Inorganica Chimica Acta, 121 (1986) 191–198

Synthesis of Mono and Binuclear Carbonyl Complexes of Manganese with Cyanide or Thiocyanate Ligands. X-ray Crystal Structure of $[\{fac\text{-Mn(CO)}_3\text{(phen)}\}_2(\mu\text{-CN})]PF_6$*

G. A. CARRIEDO, M. C. CRESPO, V. RIERA**

Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

M. L. VALIN, D. MOREIRAS

Departamento de Cristalografía y Mineralogía, Universidad de Oviedo, 33071 Oviedo, Spain

and X. SOLANS

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Gran Vía 585, 08007 Barcelona, Spain

(Received May 2, 1986; revised June 30, 1986)

Abstract

The neutral complexes *cis-trans*-$[MnX(CO)_2(bipy)(P(OPh)_3)]$ (X = I, CN or SCN) have been prepared by nucleophilic substitution of $P(OPh)_3$ by X^- in the cationic complex *cis-trans*-$[Mn(CO)_2(bipy)(P(OPh)_3)_2]^+$, or, in the case of X = CN, by reacting the iodo-dicarbonyl with AgCN. The cyanide complex reacts with MeI in the presence of KPF_6 or with $HBF_4 \cdot Et_2O$ (or $BF_3 \cdot Et_2O$) to give respectively the cationic CNMe or the neutral $CNBF_3$ derivative. The cyanide species *fac*-$[Mn(CN)(CO)_3(\widehat{NN})]$ ($\widehat{NN}$ = bipy or phen) and *cis-trans*-$[Mn(CN)(CO)_2(bipy)(P(OPh)_3)]$ react at room temperature with *fac*-$[MnBr(CO)_3(\widehat{NN})]$ or *cis-trans*-$[MnI(CO)_2(bipy)P(OPh)_3)]$ in the presence of $TlPF_6$ to give the corresponding cationic cyanide-bridged complexes $[\{Mn\}_a\text{–CN–}\{Mn\}_b]^+$ for $\{Mn\}_a$ or $\{Mn\}_b$ = $Mn(CO)_3(\widehat{NN})$ or $Mn(CO)_2(bipy)(P(OPh)_3)$. In the same way the salt $[\{fac\text{-Mn(CO)}_3\text{(bipy)}\}_2(\mu\text{-SCN})]PF_6$ can be prepared from *fac*-$[Mn(NCS)(CO)_3(bipy)]$ and *fac*-$[MnBr(CO)_3(bipy)]$. The structure of the compound $[\{fac\text{-Mn(CO)}_3\text{(phen)}\}_2(\mu\text{-CN})]PF_6$ has been established by X-ray diffraction. The reaction of the cyanide bridged complexes with $HBF_4 \cdot Et_2O$ is also discussed.

Introduction

As reported previously [1, 2] the nitrogen of a terminal CN ligand coordinated to a relatively electron rich metal center is susceptible to alkylation under very mild conditions, e.g., using MeI and KPF_6. In a similar way some cyanide complexes can be used as N-donor ligands to coordinate other metal–ligand fragments giving cyanide-bridge species [3]. Accordingly we have found that by reacting a cyanide complex $\{Mn\}_a$–CN with a halogeno complex $\{Mn\}_b$–X (X = Br or I) in the presence of $TlPF_6$ in CH_2Cl_2 at room temperature, various cationic species of the general type $[\{Mn\}_a\text{–CN–}\{Mn\}_b]PF_6$ can be obtained having equal or different manganese carbonyl moieties bridged by a CN group, a method that could also be used for the preparation of μ-SCN complexes. The preparation of the previously unknown $[MnX(CO)_2(\widehat{NN})(P(OPh)_3)]$ (X = I, CN or SCN) used for the preparation of the bridged species is also discussed.

Results and Discussion

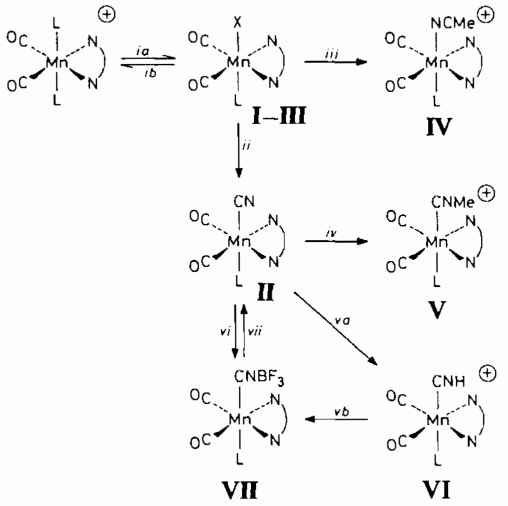
Refluxing a mixture of *cis-trans*-$[Mn(CO)_2(\widehat{NN})(P(OPh)_3)_2]ClO_4$ ($\widehat{NN}$ = bipy or phen) [4] and solid KX (X = I, CN SCN) in acetone (ia in Scheme 1) resulted in the displacement of one $P(OPh)_3$ ligand with formation of the neutral complexes *cis-trans*-$[MnX(CO)_2(\widehat{NN})(P(OPh)_3)]$ (**I–III**) data for which are given in Table I. However, for X = I or CN the conversion of the starting compound into the neutral dicarbonyl could only be completed by periodically evaporating the solvent and washing out the free $P(OPh)_3$ formed with hexane. This suggests that the equilibrium ia,ib is present in solution (see Scheme 1), showing that the $P(OPh)_3$ can replace the anionic ligand X. This method worked well for the preparation of the complexes **I** and **III** but with X = CN much decomposition took place before the total disappearance of the starting cationic complex. However, the cyanide species **II** could be prepared with a good yield by reacting **I** with AgCN in CH_2Cl_2 (reaction ii in Scheme 1). Similarly, the reactions of *fac*-$[MnBr(CO)_3(\widehat{NN})]$ and AgCN or AgNCS in CH_2Cl_2

---

*Dedicated to Prof. R. Usón on the occasion of his 60th birthday.

**Author to whom correspondence should be addressed.

0020-1693/86/$3.50



Scheme. 1. L = $P(OPh_3)$. (ia) KX (X = CN, SCN, I) in refluxing acetone; (ib) + $P(OPh_3)$; (ii) for X = I with AgCN; (iii) for X = I with $TlPF_6$ in MeCN; (iv) MeI + KPF_6 in thf; (va) $HBF_4 \cdot Et_2O$ in CH_2Cl_2; (vb) spontaneous with BF_4^-; (vi) $BF_3 \cdot Et_2O$ in CH_2Cl_2; (vii) NEt_3 in acetone or CH_2Cl_2.

lead to the sparingly soluble *fac*-tricarbonyls *fac*-$[Mn(CN)(CO)_3(\widehat{NN})]$ (**VIII**) or to the previously known *fac*-$[Mn(NCS)(CO)_3(\widehat{NN})]$ [5]. The product of the reaction ii contained variable amounts of AgCN (probably coördinated to the N atom of the MnCN group as supported by the discussion below), but this could be removed by stirring the dichloromethane solution of the product with an aqueous solution of $Na_2S_2O_3$ as reported in the preparation of some σ-alkynyl complexes of manganese [6].

The *cis-trans* stereochemistry shown in Scheme 1 for the neutral dicarbonyls is assumed because **I** reacts readily with $P(OPh)_3$ and $TlPF_6$ in CH_2Cl_2 at room temperature giving the starting *cis-trans*-$[Mn(CO)_2(bipy)(P(OPh)_3)_2]^+$, analogous to the *cis-trans*-$[Mn(CO)_2(phen)(P(OMe)_3)_2]^+$, the structure of which (in the ClO_4^- salt) has been established by X-ray diffraction [7]. Other *cis-trans* dicarbonyls such as the cationic species *cis-trans*-$[Mn(CO)_2(bipy)(P(OPh)_3)(NCMe)]PF_6$ (**IV**), can be prepared from **I** and $TlPF_6$ in the presence of the entering ligand such as NCMe (reaction iii in Scheme 1). In complex **IV** the presence of the coordinated NCMe was clearly evidenced by a singlet in the ^1H NMR at 1.97 ppm. Therefore, it appears that mixed cationic dicarbonyls of general formula *cis-trans*-$[Mn(CO)_2(\widehat{NN})LL']^+$ can be synthesized more selectively than previously reported [4] by reacting first *cis-trans*-$[Mn(CO)_2(\widehat{NN})L_2]ClO_4$ with KI followed by reaction with $TlPF_6/L'$, provided that the neutral species $[MnI(CO)_2(\widehat{NN})L]$ can be obtained in the first step, which will depend on the nature of L. Analogous to the case of the complexes *fac*-$[Mn(CO)_3(\widehat{NN})L]^+$ [4], the lability of one L ligand in the *cis-trans*-$[Mn(CO)_2(\widehat{NN})L_2]^+$ is connected with the *cis*-labilizing effect [8,9] of the $\widehat{NN}$ ligand, but the ligand in *trans* with the leaving L may also exert some *trans* effect [10] affecting the readiness of the displacement of one L.

As found in the case of the complexes *cis-cis* or *trans*-$[Mn(CN)(CO)_2(dppm)(P(OPh)_3)]$ [2], compound **II** reacted with MeI and KPF_6 in thf to give the cationic methyl-isocyanide derivative *cis-trans*-$[Mn(CO)_2(bipy)(P(OPh)_3)(CNMe)]PF_6$ (**V**) (reaction iv in Scheme 1) characterized by the data in Table I and by a broad singlet in the ^1H NMR at 3.20 ppm that can be assigned to the Me group of the CNMe ligand. Also as expected on the basis of earlier works [11], compound **II** reacted with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 to give initially the protonated derivative *cis-trans*-$[Mn(CO)_2(bipy)(P(OPh)_3)(CNH)]BF_4$ (**VI**) (reaction va in Scheme 1) as evidenced by the IR absorptions at 2079w (ν(CN)), 1982s and 1914s (ν(CO)) cm^{-1} that appeared in the CH_2Cl_2 solution just after the addition of the acid. The lowering of the ν(CN) stretching frequency in *ca.* 24 cm^{-1} with respect to the neutral cyanide complex is very close to that observed in the protonation of the species $[(arene)Mn(CO)_2(CN)]$ [11] which has a ν(CN) almost identical to that of compound **II**. The salt **VI** could not be isolated because addition of diethylether led to the neutral product *cis-trans*-$[Mn(CNBF_3)(CO)_2(bipy)(P(OPh)_3)]$ (**VII**) which had absorptions in the IR (nujol mull) at 2184m cm^{-1} (ν(CN)) and 1100s, 1120s, 1130s cm^{-1} (ν(BF)) characteristic of the coordinated $CNBF_3$ [11]. The nature of the complex **VII** was also confirmed by its synthesis from **II** and $BF_3 \cdot Et_2O$ in CH_2Cl_2 (reaction vi in Scheme 1). It was also observed that the cyano-trifluoroborate adduct **VII** dissociated slowly in acetone solution and reverted to the starting cyanide **II** by reaction with bases such as NEt_3 (vii in Scheme 1), or to the cationic CNH product by adding excess $HBF_4 \cdot Et_2O$ in CH_2Cl_2 under argon.

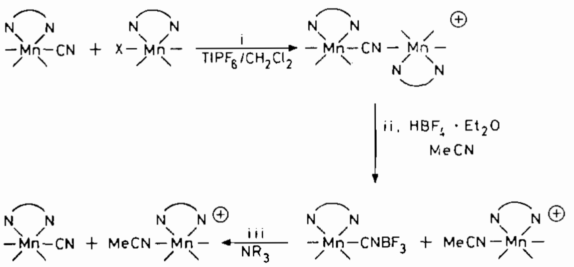
The process leading to the CNMe complex **V** (iv in Scheme 1) suggested the possibility of preparing in very mild conditions a series of cyanide bridged cationic complexes of the general type $[\{Mn\}_a{-}CN{-}\{Mn\}_b]^+$ by reacting the appropriate cyanide $\{Mn\}_a{-}CN$ and halogeno $\{Mn\}_b{-}X$ precursors in the presence of halogen abstractor such as $TlPF_6$, a reaction analogous to that used in the preparation of several –CN bridged ruthenium species [3].

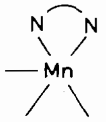
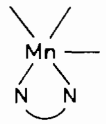
Following this procedure (i in Scheme 2) the crystalline salts **IX** to **XII** were obtained in good yields using *fac*-$[Mn(CN)(CO)_3(\widehat{NN})]$ or *cis-trans*-$[Mn(CN)(CO)_2(bipy)(P(OPh)_3)]$ and *fac*-$[MnBr(CO)_3(\widehat{NN})]$ or *cis-trans*-$[MnI(CO)_2(bipy)(P(OPh)_3)]$. The same method, but using *fac*-$[Mn(NCS)(CO)_3(bipy)]$ and *fac*-$[MnBr(CO)_3(bipy)]$, allowed the preparation of the μ-NCS complex [{*fac*-Mn-

TABLE I. Melting Points, Analytical, Conductivity and IR Data for the Complexes

Compound	Melting point[a] (°C)	Λ_M[b]	Analysis (found (calc.) (%))			IR (cm^{-1})[c]	
			C	H	N	ν(CN)	ν(CO)
cis-trans-[MnI(CO)$_2$(bipy)(P(OPh)$_3$)] (**I**)	113	11	51.0	3.27	3.88		1962s, 1892s
			(51.1)	(3.30)	(3.97)		
cis-trans-[Mn(CN)(CO)$_2$(bipy)(P(OPh)$_3$)] (**II**)	160	2.4	61.6	3.84	7.03	2105w	1966s, 1897s
			(61.7)	(3.84)	(6.96)		
cis-trans-[Mn(NCS)(CO)$_2$(bipy)(P(OPh)$_3$)] (**IIIa**)	167	8.4	58.6	3.57	7.11	2115w	1977s, 1905s
			(58.6)	(3.62)	(6.61)		
cis-trans-[Mn(NCS)(CO)$_2$(phen)(P(OPh)$_3$)] (**IIIb**)	174	3.0	60.2	3.47	6.23	2112w	1975s, 1902s
			(60.1)	(3.49)	(6.37)		
cis-trans-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(NCMe)]PF$_6$ (**IV**)	166	136	50.1	3.32	5.32	2055w	1982s, 1909s
			(50.3)	(3.41)	(5.50)		
cis-trans-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(CNMe)]PF$_6$ (**V**)	159	124	50.7	3.52	5.61	2204w	1982s, 1917s
			(50.3)	(3.41)	(5.50)		
cis-trans-[Mn(CNBF$_3$)(CO)$_2$(bipy)(P(OPh)$_3$)] (**VII**)	160	50[d]	55.1	3.49	6.03	2184m	1980s, 1912s[e]
			(55.4)	(3.43)	(6.26)		
fac-[Mn(CN)(CO)$_3$(bipy)] (**VIIIa**)	160	3.5	51.4	2.79	11.7	2115w	2029s, 1939s,br
			(52.4)	(2.52)	(13.1)		
[{Mn(CO)$_3$(phen)}$_2$(μ-CN)]PF$_6$ (**IX**)	211	127	46.0	2.12	8.49	2154w	2004s, 1948s,br
			(46.0)	(1.98)	(8.65)		
[Mn(CO)$_3$(bipy)(μ-CN)Mn(CO)$_2$(bipy)(P(OPh)$_3$)]PF$_6$ (**X**)	88	116	52.0	3.16	6.85	2154w	2042s, 1975s, 1951s, 1938s, 1903m
			(50.6)	(2.99)	(6.71)		
[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(μ-CN)Mn(CO)$_3$(bipy)]PF$_6$ (**XI**)	97	120	50.7	3.27	6.88	2135w	2036s, 1967s, 1940s, 1897m
			(50.6)	(2.99)	(6.71)		
[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(μ-CN)Mn(CO)$_2$(bipy)(P(OPh)$_3$)]PF$_6$ (**XII**)	159	114	54.6	3.48	5.29	2139w	1974s, 1903s
			(55.2)	(3.49)	(5.28)		
[{Mn(CO)$_3$(bipy)}$_2$(μ-SCN)]PF$_6$ (**XIII**)	180	125	40.8	2.19	8.49	2152m	2045s, 2036s, 1947s,br
			(40.9)	(2.03)	(8.82)		

[a] Melts with decomposition. [b] In ohm^{-1} mol^{-1} cm^2 in 5 × 10^{-4} M acetone solution. [c] In CH$_2$Cl$_2$ solution. All the PF$_6$ salts showed also a ν(PF) band at 830 cm^{-1} (nujol mull). [d] Increasing to 80. 2.3 in 1,2 dichloroethane increasing to 8.3. [e] In nujol mull 2184m, 1969s, 1909m, 1880s, and also ν(BF) bands at 1100s, 1120s, 1130s.



Compound		
IX	*fac*-Mn(CO$_3$(phen))	*fac*-Mn(CO)$_3$(phen)
X	*fac*-Mn(CO)$_3$(bipy)	*cis-trans*-Mn(CO)$_2$(bipy)(P(OPh)$_3$)
XI	*cis-trans*-Mn(CO)$_2$(bipy)(P(OPh)$_3$)	*fac*-Mn(CO)$_3$(bipy)
XII	*cis-trans*-Mn(CO)$_2$(bipy)(P(OPh)$_3$)	*cis-trans*-Mn(CO)$_2$(bipy)(P(OPh)$_3$)

Scheme 2.

(CO)$_3$(bipy)}$_2$(μ-NCS)]PF$_6$ (**XIII**) which presumably has one Mn bonded to the N and the other Mn to the S atom of the NCS ligand as suggested by the small splitting of the ν(CO) absorption of higher frequency. As might be expected on a theoretical basis [12] the ν(CN) frequency is higher in the μ-CN complexes than in the parent neutral cyanide; an effect also observed in the μ-NCS complex **XIII**.

In order to study the μ-CN bridge in more detail, an X-ray diffraction structure determination was carried out on the bis-factricarbonyl complex **IX**. The results are summarized in Tables II to IV and the structure of the cation is shown in Figs. 1 and 2.

In the solid, the group Mn(1)–C(10)–N(10)–Mn(2) is not perfectly linear, with angles Mn(1)–C(10)–N(10) (168.2(10)°) and C(10)–N(10)–Mn(2) (171.2(10)°) significantly, though not substantially, different from 180° and with a torsion angle Mn(1)–C(10)–N(10)–Mn(2) of −38.1°. Those values are very similar to the ones found in the cation [{Ru$_2$(dppe)(PPh$_3$)$_2$(C$_5$H$_5$)$_2$}(μ-CN)]$^+$ [3] although it should be noted that in some cases like for example in the polymer [Cu(dmphen)(CN)]$_n$ the deviations from the linearity of the group MCNM (CuNC = 154.8°, NCCu = 169.6°) can be attributed to packing and steric effects [13]. In accord with the large angles of the Mn(1)–C(10)–N(10)–Mn(2) group, the bond length N(10)–C(10) is short (1.107 Å) and corresponds to a C≡N triple bond as indicated by the high ν(CN) frequency (2154 cm^{-1}). The Mn(2)–N(10) distance (2.064 Å) is typical for a Mn–N single bond [14], and the Mn(1)–C(10) (2.004 Å) is very close to the values normally encountered in isocyanide manganese complexes [15, 16]. The coordination around both manganese atoms is essentially octahedral but deviations from ideal geometry are more pronounced for the Mn(2) atom. Thus, in the case of Mn(1), the main distortion from the octahedron is due to the small angle N(112)–Mn(1)–N(101) (79.3°) value that is near the range expected from the Frenz–Ibers correlation [17] for the Mn(1)–N(phen) bond length of 2.05 Å (average). Similarly to other phenanthroline complexes, the N···N nonbonding distance is 2.62 Å (average). The same distortion (originated by the angle N(201)–Mn(2)–N(212) of 78.6°) is present around the Mn(2) atom (Mn(2)–N(phen) averages 2.05 Å), but, in this case, the N(10)–Mn(2)–N(phen) angles (average 84°) deviate from 90° sufficiently to make the phenanthroline ligand appear inclined towards the group –NCMn(1) (Fig. 2), an effect reinforced by the torsion angles N(201)–Mn(2)–N(212)–C(213) (10.6°) and N(212)–Mn(2)–N(201)–C(214) (−10.5°) that are greater than the corresponding analogues in Mn(1) (N(112)–Mn(1)–N(101)–C(114) = 1.74°, N(101–Mn(1)–N(112)–C(113) = 2.24°). We cannot say whether these features are due to packing forces or to electronic effects because while the angles (and bond lengths) around the Mn(1) atom are almost identical to the observed ones in the cation *fac*-[Mn(CO)$_3$(phen)(CNBu^t)]$^+$ [15a], no X-ray structure of a *fac*-[Mn(CO)$_3$(phen)(NCR)]$^+$ complex has been published to allow comparisons with the geometrical aspects around the Mn(2) atom.

The Mn–CO bond lengths (average 1.80(3) Å) are very typical for manganese(I) carbonyls and are almost identical for both manganese atoms. Only the Mn(2)–C(21) distance (1.81 Å) is slightly shorter than the analogous Mn(1)–C(11) (1.85 Å) and, although the difference may have no statistical

TABLE II. Final Atomic Coordinates (× 10^4) and Thermal Parameters (× 10^2) of Compound **IX**

	x/a	y/b	z/c	B_{eq}
Mn(1)	8822(1)	1838(1)	7683(2)	4.08(9)
N(101)	9723(6)	1386(5)	9003(8)	3.46(53)
C(102)	10616(9)	1399(6)	9186(11)	3.57(69)
C(103)	11194(9)	1139(7)	10139(12)	4.47(76)
C(104)	10801(10)	843(7)	10933(11)	4.36(77)
C(105)	9831(9)	818(7)	10762(11)	3.56(70)
C(106)	9380(11)	505(7)	11550(11)	4.59(80)
C(107)	8472(12)	516(7)	11313(11)	4.60(83)
C(108)	7951(10)	809(7)	10350(11)	3.74(72)
C(109)	6987(13)	864(8)	10061(16)	6.34(113)
C(110)	6584(11)	1167(9)	9087(17)	6.25(103)
C(111)	7106(10)	1470(7)	8424(13)	5.02(81)
N(112)	7958(7)	1450(6)	8603(9)	1.77(53)
C(113)	8375(8)	1150(7)	9539(13)	3.96(78)
C(114)	9319(10)	1092(7)	9801(10)	3.16(68)
C(11)	8904(8)	2813(9)	8359(11)	4.39(75)
O(11)	8949(7)	3416(6)	8755(9)	6.95(64)
C(12)	9623(10)	2096(8)	6867(11)	5.30(85)
O(12)	10110(8)	2222(6)	6312(9)	7.49(69)
C(13)	7956(10)	2191(7)	6655(14)	6.10(83)
O(13)	7394(8)	2418(6)	5960(10)	11.03(79)
C(10)	8646(7)	777(7)	6961(9)	2.43(60)
N(10)	8452(7)	257(7)	6431(9)	4.33(61)
Mn(2)	7893(1)	−638(1)	5395(2)	3.73(10)
N(201)	6943(6)	−683(6)	6326(8)	2.87(51)
C(202)	6891(11)	−1182(9)	7134(13)	5.03(85)
C(203)	6255(11)	−1083(11)	7781(13)	5.79(96)
C(204)	5673(10)	−490(12)	7613(13)	5.13(93)
C(205)	5681(10)	67(11)	6794(13)	4.73(89)
C(206)	5108(10)	715(11)	6527(17)	6.65(107)
C(207)	5132(10)	1225(10)	5730(17)	6.04(103)
C(208)	5775(10)	1062(9)	5020(14)	4.92(87)
C(209)	5845(11)	1540(9)	4121(18)	6.15(104)
C(210)	6448(12)	1340(9)	3550(14)	5.43(88)
C(211)	7045(9)	676(9)	3834(12)	4.51(76)
N(212)	7015(8)	239(6)	4700(10)	4.01(60)
C(213)	6395(9)	421(7)	5294(11)	3.50(72)
C(214)	6333(10)	−76(8)	6180(11)	3.31(72)
C(21)	7377(10)	−1435(9)	4525(11)	4.49(78)
O(21)	7092(8)	−1962(7)	4003(9)	7.36(71)
C(22)	8634(11)	−1351(8)	6156(12)	4.98(81)
O(22)	9069(7)	−1842(6)	6619(10)	7.45(69)
C(23)	8659(11)	−472(8)	4547(12)	4.69(85)
O(23)	9183(8)	−390(7)	4005(10)	7.92(75)
P	3708(3)	1403(3)	8956(4)	5.08(25)
F(1)	4236(7)	1837(5)	8221(8)	8.55(61)
F(2)	3192(6)	942(6)	9723(7)	7.82(57)
F(3)	4592(15)	831(30)	9405(33)	9.66(189)
F(4)	3432(39)	765(30)	8018(42)	9.40(269)
F(5)	4066(38)	1924(20)	9968(38)	9.88(229)
F(6)	2899(21)	1880(24)	8399(28)	7.95(196)
F(3)′	4241(25)	709(23)	8979(43)	12.87(281)
F(4)′	3034(47)	993(35)	8050(47)	10.20(372)
F(5)′	4318(52)	1867(52)	9795(49)	24.51(535)
F(6)′	3027(34)	2120(24)	9011(33)	9.85(262)

TABLE III. Bond Lengths (Å) for Compound **IX**

N(101)–Mn(1)	2.069(9)
N(112)–Mn(1)	2.043(12)
C(11)–Mn(1)	1.847(15)
C(12)–Mn(1)	1.813(17)
C(13)–Mn(1)	1.748(14)
C(10)–Mn(1)	2.004(11)
C(102)–N(101)	1.328(17)
C(114)–N(101)	1.384(18)
C(103)–C(102)	1.405(18)
C(104)–C(103)	1.371(22)
C(105)–C(104)	1.445(20)
C(106)–C(105)	1.429(21)
C(114)–C(105)	1.379(17)
C(107)–C(106)	1.348(23)
C(108)–C(107)	1.397(18)
C(109)–C(108)	1.437(24)
C(113)–C(108)	1.447(22)
C(110)–C(109)	1.357(27)
C(111)–C(110)	1.373(26)
N(112)–C(111)	1.266(18)
C(113)–N(112)	1.322(17)
C(114)–C(113)	1.406(19)
O(11)–C(11)	1.132(18)
O(12)–C(12)	1.145(21)
O(13)–C(13)	1.154(18)
N(10)–C(10)	1.107(15)
Mn(2)–N(10)	2.064(11)
N(201)–Mn(2)	2.055(11)
N(212)–Mn(2)	2.062(11)
C(21)–Mn(2)	1.810(14)
C(22)–Mn(2)	1.785(14)
C(23)–Mn(2)	1.769(17)
C(202)–N(201)	1.342(19)
C(214)–N(201)	1.368(17)
C(203)–C(202)	1.407(26)
C(204)–C(203)	1.322(25)
C(205)–C(204)	1.403(25)
C(206)–C(205)	1.395(24)
C(214)–C(205)	1.406(24)
C(207)–C(206)	1.335(28)
C(208)–C(207)	1.490(27)
C(209)–C(208)	1.420(28)
C(213)–C(208)	1.428(20)
C(210)–C(209)	1.327(29)
C(211)–C(210)	1.439(21)
N(212)–C(211)	1.332(19)
C(213)–N(212)	1.362(20)
C(214)–C(213)	1.423(20)
O(21)–C(21)	1.139(18)
O(22)–C(22)	1.141(17)
O(23)–C(23)	1.166(22)

significance (about 3σ [16]), the tendency is in accordance with the possible more π-acidic ability of the CNMn(2) group as compared with that of the NCMn(1) group.

The binuclear bis-dicarbonyl complex **XII** reacted very readily with $HBF_4 \cdot Et_2O$ in NCMe giving *cis-trans*-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(NCMe)]$^+$ (**IV**) and *cis-trans*-[Mn(CNBF$_3$)(CO)$_2$(bipy)(P(OPh)$_3$)] (**VII**). This was not totally evident in the IR of the reaction mixture because of the accidental coincidence of the ν(CO) absorptions due to **IV** and **VII** (Table I), but addition of NEt_3 transformed **VII** into the neutral cyanide *cis-trans*-[Mn(CN)(CO)$_2$(bipy)(P(OPh)$_3$)]

TABLE IV. Bond Angles (°) for Compound **IX**

N(112)–Mn(1)–N(101)	79.3(4)
C(11)–Mn(1)–N(101)	89.2(5)
C(11)–Mn(1)–N(112)	90.4(5)
C(12)–Mn(1)–N(101)	98.2(5)
C(12)–Mn(1)–N(112)	175.1(5)
C(12)–Mn(1)–C(11)	93.8(6)
C(13)–Mn(1)–N(101)	172.8(7)
C(13)–Mn(1)–N(112)	93.6(6)
C(13)–Mn(1)–C(11)	90.5(6)
C(13)–Mn(1)–C(12)	89.0(7)
C(10)–Mn(1)–N(101)	92.3(4)
C(10)–Mn(1)–N(112)	86.3(5)
C(10)–Mn(1)–C(11)	176.1(5)
C(10)–Mn(1)–C(12)	89.6(6)
C(10)–Mn(1)–C(13)	87.6(5)
C(102)–N(101)–Mn(1)	127.6(9)
C(114)–N(101)–Mn(1)	113.9(8)
C(114)–N(101)–C(102)	118.3(10)
C(103)–C(102)–N(101)	125.0(13)
N(112)–C(111)–C(110)	125.7(14)
C(111)–N(112)–Mn(1)	130.3(10)
C(113)–N(112)–Mn(1)	113.1(9)
C(113)–N(112)–C(111)	116.5(13)
N(112)–C(113)–C(108)	126.2(11)
C(114)–C(113)–C(108)	113.0(12)
C(114)–C(113)–N(112)	120.6(13)
C(105)–C(114)–N(101)	120.9(13)
C(113)–C(114)–N(101)	113.0(11)
C(113)–C(114)–C(105)	126.0(14)
O(11)–C(11)–Mn(1)	178.7(12)
O(12)–C(12)–Mn(1)	176.0(12)
O(13)–C(13)–Mn(1)	178.5(16)
N(10)–C(10)–Mn(1)	168.2(10)
Mn(2)–N(10)–C(10)	171.2(10)
N(201)–Mn(2)–N(10)	84.5(4)
N(212)–Mn(2)–N(10)	83.5(4)
N(212)–Mn(2)–N(201)	78.6(5)
C(21)–Mn(2)–N(10)	177.7(6)
C(21)–Mn(2)–N(201)	93.3(6)
C(21)–Mn(2)–N(212)	96.7(5)
C(22)–Mn(2)–N(10)	91.3(5)
C(22)–Mn(2)–N(201)	95.9(6)
C(22)–Mn(2)–N(212)	172.7(6)
C(22)–Mn(2)–C(21)	88.3(6)
C(23)–Mn(2)–N(10)	92.1(6)
C(23)–Mn(2)–N(201)	172.5(6)
C(23)–Mn(2)–N(212)	94.4(6)
C(23)–Mn(2)–C(21)	90.2(7)
C(23)–Mn(2)–C(22)	90.9(7)
C(202)–N(201)–Mn(2)	128.7(9)
C(214)–N(201)–Mn(2)	115.7(9)
C(214)–N(201)–C(202)	115.2(12)
C(203)–C(202)–N(201)	122.0(14)
N(212)–C(211)–C(210)	120.4(15)
C(211)–N(212)–Mn(2)	128.1(10)
C(213)–N(212)–Mn(2)	112.8(9)
C(213)–N(212)–C(211)	118.8(11)
N(212)–C(213)–C(208)	122.4(13)
C(214)–C(213)–C(208)	119.2(14)
C(214)–C(213)–N(212)	118.4(12)
C(205)–C(214)–N(201)	126.2(13)
C(213)–C(214)–N(201)	113.1(13)
C(213)–C(214)–C(205)	120.7(13)
O(21)–C(21)–Mn(2)	176.2(13)
O(22)–C(22)–Mn(2)	175.8(13)
O(23)–C(23)–Mn(2)	177.2(13)

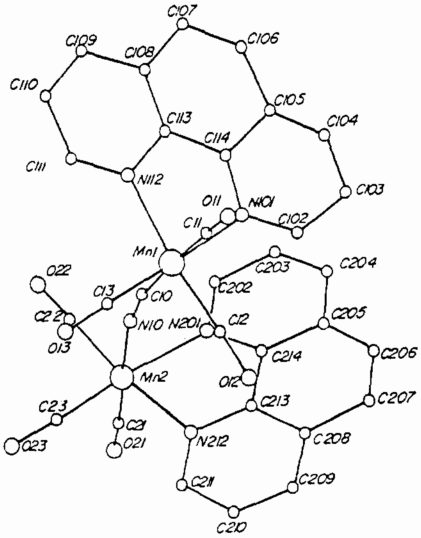


Fig. 1. The molecular structure of $[\{fac\text{-Mn(CO)}_3\text{(phen)}\}_2\text{-}(\mu\text{-CN})]^+$ with the atomic numbering scheme.

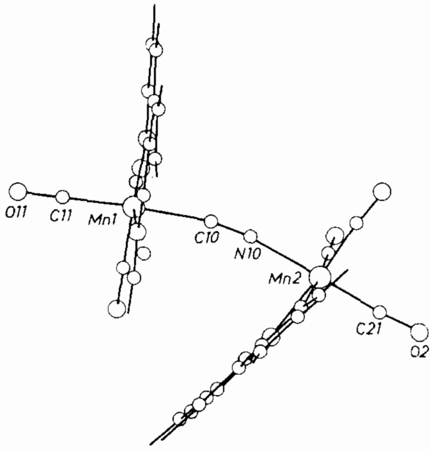


Fig. 2. Another view of the cation $[\{fac\text{-Mn(CO)}_3\text{(phen)}\}_2\text{-}(\mu\text{-CN})]^+$ showing the linearity of the MnCNMe group and the relative position of the phenanthrolines.

(**II**) which has the ν(CO) bands well separated from those of the cationic complex **IV**. Similarly, it was observed that reaction with $HBF_4 \cdot Et_2O$ in NCMe followed by addition of NEt_3 (ii and iii in Scheme 2) splitted the cyanide bridged complexes **X** and **XI** in the mononuclear species **VIIIa** + **IV** and **II** + *fac*-$[Mn(CO)_3(bipy)(NCMe)]^+$ [4] respectively, while the protonation of **IX** was slower and more difficult, leading mainly to decomposition. It therefore appears that the H^+ attacks the N atom of the μ-CN groups separating the transient cation $[\{Mn\}_a\text{–CNH}]^+$ (that subsequently gives $\{Mn\}_a\text{–CNBF}_3$*) and generating

---

*In the case of *fac*-$[Mn(CNBF_3)(CO)_3(bipy)]$, it was confirmed independently by generating it from *fac*-$[Mn(CN)-(CO)_3(bipy)]$ and $HBF_4 \cdot Et_2O$ in MeCN or CH_2Cl_2. This compound has ν(CO) maxima in CH_2Cl_2 at 2054s, 1972s and 1952s and ν(CN) at 2199 cm^{-1}.

the fragment $\{Mn\}_b^+$ that readily coordinates an MeCN molecule giving the cation $[\{Mn\}_b(NCMe)]^+$. This sequence seems plausible in view of the fact that no dissociation was detected (by IR) on the MeCN solutions of the μ-CN complexes, observations that are in consonance with other results [3]. The protonation reaction ii (Scheme 2) resembles that observed on the terminal isocyanide ligands in some electron rich complexes [18], and therefore it may be readily related with the angle $CN\{Mn\}_b$.

Experimental

All reactions were carried out under dry argon. The complexes *fac*-[MnBr(CO)$_3$(bipy)] [4] and *cis-trans*-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)$_2$]ClO$_4$ [4], were prepared by published methods. IR spectra were recorded using a Perkin-Elmer 298 spectrophotometer and calibrated against 1601.4 cm^{-1} polystyrene absorption.

cis-trans-[MnI(CO)$_2$(bipy)(P(OPh)$_3$)] (I)

To a solution of *cis-trans*-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)$_2$]ClO$_4$ (0.5 g, 0.51 mmol) in acetone (40 ml), solid KI (0.40 g, 2.41 mmol) is added and the mixture is stirred in the absence of light for 30 min. The solvent is removed *in vacuo* and the residue is washed three times with hexane (15 ml) to eliminate the free P(OPh)$_3$. Acetone (40 ml) is added and the treatment restarted. The procedure is repeated every 30 min until the ν(CO) IR spectrum of the residue no longer shows bands of the starting cationic dicarbonyl (about 6 to 7 times). The final residue is dissolved in CH$_2$Cl$_2$ (25 ml) filtered and concentrated to *ca.* 4 ml. Addition of hexane gives purple microcrystals of **I** (0.30 g, 84%).

cis-trans-[Mn(CN)(CO)$_2$(bipy)(P(OPh)$_3$)] (II)

To a solution of **I** (0.252 g, 0.36 mmol) in CH$_2$Cl$_2$ (30 ml), solid AgCN (0.058 g, 0.43 mmol) is added and the mixture is stirred in the absence of light for 20 min. The orange solution is filtered and stirred vigorously with 10 ml of a 1 M aqueous solution of Na$_2$S$_2$O$_3$ for 10 min. The organic layer is then dried with MgSO$_4$ for 30 min, filtered and concentrated to *ca.* 4 ml. Addition of hexane gives a solid that is recrystallized from CH$_2$Cl$_2$:ethanol as orange crystals (0.16 g, 74%).

cis-trans-[Mn(NCS)(CO)$_2$(bipy)(P(OPh)$_3$)] (IIIa)

A mixture of *cis-trans*-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)$_2$]ClO$_4$ (0.4 g, 0.41 mmol) and KNCS (0.048 g, 0.49 mmol) in acetone (15 ml) is refluxed for 30 min. The resulting red solution is evaporated and the resulting oil is washed three times with hexane (20 ml). The residue is extracted with a 1:2 mixture of diethylether:CH$_2$Cl$_2$ (2 × 50 ml). The extracts are evaporated *in vacuo* to give a red solid that is recrystallized from CH$_2$Cl$_2$:hexane as red microcrystals (0.11 g, 42%) of the CH$_2$Cl$_2$ solvate [Mn(NCS)(CO)$_2$(bipy)(P(OPh)$_3$)]·CH$_2$Cl$_2$ (*Anal.* Found (calc.): C, 53.9(53.4); H, 3.46(3.47); N, 6.14(5.84)) that loses the solvent on prolonged evacuation.

The compound **IIIb** was similarly prepared from *cis-trans*-[Mn(CO)$_2$(phen)(P(OPh)$_3$)$_2$]ClO$_4$.

cis-trans-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(NCMe)]PF$_6$ (IV)

To a solution of **I** (0.19 g, 0.27 mmol) in CH$_2$Cl$_2$ (15 ml), freshly distilled MeCN (3 ml) and solid TlPF$_6$ (0.3 g, 0.86 mmol) are added and the mixture is stirred for 1 h at room temperature. The resulting solution is filtered and concentrated to *ca.* 2 ml. Addition of diethylether gives yellow microcrystals of **IV** (0.12 g, 61%).

cis-trans-[Mn(CO)$_2$(bipy)(P(OPh)$_3$)(CNMe)]PF$_6$ (V)

To a solution of **II** (0.16 g, 0.27 mmol) in thf (10 ml), are added CH$_3$I (2 ml) and KPF$_6$ (0.10 g, 0.54 mmol) and the mixture is stirred for 4 days at room temperature. The resulting solution is filtered and concentrated to *ca.* 2 ml. Addition of diethylether gives a precipitate that is recrystallized from CH$_2$Cl$_2$:ethanol as orange crystals (0.13 g, 63%).

cis-trans-[Mn(CNBF$_3$)(CO)$_2$(bipy)(P(OPh)$_3$)] (VII)

To a solution of **II** (0.045 g, 0.075 mmol) in CH$_2$Cl$_2$ (5 ml), the reagent HBF$_4$·Et$_2$O (0.1 ml) is added and the mixture is stirred at room temperature for 15 min. The resulting yellow solution is concentrated to 1 ml and diethylether (20 ml) is added to give a yellow precipitate that was washed with ether, redissolved in CH$_2$Cl$_2$, reprecipitated with ether and dried *in vacuo* for 4 h to give a yellow powder (0.032 g, 63%).

fac-[Mn(CN)(CO)$_3$(bipy)] (VIIIa)

To a solution of *fac*-[MnBr(CO)$_3$(bipy)] (0.5 g, 1.3 mmol) in CH$_2$Cl$_2$ (25 ml), solid AgCN (0.22 g, 1.6 mmol) is added and the mixture is stirred overnight at room temperature. The resulting solution is filtered and concentrated to *ca.* 3 ml. Addition of hexane gave yellow solid that is crystallized from CH$_2$Cl$_2$:hexane (0.35 g, 82%).

Using AgNCS the known *fac*-[Mn(NCS)(CO)$_3$(bipy)] [5], was similarly prepared with a 73% yield.

[{fac-Mn(CO)$_3$(phen)}$_2$(μ-CN)]PF$_6$ (IX) and the other μ-CN complexes

A mixture of *fac*-[Mn(CN)(CO)$_3$(phen)] (0.15 g, 0.43 mmol), *fac*-[MnBr(CO)$_3$(phen)] (0.17 g, 0.43 mmol) and TlPF$_6$ (0.19 g, 0.6 mmol) in CH$_2$Cl$_2$ (20 ml) is stirred for 5 h in the absence of light. The resulting solution is filtered and concentrated to 2 ml. Addition of Et$_2$O gives a precipitate that is recrystallized from CH$_2$Cl$_2$:EtOH as yellow needles (0.33 g, 94%).

The complexes **X**, **XI** and **XII** were similarly prepared in CH_2Cl_2 or thf (**XII**) from **VIIIa** + **I**, **II** + *fac*-[MnBr(CO)$_3$(bipy)] and **II** + **I** respectively. Reaction times and yields are **X**, 20 h, 45%; **XI**, 3 days, 62% and **XII**, 20 h, 45%.

[{fac-Mn(CO)$_3$(bipy)}$_2$(μ-NCS)]PF$_6$ (XIII)

To a solution of *fac*-[Mn(NCS)(CO)$_3$(bipy)] (0.15 g, 0.42 mmol) and *fac*-[MnBr(CO)$_3$(bipy)] (0.16 g, 0.42 mmol) in 20 ml of CH_2Cl_2, solid $TlPF_6$ (0.2 g, 0.63 mmol) is added and the mixture is stirred at room temperature for 6 days. The solution is filtered and concentrated. Addition of Et_2O gives a precipitate that is recrystallized from CH_2Cl_2:Et_2O as yellow needles (0.27 g, 80%).

Structure determination of compound [{Mn(CO)$_3$(phen)}$_2$(μ-CN)]PF$_6$ (IX)

Crystal data

$C_{31}H_{16}N_5O_6Mn_2\cdot PF_6$, $F_w = 809.34$, monoclinic, $a = 15.202(3)$, $b = 16.886(4)$, $c = 12.694(3)$ Å, $\beta = 102.35(2)°$, $V = 3259(2)$ Å^3, $P2_1/c$, $Z = 4$, $D_x = 1.649$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, (Mo Kα) = 9.56 cm^{-1}. Room temperature.

A yellow acircular crystal (0.08 × 0.08 × 0.15 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determinated from 25 reflections ($4 \leqslant \theta \leqslant 9°$). Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, scan width 1°, scan speed 0.03° s^{-1}. Three reflections were measured each two hours as orientation and intensity control, significant variations were not observed. 1520 independent reflections were measured in the range $2 \leqslant \theta \leqslant 22.5°$; 1496 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz-polarization, but no absorption, corrections were made. The structure was solved by direct methods, using the MULTAN system of computer programs [19] and isotropically and anisotropically refined by full-matrix least-squares method, using the SHELX76 computer program [20]. The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.020|F_o|^2)^{-1}$, f, f' and f'' were taken from International Tables of X-ray Crystallography [21]. After three isotropic refinements cycles, a disorder in PF_6 ion was observed from a difference synthesis. Four F atoms were refined in two sites with 0.5 as occupancy factor according the height of peaks. The position of C and N of cyano bridge was permuted, giving the final coordinates for those positions where the thermal coefficients and R factor had the 'best' values. Hydrogen atoms were computed and refined with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R was 0.053 ($R_w = 0.057$) for all observed reflections.

Acknowledgements

We thank the Spanish C.A.I.C.Y.T. (Project 1184/81) for financial support, the Spanish Ministerio de Educación y Ciencia for a grant (M.C.C.) and the University of Barcelona for a grant.

References

1 G. J. Baird and S. G. Davies, *J. Organomet. Chem., 262,* 215 (1984).
2 G. A. Carriedo, M. C. Crespo, V. Riera, M. G. Sanchez, M. L. Valin, D. Moreiras and X. Solans, *J. Organomet. Chem., 302,* 47 (1986).
3 G. J. Baird, S. G. Davies, S. D. Moon, S. J. Simpson and R. H. Jones, *J. Chem. Soc., Dalton Trans.,* 1479 (1985) and refs. therein.
4 R. Usón, V. Riera, J. Gimeno and M. Laguna, *Transition Met. Chem., 2,* 123 (1977).
5 M. F. Farona and A. Wojcicki, *Inorg. Chem., 4,* 857 (1965).
6 D. Miguel and V. Riera, *J. Organomet. Chem., 293,* 379 (1985).
7 J. Fayos and M. Ulibarri, *Acta Crystallogr., Sect. B, 38,* 3086 (1982).
8 J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc., 98,* 3160 (1976).
9 D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc., 100,* 366 (1978).
10 M. J. Wovkulich, J. L. Atwood, L. Canada and J. D. Atwood, *Organometallics, 4,* 867 (1985) and refs. therein.
11 P. J. C. Walker and R. J. Mawby, *J. Chem. Soc. A,* 3006 (1971).
12 D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. Nucl. Chem., 21,* 33 (1961).
13 G. O. Morpurgo, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.,* 787 (1984).
14 G. L. Breneman, D. M. Chipman, C. J. Galles and R. A. Jacobson, *Inorg. Chim. Acta, 3,* 447 (1969). R. G. Little and R. J. Doedens, *Inorg. Chem., 12,* 840, 844 (1973).
15 (a) M. L. Valin, D. Moreiras, X. Solans, M. Font-Altaba, J. Solans, F. J. García-Alonso, V. Riera and M. Vivanco, *Acta Crystallogr. Sect. C, 42,* 417 (1986); (b) M. L. Valin, D. Moreiras, X. Solans, M. Font-Altaba, J. Solans, F. J. García-Alonso, V. Riera and M. Vivanco, *Acta Crystallogr. Sect. C, 41,* 1312 (1985).
16 A. C. Sarapu and R. F. Fenske, *Inorg. Chem., 11,* 3021 (1972).
17 B. A. Frenz and J. A. Ibers, *Inorg. Chem., 11,* 1109 (1972).
18 E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem., 22,* 209, 294 (1983).
19 P. Main, S. L. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, 'MULTAN', an automatic system of computer programs for crystal structure determination from X-ray diffraction data, University of York, U.K. and University of Louvain, Belgium, 1980.
20 G. M. Sheldrick, 'SHELX', a computer program for crystal structure determination, University of Cambridge, U.K., 1976.
21 'International Tables of X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974, p. 99–102 and 150.