Formation and Reactions of Cyanocyclohexadienyl Complexes of Manganese(I)

By **Peter J. C. Walker** and **Roger J. Mawby,*** Department of Chemistry, The University of York, Heslington, York YO1 5DD

Reactions of the cationic arene complexes $[(C_6H_{6-n}Me_n)Mn(CO)_3]^+$ with cyanide ion under mild conditions yield *exo*-cyanocyclohexadienyl complexes $(C_6H_{6-n}Me_nCN)Mn(CO)_3$ in which the cyano-group is attached to an unsubstituted carbon atom: the hexamethylbenzene complex reacts differently to form $(C_6Me_6)Mn(CO)_2CN$. The preference for addition to an unsubstituted carbon atom is (at least in part) kinetic rather than thermodynamic in origin, since the compound formed by cyanide addition to the mesitylene complex rearranges in chloroform solution to give some of the isomer in which the cyano-group is attached to a methyl-substituted carbon atom.

Decomposition of the cyanocyclohexadienyl complexes in the solid state or in solution yields either $(C_6H_{6-n}Me_n)$-$Mn(CO)_2CN$ or free arene and a polymeric manganese complex according to the reaction conditions used. Conventional hydride-abstracting reagents remove the cyano-group from the complexes, regenerating $[(C_6H_{6-n}Me_n)$-$Mn(CO)_3]^+$, but oxidation with ceric ion liberates the cyano-arene $C_6H_{5-n}Me_nCN$ uncontaminated by $C_6H_{6-n}Me_n$.

ALTHOUGH the susceptibility of arenes co-ordinated to metal ions to nucleophilic attack by H^- and R^- (R = alkyl or aryl) is well known,[1,2] our recent preliminary report[3] of the reaction of cations $[(arene)Mn(CO)_3]^+$ with cyanide ion to give cyanocyclohexadienyl complexes was, we believe, the first example of this type of reaction involving a nucleophile *other* than those mentioned above. This paper describes the formation and physical properties of a range of cyanocyclohexadienyl complexes of manganese(I), and some of the reactions which they undergo.

RESULTS AND DISCUSSION

Formation and Stereochemistry of Cyanocyclohexadienyl Complexes.—A range of cations $[(arene)Mn(CO)_3]^+$, required as starting materials for the preparation of cyanocyclohexadienyl complexes, was prepared by the method of Winkhaus *et al.*,[4] and isolated as salts with the anions $Y^- = I^-$, BF_4^-, BPh_4^-, and PF_6^-. Several had not previously been described in the literature, and were therefore fully characterized. Details of their i.r. and n.m.r. spectra, omitted from this paper to save space, may be obtained from the authors.

TABLE 1

N.m.r. spectra [a] of cyanocyclohexadienyl complexes (IIa—g) [b]

	Ring protons				Methyl protons			
Complex	1(*endo*)	2,6	3,5	4	1(*endo*)	2,6	3,5	4
(IIa)	3·60 (t, 1) [c]	3·01 (dd, 2) [c]	5·06 (dd, 2) [c]	6·00 (t, 1) [c]				
(IIb)	3·60 (d, 1)	2·98 (d, 1) [c]	4·78 (d, 1) [c]	5·75 (d, 1) [c]		1·70 (s, 3)	1·96 (s, 3)	
(IIc)	3·51 (c, 1)	2·93 (c, 1·5) [c]	5·06 (d, 0·5) [c]			1·76 (s, 1·5)	2·05 (s, 4·5)	2·53 (s, 3)
(IId)	3·39 (s, 1)		4·86 (s, 2)			1·73 (s, 6)		2·53 (s, 3)
(IIe)	3·43 (d, 1)	2·86 (d, 1)				1·76 (s, 3)	2·03 (s, 3) 2·07 (s, 3)	2·52 (s, 3)
(IIf)	3·46 (s, 1)			5·59 (s, 1)		1·70 (s, 6)	1·96 (s, 6)	
(IIg) [b]		2·71 (s, 2)		5·79 (s, 1)	1·82 (s, 3)		1·96 (s, 6)	

[a] In $CDCl_3$ solution at 306·5 K, using tetramethylsilane as an internal standard. Values for chemical shifts are on the δ scale. Multiplicities and relative areas of peaks are given in parentheses. s = Singlet, d = doublet, dd = doublet of doublets, t = triplet, c = complex. [b] Complex (IIg) is an isomer of (IId) (see text). [c] Further smaller splittings (due to coupling to more distant protons) were detectable.

---

[1] D. Jones and G. Wilkinson, *J. Chem. Soc.*, 1964, 2479 and references therein.

[2] E. O. Fischer and M. W. Schmidt, *Chem. Ber.*, 1967, **100**, 3782.

[3] P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 404.

[4] G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807.

Reaction of the cations $[(\text{arene})Mn(CO)_3]^+$ [arene = benzene, (Ia); *p*-xylene, (Ib); 1,2,3-trimethylbenzene, (Ic); mesitylene, (Id); 1,2,3,4-tetramethylbenzene, (Ie); 1,2,4,5-tetramethylbenzene, (If)] with cyanide ion in aqueous solution yields water-insoluble complexes, (IIa—f), of empirical formula $(\text{arene})Mn(CO)_3CN$, which may be recrystallized from light petroleum. Under the same reaction conditions the hexamethylbenzene complex $[(C_6Me_6)Mn(CO)_3]I$ forms $(C_6Me_6)Mn(CO)_2CN$. N.m.r. and i.r. spectra of the complexes (IIa—f) are given in Tables 1 and 2 respectively, while those of $(C_6Me_6)Mn(CO)_2CN$ are given in Table 3. Whereas the reaction of the hexamethylbenzene complex involves nucleophilic attack on the metal, with displacement of CO by cyanide ion, the complicated n.m.r. spectra of compounds (IIa—f) indicate that these are cyanocyclohexadienyl complexes, $(C_6H_{6-n}Me_nCN)Mn(CO)_3$, formed by nucleophilic *addition* to the *arene*.

TABLE 2

I.r. spectra of cyanocyclohexadienyl complexes (IIa—f) in the C–O and C–N stretching regions

Complex	Solvent	νC–O [a]/cm^{-1}	ν_{C-N} [b]/cm^{-1}
(IIa)	CH_2Cl_2	2038, 1961	2227
	n-pentane	2038, 1969, 1963	
(IIb)	CH_2Cl_2	2027, 1947	2224
	n-pentane	2029, 1959, 1956	
(IIc)	CH_2Cl_2	2025, 1950	2226
	n-pentane	2027, 1960, 1948	
(IId)	CH_2Cl_2	2020, 1943	2226
	n-pentane	2020, 1948	
(IIe)	CH_2Cl_2	2018, 1944	2221
	n-pentane	2020, 1957, 1940	
(IIf)	CH_2Cl_2	2020, 1943	2223
	n-pentane	2022, 1948	

[a] Strong bands. [b] Very weak bands, only observable using concentrated solutions in CH_2Cl_2.

TABLE 3

N.m.r.[a] and i.r. spectra [b] of cyanide complexes of manganese(I)

Complex	Ring protons	Methyl protons	ν_{C-N} [c]/ cm^{-1}	ν_{C-O} [d]/ cm^{-1}
$(C_6Me_6)Mn(CO)_2CN$		2·4	2097	1993, 1944
$(C_6H_3Me_3)Mn(CO)_2CN$	5·6	2·3	2103	2000, 1954
$(C_6H_6)Mn(CO)_2CN$	6·1		2106	2018, 1969
$[Mn(CO)_3CN]_4,C_6H_3Me_3$	*e*	*e*	2166, 2083	2029, 1954

[a] In $CDCl_3$ solution at 306·5 K, using TMS as an internal standard. Values for chemical shifts are on the δ scale. [b] In CH_2Cl_2 solution, except for $[Mn(CO)_3CN]_4,C_6H_3Me_3$ (Nujol mull). [c] Weak bands. [d] Strong or very strong bands. [e] Not sufficiently soluble to allow a spectrum to be obtained.

Since hexamethylbenzene is the only co-ordinated arene which does not undergo nucleophilic attack, it is logical to assume that attack on the other arenes occurs at unsubstituted carbon atoms. This is substantiated by the observation (see Table 1) that the one resonance which the n.m.r. spectra of complexes (IIa—f) have in common is that due to a single proton in the region δ 3·39—3·60 p.p.m. This compares well with the value of δ 3·5 p.p.m. for the proton attached to the carbon atom bearing the cyano-group in the *exo*-cyanocycloheptatrienyl complex $(C_7H_7CN)Cr(CO)_3$ (though not with the value of δ 2·7 p.p.m. for the corresponding proton in the *endo*-isomer).[5] It is therefore apparent that the complexes (IIa—f) have the cyano-group on a carbon atom which does not bear a methyl substituent. This conclusion is supported by the fact that the only cation to yield a mixture of products rather than a single product (Ic) is the one which is unique in that it contains an arene with more than one type of unsubstituted carbon atom. A self-consistent assignment of all the resonances for complexes (IIa—f), using a numbering system in which the ring carbon atom bearing the cyano-group is labelled 1, is given in Table 1. On the basis of this assignment, product (IIc) is seen to be an equimolar mixture of the products of nucleophilic attack at the two different types of unsubstituted carbon atom. On a statistical basis, one would expect to obtain $66\frac{2}{3}\%$ of the 2,3,4-trimethyl isomer and $33\frac{1}{3}\%$ of the 3,4,5-trimethyl isomer, so the observed ratio indicates a slight preference for attack at a carbon atom which is not adjacent to an atom bearing a methyl substituent. This result can be explained on either steric or electronic (inductive effect of methyl group) grounds. [The origin and interpretation of spectrum (IIg) are discussed later in the paper.]

Comparison with a range of related species formed by nucleophilic addition to co-ordinated cyclic hydrocarbons [5] would lead one to anticipate that complexes (IIa—f) would be *exo*- rather than *endo*-cyanocyclohexadienyl complexes, and this is implied by their n.m.r. spectra (see above) and confirmed by their i.r. spectra (Table 2). Cyclohexadienyl complexes in which a hydrogen atom occupies the *exo*-position are generally characterized by a C–H stretching band at an unusually low frequency (*ca.* 2750—2800 cm^{-1}) [5]: no such band is observed for complexes (IIa—f). The C–N stretching frequency for the complexes (2221—2227 cm^{-1}) is very close to that for *exo*-$(C_7H_7CN)Cr(CO)_3$ (2229 cm^{-1}),[6] but well removed from that for the *endo*-isomer (2250 cm^{-1}).[7]

Reactions of Cyanocyclohexadienyl Complexes: (a) Isomerization.—Although complexes (IIa—f) are fairly long-lived under a nitrogen atmosphere at room temperature in the solid state, they do not survive for long periods in solution. While studying the decomposition of the complexes in solution, we also discovered an example of isomerization. The n.m.r. spectrum of the complex (IId) in $CDCl_3$ solution changes over a period of days at room temperature. As the areas of the resonances listed for (IId) in Table 1 diminish (*relative* areas remaining the same), six new singlet resonances appear. Two, at δ 2·26 and 6·81 p.p.m., with relative areas 3 : 1, increase steadily in area; these are due to free mesitylene, formed in a decomposition reaction mentioned later. The other four increase and then decrease in area, their *relative* areas remaining constant throughout, implying

---

[5] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. (C)*, 1969, 2024.

[6] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3484.

[7] J. D. Munro and P. L. Pauson, *J. Chem. Soc. (C)*, 1967, 1061.

that all four are due to a single new species [which we have labelled (IIg)]. In Table 1, it can be seen that the spectrum of (IIg) fits well into the pattern established by (IIa—f) [*i.e.* that (IIg) is another cyanocyclohexadienyl complex], except that it is necessary to assume that the cyano-group is attached to a methyl-substituted carbon atom. Conversion of (IId) into (IIg) therefore involves the migration of the cyano-group from an unsubstituted to a substituted carbon atom. Comparison of the areas of the (IId) and (IIg) resonances indicates that an equilibrium is reached in $CDCl_3$ solution in which the two isomers are present in a 5 : 1 ratio. Thereafter, the concentrations of both isomers decrease owing to decomposition to yield free mesitylene.

This finding must be compared with our observation that the reactions of the cations (Ia—f) with cyanide ion yield *only* complexes (IIa—f) in which the cyano-group is attached to an unsubstituted carbon atom. Evidently the difference in rates of attack at unsubstituted and substituted carbon atoms is appreciably greater than the difference in thermodynamic stability between the isomers formed by the two modes of attack. It also follows that it must be the slowness of attack on the arene (compared with the rate of attack on the metal) rather than the instability of $(C_6Me_6CN)Mn(CO)_3$, which leads to the exclusive formation of $(C_6Me_6)Mn(CO)_2CN$ from $[(C_6Me_6)Mn(CO)_3]^+$ and cyanide ion in aqueous solution.

The observation that the cyano-group in complex (IId) can migrate from one ring carbon atom to another prompted us to examine the n.m.r. spectrum of complex (IIe) as a function of temperature. *Rapid* reversible movement of the cyano-group between the two *unsubstituted* carbon atoms would average the resonances due to the protons in the 1 and 6 positions, those due to the methyl groups in the 2 and 5 positions, and those due to the methyl groups in the 3 and 4 positions. The spectrum of (IIe), however, does not change between 306·5 and 333 K: above 333 K spectra cannot be obtained because decomposition to give free $C_6H_2Me_4$ is too rapid. We conclude that, at accessible temperatures, migration is slow on the n.m.r. time scale.

(*b*) *Decomposition.* The cyanocyclohexadienyl complexes decompose on heating in water, methanol, or chloroform, but the products of decomposition are not the same in all three solvents. In the polar solvents, water and methanol, carbon monoxide is evolved and complexes (arene)$Mn(CO)_2CN$ are formed. The complexes $(C_6H_6)Mn(CO)_2CN$ and $(C_6H_3Me_3)Mn(CO)_2CN$, obtained from (IIa) and (IId) respectively, were fully characterized; details of their n.m.r. and i.r. spectra are given in Table 3. The most obvious mechanism for the decomposition is one involving preliminary dissociation into ions, followed by attack at the metal with displacement of carbon monoxide.

$$(C_6H_{6-n}Me_nCN)Mn(CO)_3 \rightleftharpoons [(C_6H_{6-n}Me_n)Mn(CO)_3]^+ + CN^- \longrightarrow (C_6H_{6-n}Me_n)Mn(CO)_2CN + CO$$

The fact, mentioned earlier, that $[(C_6Me_6)Mn(CO)_3]^+$ reacts fairly rapidly with cyanide ion to yield $(C_6Me_6)Mn(CO)_2CN$ even at room temperature, whereas the decompositions of (IIa) and (IId) require more forcing conditions, implies that the major barrier to the decompositions is not the slowness of attack by cyanide ion at the metal but the unfavourable position of the prior equilibrium.

In the much less polar solvent, chloroform, the products of decomposition, either at room temperature or (more rapidly) on heating, are free arene and an insoluble yellow complex. Comparison of the i.r. spectra in the C–O and C–N stretching regions of the solids obtained from the decomposition of the different cyanocyclohexadienyl complexes (IIa—f) strongly suggests that they are all identical. Details of the spectrum of the product from the decomposition of complex (IId), given in Table 3, indicate the presence of carbonyl and cyano-groups. The simplest possible formulation for the product would be $[Mn(CO)_3CN]_n$, with n (according to molecular-weight determination in acetone) apparently 4. The mass spectrum of the compound, however, shows that it contains mesitylene, which is not removed by washing with chloroform, and elemental analysis fits the formula $[Mn(CO)_3CN]_4,C_6H_3Me_3$. It is probable that the mesitylene is present as solvent of crystallization rather than as a ligand bonded to one or more manganese atoms, since repeated recrystallization of the complex from acetone yields a product which analyses for $[Mn(CO)_3CN]_4,2CH_3COCH_3$. We are uncertain about the structure of the tetrameric unit, noting only that its i.r. spectrum contains no bands in the region expected for the C–O stretching modes of bridging carbonyl groups.

The mechanism of the decomposition in chloroform is not obvious. In view of the *exo*-positioning of the cyano-group in complexes (IIa—f), an intramolecular migration to the metal is difficult to visualize. A preliminary dissociation into the ions $[(arene)Mn(CO)_3]^+$ and CN^- may occur, despite the low dielectric constant of the solvent, but if so it is remarkable that the cyanide ion then displaces the arene in this solvent, when in water or methanol it displaces carbon monoxide.

Decomposition in the solid state can follow either of the two paths observed for decomposition in solution. Over a period of months at room temperature, complex (IId) decomposes to mesitylene and $[Mn(CO)_3CN]_4,C_6H_3Me_3$, whereas when heated to its melting point the same complex yields $(C_6H_3Me_3)Mn(CO)_2CN$ and carbon monoxide. We have found that this latter conversion can also be brought about by irradiating a solution of complex (IId) in light petroleum with u.v. light. In this case it seems likely that the first step in the decomposition is the dissociation of carbon monoxide rather than a breakdown into $[(arene)Mn(CO)_3]^+$ and cyanide ion.

(*c*) *Conversion to cyanoarenes.* The ease with which co-ordinated arenes can be converted into cyanocyclohexadienyl complexes suggests a novel route to cyanoarenes, the necessary second step being the removal of hydride ion from the cyanocyclohexadienyl complexes.

In attempts to perform this ' abstraction ' of hydride ion, we treated complex (IId) with the trityl (Ph_3C^+) and triethyloxonium cations. In both cases, the product was the mesitylene complex $[(C_6H_3Me_3)Mn(CO)_3]^+$ (Id) indicating that the reagents had removed the *exo*-cyano-group rather than the *endo*-hydrogen atom. Complex (IIa) reacted in the same way. Treatment of complex (IId) with *N*-bromosuccinimide also yielded cation (Id), even though this reagent is known to remove hydride ion from the *endo*-position in the complex $(C_6H_6Bu)(C_4Ph_4)Co$.[8] Acidification of (IId) with fluoroboric acid in propionic anhydride also produced (Id).

As an alternative to direct abstraction of hydride ion, the possibility of inducing a hydride ion shift from the cyanocyclohexadienyl ligand to the metal was considered. Removal of a carbonyl ligand to generate a vacant co-ordination site on the metal seemed a sensible first step. Treatment of complex (IId) with the compound $Rh(PPh_3)_3Cl$, which is an avid acceptor of carbon monoxide,[9] gives a reaction mixture which contains only one manganese complex, namely (Id). U.v. light, which has also been used as a means of promoting loss of a carbonyl ligand,[10] did have this effect on complex (IId), but the product (as mentioned earlier) was $(C_6H_3Me_3)Mn(CO)_2CN$ rather than $(C_6H_2Me_3CN)Mn(CO)_2H$.

A third possibility was the removal of the hydrogen, under oxidising conditions, as H^+. Whereas the relatively mild oxidising agents *p*-benzoquinone, iodine, and ferric ion all convert (IId) into (Id), oxidation of (IId) with ceric sulphate in sulphuric acid yields free mesitonitrile in a yield of 73%. No mesitylene is found among the products of the oxidation. The same procedure gives an 80% yield of benzonitrile, uncontaminated by benzene, from complex (IIa). Whether the reaction goes by way of the complex $[(C_6H_{5-n}Me_nCN)Mn(CO)_3]^+$ (which one would expect to be relatively unstable because of the electron-withdrawing effect of the cyano-group in the arene) or by some other route remains to be established.

$$(C_6H_{6-n}Me_nCN)Mn(CO)_3 - 2\varepsilon \longrightarrow [(C_6H_{5-n}Me_nCN)Mn(CO)_3]^+ + H^+$$

TABLE 4

Analytical data

Complex	M.p. (*T*/K)	Found (%) C	Found (%) H	Found (%) N	Calculated (%) C	Calculated (%) H	Calculated (%) N
(IIa)	76—77	49·1	2·6	5·8	49·4	2·5	5·75
(IIb)	73—75	52·75	4·0	5·15	53·15	3·7	5·15
(IIc)	98—103 [a]	52·75	4·05	5·0	54·75	4·25	4·9
(IId)	108—109	54·2	4·3	5·4	54·75	4·25	4·9
(IIe)	96—98	56·3	4·8	4·7	56·2	4·7	4·7
(IIf)	113—115	56·1	4·75	4·7	56·2	4·7	4·7
$(C_6Me_6)Mn(CO)_2CN$	195—197 [b]	60·15	6·1	4·6	60·2	6·05	4·7
$(C_6H_3Me_3)Mn(CO)_2CN$	163—165 [b]	55·65	4·7	5·1	56·05	4·7	5·45
$(C_6H_6)Mn(CO)_2CN$	153—156 [b]	49·25	2·9	6·0	50·25	2·8	6·5

[a] Mixture of isomers. [b] Decomposes.

CONCLUSIONS

Despite the ultimate success in converting the cyanocyclohexadienyl complexes into cyanoarenes, the major feature which emerges from the study of the reactions of these complexes is the lability of the bond between the cyano-group and the rest of the cyclohexadienyl ligand. The driving force for the loss of this group as CN^- is presumably the regeneration of the planar aromatic ring.

Another feature of interest is the very delicate balance which clearly exists for nucleophilic attack on cations $[(arene)Mn(CO)_3]^+$ between attack on the arene, attack on the metal with displacement of a carbonyl ligand, and attack on the metal with displacement of arene. A fourth mode of attack, on the carbon atom of a carbonyl group, though not observed with cyanide ion as a nucleophile, was found to occur with other nucleophiles; this will be discussed in a later paper.

EXPERIMENTAL

All the work described below was performed under an atmosphere of dry nitrogen. Complexes were stored under dry nitrogen and protected from light. Analytical data, except where given below, are collected in Table 4.

Salts of Cations (Ia—f).—These compounds were prepared from bromopentacarbonylmanganese and the appropriate arene by the method of Winkhaus *et al.*,[4] and recrystallized from acetone or from water.

Complexes (IIa—f): *Complex* (IIe).—The iodide salt of cation (Ie) (4·0 g) was dissolved in the minimum volume of water and treated with a solution of potassium cyanide (1·0 g) in water (5 ml). When precipitation was complete (*ca.* 2 h), the white solid was filtered off and treated with successive portions of light petroleum (b.p. 313—333 K) until the extracts were no longer coloured. The combined extracts were dried ($MgCl_2$) and concentrated by evaporation under a nitrogen stream. The yellow crystals which formed were filtered off and dried.

The remaining complexes, (IIa—d) and (IIf), were prepared in the same way. Yields of purified products ranged from 50 to 80%.

Cyanodicarbonyl(π-*hexamethylbenzene*)*manganese*.— This complex was obtained from the reaction of the iodide salt of the tricarbonyl(π-hexamethylbenzene)manganese cation,

---

[8] A. Efraty and P. M. Maitlis, *Tetrahedron Letters*, 1966, 4025.

[9] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[10] W. Strohmeier and H. Hellmann, *Chem. Ber.*, 1963, **96**, 2859.

using the same conditions as those employed in the preparation of complex (IIe). The product was extracted from the reaction mixture with successive portions of dichloromethane until the extracts were no longer coloured. The combined extracts were washed with water, dried ($MgCl_2$), and then concentrated by evaporation under a nitrogen stream. The yellow crystals which formed were filtered off and dried.

Cyanodicarbonyl(π-*benzene*)*manganese*.—A stirred suspension of complex (IIa) in water was warmed on a steam-bath until a clear yellow solution was obtained. The solution was then cooled and treated in the same way as the hexamethylbenzene reaction mixture above. (The reaction could also be carried out by heating in methanol at 323 K for 1 h.)

Cyanodicarbonyl(π-*mesitylene*)*manganese*.—This compound was prepared from complex (IId) in the same way as its benzene analogue was obtained from (IIa).

Decomposition of Complexes (IIa—f) *in Deuteriochloroform: Complex* (IId).—A solution of complex (IId) in deuteriochloroform was kept at 313 K for 3 h; the solution was then decanted from the yellow precipitate which had formed. The presence of free mesitylene in the solution was indicated by both n.m.r. spectroscopy and g.l.c.; there was no evidence for the formation of any mesitonitrile. The precipitate was washed with chloroform and dried; *M* (in acetone) 665. Analytical data for this sample and a sample recrystallized three times from acetone are shown below.

	C	H	N
Initial sample:	38·75%	1·8%	6·95%
Recrystallized sample:	33·8	1·3	7·35
$[Mn(CO)_3CN]_4$ requires:	29·1	0·0	8·5
$[Mn(CO)_3CN]_4,C_6H_3Me_3$ requires:	38·5	1·55	7·2
$[Mn(CO)_3CN]_4,2CH_3COCH_3$ requires:	34·05	1·55	7·2

Effect of Heat on Complex (IId).—A sample of complex (IId) was heated to its melting point. As the solid melted, bubbles of gas were evolved and the liquid resolidified. Recrystallization from dichloromethane yielded cyanodicarbonyl(π-mesitylene)manganese.

Reaction of Complex (IId) *with Triphenylmethyl Fluoroborate*.—A solution of complex (IId) (0·28 g) and triphenylmethyl fluoroborate (0·33 g) in dichloromethane (30 ml) was stirred under reflux for 0·5 h. The precipitate which formed was filtered off and recrystallized from water; analysis and n.m.r. and i.r. spectroscopy showed it to be the fluoroborate salt of cation (Id). The same product was obtained using triethyloxonium fluoroborate in dichloromethane, or triphenylmethyl fluoroborate in tetrahydrofuran. Similar results were achieved using complex (IIa), which was converted into the fluoroborate salt of cation (Ia).

Reaction of Complex (IId) *with N-Bromosuccinimide*.—A solution of complex (IId) (0·28 g) and *N*-bromosuccinimide (0·36 g) in methanol (20 ml) and light petroleum (b.p. 313—333 K; 5 ml) was stirred for 2 min and then treated with ammonium hexafluorophosphate (0·16 g) in methanol (2 ml). Removal of the solvent and recrystallization from acetone yielded the hexafluorophosphate salt of cation (Id).

Reaction of Complex (IId) *with Fluoroboric Acid*.—Solutions of fluoroboric acid (42% aqueous solution; 1·5 ml) in propionic anhydride (4 ml) and of complex (IId) (0·28 g) in the same solvent (2 ml) were mixed at 273 K. After a few minutes an ice-cold solution of ammonium hexafluorophosphate (0·24 g) in water (20 ml) was added. Crystals of the hexafluorophosphate salt of cation (Id) formed slowly.

Reaction of Complex (IId) *with Chlorotris*(*triphenylphosphine*)*rhodium*.—A solution of complex (IId) (0·28 g) and chlorotris(triphenylphosphine)rhodium (0·93 g) in benzene (25 ml) was stirred for 6 h. The yellow solid formed was filtered off, dissolved in methanol, and treated with ammonium hexafluorophosphate (0·16 g) in methanol (2 ml). Removal of the solvent and recrystallization from acetone yielded the hexafluorophosphate salt of cation (Id).

Effect of U.v. Irradiation on Complex (IId).—A solution of complex (IId) (0·27 g) in light petroleum (b.p. 333—353 K; 40 ml) was stirred under u.v. irradiation for 20 h at 323 K. The solvent was decanted from the precipitate which had formed, and the latter was then washed with ether and dried. This product was found to be cyanodicarbonyl(π-mesitylene)manganese.

Reaction of Complex (IId) *with Oxidising Agents*.—(a) A solution of complex (IId) (0·28 g) and *p*-benzoquinone (0·13 g) in acetone (10 ml) was stirred for 12 h in the absence of light. The solution was evaporated to dryness and the residue extracted with water. The aqueous solution was treated with ammonium hexafluorophosphate (0·16 g) in water (5 ml). Crystals of the hexafluorophosphate salt of cation (Id) formed slowly.

Similar results were achieved by treating complex (IId) (0·28 g) either with iodine (0·51 g) in light petroleum (b.p. 333—353 K; 10 ml) or with hydrated ferric chloride (1·35 g) in 95% aqueous ethanol (5 ml).

(b) *With ceric sulphate*. Complex (IId) (0·16 g) was added to a 4M-solution of ceric sulphate in 2M-sulphuric acid (10 ml), and the mixture was shaken for 4 days. The mixture was then extracted with three portions of ether (20 ml) and the ether extracts dried ($MgCl_2$) and filtered. The ether was removed by fractional distillation, and the residue was analysed by g.l.c. Mesitonitrile was present (in a yield of 73%), mesitylene was not.

Oxidation of complex (IIa) by the same method gave an 80% yield of benzonitrile. No benzene was produced.

Instruments used in the work described in this paper were: Mechrolab vapour pressure osmometer, model 301A; Perkin-Elmer R10 60 MHz and J.E.O.L. 100 MHz n.m.r. spectrometers; Perkin-Elmer 257 grating i.r. spectrometer; A.E.I. M.S. 12 mass spectrometer; Perkin-Elmer 240 elemental analyser; Pye 104 chromatograph.

We thank I.C.I. (Petrochemicals Division) for a maintenance grant (to P. J. C. W.)

[2/2298 *Received, 6th October*, 1972]