Addition of Proton and Boron Trifluoride at Terminal and Bridging Cyano-ligands in Dinuclear Manganese Compounds

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The addition of $HBF_4 \cdot Et_2O$ to dichloromethane solutions of $[Mn_2H(CN)(CO)_5(dppm)_2]$ and of $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) leads to complexes containing terminal and η^2-bridging HNC respectively. The terminal cyano-ligand protonates more readily and the product was isolated as $[Mn_2H(CNH)(CO)_5(dppm)_2][BPh_4]$. Protonation of the $\mu\text{-}\eta^2$-CN ligand (confirmed by ^{15}N n.m.r. spectroscopy) lowers the rate of the 'windshield-wiper' oscillation of the ligand between the manganese atoms and apparently destabilises the compound since above −20 °C uptake of CO (scavenged from solution) gives $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$. The addition of BF_3 produces the corresponding $CNBF_3$ compounds. Spectroscopic analysis was assisted by ^{13}C and ^{15}N enrichment at the cyanide ligand.

We have previously reported the synthesis and dynamic behaviour of the bridging dihapto cyano-compound $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) in which the cyano-ligand rapidly oscillates between the manganese atoms.[1] The only other compound reported to contain a $\mu\text{-}\eta^2$-cyanide is the dimolybdenum anion $[Mo_2(CN)(CO)_4(C_5H_5)_2]^-$, in which the cyanide also oscillates.[2] There are several examples of electrophilic attack at co-ordinated cyanide in mononuclear compounds. The anion $[Mn(CN)(CO)_2(C_5H_5)]^-$ is protonated to give $[Mn(CNH)(CO)_2(C_5H_5)]$,[3] and $[Mn(CN)(CO)_2(arene)]$ (arene = C_6H_6 or $C_6H_3Me_3$-2,4,6) is apparently protonated at nitrogen in aqueous solution,[4] although attempts to isolate the BF_4^- salt led to the BF_3 adduct $[Mn(CNBF_3)(CO)_2(arene)]$ where arene = $C_6H_3Me_3$-2,4,6. With other electrophiles (Et_3O^+ and Ph_3C^+) cationic species were isolated as the PF_6^- salts.[4] Other examples of electrophilic addition at nitrogen of cyanide ligands have been reported for $[M(CN)(CO)_5]^-$ (M = Cr, Mo, or W)[5] and $[Fe(CN)(CO)_2(diene)]^-$ (various dienes),[6] and $[Mn(CN)(CO)_2(C_5H_5)]^-$ is attacked at nitrogen by various electrophiles including $COCl_2$ which gives $[(C_5H_5)(OC)_2Mn\text{–}CNCONC\text{–}Mn(CO)_2(C_5H_5)]$.[7] The BF_3 adducts of mononuclear cyano-complexes are rather more common than protonated adducts.[4,8]

Our present report on the protonation of the terminal cyanide in $[Mn_2H(CN)(CO)_5(dppm)_2]$, (**1**), to give terminally co-ordinated isohydrocyanic acid is an extension of these earlier reports, but protonation of the $\mu\text{-}\eta^2$-cyanide in $[Mn_2H(CN)(CO)_4(dppm)_2]$, (**2**), gives the first example of $\mu\text{-}\eta^2$-isohydrocyanic acid.

Results and Discussion

Protonation of Terminal Cyanide.—Treatment of $[Mn_2H(CN)(CO)_5(dppm)_2]$, (**1**), in dichloromethane with an excess of $HBF_4 \cdot Et_2O$ gave $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$, (**3**), which was isolated as the BPh_4 salt in the absence of water, which readily reverses the protonation. Spectroscopic and analytical data are given in the Tables and Experimental section. We observe that ν(CN) increases by 50 cm^{-1} on protonation, in contrast to the small decrease observed for the protonation of $[Mn(CN)(CO)_2(arene)]$ and $[Mn(CN)(CO)_2(C_5H_5)]^-$,[3,4] but similar to the increase (76 cm^{-1}) observed on protonating acetonitrile to give the acetonitrilium ion $[MeCNH][SbCl_6]$.[9] Our main evidence for the CNH ligand in compound (**3**) is the doublet $[|^1J(^{15}NH)| = 106$ Hz] in the undecoupled ^{15}N n.m.r. spectrum of the 98.8% ^{15}N-enriched compound (**1**) in the presence of $HBF_4 \cdot Et_2O$ at −90 °C (Table 1 and Figure 1). At higher temperatures a broad singlet is observed because of proton exchange between co-ordinated CNH and $HBF_4 \cdot Et_2O$. The ^{15}N signal of compound (**1**) shifts upfield by around 126 p.p.m. on protonation to give (**3**), a characteristic shift for protonation of unsaturated nitrogen. Compare, for example, the ^{15}N signal for acetonitrile which moves upfield by 102.4 p.p.m. on protonation.[10] Similar differences were obtained between $\delta(^{15}N)$ for the terminal (β) nitrogen atoms in dinitrogen complexes ($M\text{–}N\equiv N_\beta$) and diazenido-complexes ($M\text{–}N\equiv NH_\beta$) of Mo and W.[11] The ^{14}N n.m.r. chemical shifts for $[M(CNH)(CO)_5]$ (M = Cr or W) (−202 and −200 p.p.m. relative to $MeNO_2$) and for $[Mn(CNH)(CO)_2(C_5H_5)]$ (−218 p.p.m.)[12] may be compared with −183.4 p.p.m. for compound (**3**) (see Table 1). A ^1H n.m.r. doublet at δ 11.45 p.p.m. $[|^1J(^{15}NH)| = 103$ Hz] was obtained on treating a 98.8% ^{15}N-enriched sample of compound (**1**) in dichloromethane with $HBF_4 \cdot Et_2O$ at −90 °C. This was assigned to CN*H* in (**3**) and is consistent with the ^{15}N n.m.r. result. The proton–nitrogen coupling was not observed in the room-temperature spectrum indicating that rapid exchange was occurring. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of compound (**1**) and its protonated form, (**3**), both appear as AA′BB′ patterns. The effect of protonation is to shift the lower-field branch upfield by 2.4 p.p.m. leaving the other branch unchanged; it is the lower-field branch that we have assigned to the phosphorus atoms at the manganese atom bonded to cyanide, so this is as expected.

Reaction of compound (**1**) with $BF_3 \cdot Me_2O$ in dichloromethane produces the analogous BF_3 adduct $[Mn_2H(CNBF_3)(CO)_5(dppm)_2]$, (**4**). The ν(CN) value for (**1**) increases by 64 cm^{-1} to 2 153 cm^{-1} on addition of BF_3 compared with an increase of 50 cm^{-1} on protonation (see Table 3 and the Experimental section for spectroscopic and analytical data).

Protonation of $\mu\text{-}\eta^2$-Cyanide.—The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$, (**2**), at −60 °C in $CD_2Cl_2\text{–}CH_2Cl_2$ contains two very broad signals (δ 64.5 and 52.3 p.p.m.) because of the onset of coalescence (T_c *ca.* −50 °C) resulting from an oscillating CN ligand.[1] Immediately after adding an excess of $HBF_4 \cdot Et_2O$ at this temperature these signals were replaced by a well resolved AA′BB′ pattern for the protonated species $[Mn_2H(\mu\text{-}\eta^2\text{-}CNH)(CO)_4(dppm)_2]^+$, (**5**) (δ 62.66 and 48.99 p.p.m.) (see Figure 2 and Table 1). The coalescence temperature for these signals is about 0 °C so that the effect of protonation at nitrogen of compound (**2**) is to raise the barrier to oscillation. However, these line-shape changes are partly obscured by the formation above 0 °C of another set of signals corresponding to $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$,

Table 1. Multinuclear n.m.r. data[a] for the cyano-compounds (**1**) and (**2**) and their protonated forms (**3**) and (**5**) formed *in situ* by the addition of $HBF_4 \cdot Et_2O$

Compound	δ(^{1}H) (hydride)	δ(^{31}P)[b]	δ(^{15}N)[c]	δ(^{13}C) (cyanide)
(**1**) $[Mn_2H(CN)(CO)_5(dppm)_2]$	−23.97 (21 °C, J_{PH} 16)	67.6 (m), 61.9 (m) (22 °C, AA′BB′)	−57.6 (s) (22 °C)	160.5 (t)[d] (J_{PC} 23.8)
(**3**) $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$	−26.2 (−90 °C)[e] −25.3 (21 °C)	65.2 (m), 61.9 (m) (22 °C, AA′BB′)	−183.4 (s) (22 °C) −172.4 (d) (−80 °C, J_{NH} 106)	
(**2**) $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$	−14.9 (−50 °C)	59.2 (s) (22 °C) 64.5 (br), 52.3 (br) (−60 °C, AA′BB′)	−139.7 (s) (22 °C)	160.7 (quintet)[d] (25 °C, J_{PC} 10)
(**5**) $[Mn_2H(\mu\text{-}\eta^2\text{-}CNH)(CO)_4(dppm)_2]^+$	−13.6[f] (−90 °C)	62.66 (m), 48.99 (m) (−60 °C, AA′BB′)[g]	−235.6 (d) (−80 °C, J_{NH} 114)	192.5 (t) (−60 °C, J_{PC} 19)

[a] In CD_2Cl_2 or CD_2Cl_2–CH_2Cl_2 solutions, *J* values in Hz. [b] At 80.984 MHz, relative to 85% H_3PO_4 (external). [c] At 40.5 MHz, measured relative to 5 mol dm^{-3} NH_4NO_3 in 2 mol dm^{-3} HNO_3 (external, converted to $MeNO_2$ scale by subtracting 359.0 p.p.m.). [d] In $CDCl_3$. [e] In the low-field region there are two singlets at δ 11.65 (HBF_4) and at 11.45 p.p.m. (CNH), the latter giving a doublet (J_{NH} *ca.* 103 Hz) for the 98.8% ^{15}N-enriched material. [f] In the low-field region there are two singlets at δ 11.51 (HBF_4) and 10.96 p.p.m. (CNH), the latter giving a doublet (J_{NH} *ca.* 118 Hz) for the 98.8% ^{15}N-enriched material. [g] For $[Mn_2H(^{13}CNH)(CO)_4(dppm)_2]^+$ the lower-field branch of the AA′BB′ spectrum shows further coupling to ^{13}C.

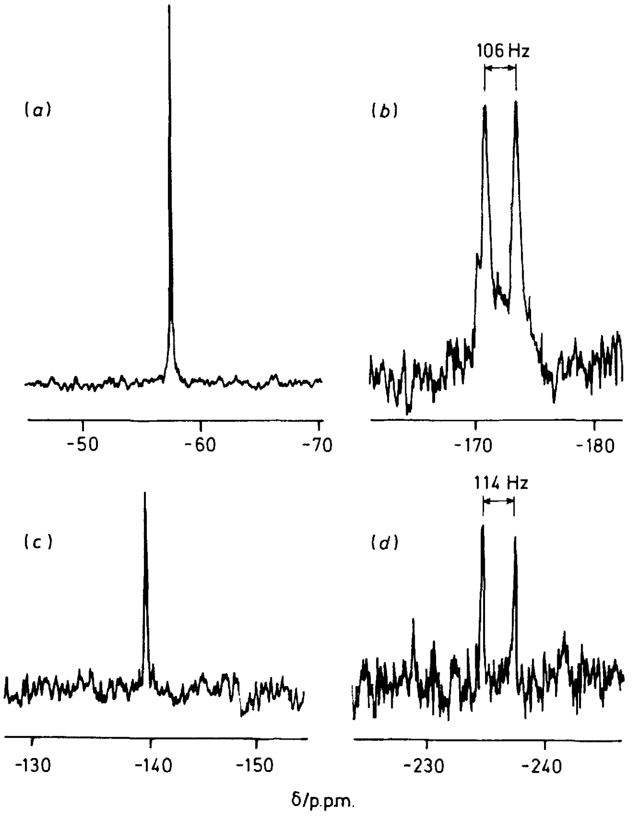


Figure 1. ^{15}N N.m.r. spectra for 98.8% enriched samples in CD_2Cl_2 solutions of (*a*) $[Mn_2H(C^{15}N)(CO)_5(dppm)_2]$, (**1**), (*b*) $[Mn_2H(C^{15}NH)(CO)_5(dppm)_2][BF_4]$, (**3**), formed by adding $HBF_4 \cdot Et_2O$ to compound (**1**) at −90 °C, (*c*) $[Mn_2H(\mu\text{-}\eta^2\text{-}C^{15}N)(CO)_4(dppm)_2]$, (**2**), and (*d*) $[Mn_2H(\mu\text{-}\eta^2\text{-}C^{15}NH)(CO)_4(dppm)_2][BF_4]$, (**5**), formed by treating compound (**2**) with $HBF_4 \cdot Et_2O$ at −80 °C

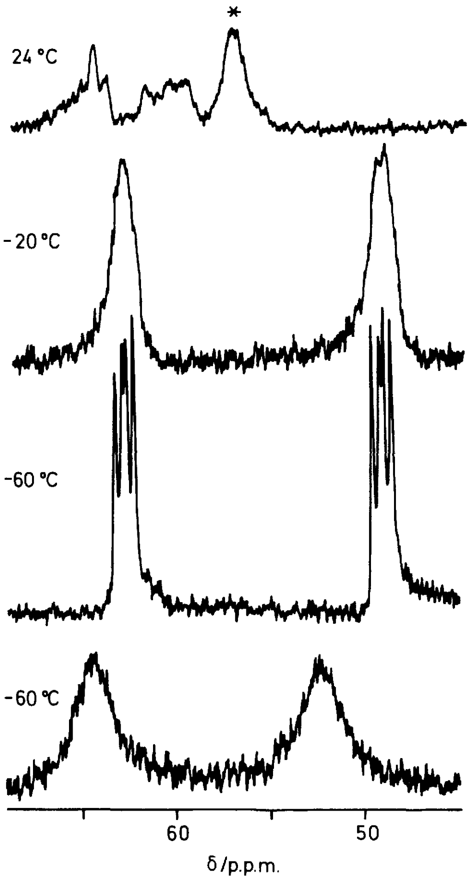


Figure 2. ^{31}P-{^{1}H} N.m.r. spectra for dichloromethane solutions of $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$, (**2**) (bottom spectrum) and on addition of $HBF_4 \cdot Et_2O$ (other spectra). The asterisk indicates the coalesced signal for compound (**5**) while the remaining signals at 24 °C are for compound (**3**)

(**3**). As the signals for cation (**5**) are replaced by those of cation (**3**) the solution changes from yellow to orange and we were unable to isolate compound (**5**). This behaviour exactly parallels that we have found for the isoelectronically related compounds $[Mn_2H(\mu\text{-}\eta^2\text{-}CO)(CO)_4(dppm)_2]^+$ and $[Mn_2H(\mu\text{-}\eta^2\text{-}CNR)(CO)_4(dppm)_2]^+$ (R = 4-MeC_6H_4) formed by protonating the neutral species at the metal–metal bond. These cations contain oscillating μ-η^2 ligands, but are readily converted at room temperature by uptake of CO into $[Mn_2H(CO)_6(dppm)_2]^+$ and $[Mn_2H(CNR)(CO)_5(dppm)_2]^+$ containing only terminal CO and CNR ligands.[13]

Compound (**2**) and the CNH complexes (**3**) and (**5**) are further characterised by ^{1}H n.m.r. signals for the hydride. Simple protonation of (**2**) at −60 °C leads to a fairly small shift

Table 2. I.r. data[a] for compounds (**1**), (**2**) and their protonated forms

Compound	Isotopomer	$\tilde{\nu}$(CO)/cm^{-1}	$\tilde{\nu}$(CN)/cm^{-1}
(**1**) $[Mn_2H(CN)(CO)_5(dppm)_2]$	σ-$^{12}C^{14}N$	2 037w, 1 960vs, 1 930s, 1 873m	2 091w
	σ-$^{13}C^{14}N$	2 037w, 1 961vs, 1 932s, 1 874m	2 046w
	σ-$^{12}C^{15}N$	2 037w, 1 961vs, 1 927vs, 1 874m	2 059w
(**3**) $[Mn_2H(CNH)(CO)_5(dppm)_2]^+$	σ-$^{12}C^{14}N^1H$	1 962vs, 1 936m, 1 888m	2 141
	σ-$^{12}C^{14}N^1H$[b]	2 035w, 1 955vs, 1 929s, 1 879m	2 143
	σ-$^{12}C^{15}NH$[c]	2 036w, 1 959vs, 1 928s, 1 885s	2 106
	σ-$^{12}C^{14}N^2H$[d]	2 036w, 1 958vs, 1 945s, 1 929s, 1 896m	2 106
(**2**) $[Mn_2H(CN)(CO)_4(dppm)_2]$	μ-η^2-$^{12}C^{14}N$	1 944m, 1 929vs, 1 875s	*e*
(**5**) $[Mn_2H(CNH)(CO)_4(dppm)_2]^+$	μ-η^2-$^{12}C^{14}N^1H$	1 992m, 1 961vs, 1 921s	1 833w (br)
	μ-η^2-$^{13}C^{14}N^1H$	1 992m, 1 960vs, 1 920s	1 795w (br)
	μ-η^2-$^{12}C^{15}N^1H$	1 990m, 1 961vs, 1 920s	1 813w (br)

[a] Recorded in CH_2Cl_2 solution, complexes (**3**) and (**5**) being prepared *in situ*, except where stated. [b] For isolated BPh_4 salt in hexachlorobutadiene. [c] For isolated BPh_4 salt in Nujol. [d] Prepared from $CF_3CO_2{}^2H$ and recorded as a solid in hexachlorobutadiene mull. [e] Not observed.

Table 3. Spectroscopic data for $CNBF_3$ complexes

	I.r. (cm^{-1})				
Compound	ν(CO)	ν(CN)	ν(BF)	δ(^{1}H)(Mn*H*Mn)	δ(^{31}P)
(**4**) $[Mn_2H(CNBF_3)(CO)_5(dppm)_2]$	2 038w, 1 966vs, 1 946s, 1 933 (sh), 1 899m[a]	2 153m[a,b]	*c*	−24.73 (quintet) (J_{PH} 16.9 Hz)	64.2 (m) 60.2 (m) (AA′BB′)
	2 037w, 1 967vs, 1 922s, 1 891m	2 154m[d]	1 091, 1 120, 1 142		
(**6**) $[Mn_2H(CNBF_3)(CO)_4(dppm)_2]$	1 995m, 1 962vs, 1 922s	1 819w (br)	*c*	−13.6 (br)[e]	62.4 (m) 49.4 (m) (AA′BB′, −60 °C)

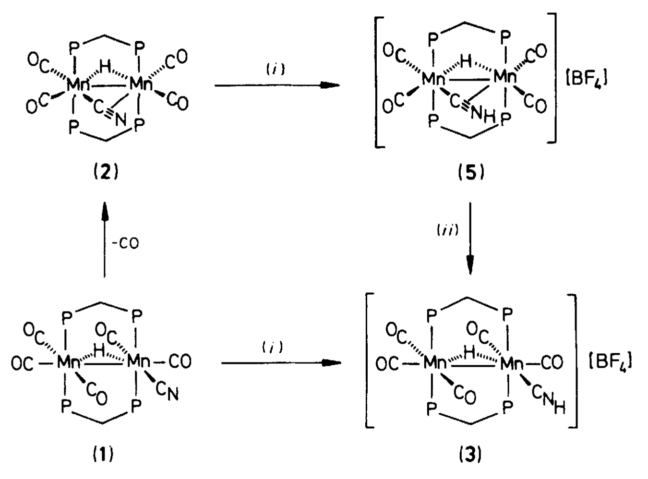
[a] In CH_2Cl_2. [b] For corresponding $^{13}CNBF_3$ compound ν(CN) 2 119m cm^{-1}. [c] Outside range scanned in CH_2Cl_2 solution. [d] For isolated material in Nujol. [e] Phosphorus coupling not resolved.

of the hydride signal from δ −14.9 to −13.6 p.p.m., while conversion at higher temperatures into compound (**3**) gives a signal at δ −24.8 p.p.m. The small downfield shift on forming (**5**) supports the idea that protonation at nitrogen occurs without other structural rearrangement. These spectra also show a signal for CN*H* for compound (**5**) at δ 10.9 p.p.m. showing coupling to ^{15}N in the enriched compound [$|^1J(^{15}NH)|$ = 118 Hz] at −90 °C. The ^{15}N resonance at −80 °C also shows this coupling (114 Hz in this case). Further, on protonation, the ^{15}N resonance shifts upfield by 95.9 p.p.m., a similar but smaller shift to that observed on protonating the cyanide ligand in compound (**1**) (Figure 1). Not only does ^{15}N n.m.r. spectroscopy confirm protonation at nitrogen, but it also apparently distinguishes clearly between terminal and μ-η^2-cyanide (Table 1), since there is a difference in δ(^{15}N) of around 80 p.p.m. between these two modes. This distinction is not always apparent from other data: δ(^{13}*C*N) is almost the same for the two forms, while ν(CN) is not always assignable; ν(CN) was not reported[2] for $[Mo_2(\mu\text{-}\eta^2\text{-}CN)(CO)_4(\eta\text{-}C_5H_5)_2]^-$ and we were unable to identify this absorption for compound (**2**). More ^{15}N n.m.r. data on μ-η^2-cyanide complexes (which still have to be synthesised) will be necessary to evaluate fully the chemical shift differences. The ^{13}C-{^{1}H} n.m.r. spectrum of compound (**5**) generated in CD_2Cl_2–CH_2Cl_2–$HBF_4{\cdot}Et_2O$ at −60 °C shows a triplet [δ(^{13}*C*N) 192.5 p.p.m., $J(^{31}P^{13}C)$ 19 Hz], downfield by 32 p.p.m. from that for the unprotonated compound (**2**), in a region expected for co-ordinated isocyanides.

The rapid transformation of compound (**2**) to cation (**5**) on protonation in CH_2Cl_2 and the relatively slow subsequent conversion into cation (**3**) could be conveniently followed by changes in the i.r. spectra. The ν(CO) absorption frequencies increased on protonation [unlike on protonation of (**1**)], while a fairly weak absorption at 1 833 cm^{-1} could be assigned to ν(CN) in the bridging CNH cation (**5**). Assignment was confirmed by separate isotopic labelling with ^{13}C, ^{15}N, and ^{2}H (Table 2). This absorption is replaced by ν(CN) at 2 143 cm^{-1} on conversion of compound (**5**) into the terminal CNH compound (**3**). The assignment was likewise confirmed by isotopic substitution. The value of ν(CN) in the μ-η^2-CNH compound (**5**) is rather similar to that observed for the μ-η^2-isocyanide ligand in $[Mn_2H(CNC_6H_4Me\text{-}4)(CO)_4(dppm)_2][BF_4]$ [ν(CN) 1 787 cm^{-1}], formed by protonation of $[Mn_2(CNC_6H_4Me\text{-}4)(CO)_4(dppm)_2]$ with $HBF_4{\cdot}Et_2O$.[13]

Thus all of the spectroscopic data are consistent with an oscillating μ-η^2-CNH ligand, the first example of its kind (see Scheme). We have observed that the terminal cyano-ligand is more basic than the μ-η^2 ligand since compound (**1**) is protonated preferentially in solutions containing both (**1**) and (**2**).

Reaction of $[Mn_2H(\mu\text{-}\eta^2\text{-}CN)(CO)_4(dppm)_2]$, (**2**), *with* BF_3.—On bubbling BF_3 gas into a dichloromethane solution of compound (**2**) at −60 °C, observations closely related to those on protonation were made. Thus the adduct $[Mn_2H(CNBF_3)(CO)_4(dppm)_2]$, (**6**), gives sharply resolved ^{31}P-{^{1}H} n.m.r. signals unlike the broad signals observed for (**2**) at −60 °C. The energy barrier to oscillation of $CNBF_3$ in (**6**) is greater than that of CN in (**2**); the coalescence temperature for (**6**) is above 25 °C. At room temperature slow irreversible conversion of complex (**6**) into (**4**) occurs. An observation unique to this system is that a ^{31}P-{^{1}H} n.m.r. singlet at δ 59.3 p.p.m. for some other unidentified species is observed along with those for (**6**) on bubbling BF_3 into a solution of compound (**2**) at −60 °C. The singlet is more intense the more BF_3 is used. Both (**6**) and this other species are slowly converted into compound (**4**) at room temperature. The ^{31}P-{^{1}H} n.m.r. singlet at δ 59.3 p.p.m. was



Scheme. (*i*) $HBF_4 \cdot Et_2O$, CH_2Cl_2; (*ii*) CO, >0 °C

shown to result from coalescence since at −100 °C it had resolved into broad equal-intensity signals (AA′BB′) at δ 64.8 and 60.4 p.p.m. Data for compound (**6**) are given in Table 3.

Experimental

The complexes $[Mn_2H(CN)(CO)_4(dppm)_2]$ and $[Mn_2H(CN)(CO)_5(dppm)_2]$ were prepared as reported earlier;[1] $K^{13}CN$ (90% ^{13}C) and $KC^{15}N$ (98.8% ^{15}N) were purchased from Merck Sharp and Dohme Isotopes.

Proton, ^{13}C-{^1H}, and ^{31}P-{^1H} n.m.r. spectra were recorded on a Varian XL200 spectrometer, while ^{15}N n.m.r. spectra were recorded without proton decoupling at 40.5 MHz on a Brüker WH400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer.

Protonation Reactions.—The n.m.r. protonation experiments were carried out by adding $HBF_4 \cdot Et_2O$ from a microsyringe (typically 0.005 cm^3 for ^1H, 0.05 cm^3 for other nuclei) to a solution of complex (**1**) or (**2**) (0.015 g for ^1H, 0.04—0.05 g for other nuclei) in CD_2Cl_2 or CD_2Cl_2–CH_2Cl_2 mixtures in the n.m.r. tube whilst cooling in solid CO_2. Spectral accumulation was commenced within a few minutes.

Preparation of $[Mn_2H(CNH)(CO)_5(dppm)_2][BPh_4]$, (**3**).—The $HBF_4 \cdot Et_2O$ (0.050 cm^3, 6.8 mol per mol Mn_2) was added to a solution of $[Mn_2H(CN)(CO)_5(dppm)_2]$ (0.0568 g) in CH_2Cl_2–CD_2Cl_2 (3 cm^3) in an n.m.r. tube for monitoring ^{31}P-{^1H} spectra. After observing the changes described in the Results and Discussion section, the solution was stored at 5 °C overnight, diluted (to *ca.* 20 cm^3) with CH_2Cl_2, and the excess of acid neutralised (pH 7) by stirring with solid $NaHCO_3$. Filtration through Celite gave a clear orange solution from which the solvent was removed under reduced pressure. The residue was taken up in methanol (*ca.* 15 cm^3) and solid $NaBPh_4$ added until precipitation of an orange solid was complete. The solid was filtered off, washed with methanol, and dried *in vacuo*. Yield 0.0265 g (43%) (Found: C, 67.8; H, 4.7; N, 1.05. $C_{80}H_{66}BMn_2NO_5P_4$ requires C, 70.35; H, 4.85; N, 1.0%). Attempted recrystallisation led to some deprotonation so the product could not be purified further. I.r. (CH_2Cl_2): ν(CO) 2 038w, 1 962vs, 1 936s, and 1 888m; ν(CN) 2 141w cm^{-1}.

Preparation of $[Mn_2H(CNBF_3)(CO)_5(dppm)_2]$, (**4**).—The adduct $BF_3 \cdot Me_2O$ (0.4 cm^3) was added to a stirred solution of $[Mn_2H(CN)(CO)_5(dppm)_2]$ (0.279 g, 0.27 mmol) in CH_2Cl_2 (40 cm^3). The solvent was removed *in vacuo* from the solution, which had become paler orange, after about 30 min to give an orange oil which on treatment with diethyl ether gave an orange solid (0.258 g, 86%) (Found: C, 59.3; H, 4.0; N, 1.4. $C_{55}H_{45}BF_3Mn_2NO_4P_4$ requires C, 60.4; H, 4.05; N, 1.25%). N.m.r.: ^1H ($CDCl_3$, 22 °C), δ 7.3 (m, C_6H_5), 4.10 (m) and 3.90 (m) (PCH_2P), and −24.73 p.p.m. (quintet, J_{PH} 16.9 Hz, Mn*H*Mn); ^{11}B, −4.7 p.p.m. (s, br) (relative to $BF_3 \cdot Et_2O$).

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