Contribution from the Department of Chemistry,
University of Miami, Coral Gables, Florida 33124

Heats of Reaction of $RMo(CO)_3C_5H_5$ (R = H, CH_3, C_2H_5) with Phosphines and Phosphites: Thermodynamic Study of the CO-Insertion Reaction

Steven P. Nolan, Ramon Lopez de la Vega, Shakti L. Mukerjee, and Carl D. Hoff*

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The heats of reaction of $HMo(CO)_3C_5H_5$ with a series of phosphines and phosphites, producing $HMo(CO)_2(PR_3)C_5H_5$, have been measured by solution calorimetry. The order of relative Mo–PR_3 bond strengths, $PMe_3 \approx P\text{-}n\text{-}Bu_3 > P(OMe)_3 > PMe_2Ph > PMePh_2$, closely resembles that determined earlier for the complexes *fac*-$(PR_3)_3Mo(CO)_3$. The heats of reaction of $RMo(CO)_3C_5H_5$ (R = CH_3, C_2H_5), producing the phosphine-substituted acyl complexes $RC(O)Mo(CO)_2(PR_3)C_5H_5$, were also studied thermochemically. This reaction can be viewed as involving both phosphine substitution and carbonyl insertion. With use of the enthalpy of phosphine substitution of $HMo(CO)_3C_5H_5$ as a model, the enthalpy of carbonyl insertion is calculated. For both R = CH_3 and R = C_2H_5 the carbonyl-insertion reaction is favored for more basic phosphines with a difference of about 2 kcal/mol between PMe_3 (most favored) and $P(OMe)_3$ (least favored). Carbonyl insertion into the Mo–Et bond is about 3 kcal/mol more favorable than into the Mo–CH_3 bond. Attempts to prepare the unsubstituted acyls $RC(O)Mo(CO)_3C_5H_5$ by carbonylation of the alkyls in THF led to facile reductive elimination of $RC(O)C_5H_5$ (35 °C, 1 atm of CO), producing $Mo(CO)_6$. Migration of the acyl group to the coordinated cyclopentadienyl ring in the presence of CO pressure and thermodynamic instability in the absence of CO pressure explain the lack of success in preparing $RC(O)Mo(CO)_3C_5H_5$ for simple alkyl groups.

Introduction

Insertion of carbon monoxide into a metal–alkyl bond to form a metal–acyl complex is one of the fundamental steps of hydroformylation and related catalytic processes.[1] Detailed theoretical and mechanistic studies of carbonyl insertion on a number of transition metals have appeared in the literature;[2] however, relatively little thermodynamic data are available for this reaction. Such information is important since under catalytic conditions preequilibria may be established where the thermodynamic properties of the intermediates would be important in determining the overall reaction profile.

Four general approaches have been used to obtain thermodynamic data for the carbonyl-insertion reaction:[2] (i) temperature variation of the equilibrium constant; (ii) differential scanning calorimetry; (iii) high-temperature thermal decomposition and halogenation reactions; (iv) solution calorimetric measurements. Representative examples of these methods are discussed below.

The majority of thermochemical data have been generated through temperature variation of the equilibrium constant. Perhaps the best example of this is the original study by Cotton and Calderazzo of reaction 1.[3] The equilibrium constant for this

$$H_3CMn(CO)_5 + CO \rightleftarrows H_3CC(O)Mn(CO)_5 \qquad (1)$$

reaction in the range 20–50 °C was evaluated in several solvents. In bis(β-ethoxyethyl) ether at 30 °C the thermodynamic values $\Delta H = -12.6$ kcal/mol and $\Delta S = -30$ eu were calculated. A recent general estimate for the loss of rotational and translational entropy of CO gas in the carbonyl-insertion reaction was 36 eu.[7b] In the temperature range 25–100 °C this corresponds to 10–14 kcal/mol, which must be overcome by the enthalpy term to obtain net thermodynamic stability. This illustrates the close balance of the favorable enthalpy and unfavorable entropy for reaction 1. A small change in the enthalpy of reaction could have a pronounced effect in the position of the acyl/alkyl equilibrium.

A number of additional studies of equilibria similar to eq 1 have been reported.[4] It is not always possible to use this method since a single equilibrium over a suitable temperature range is required. For analytical reasons it also requires that the net free energy change be relatively small, i.e. a system that is not driven too far to either side.

Differential scanning calorimetry of the solid-state reaction shown in eq 2 yielded an enthalpy of decarbonylation of ΔH = 8.1 kcal/mol in the temperature range 172–222 °C.[5] Several

$$(PPh_3)_2(Cl)PtC(O)C_6H_5 \rightarrow (PPh_3)_2(Cl)PtC_6H_5 + CO \qquad (2)$$

related compounds were investigated, and a number of other studies have appeared in the literature.[6] The major drawback to this approach is the need for clean decomposition of the reactants. Great care must be taken to analyze the solid products, since at high temperatures organometallic compounds can decompose through a number of different pathways.

High-temperature thermal decomposition and halogenation provide, in principle, a general approach to the thermochemistry of carbonyl insertion. Data from these techniques have been used to calculate the enthalpy of eq 1 for R = CH_3, CF_3, and C_6H_5.[7] The values obtained indicate decreasing enthalpy of CO insertion for C_6H_5 (15.1 ± 1.9 kcal/mol), CH_3 (12.9 ± 1.9 kcal/mol), and CF_3 (2.86 ± 1.7 kcal/mol). These values are in reasonable agreement with the original work of Cotton and Calderazzo.[3] The thermal decomposition and iodination reactions are often determined at temperatures in excess of 200 °C. Under these conditions side reactions can occur, making determination of the exact stoichiometry of the reaction under study difficult for complex molecules.[8]

Reactions in solution are generally easier to monitor than the solid–solid transformations in DSC or the products of high-temperature microcalorimetry. The only solution calorimetric study we have found in the literature in relation to carbonyl insertion is that of Yoneda and Blake.[9] The enthalpy change of CO

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(1) (a) Henrici-Olive, G.; Olive, S. "The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide"; Springer-Verlag: New York, 1984. (b) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*. (c) Tkatchenko, I. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982.

(2) (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *31*, 195. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(3) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 31.

(4) (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (b) Moloy, K. J.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (c) Lee, C.; James, B. R.; Nelson, D. R.; Haller, R. T. *Organometallics* **1984**, *3*, 1360.

(5) Ashcroft, S. J.; Maddock, A.; Beech, G. *J. Chem. Soc., Dalton Trans.* **1974**, 462.

(6) (a) Blake, D. M.; Winkelman, A.; Chung, Y. L. *Inorg. Chem.* **1975**, *14*, 1327. (b) Blake, D. M.; deFaller, J.; Chung, Y. L.; Winkelman, A. *J. Am. Chem. Soc.* **1975**, *96*, 5569.

(7) (a) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J. B.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1981**, *1*, 1166.

(8) Results of solution calorimetric studies of cycloheptatriene complexes of Cr[10a] and Mo[10b] have disagreed with those obtained through high-temperature microcalorimetry.

(9) (a) Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67. (b) Yoneda, G.; Blake, D. M. *J. Organomet. Chem.* **1980**, *190*, C71.

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Table I. Heats of Reactions,[a] Heats of Solution,[a] and Infrared Data[b] for $RMo(CO)_3C_5H_5$

	R = H		R = Me		R = Et	
phosphine	ΔH_{reacn}	IR	ΔH_{reacn}	IR	ΔH_{reacn}	IR
PMe_3	−3.3 (±0.3)	1932 1850	−17.1 (±0.3)	1929 1845 1619	−17.9 (±0.3)	1927 1843 1618
P-*n*-Bu_3	−2.9 (±0.1)	1931 1852	−16.0 (±0.3)	1927 1845 1621	−17.2 (±0.1)	1925 1842 1629
$P(OMe)_3$	−2.5 (±0.1)	1954 1878	−14.6 (±0.1)	1947 1869 1632	−15.2 (±0.3)	1945 1866 1630
PMe_2Ph	−1.7 (±0.2)	1935 1853	−14.5 (±0.2)	1930 1846 1621	−15.1 (±0.1)	1929 1844 1620
$PMePh_2$	+0.5 (±0.1)	1936 1855	−11.6 (±0.2)	1933 1851 1624	−13.6 (±0.1)	1931 1849 1623
PPh_3	+0.9 (±0.7)	1940 1862	*c*	1937 1857 1626	−10.8 (±0.4)	1935 1855 1624
soln in THF	+2.1 (±0.1)	2022 1935	+2.6 (±0.1)	2018 1927	+4.6 (±0.1)	2010 1924

[a] Reaction of solid complexes as described in Experimental Section; R = H refers to reaction 10, R = Me, Et refers to reaction 5. All units are in kcal/mol. [b] IR data in THF for terminal CO and acyl groups in cm^{-1}. [c] Reaction did not go to completion.

Table II. Enthalpies of CO Substitution by Phosphines for $TolMo(CO)_3$ and $HMo(CO)_3C_5H_5$[a]

phosphine	$\Delta H_{react}(tolMo(CO)_3)$	$\Delta H_{react}(HMo(CO)_3Cp)$	$^1/_3\Delta H_{exc}((PR_3)_3Mo(CO)_3)$[b]	$\Delta H_{exc}((HMoCO)_2(PR_3)Cp)$[c]
PMe_3	−47.1	−5.1	3.3	3.5
P(OMe)	−47.5	−4.6	3.4	3.0
P-*n*-Bu_3	−44.3	−5.0	2.4	3.4
PMe_2Ph	−43.8	−3.8	2.2	2.2
$PMePh_2$	−37.2	−1.6	0	0

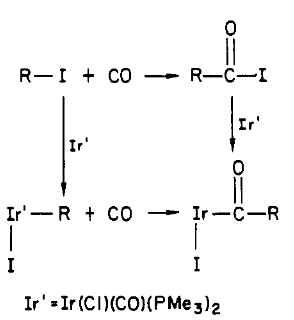
[a] All units in kcal/mol; tol = tolyl; Cp = cyclopentadienyl. [b] This refers to $^1/_3\Delta H$ for the reaction $(PMePh_2)_3Mo(CO)_3 + 3PR_3 \rightarrow (PR_3)_3Mo(CO)_3 + PMePh_2$; see text for further discussion. [c] This refers to ΔH for the reaction $HMo(CO)_2(PMePh_2)Cp + PR_3 \rightarrow HMo(CO)_2(PR_3)Cp + PMe_2Ph$; see text for further discussion.

Table III. Enthalpies of the Reaction $RMo(CO)_3C_5H_5 + PR_3 \rightarrow RC(O)Mo(CO)_2(PR_3)C_5H_5$: Calculated Enthalpies of CO Insertion and Infrared Data[a]

	R = Me			R = Et		
phosphine	ΔH_{react}	$\Delta H_{CO\ ins}$	acyl str	ΔH_{react}	$\Delta H_{CO\ ins}$	acyl str
PMe_3	19.9	14.8	1619	22.6	17.5	1618
P-*n*-Bu_3	19.1	14.1	1621	21.8	16.8	1619
PMe_2Ph	17.3	13.5	1621	19.7	15.9	1620
$PMePh_2$	14.4	12.8	1624	18.1	16.5	1623
PPh_3				15.4	16.3	1624
$P(OMe)_3$	17.4	12.8	1632	19.8	15.2	1630

[a] All ΔH values in kcal/mol; experimental error listed in Table I. IR data in cm^{-1} is ±1 cm^{-1}. [b] Calculated as described in text.

insertion on $Ir(Cl)(CO)(PMe_3)_2(R)(I)$ was determined through the use of the thermodynamic cycle



(3)

A value of −11.2 ± 3.4 kcal/mol was obtained for the enthalpy of carbonylation of the Ir(III) complex. The success of this method depended on the quantitative nature of the oxidative addition to the Ir(I) species of both methyl iodide and acetyl iodide. The major drawback to solution calorimetry is that it is difficult to generalize and each metal must be worked out individually. We have recently reported thermochemical studies of the group VI (6)[27] metals for arene exchange,[10a,b] ligand[10c,f] and phosphine exchange,[10d] and oxidative addition of hydrogen.[10e] We now report results for CO insertion in a series of organomolybdenum complexes.

Experimental Section

All manipulations were carried out under an argon atmosphere with use of standard Schlenk-tube techniques or in a glovebox purchased from Vacuum Atmospheres, Hawthorne, CA. Gas-uptake measurements and manipulations were done on a high-vacuum line of standard design.

The complexes $RMo(CO)_3C_5H_5$ (R = H, CH_3, C_2H_5) were prepared by standard procedures. Purification normally involved recrystallization from methylene chloride/heptane solution followed by high-vacuum sublimation. Only materials of high crystalline quality and spectroscopic purity were used in calorimetric measurements. Tetrahydrofuran was purified by distillation from calcium hydride followed by distillation from sodium benzophenone ketyl under argon. Phosphines and phosphites were purchased from Strem Chemical and typically purified by recrystallization or distillation prior to use. Infrared spectra were run in 0.1-

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(10) (a) Hoff, C. D. *J. Organomet. Chem.* **1983**, *246*, C53. (b) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201. (c) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357. (d) Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 215. (e) Hoff, C. D.; Nolan, S. P. *J. Organomet. Chem.* **1985**, *290*, 365. (f) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D., unpublished results.

mm KBr solution cells on a Perkin-Elmer 267 or 599 spectrometer. NMR spectra were obtained with a Varian FT-80A spectrometer.

Calorimetric Measurements. The heats of reaction were measured with a Setaram C-80 calorimetric, which has been described previously.[10e] A typical procedure is described for reaction of $EtMo(CO)_3C_5H_5$ and $P(OMe)_3$. The mixing cells of the C-80 were dried in an oven at 150 °C for several hours and then taken into the glovebox. A 0.15-g sample of $EtMo(CO)_3C_5H_5$ was weighed into the lower vessel of the mixing cell. The mixing cell was capped, loaded, and sealed with 1.5 mL of Hg. A solution of $P(OCH_3)_3$ in THF (25%) was prepared and 4 mL added to the cell. The sample cell was closed and the reference cell loaded in an identical fashion except no $EtMo(CO)_3C_5H_5$ was placed in the lower vessel. The cells were removed from the glovebox and loaded in the calorimeter. After thermal equilibration at 30 °C (about 2 h) the reaction was initiated by rotating the calorimeter. After the signal returned to base line (2–4 h) the recorder was stopped, the cells were removed, and an IR spectrum of the product revealed that the reaction was quantitative. There was no sign of decomposition in the clear yellow solution. Values of −15.2, −15.4, −14.6, and −15.7 kcal/mol were obtained for an average of -15.2 ± 0.3 kcal/mol.

The measured heat corresponds to the reaction

$$EtMo(CO)_3C_5H_5(cryst) + P(OMe)_3(soln) \rightarrow EtC(O)Mo(CO)_2(P(OMe)_3)C_5H_5(soln) \quad (4)$$

Data corresponding to this reaction are reported in Table I. The data in Tables II and III incorporate the heat of solution of $RMo(CO)_3C_5H_5$ ($R = H$, 2.1 ± 0.1 kcal/mol, $R = CH_3$, 2.6 ± 0.2 kcal/mol, $R = C_2H_5$, 4.6 ± 0.1 kcal/mol. In the case of $EtMo(CO)_3C_5H_5$ a value of $-15.2 - 4.6 = -19.8$ kcal/mol is obtained for the heat of reaction in solution. In the event that a new batch of complex was used, after purification its heat of solution and a previously determined heat of reaction were measured before its use in new reactions. This was done to reduce the chances that a complex whose IR and NMR spectra were identical with those of a previous sample would have a different enthalpy of formation due to a difference in crystal lattice energy.

Reaction of $Mo(CO)_6$ with PPh_2Me. The heat of this reaction was measured with the C-80 in the scanning mode in the temperature range 30–150 °C at a rate of 0.5 °C/min. The high-vacuum cells were cleaned and taken into the glovebox. Both the reference and sample cells were loaded with 0.200 g of $Mo(CO)_6$. A solution of diphenylmethylphosphine in bis(β-ethoxyethyl) ether (25%) was added to the sample cell and an equal amount of pure β(bis-ethoxyethyl) ether was added to the reference cell. The cells were closed, connected by high-vacuum tubing to an oil bubbler, taken out of the glovebox, and loaded into the calorimeter. After thermal equilibration (2 h) the temperature program was started. At about 80 °C bubbles of gas evolved from the bubbler and the thermogram began to deviate from the base line. At about 135 °C it returned to the base line and there was no apparent evolution of gas. After the samples were cooled back to room temperature, both cells were opened and infrared spectra were run on each sample. Neither cell showed signs of $Mo(CO)_6$ sublimation out of the cell. The infrared spectrum of the sample showed it to be a mixture of *cis*- and *trans*-$(PPh_2Me)_2Mo(CO)_4$ with a trace of $(PPh_2Me)Mo(CO)_5$, but no $Mo(CO)_6$ or $(PPh_2Me)_3Mo(CO)_3$ was present. There was no sign of thermal decomposition or oxidation in either cell. The value -1.6 ± 0.4 kcal/mol is the average of three separate determinations.

Reaction of $RMo(CO)_3C_5H_5$ with CO. a. High-Vacuum Line. Reaction of $EtMo(CO)_3C_5H_5$ and CO was studied on a high-vacuum line equipped with a Toepler pump in order to determine the number of moles of CO taken up in this reaction. Research grade CO was further purified by storage over a solution of Na/benzophenone in THF prior to use. A solid sample of $EtMo(CO)_3C_5H_5$ (0.1881 g, 0.6865 mmol) was placed in the reaction vessel and filled with freshly distilled THF (about 200 mL). The vessel was attached to the high-vacuum line and degassed. The Toepler system was used to pump a measured amount of pure CO from a calibrated storage vessel to the reaction system. The reaction was allowed to proceed to completion, and then the CO was pumped back to the original storage vessel through a series of traps to remove any THF entrained. The infrared spectrum of the solution showed complete conversion to $Mo(CO)_6$. The gas uptake was 2.75 mmol of CO, a ratio of 4.01:1 for CO:Mo. Additional confirmation of stoichiometry was obtained by observation of the IR and NMR spectra of the organic product of $MeMo(CO)_3C_5H_5$ and CO. The spectra were in agreement with literature data for $MeC(O)C_5H_5$.[11a,b] Analogous spectra were obtained for $EtC(O)C_5H_5$ and also for $MeC(O)C_5Me_5$.

b. Kinetic Studies. The kinetic studies of the rate of cleavage of $Et\text{-}C\text{-}C_5H_5$ were performed in a thermostated reaction vessel equipped with a thermostated gas buret. Approximately 20 mL of freshly distilled THF was allowed to equilibrate and absorb CO at 1 atm pressure and at the reaction temperature. The reaction was initiated by injecting a concentrated solution of the molybdenum alkyl into the reaction vessel. The rate of reaction was followed by the rate of gas uptake and also by infrared spectroscopy. Both the rate of decrease in the concentration of $RMo(CO)_3C_5H_5$ and the rate of increase in concentration of $Mo(CO)_6$ and $RC(O)C_5H_5$ were monitored. The cleavage reaction occurred at room temperature for both R = Me and R = Et, but more rapidly for R = Et. Under pseudo-first-order conditions at 1 atm total pressure in THF the half-lives in minutes were as follows: $EtMo(CO)_3C_5H_5$, at 35 °C $t_{1/2} = 34.8 \pm 2$, at 50 °C $t_{1/2} = 28.7 \pm 2$; $MeMo(CO)_3C_5H_5$, at 50 °C $t_{1/2} = 586 \pm 9$; $EtMo(CO)_3C_5Me_5$, at 50 °C $t_{1/2} = 147$.

Reaction of $MeMo(CO)_3C_5H_5$ with PR_3/CO. Reactions were conducted in the thermostated reaction vessel equipped with a gas buret described above. A 20-mL solution of P-*n*-Bu_3 (2 mL) in bis(β-ethoxyethyl) ether was allowed to equilibrate with 1 atm of CO. Approximately 0.2 g of $MeMo(CO)_3C_5H_5$ was added, the gas uptake was followed on the gas buret, and periodically infrared spectra were run. In the temperature range 50–70 °C the reaction was slow, and after several days the only peaks observed in the infrared spectra were those of $MeC(O)Mo(CO)_2(P\text{-}n\text{-}Bu_3)C_5H_5$, $(P\text{-}n\text{-}Bu_3)Mo(CO)_5$,[11c] and $MeC(O)C_5H_5$. Similar results were obtained with toluene as solvent. Reactions of $P(OMe)_3$ differed in that both $(P(OMe)_3)_2Mo(CO)_4$ and $(P(OMe)_3)_3Mo(CO)_3$[11d] appeared in the infrared spectrum.

Results and Discussion

General Methods. Reaction of $RMo(CO)_3C_5H_5$ with a number of phosphines and phosphites proceeds rapidly and quantitatively according to reaction 5. This reaction has been widely studied[12]

$$RMo(CO)_3C_5H_5 + PR_3 \rightarrow RC(O)Mo(CO)_2(PR_3)C_5H_5 \quad (5)$$

as have analogous reactions of $RMn(CO)_5$,[13] $RCo(CO)_4$,[14] and a number of other alkylmetal carbonyls. Ligand-induced carbonyl insertion is best viewed thermodynamically (but not mechanistically) as occurring in two steps, phosphine substitution and carbonyl insertion:

$$RMo(CO)_3C_5H_5 + PR_3 \rightarrow RMo(CO)_2(PR_3)C_5H_5 + CO \quad (6)$$

$$RMo(CO)_2(PR_3)C_5H_5 + CO \rightarrow RC(O)Mo(CO)_2(PR_3)C_5H_5 \quad (7)$$

The enthalpy of eq 6 reflects the difference in the Mo–CO and Mo–PR_3 bond strengths. As such, it should vary as a function of phosphine. Reaction 7 corresponds to carbonylation of the phosphine-substituted metal alkyl. The enthalpy of this reaction might be expected to depend less strongly on the nature of the phosphine substituent, since the Mo–PR_3 bond is not directly involved. The dependence of these reactions on the phosphine substituents is important since phosphines and phosphites are widely used to modify the behavior of both Co- and Rh-based hydroformylation catalysts.[15] The total effect of phosphine modification on a catalyst is complex, involving both kinetic and thermodynamic factors. The goal of this research was to understand the thermodynamic influence of the phosphine ligand on both the ligand-induced migratory insertion (eq 5) and carbonyl insertion (eq 7).

The enthalpy of eq 5 is readily obtained since it can be measured directly. Due to cleavage of the cyclopentadienyl group (discussed below) the enthalpy of reaction 7 cannot be measured directly.

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(11) (a) Hafner, K.; Kramer, H. E. A.; Musso, H.; Plusso, G.; Schultz, G. *Chem. Ber.* **1964**, *97*, 2067. (b) King, R. B. *Org. Synth.* **1968**, *56*, 1. (c) Delbeke, F. T.; Claeys, E. G.; Van Der Kellen, G. P. *J. Organomet. Chem.* **1970**, *25*, 223. (d) Darensbourg, T. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959.

(12) (a) Barnett, K. W.; Beach, D. L.; Gaydos, S. P.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 121. (b) Barnett, K. W. *Inorg. Chem.* **1969**, *8*, 2009. (c) Barnett, K. W.; Pollman, T. G.; Solomon, T. W. *J. Organomet. Chem.* **1972**, *26*, C23. (d) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 295. (e) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1. (f) Barnett, K. W.; Pollman, T. G. *J. Organomet. Chem.* **1974**, *69*, 413.

(13) (a) Green, M.; Hancock, R. J.; Wood, D. C. *J. Chem. Soc. A* **1968**, 2718. (b) Noack, K.; Ruch, M.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 345.

(14) Galamb, V.; Palyi, G. *Coord. Chem. Rev.* **1984**, *59*, 203.

(15) Pignolet, L. H., Ed. "Homogeneous Catalysis with Metal Phosphine Complexes"; Plenum Press: New York, 1983.

Since reaction 5 is the sum of reactions 6 and 7, measurement of the enthalpy of reaction 6 would yield the enthalpy of CO insertion:

$$\Delta H(\text{eq } 7) = \Delta H(\text{eq } 5) - \Delta H(\text{eq } 6) \qquad (8)$$

It is not possible to measure the enthalpy of eq 6 calorimetrically, and attempts to establish equilibrium constants by reacting $RMo(CO)_2(PR_3)C_5H_5$ with CO/PR_3 mixtures are also hindered by the irreversible cleavage of the cyclopentadienyl ring as discussed below.

In order to calculate the enthalpy of reaction 7, we have chosen to estimate the enthalpy of PR_3 substitution for CO in eq 6. We recently reported thermochemical data and bond strength estimates for a number of $Mo-PR_3$ complexes[10e] based on reaction 9. While

$$\text{areneMo(CO)}_3 + 3PR_3 \rightarrow \textit{fac-}(PR_3)_3Mo(CO)_3 + \text{arene} \qquad (9)$$

this data could be used to estimate the enthalpy of eq 6, we considered a better model to be eq 10. Calorimetric measurement

$$HMo(CO)_3C_5H_5 + PR_3 \rightarrow HMo(CO)_2(PR_3)C_5H_5 + CO \qquad (10)$$

of reaction 10 is straightforward since there is no formation of the metal formyl,[16] which is presumably thermodynamically disfavored:[17]

$$HMo(CO)_2(PR_3)C_5H_5 + CO \nrightarrow HC(O)Mo(CO)_2(PR_3)C_5H_5 \qquad (11)$$

As discussed in the next part, there is good agreement between estimates for phosphine substitution based on eq 9 and those based on eq 10. This gives confidence to the assumption that the enthalpy of PR_3 substitution is similar in the complexes $RMo(CO)_3C_5H_5$.

The general approach we have taken is to measure the enthalpies of reactions 5 and 10 and use their difference to estimate the enthalpy of eq 7:

$$\Delta H(\text{eq } 7) = \Delta H(\text{eq } 5) - \Delta H(\text{eq } 10) \qquad (12)$$

This provides a new method to estimate the enthalpy of carbonyl insertion. Since reactions analogous to those shown in eq 5 and 10 proceed rapidly for a number of organometallic complexes, this technique should be applicable to other metals as well.[18]

Heats of Reaction of $HMo(CO)_3C_5H_5$ and PR_3. This reaction is rapid and quantitative at room temperature, and calorimetric data for it are reported in Table I. These data refer to reaction of the crystalline hydride with a solution of PR_3 to yield a solution of the phosphine-substituted hydride. The data reported in Table I can be used to calculate the enthalpy of phosphine substitution. Subtracting eq 13 from eq 14 yields directly the enthalpy of

$$HMo(CO)_3C_5H_5 + PR_3 \rightarrow HMo(CO)_2(PR_3)C_5H_5 + CO \qquad (13)$$

$$HMo(CO)_3C_5H_5 + PR'_3 \rightarrow HMo(CO)_2(PR'_3)C_5H_5 + CO \qquad (14)$$

$$HMo(CO)_2(PR_3)C_5H_5 + PR'_3 \rightarrow HMo(CO)_2(PR'_3)C_5H_5 + PR_3 \qquad (15)$$

substitution of one phosphine for another in eq 15 indicative of the relative $Mo-PR_3$ bond strengths. These data, which also include correction of the calorimetric data in Table I for heats of solution, are shown in Table II. The most weakly bound phosphine (PPh_2Me) is used as reference.

The order of stability $PMe_3 \approx P\text{-}n\text{-}Bu_3 > P(OMe)_3 > PMe_2Ph > PMePh_2$ is similar to that which we determined for *fac*-$(PR_3)_3Mo(CO)_3$. These data, also collected in Table II, can be used to calculate the enthalpy of phosphine exchange shown in eq 16. Comparing one-third of this value (since 3 mol of

$$\textit{fac-}(PR_3)_3Mo(CO)_3 + 3PR'_3 \rightarrow \textit{fac-}(PR'_3)_3Mo(CO)_3 + 3PR_3 \qquad (16)$$

phosphine is exchanged) with the value for the enthalpy of reaction 14 shows that the relative $Mo-PR_3$ bonds are similar. In order to compare those to CO on an absolute basis, we have measured the enthalpy of reaction 17 by differential scanning calorimetry.

$$Mo(CO)_6 + 2PPh_2Me \rightarrow Mo(CO)_4(PMePh_2)_2 + 2CO \qquad (17)$$

The enthalpy of this reaction is -1.6 ± 1.0 kcal/mol, or -0.8 kcal/mol per $Mo-PR_3$ bond. While the error limits are rather high, it shows that the absolute bond strengths are not much different since the enthalpy of phosphine substitution on the hydride complex (reaction 8) for $PMePh_2$ is -1.6 ± 0.2 kcal/mol. We expected a greater difference in $Mo-PR_3$ bond strengths between the formally divalent $HMo(CO)_2(PR_3)C_5H_5$ and zerovalent $Mo(CO)_3(PR_3)_3$. This similarity makes it seem unlikely that the $Mo-PR_3$ bond is greatly different in $RMo(CO)_2(PR_3)C_5H_5$ compared to that in $HMo(CO)_2(PR_3)C_5H_5$.

Heat of Phosphine-Promoted CO Insertion. The enthalpies of reaction 5 in THF solutions are reported in Table III. These reactions incorporate both CO substitution by phosphine and also CO insertion. They are exothermic by an average value of 20.4 kcal/mol for $EtMo(CO)_3C_5H_5$ and 17.6 kcal/mol for $MeMo(CO)_3C_5H_5$. The heats of reaction as a function of ligand span a range of about 6 kcal/mol in the order $PMe_3 > P\text{-}n\text{-}Bu_3 > P(OMe)_3 > PMe_2Ph > PPh_2Me > PPh_3$. The enthalpy of this reaction thus depends strongly on the nature of the phosphine ligand. This would be expected to extend to other ligands as well. We have recently generated data for a number of Mo–L bond strengths[10] and hope to be able to use them to predict equilibrium constants for general ligand-induced CO insertion.

The 2.8 kcal/mol difference between the average value for insertion into the $Mo-CH_3$ bond vs. that for the $Mo-C_2H_5$ bond can be used to estimate bond strength differences for these compounds. Assuming the acyl bond strengths are the same for the propionyl and acetyl complexes implies the Mo–Et bond is at least 2.8 kcal/mol and probably on the order of 6 kcal/mol weaker than the Mo–Me bond.[19] This is in keeping with the kinetic results, where the ethyl complex is more reactive by 1–2 orders of magnitude.[20] It is also consistent with several other thermochemical estimates. Yoneda and Blake have estimated that the $Ir-CH_3$ bond is 4.3 kcal/mol stronger than the $Ir-C_2H_5$ bond.[9] An average estimated difference of about 5 kcal/mol seems to be generally applicable to main-group metals.[21] While we refer to this reaction as "carbonyl insertion", it is often termed "alkyl migration" since it is generally held that the transition state originates from migration of the alkyl group to the coordinated carbon monoxide. If the transition state involved complete breakage of the Mo–alkyl bond, the thermodynamic estimate of a 3–6 kcal/mol difference in the Mo–Me and Mo–Et bonds would imply a difference in kinetic behavior of 2–4 orders of magnitude. Since this is more than the 1–2 order of magnitude rate difference observed,[20] it implies incomplete bond breaking in the transition state. This conclusion is in keeping with extended Hückel calculations.[22]

Calculated Heats of CO Insertion. The enthalpies of reaction 7, calculated by using the formula in eq 11, are included in Table III. These values refer to the heats of carbonylation in solution and show a narrower range of enthalpies for this reaction, 2.0 kcal/mol for the Mo–Me complex and 2.3 kcal/mol for the Mo–Et complex. The average values are -13.6 kcal/mol for Mo–Me and

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(16) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715.

(17) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 232.

(18) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, D. C., work in progress.

(19) The estimate of a 6 kcal/mol difference in the Mo–Me and Mo–Et bond strengths is an upper limit. It incorporates the difference in the enthalpies of carbonyl insertion plus an additional 3 kcal/mol term since the Et–CO bond is probably weaker than the Me–CO bond by about this amount.[23]

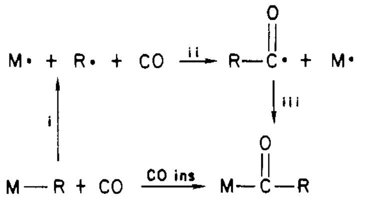
(20) (a) Jones, D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447. (b) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(21) (a) Skinner, H. A. *Adv. Organomet. Chem.* **1964**, *2*, 49. (b) Pilcher, B.; Skinner, H. A. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 2.

(22) Berke, H.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 7231.

−16.4 kcal/mol for Mo–Et. The relative order for R = Me is $PMe_3 > PBu_3 > PMePh_2 > PPh_3 > PMe_2Ph > P(OMe)_3$. Aside from the anomalous position of PMe_2Ph in the ethyl series there appears to be a steady decrease in the enthalpy of reaction with decreasing basicity of the phosphine ligand. This also parallels the acyl stretching frequency, which increases with decreasing basicity of the phosphine.

The carbonyl insertion can be viewed in terms of the thermochemical cycle shown in eq 18. It is clear that the enthalpy of

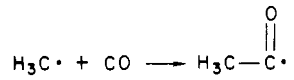


(18)

reaction involves the difference in M–R and M–C(O)–R bond strengths (steps i and iii) and the enthalpy of the organic reaction (step ii):

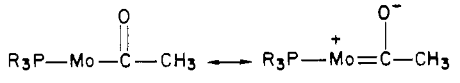
$$\Delta H_{\mathrm{CO\,ins}} = \Delta H_{\mathrm{i}} + \Delta H_{\mathrm{ii}} + \Delta H_{\mathrm{iii}} = \Delta H_{\mathrm{org\,radical}} + D^{\mathrm{M-R}} - D^{\mathrm{M-C(O)-R}} \quad (19)$$

Gas-phase data for the reaction shown in eq 20 indicate ΔH =



$$H_3C\bullet + CO \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}\bullet \quad (20)$$

−13.2 kcal/mol.[23] The average value of the enthalpy of CO insertion for the $MeMo(CO)_2(PR_3)C_5H_5$ system is −13.6 kcal/mol and is close to that of the organic reaction (eq 20). This implies that the Mo–CH_3 and Mo–C(O)CH_3 bonds are similar in strength and that the dominant thermodynamic factor for this process is the organic radical reaction. It is of interest that the difference in metal–alkyl vs. metal–acyl bond strength can be "fine tuned" by the ancillary ligands. Since the acyl group is electron-withdrawing compared to the methyl group, and significant π back-bonding has been demonstrated for acetyl complexes of molybdenum,[24] the more basic phosphines stabilize preferentially the insertion product. A decrease in the stretching frequency of the acyl group also occurs with more basic phosphines, in keeping with the resonance structure shown in eq 21.


(21)

I II

Stability of $RC(O)Mo(CO)_2(L)C_5H_5$. The only stable complexes of the type $RC(O)Mo(CO)_3C_5H_5$ contain electron-withdrawing alkyl groups such as trifluoromethyl.[25] Even in this case the stability is of kinetic origin since decarbonylation is irreversible:

$$F_3CC(O)Mo(CO)_3C_5H_5 \rightleftharpoons\!\!\!\!\!\!/\;\; F_3CMo(CO)_3C_5H_5 + CO \quad (22)$$

While the tricarbonyl complexes are unstable, substitution of one of the terminal carbonyls by a phosphine ligand has led to a number of stable complexes of the type $RC(O)Mo(CO)_2PR_3C_5H_5$. This situation is reminiscent of a number of metals, particularly the alkyl- and acylcobalt tetracarbonyls. The bulky phosphine ligand in the coordination sphere of the metal will increase the kinetic stability of the acyl complex with regard to decomposition, particularly through associative pathways. Also the presence of the electron-donating phosphine ligand will favor thermodynamically the acyl complex through resonance structure II in eq 18. Considering the poor σ-donating ability of CO compared to even that of $P(OMe)_3$,[26] the enthalpy of reaction 23 should be less than the −12.8 kcal/mol observed for the analogous phosphite complex:

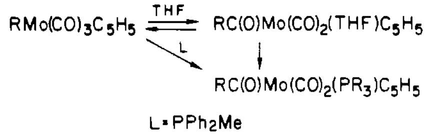
$$H_3CMo(CO)_3C_5H_5 + CO \rightarrow H_3CC(O)Mo(CO)_3C_5H_5 \quad (23)$$

This would place it in the range where the unfavorable entropy (10–14 kcal/mol) would yield a net positive free energy for eq 23.

The generally more favorable enthalpies of carbonylation of $EtMo(CO)_2LC_5H_5$ (17.5–15.2 kcal/mol from PMe_3 to $P(OMe)_3$) suggested that carbonylation of $EtMo(CO)_3C_5H_5$ offered promise for generating a stable acyl complex:

$$H_3CH_2CMo(CO)_3C_5H_5 + CO \rightarrow H_3CH_2CC(O)Mo(CO)_3C_5H_5 \quad (24)$$

Wax and Bergman[20b] have recently proposed $EtC(O)Mo(CO)_2(THF)C_5H_5$ as the key intermediate in the phosphine-promoted carbonyl insertion as shown in eq 25. It seemed likely that reaction of $EtMo(CO)_3C_5H_5$ under a CO atmosphere in THF would provide a convenient route to prepare $EtC(O)Mo(CO)_3C_5H_5$ where L = CO. At room temperature under CO at 1 atm total pressure there is no sign of formation of the desired complex, only a smooth uptake of 4 mol of CO according to eq 26. This facile migration of the acyl group from molybdenum to the cyclopentadienyl ring is of interest and is receiving more detailed mechanistic investigation.[18]



(25)

$$EtMo(CO)_3C_5H_5 + 4CO \xrightarrow{THF} EtC(O)C_5H_5 + Mo(CO)_6 \quad (26)$$

We have recently reported thermodynamic data[10c] that indicate the enthalpy of reaction 27 should be on the order of −40 kcal/mol.

$$HMo(CO)_3C_5H_5 + 3CO \rightarrow C_5H_6 + Mo(CO)_6 \quad (27)$$

On this basis, since the Mo–H bond is presumably stronger than the MoC(O)Et bond,[17] the enthalpy of reaction 26 should be even more favorable. This demonstrates the ability of $Mo(CO)_6$ to act as a "thermodynamic sink" for these complexes. In the absence of CO pressure, the acyl complexes $RC(O)Mo(CO)_3C_5H_5$ are thermodynamically unstable with respect to decarbonylation. In the presence of CO pressure they are unstable with respect to further cleavage, forming $Mo(CO)_6$.

Since the Mo–CO and Mo–PR_3 bonds are roughly similar in strength,[10c] cleavage of the Mo–C_5H_5 bond in these phosphine-substituted acyl complexes should also be thermodynamically favored:

$$RC(O)Mo(CO)_2(PR_3)C_5H_5 + nCO \rightarrow Mo(CO)_{6-n}(PR_3)_n \quad (28)$$

Cleavage of the Mo–C_5H_5 bond does occur in this system, but much more slowly than reaction 26. This is due to the kinetic and thermodynamic stabilization of the phosphine-substituted acyl complexes as already discussed. This reaction was discovered in an attempt to determine the equilibrium constant for reaction 29.

$$RC(O)Mo(CO)_2(PR_3)C_5H_5 \rightarrow RMo(CO)_2(PR_3)C_5H_5 + CO \quad (29)$$

Kinetic studies of this system by Barnett and co-workers[12] had shown the rate of decarbonylation to be unaffected by the presence of CO. In spite of this, attempts to determine the equilibrium constant were frustrated. In the presence of a 10-fold excess of

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(23) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976.

(24) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953.

(25) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(26) (a) Yarbrough, L. W., II; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269. (b) Bursten, B. E.; Darensbourg, D. J.; Kelly, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361.

(27) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

phosphine we found (under 1 atm of CO) slow cleavage of the cyclopentadienyl ring as shown in eq 30. The increased stability

$$RC(O)Mo(CO)_2(PR_3)C_5H_5 \xrightarrow[\text{slow}]{CO/PR_3} Mo(CO)_{6-n}(PR_3)_n \quad (30)$$

of $RC(O)Mo(CO)_2(L)C_5H_5$ complexes ($L = PR_3 > L = CO$) is twofold: They are thermodynamically more stable to decarbonylation in the absence of CO. In addition, they are protected by kinetic barriers from further reaction with CO/PR_3. Nevertheless, $Mo(CO)_{6-n}(PR_3)_n$ is a thermodynamic sink for these systems and it is a dominant factor in determining the catalytic chemistry in molybdenum.

Conclusion

The enthalpy of carbonyl insertion depends on both the alkyl and phosphine substituents on molybdenum. Reaction of the Mo–Et complex is on average 2.8 kcal/mol more exothermic than that of the Mo–Me complex due to the weaker Mo–Et bond. The enthalpy of the Mo–Me reaction is close to that predicted on the assumption that the Mo–Me and $Mo–C(O)CH_3$ bonds are similar in strength. For both the ethyl and methyl complexes more basic phosphines favor carbonyl insertion. This is interpreted in terms of preferential stabilization of the Mo–acyl bond through resonance delocalization. The range of influence of the phosphine is only 2 kcal/mol, but this is important since the entropy of carbonyl insertion is unfavorable and nearly cancels the favorable enthalpy of reaction. Any small variation in the enthalpy of reaction could have a pronounced effect on the position of the alkyl/acyl equilibrium.

The phosphine-promoted carbonyl insertion shows a wider range of behavior as a function of phosphine ligand, since this reaction incorporates both CO displacement (by PR_3) and CO insertion. A range of about 6 kcal/mol exists, reflecting primarily the greater difference in $Mo–PR_3$ bond strengths. These reactions are generally more favorable than CO insertion. Only in the case of the PPh_3 complex, which has a $Mo–PPh_3$ bond weaker than a Mo–CO bond, is the reaction less favored than the catalytic insertion. The choice of incoming ligand and alkyl group can span about 10 kcal/mol for $CO/MeMo(CO)_2(P(OMe)_3)C_5H_5$ (−12.8 kcal/mol) to $PMe_3/EtMo(CO)_3C_5H_5$ (−22.6 kcal/mol). Coupled with entropy estimates, these measurements can be used as a guide in predicting equilibrium constants for ligand-promoted carbonyl insertion.

Due to its weaker donor ability relative to that for phosphine ligands, the simple acyl complexes $RC(O)Mo(CO)_3C_5H_5$ are predicted to have marginal thermodynamic stability with regard to decarbonylation. Attempts to prepare $EtC(O)Mo(CO)_3C_5H_5$ under mild conditions led to facile cleavage of the $EtC(O)C_5H_5$ group and production of $Mo(CO)_6$, which is a "thermodynamic sink" under these conditions. Similar migrations from the metal to the coordinated cyclopentadienyl ring occur under more forcing conditions for related compounds. Extension of the thermochemical methods discussed here to other systems as well as additional kinetic studies are in progress.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-8314497) is gratefully acknowledged.

Registry No. $HMo(CO)_3C_5H_5$, 12176-06-6; $MeMo(CO)_3C_5H_5$, 12082-25-6; $EtMo(CO)_3C_5H_5$, 12083-68-0; PMe_3, 594-09-2; PBu_3, 998-40-3; $P(OMe)_3$, 121-45-9; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0.

Contribution from the Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland,
and Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, West Germany

Kinetics and Equilibria of Ag^+ and Pb^{2+} Cryptates in Dimethyl Sulfoxide

B. G. Cox,*[†] J. Garcia-Rosas,[‡] H. Schneider,*[‡] and Ng. van Truong[†]

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Rates and equilibria of complex formation between Ag^+ and Pb^{2+} and several cryptands have been investigated in dimethyl sulfoxide. Both Ag^+ and Pb^{2+} complexes show considerably enhanced stabilities compared with those formed by alkali-metal and alkaline-earth-metal cations of similar size, attributable to additional covalent interactions in the complexes. For Ag^+ complexes, the higher stabilities are reflected primarily in lower dissociation rate constants, whereas for Pb^{2+} cryptates, the formation rate constants are considerably higher than those of corresponding alkaline-earth cryptates and the dissociation rate constants are very similar. Implications of these results for transition-state structures and interactions are discussed.

Introduction

The ability of diaza polyoxa macrobicyclic or cryptand (Cry)[1] ligands to form very stable and selective complexes (cryptates) with alkali-metal and alkaline-earth-metal cations is well documented. Extensive studies of both the rates and equilibria of complexation reactions have appeared in recent years.[2-5]

Much less is known about cryptate complexes of transition-metal and heavy-metal cations, especially their kinetic properties, which have received almost no attention. Stability constants of Ag^+, Hg^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} complexes in several solvents are available from the work of Anderegg[6] and in particular Arnaud-Neu, Schwing-Weill, and co-workers.[7,8] An extensive set of Ag^+ cryptate stabilities in different solvents has also been reported, in conjunction with its use as an indicator ion in stability constant determinations for complexes of other cations.[4,5] Kinetic measurements on the other hand are limited to silver(I) complexes of cryptands and diaza polyethers in acetonitrile–water mixtures,[9] copper(II) complexes of cryptand (2,2,1) in dimethyl sulfoxide,[10] and lead(II) complexation by cryptand (2,1,1) in methanol.[11]

In this paper we report on the kinetics and stabilities of complex formation between silver(I) and lead(II) with a series of five cryptand ligands (I–V) in dimethyl sulfoxide (Me_2SO). Both cations form an extensive range of very stable complexes[12,13] with

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[†] University of Stirling.

[‡] Max-Planck-Institut für Biophysikalische Chemie.

(1) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1.

(2) Lehn, J. M.; Sauvage, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6700.

(3) Loyola, V. M.; Pizer, R.; Wilkins, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7185.

(4) (a) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054. (b) *Ibid.* **1981**, *103*, 1381.

(5) Cox, B. G.; van Truong, Ng.; Schneider, H. *J. Am.* Chem. *Soc.* **1984**, *106*, 1273.

(6) Anderegg, G. *Helv. Chim. Acta* **1975**, *58*, 1218.

(7) Spiess, B.; Martin-Faber, D.; Arnaud-Neu, F.; Schwing-Weill, M. J. *Inorg. Chim. Acta* **1981**, *54*, L91.

(8) Arnaud-Neu, F.; Spiess, B.; Schwing-Weill, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 5641.

(9) Cox, B. G.; Stroka, J.; Firman, P.; Schneider, I.; Schneider, H. *Aust. J. Chem.* **1983**, *36*, 2133.

(10) Cox, B. G.; Firman, P.; Schneider, H. *Inorg. Chem.* **1982**, *21*, 2320.

(11) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *Nouv. J. Chim.* **1982**, *6*, 397.

(12) Abel, E. W. In "Comprehensive Inorganic Chemistry"; Trotman-Dickenson, A. F., Ed.; Pergamon: Oxford, 1973; Vol. 2, p 105.

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