(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 Brown[21] as to whether the incoming ^{13}CO molecule binds to the molybdenum atom which originally bore the PPh_3 ligand or whether a CO group from the other molybdenum center bridges the two metals with the incoming ^{13}CO 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 ^{13}CO label was also verified by ^{13}C NMR. Chemical shifts relative to Me_4Si 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 ^{13}C NMR spectrum of $[Et_4N]^+[(\mu\text{-}H)[Mo(CO)_5][Mo(CO)_4{}^{13}CO]]^-$, CO chemical shifts at 232.0 and 228.4 ppm were in an intensity ratio of 4:97. Thus, the fraction of molecules ^{13}CO labeled equatorially may be estimated at 91%, and the fraction of molecules labeled axially at 2% (neglecting natural abundance ^{13}C).

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

A Convenient Synthesis of *cis*-$Mo(CO)_4L_2$ Derivatives (L = Group 5A Ligand) and a Qualitative Study of Their Thermal Reactivity toward Ligand Dissociation

Donald J. Darensbourg* and Robin L. Kump

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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*-$M(CO)_4L_2$ 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 $M(CO)_4L_2$.[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 $NaBH_4$ at refluxing methanol temperature.[4] The bridging hydride $\mu\text{-}H[M(CO)_5]_2^-$ has also been shown to react with phosphines and phosphites to yield $L_2M(CO)_4$ complexes and has been proposed as an intermediate in the Chatt synthesis.[5,6]

Although there are other specialized reactions for the synthesis of $Mo(CO)_4L_2$ derivatives, no general large-scale preparation of *cis*-$Mo(CO)_4L_2$ derivatives has been available.[7,8] Here we describe a particularly convenient and inexpensive route to the synthesis of *cis*-$Mo(CO)_4L_2$ 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 puchased from Strem Chemicals.

Compound Preparations. (a) *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$. 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 yellow product precipitated from solution. The reaction mixture was filtered hot to remove any heptane-soluble $Mo(CO)_5(NHC_5H_{10})$. The isolated yellow solid was washed with cold heptane and dried under vacuum to afford a yield of 13.1 g or 91%.

Scheme I

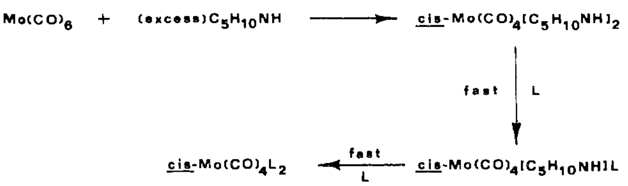

Table I. Infrared Spectra in the ν(CO) Stretching Region of *cis*-$Mo(CO)_4L_2$ Derivatives[a]

L	ν(CO),[b] cm^{-1}			
	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2
$PPhCy_2$	2012	1908	1890	1877
$P(n\text{-}Bu)_3$	2013	1910	1895	1879
$PPhMe_2$	2018	1920	1900	1891 s
PPh_2Me	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
$P(OCH_2)_3CEt$	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}.

(b) *cis*-$W(CO)_4[NHC_5H_{10}]_2$. 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*-$Mo(CO)_4L_2$ Derivatives. In a typical preparation, 1–2 g (or 2–5 mmol) of $Mo(CO)_4[NHC_5H_{10}]_2$ was stirred under reflux in dichloromethane (bp 40 °C) with a slightly greater than two molar excess of ligand (L) (L = $SbPh_3$, Me_2PhP, $P(OCH_2)_3CEt$, $MePh_2P$, $(C_6H_{11})_2PhP$, $P(OC_6H_5)_3$, PBu_3, PPh_3, and $PN_3(CH_2)_6$[9]) 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 $Mo(CO)_4[PPh_3]_2$: C, 65.58; H, 4.13. Found: C, 65.68; H, 4.12. Calcd for $Mo(CO)_4[P(Me)Ph_2]_2$: C, 59.23; H, 4.30. Found: C, 59.19; H, 4.43. Calcd for $Mo(CO)_4[P(C_6H_{11})_2Ph]_2$: C, 63.49; H, 7.19. Found: C, 63.27; H, 7.36.

Reactions carried out in an analogous manner between *cis*-$W(CO)_4[NHC_5H_{10}]_2$ and L (L = PPh_3, *n*-Bu_3P) provided an efficient means for the production of the mixed species *cis*-$W(CO)_4[NHC_5H_{10}]L$. 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*-$W(CO)_4L_2$ derivatives. Anal. Calcd for $W(CO)_4[NHC_5H_{10}]PPh_3$: C, 50.40; H, 4.04. Found: C, 51.00; H, 4.05. Calcd for $W(CO)_4[NHC_5H_{10}]P\text{-}n\text{-}Bu_3$: C, 43.24; H, 6.52. Found: C, 42.93; H, 6.49.

(d) *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$. One gram of $Mo(CO)_4[NHC_5H_{10}]_2$ 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*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ (fully characterized, including X-ray

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structure determination) which we have previously reported resulting from the photochemical reaction of $Mo(CO)_5P(OMe)_3$ with NHC_5H_{10}.[10]

(e) *trans*-$Mo(CO)_4[PPh_3]_2$. This complex was prepared by the thermal isomerization of *cis*-$Mo(CO)_4[PPh_3]_2$ 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 $Mo(CO)_4[PPh_3]_2$: C, 65.58; H, 4.13. Found: C, 65.72; H, 4.20. The trans stereochemistry was assessed by the ν(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*-$Mo(CO)_4L_2$ 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 ν(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*-$Mo(CO)_4L_2$ derivatives in good yields has been developed. The complexes which have been synthesized are shown in Table I along with values of their ν(CO) absorptions. This process is based on the ready availability of *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$ 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*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ and *cis*-$Mo(CO)_4[^{13}CO]NHC_5H_{10}$, 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*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivative was found to occur at room temperature at a rate comparable with that in the unsubstituted derivative ($t_{1/2} \approx 24$ h) $Mo(CO)_5NHC_5H_{10}$, and about 100 times slower than that in the $P(C_6H_5)_3$ 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

$$cis\text{-}Mo(CO)_4L_2 \rightleftharpoons trans\text{-}Mo(CO)_4L_2 \qquad (1)$$

conditions (Scheme I) starting with *cis*-$W(CO)_4[NHC_5H_{10}]_2$ provide the *cis*-$W(CO)_4[NHC_5H_{10}]L$ species[16] 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 $W(CO)_4L_2$ derivatives in many instances lead to the production of mixtures of *cis*- and *trans*-$W(CO)_4L_2$ species, e.g., when L = PPh_3. However, the C_s form of the $[W(CO)_4L]$ intermediate[17–19] appears to be dominant in solution since *cis*-$W(CO)_4[^{13}CO]L$ species are prepared upon substitution of piperidine with ^{13}CO (eq 2).[20] Indeed this procedure should

$$cis\text{-}W(CO)_4[NHC_5H_{10}]L + {}^{13}CO \rightarrow cis\text{-}W(CO)_4[^{13}CO]L \qquad (2)$$

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

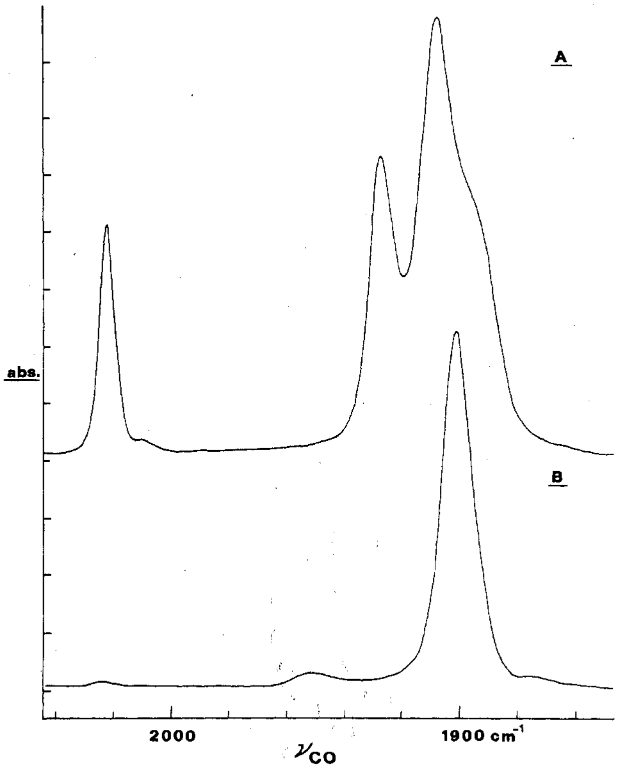

Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $Mo(CO)_4[PPh_3]_2$: A, *cis*-$Mo(CO)_4[PPh_3]_2$; B, *trans*-$Mo(CO)_4[PPh_3]_2$.

In the original report of the Chatt synthesis[4] for the bis(triphenylphosphine)molybdenum tetracarbonyl derivative, the geometry of this complex was identified as the trans isomer. However, the initially formed neutral product, $Mo(CO)_4[PPh_3]_2$, has since been correctly shown to be of cis geometry with cis → 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*-$Mo(CO)_4[PPh_3]_2$. It should be pointed out here parenthetically that the ν(CO) spectral regions for *cis*- and *trans*-$M(CO)_4L_2$ 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 ν(CO) spectra of pure cis and trans isomers of $Mo(CO)_4[PPh_3]_2$.

Preliminary mechanistic studies on the cis → trans isomerization process of $Mo(CO)_4[PPh_3]_2$ have revealed that this reaction involves initial dissociation of phosphine.[22–24] Although phosphine dissociation occurs in the *trans*-$Mo(CO)_4[PPh_3]_2$ species, this dissociative process is less facile than in the cis isomer. On the other hand *cis*-$Mo(CO)_4[P\text{-}n\text{-}Bu_3]_2$ 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*-$Mo(CO)_4L_2$ 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*-$Mo(CO)_4L_2$ Derivatives[a]

L	cone angle,[b] deg	rate of L dissocn
$P(OCH_2)_3CEt$	101	very slow
$PN_3(CH_2)_6$	102[c]	very slow
$PPhMe_2$	122	very slow
$P(OPh)_3$	128	very slow
$P(n\text{-}Bu)_3$	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 $Mo(CO)_5P(n\text{-}Bu)_3$. [e] $t_{1/2}$ for this reaction is ~30 min. [f] Weighted average of Tolman's PPh_3 and PCy_3 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*-$Mo(CO)_4L_2$ 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]

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Registry No. *cis*-$Mo(CO)_4(PPhCy_2)_2$, 66966-52-7; *cis*-$Mo(CO)_4(P(n\text{-}Bu)_3)_2$, 16244-54-5; *cis*-$Mo(CO)_4(PPhMe_2)_2$, 24554-47-0; *cis*-$Mo(CO)_4(PPh_2Me)_2$, 37438-49-6; *cis*-$Mo(CO)_4(PN_3(CH_2)_6)_2$, 66966-51-6; *cis*-$Mo(CO)_4(PPh_3)_2$, 16742-93-1; *cis*-$Mo(CO)_4(SbPh_3)_2$, 16742-98-6; *cis*-$Mo(CO)_4(P(OPh)_3)_2$, 59599-01-8; *cis*-$Mo(CO)_4(P(OCH_2)_3CEt)_2$, 66966-50-5; *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$, 65337-26-0; *cis*-$W(CO)_4[NHC_5H_{10}]_2$, 56083-13-7; $W(CO)_4[NHC_5H_{10}]PPh_3$, 67010-37-1; *trans*-$Mo(CO)_4[PPh_3]_2$, 16244-53-4; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $W(CO)_4[NHC_5H_{10}]P(n\text{-}Bu)_3$, 66966-49-2.

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Contribution from the Department of Chemistry,
York University, Downsview, Ontario, Canada M3J 1P3

Photochemistry of Carbon Monoxide and Benzyl Isocyanide Complexes of Heme Models

Colin Irwin and Dennis V. Stynes*

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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 $Fe(CNCH_3)_4(CN)_2$ (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

$$Fe(N_4)L_2 + X \rightleftharpoons Fe(N_4)(L)(X) + L \qquad (1)$$

where L is a nitrogen base, X is CO or BzNC, and N_4 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 Zink[10] 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

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