ordering in the crystal. The magnetic moment was found to be independent of magnetic field between approximately 1000 and 6000 G.

(25) The redox properties of TCNE and O_2 can be found respectively in ref 17 and in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution", Prentice-Hall, Englewood Cliffs, N.J., 1952.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Preparation of Oxygen-18-Labeled Derivatives of $[Mn(CO)_3(diphos)H]$ via Reaction of $[Mn(CO)_4(diphos)][PF_6]$ with $H_2{}^{18}O$ in the Presence of Triethylamine. Decarboxylation of a [Mn(COOH)] Intermediate

Donald J. Darensbourg* and Joseph A. Froelich

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During our studies of the exchange of oxygen atoms between cationic group 7B metal carbonyl derivatives and H_2O, we observed that in species where two electronically distinct CO groups were present, the less electron-rich carbonyl ligands were preferentially more reactive to oxygen exchange.[1-3] Further, it was noted that there was a dramatic effect on the rate of oxygen exchange as the electron density about the metal center was altered, i.e., the oxygen exchange decreased in the order $M(CO)_6^+ > M(CO)_5L^+ >> M(CO)_4L_2^+$. This process was proposed to proceed via neutral metal carbonyl intermediates containing the hydroxycarbonyl ligand, i.e., $L_n(CO)_{5-n}M(COOH)$ species where $n = 0$–2. For the reaction intermediate where M = Mn and $n = 0$, an important secondary reaction sequence was observed which involved CO_2 elimination with oxygen-enriched metal carbonyl hydride formation (eq 1).[2] Nevertheless, oxygen incorporation was

$$\mathrm{Mn(CO)_6^+ + H_2O \xrightleftharpoons{CH_3CN} \{(CO)_5Mn(COOH)\} \rightarrow Mn(CO)_5H + CO_2} \quad (1)$$

observed to be appreciably more rapid than hydride formation.

On the other hand, for the monosubstituted derivatives, this secondary process was not observed to be very important except when the reaction was carried out in the presence of dibenzo-18-crown-6 solubilized NaOH in acetonitrile.[4] Similarly, hydride formation was noted in the reaction of $M(CO)_5L^+$ species with NaSH in acetonitrile (eq 2). During

$$\mathrm{M(CO)_5L^+ + SH^- \rightleftharpoons \{M(CO)_4(L)(COSH)\} \rightarrow \mathit{cis}\text{-}HM(CO)_4L + COS} \quad (2)$$

the extended period (78 days) required for partial incorporation of labeled oxygen into $Mn(CO)_4(diphos)^+$ (diphos = bis(1,2-diphenylphosphino)ethane) via the exchange reaction with water, no metal hydride production was observed. However, upon the addition of triethylamine, although oxygen incorporation was greatly accelerated, the formation of $HMn(CO)_3(diphos)$ with concomitant CO_2 elimination was enhanced to an even greater extent (eq 3). That is, as was the

$$\mathrm{[Mn(CO)_4(diphos)]^+ + H_2{}^{18}O \xrightleftharpoons{Et_3N} \{(diphos)Mn(CO)_3COOH\} \rightarrow (diphos)Mn(CO)_3H + CO_2} \quad (3)$$

case for the reaction of the monosubstituted derivatives with H_2O in the presence of sodium hydroxide, the hydroxycarbonyl intermediate is particularly susceptible to the expulsion of CO_2 in the presence of added base.

We have examined further the effect of added amine on the relative rates of oxygen exchange vs. metal hydride production in $[Mn(CO)_4(diphos)]^+$ and wish to report the details of our investigation in this Note.

Experimental Section

Materials and Preparations. $[Mn(CO)_4(diphos)][PF_6]$ was prepared and purified by the published procedure.[3] Triethylamine was purified by distillation and reagent grade acetonitrile was dried by refluxing over sodium hydride or calcium sulfate and distilled prior to use. $H_2{}^{18}O$ (99.0% by weight oxygen-18) was obtained from Norsk Hydro (Norway). All operations on complexes in solution were carried out under an atmosphere of nitrogen.

Reactions of $[Mn(CO)_4(diphos)][PF_6]$ with $H_2{}^{18}O$. $[Mn(CO)_4(diphos)][PF_6]$ (0.09 g, 0.12 mmol) was dissolved in 3.0 mL of dry acetonitrile under nitrogen with stirring and 0.05 mL (2.5 mmol) of 99% $H_2{}^{18}O$ was added using a microsyringe. Triethylamine (2.5 μL, 0.018 mmol) was added as a catalyst for the reaction described in eq 3. The resulting concentrations of substrate and amine were 0.039 M and 5.9×10^{-3} M, respectively. The rate of oxygen-18 incorporation as well as metal hydride formation was monitored by removal of 0.5-mL samples of the reaction solution and the infrared spectrum in the ν(CO) region was recorded. Spectra of the neutral metal hydride derivative were also recorded in the absence of the cationic $[Mn(CO)_4(diphos)]^+$ species by removing the acetonitrile solvent from the 0.5-mL sample followed by the addition of 0.6 mL of dry hexane which led to the redissolution of only $HMn(CO)_3[diphos]$.

Additional reactions were performed in an identical manner (substrate concentration 0.039 M) employing varying quantities of triethylamine, namely, 10.0 μL (0.072 mmol or 0.024 M), 15.0 μL (0.108 mmol or 0.035 M), and 42.0 μL (0.301 mmol or 0.099 M), respectively. All reactions were monitored initially at 10–15-min intervals.

Infrared Measurements and Vibrational Analysis. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorption 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 $HMn(CO)_3[diphos]$ species were performed using the Cotton–Kraihanzel approach[5] employing the $C^{16}O$ frequency data. The trial force constants were refined using the $C^{18}O$ frequency data and an iterative computer program 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 molecules.[6] The trial force constants were refined to reproduce the observed ν(CO) vibrations for all $HMn(C^{16}O)_{3-x}(C^{18}O)_x[diphos]$ ($x = 0$–3) species within an average of 0.9 cm^{-1} or 0.045%.

Results and Discussion

The oxygen-exchange reaction of $[Mn(CO)_4(diphos)][PF_6]$ with $H_2{}^{18}O$ in acetonitrile to afford oxygen-18-labeled $[Mn(CO)_4(diphos)]^+$ derivatives in the absence of added base has been observed to be an extremely slow process with preferential production of axially enriched CO ligand sites.[3] Figure 1A illustrates the progress of this reaction, as monitored in the ν(CO) infrared region, after 49 days during which time only about half the molecules have at least one $C^{18}O$ group (all the observed bands have been assigned to the various $[Mn(C^{16}O)_{4-x}(C^{18}O)_x(diphos)]^+$ species). On the other hand in the presence of a "nonreactive" amine such as triethylamine the oxygen-exchange process is greatly accelerated.[7,8] For example, Figure 1B depicts oxygen-exchange reactions with $H_2{}^{18}O$ carried out in the presence of base (NEt_3) at two different concentrations, 0.024 and 0.099 M, with the cationic metal carbonyl substrate concentration equal to 0.039 M in both cases. In contrast to the relatively inert behavior observed in the absence of base, after only 45 min, ca. one-third and ca. two-thirds of the molecules have at least one $C^{18}O$ group as the NEt_3 concentration is quadrupled from 0.024 to 0.099 M. However, as noted in Figure 1B when compared with Figure 1A, there are additional ν(CO) bands at 1992 and 1906

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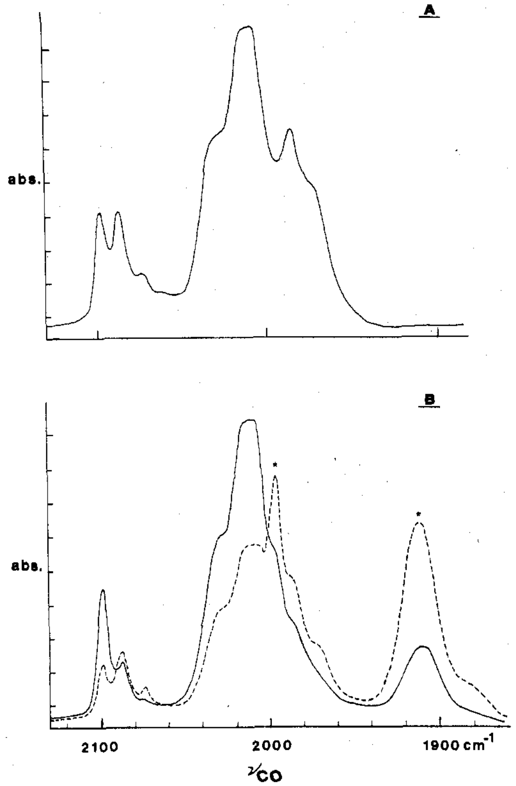


Figure 1. ν(CO) spectra for the incorporation of oxygen-18 into $[Mn(CO)_4(diphos)]^+$ in acetonitrile: A, after 49 days reaction period in the absence of triethylamine; B, after 45 min reaction period in the presence of triethylamine ((—) $[NEt_3]$ = 0.024 M, (- - -) $[NEt_3]$ = 0.099 M). Substrate concentration equals 0.039 M in both cases. Bands marked with asterisks are due to the hydride species.

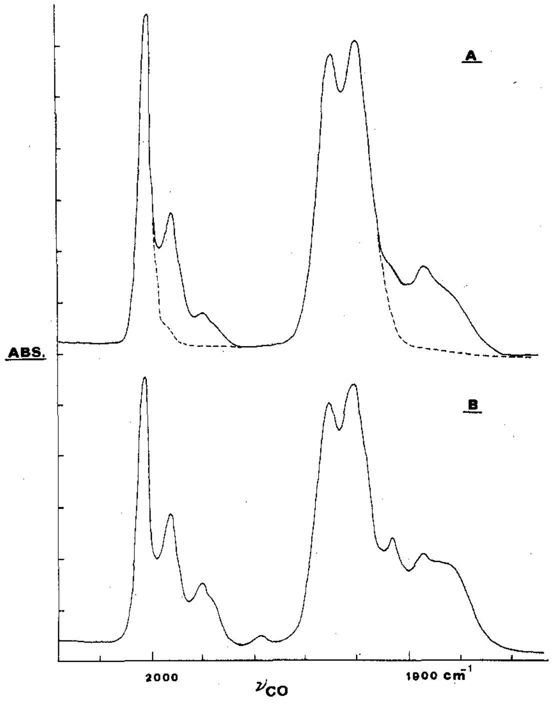
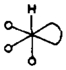
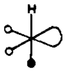
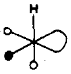
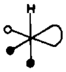
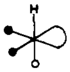
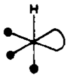


Figure 2. ν(CO) spectra of the oxygen-18 enriched $HMn(CO)_3$[diphos] species in hexane solution prepared under the conditions given in Figure 1B: A, $[NEt_3]$ = 0.024 M (- - -, spectrum due to all $C^{16}O$ species); B, $[NEt_3]$ = 0.099 M.

cm^{-1} for the oxygen-exchange reactions performed in added base (bands indicated by asterisks in Figure 1B). These ν(CO) bands have been attributed to the $HMn(CO)_3$[diphos] species. This manganese hydride derivative has previously been prepared by a facile CO substitution process in the $HMn(CO)_5$ derivative with 1,2-bis(diphenylphosphino)ethane (eq 4) and

Table I. Calculated and Observed Infrared Frequencies in the Carbonyl Stretching Region for the Six Possible Isotopic Species of $HMn(CO)_3$[diphos]

isotope	geometry	ν(CO) freq,[a] cm^{-1}		
1		2003.5 (2002.1)	1933.1 (1932.8)	1923.0 (1923.6)
2		1993.2 (1995.3)	1896.2 (1896.7)	1923.0
3		1992.3	1931.1	1889.2 (1888.7)
4		1978.8	1903.4	1883.2
5		1978.9	1909.9	1876.6
6		1955.1	1886.5	1876.6

[a] Observed frequencies used in force field fit are listed in parentheses directly below the calculated values. Spectra were measured in hexane solution. Force field calculated: k_1 = 15.45_1, $k_2 = 15.38_7$, $k_c' = 0.45_6$, and $k_c = 0.37_0$ (see Figure 3 for force constant designations).

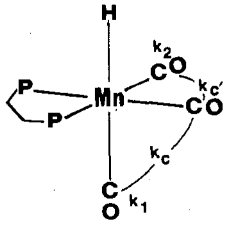


Figure 3. ν(CO) force constant designations in $HMn(CO)_3$[diphos].

$$HMn(CO)_5 + diphos \xrightarrow[22\ ^\circ C]{benzene} HMn(CO)_3[diphos] + 2CO \quad (4)$$

has been assigned an all cis geometry.[9] The rhenium analogue has similarly been prepared.[10] As noted in Figure 1B, the extent of hydride formation as well as oxygen exchange is proportional to the concentration of triethylamine.

It was necessary to isolate the hydride species $HMn(CO)_3$[diphos] from the cationic $[Mn(C^{16}O)_{4-x}(C^{18}O)_x(diphos)]^+$ derivatives in order to assess the quantity of oxygen-18 incorporation into the hydride derivative. This was easily accomplished by selective dissolution of the neutral hydride species in saturated hydrocarbon solvent once the reaction solution had been taken to dryness. Figure 2 shows the ν(CO) infrared spectra of the oxygen-18 enriched $HMn(CO)_3$[diphos] species in hexane solution. All of the observed ν(CO) bands were assigned to the various $HMn(C^{16}O)_{3-x}(C^{18}O)_x$[diphos] derivatives based on restricted CO force field calculations (see Table I). These CO stretching force constant computations were performed initially using the C–K equations[5] for a C_{3v} $M(CO)_3$ fragment (A_1 + E modes) by employing the average of the two lower frequency bands (1932.8 and 1923.6 cm^{-1}) as the E mode vibration and assigning the 2002.1-cm^{-1} vibration to the A_1 mode. This resulted in trial CO stretching force constants of k = 15.41 and k_i = 0.39. An iterative calculation has been carried out using both $C^{16}O$ and $C^{18}O$ frequency data and releasing the constraints on the CO force field such that k_1 is slightly different from k_2 which is approximately equal to k, and k_c slightly different from $k_{c'} \approx k_i$, i.e., consistent with the C_s symmetry of the carbonyl species (see Figure 3). The results of this calculation are found in Table I along with the CO stretching force field. As noted in Table I, the CO stretching force constant trans to the hydride (k_1) is slightly greater than that which is trans to the phosphine ligand (k_2) as would be anticipated.

The degree to which oxygen-18 has been incorporated into the $HMn(CO)_3$[diphos] species is considerably less than that in the corresponding $[Mn(CO)_4(diphos)]^+$ precursor at high amine concentration. This observation would of course be anticipated since both processes, oxygen exchange and metal hydride production, are occurring at comparable rates and the once formed $HMn(CO)_3$[diphos] derivative has been demonstrated not to exchange oxygen atoms with $H_2{}^{18}O$ directly. Contrasting the extent of oxygen-18 incorporation into the parent $[Mn(CO)_4(diphos)]^+$ species vs. that in the $HMn(CO)_2$[diphos] (i.e., comparing Figures 1B and 2), it is quite obvious that the intermediate common to both processes is proceeding to hydride to a greater degree as the concentration of base is increased (eq 5, where rate$_2$ is enhanced by the presence of base). For the various concentrations of added triethylamine there was a dependence on the relative rates of oxygen-18 incorporation of about $[Et_3N]^{1/2}$ as would be expected for ^-OH catalysis (i.e., $Et_3N + H_2O \rightleftharpoons Et_3NH^+ + {}^-OH$). On the other hand, there was observed a greater dependence of the relative rates of hydride production on the initial triethylamine concentration.

$$\begin{aligned}[\mathrm{MnCO}]^+ + {}^{18}\mathrm{OH}^- \rightarrow [\mathrm{MnCO}^{18}\mathrm{OH}] &\xrightarrow{\text{rate}_1} [\mathrm{MnC}^{18}\mathrm{O}] \\ &\xrightarrow{\text{rate}_2} [\mathrm{MnH}] + \mathrm{C}^{16}\mathrm{O}^{18}\mathrm{O}\end{aligned} \tag{5}$$

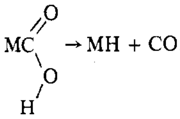
These observations have previously been ascribed to a deprotonation of the hydroxycarbonyl intermediate by base followed by hydrolysis of the reduced metal species produced via loss of CO_2, in this case $[Mn(CO)_3(diphos)]^-$ (eq 6).[3]

$$\begin{tikzcd}
{[\mathrm{Mn(COOH)}] + {}^-\mathrm{OH}(\mathrm{Et_3N})} \arrow[r, leftrightarrow] & {[\mathrm{MnCOO}]^- + \mathrm{H_2O}(\mathrm{Et_3NH^+})} \arrow[d] \\
 & {[\mathrm{Mn}]^- + \mathrm{CO_2}} \arrow[d, "\mathrm{H_2O}"'] \\
 & {[\mathrm{MnH}] + {}^-\mathrm{OH}}
\end{tikzcd} \tag{6}$$

Other reductive processes where the MCO_2H group has been postulated as an intermediate have appeared in the literature,[11-13] including the $[HgCO_2H]^+$ moiety in the reduction of Hg(II) to Hg(0) by carbon monoxide.[12] Similarly, a complex containing the closely related $[MCONHCH_3]$ grouping has been found to react with base to afford the reduced metal species (eq 7).[14]

$$(C_5H_5)W(CO)_3C(O)NHCH_3 + Et_3N \rightarrow (C_5H_5)W(CO)_3^- + CH_3N{=}C{=}O + Et_3NH^+ \tag{7}$$

Nonetheless, there are probably two mechanisms operative in [MH] formation via CO_2 elimination from the [MCOOH] intermediates; these being a concerted β-H migration (eq 8)



$$\mathrm{MC(=O)OH} \rightarrow \mathrm{MH} + \mathrm{CO_2} \tag{8}$$

which usually requires a vacant site on the metal or the base-catalyzed reductive process (eq 6). Indeed pyrolysis of the only stable example of a metal complex containing the hydroxycarbonyl ligand, $[IrCl_2(CO_2H)(CO)L_2]$ (L = Me_2PhP or Me_2PhAs), in the solid state affords the corresponding IrH complex plus carbon dioxide.[15]

In conclusion, it is apparent from the studies reported here that in order to influence the rate of MH formation from the reaction of KOH with metal carbonyl derivatives where this step is reluctant, it would be advantageous to use excess quantities of KOH even though the reaction may be catalytic in hydroxide ion (e.g., eq 9).[16] This process is indeed highly desirable in the homogeneous catalyzed water–gas shift reaction by metal carbonyl derivatives. On the other hand if it is desirable to enrich the metal carbonyl derivative with oxygen-18 or oxygen-17 it is preferable to carry out the reaction in a minimum of hydroxide ion.[17] However, in cases where metal hydride formation is quite rapid relative to the reverse process involving loss of ^-OH from the hydroxycarbonyl intermediate (e.g., the reaction of $Ru_3(CO)_{12}$ with OH^-)[16-19] large concentrations of ^-OH should be much less important for production of metal hydride species.

$$\begin{tikzcd}
{\mathrm{Cr(CO)_6} + {}^-\mathrm{OH}} \arrow[r, leftrightarrow] & {[\mathrm{Cr(CO)_5COOH}]^-} \arrow[d] \\
{[\mathrm{Cr(CO)_5H_2}] + {}^-\mathrm{OH}} \arrow[u, "\text{excess CO}", "-\mathrm{H_2}"'] & {\mathrm{Cr(CO)_5H^-} + \mathrm{CO_2}} \arrow[l, "\mathrm{H_2O}"']
\end{tikzcd} \tag{9}$$

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Registry No. **1**, 36352-75-7; **2**, 67530-47-6; **3**, 67576-70-9; **4**, 67530-48-7; **5**, 67597-59-5; **6**, 67530-49-8; $[Mn(CO)_4(diphos)](PF_6)$, 6443-17-0; $H_2{}^{18}O$, 14314-42-2.

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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Reaction of Trimethylamine–Fluoroboranes with Phosphine and Amine Bases

J. M. VanPaasschen and R. A. Geanangel*

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Reactions where two donor molecules compete for one acceptor have been used to compare the preferences of ac-