

- (19) See also the related discussion by Hayter: R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).
- (20) This result, however, does not address the question put forth by Atwood and Brown²¹ as to whether the incoming ¹³CO molecule binds to the molybdenum atom which originally bore the PPh₃ ligand or whether a CO group from the other molybdenum center bridges the two metals with the incoming ¹³CO appearing with equal probability on either of the molybdenum atoms.
- (21) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 3160 (1976).
- (22) The stereochemical position of the ¹³CO label was also verified by ¹³C NMR. Chemical shifts relative to Me₄Si were observed at 232.0 ppm for axial carbonyl ligands and at 228.4 ppm for equatorial carbonyl ligands in the natural-abundance sample. In the ¹³C NMR spectrum of [Et₄N]⁺[(μ-H)[Mo(CO)₅][Mo(CO)₄¹³CO]]⁻, CO chemical shifts at 232.0 and 228.4 ppm were in an intensity ratio of 4:97. Thus, the fraction of molecules ¹³CO labeled equatorially may be estimated at 91%, and the fraction of molecules labeled axially at 2% (neglecting natural abundance ¹³C).

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A Convenient Synthesis of *cis*-Mo(CO)₄L₂ Derivatives (L = Group 5A Ligand) and a Qualitative Study of Their Thermal Reactivity toward Ligand Dissociation

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It is often desirable to prepare disubstituted Lewis base derivatives of the group 6B hexacarbonyls. This is generally not a trivial task; in particular the synthesis of *cis*-M(CO)₄L₂ derivatives can be quite difficult since several of these species readily isomerize thermally to the trans isomer. Therefore, when brute force is employed with M(CO)₆ plus 2L in refluxing diglyme, one has to settle for the thermodynamically more stable isomer of M(CO)₄L₂.¹ The most commonly used alternate synthesis which operates under milder conditions involves the reaction of M(CO)₄(NBD) (NBD = norbornadiene or bicyclo[2.2.1]hepta-2,5-diene) with 2L.² This procedure suffers from the necessity of having to prepare and purify M(CO)₄(NBD) derivatives which is itself often a lengthy process.³ On the other hand, Chatt et al. have reported an improved, one-step synthesis of tertiary phosphine and related substitution products of group 6B metal carbonyls which involves the use of NaBH₄ at refluxing methanol temperature.⁴ The bridging hydride μ-H[M(CO)₅]⁻ has also been shown to react with phosphines and phosphites to yield L₂M(CO)₄ complexes and has been proposed as an intermediate in the Chatt synthesis.^{5,6}

Although there are other specialized reactions for the synthesis of Mo(CO)₄L₂ derivatives, no general large-scale preparation of *cis*-Mo(CO)₄L₂ derivatives has been available.^{7,8} Here we describe a particularly convenient and inexpensive route to the synthesis of *cis*-Mo(CO)₄L₂ derivatives (Scheme I). In addition, a qualitative comparison has been made of the ease of ligand (L) dissociation in the *cis*-disubstituted metal derivatives synthesized.

Experimental Section

Materials. All solvents were reagent grade chemicals by Matheson Coleman and Bell with the lone exception of decahydronaphthalene (decalin) which was Eastman practical grade. Molybdenum and tungsten hexacarbonyl were generous gifts of Climax Molybdenum Corp. Phosphine ligands were generally purchased from Strem Chemicals.

Compound Preparations. (a) *cis*-Mo(CO)₄[NHC₅H₁₀]₂. Ten grams of Mo(CO)₆ (0.0378 mol) and 25 mL of piperidine (0.253 mol) were refluxed in 120 mL of heptane for 4 h during which time the bright

Scheme I

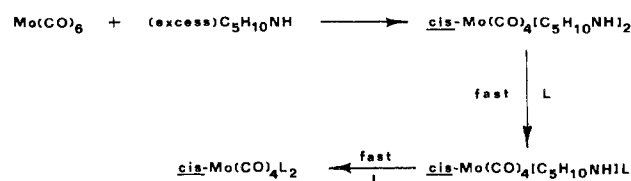


Table I. Infrared Spectra in the ν(CO) Stretching Region of *cis*-Mo(CO)₄L₂ Derivatives^a

L	ν(CO), ^b cm ⁻¹			
	A ₁ (2)	A ₁ (4)	B ₁	B ₂
PPhCy ₂	2012	1908	1890	1877
P(<i>n</i> -Bu) ₃	2013	1910	1895	1879
PPhMe ₂	2018	1920	1900	1891 s
PPh ₂ Me	2020	1925	1902	1891 s
PN ₃ (CH ₂) ₆	2022	1930	1910	1904 s
PPh ₃	2023	1927	1908	1897
SbPh ₃	2025	1934	1919	1905
P(OPh) ₃	2047	1958	1943	1935 s
P(OCH ₂) ₃ CEt	2051	1963	1944	1942 s

^a Spectra were measured in tetrachloroethylene solution. ^b Frequencies are accurate to ±1.0 cm⁻¹ except for shoulders which are probably only accurate to ±2–3 cm⁻¹.

yellow product precipitated from solution. The reaction mixture was filtered hot to remove any heptane-soluble Mo(CO)₅(NHC₅H₁₀). The isolated yellow solid was washed with cold heptane and dried under vacuum to afford a yield of 13.1 g or 91%.

(b) *cis*-W(CO)₄[NHC₅H₁₀]₂. This complex was prepared in a manner similar to that described above for the molybdenum analogue except that a higher reaction temperature was required in order to minimize reaction time. Ten grams of W(CO)₆ (0.0284 mol) and 25 mL of piperidine (0.253 mol) were refluxed at 160 °C in 120 mL of decahydronaphthalene for 24 h. There is no compelling reason to use this specific solvent. Any high-boiling, inexpensive hydrocarbon solvent would work equally as well. The yellow precipitate was washed with heptane and dried under vacuum to yield 9.8 g or 74% of the desired material.

(c) *cis*-Mo(CO)₄L₂ Derivatives. In a typical preparation, 1–2 g (or 2–5 mmol) of Mo(CO)₄[NHC₅H₁₀]₂ was stirred under reflux in dichloromethane (bp 40 °C) with a slightly greater than two molar excess of ligand (L) (L = SbPh₃, Me₂PhP, P(OCH₂)₃CEt, MePh₂P, (C₆H₁₁)₂PhP, P(OC₆H₅)₃, PBu₃, PPh₃, and PN₃(CH₂)₆) for 10–15 min. The reaction mixture was filtered through Celite, and the filtrate was reduced in volume followed by the addition of methanol. Upon cooling below 0 °C, crystals formed which were isolated by filtration. Further purification was accomplished by recrystallization from chloroform–methanol. Yields were always greater than 50%. The complexes were analyzed via ν(CO) infrared spectroscopy (see Table I) and elemental analysis. For example: Anal. Calcd for Mo(CO)₄[PPh₃]₂: C, 65.58; H, 4.13. Found: C, 65.68; H, 4.12. Calcd for Mo(CO)₄[P(Me)Ph₂]₂: C, 59.23; H, 4.30. Found: C, 59.19; H, 4.43. Calcd for Mo(CO)₄[P(C₆H₁₁)₂Ph]₂: C, 63.49; H, 7.19. Found: C, 63.27; H, 7.36.

Reactions carried out in an analogous manner between *cis*-W(CO)₄[NHC₅H₁₀]₂ and L (L = PPh₃, *n*-Bu₃P) provided an efficient means for the production of the mixed species *cis*-W(CO)₄[NHC₅H₁₀]₂L. In order to effect formation of bis L substituted derivatives of tungsten, more rigorous conditions were needed and, in general, afforded a mixture of *cis*- and *trans*-W(CO)₄L₂ derivatives. Anal. Calcd for W(CO)₄[NHC₅H₁₀]₂PPH₃: C, 50.40; H, 4.04. Found: C, 51.00; H, 4.05. Calcd for W(CO)₄[NHC₅H₁₀]P-*n*-Bu₃: C, 43.24; H, 6.52. Found: C, 42.93; H, 6.49.

(d) *cis*-Mo(CO)₄[P(OMe)₃]₂NHC₅H₁₀. One gram of Mo(CO)₄[NHC₅H₁₀]₂ was reacted with 1.0 mL of trimethyl phosphite in 40 mL of refluxing dichloromethane for 5 min. Methanol was added to the reaction mixture to precipitate a yellow product. The complex was purified by recrystallization from chloroform–methanol. The yellow crystalline product was shown to have physical properties and ν(CO) absorptions identical with an authentic sample of *cis*-Mo(CO)₄[P(OMe)₃]₂NHC₅H₁₀ (fully characterized, including X-ray

structure determination) which we have previously reported resulting from the photochemical reaction of $\text{Mo(CO)}_5\text{P(OMe)}_3$ with $\text{NHC}_5\text{H}_{10}$.¹⁰

(e) *trans*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$. This complex was prepared by the thermal isomerization of *cis*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$ in refluxing toluene. The reaction time was approximately 30 min. Upon removal of toluene, the desired product was purified by recrystallization from chloroform-methanol at 0 °C. The off-white crystalline product was obtained in a yield of 55%. Anal. Calcd for $\text{Mo(CO)}_4[\text{PPh}_3]_2$: C, 65.58; H, 4.13. Found: C, 65.72; H, 4.20. The *trans* stereochemistry was assessed by the $\nu(\text{CO})$ spectrum; i.e., a strong absorption was observed at 1901 cm^{-1} in C_2Cl_4 .

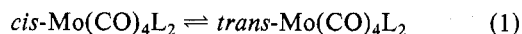
Phosphine Substitution Reactions. These processes were carried out at 55 °C in tetrachloroethylene in a reaction vessel similar to that described by Dobson and Smith.¹¹ This reactor allows the solution of *cis*- $\text{Mo(CO)}_4\text{L}_2$ to stand over a fritted disk while CO gas enters the solution by way of a side arm and is dispersed through the frit. The pressure of the CO gas prevented the solution from entering the gas inlet arm. Unreacted CO was oxidized to CO_2 by passing the excess gas through a solution of KMnO_4 . Samples were periodically withdrawn for analysis via a syringe and their infrared spectra in the $\nu(\text{CO})$ region recorded.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance potentiometer. The spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1} . Sodium chloride solution cells (1.0 mm) were used with the appropriate solvent in the reference cell.

Results and Discussion

A particularly convenient and inexpensive route to the preparation of *cis*- $\text{Mo(CO)}_4\text{L}_2$ derivatives in good yields has been developed. The complexes which have been synthesized are shown in Table I along with values of their $\nu(\text{CO})$ absorptions. This process is based on the ready availability of *cis*- $\text{Mo(CO)}_4[\text{NHC}_5\text{H}_{10}]_2$ in large quantities and the very facile replacement of the piperidine ligands in these species by phosphines and related ligands. That the reaction as shown in Scheme I proceeds stepwise was demonstrated by the isolation of the intermediates in the cases where L equals P(OMe)_3 or ^{13}CO .¹² *cis*- $\text{Mo(CO)}_4[\text{P(OMe)}_3]\text{NHC}_5\text{H}_{10}$ and *cis*- $\text{Mo(CO)}_4[^{13}\text{CO}]\text{NHC}_5\text{H}_{10}$, respectively. It has indeed been shown that the trimethyl phosphite species is highly stabilized via hydrogen bonding of the N-H grouping of the bound piperidine ligand with one of the oxygen atoms of the trimethyl phosphite.¹⁰ On the other hand, phosphorus ligands which do not possess this capability for specific stabilizing interaction, in particular, the bulky phosphines, have been demonstrated to labilize the loss of the piperidine ligand.¹³ For example, piperidine dissociation in the *cis*- $\text{Mo(CO)}_4[\text{P(OMe)}_3]\text{NHC}_5\text{H}_{10}$ derivative was found to occur at room temperature at a rate comparable with that in the unsubstituted derivative ($t_{1/2} \approx 24\text{ h}$) $\text{Mo(CO)}_5\text{NHC}_5\text{H}_{10}$, and about 100 times slower than that in the $\text{P(C}_6\text{H}_5)_3$ analogue.^{10,13-15}

The key to our ability to isolate the *cis* isomers in those cases where alternative procedures afford the *trans* isomer or isomeric mixtures of *cis* and *trans* species lies in the rapidity with which the reaction in Scheme I goes to completion (10–15 min) under mild reflux conditions (40 °C). These conditions are not strenuous or lengthy enough to effect the isomerization reaction 1. On the other hand, the analogous reaction



conditions (Scheme I) starting with *cis*- $\text{W(CO)}_4[\text{NHC}_5\text{H}_{10}]_2$ provide the *cis*- $\text{W(CO)}_4[\text{NHC}_5\text{H}_{10}]\text{L}$ species¹⁶ in good yields; i.e., substitution of the second amine is a much less facile process than in the corresponding molybdenum species. The more rigorous conditions necessary to promote formation of $\text{W(CO)}_4\text{L}_2$ derivatives in many instances lead to the production of mixtures of *cis*- and *trans*- $\text{W(CO)}_4\text{L}_2$ species, e.g., when $\text{L} = \text{PPh}_3$. However, the C_s form of the $[\text{W(CO)}_4\text{L}]$ intermediate¹⁷⁻¹⁹ appears to be dominant in solution since

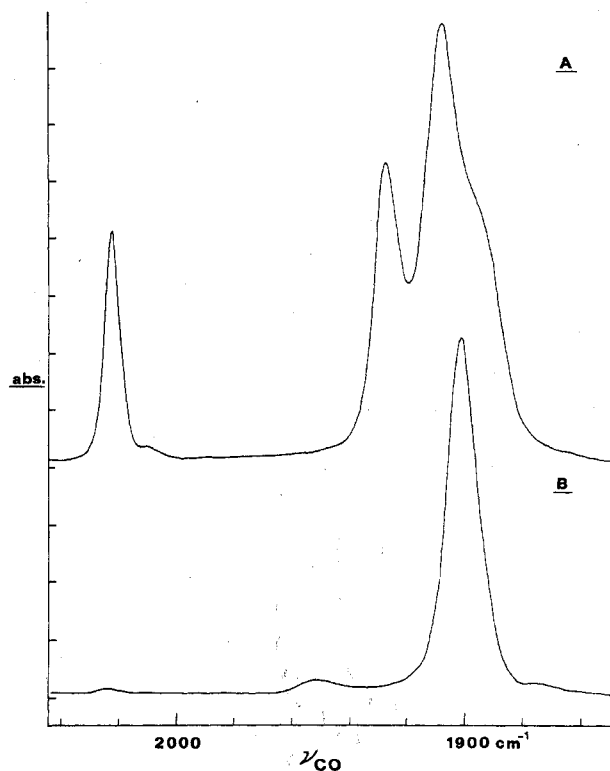
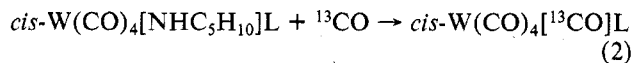


Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $\text{Mo(CO)}_4[\text{PPh}_3]_2$: A, *cis*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$; B, *trans*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$.

cis- $\text{W(CO)}_4[^{13}\text{CO}]\text{L}$ species are prepared upon substitution of piperidine with ^{13}CO (eq 2).²⁰ Indeed this procedure should



prove to be extremely useful as a general synthesis of stereospecifically labeled *cis*- $\text{W(CO)}_4[^{13}\text{CO}]\text{L}$ derivatives.

In the original report of the Chatt synthesis⁴ for the bis-(triphenylphosphine)molybdenum tetracarbonyl derivative, the geometry of this complex was identified as the *trans* isomer. However, the initially formed neutral product, $\text{Mo(CO)}_4[\text{PPh}_3]_2$, has since been correctly shown to be of *cis* geometry with *cis* $\rightarrow$ *trans* isomerization occurring after longer reflux periods.⁶ Similarly, Hui and Shaw,²¹ in a closely related synthesis of group 6B derivatives, have reported initial formation of *cis*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$. It should be pointed out here parenthetically that the $\nu(\text{CO})$ spectral regions for *cis*- and *trans*- $\text{M(CO)}_4\text{L}_2$ derivatives (the usually employed spectroscopic tool for assigning stereochemistry in these species) are grossly overlapped. Therefore, there are often small quantities of the *trans* isomer present in complexes that are assigned to be of *cis* stereochemistry. See, e.g., Figure 1 for $\nu(\text{CO})$ spectra of pure *cis* and *trans* isomers of $\text{Mo(CO)}_4[\text{PPh}_3]_2$.

Preliminary mechanistic studies on the *cis* $\rightarrow$ *trans* isomerization process of $\text{Mo(CO)}_4[\text{PPh}_3]_2$ have revealed that this reaction involves initial dissociation of phosphine.²²⁻²⁴ Although phosphine dissociation occurs in the *trans*- $\text{Mo(CO)}_4[\text{PPh}_3]_2$ species, this dissociative process is less facile than in the *cis* isomer. On the other hand *cis*- $\text{Mo(CO)}_4[\text{P-n-Bu}_3]_2$ undergoes isomerization to a *cis*/*trans* mixture, with the *trans* isomer being dominant, without phosphine dissociation.

We have qualitatively examined the ease of dissociation of phosphine ligands from the *cis*- $\text{Mo(CO)}_4\text{L}_2$ derivatives prepared in this study. The phosphine dissociation process was studied in the presence of excess CO thus leading to the

Table II. Qualitative Observations on the Dissociative Loss of Phosphines (L) from *cis*-Mo(CO)₄L₂ Derivatives^a

L	cone angle, ^b deg	rate of L dissoen
P(OCH ₂) ₃ CEt	101	very slow
PN ₃ (CH ₂) ₆	102 ^c	very slow
PPhMe ₂	122	very slow
P(OPh) ₃	128	very slow
P(<i>n</i> -Bu) ₃	132	very slow ^d
PPh ₃	145	fast ^e
PPhCy ₂	162 ^f	very fast

^a Reactions carried out in CO saturated tetrachloroethylene at 55 °C. Very slow defined as $t_{1/2}$ greater than 48 h. ^b Taken from C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977), unless otherwise noted. ^c J. R. DeLerno, L. M. Trefonas, M. Y. Darensbourg, and R. J. Majeste, *Inorg. Chem.*, **15**, 816 (1976). ^d This derivative undergoes isomerization to the trans isomer much faster than phosphine loss with formation of Mo(CO)₅P(*n*-Bu)₃. ^e $t_{1/2}$ for this reaction is ~30 min. ^f Weighted average of Tolman's PPh₃ and PCy₃ cone angles.

production of the readily identifiable Mo(CO)₅L species. Table II contains a qualitative comparison of the ease of ligand (L) dissociation in the *cis*-disubstituted molybdenum tetracarbonyl derivatives. As illustrated in Table II, the dissociative loss of phosphine closely parallels the steric requirement of the phosphine ligand as determined by its cone angle,²⁵ i.e., bulky ligands are readily lost whereas small ligands do not undergo dissociative loss easily. It should as well be noted that an additional driving force for the dissociation of phosphine in *cis*-Mo(CO)₄L₂ derivatives is the formation of [Mo(CO)₄L] intermediates where L is in an equatorial position (the C_s isomer), that is, Brown's *cis*-labilization arguments.^{26,27}

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 76-04494 is greatly appreciated.

Registry No. *cis*-Mo(CO)₄(PPhCy₂)₂, 66966-52-7; *cis*-Mo(CO)₄(P(*n*-Bu)₃)₂, 16244-54-5; *cis*-Mo(CO)₄(PPhMe₂)₂, 24554-47-0; *cis*-Mo(CO)₄(PPh₃Me)₂, 37438-49-6; *cis*-Mo(CO)₄(PN₃(CH₂)₆)₂, 66966-51-6; *cis*-Mo(CO)₄(PPh₃)₂, 16742-93-1; *cis*-Mo(CO)₄(SbPh₃)₂, 16742-98-6; *cis*-Mo(CO)₄(P(OPh)₃)₂, 59599-01-8; *cis*-Mo(CO)₄(P(OCH₂)₃CEt)₂, 66966-50-5; *cis*-Mo(CO)₄[NHC₅H₁₀]₂, 65337-26-0; *cis*-W(CO)₄[NHC₅H₁₀]₂, 56083-13-7; W(CO)₄[NHC₅H₁₀]PPh₃, 67010-37-1; *trans*-Mo(CO)₄[PPh₃]₂, 16244-53-4; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; W(CO)₄[NHC₅H₁₀]P(*n*-Bu)₃, 66966-49-2.

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Photochemistry of Carbon Monoxide and Benzyl Isocyanide Complexes of Heme Models

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In view of the well-known photodissociation of carbon monoxide and alkyl isocyanides from hemoglobin^{1,2} it is of interest to determine if a similar photolability of these π -acceptor ligands is possible in simple iron complexes analogous to the iron porphyrin in hemoglobin. Photoaquation of [Fe(CN)₅CO]⁻³ has a reported quantum yield of 0.9.³ A quantum yield of 0.14 is reported for photoaquation of Fe(CNCH₃)₄(CN)₂ (the isocyanide ligand is aquated).⁴ We have previously reported that benzyl isocyanide (BzNC) complexes of ferrous phthalocyanine are photochromic.⁵ We have now investigated several macrocyclic complexes of iron including ferrous phthalocyanine^{5,6}, ferrous 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (Fe(TIM)),^{7,8} and ferrous bis(dimethylglyoxime).⁹ All of these systems undergo a photochromic reaction based on the shift of the equilibrium



where L is a nitrogen base, X is CO or BzNC, and N₄ is the tetradentate macrocycle. We report on the synthesis, characterization, and thermal kinetics of these complexes elsewhere. Herein we report measurements of the quantum yield for photodissociation of CO and BzNC from these complexes (the reverse of eq 1). While this work was being considered for publication, Incorvia and Zink¹⁰ published their independent study which overlaps in part with this report.

Experimental Section

The complexes and their spectral features are given in Table I. Stirred solutions of the complexes were irradiated using a 200-W quartz-halogen lamp in 5-cm optical glass cells contained in a close-fitting brass block thermostated at 20 °C by means of a Lauda circulator. Wavelengths were isolated with interference filters of 100 Å band-pass (Optically Thin Films, North Andover, Mass.). Incident light intensities were typically 10⁻⁷ einstein/min as determined by