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Heat of Reaction of (Norbornadiene)molybdenum Tetracarbonyl with Monodentate and Bidentate Ligands. Solution Thermochemical Study of Ligand Substitution in the Complexes *cis*-$L_2Mo(CO)_4$

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The enthalpy of reaction of $(NBD)Mo(CO)_4$ (NBD = norbornadiene) with a number of monodentate and bidentate ligands forming *cis*-$L_2Mo(CO)_4$ has been measured at 30 °C in THF solution. The heats of reaction span a range of 33 kcal/mol. The order of stability for monodentate ligands is $PCl_3 < As(C_6H_5)_3 < py < P(C_6H_5)_3 < AsEt_3 < P(OC_6H_5)_3 < P(C_6H_5)_2(CH_3) < CO < P(C_6H_5)(CH_3)_2 < P(OCH_3)_3 < P(n\text{-}Bu)_3 < (C_6H_{11})NC < PEt_3 < PMe_3$. The series of chelating bidentate phosphines $R_2P(CH_2)_nPR_2$ ($n = 1$–4, $R = C_6H_5$; $n = 1, 2$, $R = CH_3$) and several related ligands were investigated. The chelating ring systems in the metallacycles show strain energies of about 8 kcal/mol for four-membered rings. The mixed ligand $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ shows a heat of binding midway between the heats of binding of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$, implying group additivity in this system. The complex $(phen)Mo(CO)_4$ is some 5 kcal/mol more stable than $(bpy)Mo(CO)_4$, presumably due to conformational effects in the free ligand. The ligand 1,5-cyclooctadiene forms a complex 2 kcal/mol less stable than that of norbornadiene. The influences of steric and electronic factors in determining the Mo–L bond strength are discussed.

Introduction

Chelating ditertiary phosphines have been widely used as ligands in organometallic chemistry. Kinetic, catalytic, and structural studies have been made of these complexes.[1] There are no thermodynamic data regarding strain energy or heats of binding for these ligands. Several calorimetric studies for monodentate phosphines have been reported: Manzer and Tolman investigated the solution thermochemistry of square-planar platinum(II) complexes, shown in eq 1, for a series of phosphine ligands.[2] A similar series of ligands was then investigated[3] for the Ni(0) complexes shown in eq 2. These data were interpreted in terms of the steric and electronic parameters of the phosphine ligand by using the cone angle as a measure of steric bulk and the A_1 vibrational frequency in $Ni(CO)_3L$ as a measure of ligand basicity.[4]

$$\textit{trans}\text{-}[CH_3PtQ_2(THF)]^+ + PR_3 \rightarrow \textit{trans}\text{-}[CH_3PtQ_2(PR_3)]^+ + THF \quad (1)$$
$$Q = PMe_2Ph$$

$$Ni(COD)_2 + 4PR_3 \rightarrow Ni(PR_3)_4 + 2COD \quad (2)$$

Recently, we reported a solution thermochemical study of ligand substitution in the complexes *fac*-$L_3Mo(CO)_3$ for phosphine[5] and other ligands:[6]

$$(arene)Mo(CO)_3 + 3L \rightarrow \textit{fac}\text{-}L_3Mo(CO)_3 + arene \quad (3)$$

The present study extends our work on solution thermochemistry to a series of *cis*-$L_2Mo(CO)_4$ complexes. In addition to measuring heats of binding of monodentate ligands, we report the first extensive data on the effect of chelate ring size on complex stability for bidentate phosphines.

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. Other reagents were obtained from commercial sources and purified by standard procedures. Organomolybdenum compounds were prepared by using procedures described in the literature[7] 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 that were pure as determined by IR and NMR spectroscopy and were 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. All calorimetric measurements were made at 30 °C by using the Calvet calorimeter (Setaram C-80) described previously.[5]

Reaction of $(NBD)Mo(CO)_4$ with 1,2-Bis(diphenylphosphino)ethane (diphos). In a typical procedure the mixing cells of the calorimeter were dried in an oven at 150 °C for 2 h and then taken into the glovebox. The lower chamber was filled with approximately 0.15 g of $(NBD)Mo(CO)_4$, closed, and sealed with 1.5 mL of mercury. Four milliliters of a 25% solution of diphos in THF was added to the cell. It was then closed, taken out of the glovebox, placed in the sample compartment of the calorimeter, and allowed to equilibrate at 30 °C for 2 h. After the temperature reached a stable base line, the reaction was initiated by inverting the calorimeter. After return to the base line, the trace was integrated and the enthalpy of reaction calculated. At the end of the run, IR spectra confirmed that reaction was complete and produced $(diphos)Mo(CO)_4$ as the only organometallic product. The value of −20.5 ± 0.3 kcal/mol represents the average of five different measurements. This value refers to reaction of the crystalline solid with diphos producing the diphos complex in solution. The enthalpy of solution of the crystalline solid (+3.8 kcal/mol) must be subtracted from the measured heat of reaction −20.5 kcal/mol) in order to obtain the enthalpy of reaction with all species in solution (−24.3 kcal/mol).

Reaction of $(NBD)Mo(CO)_4$ with CO: High-Pressure Calorimetry. In a typical reaction the high-pressure cells of the Calvet calorimeter were taken into the glovebox and loaded under an argon atmosphere. The reference cell was loaded with 4.0 mL of THF and the sample cell loaded with 0.1 g of $(NBD)Mo(CO)_4$ in 4.0 mL of THF. Matheson research grade CO containing less than 1 ppm of O_2 was transferred to an autoclave containing a THF solution of sodium benzophenone and thermostated at 30 °C. Gas lines leading to the calorimeter were also thermostated at 30 °C. After the cells had equilibrated, both were pressurized with CO at 500 psi. The enthalpy of reaction, −22.6 (0.8) kcal/mol, is the average of six determinations. The infrared spectrum showed $Mo(CO)_6$ as the sole metal-containing product. Reactions on samples of more than 0.1 g of $(NBD)Mo(CO)_4$ went to completion more slowly, since it appears that the carbonylation reactions are inhibited by the norbornadiene produced in the reaction.

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Table I. Enthalpies of Ligand Exchange (kcal/mol)

$$(NBD)Mo(CO)_4 + 2L \rightarrow L_2Mo(CO)_4 + NBD$$

and Bond Strength Estimates (kcal/mol) for Monodentate Ligands

ligand	complex	$-\Delta H$	bond strength
norbornadiene	$(NBD)Mo(CO)_4$	0	26.7[a]
phosphorus trichloride	$(PCl_3)_2Mo(CO)_4$	7.4 (0.2)	30.4
triphenylarsine	$(Ph_3As)_2Mo(CO)_4$	10.5 (0.3)	32.0
pyridine	$(py)_2Mo(CO)_4$	12.1 (0.1)	32.8
triphenylphosphine	$(Ph_3P)_2Mo(CO)_4$	17.1 (0.1)	35.2
triethylarsine	$(Et_3As)_2Mo(CO)_4$	19.7 (0.2)	36.6
triphenyl phosphite	$[P(OPh)_3]_2Mo(CO)_4$	21.9 (0.1)	37.7
diphenylmethylphosphine	$(PPh_2Me)_2Mo(CO)_4$	22.2 (0.2)	37.8
carbon monoxide	$Mo(CO)_6$	22.6 (0.8)	38 ± 3
phenyldimethylphosphine	$(PPhMe_2)_2Mo(CO)_4$	26.8 (0.4)	40.1
trimethyl phosphite	$[P(OMe)_3]_2Mo(CO)_4$	27.5 (0.1)	40.5
tri-*n*-butylphosphine	$(P\text{-}n\text{-}Bu_3)_2Mo(CO)_4$	30.1 (0.1)	41.8
cyclohexyl isocyanide	$(CyNC)_2Mo(CO)_4$	30.1 (0.1)	41.8
triethylphosphine	$(PEt_3)_2Mo(CO)_4$	32.1 (0.1)	42.8
trimethyl phosphine	$(PMe_3)_2Mo(CO)_4$	32.9 (0.1)	43.2

[a] Per olefin.

Results and Discussion

The goal of this work was investigation of the enthalpy of ligand exchange and evaluation of strain energies in the complexes *cis*-$L_2Mo(CO)_4$. The entryway to the thermochemistry in this system is reaction of $(NBD)Mo(CO)_4$ with excess ligand as illustrated in reaction 4 for trimethylphosphine. These reactions

$$(NBD)Mo(CO)_4 + 2PMe_3 \rightarrow (PMe_3)_2Mo(CO)_4 + NBD \quad (4)$$

$$\Delta H = -32.9\ (0.1)\ \text{kcal/mol}$$

are rapid and quantitative at room temperature. The initially formed cis products are known to undergo thermal isomerization to yield cis/trans mixtures, but this reaction is relatively slow.[8] Infrared spectra run immediately after calorimetry showed no detectable amount of trans product. In addition, it appears that there is little difference in energy between the cis and trans isomers for small phosphines.[8] All data in this paper refer to the cis isomer.

Thermochemical results for monodentate ligands are collected in Table I and provide a basis for calculating enthalpies of ligand substitution. For example, reaction with trimethyl phosphite proceeds as shown in eq 5. Subtraction of eq 5 from eq 4 leads

$$(NBD)Mo(CO)_4 + 2P(OMe)_3 \rightarrow [P(OMe)_3]_2Mo(CO)_4 + NBD \quad (5)$$

$$\Delta H = -27.5\ (0.1)\ \text{kcal/mol}$$

directly to the enthalpy of the substitution reaction shown in eq 6, since all other terms cancel. In a similar fashion the enthalpy

$$[P(OMe)_3]_2Mo(CO)_4 + 2PMe_3 \rightarrow (PMe_3)_2Mo(CO)_4 + 2P(OMe)_3 \quad (6)$$

$$\Delta H = -5.4\ (0.2)\ \text{kcal/mol}$$

of interconversion of any of the complexes can be calculated.

Bond Strength Estimates. The bond strength estimates shown in Table I refer to solution-based values. The heat of reaction with carbon monoxide, shown in eq 7, provides the platform for

$$(NBD)Mo(CO)_4 + 2CO \rightarrow Mo(CO)_6 + NBD \quad (7)$$

$$\Delta H = -22.6\ (0.8)\ \text{kcal/mol}$$

assigning absolute values to the bond strengths shown. Recent laser photolysis studies of $Mo(CO)_6$, in the gas phase, led to estimation of the first bond dissociation energy as 40.5 kcal/mol.[9]

Table II. Heats of Reaction, Cone Angles, and Electronic Parameters for Selected Phosphines

$$(NBD)Mo(CO)_4 + 2PR_3 \rightarrow (PR_3)_2Mo(CO)_4 + NBD$$

phosphine or phosphite	$-\Delta H^a$	θ^b	ν^c
PPh_3	17.1	145	2068.9
$P(OPh)_3$	21.9	128	2085.3
PPh_2Me	22.2	136	2067.0
PMe_2Ph	26.8	122	2065.3
$P(OMe)_3$	27.5	107	2079.5
$P\text{-}n\text{-}Bu_3$	30.1	132	2060.3
PEt_3	32.1	132	2061.7
PMe_3	32.9	118	2064.1

[a] Reaction enthalpies are reported in kcal/mol. [b] Cone angles are in degrees and are taken from ref 4. [c] Electronic parameters are in cm^{-1} and are taken from ref 4.

Table III. Heats of Reaction and X-ray Crystallographic Data for Selected Phosphines

phosphine	$-\Delta H^a$	$\Delta H_{rel}{}^b$	Mo–P^c	d(Mo–P)^d	ϕ^e
PMe_3	32.9	0	2.522	0	97.54
PEt_3	32.1	0.8	2.544	0.022	100.27
$P\text{-}n\text{-}Bu_3$	30.1	2.8	2.552	0.030	99.29
PMe_2Ph	26.8	6.1	2.529	0.007	94.78
PPh_2Me	22.2	10.7	2.555	0.033	92.52
PPh_3	17.1	15.8	2.577	0.055	104.62

[a] All values reported are in kcal/mol. [b] Relative stabilities (in kcal/mol) with PMe_3 as reference. [c] Bond distances (in angstroms) are taken from ref 8. [d] Bond length difference with PMe_3 (in angstroms). [e] P–W–P angle (in degrees).

The average bond dissociation energy for all six carbonyl ligands was determined as 36 kcal/mol.[10] The value 38 ± 3 kcal/mol is adopted here and leads directly to assignment of the bond strength estimates in Table I. Due to uncertainties in the transferability of bond strength data from the gas phase to the solution phase, we consider these bond strength estimates accurate to within 5 kcal/mol. The enthalpies of substitution in solution are known to greater accuracy (typically to 0.5 kcal/mol), and these are used directly to estimate complex stability.

Enthalpy of Phosphine Substitution and Its Relation to Steric and Electronic Properties of the Phosphine Ligand. The steric and electronic properties of phosphine ligands are readily described in terms of the cone angle and electronic factor, originally proposed by Tolman.[4] The enthalpy of reaction 4 was shown[5] to fit eq 8

$$\Delta H = A_0 + A_1\theta + A_2\nu \quad (8)$$

with a correlation coefficient of 0.95 ($A_0 = -613.00$, $A_1 = 0.36$, $A_2 = 0.24$). Attempts to fit the enthalpy of reaction for the monodentate phosphines listed in Table II (along with cone angles and electronic parameters) to eq 8 yielded $R = 0.86$ ($A_0 = -993.13$, $A_1 = 0.36$, and $A_2 = 0.445$). Despite the low correlation coefficient, useful information may be obtained from this type of analysis. The ratio of A_1/A_2 can be taken as a measure of the relative importance of steric versus electronic factors. It would be expected that steric factors would become less important in going from the $L_3Mo(CO)_3$ system to the $L_2Mo(CO)_4$ system. The change in the A_1/A_2 ratio shows a decreasing dependence on steric factors in going from $L_3Mo(CO)_3$ (1.42) to $L_2Mo(CO)_4$ (0.81). Work in progress on the thermochemistry of $LMo(CO)_5$ complexes should show a continued decrease in the A_1/A_2 ratio.

Enthalpy of Phosphine Substitution and Its Relation to Structural Features of the Complexes. The analysis of ligand behavior in terms of the cone angle and electronic factors is simple and is perhaps the best way to first view data of this kind. For many of the complexes studied X-ray structures have been reported[8]

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and this allows a second comparison. It must be kept in mind, of course, that thermochemical data are generated in solution and that solid-state structures may show significant differences from those in solution.

Molybdenum-phosphorus bond lengths, P-Mo-P angles, and heats of reaction are reported in Table III for complexes with known crystal structures. Relative heats of displacement and bond lengths (with $(PMe_3)_2Mo(CO)_4$ as reference) are also shown. There is no obvious correlation between the complex stability and the P-Mo-P bond angle. There is a rough correlation with the Mo-P bond length. It should be noted that sequential replacement of methyl groups by phenyl results in a steady decrease in the enthalpy of reaction. There is a smooth transition from PMe_3 to PMe_2Ph to $PMePh_2$ to PPh_3 in steps of about 5 kcal/mol (see Table III). This corresponds to individual bond strength decreases on the order of 2.5 kcal/mol (since 2 mol of phosphine is bound) as methyl is replaced by phenyl.

Electronic Requirements of the Metal Center. The enthalpies of substitution for the monodentate ligands are, in most cases, close to those that would be predicted from earlier work on *fac*-$L_3Mo(CO)_3$. For example, the enthalpy of reaction 9 is −44.4

$$(CHPT)Mo(CO)_3 + 3P(OMe)_3 \rightarrow [P(OMe)_3]_3Mo(CO)_3 + CHPT \quad (9)$$

$$CHPT = \text{cycloheptatriene}$$

kcal/mol.[6] This involves replacement of three Mo-olefin bonds by 3 mol of $P(OMe)_3$. An estimate for the enthalpy of reaction 5 could reasonably be made by taking two-thirds of the value for the enthalpy of reaction 9. The estimated value (−29.6 kcal/mol) is close to the experimental value (−27.5 kcal/mol). For many of the ligand-exchange reactions studied here, the enthalpies of reaction could have been predicted to fair accuracy from the earlier work on $L_3Mo(CO)_3$. However, such calculations do show unexpected differences as illustrated below.

In the *fac*-$L_3Mo(CO)_3$ system, trimethyl phosphite and trimethylphosphine are nearly equal in strength. The enthalpy of reaction 10 is +1.4 (0.8) kcal/mol, implying that the phosphite

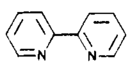
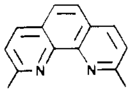
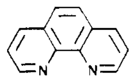
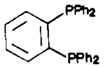
$$fac\text{-}[P(OMe)_3]_3Mo(CO)_3 + 3PMe_3 \rightarrow (PMe_3)_3Mo(CO)_3 + 3P(OMe)_3 \quad (10)$$

is a slightly stronger binding ligand. This situation is reversed in the complexes *cis*-$L_2Mo(CO)_4$. The enthalpy of reaction 6 is −5.4 (0.2 kcal/mol, indicating that trimethylphosphine is a stronger ligand in this system. Since trimethylphosphine has a smaller cone angle than trimethyl phosphite, this change cannot be ascribed to steric factors. The origin must be in the changing electronic requirements of the metal center. Addition of the highly basic PMe_3 becomes less favorable with successive substitution due to buildup of excess electron density at the metal center. When complete data are in for the $LMo(CO)_5$ system, it may be possible to examine electronic effects in more detail.

Additional Monodentate Ligands. The data in Table I include monodentate amine, arsine, and isocyanide ligands as well as carbon monoxide. The general trend observed for *fac*-$L_3Mo(CO)_3$, amine ≈ arsine < phosphine, is retained in this series. It was shown earlier that the nature of the substituents in PR_3 complexes affects complex stability. This is true for arsines as well; the $AsEt_3$ complex is 9.2 kcal/mol more stable than the corresponding $AsPh_3$ complex. The difference between PEt_3 and PPh_3 is 15 kcal/mol. As was the case for $L_3Mo(CO)_3$, carbon monoxide and isocyanides are among the strongest ligands. They have bond strengths comparable to those of phosphine ligands, as would be expected from the synthetic chemistry.

Table IV. Enthalpies of Reaction and Bond Strength Estimates for Bidentate Ligands[a]

$$(NBD)Mo(CO)_4 + LL \rightarrow (LL)Mo(CO)_4 + NBD$$

ligand	complex	$-\Delta H$	bond strength
	(COD)Mo(CO)$_4$	−2.0 (0.2)	25.7
	(NBD)Mo(CO)$_4$	0	26.7
	(bpy)Mo(CO)$_4$	11.8 (0.3)	32.6
$Ph_2AsCH_2CH_2AsPh$	(dpae)Mo(CO)$_4$	11.9 (0.3)	32.7
$Me_2NCH_2CH_2NMe_2$	(tmeda)Mo(CO)$_4$	13.4 (0.3)	33.4
	(Me$_2$phen)Mo(CO)$_4$	15.8 (0.2)	34.6
$Ph_2PCH_2PPh_2$	(dppm)Mo(CO)$_4$	16.0 (0.2)	34.7
	(phen)Mo(CO)$_4$	17.0 (0.2)	35.2
$Ph_2PCH_2CH_2AsPh_2$	(Arphos)Mo(CO)$_4$	19.3 (0.1)	36.4
$Ph_2PCH_2CH_2CH_2CH_2$-PPh_2	(dppb)Mo(CO)$_4$	22.1 (0.1)	37.8
$Ph_2PCH_2CH_2CH_2PPh_2$	(dppp)Mo(CO)$_4$	23.0 (0.1)	38.2
$Ph_2PCH_2CH_2PPh_2$	(dppe)Mo(CO)$_4$	24.3 (0.3)	38.9
$Me_2PCH_2PMe_2$	(dmpm)Mo(CO)$_4$	24.5 (0.5)	39.0
	(dppbz)Mo(CO)$_4$	24.7 (0.8)	39.1
$Me_2PCH_2CH_2PMe_2$	(dmpe)Mo(CO)$_4$	32.4 (0.1)	42.9

[a] Enthalpies and bond strengths are given in kcal/mol.

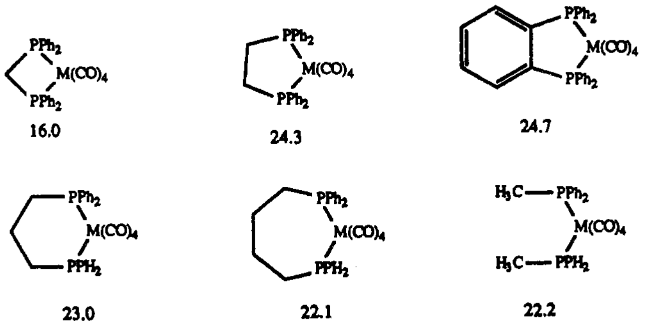


Figure 1. Relative stabilities (kcal/mol) for $[Ph_2P(CH_2)_nPPh_2]Mo(CO)_4$ complexes.

Bidentate Ligands. The enthalpies of reaction for bidentate ligands are listed in Table IV. Examination of the bond strength data and heats of ligand substitution for monodentate ligands revealed the general pattern in bond strengths P > As ≈ N. In the absence of special steric features, the heats of reaction of bidentate ligands follow this pattern and are largely predictable on the basis of the choice of an appropriate monodentate ligand model. For example, the heat of reaction of 2 mol of diphenylmethylphosphine (−22.2 kcal/mol) is close to that of 1,2-bis(diphenylphosphino)ethane (dppe); −24.3 kcal/mol). The heat of reaction of bipyridine (−11.8 kcal/mol) is quite close to that of 2 mol of pyridine (−12.1 kcal/mol). Significant differences from expected heats of binding will be referred to as "strain energy". It should be noted that bidentate ligands should have more favorable entropies of binding leading to greater thermodynamic stability even in the absence of favorable enthalpies of ligand displacement.

Chelating Phosphines and Arsines. The strain energies in cyclic organic compounds have been extensively investigated. Conventional ring strain estimates for four-, five-, and six-membered rings are on the order of 26, 6, and 0 kcal/mol.[11] Incorporation of molybdenum into the chelate structures, shown below, yields four- to seven-membered rings with the heats of reaction as shown

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(11) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

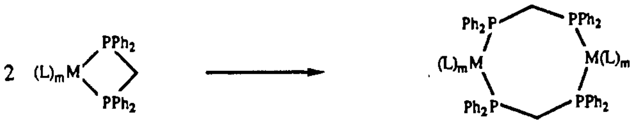
in Figure 1. The five-membered ring system based on either diphos or 1,2-(diphenylphosphino)benzene (dppbz) is most stable and slightly more so than 2 mol of Ph_2MeP. The six- and seven-membered ring systems are slightly less stable. Only for the four-membered system is a significant "ring strain" observed (8.3 kcal/mol). This is on the same order of magnitude as a recent estimate for thorium metallacyclobutanes (10 kcal/mol).[12] As shown in Table IV, the methyl-substituted analogues dmpm and dmpe present a similar behavior with a enthalpy difference of 7.9 kcal/mol between the four- and five-membered metallacycles. In this case, the more basic substituents lead to higher values and greater overall stability. Thus the enthalpy of replacement of dmpm by diphos, in reaction 11, is near zero. The strain energy

$$\text{dppmMo(CO)}_4 + \text{diphos} = \text{diphosMo(CO)}_4 + \text{dppm} \qquad (11)$$

in the four-membered ring of dppmMo$(CO)_4$ is nearly balanced by stronger binding of the more basic trialkylphosphine donors (dppm) versus that of the diaryl alkyl ligands (diphos). In this regard, it is also of interest that, whereas diphos was slightly more stable than 2 mol of diphenylmethylphosphine, dmpe is slightly less stable than 2 mol of trimethylphosphine. A possible explanation is that the phenyl groups of diphos may be held out of the way due to the structural demands of the chelate ring. This would lead to decreased steric repulson relative to that for diphenylmethylphosphine. For the methyl-substituted phosphines, this should be of little importance.

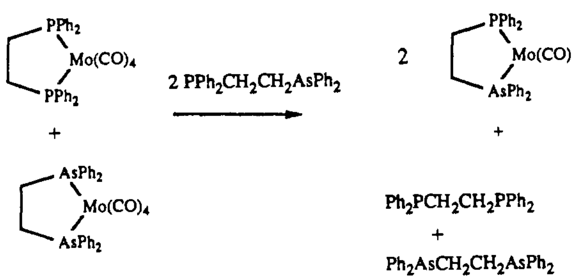
Spectroscopic data also highlight the special position of the four-membered ring systems. The $^{183}W-^{31}P$ and the $^{95}Mo-^{31}P$ coupling constants[13] are anomalously low for the four-membered metallacycles. The structure of (dppm)Mo$(CO)_4$ shows no lengthening of the Mo–P bond[14] compared to that in other diphenylalkylphosphines. The P–Mo–P angle (67.3°) shows considerable distortion and does give indication of the strain present in the system.

Phosphine ligands with small "bites" are known to form bridged structures as shown in reaction 12.[1] The entropy of reaction 12 should be unfavorable and can be estimated to be on the order of 10 kcal/mol at room temperature.[15] For the molybdenum system, we estimate the enthalpy of reaction 12 to be on the order of −16 kcal/mol, clearly offsetting the unfavorable entropy term. Thus, the mononuclear complex is probably a kinetic product.



(12)

Chelating arsine and mixed phosphine/arsine chelates were also studied. As expected, replacement of phosphorus by arsenic resulted in decreased stability. Bond strength estimates for five-membered rings appear to be roughly additive. The enthalpy of reaction 13 is calculated to be −1.3 (0.3) kcal/mol per mole of arphosMo$(CO)_4$ produced. As thermochemical data for this system increase, it should be possible to make good estimates for stabilities of a number of complexes and proposed intermediates.



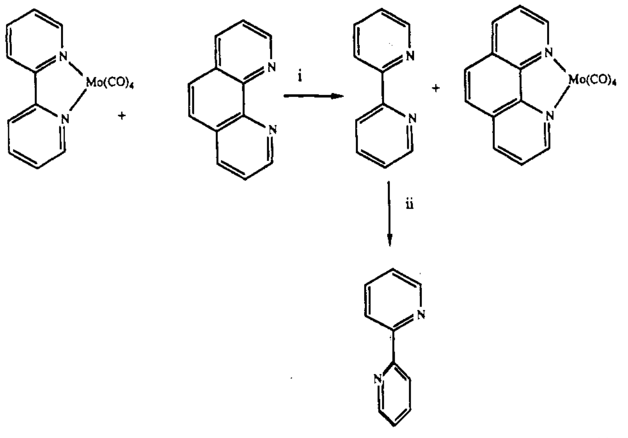
(13)

Table V. Infrared Carbonyl Bands (cm^{-1}), Enthalpies of Reaction (kcal/mol), and Bond Strength Estimates (kcal/mol) for *cis*-L_nMo$(CO)_4$ Complexes

complex	IR (CO) bands[a]	$-\Delta H$	bond strength
(COD)Mo$(CO)_4$	2041, 1953, 1905	−2.0	25.7
(NBD)Mo$(CO)_4$	2022, 1958, 1918	0	26.7
$(PCl_3)_2$Mo$(CO)_4$	2070, 1987	7.4	30.4
$(Ph_3As)_2$Mo$(CO)_4$	2045, 1948, 1900	10.5	32.0
(bpy)Mo$(CO)_4$	2039, 1938, 1900, 1838	11.8	32.6
(diars)Mo$(CO)_4$	2043, 1914, 1884	11.9	32.7
$(py)_2$Mo$(CO)_4$	2015, 1889, 1860	12.1	32.8
(tmeda)Mo$(CO)_4$	2038, 1878, 1836	13.4	33.4
(Me_2phen)Mo$(CO)_4$	2035, 1900, 1836	15.8	34.6
(dppm)Mo$(CO)_4$	2045, 1956, 1932, 1920, 1900	16.0	34.7
(phen)Mo$(CO)_4$	2041, 1900, 1884, 1844	17.0	35.2
$(Ph_3P)_2$Mo$(CO)_4$	2036, 1956, 1926, 1908, 1894	17.1	35.2
(arphos)Mo$(CO)_4$	2040, 1900	19.3	36.2
$(Et_3As)_2$Mo$(CO)_4$	2042, 1900, 1869	19.7	36.6
$[P(OPh)_3]_2$Mo$(CO)_4$	2065, 1966, 1942	21.9	37.7
(dppb)Mo$(CO)_4$	2022, 1916, 1900, 1884	22.1	37.8
$(Ph_2MeP)_2$Mo$(CO)_4$	2038, 1920, 1910	22.2	37.8
Mo$(CO)_6$	1986	22.6	38.0
(dppp)Mo$(CO)_4$	2030, 1932, 1906	23.0	38.2
(dppe)Mo$(CO)_4$	2040, 1956, 1932, 1924, 1900	24.3	38.9
(dmpm)Mo$(CO)_4$	2023, 1891, 1872	24.5	39.0
(dppbz)Mo$(CO)_4$	2018, 1926, 1887	24.7	39.1
$(Me_2PhP)_2$Mo$(CO)_4$	2036, 1954, 1922, 1900	26.8	40.1
$[(MeO)_3P]_2$Mo$(CO)_4$	2040, 1976, 1924	27.5	40.5
(n-$Bu_3P)_2$Mo$(CO)_4$	2038, 1954, 1914, 1900, 1884	30.1	41.8
$(CyNC)_2$Mo$(CO)_4$	2040, 1926	30.1	41.8
$(Et_3P)_2$Mo$(CO)_4$	2038, 1952, 1914, 1900, 1884	32.1	42.8
(dmpe)Mo$(CO)_4$	2020, 1954, 1920, 1900	32.4	42.9
$(Me_3P)_2$Mo$(CO)_4$	2036, 1942, 1920, 1900	32.9	43.2

[a] Infrared spectra were recorded in THF solution.

Chelating Nitrogen Donors. As mentioned before, the heat of binding of bpy agrees within experimental error with that of 2 mol of pyridine. The heat of binding of the tertiary aliphatic amine TMED is only slightly more negative than for the less basic pyridine system. It was surprising to find that the 1,10-phenanthroline complex was some 5 kcal/mol more stable than the corresponding bpy complex. Two rationalizations come to mind. The first is that the phen ligand has increased ability to function as a π acceptor due to its more delocalized π orbitals. The second is that the configuration of free bpy has the two pyridines perpendicular to each other. Displacement of bound bpy by phen will allow relaxation to the preferred geometry of the free ligand as shown in eq 14. Molecular mechanics calculations[16] appear to support this second explanation. The complex



(14)

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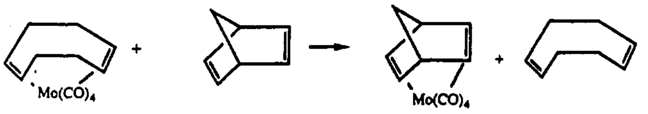
of dimethylphenanthroline is 1.2 kcal/mol less stable than the unsubstituted phenanthroline ligand, presumably due to steric repulsion between the methyl groups and coordinated carbon monoxide ligands.

Cyclooctadiene versus Norbornadiene. As discussed in this section, substitution of norbornadiene for cyclooctadiene as shown in eq 15 is exothermic by about 2 kcal/mol. This is opposite to the heat of binding to Pd(II), where cyclooctadiene was 0.3 kcal/mol more stable.[17] The reasons for these relatively small differences are not clear.



(15)

Conclusion

Data for monodentate and bidentate ligands are combined in Table V, which also includes IR spectral data. In general, the stabilities of $L_2Mo(CO)_4$ complexes are similar to those in our earlier work on $L_3Mo(CO)_3$. The importance of steric factors is reduced, as expected. The changing electronic nature of the metal center may also play a role in influencing complex stability. For bidentate ligands forming metallacycles, four-membered rings are less stable than five-membered rings by 8 kcal/mol. Six- and seven-membered rings are slightly less stable than four-membered rings (1–2 kcal/mol). In the absence of ring strain, or special steric effects, heats of reaction can be estimated to fair accuracy on the basis of data for related complexes. Additional work in progress is aimed at extending those data in order to generate a complete picture of the factors controlling stability in these and other organomolybdenum systems.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-8618753) is gratefully acknowledged.

Registry No. dppe, 1663-45-2; COD, 111-78-4; NBD, 121-46-0; bpy, 366-18-7; dpae, 4431-24-7; tmeda, 110-18-9; Mephen, 484-11-7; dppm, 2071-20-7; phen, 66-71-7; arphos, 23582-06-1; dppb, 7688-25-7; dppp, 6737-42-4; dmpm, 64065-08-3; dppbz, 13991-08-7; dmpe, 23936-60-9; py, 110-86-1; $(PCl_3)_2Mo(CO)_4$, 16244-51-2; $(Ph_3As)_2Mo(CO)_4$, 16742-97-5; $[P(OMe)_3]_2Mo(CO)_4$, 15631-22-8; $(py)_2Mo(CO)_4$, 16742-99-7; $(Ph_3P)_2Mo(CO)_4$, 16742-93-1; $(Et_3As)_2Mo(CO)_4$, 111265-67-9; $[P(OPh)_3]_2Mo(CO)_4$, 59599-01-8; $(PPh_2Me)_2Mo(CO)_4$, 37438-49-6; $(PPhMe_2)_2Mo(CO)_4$, 24554-47-0; $(P\text{-}n\text{-}Bu_3)_2Mo(CO)_4$, 16244-54-5; $(CyNC)_2Mo(CO)_4$, 15227-72-2; $(PEt_3)_2Mo(CO)_4$, 19217-80-2; $(PMe_3)_2Mo(CO)_4$, 16027-45-5; $(COD)Mo(CO)_4$, 12109-74-9; $(bpy)Mo(CO)_4$, 15668-64-1; $(dpae)Mo(CO)_4$, 38536-63-9; $(dppe)Mo(CO)_4$, 14971-45-0; $(tmeda)Mo(CO)_4$, 23301-98-6; $(dppm)Mo(CO)_4$, 26743-81-7; $(phen)Mo(CO)_4$, 15740-78-0; $(arphos)Mo(CO)_4$, 53557-42-9; $(dppb)Mo(CO)_4$, 15553-69-2; $(dppp)Mo(CO)_4$, 15553-68-1; $(dppe)Mo(CO)_4$, 15444-66-3; $(dmpm)Mo(CO)_4$, 90624-09-2; $(dppbz)Mo(CO)_4$, 111189-30-1; $(dmpe)Mo(CO)_4$, 40544-97-6; $(NBD)Mo(CO)_4$, 12146-37-1; $Mo(CO)_6$, 13939-06-5; Ph_3As, 603-32-7; Ph_3P, 603-35-0; Et_3As, 617-75-4; $P(OPh)_3$, 101-02-0; PPh_2Me, 1486-28-8; CO, 630-08-0; $PPhMe_2$, 672-66-2; $P(OMe)_3$, 594-09-2; $P\text{-}n\text{-}Bu_3$, 998-40-3; CyNC, 931-53-3; PEt_3, 554-70-1; PMe_3, 594-09-2; PCl_3, 7719-12-2; P, 7723-14-0; Mo, 7439-98-7.

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Transition-Metal-Promoted Cyclization Reactions of Isocyanide Ligands. Synthesis of Cyclic Aminooxycarbene Complexes of Platinum(II) and X-ray Structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$

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Electrophilic isocyanide CNR ligands in cationic Pt(II) complexes of the type *trans*-$[(PR'_3)_2Pt(CNR)Cl]BF_4$ (I) ($PR'_3 = PPh_3$, PMe_2Ph; R = p-$MeOC_6H_4$, p-MeC_6H_4, p-$NO_2C_6H_4$, Me, C_6H_{11}) are converted to the corresponding 5-membered cyclic aminooxycarbene derivatives *trans*-$\{(PR'_3)_2Pt[\overline{CN(R)CH_2CH_2O}]X\}BF_4$ (II) (X = Cl, Br) by reaction in THF with 2-bromoethanol in the presence of n-BuLi. These reactions are likely to proceed by nucleophilic attack of the alkoxide on the isocyanide carbon atom to give an imidoyl intermediate, which cyclizes intramolecularly to yield the carbene products. The less sterically hindered CNMe and aryl isocyanide ligands in I are converted in a few minutes to the final products II in ca. 70–90% yield; the more bulky CNC_6H_{11} derivative gives only a 25% yield. The t-BuNC ligand in the complex *trans*-$[(PPh_3)_2Pt(CN\text{-}t\text{-}Bu)Cl]BF_4$ does not react at all, nor does p-$MeOC_6H_4NC$ in *trans*-$[(PCy_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$ with bulky PCy_3 ligands. Treatment of *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2$ with 2 equiv of 2-bromoethoxide gave the bis(aminooxycarbene) $Br_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}]_2$. The Pt(II)–cyclic aminooxycarbenes II were characterized by their elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectra. An X-ray-determined structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$, space group $P2_1/a$, $a = 12.175$ (2) Å, $b = 26.137$ (3) Å, $c = 13.274$ (4) Å, $\beta = 91.61$ (2)°, and $Z = 4$, was refined to $R = 0.039$ ($R_w = 0.044$) for 5325 independent reflections. The coordination geometry around the Pt(II) atom is square planar with the carbene ligand perpendicular to the plane. The cyclic aminooxycarbene ligand is planar with $C(sp^2)$–N and $C(sp^2)$–O bond distances of 1.30 (1) and 1.33 (1) Å, indicating significant π-bonding between the nitrogen, oxygen, and carbene carbon.

Introduction

Cyclization reactions of electrophilic metal-coordinated isocyanide ligands leading to heterocyclic carbene complexes have been accomplished by different synthetic strategies (Scheme I).[2-6] For instance, paths a and b of Scheme I take advantage of the reactivity of suitably functionalized isocyanides which undergo

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