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 [TlR_3(diox)] (diox = 1,4-dioxan) has been prepared by the reaction of $TlCl_3$ with LiR (R = 2,4,6-$C_6F_3H_2$), or of [NBu_4][TlR_4] with HBF_4 (R = C_6F_5) and subsequent addition of dioxan. The displacement of dioxan by (*a*) neutral ligands leads to [TlR_3L] (L = $OPPh_3$, pyridine, PPh_3, or $Ph_2PCH_2PPh_2$); (*b*) anionic ligands affords Q[TlR_3X] {Q = $[NBu_4]^+$ or $[N(PPh_3)_2]^+$; X = Cl^-, CN^-, NO_3^-, or $CF_3CO_2^-$}; and (*c*) metal carbonylate gives Q[TlR_3M^*] {M* = $[Mo(cp)(CO)_3]^-$ (cp = η-C_5H_5), $[W(cp)(CO)_3]^-$, $[Co(CO)_4]^-$ or $[Mn(CO)_5]^-$}.

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.[1,2] The synthesis of tris(polyfluorophenyl)thallium(III) derivatives by the reaction of TlR_2Br with Cu metal [3,4] or with $Ba(O_2SR)_2$ [5] followed by isolation as the dioxan adducts [TlR_3(diox)] (R = C_6F_5, *p*-C_6F_4H, *m*-C_6F_4H, *o*-C_6F_4H, or 2,4,6-$C_6F_3H_2$) has been reported.

In the present paper we describe how [TlR_3(diox)] (R = C_6F_5 or 2,4,6-$C_6F_3H_2$) can be obtained more straightforwardly and in higher yields by the reaction of $TlCl_3$ with Li(2,4,6-$C_6F_3H_2$) or of [NBu_4][$Tl(C_6F_5)_4$] with HBF_4. The dioxan ligand can readily be replaced by other neutral ligands [L = $OPPh_3$, pyridine (py), PPh_3, or bis(diphenylphosphino)methane (dppm)], or anionic ligands (X = Cl^- or CN^-), or by metal carbonylate {M* = $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, $[Mo(cp)(CO)_3]^-$ or $[W(cp)(CO)_3]^-$ (cp = η-C_5H_5)} to give novel derivatives of the types [TlR_3L], Q[TlR_3X], or Q[TlR_3M^*] (Q = $[NBu_4]^+$ or $[N(PPh_3)_2]^+$), respectively.

Results and Discussion

Preparation of the Starting Complexes.—Recently [6] we have reported the preparation of TlR_2Cl (R = C_6F_5 or 2,4,6-$C_6F_3H_2$) by arylation of $TlCl_3$ with 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 LiR (R = C_6F_5) leads to $[TlR_4]^-$, or even to $[TlR_6]^{3-}$, which can be isolated upon addition of a bulky cation.[7] Formation of TlR_3, however, was not observed; use of a 1 : 3 molar ratio gives a mixture of TlR_2Cl and $[TlR_4]^-$.

(*b*) An excess of LiR (R = 2,4,6-$C_6F_3H_2$) does not afford $[TlR_4]^-$ but gives stable diethyl ether solutions of 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 [$Tl(C_6F_3H_2)_3$(diox)] (1).

$$TlCl_3 + 3\,Li(C_6F_3H_2) \longrightarrow 3\,LiCl + Tl(C_6F_3H_2)_3 \qquad (i)$$

Ether solutions of $Tl(C_6F_5)_3$ can be obtained by the reaction between $[TlR_4]^-$ and inorganic acids with poorly co-ordinating anions [equation (ii)]. Addition of diox permits the isolation of [$Tl(C_6F_5)_3$(diox)] (2).

$$[NBu_4][Tl(C_6F_5)_4] + HBF_4 \longrightarrow [NBu_4][BF_4] + C_6F_5H + Tl(C_6F_5)_3 \qquad (ii)$$

These methods allow the isolation of compounds (1) and (2) in better yields (68 and 83%, respectively) than those reported.[3-5] 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)

$$[TlR_3(diox)] + L \longrightarrow [TlR_3L] + diox \qquad (iii)$$

$$R = C_6F_3H_2;\ L = OPPh_3\ (3),\ py\ (4),\ PPh_3\ (5),\ or\ dppm\ (6)$$

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

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

$$[TlR_3(diox)] + QX \longrightarrow Q[TlR_3X] + diox \qquad (iv)$$

$$\begin{gathered} Q = [NBu_4]^+ \text{ or } [N(PPh_3)_2]^+ \\ R = C_6F_3H_2;\ X = Cl\ (7) \text{ or } CN\ (8) \\ R = C_6F_5;\ X = Cl\ (9) \text{ or } CN\ (10) \end{gathered}$$

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

$$Q[TlR_3(CN)] + AgX \longrightarrow AgCN \begin{cases} +QX + TlR_3 & (v) \\ \quad X = ClO_4 & \\ + Q[TlR_3X] & (vi) \end{cases}$$

$$R = C_6F_5;\ X = NO_3\ (11) \text{ or } CF_3CO_2\ (12)$$

and two different reaction courses; if X is a non-co-ordinating anion (ClO_4) the process represented in equation (v) takes place and addition of dioxan (after removal of AgCN and QX by filtration) allows isolation of (1) or (2). If X is a co-ordinating anion (NO_3 or CF_3CO_2) the reaction takes place according to equation (vi), and complex (11) or (12), respectively, can be isolated after removal of AgCN.

The presence of the CF_3CO_2 group is supported by a strong band at 1 680 cm^{-1} [ν_{asym}(CO)].[12] Other absorptions, as well as those expected for X = NO_3,[13] are masked by vibrations

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

	M.p. (°C)	Λ_M/ ohm^{-1} cm^2 mol^{-1}	*M* Found (calc.)
(1) $[Tl(C_6F_3H_2)_3(diox)]$	182 (decomp.)	1	
(2) $[Tl(C_6F_5)_3(diox)]$	259 (decomp.)	1	
(3) $[Tl(C_6F_3H_2)_3(OPPh_3)]$	141	1	897 (876)
(4) $[Tl(C_6F_3H_2)_3(py)]$	133	2	694 (677)
(5) $[Tl(C_6F_3H_2)_3(PPh_3)]$	209 (decomp.)	3	835 (860)
(6) $[Tl(C_6F_3H_2)_3(dppm)]$	100	2	933 (982)
(7) $[N(PPh_3)_2][Tl(C_6F_3H_2)_3Cl]$	115	85	
(8) $[N(PPh_3)_2][Tl(C_6F_3H_2)_3(CN)]$	115	89	
(9) $[NBu_4][Tl(C_6F_5)_3Cl]$	83	97	
(10) $[N(PPh_3)_2][Tl(C_6F_5)_3(CN)]$	90	98	
(11) $[N(PPh_3)_2][Tl(C_6F_5)_3(NO_3)]$	123 (decomp.)	105	
(12) $[N(PPh_3)_2][Tl(C_6F_5)_3(O_2CCF_3)]$	106	98	

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

	M.p. (decomp.) (°C)	Λ_M/ ohm^{-1} cm^2 mol^{-1}	ν(CO) */cm^{-1}
(13) $[NBu_4][Tl(C_6F_3H_2)_3\{Mo(cp)(CO)_3\}]$	48	120	1 962vs, 1 879vs (sh), 1 868vs, br
(14) $[NBu_4][Tl(C_6F_3H_2)_3\{W(cp)(CO)_3\}]$		138	1 956vs, 1 880vs (sh), 1 867vs, br
(15) $[N(PPh_3)_2][Tl(C_6F_3H_2)_3\{Co(CO)_4\}]$	58	115	2 042m, 1 968m (sh), 1 956s
(16) $[N(PPh_3)_2][Tl(C_6F_3H_2)_3\{Mn(CO)_5\}]$	90	112	2 070m, 1 967vs, br
(17) $[NBu_4][Tl(C_6F_5)_3\{Mo(cp)(CO)_3\}]$	107	91	1 977vs, 1 900vs (sh), 1 888vs
(18) $[NBu_4][Tl(C_6F_5)_3\{W(cp)(CO)_3\}]$	84	90	1 973vs, 1 892vs (sh), 1 878vs
(19) $[N(PPh_3)_2][Tl(C_6F_5)_3\{Co(CO)_4\}]$	139	127	2 055m, 1 990m (sh), 1 970s
(20) $[N(PPh_3)_2][Tl(C_6F_5)_3\{Mn(CO)_5\}]$	100	84	2 065m, 1 985vs, br

* In dichloromethane.

arising from the cation. A similar reaction is observed for $R = C_6F_3H_2$, $X = CF_3CO_2$, 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 $\nu_{asym}(CO)$ at 1 658 cm^{-1}.

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 $[Au(C_6F_5)_3(tht)]$, where the substitution of halide or pseudohalide for tetrahydrothiophen (tht) leads to organoaurate(III),[14] or the use of metal carbonylate gives anions containing gold(III)–transition metal bonds.[15] Since $[AsPh_4][Tl\{Co(CO)_4\}_4]$ [16] is the only reported anionic complex with a thallium(III)–transition metal bond, it seemed of interest to explore analogous reactions of $[TlR_3(diox)]$. In fact, addition of an equimolecular amount of QM* [$Q = NBu_4$ or $N(PPh_3)_2$] to a suspension of $[TlR_3(diox)]$ 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). $[TlR_3(diox)]$ need not necessarily be isolated, since the complexes can also be prepared directly by adding the carbonylate to ethereal solutions of TlR_3 [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 $[Co(CO)_4]^-$, as may be seen from the appearance of ν(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.

$$[TlR_3(diox)] + QM^* \longrightarrow Q[R_3Tl{-}M^*] + diox \quad (vii)$$

$R = C_6F_3H_2$; $M^* = [Mo(cp)(CO)_3]^-$ (13), $[W(cp)(CO)_3]^-$ (14), $[Co(CO)_4]^-$ (15), or $[Mn(CO)_5]^-$ (16)

$R = C_6F_5$; $M^* = [Mo(cp)(CO)_3]^-$ (17), $[W(cp)(CO)_3]^-$ (18), or $[Co(CO)_4]^-$ (19)

$$Tl(C_6F_5)_3 + [N(PPh_3)_2]M^* \longrightarrow [N(PPh_3)_2][(C_6F_5)_3Tl{-}M^*] \quad (viii)$$

$M^* = [Co(CO)_4]^-$ (19) or $[Mn(CO)_5]^-$ (20)

The i.r. spectra of complexes (13)—(20) in the carbonyl region are in agreement with the expected pattern; the ν(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[17] ($2a_1 + e$); 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[18] and $2a' + a''$ for Mo and W[19]). As may be seen from Table 2, the absorption bands of the $R = C_6F_5$ derivatives are at higher energies than those where $R = 2,4,6\text{-}C_6F_3H_2$, which seems in accord with the higher electronegativity of the former.

All the complexes with $R = C_6F_5$ described in the present paper are characterized by two bands at 780 and 770 cm^{-1}.

This *X*-sensitive vibration of the C_6F_5 group is assignable [9,20] to a mode involving predominantly Tl–C stretching and can be related to the symmetry of the compounds as has been shown for Tl,[6] Au,[21] and Pd or Pt [22] derivatives. A similar situation is also observed for compounds containing the 2,4,6-$C_6F_3H_2$ group; [21] 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.* 5×10^{-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 °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 °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 $[NBu_4][Tl(C_6F_5)_4]$ [7] (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 dichloromethane–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 °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. $C_{42}H_{47}F_9NO_3TlW$ 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. $C_{42}H_{41}F_{15}NO_3TlW$ 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-

$(C_6F_5)_3$ (prepared by treating $[NBu_4][Tl(C_6F_5)_4]$[7] (0.178 g, 0.16 mmol) with an excess of HBF_4 in diethyl ether (20 cm^3) was added to $[N(PPh_3)_2][Mn(CO)_5]$[25] (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. $C_{59}H_{30}F_{15}MnNO_5P_2Tl$ requires C, 49.25; H, 2.1; N, 0.95%).

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

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