^3J(PtH^e) = 30 Hz, H^e], 8.98 [d, br, 2 H, ^3J(PtH^a) = 13 Hz, H^a]; second isomer, δ 1.44 [s, 6 H, ^3J(PtH) = 71 Hz, *Me*^{a} or *Me*^{b}*Pt*], 1.20 [s, 6 H, ^3J(PtH) = 72 Hz, *Me*^{a} or *Me*^{b}*Pt*], 0.68 [s, 6 H, ^3J(PtH) = 72 Hz, *Me*^{c}*Pt*], 9.43 [s, br, 2 H, ^3J(PtH^e) = 30 Hz, H^e]; the signal for H^a is superimposed with the signal for H^a listed above. The spectrum containing both isomers **19b** also have multiplets due to H^{b-d} between 7.81 and 8.29 ppm and due to the nonequivalent methylene protons at 4.55–4.87 ppm.

[PtMe$_2$(pyox)] (23). To a solution of pyox (0.103 g) in CH_2Cl_2 (5 mL) was added 0.5 equiv of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.132 g) as a CH_2Cl_2 (10 mL) solution. The solution immediately turned dark orange, and on standing for 1 h some of the prodduct precipitated from solution. The solvent was removed, and the orange product was washed with diethyl ether and dried under vacuum: yield 97%; mp 186 °C dec. Anal. Calcd for $C_{14}H_{14}N_4OPt$: C, 37.4; H, 3.1; N, 12.5. Found: C, 37.3; H, 2.9; N, 12.1. ^{1}H NMR (CD_2Cl_2) δ 1.03 [s, 3 H, ^2J(PtH) = 92 Hz, Me^{a}Pt], 1.03 ppm [s, 3 H, ^2J(PtH) = 90 Hz, Me^{b}Pt], 9.20 [d, br, 1 H, ^3J(PtH) = 19.5 Hz, ^3J(H^{a}H^b) = 6 Hz, H^a], 8.82 [ddd, 1 H, ^3J(H^{h}H^g) = 6 Hz, ^4J(H^{h}H^f) = 3 Hz, ^5J(H^{h}H^e) = 1 Hz, H^h], 7.54–8.42 [m, 6 H, H^{b-d}, H^{e-g}]; the labels Me^a and Me^b may be interchanged.

[PtIMe$_3$(pyox)] (24). To a solution of [PtMe$_2$(pyox)] (0.063 g) in CH_2Cl_2 (15 mL) was added an excess of MeI (0.5 mL). The orange solution immediately turned bright yellow, and after 0.5 h the solvent was removed. The solid yellow product was washed with *n*-pentane and dried under vacuum: yield, quantitative ; mp 237 °C dec. Anal. Calcd for $C_{15}H_{17}H_4OIPt$: C, 30.5; H, 2.9; N, 9.5. Found: C, 30.1; H, 2.9; N, 9.3. ^{1}H NMR (CD_2Cl_2): δ 1.77 [s, 3 H, ^2J(PtH) = 76 Hz, Me^{a}Pt], 1.57 [s, 3 H, ^2J(PtH) = 72 Hz, Me^{b}Pt], 0.79 [s, 3 H, ^2J(PtH) = 72 Hz, Me^{c}Pt], 9.00 [d, br, 1 H, ^3J(PtH) = 14 Hz, ^3J(H^{a}H^b) = 6 Hz, H^a], 8.83 [d, br, 1 H, ^3J(H^{h}H^g) = 6 Hz, H^h], 7.55–8.47 [m, 6 H, H^{b-d}, H^{e-g}]; the assignments Me^a and Me^b may be reversed.

[Pt$_2$Me$_4$(μ-azpy)] (25). To a solution of azpy (0.026 g) in acetone (10 mL) was added 1 equiv of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.080 g) as an acetone solution (15 mL). The solution immediately turned dark brown, and the product precipitated from solution over 1 h. The brown solid product was collected by filtration, washed with acetone, and dried under vacuum: yield 94%; mp 205 °C dec. Anal. Calcd for $C_{14}H_{20}N_4Pt_2$: C, 26.5; H, 3.2; N, 8.8. Found: C, 27.0; H, 3.6; N, 8.8. This complex is insoluble in all common organic solvents. Attempts to prepare the mononuclear [PtMe$_2$(azpy)] were unsuccessful.

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. **8**, 90144-57-3; **9**, 105040-48-0; **10**, 105040-55-9; **11**, 90191-00-7; **12**, 105040-49-1; **13**, 105040-56-0; **14a**, 102615-01-0; **14b**, 93708-95-3; **14c**, 102615-00-9; **14d**, 102614-99-3; **14e**, 105118-47-6; **15a**, 105040-50-4; **15b**, 105040-52-6; **18a**, 105040-51-5; **18b**, 105040-53-7; **18c**, 105040-54-8; **19a**, 105064-11-7; **19b**, 105040-58-2; **21**, 93708-89-5; **22**, 105040-57-1; **23**, 105040-59-3; **24**, 105064-12-8; **25**, 105040-60-6; pyox, 1671-89-2; [PtMe$_2$(azpy)], 105040-61-7; [Pt$_2$Me$_4$(μ-S-SMe$_2$)$_2$], 79870-64-7; [Pt$_2$Me$_8$(μ-SMe$_2$)$_2$], 92784-98-0; [PtIMe$_3$]$_4$, 18253-26-4.

Heats of Reaction of (Toluene)Mo(CO)$_3$ with Substituted Arenes, Sodium Cyclopentadiene, Nitriles, Isocyanides, and Other Ligands. Solution Thermodynamic Study of Ligand Exchange in the Complexes *fac*-L$_3$Mo(CO)$_3$

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Received March 28, 1986

The results of solution calorimetric studies are used to measure the relative stability in solution of the following complexes: (arene)Mo(CO)$_3$ (arene = *o*-xylene, *m*-xylene, *p*-xylene, *N*,*N*-dimethylaniline, *p*-bis(dimethylamino)benzene, (trimethylsilyl)benzene, sodium tetraphenylborate, and sodium cyclopentadiene), L$_3$Mo(CO)$_3$ (L = acetone, acetonitrile, benzonitrile, *tert*-butyl cyanide, *tert*-butyl isocyanide, cyclohexyl isocyanide, piperidine, and tributylphosphine oxide), and L*Mo(CO)$_3$ (L* = bis(methoxyethyl) ether and potassium hydridotris(pyrazoyl)borate). The enthalpy of deprotonation of H–Mo(CO)$_3$C$_5$H$_5$ by NaC$_5$H$_5$ has been measured and used to complete a thermochemical cycle comparing the heats of reaction of (toluene)Mo(CO)$_3$ with C_5H_6 and NaC$_5$H$_5$. These results are combined with earlier data to yield enthalpies of ligand exchange: $L_nMo(CO)_3 + n L' \rightarrow L'_{n'}Mo(CO)_3 + nL$ which span over 50 kcal/mol and encompass a broad range of organometallic ligands. Factors involved in controlling Mo–L bond strengths are discussed.

Introduction

Knowledge of metal–ligand bond strengths is fundamental to understanding organometallic chemistry. Dissociation of a ligand to generate a vacant site at a metal center is a required step in many reactions of importance to catalysis.[1] An active catalyst, due to low-energy barriers with regard to ligand exchange and interconversion, may be subject to thermodynamic constraints within a limited domain of reactivity. Solution thermochemistry can provide essential information in understanding and predicting such behavior. Despite an increased interest in this area,[2] there are few studies of the thermochemistry of organometallic reactions in solution.

Several methods are available to generate metal–ligand bond strength estimates, particularly in the gas phase.[3]

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The relationship of such gas-phase studies to solution phase work is not clear since in many cases heats of solution and sublimation are not known. For determination of enthalpies of reaction, solution calorimetry and temperature variation of the equilibrium constant provide practical and direct methods. For air-sensitive compounds great care must be taken to avoid atmospheric oxidation or hydrolysis which can be highly exothermic. When side processes cannot be precluded, or in cases where the reaction does not proceed to completion, a thermodynamic cycle may be established which can be used to calculate the heat of the desired reaction. Once these obstacles have been overcome, solution calorimetry offers the advantage that enthalpies can be determined relatively accurately for a large number of organometallic reactions.

The thermochemistry of ligand exchange in organometallic systems was first studied, using solution calorimetry, by Partenheimer.[4] The enthalpy of reaction 1 was

$$\mathrm{PdCl_2(C_6H_5CN)_2 + L{-}L \rightarrow PdCl_2(L{-}L) + 2C_6H_5CN} \qquad (1)$$

investigated for a number of ligands and the following order of stability derived: diene < pyridine < tetramethylene diamine < diars < diphos.

From the heats of reaction of dimeric olefin complexes of Rh(I), it was also shown that triphenyl phosphite is a stronger ligand than 1,5-cyclooctadiene and that triphenylphosphine is a better donor than pyridine.[5]

The enthalpy of reaction 2 was investigated by Manzer and Tolman[6] for a series of phosphines and phosphites as

$$trans\text{-}\mathrm{H_3CPt(PMe_2Ph)_2(THF) + L \rightarrow}\ trans\text{-}\mathrm{H_3CPt(PMe_2Ph)_2(L) + THF} \qquad (2)$$

well as other ligands. A similar series of ligands was later investigated for reaction 3.[7] These results wre interpreted

$$\mathrm{Ni(COD)_2 + 4L \rightarrow NiL_4 + 2COD} \qquad (3)$$

in terms of steric and electronic factors, using the cone angle[8] of the phosphine ligand as a measure of steric repulsion and the A_1 carbonyl stretching frequency of $Ni(CO)_3L$ as a measure of ligand basicity.

The orders of stabilities for these four systems show broad similarities, and these results are consistent with various kinetic observations.[9] This may simply reflect the basic "hard–soft"[10] (or equivalent) concept in which organometallic complexes are relatively "soft" and generally bind softer ligands such as phosphines in preference to harder ligands such as amines. While such interpretations are useful, it seems likely that the specific metal, its oxidation state, and ancillary ligands play a vital role in determining the strength of the metal–ligand interaction.

The chemistry of the $-M(CO)_3$ fragment (M = Cr, Mo, W) is one of the most intensely studied in organometallic chemistry.[11] Since a wide range of relatively stable compounds can be prepared, the opportunity exists to study in detail the factors influencing metal–ligand bond strengths for a series of related complexes. Previous work on the thermochemistry of ligand exchange include arene and olefin,[12,13] cyclopentadienyl,[14] pentamethylcyclopentadienyl,[15] and phosphine and phosphite ligands.[16] We now report additional results on the solution thermochemistry of ligand exchange in the $L_nMo(CO)_3$ system.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard Schlenk tube techniques or in a Vacuum/Atmospheres glovebox with less than 1 ppm of oxygen and water. Tetrahydrofuran was purified by distillation from calcium hydride to a second flask where it was distilled from sodium benzophenone ketyl under argon into flame dried glassware. Methylene chloride was refluxed over phosphorus pentoxide and then distilled under argon. Toluene was distilled from sodium benzophenone ketyl. Other reagents were obtained from commercial sources and purified by standard procedures. Organomolybdenum compounds were prepared by using procedures described in the literature[11] or slight modifications thereof. Complexes used in calorimetry were subjected to at least two purification steps involving either recrystallization or high vacuum sublimation. Only materials which where pure as determined by IR and NMR spectroscopy and of high crystalline quality were used in the calorimetric measurements. If a new batch of material was used, measurements of heats of solution and heats of reaction were repeated to ensure that the material was not only chemically pure but had the same heat content. Infrared spectra were obtained by using a Perkin-Elmer 267 or 501 spectrophotometer in 0.1-mm KBr solution cells. NMR spectra were obtained on a Varian FT-80A spectrometer. Calorimetric measurements were made as described below by using either a Calvet calorimeter(Setaram C-80) or a modified Guild calorimeter installed in a glovebox which has been previously described.[13]

Calorimetric Measurements for Reaction of η^6-$Me_2NC_6H_5$–$Mo(CO)_3$ and Pyridine. Samples of purified η^6-$Me_2NC_6H_5$–$Mo(CO)_3$ in the range of 0.1–0.2 g were sealed in glass ampules under vacuum. The Guild solution calorimeter[13] was filled with a solution of 400 mL of freshly distilled methylene chloride and 50 mL of pyridine which had been refluxed and distilled from BaO. The glass ampule was placed in the Teflon holder, and the temperature allowed to equilibrate. A series of electrical calibrations were done followed by breaking of the ampule and a second set of electrical calibrations. The heat of the reaction, −20.6 ± 0.7 kcal/mol is the average of six separate determinations. In a similar fashion the heat of solution was determined in pure methylene chloride. The endothermic value, +3.8 ± 0.2 kcal/mol, is the average of three measurements. Periodically, empty ampules were broken to ensure there was no heat associated with the ampule breaking process itself. The calorimeter system has been calibrated on several occasions using standard reactions.[13]

Calorimetric Measurements of Reactions of NaC_5H_5. The Guild calorimeter described above was also used to measure the heats of reaction of NaC_5H_5 with (toluene)$Mo(CO)_3$ and $HMo(CO)_3C_5H_5$. A solution of NaC_5H_5 in THF was prepared in the glovebox by slow addition of 50 mL of freshly cracked C_5H_6 to 400 mL of THF stirred over an excess of NaH. After addition was complete and there was no further hydrogen evolution, the solution was filtered and placed in the calorimeter. Ampules containing (toluene)$Mo(CO)_3$ (or $HMo(CO)_3C_5H_5$) were then broken in this solution to measure the heats of reaction in a manner analogous to that described above. The Guild calorimeter was used for all isoperibol measurements of reactions which went to completion within 30 min.

Calorimetric Measurements for Reactions of (*p*-Xylene)$Mo(CO)_3$ with CH_3CN. Reactions, which were longer than 30 min or for which there was not a large amount of material

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available, were run in a Calvet calorimeter. In a typical procedure the mixing cells were dried in an oven at 150 °C for 2 h and then taken into the glovebox. The lower chamber was filled with approximately 0.2 g of (*p*-xylene)$Mo(CO)_3$, closed, and sealed with 1.5 mL of Hg. Four mL of a 25% solution of CH_3CN (freshly distilled from P_2O_5) in THF was added to the cell; it was closed, taken out of the glovebox, and allowed to equilibrate at 30.0 °C for 2 h. After a stable base line was reached, reaction was initiated by inverting the calorimeter. An initial endothermic peak (due to the heat of solution) was followed by an exothermic heat of reaction. After return to base line (1–2 h), the trace was integrated to determine the heat of reaction. The value of −16.2 ± 0.4 kcal/mol represents the average of six separate measurements. At the end of the run IR spectra confirmed that reaction was complete and produced only *fac*-$(CH_3CN)_3Mo(CO)_3$.

Results

This work is based on the thermochemical study of two general reactions. The first relies on reaction of the crystalline organomolybdenum complex with pyridine as shown in 4 and 5.

$$C_6H_6Mo(CO)_3 + 3py \rightarrow (py)_3Mo(CO)_3 + C_6H_6 \quad (4)$$

$$L_3Mo(CO)_3 + 3py \rightarrow (py)_3Mo(CO)_3 + 3L \quad (5)$$

These reactions are rapid and quantitative for a number of complexes.[13,15,17] Subtraction of eq 5 from eq 4 leads directly to the enthalpy of ligand exchange shown in eq 6. The benzene complex is taken as reference since it is the least stable.

$$C_6H_6Mo(CO)_3 + 3L \rightarrow L_3Mo(CO)_3 + C_6H_6 \quad (6)$$

The second general procedure is based on the in situ formation of $L_3Mo(CO)_3$ from (toluene)$Mo(CO)_3$ (or (*p*-xylene)$Mo(CO)_3$) in THF. Solvolysis of the arene complexes by THF was first reported by Muetterties, Bleeke, and Sievert.[18] The reaction with excess L may proceed through the $(THF)_3Mo(CO)_3$ complex as shown in eq 7.

$$\text{(toluene)}Mo(CO)_3 \xrightarrow{\text{THF}} (THF)_3Mo(CO)_3 + 3L \xrightarrow{\text{THF}} L_3Mo(CO)_3 \quad (7)$$

These two methods, eq 5 and 7, are complementary. Degradation with pyridine, eq 5, is suitable for complexes less stable than $(py)_3Mo(CO)_3$. Formation of the $L_3Mo(CO)_3$ complex in THF solution, eq 7, requires that the complex be more stable than $(THF)_3Mo(CO)_3$. Complexes whose stabilities fall between $(THF)_3Mo(CO)_3$ and $(py)_3Mo(CO)_3$, in Table III, can be studied by either method. We have done this for several compounds, and the results agree within experimental error.[13]

We have reported data for a number of arene and olefin complexes of molybdenum tricarbonyl.[13] The enthalpies of arene exchange were measured in methylene chloride since equilibrium constants had also been measured in this solvent.[18] In order to convert the thermochemical data to the enthalpy of arene exchange in methylene chloride, various heats of solution must be added according to eq 8. Within experimental error the heats of solution of the

$$\text{M–arene} + \text{arene}' \rightarrow \text{M–arene}' + \text{arene}$$

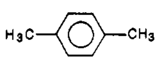
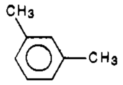
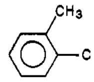
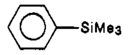
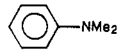
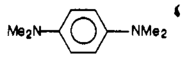
$$\Delta H_{\text{exchange}} = \Delta H^{\text{M–arene}}_{\text{react.py}} - \Delta H^{\text{M–arene}'}_{\text{react.py}} + \Delta H^{\text{M–arene}'}_{\text{soln.CH}_2\text{Cl}_2} - \Delta H^{\text{M–arene}}_{\text{soln.CH}_2\text{Cl}_2} + \Delta H^{\text{arene}'}_{\text{soln.py}} - \Delta H^{\text{arene}}_{\text{soln.py}} + \Delta H^{\text{M–arene}}_{\text{soln.CH}_2\text{Cl}_2} - \Delta H^{\text{arene}'}_{\text{soln.CH}_2\text{Cl}_2} \quad (8)$$

arenes cancel, and so the difference between the heat of reaction of the crystalline complex and its heat of solution in methylene chloride provides a gage for the stability of the complex as shown in eq 9. Data for the complexes,

$$\Delta H_{\text{exchange}} \approx \Delta H^{\text{M–arene}}_{\text{react.py}} - \Delta H^{\text{M–arene}}_{\text{soln.CH}_2\text{Cl}_2} - \Delta H^{\text{M–arene}'}_{\text{react.py}} + \Delta H^{\text{M–arene}'}_{\text{soln.CH}_2\text{Cl}_2} \quad (9)$$

their heats of solution, and enthalpies of exchange relative to benzene are reported in Table I. Additional data for arene complexes reported earlier are listed in Table III. We have measured the heats of solution of several of these complexes in toluene, methylene chloride, and tetrahydrofuran. Within 1 kcal/mol for the covalent complexes studied, there appears to be no solvent dependence in these systems with regard to enthalpy of arene exchange.[17]

Table I. Heats of Reaction,[a] Heats of Solution,[b] and Calculated Heats of Arene Exchange[c] for (Arene)$Mo(CO)_3$ Complexes

arene	ΔH^{rxn}	ΔH^{soln}	$\Delta H^{\text{arene exc}}$
	−24.0 ± 1.4	4.6 ± 0.1	−2.3
	−24.0 ± 1.4	3.9 ± 0.4	−3.0
	−23.2 ± 0.8	4.4 ± 0.4	−3.3
	−20.3 ± 0.3	5.0 ± 0.2	−5.6
	−20.6 ± 0.7	3.8 ± 0.2	−7.0
	−18.9 ± 0.5	4.5 ± 0.1	−7.5

[a] Heats of reaction refer to the enthalpy of (arene)$Mo(CO)_3$(cryst) + py(soln) → $py_3Mo(CO)_3$(soln) + arene(soln). [b] Heats of solution refer to the enthalpy of solution of the crystalline (arene)$Mo(CO)_3$ in CH_2Cl_2. [c] The enthalpy of arene exchange relative to (benzene)$Mo(CO)_3$ is calculated as described in the text. All units are in kcal/mol.

Heats of Reaction of (Toluene)$Mo(CO)_3$ or (*p*-Xylene)$Mo(CO)_3$ with Excess L. The second major entryway into the thermochemistry of $L_3Mo(CO)_3$ is the direct measurement of the enthalpy of reaction 7. Since the complexes studied are generated in THF solution, isolation, and separate determination of the heats of solution of the crystalline compounds are not necessary. Due to ease of preparation relative to (benzene)$Mo(CO)_3$ we have used either (toluene)$Mo(CO)_3$ or (*p*-xylene)$Mo(CO)_3$ in these reactions. These values were then adjusted to reflect their stabilities relative to (benzene)$Mo(CO)_3$. When (toluene)$Mo(CO)_3$ was used, a correction of 5.0 kcal (2.0 kcal/mol increased stability of (toluene)$Mo(CO)_3$ relative to (benzene)$Mo(CO)_3$ and 3.0 kcal/mol for its heat of solution in THF) must be subtracted from the measured heat of reaction. When (*p*-xylene)$Mo(CO)_3$ was used, 5.6 kcal/mol is subtracted due to a 2.3 kcal/mol greater stability relative to benzene and a 3.3 kcal/mol heat of solution. Measured enthalpies of reaction for new ligands and their related heats of arene exchange are reported in Table II. A compilation of data gathered up to this point on the $L_nMo(CO)_3$ system is shown in Table III.

Three of the complexes examined in this report, $Na[B(C_6H_5)_4]Mo(CO)_3$, $Na[C_5H_5]Mo(CO)_3$, and K[Tp]$Mo(CO)_3$,[7] are ionic. For these complexes it can be expected that significant heats of solution will appear. Transfer of these data to other solvents or the gas phase would yield sizable errors. In these systems bond strength estimates, discussed in more detail later, refer only to solution values.

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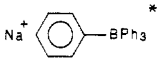
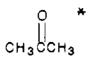
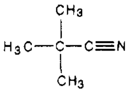
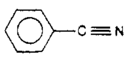
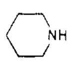
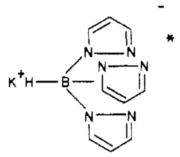
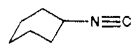
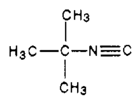
Table II. Heats of Reaction with (Toluene)Mo(CO)$_3$,[a] and Calculated Heats of Ligand Exchange for L$_3$Mo(CO)$_3$[b]

ligand	$\Delta H^{\rm rxn}$	$\Delta H^{\rm exc}$
 *	-1.1 ± 0.2	6.7
 $CH_3C(O)CH_3$ *	-6.2 ± 0.5	11.8
$O(CH_2CH_2OCH_3)_2$	-9.2 ± 0.2	14.8
 $(CH_3)_3C{-}C{\equiv}N$	-15.0 ± 0.3	20.0
	-15.5 ± 0.2	20.5
$H_3C{-}C{\equiv}N$	-16.8 ± 0.6	21.8
n-BuP=O*	-16.4 ± 0.2	22.0
	-26.6 ± 0.8	31.6
Ph_2MeAs*	-26.4 ± 0.2	32.0
Et_3As*	-31.9 ± 0.2	37.5
	-30.1 ± 0.4	35.1
 *	-31.9 ± 0.2	37.5
	-44.9 ± 0.3	49.9
 $(CH_3)_3C{-}N{\equiv}C$	-45.1 ± 0.5	50.1

[a] Refers in most cases to the enthalpy of the reaction. TolMo(CO)$_3$(cryst) + 3L(soln) → L$_3$Mo(CO)$_3$(soln) + tol(soln). In some cases p-xylMo(CO)$_3$ was used (designated by an asterisk). In all cases the amount of ligand L was in excess. [b] The enthalpy of exchange is relative to (benzene)Mo(CO)$_3$ and is calculated as discussed in the text. All units are in kcal/mol.

Heat of Protonation of NaC$_5$H$_5$ by HMo(CO)$_3$C$_5$H$_5$. The heat of reaction 10 was measured in tetrahydrofuran.

$$\text{H-Mo(CO)}_3\text{C}_5\text{H}_5 + \text{NaC}_5\text{H}_5 \rightarrow \text{Na-Mo(CO)}_3\text{C}_5\text{H}_5 + \text{C}_5\text{H}_6 \quad (10)$$

The measured enthalpy is −21.1 ± 1.0 kcal/mol for reaction of the crystalline hydride with a solution of NaC$_5$H$_5$ in THF. The enthalpy of solution of H-Mo(CO)$_3$C$_5$H$_5$ is +2.1 ± 0.1 kcal/mol, and so the enthalpy of reaction 10 in solution is −23.2 ± 1.1 kcal/mol. Additional measurements on the enthalpies of organometallic acid–base and redox reactions are in progress.[19]

Discussion

The primary goal of this work is understanding the solution thermochemistry of organometallic reactions. We have previously reported thermochemical data on ligand exchange,[12-16] hydrogen activation,[14] and carbonyl insertion[20] for the group VI metals. This paper includes new data for ligand exchange in the complexes *fac*-L$_3$Mo(CO)$_3$ and summarizes earlier work. Emphasis is placed on the relative stability in solution with regard to the enthalpy of the ligand exchange reaction shown in eq 11.

$$\text{L}_n\text{Mo(CO)}_3 + n\text{L}' \rightarrow \text{L}'_{n'}\text{Mo(CO)}_3 + n\text{L} \quad (11)$$

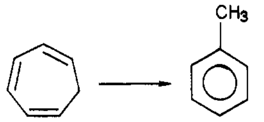
The ligands studied include arenes, olefins, ethers, cyclopentadiene, cyanides, phosphine oxides, amines, arsines, isocyanides, phosphines, and phosphites. To our knowledge this represents the widest range of ligands which have been studied thermodynamically for an organometallic system. The enthalpies of ligand exchange span a range of over 50 kcal/mol and are collected in Table III. They provide a means of predicting the position of thermodynamic equilibrium since entropies of reactions can be estimated.[21]

The enthalpy of ligand exchange (eq 11) for any two ligands L and L′ is the difference between the heats of reaction of L and L′ with (benzene)Mo(CO)$_3$. These heats of reaction are listed in Table III. For example, the formation of HMo(CO)$_3$C$_5$Me$_5$ from (CH$_3$CN)$_3$Mo(CO)$_3$, as shown in eq 12, has an estimated enthalpy (using Table III) of +11.9 kcal/mol.

$$(\text{CH}_3\text{CN})_3\text{Mo(CO)}_3 + \text{C}_5\text{Me}_5\text{H} \rightarrow \text{HMo(CO)}_3\text{C}_5\text{Me}_5 + 3\text{CH}_3\text{CN} \quad (12)$$

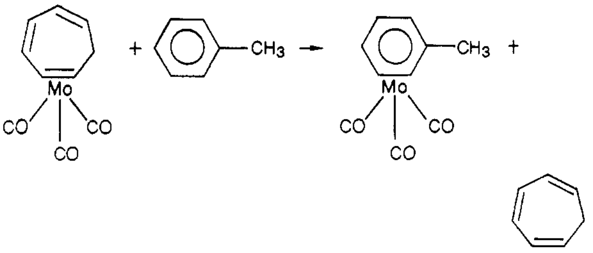
This is in good agreement with an independent study of the temperature variation of the equilibrium constant which yielded +10.8 kcol/mol.[22] In addition to quantitative checks on the data in Table III, we have made numerous qualitative competition studies[17] which verify the relative metal–ligand bond strengths in this system.

The results in Table III can be coupled with organic thermochemical data to estimate the effect of metal binding on the heats of ligand transformations. The isomerization of cycloheptatriene to toluene (eq 13) is exothermic by 31.74 kcal/mol,[23] approximately the resonance energy of the arene.



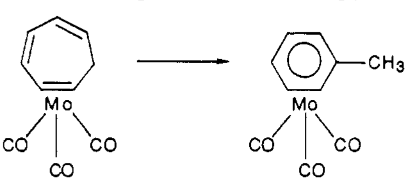
(13)

Equation 14 shows that ligand exchange of toluene for cycloheptatriene is endothermic by 7.1 kcal/mol.



(14)

Addition of eq 13 and 14 yields the enthalpy of isomerization of bound cycloheptatriene to toluene as shown in eq 15.



(15)

The enthalpy of this isomerization (−24.6 kcal/mol) is reduced upon coordination relative to the free ligand. This result can be interpreted either as destruction of the resonance energy of the coordinated toluene or as a gain in stability of cyclo-

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

(20) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160.

(21) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience; New York, 1976. (b) Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449.

(22) Kubas, G. J., unpublished results.

(23) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press; New York, 1970. (b) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

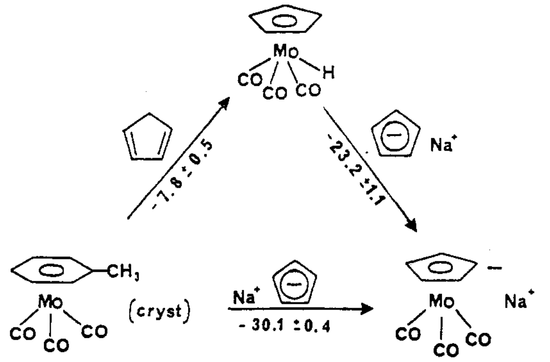
Table III. Calculated Enthalpies for the Ligand Exchange Reaction in Solution[a,b]

$(benzene)Mo(CO)_3 + nL \rightarrow LnMo(CO)_3 + benzene$

ligand	complex	enthalpy	bond strength
benzene	$C_6H_6Mo(CO)_3$	0	63.2
toluene	(tol)Mo(CO)$_3$	−2.0	65.2
p-xylene	(*p*-xyl)Mo(CO)$_3$	−2.3	65.5
cyclooctatetraene	(COT)Mo(CO)$_3$	−2.5	65.7
m-xylene	(*m*-xyl)Mo(CO)$_3$	−3.0	66.2
o-xylene	(*o*-xyl)Mo(CO)$_3$	−3.3	66.2
mesitylene	MesMo(CO)$_3$	−3.5	66.7[b]
phenyltrimethylsilane	$PhMe_3SiMo(CO)_3$	−5.6	68.8
hexamethylbenzene	(HMB)Mo(CO)$_3$	−5.7	68.9
tetraphenylborate	$NaPh_4BMo(CO)_3$	−6.7	69.9
dimethylaniline	(DMA)Mo(CO)$_3$	−7.0	70.3
N,N,N',N'-tetramethylaniline	(TMA)Mo(CO)$_3$	−7.5	70.7
cycloheptatriene	(CHPT)Mo(CO)$_3$	−9.1	72.3
pentamethylcyclopentadiene	$HMo(CO)_3C_5Me_5$	−10.5	91 (Mo–Cp*) 66 (Mo–H)
tetrahydrofuran	$(THF)_3Mo(CO)_3$	−11.3	24.8
acetone	$((CH_3)_2CO)_3Mo(CO)_3$	−11.3	25.0
tri-*tert*-butylphosphine	$(t\text{-}Bu_3P)_2Mo(CO)_3$	−11.8	37.5
cyclopentadiene	$HMo(CO)_3C_5H_5$	−12.8	93 (Mo–Cp) 66 (Mo–H)
bis(methoxyethyl) ether	(diglyme)Mo(CO)$_3$	−14.8	26.0
tert-butyl cyanide	$(t\text{-}BuCN)_3Mo(CO)_3$	−20.0	27.7
benzonitrile	$(C_6H_5CN)Mo(CO)_3$	−20.5	27.9
acetonitrile	$(CH_3CN)_3Mo(CO)_3$	−21.8	28.2
tri-*n*-butylphosphine oxide	$(n\text{-}Bu_3PO)_3Mo(CO)_3$	−22.0	28.4
tricyclohexylphosphine	$(PCy_3)_xMo(CO)_3$	−23.1	
trichlorophosphine	$(PCl_3)_3Mo(CO)_3$	−27.3	30.2
pyridine	$(py)_3Mo(CO)_3$	−30.9	31.4
piperidine	$(pip)_3Mo(CO)_3$	−31.6	31.6
diphenylmethylarsine	$(Ph_2MeAs)_3Mo(CO)_3$	−32.6	31.9
sodium cyclopentadiene	$NaC_5H_5Mo(CO)_3$	−35.1	98.3
potassium hydridotris(pyrazolyl)borate	KTpMo(CO)$_3$	−37.5	33.6
triethylarsine	$(Et_3As)_3Mo(CO)_3$	−37.5	33.6
triphenylphosphine	$(Ph_3P)_3Mo(CO)_3$	−42.2	35.1
methyldiphenylphosphine	$(MePh_2P)_3Mo(CO)_3$	−42.2	35.1
triphenylphosphite	$[P(OPh)_3]_3Mo(CO)_3$	−42.5	35.2
triphos	triphosMo(CO)$_3$	−46.0	36.4
triethylphosphine	$(PEt_3)_3Mo(CO)_3$	−46.7	36.6
dimethylphenylphosphine	$(PMe_2Ph)_3Mo(CO)_3$	−48.8	37.3
tri-*n*-butylphosphine	$(n\text{-}Bu_3P)_3Mo(CO)_3$	−49.3	37.5
cyclohexyl isocyanide	$(CyNC)_3Mo(CO)_3$	−49.9	37.7
tert-butyl isocyanide	$(t\text{-}BuNC)_3Mo(CO)_3$	−50.1	37.8
trimethylphosphine	$(PMe_3)_3Mo(CO)_3$	−52.1	38.4
trimethyl phosphite	$(POMe_3)_3Mo(CO)_3$	−53.5	38.9
carbon monoxide	$Mo(CO)_6$		40.5[c]

[a] Al units are in kcal/mol. The enthalpy of exchange is calculated based on all species being in solution, normally THF, but some arenes in CH_2Cl_2. [b] Bond strength estimates are based on the gas-phase value for Mo–mesitylene reported in ref 27. [c] Refers to first dissociation determined by laser pyrolysis.[41] The average energy has been reported as 36 kcal/mol.[42] Measurement of the exact position of $Mo(CO)_6$ is planned.[19]

Scheme I



heptatriene through "metalloaromaticity".[24] In either case, the energy gap between the two structures is reduced. This type of effect can be of significance in understanding transition-metal-catalyzed isomerizations. Additional studies on related systems are in progress.

A second illustration involves a coordinated ligand reaction rather than an isomerization. Formation of dimethylaniline from benzene and dimethyl amine as shown in eq 16 is thermodynamically disfavored in the gas phase ($\Delta H° = 4.95$ kcal/mol).[23] Combination of eq 16 with the

(16)

ligand displacement reaction 17 leads to reaction 18 which is the stoichiometric conversion of coordinated benzene to coordinated dimethylaniline. Due to the stronger Mo–dimethylaniline bond relative to the Mo–benzene bond (by 7.0 kcal/mol), this process should now be thermodynamically allowed. To our knowledge, a reaction of this type has never been observed[25] and this estimate is made to

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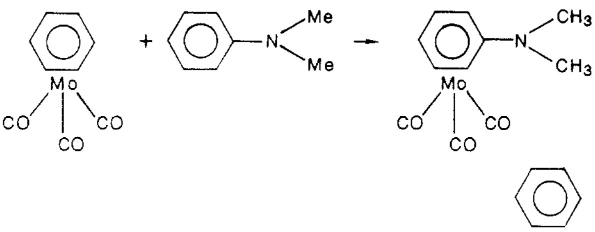
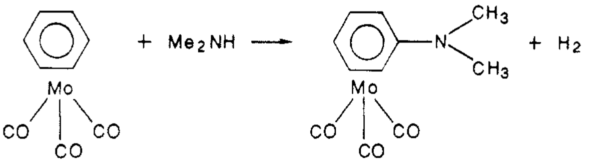
(24) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760.

(25) This hypothetical reaction would represent a stoichiomeric rather than a catalytic conversion. Any catalytic cycle would necessarily involve replacement of bound aniline with free benzene which would cancel the 7.0 kcal/mol gained by preferential coordination of dimethylaniline to molybdenum. It is of interest that converstion of (fluorobenzene)Cr(CO)$_3$ to (aminobenzene)Cr(CO)$_3$ has been reported. Mahaffy, C. A. L.; Paulson, P. L. *J. Chem. Res.* **1978**, 1762.


(17)


(18)

indicate the thermodynamic influence of the metal on the ligand transformation. It is clear that coordination to molybdenum thermodynamically allows a stoichiometric conversion of benzene to dimethylaniline.[25]

Bond Strength Estimates. The generation of bond strength estimates is best done in the gas phase. This is difficult for organometallic complexes other than those of the simplest kind. Due to thermal instability there are few reliable measurements of heats of sublimation. Although for the covalent complexes discussed here it is reasonable to assume that solution phase results reflect the gas-phase data,[26] we consider that our bond strength estimates refer to solution-phase values only. This allows better comparison to kinetically generated estimates. The bond strengths listed in Table III are all based on the calorimetric determination of the Mo–mesitylene bond strength[27] determined by other workers. Comparison to a recent laser pyrolysis value for the Mo–CO bond strength[28] gives confidence to this value as discussed later.

A second problem in discussing individual bond strengths is partitioning of total energy changes within the molecule. For example, the enthalpy of eq 17 is −7.0 kcal/mol in solution and is likely to be similar in the gas phase. We take this to mean that the Mo–dimethylaniline bond is 7.0 kcal/mol stronger than the Mo–benzene bond, since this is the net effect. In reality this energy change is distributed throughout the molecule. The terminal CO ligands may be more strongly bound in the dimethylaniline complex. This point has recently been discussed in detail elsewhere.[29] For this reason, we prefer using the primary data to calculate the enthalpy of a given reaction. We use bond strength estimates only to obtain a qualitative understanding of its thermochemistry.

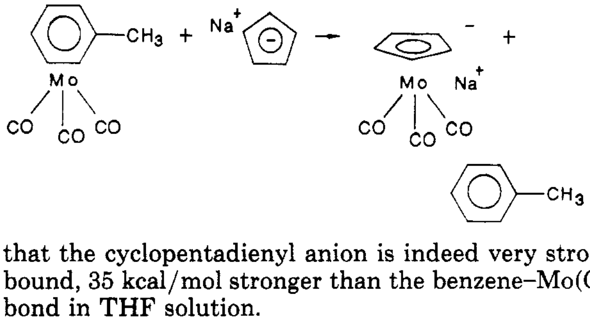
Arene, Olefin, and Cyclopentadienyl Ligands. The order of stability for arenes shown in Table III, benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene < (trimethylsilyl)benzene < hexamethylbenzene < tetraphenylborate < dimethylaniline < *p*-bis(dimethylamino)benzene, spans a range of 7.5 kcal/mol. This is similar in order but smaller in range to that determined for analogous (arene)$Cr(CO)_3$ complexes.[12] It is also in the order of decreasing force constant for the terminal CO stretch and ionization potential of the complexes.[30] It is clear that a major factor in determining the metal–arene bond strengths in these complexes is the ability to donate electron density to the metal and into the antibonding CO orbitals of the $-M(CO)_3$ fragment. The opposite order of stability has been observed for the bis(arene) complexes (arene)$_2$M (M = Cr, Mo, W),[31] where the absence of terminal CO ligands reduces the acidity of the metal center.

As was the case with chromium,[2] the cycloheptatriene–metal bond was found to be stronger than the benzene–metal bond. The cyclooctatetraene complex is 6.6 kcal/mol less stable than the cycloheptatriene complex, probably reflecting the relative inability of cyclooctatetraene to assume a configuration with good metal–ligand overlap. Although the (polyene)$M(CO)_3$ is thermodynamically more stable than the (arene)$M(CO)_3$ complexes for both Cr and Mo, polyene complexes are apparently more reactive. This may be due to lower activation energy in the η^6 to η^4 conversion for the triolefin complexes. While the arene and olefin complexes are among the least stable, with regard to enthalpy of formation, as η^6 ligands, they do have favorable entropies of formation. We measured the equilibrium constant for reaction 19 as a function of temperature.[13] The entropy change for this reaction (−41.5

$$(\mathrm{toluene})\mathrm{Mo(CO)_3} + 3\mathrm{THF} \rightleftharpoons (\mathrm{THF})_3\mathrm{Mo(CO)_3} + \mathrm{toluene} \quad (19)$$

cal/(mol deg)) represents a term of 12.5 kcal/mol at room temperature which favors formation of the arene complex. This value is in agreement with estimates from an entropy cycle[13] and can be used as a rough guide in analogous ligand replacement reactions.

The range of arene–molybdenum bond strengths is small. Caution should be used when drawing conclusions on a case such as the xylenes, where only 0.7 kcal/mol separate their relative bond strength estimates. In this particular case, one should be aware of the experimental error limits (ca. ±1 kcal/mol) and of the operational assumption that solvent effects are unimportant. It is likely that electron-withdrawing substituents on the arene will lead to decreased stability. This is the case with $ClC_6H_5Cr(CO)_3$ which is less stable than $C_6H_6Cr(CO)_3$ by about 2 kcal/mol.[13] It seemed reasonable that the strongest six-electron aromatic donor would be the cyclopentadienyl anion. In this work we have measured the enthalpy of the ionic reaction (20). The enthalpy of this reaction indicates that the cyclopentadienyl anion is indeed very strongly bound, 35 kcal/mol stronger than the benzene–$Mo(CO)_3$ bond in THF solution.


(20)

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[26] To illustrate this, consider the substitution shown:

$$\underset{40.7}{\mathrm{Cr(CO)_5PPh_3}} + \underset{6.7}{\mathrm{PMe_3}} \rightarrow \underset{23.2}{\mathrm{Cr(CO)_5PMe_3}} + \underset{21.8}{\mathrm{PPh_3}}$$

The enthalpies of sublimation in kcal/mole are shown beneath each compound. Data for the phosphines is taken from ref 23 and for the Cr complexes from: Boxhoorn, G.; Ersting, J. M.; Stufkens, D. J.; Oskam, A. *Thermochim. Acta* **1980**, *42*, 315. The difference in the sublimation energies of the complexes (17.5 kcal/mol) is nearly offset by the difference in enthalpy of sublimation of the ligand (15.1 kcal/mol). It seems likely that for nonionic complexes the solution values *may* reflect the gas-phase values, but all bond strength values reported here are solution based values.

[27] Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani-Moatyar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321.

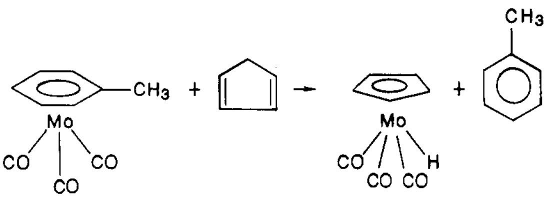
[28] Lewis, M. D.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

[29] Calhorda, M. J.; Frazao, C. F.; Martinho-Simoes, J. A. *J. Organomet. Chem.* **1984**, *262*, 305.

[30] (a) Muller, J. *J. Organomet. Chem.* **1969**, *18*, 321. (b) Neuse, E. W. *J. Organomet. Chem.* **1975**, *99*, 287.

[31] Connor, J. A.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani-Moatyar, M. T. *J. Organomet. Chem.* **1979**, *179*, 331.

We had previously reported the enthalpy of reaction 21.

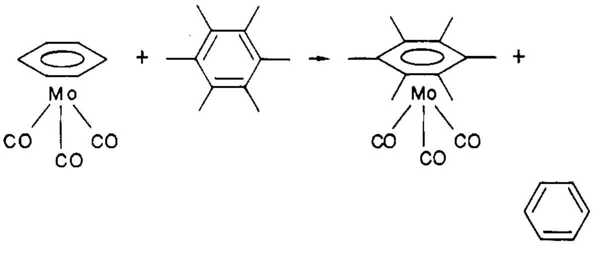


(21)

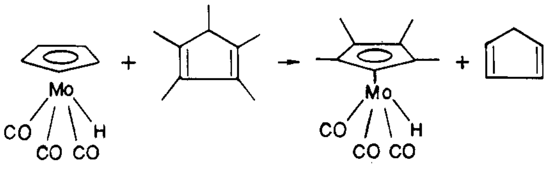
This led to estimations of the Mo–H bond strength as 66 kcal/mol and the Mo–Cp bond strength as 91 kcal/mol.[13] Later work on the heats of hydrogenation of $[Mo(CO)_3C_5H_5]_2$[14] yielded an independent estimate of the Mo–H bond strength of 65 kcal/mol, which agrees with that obtained from reaction 21. This estimate is based on the kinetic determination of the Mo–Mo bond as described by Poe.[32] The value for the Mo–Cp bond strength is quite close to a recent estimate of the Fe–Cp bond strength obtained from laser pyrolysis studies.[33]

Since we had measured the enthalpies of reactions 20 and 21, it was of interest to complete the thermochemical cycle shown in Scheme I. The enthalpy of protonation of NaCp by $HMo(CO)_3Cp$ is –23.2 kcal/mol which compares favorably with the predicted value of –22.3 kcal/mol. Jordan and Norton[34] have recently determined the pK_a value of $HMo(CO)_3Cp$. Assuming that the entropies of deprotonation are similar, we estimate that HMp should be 16.2 pK_a units more acidic than C_5H_6. This is in reasonable agreement with literature values.[34]

The relative stability of pentamethylcyclopentadiene is also of interest since this ligand is present in a number of important organometallic complexes.[35] The substitution of hexamethylbenzene for benzene in eq 22 is exothermic by about 6 kcal/mol. The enthalpy of reaction 21 was measured with C_5Me_5H replacing C_5H_6[15] and indicates that the enthalpy of eq 23 is actually endothermic. This result was surprising and indicates that, assuming that the C_5R_5–H (R = H, CH_3) bond strengths are the same for the free ligands, the pentamethylcyclopentadienyl–molybdenum bond is not appreciably stronger and may actually be slightly weaker than the cyclopentadienyl–metal bond for these complexes. It is interesting that although increased methyl substitution causes net strengthening of the metal–arene bond, analogous substitution in the cyclopentadienyl group does not induce similar behavior.



(22)



(23)

Phosphine, Arsine, and Amine Donors. Thermochemical data for a series of phosphine and phosphite ligands were reported earlier.[16] The relative stabilities of these complexes were shown to depend on both steric and electronic factors. As defined by Tolman,[8] the cone angle θ measures the steric bulk of a phosphine ligand. The totally symmetric vibrational frequency ν of $LNi(CO)_3$ measures the relative basicity of the phosphine ligand. The enthalpy of reaction with (toluene)$Mo(CO)_3$ was shown to obey the relationship (24). Work in progress is aimed at

$$\Delta H = A_0 + A_1\theta + A_2\nu \qquad (24)$$

determining the relative thermochemistry in the less crowded complexes $L_2Mo(CO)_4$ and $LMo(CO)_5$. Finally, it is worth pointing out that, with regard to enthalpy of reaction, 2 mol of strong ligand such as PR_3, CO, or RNC are sufficient to replace an η^6-arene ligand.

Extension of this work to the heavier group V ligands Et_3As and Ph_2AsMe shows that these are more weakly bound than are the analogous phosphines. The difference between the Et_3E and Ph_2MeE (E = P, As) is 4.5 kcal/mol for phosphorous and 4.9 kcal/mol for arsenic, implying a similar group contribution from the substituents. In both cases the arsenic complex is about 10 kcal/mol less stable or an average bond strength energy difference of 3.3 kcal/mol between the Mo–As and Mo–P bonds.

It was not possible to obtain analogous thermochemical data for amine complexes. No evidence was found for formation of $(Et_3N)_3Mo(CO)_3$.[17] Due to the smaller Mo–N bond length compared to phosphorous, greater steric repulsion between the amine alkyl groups would be expected. The complexes *fac*-$py_3Mo(CO)_3$ and *fac*-$pip_3Mo(CO)_3$ (pip = piperidine) showed similar stabilities in solution. They were comparable to the arsine ligands. The stability of the group V ligands appears to decrease in the order P > As > N. This is, of course, subject to wide variation depending on the substituents. For example, PCl_3 is held more weakly than the arsine and amine ligands studied. The lability of PCl_3 complexes of group VI metals is well-known.[9]

The presence of additional charge density on a donor ligand, such as Ph_4B^- and $C_5H_5^-$ was shown to increase the stability of these complexes. The anion Tp^- (hydridotris(pyrazoyl)borate) has been shown to form a number of interesting complexes which are formally similar to the corresponding $C_5H_5^-$ complexes.[36] The qualitative differences in the nature of the bonding in these complexes has been pointed out.[37] The increased electron density on the nitrogen donors in Tp^- results in a 6.6 kcal/mol increase in stability relative to $py_3Mo(CO)_3$, an analogous donor. It is also of interest that the Tp^- ligand is close to and slightly stronger than Cp^- in this system. These chelating ligands would also be favored with regard to entropy of binding. The other chelating ligand investigated, triphos, $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$, which consists of two diphenylalkyl- and one phenyldialkylphosphine groups is in between Ph_2PMe and $PhPMe_2$ in

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[34] (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) As shown in ref 33a, $HMo(CO)_3Cp$ has a pK_a 2.1 units greater than 2,4 dinitrophenol in acetonitrile. Cyclopentadiene is 11 pK_a units weaker than 2,4-DNP (Gordon, A. J.; Ford, R. A. *The Chemists Companion*, Wiley: New York, 1972; p 61). This implies a 13.1 pK_a unit difference between $HMo(CO)_3Cp$ and C_5H_6. The enthalpy of protonation, –22.3 kcal/mol, implies a difference of 16.2 pK_a units. We have not been able to find pK_a data for C_5H_6 in acetonitrile solution, and our measurements are in tetrahydrofuran. Despite this the agreement is reasonable.

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formation enthalpy, indicating little ring strain in (triphos)Mo(CO)$_3$. Detailed investigation of ring strain in chelating phosphine ligands is in progress.[19]

Cyanides, Isocyanides, Oxygen Donors, and Carbon Monoxide. The phosphine ligands PR$_3$ showed a strong dependence on the nature of the substituents bound to phosphorous. This would not be expected to be true with nitriles R$_3$CCN where two additional atoms insulate the electronic effect of the R group on the donor atom. In a similar fashion, steric repulsions would be expected to be less severe. The data for *tert*-butyl cyanide, benzonitrile, and acetonitrile illustrate this, with heats of exchange with (benzene)Mo(CO)$_3$ of −20.0, −20.5, and −21.8 kcal/mol. The same situation exists with the isocyanides, where the heats of exchange are −49.9 and −50.1 kcal/mol for cyclohexyl and *tert*-butyl isocyanide, respectively. It is well-known in organometallic chemistry that nitriles are relatively weak, labile ligands and that isocyanides form strong bonds. From the data in Table III we can calculate the enthalpy of reaction 25, substitution of three cyanides

$$fac\text{-}(CO)_3Mo(NCR)_3 + 3CNR \rightarrow fac\text{-}(CO)_3Mo(CNR)_3 + 3RCN \quad (25)$$

by three isocyanides as −30 kcal/mol or a difference in the metal ligand bond strengths of 10 kcal/mol. In this regard, it is of interest that a recent gas-phase study has shown the heat of protonation of CH$_3$NC to be 13.4 kcal/mol more exothermic than CH$_3$CN,[38] close to the difference in heats of binding to molybdenum. For the free organic compound the isomerization of a cyanide to an isocyanide is +15 kcal/mol.[23] From eq 25 and 26, we can approximate

$$H_3C\text{–}CN \rightarrow H_3C\text{–}NC \quad (26)$$

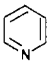
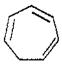
the enthalpy of coordinated cyanide to isocyanide isomerization to be +15 kcal/mol or +5 kcal/mol/cyanide unit. Thus, it is clear that although formation of isocyanide as shown in eq 27 is kinetically controlled, coordination to molybdenum does reduce the total energy difference between the cyanide and isocyanide isomers.

$$fac\text{-}(CO)_3Mo(NCR)_3 \rightarrow fac\text{-}(CO)_3Mo(CNR)_3 \quad (27)$$

Four oxygen donors were investigated in this series. The complex (THF)$_3$Mo(CO)$_3$ is slightly more stable than arene and olefin complexes, with an average Mo–THF bond strength of 24.8 kcal/mol. The acetone complex is virtually identical in thermodynamic stability with the tetrahydrofuran complex. In addition to a presumably more favorable entropy of formation, the tridentate ether, diglyme, shows a slightly greater enthalpy of exchange with (benzene)Mo(CO)$_3$. This could be due to reduced steric repulsion in the chelating system. In this work, we also report the first organometallic bond strength estimate for a phophine oxide. The complex (n-Bu$_3$P=O)$_3$Mo(CO)$_3$ is considerably more stable with regard to ligand exchange than (THF)$_3$Mo(CO)$_3$ and of approximately equal stability to (RCN)$_3$Mo(CO)$_3$. The average bond strength difference between the n-Bu$_3$P–Mo and n-Bu$_3$P=O—Mo bonds is 9.1 kcal/mol. In several systems, it has been observed that, when phosphine-substituted catalysts are used, there is conversion by traces of oxygen of the phosphine ligand to a phosphine oxide.[39] In some cases, this is essential to the generation of an active catalyst. The work shows that the Mo–OPR$_3$ bond is of intermediate strength and should be considerably more labile than the corresponding metal–phosphine bond.

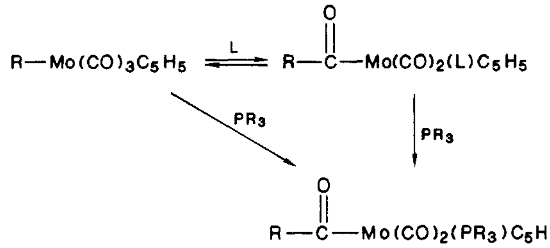
Table IV. Average Enthalpies of Exchange for the Reactions

$L_xM[P(OMe)_3]_n + nL \rightarrow L_xm[L]_n + nP(OMe)_3{}^a$

L	$^1/_3\Delta H_{Mo}{}^b$	$\Delta H_{Pt}{}^c$	$^1/_4\Delta H_{Ni}{}^d$
P(OMe)$_3$	0	0	0
PMe$_3$	0.5	0	3.8
t-BuNC	1.1		3.2
PMe$_2$Ph	1.6	1.2	3.2
PEt$_3$	2.3	1.9	4.5[e]
P(OPh)$_3$	3.7	4.8	3.0
PPh$_2$Me	3.8	4.1	4.8
AsEt$_3$	5.3	10.8[f]	
	7.5	14	
H$_3$C–CN	10.4	22.0	
Ph–CN	11.0	21.5	
	14.0	26.2	
	14.8		12.8[g]

[a] Enthalpies of reaction refer to solution values and are expressed in kcal/mol. [b] Refers to one-third of the enthalpy of reaction in THF solution: [P(OMe)$_3$]$_3$Mo(CO)$_3$ + 3L → L$_3$Mo(CO)$_3$ + 3P(OMe)$_3$. [c] Refers to the enthalpy of reaction in THF solution: (CH$_3$)Pt(PMe$_2$Ph)$_2$[P(OMe)$_3$] + L → (CH$_3$)Pt(PMe$_2$Ph)$_2$L + P(OMe)$_3$. [d] Refers to one-fourth the enthalpy of reaction in toluene: Ni[P(OMe)$_3$]$_4$ + 4L → NiL$_4$ + 4P(OMe)$_3$. Data calculated from ref 7a. [e] Only the NiL$_3$ complex was formed when Ni(COD)$_2$ was treated with excess PEt$_3$. The value of 4.5 can be calculated from ΔH = 16 kcal/mol for the reaction Ni(PEt$_3$)$_4$ ⇌ Ni(PEt$_3$)$_3$ + PEt$_3$. Data calculated from ref 7b. [f] This value is based on calculation for Me$_3$As rather then Et$_3$As. [g] This value is based on calculation for cyclooctadiene rather than cycloheptatriene.

Carbonyl insertion for the organomolybdenum complexes has been shown to be promoted[40] by ligands according to the mechanism shown in eq 28. Tetrahydrofuran, cyanides, and phosphine oxides have been shown to serve as promoters of this reaction. These ligands all share the quality of being intermediate in bond strength to molybdenum, i.e., strong enough to form the acyl intermediate, and weak enough to be readily replaced by the stronger phosphine ligand.



(28)

It is clear from Table III that the strongest ligands are phosphines and isocyanides. The position of carbon monoxide is of real interest. The first dissociation energy of CO from Mo(CO)$_6$ has been determined as 40.5 kcal/mol by laser pyrolysis.[28] This compares to an average value estimated from calorimetric measurements of 36.0 kcal/mol.[41] Therefore the exact position of Mo(CO)$_6$ remains a question, but it is clear that the relative order of stability for two-electron donors is THF < cyanide ≈ phosphine

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oxide < PCl_3 < pyridine < arsines < phosphines ≈ phosphites ≈ isocyanides ≈ carbon monoxide.

Comparison to Other Thermodynamic Data. Several zerovalent group VI complexes similar or identical with those in Table III have been studied by other groups. Differential scanning calorimetry has been used to investigate reactions of the complexes $AmMo(CO)_5$ (Am = pyridine, piperidine, etc.).[42,43] High-temperature thermal decomposition and iodination studies have appeared for some of the complexes we have examined.[2,27,44,45] Our solution thermochemical results are qualitatively in agreement with these gas-phase values. Quantitative disagreements may be attributed to differences between the gas and solution phases. The absolute value for the Mo–mesitylene[27] bond strength in the gas phase is taken as a benchmark for our solution results. A second gas-phase value for Mo–CO in $Mo(CO)_6$[28] determined by laser pyrolysis also seems to be in accord with our solution bond strength estimates.

Since the primary use of bond strength data is to calculate heats of reaction in solution, we prefer doing this directly, without recourse to bond strength estimates. The data for ligand exchange reported in Table III are subject only to experimental errors such as those shown in Tables I and II and are typically accurate to ±1 kcal/mol. Uncertainties in bond strength assignments due to comparison between gas-phase and solution-phase values make the absolute bond strength assignments considerably less reliable, probably on the order of ±5 kcal/mol. However, these values have an internal relative accuracy which is considerably better.

Extensive solution thermochemical data, more readily comparable to our work, has appeared for three systems. Partenheimer[4] has reported the enthalpies of reaction on the Pd–L system (eq 1). The order of bond strengths was triphenylphosphine > triphenyl phosphite > pyridine > cyclooctadiene. More extensive data have been reported for reactions 2 and 3. In both of these cases and in our system, $P(OMe)_3$ was the strongest ligand. In Table IV, we report the normalized enthalpies of substitution for ligands in our study which overlap with these systems. Dividing the enthalpies of reaction 29 by n gives an average

$$AxM[P(OMe)_3]_n + nL \rightarrow AxML_n + nP(OMe)_3 \qquad (29)$$

relative bond strength for the different metals. Trimethyl phosphite is taken as the reference in eq 29, since it is the strongest ligand for all three systems and since the complexes in eq 2 and 3 do not form stable benzene complexes. Thus, the compounds in Table IV are listed in order of decreasing stability relative to their respective $P(OMe)_3$ complexes. There are some remarkable similarities but also some important differences in the three metals studied.[46] Preliminary work on the $L_2Mo(CO)_4$ and $LMo(CO)_5$ sytems shows that even for complexes of the same metal and oxidation state, the changing steric and electronic factors of the metal can vary the order of stability.[17] Extrapolation of results from this system to others is not yet warranted. Additional work in progress is aimed at determining a complete thermodynamic surface for the reactions of these organomolybdenum complexes.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE 8314497) is gratefully acknowledged. We also thank Dr. John Connolly of the University of Missouri at Kansas City for a gift of KTp. We also wish to thank Mr. Shakti Mukerjee for experimental assistance in some of the measurements.

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Lithiophosphinoferrocenes. A Route to Polyphosphines and Ring-Substituted Ferrocenophanes

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Received October 29, 1985

The metalation of $Fe(C_5H_4PPh_2)(C_5H_5)$ (**7**) by *n*-BuLi affords predominantly hetero-ring dilithiated products **8** best characterized by their reaction with S_8 which yields the [3]ferrocenophanes $Fe(C_5H_3(P(S)Ph_2)S\text{-}1,n)(C_5H_4S_2)$ (n = 3 (~75%) or 2 (~25%). The PPh_2 group has some effect in directing the metalation of **7** to the 2-position. Reaction of **8** with $ClPPh_2$ affords tris(tertiary phosphines) and with Cl_2PPh affords [1]ferrocenophanes such as $Fe(C_5H_3(PPh_2)PPh\text{-}1,3)(C_5H_4)$ (**12a**). Cleavage of **12a** with RLi takes place so that the anion is formed predominantly in the PPh_2-substituted ring allowing the preparation of compounds such as $Fe(C_5H_3(PPh_2)SiMe_3\text{-}1,3)(C_5H_4PPhMe)$. Some arsenic derivatives and related chemistry of $Fe(C_5H_4PPh_2)_2$ are also described.

Introduction

The lithiation of ferrocene has proven to be a useful initial reaction step in the synthesis of a wide range of substituted ferrocenes.[1-3] In particular this route is well established for the preparation of ferrocenylphosphines which form many useful transition-metal complexes.

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