corresponding P=O and P–O–P spectral regions. It is evident that there is an almost exact parallel regarding the number of prominent bands and their relative spacings. The difference in relative intensities is due to the different extents of $^{18}O$ enrichment.

A detailed interpretation of all these isotope patterns will be presented elsewhere,[8] but it has already been shown that pattern B in particular is distinctive[9] of the highest $T_2$ vibration in $M_4O_6$ cage units. We believe that the similarity in isotope patterns strongly supports our identification of matrix-isolated $V_4O_{10}$ ($T_d$ symmetry), and these results therefore confirm the basic conclusions of the mass spectrometric studies.

**Registry No.** $V_4O_{10}$, 12503-98-9.

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# A Tetracyanoethylene Complex of (*meso*-Tetraphenylporphinato)manganese(II)

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Recently we have been investigating the chemical and spectroscopic properties[1,2] of porphyrinatomanganese–dioxygen complexes formed from the reaction of molecular oxygen with high-spin $d^5$ porphyrinatomanganese(II) complexes in toluene at −78 °C. The resulting dioxygen complexes have the form $Mn(por)(O_2)$ (por = porphyrin), and on the basis of EPR evidence[2] have been described in terms of a $Mn^{IV}(O_2^{2-})$ formalism. Although the structures of these manganese–dioxygen complexes have not yet been determined, on the basis of analogy with other metal–dioxygen systems containing a coordinated peroxide ($O_2^{2-}$) moiety as well as on the basis of recent chemical evidence,[1] it has been postulated that the dioxygen is bound to the manganese in a $\pi$-bonded symmetrical, Griffith-type conformation.

During our investigation of the reactivity of porphyrinatomanganese(II) complexes we have observed that in nonpolar aromatic hydrocarbon solvents, complexes of the type $Mn^{II}(TPP)(L)$[3] react with TCNE to form an adduct which is reversible upon the addition of a strongly coordinating neutral ligand such as pyridine. Since TCNE has been shown to be capable of reacting with low-valent organometallic complexes to form adducts in which the TCNE is bound to the metal center in a $\pi$-bonded olefin structure,[4] similar to the structure proposed for the bonding of $O_2$ in the manganese–dioxygen complexes, we have characterized the complex formed between (tetraphenylporphinato)manganese(II) complexes and TCNE.

## Experimental Section

Tetracyanoethylene was obtained from Aldrich Chemical Co. and was used without further purification. Toluene was reagent grade and was distilled from sodium–benzophenone ketyl immediately prior to use. All procedures were carried out under a $N_2$ atmosphere using standard Schlenk-type glassware and techniques.

The resonance Raman spectra were obtained by excitation with a Coherent Radiation Model CR-3 $Ar^+$ laser. The spectra were collected with a 0.75-m Spex Model 1400-II double monochormater equipped with a cooled RCA C31034A photomultiplier tube with standard low-level threshold photocounting electronics. The samples were spun rapidly in evacuated 5 mm o.d. Pyrex tubes to avoid laser-induced thermal decomposition.

*meso*-Tetraphenylporphine was synthesized by the method of Adler et al.[5] The complex $Mn^{II}(TPP)(py)$ was prepared by the literature method.[1] In a typical preparation of Mn(TPP)(TCNE) a toluene solution of TCNE (150 mg in 20 mL of toluene) was added via a gastight syringe to a toluene solution of $Mn^{II}(TPP)(py)$ (300 mg in 30 mL of toluene). The solution was stirred briefly at room temperature and was allowed to stand for 0.5 h. The purple crystalline product was collected by filtration and washed twice with 10-mL portions of toluene. The solid was dried overnight in vacuo to yield 270 mg (84%) of product. Anal.[6] Calcd for $C_{50}H_{28}N_8Mn$: C, 75.47; H, 3.55; N, 14.08; Mn, 6.90. Found: C, 75.82; H, 3.90; N, 13.55; Mn, 6.58.

## Results

Mixing toluene solutions of $Mn^{II}(TPP)(py)$ and TCNE in an inert atmosphere at room temperature results in the precipitation of a solid complex having the empirical formula Mn(TPP)(TCNE). The solid, which is moderately air stable, is insoluble in aromatic hydrocarbons but dissolves readily in deoxygenated weakly coordinating polar solvents, such as methanol, to give solutions having optical spectra characteristic of (tetraphenylporphinato)manganese(III) complexes. The optical spectrum of Mn(TPP)(TCNE) exhibits absorption maxima between 650 and 350 nm identical with those obtained from a methanol solution of $Mn^{III}(TPP)(Cl)$. Dissolving solid Mn(TPP)(TCNE) in deoxygenated pyridine results in an optical spectrum showing a mixture of both manganese(II) and manganese(III) tetraphenylporphinato species.[8]

When spectroscopic amounts of $Mn^{II}(TPP)(py)$ are dissolved in toluene (concentration $\sim 10^{-5}$ M) a characteristic (tetraphenylporphinato)manganese(II) type spectrum is observed.[9] Adding a toluene solution of TCNE to the metalloporphyrin solution results in the disappearance of the Mn(TPP)(py) spectrum. The addition of pyridine to the Mn(TPP)(TCNE) solution results in the regeneration of the $Mn^{II}(TPP)(py)$ spectrum in about 85% yield with the rest of the material being present as a manganese(III) porphyrin species.[10]

The optical spectrum of solid Mn(TPP)(TCNE) in Nujol was obtained, Figure 1. This spectrum is not characteristic of either a manganese(II) or manganese(III) tetraphenylporphinato complex. This spectrum is identical with that obtained when an excess of a toluene solution of TCNE is added to a toluene solution containing spectral amounts of $Mn^{II}(TPP)(TCNE)$ with the exception that a broad band is observed at 405 nm which is attributable to the presence of a TCNE–toluene charge-transfer band arising from the presence of excess TCNE.

The X-band EPR spectrum of a frozen toluene solution of $Mn^{II}(TPP)(py)$ shows a spectrum characteristic of high-spin $d^5$ systems having a large zero-field splitting.[11] The addition of TCNE as either a solid or in toluene solution to an EPR tube containing a toluene solution of $Mn^{II}(TPP)(py)$ and rapidly cooling the mixture to 78 K result in the the disappearance of the $Mn^{II}(TPP)(py)$ spectrum and the replacement by a featureless spectrum between 0 and 7000 G. When tetrafluoroethylene was added to an EPR tube containing a toluene solution of $Mn^{II}(TPP)(py)$, no adduct formation was observed, as indicated by no change in the EPR spectrum.[12]

Both resonance Raman (Figure 2) and infrared spectra were taken of the solid Mn(TPP)(TCNE) complex and indicate extensive transfer of electron density from the manganese center to the coordinated TCNE moiety (see Discussion).

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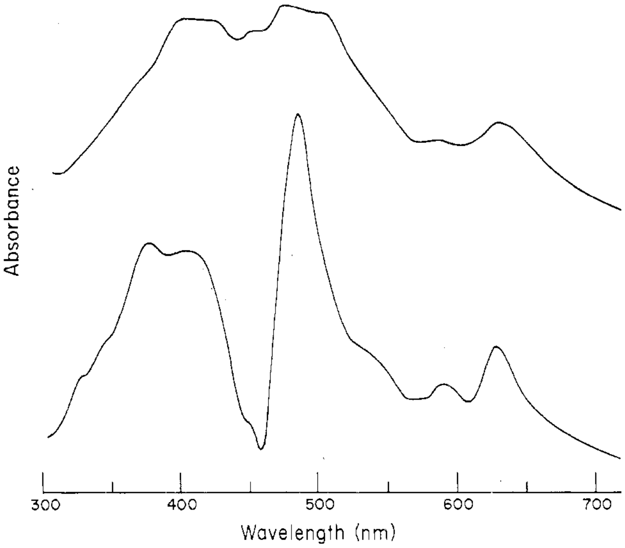

**Figure 1.** Optical spectra of solid Mn(TPP)(TCNE), top, and $Mn^{III}(TPP)(Cl)$, bottom, in Nujol. The absorptivities of the bands of Mn(TPP)(TCNE) in the 300–500-nm region are significantly less than normally observed in $Mn^{III}(TPP)$ complexes.

Table I. Magnetic Susceptibility Data for Solid Mn(TPP)(TCNE)

| $T$, K | $10^5\chi_g$, cgsu | $\mu_{eff}$,[a] $\mu_B$ | $T$, K | $10^5\chi_g$, cgsu | $\mu_{eff}$,[a] $\mu_B$ |
|---|---|---|---|---|---|
| 293 | 1.11 | 4.66 | 169 | 2.20 | 4.93 |
| 232 | 1.42 | 4.66 | 150 | 2.62 | 5.05 |
| 217 | 1.54 | 4.69 | 130 | 3.35 | 5.31 |
| 202 | 1.70 | 4.74 | 106 | 4.66 | 5.64 |
| 186 | 1.91 | 4.82 | 78 | 8.93 | 6.68 |

[a] Calculated per mole of Mn(TPP)(TCNE). A correction of $-396 \times 10^{-6}$ cgsu/mol was made for the diamagnetism of the porphyrin.

Magnetic susceptibility measurements of the solid Mn(TPP)(TCNE) complex were made by the Faraday method between 293 and 78 K. The results are summarized in Table I.

## Discussion

Few reactions of TCNE with metal complexes exhibiting a porphyrin-like chelate structure have been reported. Tetracyanoethylene has been shown[13] to interact with the Schiff base complex $Co^{II}(acacen)(py)$ to yield two complexes containing 2 mol of $Co^{II}(acacen)(py)$/mol of TCNE. In both complexes the TCNE ligand is said to be bonded to the cobalt centers through the nitrile nitrogen atom and there appears to be some transfer of electron density from the cobalt centers to the coordinated TCNE ligand. Further, toluene solutions containing either $Co^{II}(TPP)$ or $Co^{II}(TPP)(py)$ have been shown[14] to react reversibly with TCNE to form complexes in which the TCNE has been reduced to the $TCNE^{-}\cdot$ anion radical. A comparison of the $M^{III}/^{II}$ redox potentials of cobalt and manganese tetraphenylporphinato complexes indicates that reduction of TCNE to the anion radical should be more favorable for the manganese porphyrin complex than for the cobalt porphyrin complexes.[15] In agreement with the above prediction, $Mn^{II}(TPP)(py)$ reacts with TCNE in toluene solution to give an adduct in which there is a substantial transfer of electron density from the manganese center to the coordinated TCNE ligand. As is discussed below, such a conclusion is consistent with both the chemical behavior and spectroscopic properties of Mn(TPP)(TCNE).

The reaction of $Mn^{II}(TPP)(py)$ and TCNE in toluene solution does not involve either the formation of a charge-transfer type of complex having a neutral ground state or the formation of a $Mn^{II}(TPP)(TCNE)$ complex involving a neutral TCNE bound to a manganese(II) center through a nitrile nitrogen atom of the TCNE ligand. This is confirmed by the following experimental observations: (1) the formation of the Mn(TPP)(TCNE) complex results in the disappearance of the typical (tetraphenylporphinato)manganese(II) type optical spectrum. For either a neutral ground-state charge-transfer complex or a neutral TCNE ligation of the $Mn^{II}(TPP)$, a typical porphyrinatomanganese(II) spectrum should be observed.[16] (2) Dissolution of solid Mn(TPP)(TCNE) in a polar, weakly coordinating, solvent such as methanol results in the quantitative formation of a $Mn^{III}(TPP)$ species. This observation suggests that there is a transfer of electron density from the manganese center to the TCNE ligand. Further, the formation of large amounts of a manganese(III) porphyrin species upon dissolution of solid Mn(TPP)(TCNE) in pyridine is incompatible with the presence of a coordinated neutral TCNE ligand. For such a complex, the addition of pyridine would result in simple ligand replacement to give $Mn^{II}(TPP)(py)$. (3) The disappearance of the characteristic $Mn^{II}(TPP)(L)$ EPR spectrum upon complexation with TCNE is consistent with a Mn(II) ground state for the complex. (4) There is no disruption of the optical spectra when TCNE is added to toluene solutions containing either $TPPH_2$ or $Zn^{II}(TPP)$.

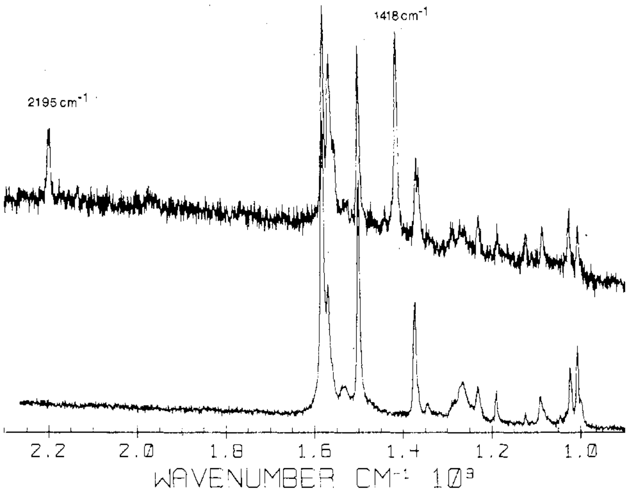

**Figure 2.** Resonance Raman spectra of solid Mn(TPP)(Cl), bottom, and Mn(TPP)(TCNE), top. The spectra were taken using an $Ar^+$ laser with 5145-Å excitation at 50 mW laser power, 0.25 Å/s scan rate, and 1.0 s counting interval. The presence of TCNE associated resonances at 1418 and 2195 $cm^{-1}$ indicate that the coordinated TCNE resembles the anion radical, $TCNE^{-}\cdot$.

Having established that the reaction between $Mn^{II}(TPP)(py)$ and TCNE involves a significant transfer of electron density from the manganese center to the TCNE ligand, we now turn our attention to the nature of the interaction between the metalloporphyrin and the coordinated TCNE moiety. An indication of the nature of the Mn(TPP)(TCNE) complex comes from the resonance Raman spectrum of solid Mn(TPP)(TCNE). Resonance Raman spectroscopy can be utilized to probe the oxidation state of the TCNE moiety by comparing the frequencies of the totally symmetric Raman-active modes of the coordinated TCNE with the frequencies observed for both neutral TCNE and the anion radical $TCNE^{-}\cdot$.[17] Of the four $A_g$ modes of TCNE the $\nu_1$ mode, which is predominently associated with the C≡N stretch, and the $\nu_2$ mode, which is associated largely with the C=C stretch, undergo the largest frequency shifts upon reduction of TCNE to $TCNE^{-}\cdot$.[17] In the resonance Raman spectrum of solid Mn(TPP)(TCNE), Figure 2, these bands, $\nu_1$ and $\nu_2$, occur at 2195 and 1418 $cm^{-1}$, respectively. These values are vitually identical with those obtained for

**Table II.** The C≡N IR Stretching Frequencies for Several TCNE Compounds (cm$^{-1}$)

| | band I | band II |
|---|---|---|
| TCNE$^{a}$ | 2260 | 2225 |
| TCNE$^{-\cdot\, a}$ | 2200 | 2175 |
| TCNE$^{2-\, a}$ | 2160 | 2095 |
| Mn(TPP)(TCNE)$^{b}$ | 2195 | 2150 |

$^{a}$ Alkali halide pellets.[20] $^{b}$Nujol.

$[(C_4H_9)_4N]^+[TCNE]^{-\cdot}$,[17] i.e., 2194 and 1421 cm$^{-1}$.[18] Values for $\nu_1$ and $\nu_2$ for neutral TCNE have been measured[17] as 2231 and 1562 cm$^{-1}$, respectively.[19]

Further evidence that the coordinated TCNE can be represented as the anion radical, TCNE$^{-\cdot}$, comes from infrared evidence. The C≡N stretching region of the infrared spectrum has been used to probe the nature of coordinated TCNE ligands.[4,13,20] In alkali halide pellets, TCNE, TCNE$^{-\cdot}$, and TCNE$^{2-}$ are all characterized by doublets in the 2100–2300-cm$^{-1}$ region, Table II. A comparision of the stretching frequencies obtained from Mn(TPP)(TCNE),[21] which similarly shows a doublet in the 2100–2300-cm$^{-1}$ region, with those obtained for neutral TCNE and its anions, Table II, supports the evidence obtained from resonance Raman spectroscopy that the coordinated TCNE in Mn(TPP)(TCNE) resembles the anion radical, TCNE$^{-\cdot}$. On the basis of both infrared and resonance Raman spectroscopy, the complex formed between (tetraphenylporphinato)manganese(II) and TCNE can be represented as Mn$^{III}$(TPP)(TCNE$^{-\cdot}$).

Despite the assignment of the complex as having a Mn(III) center coordinated to a TCNE$^{-\cdot}$ ion, the optical spectrum of Mn$^{III}$(TPP)(TCNE$^{-\cdot}$) is not characteristic of a typical manganese(III) porphyrin. Rather, the absence of bands in the optical spectrum normally associated with $\pi$ to $\pi^*$ transitions of the porphyrin $\pi$ orbitals[22] implies that there is a substantial disruption of the porphyrin $\pi$ cloud. Such a disruption of the porphyrin would not be expected were the TCNE$^{-\cdot}$ anion bonded to the porphyrin via a nitrile–nitrogen atom but rather implies that the C=C axis of the coordinated TCNE$^{-\cdot}$ lies parallel to the plane of the porphyrin ring.[23] The actual geometric structure of the complex and the nature of the bonding between the coordinated TCNE$^{-\cdot}$ ion and the manganese porphyrin moiety await a single-crystal X-ray structure determination. Attempts to obtain single crystals of Mn(TPP)(TCNE) suitable for an X-ray structure determination have so far proven unsuccessful.

The solid complex Mn(TPP)(TCNE) exhibits unusual magnetic properties, Table I. The effective magnetic moment per manganese increases from 4.66 $\mu_B$ at 293 K to 6.68 $\mu_B$ at 78 K, indicative of an ordering of the unpaired electrons at low temperatures.[24]

Finally, it is interesting to note the different properties observed for Mn(TPP)(TCNE) and the dioxygen complex Mn(TPP)($O_2$). Whereas adding TCNE or $O_2$ to a toluene solution of Mn$^{II}$(TPP)(py) results in the substitution of the pyridine ligand by TCNE and $O_2$, respectively, both the optical spectra and the EPR behavior of the TCNE and dioxygen complexes are distinctly different. In addition we note that the addition of $C_2F_4$ to a toluene solution of Mn$^{II}$(TPP)(py) gives no evidence of complex formation as evidenced by EPR and optical spectra. We therefore conclude that the olefins TCNE and $C_2F_4$ do not react with manganese(II) porphyrins in the same manner as dioxygen. The differences observed for the interaction of manganous porphyrin with dioxygen and TCNE may reflect the different redox properties of $O_2$ and TCNE.[25]

**Acknowledgment.** We thank Professor Richard P. Van Duyne for helpful discussions and Mr. James R. Anderson for his diligent technical assistance. This research was supported by grants from the National Institutes of Health and the National Science Foundation.

**Registry No.** Mn(TPP)(TCNE), 67674-04-8; Mn$^{II}$(TPP)(py), 57034-31-8; Mn(TPP)(Cl), 32195-55-4.

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(3) Abbreviations: TPP, the dianion of *meso*-tetraphenylporphine; TCNE, tetracyanoethylene; L represents a neutral basic ligand such as pyridine; py, pyridine; acacen, the *N,N'*-ethylenebis(acetylacetoniminato) dianion.
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(8) The amount of Mn(II) and Mn(III) tetraphenylporphinato species varied somewhat with concentration but the solution in general appeared about equimolar in the two species.
(9) When Mn$^{II}$(TPP)(py) is dissolved in toluene, the following equilibrium is established: Mn$^{II}$(TPP)(py) $\rightleftharpoons$ Mn$^{II}$(TPP) + py. The resulting spectrum reflects this equilibrium and the absorption maxima and absorptivities therefore depend upon the initial concentration of Mn$^{II}$(TPP)(py). See ref 1 and references cited therein.
(10) Two equivalents of TCNE are necessary to remove all traces of the Mn(II) Soret peak from the visible spectrum on the addition of TCNE to a toluene solution of Mn$^{II}$(TPP)(py). In a specific instance, 1 mL of pyridine added to 20 mL of the Mn(TPP)(TCNE) solution was required to bring back the Mn(II) Soret band to its maximum (i.e., 88% Mn(II) regenerated).
(11) The frozen toluene solution of Mn$^{II}$(TPP)(py) shows a low-field six-line $^{55}$Mn hyperfine pattern having a $g_\perp = 5.96$ and a $g_\parallel = 2.00$.[2]
(12) No complex formation between Mn$^{II}$(TPP)(py) and tetrafluoroethylene was observed in the optical spectra when gaseous tetrafluoroethylene was added to a toluene solution of Mn$^{II}$(TPP)(py).
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(19) These values are similar to those reported by R. A. Miller, O. Sala, P. Devlin, J. Overend, F. Lippert, W. Lindes, H. Moser, and J. Varchinin, *Spectrochim. Acta*, **20**, 1233 (1964).
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(21) The infrared spectra of Mn(TPP)(TCNE) were run as either Nujol or perfluorinated hydrocarbon mulls. In KBr the complex reacts to give Mn$^{III}$(TPP)(Br) as evidenced by resonance Raman spectroscopy of the pellet. Data for TCNE and its anions were obtained from ref 20.
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(23) That the coordinated TCNE$^-$ is not bonded via the nitrile nitrogen atom is also consistent with resonance Raman data. The resonance Raman spectra of five-coordinate Mn$^{III}$(TPP) complexes have been shown to exhibit certain modes characteristic of five-coordination (R. R. Gaughan, D. F. Shriver, and L. Boucher, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 433 (1975)). The absence of these modes in the spectrum of solid Mn(TPP)(TCNE) implies that the coordinated TCNE$^-$ is not acting as a simple monodentate ligand.
(24) The value for $\mu_{eff}$ of 6.68 $\mu_B$ at 78 K is larger than expected for an essentially infinite ferromagnetic coupling of the unpaired species at 78 K. A strong ferromagnetic interaction would give a spin-only value for $\mu_{eff}$ of 5.91 $\mu_B$ (W. Wojciechowski, *Inorg. Chim. Acta*, **1**, 329 (1967)). The large value for $\mu_{eff}$ at 78 K may indicate some long-range magnetic

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.

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# 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

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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

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

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

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

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

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

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 $5.9 \times 10^{-3}$ 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 $\nu$(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 $\nu$(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 $\nu$(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 $\nu$(CO) bands at 1992 and 1906

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