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Steric Contributions to the Solution Dynamics Involving Phosphorus Ligand Dissociation in Substituted Derivatives of Molybdenum Hexacarbonyl

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Kinetic and mechanistic studies of *cis*-$Mo(CO)_4L_2$ derivatives (L = phosphine or phosphite) are presented for the substitution reaction of one of the ligands (L) by carbon monoxide. These processes were observed to proceed by a dissociative mechanism with the rate of substitution being greatly enhanced as the size of the phosphorus ligand increases within a series of phosphine or phosphite derivatives. The *cis*-$Mo(CO)_4L_2$ species were found to react stereospecifically with ^{13}CO to afford *cis*-$Mo(CO)_4(^{13}CO)L$ derivatives. In addition, the $[Mo(CO)_4L]$ intermediate produced by phosphine loss from a stereospecifically ^{13}CO-labeled *cis*-$Mo(CO)_4L_2$ derivative was observed to be nonfluxional during its solution lifetime. Rate studies of phosphine dissociation in *trans*-$Mo(CO)_4(PPh_3)_2$ are reported which demonstrate this process to be less facile when compared with the analogous process in *cis*-$Mo(CO)_4(PPh_3)_2$. Observations on the cis → trans isomerization reaction of $Mo(CO)_4(PPh_3)_2$ resulting from dissociative phosphine loss are also discussed.

Introduction

Thermally activated ligand-dissociation processes in substituted group 6B metal carbonyl derivatives involving the tightly bound, ubiquitous phosphine or phosphite ligands have rarely been studied quantitatively.[1,2] This can be attributed to a large extent to the lack of complexes where phosphine dissociation is energetically more favored than other reaction pathways. Nevertheless, it is well-known that ligand size can have a pronounced influence on the rate of ligand dissociation.[3a] The steric versatility of tertiary phosphines and phosphites achieved by varying the substituent groups on phosphorus can often be accomplished without dramatically altering the ligands' electronic properties; however, some caution must always be exercised when separating electronic and steric effects since these properties tend to be interrelated.[3b] Therefore, the need for accurately determined activation parameters is essential in investigations intended to distinguish between these effects.

In the work reported in this contribution we have exploited this rate enhancement for phosphorus ligand dissociation based on steric effects in *cis*-$Mo(CO)_4L_2$ derivatives in order to examine the activation parameters for phosphine or phosphite dissociation (eq 1).[4] The use of carbon monoxide as the

$$cis\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L \qquad (1)$$

incoming ligand is advantageous not only because thermally stable $Mo(CO)_5L$ species are afforded but also because it eliminates consideration of the associative or dissociative interchange term which is common to many such substitution processes. It is important that we know more about the solution geometry and reactivity of the postulated $[Mo(CO)_4L]$ intermediates formed during these dissociative processes.[5,6] Therefore, these investigations have also involved a determination of the stereochemical site occupied by the incoming CO ligand, as well as a determination of the scrambling of a stereospecifically incorporated labeled carbon monoxide ligand in the $[Mo(CO)_4L]$ intermediate. Studies have clearly established that in the substitution process described in eq 1 the environment about the metal center in the transition state closely resembles the products of dissociation, $[Mo(CO)_4L]$ and L.[7,8] Consequently, it is appropriate to employ ΔH^* values as means of comparing metal–phosphorus bond strengths.

The *trans*-$Mo(CO)_4L_2$ derivatives are often the thermodynamically more stable isomeric form of the disubstituted monoligated molybdenum tetracarbonyl species where L = phosphine or phosphite. This has been substantiated for L = PPh_3,[4] P-*n*-Bu_3,[9] and PEt_3.[9,10] Hence, in our consideration of the reaction described in eq 1 it was necessary to explore simultaneously the kinetic parameters for the *trans*-$Mo(CO)_4L_2$ derivatives (eq 2), along with the coordination site

$$trans\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L \qquad (2)$$

occupied by the incoming CO ligand. Observations on the cis → trans isomerization process resulting from dissociative phosphine loss are also discussed.

Table I. Rates of Ligand (L) Replacement by CO at 70 °C in CO-Saturated Tetrachloroethylene for *cis*-$Mo(CO)_4L_2$ Derivatives

L	cone angle, deg[a]	rate, s^{-1}
$PN_3(CH_2)_6$	102[b]	$<1.0 \times 10^{-6}$
PMe_2Ph	122	$<1.0 \times 10^{-6}$
$PMePh_2$	136	1.33×10^{-5}
PPh_3	145	3.16×10^{-3} [c]
$PPhCy_2$	162[d]	6.40×10^{-2} [c]
$P(OCH_2)_3CEt$	101	$<1.0 \times 10^{-6}$
$P(OPh)_3$	128	$<1.0 \times 10^{-5}$
$P(O\text{-}o\text{-}tol)_3$	141	1.60×10^{-4}

[a] Taken from ref 3a unless otherwise noted. When the concept of cone angle as defined by Tolman is used, it is important to consider ligand intermeshing as illustrated by Clark.[3b] [b] DeLerno, J. R.; Trefonas, L. M.; Darensbourg, M. Y.; Majeste, R. J. *Inorg. Chem.* **1976**, *15*, 816. [c] Extrapolated from the Arrhenius plots. [d] Reference 4.

Results and Discussion

The rate of substitution of the phosphine or phosphite ligand (eq 1) in *cis*-$Mo(CO)_4L_2$ complexes (where L = $P(OCH_2)_3CEt$, $PN_3(CH_2)_6$, PMe_2Ph, $PMePh_2$, PPh_3, $PPhCy_2$, $P(OPh)_3$, and $P(O\text{-}o\text{-}tol)_3$) has been observed to follow the first-order rate law (3) in CO-saturated tetrachloroethylene

$$\text{rate} = k_1[cis\text{-}Mo(CO)_4L_2] \qquad (3)$$

solution. Comparative values of the rate constants k_1 at 70.0 °C, calculated from the first-order rate expression, are given in Table I. The reactions were observed to be clean, with $Mo(CO)_5L$ being the only product. Further reactions of the $Mo(CO)_5L$ derivatives with carbon monoxide to afford $Mo(CO)_6$ or to exchange CO groups require more rigorous conditions.[11] As is noted in Table I, the rates within a series of phosphines or phosphites parallel the steric requirements of the dissociating ligand L, with rates increasing as the Tolman cone angle increases.

We have chosen to investigate the kinetic and mechanistic details for displacement of L by CO from *cis*-$Mo(CO)_4L_2$ species where L = PPh_3, $P(O\text{-}o\text{-}tol)_3$, and $PPhCy_2$. Rate data and activation parameters are given in Tables II and III, and it can be seen that rates at 70 °C vary, L = $PPhCy_2 \gg PPh_3 \gg P(O\text{-}o\text{-}tol)_3$. The faster rate for $PPhCy_2$ can be seen to arise from an entropy effect (steric acceleration), as is reflected in

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Table II. Rate Constants for the Dissociation of Phosphines in *cis*-$Mo(CO)_4L_2$ Derivatives[a]

L	temp, °C	10^4k_1, s^{-1}
PPh_3	40.0	0.449
	50.0	2.06
	60.0	8.27
	64.9	16.4
$PPhCy_2$	29.7	1.51
	31.4	2.09
	35.4	4.04
	37.8	6.09
	39.8	8.43
	40.7	8.73
	43.0	13.3
$P(O\text{-}o\text{-}tol)_3$	56.0	0.205
	62.6	0.552
	70.0	1.60
	75.4	3.22

[a] Reactions carried out in CO-saturated tetrachloroethylene.

Table III. Comparative Rate Constants and Activation Parameters for Dissociative Processes in $Mo(CO)_4L_2$ Species

L	10^4k(70 °C), s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu	cone angle, deg
$P(O\text{-}o\text{-}tol)_3$[a]	1.60	31.9 (11)	14.4 (35)	141
PPh_3[a]	31.6	29.7 (5)	14.2 (14)	145
$PPhCy_2$[a]	640.0	30.2 (16)	21.7 (54)	162
PPh_3[b]	0.471	22.9 (15)	−14.0 (76)	145
PPh_3[c]	0.674	23.6 (14)	−11.1 (39)	145

[a] Dissociation from *cis*-$L_2Mo(CO)_4$. [b] Dissociation from *trans*-$L_2Mo(CO)_4$; value of *k* extrapolated from Arrhenius plot of data at 74.5–96.0 °C. [c] Isomerization of *cis*-$Mo(CO)_4(PPh_3)_2$ → *trans*-$Mo(CO)_4(PPh_3)_2$ in excess PPh_3; value of *k* extrapolated from Arrhenius plot of data at 75.5–82.5 °C.

the greater Tolman cone angle for $PPhCy_2$ than for PPh_3 or $P(O\text{-}o\text{-}tol)_3$. The slowest rate, for $P(O\text{-}o\text{-}tol)_3$, results from a greater enthalpy of activation for Mo–L bond breaking and probably reflects greater Mo–L bond strength for this ligand,[12] the consequence of stronger π bonding of L to Mo.

It was of additional interest to perform *competitive dissociative loss* studies of these phosphorus ligands from a single metal center to observe which ligand was displaced as a result of steric crowding about the metal in *cis*-$Mo(CO)_4LL'$ species. This was accomplished by synthesizing the mixed-ligand derivatives (eq 4) and examining the distribution of products from their reactions with CO (eq 5 and 6). Hence, the effect

$$cis\text{-}Mo(CO)_4(PPh_3)(NHC_5H_{10}) + L \rightarrow cis\text{-}Mo(CO)_4(PPh_3)L \quad (4)$$

$$L = PCy_2Ph \text{ and } P(O\text{-}o\text{-}tol)_3$$

$$cis\text{-}Mo(CO)_4(PPh_3)(PCy_2Ph) + CO \rightarrow Mo(CO)_5(PCy_2Ph) + PPh_3 \quad (5)$$

$$cis\text{-}Mo(CO)_4(PPh_3)(P(O\text{-}o\text{-}tol)_3) + CO \begin{array}{l} \nearrow \begin{array}{c} Mo(CO)_5PPh_3 + P(O\text{-}o\text{-}tol)_3 \\ 55\% \end{array} \\ \searrow \begin{array}{c} Mo(CO)_5(P(O\text{-}o\text{-}tol)_3) + PPh_3 \\ 45\% \end{array} \end{array} \quad (6)$$

of the bulkier ligand is to cause a *steric labilization* of the smaller phosphorus ligand.[13] In support of this contention, the reaction of *cis*-$Mo(CO)_4[P(OMe)_3](PCy_3)$ species with CO affords $Mo(CO)_5(PCy_3)$ (cone angles of $P(OMe)_3$ and PCy_3 being 107 and 170°, respectively[3a]). Further, we have previously reported a large steric enhancement in the dissociation of piperidine from *cis*-$Mo(CO)_4(PPh_3)(NHC_5H_{10})$ as compared with its pentacarbonyl analogue.[7] Steric labilization may be a general phenomenon and will require further investigation. For example experiments to test bulky phosphine labilization effects on other ligands such as carbon monoxide in both mononuclear and metal-cluster derivatives are under way. Preliminary observations on $Mo(CO)_5L$ derivatives are encouraging, for CO loss is found to occur preferentially from an equatorial site and increases in the order PPh_3 > P-*n*-Bu_3 > $P(OCH_2)CC_2H_5$.[14]

Scheme I

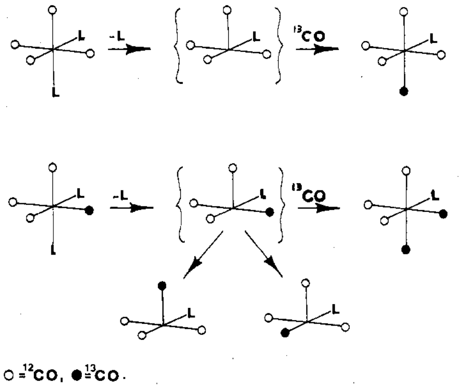


Table IV. Rate Constants for the Dissociation of Triphenylphosphine in *trans*-$Mo(CO)_4(PPh_3)_2$ and the Isomerization of *cis*-$Mo(CO)_4(PPh_3)_2$ → *trans*-$Mo(CO)_4(PPh_3)_2$

process	temp, °C	10^5k, s^{-1}	process	temp, °C	10^5k, s^{-1}
dissocn[a]	74.5	8.14	isomerizn[b]	75.5	11.7
	77.5	9.80		76.1	12.5
	87.5	25.8		82.5	23.4
	96.0	57.4			

[a] Reactions carried out in CO-saturated tetrachloroethylene. [b] Reactions carried out in excess PPh_3 in tetrachloroethylene.

Intimate mechanistic aspects for the overall ligand substitution process described in eq 1 have been derived from studies of trapping experiments of the intermediate $[Mo(CO)_4L]$ species with labeled carbon monoxide. The reactions of *cis*-$Mo(CO)_4L_2$ (L = PPh_3 or $P(O\text{-}o\text{-}tol)_3$) derivatives with ^{13}CO have led to the production of $Mo(CO)_4(^{13}CO)L$ species which are exclusively labeled in an equatorial position as indicated by ^{13}C NMR spectroscopy (Figure 1). This result indicates that the intermediate resulting from loss of a cis phosphine ligand in *cis*-$Mo(CO)_4L_2$ closely resembles the transition state. That is, the transition state which presumably involves a great deal of bond breaking[12] (Figure 2) requires little reorganization in going to the intermediate. It was further demonstrated from the reaction of axially labeled *cis*-$Mo(CO)_3(^{13}CO)(PPh_3)_2$ with ^{13}CO that the square-pyramidal intermediate $[Mo(CO)_4(PPh_3)]$ is nonfluxional during its solution lifetime.[15-17] When the $[Mo(CO)_3(^{13}CO)(PPh_3)]$ transient is trapped with ^{13}CO, the resulting $Mo(CO)_3(^{13}CO)_2(PPh_3)$ derivative was shown by ^{13}C NMR (Figure 1) to contain *only* equatorially labeled carbon monoxide groups, and ν(CO) infrared spectroscopy indicated the two ^{13}CO ligands to be cis to one another.[18] This result is totally congruous with our recent report of the reaction of (bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tetracarbonyl, stereospecifically labeled with ^{13}CO, with PPh_3 in hydrocarbon solvent to afford *fac*-$Mo(CO)_3(^{13}CO)(PPh_3)_2$.[19] Scheme I summarizes these observations along with the reaction coordinate/energy diagram given in Figure 2.[20-23]

The *trans*-$Mo(CO)_4(PPh_3)_2$ derivative also has been found to undergo phosphine ligand substitution (eq 2), albeit more reluctantly than its cis analogue. The reaction of *trans*-$Mo(CO)_4(PPh_3)_2$ with CO to afford $Mo(CO)_5(PPh_3)$ was observed to follow the first-order rate expression (eq 7), and

$$\text{rate} = k_1'[trans\text{-}Mo(CO)_4(PPh_3)_2] \quad (7)$$

values of the rate constants, k_1', obtained at several tem-

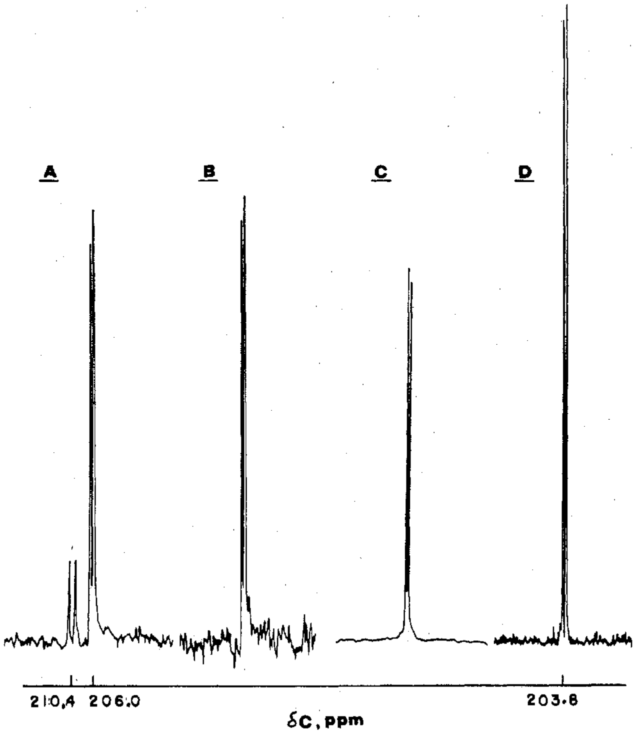


Figure 1. ^{13}C NMR spectra in carbonyl region in $CDCl_3$ solvent. (A) Natural-abundance spectrum of $Mo(CO)_5(PPh_3)$; $\delta(C_{trans})$ 210.4 (J_{P-C} = 22.5 Hz), $\delta(C_{cis})$ 206.0 (J_{P-C} = 8.8 Hz). (B) Spectrum of $Mo(CO)_5(PPh_3)$ from the reaction of *cis*-$Mo(CO)_4(PPh_3)_2$ and ^{13}CO at 55 °C. (C) Spectrum of $Mo(CO)_5(PPh_3)$ from the reaction of *fac*-$Mo(CO)_3(^{13}CO)(PPh_3)_2$ and ^{13}CO at 55 °C. (D) Spectrum of $Mo(CO)_5[P(O\text{-}o\text{-}tol)_3]$ from the reaction of *cis*-$Mo(CO)_4[P(O\text{-}o\text{-}tol)_3]_2$ and ^{13}CO; $\delta(C_{cis})$ 203.8 (J_{P-C} = 12.7 Hz).

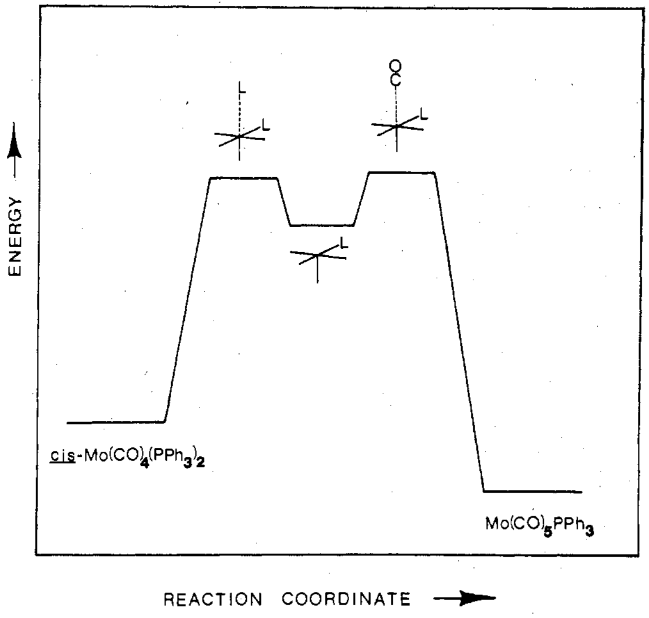


Figure 2. Plot of free energy vs. reaction coordinate for the reaction of *cis*-$Mo(CO)_4(PPh_3)_2$ + CO → $Mo(CO)_5(PPh_3)$. The relative heights of the barriers to reactions of $[Mo(CO)_4(PPh_3)]$ with CO and PPh_3 have been shown to be very similar (with the CO barrier somewhat higher) via competitive studies.[7] The energy of activation for the right-hand pathway has indeed been observed to be large (E_{act} $\gtrsim$ 36 kcal).[14]

peratures, are listed in Table IV.

A comparison of activation enthalpies for the substitution reactions (1) and (2) (see Table III) indicates that the enhanced rate of dissociation of the triphenylphosphine ligand in *cis*-$Mo(CO)_4(PPh_3)_2$ is due to the large positive ΔS^* associated with this process.[24] In other words, the kinetic stability of the *trans*-$Mo(CO)_4(PPh_3)_2$ isomer over that of the cis form is due to steric interference of the two bulky triphenylphosphine ligands in the latter derivative (ΔG^*(trans) = 27.8 kcal and ΔG^*(cis) = 25.3 kcal).

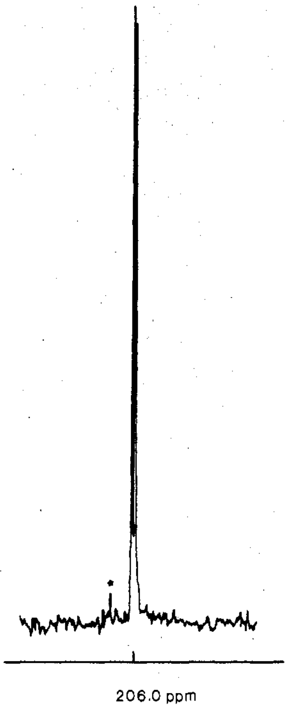
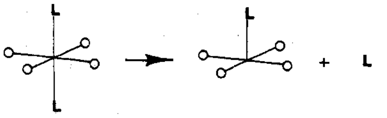
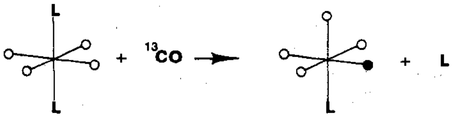


Figure 3. ^{13}C NMR spectrum in $CDCl_3$ of $Mo(CO)_5(PPh_3)$ afforded from *trans*-$Mo(CO)_4(PPh_3)_2$ and ^{13}CO (results were the same at 55 and 91 °C). Peak with asterisk is due to *trans*-$Mo(CO)_4(PPh_3)_2$.

The large negative entropy of activation associated with reaction 2 is suggestive of gross reorganization in the transition state along the reaction coordinate for this transformation, since a simple dissociative process analogous to that in Scheme I (e.g., the process described in eq 8) in relatively noninteracting solvent should afford a positive ΔS^* value. Other evidence indicative of reorganization in either the transition state or the intermediate is obtained when labeled carbon monoxide is employed as the entering ligand. As shown in eq 9, the stereochemical position occupied by the ^{13}CO in the pentacarbonyl product is specifically equatorial. Figure 3 contains the ^{13}C NMR spectrum of the product of reaction 9 (a single ^{13}C resonance at 206.0 ppm) which demonstrates the process to be stereospecific within an experimental error of 3%.[25-27]



(8)



(9)

The pathway for cis ⇌ trans isomerization of $Mo(CO)_4(PPh_3)_2$ (eq 10) has been demonstrated from these studies to

$$cis\text{-}Mo(CO)_4(PPh_3)_2 \rightleftharpoons trans\text{-}Mo(CO)_4(PPh_3)_2 \quad (10)$$

involve dissociation of a PPh_3 ligand, i.e., reaction 10 when carried out in a CO atmosphere affords $Mo(CO)_5(PPh_3)$ quantitatively. The rate for this cis → trans isomerization process is significantly slower than the dissociative loss of PPh_3 from *cis*-$Mo(CO)_4(PPh_3)_2$ (see Tables III and IV). That is, there is definitely a higher energy barrier for the intermediate $[\mathrm{Mo(CO)_4(PPh_3)}]$ (C_s isomer) to react with $\mathrm{PPh_3}$ to form the *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ isomer than for it to recombine with $\mathrm{PPh_3}$ and revert to *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$. A comparison of the activation parameters (Table III) for the replacement of $\mathrm{PPh_3}$ by CO in *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ and the *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ → *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ isomerization process indicates that there must be more bond making in the reaction of the intermediate $[\mathrm{Mo(CO)_4PPh_3}]$ with $\mathrm{PPh_3}$ to afford *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$. Thus during the cis → trans isomerization reaction, the experimental observation may be explained with only the C_s $[\mathrm{Mo(CO)_4(PPh_3)}]$ intermediate; i.e., there is no reason to invoke the presence of the alternative C_{4v} $[\mathrm{Mo(CO)_4(PPh_3)}]$ species. This conclusion is consistent with the results for replacement of $\mathrm{PPh_3}$ in *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ by CO. Nevertheless, both stereochemistries for $[\mathrm{Mo(CO)_4L}]$ intermediates (C_s and C_{4v}), generated photochemically, have been observed by matrix-isolation spectroscopy.[28,29] Because of the dissociative nature of the cis → trans isomerization reaction (10), the preparative yield of *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ afforded from thermolysis of the cis isomer (see Experimental Section) is increased in the presence of added triphenylphosphine; e.g., when the reaction is carried out in a twofold excess of $\mathrm{PPh_3}$ the isolated, purified yield increases from 55 to 87%.

Contrary to these observations, the lowest energy mechanism for the isomerization of the analogous P-*n*-$\mathrm{Bu_3}$ and $\mathrm{PEt_3}$ derivatives has been unequivocally shown to occur via a non-bond-breaking, intramolecular process.[9] This isomerization reaction has been described as proceeding along a reaction coordinate involving a trigonal-prismatic transition state or intermediate. Therefore, the barrier to an intramolecular rotation process in the disubstituted derivatives containing the smaller P-*n*-$\mathrm{Bu_3}$ and $\mathrm{PEt_3}$ ligands (cone angles = 132°)[3a] is less than that for Mo–P bond cleavage by about 5–6 kcal.[30] The energy difference between the two isomeric forms of $\mathrm{Mo(CO)_4L_2}$ (L = P-*n*-$\mathrm{Bu_3}$ and $\mathrm{PEt_3}$) is ~1 kcal, with the trans isomers being thermodynamically more stable (equilibrium mixture ~85% trans). On the other hand, the *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ derivative is somewhat more stable than its cis analogue (perhaps 2–3 kcal) since reaction 10 is observed to go essentially completely to the right.

Experimental Section

Materials. Tetrachloroethylene was Spectro Grade solvent obtained from Matheson Coleman and Bell. Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Corp. The phosphine ligands were purchased from Strem Chemicals. $^{12}\mathrm{C}$ carbon monoxide was supplied by Matheson, whereas $^{13}\mathrm{CO}$ gas enriched to >90% was obtained from Prochem, B.O.C. Ltd., London. *cis*-$\mathrm{Mo(CO)_4(NHC_5H_{10})_2}$ was prepared from $\mathrm{Mo(CO)_6}$ and excess piperidine in refluxing heptane.[4]

Compound Preparations. (a) *cis*-$\mathrm{Mo(CO)_4L_2}$ (L = Phosphine or Phosphite). All *cis*-$\mathrm{Mo(CO)_4L_2}$ derivatives were prepared from *cis*-$\mathrm{Mo(CO)_4(NHC_5H_{10})_2}$ and excess ligand (L) in refluxing dichloromethane as previously described.[4]

(b) *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$. This complex was prepared by the thermal isomerization of *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ in refluxing toluene. The product was purified by recrystallization from chloroform/methanol at 0 °C.

(c) *cis*-$\mathrm{Mo(CO)_4(PPh_3)(PPhCy_2)}$. *cis*-$\mathrm{Mo(CO)_4(PPh_3)(NHC_5H_{10})}$ was prepared and purified as previously described by photolysis of $\mathrm{Mo(CO)_5(PPh_3)}$ in the presence of excess $\mathrm{NHC_5H_{10}}$ in THF.[31] This complex was reacted with a 2 molar excess of $\mathrm{PPhCy_2}$ in hydrocarbon solvent for several hours (~10) at 22 °C. The reaction solution contained about 85–90% product (ν(CO) for *cis*-$\mathrm{Mo(CO)_4(PPh_3)(PPhCy_2)}$ 2017, 1917, 1899, 1884 $\mathrm{cm^{-1}}$). The 10–15% impurity was the starting material *cis*-$\mathrm{Mo(CO)_4(PPh_3)(NHC_5H_{10})}$. The reaction was quenched at this stage to avoid formation of the *cis*-$\mathrm{Mo(CO)_4(PPhCy_2)_2}$ derivative. Reaction 5 was carried out at 50 °C for ~45 min in tetrachloroethylene to afford mostly $\mathrm{Mo(CO)_5(PPhCy_2)}$ (ν(CO) 2069.4, 1946.0, 1934.2 $\mathrm{cm^{-1}}$) with a small quantity (~10–15%) of $\mathrm{Mo(CO)_5(PPh_3)}$ believed to arise from the reaction of the *cis*-$\mathrm{Mo(CO)_4(PPh_3)(NHC_5H_{10})}$ impurity with CO.

(d) *cis*-$\mathrm{Mo(CO)_4(PPh_3)}$[P(O-*o*-tol)$_3$]. *cis*-$\mathrm{Mo(CO)_4(PPh_3)(NHC_5H_{10})}$ was prepared by an alternative route to the photolysis method (vide supra) in order to more readily acquire larger quantities of this material. A 1.23-g sample (3.26 mmol) of *cis*-$\mathrm{Mo(CO)_4(NHC_5H_{10})_2}$ and 0.86 g (3.28 mmol) of $\mathrm{PPh_3}$ were refluxed in $\mathrm{CH_2Cl_2}$ for *exactly* 2 min during which time the solution became clear. The reaction mixture was immediately placed in an ice bath, and the solvent was removed at 0 °C. The solid was dissolved in chloroform and filtered through Celite. Upon the addition of methanol and cooling of the solution below 0 °C, yellow crystals of the pure product were obtained. These crystals were isolated by filtration and dried under vacuum (yield 80%). This complex was then reacted with a 2 molar excess of tri-*o*-tolyl phosphite in refluxing $\mathrm{CH_2Cl_2}$ for about 25 min. The solvent was removed under vacuum and the product recrystallized from $\mathrm{CHCl_3/CH_3OH}$ as described above to yield yellow crystals of *cis*-$\mathrm{Mo(CO)_4(PPh_3)}$[P(O-*o*-tol)$_3$] (ν(CO) 2035.5, 1943.5, 1923.5, 1911.5 $\mathrm{cm^{-1}}$ in $\mathrm{C_2Cl_4}$). Reaction 6 was carried out at 50 °C for 18 h in CO-saturated tetrachloroethylene to afford a 55:45 mixture of $\mathrm{Mo(CO)_5(PPh_3)}$ and $\mathrm{Mo(CO)_5}$[P(O-*o*-tol)$_3$].

Kinetic Measurements. Reactions were carried out in tetrachloroethylene solution at a variety of temperatures. Solutions of pure $\mathrm{Mo(CO)_4L_2}$ derivatives were introduced into the reaction vessel, allowed to attain thermal equilibrium, and then monitored by infrared spectroscopy in the ν(CO) region. At temperatures less than 65 °C, the reaction vessel employed was similar to that described by Dobson and Smith[2] in which the reactant solvent is held over a fritted disk by the pressure of CO entering the vessel through a side arm and then bubbling through the solution. Unreacted CO was passed through a solution of $\mathrm{KMnO_4}$ and oxidized to $\mathrm{CO_2}$. At higher temperatures, solvent evaporation due to the large volume of CO swept through the solution became a problem; thus these reactions were carried out in a 50-mL round-bottomed flask with condenser and with two side arms closed with serum caps. CO was bubbled through the solution via a hypodermic needle, and excess CO was oxidized by $\mathrm{KMnO_4}$ (vide supra). In both reactors, CO bubbling provided considerable agitation, ensuring homogeneity of the solution and their being saturated with CO.

Isomerization reactions of *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ to *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ were performed in a 50-mL round-bottom flask sealed with a wire-secured serum cap. The flask was then purged with nitrogen to reduce the possibility of air oxidation, and a solution of *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$ in excess $\mathrm{PPh_3}$ (200-fold) was added.

^{13}C Nuclear Magnetic Resonance Measurements. ^{13}C resonances were measured on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in $\mathrm{CDCl_3}$ solvent in 10-mm tubes. Chemical shifts are expressed in ppm relative to $\mathrm{(CH_3)_4Si}$, with positive δ(C) values being at lower field than $\mathrm{(CH_3)_4Si}$.

Infrared Measurements. The infrared spectra were recorded on either a Perkin-Elmer 521 or 283 spectrophotometer, both equipped with a linear-absorbance potentiometer. The spectra were calibrated against a water vapor spectrum below 2000 $\mathrm{cm^{-1}}$ and against a CO spectrum above 2000 $\mathrm{cm^{-1}}$. Matched sodium chloride cells (1.0 mm) were used in the measurements.

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Registry No. *cis*-$\mathrm{Mo(CO)_4(PN_3(CH_2)_6)_2}$, 66966-51-6; *cis*-$\mathrm{Mo(CO)_4(PMe_2Ph)_2}$, 24554-47-0; *cis*-$\mathrm{Mo(CO)_4(PMePh_2)_2}$, 37438-49-6; *cis*-$\mathrm{Mo(CO)_4(PPh_3)_2}$, 16742-93-1; *cis*-$\mathrm{Mo(CO)_4(PPhCy_2)_2}$, 66966-52-7; *cis*-$\mathrm{Mo(CO)_4(P(OCH_2)_3CEt)_2}$, 66966-50-5; *cis*-$\mathrm{Mo(CO)_4(P(OPh)_3)_2}$, 59599-01-8; *cis*-$\mathrm{Mo(CO)_4}$(P(O-*o*-tol)$_3$)$_2$, 69439-85-6; *trans*-$\mathrm{Mo(CO)_4(PPh_3)_2}$, 16244-53-4; $\mathrm{Mo(CO)_5(PPh_3)}$, 14971-42-7; *fac*-$\mathrm{Mo(CO)_3(^{13}CO)(PPh_3)_2}$, 67361-39-1; $\mathrm{Mo(CO)_5}$[P(O-*o*-tol)$_3$], 18475-10-0; *cis*-$\mathrm{Mo(CO)_4(PPh_3)(PPhCy_2)}$, 69439-86-7; *cis*-$\mathrm{Mo(CO)_4(PPh_3)}$[P(O-*o*-tol)$_3$], 69439-87-8; *cis*-$\mathrm{Mo(CO)_4(PPh_3)(NHC_5H_{10})}$, 38780-82-4; *cis*-$\mathrm{Mo(CO)_4(NHC_5H_{10})_2}$, 65337-26-0; $\mathrm{Mo(CO)_5(PPhCy_2)}$, 69439-88-9; CO, 630-08-0.

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(11) For example, $Mo(CO)_5(PPh_3)$ was heated in ^{13}CO-saturated C_2Cl_4 for 24 h at 55 °C with no measurable CO exchange or formation of $Mo(CO)_5(^{13}CO)$.

(12) On the basis of kinetic evidence, i.e., the fairly nondiscriminating ability of $[Mo(CO)_4(PPh_3)]$, these displacement reactions are thought to proceed with essentially complete molybdenum–phosphorus bond breaking.[7]

(13) It is however expected that in cases where L and L′ differ significantly in electronic character this generalization will not necessarily hold true.

(14) Darensbourg, D. J., unpublished results.

(15) The related 16-electron group 6B metal derivatives, $[Cr(CO)_5]$, have an average characteristic inverse lifetime in CO-saturated cyclohexane solution of $\sim 3 \times 10^4$ s^{-1}.[16,17]

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(18) It is nevertheless possible to scramble CO groups via a TBP transition state such that an incoming ^{13}CO ligand leads to a $Mo(CO)_5(PPh_3)$ species where the two ^{13}CO ligands are trans to one another without concomitant formation of a ^{13}CO axially labeled $Mo(CO)_5(PPh_3)$ species.

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(20) Although the intermediates in Scheme I are represented as nonsolvated species, it is likely in tetrachloroethylene that transient solvated species are present; e.g., unstable $M(CO)_5(TCNE)$ (M = Cr, Mo, W)[21] and $Fe(CO)_4(C_2Cl_4)$[22] derivatives have been reported as well as $(PPh_3)_2Pt(C_2Cl_4)$.[23]

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(24) Qualitatively similar observations have been reported for this process carried out in toluene in ref 1.

(25) We have previously incorrectly reported a somewhat higher quantity of *trans*-$Mo(CO)_4(^{13}CO)(PPh_3)$ afforded by this reaction based on rather difficult to analyze ν(CO) infrared data alone.[26,27]

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(30) The activation enthalpy for the cis → trans isomerization of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ has been found to be 24.5 kcal.[9] The electronic influences on the metal center of P-*n*-Bu_3 or $PPhCy_2$ in the *cis*-$Mo(CO)_4L_2$ derivatives are quite similar as indicated by their ν(CO) infrared frequencies.[4] Thus, we would expect the ΔH^* values for Mo–P bond cleavage in these two derivatives to be essentially the same (ΔH^* observed for Mo–P dissociation in *cis*-$Mo(CO)_4(PPhCy_2)_2$ is 30.2 kcal/mol).

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Synthesis, Characterization, and Electrochemical Properties of Dithiocarbamato Complexes of Osmium(III) and -(IV)

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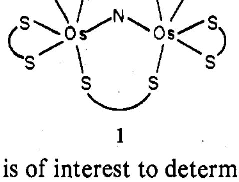
Several new *N,N*-dialkyldithiocarbamato (R_2dtc) complexes of osmium(III) and -(IV) have been synthesized and characterized. An electrochemical study on $Os(Et_2dtc)_3$, $ClOs(Et_2dtc)_3$, and $Os_2N(Et_2dtc)_5$ has been carried out and the results compared with those of analogous ruthenium and iron complexes. In propylene carbonate solution, $Os(dtc)_3$ exhibits a four-membered electron-transfer series $[Os(Et_2dtc)_3^- \rightleftarrows Os(Et_2dtc)_3 \rightleftarrows Os(Et_2dtc)_3^+ \rightleftarrows Os(Et_2dtc)_3^{2+}]$ while in acetonitrile solution the redox chemistry is complex with $Os(Et_2dtc)_3$ showing a one-electron irreversible oxidation to $[(CH_3CN)Os(Et_2dtc)_3]^+$ in a manner similar to $Ru(Et_2dtc)_3$. The ^1H NMR properties of the complexes $XOs(R_2dtc)_3$ (X = Cl, I, and PPh_3), $[Os_2(R_2dtc)_5]Cl$, and $Os(Et_2dtc)_3$ have been determined.

Introduction

Only a few reports have appeared on the synthesis, characterization, and properties of osmium dithiocarbamate complexes. The preparation of tris(*N,N*-diethyldithiocarbamato)osmium(III), $Os(Et_2dtc)_3$, and the tetrakis osmium(IV) complex, $Os(Et_2dtc)_4$, has recently been reported.[1] A number of mixed-ligand dithiocarbamate complexes of Os(II) with carbonyl and phosphine ligands have also recently been prepared.[2,3] Almost no work has been done on the structural, redox, and reactivity properties of osmium dithiocarbamate complexes, and therefore we have undertaken a comprehensive study of osmium R_2dtc (R = Me or Et) chemistry and its relation to the well-developed chemistry of iron[4] and ruthenium.[5] We recently reported the structural characterization of a novel μ-nitrido complex of Os(IV), $Os_2N(Me_2dtc)_5$ (**1**).[6] Although **1** does not have a ruthenium or iron analogue, it is of interest to determine if the reactions of $Os(R_2dtc)_3$ with HCl, I_2, and BF_3 mimic those of iron and ruthenium. The products of these reactions are $ClFe(R_2dtc)_2$,[7] $IFe(R_2dtc)_2$,[8] and $[Fe(R_2dtc)_3]BF_4$,[9] respectively, for iron and $ClRu(R_2dtc)_3$ (**2**),[10] $IRu(R_2dtc)_3$,[8] and β-$[Ru_2(R_2dtc)_5]BF_4$ (**3**),[11] respectively, for ruthenium. α-$[Ru_2(R_2dtc)_5]Cl$ (**4**), an isomeric form of the cation **3**, has also been prepared by photolysis of $Ru(R_2dtc)_3$ in chlorocarbon solvents[12] or by reaction of $RuCl_3 \cdot xH_2O$ with NaR_2dtc in aqueous solution and separation from $Ru(R_2dtc)_3$ by column chromatography.[13]



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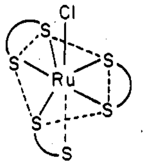

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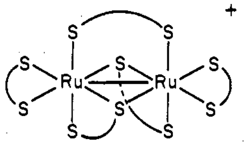

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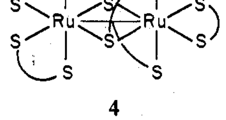

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It is also important to compare the electrochemistry of the various (dithiocarbamato)osmium complexes to that of iron and ruthenium. The oxidative electrolysis of $M(R_2dtc)_3$ in

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