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Oxygen Exchange Reactions of $H_2{}^{18}O$ with the Hexacarbonyl Cations of Manganese and Rhenium

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Abstract: The reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with labeled water are described. The carbonyl ligands in these cationic carbonyl derivatives are found to undergo facile oxygen exchange reactions with $H_2{}^{18}O$, presumably through a hydroxycarbonyl intermediate, $[M(CO)_5C(O)OH]$, to afford $[M(C^{16}O)_{6-n}(C^{18}O)_n]^+$ species. In the manganese derivative β-hydrogen transfer in the intermediate is noted with the formation of oxygen-18 enriched $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ derivatives. The relative frequency for β-hydrogen transfer vs. oxygen exchange was found to be dependent on the nature of the metal center, with hydrogen transfer being retarded in the more electron-rich metal carbonyl centers such as $[Mn(CO)_5L]^+$ (L = phosphine, pyridine, CH_3CN) and $[Re(CO)_6]^+$.

Reactions of parent metal carbonyl species with hydroxide ion have been known for some time to result in the production of metal carbonyl hydride derivatives. In this manner $[HFe(CO)_4]^-$ and $[Cr_2H(CO)_{10}]^-$ have been prepared from the reaction of $Fe(CO)_5$ and $Cr(CO)_6$ with hydroxide, respectively.[1] Activated metal carbonyl derivatives similarly are reactive toward water. For example, $[Mn(CO)_6]^+$ readily reacts with water according to the overall reaction

$$[Mn(CO)_6]^+ + H_2O \rightarrow HMn(CO)_5 + H^+ + CO_2 \quad (1)$$

It has been proposed that this reaction proceeds via reduction of $[Mn(CO)_6]^+$ to $[Mn(CO)_5]^-$ which in turn hydrolyzes to $HMn(CO)_5$.[1] On the other hand, $[Re(CO)_6]^+$ is perfectly stable in water. Nevertheless, Muetterties has observed that this species exchanges oxygen with oxygen atoms in water, probably through nucleophilic attack of ^-OH on the carbonyl carbon atom to give the intermediate $Re(CO)_5COOH$.[2] Recently we have extended these studies to include stereospecific incorporation of oxygen-18 into manganese and rhenium pentacarbonyl derivatives.[3,4]

$$M(CO)_5L^+ + H_2{}^{18}O \rightarrow \{M(CO)_4(L)C(=O){}^{18}OH\} \rightarrow M(CO)_4(C^{18}O)L^+ \quad (2)$$

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

Presumably proton exchange readily occurs between the two oxygen atoms in the hydroxycarbonyl intermediate species which is in chemical equilibrium with the starting material.[5]

In an effort to define more precisely the nature of these metal-bound carbon monoxide oxygen exchange reactions with water, we have studied the reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with $H_2{}^{18}O$.

Experimental Section

Material and Equipment. Reagent grade acetonitrile (Matheson Coleman and Bell) was purified by distillation from sodium hydride or calcium sulfate. Similarly, reagent grade hexane (Matheson Coleman and Bell) was purified by refluxing over calcium sulfate and distilled prior to use. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were purchased from Strem Chemical Co. $H_2{}^{18}O$ (96.5% by weight oxygen-18) was obtained from Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio.

Preparations. $[Mn(CO)_6][BF_4]$ was prepared by the published procedure of Beach and Gray.[6] Similarly, $[Re(CO)_6][BF_4]$ was synthesized in an analogous manner. $Re_2(CO)_{10}$ (1.0 g, 1.9 mmol) dissolved in 20 mL of THF was reduced under nitrogen with an excess of sodium amalgam. After stirring for 30 min the orange solution was filtered under N_2 into 5 mL of ethyl chloroformate and the solution was stirred for an additional 2 h. The cloudy orange solution was filtered under N_2 to remove the NaCl precipitate. BF_3 was slowly bubbled into the filtrate for 15 min causing a white precipitate to form. (Alternatively, an excess of $BF_3 \cdot Et_2O$ was added to the solution which was stirred for 15 min to obtain the white precipitate.) The product was filtered, washed with 20 mL of THF, and vacuum dried. The purified yield was 0.30 g or 44%.

Reactions of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ with H_2O. $[Mn(CO)_6][BF_4]$ (0.103 g, 0.331 mmol) was dissolved in 8.0 mL of dry acetonitrile under nitrogen and an initial infrared spectrum in the $\nu(CO)$ region was obtained in a 0.1-mm sealed solution cell. To the stirred solution at room temperature was added 0.05 mL (2.5 mmol) of 95% $H_2{}^{18}O$ using a microsyringe. The reaction was monitored by periodically withdrawing samples and observing the $\nu(CO)$ infrared spectra. A similar reaction was carried out with $[Re(CO)_6][BF_4]$. Control reactions employing $H_2{}^{16}O$ were simultaneously performed.

A heterogeneous reaction was carried out between $[Mn(CO)_6][BF_4]$ and $H_2{}^{18}O$ by adding 1.0 mL of dry hexane to a degassed sample of $[Mn(CO)_6][BF_4]$ (0.203 g, 0.65 mmol) followed by the addition of 0.10 mL (5.0 mmol) of 95% $H_2{}^{18}O$. The extent of oxygen-18 enriched $(CO)_5MnH$ production was followed by withdrawing samples of the solution phase with a hypodermic syringe at various time intervals and obtaining their infrared spectra in the $\nu(CO)$ 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 $[M(CO)_6]^+$ (M = Mn and Re) species were performed using the Cotton-Kraihanzel approach[7] employing the $C^{16}O$ frequency data (T_{1u} mode) and assuming interaction force constants to be similar to those obtained in the monosubstituted pentacarbonyl derivatives.[4,8] The trial force constants were refined using the $C^{18}O$ frequency data and an iterative computer program[9] 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 three trial force constants were refined to reproduce the observed $C^{16}O$ and $C^{18}O$ vibrations to within an average of <1.5 cm^{-1}.

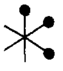
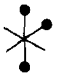
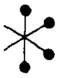
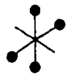
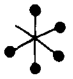
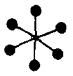
Calculation of the $\nu(CO)$ bands due to the various manganese pentacarbonyl hydride species, $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ (n = 0–5), was carried out using the carbonyl stretching parameters ($k_1 = 16.46$, $k_2 = 16.88$, $k_c' = 0.266$, $k_c = 0.299$, and $k_t = 0.480$) obtained by Kaesz and co-workers[10] based on a restricted carbonyl force field.

Results and Discussion

The reactions of $[M(CO)_6]^+$ (M = Mn and Re) with $H_2{}^{18}O$ have been followed in dry acetonitrile via infrared spectroscopy in the $\nu(CO)$ region aided by calculations involving a restricted CO force field. Figures 1 and 2 illustrate, respectively, the time-dependent $\nu(CO)$ spectra of oxygen-18 enrichment of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ in acetonitrile. The observed and calculated $\nu(CO)$ values for the ten possible isotopically substituted metal hexacarbonyl species, $[M(C^{16}O)_{6-n}(C^{18}O)_n]^+$ (n = 0–6), are listed in Table I. The carbonyl stretching parameters obtained from the approximate force field are the following: $[Mn(CO)_6]^+$ $k_1 = 18.16$, $k_c = 0.15_9$, and $k_t = 0.40_7$; $[Re(CO)_6]^+$ $k_1 = 18.10$, $k_c = 0.20_9$, and $k_t = 0.56_9$. The principal features of these spectra other than the parent absorptions at 2094.8 and 2082.9 cm^{-1} are bands due to the presence of $C^{18}O$ trans to $C^{16}O$ (2061 and 2049 cm^{-1}) or trans to $C^{18}O$ (2048 and 2034 cm^{-1}) for the manganese and rhenium derivatives, respectively. There are, however, slight shifts in some of these absorptions due to vibrational mixing in several of the isotopically substituted species.

Although the reaction of $[Re(CO)_6]^+$ with $H_2{}^{18}O$ is quite clean, affording only $\nu(CO)$ absorptions ascribable to the various $[Re(C^{16}O)_{6-n}(C^{18}O)_n]^+$ (n = 0–6) species, the reaction of $[Mn(CO)_6]^+$ with $H_2{}^{18}O$ in acetonitrile is more complex. Bands in the $\nu(CO)$ region assigned to $[Mn(C^{16}O)_{6-n}(C^{18}O)_n]^+$ species (labeled a in Figure 1) are initially predominant. However, $\nu(CO)$ absorptions due to $Mn(CO)_5(CH_3CN)^+$ (labeled b in Figure 1)[8] and $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ (labeled c in Figure 1) are also present. After the reaction mixture has been allowed to stand for extended periods of time $Mn(CO)_3(CH_3CN)_3{}^+$ ($\nu(CO)$ band labeled d in Figure 1)[8] is produced. Since $Mn(CO)_5(CH_3CN)^+$ is observed in the early stages of the reaction and $[Mn(CO)_6]^+$ was found to be inert in CH_3CN under the conditions of the reaction in the absence of H_2O, its formation must result from the displacement of the hydroxycarbonyl ligand in the intermediate by acetonitrile. Both $Mn(CO)_5(CH_3CN)^+$ and $HMn(CO)_5$ eventually afford the very stable $Mn(CO)_3(CH_3CN)_3{}^+$ derivative upon prolonged standing in wet acetonitrile. It is also worth noting that during the formation of $HMn(CO)_5$ no $\nu(CO)$ spectral evidence[11] for the presence of $[Mn(CO)_5]^-$ as an intermediate in this process was obtained. It is felt that both $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ react with

Table I. Observed and Calculated $\nu(CO)$ Frequencies for the Ten Possible Isotopic Species of $[M(CO)_6]^+$ with $C^{18}O$

		$\nu(CO)$ freq (cm^{-1})			
		M = Mn		M = Re	
Isotope	Geometry	Obsd[a]	Calcd	Obsd[a]	Calcd
1			2180.8		2198.0
		2125.5	2126.0		2126.1
		b	2126.0		2126.1
		2094.8	2096.9	*2082.9*	2083.7
		b	2096.9	*b*	2083.7
		b	2096.9	*b*	2083.7
2			2175.5		2192.1
		2125.5	2126.0		2126.1
		2116.6	2117.7	2116.4	2115.9
		2094.8	2096.9	2082.9	2083.7
		b	2096.9	*b*	2083.7
		2060.9	2059.2	*2049.0*	2048.8
3			2169.5		2185.3
			2121.1		2120.2
		2115.1	2115.2		2112.4
		2094.8	2096.9	2082.9	2083.7
		c	2061.8	*c*	2050.9
		c	2056.7	*c*	2046.6
4			2170.9		2186.7
		2125.5	2126.0		2126.1
		2094.8	2096.9	*c*	2085.5
		b	2096.9	2082.9	2083.7
			2084.2	*b*	2083.7
		2048.1	2046.3	*2034.1*	2033.5
5			2161.9	2178.0	2177.1
		2115.1	2115.2		2112.4
		b	2115.2		2112.4
			2064.2		2053.0
		c	2056.7	*c*	2046.6
		c	2056.7	*c*	2046.6
6			2164.0	2178.0	2179.1
			2119.3		2118.1
		2094.8	2096.9		2085.4
			2084.9	2082.9	2083.7
		c	2058.5	*c*	2048.3
		2048.1	2046.3	2034.1	2033.5
7			2154.8	2169.1	2069.4
		2115.1	2115.2		2112.4
			2085.7		2085.3
		c	2060.0	*c*	2049.6
		c	2056.7	*c*	2046.6
		2048.1	2046.3	2034.1	2033.5
8			2157.9		2172.2
			2096.9		2099.4
		2094.8	2096.6	2082.9	2083.7
			2074.7		2074.8
		2048.1	2046.3	2034.1	2033.5
		b	2046.3	*b*	2033.5
9			2145.6	2159.1	2159.7
			2096.7		2096.6
			2074.7		2074.8
		c	2058.1	*c*	2048.0
		2048.1	2046.3	2034.1	2033.5
		b	2046.3	*b*	2033.5
10			2128.2		2145.0
			2074.7		2074.8
			2074.7		2074.8
		2048.1	2046.3	2034.1	2033.5
		b	2046.3	*b*	2033.5
		b	2046.3	*b*	2033.5

[a] Frequencies were determined in acetonitrile and are accurate to ±1 cm^{-1}. Italicized frequencies were used as input data. [b] Degenerate vibration with observed band immediately above. [c] Buried beneath other, more prominent bands; however, some broadening in these regions was generally noted.

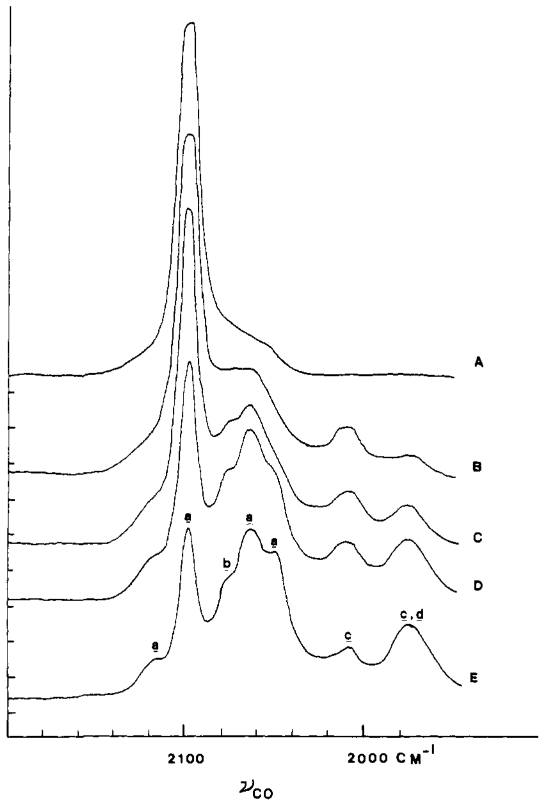


Figure 1. Time-dependent ν(CO) spectra for the reaction of $[Mn(CO)_6]^+$ with $H_2{}^{18}O$ in acetonitrile: A, initial spectrum; B, 0.5 h; C, 1.5 h; D, 4.0 h; E, 7.0 h.

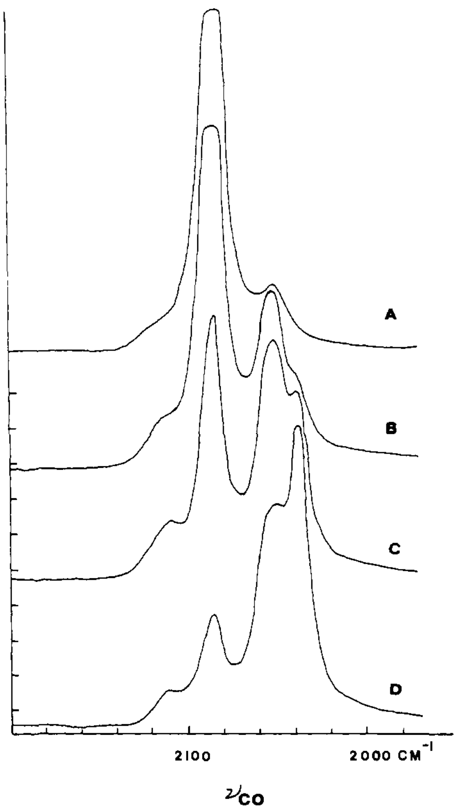


Figure 2. Time-dependent ν(CO) spectra for the reaction of $[Re(CO)_6]^+$ with $H_2{}^{18}O$ in acetonitrile: A, 0.25 h; B, 1.3 h; C, 4.0 h; D, 22.0 h.

water via a common hydroxycarbonyl intermediate, $[(CO)_5MC(O)OH]$, with the difference in reaction products being due to the relative ease of CO_2 elimination in the two metal species.

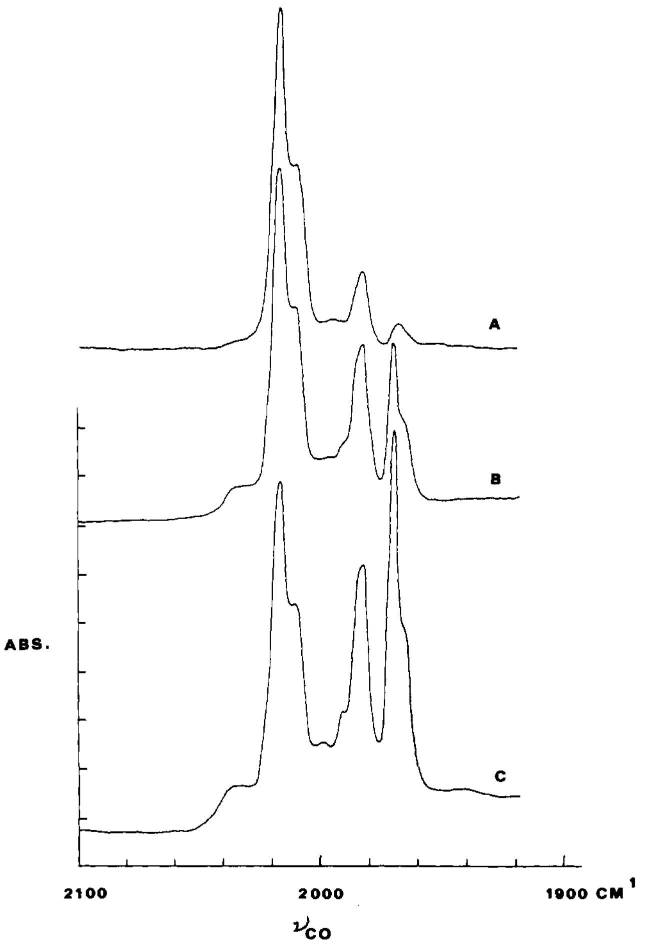


Figure 3. Variation in ν(CO) spectra of $HMn(CO)_5$ in hexane, produced via reaction of $[Mn(CO)_6]^+$ with $H_2{}^{18}O$, as a function of time. The large absorbances due to $HMn(C^{16}O)_5$ initially formed undergo no significant changes during the latter stages of the reaction: A, 10 min; B, 60 min; C, 120 min.

$$[M(CO)_6]^+ + H_2O \rightleftharpoons \{M(CO)_5C(=O)OH\} \rightarrow HM(CO)_5 + CO_2 \quad (3)$$

In order to better assess the relative magnitude of oxygen exchange vs. CO_2 elimination in the hydroxycarbonyl intermediate in the absence of secondary acetonitrile substitution processes, we have carried out biphasic reactions where the manganese pentacarbonyl hydride is extracted into hexane solvent. Thus, the extent of oxygen-18 incorporation into $[Mn(CO)_6]^+$ was noted from the appearance of labeled oxygen in the $HMn(CO)_5$ species. Calculated ν(CO) band positions for the $C^{18}O$ labeled $HMn(CO)_5$ derivatives, computed from a restricted force field, are given in Table II. Figure 3 contains the ν(CO) spectra obtained in hexane for the various $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ species. A control experiment where initially a quantity of $HMn(C^{16}O)_5$ was present, as evidence in Figure 3, indicated no oxygen exchange reactions of $HMn(CO)_5$ with $H_2{}^{18}O$ occur.

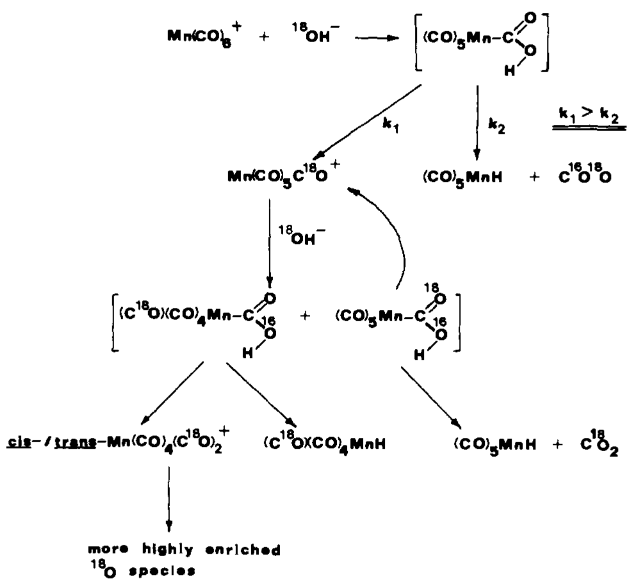
The appearance of oxygen-18 in $HMn(CO)_5$ was readily followed by observing the absorbances at 1981.5, 1968.7, and 1963.9 cm^{-1} which correspond respectively to substitution of $C^{18}O$ into the monoequatorial (**2**), the trans diequatorial (**5**), and the axial (**3**) positions. There is as well a band at ~1984 cm^{-1} (shoulder on band in species **2**) which is due to the cis diequatorial species (**4**). As can be seen in Table II, more highly enriched species, which are produced with longer reaction times, afford some absorbances slightly shifted from these noted above. Indeed some broadening of these absorbances mentioned above is seen with longer enrichment periods. From

Table II. Calculated Infrared Frequencies in the ν(CO) Region for the 12 Possible Isotopic Species of $HMn(CO)_5$ Enriched with $C^{18}O$[a]

Molecule	Freq, cm^{-1} [b]				
1. $HMn(C^{16}O)_5$	2117.8	2041.5	2015.4	2015.4	2005.7
2. $HMn(C^{16}O)_4(C^{18}O)$, eq	2110.0	2035.7	2006.4	2015.4	*1979.1*
3. $HMn(C^{16}O)_4(C^{18}O)$, ax	2113.6	2041.5	2015.4	2015.4	*1961.3*
4. $HMn(C^{16}O)_3(C^{18}O)_2$, cis eq	2100.6	2031.7	2007.1	*1981.5*	1976.3
5. $HMn(C^{16}O)_3(C^{18}O)_2$, trans eq	2102.1	2017.3	*1966.8*	2015.4	1995.6
6. $HMn(C^{16}O)_3(C^{18}O)_2$, ax-eq	2105.4	2035.6	1982.2	2015.4	1959.3
7. $HMn(C^{16}O)_2(C^{18}O)_3$, eq	2090.4	2016.9	1966.8	1995.7	1978.1
8. $HMn(C^{16}O)_2(C^{18}O)_3$, ax-eq (cis)	2095.3	2031.7	1987.2	1976.3	1958.1
9. $HMn(C^{16}O)_2(C^{18}O)_3$, ax-eq (trans)	2097.0	2010.5	1966.8	2015.4	1958.8
10. $HMn(C^{16}O)(C^{18}O)_4$, eq	2076.0	1992.3	1966.8	1966.8	1996.8
11. $HMn(C^{16}O)(C^{18}O)_4$, ax-eq	2084.1	2011.6	1966.8	1979.0	1957.7
12. $HMn(C^{18}O)_5$	2066.7	1992.3	1966.8	1966.8	1957.4

[a] Calculated using carbonyl force field in ref 10. [b] Italicized frequencies were employed in assessing the extent of oxygen-18 incorporation into $HMn(CO)_5$. These were observed at 1981.5, 1963.9, ~1984, and 1968.7 cm^{-1}, respectively.

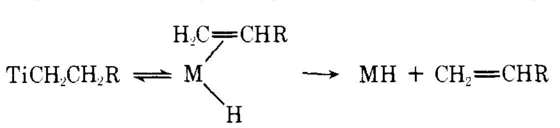
Scheme I



the relative growth of these absorbances it is readily discernible that there is progressively more highly oxygen-18 enriched $HMn(CO)_5$ species produced with time with no concomitant loss of previously afforded $HMn(C^{16}O)_{5-n}(C^{18}O)_n$ species. It is also clear from the initial growth rates of absorbances 1981.5 (due to species **2**) and 1963.9 cm^{-1} (due to species **3**) that there is no preference of $C^{18}O$ for the axial or equatorial position in the pentacarbonylhydride species as is dictated via reaction 3 where $[Mn(CO)_6]^+$ is statistically enriched in oxygen-18.

It therefore followed from these observations that CO_2 elimination with formation of metal hydride is considerably slower than simple oxygen-18 exchange; i.e., as shown in Scheme I, $k_1 > k_2$.[12]

Under similar conditions $[Mn(CO)_5L]^+$ derivatives (L = phosphine, pyridine, CH_3CN) as well as their rhenium analogues undergo oxygen-18 exchange reactions with H_2O albeit much slower than the parent hexacarbonyl species; CO_2 elimination is virtually excluded in these cases.[13] That is, there is even greater disparity in the rate constants, k_1 and k_2, when the metal center is more electron rich as is the case with the substituted species or $[Re(CO)_6]^+$. This trend in reactivity is analogous to that observed in the oligomerization of 1-olefins via Ziegler-Natta catalysts (eq 4) where the relative frequency


$$\mathrm{TiCH_2CH_2R} \rightleftharpoons \overset{\mathrm{H_2C{=}CHR}}{\underset{\mathrm{H}}{\mathrm{M}}} \longrightarrow \mathrm{MH} + \mathrm{CH_2{=}CHR} \quad (4)$$

of β-hydrogen transfer depends on the electron affinity of the metal.[14] As the electron affinity of titanium is reduced by the addition of donor ligands, the hydrogen transfer occurs less frequently.

We are in the process of developing synthetic methods for the production of oxygen-17 labeled $HMn(CO)_5$ and related compounds employing the water exchange reactions described above for nuclear resonance studies, i.e., NQR and NMR measurements.

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 76-04494 is greatly appreciated.

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