Spectroscopic Studies on Isotopically Enriched Molecules. IV. The Displacement of Olefins by Carbon Monoxide in Complexes of Molybdenum[1]

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Abstract: The facile displacement by CO of olefins in $C_7H_8Mo(CO)_4$ and $C_8H_{10}Mo(CO)_3$ has been followed using ^{13}C-enriched CO. The $Mo(CO)_6$ thus formed contains various multiple ^{13}C-enriched species. Of the bis-^{13}CO species, both *cis* and *trans* isomers were observed, indicating that the stereochemistry of the carbonyl groups is not preserved during the displacement of olefin by CO.

It was recently reported by Kaesz, Winstein, and Kreiter[2] that CO under atmospheric pressure would substitute into $C_8H_8Mo(CO)_3$ and $C_8H_{10}Mo(CO)_3$ to give the olefin–metal tetracarbonyl complexes. In the latter case, $Mo(CO)_6$ was ultimately observed while in the former case insoluble $C_8H_8[Mo(CO)_4]_2$ was the final product. In addition, we have shown that the CO substitution reaction also takes place in the complex norbornadienemolybdenum tetracarbonyl ($C_7H_8Mo(CO)_4$).

With labeled CO it is possible to follow the stereochemistry of the substitution reactions.[1b,3] The presently available ^{13}C enrichment in CO is 50%; thus various proportions of ^{13}CO-substituted products are expected. For instance, $C_7H_8Mo(CO)_4$ with ^{13}CO in natural abundance consists essentially of 4% of mono-^{13}CO-substituted species while 96% is all-^{12}CO. From this material and 50% ^{13}C-enriched CO, we obtain $Mo(CO)_6$ in the following distribution: 24% all-^{12}CO, 49% mono-^{13}CO, 26% bis-^{13}CO, and 1% tris-^{13}CO (and smaller amounts of higher enrichment, which we shall disregard for the purposes of the present study because of our limits of detection; see below). A tricarbonyl starting material, such as $C_8H_{10}Mo(CO)_3$, consists of 3% mono-^{13}CO and 97% all-^{12}CO. With 50% ^{13}C-enriched CO this would give $Mo(CO)_6$ in the distribution (to the nearest 1%) 12% all-^{12}CO, 37% mono-^{13}CO, 38% bis-^{13}CO, and 13% tris-^{13}CO. It was our goal to analyze the CO absorptions in these products in order to determine the stereochemical distribution of labeled molecules.

Experimental Section

Reagents. Norbornadienemolybdenum tetracarbonyl was prepared from the olefin and $Mo(CO)_6$.[4] $Mo(CO)_6$ was purchased from Climax Molybdenum Co. 1,3,5-Cyclooctatrienemolybdenum tricarbonyl was obtained by methods described previously.[2] The CO, 50% ^{13}CO-enriched, was purchased from Merck Sharpe and Dohme of Canada Ltd. and was stored and handled as described in previous publications.[3] All solvents used in the syntheses and spectroscopic studies were redistilled and stored under an atmosphere of nitrogen.

CO Substitution and Exchange Reactions. About 50 mg of the appropriate olefin complex in 3 ml of cyclohexane was placed in an atmosphere of ^{13}C-enriched CO for several days. The excess CO was then recovered and solvent removed under reduced pressure. From the residue molybdenum hexacarbonyl was sublimed out at 40° (0.1 mm).

The features observed in the spectrum of $Mo(CO)_6$ obtained from this procedure (see Discussion below) result only from the substitution reaction since exchange of ^{13}C-enriched CO with $Mo(CO)_6$ under identical conditions gave no observable change in its carbonyl spectrum.

One substitution reaction was arrested at an early stage in the formation of $Mo(CO)_6$ from $C_7H_8Mo(CO)_4$. Unconverted olefin complex was recovered; its spectrum showed only slight enrichment due to its own exchange with ^{13}C-enriched CO.[5] This exchange reaction was very much slower than the CO substitution reaction to produce $Mo(CO)_6$. A qualitative comparison of the growth of the ^{13}CO absorptions in the recovered olefin to the amount of $Mo(CO)_6$ produced leads us to estimate that the exchange reaction is only about one-tenth or less the rate of the substitution reaction.

Infrared Spectra. All spectra were recorded on the Beckman IR 4 spectrophotometer (LiF prism) and calibrated against the ν_2 fundamental of water vapor.[6] Cyclohexane was used as solvent in all cases in order to obtain optimum resolution in solution.

Calculations. Approximate force constants were calculated using the iterative program of Schachtschneider and Snyder.[7]

Results and Discussion

Carbonyl Absorptions of $Mo(CO)_6$ with ^{13}CO in Natural Abundance. The infrared spectrum of $Mo(CO)_6$ in the CO stretching region is shown in Figure 1, upper trace. The measured frequencies for the peaks identified by the letters are: a, 2108.7; b, 2009.3; c, 1988.4; d, 1956.3 cm^{-1}. Since the all-^{12}CO derivative is expected to give rise to only one infrared band, T_{1u} mode[8] (band c), the other peaks of much lower intensity most likely belong to molecules containing ^{13}CO; the mono-^{13}CO substituted derivative will be present in 6% natural abundance (other species more highly substituted by ^{13}CO will not be detectable in natural abundance at these concentrations).

Substitution of one ^{13}CO group into $Mo(CO)_6$ lowers the molecular symmetry to C_{4v} for which four infrared-active (3 A_1 and an E) and five Raman-active (the ir active plus a B_1) modes are expected. The symmetry co-

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(1) (a) Work supported by National Science Foundation Grant GP 6720. (b) For the previous paper in this series, see P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

(2) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966).

(3) (a) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *ibid.*, **89**, 2844 (1967); (b) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, **89**, 2851 (1967).

(4) R. Pettit, *ibid.*, **81**, 1266 (1959).

(5) R. W. Harrill, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1967, to be published.

(6) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Natl. Bur. Std.*, **64A**, 1 (1960).

(7) See footnote 14 in ref 3a.

(8) (a) L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962); (b) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963a); (c) J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

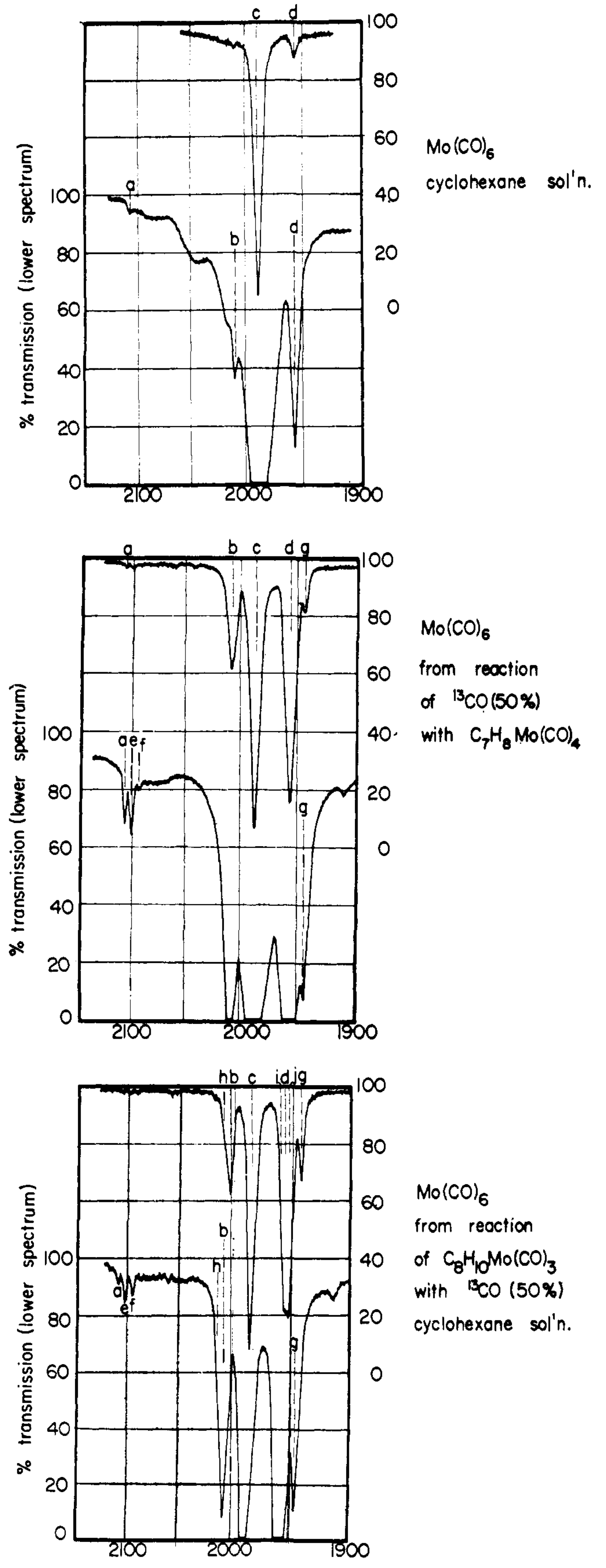


Figure 1. High-resolution infrared spectrum (LiF prism) in the carbonyl-stretching region for molybdenum hexacarbonyl containing ^{13}CO in natural abundance (upper trace) and for product obtained in the displacement of olefin by 50% ^{13}C-enriched CO from $C_7H_8Mo(CO)_4$ (middle trace) and $C_8H_{10}Mo(CO)_3$ (lower trace).

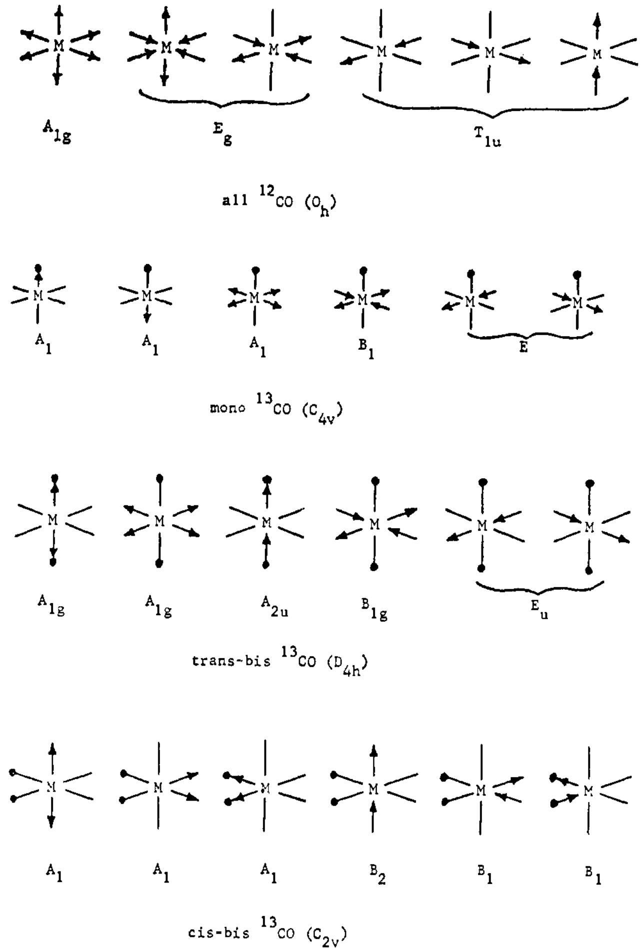


Figure 2. Internal symmetry coordinates for the all-^{12}CO and some ^{13}CO-substituted $Mo(CO)_6$ species. The position of ^{13}CO substitution is indicated by a heavy dot.

ordinates for these vibrations are given in Table I and are shown in Figure 2. Inspection of these shows that the E mode of the C_{4v} molecule is identical with the T_{1u} vibration of the all-^{12}CO molecule; these two will therefore appear at the same energy in the spectrum, under band c. The weak peaks, bands a, b, and d, are assigned to the three A_1 vibrations of the mono-^{13}CO molecule. Band a is assigned to the radial A_1 mode, band b to the mode of axial ^{12}CO, and band d to the mode of axial ^{13}CO. The observed A_1 modes of course will not be exactly those described by the symmetry coordinates, since these will interact and mix in the "normal" modes which correspond to the bands actually observed.

Within the carbonyl block there are only three force constants to be determined: the carbonyl stretching force constant k and the interaction force constants k_{cis} (k_c) and k_{trans} (k_t).[8] These are calculated from the available data. Band c is obviously the T_{1u} vibration of the all-^{12}CO species while bands a, b, and d are the absorptions of the mono-^{13}CO-substituted species in natural abundance. The assignments and results are summarized in Table II.

From these particular force constants, and with the appropriate changes in the G-matrix elements, frequencies of all possible ^{13}CO-substituted $Mo(CO)_6$ molecules can be obtained; the computer is in that case instructed to stop after zero perturbations. The

Table I. Symmetry Coordinates and Secular Equations for the All-^{12}CO and Some ^{13}CO-Substituted Species of Mo(CO)$_6$

Molecule	Symmetry species	Symmetry coordinate	Secular equation[a]
All-^{12}CO	A$_{1g}$	$S_1 = \frac{1}{\sqrt{6}}(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$	$\lambda_1 = \mu_{^{12}\text{CO}}(k + k_t + 4k_c)$
	E$_g$	$S_{2a} = \frac{1}{2\sqrt{3}}(2r_1 - r_2 - r_3 - r_4 - r_5 + 2r_6)$	$\lambda_2 = \mu_{^{12}\text{CO}}(k + k_t - 2k_c)$
		$S_{2b} = \frac{1}{2}(r_2 - r_3 + r_4 - r_5)$	
	T$_{1u}$	$S_{3a} = \frac{1}{\sqrt{2}}(r_1 - r_6)$	$\lambda_3 = \mu_{^{12}\text{CO}}(k - k_t)$
		$S_{3b} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	
		$S_{3c} = \frac{1}{\sqrt{2}}(r_3 - r_5)$	
Mono-^{13}CO C$_{4v}$	A$_1$	$S_4 = r_1$	$\lambda_4 = \mu_{^{13}\text{CO}}k$
	A$_1$	$S_5 = \frac{1}{2}(r_2 + r_3 + r_4 + r_5)$	$\lambda_5 = \mu_{^{12}\text{CO}}(k + k_t + 2k_c)$
	A$_1$	$S_6 = r_6$	$\lambda_6 = \mu_{^{12}\text{CO}}k$
	B$_1$	$S_7 = \frac{1}{2}(r_2 - r_3 + r_4 - r_5)$	$\lambda_7 = \mu_{^{12}\text{CO}}(k + k_t - 2k_c)$
	E	$S_{8a} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_8 = \mu_{^{12}\text{CO}}(k - k_t)$
		$S_{8b} = \frac{1}{\sqrt{2}}(r_3 - r_5)$	
trans-Bis-^{13}CO D$_{4h}$	A$_{1g}$	$S_9 = \frac{1}{\sqrt{2}}(r_1 + r_6)$	$\lambda_9 = \mu_{^{13}\text{CO}}(k + k_t)$
	A$_{1g}$	$S_{10} = \frac{1}{2}(r_2 + r_3 + r_4 + r_5)$	$\lambda_{10} = \mu_{^{12}\text{CO}}(k + k_t + 2k_c)$
	A$_{2u}$	$S_{11} = \frac{1}{\sqrt{2}}(r_1 - r_6)$	$\lambda_{11} = \mu_{^{13}\text{CO}}(k - k_t)$
	B$_{1g}$	$S_{12} = \frac{1}{2}(r_2 - r_3 + r_4 - r_5)$	$\lambda_{12} = \mu_{^{12}\text{CO}}(k + k_t - 2k_c)$
	E$_u$	$S_{13a} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_{13} = \mu_{^{12}\text{CO}}(k - k_t)$
		$\mathrm{S}_{13b} = \frac{1}{\sqrt{2}}(r_3 - r_5)$	
cis-Bis-^{13}CO C$_{2v}$	A$_1$	$S_{14} = \frac{1}{\sqrt{2}}(r_1 + r_6)$	$\lambda_{14} = \mu_{^{12}\text{CO}}(k + k_t)$
	A$_1$	$S_{15} = \frac{1}{\sqrt{2}}(r_2 + r_3)$	$\lambda_{15} = \mu_{^{13}\text{CO}}(k + k_c)$
	A$_1$	$S_{16} = \frac{1}{\sqrt{2}}(r_4 + r_5)$	$\lambda_{16} = \mu_{^{12}\text{CO}}(k + k_c)$
	B$_1$	$S_{17} = \frac{1}{\sqrt{2}}(r_2 - r_3)$	$\lambda_{17} = \mu_{^{13}\text{CO}}(k - k_c)$
	B$_1$	$S_{18} = \frac{1}{\sqrt{2}}(r_4 - r_5)$	$\lambda_{18} = \mu_{^{12}\text{CO}}(k - k_c)$
	B$_2$	$S_{19} = \frac{1}{\sqrt{2}}(r_1 - r_6)$	$\lambda_{19} = \mu_{^{12}\text{CO}}(k - k_t)$

[a] Diagonal elements.

Table II. Comparison of Calculated and Observed Frequencies for Mo(CO)$_6$

Molecule	Vib activity		Input	Calcd[a]	Obsd	Band designation
All-^{12}CO O$_h$	A$_{1g}$	R		2114.5	(2119)[b]	
	E$_g$	R		2016.8	(2021)[b]	c
	T$_{1u}$	ir	1988.4	1988.2	1988.4	
Mono-^{13}CO C$_{4v}$	A$_1$	R-ir	2108.7	2108.7	2108.7	a
	A$_1$	R-ir	2009.3	2009.3	2009.3	b
	A$_1$	R-ir	1956.3	1956.6	1956.6	d
	B$_1$	R		2016.8	. . .[c]	
	E	R-ir		1988.2	. . .[c]	

[a] These are associated with the following force constants: $k = 16.473$, $k_c = 0.272$, and $k_t = 0.504$ mdynes/Å. [b] From ref 8, in CHCl$_3$ solution. [c] Obscured by mode of all-^{12}CO molecule.

new bands appearing in multiple ^{13}CO-substituted Mo(CO)$_6$ can now be compared with the calculated values.

Carbonyl Absorptions of Mo(CO)$_6$ Obtained from C$_7$H$_8$Mo(CO)$_4$ and 50% ^{13}C-Enriched CO. The absorptions of Mo(CO)$_6$ produced from the reaction of C$_7$H$_8$Mo(CO)$_4$ and 50% ^{13}C-enriched CO have been shown in Figure 1, middle spectrum. As expected the peaks labeled a, b, and d due to mono-^{13}CO species have increased substantially in intensity compared to band c, which is the T$_{1u}$ fundamental of the all-^{12}CO molecule. It was expected that the product would contain 49% of the mono-^{13}CO species with only 24% of the all-^{12}CO molecules remaining. In addition, three new peaks have appeared: bands e, f, and g which are measured at 2102.2, 2094.0, and 1944.0 cm^{-1}, respectively. Bands b and d appear to be somewhat broadened.

Table III. Comparison of Calculated and Observed Frequencies for Bis- and Tris-^{13}CO-Substituted $Mo(CO)_6$

	Vib species	Activity	Calcd	Observed from $C_7H_8Mo(CO)_4$	Observed from $C_8H_{10}Mo(CO)_3$	Letters[a]
trans-Bis-^{13}CO	A_{1g}	R	2102.9			
D_{4h}	A_{1g}	R	1982.8	...	...	
	B_{1g}	R	2016.8	...	...	
	A_{2u}	ir	1943.9	1944.0	1943.7	g
	E_u	ir	1988.2	...[b]	...[b]	
cis-Bis-^{13}CO	A_1	ir, R	2102.3	2102.2	2102.2	e
C_{2v}	A_1	ir, R	2012.6	...	2011.8	h
	B_1	ir, R	2006.6	...	2007.8	b
	A_1	ir, R	1959.3	...	1957.5[c]	i
	B_1	ir, R	1953.8	...	1954.8	j
	B_2	ir, R	1988.2	...[b]	...[b]	
All-*cis*-tris-^{13}CO	A_1	ir, R	2095.0	2094.0	2094.5	f
C_{3v}	E	ir, R	2006.0	...[d]	...[d]	
	A_1	ir, R	1962.0			
	E	ir, R	1953.8			
cis–trans-Tris-^{13}CO	A_1	ir, R	2095.8			
C_{2v}	A_1	ir, R	2011.0			
	A_1	ir, R	1983.3	...[d]	...[d]	
	A_1	ir, R	1943.9			
	B_1	ir, R	1955.6			
	B_2	ir, R	1988.2			

[a] See Figure 1 for identification of peaks corresponding to each letter. [b] Degenerate with E mode of all-^{12}CO molecule. [c] Probably a combination of the 1956.6-cm^{-1} band of the mono-^{13}CO molecule and the 1959.3-cm^{-1} band of the *cis*-bis-^{13}CO molecule. [d] Probably not observed because of a mono- or disubstituted $Mo(CO)_6$ absorption.

Two bis-^{13}CO isomers totaling to 26% of this $Mo(CO)_6$ mixture are possible. If the $Mo(CO)_4$ groups of the original olefin complex were to retain their relative configuration, only the *cis*-bis-^{13}CO species (C_{2v} symmetry) would be produced. The other possibility is the *trans*-bis-^{13}CO isomer of D_{4h} symmetry. For the latter, two infrared-active (an A_{2u} and an E_u) and three Raman-active (2 A_{1g} and a B_{1g}) modes are expected. The symmetry coordinates for these modes have been given in Table I and are illustrated in Figure 2. Comparison of these symmetry coordinates to those of the all-^{12}CO molecule shows that the E_u mode is identical with the T_{1u} vibration. The A_{2u} vibration is related to the T_{1u}, but should be shifted to lower energy due to the expected isotope shift for ^{13}CO. The other modes are Raman active only. Therefore, the presence of the *trans*-bis-^{13}CO-$Mo(CO)_6$ can be confirmed in the infrared in this mixture only by the appearance of the A_{2u} absorption.

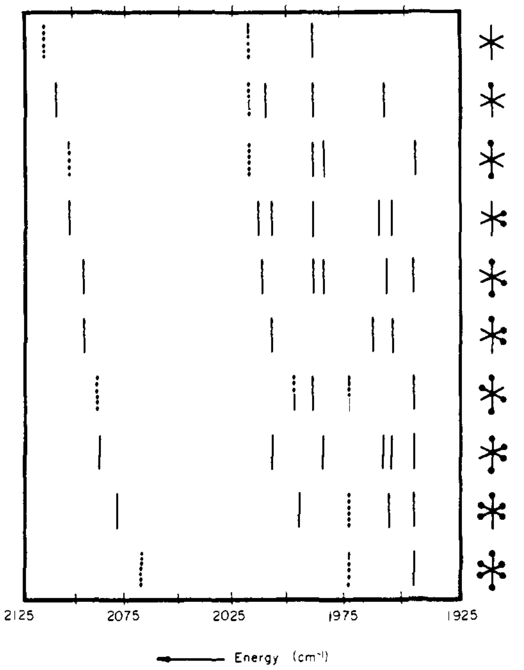


Figure 3. Calculated frequencies for all possible ^{13}CO-substituted $Mo(CO)_6$ species using the force constants obtained from the frequencies of the all-^{12}CO species (top line). The position of ^{13}CO substitution is indicated by a heavy dot. The vertical dashed lines represent Raman-active modes, while the heavy blacklines represent either ir- or Raman–ir-active modes.

Six modes are expected for the C_{2v} molecule (three A_1, two B_1, and a B_2), all of which are active in the infrared and in the Raman. The symmetry coordinates for these modes have been given in Table I and are also shown in Figure 2. The B_2 vibration is identical with the T_{1u} of the all-^{12}CO molecule. Two of the remaining modes, an A_1 and a B_1, which involve motions of the ^{13}CO groups, will be expected at lower energy from the B_2 vibration (actually in the spectrum these will appear at lower energy from the T_{1u} vibration) due to the effect of ^{13}C-isotopic substitution.

The frequencies expected for these molecules were calculated starting from the force constants of the all-^{12}CO molecule. These are given in Table III, third column, and are illustrated in Figure 3.

In order to identify the calculated frequencies of the ^{13}CO-substituted molecules, it is necessary to correlate the species of the molecules of lower symmetry with those of the symmetry group O_h belonging to the all-^{12}CO species. This correlation is given in Table IV. The calculated frequencies of molecules of lower symmetry will then appear in the symmetry block of the species of O_h symmetry with which they are correlated. Thus the two infrared-active vibrations for the D_{4h} molecule are identified as the A_{2u} mode at 1943.9 and the E_u mode at 1988.2 cm^{-1}. Since the latter will be accidentally degenerate with the T_{1u} mode of the all-^{12}CO derivative, the A_{2u} band will be the only inde-

Table IV. Correlation between Symmetry Species for Isotopically Substituted $Mo(CO)_6$ Molecules and for All-^{12}CO $Mo(CO)_6$

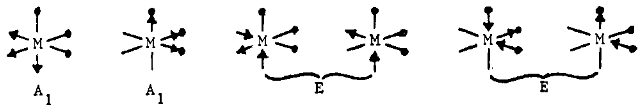
	All-^{12}CO	Mono-^{13}-CO	Bis-^{13}CO (*trans*)	Bis-^{13}CO (*cis*)
Group	O_h	C_{4v}	D_{4h}	C_{2v}
Species	A_{1g}	A_1	A_{1g}	A_1
	E_g	$A_1 + B_1$	$A_{1g} + B_{1g}$	$A_1 + A_2$
	T_{1u}	$A_1 + E$	$A_{2u} + E_u$	$A_1 + B_1 + B_2$

pendent absorption through which the presence of the D_{4h} molecule can be detected. For the C_{2v} isomer, six infrared-active modes are expected at 2102.3, 2012.6, and 1959.3 cm^{-1} for the A_1 modes, 2006.6 and 1988.2 cm^{-1} for the B_1 modes, and 1953.8 cm^{-1} for the B_2 mode.

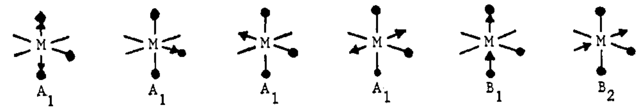
We are now ready to complete our assignment of the spectrum of $Mo(CO)_6$ obtained from $C_7H_8Mo(CO)_4$ and 50% ^{13}C-enriched CO. Band e at 2102.2 cm^{-1} undoubtedly belongs to the *cis*-bis-^{13}CO species; it compares excellently with the predicted high-energy A_1 mode of that molecule, calculated at 2102.3 cm^{-1}. Band g which appears at 1944.0 cm^{-1} must be the A_{2u} mode of the *trans*-bis-^{13}CO molecule, calculated at 1943.9 cm^{-1}. No peak near this value is calculated for the *cis*-bis-^{13}CO isomer. *It thus appears that the configuration of the four CO groups in $C_7H_8Mo(CO)_4$ starting material is not preserved in the $Mo(CO)_6$ product.*

In concluding our analysis of the spectrum of this product, we explain the broadening of band b by the appearance of the A_1 and B_2 modes from the C_{2v} molecule, which are calculated at 2012.6 and 2006.6 cm^{-1}, respectively. Similarly, the broadening of band d results from the A_1 and B_1 modes of the *cis*-substituted molecule calculated at 1959.3 and 1953.8 cm^{-1}, respectively. The small peak, band f, is due to a tris-^{13}CO species, expected at a concentration of at least 1% (starting from $C_7H_8Mo(CO)_4$ with ^{13}CO at natural abundance) or more because of some slow exchange of olefin complex before its conversion to $Mo(CO)_6$; see Experimental Section.

Carbonyl Absorptions of $Mo(CO)_6$ Obtained from $C_8H_{10}Mo(CO)_3$ and 50% ^{13}C-Enriched CO. The absorptions of $Mo(CO)_6$ obtained from $C_8H_{10}Mo(CO)_3$ and ^{13}C-enriched CO are shown on Figure 1, lower trace. As expected, even less of the all-^{12}CO species is present with larger amounts of ^{13}CO-substituted species (see introductory section). Owing to the several near-coincidences of bands expected for the various multiple ^{13}CO-substituted species, the maximum of band b (originally assigned to mono-^{13}CO in $Mo(CO)_6$ at natural abundance) is observed to have shifted to 2007.0 cm^{-1} (compared to 2009.3 cm^{-1} before). Also, a shoulder at about 2012 cm^{-1} is detected on this band. The *cis*-bis-^{13}CO derivative (discussed above) is expected to display a B_2 mode (calculated, 2006.6 cm^{-1}) and one of its A_1 modes (2012.6 cm^{-1}) in this vicinity. In addition two maxima i and j are resolved on both sides of the peak labeled b, which also account for a perceptible broadening of this band; the two maxima are measured at 1957.5 and 1954.8 cm^{-1}. Band i appears to be a composite peak at an average position between an A_1 mode of the mono-^{13}CO species (calculated 1956.3 cm^{-1}) and an A_1 mode of the *cis*-bis-^{13}CO species (calculated 1959.3 cm^{-1}). Band j corresponds to the B_1 vibration of this latter species (calculated 1953.8 cm^{-1}). We also observe evidence for the *trans*-bis-^{13}CO species by the band g at 1943.7 cm^{-1}. *Thus in this substitution reaction like that in $C_7H_8Mo(CO)_4$ discussed above, the configuration of the original tricarbonyl grouping in $C_8H_{10}Mo(CO)_3$ was not retained.* In the resulting mixture of isotopically substituted $Mo(CO)_6$ a significant amount of tris-^{13}CO species is expected. At least 13% would result from $C_8H_{10}Mo(CO)_3$ containing ^{13}CO in natural abundance, or more if appreciable exchange of olefin complex with ^{13}CO occurred before conversion to $Mo(CO)_6$; see Experimental Section. However, the complexity of the carbonyl region does not permit a clear-cut assignment for any but band f; see Table III, above.



all cis-tris ^{13}CO (C_{3v})



cis-trans-tris ^{13}CO (C_{2v})

Figure 4. Internal symmetry coordinates for tris-^{13}CO-substituted $Mo(CO)_6$. The position of ^{13}CO substitution is indicated by a heavy dot.

Two isomers are possible for tris-^{13}CO-substituted $Mo(CO)_6$. One, in which the three ^{13}CO groups are *cis* to each other (all *cis*), possesses C_{3v} symmetry. The other, in which two of the ^{13}CO groups are *trans* to each other (*cis–trans* isomer), has C_{2v} symmetry. Four infrared- (and Raman-) active modes, 2 A_1 and 2 E modes, are expected for the C_{3v} molecule. These modes are described by the symmetry coordinates shown in Figure 4. From symmetry considerations, these vibrations can be considered as two independent groups, $M(^{12}CO)_3$ and $M(^{13}CO)_3$, each giving rise to an A_1 and an E mode, with the ^{12}CO at high energy and the ^{13}CO group at low energy. Six modes are expected for the C_{2v} molecule of symmetry species A_1 (four), B_1, and B_2. The symmetry coordinates for these have been given in Table V. The B_2 mode is identical with the T_{1u} mode of the all-^{12}CO molecule. The frequencies calculated for the tris-^{13}CO-substituted species are shown in Table III. From this it is seen that band f, which appears at 2094.5 cm^{-1}, could result from the high-energy A_1 mode of one or *both* isomers, calculated at 2095.0 and 2095.8 cm^{-1} for the C_{3v} and C_{2v} isomers, respectively. All the other peaks expected for these molecules either are obscured by the absorptions of the less substituted molecules or are too weak to be observed. A higher degree of ^{13}C enrichment would be needed to sort out the vibrations of the tris (and higher substituted) species comparable to the analyses which were possible for the bis-^{13}CO species.

Table V. Symmetry Coordinates and Secular Equations for the Tris-^{13}CO-Substituted Species of Mo(CO)$_6$

Molecule	Vib	Symmetry coordinate	Secular equation
All-*cis*-tris-^{13}CO C_{3v}	A_1	$S_1 = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$	$\lambda_1 = \mu_{^{12}\mathrm{CO}}(k + 2k_c)$
	A_1	$S_2 = \frac{1}{\sqrt{3}}(r_4 + r_5 + r_6)$	$\lambda_2 = \mu_{^{13}\mathrm{CO}}(k + 2k_c)$
	E	$S_{3a} = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$	$\lambda_3 = \mu_{^{12}\mathrm{CO}}(k - k_c)$
		$S_{3b} = \frac{1}{\sqrt{2}}(r_2 - r_3)$	
	E	$S_{4a} = \frac{1}{\sqrt{6}}(2r_4 - r_5 - r_6)$	$\lambda_4 = \mu_{^{13}\mathrm{CO}}(k - k_c)$
		$S_{4b} = \frac{1}{\sqrt{2}}(r_5 - r_6)$	
cis-trans-Tris-^{13}CO C_{2v}	A_1	$S_5 = r_1$	$\lambda_5 = \mu_{^{12}\mathrm{CO}}k$
	A_1	$S_6 = \frac{1}{\sqrt{2}}(r_2 + r_4)$	$\lambda_6 = \mu_{^{12}\mathrm{CO}}(k + k_t)$
	A_1	$S_7 = \frac{1}{\sqrt{2}}(r_3 + r_5)$	$\lambda_7 = \mu_{^{13}\mathrm{CO}}(k + k_t)$
	A_1	$S_8 = r_6$	$\lambda_8 = \mu_{^{13}\mathrm{CO}}k$
	B_1	$S_9 = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_9 = \mu_{^{12}\mathrm{CO}}(k - k_t)$
	B_2	$S_{10} = \frac{1}{\sqrt{2}}(r_3 - r_5)$	$\lambda_{10} = \mu_{^{13}\mathrm{CO}}(k - k_t)$

Conclusion

It has been possible to assign the bands for ^{13}CO-substituted species in mixtures of ^{13}CO-enriched Mo(CO)$_6$. For the bis-^{13}CO species both possible isomers, the *cis* and *trans*, were observed to be present, indicating that the carbonyl groups in the original olefin complexes did not preserve their stereochemistry during the displacement of olefin by CO. It is evident that substitution proceeds through some intermediate in which the CO groups lose their stereochemical distinction, perhaps by a valence tautomerism at a rate that is rapid compared to the half-life of such a species. We can envisage rapid valence tautomerism in either a five-coordinate intermediate (achieved *via* a dissociative mechanism) or a seven-coordinate intermediate (*via* a bimolecular process). This system certainly offers rich promise for future studies. Quantitative information about the distribution of stereoisomers would also be highly desirable.

If valence tautomerism in the final product itself is sufficiently slow (or even possibly nonexistent) the use of ^{13}C nmr would certainly give some important additional information. Further studies on these systems are now in progress in our laboratory.

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