

Novel N-bound thallium(I) complexes of redox-active cyanomanganese carbonyl ligands: cyanide as a μ_3 - $\kappa C:\kappa N:\kappa N$ 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 = Ph₂PCH₂PPh₂) react with TlPF₆ to give [(thf)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆]**1**, [Tl(μ-NC)MnL_x]₂[PF₆]₂ [L_x = *cis*-(CO)₂{P(OR)₃}(dppm), R = Ph **2** or Et **3**] and [Tl{(μ-NC)MnL_x}]₂[PF₆]₂ [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 μ_3 - $\kappa C:\kappa N:\kappa N$ cyanide ligand N-bonded to two thallium atoms and C-bonded to manganese.

Thallium(I) salts of poorly co-ordinating anions, such as TlPF₆, 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)₂Rh{(μ-NC)MnL_x}]₂[PF₆]₂ [L_x = *trans*-(CO)₂{P(OEt)₃}(dppm), dppm = Ph₂PCH₂PPh₂], 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 [TlPt₃(CO)₃(PCy₃)₃][RhCl₂(η-cod)] (Cy = cyclohexyl, cod = cycloocta-1,5-diene), synthesised from TlPF₆, [Pt₃(CO)₃(PCy₃)₃] and [Rh(μ-Cl)(cod)]₂.³

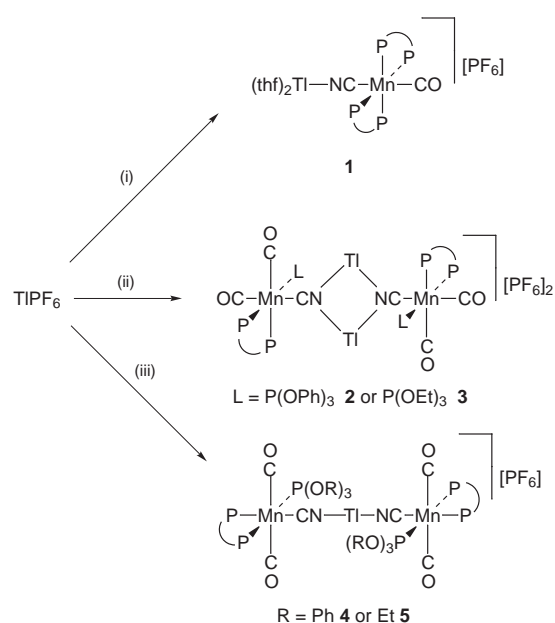
Thallium(I) is rarely bound to simple monodentate N-donors such as NH₃² though complexes of polydentate ligands are more stable.⁴ However, we now report the surprising observation that Tl⁺ acts as a Lewis acid towards the cyanomanganese carbonyls *trans*-[Mn(CN)(CO)(dppm)₂]⁵ and *cis*- and *trans*-[Mn(CN)(CO)₂{P(OR)₃}(dppm)] (R = Ph or Et),⁶ giving novel bi-, tri- and tetra-nuclear, Tl–N bonded cyanide complexes, including [(thf)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆], which shows pyramidal geometry at thallium, and [Tl(μ-NC)MnL_x]₂[PF₆]₂ [L_x = *cis*-(CO)₂{P(OEt)₃}(dppm)], which contains an unusual μ_3 - $\kappa C:\kappa N:\kappa N$ bridge.

Results and Discussion

Synthesis of [(thf)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆]**1**

On adding solid TlPF₆ 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)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆]**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][PF₆].

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



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 $\nu(\text{CN})$.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 $\nu(\text{CN})$ 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 $\pi^*(\text{CN})$ orbital.

One cyanide absorption is also observed in Nujol but in CH₂Cl₂ 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 Tl₂[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

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Table 1 Analytical and IR spectroscopic data for $[\text{Tl}_m\{\mu\text{-NC}\}\text{MnL}_x]_n^{2+}$

L_x	m	n	z^c	Colour	Yield (%)	Analysis (%) ^a			IR ^b /cm ⁻¹	
						C	H	N	v(CN)	v(CO) ^d
1 <i>trans</i> -(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 <i>cis</i> -(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	1973vs, 1924s
3 <i>cis</i> -(CO) ₂ {P(OEt) ₃ }(dppm)	2	2	2	White	45	39.1 (39.4)	3.5 (3.6)	1.2 (1.4)	2083 (sh), 2063w ^g	1969vs, 1917vs ^g
4 <i>trans</i> -(CO) ₂ {P(OPh) ₃ }(dppm)	1	2	1	Cream	61	54.9 (54.4)	3.7 (4.2)	1.4 (1.2)	2072w, 2053m	1961vs, 1907s
5 <i>trans</i> -(CO) ₂ {P(OEt) ₃ }(dppm)	1	2	1	Pale yellow	45	47.6 (47.4)	4.4 (4.3)	1.6 (1.6)	2049s ^g	1956vs, 1907vs ^g
									2080vw (sh), 2066w	1933vs (2011)
									2067m, 2042 (sh) ^g	1925vs (2010) ^g
									2078, 2061, 2054w	1918vs (2000)
									2078w, 2070 (sh) ^g	1912vs (2030) ^g

^a Calculated in parentheses. ^b In CH₂Cl₂ unless stated otherwise; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. ^c Cations isolated as [PF₆]⁻ 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.

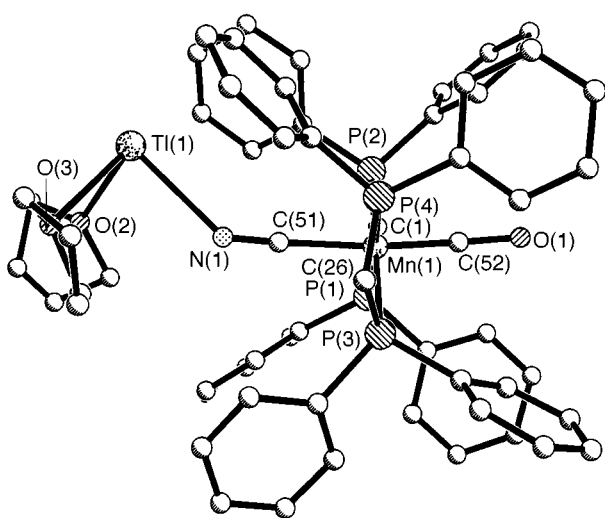


Fig. 1 Molecular structure of $[(\text{thf})_2\text{Ti}(\mu\text{-NC})\text{Mn}(\text{CO})(\text{dppm})_2][\text{PF}_6] \mathbf{1}$ showing the atom labelling scheme; only the major image of the molecule is shown. All hydrogen atoms and the [PF₆]⁻ anion have been omitted for clarity

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 $[(\text{thf})_2\text{Ti}(\mu\text{-NC})\text{Mn}(\text{CO})(\text{dppm})_2][\text{PF}_6] \mathbf{1}$

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] itself¹¹ and its N-bound complexes with RhCl(CO)₂¹ 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)–Ti(1)–O(2)	87.0(6)	N(1)–C(51)–Mn(1)	175.6(14)
N(1)–Ti(1)–O(3)	86.0(6)	O(1)–C(52)–Mn(1)	178.0(12)
O(2)–Ti(1)–O(3)	81.7(9)	P(2)–Mn(1)–P(1)	74.0(2)
C(51)–N(1)–Ti(1)	139.7(12)	P(3)–Mn(1)–P(4)	73.76(14)
C(51)–N(1)–Ti(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) [Ti(1) and Ti(1') respectively]; the thf ligands are also disordered. In the majority thallium atom position, Ti(1) is N-bound to the cyanide group of the manganese ligand [Ti(1)–N(1) = 2.63(2) Å] and further co-ordinated to the oxygen atoms of two thf molecules [Ti(1)–O(2) = 2.74(3), Ti(1)–O(3) = 2.75(3) Å]. There is one short [PF₆]⁻ ··· Ti contact [Ti(1) ··· F(1) 3.27(3) Å]. The valence angles at Ti(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 ··· Ti contact this shielding is not complete.

Synthesis of $[\{\text{Ti}(\mu\text{-NC})\text{MnL}_x\}_2][\text{PF}_6]_2$ [$L_x = \text{cis}(\text{CO})_2\text{-P}(\text{OR})_3(\text{dppm})$, R = Ph **2** or Et **3**]

The complexes *cis*-[Mn(CN)(CO)₂{P(OR)₃}(dppm)] (R = Ph or Et) also react with TlPF₆ 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 $[\{\text{Ti}(\mu\text{-NC})\text{MnL}_x\}_2][\text{PF}_6]_2$ [$L_x = \text{cis}(\text{CO})_2\text{-P}(\text{OR})_3(\text{dppm})$, 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-coordination to Tl^I, cf. **1**.} For example, in CH₂Cl₂ 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 CH₂Cl₂, 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

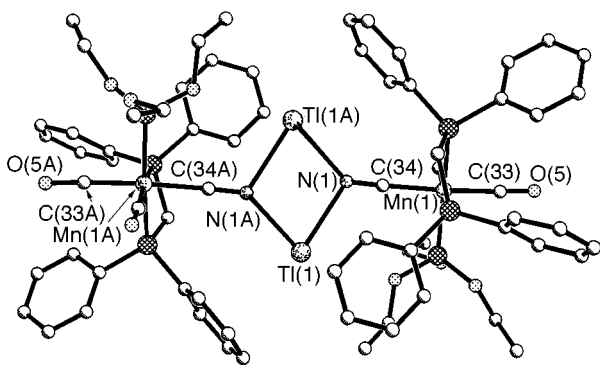


Fig. 2 Molecular structure of $[\text{Ti}_2\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]_2$ [$\text{L}_x = \text{cis}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})$] **3**. All hydrogen atoms and the $[\text{PF}_6]^-$ anions have been omitted for clarity

is observed at 2049 cm^{-1} . In an attempt to explain these apparently anomalous IR spectra the crystal structure of $[\{\text{Ti}(\mu\text{-NC})\text{MnL}_x\}_2][\text{PF}_6]_2$ [$\text{L}_x = \text{cis}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})$] **3** was determined.

Crystal structure of $[\{\text{Ti}(\mu\text{-NC})\text{MnL}_x\}_2][\text{PF}_6]_2$ [$\text{L}_x = \text{cis}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})$] **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°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 $\mu_3\text{-}\kappa\text{C}:\kappa\text{N}:\kappa\text{N}$ cyanide bridge. Thus, the CN ligand is C-bound to the manganese centre and N-bound to *two* thallium atoms, forming a Ti_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 $\text{Li}_3[\text{Co}(\text{CN})_5]\cdot 2\text{dmf}$, 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 Ti_2N_2 core is planar and somewhat asymmetric such that there are two different Ti–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 Ti^{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 Ti–N bonds in **1** but are shorter than the distances in the complexes $\text{Ti}_2[\text{Pt}(\text{CN})_4]$ and $\text{Ti}[\text{Au}(\text{CN})_4]$ noted above. In **3** the N–Ti–N and Ti–N–Ti angles are 76.4(1) and 103.7(1)° respectively reflecting the diamondoid shape of the Ti_2N_2 unit [Ti⋯Ti 4.253(7), N⋯N 3.345(5) Å]. The geometry at each nitrogen atom of the ring is distorted trigonal [C(34)–N(1)–Ti(1) 116.0(2); C(34)–N(1)–Ti(1A) 134.8(2); Ti(1)–N(1)–Ti(1A) 103.7(1)°] with the nitrogen atom out of the plane formed by C(34), Ti(1) and Ti(1A) by 0.238(1) Å. The N–Ti–N angle at Ti is again very acute [76.4(1)°]; similarly acute O–Ti–O angles [70.8(4) and 76.7(4)°] are found in the Ti_2O_2 rings of $[\{\text{TiO}-\text{C}_6\text{H}_2(\text{CF}_3)_3\}_2]^{15}$ and $[\{\text{Ti}(\mu\text{-OC}_6\text{H}_4\text{C}_6\text{H}_4\text{OH})\}_2]^{16}$ respectively. The cyanide bridge is, as usual, near linear at carbon, Mn–C–N angle 177.7(3)° while the C–N–Ti(1) and C–N–Ti(1A) angles are bent (see above). There are two short (less than 3.5 Å) $[\text{PF}_6]^-$ ⋯Ti contacts [Ti(1)⋯F(2) 3.095(3) Å, Ti(1)⋯F(4) 3.089(3) Å].

In the light of the structural analysis, the IR spectra can be partly rationalised. One might expect the $\{\text{Ti}(\mu\text{-NC})\text{Mn}\}_2$ 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(μ-CN)M' linkages are present, for example $\text{cis}[(\text{CO})_2\text{Rh}\{\mu\text{-NC}\}\text{MnL}_x]_2^+$ [$\text{L}_x = \text{cis}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})$],¹ the expected two $\nu(\text{CN})$ bands were not detected. Moreover, Nujol complex **3** shows the lower

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

Ti(1)–N(1)	2.636(3)	Mn(1)–C(33)	1.800(4)
Ti(1)–N(1A)*	2.773(3)	O(4)–C(32)	1.146(5)
Ti(1)⋯Ti(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)–Ti(1)–N(1A)	76.4(1)	N(1)–C(34)–Mn(1)	177.7(3)
Ti(1)–N(1)–Ti(1A)	103.7(1)	O(4)–C(32)–Mn(1)	176.3(4)
C(34)–N(1)–Ti(1A)	134.8(2)	O(5)–C(33)–Mn(1)	174.7(4)
C(34)–N(1)–Ti(1)	116.0(2)		

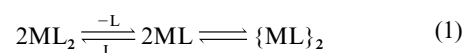
* Symmetry transformations used to generate atoms suffixed A: $-x, -y, -z + 2$.

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 Ti–N bonds in **2** and **3**.

Synthesis of $[\text{Ti}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]_2$ [$\text{L}_x = \text{trans}(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})$, R = Ph **4** or Et **5**]

Surprisingly, a third type of complex is isolated when TIPF_6 is reacted with $\text{trans}[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]$. 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 $[\text{Ti}\{\mu\text{-NC}\}\text{MnL}_x]_2[\text{PF}_6]_2$ [$\text{L}_x = \text{trans}(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})$, 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:Ti) 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 Ti–N bonds in the cyanomanganese adducts, the equilibria shown in equation (1)



(M = Ti, L = cyanomanganese carbonyl ligand) may account for the rather complex solution IR spectra.

Conclusion

Complexes **1–5** are rare in containing not only Ti^{I} -bound monodentate N-donor ligands but also a cyanide bridge N-bound to thallium(I). Moreover, very different core geometries, namely $\text{Ti}(\mu\text{-NC})\text{Mn}$, $\{\text{Ti}(\mu\text{-NC})\text{Mn}\}_2$ and $\text{Ti}\{\mu\text{-NC}\}\text{Mn}\}_2$, are observed for the complexes of Ti^{I} with $\text{trans}[\text{Mn}(\text{CN})(\text{CO})(\text{dppm})_2]$, $\text{cis}[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]$ and $\text{trans}[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]$ respectively. We have noted before the different electronic properties associated with the oxidised forms of the cyanomanganese ligands {the singly occupied molecular orbitals of $\text{trans}[\text{Mn}^{\text{II}}(\text{CN})(\text{CO})(\text{dppm})_2]^+$ and $\text{trans}[\text{Mn}^{\text{II}}(\text{CN})(\text{CO})_2\{\text{P}(\text{OR})_3\}(\text{dppm})]^+$ 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 = Et¹⁷ or Ph¹⁸) and *trans*-[Mn(CN)(CO)(dppm)₂]^{5,19} were prepared by published methods. The salt TlPF₆ 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)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆] **1.** To a stirred solution of *trans*-[Mn(CN)(CO)(dppm)₂] (0.10 g, 0.11 mmol) in thf (20 cm³) was added TlPF₆ (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, CH₂Cl₂ or thf to give solutions which decompose under nitrogen in hours.

[Tl₂{(μ-NC)MnL_x}₂][PF₆]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 TlPF₆ (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 CH₂Cl₂, 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 CH₂Cl₂ solution of the complex, yield 42 mg (30%).**

The complex is stable in the solid state and is soluble in acetone, CH₂Cl₂ and thf to give solutions which are moderately stable in air.

The complex [Tl₂{(μ-NC)MnL_x}₂][PF₆]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 CH₂Cl₂ extract to give a precipitate which was then redissolved in CH₂Cl₂ and treated with *n*-hexane.

[Tl{(μ-NC)MnL_x}₂][PF₆] [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 TlPF₆ (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 CH₂Cl₂. 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 cm³) 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, CH₂Cl₂ or thf slowly decompose in air.

The complex [Tl{(μ-NC)MnL_x}₂][PF₆] [L_x = *trans*-(CO)₂-{P(OEt)₃}(dppm)] **5** was prepared by the same method.

Structure determinations of [(thf)₂Tl(μ-NC)Mn(CO)(dppm)₂][PF₆] **1** and [Tl(μ-NC)MnL_x]₂[PF₆]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
<i>M</i>	1357.38	2073.68
Crystal system	Orthorhombic	Triclinic
Space group (no.)	<i>Pbca</i> (61)	<i>P</i> $\bar{1}$ (2)
<i>a</i> /Å	19.113(2)	10.0840(8)
<i>b</i> /Å	22.637(2)	13.297(2)
<i>c</i> /Å	28.076(5)	15.921(2)
<i>α</i> /°	90	71.423(9)
<i>β</i> /°	90	77.844(8)
<i>γ</i> /°	90	78.945(6)
<i>T</i> /K	173	173
<i>U</i> /Å ³	121 473(3)	1960.3(4)
<i>Z</i>	8	1
μ/mm ⁻¹	3.050	4.659
Reflections collected	51 247	12 579
Independent reflections (<i>R</i> _{int})	8451 (0.0730)	8662 (0.0244)
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>): <i>R</i> ₁ , <i>wR</i> ₂]	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 [PF₆]⁻ anions. One phosphorus atom is located at a crystallographic inversion centre. The second [PF₆]⁻ 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 [PF₆]⁻ 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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