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Photochemical Substitution Reactions of Group 6B Metal Tetracarbonyl Norbornadiene Complexes with ^{13}CO , Kinetics of Subsequent Thermal Rearrangements in the Stereospecifically Labeled Species, and Relationship of These Results to the Photoinduced Hydrogenation Process

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Abstract: Photochemical substitution reaction ($\lambda > 2800 \text{ \AA}$) of $\text{M}(\text{CO})_4(\text{NBD})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$ and $\text{NBD} = \text{norbornadiene}$) with ^{13}CO have been shown via infrared spectroscopy, coupled with ^{13}C NMR, to occur with preferential loss of an axial CO ligand. Further rearrangement of the stereospecifically ^{13}CO labeled $\text{M}(\text{CO})_4(\text{NBD})$ species results upon thermal and/or photochemical activation. A mechanism for this rearrangement in the tungsten derivative has been proposed based on kinetic measurements (both for the rearrangement process and diolefin substitution with phosphines) which involves cleavage of one metal-olefin bond, followed by a Berry permutation. The results of thermal and photochemical hydrogenation of norbornadiene in the presence of group 6b hexacarbonyls are explained employing CO dissociation as well as metal-olefin bond cleavage.

Introduction

Several studies on photoinduced hydrogenation of conjugated dienes in the presence of chromium carbonyl complexes have been published in recent years.¹⁻⁴ Chromium tetracarbonyl norbornadiene has been implicated as an intermediate in the photoassisted hydrogenation² and dimerization⁵ of norbornadiene with chromium hexacarbonyl. Although metal carbonyl derivatives have been demonstrated to readily lose carbonyl ligands upon photolysis,⁶⁻⁸ Platbrood and Wilputte-Steinert have concluded, based on an extensive mechanistic investigation of the photoinduced hydrogenation of (norbornadiene) $\text{Cr}(\text{CO})_4$, that the primary photochemical process in these reactions involves a metal-olefin bond rupture.² Similarly, thermal hydrogenation of 1,3-dienes involving chromium carbonyl complexes as catalysts have been investigated,^{9,10} and Schroeder and Wrighton¹⁰ have proposed that these reactions proceed through an intermediate common with that of the photocatalyzed process, (diene) $\text{Cr}(\text{CO})_3\text{H}_2$. During this time we published our initial investigation of photochemical substitution reactions of group 6b metal tetracarbonyl norbornadiene with ^{13}CO which indicated that these species were rapidly enriched with ^{13}CO .¹¹ Recently, Platbrood

and Wilputte-Steinert¹² have as well shown that photochemical reaction of (norbornadiene) $\text{Cr}(\text{CO})_4$ with triphenylphosphine leads to the production of *mer*-(norbornadiene) $\text{Cr}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ which was in agreement with earlier, less definitive work of King and Korenowski¹³ on photochemical reactions of (norbornadiene) $\text{W}(\text{CO})_4$ with $\text{As}(\text{C}_6\text{H}_5)_3$ and $\text{Sb}(\text{C}_6\text{H}_5)_3$. These workers¹² also observed that the rate of $\text{P}(\text{C}_6\text{H}_5)_3$ substitution into (norbornadiene) $\text{Cr}(\text{CO})_4$ and the rate of hydrogenation of (norbornadiene) $\text{Cr}(\text{CO})_4$ were similar, thus indicating that CO dissociation is possibly the rate-determining step in the hydrogenation process.

In addition to the interest in (norbornadiene) $\text{M}(\text{CO})_4$ derivatives as catalysts in the photochemical hydrogenation process of norbornadiene, a model system for the general diene photoinduced hydrogenation in the presence of hexacarbonyls, we have been interested in the stereospecificity of photochemical substitution reactions of substituted metal carbonyl derivatives in general.^{14,15} For these reasons we have examined the stereoselectivity of group 6b metal tetracarbonyl norbornadiene species toward photochemical substitution processes with ^{13}CO as well as subsequent thermal rearrangements of some of the ^{13}CO substituted species. This report represents a detailed presentation of our earlier communication,¹¹ as well

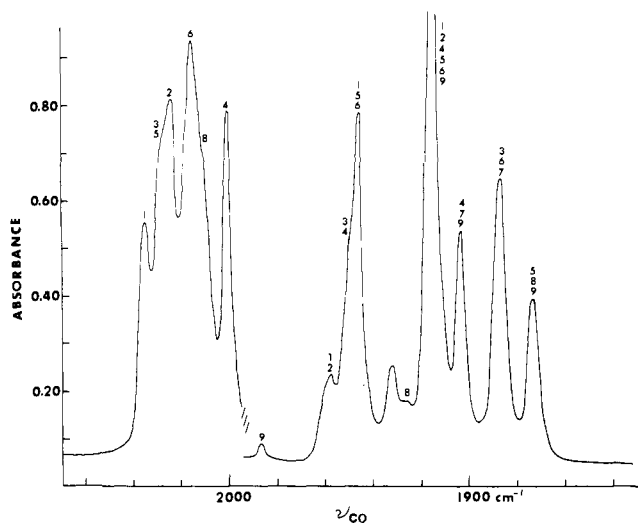


Figure 1. $\nu(\text{CO})$ infrared spectrum of ^{13}CO enriched $(\text{NBD})\text{Cr}(\text{CO})_4$ in hexane solution. The numbers refer to the species which afford these absorptions as listed in Table I.

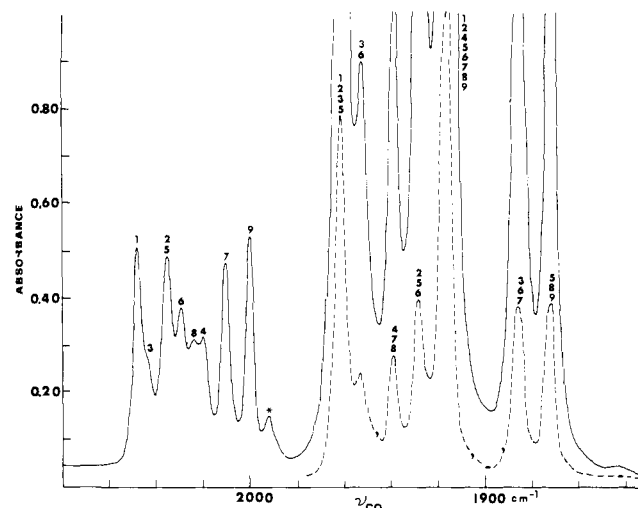


Figure 2. $\nu(\text{CO})$ infrared spectrum of ^{13}CO enriched $(\text{NBD})\text{Mo}(\text{CO})_4$ in hexane solution. The numbers refer to the species which afford these absorptions as listed in Table I. The band due to a trace quantity of hexacarbonyl is indicated by an asterisk.

as further studies defining the mechanism of the photochemical hydrogenation of norbornadiene in the presence of group 6b metal carbonyls.

Experimental Section

Chromium, molybdenum, and tungsten tetracarbonyl norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) were synthesized by previously described methods.¹⁶ Reagent grade hexane (Mallinckrodt) was distilled from silica gel. Carbon monoxide of 93% ^{13}C isotopic abundance was obtained from Monsanto Research Corp., Miamisburg, Ohio.

Photochemical ^{13}CO Incorporation Experiments. Irradiation of the $\text{M}(\text{CO})_4(\text{NBD})$ complexes was carried out in a water-cooled 25-ml Pyrex cell employing a 450-W Hanovia Mercury lamp ($\lambda > 2800 \text{ \AA}$) for $\text{M} = \text{Cr}, \text{W}$ and a 100-W lamp for the photochemically less stable species where $\text{M} = \text{Mo}$. A carbon monoxide atmosphere enriched in carbon-13 to 93% was continuously recirculated through a hexane solution of the complex in a closed system by means of a variable-speed Masterflex tubing pump (Cole-Parmer Co.).¹⁷

The course of the ^{13}CO enrichment reactions was followed by withdrawing samples with a hypodermic syringe at various time intervals. Infrared spectral measurements in the $\nu(\text{CO})$ region were used to monitor the extent of ^{13}CO enrichment. Samples prepared for infrared spectral analysis containing a high degree of CO incorporation

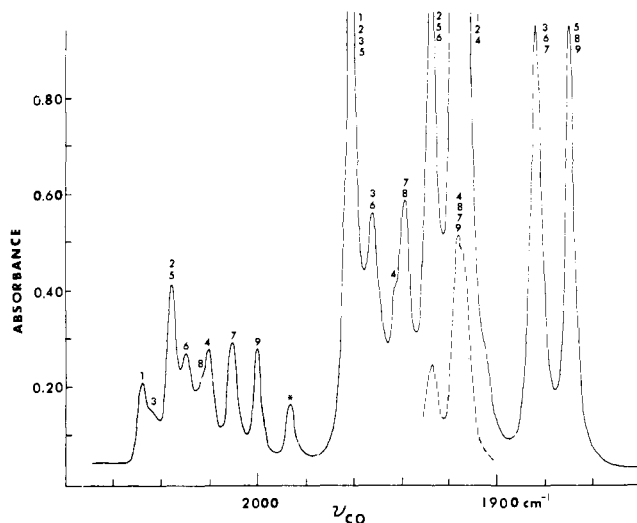


Figure 3. $\nu(\text{CO})$ infrared spectrum of ^{13}CO enriched $(\text{NBD})\text{W}(\text{CO})_4$ in hexane solution. The numbers refer to the species which afford these absorptions as listed in Table I. The band due to a trace quantity of hexacarbonyl is indicated by an asterisk.

were purified by vacuum removal of hexane, followed by sublimation of the ^{13}CO enriched complex. The irradiation times required for obtaining highly enriched ^{13}CO samples were 15, 40, and 10 min for the Cr, Mo, and W derivatives, respectively. Figures 1–3 illustrate the $\nu(\text{CO})$ spectra obtained from this procedure. On the other hand, in order to obtain more meaningful results on the initial products of photochemical substitution reactions as well as for studies involving rearrangements of mono- ^{13}CO substituted species, it was necessary to isolate samples after shorter reaction times (2–20 min). These samples were handled by rapid filtration of the irradiated solutions, followed by removal of the solvent at $\sim 0^\circ\text{C}$ with no further purification.

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.

The observed $\nu(\text{CO})$ frequencies ($\pm 0.5 \text{ cm}^{-1}$) and their assignments are listed in Table I along with the calculated values. Initial CO stretching force constant calculations were performed using only the ^{12}CO frequency data and a modified Cotton-Kraihanzel¹⁸ approach refined by Jernigan, Brown, and Dobson,¹⁹ and employing a program developed in our laboratories.²⁰ The trial force constants were refined using the ^{13}CO frequency data and an iterative computer program²¹ 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 to within an average of $< 1.0 \text{ cm}^{-1}$.

Kinetics of Thermal Rearrangement. Samples were enriched with ^{13}CO as described in the previous section. $(\text{NBD})\text{W}(\text{CO})_4$ was irradiated for 5 min with a 450-W lamp in hexane. The solution was immediately cooled with dry ice-acetone, and the solvent was removed under vacuum, taking care to keep the solution below room temperature. The enriched product was generally not further purified to avoid loss of some of the desired stereospecificity. One enriched sample of $(\text{NBD})\text{W}(\text{CO})_4$ was purified by sublimation at 80°C with a loss of about 30% of the stereospecificity. Rearrangement rates were observed to be the same, however, whether purified or unpurified ^{13}CO enriched complexes were employed in the measurements. It should be noted parenthetically that the impurity appears to be insoluble in hexane solvent. Typical samples for carrying out thermal rearrangement studies had an axial-equatorial mono- ^{13}CO ratio of 3.0–3.5 (see Figure 4, bands a and e; the corresponding ratio for the natural abundance ^{13}CO sample is 1.1) and were about 30% enriched with one ^{13}CO ligand. These samples contained only trace quantities of disubstituted ^{13}CO species (see Figure 4, bands a_2 and e_2).

Similarly, enriched samples of the analogous molybdenum complex were prepared by radiation with a 100-W lamp for 20 min. These

Table I. Observed and Calculated Wave Numbers for (NBD)M(CO)₄ in Hexane (cm⁻¹)

Molecule	Symmetry	M = Cr		M = Mo		M = W	
		Obsd ^a	Calcd	Obsd ^a	Calcd	Obsd ^a	Calcd
(NBD)M(¹² CO) ₄ (C _{2v})	A ₁	(2030.2)	2030.0	(2044.0)	2041.9	(2042.0)	2041.3
	A ₁	(1955.7)	1955.9	(1959.4)	1959.7	(1956.0)	1956.0
	B ₁	(1944.2)	1944.2	1959.4	1957.3	1956.0	1955.5
	B ₂	(1913.2)	1913.9	(1914.2)	1914.1	(1909.2)	1908.8
(NBD)M(¹² CO) ₃ (¹³ CO) (C _s) ax	A'	2019.1	2015.7	2031.1	2030.8	(2029.0)	2029.2
	A'	<i>b</i>	1954.8	<i>b</i>	1959.1	<i>b</i>	1955.9
	A'	<i>b</i>	1915.5	(1926.2)	1924.7	(1924.5)	1923.6
	A''	1913.2	1913.9	1914.2	1914.1	1909.2	1908.8
(NBD)M(¹² CO) ₃ (¹³ CO) (C _s) eq	A'	2026.0 (s)	2027.9	2037.0 (s)	2036.9	2038.5 (s)	2037.0
	A'	<i>c</i>	1944.5	1950.8	1949.9	1948.0	1945.4
	A'	(1884.9)	1884.2	(1884.1)	1885.8	(1879.6)	1880.5
	A''	1944.2	1944.2	1959.4	1957.3	1956.0	1955.5
(NBD)M(¹² CO) ₂ (¹³ CO) ₂ (C _{2v}) ax	A ₁	1998.7	1996.2	2015.9	2017.0	2015.5	2013.4
	A ₁	<i>c</i>	1944.7	1937.0	1939.7	1939.1	1939.0
	B ₁	(1901.0)	1900.9	<i>b</i>	1913.7	1912.6	1912.0
	B ₂	1913.2	1913.9	1914.2	1914.1	1909.2	1908.8
(NBD)M(¹² CO) ₂ (¹³ CO) ₂ (C _{2v}) eq	A ₁	<i>b</i>	2026.0	<i>b</i>	2031.7	<i>b</i>	2032.9
	A ₁	<i>b</i>	1916.2	<i>b</i>	1925.7	<i>b</i>	1920.4
	B ₁	1944.2	1944.2	1959.4	1957.3	1956.0	1955.5
	B ₂	(1871.3)	1871.3	(1870.2)	1871.5	(1866.5)	1866.3
(NBD)M(¹² CO) ₂ (¹³ CO) ₂ (C ₁) ax-eq	A	2012.1	2012.7	2024.8	2024.2	2024.2	2023.6
	A	<i>c</i>	1944.5	<i>b</i>	1951.5	<i>b</i>	1947.5
	A	<i>b</i>	1915.5	<i>b</i>	1924.2	<i>b</i>	1922.8
	A	<i>b</i>	1884.0	<i>b</i>	1885.5	<i>b</i>	1880.2
(NBD)M(¹² CO)(¹³ CO) ₃ (C _s) diax-eq	A'	<i>d</i>	1990.3	2006.2	2007.1	2005.1	2004.8
	A'	<i>b</i>	1937.5	<i>b</i>	1935.1	1934.8	1933.1
	A'	<i>b</i>	1883.9	<i>b</i>	1885.3	<i>b</i>	1880.1
	A''	<i>b</i>	1900.0	<i>b</i>	1913.7	1912.6	1912.0
(NBD)M(¹² CO)(¹³ CO) ₃ (C _s) dieq-ax	A'	2008.0 (s)	2010.1	2018.6	2017.8	2018.5 (s)	2018.5
	A'	1923.4	1922.3	<i>b</i>	1937.1	1934.8	1933.7
	A'	<i>b</i>	1909.8	<i>b</i>	1915.5	<i>b</i>	1912.4
	A''	1871.3	1871.3	1870.2	1871.5	1866.5	1866.3
(NBD)M(¹³ CO) ₄	A ₁	1984.5	1984.9	1998.0	1996.5	1994.3	1995.9
	A ₁	<i>b</i>	1912.3	<i>b</i>	1916.1	<i>b</i>	1912.5
	B ₁	1901.0	1900.9	<i>b</i>	1913.7	1912.6	1912.0
	B ₂	1871.3	1871.3	1870.2	1871.5	1866.5	1866.3

^a Frequencies in parentheses used as input data. ^b Buried beneath other, more prominent bands. ^c A shoulder on the 1944.2 cm⁻¹ band at about 1948 cm⁻¹ may be attributed to these vibrational modes. ^d This vibration was not observed.

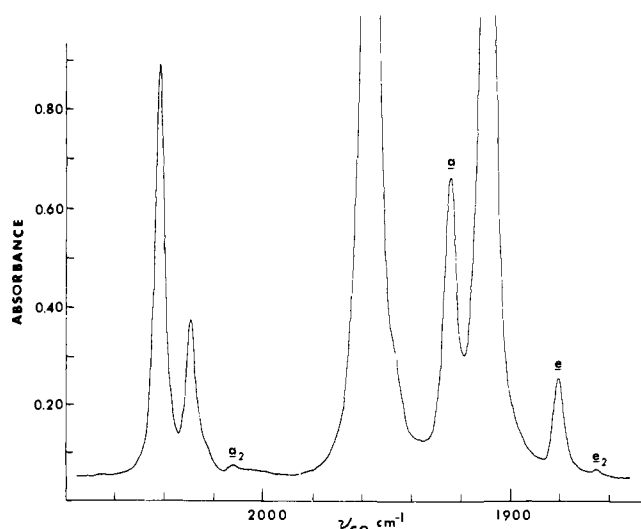


Figure 4. $\nu(\text{CO})$ spectrum of $\text{W}(\text{CO})_4(\text{NBD})$ in hexane. Sample primarily enriched with one ¹³CO prior to carbonyl ligand rearrangement.

samples had an axial-equatorial mono-¹³CO ratio of about 4.0 (see Figure 5). The natural abundance ratio was determined to be ~1.3.

The kinetic studies were run in hexane solution in 20-ml thick-walled tubes fitted with Teflon stopcocks and rubber septum caps. The reaction flasks were placed in a Tamson constant-temperature bath equipped with a Portable Bath Cooler with a constant-temperature control of ± 0.05 °C. Samples for IR spectral analysis were withdrawn periodically with a hypodermic syringe. In most instances it was possible to follow both the disappearance of the mono-¹³CO axial species (band a in Figure 4) and the appearance of the mono-¹³CO equatorial species (band e in Figure 4). Figure 6 illustrates the $\nu(\text{CO})$ spectrum after rearrangement has occurred.

Rate constants were calculated using a linear least-squares computer program for the first-order rate plots of $\ln(A_1 - A_e)$ vs. time, where A_1 is the absorbance of band a or e in Figure 4 and A_e is the absorbance of the respective band at equilibrium. The reactions were observed to yield linear plots over several half-lives.

In the case of the molybdenum complex much decomposition occurred during the rearrangement process. The decomposition rate was independently measured on nonenriched samples and, therefore, provides an approximate correction to the rearrangement kinetic data.

Photochemical and Thermal Hydrogenation Experiments. Hydrogenation reactions were carried out in spectrograde hydrocarbon solvents under 1 atm of hydrogen pressure. The photochemical hydrogenation studies were performed in the vessel used in the ¹³CO enrichment experiments previously described employing a 450-W Hanovia mercury lamp ($\lambda > 2800$ Å). All solutions were purged with H₂ for approximately 30 min prior to the introduction of the metal catalyst and substrate. A slow stream of hydrogen gas was passed through the reaction flask during the entire hydrogenation process.

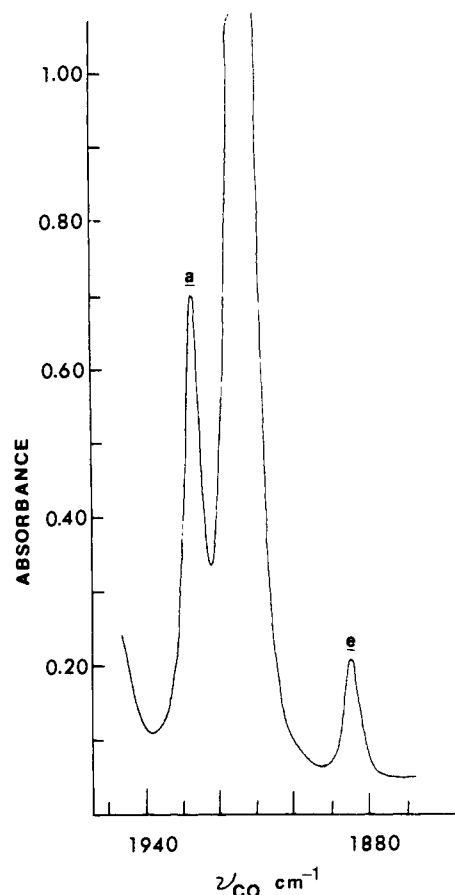


Figure 5. $\nu(\text{CO})$ spectrum of $\text{Mo}(\text{CO})_4(\text{NBD})$ in hexane. Sample primarily enriched with one ^{13}C prior to carbonyl ligand rearrangement.

A dry ice-acetone cold trap was incorporated into the reaction system to avoid possible loss of volatile products. Samples were withdrawn periodically with a syringe during the hydrogenation reactions, and the products were analyzed by gas-liquid chromatography (Fisher Model 2400 with a thermal conductivity detector). The column was a 9 ft, $\frac{1}{4}$ in. diameter aluminum tube packed with GE-SE-30 on Chromosorb W (80-100 mesh). Authentic samples of nortricyclene and norbornene were prepared by established procedures. Areas under the chromatograms were determined using a planimeter.

Results and Discussion

Photochemical Reactions. The $\text{M}(\text{CO})_4(\text{NBD})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) species were all found to readily incorporate ^{13}C upon photolysis employing wavelengths greater than 2800 \AA . Figures 1-3 illustrate the large degree of photoinduced carbonyl substitution which was observed. By following the time dependence of ^{13}C incorporation as indicated by the $\nu(\text{CO})$ spectra, and with the aid of restricted $\nu(\text{CO})$ force field calculations, it was possible to assign bands belonging to the same molecule. Table I contains the calculated and observed $\nu(\text{CO})$ bands with their assignments for the ^{13}C enriched species of the group 6b metal $\text{M}(\text{CO})_4(\text{NBD})$ derivatives. These various species are depicted in Figure 7. As noted in Table I the $\nu(\text{CO})$ frequencies for $\text{M}(\text{CO})_{4-x}(\text{CO})_x(\text{NBD})$ ($x = 0-4$) can be fitted with a mean error of $<1.0 \text{ cm}^{-1}$. The refined force constants for the tetracarbonyl derivatives are shown in Table II.

Perutz and Turner have demonstrated the usefulness of restricted CO stretching force fields in predicting isotopic spectra and structural information of metal carbonyl fragments.^{22,23} Our observations reported here, as well as elsewhere,²⁴ clearly add further credibility to calculations of isotopically labeled species employing restricted CO force fields. The lack of direct chemical meaning in the absolute value of

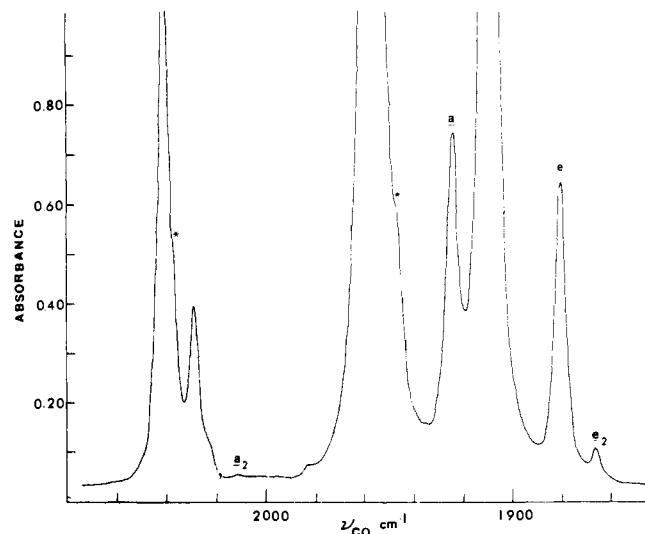


Figure 6. $\nu(\text{CO})$ spectrum of mono- ^{13}C enriched $\text{W}(\text{CO})_4(\text{NBD})$ in hexane after carbonyl ligand rearrangement.

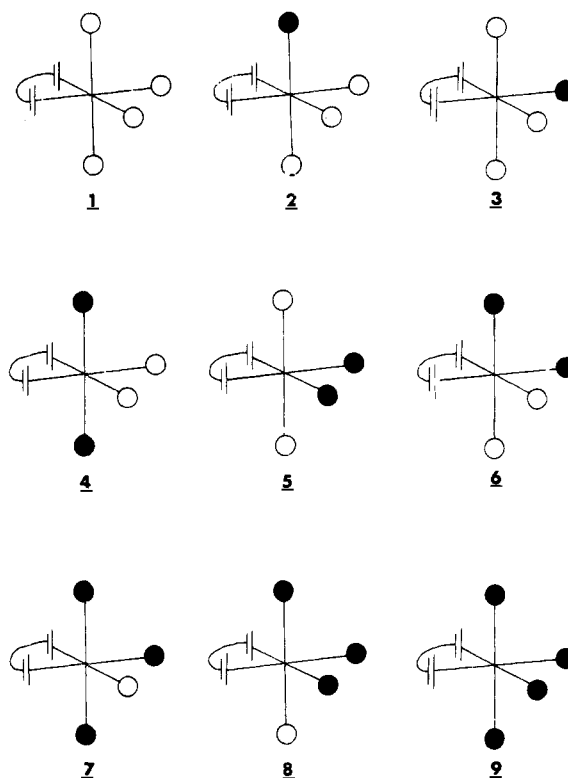


Figure 7. Illustration of the observed arrangements of ^{13}C groups (represented as closed circles) in $\text{M}(\text{CO})_4(\text{NBD})$ derivatives.

the force constants (in particular in the interaction force constants) is nevertheless still under discussion.²⁵ However, certainly within a series of related complexes, the stretching force constants provide relevant bonding information.²⁶

In the initial stages of the photoinduced ^{13}C substitution process in the molybdenum and tungsten derivatives ^{13}C incorporation occurs preferentially at an axial position (2 in Figure 7). This conclusion is based on the ratio of the absorbances of bands a and e (see e.g., Figures 4 and 5) as compared with their natural abundance ratio. Further confirmation that the incoming ^{13}C ligand occupied an axial position was obtained from the greatly enhanced ^{13}C NMR signal ascribed to an axial CO group in an enriched monosubstituted ^{13}C sample of $(\text{NBD})\text{W}(\text{CO})_4$ (see Table III).^{27,29} However, upon

Table II. $\nu(\text{CO})$ Force Constants for (NBD)M(CO)₄ Derivatives^a

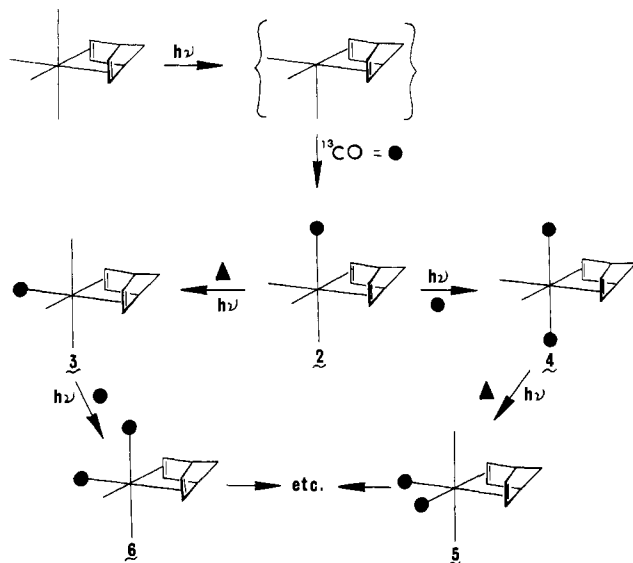
M	Force constants, mdyn/Å				
	k_1	k_2	k_c	$k_{c'}$	k_t
Cr	15.20 ₆	15.86 ₇	0.206	0.411	0.608
Mo	15.36 ₁	15.93 ₉	0.309	0.568	0.472
W	15.26 ₀	15.96 ₀	0.305	0.548	0.518

^a k_1 and k_2 are equatorial and axial CO stretching force constants, respectively; whereas $k_c(\text{CO}_{ax} - \text{CO}_{eq})$, $k_{c'}(\text{CO}_{eq} - \text{CO}_{eq})$, and $k_t(\text{CO}_{ax} - \text{CO}_{ax})$ are the interaction force constants.

allowing the solution to stand in the dark, or during further irradiation, a secondary process occurs which leads to a decrease in the quantity of mono-¹³CO axially substituted species (2) with a concomitant increase in the quantity of corresponding equatorially substituted species (3). The major disubstituted ¹³CO species observed initially is the diaxial molecule (4). This species (4) rearranges to the disubstituted equatorial species (5) during the same process which transforms 2 into 3, with no simultaneous formation of the disubstituted equatorial-axial species (6). The $\nu(\text{CO})$ spectral changes involved in these processes may be seen in our earlier communication of this work.¹¹

The proposed mechanism for the photoinduced ¹³CO enrichment involves initial loss of an axial CO ligand (Scheme I) to yield species 2 which can undergo a second loss of an axial ¹²CO or ¹³CO ligand to yield species 4 or reproduce species 2, respectively. At the same time a secondary isomerization process is occurring which yields species 3 from species 2, as well as species 5 from species 4. Similarly, species 3 can photochemically dissociate an axial CO ligand to yield the disubstituted axial-equatorial species 6. Scheme I assumes that

Scheme I



the stable form of the intermediate produced via loss of carbon monoxide is square pyramidal and further that it does not intramolecularly scramble CO groups. These assumptions are borne out by the preferential production of the axially di-¹³CO substituted species 4. This observation is in agreement with a 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.^{22,23,30-36}

It is important to note that this mechanism, as well as all other mechanisms involving photochemical elimination of CO followed by thermal incorporation of ¹³CO, assumes the oc-

Table III. ¹³C NMR Chemical Shifts of (NBD)M(CO)₄ Derivatives^a

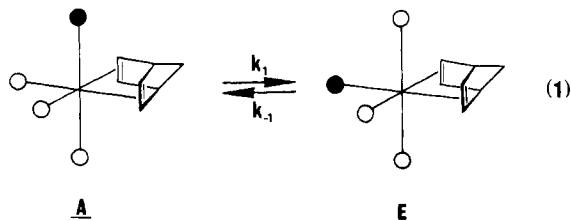
M	δ_c , ppm ^b				
	Axial-CO	Equatorial-CO	C ₁	C ₂	C ₃
Cr	225.5	228.6 ^c	74.7	47.3	61.6
Mo	213.8	217.7	78.5	48.8	64.8
W	203.3	209.3	68.9	48.6	67.3
W(¹³ C-enriched) ^d	(203.1)	209.4	69.4	48.4	67.3

^a Measured in chloroform solvent on natural abundance samples except where noted. ^b Shifts are relative to (CH₃)₄Si and increasing frequency is regarded as being positive. The norbornadiene ligand's carbon atoms are labeled C₁, C₂, and C₃ for olefinic, bridgehead, and methylenic carbons, respectively. ^c This shift is quite different from that previously reported by Mann.²⁹ ^d $J_{W-C} = 117.9$ Hz on the greatly enhanced axial-CO signal of the enriched sample.

currence of a microscopic reversible process (i.e., the transition state for the forward, photochemical reaction is the same as the reverse, thermal reaction) which is not necessarily the case. However, our data do indeed indicate that in this instance it is an axial CO group which is lost in the primary photochemical process. For example, if we consider the opposite result, i.e., equatorial CO loss being the primary photochemical process, the intermediate produced in this process would have to rearrange prior to ¹³CO substitution since the preferred coordination site is axial. This would in turn necessitate that one of the original axial CO groups in the photogenerated intermediate becomes an equatorial group in the tetracarbonyl species. Therefore, if equatorial CO loss occurs in the mono-¹³CO axially labeled species, 50% of the disubstituted ¹³CO species would be the axial-equatorial derivatives. Since diaxial ¹³CO product is formed exclusively, the initial photochemical process must involve loss of an axial CO group.

Unfortunately, in the case of Cr(CO)₄(NBD), the band due to the mono-¹³CO axially substituted species is buried beneath one of the intense bands in the all ¹²CO molecule (~1915 cm⁻¹). Therefore, it was not possible to accurately assess by means of the infrared technique whether there was preferential coordination of ¹³CO at an axial site initially. It does appear likely, however, that this process is indeed analogous to that observed for the molybdenum and tungsten derivatives.

Thermal Rearrangement Reactions. We have investigated the thermal rearrangement of the stereospecifically labeled M(CO)₃(¹³CO)(NBD) (M = Mo and W) and W(CO)₂(¹³CO)₂(NBD) species in order to obtain evidence for the mechanistic details of this process. For the reversible rearrangement of the mono-¹³CO labeled species (eq 1), k_1 is equal



to k_{-1} or the equilibrium constant (K_{eq}) equals 1. That is, since the arrangement of nuclei are equivalent in the two species, A and E are of equal free-energy content.

Starting with an excess of species A the approach to equilibrium can be expressed by the following equation:³⁷

$$\ln \frac{[A]_0 - [A]_e}{[A]_t - [A]_e} = kt = (k_1 + k_{-1})t = 2k_1t \quad (2)$$

where $[A]_0$, $[A]_e$, and $[A]_t$ represent the concentration of

Table IV. First-Order Rate Constants for Thermal Rearrangement of Axially Mono-¹³CO Substituted (NBD)W(CO)₄ in Hexane

Temp, °C	10 ⁴ <i>k</i> , s ⁻¹ ^a	Comments
25.1	2.35 ± 0.28	<i>b</i>
25.1	2.30 ± 0.13	<i>b</i>
25.2	2.36 ± 0.31	<i>c</i>
40.0	13.2 ± 1.9	<i>b</i>
40.0	12.9 ± 1.1	<i>b</i>
40.0	10.8 ± 0.5	<i>b</i>
40.0	13.7 ± 1.8	<i>b</i>
40.0	11.6 ± 0.7	<i>d</i>
50.0	28.6 ± 3.3	<i>b</i>
50.0	26.9 ± 1.3	<i>b</i>
50.1	24.7 ± 4.8	<i>c</i>

^a Error limits for rate constant data are one standard deviation.

^b These values represent the rates determined simultaneously from axial species decay and equatorial species production, respectively.

^c This value represents the rate as determined from axial species decay.

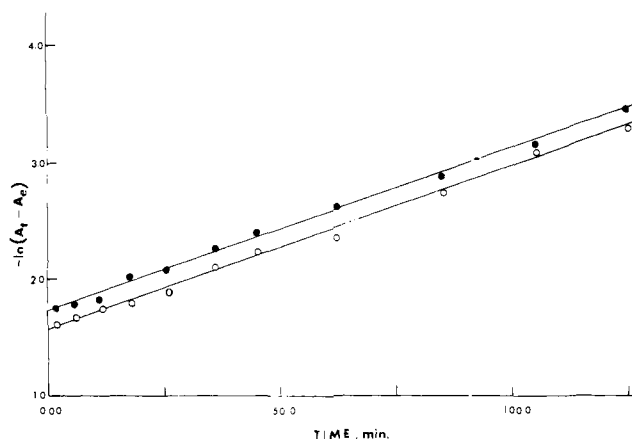
^d This value represents the rate as determined from equatorial species decay.

species A initially, at equilibrium, and at time = *t*, respectively. The rate constant, *k*, obtained from the expression 2 above is therefore twice the rate constant for species A going to species E or vice versa. That is, *k* represents the rate constant for going to the intermediate or transition state species in the rearrangement process. Figure 8 illustrates representative plots of eq 2 approached from either direction for the rearrangement in the dark of axially substituted W(CO)₃(¹³CO)(NBD) in hexane at 25.1 °C.

Table IV list values of *k*, the rate constant for rearrangement, as a function of temperature for (NBD)W(CO)₄. The activation energy for the axial–equatorial CO rearrangement process, *E*_a, was calculated to be 19.0 ± 1.1 kcal mol⁻¹ from an Arrhenius plot. The calculated activation parameters (95% confidence limits) were Δ*H** = 18.4 ± 1.1 kcal mol⁻¹ and Δ*S** = -12.3 ± 3.8 eu.

The analogous rearrangement reaction for the molybdenum derivative was not clean, i.e., a considerable amount of decomposition occurred simultaneously with the axial–equatorial carbonyl scrambling process. Although an attempt was made to compensate for this by measuring the rate of decomposition independently on nonenriched samples, the rate data were inherently more inaccurate than that reported for the tungsten analogue. Nevertheless, it was clear that the rearrangement of axial and equatorial carbonyl groups in the molybdenum tetracarbonyl species is considerably slower (Table V) than that in the tungsten derivative with corresponding activation parameters of Δ*H** = 25.3 ± 2.4 kcal mol⁻¹ and Δ*S** = 1.2 ± 7.8 eu.

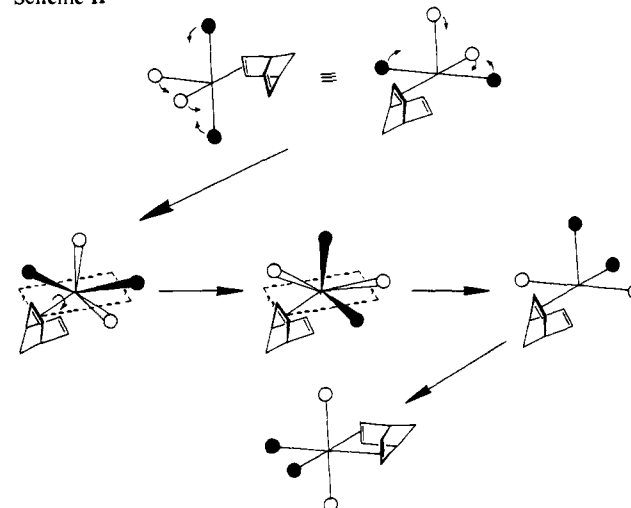
Since stereochemical nonrigidity is such an ubiquitous feature of five-coordinate molecules or reaction intermediates we have proposed a mechanism for CO scrambling which involves chelate ring opening as the rate-determining step followed by a facile rearrangement, based on a square-pyramidal ground state, of carbonyl groups by the Berry process.^{11,38} The fluxionality of the carbonyl ligands in the monoligated W(CO)₄(NBD) intermediate is similar to that observed in Fe(CO)₄(olefin) derivatives,^{39,40} the difference being that the ground state is most likely square pyramidal in the group 6b case as opposed to trigonal bipyramidal. This exchange of CO coordination sites in the monoligated intermediate involves partial rotation about the metal–olefin bond, where the geometry of the transition state is a distorted square pyramid with the monoligated olefin occupying the apical position (see Scheme II where ● = an axial carbonyl ligand, ¹²CO, or ¹³CO, or both). The barrier to rotation should be relatively small

**Figure 8.** First-order rate plots of the thermal axial–equatorial carbonyl exchange reaction in W(CO)₄(NBD) in hexane at 25.1 °C; (●) axial W(CO)₃(¹³CO)(NBD) decay; (○) equatorial W(CO)₃(¹³CO)(NBD) production.**Table V.** First-Order Rate Constants for Thermal Rearrangement of Axially Mono-¹³CO Substituted (NBD)Mo(CO)₄ in Hexane^a

Temp, °C	10 ⁵ <i>k</i> , s ⁻¹ ^b
40.0	4.33 ± 0.36
40.0	3.99 × 0.38
40.0	4.94 × 0.16
50.0	12.9 ± 1.9
60.0	47.8 ± 0.4
60.0	55.5 ± 4.1

^a Error limits for rate constant data are one standard deviation.

^b Values represent the rate as determined from the decay of the axially ¹³CO enriched species with corrections being made for some thermal decomposition of the complex (~10–20%).

Scheme II

(<10 kcal mol⁻¹) since electron-withdrawing groups which enhance the π asymmetric component of the metal–olefin bond are absent in the W(CO)₄(NBD) intermediate. Therefore, the rate of ring opening should be an upper limit to the rate of carbonyl rearrangement.⁴¹

In addition, we have measured the rate of carbonyl rearrangement in a tungsten sample enriched diaxially in ¹³CO, species 4. This species was found to rearrange, by monitoring the growth of the diequatorial-¹³CO band at 1866.5 cm⁻¹, at exactly the same rate as the monoaxial ¹³CO species (2) transform to the mono-equatorial ¹³CO species (3) at 40 °C. More importantly, only the diequatorial ¹³CO species is produced, i.e., there was no increase in the quantity of species 6

(the axial-equatorial disubstituted ^{13}C O species) as noted by the absorbance of the highest frequency band labeled 6 in Figure 3. This result is consistent with a rearrangement process as indicated in Scheme II which dictates that the two axial CO groups interchange simultaneously with the two equatorial CO groups, a necessary consequence of the Berry pseudo-rotation mechanism.

The observed activation parameters for the CO interchange process in $\text{W}(\text{CO})_4(\text{NBD})$, $\Delta H^* = 18.4 \text{ kcal mol}^{-1}$ and $\Delta S^* = -12.3 \text{ eu}$, are about the same as those obtained for the substitution process⁴¹ and are also consistent with other reported ring-opening, rate-determining mechanisms. For example, Schultz and Dodson have observed values of $\Delta H^* = 21.3 \text{ kcal mol}^{-1}$ and $\Delta S^* = -14 \text{ eu}$ for ring opening in the reaction of $(\text{DTO})\text{W}(\text{CO})_4$ (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane) with phosphines and phosphites in decalin.⁴²

On the other hand, since the rate of thermal CO interchange in $\text{Mo}(\text{CO})_4(\text{NBD})$ occurs so much less readily than that in the tungsten analogue, we feel that an alternative mechanism is probably operative in this case. Indeed, if metal-olefin bond cleavage is rate determining, this process would be expected to be more facile in the molybdenum derivative. Unfortunately, ligand substitution reactions of $\text{Mo}(\text{CO})_4(\text{NBD})$ as well appear to be proceeding principally via an alternative mechanism to simply ring opening, thereby, prohibiting the measurement of the rate of ring opening employing the substitution reaction approach.⁴³⁻⁴⁵ It is not unprecedented for molybdenum and tungsten tetracarbonyl derivatives to undergo similar substitution reactions by way of different mechanisms.⁴⁶

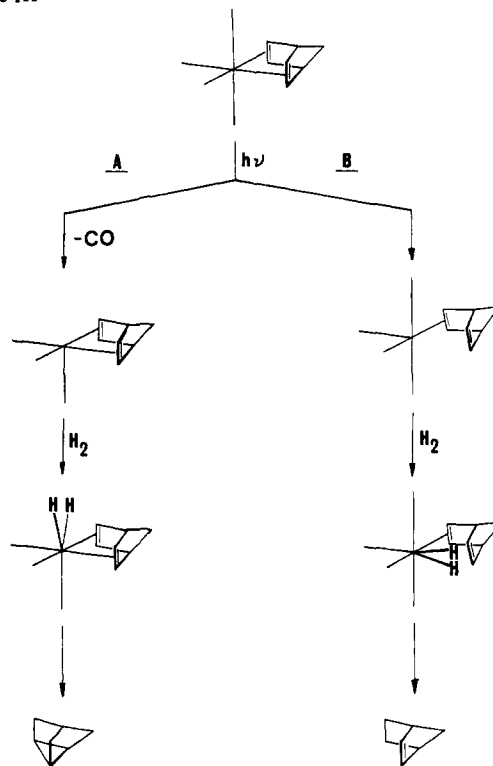
An alternate mechanism for axial-equatorial CO equilibration in $\text{Mo}(\text{CO})_4(\text{L-L})$ complexes, where L-L is glyoxal-bis(arylimines) or glyoxal-bis(*tert*-butylimine), has been presented by Majunke, Leibfritz, Mack, and tom Dieck.⁴⁷ These workers have proposed an intramolecular twisting mechanism proceeding through a trigonal-prismatic transition state where all metal-ligand bonds remain intact. The rigidity of the norbornadiene ligand should, however, greatly increase the energy barrier for this type of a process.^{48,49}

Photochemical and Thermal Hydrogenation Processes. The mechanism of the photoinduced hydrogenation of norbornadiene catalyzed by $\text{Cr}(\text{CO})_6$ has recently been studied by Platbroad and Wilputte-Steinert.^{2,3} $\text{Cr}(\text{CO})_4(\text{NBD})$ was observed to undergo photoinduced hydrogenation to yield a mixture of nortricyclene and norbornene in a ratio of 2.8 to 1, respectively. The primary photochemical process, employing irradiation at λ 366 nm, was proposed to involve an open complex where one bond of the chelate is broken, i.e., an intermediate which is uncommon to that in the analogous thermal process.^{9,10} In view of our observed rapid photochemical incorporation of ^{13}C O into $(\text{NBD})\text{M}(\text{CO})_4$ species, as well as a secondary process involving metal-olefin bond cleavage, we have carried out further investigations of both the photochemical and thermal hydrogenation of norbornadiene.

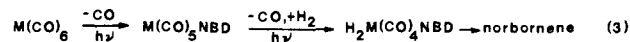
The photochemical hydrogenation of norbornadiene ($2.0 \times 10^{-2} \text{ M}$) in the presence of $\text{Cr}(\text{CO})_6$ ($8.0 \times 10^{-3} \text{ M}$) in *n*-pentane formed nortricyclene and norbornene in a constant ratio of 1.9, a result only slightly different from that previously reported.⁵⁰ When the metal center was changed to tungsten or molybdenum, results quite different from those of chromium were observed. Photoassisted hydrogenation of norbornadiene ($2 \times 10^{-2} \text{ M}$) in the presence of $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ ($8 \times 10^{-3} \text{ M}$) in *n*-pentane afforded mostly norbornene with only small (<7%) quantities of nortricyclene being formed. However, photoassisted hydrogenation of norbornadiene starting from the $(\text{NBD})\text{M}(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$) derivatives provided product ratios of nortricyclene and norbornene (which varied somewhat with time) of 0.25-0.50 and 2.0-4.0 for molybdenum and tungsten, respectively.

A proposal for the production of the alkane and alkene products is presented in Scheme III which incorporates both

Scheme III



phenomena observed upon irradiation of $(\text{NBD})\text{M}(\text{CO})_4$ derivatives (CO loss and metal-olefin bond opening). This scheme readily accommodates the observations made on the hydrogenation of norbornadiene with group 6b carbonyl catalysts. Firstly, irradiation of $\text{Cr}(\text{CO})_6$ or $(\text{NBD})\text{Cr}(\text{CO})_4$ and norbornadiene under D_2 in pentane has been shown to yield nortricyclene-3,5,*d*₂ and *endo,endo*-norbornene-5,6-*d*₂.⁵¹ Secondly, the product distribution as a function of the nature of the precatalyst employed can be explained if we assume that upon photochemical loss of CO from the monoolefinic species $\text{M}(\text{CO})_5(\text{NBD})$, H_2 is absorbed by the complex proceeding directly to norbornene via route B in Scheme III. Whereas



starting with $\text{M}(\text{CO})_4(\text{NBD})$ as the catalyst results in a product distribution which is dependent on the relative importance of routes A and B in Scheme III. In this connection the $\text{W}(\text{CO})_5(\text{NBD})$ species was observed spectroscopically in large quantities upon irradiation of $\text{W}(\text{CO})_6$ in the presence of norbornadiene [$\nu(\text{CO})$ in pentane: 2080 (A_1), 1960 (A_1) and 1952 (E)].

Thirdly, we have observed thermal hydrogenation of norbornadiene in the $\text{M}(\text{CO})_4(\text{NBD})$ derivatives, under conditions where an opening of the metal-olefin chelate (60 °C in saturated hydrocarbon solvent) occurs, resulting in the exclusive production of the alkene product, norbornene. This provides strong evidence for the proposed intermediate in the production of norbornene photochemically in Scheme III in that it is analogous to that proposed in the thermal intramolecular CO rearrangement or decomposition reactions of $\text{M}(\text{CO})_4(\text{NBD})$ species.

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- (41) We are presently investigating the rate of substitution of $W(CO)_4(NBD)$ with phosphines and phosphites and have observed that these reactions proceed via a chelate ring-opening mechanism with a limiting rate being observed at high phosphine concentrations. These rate data clearly indicate that the rate of ring opening is somewhat faster than intramolecular CO interchange. Therefore, ring opening and closing can take place without concomitant axial-equatorial CO exchange necessarily occurring, i.e., the barrier to ring closure for the intermediate is slightly less than the barrier to Berry rearrangement which involves olefin rotation; D. J. Darensbourg and B. Rupp, unpublished results.
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- (43) Our initial results involving substitution reactions of the diene ligands, norbornadiene and bicyclo[6.1.0]nona-2,4,6-triene (bound through two olefinic bonds only), suggest some sort of incoming ligand assisted ring-opening mechanism where the nature of the leaving group plays an important role in the process.^{24,41} For example, the stereochemistry of products is different for replacement of the diene ligand from those involving displacement of diamine ligands (where a ring-opening mechanism is operative) in molybdenum complexes with the same incoming ligands. On the other hand, the tungsten derivatives afford products of the same stereochemistry regardless of the nature of the leaving group. In addition, stereospecifically axially labeled $Mo(CO)_3(^{13}CO)(NBD)$ and $Mo(CO)_3(^{13}CO)$ (bicyclo[6.1.0]nona-2,4,6-triene) undergo substitution reactions with a variety of incoming ligands to form *cis*- $Mo(CO)_3(^{13}CO)(L_2)$ with retention of the stereospecific ^{13}CO label.²⁴ It should also be pointed out that, contrary to CO rearrangement reactions, the rate of olefin substitution in $Mo(CO)_4(NBD)$ is much more rapid than that in $W(CO)_4(NBD)$. See also related work on $Mo(CO)_4$ (cyclooctadiene) in ref 44 and 45.
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An Easy Access to *exo*-Brevicomin¹

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Abstract: Selective irradiation (or singlet sensitization and triplet quenching) of the carbonyl group of 2-propionyl-6-methyl-2,3-dihydro-4*H*-pyran gives stereoselectively the *exo* isomer of $\Delta^{2,3}$ -dehydrobrevicomin. Catalytic hydrogenation of the latter leads to *exo*-brevicomin, the principal component of the sex attractant of *Dendroctonus brevicomis*.

2,3-Dihydro-4*H*-pyrans have been shown to undergo the *retro*-Diels-Alder reaction as well as ring contraction leading to cyclobutanes when irradiated in the absorption band of the double bond.^{2,3}

On the other hand, selective irradiation⁴ of the carbonyl group of 4-acylcyclohex-1-ene,⁵ or of 2-acyl-2,3-dihydro-4*H*-pyrans,³ induces the creation of a bond between the oxygen atom of the carbonyl group and the C(6) carbon atom of the