Chemical and Infrared Spectral Details of Reactions Involving Stereospecific Incorporation of Oxygen-18 into Substituted Manganese and Rhenium Carbonyl Derivatives via Exchange Reactions with $H_2{}^{18}O$

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Abstract: The reactions of substituted group 7B metal carbonyl cationic derivatives, $[M(CO)_5L]^+$ (M = Mn, Re and L = phosphine, C_5H_5N, CH_3CN) and $[Mn(CO)_4(diphos)]^+$, with labeled water are described. The carbonyl ligands in these derivatives are found to undergo facile oxygen-exchange reactions with $H_2{}^{18}O$, presumably through hydroxycarbonyl intermediates, to afford $C^{18}O$ enriched species. In all cases investigated, the carbonyl sites with the higher CO stretching force constant (implying more positive character at carbon as well as a more stable LUMO) were found to be more susceptible to oxygen exchange, thus leading to stereospecifically labeled species. In addition, the reactivity of the substrate toward oxygen exchange with water was found to decrease in the order $[M(CO)_6]^+ > [M(CO)_5L]^+ \gg [M(CO)_4(L\text{-}L)]^+$. The preparation of *cis*-$[Mn(CO)_4({}^{13}CO)L]^+$ (L = PMe_2Ph, PPh_3, and $AsPh_3$) species is reported along with oxygen-18 exchange reactions of these derivatives to yield mixed labeled (${}^{13}C^{18}O$) metal carbonyls. The incorporation of oxygen-18 into metal carbonyl cations was found to be greatly accelerated by the addition of small quantities of triethylamine.

Although $[Re(CO)_6]^+$ is perfectly stable in water, Muetterties has observed that this species exchanges oxygen with oxygen atoms in water.[1] We have previously reported on the stereospecific incorporation of oxygen-18 into manganese and rhenium pentacarbonyl derivatives via exchange reactions with $H_2{}^{18}O$, where the equatorial CO positions were enriched at a faster rate than the axial CO position.[2] These processes were proposed to proceed through an intermediate resulting from hydroxide attack at a carbonyl carbon site, which is in chemical equilibrium with the starting material and where proton exchange readily occurs between the two oxygen atoms (eq 1).

$$M(CO)_5L^+ + H_2{}^{18}O \rightarrow \{M(CO)_4(L)C(=O)^{18}OH\} \rightarrow M(CO)_4(C^{18}O)L^+ \quad (1)$$

$$(M = Mn, Re \text{ and } L = \text{phosphine, pyridine, } CH_3CN)$$

In the manganese hexacarbonyl cationic derivative a secondary process occurs as well as the oxygen exchange reaction which involves β-hydrogen transfer in the $[Mn(CO)_5COOH]$ intermediate with concomitant formation of $HMn(CO)_5$ and CO_2.[3] Similarly, the reaction of $Fe(CO)_5$ with ^-OH to afford $Fe(CO)_4H^-$ and CO_2 has been proposed to proceed through the intermediate $[Fe(CO)_4COOH]^-$.[4] Hydroxycarbonyl intermediates have also been implicated in the reaction of $[PtCl(CO)(PEt_3)_2]^+$ and water to yield the Pt(II) hydride species and CO_2[5] and in the catalytic reduction of nitric oxide by carbon monoxide using $[RhCl_2(CO)_2]^-$.[6] Hui and Shaw[7] have also proposed the intermediacy of a hydroxycarbonyl species, $[M(CO)_5COOH]^-$, in substitution reactions of the group 6B hexacarbonyls with phosphines in the presence of aqueous sodium hydroxide. Recently, we have postulated an analogous sulfhydrocarbonyl intermediate in the reaction of $[M(CO)_5L]^+$ species (M = Mn, Re) with NaSH to afford $HMn(CO)_4L$ derivatives and COS.[8]

On the other hand a stable Ir(III) hydroxycarbonyl species, $IrCl_2(COOH)(CO)(PMe_2Ph)_2$, has been prepared from the reaction of the dicarbonyl cation with water.[9] Indeed this reaction was found to be readily reversible in that the dicarbonyl cation was re-formed upon reaction of the hydroxycarbonyl derivative with dry HCl.

In addition to our interest in the preparation of stereospecifically labeled metal carbonyl derivatives with either ^{13}CO or $C^{18}O$ for both photochemical and thermal mechanistic studies,[10-15] we have been for a long period interested in understanding the electronic factors responsible for controlling the specific site of nucleophilic attack in metal carbonyl derivatives.[16-18] This report represents a detailed extension of our earlier communication,[2] as well as further studies defining the mechanism of these metal-bound carbon monoxide oxygen exchange reactions with water.

Experimental Section

Material and Equipment. $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, bis(1,2-diphenylphosphino)ethane, triphenylarsine, and dimethylphenylphosphine were purchased from Strem Chemical Co. Triphenylphosphine was the generous gift of M and T Chemical Co. Nitrosylhexafluorophosphate ($NOPF_6$) was obtained from Aldrich, whereas NH_4PF_6 was purchased from Ozark-Mahoning Co. Carbon monoxide, 90% enriched in ^{13}CO, was acquired from Prochem. $H_2{}^{18}O$ (96.5% by weight oxygen-18) and $D_2{}^{18}O$ (99.0% by weight oxygen-18) were obtained from Monsanto Research Corp. (Mound Laboratory) and Norsk Hydro (Norway), respectively. Reagent grade acetonitrile (Matheson Coleman and Bell) was purified by refluxing over sodium hydride or calcium sulfate and distilled prior to use.

Melting points were taken in open capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses on the complexes were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparations. All operations on complexes in solution were carried out under an atmosphere of nitrogen. Manganese pentacarbonyl bromide and $Mn(CO)_4(L)Br$ derivatives were prepared according to the procedures in the literature.[19] The $M({}^{12}CO)_5L^+$ (M = Mn, Re) complexes were synthesized by methods we have previously described.[20] $Mn(CO)_3(diphos)Br$ was prepared from $Mn(CO)_5Br$ and bis(1,2-diphenylphosphino)ethane in THF under a CO atmosphere as described by Angelici and Brink.[21] The material was purified by recrystallization from CH_2Cl_2/hexane.

$[Mn(CO)_4(diphos)][PF_6]$. This complex was prepared by employing a procedure analogous to that described by Anglin and Graham[22] for the synthesis of the rhenium derivative. $Mn(CO)_3(diphos)Br$ (0.76 g, 1.2 mmol) dissolved in 50 mL of benzene under a nitrogen atmosphere underwent a color change from yellow to red upon the addition of 2 g of $AlCl_3$. The solution was then pressurized with CO (~2-3 atm) and heated to 60 °C for 1 h. Upon cooling to room temperature, the solvent was removed in vacuo. Addition of a methanolic solution of NH_4PF_6 (10.0 mmol in 10 mL) to the residue dissolved in 20 mL of methanol resulted in immediate precipitation of white crystals. These were collected by filtration and washed with methanol and hexane, mp >232 °C. Anal. Calcd for $C_{30}H_{24}O_4P_3F_6Mn$: C, 50.72; H, 3.41. Found: C, 50.72; H, 3.40.

[*cis*-$Mn(CO)_4(^{13}CO)L$][PF_6]. These complexes, where L = Me_2PhP, Ph_3P, Ph_3As, were prepared in low yields (10–15%) from the corresponding *cis*-$Mn(CO)_4(L)Br$ species and ^{13}CO (90% enrichment) in the presence of $AlCl_3$ as described above for the preparation of the [$Mn(CO)_4$(diphos)][PF_6] derivative. The stereochemical site of ^{13}CO addition was determined by infrared spectroscopy in the ν(CO) region. There was no infrared spectral evidence for rearrangement of the stereospecifically incorporated ^{13}CO in these derivatives in solution at ordinary temperatures. IR spectra (ν(CO) in acetonitrile): $[Me_2PhPMn(CO)_5]^+$ 2135.6 (m), 2078.2 (w, sh), 2062 (sh), 2050.3 (s), 2018.9 (s) cm^{-1}; $[Ph_3PMn(CO)_5]^+$ 2134.9 (m), 2080 (w, sh), 2065 (sh), 2052.1 (s), 2021.0 (s) cm^{-1}; $[Ph_3AsMn(CO)_5]^+$ 2135.1 (m), 2080 (w, sh), 2064 (sh), 2053.9 (s), 2021.8 (s) cm^{-1}.

Reactions of [$Mn(CO)_4$(diphos)][PF_6] with $H_2{}^{18}O$. [$Mn(CO)_4$(diphos)][PF_6](0.114 g, 0.160 mmol) was dissolved in 4.0 mL of dry acetonitrile under nitrogen with stirring and 0.15 mL (8.3 mmol) of 95% $H_2{}^{18}O$ was added using a microsyringe. The reaction was monitored by periodically withdrawing samples and observing the ν(CO) infrared spectra over an 80-day period. The complex was found to be perfectly stable in acetonitrile under an inert atmosphere for at least 3 months.

A similar reaction was carried out where [$Mn(CO)_4$(diphos)][PF_6] (0.0526 g, 0.074 mmol) was dissolved in 2.0 mL of dry acetonitrile with 0.05 mL (2.5 mmol) of 95% $H_2{}^{18}O$ with the addition of 5.0 μL of triethylamine (0.036 mmol). The rate of oxygen-18 incorporation was markedly enhanced in the presence of triethylamine with a concomitant production of metal-hydride complex being observed.

Reactions of [$M(CO)_5L$][PF_6] with $H_2{}^{18}O$. [$M(CO)_5L$][PF_6] complexes (M = Mn: L = Me_2PhP, Ph_3P, CH_3CN, C_5H_5N and M = Re: L = Ph_3P, Me_2PhP, CH_3CN) were reacted with $H_2{}^{18}O$ in much the same manner as that described above for the [$Mn(CO)_4$(diphos)][PF_6] derivative. In a typical experiment, [$Me_2PhPMn(CO)_5$] [PF_6] (0.040 g, 0.084 mmol) was dissolved in 1.0 mL of acetonitrile containing 0.10 cm^3 of $H_2{}^{18}O$ (5.0 mmol) with stirring. The enrichment was monitored by IR spectroscopy in the ν(CO) region. Similar experiments were carried out with the stereospecifically ^{13}CO labeled species, e.g., *cis*-[$Mn(CO)_4(^{13}CO)PMe_2Ph$][PF_6].

A heterogeneous reaction was carried out between [$Mn(CO)_5PPh_3$][PF_6] and $H_2{}^{18}O$ by adding 5.0 mL of dry hexane to a degassed sample of the pentacarbonyl complex (0.122 g, 0.212 mmol) followed by the addition of 0.05 mL (2.5 mmol) of 95% $H_2{}^{18}O$. The slow production of oxygen-18 enriched *cis*-$HMn(CO)_4PPh_3$ species was followed by withdrawing samples of the solution phase with a hypodermic syringe at various time intervals and obtaining their infrared spectra in the ν(CO) region.

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 on the $[M(CO)_5L]^+$ (M = Mn and Re, L = Lewis base) species were performed using the Cotton–Kraihanzel approach[23] employing the $C^{16}O$ frequency data. On the other hand, initial CO stretching force constant calculations on $[Mn(CO)_4(diphos)]^+$ were carried out using the $C^{16}O$ frequency data and a modified Cotton–Kraihanzel procedure refined by Jernigan, Brown, and Dobson[24] and employing a program developed in our laboratories.[25] The trial force constants were refined using the $C^{18}O$ frequency data and an iterative computer program[26] 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 trial force constants were generally refined to reproduce the observed ν(CO) vibrations within an average of <1.5 cm^{-1}.

Results and Discussion

The reactions of several substituted group 7B metal carbonyl derivatives with $H_2{}^{18}O$ have been followed in dry acetonitrile via infrared spectroscopy in the ν(CO) region. Firstly, we will discuss the results of the oxygen-18 water exchange process between metal-bound carbon monoxide in the pentacarbonyl derivatives. Figure 1 illustrates the high-frequency region of the ν(CO) spectra obtained at several time intervals for the incorporation of oxygen-18 into $[Me_2PhPMn(CO)_5]^+$.[27] It was possible to assign all the observed bands to the various oxygen-18 enriched species by noting the rates of appearance and decay of bands concomitantly aided by calculations involving a restricted CO force field. Table I lists the results for the seven observed isotopic species of $[Me_2PhPMn(CO)_5]^+$ enriched with $C^{18}O$.

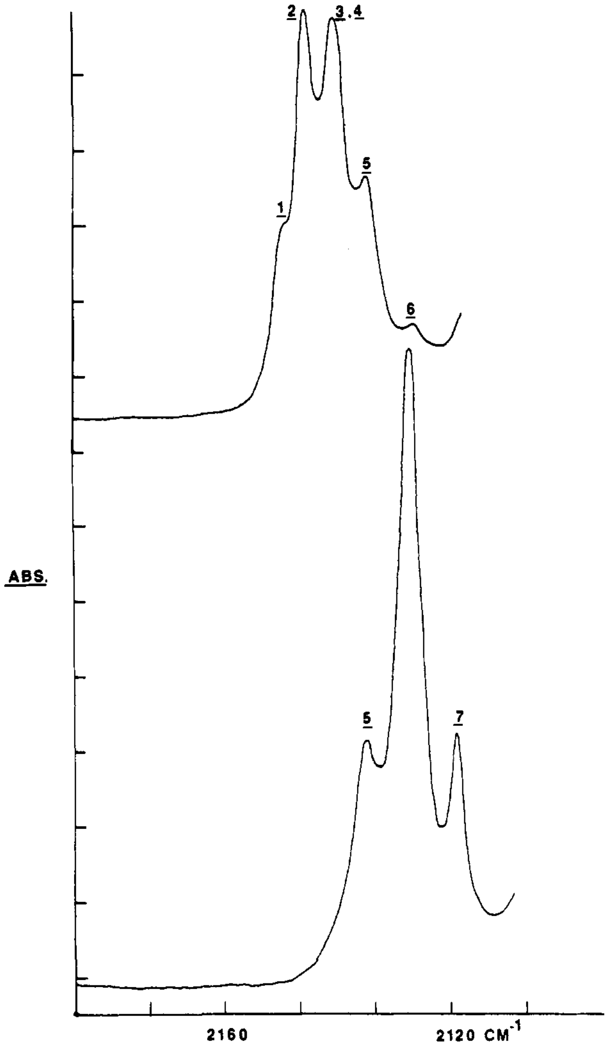


Figure 1. High-frequency region of the ν(CO) spectra for the incorporation of oxygen-18 into $[Me_2PhPMn(CO)_5]^+$. The numbers correspond to the isotopic species listed in Table I.

Although there are calculated ν(CO) band positions in mixed axial–equatorial $C^{18}O$ substituted species which are quite similar to those of equatorially only substituted species, the high-frequency band at 2094.1 cm^{-1} assigned to the all $C^{18}O$ molecule, 7, does not begin to grow in until the predominant species in solution is the equatorially substituted tetra-$C^{18}O$ derivative, 6. That all the observed bands are correctly assigned to oxygen-18 enriched carbonyl stretching vibrations in the parent derivative is revealed experimentally by carrying out the reverse reaction on the highly enriched species with $H_2{}^{16}O$, the $[Me_2PhPMn(C^{16}O)_5]^+$ derivative being afforded quantitatively. Identical observations were noted for the reactions of $[Ph_3PMn(CO)_5]^+$ and the corresponding rhenium analogues, $[Me_2PhPRe(CO)_5]^+$ and $[Ph_3PRe(CO)_5]^+$, with $H_2{}^{18}O$.

Reactions of the more labile acetonitrile and pyridine substituted complexes of manganese with $H_2{}^{18}O$ in acetonitrile were complicated by carbonyl displacement reactions, eventually leading to the production of the very stable $[Mn(CO)_3(CH_3CN)_3]^+$ derivative. Nevertheless, in the early stages of enrichment only species containing equatorial $C^{18}O$

Table I. Calculated and Observed Infrared Frequencies in the ν(CO) Region for the Seven Observed Isotopic Species of $[Me_2PhPMn(CO)_5]^+$ Enriched with $C^{18}O$

Molecule	Frequencies,[a] cm^{-1}				
1. All $C^{16}O$	2143.5 (*2141.8*)	2078.8 (2081 sh)	2051.2 (*2050.3*)	2051.2 (*2050.3*)	2064.6 (2062 sh)
2. Mono-$C^{18}O$ (eq)	2136.4 (*2135.4*)	2073.1	2051.2 (2050.3)	2014.8 *b*	2063.7
3. Di-$C^{18}O$(eq-cis)	2127.8 (2128.1)	2068.5	2017.9 (*2019.1*)	2011.7 *b*	2063.2
4. Di-$C^{18}O$(eq-trans)	2129.5 (2128.1)	2039.2	2051.2 (2050.3)	2001.8 (*2003.1*)	2067.3
5. Tri-$C^{18}O$ (eq)	2119.0 (*2118.1*)	2040.1	2013.7 *b*	2001.8 (2003.1)	2064.5 (2064.5)
6. Tetra-$C^{18}O$ (eq)	2107.0 (*2107.9*)	2028.6	2001.8 (2003.1)	2001.8 (2003.1)	2049.7 (2048.1)
7. All $C^{18}O$	2091.8 (*2094.1*)	2028.6	2001.8 (2003.1)	2001.8 (2003.1)	2014.8 *b*

[a] Observed frequencies are listed in parentheses directly below the calculated values. Italicized frequencies were employed as input data in the force field fit ($k_1 = 17.43$, $k_2 = 17.44$, $k_c' = 0.22_2$, $k_c = 0.24_6$, $k_t = 0.45_2$). Spectra were determined in acetonitrile. [b] Buried beneath other, more prominent bonds.

Table II. Calculated and Observed Infrared Frequencies in the ν(CO) Region for the Seven Observed Isotopic Species of $[(CH_3CN)Re(CO)_5]^+$ Enriched with $C^{18}O$

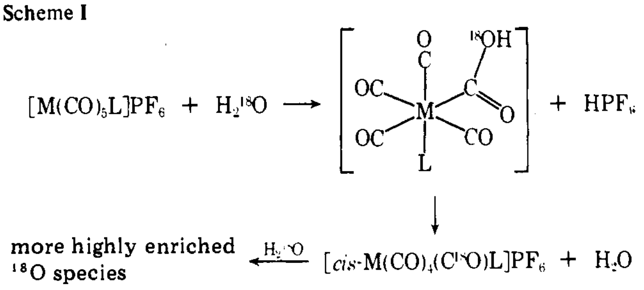
Molecule	Frequencies,[a] cm^{-1}				
1. All $C^{16}O$	2170.7 (*2168.8*)	2097.5	2059.5 (*2059.6*)	2059.5 (*2059.6*)	2029.1 (2029.0)
2. Mono-$C^{18}O$ (eq)	2162.4 (*2161.3*)	2090.0	2059.5 (2059.6)	2020.5 (*2020.1*)	2033.5
3. Di-$C^{18}O$(eq-cis)	2152.0 (2152.1)	2084.8	2022.2 (2020.1)	2019.7 (2020.1)	2036.8
4. Di-$C^{18}O$(eq-trans)	2154.3 (2152.1)	2066.8	2059.5 (2059.6)	2009.9 (2010.1)	2024.9
5. Tri-$C^{18}O$ (eq)	2141.1 (*2141.9*)	2065.5	2020.3 (2020.1)	2009.9 (*2010.1*)	2028.2
6. Tetra-$C^{18}O$ (eq)	2124.7 (2127.1)	2046.9	2009.9 (2010.1)	2009.9 (2010.1)	2023.0
7. All $C^{18}O$	2118.3	2046.9	2009.9	2009.9	1980.1

[a] Observed frequencies are listed in parentheses directly below the calculated values. Italicized frequencies were employed as input data in the force field fit ($k_1 = 16.83$, $k_2 = 17.71$, $k_c' = 0.26_4$, $k_c = 0.33_3$, $k_t = 0.58_3$).

groups were observed. On the other hand, $[Re(CO)_5(CH_3CN)]^+$ was found to be quite stable toward ligand displacement under the conditions of the oxygen-exchange process, affording only ν(CO) absorptions ascribable to the various $[Re(C^{16}O)_{5-n}(C^{18}O)_n(CH_3CN)]^+$ (n = 0-4) species (see Figure 2 and Table II). Unlike in the phosphine-substituted derivatives where the low-frequency A_1 (primarily axial CO stretching) and E vibrational modes are grossly overlapped, the low-frequency ν(CO) A_1 vibrational mode in this derivative occurs at a much lower frequency than the E mode. Consequently, it is possible to detect oxygen-18 exchange at the axial CO site in the initial stages of the reaction if indeed it is occurring. For example, a strong A_1 absorption is calculated at 1983.2 cm^{-1} for the *trans*-$[Re(CO)_4(C^{18}O)(CH_3CN)]^+$ species. As evident in Figure 2 there is no ν(CO) absorption observed in this region. Further evidence for the absence of axial carbonyl oxygen exchange is noted in the lack of shifting to lower frequency of the vibration around 2029 cm^{-1} (which corresponds primarily to an axial $C^{16}O$ motion) during all stages of the reaction.

It is therefore clear that in all the pentacarbonyl derivatives studied *the equatorial carbonyl sites are more susceptible to oxygen exchange than is the axial site* (Scheme I).

Scheme I



We have previously discussed the site of nucleophilic attack in substituted metal carbonyls in terms of the charge at a carbonyl carbon atom as implied by the CO stretching force constant.[16-18] Our prediction that carbonyl groups with higher stretching force constants will be more reactive toward nucleophiles has been quite useful in explaining the relative reactivity patterns in substituted metal carbonyl derivatives.[28-30] However, recent calculations have shown that charge is not the primary factor in determining the site of nucleophilic attack in acyl and carbene complexes of manganese and chromium carbonyls, respectively.[31-34] Similar conclusions have also been reached in the reactivity of the thiocarbonyl derivatives of group 6B, $M(CO)_5CS$, toward hard nucleophiles.[35] It has thus been proposed that it is more reasonable to discuss reactions of these types in terms of frontier orbital control.[31,35-38] It is important to note here, however, that when dealing with a system where *only* carbonyl carbon atoms are susceptible to attack by nucleophiles,[39,40] the conditions of our original proposal,[16] the CO stretching force constant predictive capa-

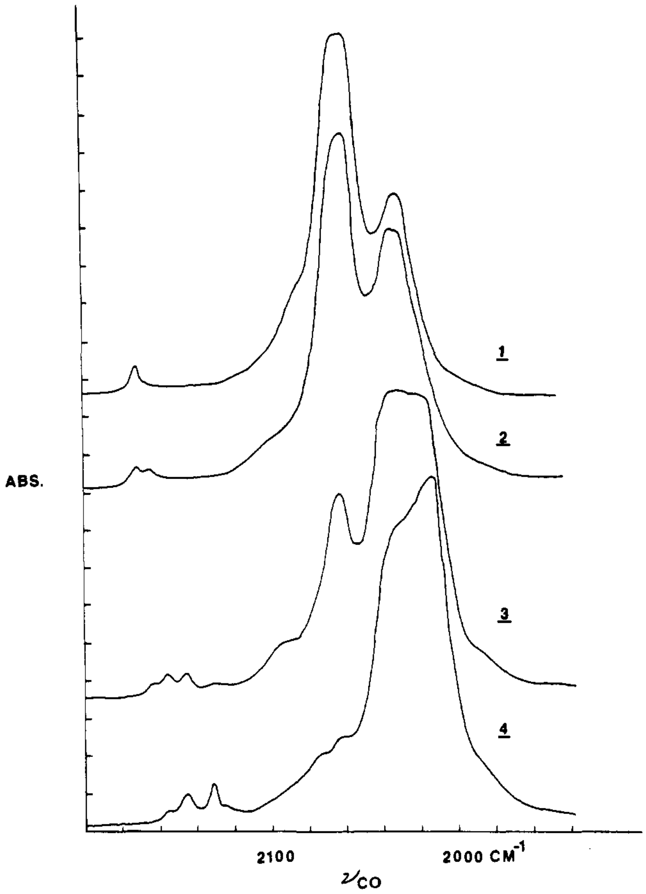


Figure 2. ν(CO) spectra for the incorporation of oxygen-18 into $[(CH_3CN)Re(CO)_5]^+$ as a function of time (0.225 mmol of substrate and 5.0 mmol of $H_2{}^{18}O$ in 5 mL of CH_3CN): (1) initial spectrum, (2) 1.0 h, (3) 7.0 h, and (4) 22.5 h.

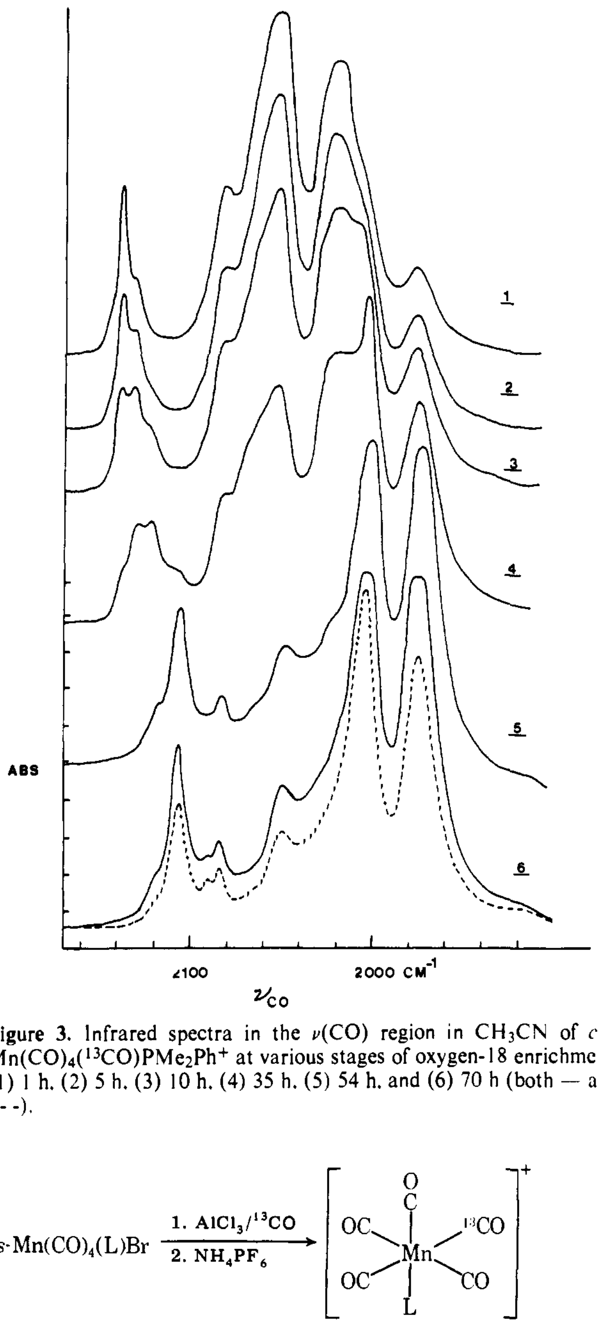
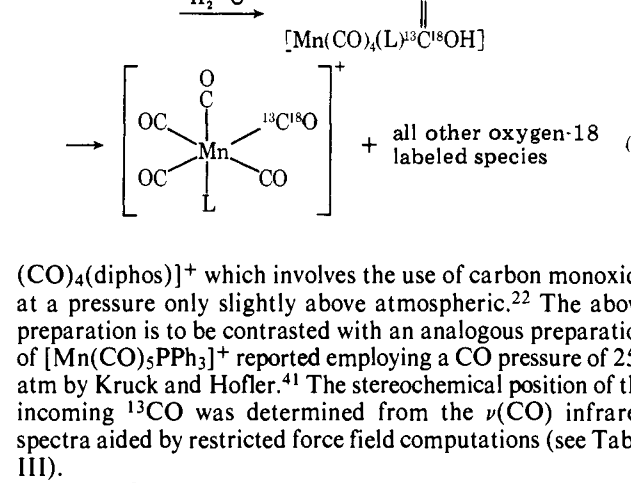


Figure 3. Infrared spectra in the ν(CO) region in CH_3CN of *cis*-$Mn(CO)_4(^{13}CO)PMe_2Ph^+$ at various stages of oxygen-18 enrichment: (1) 1 h, (2) 5 h, (3) 10 h, (4) 35 h, (5) 54 h, and (6) 70 h (both — and - - -).



(2)

bility works quite well. This is so because the same factors which influence charge at carbon in M—C≡O systems affect the stability of the LUMO (carbon-oxygen π antibond). That is, a larger CO stretching force constant (in a given complex or a series of closely related complexes) implies less metal-carbon π bonding and therefore a more stable π^* orbital on the carbonyl ligand.

Therefore, it is also possible to discuss the oxygen exchange reactions in terms of an interaction of the highest occupied molecular orbital (HOMO) of the hydroxide ion (the lone pair of electrons) and the lowest unoccupied molecular orbital (LUMO) of the complex. Combination of the hydroxide ion with the carbon-oxygen π antibonding level (which lies mostly on the carbon atom) will disrupt the multiple-bond character between carbon and oxygen, yielding the hydroxycarbonyl intermediate.

The observed reactivity pattern, a site preference for oxygen exchange to occur at an equatorial carbon monoxide ligand in $[M(CO)_5L]^+$ species where the CO stretching force constant for CO_{eq} (k_2) is larger than that for CO_{ax} (k_1), is totally consistent with this view. In addition, in the hexacarbonyl cationic species $[M(CO)_6]^+$ the rate of oxygen exchange is considerably faster than that observed in the substituted derivatives as anticipated based on the larger CO stretching force constants in the former species.[3]

We have extended our studies of $[Mn(CO)_5L]^+$ derivatives with $H_2{}^{18}O$ to include an investigation illustrating the feasibility of chemically producing mixed labeled carbon monoxide which is bound to a transition metal (eq 2). The stereospecific *cis*-$Mn(CO)_4(^{13}CO)L^+$ (L = PMe_2Ph, PPh_3, and $AsPh_3$) derivatives were prepared employing a method similar to that used by Anglin and Graham for the synthesis of $[Re(CO)_4(diphos)]^+$ which involves the use of carbon monoxide at a pressure only slightly above atmospheric.[22] The above preparation is to be contrasted with an analogous preparation of $[Mn(CO)_5PPh_3]^+$ reported employing a CO pressure of 250 atm by Kruck and Hofler.[41] The stereochemical position of the incoming ^{13}CO was determined from the ν(CO) infrared spectra aided by restricted force field computations (see Table III).

These ^{13}C-enriched cationic carbonyl derivatives were subjected to oxygen-exchange reaction with $H_2{}^{18}O$ as described for the parent ^{12}C derivatives. Figure 3 illustrates the

Table III. Calculated and Observed IR Frequencies in the Carbonyl Stretching Region for Oxygen-18 Isotopic Species of *cis*-$Mn(CO)_4(^{13}CO)PMe_2Ph^+$

Isotopic species	Frequencies,[a] cm^{-1}				
a	2136.8	2073.3	2063.7	2051.2	2018.1
	(2135.6)	(2078.2)	(2062 sh)	(2050.3)	(2018.9)
b	2133.4	2071.9	2063.4	2051.2	1971.8
					(1975.5)
c	2128.3	2068.6	2063.2	2019.8	2013.1
	(2127.1)				
d	2129.9	2067.4	2051.2	2040.9	2003.6
	(2127.1)				
e	2124.2	2067.6	2063.0	2015.3	1971.4
	(2125.6)				(1975.5)
f	2126.8	2067.0	2051.2	2028.5	1968.0
	(2125.6)				
g	2119.0	2064.5	2040.1	2013.6	2001.7
	(2118.1)				(2003.0)
h	2119.5	2064.5	2040.2	2016.9	2001.7
	(2118.1)				(2003.0)
i	2115.7	2064.4	2030.5	2013.0	1967.8
	(2114.1)				
j	2114.7	2063.9	2039.9	2001.7	1971.2
	(2114.1)			(2003.0)	
k	2102.7	2046.9	2022.3	2001.7	1967.7
	(2102.5)	(2045.9)	(2022 sh)	(2003.0)	(1972.7)
l	2085.0	2023.2	2013.9	2001.7	1967.4
	(2086.1)			(2003.0)	

[a] Calculated with force field given in Table I. Observed frequencies are listed in parentheses directly below the calculated values.

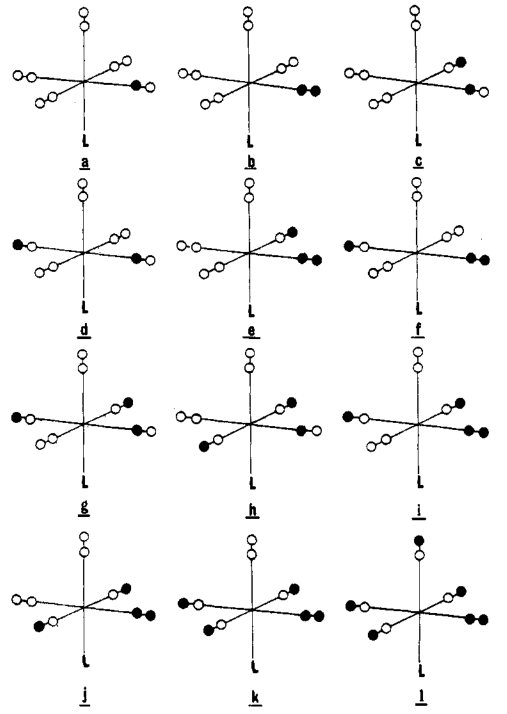


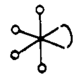
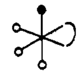
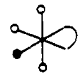
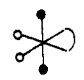
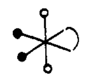
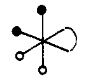
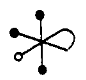
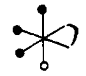
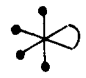
Figure 4. Illustration of the observed arrangements of $^{13}C^{18}O$ and $^{12}C^{18}O$ groups in $M(CO)_5L^+$ derivatives (closed circles represent carbon-13 or oxygen-18 atoms).

ν(CO) spectra obtained as a function of time for the incorporation of oxygen-18 into *cis*-$Mn(CO)_4(^{13}CO)PMe_2Ph^+$. Figure 4 depicts all the observed species derived from exchange reactions of *cis*-$Mn(CO)_4(^{13}CO)L^+$ with $H_2{}^{18}O$, whereas Table III shows the data for these isotopically labeled species where L = PMe_2Ph. Similar results were observed for all derivatives investigated. From Table III, it can be readily seen that the lowest frequency absorption occurring around 1970 cm^{-1} is due only to those species containing the $^{13}C^{18}O$ ligand.[42] As anticipated for preferential equatorial oxygen-18 incorporation, the ν(CO) band at 2085 cm^{-1} for the axially enriched species l was observed only after a large accumulation of the all equatorial oxygen-18 labeled species k had occurred as evidenced by the ν(CO) band at 2102 cm^{-1} [43]

In order to further test the stereochemical preference for oxygen exchange to occur at the carbonyl ligand with the highest CO stretching force constant in derivatives where a choice of carbonyl sites exists, we have explored the reaction of $[Mn(CO)_4(diphos)]^+$ with $H_2{}^{18}O$. The carbon monoxide ligands in this disubstituted derivative are more electron rich than those in the hexacarbonyl or pentacarbonyl cationic species and would in turn be expected, based on the electronic arguments presented above, to be less reactive toward nucleophilic attack. Indeed this expectation is dramatically borne out. Figure 5 depicts the ν(CO) spectra obtained as a function of time (measured in days) for the incorporation of oxygen-18 into $[Mn(CO)_4(diphos)][PF_6]$ in acetonitrile. As noted in Figure 5, the oxygen-exchange process is greatly retarded in this species.[44] Table IV contains the observed and calculated ν(CO) spectra for the possible isotopically enriched species of $[Mn(CO)_4(diphos)]^+$, along with the CO force field. As discernible in Figure 5, simultaneous growth in absorptions at 2082.5 and 1981.7 cm^{-1} corresponding to species **2** and in absorptions at 2069.7 and 1967.5 cm^{-1} corresponding to species **4** occurs in a stepwise manner (i.e., first production of **2** followed by formation of **4**). Eventually, a band grows in at 2059 cm^{-1} (species **7**) which corresponds to the diaxial-monoequatorial $C^{18}O$ derivative. These results clearly indicate that oxygen exchange occurs more readily at the axial CO ligand sites, i.e., those with the higher CO stretching force constant (see footnote *a* of Table IV).

We have examined further the mechanistic details of the oxygen-exchange process employing the relatively inert $[Mn(CO)_4(diphos)]^+$ derivative. The reaction with $H_2{}^{18}O$ was carried out in the presence of small quantities of a "nonreactive" amine, triethylamine.[20,45-48] The high-frequency overlay in Figure 5D illustrates the effect of an addition of 0.036 mmol of triethylamine (0.074 mmol of substrate and 2.5 mmol of

Table IV. Calculated and Observed IR Frequencies in the Carbonyl Stretching Region for the Nine Possible Isotopic Species of $[Mn(CO)_4(diphos)]^+$

Isotope	Geometry	ν(CO) Frequencies,[a] cm^{-1}			
1		2095.0 (*2094.0*)	2026.8 (*2026.5*)	2016.6 *b*	2001.5 *b*
2		2083.1 (*2082.5*)	2024.9	1981.1 (*1981.7*)	2001.5
3		2090.2	2019.2	2016.6	1965.1
4		2068.5 (*2069.7*)	2003.3	1967.9 (*1967.5*)	2001.5
5		2085.6	1986.8	2016.6	1953.3
6		2076.7	2018.8	1982.4	1963.9
7		2057.9 (2059.0)	2002.9	1963.7	1967.9
8		2070.5	1994.4	1974.8	1953.3
9		2044.5	1977.9	1967.9	1953.3

[a] Observed frequencies are listed in parentheses directly below the calculated values. Italicized frequencies were employed as input data in the force field fit ($k_1(eq) = 16.55$, $k_2(ax) = 16.90$, $k_c(ax-eq) = 0.25_9$, $k_c'(eq-eq) = 0.37_3$, $k_t(ax-ax) = 0.48_4$). [b] Two grossly overlapped bands centered ~2007 cm^{-1}.

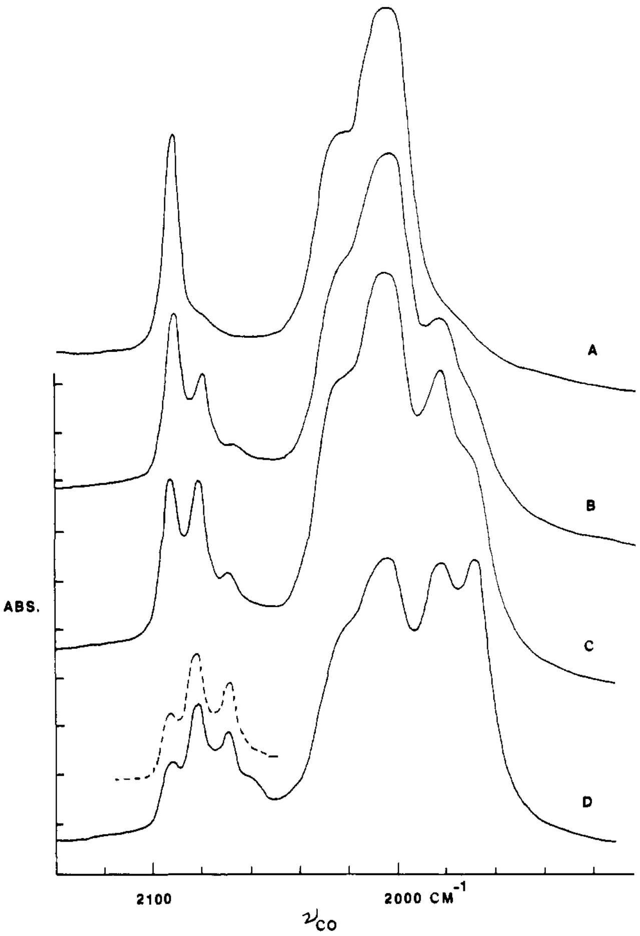
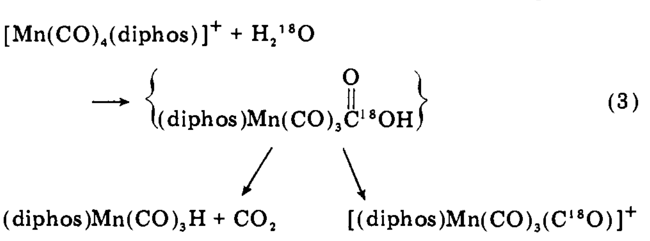


Figure 5. ν(CO) spectra as a function of time for the incorporation of oxygen-18 into $[Mn(CO)_4(diphos)]^+$ in acetonitrile: (A) 9 days, (B) 39 days, (C) 49 days, and (D) 78 days (overlay - - -, after 3 h with added Et_3N).

$H_2{}^{18}O$ in 2.0 mL of CH_3CN), the rate of oxygen-18 incorporation being markedly enhanced in the presence of triethylamine. For example, after 3 h of reaction time oxygen exchange has proceeded to approximately the same extent as that which took 78 days under similar conditions in the absence of triethylamine. This acceleration in rate can be attributed to an increase in the concentration of the reactive hydroxide species with added amine base. At the same time, however, these conditions increase the relative rate of β-hydrogen transfer in the hydroxycarbonyl intermediate with formation of CO_2 and metal hydride as compared to oxygen exchange (eq 3).[49] That is, although the reaction path leading to metal

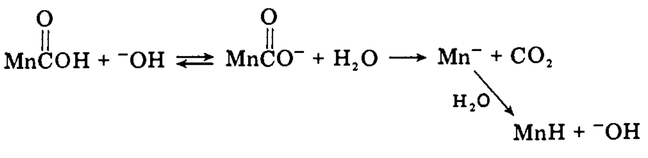


$$[Mn(CO)_4(diphos)]^+ + H_2{}^{18}O \longrightarrow \left\{(diphos)Mn(CO)_3\overset{\overset{O}{\|}}{C}{}^{18}OH\right\} \qquad (3)$$
$$\swarrow (diphos)Mn(CO)_3H + CO_2 \qquad \searrow [(diphos)Mn(CO)_3(C^{18}O)]^+$$

hydride formation is not noted for the reaction of $[Mn(CO)_4(diphos)]^+$ with water even over reaction periods as long as 78 days (where extensive oxygen-18 exchange has occurred), in the exchange reaction carried out in the presence of triethylamine substantial metal-hydride formation was observed.[50,51]

This observation that the hydroxycarbonyl intermediate is relatively more reactive toward β-hydrogen transfer vs. oxygen exchange in the presence of added base as compared to reactions carried out in the absence of base may be due to base (hydroxide ion) assistance in the β-elimination process. In other words, in the presence of relatively large concentrations of hydroxide ion, the hydroxycarbonyl intermediate may be attacked by ^-OH, presumably at the carboxylic carbon atoms,[52,53] leading to the formation of metal hydride and carbon dioxide.[54] It should be pointed out here parenthetically that reactions of metal carbonyls with potassium hydroxide have been known for some time to afford metal carbonyl hydride derivatives on a preparative scale, e.g., $Fe(CO)_5$ and $Cr(CO)_6$ yield $[HFe(CO)_4)]^-$ and $[Cr_2H(CO)_{10}]^-$, respectively.[4,55]

Alternatively, the hydroxide ion (or Et_3N itself) may serve to deprotonate the hydrocarbonyl intermediate, followed by release of CO_2 with hydrolysis of the reduced metal species, i.e.[56,57]



$$Mn\overset{\overset{O}{\|}}{C}OH + {}^-OH \rightleftharpoons Mn\overset{\overset{O}{\|}}{C}O^- + H_2O \longrightarrow Mn^- + CO_2$$
$$\xrightarrow{H_2O} MnH + {}^-OH$$

In conclusion, there is an obvious similarity between this process (metal hydride formation and CO_2 elimination) and the metal carbonyl cluster catalyzed energy-important water gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$).[58] We have, therefore, initiated a study of oxygen-exchange reactions between metal carbonyl clusters and labeled water.

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(44) Approximate CO stretching force constants for the reactive CO groups in the species, $[Mn(CO)_6]^+$, $[Mn(CO)_5PMe_2Ph]^+$, and $[Mn(CO)_4(diphos)]^+$ are 18.16, 17.44, and 16.90 mdyn/Å, respectively. It should as well be noted that sterically the carbonyl ligands are more hindered as substitution at the metal center by phosphines occurs. This has been shown to be an important consideration in reaction of $W(CO)_5L$ derivatives with the more bulky reagent $C_6H_5CH_2MgCl$.[17]
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Asymmetric Hydrogenation. Rhodium Chiral Bisphosphine Catalyst

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Abstract: Enantiomeric excesses of 95–96% are obtained by the asymmetric hydrogenation of α-acylaminoacrylic acids. The olefin configuration, whether *E* or *Z*, has a profound influence on the rate and stereospecificity. Excellent selectivity (~90% ee) was obtained with an α-enol ester, which is the first outstanding result with a nonamide substrate. A catalyst picture is presented and the stereochemical results are discussed.

The efficiency of asymmetric hydrogenation in soluble systems has greatly improved since the original development in 1968.[1,2] Enantiomeric excesses of 95–96% are now possible with α-acylaminoacrylic acids.[3] The optimum selectivity associated with earlier catalysts required rather mild reaction conditions, i.e., ambient temperature and pressure. Discovery of the catalyst precursor [rhodium(1,5-cyclooctadiene)L]$^+$ tetrafluoroborate$^-$ (**6**),[3] L = 1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine], **5**, opened new possibilities. The bisphosphine catalyst was not as sensitive to reaction variables