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Platinum–thallium cluster complexes

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The synthesis of new Pt_3Tl complexes $[Pt_3\{\mu_3\text{-}Tl(diketonate)(OH_2)\}(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]_2$, **2**, dppm = $Ph_2CH_2PPh_2$, by reversible addition of thallium(I) β-diketonates to the complex cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, is reported. The thallium(I) units are easily displaced from platinum by halide ions X^- (X = Cl, Br, I) to give $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}X)(\mu\text{-}dppm)_3]^+$, or by $SnCl_3^-$ to give $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}SnCl_3)(\mu\text{-}dppm)_3]^+$. With trifluoroacetate there was an equilibrium with $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}O_2CCF_3)(\mu\text{-}dppm)_3]^+$ and $[Pt_3\{\mu_3\text{-}Tl(diketonate)(O_2CCF_3)\}(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$. The structures of two Pt_3Tl clusters are reported, and the Pt_3Tl unit is shown to be tetrahedral.

Introduction

There has been much interest in the use of thallium(I) as a ligand in late transition metal chemistry,[1–17] and many of the known examples involve PtTl bonding.[1–13] Most Pt–Tl bonded complexes contain simple Pt–Tl or Pt–Tl–Pt units[4,6–9,11–13] but Tl–Pt–Tl units are also known.[5,10] Platinum–thallium bonds in cluster complexes are known as depicted in Chart 1,[1–3] but the only structurally characterized Pt_3Tl complex is $[Pt_3(\mu_3\text{-}Tl)(\mu\text{-}CO)_3(PCy_3)_3]^+$, isolated as the $[RhCl_2(cod)]^-$ salt, **A** in Chart 1.[1] Complex **A** has *d*(PtPt) = 2.667(1)–2.668(1) and *d*(PtTl) = 3.034(1)–3.047(1) Å so is regarded as having a distorted tetrahedral core.[1] Complex **C** (Chart 1) has an encapsulated thallium(I) ion bridging two Pt_3 triangles, with *d*(PtPt) = 2.658(3)–2.682(3) and *d*(PtTl) = 2.860(3)–2.992(3) Å.[3] The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, **1**,[18] forms bimetallic cluster complexes with many other main group and transition elements, including the Pt_3ReTl complex **B** (Chart 1), which was characterized by its spectroscopic properties.[2] Thallium(I) may act as a 2-electron donor using its $6s^2$ electrons, but it may also act as an electrophilic group, accepting an electron pair from an electron-rich metal into an empty 6p orbital.[1–17] It is possible that both of these forms of bonding may contribute to the metal–thallium bond, resulting in little net electron transfer. Since there are few Pt_3Tl cluster complexes, it was of interest to extend the series of known complexes by studying the binding of thallium(I) directly to complex **1**,[18] and this article reports that thallium(I) can bind easily and reversibly to give a series of cluster complexes containing tetrahedral Pt_3Tl units.

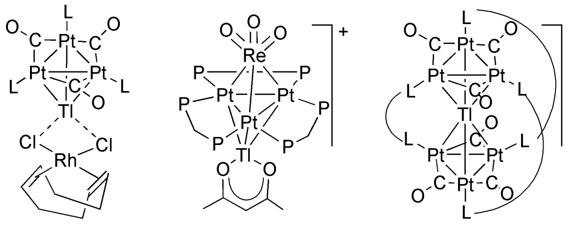

A, L = PCy_3 B, PP = dppm C, LL = dppp

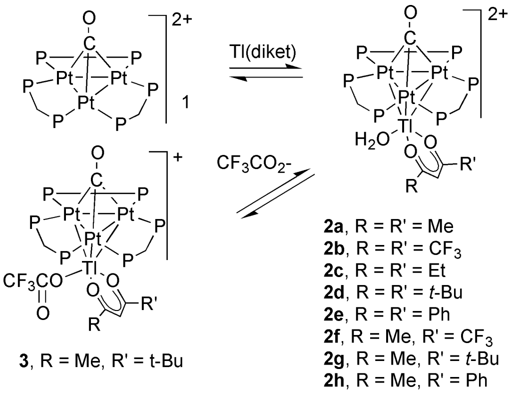
Chart 1 Some clusters having Pt_3Tl units.

Results

The synthesis of new Pt_3Tl complexes by addition of thallium(I) β-diketonates[19] to the complex cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, **1**, is shown in Scheme 1. The reactions to give complexes $[Pt_3\{\mu_3\text{-}Tl(diketonate)(OH_2)\}(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]_2$, **2**, appeared to be quantitative when monitored by ^1H and ^{31}P NMR spectroscopy, and the products could be isolated as air-stable orange solids by precipitation from acetone solution. However, the reactions are clearly equilibria and slow crystallization from acetone–ether or acetone–pentane solutions often gave single crystals of the precursor cluster complex **1**. Cyclopentadienylthallium(I) failed to form a complex with **1**, perhaps due to steric effects with the cyclopentadienyl group.

Table 1 Selected ^{31}P NMR data for the complexes

Complex	δ(P)	^1J(PtP)	^2J(TlP)	^3J(PP)
2a	−1.97	3745	487	140
2b	−1.27	3765	412	110
2c	−2.44	3783	485	100
2d	−0.10	3754	459	110
2e	−1.41	3752	485	100
2f	−1.85	3766	465	130
2g	−0.28	3774	463	150
2h	−1.71	3757	465	100



Scheme 1 Synthesis of the Pt_3Tl clusters.

The presence of the Pt_3Tl core in clusters **2** was clearly demonstrated by the ^{31}P NMR spectra, which showed the presence of a coupling ^2J(TlP) = 412–487 Hz (Table 1). A typical ^{31}P NMR spectrum is shown in Fig. 1. The spectra, especially in the ^{195}Pt satellite regions, were broad. The spectra were essentially unchanged at low temperature, suggesting that the broadening is not a result of fluxionality. The ^1H NMR spectra were also broad, but showed the expected resonances

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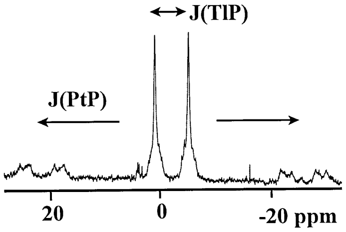
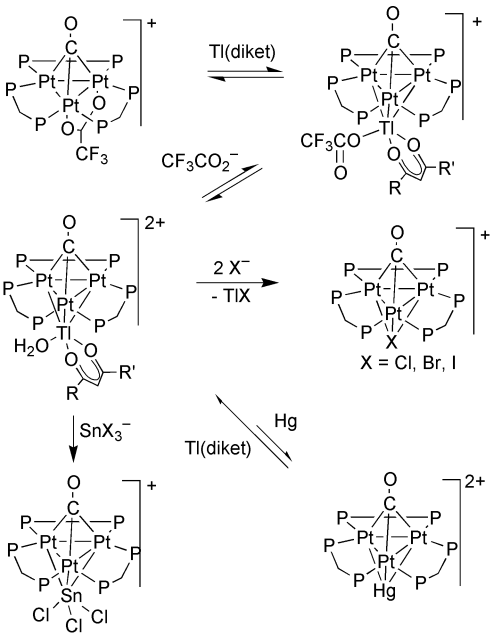


Fig. 1 The ^{31}P NMR spectrum of complex **2a**. The central doublet arises from ^{2}J(TlP) and satellite spectra from ^{1}J(PtP).

for the dppm and the β-diketonate ligands. In addition, a broad singlet resonance at $\delta = 2.3$–2.4 ppm was assigned to a water ligand. None of the resonances showed coupling to thallium, and it is possible that there is easy intermolecular exchange of the diketonate and aqua ligands between thallium centres. When the reactions of **1** with thallium diketonates are carried out in dry acetone, it is likely that the acetone solvates are formed but it has not been possible to isolate such complexes in pure form or to grow crystals for structure determination. On workup, the aqua complexes are isolated.

The binding of thallium(I) to platinum is evidently not strong and attempted ligand substitution reactions at thallium(I) tended to cause displacement from platinum. For example, reactions with halide ions X^- gave precipitation of TlX and formation of $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}X)(\mu\text{-dppm})_3]^+$, as shown in Scheme 2. The thallium(I) centre in **2a** was not displaced by mercury(0) but it was displaced by $SnCl_3^-$. With trifluoroacetate there was an equilibrium with $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}O_2CCF_3)(\mu\text{-dppm})_3]^+$ and $[Pt_3\{\mu_3\text{-}Tl(diketonate)(O_2CCF_3)\}(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, and crystals of complex **3** (Scheme 1) were isolated from one such reaction.



Scheme 2 Reactions of the Pt_3Tl clusters.

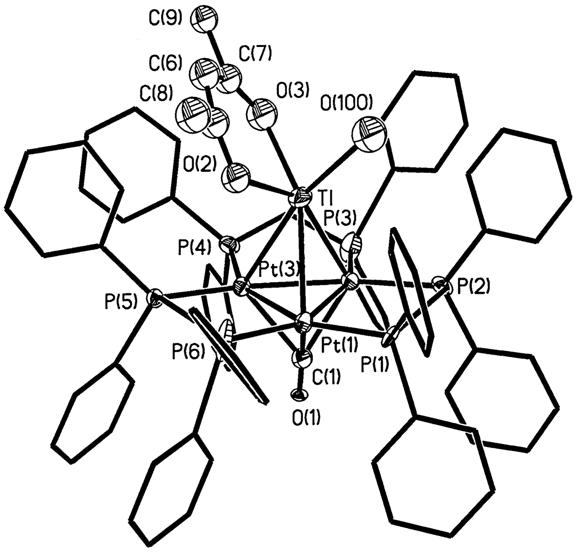


Fig. 2 A view of the structure of the dicationic cluster complex **2a**, with 30% probability ellipsoids. For clarity, thermal ellipsoids are not shown for carbon atoms of the dppm ligands.

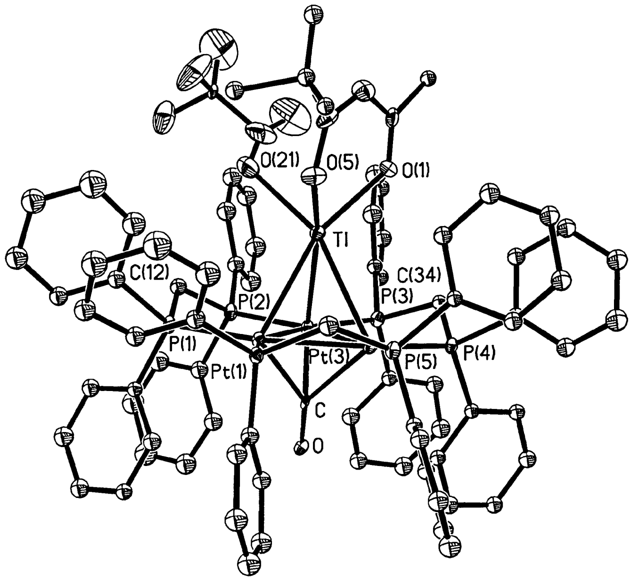


Fig. 3 A view of the structure of the cationic cluster complex **3**, with 30% probability ellipsoids.

The structures of complexes **2a** and **3** were determined crystallographically, and are shown in Fig. 2 and 3. Selected bond parameters are given in Table 2. For both complexes, the $[Pt_3\{\mu_3\text{-}Tl\}(\mu_3\text{-}CO)(\mu\text{-dppm})_3]$ core of the cluster was clearly defined but the ligands on thallium exhibited disorder and the bond parameters for them are less precise. Both **2a** and **3** contain a roughly tetrahedral Pt_3Tl core with similar mean distances d(PtPt) = 2.645 and 2.638 Å and d(PtTl) = 2.911 and 2.903 Å in **2a** and **3** respectively. The mean distance d(PtTl) is shorter than in complex **A**, Chart 1, of 3.038 Å but similar to that in complex **C** of 2.932 Å.[1,2] The cluster structure is similar to those in $[Pt_3(\mu_3\text{-}Hg)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ and in $[Pt_3(\mu_3\text{-}SnF_3)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, each of which has a roughly tetrahedral core.[20]

In terms of bonding, the units $Tl(OH_2)$(diketonate) and $[Tl(O_2CCF_3)(diketonate)]^-$ can be thought of as having thallium(I) with sp^3 hybridization and a stereochemically active lone pair of electrons, that is then donated to the a_1 acceptor orbital of the Pt_3 triangle of complex **1** to form the tetrahedral cluster. The donor group can be thought of as isoelectronic with $[SnX_3]^-$ or with PX_3. The donor $[SnX_3]^-$ forms a similar cluster as shown in Scheme 2, and is evidently a better donor than thallium(I). We have attempted to prepare the analogous lead(II) derivatives since these would be strictly isoelectronic with thallium(I) but without success. It should also be noted that the isoelectronic donors Hg(0) and Tl(I) behave somewhat differently, as seen in Scheme 2. The neutral Hg(0) does not take on extra ligands, whereas thallium(I) does. Thus, if the clusters are considered as having the main group metal acting as a 2-electron-donor to a Pt_3 cluster, the Tl(I) and Hg(0) derivatives are similar. However, considering them as tetranuclear clusters, the mercury(0) and thallium(I) derivatives are 54- and 60-electron clusters respectively. In these complexes, it is probably best to consider the main group metal as a 2-electron donor.

Table 2 Selected bond lengths [Å] and angles [°] for $[Pt_3(\mu_3\text{-CO})\{\mu_3\text{-Tl(acac)(OH}_2)\}(\mu\text{-dppm})_3][PF_6]_2\cdot CH_2Cl_2$, **2a**, and $[Pt_3(\mu_3\text{-CO})\{\mu_3\text{-Tl(MeCOCHCOBu)(OCOCF}_3)\}(\mu\text{-dppm})_3][PF_6]\cdot 0.75Me_2CO$, **3**

	2a	**3**
Pt(1)–Pt(2)	2.642(1)	2.640(1)
Pt(1)–Pt(3)	2.655(2)	2.632(1)
Pt(2)–Pt(3)	2.639(2)	2.642(1)
Pt(1)–Tl	2.894(3)	2.867(1)
Pt(2)–Tl	2.891(3)	2.906(1)
Pt(3)–Tl	2.947(1)	2.935(1)
Pt(1)–C(1)	2.17(4)	2.18(2)
Pt(2)–C(1)	2.17(4)	2.14(2)
Pt(3)–C(1)	2.26(2)	2.21(2)
Tl–O(a)	2.58(3)	2.27(2)
Tl–O(b)	2.26(3)	2.30(2)
Tl–O(c)	2.51(2)	2.39(2)
Pt(2)–Pt(1)–Pt(3)	59.76(8)	60.14(3)
Pt(3)–Pt(2)–Pt(1)	60.37(8)	59.77(3)
Pt(2)–Pt(3)–Pt(1)	59.87(3)	60.09(3)
Pt(2)–Pt(1)–Tl	62.76(10)	63.54(3)
Pt(3)–Pt(1)–Tl	63.99(6)	64.34(3)
Pt(3)–Pt(2)–Tl	64.22(6)	63.67(3)
Pt(1)–Pt(2)–Tl	62.89(10)	62.03(3)
Pt(2)–Pt(3)–Tl	62.04(6)	62.55(3)
Pt(1)–Pt(3)–Tl	61.95(7)	61.71(3)
Pt(2)–Tl–Pt(1)	54.34(3)	54.43(2)
Pt(2)–Tl–Pt(3)	53.73(5)	53.78(2)
Pt(1)–Tl–Pt(3)	54.06(5)	53.94(2)

O(a), O(b) are in diketonate ligands, O(c) is in the aqua or trifluoroacetate ligand.

Experimental

All reactions were carried out under a N_2 atmosphere using Schlenk techniques. IR spectra were recorded as Nujol mulls by using a Perkin-Elmer 2000 spectrometer. The ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded using a Varian Mercury 400 or an Inova 400 spectrometer; the Pt_3Tl complexes did not give satisfactory ^{13}C or ^{195}Pt NMR spectra. Chemical shifts are referenced to Me_4Si (^{1}H), $CFCl_3$ (^{19}F) or 85% H_3PO_4 (^{31}P). The complex $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ was prepared according to the reported method,[18] and thallium(I) diketonates were prepared and characterized by the literature methods.[19] Characterization data: **Tl(acac)**, IR: ν(CO) 1571 (s), 1514 (m) cm^{-1}. ^{1}H NMR: δ = 5.22 [s, 1H, CH]; 1.89 [s, 6H, CH_3]; **Tl(hfac)**, IR: ν(CO) 1665 (s), 1557 (w), 1530 (m) cm^{-1}. ^{1}H NMR: δ = 5.47 [s,1H, CH]; ^{19}F NMR: δ = −76.9 [s, 6F, CF_3]; **Tl(etac)**, IR: ν(CO) 1590 (s), 1509 (m) cm^{-1}. ^{1}H NMR: δ = 5.05 [s, 1H, CH]; 2.07 [q, 4H, CH_2]; 0.98 [t, 6H, CH_3]; **Tl(dpm)**, IR: ν(CO) 1602 (s), 1507 (w), 1498 (m) cm^{-1}. ^{1}H NMR: δ = 5.31 [s, 1H, CH]; 0.94 [s, 18H, ^{t}Bu]; **Tl(dbm)**, IR: ν(CO) 1593 (s), 1550 (m) cm^{-1}. ^{1}H NMR: δ = 7.4–7.95 [m, 10H, Ph]; 6.05 [s, 1H, CH]; **Tl(tfac)**; IR: ν(CO) 1617 (s), 1516 (m) cm^{-1}. ^{1}H NMR: δ = 5.38 [s, 1H, CH]; 1.96 [s, 3H, CH_3]; ^{19}F NMR: δ = −76.20 [s, CF_3]; **Tl(tbac)**, IR: ν(CO) 1585 (s), 1548 (w), 1507 (s) cm^{-1}. ^{1}H NMR (acetone): δ 5.29 [s, 1H, CH]; 1.88 [s, 3H, CH_3]; 1.05 [s, 9H, ^{t}Bu]; **Tl(bzac)**, IR: ν(CO) 1588 (s), 1569 (s) cm^{-1}. ^{1}H NMR (acetone): δ = 7.35–7.82 [m, 5H, Ph]; 5.78 [s, 1H, CH]; 1.94 [s, 3H, CH_3].

Syntheses

$[Pt_3\{\mu_3\text{-Tl(acac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2a). To a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]$ $[PF_6]_2$ (50 mg, 0.024 mmol) in acetone (5 mL) was added a solution of Tl(acac) (7.5 mg, 0.024 mmol) in acetone (5 mL). The resulting mixture was stirred at room temperature for 0.5 h, then filtered and the solution was concentrated to 3 mL. Ether was added to precipitate the complex product as an orange solid in 60% yield. IR: ν(CO) = 1792 (s) cm^{-1}. NMR in acetone-d$_6$: δ(^{1}H) = 6.3 [m, 3H, H^{a}CP$_2$, dppm]; 5.8 [m, 3H, H^{b}CP$_2$, dppm]; 5.6 [s, 1H, CH, acac]; 2.18 [s, 6H, CH_3, acac]; δ(^{31}P) = −1.97 [d, 6P, ^1J(PtP) = 3745 Hz, ^2J(TlP) = 487 Hz, ^3J(PP) = 145 Hz, dppm]. Anal. Calc. for: $C_{81}H_{75}F_{12}O_4P_8Pt_3$ Tl: C, 40.9; H, 3.2. Found: C, 41.2; H, 3.1%.

$[Pt_3\{\mu_3\text{-Tl(hfac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2b). This was prepared similarly but using Tl(hfac). The complex was isolated as an orange solid in 62% yield. IR: ν(CO) 1790 (m) cm^{-1}. NMR: δ(^{1}H) = 6.2 [m, 3H, H^{a}CP$_2$, dppm]; 5.9 [s, 1H, CH, hfac]; 5.8 [m, 3H, H^{b}CP$_2$, dppm]; δ(^{19}F) = −2.75 [d, 12F, ^1J(PF) = 175 Hz, PF$_6$]; −77.7 [s, 6F, CF$_3$, hfac]; δ(^{31}P) = −1.27 [d, ^1J(PtP) = 3765 Hz, ^2J(TlP) = 412 Hz, ^3J(PP) = 108 Hz, dppm]. Anal. Calc. for $C_{81}H_{69}F_{18}O_4P_8Pt_3Tl$: C, 39.2; H, 2.7. Found: C, 39.4; H, 2.5%.

$[Pt_3\{\mu_3\text{-Tl(etac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2c). This was prepared similarly from Tl(etac). The orange product was isolated in 58% yield. IR: ν(CO) 1790 (s) cm^{-1}. NMR: δ(^{1}H) = 6.35 [m, 3H, H^{a}CP2, dppm]; 5.7 [m, 3H, H^{b}CP$_2$, dppm]; 5.5 [s, 1H, CH, etac]; 2.3 [br, 4H, CH$_2$, etac]; 1.05 [t, 6H, J(HH) = 7 Hz, CH$_3$, etac]; δ(^{31}P) = −2.44 [d, 6P, ^1J(PtP) = 3783 Hz, ^2J(TlP) = 485 Hz, ^3J(PP) = 85 Hz, dppm]. Anal. Calc. for: $C_{83}H_{79}F_{12}O_4P_8Pt_3Tl$: C, 41.4; H, 3.3. Found: C, 41.3; H, 3.0%.

$[Pt_3\{\mu_3\text{-Tl(dpm)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2d). This was prepared similarly from Tl(dpm) and isolated in 73% yield. IR: ν(CO) 1780 (m) cm^{-1}. NMR: δ(^{1}H) = 5.8 [m, 3H, H^{a}CP$_2$, dppm]; 5.2 [m, 3H, H^{b}CP$_2$, dppm]; 5.0 [s, 1H, CH, dpm]; 1.9 [s, 18H, ^{t}Bu, dpm]; δ(^{31}P) = −0.1 [d, ^1J(PtP) = 3754 Hz, ^2J(TlP) = 459 Hz, ^3J(PP) = 108 Hz, dppm]. Anal. Calc. for $C_{87}H_{87}F_{12}O_4P_8Pt_3Tl$: C, 42.4; H, 3.6. Found: C, 42.6; H, 3.5%.

$[Pt_3\{\mu_3\text{-Tl(dbm)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2e). This was prepared similarly using Tl(dbm) and isolated in 75% yield. IR: ν(CO) = 1792 (s) cm^{-1}. NMR: δ(^{1}H) = 6.8 [m 3H, H^{a}CP$_2$, dppm]; 6.5 [m, 3H, H^{b}CP$_2$, dppm]; 5.7 [s, 1H, CH, dbm]; δ(^{31}P) = −1.4 [d, ^1J(PtP) = 3752 Hz, ^2J(TlP) = 485 Hz, ^3J(PP) = 98 Hz, dppm]. Anal. Calc. for: $C_{91}H_{79}F_{12}O_4P_8Pt_3Tl$: C, 43.7; H, 3.2. Found: C, 43.4; H, 3.0%.

$[Pt_3\{\mu_3\text{-Tl(tfac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2f). This was prepared similarly but using Tl(tfac) and the yellow–orange product was isolated in 62% yield. IR: ν(CO) = 1792 (s) cm^{-1}. NMR: δ(^{1}H) = 6.3 [m, 3H, H^{a}CP$_2$, dppm]; 5.75 [m, 3H, H^{b}CP$_2$, dppm]; 5.45 [s, 1H, CH, tfac]; 2.05 [s, 3H, CH$_3$, tfac]; δ(^{19}F) = −73.5 [d, 12F, ^1J(PF) = 708 Hz, PF$_6$]; −75.0 [s, 3F, CF$_3$, tfac]; δ(^{31}P) −1.85[d, ^1J(PtP) = 3766 Hz, ^2J(TlP) = 465 Hz, ^3J(PP) = 135 Hz, dppm]. Anal. Calc. for $C_{81}H_{72}F_{15}O_4P_8Pt_3Tl$: C, 40.0; H, 3.0. Found: C, 39.6; H, 2.7%.

$[Pt_3\{\mu_3\text{-Tl(tbac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2g). This was prepared in a similar way using Tl(tbac) and isolated in 64% yield. IR: ν(CO) = 1790 (m) cm^{-1}. NMR: δ(^{1}H) = 6.35 [m, 3H, H^{a}CP$_2$, dppm]; 5.9 [s, 1H, CH, tbac]; 5.7 [m, 3H, H^{b}CP$_2$, dppm]; 2.35 [s, 3H, CH$_3$, tbac]; 1.25 [s, 9H, ^{t}Bu, tbac]; δ(^{31}P) = −0.28 [d, ^1J(PtP) = 3774 Hz, ^2J(TlP) = 463 Hz, ^3J(PP) = 190 Hz, dppm]. Anal. Calc. for $C_{84}H_{81}F_{12}O_4P_8Pt_3Tl$: C, 41.7; H, 3.4. Found: C, 41.5; H, 3.1%.

$[Pt_3\{\mu_3\text{-Tl(bzac)(OH}_2)\}(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (2h). This was prepared similarly using Tl(bzac) and isolated as an orange–yellow solid in 75% yield. IR: ν(CO) = 1824 (s) cm^{-1}. NMR: δ(^{1}H) = 6.7 [s, 1H, CH, bzac]; 6.4 [m, 3H, H^{a}CP$_2$, dppm]; 5.8 [m, 3H, H^{b}CP$_2$, dppm]; 2.3 [s, 3H, CH$_3$, bzac]; δ(^{31}P) = −1.71 [d, ^1J(PtP) = 3757 Hz, ^2J(TlP) = 465 Hz, ^3J(PP) = 102 Hz, dppm]. Anal. Calc. for $C_{86}H_{77}F_{12}O_4P_8Pt_3Tl$: C, 42.3; H, 3.2. Found: C, 42.0; H, 2.9%.

$[Pt_3(\mu_3\text{-Cl})(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]$. To a solution of complex **1** (40 mg) in methanol (10 mL) was added KCl (2.9 mg), and the

Table 3 Crystal data and structure refinement for $[Pt_3(\mu_3\text{-}CO)\{\mu_3\text{-}Tl(acac)(OH_2)\}(\mu\text{-}dppm)_3][PF_6]_2\cdot CH_2Cl_2$, **2a**, and $[Pt_3(\mu_3\text{-}CO)\{\mu_3\text{-}Tl(MeCOCHCOBu)(OCOCF_3)\}(\mu\text{-}dppm)_3][PF_6]\cdot 0.75Me_2CO$, **3**

Complex	**2a**	**3**
Formula	$C_{81}H_{74}Cl_2F_{12}O_3P_8Pt_3Tl$	$C_{86}H_{79}F_9O_5P_7Pt_3Tl\cdot 0.75C_3H_6O$
M	2431.70	2413.48
T/K	293(2)	150(2)
Wavelength/Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$
a/Å	13.459(3)	14.692(2)
b/Å	23.090(5)	29.713(3)
c/Å	14.721(3)	21.744(2)
β/°	103.99(3)	99.054(4)
Volume/Å^3, Z	4439(1), 2	9373.6(18), 4
Density (calc.)/Mg m^{-3}	1.819	1.710
μ/mm^{-1}	6.795	6.362
Ind. refl.	13736	16840
Abs. corr.	Integration	Integration
Data/restr./param.	13736/1/428	16840/0/486
Goof on F^2	1.104	1.096
R indices $[I > 2\sigma(I)]$	$R1 = 0.0795$, $wR2 = 0.1899$	$R1 = 0.0944$, $wR2 = 0.2625$

mixture was stirred for 2 h. The solvent volume was reduced and water (5 mL) was added to precipitate the product, which was washed with water and dried under vacuum. Yield 98%. Anal. Calc. for $C_{76}H_{66}ClF_6OP_7Pt$: C, 46.9; H, 3.4. Found: C, 47.3; H, 3.8%. IR (Nujol): ν(CO) = 1767 cm^{-1}. NMR in acetone-d$_6$: $\delta(^1H) = 5.72, 5.92$ [m, J(HH) = 14 Hz, CH$_2$]; $\delta(^{31}P) = -17.6$ [s, ^1J(PtP) = 3700, ^3J(PP) = 165, dppm]; $\delta(^{13}C) = 197.0$ [sept, ^1J(PtC) = 890 Hz, ^2J(PC) = 17 Hz, CO]

Similarly were prepared: $[Pt_3(\mu_3\text{-}Br)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]$. Yield 97%. Anal. Calc. for $C_{76}H_{66}BrF_6OP_7Pt$: C, 45.9; H, 3.3. Found: C, 45.1; H, 3.5%. IR (Nujol): ν(CO) = 1753 cm^{-1}. NMR in acetone-d$_6$: $\delta(^1H) = 5.71, 5.84$ [m, J(HH) = 14 Hz, CH$_2$]; $\delta(^{31}P) = -17.1$ [s, ^1J(PtP) = 3800, ^3J(PP) = 160, dppm]; $\delta(^{13}C) = 195.8$ [sept, ^1J(PtC) = 896 Hz, ^2J(PC) = 20 Hz, CO]. $[Pt_3(\mu_3\text{-}I)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]$. Yield 97%. Anal. Calc. for $C_{76}H_{66}BrF_6OP_7Pt$: C, 44.8; H, 3.3. Found: C, 44.5; H, 3.5%. IR (Nujol): ν(CO) = 1767 cm^{-1}. NMR in acetone-d$_6$: $\delta(^1H) = 5.57, 6.08$ [m, J(HH) = 14 Hz, CH$_2$]; $\delta(^{31}P) = -17.8$ [s, ^1J(PtP) = 3890, ^3J(PP) = 165]; $\delta(^{13}C) = 192.7$ [sept, ^1J(PtC) = 850 Hz, ^2J(PC) = 18 Hz, CO].

Cluster exchange reactions

These reactions were carried out in NMR tubes containing solutions of complex **2**, and products were identified by their ^1H and ^{31}P NMR spectra. For reactions with halide ions, the solutions were filtered to remove insoluble TlX and the products $[Pt_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]$ were identified by the characteristic NMR spectra reported above.

X-Ray structure determinations

Crystals of $[Pt_3\{Tl(\text{–}OC(Me)CHC(Bu)O)(O_2CCF_3)\}(dppm)_3(CO)]\cdot 3/4$ acetone were grown by slow diffusion of hexane into an acetone solution. An orange crystal was mounted on a glass fibre. Data were collected at low temperature (150 K) using a Nonius Kappa-CCD diffractometer using COLLECT software.[21a] The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using DENZO.[21a] The data were scaled using SCALEPACK[21a] and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 3. The SHELXTL 5.1 program package was used to solve the structure by Patterson, followed by successive difference Fouriers.[21b] The Pt_3Tl cation was modelled with a 50/50 isotropic mixture of Me/Bu groups on the acac ligand, disordered across the two positions. The methylene and phenyl groups of the cation were also refined isotropically. The hexafluorophosphate anion was disordered and was refined as a 60/40 mixture with isotropic fluorine atoms. The remaining atoms of the molecule were refined anisotropically. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atom. The solvent molecule was refined isotropically complete with hydrogen atoms in the model and refined to 75% occupancy.

The crystals of $[Pt_3(\mu_3\text{-}CO)\{\mu_3\text{-}Tl(acac)(OH_2)\}(\mu\text{-}dppm)_3][PF_6]_2\cdot CH_2Cl_2$ were obtained from dichloromethane. Data were collected and treated similarly, except that room temperature collection was used. There was unresolved disorder of the acac and H_2O ligands and these were treated isotropically. All other heavy atoms were anisotropic, with disorder in the anions. There was also a high thermal parameter for methylene carbon atom C(3), probably a result of unresolved disorder.

CCDC reference numbers 169369 and 169370.

See http://www.rsc.org/suppdata/dt/b1/b107579a/ for crystallographic data in CIF or other electronic format.

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