Novel N-bound thallium(I) complexes of redox-active cyanomanganese carbonyl ligands: cyanide as a μ3-κ*C*:κ*N*:κ*N* triply bridging ligand

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The cyanomanganese carbonyls *trans*-[Mn(CN)(CO)(dppm)$_2$], and *cis*- and *trans*-[Mn(CN)(CO)$_2${P(OR)$_3$}-(dppm)] (R = Ph or Et, dppm = Ph$_2$PCH$_2$PPh$_2$) react with TlPF$_6$ to give [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$]-[PF$_6$] **1**, [{Tl(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = *cis*-(CO)$_2${P(OR)$_3$}(dppm), R = Ph **2** or Et **3**] and [Tl{(μ-NC)MnL$_x$}$_2$]-[PF$_6$] [L$_x$ = *trans*-(CO)$_2${P(OR)$_3$}(dppm), R = Ph **4** or Et **5**] respectively. Complexes **1** and **3** have been structurally characterised by single-crystal X-ray diffraction methods; the former is pyramidal at thallium while the latter provides a rare example of a μ3-κ*C*:κ*N*:κ*N* cyanide ligand N-bonded to two thallium atoms and C-bonded to manganese.

Thallium(I) salts of poorly co-ordinating anions, such as TlPF$_6$, are widely used as halide abstraction agents in the synthesis of organometallic and co-ordination complexes of transition metals. For example, we have used such salts in the preparation of cyanide-bridged complexes such as [(CO)$_2$Rh{(μ-NC)MnL$_x$}$_2$]-[PF$_6$] [L$_x$ = *trans*-(CO)$_2${P(OEt)$_3$}(dppm), dppm = Ph$_2$PCH$_2$-PPh$_2$], from [{Rh(μ-Cl)(CO)$_2$}$_2$] and *trans*-[Mn(CN)(CO)$_2$-{P(OEt)$_3$}(dppm)].[1] The main driving force for these abstraction reactions is the insolubility of thallium(I) halides although the poor co-ordinating ability of Tl$^+$, a weak Lewis acid,[2] is also important. Only rarely is thallium incorporated into the product, as for example in [TlPt$_3$(CO)$_3$(PCy$_3$)$_3$][RhCl$_2$(η-cod)] (Cy = cyclohexyl, cod = cyclooecta-1,5-diene), synthesised from TlPF$_6$, [Pt$_3$(CO)$_3$(PCy$_3$)$_3$] and [{Rh(μ-Cl)(cod)}$_2$].[3]

Thallium(I) is rarely bound to simple monodentate N-donors such as NH$_3$[2] though complexes of polydentate ligands are more stable.[4] However, we now report the surprising observation that Tl$^+$ acts as a Lewis acid towards the cyanomanganese carbonyls *trans*-[Mn(CN)(CO)(dppm)$_2$][5] and *cis*- and *trans*-[Mn(CN)(CO)$_2${P(OR)$_3$}(dppm)] (R = Ph or Et),[6] giving novel bi-, tri- and tetra-nuclear, Tl–N bonded cyanide complexes, including [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$], which shows pyramidal geometry at thallium, and [{Tl(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = *cis*-(CO)$_2${P(OEt)$_3$}(dppm)], which contains an unusual μ3-κ*C*:κ*N*:κ*N* bridge.

Results and Discussion

Synthesis of [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] 1

On adding solid TlPF$_6$ to *trans*-[Mn(CN)(CO)(dppm)$_2$] (1:1 ratio) in thf, an orange solution was formed from which an orange solid was precipitated on addition of a 1:1 mixture of diethyl ether and *n*-hexane; crystallisation, by allowing *n*-hexane to diffuse into a solution of the complex in thf, gave the pure product which analysed (C, H and N; Table 1) as [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] **1** (Scheme 1). Complex **1** slowly loses thf in the solid state and *in vacuo* complete solvent loss results in a product analysing as [Tl(μ-NC)Mn-(CO)(dppm)$_2$][PF$_6$].

The IR spectrum of **1** in thf (Table 1) shows one strong carbonyl band at 1874 cm^{-1}, shifted by *ca*. 10 cm^{-1} to higher energy from that of *trans*-[Mn(CN)(CO)(dppm)$_2$],[5] in accord with N-co-ordination of the terminal cyanide ligand. Cyanide bridge formation is usually also accompanied by an increase

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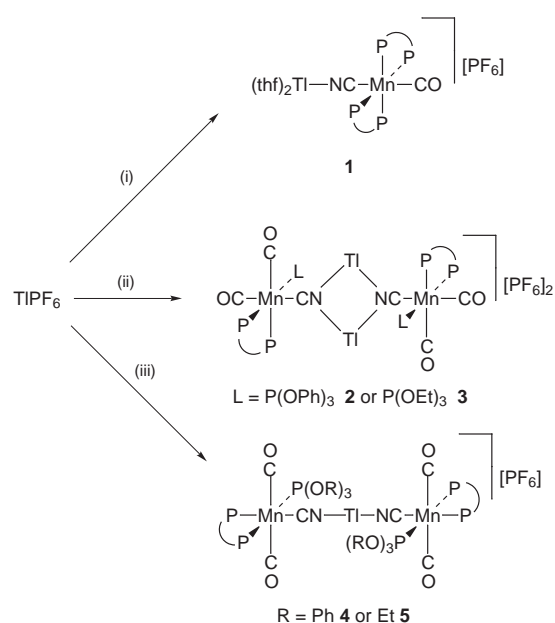
Scheme 1 (i) *trans*-[Mn(CN)(CO)(dppm)$_2$]; (ii) *cis*-[Mn(CN)(CO)$_2$-{P(OR)$_3$}(dppm)]; (iii) *trans*-[Mn(CN)(CO)$_2${P(OR)$_3$}(dppm)]

in energy of ν(CN).[7] For **1**, however, the weak cyanide band, at 2058 cm^{-1}, is shifted to *lower* energy (by *ca*. 20 cm^{-1}) from that of *trans*-[Mn(CN)(CO)(dppm)$_2$]. A decrease in ν(CN) can occur when a cyanide bridge is formed with a strongly withdrawing N-bound fragment. In **1** (and other complexes described below) the positive charge on Tl$^+$ presumably induces increased back bonding from C-bound manganese to the π*(CN) orbital.

One cyanide absorption is also observed in Nujol but in CH$_2$Cl$_2$ complex **1** shows a weak shoulder at *ca*. 2030 cm^{-1} on the main band at 2046 cm^{-1}. Moreover, the slow growth with time of a band at 1936 cm^{-1} indicates the decomposition of **1** by a pathway which affords the unco-ordinated Mn^{II} cation *trans*-[Mn(CN)(CO)(dppm)$_2$]$^+$.

Although the Tl–C bond in Tl^{III} cyanide complexes such as [Tl(CN)$_4$]$^-$ is said to be strong,[8] N-bonded cyano complexes of thallium(I) are uncommon or ill-defined. For example, although each thallium(I) atom has five nearest neighbour cyanide ions in the crystal structure of Tl$_2$[Pt(CN)$_4$] the Tl···N distances are long, at *ca*. 2.8–3.0 Å.[9] Similarly, in Tl[Au(CN)$_4$] the thallium ions are irregularly 'co-ordinated' with Tl···N distances

Table 1 Analytical and IR spectroscopic data for $[Tl_m\{(\mu\text{-}NC)MnL_x\}_n]^{z+}$

	L_x	m	n	z^c	Colour	Yield (%)	C	H	N	v(CN)	v(CO)^d
							Analysis (%)^a			**IR^b/cm^{-1}**	
1	trans-(CO)(dppm)$_2$	1	1	1	Orange	66	52.2 (52.5)	4.4 (4.1)	1.0 (1.5)^e	2058w^f	1874s^f
2	cis-(CO)$_2${P(OPh)$_3$}(dppm)	2	2	2	Cream	30	47.1 (46.8)	3.1 (3.2)	1.1 (1.2)	2080 (sh), 2060w 2083 (sh), 2063w^g	1973vs, 1924s 1969vs, 1917vs^g
3	cis-(CO)$_2${P(OEt)$_3$}(dppm)	2	2	2	White	45	39.1 (39.4)	3.5 (3.6)	1.2 (1.4)	2072w, 2053m 2049s^g	1961vs, 1907s 1956vs, 1907vs^g
4	trans-(CO)$_2${P(OPh)$_3$}(dppm)	1	2	1	Cream	61	54.9 (54.4)	3.7 (4.2)	1.4 (1.2)	2080vw (sh), 2066w 2067m, 2042 (sh)^g	1933vs (2011) 1925vs (2010)^g
5	trans-(CO)$_2${P(OEt)$_3$}(dppm)	1	2	1	Pale yellow	45	47.6 (47.4)	4.4 (4.3)	1.6 (1.6)	2078, 2061, 2054w 2078w, 2070 (sh)^g	1918vs (2000) 1912vs (2030)^g

^{a} Calculated in parentheses. ^{b} In CH$_2$Cl$_2$ unless stated otherwise; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. ^{c} Cations isolated as [PF$_6$]$^-$ salts. ^{d} Very weak A-mode given in parentheses. ^{e} Analysed as a 1:2 thf solvate (crystals grown from thf–n-hexane). ^{f} In thf. ^{g} In Nujol.
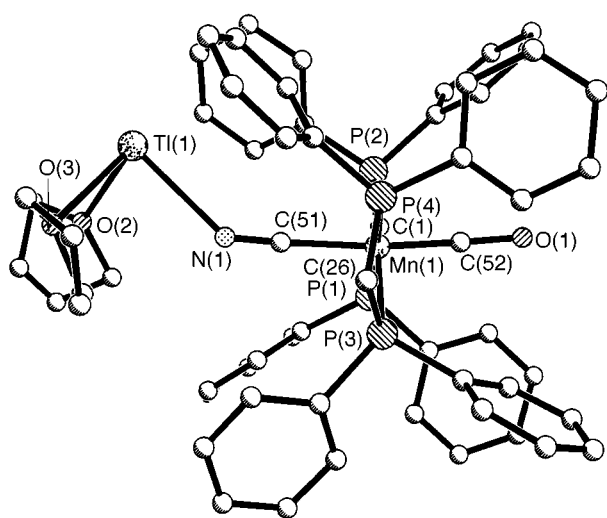

Fig. 1 Molecular structure of [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] **1** showing the atom labelling scheme; only the major image of the molecule is shown. All hydrogen atoms and the [PF$_6$]$^-$ anion have been omitted for clarity

ranging from 2.85 to 3.2 Å.[10] Thus, given the spectroscopic evidence for a Tl–NC bond in the well-defined molecular complex **1**, an attempt was made to determine the structure by a single-crystal X-ray diffraction study.

Crystal structure of [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] 1

Orange crystals of square plate-like habit were grown by allowing n-hexane to diffuse slowly into a solution of **1** in thf at −10 °C. For X-ray diffraction data collection a single crystal was rapidly mounted in silicone grease, in the presence of the mother-liquors from the crystallisation process. Even so, powdering of the crystal was still observed due to the loss of co-ordinated thf; the diffraction data were therefore relatively poor, preventing accurate modelling of the structure and resulting in large residual values. Moreover the structure is severely disordered in the region around the thallium atom further limiting the quantitative information available. Thus, the structure is discussed only qualitatively with respect to the stoichiometry and geometry of the major image of the complex cation.

The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The manganese atom has a distorted octahedral geometry, as found in the ligand trans-[Mn(CN)(CO)(dppm)$_2$] itself[11] and its N-bound complexes with RhCl(CO)$_2$[1] and FeI(NO)$_2$.[12] The two bidentate dppm ligands occupy the four equatorial sites; the axial sites are occupied by the carbonyl and cyanide ligands. The thallium

Table 2 Selected bond lengths (Å) and angles (°) for complex **1** *

Tl(1)–N(1)	2.63(2)	O(1)–C(52)	1.27(2)
Tl(1)–O(2)	2.74(3)	Mn(1)–C(52)	1.707(13)
Tl(1)–O(3)	2.75(3)	Mn(1)–P(1)	2.270(4)
Tl(1′)–N(1)	2.57(2)	Mn(1)–P(2)	2.269(4)
N(1)–C(51)	1.14(2)	Mn(1)–P(3)	2.275(4)
Mn(1)–C(51)	1.97(2)	Mn(1)–P(4)	2.282(4)
N(1)–Tl(1)–O(2)	87.0(6)	N(1)–C(51)–Mn(1)	175.6(14)
N(1)–Tl(1)–O(3)	86.0(6)	O(1)–C(52)–Mn(1)	178.0(12)
O(2)–Tl(1)–O(3)	81.7(9)	P(2)–Mn(1)–P(1)	74.0(2)
C(51)–N(1)–Tl(1)	139.7(12)	P(3)–Mn(1)–P(4)	73.76(14)
C(51)–N(1)–Tl(1′)	126.4(12)		

* Tl(1′) occupancy 0.35(2); Tl(1) occupancy 0.65(2).

atom is disordered over two sites in the ratio 65(2):35(2) [Tl(1) and Tl(1′) respectively]; the thf ligands are also disordered. In the majority thallium atom position, Tl(1) is N-bound to the cyanide group of the manganese ligand [Tl(1)–N(1) = 2.63(2) Å] and further co-ordinated to the oxygen atoms of two thf molecules [Tl(1)–O(2) = 2.74(3), Tl(1)–O(3) = 2.75(3) Å]. There is one short [PF$_6$]$^-$···Tl contact [Tl(1)···F(1) 3.27(3) Å]. The valence angles at Tl(1) are acute [81.7(9)–87.0(6)°] perhaps indicating the presence of a stereochemically active lone pair at the Tl^I centre. The bound atoms and the phenyl rings of the dppm moieties of the manganese ligand provide steric protection of the labile thallium (see Fig. 1) although given the presence of the short F···Tl contact this shielding is not complete.

Synthesis of [{Tl(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = cis-(CO)$_2$-{P(OR)$_3$}(dppm), R = Ph 2 or Et 3]

The complexes cis-[Mn(CN)(CO)$_2${P(OR)$_3$}(dppm)] (R = Ph or Et) also react with TlPF$_6$ in a 1:1 ratio to give moderate yields of white solids which analyse (Table 1) as 1:1 adducts but which are the dimeric complexes [{Tl(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = cis-(CO)$_2${P(OR)$_3$}(dppm), R = Ph 2 or Et 3] (Scheme 1). Although the carbonyl IR spectra of **2** and **3** show the two bands expected for the cis-Mn(CO)$_2$ group, the cyanide stretching region is more complex. {Note that v(CN) for cis-[Mn(CN)(CO)$_2${P(OR)$_3$}(dppm)] is again shifted to lower energy on N-co-ordination to Tl^I, cf. **1**.} For example, in CH$_2$Cl$_2$ complex **2** shows two v(CN) absorptions, one weak and sharp at 2060 cm^{-1} and another, weaker and broader, at 2080 cm^{-1}; the spectrum is similar in Nujol. For **3** in CH$_2$Cl$_2$, the two cyanide bands occur at 2053 and 2072 cm^{-1}, somewhat lower in energy than those for **2** {as expected when P(OPh)$_3$ is replaced by P(OEt)$_3$ at manganese}. However, in complex **3** the higher energy band is relatively stronger than the corresponding band for **2** but is absent in Nujol where only one, sharp, band
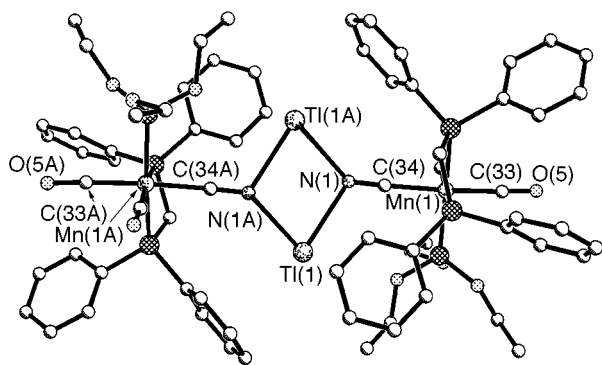
Fig. 2 Molecular structure of $[Tl_2\{(\mu\text{-NC})MnL_x\}_2][PF_6]_2$ [$L_x = cis$-$(CO)_2\{P(OEt)_3\}(dppm)]$ **3**. All hydrogen atoms and the $[PF_6]^-$ anions have been omitted for clarity

is observed at 2049 cm^{-1}. In an attempt to explain these apparently anomalous IR spectra the crystal structure of $[\{Tl(\mu\text{-NC})MnL_x\}_2][PF_6]_2$ [$L_x = cis$-$(CO)_2\{P(OEt)_3\}(dppm)]$ **3** was determined.

Crystal structure of $[\{Tl(\mu\text{-NC})MnL_x\}_2][PF_6]_2$ [$L_x = cis$-$(CO)_2\{P(OEt)_3\}(dppm)]$ 3

Colourless crystals of parallelepiped habit were grown by allowing n-hexane to diffuse slowly into a solution of **3** in CH_2Cl_2 at $-10\,^\circ C$. The molecular structure of **3** is shown in Fig. 2 and selected bond lengths and angles are given in Table 3.

The complex is dimeric and centrosymmetric with the two halves of the dimer linked by a μ_3-κC:κN:κN cyanide bridge. Thus, the CN ligand is C-bound to the manganese centre and N-bound to *two* thallium atoms, forming a Tl_2N_2 core. Such a bonding mode for the cyanide ligand has not previously been characterised by single-crystal X-ray diffraction methods though the structure of $Li_3[Co(CN)_5]\cdot 2dmf$, where each cyanide bridge is C-bound to cobalt and N-bound to two lithium atoms, has been reported based on an *ab initio* structure determination from synchrotron powder diffraction data.[13]

The Tl_2N_2 core is planar and somewhat asymmetric such that there are two different Tl–N bond lengths, at 2.636(3) and 2.773(3) Å. These distances may be compared with the sum of the ionic radius of Tl^I (1.50 Å) and the covalent radius of N (0.73 Å),[14] *i.e.* 2.23 Å. They are also longer than the Tl–N bonds in **1** but are shorter than the distances in the complexes $Tl_2[Pt(CN)_4]$ and $Tl[Au(CN)_4]$ noted above. In **3** the N–Tl–N and Tl–N–Tl angles are 76.4(1) and 103.7(1)° respectively reflecting the diamondoid shape of the Tl_2N_2 unit [$Tl\cdots Tl$ 4.253(7), $N\cdots N$ 3.345(5) Å]. The geometry at each nitrogen atom of the ring is distorted trigonal [C(34)–N(1)–Tl(1) 116.0(2); C(34)–N(1)–Tl(1A) 134.8(2); Tl(1)–N(1)–Tl(1A) 103.7(1)°] with the nitrogen atom out of the plane formed by C(34), Tl(1) and Tl(1A) by 0.238(1) Å. The N–Tl–N angle at Tl is again very acute [76.4(1)°]; similarly acute O–Tl–O angles [70.8(4) and 76.7(4)°] are found in the Tl_2O_2 rings of [$\{TlO$-$C_6H_2(CF_3)_3\}_2$][15] and [$\{Tl(\mu\text{-OC}_6H_4C_6H_4OH)\}_2$][16] respectively. The cyanide bridge is, as usual, near linear at carbon, Mn–C–N angle 177.7(3)° while the C–N–Tl(1) and C–N–Tl(1A) angles are bent (see above). There are two short (less than 3.5 Å) $[PF_6]^- \cdots Tl$ contacts [$Tl(1)\cdots F(2)$ 3.095(3) Å, $Tl(1)\cdots F(4)$ 3.089(3) Å].

In the light of the structural analysis, the IR spectra can be partly rationalised. One might expect the $\{Tl(\mu\text{-NC})Mn\}_2$ core to give rise to two cyanide stretching vibrations (symmetric and antisymmetric), as is observed in CH_2Cl_2 solution. However, in other complexes where two $Mn(\mu\text{-CN})M'$ linkages are present, for example cis-$[(CO)_2Rh\{(\mu\text{-NC})MnL_x\}_2]^+$ [$L_x = cis$-$(CO)_2\{P(OEt)_3\}(dppm)]$,[1] the expected two $\nu(CN)$ bands were not detected. Moreover, Nujol complex **3** shows the lower

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

|			
Tl(1)–N(1)	2.636(3)	Mn(1)–C(33)	1.800(4)
Tl(1)–N(1A)*	2.773(3)	O(4)–C(32)	1.146(5)
Tl(1)···Tl(1A)	4.253(7)	Mn(1)–C(32)	1.801(4)
N(1)···N(1A)	3.345(5)	Mn(1)–P(1)	2.2748(9)
N(1)–C(34)	1.159(4)	Mn(1)–P(2)	2.3220(9)
Mn(1)–C(34)	1.961(3)	Mn(1)–P(3)	2.2219(10)
O(5)–C(33)	1.153(4)		
N(1)–Tl(1)–N(1A)	76.4(1)	N(1)–C(34)–Mn(1)	177.7(3)
Tl(1)–N(1)–Tl(1A)	103.7(1)	O(4)–C(32)–Mn(1)	176.3(4)
C(34)–N(1)–Tl(1A)	134.8(2)	O(5)–C(33)–Mn(1)	174.7(4)
C(34)–N(1)–Tl(1)	116.0(2)		

* Symmetry transformations used to generate atoms suffixed A: $-x$, $-y$, $-z + 2$.

energy cyanide absorption of the two observed in CH_2Cl_2. We therefore assign that lower energy vibration to the dimeric complex (as found in the solid state) and suggest the higher frequency absorption may be due to the corresponding monomer (*i.e.* to an analogue of complex **1**), formed in solution by dissociation of **3**. Such dissociation seems possible given the length, and therefore presumably the weakness, of the Tl–N bonds in **2** and **3**.

Synthesis of $[Tl\{\mu\text{-NC})MnL_x\}_2][PF_6]$ [$L_x = trans$-$(CO)_2\{P(OR)_3\}(dppm)$, R = Ph 4 or Et 5]

Surprisingly, a third type of complex is isolated when $TlPF_6$ is reacted with $trans$-$[Mn(CN)(CO)_2\{P(OR)_3\}(dppm)]$. Thus, the addition of 1 equivalent of the former to 1 equivalent of the latter in acetone afforded only cream (R = Ph) or pale yellow (R = Et) 1:2 adducts $[Tl\{(\mu\text{-NC})MnL_x\}_2][PF_6]$ [$L_x = trans$-$(CO)_2\{P(OR)_3\}(dppm)$, R = Ph 4 or Et 5] (Scheme 1), isolated in higher yield when the syntheses were repeated with the reactants in a 2:1 (Mn:Tl) stoichiometry.

As for complexes **2** and **3**, the IR spectra of **4** and **5** are complicated in the cyanide stretching region (Table 1). For example, in CH_2Cl_2 complex **4** shows one broad band, with a shoulder, whereas **5** shows three poorly defined bands; in Nujol, one band with a shoulder is observed for both compounds. Unfortunately, single crystals of **4** and **5** could not be grown. However, given the likely lability of the Tl–N bonds in the cyanomanganese adducts, the equilibria shown in equation (1)

$$2ML_2 \xrightleftharpoons[L]{-L} 2ML \rightleftharpoons \{ML\}_2 \qquad (1)$$
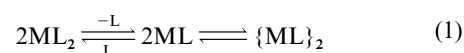
(M = Tl, L = cyanomanganese carbonyl ligand) may account for the rather complex solution IR spectra.

Conclusion

Complexes **1**–**5** are rare in containing not only Tl^I-bound monodentate N-donor ligands but also a cyanide bridge N-bound to thallium(I). Moreover, very different core geometries, namely $Tl(\mu\text{-NC})Mn$, $\{Tl(\mu\text{-NC})Mn\}_2$ and $Tl\{(\mu\text{-NC})Mn\}_2$, are observed for the complexes of Tl^I with $trans$-$[Mn(CN)(CO)(dppm)_2]$, cis-$[Mn(CN)(CO)_2\{P(OR)_3\}(dppm)]$ and $trans$-$[Mn(CN)(CO)_2\{P(OR)_3\}(dppm)]$ respectively. We have noted before the different electronic properties associated with the oxidised forms of the cyanomanganese ligands {the singly occupied molecular orbitals of $trans$-$[Mn^{II}(CN)(CO)(dppm)_2]^+$ and $trans$-$[Mn^{II}(CN)(CO)_2\{P(OR)_3\}(dppm)]^+$ have δ and π symmetry respectively relative to the cyanide π^* orbital}. The present study suggests that steric properties may also play a controlling part in the systematic design of unusual mixed-valence complexes containing cyanomanganese carbonyls as redox-active ligands.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled and deoxygenated solvents; reactions were monitored by IR spectroscopy where necessary. The compounds *cis*- and *trans*-[Mn(CN)(CO)$_2${P(OR)$_3$}(dppm)] (R = Et[17] or Ph[18]) and *trans*-[Mn(CN)(CO)(dppm)$_2$][5,19] were prepared by published methods. The salt TlPF$_6$ was purchased from Strem Chemicals. Infrared spectra were recorded on a Nicolet 5ZDX FT spectrometer. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Syntheses

[(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] 1. To a stirred solution of *trans*-[Mn(CN)(CO)(dppm)$_2$] (0.10 g, 0.11 mmol) in thf (20 cm³) was added TlPF$_6$ (0.04 g, 0.11 mmol). After 1 h the bright orange solution was filtered through Celite, concentrated to *ca.* 5 cm³, and treated with diethyl ether–*n*-hexane (1:1) (20 cm³) to give an orange solid. The product was dissolved in thf, layered with *n*-hexane and allowed to crystallise, yield 99 mg (66%).

The solid complex slowly decomposes in air. It dissolves in acetone, CH$_2$Cl$_2$ or thf to give solutions which decompose under nitrogen in hours.

[Tl$_2${(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = *cis*-(CO)$_2${P(OPh)$_3$}(dppm)] 2. To a stirred solution of *cis*-[Mn(CN)(CO)$_2${P(OPh)$_3$}(dppm)] (0.10 g, 0.12 mmol) in acetone (20 cm³) was added TlPF$_6$ (42 mg, 0.12 mmol), giving a cloudy pale yellow solution. After stirring the mixture for 12 h it was filtered through Celite and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$, filtered and reduced in volume to *ca.* 3 cm³. Addition of diethyl ether–*n*-hexane (1:1) (10 cm³) gave a cream solid which was purified twice by allowing *n*-hexane to diffuse into a concentrated CH$_2$Cl$_2$ solution of the complex, yield 42 mg (30%).

The complex is stable in the solid state and is soluble in acetone, CH$_2$Cl$_2$ and thf to give solutions which are moderately stable in air.

The complex [Tl$_2${(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = *cis*-(CO)$_2${P(OEt)$_3$}(dppm)] 3 was prepared similarly and purified by adding diethyl ether–*n*-hexane (1:1) to the CH$_2$Cl$_2$ extract to give a precipitate which was then redissolved in CH$_2$Cl$_2$ and treated with *n*-hexane.

[Tl{(μ-NC)MnL$_x$}$_2$][PF$_6$] [L$_x$ = *trans*-(CO)$_2${P(OPh)$_3$}(dppm)] 4. A mixture of *trans*-[Mn(CN)(CO)$_2${P(OPh)$_3$}(dppm)] (97 mg, 0.12 mmol) and TlPF$_6$ (20 mg, 0.06 mmol) in acetone (10 cm³) was stirred for 15 min. The pink solution was evaporated to dryness and the residue extracted into CH$_2$Cl$_2$. The extract was filtered through Celite and then reduced in volume *in vacuo*; addition of a mixture of diethyl ether–*n*-hexane (1:2) (*ca.* 10 cm⁻³) gave a cream solid which was further purified using thf–*n*-hexane, yield 71 mg (61%).

The complex is stable in air in the solid state but solutions in solvents such as acetone, CH$_2$Cl$_2$ or thf slowly decompose in air.

The complex [Tl{(μ-NC)MnL$_x$}$_2$][PF$_6$] [L$_x$ = *trans*-(CO)$_2${P(OEt)$_3$}(dppm)] 5 was prepared by the same method.

Structure determinations of [(thf)$_2$Tl(μ-NC)Mn(CO)(dppm)$_2$][PF$_6$] 1 and [{Tl(μ-NC)MnL$_x$}$_2$][PF$_6$]$_2$ [L$_x$ = *cis*-(CO)$_2${P(OEt)$_3$}(dppm)] 3

General. Many of the details of the structure analyses of 1 and 3 are presented in Table 4. A full hemisphere of reciprocal space was scanned with the area detector centre held at

Table 4 Crystal and refinement data for complexes **1** and **3**

Compound	1	3
Formula	C$_{60}$H$_{60}$F$_6$MnNO$_3$P$_5$Tl	C$_{68}$H$_{74}$F$_{12}$Mn$_2$N$_2$O$_{10}$P$_8$Tl$_2$
M	1357.38	2073.68
Crystal system	Orthorhombic	Triclinic
Space group (no.)	*Pbca* (61)	*P*Ī (2)
a/Å	19.113(2)	10.0840(8)
b/Å	22.637(2)	13.297(2)
c/Å	28.076(5)	15.921(2)
α/°	90	71.423(9)
β/°	90	77.844(8)
γ/°	90	78.945(6)
T/K	173	173
U/Å³	121 473(3)	1960.3(4)
Z	8	1
μ/mm⁻¹	3.050	4.659
Reflections collected	51 247	12 579
Independent reflections (R_{int})	8451 (0.0730)	8662 (0.0244)
Final R indices [$I > 2\sigma(I)$]: $R1$, $wR2$	0.127, 0.284	0.0284, 0.064

2θ = −27°. Absorption corrections were applied on the basis of equivalent reflections.

For complex **1** all non-hydrogen atoms, except those of the two thf molecules, and fluorine atoms F(5), F(6), F(7), F(5′), F(6′) and F(7′) were assigned anisotropic displacement parameters and refined without positional constraints. The asymmetric unit contains two [PF$_6$]⁻ anions. One phosphorus atom is located at a crystallographic inversion centre. The second [PF$_6$]⁻ anion is assigned occupancy 0.5 to provide a chemically correct charge balance for the salt although it lies at a general position; refinement with greater occupancy than 0.5 led to higher residuals. This second [PF$_6$]⁻ ion is disordered and the fluorine atoms F(5), F(6) and F(7) were assigned two positions, each of occupancy 0.25. The thallium atom is also disordered and is assigned two positions, Tl(1) and Tl(1′) with site occupancies which refined to 0.65(2):0.35(2). The two co-ordinated thf molecules are also severely disordered. The first thf consists of O(2), C(53), C(54), C(55) and C(56) with second positions assigned as C(53′), C(55′) and C(56′). The ratio of site occupancy for the two parts of the molecule was assigned as 0.65(2):0.35(2) in company with the thallium sites. Carbon atom C(54) is shared by the two halves of the molecule. Hydrogen atoms were assigned in idealised positions to C(53), C(56) and C(53′), each with isotropic displacement parameters constrained to 1.2 times the U_{eq} of their attached carbon atoms. The second thf molecule is also disordered, and consists of O(3), C(57), C(58), C(59) and C(60), with second positions assigned as C(57′) and C(60′). Thus carbon atoms C(58) and C(59) are shared by the two halves of the molecule. The site occupancies for the two parts of this molecule were assigned as 0.8(2):0.2(2) after refinement. Hydrogen atoms were assigned in idealised positions to C(57) and C(60), each with isotropic displacement parameters and again constrained to 1.2 times the U_{eq} of their attached carbon atoms. The largest remaining features of the difference electron density map are within 1.0 Å of the fluorine atoms. Except where noted above, hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.2 times the U_{eq} of their attached carbon atoms.

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See http://www.rsc.org/suppdata/dt/1998/1913/ for crystallographic files in .cif format.

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