

THE HEATS OF REACTION OF PHOSPHINES AND PHOSPHITES WITH TOLUENE-MOLYBDENUM TRICARBONYL. IMPORTANCE OF BOTH STERIC AND ELECTRONIC FACTORS IN DETERMINING THE Mo-PR₃ BOND STRENGTH

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Summary

The heats of reaction of tolueneMo(CO)₃ with a series of phosphines and phosphites have been measured by solution calorimetry. The order of stability toward formation of *fac*-(PR₃)₃Mo(CO)₃ in THF solution is: P(OCH₃)₃ > PMe₃ > PⁿBu₃ > PMe₂Ph > PEt₃ > triphos > P(OPh)₃ > PMePh₂ > PPh₃ > PCl₃ and spans a range of 25 kcal/mol reflecting individual bond strength differences up to 8 kcal/mol. The bulky phosphines PCy₃ and P^tBu₃ react with tolueneMo(CO)₃ in THF, but 30–40 kcal/mol less heat is evolved in these reactions than with the other phosphines and phosphites. The coordinately unsaturated five-coordinate complexes (PR₃)₂Mo(CO)₃ are proposed as the reaction products. The importance of both steric and electronic factors in the Mo–P bond is discussed.

Introduction

Phosphines and phosphites are key ligands in organometallic chemistry. Variation of R in PR₃ and P(OR)₃ can lead to a wide range of steric and electronic properties for the phosphine ligand and the metal center to which it coordinates [1]. The importance of metal-phosphine complexes in homogeneous catalysis is well known [2]. Detailed kinetic studies, including activation energies, have been reported for a range of different phosphines and metal complexes [3,4]. Two significant thermochemical studies dealing with a series of phosphines have been reported [5,6]. The first involved displacement of coordinated THF from square planar platinum(II) complex shown in eq. 1:



Q = PMe₂Ph

A similar series of phosphines was studied for the nickel(0) complexes based on

reaction 2:



For bulky phosphine ligands an equilibrium was shown to exist with the coordinatively unsaturated three coordinate nickel(0) complexes [6,7]



The results for platinum(II) and nickel(0) showed similarities, however, they also showed significant differences. For platinum(II) both steric and electronic factors appeared to be important whereas for nickel(0) steric factors predominated. The enthalpies of reaction 1 were -26.4 and -26.2 kcal/mol for $\text{P}(\text{OCH}_3)_3$ and PMe_3 indicating essentially the same bond strength for the phosphine and phosphite with platinum(II). The corresponding measurements for reaction 2 were -51 and -36 kcal/mol indicating that the average $\text{Ni}-\text{P}(\text{OCH}_3)_3$ bond strength is about 4 kcal/mol greater than the $\text{Ni}-\text{PMe}_3$ bond strength.

It is not clear what combination of steric and electronic properties determine metal-phosphine bond strengths. It seems likely that this will depend not only on the metal, but on its oxidation state and auxiliary ligands. The studies mentioned above were on late transition metals not containing coordinated carbon monoxide. The electron-withdrawing properties of the $\text{M}(\text{CO})_3$ fragment ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are well known [8] and we have recently reported thermochemical studies for Group VI tricarbonyl complexes [9-12]. In order to gain additional information about the metal-phosphorus bond we now extend this to include twelve phosphine and phosphite complexes of molybdenum tricarbonyl.

Experimental

All manipulations involving organometallic compounds were performed using standard Schlenk tube techniques under an argon atmosphere, or in a vacuum/atmospheres glove box containing less than 1 ppm oxygen and water. Phosphines and phosphites were obtained from Strem chemicals and were routinely distilled or recrystallized prior to use. Tetrahydrofuran was stored over calcium hydride and distilled from sodium benzophenone into flame dried glassware. Toluene $\text{Mo}(\text{CO})_3$ (= Tol $\text{Mo}(\text{CO})_3$) was prepared according to the literature [8] and recrystallized twice from methylene chloride/heptane. Infrared spectra were measured using a Perkin-Elmer 267 spectrometer in 0.1 mm KBr cells. NMR spectra were determined on a Varian FT-80A spectrometer. Calorimetric measurements were made using either the Calvet calorimeter (Setaram C-80) or the Guild solution calorimeter for isoperibol measurements. These calorimeters have been described previously [10,11] and typical procedures are described below.

Calorimetric measurement for reaction of PPh_3 and Tol $\text{Mo}(\text{CO})_3$

The mixing vessels of the Setaram C-80 were cleaned, dried in an oven at 150°C , and then taken into the glove box. A 0.2 g sample of recrystallized Tol $\text{Mo}(\text{CO})_3$ was weighed into the lower vessel, it was closed and sealed with 1.5 ml Hg. Four ml of a stock solution of $\text{P}(\text{OCH}_3)_3$ (10 ml $\text{P}(\text{OCH}_3)_3$ in 40 ml THF) was added and the vessel closed, taken out of the glove box and loaded in the calorimeter. The reference vessel was loaded in identical fashion, except no Tol $\text{Mo}(\text{CO})_3$ was added to the

lower vessel. After the calorimeter had reached thermal equilibrium at 30.0°C (about 2 h) the reaction was initiated by inverting the calorimeter. At the end of the reaction (1–2 h) the vessels were removed from the calorimeter, taken into the glove box, opened, and the infrared spectrum run of the product. Conversion to $[\text{P}(\text{OCH}_3)_3]\text{Mo}(\text{CO})_3$ was quantitative. The enthalpy of reaction, -47.7 ± 0.1 kcal/mol, is the average of six separate determinations.

Calorimetric measurement for reaction of PPh_3 and $\text{TolMo}(\text{CO})_3$

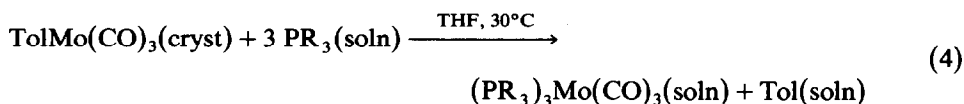
Attempts to measure this heat of reaction were frustrated due to formation of a precipitate of $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Mo}(\text{CO})_3$ under the concentrated conditions used in the Calvet calorimeter. The isoperibol Guild solution calorimeter described previously [10] was used to avoid this problem. Fifty grams of recrystallized triphenylphosphine was dissolved in 500 ml of freshly distilled THF, and loaded into the calorimeter. Sealed glass ampoules containing about 0.2 g of $\text{TolMo}(\text{CO})_3$ were placed in the Teflon holder of the ampoule breaker. Electrical calibration were done before and after the reaction. The clear light yellow solution showed no evidence of a precipitate. The value -37.2 ± 0.9 kcal/mol represents the average of eight separate determinations.

Reaction of PCy_3 and P^iBu_3 with $\text{TolMo}(\text{CO})_3$

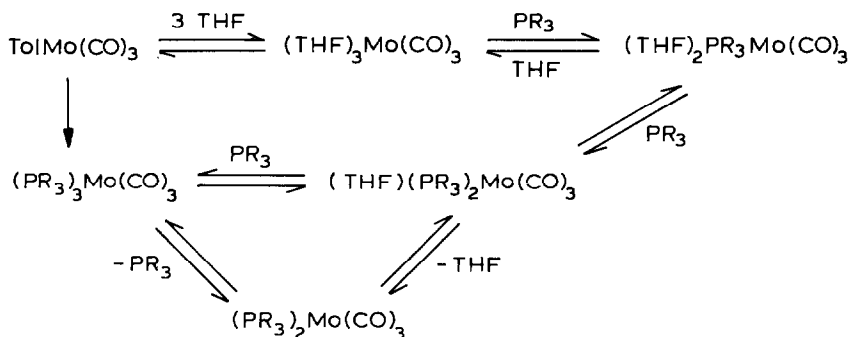
The low values for the heats of reaction of these phosphines prompted spectroscopic investigation of their reactions. In a Schlenk tube under an argon atmosphere solutions of PCy_3 and $\text{TolMo}(\text{CO})_3$ were prepared in $\text{C}_6\text{D}_6/\text{THF}$ (1/1) at P/Mo ratios of 10/1, 5/1, 3/1, and 2/1. At P/Mo ratios lower than 2/1, some precipitates were always present, and so they were not studied. The solutions were filtered into NMR tubes and sealed off under vacuum. In addition to free PCy_3 , new signals at 64.4 and 83.5 ppm (relative to external H_3PO_4) appeared which we attribute to MoP_2 and MoP_3 complexes, respectively. Integration of the signals supports this conclusion and yields $K_{\text{eq}} = 0.3 \pm 0.15$ for the equilibrium $\text{MoP}_3 \rightleftharpoons \text{MoP}_2 + \text{P}$. In parallel experiments the infrared spectra of these solutions were run, and a complex series of bands occurred which were not fully resolved. There were no signs of $\text{TolMo}(\text{CO})_3$ or $(\text{THF})_3\text{Mo}(\text{CO})_3$ or $\text{Mo}(\text{CO})_6$ in the spectra. At low P/Mo ratios and in dilute solution the limiting spectrum showed bands at 2004(w), 1886(s) cm^{-1} . This spectrum was identical when obtained from either $\text{TolMo}(\text{CO})_3$ or $\text{CHPTMo}(\text{CO})_3$. At high P/Mo ratios new bands appeared. The most intense were centered around 1912 and 1800 cm^{-1} . Similar studies with P^iBu_3 showed no evidence for species other than the disubstituted complex with IR bands at 2075(w) and 1935(s, broad) cm^{-1} . These solution were extremely air sensitive and attempts to isolate crystalline products failed.

Results and discussion

The basis for the calorimetric data reported in Table 1 is reaction 4:



The kinetics of this reaction have been studied under different conditions, but not in



SCHEME 1. Proposed equilibria for TolMo(CO)_3 in PR_3/THF solution.

TABLE 1

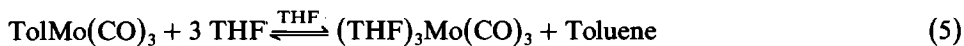
HEATS OF REACTION, CONE ANGLES, AND ELECTRONIC FACTORS FOR PHOSPHINES AND PHOSPHITES STUDIED IN THE REACTION

$\text{TolMo(CO)}_3 + 3 \text{ PR}_3 \rightarrow (\text{PR}_3)_3\text{Mo(CO)}_3 + \text{Toluene}$

Phosphine	ΔH^{rxn} (kcal/mol)	θ^a	ν_{Ni}^b	ν_{Mo}^c
$\text{P(OCH}_3)_3$	-47.5(0.5)	107	2079.5	1968
$\text{P(CH}_3)_3$	-47.1(0.1)	118	2064.1	1935
P^nBu_3	-44.3(0.2)	132	2060.3	1928
$\text{P(CH}_3)_2(\text{C}_6\text{H}_5)$	-43.8(0.3)	122	2065.3	1937
$\text{P(C}_2\text{H}_5)_3$	-41.7(0.4)	132	2061.7	1930
Triphos	-41.0(0.6)	-	-	1946
$\text{P(OC}_6\text{H}_5)_3$	-37.5(0.1)	128	2085.3	1994
$\text{P(CH}_3)(\text{C}_6\text{H}_5)_2$	-37.2(0.1)	136	2067.0	1947
$\text{P(C}_6\text{H}_5)_3$	-37.2(0.9)	145	2068.9	^d
pCl_3	-22.3(0.7)	124	2097.0	2040
$\text{P(C}_6\text{H}_{11})_3$	-18.1(0.2)	170	2056.4	^e
P^tBu_3	-6.8(0.1)	182	2056.1	^e

^a Taken from ref. 1. ^b The A_1 band of LNi(CO)_3 in CH_2Cl_2 taken from ref. 1. ^c The A_1 band of $\text{L}_3\text{Mo(CO)}_3$ measured in THF. ^d Due to low solubility not recorded. ^e These phosphines form the coordinately unsaturated species $(\text{PR}_3)_2\text{Mo(CO)}_3$, see discussion.

THF solution [13,14]. Reaction of TolMo(CO)_3 with THF [15] is known to proceed rapidly as shown in eq. 5 and we have reported the thermodynamic parameters ($\Delta H^\circ -9.3$ kcal/mol; $\Delta S^\circ -41.5$ e.u.) for this equilibrium [10].

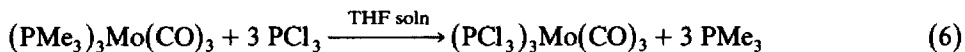


It seems likely that reaction 4 in THF proceeds through this complex with stepwise displacement of coordinated THF as shown in Scheme 1*.

In the presence of excess phosphine, reaction 4 proceeds quantitatively as shown,

* Preliminary ^{31}P NMR studies support establishment of the equilibria shown in Scheme 1. Additional ^{95}Mo NMR studies are planned for this system.

except for PCy_3 and P^iBu_3 which are discussed separately below. The data in Table 1 can be used directly to calculate the enthalpies of phosphine displacements such as that shown in eq. 6:



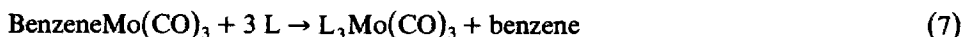
Subtracting the appropriate forms of eq. 4 for PMe_3 and PCl_3 yields eq. 6; using the data in Table 1 the calculated heat of reaction 6 is +24.8 kcal/mol. The lability of PCl_3 complexes is well known [13,14]; it is clear from these data that they are also less stable in a thermodynamic sense. Relative stabilities of the other phosphines are discussed in more detail below.

The series PMe_3 , PMe_2Ph , PMePh_2 , PPh_3 and triphos

There is a steady decrease in the thermodynamic stability of these complexes upon replacing an alkyl group by a phenyl group. These changes affect both the steric and electronic properties of the phosphine. Replacement of methyl by phenyl decreases the basicity of the phosphine and increases its cone angle [1]. Diphenylmethylphosphine appears to occupy an anomalous position in the series. The chelating ligand triphos ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$) containing two alkylidiphenyl- and one dialkylphenyl-phosphine appears between Ph_2PMe and PhPMe_2 in Table 1. The value predicted for triphos on this basis ($\Delta H = \frac{2}{3}\Delta H^{\text{Ph}_2\text{PMe}} + \frac{1}{3}\Delta H^{\text{PhPMe}_2}$) is -39.4 kcal/mol. This agrees within experimental error with the value obtained of -41.0 ± 0.6 kcal/mol indicating that any special stability of triphos complexes has its origin in entropic rather than enthalpic factors.

Comparison of the Mo-PR_3 to other Mo-L strengths

We have reported thermodynamic data [10-12] which can be used to calculate enthalpies of ligand exchange such as that shown in eq. 7:

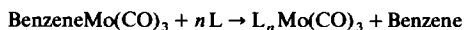


In order to compare the data for the phosphines to these ligands the heat of solution of $\text{TolMo}(\text{CO})_3$ (+3.0 kcal/mol) must be subtracted from the data in Table 1 and the enthalpy of exchange of toluene for benzene (-2.0 kcal/mol) added [10]. Combined results for the enthalpy of ligand exchange are shown in Table 2. These data combine some earlier values in methylene chloride solution with the present ones in tetrahydrofuran. We have measured the appropriate heats of solution for several of these complexes in methylene chloride, tetrahydrofuran, and toluene [15] and solvent effects cancel within 1 kcal/mol. It should be stressed that the data in Table 2 refers to enthalpy of displacement and that entropic factors can play a large role in determining stability, particularly for poly-hapto ligands such as arenes.

The individual bond strength estimates listed in Table 2 are based on the assumption that solution properties accurately reflect the gas phase values. Due to problems with thermal decomposition reactions, there are few reliable heats of sublimation available for organometallic compounds other than the simple carbonyls. The concept of individual isolated bond strengths in such complex molecules is, in any case, an approximation, albeit a useful one. The Mo-CO bond strength estimate of 40.5 kcal/mol is the result of recent laser pyrolysis studies of $\text{Mo}(\text{CO})_6$ [16]. This implies that the Mo-CO bond is stronger than the Mo-PR_3 bond, in keeping with

TABLE 2

CALCULATED ENTHALPIES FOR THE LIGAND EXCHANGE REACTION IN SOLUTION:



Ligand	Complex	$\Delta H^\circ_{\text{exch}}$ (kcal/mol)	Bond strength ^a estimate (kcal/mol)
Benzene	C ₆ H ₆ Mo(CO) ₃	0	63.2
Toluene	TolMo(CO) ₃	-2.0	65.2
Cyclooctatetraene	COTMo(CO) ₃	-2.5	65.7
Mesitylene	MesMo(CO) ₃	-3.5	66.7
Hexamethylbenzene	HMBMo(CO) ₃	-5.7	68.9
Cycloheptatriene	CHPTMo(CO) ₃	-9.1	72.3
Pentamethylcyclopentadiene	HMo(CO) ₃ C ₅ Me ₅	-10.5	91 Mo-C ₅ Me ₅ 66 Mo-H
Tetrahydrofuran	(THF) ₃ Mo(CO) ₃	-11.3	24.8
Tri- <i>t</i> -butylphosphine	(P ^{<i>t</i>} Bu ₃) ₂ Mo(CO) ₃	-11.8	37.5
Cyclopentadiene	HMo(CO) ₃ C ₅ H ₅	-12.8	93 Mo-C ₅ H ₅ 66 Mo-H
Tricyclohexylphosphine	(PCy ₃) ₃ Mo(CO) ₃	-23.1	-
Trichlorophosphine	(PCl ₃) ₃ Mo(CO) ₃	-27.3	30.2
Pyridine	py ₃ Mo(CO) ₃	-30.9	31.4
Triphenylphosphine	(PPh ₃) ₃ Mo(CO) ₃	-42.2	35.1
Methyldiphenylphosphine	(PMe ₂ Ph) ₃ Mo(CO) ₃	-42.2	35.1
Triphenylphosphite	(P(OPh) ₃) ₃ Mo(CO) ₃	-42.5	35.2
Triphos	TriphosMo(CO) ₃	-46.0	36.4
Triethylphosphine	(PEt ₃) ₃ Mo(CO) ₃	-46.7	38.6
Dimethylphenylphosphine	(PMe ₂ Ph) ₃ Mo(CO) ₃	-48.8	37.3
Tri- <i>n</i> -butylphosphine	(P ^{<i>n</i>} Bu ₃) ₃ Mo(CO) ₃	-49.3	37.5
Trimethylphosphine	(PMe ₃) ₃ Mo(CO) ₃	-52.1	38.4
Trimethylphosphite	(P(OCH ₃) ₃) ₃ Mo(CO) ₃	-52.5	38.6
Carbon Monoxide	Mo(CO) ₆	-	40.5 Mo-CO ^b

^a Data for non-phosphines reported earlier [10–12]. Bond strength estimates calculated on Mo–Toluene bond strength reported earlier [10], and assumption that solution values approximate gas phase bond strengths. Values for phosphines are the average of first three dissociation energies. ^b The bond strength estimate for Mo(CO)₆ is taken from ref. 16.

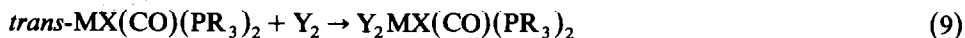
our preliminary results [15] indicating triphenylphosphine substitution in Mo(CO)₆ to be endothermic. The results of kinetic studies have been used to estimate $\Delta H = -3.9$ kcal/mol [17] for reaction 8:



This also supports a stronger M–CO bond than M–PR₃. In this regard the recent estimate of 75.3 kcal/mol for the (CO)₅W–PPh₃ bond strength [18] compared to a value of 46.0 kcal/mol for (CO)₅W–CO [24] seems likely to be incorrect. A possible source of error in the high temperature bromination experiments is failure to achieve a defined stoichiometry of reaction.

Electronic and steric factors^c

The enthalpy of oxidative addition to square planar rhodium(I) and iridium(I) complexes as shown in eq. 9 has been studied as a function of the phosphine ligand:



Relationships of the type shown in eq. 10, originally suggested by Tolman [1] were shown to be valid with correlation coefficients of 0.85–0.97 depending upon the particular system investigated [19].

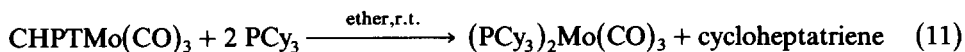
$$-\Delta H^\circ = A_0 + A_1\theta + A_2v \quad (10)$$

The enthalpy of reaction 4 can be fitted to an expression of this type for the first nine phosphines listed in Table 1 with a correlation factor of 0.95 ($A_0 = -613.00$, $A_1 = 0.36222$, $A_2 = 0.25364$). The bulky phosphines PCy_3 and P^tBu_3 yield complexes of the type $(\text{PR}_3)_2\text{Mo}(\text{CO})_3$ (discussed below) and so can not be included in this relationship. The value predicted for PCl_3 of -36.2 kcal/mol is clearly at odds with the observed value of -22.3 kcal/mol. It seems possible that the cone angle of 124° assigned to PCl_3 may not accurately reflect the steric repulsion for this ligand. The cone angle measurement [1] is based on the Van der Waals' radii of the atoms involved and does not take into account that the intrinsic repulsion between adjacent lone pairs on chlorine is probably greater than that of the bound-pair repulsions of adjacent alkyl groups. An effective cone angle of around 162° would bring the data for PCl_3 into good agreement with relationship 10. Despite a reasonable correlation coefficient, the utility of expression 10 is only in its ability to predict as yet unmeasured data. We plan to test this in the future * and extend relationships to the complexes $(\text{PR}_3)_2\text{Mo}(\text{CO})_4$ (both *cis* and *trans*) and $(\text{PR}_3)\text{Mo}(\text{CO})_5$ where steric factors should be less important as judged by the A_1/A_2 ratio. At present the qualitative conclusion that small, basic phosphines lead to the strongest $\text{Mo}-\text{PR}_3$ bond may be as useful as the empirical relationship in eq. 10. The interrelationship of steric and electronic factors has been discussed by Clark [20].

In an attempt to get a better fit to our data, we also used vibrational data for the $\text{L}_3\text{Mo}(\text{CO})_3$ complexes rather than the tabulated electronic factors based on the A_1 vibration of $\text{LNi}(\text{CO})_3$ [1]. Exactly the same correlation was achieved. This was due to the fact that the vibrational data for $\text{L}_3\text{Mo}(\text{CO})_3$ is directly related to the data for $\text{LNi}(\text{CO})_3$ (0.99 correlation). The slope of the line fit by least squares is 2.9 ± 0.2 ; close to the 3/1 ligand ratio. While this is probably fortuitous it does indicate close similarity between the two systems.

PCy₃ and P^tBu₃

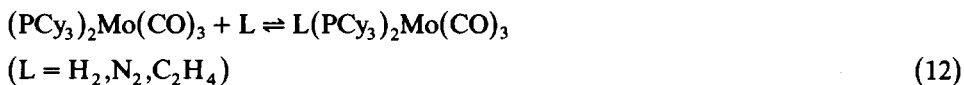
The calorimetric values for PCy_3 and P^tBu_3 were exceptionally low and prompted additional spectroscopic investigation. It was clear from the IR and NMR spectra that new $\text{Mo}-\text{P}$ complexes were formed which did not retain the coordinated arene. Kubas has reported preparation of $(\text{PCy}_3)_2\text{Mo}(\text{CO})_3$ [21] as shown in eq. 11:



The IR spectra in THF of the complex prepared in this way agrees with that of the calorimetric solutions from $\text{ToI}(\text{Mo}(\text{CO})_3)$. The coordinatively unsaturated $(\text{PCy}_3)_2\text{Mo}(\text{CO})_3$ has been shown to form adducts reversibly as shown in eq. 12

* For example we are now modifying our calorimetric system to allow gas/soln. reactions and plan to attempt measurements with $\text{PF}_3(\text{g})$ in the future.

[21,22]:



It is possible that such an adduct is formed with THF in solution, but stable adducts could not be isolated from this system [23]. At high concentrations of PCy_3 , changes in the IR and NMR spectra suggest that equilibrium 12 is established for $\text{L} = \text{PCy}_3$ but that $(\text{PCy}_3)_3\text{Mo}(\text{CO})_3$ readily dissociates. Spectroscopic studies for the bulkier ligand P^tBu_3 suggest formation of only $(\text{P}^t\text{Bu}_3)_2\text{Mo}(\text{CO})_3$. The bond strength estimate (see below) for $\text{Mo}-\text{P}^t\text{Bu}_3$ in the five coordinate complex $\text{Mo}(\text{CO})_3(\text{P}^t\text{Bu}_3)_2$ of 37.5 kcal/mol is in keeping with bond strength estimates for other trialkylphosphines in $\text{Mo}(\text{CO})_3(\text{PR}_3)_3$. The correspondence between these values implies that the average bond dissociation energy and the first bond dissociation energy are similar for small phosphines.

Conclusion

The thermochemical data in Table 2 shows that the enthalpy of ligand exchange for $\text{L}_3\text{Mo}(\text{CO})_3$ spans a range over 50 kcal/mol from $\text{C}_6\text{H}_6\text{Mo}(\text{CO})_3$ to $\text{Mo}(\text{CO})_6$. With the exception of PCl_3 the phosphines and phosphites form relatively strong bonds. The $\text{Mo}-\text{PR}_3$ bond strength depends on both steric and electronic factors of the phosphine, paralleling more closely results for platinum(II) [5] than for nickel(0) [6]. Complexes such as $\text{Ni}(\text{PMe}_3)_4$ are disfavored for nickel(0) but not for platinum(II) or molybdenum(0) (in $\text{L}_3\text{Mo}(\text{CO})_3$). This may be due to the ability of the $\text{Mo}(\text{CO})_3$ group to accept electron density. This highlights the need for additional data to determine the factors controlling the $\text{M}-\text{PR}_3$ bond strength as a function of the metal, its oxidation state, and auxiliary ligands. Work to extend the solution thermochemistry of these and related complexes is in progress.

Acknowledgement

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