solution was extracted three times with 100-mL portions of deoxygenated water. The combined aqueous solution was extracted twice with 50-mL portions of ethyl ether and then acidified with 10% hydrochloric acid. The acidified solution was then extracted three times with 30-mL portions of ethyl ether, and the extracts were dried over magnesium sulfate. Filtration and removal of the solvent left 0.40 g (56%) of **21** as an orange solid. Recrystallization of the product from ethyl ether/pentane at −25 °C gave orange crystals, mp 135–137 °C (lit.[48] mp 135–138 °C). A mixture melting point of this product with an authentic sample was undepressed: NMR (acetone-d_6, internal Me_4Si) δ 5.64 (t, 2 H, $H_{2,5}$), 5.52 (t, 2 H, $H_{3,4}$), 8.94 (s, 1 H, OH); IR (KBr) 3100–2400 (m, br), 2035 (s), 1970 (s), 1670 (s, br) 1490 (s, br) 1490 (s), 1415 (m), 1370 (m), 1290 (s), 1155 (m), 1050 (w), 1030 (w), 1010 (w), 910 (m), 815 (m), 740 (m), 615 (m) cm^{-1}.

The initial ether solution after carbonation was dried over magnesium sulfate, filtered, and deposited on 5 g of alumina. Chromatography of the coated product on a 2 × 35 cm column of dry-packed alumina using pentane as the eluant removed an orange band, which afforded 20 mg (4%) of (η^5-cyclopentadienyl)dicarbonylcobalt as a red oil. Continued pentane elution removed a second orange band, which produced 30 mg of an unidentified red oil.

(η^5-1-Methyl-1-(hydroxyethyl)cyclopentadienyl)dicarbonylcobalt (22). A solution of (η^5-lithiocyclopentadienyl)dicarbonylcobalt was prepared from 0.52 g (2.0 mmol) of (η^5-bromocyclopentadienyl)dicarbonylcobalt, 1.07 mL (2.0 mmol) of *n*-butyllithium in hexane, and 30 mL of ethyl ether as previously described. Upon completion of the *n*-butyllithium addition, 1.00 mL (13.8 mmol) of deoxygenated, reagent grade acetone was immediately added to the solution. The solution was stirred for 30 min at −78 °C, treated with 3 mL of methanol, allowed to warm to 25 °C, and hydrolyzed with 50 mL of deoxygenated water. The reaction mixture was added to a 250-mL separatory funnel, the aqueous layer was removed, and the organic layer was washed with water until the aqueous extracts remained neutral. The organic layer was dried over magnesium sulfate, filtered, treated with 5 g of alumina, and concentrated to dryness in vacuo. The coated product was added to a 2 × 25 cm column of dry-packed alumina. Elution of the column with pentane produced an orange band, which after removal of the solvent gave 20 mg (6%) of (η^5-cyclopentadienyl)dicarbonylcobalt. Continued elution with pentane and 2:1 pentane/ether removed two additional orange bands, which produced 5 and 20 mg of unidentified red oils, respectively. Elution with 1:1 pentane/ether removed a fourth (major) band. Removal of the solvent afforded 200 mg (42%) of **22** as a dark red oil. NMR (C_6D_6, internal Me_4Si) δ 5.23 (t, 2 H, $H_{2,5}$), 5.06 (t, 2 H, $H_{3,4}$), 3.78 (s, 1 H, OH), 1.49 (s, 6 H, CH_3); IR (film, NaCl) 3750–3175 (br, vs), 3125 (m), 2995 (vs), 2945 (s), 2890 (s), 2010 (vs), 1965 (vs), 1500 (m), 1475 (m), 1460 (m), 1445 (m), 1390 (vs), 1330 (m), 1160 (s), 1125 (s), 1045 (m), 950 (s), 915 (m), 830 (s), 805 (m) cm^{-1}.

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Registry No. 1, 34822-90-7; 2, 36664-93-4; 3, 41851-50-7; 4, 41851-49-4; 5, 94890-79-6; 6, 94890-67-2; 7, 94890-68-3; 8, 1293-67-0; 9, 1293-65-8; 10, 94890-69-4; 11, 94890-70-7; 12, 12079-90-2; 13, 12079-86-6; 14, 94890-71-8; 15, 94890-72-9; 16, 94890-73-0; 17, 94890-74-1; 18, 94890-75-2; 19, 94890-76-3; 20, 94890-77-4; 21, 94890-78-5; 22, 79086-57-0; $(\eta^5\text{-}c_5H_5)TiCl_3$, 1270-98-0; $TiCl_4$, 7550-45-0; $BrMn(CO)_5$, 14516-54-2; $FeCl_2$, 7758-94-3; $Co_2(CO)_8$, 15226-74-1; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-25-0; $[ClRh(CO)_2]_2$, 14523-22-9; $NiBr_2{\cdot}2DME$, 18346-62-8; $[ClCu(PEt_3)]_4$, 55606-52-5.

Destabilization of μ-η^2-Carbon Monoxide and μ-η^2-Isocyanide Bridges in Dimanganese Compounds on Protonation of the Metal–Metal Bond

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Protonation of $Mn_2(\mu\text{-}\eta^2\text{-}CO)(CO)_4(dppm)_2$ in dichloromethane with $HBF_4{\cdot}Et_2O$ at −80 °C gives $[Mn_2H(\mu\text{-}\eta^2\text{-}CO)(CO)_4(dppm)_2][BF_4]$ which was characterized by IR and NMR methods. It readily decomposes above −60 °C to $[Mn_2H(CO)_6(dppm)_2][BF_4]$ which can be isolated. Protonation of the neutral pentacarbonyl leads to a considerable destabilization of the formally four-electron-donating μ-η^2-carbonyl form as evidenced by the very large increase in ν(CO) associated with the bridging CO ligand from 1648 to 1787 cm^{-1}, by a greater than 9.4 kcal mol^{-1} lowering of the energy barrier to CO oscillation between the metal atoms, and by the facile thermal conversion to $[Mn_2H(CO)_6(dppm)_2]^+$ which contains only terminal CO ligands. The tolyl isocyanide compound $Mn_2(\mu\text{-}\eta^2\text{-}CNC_6H_4Me\text{-}4)(CO)_4(dppm)_2$ behaves almost identically, chemically, and spectroscopically, on protonation with $HBF_4{\cdot}Et_2O$.

Introduction

The μ-η^2-carbonyl ligand in $Mn_2(CO)_5(dppm)_2$ (1; dppm = $Ph_2PCH_2PPh_2$) is formally a four-electron donor.[1-4] Intuitively one might expect that enhanced reactivity toward nucleophiles would be a feature of its chemistry. However, compound 1 was found to be generally not susceptible to nucleophilic attack,[5] and calculations indicating that the predominant component of the η^2-interaction is back-donation from the metal to the CO π^*

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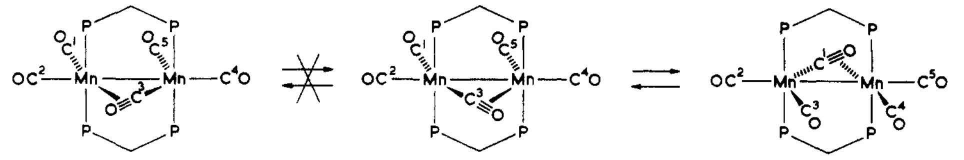

Figure 1. Dynamic behavior of $Mn_2(CO)_5(dppm)_2$ (1).[3,4]

Table I. Important NMR and Infrered Data for Compounds 1 and 2 and Their Protonated Derivatives (R = $4\text{-}C_6H_4Me$)

	$\nu(CN)^a$ or $\nu(CO)^a/cm^{-1}$	δ ($^{31}P\{^1H\}$ NMR)^b	δ (^1H NMR; μ-H)^c
$Mn_2(CO)_5(dppm)_2$ (1)	1648	76.5, 60.3 (22 °C)	
$[Mn_2H(CO)_5(dppm)_2]^+$ (4)	1787	63.4, 51.7 (−60 °C) 57.6 (0 °C)	−13.86
$[Mn_2H(CO)_6(dppm)_2]^+$ (2)		61.4 (0 °C)	−26.18
$Mn_2(CNR)(CO)_4(dppm)_2$ (3)	1657	75.6, 64.2 (−80 °C)	
$[Mn_2H(CNR)(CO)_4(dppm)_2]^+$ (6)	1791	60.9, 54.6 (−80 °C) 57.8 (0 °C)	−14.8
$[Mn_2H(CNR)(CO)_5(dppm)_2]^+$ (5)	*d*	65.3, 63.1 (24 °C)	−25.3

[a] Absorptions for μ-η^2-ligands recorded in CH_2Cl_2 solution. [b] Relative to 85% H_3PO_4 (external); downfield positive; recorded in CH_2Cl_2/CD_2Cl_2 mixtures at 80.984 MHz. When two signals were observed, these should appear as AA′BB′ patterns but the fine structure was only poorly resolved (see Figures 1 and 3) in most cases. [c] Quintet patterns from equivalent coupling to four equivalent or effectively equivalent ^{31}P nuclei; fine structure sometimes poorly resolved. Recorded at 200 MHz in $CDCl_3$. [d] $\nu(CN)$ for terminal CNR = 2117 cm⁻¹ (Nujol, BPh_4 salt), 2124 cm⁻¹ (CH_2Cl_2).

orbitals have led others to believe that the μ-η^2-CO is not a four-electron donor at all.[6] Back-donation is favored by the extensive substitution at the Mn atoms by phosphorus donors so that the μ-η^2-CO is deactivated toward nucleophilic attack. Rather, compound 1 is protonated at the metal–metal bond to yield, in the absence of neutral or anionic donor species, the hexacarbonyl cation $[Mn_2H(CO)_6(dppm)_2]^+$ (2), the X-ray crystal structure of the BBh_4^- salt of which[7] shows it to be directly related to $[M_2H(CO)_{10}]^-$ (M = Cr, Mo, or W).[8] Compound 2 arises as a result of scavenging of CO and the formation of 2 occurs quantitatively under an atmosphere of CO.[5] The paper describes low-temperature protonation studies which have established the intermediate and its dynamic behavior which differs considerably from that of the deprotonated form.

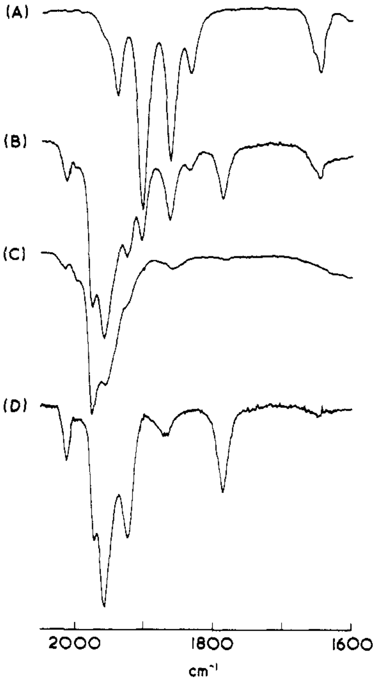

Figure 2. ν(CO) spectra of dichloromethane solutions of (A) $Mn_2(CO)_5(dppm)_2$ at 0 °C, (B) immediately after adding an excess of $HBF_4 \cdot Et_2O$ at 0 °C, and (C) 3–4 min later, corresponding to $[Mn_2H(CO)_6(dppm)_2]^+$. Spectrum D is derived from B by subtraction of spectra A and C, weighted appropriately to remove absorptions due to compounds 1 and 2.

Results and Discussion

Many μ-η^2-ligands ($CH{=}CH_2$, $C{\equiv}CR$, CNR, etc.) oscillate rapidly on an NMR time scale between the metal atoms which they bridge; for example, the manganese atoms in the μ-η^2-CN complex $Mn_2H(CN)(CO)_4(dppm)_2$ exchange as the CN oscillates.[9] A similar rapid oscillation of μ-η^2-CN was observed for $[Mo_2(C_5H_5)_2(CO)_4(CN)]^-$.[10] Ethenyl oscillations in $Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}$[11] and $Re_2H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_8$[12] are rapid as is the ethynyl oscillation in $Re_2H(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(CO)_8$.[13] This is in contrast to the μ-η^2-CO in 1 and the μ-η^2-isocyanide in the related compound $Mn_2(CNC_6H_4CH_3\text{-}4)(CO)_4(dppm)_2$ (3)[14] which do not oscillate rapidly enough to give any NMR line-broadening or coalescence effects even though, as in the other cases cited, the metal atoms are equivalent except for the unsymmetrically bridging ligand. A lower limit to the energy barrier to CO oscillation in 1 was estimated to be 15.6 kcal mol⁻¹ by observing sharply resolved $^{31}P\{^1H\}$ NMR signals at 180 °C.[15] Figure 1 summarizes the known

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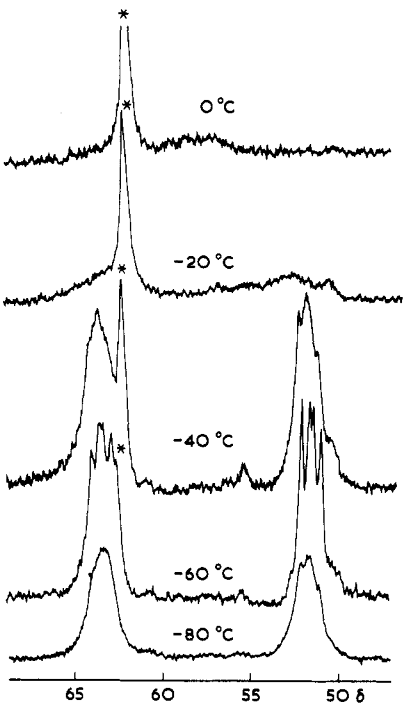

Figure 3. $^{31}P\{^1H\}$ NMR spectra of $Mn_2(CO)_5(dppm)_2$ (1) in CH_2Cl_2/CD_2Cl_2 recorded after adding $HBF_4{\cdot}Et_2O$ (excess) at -80 °C and then at intervals on warming to 0 °C. The singlet marked (*) corresponds to $[Mn_2H(CO)_6(dppm)_2]^+$.

dynamic behavior of 1.[3,4] The questions is whether CO and CN are fundamentally different in their ability to oscillate, especially as the only other known μ-η^2-cyanide in $[Mo_2(CN)(CO)_4(C_5H_5)_2]^-$ also oscillates very readily between the metal atoms (E_a = 10.4 ± 0.4 kcal mol^{-1}).[10] The related isocyanide complexes $Mo_2(\mu$-η^2-$CNR)(CO)_4(C_5H_5)_2$ (R = Me, Ph, or t-Bu) are stereochemically rigid like the isocyanide complex 3,[16] although $Mo_2(\mu$-η^2-$CNMe)(CO)_4(C_5Me_5)_2$ undergoes the windshield-wiper mechanism like the cyanide complex but with a high activation barrier.[17]

To make a more useful comparison, we wished to compare $Mn_2H(\mu$-η^2-$CN)(CO)_4(dppm)_2$ with the isoelectronic compound $[Mn_2H(\mu$-η^2-$CO)(CO)_4(dppm)_2]^+$ (4) but, as we have described above, the protonation of 1 at room temperature gives the hexacarbonyl compound 2. However, we noticed that immediately after H^+ addition the solution changed from orange to orange-red which then quickly lightened to yellow-orange indicating that there might be an intermediate. Addition of $HBF_4{\cdot}Et_2O$ to a solution of 1 in dichloromethane at -80 °C gave a new set of ^1H and $^{31}P\{^1H\}$ NMR signals assignable to cation 4 (important data in Table I). In particular, a broad ^1H NMR (hydride) signal at δ -13.86 was observed which disappeared to be replaced by that of 2 (δ -26.18) on warming to room temperature. These signals may be compared with those for the isoelectronic cyanide complexes $Mn_2H(\mu$-η^2-$CN)(CO)_4(dppm)_2$ (δ -14.84) and $Mn_2H(\eta^1$-$CN)(CO)_5(dppm)_2$ (δ -23.87).[9] A medium-strong bridging CO absorption at 1787 cm^{-1} was observed for 4 (Figure 2). $^{31}P\{^1H\}$ NMR spectra at -80 °C and on raising the temperature to 0 °C (Figure 3) showed that compound 4 is unsymmetrical with an AA′BB′ pattern but coalescence at around -10 °C gave an estimated value of $\Delta G^{\ddagger}{}_{263}$ of 11.2 kcal mol^{-1}. Better quality spectra around coalescence were prevented by the conversion above -60 °C of cation 4 to cation 2 which gave a $^{31}P\{^1H\}$ NMR singlet predominating at 0 °C. These results are summarized in Figure 4.

The large frequency shift for ν(CO) of the bridging ligand on protonation at the metal atoms of compound 1 (139 cm^{-1}) brings this absorption into a frequency region not uniquely characteristic of μ-η^2-CO. NMR and IR data would also be consistent with a semibridging carbonyl (but not a symmetrically bridging one); however, in the absence of an increased Mn–Mn bond order or solvent coordination, compound 4 would be unsaturated. Coordination of a solvent molecule as in $[Mn_2H(MeCN)(CO)_5(dppm)_2][BF_4]$[9] would give a hydride NMR signal at much higher field than δ -13.86 (see Table I). We favor the retention of the μ-η^2-bridge albeit with considerably weakened η^2-interactions, and we have illustrated 4 in this way (Figure 4).

Three consequences of protonation of compound 1 are (a) the destabilization of the μ-η^2-CO bridged form and the formation of the hexacarbonyl cation 2, (b) a reduction of at least 9.4 kcal mol^{-1} in the barrier for the windshield-wiper process, and (c) a large increase (139 cm^{-1}) in ν(CO) for the bridging carbonyl.

The isocyanide complex $Mn_2(\mu$-η^2-$CNC_6H_4CH_3$-$4)(CO)_4(dppm)_2$ (3) shows remarkably similar behavior in most respects on protonation to that of compound 1. Spectroscopic data for the intermediate 6 and the final isolable compound 5 are summarized in Table I and Figure 5 shows $^{31}P\{^1H\}$ NMR spectra. In the experiment shown in Figure 5, incomplete protonation occurred at -80 °C so that $^{31}P\{^1H\}$ NMR signals for $Mn_2(CNR)(CO)_4(dppm)_2$ (3) and $[Mn_2H(CNR)(CO)_4(dppm)_2]^+$ (5) (R = 4-C_6H_4Me) were observed. The spectra between -80 and -40 °C show well the different phosphorus exchange behavior between 3 and 6; $\Delta G^{\ddagger}{}_{228}$ for 6 was estimated to be 10.0 kcal mol^{-1}, a similar lowering (at least 8.7 kcal mol^{-1}) to that of the μ-η^2-CO compound on protonation. The ν(CN) frequency is raised from 1657 to 1791 cm^{-1} on protonation compared with the change from 1648 to 1787 cm^{-1} for the carbonyl system. The final product from the protonation, $[Mn_2H(CNC_6H_4CH_3$-$4)(CO)_5(dppm)_2]^+$ (6) contains a terminal isocyanide cis to the Mn–Mn bond and was previously synthesized by the replacement of the acetonitrile ligand in $[Mn_2H(CH_3CN)(CO)_5(dppm)_2]^+$ by 4-tolyl isocyanide.[18] The conversion of 3 to 5 corresponds directly to that for the μ-η^2-CO system shown in Figure 4 except that the intermediate 6 seems to survive rather longer at higher temperatures. If the major component of the η^2-bonding were donation from filled bonding π-CNR or CO orbitals, protonation at the metal would stabilize this η^2-coordination. Quite the reverse is observed so our results support calculations that indicate that back-donation predominates.[6] Steric effects might also lead to destabilization. One would presume that the Mn–Mn distance would increase on protonation[19] and also the terminal CO ligands

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[15] An AA′BB′ $^{31}P\{^1H\}$ NMR spectrum was observed at 20 °C in CH_2Cl_2 which gave this limit.[3] We have now observed well-separated $^{31}P\{^1H\}$ NMR signals at 180 °C for a solution of 1 in tetrahydronaphthalene although significant decomposition to $Mn_2(CO)_6(dppm)_2$ was observed. Thus we can raise the lower limit for the oscillation barrier in 1 to 20.6 kcal mol^{-1}, assuming that the coalescence temperature is >200 °C. Compound 1 is fluxional as shown by the pairwise coalescence of four of the five ^{13}CO NMR resonances. This process involves the exchange of the μ-η^2-CO with a terminal one but not of the nonequivalent Mn atoms.[4] For 3, we observed well-resolved, separated $^{31}P\{^1H\}$ NMR signals at 120 °C in xylene solution. Assuming that the coalescence temperature is >150 °C, we set a lower limit of 18.7 kcal mol^{-1} for the oscillation barrier of the p-tolyl isocyanide ligand.

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(19) Protonation across a M–M bond normally leads to an increased metal atom separation. The Mn–Mn distance in 2 (BPh_4 salt) is 3.22 Å[7] compared with 2.93 Å in 1.[2]

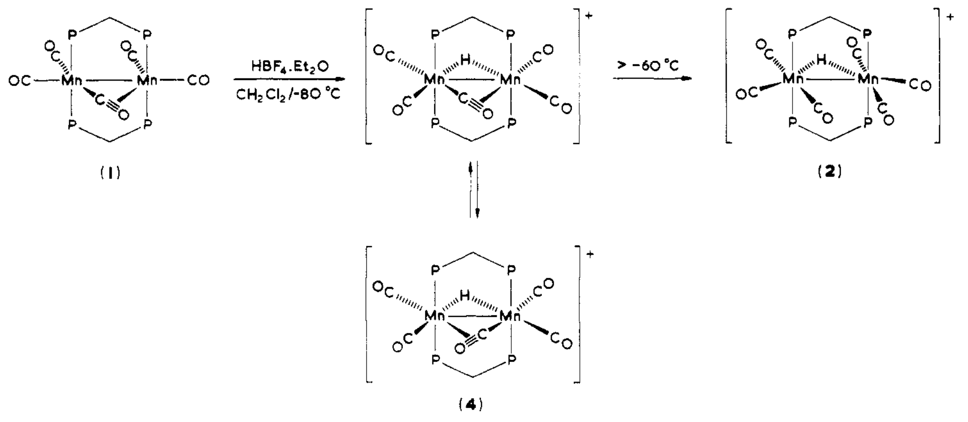

Figure 4. The protonation of $Mn_2(CO)_5(dppm)_2$ (1).

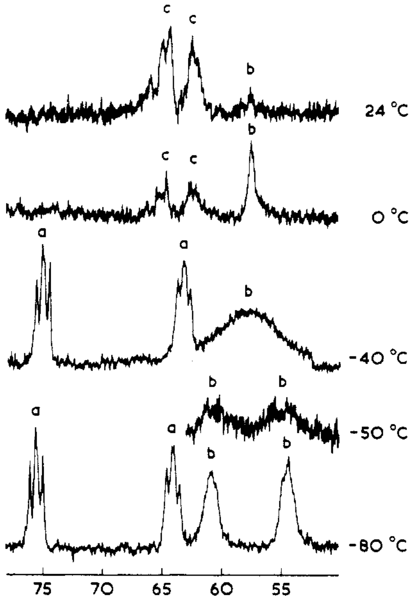

Figure 5. $^{31}P\{^1H\}$ NMR spectra of $Mn_2(CNC_6H_4Me\text{-}4)(CO)_4(dppm)_2$ in CH_2Cl_2/CD_2Cl_2 recorded after adding $HBF_4{\cdot}Et_2O$ (excess) at −80 °C and then at intervals on warming to 24 °C: singals a, compound 3; signals b, compound 6; signals c, compound 5.

would crowd the μ-CO more in 4 than in 1. Both factors might destabilize the μ-η^2-CO with respect to a μ-η^1-geometry presumed to be the transition state for CO oscillation by the windshield-wiper mechanism.

Experimental Section

$Mn_2(CO)_5(dppm)_2$ (1)[1] and $Mn_2(CNC_6H_4Me)(CO)_4(dppm)_2$ (3)[14] were prepared as reported earlier. NMR spectra were recorded on a Varian XL200 instrument and IR spectra on a Perkin-Elmer 983 instrument. The 3600 data station was used to generate difference spectra as shown in Figure 2.

Protonation of $Mn_2(CO)_5(dppm)_2$ (1). A suspension of compound 1 (0.015–0.020 g for ^1H NMR and 0.045 g for ^{31}P NMR) in CD_2Cl_2 (0.5–2.0 cm^3) in an NMR tube was cooled to −80 °C. The acid $HBF_4{\cdot}Et_2O$ (0.005–0.020 cm^3) was added to the suspension at this temperature using a microsyringe and compound 1 dissolved to give an orange solution. The first NMR data were acquired within a few minutes, and the spectra obtained on raising the temperature are shown in Figure 3. The changes are irreversible. The final solution (after 4 days at −20 °C or after a short time at 20 °C) gave spectra corresponding well with those of an authentic sample of $[Mn_2H(CO)_6(dppm)_2][BF_4]$ $\{^{31}P\{^1H\}$ NMR. ($CDCl_3$) δ 58.95; ^1H NMR ($CDCl_3$) δ −26.18 (quintet, $J = 15.2$ Hz); IR (CH_2Cl_2) ν(CO) 2035 (w), 1976 (vs), 1955 (m, sh), 1946 (m, sh) cm$^{-1}\}$.[5] The conversion of 1 to 2 occurs more readily under CO (1 atm) when one molecule of CO is absorbed.[5] We presume the extra CO in the absence of added CO comes from some decomposed complex although we could find no evidence in the ^{31}P NMR or infrared spectra for metal carbonyl or phosphorus-containing by-products. Possibly paramagnetic non-carbonyl manganese dppm complexes are formed but we did not search for these. Monitoring the protonation of compound 1 by IR, we found that within a few minutes of adding $HBF_4{\cdot}Et_2O$ to a CH_2Cl_2 solution at 0 °C, the infrared spectrum of 2 only was observed. However, immediately after the acid addition, in the spectrum around 2000 cm^{-1} absorptions due to 1, 2, and another species were observed. Computer-aided subtraction of the spectra of 1 and 2 gave a spectrum [2024 (w), 1971 (s), 1957 (vs), 1924 (s), 1872 (w), 1787 (m) cm^{-1}] which must correspond closely to that of cation 4 (Figure 2).

Protonation of $Mn_2(CNC_6H_4Me\text{-}4)(CO)_4(dppm)_2$ (3). This was studied in the same way as was compound 1. $^{31}P\{^1H\}$ NMR spectra are shown in Figure 5. A similar treatment of the first IR spectra obtained after adding $HBF_4{\cdot}Et_2O$ gave a spectrum for the intermediate 6 in CH_2Cl_2: ν(CO) 2039 (w), 1999 (m), 1967 (vs), and 1933 (s) and ν(CN) 1791 cm^{-1}. The 1791 cm^{-1} absorption was replaced by ν(CN) at 2124 cm^{-1} on conversion of 6 to 5. Carrying out the reaction at room temperature, $HBF_4{\cdot}Et_2O$ was added to a clear yellow solution of compound 3 in dichloromethane to give an orange solution after 30 min. Solid sodium hydrogen carbonate was added to neutralize the excess of acid, and the solution was filtered through Celite. Removal of the solvent gave a solid sample which gave infrared and NMR spectra essentially indistinguishable from those of an authentic sample of 5 prepared as the BPh_4^- salt by the addition of MeC_6H_4NC to a solution of $[Mn_2H(CO)_5(MeCN)(dppm)_2][BPh_4]$ $\{^1H$ NMR ($CDCl_3$) δ −25.3 (quintet); IR (CH_2Cl_2) ν(CO) 2038 (w), 1970 (vs), 1952 (s, sh), 1946 (s, sh), 1916 (m) cm^{-1} and ν(CN) 2124 (m) cm$^{-1}\}$.[7]

Acknowledgment. We thank the S.E.R.C. for support.

Registry No. 1, 56665-73-7; 2, 79519-57-6; 2·BF_4, 79519-58-7; 3, 64756-62-3; 4, 94904-53-7; 5, 79503-32-5; 5·BPh_4, 94904-54-8; 6, 94904-55-9; MeC_6H_4NC, 7175-47-5; $[Mn_2H(CO)_5(MeCN)(dppm)_2][BPh_4]$, 94904-56-0; $Mn_2(CO)_6(dppm)_2$, 37523-62-9.