The Co-ordination Chemistry of Manganese. Part 14.[1] Synthesis of Manganese(II) Complexes of Tertiary Phosphine Ligands containing 2-Cyanoethyl Groups

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Complexes of manganese(II) salts with tertiary phosphine ligands containing 2-cyanoethyl groups have been prepared and characterised, MnX_2L [X = Cl, Br, I, or NCS; L = $P(CH_2CH_2CN)_3$, $PPh(CH_2CH_2CN)_2$, or $Ph_2PCH_2CH_2CN$]. In the solid state and in dichloromethane solution, when L = $P(CH_2CH_2CN)_3$ or $PPh(CH_2CH_2CN)_2$ the complexes have pseudo-octahedral dimeric structures involving bridging and terminal X groups and tridentate PN_2 ligands, and molecular-weight measurements confirm the dimeric nature for two of these complexes in dichloromethane; however, for L = $Ph_2PCH_2CH_2CN$ the complexes are pseudo-tetrahedral and the cyano-group is not co-ordinated. In tetrahydrofuran (thf) all the complexes have been assigned a pseudo-octahedral $MnX_2(thf)_3L$ structure in which the ligands are unidentate phosphine donors only. None of the MnX_2L complexes absorbs dioxygen in thf, in contrast to their tertiary alkylphosphine analogues. This is attributed to the better π-acceptor properties of the 2-cyanoethyl ligands. The complex $MnI_2[P(CH_2CH_2CN)_3]$ can be formed by substitution of PBu^n_3 in $MnI_2(PBu^n_3)$ in thf, but the reverse reaction is not possible.

During a wide-ranging study of the reactions of $MnX_2(PR_3)$ complexes with small molecules such as dioxygen,[2] carbon monoxide,[3,4] and sulphur dioxide [5] certain trends have begun to emerge. Most of our effort has concentrated on dioxygen binding [equation (1)] primarily because it has been possible

$$MnX_2(PR_3) + O_2 \rightleftharpoons MnX_2(PR_3)(O_2) \qquad (1)$$

to determine K_{O_2} and p_{50} values for the $MnX_2(PR_3)$ complexes spectrophotometrically.[2,6] It has been found that both the steric and electronic properties of the tertiary phosphine ligands are important factors in determining the 'activity,' or otherwise, of a given $MnX_2(PR_3)$ complex.[7,8] The relative contribution of each of these factors has not, however, been determined.[8]

In reviewing the steric and electronic properties of a range of PR_3 ligands, Tolman [9] noted that the substituent groups n-C_4H_9 and CH_2CH_2CN are sterically identical. The electronic properties of the ligands were, however, significantly different. These observations led us to the work described here.

The complexes $MnX_2(PR_3)$ (X = Cl, Br, I, or NCS; R_3 = Bu^n_3, $PhBu^n_2$, or Ph_2Bu^n) have been synthesised previously and their reactions with dioxygen studied.[2,7,8] The compounds $PPh_{3-n}(CH_2CH_2CN)_n$ (n = 1—3) were readily available from commercial sources and appeared to offer a potential insight into the relative importance of steric and electronic properties of the PR_3 ligand on the 'activity' of the corresponding $MnX_2(PR_3)$ complex.

Results and Discussion

Stirring anhydrous MnX_2 salts (X = Cl, Br, I, or NCS) with $PPh_{3-n}(CH_2CH_2CN)_n$ (n = 1—3) in dry diethyl ether under argon resulted in the formation of 1 : 1 complexes of formula MnX_2(ligand), Table 1. The stoicheiometry of the product remained constant over a wide range of reaction conditions. Thus, even when a 10 molar excess of phosphine ligand was employed and the mixture refluxed for several days only the $MnX_2(PR_3)$ complex and unreacted PR_3 ligand were recovered. The complexes of each of the three ligands exhibited slightly different spectroscopic properties, and so each type will be discussed in turn.

Complexes of Tris(2-cyanoethyl)phosphine.—The i.r. data for the $MnX_2[P(CH_2CH_2CN)_3]$ complexes, as Nujol mulls, are listed in Table 2. As can be seen, both Mn–X and Mn–X–Mn linkages have been identified.[10,11] Bands assignable to ν(Mn–P)[10,11] and ν(Mn–N)[10,11] are also clearly observable. It is noticeable that the ν(CN) absorptions of the ligand appear as two bands in the spectra of the complexes, one identical to that of the free ligand and the other shifted to higher frequency, indicating co-ordination of some of the CN groups.[12]

The room-temperature magnetic moments, Table 1, are all lower than the spin-only value of 5.92 μ_B expected for high-spin manganese(II). The values decrease in the order Cl > Br > I > NCS, suggesting that bridging Mn–X–Mn moieties tend to significant spin pairing in this order in these complexes.

The presence of manganese(II) centres is also confirmed by e.s.r. measurements. In the solid state each of the $MnX_2[P(CH_2CH_2CN)_3]$ complexes exhibits a broad band at $g_{eff.}$ *ca.* 6 and 2, with no fine structure. These spectra imply a pseudo-octahedral environment for the manganese centres.[13,14] In dichloromethane solution the e.s.r. spectra consist of a broad band at $g_{eff.}$ = 6, Table 3, again suggesting a pseudo-octahedral environment. The i.r. spectra of the complexes in dichloromethane are similar to those in the solid state, namely two bands are found in the ν(CN) region, one at the position of the free-ligand band and one at a higher frequency indicating co-ordination of some of the CN groups in dichloromethane solution. The complex $MnI_2[P(CH_2CH_2CN)_3]$ was fortunately sufficiently soluble for a molecular-weight determination, and the value obtained, 985, corresponds closely to that calculated for a dimer (1 004 for $\{MnI_2[P(CH_2CH_2CN)_3]\}_2$).

All of the above observations are consistent with the $MnX_2[P(CH_2CH_2CN)_3]$ complexes being halide- or pseudo-halide-bridged dimers in the solid state and in dichloromethane solution. The i.r. evidence clearly indicates that the $P(CH_2CH_2CN)_3$ ligand is co-ordinating to manganese *via* both the phosphorus atoms and, almost certainly, two CN groups. The most likely structure is (I).

In tetrahydrofuran (thf) the complexes appear to have a different structure. The i.r. spectra, Table 4, in the ν(CN) region comprise only a single band, at the same frequency as

Table 1. Physical and analytical data for the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes

Complex	Colour	M.p. (°C)	$\mu_{eff.}/\mu_B$	Analysis (%) *					
				C	H	N	P	X	Mn
$MnCl_2[P(CH_2CH_2CN)_3]$	Off white	191	5.8	34.0 (33.9)	4.0 (3.8)	13.0 (13.2)		22.0 (22.3)	
$MnBr_2[P(CH_2CH_2CN)_3]$	Pale pink	124	5.75	27.0 (26.5)	3.0 (2.9)	9.5 (10.3)		38.5 (39.2)	
$MnI_2[P(CH_2CH_2CN)_3]$	Pink-orange	125	5.7	20.8 (21.5)	2.0 (2.4)	9.0 (8.4)		50.9 (50.6)	
$Mn(NCS)_2[P(CH_2CH_2CN)_3]$	Yellow	77	5.45	37.0 (36.3)	3.5 (3.3)	19.0 (19.2)	8.6 (8.5)		14.9 (15.1)
$MnCl_2[PPh(CH_2CH_2CN)_2]$	Off white	185	5.8	42.4 (42.5)	3.9 (3.8)	8.0 (8.2)	9.0 (9.1)	20.5 (20.7)	16.4 (16.2)
$MnBr_2[PPh(CH_2CH_2CN)_2]$	Pink	143	5.7	34.0 (33.5)	3.1 (3.3)	6.4 (6.5)	7.5 (7.4)	37.0 (36.5)	
$MnI_2[PPh(CH_2CH_2CN)_2]$	Pink-orange	135	5.6	28.0 (27.5)	2.7 (2.5)	5.5 (5.3)	6.0 (5.9)	48.0 (48.5)	10.0 (10.2)
$Mn(NCS)_2[PPh(CH_2CH_2CN)_2]$	Yellow	80	5.4	44.0 (43.4)	3.2 (3.4)	7.0 (7.2)	8.2 (8.0)		
$MnCl_2[PPh_2(CH_2CH_2CN)]$	Off white	162	5.75	49.6 (49.3)	4.0 (3.8)	3.6 (3.8)		19.0 (19.5)	
$MnBr_2[PPh_2(CH_2CH_2CN)]$	Pink	102	5.7	40.0 (39.7)	3.2 (3.1)	2.8 (3.1)	7.0 (6.8)	34.8 (35.2)	
$MnI_2[PPh_2(CH_2CH_2CN)]$	Pink-orange	92	5.6	33.0 (32.8)	3.0 (2.6)	2.4 (2.6)		47.0 (46.4)	
$Mn(NCS)_2[PPh_2(CH_2CH_2CN)]$	Yellow	62	5.35	54.5 (53.9)	4.0 (3.7)	11.8 (11.1)	8.5 (8.2)		15.0 (14.6)

* Calculated values are given in parentheses.

Table 2. Infrared spectra (cm^{-1}) of the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes in Nujol

Complex	ν(ligand) [a]	ν(Mn–X)	ν(Mn–X–Mn)	ν(Mn–P)	ν(Mn–N)
$MnCl_2[P(CH_2CH_2CN)_3]$	2 270s (sh), 2 240m, (sh)	290m	220m	390s (sh)	250m (br)
$MnBr_2[P(CH_2CH_2CN)_3]$	2 275s (sh), 2 240m, (sh)	230m	190m (br)	392m (sh)	250m (sh)
$MnI_2[P(CH_2CH_2CN)_3]$	2 280s (sh), 2 240m, (sh)	218m (sh)	160m (br)	394m—w (sh)	245w (sh)
$Mn(NCS)_2[P(CH_2CH_2CN)_3]$	2 270s (sh), 2 240m, (sh)	2 080m [b]	2 110m (sh) [c]	388m (br)	280, 250w (sh)
$MnCl_2[PPh(CH_2CH_2CN)_2]$	2 285m (sh)	300m	225m (br)	385m (br)	255w (sh)
$MnBr_2[PPh(CH_2CH_2CN)_2]$	2 290m (sh)	240m (sh)	185m (br)	395m (sh)	260w (br)
$MnI_2[PPh(CH_2CH_2CN)_2]$	2 300m (sh)	205m (br)	170s (br)	400w (sh)	255m (br)
$Mn(NCS)_2[PPh(CH_2CH_2CN)_2]$	2 280m (sh)	2 060s (sh) [b]	2 120m (sh) [c]	390m (br)	285, 250w (sh)
$MnCl_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	300s (sh)	230m (br)	400m (sh)	n.o.
$MnBr_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	240m (sh)	185m (br)	400m (sh)	n.o.
$MnI_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	205s (sh)	155m (sh)	410m (br)	n.o.
$Mn(NCS)_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	2 060s (sh) [b]	2 120m (sh) [c]	390m (br)	285m (sh)

s = Strong, m = medium, w = weak, sh = sharp, br = broad, and n.o. = not observed.

[a] ν(CN): for $P(CH_2CH_2CN)_3$, 2 240; $PPh(CH_2CH_2CN)_2$, 2 270; $PPh_2(CH_2CH_2CN)$, 2 230 cm^{-1}. [b] ν(CN) for Mn–NCS. [c] ν(CN) for Mn–NCS–Mn.

Table 3. Spectroscopic properties of the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes in dichloromethane solution

Complex	Infrared (cm^{-1}) ν(ligand) [a]	E.s.r. line positions/G [b]						
$MnCl_2[P(CH_2CH_2CN)_3]$	2 280s (sh), 2 245m (sh)	1 000s		1 600w		2 100w	3 300m	5 650w
$MnBr_2[P(CH_2CH_2CN)_3]$	2 280s (sh), 2 245m (sh)	1 125s		1 600m		2 200m	3 300w	5 750w
$MnI_2[P(CH_2CH_2CN)_3]$	2 280s (sh), 2 245m (sh)	950s		1 400m		3 300m		5 350m
$Mn(NCS)_2[P(CH_2CH_2CN)_3]$	2 280s (sh), 2 245m (sh)	1 000s		1 550w		2 200m	3 300w	
$MnCl_2[PPh(CH_2CH_2CN)_2]$	2 290s (sh)	1 000s		1 495w		2 200w	3 300m	5 700w
$MnBr_2[PPh(CH_2CH_2CN)_2]$	2 290s (sh)	1 100s		1 600m		2 100w	3 250w	5 650m
$MnI_2[PPh(CH_2CH_2CN)_2]$	2 288s (sh)	950s		1 500m		3 300m		5 400m
$Mn(NCS)_2[PPh(CH_2CH_2CN)_2]$	2 285s (sh)	1 000s		1 600w		2 200m	3 400w	
$MnCl_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)		1 650w		3 300s			
$MnBr_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)		1 500s		3 300s			
$MnI_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)		1 600w		3 300s			
$Mn(NCS)_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)		1 650m		3 300s			

[a] ν(CN) for free ligands: $P(CH_2CH_2CN)_3$, 2 245; $PPh_2(CH_2CH_2CN)$, 2 230 cm^{-1}. [b] All lines are broad and show no hyperfine coupling to ^{55}Mn; $G = 10^{-4}$ T.

that of the free ligand. This clearly shows that the CN groups are not co-ordinated in thf solution. In addition, the e.s.r. spectra are also different in thf to the spectra obtained in dichloromethane. Whereas the main feature of the dichloromethane e.s.r. spectra is the broad band at $g_{eff.} = 2$ [Figure (*a*)], the main feature of the spectra in thf is the $g_{eff.} = 6$ band [spectrum (*b*)]. The spectrum of $MnI_2[P(CH_2CH_2CN)_3]$ in thf is, in fact, very similar to that of $MnI_2(PBu^n_3)$ in thf [spectrum (*c*)], and consists of a strong $g_{eff.} = 6$ absorption with hyperfine coupling to ^{55}Mn ($I = \frac{5}{2}$) observed.

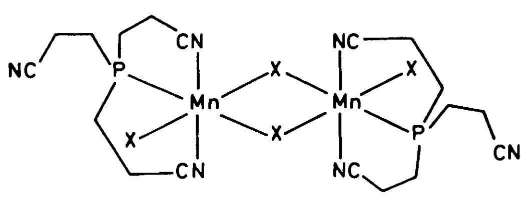
All of the above observations indicate that the $MnX_2[P(CH_2CH_2CN)_3]$ complexes in thf are similar to their trialkylphosphine analogues and presumably have the same structures, (II).[15]

Complexes of Bis(2-cyanoethyl)phenylphosphine.—The important solid-state i.r. spectral bands are listed in Table 2. The low-energy regions are very similar to those of the corresponding $P(CH_2CH_2CN)_3$ complexes, exhibiting bands attributable to both bridging and terminal Mn–X linkages, and Mn–P and Mn–N vibrations. However, in contrast to the $P(CH_2CH_2CN)_3$ complexes, there is only a single ν(CN) band,

Table 4. Spectroscopic properties of the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes in tetrahydrofuran solution

Complex	Infrared (cm^{-1}) ν(ligand) [a]	E.s.r. line positions/G [b]					
$MnCl_2[P(CH_2CH_2CN)_3]$	2 245s (sh)	1 000s	1 600m	2 100w	3 300w	5 650w	8 500w
$MnBr_2[P(CH_2CH_2CN)_3]$	2 245s (sh)	1 125s	1 450m	2 150w	3 350w	5 750m	
$MnI_2[P(CH_2CH_2CN)_3]$	2 245s (sh)	980s	1 550m	2 100w	3 350w		8 500w
$Mn(NCS)_2[P(CH_2CH_2CN)_3]$	2 245s (sh)	1 000s	1 450m		3 300m	5 700w	
$MnCl_2[PPh(CH_2CH_2CN)_2]$	2 268m (sh)	1 000s	1 550m	2 100w	3 300w		8 500w
$MnBr_2[PPh(CH_2CH_2CN)_2]$	2 268m (sh)	1 125s	1 500w	2 200w	3 300w	5 700m	
$MnI_2[PPh(CH_2CH_2CN)_2]$	2 268m (sh)	950s	1 450w	2 000w	3 400w	5 800m	
$Mn(NCS)_2[PPh(CH_2CH_2CN)_2]$	2 268m (sh)	1 000s	1 450w		3 250m	5 680w	
$MnCl_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	990s	1 600w	2 100w	3 300m	5 700w	
$MnBr_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	1 100s	1 550m	2 100w	3 250m		8 500w
$MnI_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	950s	1 450w	2 100w	3 250w	5 700m	8 700w
$Mn(NCS)_2[PPh_2(CH_2CH_2CN)]$	2 230w (sh)	1 000s	1 500w		3 200m	5 700w	

[a] ν(CN) for free ligands: $P(CH_2CH_2CN)_3$, 2 245; $PPh(CH_2CH_2CN)_2$, 2 268; $PPh_2(CH_2CH_2CN)$, 2 230 cm^{-1}. [b] All lines split into six by hyperfine coupling to $^{55}Mn(I = \frac{5}{2})$.



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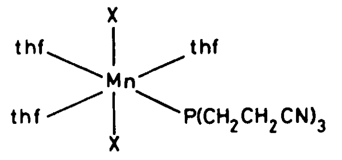

(II)

assignable to co-ordinated ligand. Hence, both CN groups are co-ordinated.

The room-temperature magnetic moments of the $MnX_2[PPh(CH_2CH_2CN)_2]$ complexes are in the same range as those of the $P(CH_2CH_2CN)_3$ compounds, Table 1, and, in addition the solid-state and dichloromethane solution e.s.r. spectra of these complexes are very similar to those of the $P(CH_2CH_2CN)_3$ ligand.

The i.r. spectra of the complexes dissolved in dichloromethane exhibit only a single ν(CN) absorption attributable to co-ordinated CN groups, Table 3. The $MnI_2[PPh(CH_2CH_2CN)_2]$ complex was sufficiently soluble in dichloromethane for a molecular-weight determination, and the value obtained, 1 020, is close to the calculated value (1 050) for dimeric $\{MnI_2[PPh(CH_2CH_2CN)_2]\}_2$.

In tetrahydrofuran solution the $MnX_2[PPh(CH_2CH_2CN)_2]$ complexes exhibit e.s.r. spectra which are almost identical to those of the $MnX_2[P(CH_2CH_2CN)_3]$ and $MnX_2(PBu^n_3)$[15] complexes in this solvent, Table 4. In addition the i.r. spectra of $MnX_2[PPh(CH_2CH_2CN)_2]$ and $MnX_2[P(CH_2CH_2CN)_3]$ are similar in exhibiting only a single ν(CN) band in the same region as that of the free ligand.

It may thus be concluded that the $MnX_2[PPh(CH_2CH_2CN)_2]$ complexes have similar co-ordination spheres, (I) and (II), to those of the $MnX_2[P(CH_2CH_2CN)_3]$ compounds in the corresponding solid or solution states.

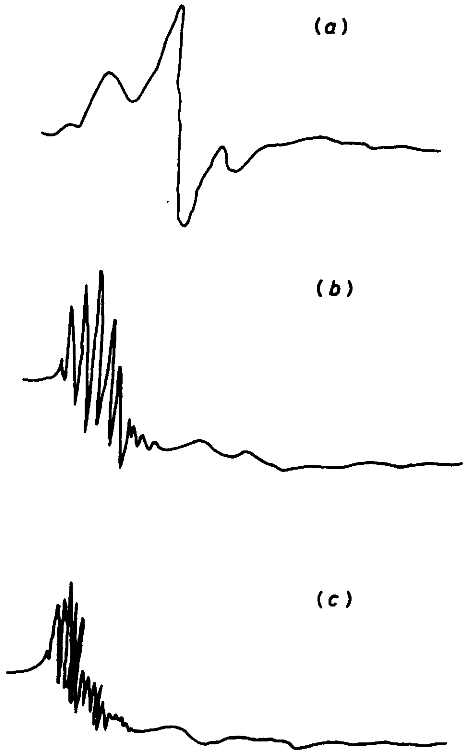

Figure. E.s.r. spectra of (*a*) $MnI_2[P(CH_2CH_2CN)_3]$ in dichloromethane, (*b*) $MnI_2[P(CH_2CH_2CN)_3]$ in tetrahydrofuran, and (*c*) $MnI_2(PBu^n_3)$ in tetrahydrofuran

Complexes of (2-Cyanoethyl)diphenylphosphine.—The important bands in the mull i.r. spectra of the $MnX_2(Ph_2PCH_2CH_2CN)$ complexes are listed in Table 2, and it can be seen that these complexes exhibit spectra different from the previously discussed compounds. Most notably, $MnX_2(Ph_2PCH_2CH_2CN)$ exhibit only a single band assignable to an unco-ordinated CN group. That the $Ph_2PCH_2CH_2CN$ ligand does not bond *via* the CN group is further substantiated by the absence of any bands in the far-i.r. region assignable to ν(Mn–N).

Although the room-temperature magnetic moments of $MnX_2(Ph_2PCH_2CH_2CN)$ are in the same range as those of the other two cyano-ligands, Table 1, the e.s.r. spectra of dichloromethane solutions indicate a different structure in solution, Table 3. These spectra consist of two major bands in the $g_{\text{eff.}} = 4$ and 2 regions, implying tetrahedral geometry for the manganese(II) centre (no hyperfine structure is observed). The i.r. spectra of the complexes in this solvent exhibit only one ν(CN) absorption in the same region as that of unco-ordinated ligand, clearly showing that bonding *via* the CN group is not occurring.

None of the $MnX_2(Ph_2PCH_2CH_2CN)$ complexes was sufficiently soluble for molecular-weight determinations, but from i.r. evidence it is clear that they are at least dimeric and it is possible that they are polymers. Recently, complexes of co-ordination sphere $MnR_2(P)$ (R = alkyl) have been shown to be anion-bridged pseudo-tetrahedral dimers by Wilkinson and co-workers[16] or have an infinite halide-bridged alternating $MnX_4(P)_2$–MnX_4 structure by King *et al.*[17]

In thf solution the $MnX_2(Ph_2PCH_2CH_2CN)$ complexes are spectroscopically similar, Table 4, to complexes of both $P(CH_2CH_2CN)_3$ and $PPh(CH_2CH_2CN)_2$ ligands and presumably have similar structures (II).

Reactions of $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ *with Dioxygen.*—Because of the apparent structural similarity of these complexes to their n-butylphosphine analogues in thf solution (see above), a study of their reactions with dioxygen was undertaken. The study took the form of both qualitative observation, *i.e.* did the intense colours normally associated with the $MnX_2(PR_3)(O_2)$ species develop,[3] and quantitative measurement, *i.e.* how much dioxygen was absorbed by a solution of a $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complex?

The initial qualitative observations suggested that reaction with dioxygen was not occurring. All the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes in thf solution, when exposed to dioxygen, showed no colour change whatsoever. In addition, such solutions were connected to a gas burette and the quantity of dioxygen absorption by the solution accurately recorded. All the samples studied absorbed no dioxygen over and above the amount absorbed by the same volume of thf solvent alone. The uptake measurements were performed at −78, 0, and 20 °C, and no uptake attributable to the complexes was observed. Moreover, the e.s.r. spectra of thf solutions of the complexes were unchanged upon exposure to dioxygen, strongly suggesting that no reaction had occurred.

As mentioned earlier, the CH_2CH_2CN group is sterically identical to an n-C_4H_9 group.[9] The non-reactivity of the $MnX_2[PPh_{3-n}(CH_2CH_2CN)_n]$ complexes in thf solution, which have identical structures to the $MnX_2(PBu^n{}_3)$ complexes in this solvent, with dioxygen cannot, therefore, be attributable to steric considerations, and must be a consequence of electronic factors. The electronic properties of the two series of ligands are significantly different.[9] The $PPh_{3-n}(CH_2CH_2CN)_n$ ligands have been shown to be better π acceptors than their $PPh_{3-n}(n\text{-}C_4H_9)_n$ analogues,[9] and the manganese(II) complexes of the former ligands would therefore be expected to be more electron deficient at the metal centre. This deficiency would, in turn, mean that the manganese would bond more strongly to other σ donors such as thf molecules. Since dioxygen co-ordination involves replacement of one thf ligand by an O_2 ligand, it seems likely that the stronger Mn–thf bond in the cyanoethyl ligand complexes inhibits substitution by an O_2 ligand.

Ligand-exchange Reactions.—Since the $PPh_{3-n}(CH_2CH_2CN)_n$ ligands are better π acceptors than their $PPh_{3-n}(n\text{-}C_4H_9)_n$ analogues and since complexes of the former are inert towards, but complexes of the latter are active towards, dioxygen binding, it seemed possible to see which of the two types of ligand were preferentially bound to manganese.

Two experiments were performed. Solutions of the complexes $MnI_2(PBu^n{}_3)$ and $MnI_2[P(CH_2CH_2CN)_3]$ in thf were prepared and their e.s.r. spectra recorded. Equimolar quantities of the complementary PR_3 ligand were then added and the solutions stirred for several days. The e.s.r. spectra of the resulting solutions were found to be identical. Each solution was then connected to a gas burette in turn and the amount of dioxygen absorbed at −78 °C measured. Neither solution absorbed more O_2 than did the solvent blanks.

These results tend to suggest that in both cases the species $MnI_2[P(CH_2CH_2CN)_3]$ was formed in solution. Evaporation of all the thf, followed by extraction with toluene, led to the isolation of solid $MnI_2[P(CH_2CH_2CN)_3]$ in both cases. Distillation of the toluene extracts led to the isolation of $PBu^n{}_3$ from both samples (identified by i.r. and ^{31}P n.m.r.). These results clearly show that, for manganese(II) iodide, $P(CH_2CH_2CN)_3$ is bound in preference to $P(n\text{-}C_4H_9)_3$, possibly because of the better π-acceptor properties of the former.

Experimental

Unless otherwise stated, all manipulations were performed under an atmosphere of dry argon. Solvents and manganese(II) salts were very carefully dried by previously published methods.[10] It is extremely important to ensure strictly anhydrous materials and solvents and inert conditions in order to isolate these simple compounds. The failure of Green and co-workers[18] to prepare manganese(II) phosphine complexes has been attributed[3] to a failure to adopt these basic precautions. All glassware was oven dried prior to use and cooled under an argon atmosphere.

All the manganese complexes were synthesised by the same general method, and the synthesis of $MnI_2[PPh(CH_2CH_2CN)_2]$ is typical. A round-bottomed flask (250 cm³) equipped with a sidearm and containing a magnetic follower was charged with dry manganese(II) iodide (1.55 g 5.0 mmol) and solid $PPh(CH_2CH_2CN)_2$ (1.08 g, 5.0 mmol). Dry diethyl ether (75 cm³) was then distilled onto the solid mixture, the flask was sealed under argon, and the mixture was stirred at room temperature for 5 d. The volume of solvent was then reduced to *ca.* 25 cm³ by application of a vacuum, and the resulting slurry filtered in a Schlenk apparatus, washed with portions of dry diethyl ether (about 3 × 20 cm³), and dried *in vacuo*.

The dioxygen-uptake experiments were performed in an apparatus and by methods previously described.[2]

Infrared and e.s.r. spectra, magnetic susceptibility measurements, and molecular-weight determinations were carried out as described previously.[10] Elemental analyses were obtained by the U.M.I.S.T. Microanalytical Service.

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