

Triphenylboron adducts of redox-active cyanomanganese ligands †

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The reaction of $[\text{Mn}(\text{CN})(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ ($\text{R} = \text{Ph}$ or OPh) with $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{tetrahydrothiophene}$) in the presence of $\text{Na}[\text{BPh}_4]$ gave $[\text{Mn}(\text{CNBPh}_3)(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$, X-ray studies on which ($\text{R} = \text{OPh}$) confirm addition of triphenylboron to the nitrogen atom of the cyanomanganese centre. Comparison of the geometry of the $\text{Ph}_3\text{B-NC}$ interaction, as measured by the mean C-B-C angle and mean B-C length, with those of L-BPh_3 species in the Cambridge Structural Database showed the manganese ligand to be a relatively weak donor comparable with a range of other N and O ligands. The complexes $[\text{Mn}(\text{CNBPh}_3)(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$, as well as *cis*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})]$ and *trans*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})(\text{dppm})_2]$, can be prepared directly from BPh_3 and the appropriate cyanomanganese ligand. Each of the complexes undergoes one-electron oxidation at a platinum disc electrode in CH_2Cl_2 and the reaction of *trans*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})(\text{dppm})_2]$ with $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ gives *trans*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})(\text{dppm})_2][\text{PF}_6]$.

Introduction

Our studies of the intramolecular electron-transfer reactions of bi- and poly-nuclear complexes have relied on the systematic variation of (i) the substitution pattern at the redox-active octahedral cyanomanganese centres $[\text{Mn}(\text{CN})(\text{CO})_{5-n}\text{L}_n]$ ($\text{L} = \text{P-donor ligand}$)¹ and (ii) the geometry at the metal to which such centres are bound through N [square planar Rh^{I} ,² tetrahedral Fe^{-1} ,³ octahedral Mn^{IV} and Ru ,⁵ linear M^{I} ($\text{M} = \text{Cu}$, Ag or Au),⁶ *etc.*]. The strongest intramolecular interaction so far detected (as measured by ΔE , the difference in potential between two successive one-electron oxidation processes) between two such redox-active cyanomanganese ligands is across the linear linkage $\text{Mn}(\text{CN})\text{Au}(\text{NC})\text{Mn}$, using the ligands *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]$ ($\text{R} = \text{Et}$ or Ph). The symmetry of the SOMO (singly occupied molecular orbital) of the manganese(II) fragments {formed by the one-electron oxidation of the co-ordinated manganese(I) ligand} in relation to that of the π^* orbitals of the cyanide bridge appears to be of prime importance in controlling the extent of intramolecular interaction. Thus, we sought to probe this control further by using cyanometal ligands with a pseudo-tetrahedral manganese centre, namely $[\text{Mn}(\text{CN})(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ ($\text{R} = \text{Ph}$ or OPh). Surprisingly, the synthetic route used to prepare $[\text{Au}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]$ [$\text{L}_x = (\text{CO})(\text{dppm})_2$ or *cis*- or *trans*- $(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})$ ($\text{R} = \text{Ph}$ or Et)]⁶ failed with the pseudo-tetrahedral complexes. Instead, we have isolated the unusual borane adducts $[\text{Mn}(\text{CNBPh}_3)(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ ($\text{R} = \text{Ph}$ or OPh). Here we report studies of the synthesis of these species by this and simpler routes, and their characterisation by spectroscopic, structural and electrochemical means. We also report a comparison of the geometry of $[\text{Mn}(\text{CNBPh}_3)\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ with those of other L-BPh_3 adducts, allowing the relative donor strength of the ligand L to be assessed on the basis of its ability to distort the BPh_3 moiety from planarity.

Results and discussion

The pseudo-tetrahedral complex $[\text{Mn}(\text{CN})(\text{PPh}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ has been prepared previously, by the reaction of $[\text{MnI}(\text{PPh}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ with NaCN in ethanol,⁷ but a more convenient preparation (one step from $[\text{Mn}(\text{CO})(\text{PPh}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]^+$) to this and $[\text{Mn}(\text{CN})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ is described in the Experimental section; spectroscopic and electrochemical data, for comparison with data for the new binuclear complexes now reported, are given in Table 1.

Synthesis of $[\text{Mn}(\text{CNBPh}_3)\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$

Treatment of $[\text{Mn}(\text{CN})(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ ($\text{R} = \text{Ph}$ or OPh) with $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{tetrahydrothiophene}$) in the presence of TlPF_6 (the method used⁶ to prepare complexes such as $[\text{Au}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]$ [$\text{L}_x = (\text{CO})(\text{dppm})_2$]) gave only an inseparable mixture of several products. The reactions were therefore repeated in acetone using $\text{Na}[\text{BPh}_4]$ as the halide abstraction reagent, to give a solution which IR spectroscopy showed contained only two products and from which orange (**1**, $\text{R} = \text{OPh}$) or red-brown (**2**, $\text{R} = \text{Ph}$) solids were isolated. (Attempts to isolate and characterise the second product were unsuccessful.)

The presence of the $[\text{Mn}(\text{CN})(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ moiety in complexes **1** and **2** was confirmed by the appearance of a strong nitrosyl absorption in the IR spectrum (Table 1), and cyanide-bridge formation by the shift to higher energy of $\nu(\text{CN})$ (*ca.* 70 cm^{-1}) from that of $[\text{Mn}(\text{CN})(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ [$\nu(\text{CN})$ 2107 cm^{-1} , $\text{R} = \text{OPh}$; 2099 cm^{-1} , $\text{R} = \text{Ph}$]. This shift was, however, much greater than expected (*cf.* *ca.* $20\text{--}30\text{ cm}^{-1}$ on forming $[\text{Au}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]$ [$\text{L}_x = (\text{CO})(\text{dppm})_2$ or *cis*- or *trans*- $(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})$ ($\text{R} = \text{Ph}$ or Et)] from *trans*- $[\text{Mn}(\text{CN})(\text{CO})(\text{dppm})_2]$ or *cis*- or *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]$ ($\text{R} = \text{Ph}$ or Et)]⁶ and the elemental analysis (C, H and N; Table 1) was inconsistent with that for the expected trimetallic complex $[\text{Au}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{BPh}_4]$ [$\text{L}_x = (\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$. In the absence of further spectroscopic data a structural analysis of **1** was carried out.

† Supplementary data available: CSD structural data for L-BPh_3 species. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/3185/>, otherwise available from BLDSC (No. SUP 57616, 3 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

Table 1 Analytical and IR spectroscopic data for BPh₃ complexes

Complex	Colour	Yield (%)	Analysis (%) ^a			IR ^b /cm ⁻¹			E°/V ^c
			C	H	N	ν(CN)	ν(CO)	ν(NO)	
[Mn(CN){P(OPh) ₃ }(NO)(η-C ₃ H ₄ Me)]	Orange-brown	46	59.9 (60.0)	4.5 (4.5)	5.5 (5.6)	2107w	—	1758	1.11
[Mn(CN)(PPh ₃)(NO)(η-C ₃ H ₄ Me)]	Purple	46	66.3 (66.4)	5.3 (4.9)	6.2 (6.2)	2099w	—	1734	0.85
[Mn(CNBPh ₃){P(OPh) ₃ }(NO)(η-C ₃ H ₄ Me)] 1	Orange	64	69.2 (69.6)	4.8 (5.0)	3.7 (3.8)	2177w	—	1774	1.44(1)
[Mn(CNBPh ₃)(PPh ₃)(NO)(η-C ₃ H ₄ Me)] 2	Red-brown	59	73.7 (74.4)	5.3 (5.4)	3.9 (4.0)	2166m	—	1749	1.09
<i>cis</i> -[Mn(CNBPh ₃)(CO) ₂ {P(OEt) ₃ }(dppm)] 3	Yellow	59	62.7 (62.7) ^d	5.3 (5.4)	1.6 (1.4)	2152w	1967, 1913ms	—	1.25(1), (0.75)
<i>trans</i> -[Mn(CNBPh ₃)(CO)(dppm) ₂] 4	Orange	68	74.4 (74.6) ^e	5.7 (5.7)	1.1 (1.2)	2110mw	1874	—	0.26
<i>trans</i> -[Mn(CNBPh ₃)(CO)(dppm) ₂][PF ₆] ⁻ 5	Red	46	64.3 (64.2) ^f	4.5 (4.7)	0.9 (1.1)	2138w	1947	—	0.26

^a Calculated values in parentheses. ^b In CH₂Cl₂; strong absorptions unless otherwise stated, m = medium, w = weak. ^c In CH₂Cl₂ at a platinum disc electrode; E°_r for reversible wave unless otherwise stated. For an irreversible (I) wave the peak potential [(E_p)_{ox} or (E_p)_{red}] is given at a scan rate of 200 mV s⁻¹. Under the conditions used the potential for the couple [FeCp₂]⁺–[FeCp₂]⁻ is 0.47 V. ^d Analysed as 1.0 CH₂Cl₂ solvate. ^e Analysed as 1.0 thf solvate. ^f Analysed as 1.5 CH₂Cl₂ solvate.

Table 2 Selected bond lengths (Å) and angles (°) for [Mn(CNBPh₃){P(OPh)₃}(NO)(η-C₅H₄Me)] **1**; values for the second independent molecule are given in square brackets^a

B–C _{av}	1.612(9) [1.620(8)]	B–N–C	177.8(5) [177.9(5)]
B–N	1.608(8) [1.591(7)]	N–C–Mn	175.6(5) [177.9(5)]
N–C	1.142(6) [1.147(6)]	Mn–N–O	174.8(5) [174.0(6)]
(N)C–Mn	1.929(6) [1.933(6)]	(O)N–Mn–C(N)	98.2(2) [100.1(2)]
Mn–N(O)	1.634(5) [1.624(6)]	(O)N–Mn–P(OPh)	94.4(2) [96.3(2)]
N–O	1.169(5) [1.127(6)]	(C)N–Mn–P(OPh)	89.2(2) [86.3(2)]
Mn–P(OPh)	2.213(4) [2.203(2)]	O–P–O _{av}	101.2(2) [100.7(2)]
P–O _{av}	1.602(4) [1.596(4)]	C–B–C _{av}	112.8(5) [112.0(5)]
		C–B–N _{av}	105.9(5) [106.8(5)]

^a Estimated standard uncertainties for individual values are given in parentheses for the least significant digit, here and throughout this paper.

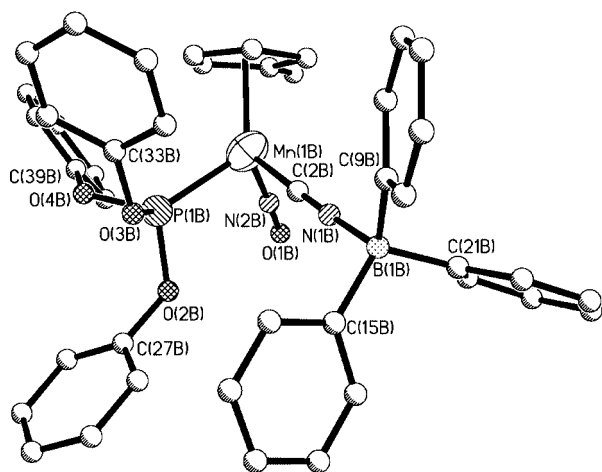


Fig. 1 Molecular structure of the ordered independent molecule of complex **1** showing atom labelling. Hydrogen atoms are omitted for clarity.

The molecular structure of [Mn(CNBPh₃){P(OPh)₃}(NO)(η-C₅H₄Me)] **1**

Crystals of **1** were grown by allowing a concentrated CH₂Cl₂ solution of the complex to diffuse into *n*-hexane at room temperature. The structural analysis unexpectedly revealed **1** to be the borane adduct [Mn(CNBPh₃){P(OPh)₃}(NO)(η-C₅H₄Me)]. One of the two independent molecules in the unit cell is shown in Fig. 1; selected structural data are given in Table 2.

Co-ordination of the cyanomanganese ligand to the boron centre in complex **1** leads to elongation of the B–C bond length compared with that in trigonal planar BPh₃ (1.576 Å,⁸ cf. 1.616 Å in **1**), while the C–B–C angle is reduced from 120 to 112.4°, consistent with substantial rehybridisation of boron from sp² towards sp³ in **1**. The B–N bond length in **1** (1.600 Å) is similar to those in the Co^{II}–CNBPh₃ and Fe^{II}–CNBPh₃ adducts [Co{κ³-(PPh₂CH₂)₃CMe}{CNBPh₃}],⁹ [FeMe(CNBPh₃)(CO)₂-(PMe₃)₂]¹⁰ and *trans*-[Fe(CNBPh₃)₂(tim)] (tim = 2,3,9,10-tetra-methyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)¹¹ (1.605, 1.592 and 1.577 Å respectively).

The manganese centre in complex **1** is significantly distorted from tetrahedral geometry in the manner expected for d⁶ [ML₃Cp] species with angles between the monodentate ligands distorted towards 90° from 109.5° (see Table 2). A comparison of the bond lengths around the Mn with those of octahedral cyanomanganese ligands shows only small differences, despite the change in geometry at Mn. For example, the Mn–P(OPh)₃ bond length is 2.199(2) Å in the octahedral manganese complex *trans*-[Cl₃Fe(μ-NC)Mn(CO)₂{P(OPh)₃}(dppm)].¹² The Mn–C–N–B linkage is close to linear (180 > all angles > 175°). The bond lengths of the Mn–C–N moiety in **1** (Mn–C 1.931 Å, C–N 1.145 Å) are in the range observed in other complexes of cyanomanganese ligands, with both transition metal and p-block element Lewis acids {cf. *trans*-[Mn(CO)(CNCH₂CMe=CH₂)(dppm)]⁺, Mn–C 1.929(9), C–N 1.132(11) Å¹³ and *trans*-

[Cl₃Fe(μ-NC)Mn(CO)₂{P(OPh)₃}(dppm)], Mn–C 1.889(8), C–N 1.182(7) Å.¹²

The determination of the structure of complex **1** allows a comparison to be made between the effect of the cyanomanganese ligand in **1** on the geometry of the BPh₃ fragment with those of other ligands, L, in other L·BPh₃ adducts (L = neutral or anionic ligand bound to B through an atom, Z). There are some 23 structures containing geometric information on L·BPh₃ moieties (excluding [BPh₄][−] anions) in the Cambridge Structural Database (CSD, see Experimental section), containing a total of 26 unique fragments. In this data set the ligands are predominantly nitrogen donors (*i.e.* Z = N, 19 examples, usually with sp² hybridisation at N) although there are also examples of oxygen (5 cases), phosphorus (1 case) and germanium(II) (1 case) donors.

We have previously shown¹⁴ that the geometry of Z–PPh₃ species can be usefully analysed through a study of the symmetric deformation of the P–C distances and C–P–C angles. In that case there was a persistent negative correlation between the mean P–C distance (⟨P–C⟩) and mean C–P–C angle (⟨C–P–C⟩) which was interpreted in terms of a qualitative molecular orbital model of the bonding in PPh₃. The main driving force for geometry distortion in the Z–PPh₃ species is the occupancy of the HOMO of PPh₃, its lone pair (2a₁, see Fig. 2 which is derived from the Walsh diagram given in ref. 14). As this orbital is depopulated by co-ordination to a Lewis acid (such as a proton) ⟨C–P–C⟩ increases from *ca.* 103° in free PPh₃ to *ca.* 112° in [PPh₃]⁺ salts while ⟨P–C⟩ contracts correspondingly from 1.83 to 1.78 Å. In L·BPh₃ we might therefore expect to monitor the effect of Lewis bases in the converse manner. As the LUMO (2a₁, see Fig. 2) of BPh₃ becomes more completely occupied as a result of donation from the ligand L the geometry would be expected to distort from planarity (as in BPh₃ where ⟨C–B–C⟩ 120°) towards tetrahedral values with ⟨C–B–C⟩ *ca.* 110° (see Fig. 2). Indeed symmetry requires that the geometry of the ubiquitous [BPh₄][−] anion has ⟨C–B–C⟩ 109.5°. Fig. 3 shows a plot of the ⟨C–B–C⟩ and ⟨C–B⟩ values for the 26 Z–BPh₃ fragments in the CSD together with the mean values for 319 [BPh₄][−] anions, those for BPh₃ itself and for the two independent molecules of **1**. The negative correlation of bond length and angle observed in the much larger Z–PPh₃ data set is seen here too, albeit in weakened form (linear correlation coefficient = −0.568, Spearman rank correlation coefficient¹⁴ ρ_s = −0.194) in part due to the relative paucity of data. The general trend is that stronger donors such as Ph[−] (in [BPh₄][−] anions) lie at the lower right of the plot and weaker donors such as thf (*e.g.* CSD refcode TEKPII, ⟨B–C⟩ 1.622 Å, ⟨C–B–C⟩ 113.7°) or oxo-metal (*e.g.* CSD refcode KENZEI, ⟨B–C⟩ 1.608 Å, ⟨C–B–C⟩ 113.5°) at the upper left of the main body of points, with the special case in which the ligand L is absent (BPh₃) at the extreme upper left of the plot. On the basis of the structure of **1** and those of the other cyanometal complex adducts referred to above, it seems clear that the M–CN moiety is one of the weaker donors in the group represented in Fig. 3. Thus, the ⟨B–C⟩ values for **1** are at the low end of the range of values observed in this data set and the ⟨C–B–C⟩ values in the mid-upper part of the distribution.

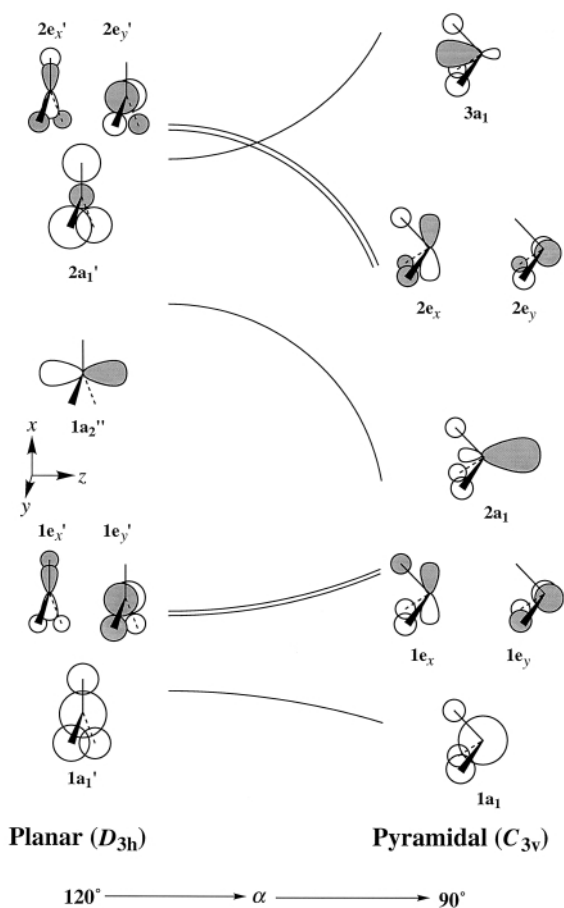


Fig. 2 Walsh diagram for EPh_3 species ($E = B$ or P) indicating schematically the energy variation for the principal orbital interactions as a function of the $C-E-C$ angles. The $2a_1$ orbital is the HOMO for $E = P$ and the LUMO for $E = B$.

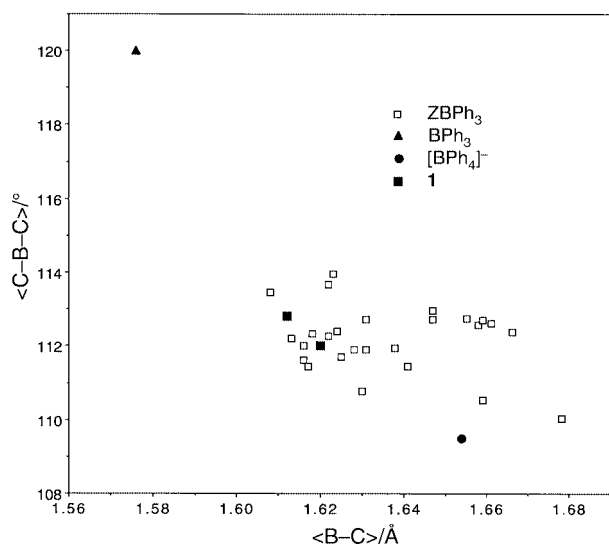


Fig. 3 Scatterplot of $\langle B-C \rangle$ vs. $\langle C-B-C \rangle$ for $L \cdot BPh_3$, BPh_3 , $[BPh_4]^-$ and complex **1**.

It would be of interest to compare other methods of gauging the donor ability of ligands with this structural approach.

Although the mechanism of formation of $[Mn^I(CNBPh_3)(PR_3)(NO)(\eta-C_5H_4Me)]$ is unknown, $[AuCl(tht)]$ is certainly required in the reaction mixture (despite the absence of gold in the isolated product) as $[Mn(CN)(PR_3)(NO)(\eta-C_5H_4Me)]$ ($R = Ph$ or OPh) does not react with $Na[BPh_4]$ alone. Recent studies have shown^{15,16} that $Na[BPh_4]$ can act as a phenylating agent towards gold complexes, for example giving $[AuPh-$

$PBu^t_3]$ with $[O\{Au(PBu^t_3)\}_3][BF_4]$,¹⁵ and $Na[BPh_4]$ does react with $[AuCl(tht)]$ in acetone. Though no products have been characterised from this last reaction, $NaCl$, BPh_3 and $[AuPh(tht)]$ are likely candidates. The last is expected to be thermally unstable¹⁷ so that, in the reaction between $[Mn(CN)(PR_3)(NO)(\eta-C_5H_4Me)]$ ($R = Ph$ or OPh), $[AuCl(tht)]$ and $Na[BPh_4]$, the Lewis acid BPh_3 would become available to react with the N-donor cyanomanganese complex. Indeed, BPh_3 does react directly with $[Mn(CN)(PR_3)(NO)(\eta-C_5H_4Me)]$ ($R = Ph$ or OPh), providing a simpler route to **1** and **2**, and to the complexes *cis*- $[Mn(CNBPh_3)(CO)_2\{P(OEt)_3\}(dppm)]$ **3** and *trans*- $[Mn(CNBPh_3)(CO)(dppm)]_2$ **4**.

The addition of BPh_3 to the cyanomanganese ligand in CH_2Cl_2 , followed by treatment with *n*-hexane and recrystallisation of the precipitated product using CH_2Cl_2 -*n*-hexane or *thf*-*n*-hexane mixtures, gave complexes **1–4** in *ca.* 50–60% yield as yellow to red powders. The complexes were characterised by elemental analysis (Table 1) and IR spectroscopy. Large shifts to higher energy in $\nu(CN)$, of the order of 30 (for **4**) to 70 (for **1**) cm^{-1} , show the BPh_3 group to act as a relatively weak Lewis acid on co-ordination; stronger withdrawing groups such as $Fe(NO)_2(PPh_3)_3$ and $SbCl_5$ ¹⁸ lead to small negative shifts in $\nu(CN)$ on co-ordination at N.

The electrochemistry of complexes **1–4**

Cyclic voltammetry at a platinum electrode in CH_2Cl_2 shows that complexes **1–4** undergo oxidation in the potential range 0.0 to 1.6 V (Table 1), with the potentials shifted to more positive values when compared with those of the free cyanomanganese ligands themselves. The oxidation of the $P(OPh)_3$ complex **1** is chemically irreversible whereas that of the PPh_3 analogue **2** is partially reversible [$(i_p)_{red}/(i_p)_{ox} = ca. 0.8$ at scan rates ≥ 100 $mV s^{-1}$]. The CV of **3** reveals the usual *cis* to *trans* oxidative isomerisation found in complexes of *cis*-dicarbonyl manganese ligands,¹⁹ with an irreversible wave at 1.25 V coupled to a product wave centred at 0.75 V. The oxidation of the monocarbonyl adduct **4** is fully reversible and, at a potential of 0.26 V, is readily achieved using mild oxidants. Thus, addition of $[Fe(\eta-C_5H_5)_2][PF_6]$ to a solution of **4** in CH_2Cl_2 gave a red solution from which the 1.5 CH_2Cl_2 solvate of the manganese(II) salt $[Mn(CNBPh_3)(CO)(dppm)_2][PF_6]$ **5** was isolated and characterised by elemental analysis, IR spectroscopy and electrochemistry (Table 1). Thus, the IR spectrum of **5** shows an increase in $\nu(CN)$ to 2138 cm^{-1} (from 2110 cm^{-1} in **4**) and an increase in $\nu(CO)$ to 1947 cm^{-1} (from 1874 cm^{-1} in **4**), in accord with one-electron oxidation at Mn. The CV of **5** shows a reduction wave centred at a potential identical to that at which oxidation of **4** occurs (0.26 V).

Conclusion

The reaction of pseudo-tetrahedral cyanomanganese ligands $[Mn(CN)(PR_3)(NO)(\eta-C_5H_4Me)]$ ($R = Ph$ or OPh) with $[AuCl(tht)]$ in the presence of $Na[BPh_4]$ unexpectedly gives the triphenylboron adducts $[Mn(CNBPh_3)(PR_3)(NO)(\eta-C_5H_4Me)]$ ($R = Ph$ or OPh); these products, as well as adducts of other cyanomanganese ligands, may be synthesised by the direct reaction of cyanomanganese ligands with BPh_3 .

The structure of $[Mn(CNBPh_3)\{P(OPh)_3\}(NO)(\eta-C_5H_4Me)]$ **1** has a pseudo-tetrahedral geometry at Mn and a linear Mn–C–N–B unit. The geometry of the $CNBPh_3$ moiety is similar to that in other M–CN adducts of this type. The CSD study shows that the $\langle B-C \rangle$ and $\langle C-B-C \rangle$ values for **1** imply the cyanomanganese ligand to be a weak donor causing only a modest distortion of the BPh_3 unit, comparable with that caused by *thf*.

Chemical oxidation of the monocarbonyl *trans*- $[Mn(CNBPh_3)(CO)(dppm)]_2$ with $[Fe(\eta-C_5H_5)_2][PF_6]$ gives the manganese(II) complex *trans*- $[Mn(CNBPh_3)(CO)(dppm)]_2[PF_6]$.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled and deoxygenated solvents; reactions were monitored by IR spectroscopy where appropriate. Unless stated otherwise, complexes (i) were purified by dissolution in CH_2Cl_2 , filtration of the solution through Celite, addition of *n*-hexane to the filtrate and reduction of the volume of the mixture *in vacuo* to induce precipitation, and (ii) are air-stable in the solid state and dissolve in polar solvents such as CH_2Cl_2 and acetone to give moderately air-sensitive solutions. The compounds $[\text{Mn}(\text{CO})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})][\text{BF}_4]$,²⁰ *trans*- $[\text{Mn}(\text{CN})(\text{CO})(\text{dppm})_2]$,²¹ *cis*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})]$,⁴ $[\text{AuCl}(\text{tht})]$ ²² and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ ²³ were prepared by published methods; BPh_3 and $[\text{NET}_4]\text{CN}$ were purchased from Fluka and $\text{Na}[\text{BPh}_4]$ from Aldrich. IR spectra were recorded on a Nicolet 5ZDX FT spectrometer. Electrochemical studies were carried out as previously described.⁶ Under these conditions, E° for the couple $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$ in CH_2Cl_2 is 0.47 V. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Syntheses

$[\text{Mn}(\text{CN})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$. A mixture of $[\text{Mn}(\text{CO})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})][\text{BF}_4]$ (3.71 g, 6.3 mmol) and $[\text{NET}_4]\text{CN}$ (0.98 g, 6.3 mmol) was heated under reflux in CH_2Cl_2 (150 cm^3) for 18 h. The solution was then filtered and evaporated to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (15 cm^3) and added to an alumina-*n*-hexane chromatography column (20 \times 2.5 cm). Elution of the orange-brown band with CH_2Cl_2 -thf (19:1) gave an orange-brown solution which was treated with *n*-hexane (300 cm^3) and reduced in volume *in vacuo* to give an orange precipitate. The precipitate was then extracted into toluene, filtered, evaporated to dryness, redissolved in CH_2Cl_2 , treated with *n*-hexane, and reduced in volume to give the product as an orange-brown powder, yield 1.44 g (46%).

The complex $[\text{Mn}(\text{CN})(\text{PPh}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ was prepared similarly. Column chromatography gave a green band, which was discarded, and a red band, eluted with CH_2Cl_2 -thf (1:1), which gave a red solution from which the product was isolated as a purple powder on treatment with *n*-hexane and partial removal of the solvent *in vacuo*.

$[\text{Mn}(\text{CNBPh}_3)\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$. *Method (i)*. To a stirred solution of $[\text{AuCl}(\text{tht})]$ (150 mg, 0.47 mmol) and $[\text{Mn}(\text{CN})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ (397 mg, 0.79 mmol) in acetone (50 cm^3) was added $\text{Na}[\text{BPh}_4]$ (270 mg, 0.79 mmol). After 2 h the reaction mixture was evaporated to dryness and the residue extracted into CH_2Cl_2 (20 cm^3). After filtration through Celite, the orange solution was evaporated to dryness, and the extraction, filtration, and evaporation processes repeated using toluene. Finally, the residue was redissolved in CH_2Cl_2 , *n*-hexane was added, and the mixture reduced in volume *in vacuo* to give an orange powder, yield 146 mg (25%).

Method (ii). To a stirred solution of $[\text{Mn}(\text{CN})\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ (50 mg, 0.10 mmol) in CH_2Cl_2 (15 cm^3) was added BPh_3 (27 mg, 0.11 mmol). After 10 min the reaction mixture was filtered through Celite, and the filtrate treated with *n*-hexane (20 cm^3). Reduction of the volume of the solvent *in vacuo* gave an orange solid which was washed with *n*-hexane (2 \times 30 cm^3) and then purified using CH_2Cl_2 -*n*-hexane to give the product, yield 47 mg (64%).

The complexes $[\text{Mn}(\text{CNBPh}_3)(\text{PR}_3)(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ (R = Ph or OPh) and *cis*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})]$ were prepared similarly as was *trans*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})(\text{dppm})_2]\cdot\text{thf}$ (after purification using thf-*n*-hexane).

trans- $[\text{Mn}(\text{CNBPh}_3)(\text{PPh}_3)(\text{CO})(\text{dppm})_2][\text{PF}_6]$. To a stirred solution of *trans*- $[\text{Mn}(\text{CN})(\text{CO})(\text{dppm})_2]$ (50 mg, 0.06 mmol) in CH_2Cl_2 (15 cm^3) was added BPh_3 (15 mg, 0.07 mmol). After 10 min, IR spectroscopy confirmed the presence of only *trans*- $[\text{Mn}(\text{CNBPh}_3)(\text{CO})(\text{dppm})_2]$ in the orange solution. Solid $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ (19 mg, 0.06 mmol) was then added to give a red solution which gave a dark oil on addition of *n*-hexane and reduction of the solvent volume *in vacuo*. The oil was then dissolved in the minimum volume of CH_2Cl_2 (*ca.* 3 cm^3). Rapid addition of diethyl ether (50 cm^3) gave a red precipitate which was washed with *n*-hexane (2 \times 30 cm^3) and dried *in vacuo*, yield 35 mg (46%). The solid decomposes slowly in the solid state.

Structure determination of $[\text{Mn}(\text{CNBPh}_3)\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta\text{-C}_5\text{H}_4\text{Me})]$ 1

Crystals were grown by allowing a concentrated CH_2Cl_2 solution of **1** to diffuse into *n*-hexane at room temperature. The structure analysis was carried out by standard area detector methods.

Crystal data. $\text{C}_{43}\text{H}_{37}\text{BMnN}_2\text{O}_4\text{P}$, $M = 742.45$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.100(3)$, $b = 17.727(5)$, $c = 42.363(9)$ Å, $\beta = 96.06(2)^\circ$, $V = 7543(4)$ Å³, $T = 293$ K, $Z = 8$, $D_x = 1.305$ g cm^{-3} , $\mu = 0.44$ mm⁻¹, 27335 reflections measured, 10652 unique, $R_{\text{int}} = 0.5096$, $R1 = 0.066$.

There are two independent molecules of complex **1** in the asymmetric unit (identified by postscripts A and B in the atom list). In molecule A there is a twofold disorder of one phenyl group at the boron; the two orientations of the ring have occupancy 0.55(1) and 0.45(1) and are related by rotation about the C15A...C18A axis. The disorder leads to artificially short intermolecular contacts (involving C17A) across an inversion centre involving this group, which are presumably avoided in practice by local short-range ordering in the crystal. Partial occupancy atoms were refined isotropically.

CCDC reference number 186/1583.

See <http://www.rsc.org/suppdata/dt/1999/3185/> for crystallographic files in .cif format.

Database study

Geometric data for ZBPh_3 fragments ($Z \neq \text{C}$), BPh_3 and $[\text{BPh}_4]^-$ anions (the latter for those structures without disorder and with $R < 0.05$) were retrieved from the October 1998 version of the Cambridge Structural Database.²⁴ Average B-C distances ($\langle \text{B-C} \rangle$) and C-B-C bond angles ($\langle \text{C-B-C} \rangle$) were calculated for each case, and for $[\text{BPh}_4]^-$ the average of all the (B-C) values taken. The CSD refcodes and molecular dimensions for the fragments shown in Fig. 3 have been deposited (SUP 57616).

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