

The Solution Behavior of Unsaturated Molybdenum Carbonyl Species as Evidenced via Stereospecific ^{13}C O Labeling Studies

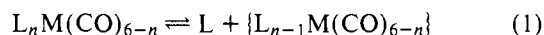
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Abstract: Stereospecific incorporation of ^{13}C O into the triene complex, (bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl, has been found to occur with the axially labeled ^{13}C O tetracarbonyl derivative being formed where the triene ligand is acting as a four-electron donor. A facile, high-yield synthesis of other stereospecific ^{13}C O-labeled cis-disubstituted derivatives of molybdenum has been developed which involves displacement of the olefin with a variety of incoming ligands, namely, norbornadiene, diamines, PPh_3 , P(OPh)_3 , SbPh_3 , and diphos. The retention of the axial ^{13}C O label in these *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ derivatives is ascribed to a site preference of these ligands(L) for an equatorial position in the square-pyramidal structure of the five-coordinate intermediates involved in this process where the barrier to CO rearrangement is large. On the other hand, when the incoming ligand is the small, relatively good π acceptor, P(OMe)_3 , CO rearrangement was found to readily occur. Similarly, reaction of $\text{Mo}(\text{CO})_4(\text{triene})$ with ^{13}C O afforded a statistical distribution of *cis* and *trans* bis- ^{13}C O species, thus indicating that the CO groups in the $[\text{Mo}(\text{CO})_5]$ intermediate lose their stereochemical integrity at a rate which is rapid relative to their solution lifetime. The infrared spectral details in the $\nu(\text{CO})$ region of the ^{13}C O labeled derivatives prepared in this investigation are discussed.

Introduction

Mechanistic studies of thermal ligand substitution processes of substituted group 6B metal carbonyl derivatives continue to play an exceedingly important role in the elucidation of the intimate details of reactions in general which involve the replacement of neutral ligands from metal centers in low oxidation states.²⁻⁵ An analysis of reactivity patterns in these octahedral metal carbonyl derivatives has been quite informative with respect to understanding the geometry of transition states and/or intermediates afforded in the ligand dissociation step⁶⁻⁸



Much of the impetus for a thorough investigation of these processes is provided by the ubiquitous presence of these coordinatively unsaturated species in homogeneous transition metal carbonyl catalysis. Indeed, the selectivity of many transition metal carbonyl catalysts is based on the relative reactivity of the unsaturated intermediate toward one substrate over another, whether this be due to electronic or steric factors.

In recent years we have been interested in examining the reactivity of coordinatively unsaturated species, procreated by the thermal⁸⁻¹⁰ or photochemical¹¹⁻¹³ initiated loss of a labile ligand in substituted metal carbonyl derivatives, with regard to their discriminating behavior toward various incoming ligands. An additional concern of ours has been to enhance the understanding of the degree of fluxionality of the remaining ligands in the five-coordinate, 16-electron intermediates. Our approach to this latter mechanistic problem has been centered around our ability to synthesize and spectroscopically characterize stereospecifically or stereoselectively ^{13}C O or C^{18}O labeled metal carbonyl derivatives. We wish to report in this communication the reaction of the triene complex, (bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl, with ^{13}C O in solution to afford stereospecifically the axially labeled ^{13}C O tetracarbonyl derivatives, along with subsequent reactions of this labeled derivative with a variety of Lewis bases.

Results and Discussion

An investigation of the reaction of (triene) $\text{Mo}(\text{CO})_3$ (triene = bicyclo[6.1.0]nona-2,4,6-triene) with phosphite ligands and

carbon monoxide to afford (triene) $\text{Mo}(\text{CO})_3\text{L}$ derivatives, where $\text{L} = \text{P(OMe)}_3$, P(OPh)_3 , CO and the triene ligand is acting as a four-electron donor, has been described.^{14,15} It was of interest to determine the coordination site of the incoming CO ligand; therefore, we have carried out the substitution reaction with ^{13}C -labeled carbon monoxide (eq 2). Figure 1 il-



lustrates the $\nu(\text{CO})$ spectra of both $\text{Mo}({}^{12}\text{C}\text{O})_4(\text{triene})$ and $\text{Mo}({}^{12}\text{C}\text{O})_3({}^{13}\text{C}\text{O})(\text{triene})$ observed in hexane solution. The weak $\nu(\text{CO})$ absorptions in Figure 1A (indicated by asterisks) are most likely due to molecules containing ^{13}C O; the mono- ^{13}C O substituted derivatives (axial and equatorial substitution) will each be present in 2.2% natural abundance. The assignment of the two weak, higher frequency absorptions (at 2027 and 1937 cm^{-1}) in Figure 1A to mono- ^{13}C O species is confirmed by the great enhancement in the intensity of these bands with a concomitant decrease in the absorptions at 2044 and 1969 cm^{-1} as shown in Figure 1B, which contains the $\nu(\text{CO})$ spectrum of $\text{Mo}({}^{12}\text{C}\text{O})_3({}^{13}\text{C}\text{O})(\text{triene})$. As is noted in Figure 1, the band at 1884 cm^{-1} did not undergo any increase in intensity in the mono- ^{13}C O species prepared via eq 2.

Substitution of one ^{13}C O group into the *cis*- $\text{M}(\text{CO})_4\text{L}_2$ derivative lowers the local molecular symmetry of the $\text{M}(\text{CO})_4$ moiety (C_{2v}), where all four $\nu(\text{CO})$ infrared modes are active ($2A_1 + B_1 + B_2$), to C_s for which four $\nu(\text{CO})$ infrared-active modes are also expected ($3A' + A''$). This is the case whether the labeled carbon monoxide occupies an axial or equatorial position in the metal tetracarbonyl framework. The antisymmetric vibration (A'') in the mono- ^{13}C O substituted species is identical with either the B_2 or B_1 mode of the all- ^{12}C O molecule when ^{13}C O is located in an axial or equatorial site, respectively. Therefore, the band at 1914.2 cm^{-1} which does not undergo a frequency shift upon ^{13}C O substitution must be ascribed to either of these two modes (B_1 or B_2). If it is further required that the CO groups *trans* to the olefinic ligands have CO stretching force constants less than those CO groups mutually *trans* to one another, it can be concluded that the $\nu(\text{CO})$ vibrational mode at 1914.2 cm^{-1} is of B_2 symmetry.

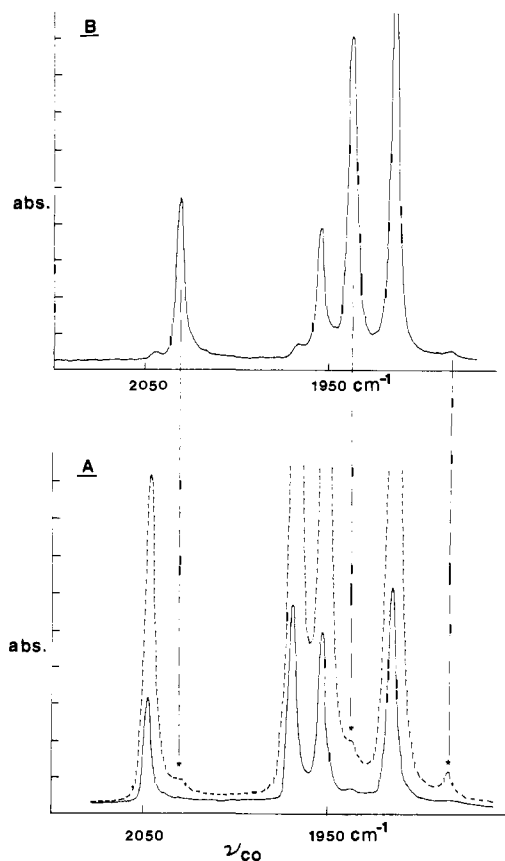
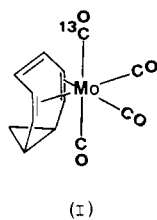


Figure 1. Infrared spectra in CO stretching region in hexane of $\text{Mo}(\text{CO})_4(\text{triene})$: (A) natural abundance ^{13}C spectra, — and - - - refer to two different solution concentrations; (B) ^{13}C enriched spectrum.

The symmetry coordinates for the vibrations in the all- ^{12}C and mono- ^{13}C axially substituted species are depicted in Figure 2. It can be readily seen in Figure 2 that the two vibrations (A_1 and B_1) should be significantly affected by the introduction of an axial ^{13}C ligand, whereas the other A_1 mode will be only slightly shifted due to mixing. Figure 1b bears these expectations out. Using these assignments, the C-K force constants were refined with the results being summarized in Table I. Thus, reaction 2 leads to the exclusive production of the axially labeled $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$ species (I).¹⁶



This result is consistent with our previous studies on the photochemical incorporation of ^{13}C in $\text{Mo}(\text{CO})_4(\text{NBD})$ (NBD = bicyclo[2.2.1]hepta-2,5-diene), where the intermediate is of square pyramidal geometry and further does not intramolecularly scramble CO groups on the time scale of ^{13}C addition (eq 3). Therefore, this observation is in agreement with an ever growing body of evidence in support of 16 valence electron, pentacoordinate metal carbonyls and derivatives exhibiting square-pyramidal rather than trigonal-bipyramidal geometry, both in solution and in inert matrices.^{7,11,17-24}

Reaction of the stereospecifically ^{13}C -labeled, $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$ derivative with a large variety of ligands has led to the development of an extremely efficient synthesis of stereospecifically ^{13}C -labeled *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ complexes

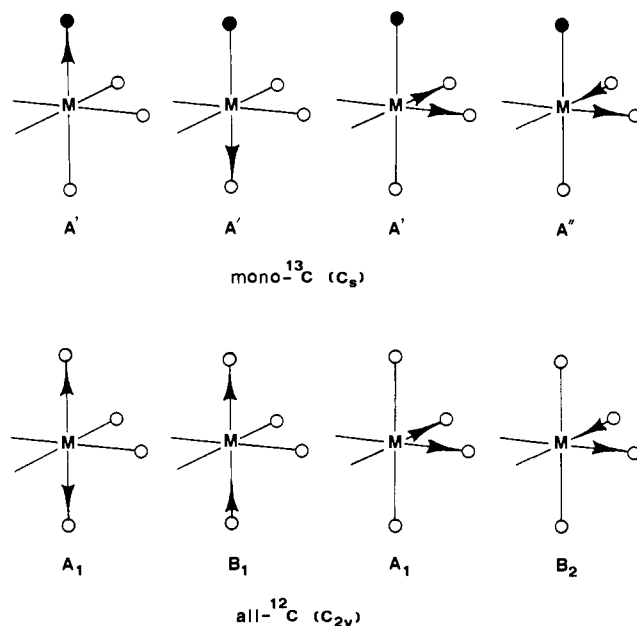


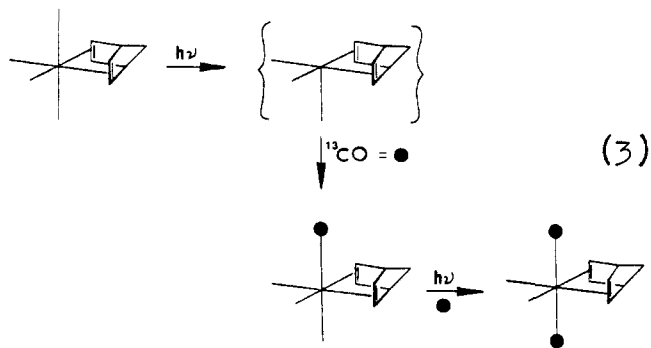
Figure 2. Internal symmetry coordinates for the all- ^{12}C and mono- ^{13}C axially substituted $\text{L}_2\text{M}(\text{CO})_4$ species. The position of ^{13}C substitution is indicated by the solid dot.

Table I. Calculated and Observed CO Stretching Frequencies in (Triene) $\text{Mo}(\text{CO})_4$ Species^a

Molecule	Symmetry	Obsd ^b	Calcd
All ^{12}C species	A_1	<i>2044.0</i>	2043.7
	A_1	<i>1952.3</i>	1951.9
	B_1	<i>1969.0</i>	1969.4
	B_2	<i>1914.2</i>	1914.5
Mono- ^{13}C axially substituted	A'	<i>2027.2</i>	2028.6
	A'	<i>1954.2</i>	1954.3
	A'	<i>1937.1</i>	1937.4
	A''	<i>1914.2</i>	1914.5
Mono- ^{13}C equatorially substituted	A'	<i>c</i>	2042.4
	A'	<i>c</i>	1940.7
	A'	<i>1884.0^d</i>	1883.8
	A''	<i>c</i>	1969.4

^a Frequencies were measured in hexane solution. ^b The eight frequencies (italics) were used as input and were calculated with an average error of 0.4 cm^{-1} or 0.022% . ^c These frequencies were absent in the ^{13}C labeled species. ^d This frequency was observed in the natural abundance ^{13}C spectrum at high concentration.

(with isolated, purified yields generally being greater than 80%). For example, it is possible to prepare the mono- ^{13}C CO



axially labeled $\text{Mo}(\text{CO})_4(\text{NBD})$ derivative in its pure form via reaction 4, i.e., in the absence of further CO substitution reactions as is operative in its photochemical synthesis.¹¹ Other mono- ^{13}C CO axially labeled Lewis base derivatives, *cis*-

Table II. Calculated and Observed CO Stretching Frequencies in *cis*-Mo(CO)₄L₂ Species (cm⁻¹)^a

Molecule	Symmetry	$\nu(\text{CO})$							
		PPh ₃		P(OPh) ₃		Diphos		TMPA	
		Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
All ¹² CO species	A ₁	2023.4	2025.1	2045.6	2044.6	2023.1	2022.6	2015.9	2015.4
	A ₁	1930.2	1929.5	1965.5	1965.4	1931.4	1931.0	1890.6	1889.4
	B ₁	1911.2	1911.7	1945.2	1946.1	1917.1	1917.9	1885.8	1887.9
Mono- ¹³ CO, axially substituted	B ₂	1900.2	1899.6	1940.4	1940.7	1904.0	1903.9	1853.0	1853.2
	A'	2011.4	2012.0	2033.9	2034.2	2010.0	2011.0	2003.0	2004.8
	A'	1926.1	1927.0	1961.6	1961.7	1928.3	1928.6	1888.7	1889.0
Mono- ¹³ CO, equatorially substituted	A'	1882.9	1883.7	1918.0	1916.2	1889.1	1888.4	1858.5	1856.1
	A''	1900.2	1899.6	1940.4	1940.7	1904.0	1903.9	1853.2	1853.2
	A'	<i>b</i>	2020.8	<i>b</i>	2038.6	<i>b</i>	2017.3	<i>b</i>	2008.0
	A'	<i>b</i>	1921.2	<i>b</i>	1958.8	<i>b</i>	1923.7	<i>b</i>	1881.9
	A''	<i>b</i>	1869.3	<i>b</i>	1909.5	<i>b</i>	1873.5	<i>b</i>	1825.9
	A''	1911.2 ^c	1911.7	1945.2 ^c	1946.1	1917.1 ^c	1917.9	1885.8 ^c	1887.9

^a Frequencies were measured in hexane solution. ^b These frequencies were absent in the ¹³CO labeled species. ^c This frequency was not observed in the ¹³CO enriched species. It is assigned based on the fact that it should be the same as the B₁ vibration in the all ¹²CO species.

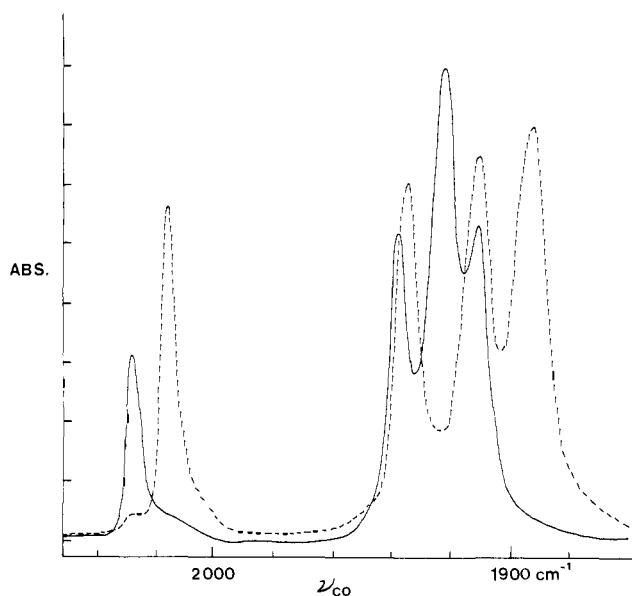


Figure 3. Infrared spectra in $\nu(\text{CO})$ region of *cis*-Mo(CO)₄[SbPh₃]₂ in hexane: —, natural abundance ¹³CO spectrum; - - -, axially mono-¹³CO, *cis*-Mo(CO)₃(¹³CO)[SbPh₃]₂ spectrum.

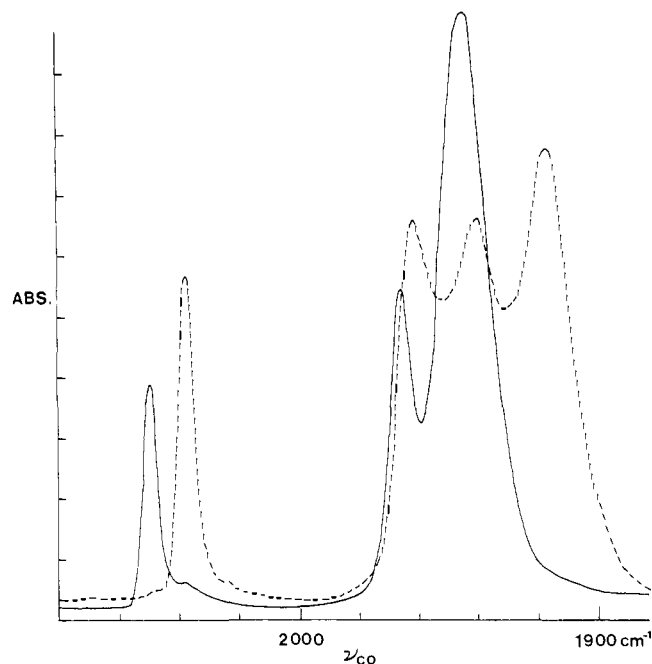
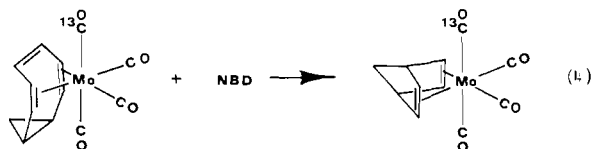


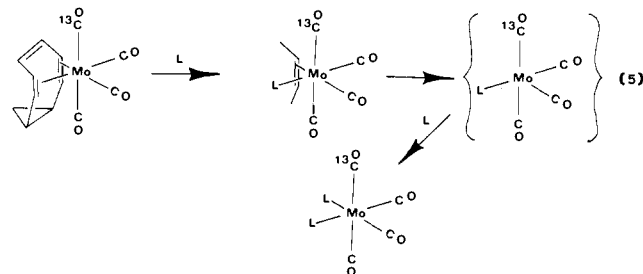
Figure 4. Infrared spectra in $\nu(\text{CO})$ region of *cis*-Mo(CO)₄[P(OPh)₃]₂ in hexane: —, natural abundance ¹³CO spectrum; - - -, axially mono-¹³CO, *cis*-Mo(CO)₃(¹³CO)[P(OPh)₃]₂ spectrum.

Mo(CO)₄L₂, which have been prepared employing this procedure include L₂ = diphos (bis(1,2-diphenylphosphino)eth-



ane), TMED (*N,N,N',N'*-tetramethylethylenediamine), TMPA (*N,N,N',N'*-tetramethyl-1,3-diaminopropane), and L = PPh₃, SbPh₃, and P(OPh)₃. The stereochemical position of the ¹³CO ligand in these substituted *cis*-Mo(CO)₄L₂ derivatives was determined simultaneously by $\nu(\text{CO})$ spectra (assigning all bands, both with respect to position and relative intensity pattern, with the aid of computations using a restricted CO force field), and by ¹³C NMR measurements. Figures 3 and 4 illustrate typical $\nu(\text{CO})$ spectral results, whereas Table II contains the calculated and observed $\nu(\text{CO})$ frequency values for the derivatives studied.^{25,26} The refined force constants for the tetracarbonyl derivatives are given in Table III. As is readily apparent from the arguments presented earlier, these $\nu(\text{CO})$ spectra can be explained in terms of a

¹³CO group being stereospecifically located in an axial position. In other words, during the course of the substitution reaction (eq 5), there is no equilibration of axial and equatorial



carbonyl ligands, i.e., the axial and equatorial carbonyl groups maintain their integrity in all transition states and intermediates during this substitution process.

Further confirmation that the ¹³CO remains incorporated in an axial position during the substitution of the triene is seen in the ¹³C NMR data for the carbonyl ligands of the thus formed *cis*-Mo(CO)₄L₂ derivatives. Only one strong signal

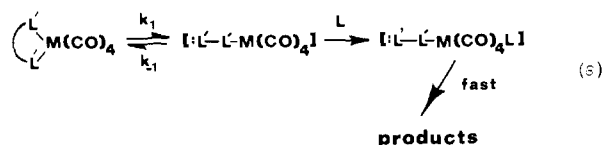
Table III. $\nu(\text{CO})$ Force Constants for *cis*-Mo(CO)₄L₂ Derivatives

L or L ₂	Force constants, mdyn/Å				
	k_1	k_2	k_c	k_c'	k_t
Triene ^a	15.14 ₈	16.20 ₄	0.19 ₈	0.34 ₉	0.54 ₅
NBD ^b	15.36 ₁	15.93 ₉	0.30 ₉	0.56 ₈	0.47 ₂
P(OPh) ₃	15.64 ₁	15.84 ₆	0.31 ₀	0.43 ₅	0.55 ₄
SbPh ₃	15.12 ₉	15.50 ₀	0.31 ₉	0.41 ₄	0.61 ₄
Diphos	15.08 ₀	15.45 ₀	0.34 ₁	0.44 ₄	0.59 ₉
PPh ₃	14.99 ₇	15.46 ₀	0.33 ₄	0.42 ₈	0.70 ₄
TMED ^c	14.59 ₀	14.90 ₆	0.48 ₆	0.68 ₁	0.57 ₆
TMPA ^d	14.54 ₅	14.99 ₆	0.48 ₈	0.67 ₈	0.60 ₀

^a Triene = bicyclo[6.1.0]nona-2,4,6-triene. ^b NBD = bicyclo[2.2.1]hepta-2,5-diene. ^c TMED = *N,N,N',N'*-tetramethylethylenediamine. ^d TMPA = *N,N,N',N'*-tetramethyl-1,3-diaminopropane.

was observed in the ¹³C-enriched samples corresponding in chemical shift to the axial carbon monoxide ligand, e.g., in the *cis*-Mo(CO)₃(¹³CO)(PPh₃)₂ species only a triplet centered at 210.2 ppm was observed.²⁷ It should be again noted here that all previous experience with two-electron ligands of poorer π acidity than CO indicates that carbonyl ligands trans to other carbonyl ligands yield a carbon resonance at lower frequency than carbonyl ligands trans to the substituted ligand.²⁸

At this point it is important to discuss in more detail the proposed mechanism involving stepwise displacement of the triene from Mo(CO)₄(triene) as illustrated in eq 5. Unfortunately, the substitution reaction of the triene proceeds too rapidly in excess ligand (L) to allow for the determination of an accurate rate profile as a function of ligand concentration via conventional techniques. However, qualitatively it was observed that the reaction rate was dependent on the nature of the incoming ligand as well as its concentration. This rate behavior in reactions involving displacement of bidentate chelate rings has been best attributed to a ring-opening mechanism where the intermediate can return to starting material by way of ring closure or go on to product(s) (see eq 6).^{5,29-31} In any case, the resulting stereochemistry of the ¹³CO

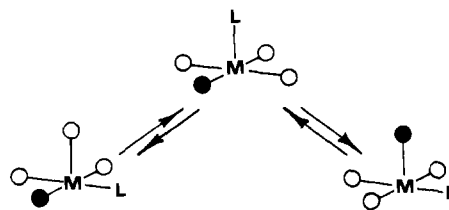


labeled *cis*-L₂Mo(CO)₄ derivatives was not dependent on the concentration of L, i.e., variation in incoming ligand concentration ([L]) over a 2- to 50-fold excess leads to no differences in the stereochemical position of ¹³CO in these disubstituted species for the ligands investigated.

The lack of intramolecular carbonyl ligand rearrangement in the formation of *cis*-Mo(CO)₄L₂ species from Mo(CO)₄(triene) clearly demonstrates the rigidity of substituted, five-coordinate molybdenum carbonyl species during their solution lifetime at room temperature,³²⁻³⁴ i.e., the $[\text{Mo(CO)}_4]$ and $[\text{LMo(CO)}_4]$ intermediates afforded during the process described in eq 6. Similar results were noted by us for Mo(CO)₄(NBD),¹¹ where the barrier to scrambling CO ligands in the stereospecifically, axially labeled Mo(CO)₃(¹³CO)(NBD) was found to be quite high (>25 kcal/mol). The rigidity of the Mo(CO)₄ moiety has also been observed in Mo(CO)₄BH₄⁻.^{35,36} On the other hand, nonrigidity has been reported in the *cis*-L₂Mo(CO)₄ (L₂ = substituted diazabutadienes) derivatives.³⁷

Contrary to the nonfluxional behavior in molybdenum derivatives, the barrier to carbonyl ligand rearrangement in the W(CO)₄(NBD) analogue was found to be considerably lower.¹¹ We have ascribed the fluxional behavior in this derivative to chelate ring opening as the rate-determining step

Scheme I



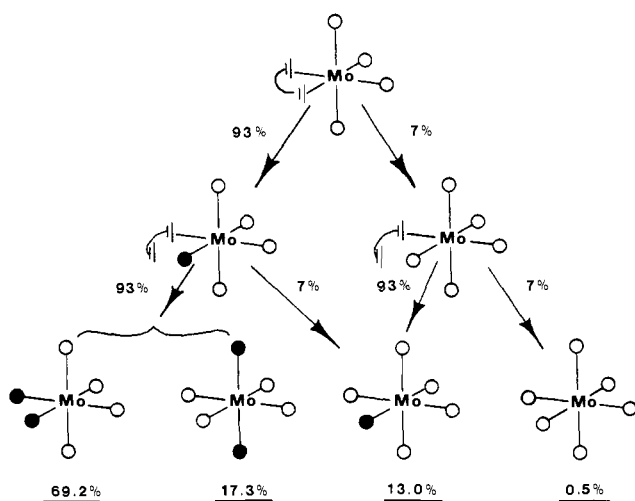
followed by a facile rearrangement of carbonyl groups by the Berry process,³⁸ based on a square-pyramidal ground state. During this fluxional process the unique ligand occupies an apical position in the square pyramidal or distorted square pyramidal structure, a situation which is evidently much less favored in molybdenum derivatives when compared with their tungsten analogues (Scheme I). It would be expected that this barrier decreases in size upon going to unique ligands which approach carbon monoxide in σ and π bonding capabilities.

Rossi and Hoffmann³⁹ have predicted that in d⁶ square-pyramidal species weak σ donors should occupy an equatorial site. In other words, when considering only σ bond strengths in square pyramid d⁶ species the anticipated trend for metal-ligand bonding is M-L_{ax} stronger than M-L_{eq}. Thus ligands which are weak σ donors and non- π -acceptors (saturated amines) or weak π acceptors (olefins without electron-withdrawing substituents, phosphines, etc.) should show a preference for an equatorial site in the square pyramidal structure of d⁶ species. This preference would be greater for the weak σ donor and non- π -acceptor ligands, diminishing as the ligands approach the bonding characteristics of CO. These are indeed the arguments put forth by Atwood and Brown in their description of cis labilization of ligand dissociation processes.⁴⁰

That steric effects also influence the ease with which the rearrangement process depicted in Scheme I proceeds is demonstrated in the reaction of the stereospecifically labeled Mo(CO)₃(¹³CO)(triene) with P(OMe)₃. Unlike the other reactions investigated here where only the *cis*-L₂Mo(CO)₄ isomer is formed, the reaction of P(OMe)₃ with Mo(CO)₄(triene) affords the *trans*-Mo(CO)₄[P(OMe)₃]₂ derivative predominantly with only ~25% of the product existing as the *cis* isomer. Although this isomeric distribution itself implies that the intermediate, [Mo(CO)₄P(OMe)₃], with P(OMe)₃ in an apical site is readily accessible even down to 0 °C, direct evidence for fluxional behavior in this species is obtained from the location of the ¹³CO label in the *cis*-Mo(CO)₃(¹³CO)[P(OMe)₃]₂ derivative. It was noted that rearrangement of the ¹³CO ligand had occurred with both *mer*- and *fac*-Mo(CO)₃(¹³CO)[P(OMe)₃]₂ being observed.⁴¹ Whereas triphenyl phosphite (cone angle = 128°)⁴² and trimethyl phosphite (cone angle = 107°)⁴² are both generally considered to be more like CO in π and σ bonding capabilities than triphenylphosphine (cone angle = 145°),⁴² with triphenyl phosphite being somewhat more similar to CO electronically than P(OMe)₃, the sterically more demanding P(OPh)₃ ligand affords stereochemical results in reaction 5 identical with PPh₃ and in direct contrast with P(OMe)₃. Thus, the nature of the [Mo(CO)₄L] intermediate is sensitive to the number of 90° interactions of L with MCO units.

The reaction of Mo(CO)₄(triene) with 93% enriched ¹³CO has been found to proceed with complete fluxionality in the [Mo(CO)₄(¹³CO)] intermediate afforded during the triene substitution process. This result is analogous to that previously reported by Harrill and Kesz⁴³ for the reaction of C₇H₈Mo(CO)₄ with 50% enriched ¹³CO, where it was also observed that the stereochemistry of the carbonyl groups was not preserved during the displacement of the olefin by CO.

Scheme II



However, these workers did not present any quantitative information on the distribution of stereoisomers (*cis* and *trans* bis- ^{13}CO species). Figure 5 contains the infrared spectra of $\text{Mo}(\text{CO})_6$ enriched with ^{13}CO from the reaction of $\text{Mo}(\text{CO})_4$ (triene) with ^{13}CO . The assignments of the various $\nu(\text{CO})$ vibrations shown in Figure 5 have been provided in the literature.^{43,44} Using the intensity ratio of the band at 1944.7 cm^{-1} (due to the A_{2u} motion in the *trans* bis- ^{13}CO species only, an antisymmetric stretching of *trans* ^{13}CO groups) and the 1989.9-cm^{-1} band (due to the E_u mode of the mono- ^{13}CO , E_u mode of the *trans* bis- ^{13}CO , and the B_2 mode of the *cis* bis- ^{13}CO species; an antisymmetric stretching of *trans* ^{12}CO groups) it is only possible to fit the observed and calculated band ratio if the $[\text{Mo}(\text{CO})_5]$ intermediate is assumed to be totally fluxional (see Scheme II).⁴⁵ Therefore, the CO groups in $[\text{Mo}(\text{CO})_5]$ lose their stereochemical identity at a rate that is rapid relative to their CO-saturated hydrocarbon solution lifetime.⁴⁶ In other words, in the absence of an L ligand with a site preference in the pentacoordinate d^6 structure of the intermediate afforded from the dissociation of a ligand in the hexacoordinate group 6B carbonyl derivatives, the species is nonrigid.

Finally, the availability of a large variety of stereospecifically ^{13}C labeled *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$ derivatives has as well provided for a more detailed knowledge of the intimate mechanism of diamine displacement in $\text{Mo}(\text{CO})_4(\text{diamine})$ species.²⁶ In addition, these labeled derivatives will provide for unequivocal answers of the site of CO loss in reactions involving thermal or photochemical substitution of carbon monoxide; e.g., see the very elegant recent thermal investigation by Dobson and coworkers.^{47,48}

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. The ligand, bicyclo[6.1.0]nona-2,4,6-triene, was prepared according to the procedure in the literature.⁴⁹ Cyclooctatetraene was the generous gift of BASF. (Bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl was synthesized by the room temperature displacement of diglyme from (diglyme) $\text{Mo}(\text{CO})_3$ ⁵⁰ with bicyclo[6.1.0]nona-2,4,6-triene in tetrahydrofuran.¹⁴ The olefinic complex was purified by recrystallization from hexane at $-30\text{ }^\circ\text{C}$. Carbon monoxide of 93% ^{13}C isotopic abundance was obtained from Monsanto Research Corp., Miamisburg, Ohio.

Preparations. $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$. (Bicyclo[6.1.0]nona-2,4,6-triene)molybdenum tricarbonyl (1.0 g, 3.35 mmol) was placed in a 100-mL reaction vessel equipped with a side arm stopcock and a serum cap. The vessel was evacuated and 30 mL of dry hexane was admitted by means of a hypodermic syringe. The reaction flask was then pressurized with 93% enriched ^{13}CO at slightly greater than 2 atm and

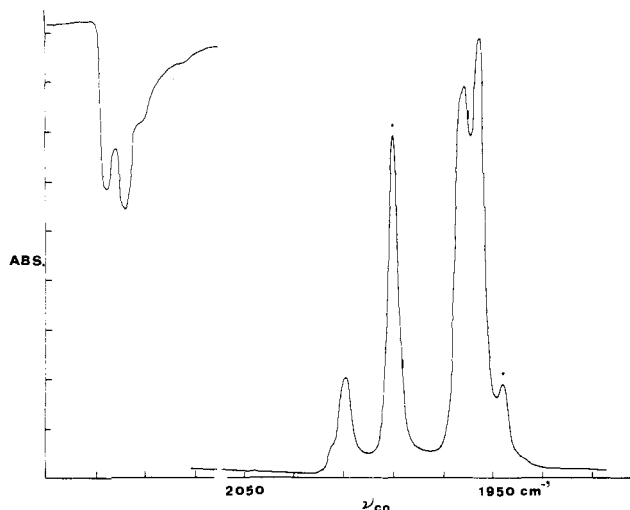


Figure 5. Infrared spectrum in $\nu(\text{CO})$ region of ^{13}C -enriched $\text{Mo}(\text{CO})_6$ in hexane prepared from $\text{Mo}(\text{CO})_4(\text{triene})$ and 93% ^{13}C -enriched CO. The weak absorptions in the high-frequency $\nu(\text{CO})$ region are displayed in the top left-hand corner on an expanded % T scale. The peaks labeled with asterisks denote the bands at 1989.0 and 1944.7 cm^{-1} employed in quantitatively assessing the extent of CO rearrangement in the $[\text{Mo}(\text{CO})_5]$ intermediate; predicted and observed ratios were the same, 7.5:1.

the solution was magnetically stirred for 30 min at room temperature during which time the solution changed from reddish-orange to yellow. The solvent was removed under vacuum and the complex was purified by recrystallization from hexane at $-30\text{ }^\circ\text{C}$. The yield of yellow crystals of products was $\sim 90\%$.

***cis*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{PPh}_3]_2$.** $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$ (0.80 g, 2.45 mmol) and 1.49 g (5.68 mmol) of triphenylphosphine were stirred in 30 mL OF CH_2Cl_2 under nitrogen for 2 h at room temperature. The solvent was removed at reduced pressure and the resulting solid material was extracted with chloroform and filtered through Celite. Upon the addition of methanol and cooling the solution below $0\text{ }^\circ\text{C}$ yellow crystals of the pure bis(triphenylphosphine)molybdenum tetracarbonyl formed. These crystals were isolated by filtration and dried under vacuum at ambient temperature (yield 75%).

The other labeled derivatives were prepared in much the same manner except for the more solution unstable diamines which are described separately. Typical analytical data are given below. Anal. Calcd for $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{PPh}_3]_2$: C, 65.63; H, 4.12. Found: C, 65.67; H, 4.12. Calcd for $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{SbPh}_3]_2$: C, 47.86; H, 3.01. Found: C, 47.82; H, 2.99.

$\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{diamine})$. An excess of diamine ligand (*N,N,N',N'*-tetramethylethylenediamine or *N,N,N',N'*-tetramethyl-1,3-diaminopropane) was added to a hexane saturated solution of the $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$ derivative with stirring. The yellow diamine product, which is not very soluble in hydrocarbon solvents, began to settle out of solution almost immediately. After the reaction solution was stirred for an additional 1 h the bright yellow complex was isolated by filtration and washed with hexane. Anal. Calcd for the ethylenediamine derivative, $\text{Mo}(\text{CO})_3(^{13}\text{CO})[\text{N}_2\text{C}_6\text{H}_{16}]$: C, 37.24; N, 8.61; H, 4.96. Found: C, 37.10; N, 8.53; H, 4.93.

Infrared Measurements and Vibrational Analysis. 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} . Matched sodium chloride cells were used in the measurements.

Initial CO stretching force constant calculations were performed using only the ^{12}CO frequency data and a modified Cotton-Kraihanzel⁵¹ approach refined by Jernigan, Brown, and Dobson,⁵² and employing a program developed in our laboratories.⁵³ The trial force constants were refined using the ^{13}CO frequency data and an iterative computer program⁵⁴ 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. The five trial force constants were refined to reproduce the observed ^{12}CO and ^{13}CO vibrations generally to within an average of $<1.0\text{ cm}^{-1}$.

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- (46) This result is consistent with our earlier observation on the $[\text{Mo}(\text{CO})_5]$ intermediate afforded thermally from $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$,⁸ as well as observations in the matrix photochemistry of group 6B hexacarbonyl species.²¹
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Metal-Stabilized Carbonium Ions Derived from Bis(tricarbonylchromium) Complexes of Diarylmethanes¹

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Abstract: (π, π' -Diarylcarbinol)bis(tricarbonylchromium) complexes, prepared either by direct reaction of a diarylcarbinol with chromium hexacarbonyl or by reduction of the appropriate (π, π' -diaryl ketone)bis(tricarbonylchromium) with sodium borohydride, react with $\text{HPF}_6/(\text{EtCO})_2\text{O}$ to give the respective very stable (π, π' -diarylcarbonium hexafluorophosphate)bis(tricarbonylchromium) complexes. These blue carbonium ion salt complexes are carbon electrophiles which alkylate alcohols, primary and secondary amines, and highly nucleophilic aromatic and heterocyclic compounds such as *N,N*-dimethylaniline, pyrrole, and *N*-methylpyrrole. A ^{13}C NMR study of the (π, π' -di-*p*-tolylcarbonium chlorostannate)bis(tricarbonylchromium) complex in dichloromethane solution, as well as an IR study, provided evidence of extensive delocalization of positive charge from carbon to chromium in these carbonium ion complexes.

Introduction

There has been much interest in carbonium ions which are stabilized by π -ligand complexes of transition metals.² Ferrocenyl-substituted carbonium ions, I, have been studied most extensively,^{2,3} but other systems, II,⁴ III,⁵ IV,⁶ V,⁸ and

VI,⁷ also have been investigated. During a study of the electronic effects of the $\text{Cr}(\text{CO})_3$ group on arene ligands, Holmes, Jones, and Pettit attempted the synthesis of a stable π -complexed carbonium ion salt of type VII.⁹ Treatment of (π -benzyl alcohol)tricarbonylchromium with perchloric or tetrafluoro-