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SYNTHESIS OF OCTAHEDRAL CARBONYL COMPLEXES OF MANGANESE(I) WITH SCN OR CN LIGANDS. CRYSTAL STRUCTURE OF *fac*-[SCNMn(CO)$_3$(dppm)]

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Summary

The complexes *fac*-[XMn(CO)$_3$(dppm)], *cis,cis*-[XMn(CO)$_2$(dppm)(P(OPh)$_3$)] and *trans*-[XMn(CO)(dppm)$_2$] with X = SCN or CN have been prepared from the corresponding bromocarbonyls and the salts AgX or KX, or, in the case of the di- and mono-carbonyls, from *fac*-[XMn(CO)$_3$(dppm)] with X = SCN or CN by thermal or photochemical CO substitution by the ligands P(OPh)$_3$ or dppm. The structure of *fac*-[SCNMn(CO)$_3$(dppm)] has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, and the structure has been refined to $R = 0.058$ for 4123 reflexions measured in the range $2 \leqslant \theta \leqslant 30$ at room temperature. The *cis,cis*-[NCMn(CO)$_2$(dppm)(P(OPh)$_3$)] complex can be oxidized and subsequently reduced to the isomer *trans*-[NCMn(CO)$_2$(dppm)(P(OPh)$_3$)]. All the neutral cyanide complexes react readily with MeI and KPF$_6$ to give the corresponding methylisocyanide derivatives [Mn(CO)$_2$(dppm)(P(OPh)$_3$)(CNMe)]PF$_6$ and [Mn(CO)(dppm)$_2$(CNMe)]PF$_6$. The stereochemistries of the compounds is discussed in relation to the ^{31}P NMR spectra.

Introduction

Neutral pseudohalide carbonyl complexes of manganese(I) of the general type [XMn(CO)$_{5-n}$L$_n$] (X = CN or SCN, $n = 0$ to 2) are known with monodentate and bidentate ligands and with various geometries [1], but to our knowledge no neutral mononuclear cyano or thiocyanate di- or mono-carbonyl species have been reported.

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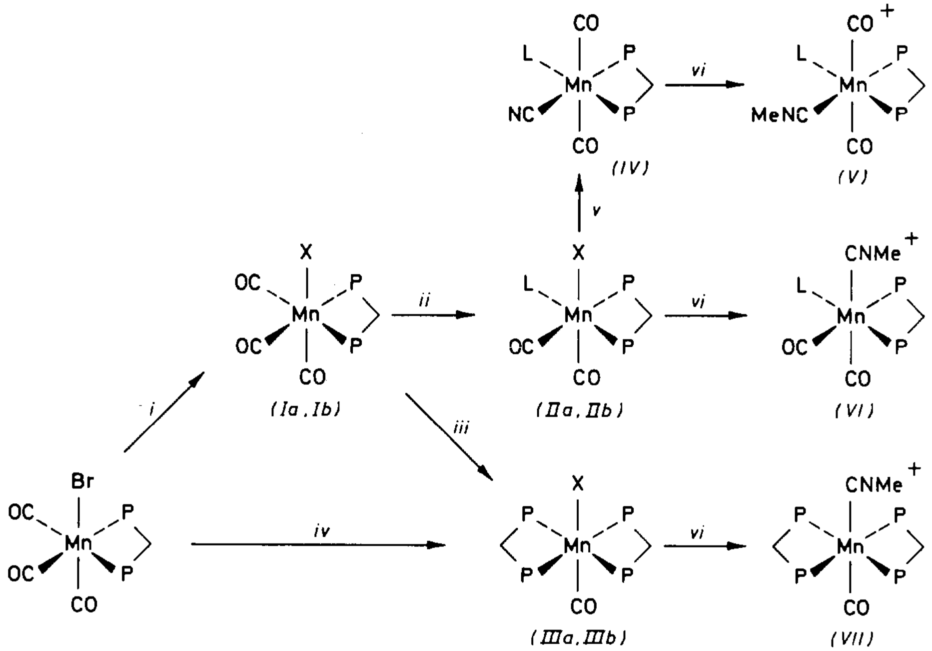
TABLE 1

MELTING POINTS, CONDUCTIVITY, ANALYTICAL AND IR DATA FOR THE COMPLEXES

Compound	M.p. [a] (°C)	Λ_M [b]	Analysis (Found (calcd.) (%))			IR [c] (cm^{-1})	
			C	H	N	ν(CN)	ν(CO)
fac-[SCNMn$(CO)_3$(dppm)] [d]	171	21	59.1	3.70	2.48	2102w	2035s, 1962s, 1932s
(Ia)			(59.9)	(3.79)	(2.41)		
fac-[NCMn$(CO)_3$(dppm)]	188	2.3	62.3	3.96	3.07	2114w	2015s, 1956s, 1947s
(Ib)			(63.4)	(4.04)	(2.55)		
cis,cis-[SCNMn$(CO)_2$(dppm)(P$(OPh)_3$)]·CH_2Cl_2 [d]	145	10	58.8	4.09	1.42	2105m	1970s, 1900s
(IIa)			(59.5)	(4.11)	(1.47)		
cis,cis-[NCMn$(CO)_2$(dppm)(P$(OPh)_3$)]	171	2.2	65.3	4.33	1.78	2095w	1969s, 1910s
(IIb)			(66.4)	(4.49)	(1.68)		
trans-[SCNMn(CO)$(dppm)_2$] [d]	129	10	67.6	4.84	1.90	2097m	1847s,br
(IIIa)			(68.6)	(4.88)	(1.54)		
trans-[NCMn(CO)$(dppm)_2$]	178	10	69.6	5.15	1.64	2091w	1864s,br
(IIIb)			(71.1)	(5.06)	(1.60)		
trans-[NCMn$(CO)_2$(dppm)(P$(OPh)_3$)]	150	6	65.8	4.87	1.53	2085w	1929s
(IV)			(66.4)	(4.49)	(1.68)		
cis,cis-[Mn$(CO)_2$(dppm)(P$(OPh)_3$)(CNMe)]PF_6·0.5CH_2Cl_2 [e]	203	117	54.9	4.10	1.33	2197w	1990s, 1942s
(V)			(55.1)	(3.96)	(1.35)		
trans-[Mn$(CO)_2$(dppm)(P$(OPh)_3$)(CNMe)]PF_6 [e]	130	115	56.5	4.29	1.42	2174w	1952s
(VI)			(56.9)	(4.07)	(1.41)		
trans-[Mn(CO)$(dppm)_2$(CNMe)]PF_6 [e]	184	122	59.4	4.51	1.35	2152w	1902s
(VII)			(61.3)	(4.57)	(1.35)		

[a] With decomposition. [b] In ohm^{-1} mol^{-1} cm^2 measured in 5×10^{-4} *M*, Me_2CO solution at 25°C. [c] In CH_2Cl_2 solution. [d] ν(CS) (cm^{-1}) (Nujol mull): (Ia) 818, (IIa) 813, (IIIa) 802. [e] ^1H NMR (δ (ppm)) in $CDCl_3$, ref. TMS: (V) 2.42 (s, br, 3H, CNMe), 4.74 (m, 2H, CH_2), 5.27 (s, 1H, $\frac{1}{2}CH_2Cl_2$), 7.22 (m, 35H, C_6H_5); (VI) 3.04 (s, br, 3H, CNMe), 4.68 (decep. simple triplet, 2H, CH_2), 7.19 (m, 35H, C_6H_5); (VII) 2.6 (s, br, 3H, CNMe), 4.80 (m, 2H, CH_2), 7.27 (m, 40H, C_6H_5).



SCHEME 1. (i) AgX in CH_2Cl_2 (X = SCN, CN); (ii) $P(OPh)_3$ in toluene reflux (X = SCN, CN); (iii) dppm, in CH_2Cl_2, $h\nu$ (X = SCN); (iv) dppm, $h\nu$ followed by AgX (X = CN, SCN) or KX (X = SCN); (v) $NOPF_6$ followed by NH_2NH_2; (vi) MeI and KPF_6 in THF.

On the other hand, it is known that in some cases a coordinated cyanide ligand can be alkylated under very mild conditions, e.g. with RI, to give alkylisocyanide complexes [2]. Therefore, as part of our work on the specific synthesis of neutral and cationic octahedral carbonyls of manganese(I) [3], we have studied the preparation of a series of neutral thiocyanate and cyanide di- and mono-carbonyl complexes of the type $[XMn(CO)_{3-n}(dppm)L_n]$ (L = $P(OPh)_3$ or dppm, $n = 0$, 1 or 2), which for X = CN, react with MeI and KPF_6 to generate cationic species containing the CNMe ligand.

Results and discussion

Treatment of *fac*-$[BrMn(CO)_3(dppm)]$ with AgX (X = SCN or CN) in CH_2Cl_2 (reaction i in Scheme 1) gave the complexes *fac*-$[SCNMn(CO)_3(dppm)]$ (Ia) and *fac*-$[NCMn(CO)_3(dppm)]$ (Ib) in good yields. The IR spectra in solution of these compounds (Table 1) showed the three ν(CO) strong absorptions characteristic of a *fac*-tricarbonyl and a medium (Ia) or week (Ib) band due to the ν(CN) stretching. The thiocyanate complex (Ia) is analogous to the known *fac*-$[SCNMn(CO)_3(dppe)]$, for which it was assumed that the SCN ligand is N-bonded to the manganese [4]. This assumption is based on the ν(CN) and ν(CS) stretching frequencies near 2100 and 818 cm^{-1} respectively, in the range observed for the N-bonded thiocyanates. It is thus to be expected that the SCNMn group is almost linear. These two features were confirmed in the case of compound Ia by an X-ray diffraction study. The results are summarized in Tables 2 and 3, and the structure is shown in Fig. 1

TABLE 2

FINAL ATOMIC COORDINATES ($\times 10^5$ for Mn, P, and S; $\times 10^4$ otherwise) AND THERMAL PARAMETERS FOR COMPOUND Ia

Atom	x/a	y/b	z/c	B_{eq}
Mn	73315(3)	−20180(5)	−11648(6)	3.30(3)
P(1)	74029(6)	−12848(8)	6010(10)	3.22(5)
C(111)	8161(2)	−412(3)	1195(4)	3.57(19)
C(112)	8371(3)	−324(4)	2313(4)	4.42(23)
C(113)	8935(3)	347(4)	2760(5)	5.23(26)
C(114)	9299(3)	928(5)	2080(6)	6.45(34)
C(115)	9099(4)	859(5)	966(7)	7.95(42)
C(116)	8527(4)	184(5)	497(5)	6.12(30)
C(121)	6573(3)	−689(4)	1003(4)	3.83(20)
C(122)	5993(3)	−1258(4)	1354(4)	4.71(24)
C(123)	5356(3)	−753(6)	1585(6)	6.66(35)
C(124)	5284(4)	306(7)	1486(6)	7.70(41)
C(125)	5849(4)	874(5)	1154(6)	7.33(38)
C(126)	6499(3)	383(4)	909(5)	5.52(27)
C(12)	7572(2)	−2550(3)	1304(4)	3.35(18)
P(2)	79037(6)	−32118(9)	1379(9)	2.99(4)
C(211)	8927(2)	−3191(3)	393(4)	3.10(17)
C(212)	9292(3)	−3671(4)	−369(4)	4.49(23)
C(213)	10075(3)	−3660(4)	−250(5)	5.09(26)
C(214)	10484(3)	−3172(4)	630(5)	4.95(25)
C(215)	10132(3)	−2675(5)	1390(4)	5.08(26)
C(216)	9347(2)	−2682(4)	1282(4)	4.06(21)
C(221)	7674(2)	−4591(3)	165(4)	3.41(19)
C(222)	7039(3)	−4970(4)	−526(4)	4.37(23)
C(223)	6864(3)	−6032(4)	−498(5)	5.23(27)
C(224)	7326(3)	−6702(4)	189(5)	5.25(27)
C(225)	7944(3)	−6331(4)	881(5)	4.92(25)
C(226)	8116(3)	−5268(3)	886(4)	3.87(20)
N	6342(2)	−2554(3)	−829(3)	3.67(16)
C(N)	5795(2)	−2919(3)	−676(4)	3.55(18)
S	50115(7)	−34663(11)	−4395(15)	6.12(8)
C(1)	8228(3)	−1599(4)	−1446(4)	4.38(22)
O(1)	8798(2)	−1342(3)	−1676(4)	6.79(22)
C(2)	7243(3)	−2847(4)	−2385(4)	4.53(23)
O(2)	7193(3)	−3365(3)	−3157(4)	7.19(23)
C(3)	6873(3)	−896(4)	−1899(4)	4.51(22)
O(3)	6602(2)	−187(3)	−2357(4)	7.17(22)

together with the atom numbering scheme. To date no other X-ray structure determination of a mononuclear thiocyanate carbonyl complex of manganese(I) has been published.

In the complex Ia the manganese atom displays a distorted octahedral coordination with the three linear carbonyl ligands (the mean Mn–C–O angle is 178.2°) *cis* to each other (*fac*-geometry). The other atoms coordinated to the manganese are the two phosphorus atoms of the dppm ligand and the nitrogen of the NCS group. The angles S–C–N (178.9(4)°) and Mn–N–C (175.2(4)°) showed that the ligand is essentially linear and the distances N–C (1.132(6) Å) and C–S (1.645(5) Å) are in the range usually observed for typical terminal NCS ligands [5]. These bond lengths

TABLE 3

MAIN BOND LENGTHS (Å) AND ANGLES (°) IN COMPOUND Ia

P(1)–Mn	2.342(1)
P(2)–Mn	2.335(1)
N–Mn	2.015(4)
C(1)–Mn	1.787(5)
C(2)–Mn	1.820(5)
C(3)–Mn	1.827(5)
C(12)–P(1)	1.842(4)
P(2)–C(12)	1.840(5)
C(N)–N	1.132(6)
S–C(N)	1.645(5)
O(1)–C(1)	1.156(6)
O(2)–C(2)	1.148(7)
O(3)–C(3)	1.140(6)
P(2)–Mn–P(1)	71.3(1)
N–Mn–P(1)	82.7(1)
N–Mn–P(2)	87.0(1)
C(1)–Mn–P(1)	97.7(2)
C(1)–Mn–P(2)	90.7(2)
C(1)–Mn–N	177.4(2)
C(2)–Mn–P(1)	167.7(2)
C(2)–Mn–P(2)	98.6(2)
C(2)–Mn–N	89.9(2)
C(2)–Mn–C(1)	89.2(2)
C(3)–Mn–P(1)	95.3(2)
C(3)–Mn–P(2)	166.6(2)
C(3)–Mn–N	91.3(2)
C(3)–Mn–C(1)	91.2(2)
C(3)–Mn–C(2)	94.7(2)
C(12)–P(1)–Mn	93.3(1)
P(2)–C(12)–P(1)	95.5(2)
C(12)–P(2)–Mn	93.6(1)
C(N)–N–Mn	175.2(4)
S–C(N)–N	178.9(4)
O(1)–C(1)–Mn	176.9(4)
O(2)–C(2)–Mn	179.3(5)
O(3)–C(3)–Mn	178.5(4)

suggest the presence of an N≡C triple bond and a C–S single bond, and so are indicative of an electron distribution approaching Mn–N≡C–S. The Mn–N bond length (2.015(4) Å) is short for a typical Mn–N single bond (about 2.1 Å [6]), but is very long compared with other Mn–N(*sp*) bonds with some multiple character [7]. It is known that electronic as well as steric factors are significant in determining the coordination of the ambivalent NCS ligand [8], and it has been shown that steric factors are responsible for the S-thiocyanate structures observed for some [NCSMn(CO)$_3$L$_2$] complexes [4]. The structure of compound Ia shows no steric interactions between the linear NCS group and the dppm ligand which could favour an SCN bonding to the manganese, in accord with arguments advanced previously for the analogous *fac*-[SCNMn(CO)$_3$(dppe)] [4]. In fact, while the angles C(2)–Mn–N and C(3)–Mn–N are nearly 90° (mean value 90.6°), the P(1)–Mn–N angle is only

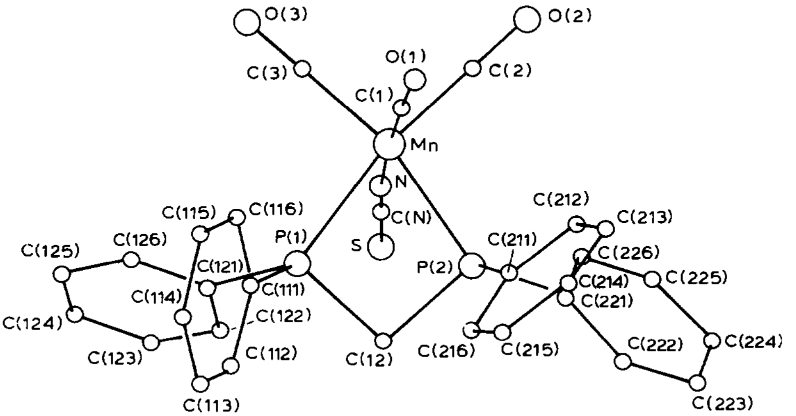


Fig. 1. Structure of *fac*-[SCNMn(CO)$_3$(dppm)].

82.7° showing a slight bending of the group MnNCS towards the dppm ligand instead of away from it. The Mn–P bond length (average 2.338(4) Å) is similar to values observed for other Mn–P bonds [9], and the angle P(1)–Mn–P(2) (71.2°) and the dihedral angle C(12)–P(2)–P(1)–Mn (−17.08°) are reasonable for a chelated dppm ligand [10]. The Mn–C bond lengths of the carbonyl ligands are normal for *fac*-tricarbonyl complexes of manganese [11], and vary only slightly depending on the ligands *trans* to them. Thus the Mn–C(1) distance (1.787(5) Å) is only 0.036 Å shorter than the mean value of the other two Mn–C bonds (1.823(3) Å). Although small, this difference is in the direction expected on the basis of the lower π-aceptor ability of the NCS ligand compared with the dppm ligand.

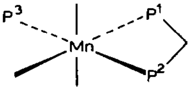
The fact that the NCS ligand is a harder base than the phosphines [12] and therefore more *cis*-labilizing [13] suggested that one CO *cis* to it in Ia could be replaced by another ligand, as previously found for *fac*-[BrMn(CO)$_3$(dppm)] [3b]. In accord with this it was observed that Ia reacted readily with P(OPh)$_3$ in refluxing toluene (ii in Scheme 1) to give *cis,cis*-[SCNMn(CO)$_2$(dppm)(P(OPh)$_3$)] (IIa) (crystallized from CH$_2$Cl$_2$/hexane as a CH$_2$Cl$_2$ solvate), data for which are given in Table 1. The IR in solution of this product showed the two ν(CO) absorptions of the same intensity characteristic of a *cis*-dicarbonyl. The ν(CN) and ν(CS) stretching frequencies of the NCS ligand in IIa (2105 and 813 cm^{-1}, respectively) showed no significant changes from the values for the starting complex Ia. The structure of IIa shown in the scheme was assumed on the basis of earlier work [3b], and was supported by the ^{31}P{^{1}H} NMR spectrum (Table 4). At room temperature the spectrum showed three very broad signals, which upon cooling to −60°C were resolved into a broad doublet of doublets and two other sharp doublets of doublets at lower frequencies. An approximate first order analysis of the spectrum (AMX system) yielded the chemical shifts and coupling constants shown in Table 4. (The assignments are discussed later).

Additional support for the structure of IIa came from its synthesis from *cis,cis*-[BrMn(CO)$_2$(dppm)(P(OPh)$_3$)] [3b] and AgSCN in CH$_2$Cl$_2$ at room temperature, in which it can be confidently assumed that the NCS replaces the Br with retention of the stereochemistry of the starting complex.

Further replacement of CO in IIa by another P(OPh)$_3$ ligand could only be

TABLE 4

^{31}P NMR DATA[a] FOR THE COMPLEXES



Compound	X	δ(P)	δ(P^1)	δ(P^2)	δ(P^3)	J_{12}	J_{13}	J_{23}
fac-[XMn(CO)$_3$(dppm)]	Br	10.9 [b]						
	SCN (Ia)	13.4						
	CN (Ib)	19.7						
cis,cis-[XMn(CO)$_2$(dppm)(P(OPh)$_3$)]	Br		7.4	24.0	154	43	77	140
	SCN (IIa) [c]		10.2	25.3	171	46	73	117
	CN (IIb)		17.0	31.0	172	51	77	75
	CNMe$^+$ (V)		14.8	26.3	169	50	70	50
trans-[XMn(CO)$_2$(dppm)(P(OPh)$_3$)]	Br		57.7	14.1	154	30	60	66
	CN (IV) [c]		26.2	34.4	179	34	34	59
	CNMe$^+$ (VI)		27.0	27.0	170			
trans-[XMn(CO)(dppm)$_2$]	Br	34.4						
	SCN (IIIa)	36.1						
	CN (IIIb)	41.3						
	CNMe$^+$ (VII)	42.3						

[a] Proton decoupled. Measured in CDCl$_3$ solution at room temperature, to high frequency of external 85% H$_3$PO$_4$ δ in ppm, J(PP) in Hz. [b] From ref. 26 (12.7 in ref. 27). [c] Measured at −60°C.

achieved in very low yield by low temperature irradiation in the presence of excess P(OPh)$_3$; a yellow product was formed, and was characterized by IR (ν(CN) 2110, ν(CO) 1882, ν(CS) 818 cm^{-1}) as [SCNMn(CO)(dppm)(P(OPh)$_3$)$_2$].

Similarly, low temperature irradiation of Ia with dppm led to the replacement of two CO ligands with formation of *trans*-[SCNMn(CO)(dppm)$_2$] (IIIa), also in poor yield. However, this orange air-sensitive compound was prepared in good yield by treating *trans*-[BrMn(CO)(dppm)$_2$] (obtained from *fac*-[BrMn(CO)$_3$(dppm)] and dppm as in ref. 14) with KSCN in CH$_2$Cl$_2$ at room temperature (path iv in Scheme 1). The IR and ^{31}P NMR spectra of compound IIIa (Tables 1 and 4) were in accord with the proposed structure, which is the same as that of the starting bromocarbonyl complex.

Like compound Ia, the analogous cyanide complex Ib reacted with P(OPh)$_3$ in refluxing toluene to give the corresponding cyano-dicarbonyl species *cis,cis*-[NCMn(CO)$_2$(dppm)(P(OPh)$_3$)] (IIb) (reaction ii in Scheme 1), which was characterized on the basis of the data shown in Tables 1 and 4. Like IIa it could also be prepared from *cis,cis*-[BrMn(CO)$_2$(dppm)(P(OPh)$_3$)] and AgCN in CH$_2$Cl$_2$. From qualitative experiments it was observed that the rate of the thermally promoted CO substitution reaction ii shown in the scheme varied in the order SCN $\simeq$ Br $\gg$ CN, suggesting that the CN ligand is less *cis*-labilizing than Br or SCN in the species *fac*-[XMn(CO)$_3$(dppm)]. This correlates with the Mn–CO(*cis*) bond strengths, estimated from the variations of the Cotton–Kraihanzel CO parameters [15] for these C–O bonds (K_2), namely 1599 (SCN), 1590 (Br) and 1584 (CN) N m^{-1} (the SCN and CN values were calculated by neglecting any interaction between CO and CN oscillators). Analogous correlations can be found in the literature for the rates of

CO substitution in $[XMn(CO)_5]$ (X = Cl, Br, I) and the K(CO) of the CO in *cis* with X [16]. Interestingly, the compound *fac*-$[PhC{\equiv}CMn(CO)_3(dppm)]$, for which K_2 is 1572 N m^{-1}, has been found to react very slowly with $P(OPh)_3$ in refluxing toluene [17].

The lower ability of the CN ligand than of the SCN group to promote CO substitution is also reflected in the fact that no further reaction with $P(OPh)_3$, or even, dppm, to give monocarbonyl species could be achieved. However, treatment of *trans*-$[BrMn(CO)(dppm)_2]$ with AgCN in CH_2Cl_2 gave *trans*-$[NCMn(CO)(dppm)_2]$ (IIIb), but only in moderate yield (reaction iv in Scheme 1) because of side reactions that led to unidentified products. Attempts to prepare IIIb using KCN instead of AgCN were unsuccesful.

It has been reported that the species *cis,cis*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$ can be oxidized with $NOPF_6$ and the product subsequently reduced to give the isomer *trans*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$ [3b]. Similarly, the cyanide dicarbonyl IIb was oxidized by $NOPF_6$ in CH_2Cl_2 to give a violet solution showing a ν(CO) absorption in the IR at 2000 cm^{-1}, probably corresponding to the manganese(II) species *trans*-$[NCMn(CO)_2(dppm)(P(OPh)_3)]^+$, which was not isolated but which gave *trans*-$[NCMn(CO)_2(dppm)(P(OPh)_3)]$ (IV) upon addition of hydrazine (path v in Scheme 1). The oxidation of the thiocyanate complex IIa, followed by reduction with NH_2NH_2, gave an unstable mixture that showed bands in the IR spectrum at 2084w, and 1930s cm^{-1}, attributable to the *trans*-isomer but no pure SCN analogue of IV could be prepared by this method. The compound IV was also formed, together with some of the *cis,cis*-isomer IIb in the reaction of *trans*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$ and AgCN in CH_2Cl_2, but in the analogous reaction with AgSCN only very slow formation of the *cis,cis*-dicarbonyl (IIa) was observed. As in previous cases [3b], the latter result may be attributed to the slow oxidation of the *trans*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$ to give, after decomposition of the Mn^{II} species, the *cis,cis*-bromodicarbonyl isomer, which reacts with AgX to give IIa or IIb.

The spectroscopic properties of compound IV (Tables 1 and 4) are in accord with the structure proposed. Thus, the IR spectrum showed only one ν(CO) absorption, as expected for a *trans* dicarbonyl. The ν(CN) stretching frequency is similar to the corresponding ones for the complexes Ib, IIb and IIIb; they fall in the range observed for other coordinate CN ligands (ca. 2100 cm^{-1}) [18] and are only slightly higher than ν(CN) for the free CN^- anion (2085 cm^{-1} in Nujol [19]), and lower than 2145 cm^{-1} observed for $[NCMn(CO)_5]$, as would be expected on the basis of the bonding characteristics of the CN^- ligand [20]. The $^{31}P\{^1H\}$ NMR of IV at room temperature showed three broad signals, which were resolved at -60°C into three sets of multiplets (approximate AMX system). For the other spectra in Table 4 the chemical shifts and coupling constants were calculated by a first order analysis and the assignments were made by taking account of *trans* influences [21]. Thus, in the case of the compounds *cis,cis*-$[XMn(CO)_2(dppm)(P(OPh)_3)]$ for X = Br, SCN (IIa) or CN (IIb), the chemical shift corresponding to the lowest frequency was assigned to the P(1) phosphorus, which is the one *trans* to a CO ligand while in the *trans*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$, the smallest chemical shift was assigned to the P(2) atom, which is *trans* to a $P(OPh)_3$ ligand. For compound IV the assignment was made by assuming that the CN has a stronger *trans* influence ligand than $P(OPh)_3$ [22].

The low ν(CN) frequencies of the compounds IIb, IIIb and IV suggested that the CN group is sufficiently nucleophilic to react with the very mild methylating agent MeI, as found recently in other cases [2]. In agreement with this, the cyanide complexes were found to react with MeI in THF in the presence of KPF_6 (path vi in Scheme 1) to give the cationic methyl isocyanide derivatives *cis,cis*-[Mn(CO)$_2$(dppm)(P(OPh)$_3$)(CNMe)]PF$_6$ (V), *trans*-[Mn(CO)$_2$(dppm)(P(OPh)$_3$)(CNMe)]PF$_6$ (VI) and *trans*-[Mn(CO)(dppm)$_2$(CNMe)]PF$_6$ (VII), data for which are given in Tables 1 and 4. The ν(CN) frequency of the CNMe group in the IR spectrum of the monocarbonyl compound VII is very close to that for the corresponding band in the free CNMe ligand (2158 cm^{-1} [23]), whereas slightly higher values were observed for the dicarbonyls V and VI. It was also noticed that in V, in which the CNMe ligand is *trans* with the CO, the ν(CN) is higher than in VI, in which the CNMe is *trans* to a phosphorus atom. These observations can be explained in terms of the bonding properties of the CNMe ligand [24]. The relatively large increase in the ν(CO) frequencies on going from the cyanide complexes to the CNMe derivatives is also consistent with the formation of cationic species.

The presence of the CNMe group in the cationic complexes was also confirmed by the slightly broad signal in the ^{1}H NMR spectra in the 2.5–3.0 region (Table 1) (the free ligand Me resonance is 2.73 ppm (J(NH) 2.4 Hz) [23]). The observed values for the compounds V, VI and VII are higher than those reported for other cationic CNMe complexes of manganese(I) which do not contain phosphorus ligands [25], and vary considerably with the ligand *trans* with the CNMe. Thus, while V has the Me resonance at 2.42 ppm (CNMe *trans* to a CO), in VI it is at 3.04 ppm (CNMe *trans* to a phosphorus of the dppm).

Finally, it was observed that the room temperature $^{31}P\{^1H\}$ NMR spectrum of the *trans* dicarbonyl V showed only one broad signal for the two phosphorus of the dppm ligand, which can be accounted for by assuming that the P(OR)$_3$ and CNR ligands have similar *trans*-influences [22].

Experimental

The reactions were carried out under argon. The IR spectra were recorded with a Perkin–Elmer 298 Spectrometer and calibrated with reference to the 1602 cm^{-1} band of polystyrene. The NMR spectra were recorded with a JEOL FX90Q instrument. The complexes *fac*-[BrMn(CO)$_3$(dppm)] [3a], *cis,cis*- and *trans*-[BrMn(CO)$_2$(dppm)(P(OPh)$_3$)] [3b] and *trans*-[BrMn(CO)(dppm)$_2$] [14] were prepared by published methods.

Preparation of fac-[XMn(CO)$_3$(dppm)] (X = SCN (Ia), CN (Ib))

A mixture of *fac*-[BrMn(CO)$_3$(dppm)] (1 g, 1.6 mmol) and AgX (3 mmol) in CH_2Cl_2 (25 ml) was stirred for 24 h at room temperature in the absence of light then filtered. The filtrate was concentrated to 5 ml and sufficient hexane was added to precipitate the yellow *fac*-[XMn(CO)$_3$(dppm)], which was recrystallized from CH_2Cl_2/hexane. Yield ca. 80%.

Preparation of cis,cis-[XMn(CO)$_2$(dppm)(P(OPh)$_3$)] (X = SCN (IIa), CN (IIb))

a. From cis,cis-[BrMn(CO)$_2$(dppm)(P(OPh)$_3$)]. A mixture of *cis,cis*-[BrMn-

$(CO)_2(dppm)(P(OPh)_3)]$ (0.47 g, 0.53 mmol) and AgSCN (0.11 g, 0.69 mmol) in CH_2Cl_2 (25 ml) was stirred at room temperature in the absence of light for 7 h then filtered through Celite. The filtrate was concentrated in vacuo to ca. 3 ml and hexane was added to precipitate a yellow solid, which was recrystallized from CH_2Cl_2/hexane to give IIa (0.22 g, 48%).

The compound IIb was similarly prepared (but with a reaction time of 16 h) and reacrystallized from CH_2Cl_2/ethanol to give yellow crystals (30% yield).

b. From fac-[XMn(CO)$_3$(dppm)]. A mixture of *fac*-$[SCNMn(CO)_3(dppm)]$ (0.3 g, 0.5 mmol) and $P(OPh)_3$ (0.78 g, 2.5 mmol) in toluene (20 ml) was refluxed for 1 h, then cooled to room temperature and filtered. The filtrate was concentrated in vacuo almost to dryness, and the remaining oil was washed with hexane (2 × 20 ml) to give a solid. This was recrystallized from CH_2Cl_2/hexane to give IIa as yellow crystals (0.37 g, 83%).

The yellow compound IIb was similarly prepared (reaction time 16 h) in 30% yield. Recrystallization was from CH_2Cl_2/ethanol.

Preparation of trans-[XMn(CO)(dppm)$_2$]

X = SCN (IIIa). A mixture of *trans*-$[BrMn(CO)(dppm)_2]$ (0.30 g, 0.32 mmol) and KSCN (0.4 g, 4 mmol) in CH_2Cl_2 (25 ml) was stirred for 2 d then filtered. The orange filtrate was concentrated in vacuo to ca. 3 ml and hexane was added to precipitate a solid, which was recrystallized from CH_2Cl_2/hexane to give orange crystals of IIIa (0.12 g, 41%).

When AgSCN was used the compound was obtained in 7 h in 10% yield. It was also made in 26% yield by irradiation with UV light at −10°C of *fac*-$[SCNMn(CO)_3(dppm)]$ in the presence of a five-fold excess of dppm in CH_2Cl_2.

X = CN (IIIb). A mixture of *trans*-$[BrMn(CO)(dppm)_2]$ (0.31 g, 0.33 mmol) and AgCN (0.06 g, 0.45 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature in the absence of light for 15 min then filtered. The filtrate was concentrated in vacuo to 5 ml and hexane was added to precipitate a yellow product, which was discarded. The liquid was concentrated and more hexane was added to give an orange powder, which was recrystallized from CH_2Cl_2/hexane to give microcrystals of IIIb (0.02 g, 7%).

Preparation of trans-[NCMn(CO)$_2$(dppm)(P(OPh)$_3$)] (IV)

A solution of IIb (0.53 g, 0.64 mmol) in CH_2Cl_2 (20 ml) was cooled in an ice bath, $NOPF_6$ (0.15 g, 0.86 mmol) was added, and the mixture was stirred for 90 min to give a deep violet solution. To this was added 80% hydrazine monohydrate (2 ml), and the red mixture was filtered through Celite. The filtrate was concentrated in vacuo to 5 ml and hexane was added to precipitate the crude product. Recrystallization from CH_2Cl_2/ethanol afforded orange crystalline IV (0.203 g, 38%).

The compound was also prepared by treating *trans*-$[BrMn(CO)_2(dppm)(P(OPh)_3)]$ with AgCN in CH_2Cl_2 for 3 h (48% yield).

Preparation of the cationic complexes V, VI and VII

To a solution of IIb (0.30 g, 0.36 mmol) in THF (20 ml) were added CH_3I (2 ml) and KPF_6 (0.1 g, 0.56 mmol), and the mixture was stirred at room temperature for 4 d then filtered. The yellow filtrate was evaporated and the residual oil was dissolved in CH_2Cl_2. Diethyl ether was added to precipitate a solid, which was recrystallized from CH_2Cl_2/ethanol to give pale microcrystalline V (0.2 g, 56%).

The yellow compound VI was similarly prepared from IV in 51% yield, and the orange complex VII by the same procedure (but with a reaction time of 24 h) in 42% yield.

Crystal structure determination of Ia

Crystal data. $C_{29}H_{22}NO_3SP_2Mn$, *M* 571.4, monoclinic, *a* 18.040(3), *b* 12.850(2), *c* 12.235(2) Å, β 98.89(2)°, *V* 2802(1) Å^3, $P2_1/n$, D_x 1.354 g cm^{-3}, $Z = 4$, $F(000) = 1152$, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 7.11 cm^{-1}. Room temperature.

Crystals were obtained as yellow prisms from CH_2Cl_2/hexane. A small crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 9°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo-K_α radiation, using the ω-scan technique, (scan width 1.2°, scan speed 0.03° s^{-1}). Three reflections were measured each 2 h as orientation and intensity control and no significant variations were observed. 4504 independent reflections were measured in the range $2 \leqslant \theta \leqslant 30°$ and 4123 of these, with $I \geqslant 2.5\sigma(I)$, were used. Lorentz-polarization but no absorption corrections were made. The Mn and P atoms were located by direct methods using the MULTAN system [28]. The remaining non-hydrogen atoms were located by use of the DIRDIF system [29]. The structure was isotropically and anisotropically refined by full-matrix least-squares method using the SHELX76 program [30]. The function minimized was $w\,[\,|F_0| - |F_c|\,]^2$, where $w = (\sigma^2(F_0) + 0.0017|F_0|^2)^{-1}$, f, f' and f'' were taken from ref. 31. All the hydrogen atoms were located from a difference synthesis, and refined with an overall isotropic temperature factor and the remaining atoms were refined anisotropically. The final R factor was 0.058 ($R_w = 0.061$) for all observed reflections.

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