Inorg. Chem. **1992**, *31*, 4885–4889

Heats of the Reactions of (Naphthalene)Cr(CO)$_3$, (Cycloheptatriene)Cr(CO)$_3$, (Cycloheptatriene)W(CO)$_3$, and (EtCN)$_3$W(CO)$_3$ with Pyridine, Phosphines, Phosphites, and Other Ligands. Comparative Thermochemical Study of L$_3$M(CO)$_3$ Complexes (M = Cr, Mo, W)

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Received July 30, 1991

Enthalpies of ligand substitution based on reaction of (cycloheptatriene)Cr(CO)$_3$, (naphthalene)Cr(CO)$_3$, (cycloheptatriene)W(CO)$_3$, (EtCN)$_3$W(CO)$_3$, and (arene)W(CO)$_3$ complexes with a series of ligands have been measured by solution calorimetry. These data generate an order of thermochemical stability for the complexes L$_n$M(CO)$_3$ (M = Cr, W). These data are combined with earlier data reported for analogous organomolybdenum complexes and allow comparison of relative enthalpies of ligand substitution as a function of the metal. Referenced to the (η^6-C$_6$H$_6$)M(CO)$_3$ complex, ligand substitution reactions producing L$_n$M(CO)$_3$ become increasingly exothermic in going from Cr to Mo to W, in keeping with the expected increase in bond strength in going from a first- to a second- to a third-row metal.

Introduction

Thermochemical studies of inorganic/organometallic complexes in the gas phase[1] and in solution[2] provide information about reaction energetics and complex stability. There are relatively few cases where first-, second-, and third-row transition metals can be directly compared. One such example was reported by Smith,[3] who determined the bond dissociation energies of group VI hexacarbonyls:

$$M(CO)_6(g) \rightarrow M(CO)_5(g) + CO \qquad (1)$$

M, D (kcal/mol): Cr, 36.5; Mo, 40.0; W, 46.0

These data parallel the data of Connor[4] for average bond dissociation energies (one-sixth the calculated enthalpy of reaction 2).

$$M(CO)_6(g) \rightarrow M(g) + 6CO \qquad (2)$$

M, D (kcal/mol): Cr, 26.0; Mo, 36.0; W, 43.0

We have studied ligand substitution for a number of organomolybdenum complexes in solution.[5] In particular, the enthalpies of substitution based largely on reaction 3 have been determined[6] for a wide range of ligands. In this paper, we report analogous enthalpies of substitution for chromium and tungsten complexes. These data highlight the role of the metal in organometallic solution thermochemistry for ligand substitutions of an isostructural set of complexes.

$$(p\text{-xylene})Mo(CO)_3 + nL \xrightarrow{THF} L_nMo(CO)_3 + p\text{-xylene} \qquad (3)$$

Experimental Section

All manipulations of organometallic complexes and solutions were done under an argon atmosphere either in a Vacuum/Atmospheres glovebox or with standard Schlenk tube techniques. Toluene and THF were purified by distillation from sodium benzophenone ketyl under argon. Acetonitrile was purified by distillation from P$_2$O$_5$ under argon. The complexes (naphthalene)Cr(CO)$_3$, (cycloheptatriene)Cr(CO)$_3$, (CH$_3$CN)$_3$Cr(CO)$_3$, (cycloheptatriene)W(CO)$_3$, (EtCN)$_3$W(CO)$_3$, and (arene)M(CO)$_3$ were prepared and recrystallized according to standard literature procedures.[7] Enthalpies of solution and reaction were measured by solution calorimetric techniques similar to those described in detail elsewhere[5,6] using a Setaram C-80 Calvet calorimeter. A typical procedure is described below. Infrared spectra were recorded using a Perkin-Elmer 1850 FTIR in solution cells obtained from Harrick Scientific with KBr, CaF$_2$, or Ge windows. In all cases, carbonyl bands in agreement with literature data[7] were obtained, and the infrared data indicated quantitative production of product in solution.

Measurement of Enthalpy of Reaction of (CHPT)Cr(CO)$_3$ and Pyridine. A sample of the complex (CHPT)Cr(CO)$_3$ which had been recently purified by vacuum sublimation was taken into the glovebox with the mixing cell for the Calvet calorimeter along with THF which had been purified by distillation from sodium benzophenone. Pyridine which had been refluxed for 24 h over anhydrous BaO was distilled into flame-dried glassware. A stock solution of 10% pyridine in THF was prepared. A sample of approximately 0.05 g of (CHPT)Cr(CO)$_3$ was loaded into the mixing cell of the calorimeter, which was closed and sealed with triply distilled Hg. The solution of pyridine in THF was "seeded" by addition

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Table I. Combined Data for Enthalpies of Reaction

$$C_6H_6Cr(CO)_3 + 3L \rightarrow L_3Cr(CO)_3 + C_6H_6$$

ligand	ΔH (kcal/mol)	ligand	ΔH (kcal/mol)
naphthalene	+6.3 ± 0.6	P^nBu_3	−40.8 ± 1.6
benzene	0.0 ± 1.2	triphos	−40.9 ± 2.4
mesitylene	−4.3 ± 1.2	PEt_3	−42.1 ± 1.8
CHPT	−6.5 ± 0.6	PMe_2Ph	−43.4 ± 1.8
C_5Me_5H	−10.0 ± 1.0	$P(OMe)_3$	−44.0 ± 1.6
CH_3CN	−10.7 ± 1.2	CyNC	−44.5 ± 2.4
py	−21.3 ± 1.3	PMe_3	−48.2 ± 2.4
PPh_2Me	−31.8 ± 1.4		

of a small amount of (CHPT)$Cr(CO)_3$, and 4.0 mL of the resulting solution was added to the upper chamber of the mixing cell. The cell was sealed in the glovebox and loaded into the calorimeter for equilibration. After about 2 h, the reaction was initiated by rotation of the calorimeter and followed over the next 2 h until the thermogram indicated complete reaction. Following completion of the calorimetric run, the cell was taken into the glovebox and opened and an infrared spectrum run of the clear red-orange solution, which indicated quantitative conversion to *fac*-$(py)_3Cr(CO)_3$.[7] The enthalpy of reaction so measured was −11.7 ± 0.5 kcal/mol and is based on five separate measurements. Subtraction of the enthalpy of solution of (CHPT)$Cr(CO)_3$ in THF (+3.1 ± 0.2 kcal/mol, average of four measurements) yields an enthalpy of reaction in solution of −14.8 ± 0.7 kcal/mol.

Results

Enthalpies of Substitution Based on Reactions of (Cycloheptatriene)$Cr(CO)_3$. Reaction of (CHPT)$Cr(CO)_3$ with excess ligand (L) in THF occurs at variable rates, depending on the nature of L. For most ligands, reaction is complete in 20–120 min when 10% solutions of L in THF are used and the reaction temperature is 30 °C. All reactions reported were quantitative as determined by FTIR spectroscopy and proceed as shown in eq 4. The direct experimental data for eq 4 have been adjusted to

$$(\mathrm{CHPT})Cr(CO)_3(s) + nL(soln) \xrightarrow[30\,°C]{THF} \textit{fac}\text{-}L_nCr(CO)_3(soln) + \mathrm{CHPT}(soln) \quad (4)$$

calculate the enthalpies of substitution with all species in solution by subtraction of the enthalpy of solution of (CHPT)$Cr(CO)_3$ (+3.1 ± 0.2 kcal/mol). As shown in previous work on related systems,[5,6] for these relatively nonpolar complexes heats of solution largely cancel. Experimental data for reaction 4 as a function of ligand are listed in supplementary Table I. These data are combined with other data below and listed as a general order of stability in Table I in the text.

Enthalpies of Substitution Based on Reactions of (Naphthalene)$Cr(CO)_3$. The above method was useful for complexes more stable than (CHPT)$Cr(CO)_3$; however, the complex (naphthalene)$Cr(CO)_3$ made possible the thermochemical study of a wider range of ligands, as shown in eq 5. These reactions probably

$$(\mathrm{naphthalene})Cr(CO)_3(s) + nL(soln) \xrightarrow[50\,°C]{THF} \textit{fac}\text{-}L_nCr(CO)_3(soln) + \mathrm{naphthalene}(soln) \quad (5)$$

proceed through the complex $(THF)_3Cr(CO)_3$ formed upon solvolysis[8] (eq 6). The complex $(THF)_3Cr(CO)_3$ is unstable and in the absence of added ligand slowly decomposes. For this reason, the enthalpy of solution of (naphthalene)$Cr(CO)_3$ in THF could not be measured directly. Calorimetric attempts to measure this did not return to the baseline due to the slow but exothermic solvolysis reaction. The enthalpy of solution in toluene at 30 °C was measured to be +4.8 ± 0.1 kcal/mol, and we adopt the value in THF of +4.8 ± 1.0 kcal/mol. That value is in keeping with estimates of the thermograms for solution in THF and the fact that for low-valent complexes of this type the enthalpies of solution in toluene and THF are similar.[6] Enthalpies of substitution based on reactions of (naphthalene)$Cr(CO)_3$ are collected in supplementary Table II.

$$(\mathrm{naphthalene})Cr(CO)_3 \overset{THF}{\rightleftharpoons} (THF)_3Cr(CO)_3 + \mathrm{naphthalene} \quad (6)$$

Combined Data for $L_nCr(CO)_3$ Series. The studies described above based on reactions 4 and 5 were made for both PMe_3 and PMe_2Ph for both complexes. Comparisons of data for these two complexes in supplementary Tables I and II show that reactions based on (naphthalene)$Cr(CO)_3$ are more exothermic by 12.8 ± 0.6 kcal/mol. Combined data for chromium are shown in Table I, where average values have been incorporated for PMe_3 and PMe_2Ph. The enthalpies of reaction shown in Table I are all relative to $C_6H_6Cr(CO)_3$ and correspond to reaction 7. Also

$$C_6H_6Cr(CO)_3(soln) + nL(soln) \rightarrow L_nCr(CO)_3(soln) + C_6H_6(soln) \quad (7)$$

included in Table I are data for formation of $HCr(CO)_3C_5Me_5$ as measured earlier on the basis of reaction 8.[9]

$$(\mathrm{naphthalene})Cr(CO)_3 + C_5Me_5H \rightarrow (\eta^5\text{-}C_5Me_5)Cr(CO)_3H + \mathrm{naphthalene} \quad (8)$$

As an additional check, the enthalpy of reaction 9 was determined by direct measurement. The directly measured

$$(CH_3CN)_3Cr(CO)_3 + 3py \xrightarrow[30\,°C]{THF} (py)_3Cr(CO)_3 + 3CH_3CN \quad (9)$$

enthalpy of reaction 9 (−11.5 ± 0.9 kcal/mol) is in reasonable agreement with the value calculated from data in Table I (−10.6 ± 2.5 kcal/mol). Independent checks of this type were made to give confidence to the experimental data.

Enthalpies of Substitution Based on Reactions of (Cycloheptatriene)$W(CO)_3$. Reaction of (CHPT)$W(CO)_3$ with excess ligand L in THF proceeds quantitatively as shown in eq 10.

$$(\mathrm{CHPT})W(CO)_3(s) + nL(soln) \xrightarrow[30\,°C]{THF} \textit{fac}\text{-}L_nW(CO)_3(soln) + \mathrm{CHPT}(soln) \quad (10)$$

Experimental data for eq 10, adjusted for the enthalpy of solution of (CHPT)$W(CO)_3$ in THF (+3.4 ± 0.2 kcal/mol), are collected in supplementary Table III.

Enthalpies of Substitution Based on Reactions of $(EtCN)_3W(CO)_3$. In order to include data on the thermochemical stability of nitrile complexes, we measured the enthalpies of reactions 11 and 12. The data shown correspond to reactions with all species in solution. Thus the values include the enthalpy of solution of $(EtCN)_3W(CO)_3$ in 10% EtCN/THF: +4.3 ± 0.2 kcal/mol. It was found that addition of nitrile was added to suppress formation of small amounts of solvation by THF. Careful examination of the infrared spectrum of $(EtCN)_3W(CO)_3$ in pure THF showed formation of shoulder peaks and broadening which were concentration dependent and fully reversible upon addition of EtCN. This was consistent with establishment of the equilibrium shown in eq 13. Addition of EtCN completely suppresses this reaction and allows accurate determination of the enthalpy of solution. The difference between the enthalpies of

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$$(Et_3CN)_3W(CO)_3 + 3py \xrightarrow[30\,°C]{THF} (py)_3W(CO)_3 + 3EtCN \quad (11)$$

$$\Delta H = -12.7 \pm 1.2 \text{ kcal/mol}$$

$$(Et_3CN)_3W(CO)_3 + 3P(OMe)_3 \xrightarrow[30\,°C]{THF} (P(OMe)_3)_3W(CO)_3 + 3EtCN \quad (12)$$

$$\Delta H = -31.9 \pm 2.2 \text{ kcal/mol}$$

$$(EtCN)_3W(CO)_3 + THF \rightleftharpoons (EtCN)_2(THF)W(CO)_3 + EtCN \quad (13)$$

reactions 11 and 12 (19.2 ± 3.0 kcal/mol is in reasonable agreement with the calculated difference in stability between $(py)_3W(CO)_3$ and $(P(OMe)_3)_3W(CO)_3$ of 22.6 ± 4.2 kcal/mol from the data in supplementary Table III.

Reaction of (Arene)$W(CO)_3$ Complexes with Pyridine. Thermochemical stability of (arene)$W(CO)_3$ complexes was determined by investigating the enthalpy of reaction with pyridine according to eq 14. These reactions proceed to completion at

$$(arene)W(CO)_3(s) + 3py(soln) \xrightarrow{py/THF} (py)_3W(CO)_3(soln) + arene(soln) \quad (14)$$

50–60 °C in py/THF solution. Experimental data are collected in supplementary Table IV. These data place the thermochemical position of the arene complexes relative to pyridine. Combined data for the tungsten complexes, also including enthalpy of formation data for $(\eta^5\text{-}C_5Me_5)W(CO)_3H$,[9] are collected in Table II.

Discussion

The goal of this work was to investigate the thermodynamic role played by the metal with regard to the relative stability of organometallic complexes in solution. In spite of the generally held view that metal–ligand bond strengths increase in descending a given transition metal triad,[4] there are surprisingly few thermodynamic data for isostructural complexes of first-, second-, and third-row metals. This is particularly true of metal complexes in solution. As mentioned in the Introduction, Smith[3] has determined the first bond dissociation energies of Cr, Mo, and W hexacarbonyls. Blake[10] concluded in his thermodynamic study of oxidative addition reactions that those of Rh(I) are about 0.8 times as exothermic as reactions of corresponding Ir(I) complexes:

$$L_nM + X\text{–}Y \rightarrow L_nM(X)Y \quad (15)$$

$$\Delta H_{Ir} = 1.25\Delta H_{Rh}$$

We have recently investigated[11] binding of ligands to the sterically crowded Kubas type complexes:

$$(P(C_6H_{11})_3)_2M(CO)_3 + L \rightarrow (P(C_6H_{11})_3)_2M(CO)_3L \quad (16)$$

$$M = Cr, Mo, W$$

The enthalpies of binding were in the general order Cr < Mo < W; however, there were some exceptions. Molecular H_2 and N_2 bound roughly the same to Cr and Mo. For larger ligands such as pyridine and trimethyl phosphite, the order Cr < Mo < W was strictly followed; however, steric factors probably play a significant role in these complexes, particularly for the first-row metal.

Table II. Combined Data for Enthalpies of Reaction

$$C_6H_6W(CO)_3 + 3L \rightarrow L_3W(CO)_3 + C_6H_6$$

ligand	ΔH (kcal/mol)	ligand	ΔH (kcal/mol)
benzene	0 ± 1.5	PPh_2Me	−53.8 ± 1.8
mesitylene	−5.6 ± 1.9	triphos	−56.7 ± 1.5
$Me_2NC_6H_5$	−8.5 ± 1.7	PEt_3	−60.2 ± 1.7
CHPT	−12.5 ± 1.5	PMe_2Ph	−60.8 ± 1.7
C_5Me_5H	−22.3 ± 3.0	PBu_3	−61.1 ± 1.4
ETCN	−27.7 ± 3.0	$P(OMe)_3$	−63.0 ± 1.4
py	−40.4 ± 2.8	CyNC	−65.8 ± 1.4
$P(OPh)_3$	−53.1 ± 1.3	PMe_3	−65.8 ± 1.3

Table III. Relative Thermochemical Stability [$-\Delta H_{reacn}$ (kcal/mol)]

$$C_6H_6M(CO)_3 + nL \rightarrow L_nM(CO)_3 + C_6H_6 \quad (M = Cr, Mo, W)$$

ligand	Cr	Mo	W
benzene	0.0	0.0	0.0
mesitylene	4.3	3.5	5.6
$Me_2NC_6H_5$		7.5	8.5
CHPT	6.5	9.1	12.7
C_5Me_5H	10.0	10.5	22.3
CH_3CN	10.7	21.8	27.7
py	21.3	30.9	40.4
$P(OPh)_3$		42.5	53.1
PPh_2Me	31.8	42.2	53.8
P^nBu_3	40.8	49.3	61.1
triphos	40.9	46.0	56.7
PEt_3	42.1	46.7	60.2
PMe_2Ph	43.4	48.8	60.8
$P(OMe)_3$	44.0	53.5	63.0
$C_6H_{11}NC$	44.5	49.9	65.8
PMe_3	48.2	52.1	65.8

Burkey[12] recently investigated agostic bond strengths for hydrocarbons and silanes via photoacoustic calorimetry:

$$M(CO)_6 \rightarrow CO + M(CO)_5 + R\text{–}H \rightarrow M(CO)_5(H\text{–}R) \quad (17)$$

Enthalpies of alkane binding were calculated to be 9.6 ± 2.3, 8.7 ± 2.7, and 13.4 ± 2.0 kcal/mol for Cr, Mo, and W, respectively. Thus the binding was significantly stronger to W but nearly the same for Cr and Mo. Binding of silanes was exothermic by 21.1 ± 2.3, 22.0 ± 2.1, and 27.8 ± 2.1 kcal/mol for Cr, Mo, and W, respectively.

This work reports new data for enthalpies of substitution of the complexes $L_nM(CO)_3$ (M = Cr, W). These data are combined with previously reported data on corresponding molybdenum complexes[6] and give a good picture of relative bond strengths in solution for a complete metal triad. Enthalpies of substitution are combined in Table III for reaction 18. These data are also shown graphically in Figure 1.

$$C_6H_6M(CO)_3 + nL \rightarrow L_nM(CO)_3 + C_6H_6 \quad (18)$$

$$M = Cr, Mo, W$$

Examination of the data in Table III and Figure 1 shows that, except for binding of arenes and C_5Me_5H, the enthalpies of ligand substitution become progressively more exothermic in going from

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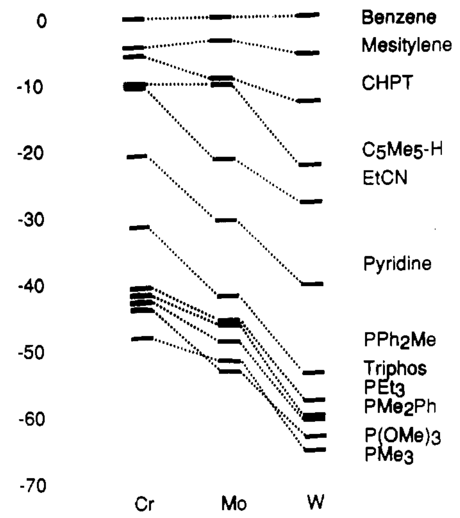

Figure 1. Relative stability of *fac*-$L_3M(CO)_3$ complexes.

Cr to Mo to W. It appears as if a uniform projection of the bond strengths as a function of donor ability is occurring. In order to determine absolute bond strengths, it would be necessary to know the heat of formation of the tricarbonyls. Thus, the net enthalpies of binding of the ligands we have studied can be thought of as being the second stage of the two-part reaction shown in eq 19.

$$M(CO)_3(g) + C_6H_6 \xrightarrow{\text{i}} (C_6H_6)M(CO)_3 + nL \xrightarrow{\text{ii}} L_nM(CO)_3 \quad (19)$$

Determination of absolute bond strengths in these systems would require knowledge of the heat of formation of the tricarbonyl fragments. We were not able to find accurate data for the heat of formation of the tricarbonyl fragments of Cr, Mo, and W. That might allow determination or quantitative estimation of the enthalpy of step i, allowing us to make absolute bond strength estimates. Rigorous analysis of bond strength data based on our study of the relative bond strengths (step ii) can only be accomplished when such data are generated. Nevertheless, reasonable estimates for the understanding of qualitative bonding trends can be made by estimation of the energy necessary to produce the tricarbonyls coupled with DSC results as discussed below.

Differential scanning calorimetry shows that, for all three metals, replacement of 3 mol of CO by triphos is nearly thermoneutral:[14]

$$M(CO)_6 + \text{triphos} \xrightarrow{25\text{–}150\ °C} (\text{triphos})M(CO)_3 + 3CO \quad (20)$$

$$\Delta H = 0 \pm 5 \text{ kcal/mol}$$

Thus, the position of the metal hexacarbonyl in Figure 1 is approximately the same as that of triphos.

Data shown in eqs 1 and 2 can be used to generate a *rough* estimate of the energy needed to generate the $M(CO)_3$ fragment from $M(CO)_6$: Taking an average of the first dissociation energy

$$M(CO)_6 \rightarrow M(CO)_3 + 3CO \quad (21)$$

(eq 1) and of the average dissociation energy (eq 2) and multiplying by 3 yield a rough estimate of the energy necessary to produce the tricarbonyl fragments *in the absence of significant electronic rearrangements of these fragments*. Estimates for the energy required to dissociate 3 mol of CO from these metals would then be 94, 114, and 134 kcal/mol for Cr, Mo, and W, respectively. Equating these values to the value for triphos allows *estimation* of the absolute bond energies shown in Table IV.

Table IV. Estimated[a,b] Relative Thermochemical Stability [$-\Delta H_{\text{reacn}}$ (kcal/mol)]

$$\text{“}M(CO)_3\text{”} + nL \rightarrow L_nM(CO)_3 \quad (M = Cr, Mo, W)$$

ligand	Cr	Mo	W	ΔH(Mo/Cr)	ΔH(W/Cr)
benzene	53	68	77	1.28	1.45
CHPT	60	77	90	1.28	1.50
CH_3CN	64	90	105	1.40	1.64
py	74	99	117	1.34	1.58
PPh_2Me	85	110	131	1.29	1.54
P^nBu_3	94	117	138	1.24	1.47
triphos	94	114	134	1.21	1.43
PEt_3	95	115	137	1.21	1.44
PMe_2Ph	96	117	138	1.22	1.44
$P(OMe)_3$	97	122	140	1.26	1.44
$C_6H_{11}NC$	98	118	143	1.20	1.46
PMe_3	101	120	143	1.19	1.42
av				1.26	1.48

[a] Based on estimate for enthalpy of formation of “$M(CO)_3$” based on literature data. See text for discussion. [b] The columns ΔH(Mo/Cr) and ΔH(W/Cr) refer to the ratio of the enthalpies of ligand binding for the indicated metals.

In spite of the fact that the data in Table IV are estimates based on literature values for M–CO first and average bond strengths, several conclusions are apparent. The first is that arenes such as benzene bind with roughly half the total enthalpy of binding of the strongest ligands (CO, phosphines, phosphites, isonitriles). The second conclusion that can be reached by examination of Figure 1 is that the relative enthalpies of ligand substitution support the greater metal–ligand bond strengths in going from a first- to a second- to a third-row metal. Due to the uncertainties in estimating the absolute enthalpies of formation of the tricarbonyl fragments $M(CO)_3$, the apparent ratio of bond enthalpies of Cr/Mo/W of 1.0/1.26/1.48 is subject to larger errors than may be apparant. The individual first bond dissociation energies determined by Smith[3] (see eq 2) are in the ratio Cr/Mo/W = 1.0/1.1/1.26. **It seems most reasonable to expect an increase of 10–20% in the bond strengths for each step in going from Cr to Mo to W for these complexes.** Steric influences, expected to be more severe for the chromium complexes, add an additional uncertainty in interpreting these results.

The data in Figure 1 clearly show that, whatever the absolute values for ligand addition to the “$M(CO)_3$” fragments are, the relative enthalpies in solution increase steadily in going from Cr to Mo to W. A practical consequence of this steady increase in enthalpy on descending the triad can be considered in the replacement of a weak polydentate ligand (such as an arene) by a stronger monodentate ligand (such as nitrile or pyridine):

$$PM(CO)_3 + 3L \rightarrow L_3M(CO)_3 + P \quad (22)$$

$$P = \text{polydentate ligand}$$

Enthalpic factors will normally favor formation of the $PM(CO)_3$ complex—on the basis of strength per bond, only agostic interactions appear to be weaker than bonds to arenes. Entropic factors will normally favor formation of the $PM(CO)_3$ complex. The entropy of reaction 22 should be relatively constant in going from Cr to Mo to W. At higher temperatures, the polydentate ligand will be preferred—as we have shown in NMR studies of binding of arenes[5] and cyclopentadienyl hydrides.[9] Since the gap in bond strengths normally increases in going from Cr to Mo to W, the thermodynamic stability of the weakly bound polyhapto complexes will increase in going from Cr to Mo to W. This can

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have important practical consequences regarding equilibrium constants for binding modes as a function of the metal.

Conclusion

This work is part of our continuing investigation of solution thermochemistry of group VI complexes. This paper reports data for enthalpies of binding in the $L_3M(CO)_3$ system for chromium, molybdenum, and tungsten. These data provide needed documentation of the general increase in coordinate bond strength in descending a given metal triad. Enthalpies of ligand binding, relative to benzene, show clearly the increase in enthalpy of ligand substitution in going from Cr to Mo to W. Estimates of the absolute values of ligand binding to the "$M(CO)_3$" fragments indicate the ratios of the bond strengths are approximately 1.0, 1.26, and 1.48 for Cr, Mo, and W, respectively. Since entropic factors may remain relatively constant in reactions such as arene displacement, the more favorable enthalpies of ligand substitution for the heavier metals may be able to override unfavorable entropic factors. Additional work is in progress to map the thermodynamic surface for ligand binding to group VI metals as a function of ligand donor and oxidation state on the metal.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE 8618753) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Tables of experimental data on enthalpies of reaction (2 pages). Ordering information is given on any current masthead page.