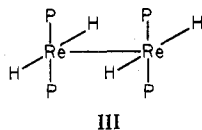


analogue<sup>7</sup> and is independent evidence for the presence of multiple bonding involving the two rhenium atoms in the octahydrido complexes.

**Comments Concerning the Bonding in  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$ .** The octahydrido dimers,  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$ , can formally be considered as derivatives of  $\text{Re}(\text{IV})$ ,<sup>7</sup> and the presence of a Re-Re triple bond follows upon applying the EAN rule. We believe that one way of viewing the bonding in these species is to consider them to be products of the hydrogenation of the rhenium(II) dimers  $\text{Re}_2\text{H}_4(\text{PR}_3)_4$ . Although these dimers are unknown, the halide analogues  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  are well characterized.<sup>4,14</sup> The tetrahydrido moiety (structure III) is assigned a structure



which is analogous to that of the tetrahalo complexes  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  (structure I),<sup>14</sup> with the exception that the hydrido complex is centrosymmetric while the tetrahalo dimers are noncentrosymmetric.<sup>14</sup> The effect of eclipsing the phosphines as in III will be to decrease the P-Re-P angle (due to increased nonbonded repulsion between the phosphine ligands of adjacent  $\text{ReP}_2$  sets) relative to that observed in the noncentrosymmetric complex, but one might consider that the Re-Re bonding order ( $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ ) remains intact.

We prefer to consider the bonding in the hydride bridges in the following manner. There is no net bonding provided by the  $(\delta)^2(\delta^*)^2$  orbital set in the  $\text{Re}_2^{4+}$  fragment of  $\text{Re}_2\text{H}_4(\text{PR}_3)_4$ . However, the hydride bridges in  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$  mix with the  $\delta$ - $\delta^*$  set, and net bonding is now possible in a  $\text{Re}_2(\mu\text{-H})_4^{4+}$  moiety in which the eight electrons (four from the two  $\text{Re } d_{xy}$  orbitals and four from the four hydrogen atoms) are distributed among six orbitals (arising from the two  $5d_{xy}$  orbitals from the Re atoms and the four H 1s orbitals). Since the set of four orbitals which are filled will be predominantly bonding in character, while the two highest energy antibonding orbitals are empty, there will likely be a net stabilization of the  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$  molecules. This approach to the bonding of the octahydrido dimers raises the question as to whether the "parent" dimers  $\text{Re}_2\text{H}_4(\text{PR}_3)_4$  exist. The isolation of these species is of interest both from the point of view of exploring their reactivity toward hydrogen and other molecules and as subjects for theoretical calculations (especially those of the SCF-X $\alpha$ -SW type).<sup>15</sup> Efforts to synthesize the hydride dimers  $\text{Re}_2\text{H}_4(\text{PR}_3)_4$  are currently underway in our laboratory.

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**Registry No.**  $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ , 55400-06-1;  $\text{Re}_2\text{Cl}_4(\text{P}(n\text{-Pr})_3)_4$ , 55400-08-3;  $\text{Re}_2\text{Cl}_4(\text{PEtPh}_2)_4$ , 66984-39-2;  $\text{Re}_2\text{H}_8(\text{PEtPh}_2)_4$ , 66984-38-1;  $\text{Re}_2\text{H}_8(\text{PPh}_3)_4$ , 66984-37-0;  $(\text{Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ , 14023-10-0;  $\text{NaBH}_4$ , 16940-66-2.

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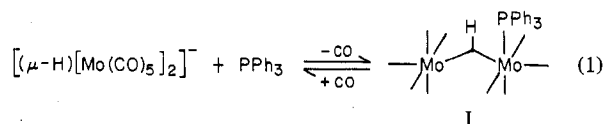
Contribution from the Department of Chemistry,  
Tulane University, New Orleans, Louisiana 70118

## Preparation of a Stereospecifically $^{13}\text{C}$ -Labeled $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$ Species and Analysis of Its CO Stretching Vibrational Modes

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and Marcetta Y. Darensbourg\*

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The extent to which reactive sites on metal atoms are influenced by chemically bound adjacent metal centers continues to be a perplexing problem, demanding both chemical and physical approaches. An investigation of the reactions of  $[\text{Et}_4\text{N}]^+[(\mu\text{-H})[\text{M}(\text{CO})_5]_2]^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) with phosphines and phosphites to afford  $\text{L}_2\text{M}(\text{CO})_4$  complexes was recently reported.<sup>1,2</sup> For the reaction of  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  with  $\text{PPh}_3$  it was possible to isolate an intermediate prior to dimer disruption. This asymmetric bridging hydride carbonylate (I) has been shown to contain  $\text{PPh}_3$  in an equatorial position by single-crystal X-ray diffraction methods<sup>3-6</sup> as well as by infrared spectroscopy in the  $\nu(\text{CO})$  region. As is indicated in eq 1, this process is readily reversible, with dis-

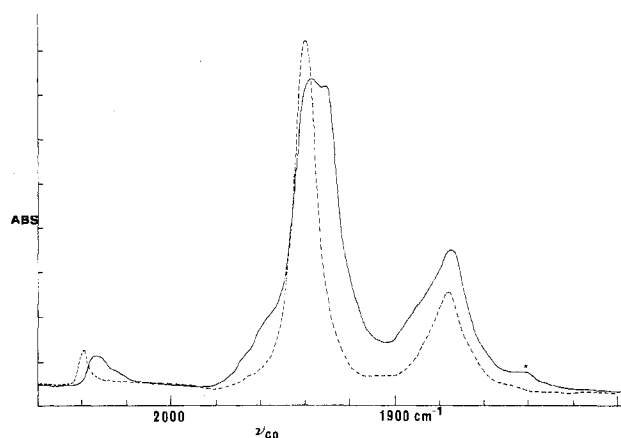


sociation of  $\text{PPh}_3$  occurring under rather mild conditions. Thus, it has been possible to carry out the reverse reaction of eq 1 in the presence of  $^{13}\text{C}$ -labeled carbon monoxide to afford  $[(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4(^{13}\text{CO})]^-$ . We wish to communicate the details of the preparation of this labeled species along with an analysis of its  $\nu(\text{CO})$  infrared spectral data. The impetus for this investigation was a desire to determine whether the two  $\text{M}(\text{CO})_5$  moieties interact across the hydride bridge in such a way as to affect  $\nu(\text{CO})$ .

## Experimental Section

**Preparation of  $[\text{Et}_4\text{N}]^+[(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4(^{13}\text{CO})]^-$ .**  $[\text{Et}_4\text{N}]^+[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  was prepared by the procedure previously described.<sup>2</sup> A solution of 0.060 g of  $[\text{Et}_4\text{N}]^+[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  in 8.0 mL of THF (distilled from Na-benzophenone) was prepared under a nitrogen atmosphere. The solution was transferred via syringe to a nitrogen-flushed tube of volume 25 mL equipped with a stopcock and serum cap at its sole outlet. A stream of  $^{13}\text{C}$  (>90% enriched, Prochem, BOC Ltd., London) was introduced to the solution by means of a syringe needle through the serum cap until a pressure of approximately 2 atm was attained. The reaction vessel was then placed in a constant temperature bath thermostated at 51.6 °C, and the reaction was allowed to proceed in the dark for 90 min, at which time the reaction had gone to completion as indicated by the  $\nu(\text{CO})$  infrared spectrum of the reaction mixture.

**Infrared Spectra.** The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance



**Figure 1.**  $\nu(\text{CO})$  spectra of  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  in tetrahydrofuran: ---,  $[(\mu\text{-H})[\text{Mo}({}^{12}\text{CO})_5]_2]^-$ ; —,  ${}^{13}\text{CO}$ -enriched  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$ ; \*, peak assigned to the mono- ${}^{13}\text{CO}$  axial species.

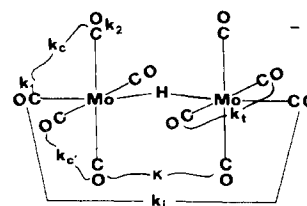
potentiometer. The spectra were calibrated against a water vapor spectrum below  $2000\text{ cm}^{-1}$  and against a CO spectrum above  $2000\text{ cm}^{-1}$ . Sodium chloride solution cells (0.1-mm path length) were used with tetrahydrofuran solvent in the reference cell.

**Vibrational Analysis in the  $\nu(\text{CO})$  Region.** Initial CO stretching force constants were calculated using the secular equations of Cotton and Kraihanzel for two noninteracting  $C_{4v}$  metal centers.<sup>7</sup> The trial force constants were refined with the addition of interaction force constants across the hydride bridge using the  ${}^{12}\text{CO}$  and  ${}^{13}\text{CO}$  frequency data and an iterative computer program<sup>8</sup> that adjusts a set of force constants common to a group of isotopically substituted molecules to give simultaneously a least-squares fit between the observed and calculated frequencies for all the molecules. Force constants were refined to reproduce the observed  ${}^{12}\text{CO}$  and  ${}^{13}\text{CO}$  vibrations to within an average error of  $1.0\text{ cm}^{-1}$ .

## Results and Discussion

The phosphine substituted bridging hydride species  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4\text{PPh}_3]]^-$  has been found to react with  ${}^{13}\text{CO}$  in tetrahydrofuran solution to afford  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4({}^{13}\text{CO})]]^-$  in near-quantitative yield. Figure 1 illustrates the  $\nu(\text{CO})$  infrared spectrum of this  ${}^{13}\text{CO}$  species along with the corresponding spectrum of its all  ${}^{12}\text{CO}$  analogue,  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$ . The three-band pattern observed for the  $\nu(\text{CO})$  vibrational modes in the all- ${}^{12}\text{CO}$   $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  molecular ion can be initially treated as arising from two noninteracting  $C_{4v}$   $[\text{Mo}(\text{CO})_5]$  moieties of symmetry  $2A_1 + E$  (2040.5 ( $A_1$ ), 1876.5 ( $A_1$ ), and 1940.5 (E)). The Cotton-Kraihanzel force constants calculated employing this assignment are  $k_1 = 14.35$ ,  $k_2 = 15.71$ , and  $k_3 = 0.24$ . If one  ${}^{13}\text{CO}$  group is inserted into either an equatorial or axial position and this force field is used to calculate the  $\nu(\text{CO})$  frequencies in these isotopically labeled molecules, it is not possible to account for the observed  $\nu(\text{CO})$  band pattern in the derivative prepared by reaction 1.<sup>9</sup> Specifically, bands are calculated at 1912.6 and 1838.3  $\text{cm}^{-1}$  for the equatorially and axially labeled mono- ${}^{13}\text{CO}$  species, respectively, both of which are absent in the observed spectrum of the  ${}^{13}\text{CO}$ -enriched species. These calculated  $\nu(\text{CO})$  shifts upon  ${}^{13}\text{CO}$  incorporation are analogous to those observed in a variety of mononuclear  $\text{M}(\text{CO})_5\text{L}$  species,<sup>10-12</sup> including the related  $\text{HMn}(\text{CO})_5$  derivative.<sup>13-15</sup>

Therefore, in order to explain the observed infrared band pattern in  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5][\text{Mo}(\text{CO})_4({}^{13}\text{CO})]]^-$  it was necessary to include coupling of carbonyl groups across the Mo-H-Mo bridge. We have adopted the approach employed by Cotton and Wing<sup>16</sup> for  $\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Mn}, \text{Re}$ ) in approximating a restricted CO force-field calculation which considers interactions of carbonyl groups on the two metal centers. This model involves, in addition to interactions between CO stretching vibrations within each  $\text{Mo}(\text{CO})_5$  unit,



**Figure 2.**  $\nu(\text{CO})$  force constant designations in the  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  species.

**Table I.** Calculated and Observed  $\nu(\text{CO})$  Vibrational Modes in  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  Species<sup>a</sup>

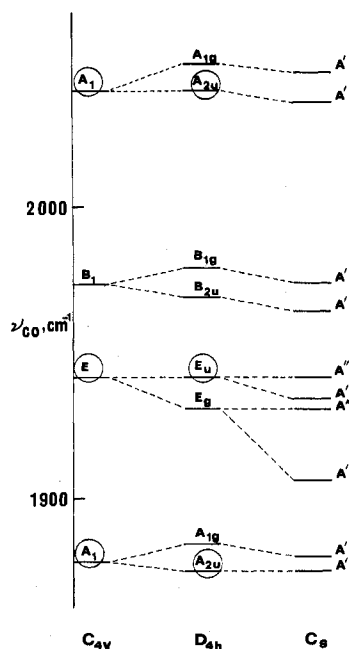
molecule	vibration	$\nu(\text{CO}), \text{cm}^{-1}$		
		obsd <sup>b</sup>	calcd	
all- ${}^{12}\text{CO}$ species ( $D_{4h}$ )	$A_{1g}$		2047.6	
	$A_{2u}$	2040.5	2040.9	
	$B_{1g}$		1975.0	
	$B_{2u}$	1968.0	1967.9	
	$E_u$	1940.5	1938.5	
	$E_g$		1931.3	
	$A_{1g}$		1880.4	
	$A_{2u}$	1876.5	1876.1	
	monosubstituted ${}^{13}\text{CO}$ , <sup>c</sup> equatorially ( $C_s$ )	$A'$		2045.4
		$A'$	2036.0	2035.3
$A'$			1972.8	
$A'$			1963.3	
$A''$		1940.5	1938.5	
$A'$		1932.0	1935.3	
$A''$			1931.3	
$A'$			1906.6	
$A'$		1875.0	1879.8	
monosubstituted ${}^{13}\text{CO}$ , axially ( $C_{4v}$ )	$A_1$		2047.0	
	$A_1$		2040.1	
	$B_1$		1975.0	
	$B_1$		1967.9	
	E		1938.5	
	E		1931.3	
	$A_1$		1878.3	
	$A_1$	1840.5 <sup>d</sup>	1838.0	

<sup>a</sup> Spectra were determined in THF solvent. The refined CO force constants calculated were  $k_1 = 14.38$ ,  $k_2 = 15.66$ ,  $k_{c'} = 0.26$ ,  $k_c = 0.29$ ,  $k_t = 0.54$ ,  $K = 0.05$ ,  $k_j = 0.031$ , with an average error in frequencies of  $1.0\text{ cm}^{-1}$  or 0.050%. <sup>b</sup> Italic frequencies were used as input in the refinement process. <sup>c</sup> Although all nine bands are predicted to be infrared active, the dipole moment changes are negligible for several of these symmetry modes.

<sup>d</sup> A weak vibration observed in the enriched sample.

coupling between CO stretching vibrations in different  $\text{Mo}(\text{CO})_5$  units. This latter coupling is introduced using the two interaction force constants,  $K$  (interaction of two nearest-neighbor equatorial CO groups on different metal centers), and  $k_j$  (interaction of axial CO groups on different metal centers) (see Figure 2).<sup>17,18</sup> Small positive values for  $K$  and  $k_j$  terms (0.20 and 0.02) were used in the initial calculation in accordance with the approximation of Cotton and Wing.<sup>16</sup> The refined force constants along with the observed and calculated  $\nu(\text{CO})$  frequencies are given in Table I. The refined values of  $K$  and  $k_j$  remain small and positive, 0.056 and 0.031, respectively, or an order of magnitude smaller than the CO interaction force constants on the same metal center.

The repulsive interaction between  $d_{\pi}$  orbitals of adjacent metal centers has been used to account for differences in both intensities and frequencies of  $\nu(\text{CO})$  spectra of mononuclear  $\text{XMn}(\text{CO})_5$  and  $\text{M}_2(\text{CO})_{10}$ ,  $\text{M} = \text{Mn}, \text{Tc}, \text{and Re}$ .<sup>16</sup> Cotton and Wing convincingly argued that a simultaneous stretching of the four equivalent CO groups on adjacent  $\text{M}(\text{CO})_5$  units is less favorable than a stretching of one set and a contraction of the other. The resultant contribution to the dipole moment is unavailable to mononuclear systems. Since the interaction



**Figure 3.** Diagram illustrating how the CO stretching spectrum of  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  ( $D_{4h}$ ) is derived from that of the  $\text{Mo}(\text{CO})_5$  groups ( $C_{4v}$ ). The circle frequencies are infrared active. The  $\nu(\text{CO})$  frequency values (all infrared active) in the mono- $^{13}\text{CO}$  equatorially labeled species are given on the right.

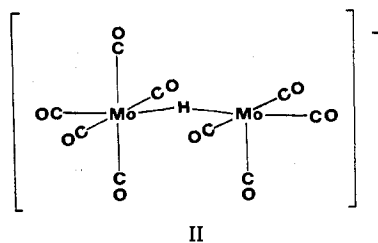
constant is positive, the two highest frequency bands, arising from symmetric stretching of axial and equatorial CO groups will be closer in frequency for  $\text{M}_2(\text{CO})_{10}$  than in the mononuclear complexes. The important point to be correlated with our studies is that the separation of these highest frequency bands varies with M–M bond length and is 31, 48, and  $56\text{ cm}^{-1}$  for  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Tc}_2(\text{CO})_{10}$ , and  $\text{Re}_2(\text{CO})_{10}$ , respectively. Thus a direct correlation between M–M interaction and CO interaction apparently exists.<sup>19</sup>

A substantial amount of M–M interaction in  $[(\mu\text{-H})[\text{M}(\text{CO})_5]_2]^-$  species is supported by various solid-state structural studies. Neutron diffraction analyses of  $[\text{Et}_4\text{N}]^+[(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2]^-$ ,<sup>6</sup>  $(\mu\text{-H})\text{W}_2(\text{CO})_8(\text{NO})\text{P}(\text{OME})_3$ ,<sup>4</sup> and  $(\mu\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$ <sup>5</sup> clearly show that the hydride does not occupy the sixth octahedral coordination site about the metal carbonyl (or derivative) center but rather is positioned off the M–M axis so as to define a three-center, two-electron closed-type bond.<sup>4-6</sup>

The impossibility of surmising a physical interpretation of the cross-metal CO interaction constants was discussed by Cotton and Wing<sup>16</sup> and similarly the values obtained here are of significance only in the fact of their existence. It is important to point out parenthetically here that there are other ways to introduce coupling across the Mo–H–Mo bridge into the potential energy function; i.e., the solution presented here is not unique and we do not wish to place any physical significance on the values of  $K$  and  $k_j$ . Perhaps a fortuitous consistency is the fact that the values obtained for the hydride-bridged cross-metal CO interactions are smaller than the absolute values obtained on the direct M–M bonded systems ( $K = 0.33$  and  $0.24$ , and  $k_j = 0.12$  and  $-0.04$  for  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$ , respectively).<sup>16</sup>

It can be seen from Figure 1 and Table I that the principal mono- $^{13}\text{CO}$  species produced via reaction 1 is the equatorially substituted species; i.e., replacement of  $\text{Ph}_3\text{P}$  is essentially stereospecific with perhaps a trace of axially  $^{13}\text{CO}$ -labeled species being afforded as evidence by the weak absorption at  $\sim 1840\text{ cm}^{-1}$  in Figure 1. There was no observed tendency for  $^{13}\text{CO}$  to intramolecularly scramble in solution in this

labeled derivative at ambient temperature. This observation would suggest that the intermediate afforded by  $\text{PPh}_3$  dissociation (the vacant site will undoubtedly be temporarily occupied by the labile THF ligand) is square pyramidal in geometry with the bridging hydride ligand being in an equatorial position (species II).<sup>20-22</sup> Figure 3 shows how the



CO stretching modes in the  $\text{Mo}(\text{CO})_5$  units are related to those in the  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$  species. As is readily apparent, the three infrared-active bands expected (and observed) in the dimeric  $D_{4h}$  species should have a similar band pattern as that anticipated for noninteracting  $\text{Mo}(\text{CO})_5$  moieties. Indeed, the calculated CO stretching force constants assuming isolated metal centers are not significantly altered upon inclusion of interaction constants across the M–H–M bridge ( $14.35$  and  $15.71$  vs.  $14.38$  and  $15.67\text{ mdyn/\AA}$ ). It is also worth noting the sizable difference in the CO stretching force constants  $k_1$  and  $k_2$  for CO groups trans and cis to the Mo–H–Mo bridge, respectively. This result is consistent with the shorter M–C<sub>axial</sub> ( $\sim 0.07\text{ \AA}$  shorter) bond distance as determined by X-ray diffraction measurements for the analogous  $[(\mu\text{-H})[\text{W}(\text{CO})_5]_2]^-$  and  $[(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2]^-$  salts<sup>6,18</sup> which presumably will hold true for the molybdenum anion.

**Acknowledgment.** Partial financial support from the National Science Foundation through Grant CHE 76-04494 for this project is greatly appreciated.

**Registry No.**  $[\text{Et}_4\text{N}]^+[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$ , 64600-03-9;  $[\text{Et}_4\text{N}]^+[(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4(^{13}\text{CO})]^-$  ( $C_s$ ), 66984-41-6;  $[\text{Et}_4\text{N}]^+[(\text{CO})_5\text{Mo-H-Mo}(\text{CO})_4(^{13}\text{CO})]^-$  ( $C_{4v}$ ), 67110-77-4;  $[(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2]^-$ , 45270-68-6.

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- Although the M–H–M bond has been observed to be bent rather than a linear M–H–M fragment, the equatorial carbonyls in the two  $\text{M}(\text{CO})_5$  units have been observed to be in an eclipsed array.<sup>6,18</sup>
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- (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<sup>21</sup> as to whether the incoming <sup>13</sup>CO molecule binds to the molybdenum atom which originally bore the PPh<sub>3</sub> ligand or whether a CO group from the other molybdenum center bridges the two metals with the incoming <sup>13</sup>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 <sup>13</sup>CO label was also verified by <sup>13</sup>C NMR. Chemical shifts relative to Me<sub>4</sub>Si 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 <sup>13</sup>C NMR spectrum of [Et<sub>4</sub>N]<sup>+</sup>[(μ-H)[Mo(CO)<sub>5</sub>][Mo(CO)<sub>4</sub><sup>13</sup>CO]]<sup>-</sup>, CO chemical shifts at 232.0 and 228.4 ppm were in an intensity ratio of 4:97. Thus, the fraction of molecules <sup>13</sup>CO labeled equatorially may be estimated at 91%, and the fraction of molecules labeled axially at 2% (neglecting natural abundance <sup>13</sup>C).

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### A Convenient Synthesis of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> 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)<sub>4</sub>L<sub>2</sub> 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)<sub>6</sub> plus 2L in refluxing diglyme, one has to settle for the thermodynamically more stable isomer of M(CO)<sub>4</sub>L<sub>2</sub>.<sup>1</sup> The most commonly used alternate synthesis which operates under milder conditions involves the reaction of M(CO)<sub>4</sub>(NBD) (NBD = norbornadiene or bicyclo[2.2.1]hepta-2,5-diene) with 2L.<sup>2</sup> This procedure suffers from the necessity of having to prepare and purify M(CO)<sub>4</sub>(NBD) derivatives which is itself often a lengthy process.<sup>3</sup> 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<sub>4</sub> at refluxing methanol temperature.<sup>4</sup> The bridging hydride μ-H[M(CO)<sub>5</sub>]<sup>-</sup> has also been shown to react with phosphines and phosphites to yield L<sub>2</sub>M(CO)<sub>4</sub> complexes and has been proposed as an intermediate in the Chatt synthesis.<sup>5,6</sup>

Although there are other specialized reactions for the synthesis of Mo(CO)<sub>4</sub>L<sub>2</sub> derivatives, no general large-scale preparation of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> derivatives has been available.<sup>7,8</sup> Here we describe a particularly convenient and inexpensive route to the synthesis of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> 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)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>. Ten grams of Mo(CO)<sub>6</sub> (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

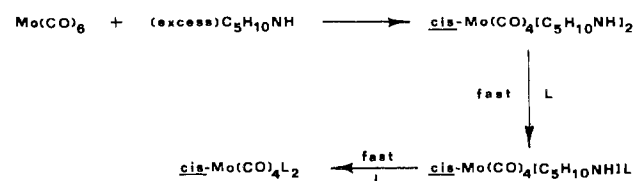


Table I. Infrared Spectra in the ν(CO) Stretching Region of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> Derivatives<sup>a</sup>

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

<sup>a</sup> Spectra were measured in tetrachloroethylene solution. <sup>b</sup> Frequencies are accurate to ±1.0 cm<sup>-1</sup> except for shoulders which are probably only accurate to ±2–3 cm<sup>-1</sup>.

yellow product precipitated from solution. The reaction mixture was filtered hot to remove any heptane-soluble Mo(CO)<sub>5</sub>(NHC<sub>5</sub>H<sub>10</sub>). 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)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>. 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)<sub>6</sub> (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)<sub>4</sub>L<sub>2</sub> Derivatives. In a typical preparation, 1–2 g (or 2–5 mmol) of Mo(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub> was stirred under reflux in dichloromethane (bp 40 °C) with a slightly greater than two molar excess of ligand (L) (L = SbPh<sub>3</sub>, Me<sub>2</sub>PhP, P(OCH<sub>2</sub>)<sub>3</sub>CEt, MePh<sub>2</sub>P, (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>PhP, P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, PBu<sub>3</sub>, PPh<sub>3</sub>, and PN<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>) 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)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub>: C, 65.58; H, 4.13. Found: C, 65.68; H, 4.12. Calcd for Mo(CO)<sub>4</sub>[P(Me)Ph<sub>2</sub>]<sub>2</sub>: C, 59.23; H, 4.30. Found: C, 59.19; H, 4.43. Calcd for Mo(CO)<sub>4</sub>[P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>Ph]<sub>2</sub>: C, 63.49; H, 7.19. Found: C, 63.27; H, 7.36.

Reactions carried out in an analogous manner between *cis*-W(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub> and L (L = PPh<sub>3</sub>, *n*-Bu<sub>3</sub>P) provided an efficient means for the production of the mixed species *cis*-W(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>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)<sub>4</sub>L<sub>2</sub> derivatives. Anal. Calcd for W(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>PPH<sub>3</sub>: C, 50.40; H, 4.04. Found: C, 51.00; H, 4.05. Calcd for W(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>P(*n*-Bu)<sub>3</sub>: C, 43.24; H, 6.52. Found: C, 42.93; H, 6.49.

(d) *cis*-Mo(CO)<sub>4</sub>[P(OMe)<sub>3</sub>]<sub>2</sub>NHC<sub>5</sub>H<sub>10</sub>. One gram of Mo(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]<sub>2</sub> 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)<sub>4</sub>[P(OMe)<sub>3</sub>]<sub>2</sub>NHC<sub>5</sub>H<sub>10</sub> (fully characterized, including X-ray