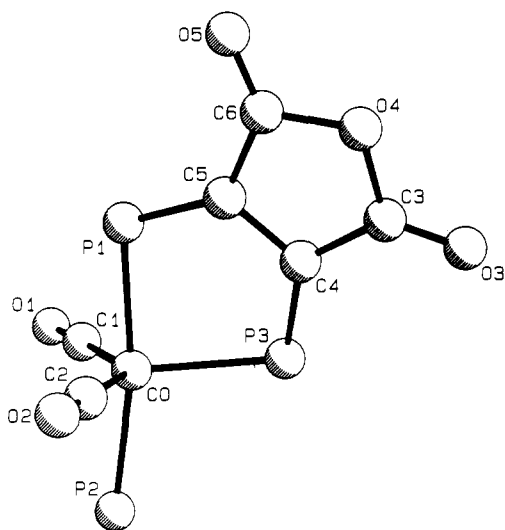
**Kinetics.** These studies were carried out with the aid of a Beckman DU-7 UV-visible spectrophotometer equipped with a thermostated cell holder with a temperature precision of 0.25 °C. The disappearance of  $\text{Co}(\text{CO})_3\text{L}_2$  in  $\text{CH}_2\text{Cl}_2$  was monitored at 758 nm. For reactions with  $\text{PPh}_3$ , the reaction vessel consisted of a Pyrex cell with a side arm at the top. The solution containing  $\text{Co}(\text{CO})_3\text{L}_2$  was placed in the side arm and the solution containing  $\text{PPh}_3$  was placed in the cell. The cell was stoppered with a Teflon valve and brought out of the glovebox. The two solutions were mixed immediately before each measurement. In the case of other phosphine or phosphite ligands, a double-valve, two-compartment cell was used. (A sketch is provided in the Supplementary Material.) The double-valve arrangement was necessary to prevent escape of phosphine or phosphite into the glovebox atmosphere and subsequent poisoning of the oxygen-scrubbing catalyst. For reactions carried out at 25 °C or above, rate constants were obtained directly from the slope of  $\ln(A_t - A_\infty)$  vs  $t$  plots. For reactions at temperatures lower than 25 °C, final absorbances were difficult to obtain. Rate constants were obtained by the method described in Moore and Pearson.<sup>16</sup>

**Electrochemistry.** Electrochemical experiments were performed with a PAR Electrochemical Station including a Model 175 Universal Programmer, a Model 173 Potentiostat-Galvanostat, and a Model 174 A Polarographic Analyzer. The recordings were made with a Gould Model 3054 XY-recorder. All experiments were performed inside the drybox. The electrolyte used was tetra-*n*-butylammonium perchlorate (TBAP), which was purchased from Fisher and recrystallized twice from spectrum-grade ethyl acetate/isooctane, and then dried under high vacuum at 40 °C for 1 day.

Cyclic voltammetry was performed with a three-electrode cell. The auxiliary electrode consisted of a 24-gauge wire coiled around the Pt bead working electrode which we made from a 1 cm long 18-gauge Pt wire with one end melted into the form of a spherical bead. This Pt wire was sealed into the end of a 10 cm long Flint glass tube (4 mm in diameter). A copper wire was then inserted into the glass tube and connected to the Pt wire with a small amount of solder. A 24-gauge Ag wire was used as a quasireference electrode separated from the test solution by a fine glass frit and a Luggin capillary.

Potentials were calibrated against the ferrocene/ferrocenium ( $\text{Fe}/\text{Fe}^+$ ) couple by adding ferrocene as an internal standard directly to the solution under investigation and are referred to the aqueous saturated calomel electrode (SCE). The redox potential of  $\text{Fe}/\text{Fe}^+$  in THF was  $0.530 \pm 0.003$  V vs SCE. TBAP (0.1 M) was used as the supporting electrolyte

(16) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley-Interscience: New York, 1981; p 70.



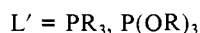
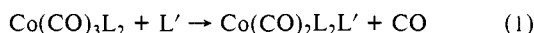
**Figure 1.** Crystal structure of the  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  complex [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride]. The phenyl groups on the P atoms have been removed for clarity.

with  $\approx 10^{-4}$  M of the substances under investigation.

**Other Physical Measurements.** Infrared spectra were obtained with a Nicolet 5DBX FT-IR spectrometer. UV/visible spectra were recorded on a Beckman DU-7 spectrophotometer. ESR spectra were obtained with a Varian E-3 EPR spectrometer or Varian E-line Century Series EPR spectrometer.

## Results and Discussion

**Substitution Reactions of the  $\text{Co}(\text{CO})_3\text{L}_2$  Complex.**  $\text{Co}(\text{CO})_3\text{L}_2$  reacts thermally with phosphine and phosphite ligands in  $\text{CH}_2\text{Cl}_2$  to form monosubstituted products of the type  $\text{Co}(\text{CO})_2\text{L}_2\text{L}'$  (eq 1). The products were characterized by elemental analysis,



infrared spectroscopy, cyclic voltammetry, and in the case of  $\text{L}' = \text{PPh}_3$  X-ray diffraction (Figure 1).<sup>17</sup> Table I summarizes the infrared frequencies of the terminal CO ligands and the carbonyl groups in the chelating  $\text{L}_2$  ligand for the  $\text{Co}(\text{CO})_2\text{L}_2\text{L}'$  complexes, free  $\text{L}_2$ , and  $\text{Co}(\text{CO})_3\text{L}_2$ . In general, the replacement of CO by  $\text{L}'$  lowers the stretching frequencies of both types of CO; among the substituted complexes, the extent to which the frequencies are lowered is parallel to the electron donating ability<sup>6,18</sup> of the ligands:  $\text{P}(n\text{-Bu})_3 > \text{PPh}_3 > \text{P}(\text{OMe})_3 > \text{P}(\text{OPh})_3$ . This result is an example of the familiar phenomenon that increased electron donation to a metal increases the amount of metal-ligand  $\pi$ -back-bonding.<sup>19</sup> Similar arguments explain the ESR data presented in a later section.

**Reactivity of the  $\text{Co}(\text{CO})_3\text{L}_2^+$  Complex.** For comparison purposes, we attempted substitution reactions on the 18-electron  $\text{Co}(\text{CO})_3\text{L}_2^+$  complex. Under the same conditions as with the neutral 19-electron complex, substitution of the  $\text{Co}(\text{CO})_3\text{L}_2^+$  complex did not occur. In a typical experiment, addition of  $\text{PPh}_3$  [ $4 \times 10^{-2}$  M] to a  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{Co}(\text{CO})_3\text{L}_2^+]\text{I}^-$  [ $10^{-2}$  M] at room temperature gave no reaction even after 24 h. Similar results were obtained with other nucleophiles. Consistent with

(17) The complex crystallizes in the monoclinic space group  $P2_1/n$  with cell dimensions  $a = 10.367$  (4) Å,  $b = 24.096$  (5) Å,  $c = 18.417$  (3) Å,  $\beta = 94.07$  (2)°, and  $Z = 4$ . The structure was refined to  $R = 0.074$  for 2063 data with  $F^2 > 3.0\sigma(F^2)$ . In contrast to the square-pyramidal geometry of the unsubstituted parent complex  $\text{Co}(\text{CO})_3\text{L}_2$ , the substituted complex crystallizes as a distorted trigonal bipyramid with the atoms C1, C2, and P3 defining the equatorial plane and the atoms P1 and P2 occupying the axial positions. Important angles are C1-Co-P1, 87.4 (6)°, C1-Co-P2, 87.2 (6)°, C1-Co-P3, 121.2 (7)°, and P1-Co-P2, 170.2 (2)°; distortions within the equatorial plane are reflected by the angles C1-Co-C2, 134 (1)°, and C2-Co-P3, 103.8 (8)°. The bond distances are similar to those of the parent complex.<sup>8</sup>

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**Table II.** Electrochemical Data<sup>a</sup>

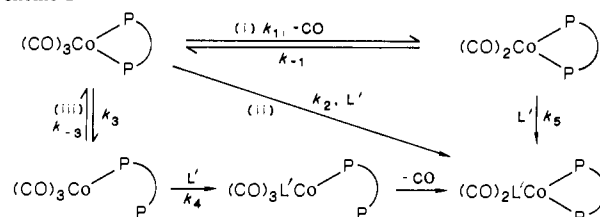
complex	$E_{1/2(1)}^b$	$I_{pa1}/I_{pc1}$	$E_{1/2(2)}^b$	$I_{pa2}/I_{pc2}$
$\text{L}_2$	-0.76	$\sim 1$	-1.52	$\sim 0.5$
$\text{Co}(\text{CO})_3\text{L}_2$	+0.07	$\sim 1$	-0.74	$\sim 0.65$
$\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$	-0.07	$\sim 1$	-0.82	$\sim 0.29$
$[\text{NBu}_4][\text{Co}(\text{CO})_2\text{L}_2\text{I}^-]$	-0.29	$\sim 1.2$	<i>c</i>	<i>c</i>

<sup>a</sup>In THF with 0.1 M TBAP at 100 mV/s. <sup>b</sup>Volts vs SCE. <sup>c</sup>Irreversible,  $E_{pc} = -1.33$  V vs SCE.

**Table III.** Rate Constants for Substitution of  $\text{Co}(\text{CO})_3\text{L}_2$  ( $1.40 \times 10^{-3}$  M) at 25 °C in  $\text{CH}_2\text{Cl}_2$  as a Function of  $[\text{PPh}_3]$

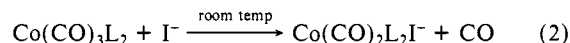
$[\text{PPh}_3]$ , M	0.148	0.296	0.371	0.445	0.556	0.704
$k$ ( $\text{s}^{-1}$ ) $\times 10^3$	5.48	5.45	5.47	5.52	5.42	5.50

**Scheme I**



these results, we note that substitution reactions of 18-electron organometallic cobalt complexes generally require quite vigorous conditions ( $T > 80$  °C).<sup>20</sup> Our conclusion is that the lability of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex is attributable to the extra electron.

It is noteworthy that whereas  $\text{Co}(\text{CO})_3\text{L}_2^+$  does not react with iodide, the corresponding  $\text{Co}(\text{CO})_3\text{L}_2$  complex reacted readily with  $[\text{NBu}_4^+]\text{I}^-$  at room temperature to give a substituted complex we formulate as  $\text{Co}(\text{CO})_2\text{L}_2\text{I}^-$ .



The infrared spectrum of the complex (Table I) shows  $\nu(\text{C}\equiv\text{O})$  bands at lower frequencies than the phosphine- or phosphite-substituted complexes, consistent with an electron-rich Co center. The  $[\text{NBu}_4^+][\text{Co}(\text{CO})_2\text{L}_2\text{I}^-]$  complex oxidizes at -0.29 V vs SCE, showing a much stronger reducing ability than  $\text{Co}(\text{CO})_3\text{L}_2$  or the substituted complexes (Table II).

**Kinetics and Mechanism of the  $\text{Co}(\text{CO})_3\text{L}_2$  Substitution Reactions.** Three possible pathways for the substitution reaction are outlined in Scheme I. Pathway (i) is a dissociatively activated mechanism in which CO dissociates reversibly to give a four-coordinate intermediate, followed by reaction with  $\text{L}'$  to give the products. Pathway (ii) is an associatively activated pathway, and pathway (iii) is a dissociatively activated mechanism involving initial dissociation of one end of the chelate ligand followed by subsequent steps. The rate expression incorporating all three pathways is as follows:

$$-\frac{d[\text{S}]}{dt} = \frac{k_1 k_5 [\text{S}][\text{L}']}{k_{-1}[\text{CO}] + k_5[\text{L}']} + k_2 [\text{S}][\text{L}'] + \frac{k_3 k_4 [\text{S}][\text{L}']}{k_{-3} + k_4[\text{L}']} \quad (3)$$

$$\text{where } \text{S} = \text{Co}(\text{CO})_3\text{L}_2$$

The reactions were monitored by following the absorbance decay of  $\text{Co}(\text{CO})_3\text{L}_2$  at 758 nm in  $\text{CH}_2\text{Cl}_2$ . Linear plots of  $-\ln \{(A_t - A_\infty)/(A_0 - A_\infty)\}$  vs  $t$  were obtained, indicating a (pseudo-) first-order reaction. The data in Table III show that the rate constant is independent of ligand concentration, even at very low concentrations of  $\text{L}'$ . This result eliminates from consideration the associatively activated mechanism [pathway (ii)].<sup>21</sup> Note, however, that these data cannot differentiate between the two dissociatively activated pathways because the rate expression for

(20) For example, the substitution reactions of  $\text{Co}(\text{CO})_3(\text{P}(\text{OMe})_2)^+$  with phosphines and phosphites required reaction temperatures in excess of 80 °C. See: Attali, S.; Pollblanc, R. *Inorg. Chim. Acta* **1972**, *6*, 475-479. For comparison purposes, we note that  $\text{Co}(\text{CO})_3\text{L}_2$  decomposes quickly in benzene solution above 50 °C.

(21) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1974.

**Table IV.** Rate Constants for the Substitution of  $\text{Co}(\text{CO})_3\text{L}_2$  ( $1.4 \times 10^{-3}$  M) by  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$  as a Function of Temperature

$t$ ( $^\circ\text{C}$ )	$k$ ( $\text{s}^{-1}$ ) ( $\times 10^4$ ) <sup>a</sup>
10.0	$5.98 \pm 0.17$
15.0	$12.6 \pm 0.4$
20.0	$26.7 \pm 0.3$
25.0	$54.7 \pm 0.3$
30.0	$102 \pm 1$

<sup>a</sup>The rates were independent of  $\text{PPh}_3$  concentration. The rate constants shown are the average of at least five determinations. Typical concentration ranges used for  $\text{PPh}_3$  are found in Table III.

**Table V.** Rate Constants for the Substitution of  $\text{Co}(\text{CO})_3\text{L}_2$  ( $1.4 \times 10^{-3}$  M) by Various Ligands<sup>a</sup> in  $\text{CH}_2\text{Cl}_2$  at 25  $^\circ\text{C}$ 

L	$k$ ( $\text{s}^{-1}$ ) ( $\times 10^3$ ) <sup>a</sup>
$\text{PPh}_3$	$5.47 \pm 0.03$
$\text{P}(\text{OPh})_3$	$5.18 \pm 0.18$
$\text{PMePh}_2$	$5.20 \pm 0.13$
$\text{PBu}_3$	$5.58 \pm 0.08$
$\text{P}(\text{OMe})_3$	$5.03 \pm 0.08$

<sup>a</sup>The rates were independent of ligand concentrations. The rate constants shown are the average of at least five determinations. Typical ligand concentration ranges are found in Table III.

either pathway can be reduced to a simple first-order expression under the appropriate conditions. Thus, for pathway (iii) (the ring-opening pathway) the rate is given by rate =  $k_3[\text{S}]$  if  $k_4[\text{L}'] \gg k_{-3}$ . However, this inequality is probably not valid in this reaction (or many other related reactions of chelated complexes).<sup>22</sup> In terms of electron-donating ability and steric size, the uncoordinated end of the bidentate ligand and the entering ligand are comparable to each other. In addition, the rigidity of the chelate ligand (caused by the carbon-carbon double bond) assures that the dissociated phosphorus of the bidentate ligand has a high "effective concentration" in the vicinity of the metal center. Thus, a strong argument can be made that  $k_4[\text{L}']$  is much smaller than  $k_{-3}$ . In fact, in numerous studies it has been shown that the "competition ratio",  $k_{-3}/k_4$ , is generally much greater than one.<sup>22</sup> The conclusion is that  $k_{-3}$  is probably much greater than  $k_4[\text{L}']$ , and, therefore, if pathway (iii) were followed then the rate would be first order in  $[\text{L}']$ .

Assume, however, that pathway (iii) is occurring but that  $k_{-3}$  is anomalously small so that the reaction rate is simply first order in  $[\text{S}]$ , as found. This assumption was tested by lowering the concentration of both the entering ligand ( $10^{-3}$  M) and the complex ( $10^{-3}$  M) in order to decrease the magnitude of  $k_4[\text{L}']$ . Under these conditions, the dependence of the rate on the ligand concentration would be more obvious. However, first-order rate constants essentially identical with those in Table III were obtained in these experiments. The ring-opening mechanism can, therefore, be reasonably excluded, and the data are thus consistent only with the dissociatively activated route involving CO loss in pathway (i).<sup>23</sup>

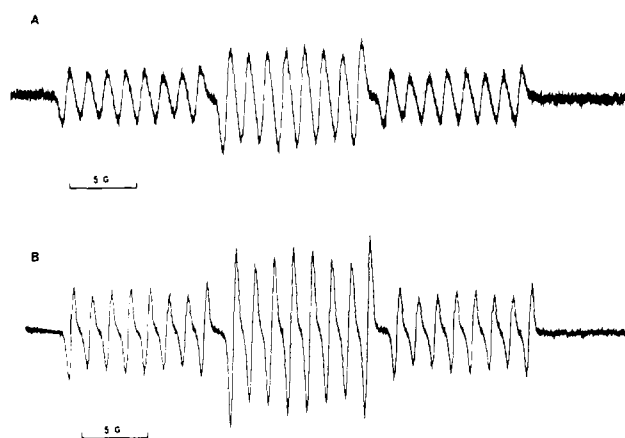
Table IV lists the rate constants obtained at different temperatures. A plot of  $-\ln(k/T)$  vs  $(1/T)$  yielded the following activation parameters:  $\Delta H^\ddagger = 23.8 \pm 0.6$  kcal/mol;  $\Delta S^\ddagger = 11.1 \pm 2.2$  cal mol<sup>-1</sup> K<sup>-1</sup>. The positive entropy is consistent with the dissociative pathway; the enthalpy can be roughly viewed as the Co-CO bond energy.

As a further test of the proposed dissociative pathway, other ligands were reacted with  $\text{Co}(\text{CO})_3\text{L}_2$ . As shown in Table V,

(22) (a) Cohen, M. A.; Brown, T. L. *Inorg. Chem.* **1976**, *15*, 1417-1423. (b) Dobson, R.; Houk, L. W. *Inorg. Chim. Acta* **1967**, *1*, 287-293. (c) Dobson, G. R.; Asali, K. J.; Marshall, J. L.; McDaniel, C. R., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 8100-8102. (d) Faber, G. C.; Dobson, G. R. *Inorg. Chim. Acta* **1968**, *2*, 479-481.

(23) Although the exact rate expression for a dissociatively activated Co-loss pathway is given by the first term in eq 3, in practice this expression nearly always reduces to the simple first-order expression rate =  $k[\text{complex}]$  because  $k_3[\text{L}'] \gg k_{-3}[\text{CO}]$ . For discussions of the kinetics of dissociatively activated metal carbonyl complex substitution reactions, see ref 24 and the extensive list of references therein.

(24) (a) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557-599. (b) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173-216.

**Figure 2.** ESR spectra of the (a)  $\text{Co}^{13}\text{CO}_3\text{L}_2$  and (b)  $\text{Co}(\text{CO})_3\text{L}_2$  complexes in THF at 25  $^\circ\text{C}$ .**Table VI.** ESR Coupling Constants<sup>a</sup>

complex	$g$	$A_p$ (G)	$A_{\text{Co}}$ (G)
$\text{L}_2^-$ <sup>b</sup>	2.0077	3.10	
$\text{Co}(\text{CO})_3\text{L}_2$ <sup>c</sup>	2.0041	9.72	1.05
$\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ <sup>c</sup>	2.0034	8.22	0.15

<sup>a</sup>The magnetic field was calibrated with di-*tert*-butyl nitroxide. <sup>b</sup>THF. <sup>c</sup> $\text{CH}_2\text{Cl}_2$ .

similar rate constants were obtained with all of the ligands, a result consistent with a dissociatively activated mechanism.<sup>21</sup>

**The ESR Spectrum of  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ .** The  $g$  values and coupling constants in the ESR spectra of the  $\text{Co}(\text{CO})_3\text{L}_2$ ,  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ , and  $\text{L}_2^-$  complexes are reported in Table VI. The coupling constants are a sensitive way to probe the electronic structure of the substituted complex. Thus, the small phosphorus coupling constant of the reduced ligand ( $A_p = 3.10$  G) indicates that the odd electron density is polarized toward the oxygen atoms. In contrast, the odd electron has a much greater interaction with the phosphorus atoms in the complexes due to the delocalization of the electron onto the  $\text{Co}(\text{CO})_2\text{L}'$  ( $\text{L}' = \text{CO}$  or  $\text{PPh}_3$ ) portion of the molecule. As a result, the phosphorus coupling constants are larger ( $A_p = 8.22; 9.72$  G). Note that the Co atom is more electron-rich in the substituted complex than in the unsubstituted complex; smaller  $A_{\text{Co}}$  and  $A_p$  values for  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  than  $\text{Co}(\text{CO})_3\text{L}_2$  are indicative of less delocalization onto the more electron-rich  $\text{Co}(\text{CO})_2\text{PPh}_3$  moiety. A complete interpretation of the ESR spectra will be reported in a separate publication.<sup>25</sup>

**Electrochemistry of  $\text{L}_2$ ,  $\text{Co}(\text{CO})_3\text{L}_2$ , and  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ .** As mentioned above, the stability of the  $\text{Co}(\text{CO})_3\text{L}_2$  and  $\text{Co}(\text{CO})_2\text{L}_2\text{L}'$  complexes can be attributed to the ability of the  $\text{L}_2$  ligand to delocalize the extra electron. This ability of the ligand to accept an electron without decomposition is reflected in the electrochemistry of the uncoordinated ligand and its complexes. The data, summarized in Table II, show that  $\text{Co}(\text{CO})_3\text{L}_2$  is oxidized at a much higher potential than the one-electron reduced free ligand. (Coulometry showed that the oxidation is a one-electron process.) The higher, more positive, oxidation potential of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex relative to  $\text{L}_2^-$  can be attributed to the stabilization of the odd electron caused by interaction with and delocalization onto the Co atom. Simple electrostatic arguments also lead one to predict a more positive potential for the  $\text{Co}(\text{CO})_3\text{L}_2$  complex compared to  $\text{L}_2^-$ .<sup>26</sup>

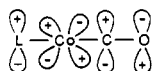
**Concluding Remarks, Why Is the  $\text{Co}(\text{CO})_3\text{L}_2$  Complex Labile?** The unreactivity of the 18-electron  $\text{Co}(\text{CO})_3\text{L}_2^+$  complex strongly suggests that the reactivity of the 19-electron  $\text{Co}(\text{CO})_3\text{L}_2$  complex

(25) Mao, F.; Tyler, D. R., manuscript in preparation.

(26) According to the potentials in Table IV, the  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  complex should reduce ferrocenium. Indeed, when  $[\text{Cp}_2\text{Fe}^+][\text{FeCl}_4^-]$  (1 mL;  $6.0 \times 10^{-2}$  M) was mixed with  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  (1 mL;  $2.0 \times 10^{-2}$  M), a product formed with CO stretching bands at 2029 (s), 1979 (vs), 1850 (w), and 1783 (s)  $\text{cm}^{-1}$ . The blue shift of these bands relative to  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$  is consistent with oxidation of the complex to  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3^+$ .

can be attributed to the extra electron. To account for the lability of the 19-electron complex, we propose there is a delocalization of the odd electron into an orbital that is Co-CO antibonding ( $\pi^*$ );<sup>27</sup> occupation of these orbitals will weaken the Co-CO bond and labilize the complex toward CO dissociation. The ESR spectrum of the  $\text{Co}(\text{CO})_3\text{L}_2$  complex is consistent with this hypothesis. Spectra a and b of Figure 2 show the ESR spectra of the  $\text{Co}(\text{CO})_3\text{L}_2$  and  $\text{Co}(\text{CO})_3\text{L}_2$  complexes, run under identical conditions. The spectra are nearly identical, but note the line broadening in the  $\text{Co}(\text{CO})_3\text{L}_2$  spectrum. As tested by varying the conditions, this line broadening was not caused by the instrument, the concentration of the compound, or the presence of oxygen, and therefore it must reflect a slight electronic coupling to the  $^{13}\text{C}$  atoms. Note that only a slight weakening of the Co-CO bond is required for labilization. Although exact numbers are not available, the 24 kcal/mol enthalpy for the Co-CO bond from  $\Delta H^\ddagger$  is probably about 5 to 10 kcal/mol less than typical Co-CO bond energies of 18-electron complexes.<sup>28</sup> A 5 to 10 kcal/mol decrease in activation energy corresponds to an increase in the rate constant for dissociation of about  $10^4$ - $10^8$ .<sup>29</sup> Thus, the delocalization of the 19th electron and the concomitant decrease in the Co-CO bond energy (as reflected in  $\Delta H^\ddagger$ ) give the Co-

(27) The molecular orbital containing the odd electron would be primarily an  $\text{L}_2 \pi^*$  orbital mixed with an antibonding combination of a Co d orbital and a CO ( $\pi^*$ ) orbital:



The Co/CO portion of this MO is the antibonding combination of the Co and CO ( $\pi^*$ ) orbitals used in "back-bonding."

(28) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71-110.

(29) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 211.

$(\text{CO})_3\text{L}_2$  complex its substitutional lability.

The conclusion above can be extended to other 19-electron complexes. Note that in type I complexes<sup>9</sup> [e.g.,  $\text{Fe}(\text{CO})_5$ ] there is a greater likelihood that the extra electron will occupy a metal-ligand antibonding orbital because low-energy  $\pi^*$  ligand orbitals are not available [as in  $\text{Co}(\text{CO})_3\text{L}_2$  and other type III complexes]. Thus, the M-L bond will be significantly weakened in these complexes and fast dissociative processes are predicted and apparently observed.<sup>30</sup> The point is that if the  $\text{Co}(\text{CO})_3\text{L}_2$  complex, especially chosen because it might undergo associatively activated substitution, reacts dissociatively, then certainly other 19-electron complexes are also going to react dissociatively.

**Acknowledgment.** This work was supported by the National Science Foundation. The Sloan Foundation is acknowledged for a fellowship to D.R.T. Drs. P. Krusic, W. Kaim, and P. Rieger are thanked for helpful discussions.

**Supplementary Material Available:** A description and tables giving the details of crystallographic data collection, bond distances and angles, intra- and intermolecular distances and angles, positional parameters, and thermal parameters for  $\text{Co}(\text{CO})_2\text{L}_2\text{PPh}_3$ , a plot of  $-\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$  vs time for the reaction of  $\text{Co}(\text{CO})_3\text{L}_2$  with  $\text{PPh}_3$ , a plot of  $-\ln (k/T)$  vs  $T^{-1}$  for the reaction of  $\text{Co}(\text{CO})_3\text{L}_2$  with  $\text{PPh}_3$ , and a sketch of the double-valve reaction cell used for the kinetics studies (22 pages); listings of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

(30) Examples of reactions in which the dissociative behavior of 19-electron complexes can be inferred are found in: (a) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879-886. (b) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 749-752. (c) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817-819. (d) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

## A Study of Asymmetric Induction during the Addition of Enolate Nucleophiles, Having Sulfoximine Chiral Auxiliaries, to Diene-Molybdenum and Dienyliron Complexes

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**Abstract:** Asymmetric induction as high as 90% ee was obtained during the reaction of enolates, derived from optically pure sulfoximinyl esters of type **16**, with the cycloheptadiene-Mo(CO)<sub>2</sub>Cp cation. Lower, but still significant asymmetric induction was observed during the reaction of these enolates with cyclohexadiene-Mo(CO)<sub>2</sub>Cp, cycloheptadienyl-Fe(CO)<sub>2</sub>P(OPh)<sub>3</sub>, and cyclohexadienyl-Fe(CO)<sub>3</sub> complexes. It was established that enolates derived from the (-)-(R)-sulfoximine preferentially add to the *pro-R* terminus of the diene and dienyl complexes, by determination of absolute stereochemistry of derived alcohols using Mosher's method and by X-ray crystal structure determination of a major adduct **33** from reaction with cyclohexadiene-Mo(CO)<sub>2</sub>Cp hexafluorophosphate. Desulfonylation of the sulfoximine ester adducts gave enantiomerically enriched monoester derivatives **21-24**, which could, in some cases, be further functionalized by hydride abstraction and second nucleophile addition. An attempt is made in this paper to rationalize the observed stereoselectivity on the basis of Seebach's topological rule for somewhat related Michael additions of enamines to nitroolefins.

The control of stereochemistry during carbon-carbon bond formation is one of the central issues in contemporary organic synthesis.<sup>2</sup> The definition of relative stereochemistry during the attachment of substituents to six- and seven-membered rings, with

a transition-metal moiety as a stereodirecting template, is currently being studied in our laboratory and has led to new methodology for the construction of subunits of potential value in natural products synthesis.<sup>3</sup> For example, the cyclohexadiene-Mo-

(1) (a) Case Western Reserve University. (b) University of Toledo.  
(2) Morrison, J. D. *Asymmetric Synthesis*; Academic: Orlando, FL, 1983-1985; Vol. 1-5.

(3) (a) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. (b) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276. (c) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. Pearson, A. J.; Ray, T. *Tetrahedron* **1985**, *41*, 5765.