

## Preparation of Monomeric Neutral or Anionic Tris(polyfluorophenyl)-thallium(III) and of Anionic Heteronuclear Tris(polyfluorophenyl)-thallium-Metal Carbonyl Complexes

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The complex  $[\text{TlR}_3(\text{diox})]$  (diox = 1,4-dioxan) has been prepared by the reaction of  $\text{TlCl}_3$  with  $\text{LiR}$  ( $\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ), or of  $[\text{NBu}_4][\text{TlR}_4]$  with  $\text{HBF}_4$  ( $\text{R} = \text{C}_6\text{F}_5$ ) and subsequent addition of dioxan. The displacement of dioxan by (a) neutral ligands leads to  $[\text{TlR}_3\text{L}]$  ( $\text{L} = \text{OPPh}_3$ , pyridine,  $\text{PPh}_3$ , or  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ); (b) anionic ligands affords  $\text{Q}[\text{TlR}_3\text{X}]$  ( $\text{Q} = [\text{NBu}_4]^+$  or  $[\text{N}(\text{PPh}_3)_2]^+$ ;  $\text{X} = \text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_3^-$ , or  $\text{CF}_3\text{CO}_2^-$ ); and (c) metal carbonylate gives  $\text{Q}[\text{TlR}_3\text{M}^*]$  ( $\text{M}^* = [\text{Mo}(\text{cp})(\text{CO})_3]^-$  ( $\text{cp} = \eta\text{-C}_5\text{H}_5$ ),  $[\text{W}(\text{cp})(\text{CO})_3]^-$ ,  $[\text{Co}(\text{CO})_4]^-$  or  $[\text{Mn}(\text{CO})_5]^-$ ).

Triaryl- (or alkyl)-thallium(III) complexes are only poorly represented in the literature, especially in comparison with the large number of organothallium derivatives with one or two organic groups attached to the thallium atom.<sup>1,2</sup> The synthesis of tris(polyfluorophenyl)thallium(III) derivatives by the reaction of  $\text{TlR}_2\text{Br}$  with  $\text{Cu}$  metal<sup>3,4</sup> or with  $\text{Ba}(\text{O}_2\text{-SR})_2$ <sup>5</sup> followed by isolation as the dioxan adducts  $[\text{TlR}_3(\text{diox})]$  ( $\text{R} = \text{C}_6\text{F}_5$ ,  $p\text{-C}_6\text{F}_4\text{H}$ ,  $m\text{-C}_6\text{F}_4\text{H}$ ,  $o\text{-C}_6\text{F}_4\text{H}$ , or  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) has been reported.

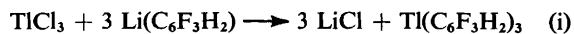
In the present paper we describe how  $[\text{TlR}_3(\text{diox})]$  ( $\text{R} = \text{C}_6\text{F}_5$  or  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) can be obtained more straightforwardly and in higher yields by the reaction of  $\text{TlCl}_3$  with  $\text{Li}(2,4,6\text{-C}_6\text{F}_3\text{H}_2)$  or of  $[\text{NBu}_4][\text{Ti}(\text{C}_6\text{F}_5)_4]$  with  $\text{HBF}_4$ . The dioxan ligand can readily be replaced by other neutral ligands [ $\text{L} = \text{OPPh}_3$ , pyridine (py),  $\text{PPh}_3$ , or bis(diphenylphosphino)methane (dppm)], or anionic ligands ( $\text{X} = \text{Cl}^-$  or  $\text{CN}^-$ ), or by metal carbonylate ( $\text{M}^* = [\text{Co}(\text{CO})_4]^-$ ,  $[\text{Mn}(\text{CO})_5]^-$ ,  $[\text{Mo}(\text{cp})(\text{CO})_3]^-$  or  $[\text{W}(\text{cp})(\text{CO})_3]^-$  ( $\text{cp} = \eta\text{-C}_5\text{H}_5$ )) to give novel derivatives of the types  $[\text{TlR}_3\text{L}]$ ,  $\text{Q}[\text{TlR}_3\text{X}]$ , or  $\text{Q}[\text{TlR}_3\text{M}^*]$  ( $\text{Q} = [\text{NBu}_4]^+$  or  $[\text{N}(\text{PPh}_3)_2]^+$ ), respectively.

### Results and Discussion

**Preparation of the Starting Complexes.**—Recently<sup>6</sup> we have reported the preparation of  $\text{TlR}_2\text{Cl}$  ( $\text{R} = \text{C}_6\text{F}_5$  or  $2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) by arylation of  $\text{TlCl}_3$  with  $\text{LiR}$  in 1:2 molar ratio. Moreover, use of an excess of the lithium derivative gives rise to two different types of behaviour:

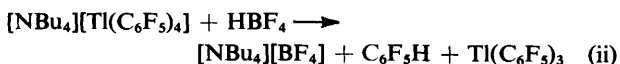
(a) An excess of  $\text{LiR}$  ( $\text{R} = \text{C}_6\text{F}_5$ ) leads to  $[\text{TlR}_4]^-$ , or even to  $[\text{TlR}_6]^{3-}$ , which can be isolated upon addition of a bulky cation.<sup>7</sup> Formation of  $\text{TlR}_3$ , however, was not observed; use of a 1:3 molar ratio gives a mixture of  $\text{TlR}_2\text{Cl}$  and  $[\text{TlR}_4]^-$ .

(b) An excess of  $\text{LiR}$  ( $\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ ) does not afford  $[\text{TlR}_4]^-$  but gives stable diethyl ether solutions of  $\text{TlR}_3$  [equation (i)]. Evaporation of these solutions yields a dense



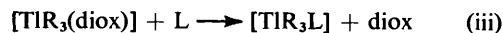
oil, which tends to decompose rapidly. Moreover, previous addition of 1,4-dioxan (diox) allows the isolation of  $[\text{Ti}(\text{C}_6\text{F}_3\text{H}_2)_3(\text{diox})]$  (1).

Ether solutions of  $\text{Ti}(\text{C}_6\text{F}_5)_3$  can be obtained by the reaction between  $[\text{TlR}_4]^-$  and inorganic acids with poorly co-ordinating anions [equation (ii)]. Addition of diox permits the isolation of  $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (2).



These methods allow the isolation of compounds (1) and (2) in better yields (68 and 83%, respectively) than those reported.<sup>3-5</sup> The properties of the compounds coincide with those previously described.

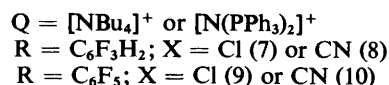
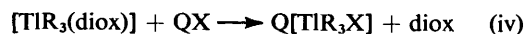
**Neutral Mononuclear Complexes.**—The dioxan in compounds (1) and (2) can be readily replaced by other neutral ligands [equation (iii)]. The white complexes (3)–(6)



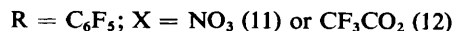
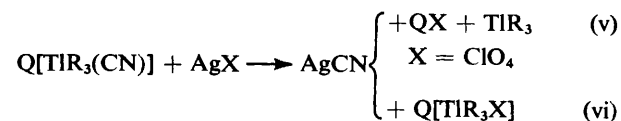
$\text{R} = \text{C}_6\text{F}_3\text{H}_2$ ;  $\text{L} = \text{OPPh}_3$  (3), py (4),  $\text{PPh}_3$  (5), or dppm (6)

are air- and moisture-stable solids, non-conducting in acetone solution and monomeric in chloroform (see Table 1).

**Anionic Complexes.**—Substitution of  $\text{X} = \text{Cl}$  or  $\text{CN}$  for dioxan leads to organothallate(III) derivatives [equation (iv)].



The i.r. spectra of the chloro-complexes (7) and (9) show bands arising from  $\nu(\text{Ti-Cl})$ <sup>8,9</sup> at 230 and 250  $\text{cm}^{-1}$ , respectively. Complexes (8) and (10) do not exhibit vibrations due to  $\nu(\text{C}\equiv\text{N})$ .<sup>10,11</sup> Nonetheless, the presence of the CN group is clearly shown by addition of a silver salt, which in both cases causes precipitation of  $\text{AgCN}$  [equations (v) and (vi)]



and two different reaction courses; if  $\text{X}$  is a non-co-ordinating anion ( $\text{ClO}_4$ ) the process represented in equation (v) takes place and addition of dioxan (after removal of  $\text{AgCN}$  and  $\text{QX}$  by filtration) allows isolation of (1) or (2). If  $\text{X}$  is a co-ordinating anion ( $\text{NO}_3$  or  $\text{CF}_3\text{CO}_2$ ) the reaction takes place according to equation (vi), and complex (11) or (12), respectively, can be isolated after removal of  $\text{AgCN}$ .

The presence of the  $\text{CF}_3\text{CO}_2$  group is supported by a strong band at 1680  $\text{cm}^{-1}$  [ $\nu_{\text{asym}}(\text{CO})$ ].<sup>12</sup> Other absorptions, as well as those expected for  $\text{X} = \text{NO}_3$ ,<sup>13</sup> are masked by vibrations

Table 1. Physical data for complexes (1)–(12)

	M.p. (°C)	$\Lambda_M /$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	M Found (calc.)
(1) [Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (diox)]	182 (decomp.)	1	
(2) [Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (diox)]	259 (decomp.)	1	
(3) [Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (OPPh <sub>3</sub> )	141	1	897 (876)
(4) [Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (py)]	133	2	694 (677)
(5) [Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (PPh <sub>3</sub> )	209 (decomp.)	3	835 (860)
(6) [Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (dppm)]	100	2	933 (982)
(7) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> Cl]	115	85	
(8) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> (CN)]	115	89	
(9) [NBu <sub>4</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> ) <sub>3</sub> Cl]	83	97	
(10) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (CN)]	90	98	
(11) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (NO <sub>3</sub> )	123 (decomp.)	105	
(12) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (O <sub>2</sub> CCF <sub>3</sub> )	106	98	

Table 2. Physical data for complexes (13)–(20)

	M.p. (decomp.) (°C)	$\Lambda_M /$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	$\nu(\text{CO})^* / \text{cm}^{-1}$
(13) [NBu <sub>4</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> {Mo(cp)(CO) <sub>3</sub> }]	48	120	1 962vs, 1 879vs (sh), 1 868vs, br
(14) [NBu <sub>4</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> {W(cp)(CO) <sub>3</sub> }]		138	1 956vs, 1 880vs (sh), 1 867vs, br
(15) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> {Co(CO) <sub>4</sub> }]	58	115	2 042m, 1 968m (sh), 1 956s
(16) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>3</sub> H <sub>2</sub> ) <sub>3</sub> {Mn(CO) <sub>5</sub> }]	90	112	2 070m, 1 967vs, br
(17) [NBu <sub>4</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> {Mo(cp)(CO) <sub>3</sub> }]	107	91	1 977vs, 1 900vs (sh), 1 888vs
(18) [NBu <sub>4</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> {W(cp)(CO) <sub>3</sub> }]	84	90	1 973vs, 1 892vs (sh), 1 878vs
(19) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> {Co(CO) <sub>4</sub> }]	139	127	2 055m, 1 990m (sh), 1 970s
(20) [N(PPh <sub>3</sub> ) <sub>2</sub> ][Tl(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> {Mn(CO) <sub>5</sub> }]	100	84	2 065m, 1 985vs, br

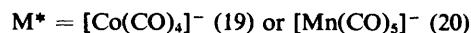
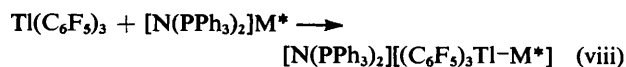
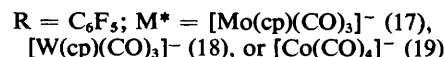
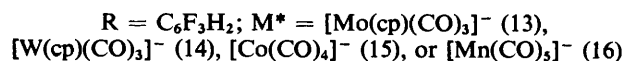
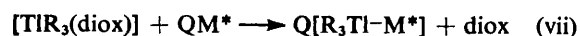
\* In dichloromethane.

arising from the cation. A similar reaction is observed for R = C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>, X = CF<sub>3</sub>CO<sub>2</sub>, though evaporation of the filtrate (after removal of AgCN) leads to oils, which could not be separated and whose i.r. spectra show absorption due to  $\nu_{\text{asym}}(\text{CO})$  at 1 658 cm<sup>-1</sup>.

Complexes (7)–(12) are white air- and moisture-stable solids, conducting in acetone solution (1 : 1 electrolytes), as may be seen from Table 1.

**Anionic Heteronuclear Complexes with Thallium–Transition Metal Bonds.**—The foregoing behaviour is similar to that observed for [Au(C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>)<sub>3</sub>(tht)], where the substitution of halide or pseudohalide for tetrahydrothiophen (tht) leads to organoaurate(III),<sup>14</sup> or the use of metal carbonylate gives anions containing gold(III)–transition metal bonds.<sup>15</sup> Since [AsPh<sub>4</sub>][Tl{Co(CO)<sub>4</sub>}]<sub>4</sub><sup>16</sup> is the only reported anionic complex with a thallium(III)–transition metal bond, it seemed of interest to explore analogous reactions of [TlR<sub>3</sub>(diox)]. In fact, addition of an equimolecular amount of QM\* [Q = NBu<sub>4</sub> or N(PPh<sub>3</sub>)<sub>2</sub>] to a suspension of [TlR<sub>3</sub>(diox)] in dichloromethane leads to the ready substitution of the carbonylate anion M\* for dioxan and to the formation [equation (vii)] of the thallium–metal bonded (M = Mo, W, Co, or Mn) complexes (13)–(19). [TlR<sub>3</sub>(diox)] need not necessarily be isolated, since the complexes can also be prepared directly by adding the carbonylate to ethereal solutions of TlR<sub>3</sub> [equation (viii)]. The colour of the resulting complexes varies from white [(19), (20)] to orange (14). They are conducting in acetone solution (Table 2). At room temperature the solids are air- and moisture-stable, except for (14) which must be stored at low temperature.

Solutions of (16)–(20) are stable under nitrogen. Above –20 °C the solutions of (15) yield [Co(CO)<sub>4</sub>]<sup>-</sup>, as may be seen from the appearance of  $\nu(\text{CO})$  bands arising from the



free carbonylate. Lowering the temperature causes regeneration of the complex with re-formation of the thallium–cobalt bond. Solutions of (13) and (14) are also unstable above –20 °C. Appearance of free carbonylate followed by release of CO (more rapid in the tungsten derivative) can be observed; no regeneration is therefore possible in these cases.

The i.r. spectra of complexes (13)–(20) in the carbonyl region are in agreement with the expected pattern; the  $\nu(\text{CO})$  bands in all cases are displaced towards higher energies, relative to the metal carbonylate anions. The manganese derivatives show only two of the three expected absorptions<sup>17</sup> ( $2a_1 + e$ ); probably the broad lower-energy band results from overlapping of the two vibrations due to ( $a_1 + e$ ). The Co, Mo, and W complexes exhibit the three expected absorptions ( $2a_1 + e$  for Co<sup>18</sup> and  $2a' + a''$  for Mo and W<sup>19</sup>). As may be seen from Table 2, the absorption bands of the R = C<sub>6</sub>F<sub>5</sub> derivatives are at higher energies than those where R = 2,4,6-C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>, which seems in accord with the higher electronegativity of the former.

All the complexes with R = C<sub>6</sub>F<sub>5</sub> described in the present paper are characterized by two bands at 780 and 770 cm<sup>-1</sup>.

This X-sensitive vibration of the  $C_6F_5$  group is assignable<sup>9,20</sup> to a mode involving predominantly Tl-C stretching and can be related to the symmetry of the compounds as has been shown for Tl,<sup>6</sup> Au,<sup>21</sup> and Pd or Pt<sup>22</sup> derivatives. A similar situation is also observed for compounds containing the 2,4,6- $C_6F_3H_2$  group;<sup>21</sup> the complexes described herein show these two bands at ca. 845 and 838  $cm^{-1}$ .

### Experimental

I.r. spectra were recorded with a Perkin-Elmer 599 spectrophotometer for solutions in dichloromethane, or for Nujol mulls between polyethylene sheets. Conductivities were measured for ca.  $5 \times 10^{-4}$  mol  $dm^{-3}$  solutions in acetone with a Philips 9501/01 conductometer. Molecular weights were determined for solutions in chloroform with a Hitachi-Perkin-Elmer 115 osmometer. Analyses (C, H, N) were carried out with a Perkin-Elmer 240 microanalyser. All solvents were distilled from drying agents under nitrogen, and all operations were conducted in oxygen-free anhydrous nitrogen.

[ $Tl(C_6F_3H_2)_3(diox)$ ] (1).—To a solution of  $Li(2,4,6-C_6F_3H_2)_6$  (21 mmol) in diethyl ether (100  $cm^3$ ) at  $-78^\circ C$  was added anhydrous  $TlCl_3$  (0.93 g, 3 mmol) and the mixture was stirred for 10 min. Dioxan (4  $cm^3$ ) was added and the mixture stirred for 1 h; the solution was then warmed to  $-40^\circ C$  and stirred for 45 min. After warming to room temperature the excess of lithium derivative was destroyed with solid  $CO_2$ . Evaporation to dryness and treatment of the residue with a mixture of dioxan (10  $cm^3$ ) and hexane (30  $cm^3$ ), filtration, and subsequent evaporation of the filtrate to dryness gave white solid (1), which was recrystallized from ether-hexane (1.40 g, 68%) (Found: C, 38.05; H, 2.0.  $C_{22}H_{14}F_9O_2Tl$  requires C, 38.55; H, 2.05%).

[ $Tl(C_6F_5)_3(diox)$ ] (2).—To a solution of  $[NBu_4][Tl(C_6F_5)_4]^-$  (1.12 g, 1 mmol) in diethyl ether (50  $cm^3$ ) was added  $HBF_4$  (1  $cm^3$  of a 50% ethereal solution) and the mixture was stirred for 30 min at room temperature. The precipitated  $[NBu_4][BF_4]$  was removed by filtration and dioxan (1  $cm^3$ ) was added to the filtrate. The white complex (2) crystallized upon evaporation (0.66 g, 83%) (Found: C, 33.4; H, 1.05.  $C_{22}H_8F_{15}O_2Tl$  requires C, 33.3; H, 1.0%).

[ $Tl(C_6F_3H_2)_3L$ ] [ $L = OPPh_3$  (3), py (4),  $PPh_3$  (5), or  $dppm$  (6)].—To a suspension of (1) (0.172 g, 0.25 mmol) in dichloromethane (10  $cm^3$ ) was added L [ $L = OPPh_3$  (0.070 g, 0.25 mmol), py (0.10  $cm^3$ , 1.2 mmol),  $PPh_3$  (0.666, 0.25 mmol), or  $dppm$  (0.096 g, 0.25 mmol)]; instantaneous formation of a clear solution was observed. The solution was stirred for 10 min and evaporated to dryness. The resulting white solid was recrystallized from dichloromethane-hexane to give (3) (0.130 g, 60%) (Found: C, 49.7; H, 2.6.  $C_{36}H_{21}F_9OPTl$  requires C, 49.35; H, 2.4%); (4) (0.091 g, 54%) (Found: C, 40.45; H, 1.85; N, 2.0.  $C_{23}H_{11}F_9NTl$  requires C, 40.8; H, 1.65; N, 2.05%); (5) (0.165 g, 77%) (Found: C, 50.15; H, 2.5.  $C_{36}H_{21}F_9PTl$  requires C, 50.3; H, 2.45%); or (6) (0.20 g, 81%) (Found: C, 52.3; H, 3.0.  $C_{43}H_{28}F_9P_2Tl$  requires C, 52.6; H, 2.85%).

$Q[TlR_3Cl]$  [ $Q = N(PPh_3)_2$ ,  $R = C_6F_3H_2$  (7); or  $Q = NBu_4$ ,  $R = C_6F_5$  (9)].—To a suspension of (1) (0.343 g, 0.5 mmol) or (2) (0.397 g, 0.5 mmol) in dichloromethane (20  $cm^3$ ) was added  $[N(PPh_3)_2]Cl$  (0.287 g, 0.5 mmol) or  $[NBu_4]Cl$  (0.139 g, 0.5 mmol), respectively. After 10 min stirring at room temperature the clear solution was evaporated to dryness and the white residue was recrystallized from dichloro-

methane-hexane to give complex (7) (0.89 g, 69%) (Found: C, 54.85; H, 3.1; N, 1.55.  $C_{52}H_{36}ClF_9NP_2Tl$  requires C, 55.35; H, 3.1; N, 1.2%); or (9) (0.38 g, 77%) (Found: C, 41.25; H, 3.45; N, 1.4.  $C_{34}H_{36}ClF_{15}NTl$  requires C, 41.5; H, 3.7; N, 1.4%).

$[N(PPh_3)_2][TlR_3(CN)]$  [ $R = C_6F_3H_2$  (8) or  $C_6F_5$  (10)].—To a solution of (1) (0.172 g, 0.25 mmol) or (2) (0.198 g, 0.25 mmol) in methanol (15  $cm^3$ ) was added NaCN (0.025 g, 0.5 mmol) and the mixture was stirred for 45 min.  $[N(PPh_3)_2]ClO_4$  (0.155 g, 0.25 mmol) was added, the stirring was continued for 20 min, and the solution was evaporated to dryness. The residue was treated with dichloromethane (30  $cm^3$ ), and the solution was filtered and evaporated to dryness. The resulting solid was recrystallized from diethyl ether-hexane to give (8) (0.130 g, 45%) (Found: C, 56.45; H, 3.25; N, 2.4.  $C_{55}H_{36}F_9N_2P_2Tl$  requires C, 56.85; H, 3.1; N, 2.4%); or (10) (0.096 g, 27%) (Found: C, 51.9; H, 2.4; N, 2.45.  $C_{55}H_{30}F_{15}N_2P_2Tl$  requires C, 52.0; H, 2.4; N, 2.2%).

$[N(PPh_3)_2][Tl(C_6F_5)_3X]$  [ $X = NO_3$  (11) or  $CF_3CO_2$  (12)].—A mixture of (10) (0.184 g, 0.14 mmol) and  $AgX$  [ $X = NO_3$  (0.025 g, 0.14 mmol) or  $CF_3CO_2$  (0.036 g, 0.14 mmol)] was dissolved in acetone (20  $cm^3$ ) and stirred for 1 h at room temperature. The  $AgCN$  formed was filtered off, the filtrate was evaporated to dryness, and the white residue was recrystallized from diethyl ether-hexane to give (11) (0.100 g, 55%) (Found: C, 49.25; H, 2.75; N, 2.45.  $C_{54}H_{30}F_{15}N_2O_3P_2Tl$  requires C, 49.65; H, 2.3; N, 2.15%); or (12) (0.078 g, 36%) (Found: C, 49.35; H, 2.25; N, 1.1.  $C_{56}H_{30}F_{18}NO_2P_2Tl$  requires C, 49.55; H, 2.25; N, 1.05%).

$Q[Tl(C_6F_3H_2)_2M^*]$  [ $Q = NBu_4$ ,  $M^* = [Mo(cp)(CO)_3]^-$  (13) or  $[W(cp)(CO)_3]^-$  (14); or  $Q = N(PPh_3)_2$ ,  $M^* = [Co(CO)_4]^-$  (15) or  $[Mn(CO)_5]^-$  (16)].—To a suspension of (1) (0.172 g, 0.25 mmol) in dichloromethane (10  $cm^3$ ) at  $-50^\circ C$  was added  $QM^*$  (0.25 mmol) [ $[NBu_4][Mo(cp)(CO)_3]^{23}$  (0.125 g),  $[NBu_4][W(cp)(CO)_3]^{23}$  (0.144 g),  $[N(PPh_3)_2][Co(CO)_4]^{24}$  (0.177 g), or  $[N(PPh_3)_2][Mn(CO)_5]^{25}$  (0.184 g)]. The resulting solution was stirred for 10 min; addition of hexane (25  $cm^3$ ) then caused separation of an oil, which was decanted and separated by vigorous stirring with hexane to give (13) (0.142 g, 52%) (Found: C, 45.55; H, 4.5; N, 1.4.  $C_{42}H_{47}F_9MoNO_3Tl$  requires C, 46.45; H, 4.35; N, 1.3%); (14) (0.207 g, 71%) (Found: C, 41.65; H, 4.55; N, 1.2.  $C_{42}H_{47}F_9NO_3TIW$  requires C, 43.0; H, 4.05; N, 1.2%; discrepancies can be explained by lack of stability at room temperature); (15) (0.244 g, 74%) (Found: C, 53.1; H, 3.0; N, 1.1.  $C_{58}H_{36}CoF_9NO_4P_2Tl$  requires C, 53.3; H, 2.8; N, 1.05%); or (16) (0.209 g, 87%) (Found: C, 52.85; H, 2.95; N, 1.0.  $C_{59}H_{36}F_9MnNO_5P_2Tl$  requires C, 53.25; H, 2.75; N, 1.05%).

$Q[Tl(C_6F_5)_3M^*]$  [ $Q = NBu_4$ ,  $M^* = [Mo(cp)(CO)_3]^-$  (17) or  $[W(cp)(CO)_3]^-$  (18); or  $Q = N(PPh_3)_2$ ,  $M^* = [Co(CO)_4]^-$  (19)].—To a suspension of (2) (0.24 g, 0.30 mmol) in dichloromethane (30  $cm^3$ ) was added  $QM^*$  (0.30 mmol) [ $[NBu_4][Mo(cp)(CO)_3]^{23}$  (0.150 g),  $[NBu_4][W(cp)(CO)_3]^{23}$  (0.173 g), or  $[N(PPh_3)_2][Co(CO)_4]^{24}$  (0.208 g)] and the mixture was stirred for 15 min at room temperature. Concentration to ca. 5  $cm^3$  and addition of hexane led to the separation of (17) (0.257 g, 72%) (Found: C, 42.5; H, 3.5; N, 1.25.  $C_{42}H_{41}F_{15}MoNO_3Tl$  requires C, 42.3; H, 3.45; N, 1.15%); (18) (0.288 g, 75%) (Found: C, 38.8; H, 3.2; N, 1.05.  $C_{42}H_{41}F_{15}NO_3TIW$  requires C, 39.4; H, 3.25; N, 1.1%); or (19) (0.242 g, 57%) (Found: C, 49.9; H, 2.55; N, 1.2.  $C_{58}H_{30}CoF_{15}NO_4P_2Tl$  requires C, 49.25; H, 2.15; N, 1.0%).

$[N(PPh_3)_2][Tl(C_6F_5)_3\{Mn(CO)_5\}]$  (20).—A solution of Tl-

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (prepared by treating [NBu<sub>4</sub>][Ti(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>7</sup> (0.178 g, 0.16 mmol) with an excess of HBF<sub>4</sub> in diethyl ether (20 cm<sup>3</sup>) was added to [N(PPh<sub>3</sub>)<sub>2</sub>][Mn(CO)<sub>5</sub>]<sup>25</sup> (0.114 g, 0.16 mmol) and the mixture was stirred at room temperature for 15 min. The solution was evaporated to dryness and the resulting (20) was recrystallized from diethyl ether-hexane (0.132 g, 59%) (Found: C, 50.05; H, 2.45; N, 0.85. C<sub>59</sub>H<sub>30</sub>F<sub>15</sub>MnNO<sub>5</sub>P<sub>2</sub>Tl requires C, 49.25; H, 2.1; N, 0.95%).

Complex (19) was obtained similarly (0.106 g, 47%).

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