Synthesis and characterization of $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$: an anionic cluster containing an unusual μ_3-PPh_2 bridging system

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$[NBu_4]_2[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ reacts with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (1:2 molar ratio) yielding $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$ which contains unusual μ_3-PPh(1,2-η^2-Ph)-κ^3P phosphido and semi-bridging C_6F_5 ligands and two Pt–Pt bonds of length 2.899(1) and 2.772(1) Å.

The ability of phosphido groups to bridge two metal centres and to support a wide range of bonding and non-bonding M–M distances is well known.[1] Only rarely do such ligands display μ_3-PR_2 coordination in which three metal centres are involved.[2]

In the course of our current research on phosphido palladium and platinum complexes[3] and while exploring the reactivity of the anion $[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]^{2-}$ [3a] we have prepared $[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]$ **1**, a trinuclear anionic platinum(II) complex which contains a triply bridging diphenylphosphido ligand in which the phosphorus is bound to all three platinum atoms and one phenyl group is η^2-coordinated.

When *cis*-$[Pt(C_6F_5)_2(thf)_2]$[4] is added to a CH_2Cl_2 solution of $[NBu_4]_2[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ (2:1 molar ratio), **1** and $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[5] are obtained [eqn. (1)].†

$$\begin{aligned}&[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]\\&\quad + 2\ cis\text{-}[Pt(C_6F_5)_2(thf)_2] \rightarrow \underset{\mathbf{1}}{[NBu_4][Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]}\\&\qquad\qquad + 1/2\,[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \quad (1)\end{aligned}$$

If the reaction is carried out in 1:1 molar ratio, the two reaction products and the phosphido complex used as starting material are obtained, indicating that the reaction requires a 2:1 molar ratio for completion. These observations suggest that *cis*-$[Pt(C_6F_5)_2(thf)_2]$ acts as a C_6F_5 scavenger from $[NBu_4]_2[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ and that $[(C_6F_5)Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)]$ **A** and $[Pt(C_6F_5)_3]^-$ **B** may be plausible intermediates. The reaction between **A** and **B** would yield **1**, while the dimerization of **B** would result in the formation of $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$.

A single-crystal X-ray diffraction study of **1** as its dichloromethane solvate (Fig. 1)‡ reveals that the structure adopted by the anion in the crystal contains a triply bridging PPh_2^- ligand that donates six electrons to the complex through P–Pt interactions and η^2-coordination of one phenyl group. This gives a total valence electron count of 44, which is consistent with the presence of two Pt–Pt bonds between the Pt^{II} centres in **1**. The anion structure can formally be regarded as arising from union of $[(C_6F_5)Pt(2)(\mu\text{-}PPh_2)_2Pt(3)(C_6F_5)]$ **A** and $[Pt(1)(C_6F_5)_3]^-$ **B**. In effect the fourth coordination site at Pt(1) in **B** is taken by the Pt(2)–P(1) bond with both Pt(2) and P(1) within bonding distance of Pt(1) [Pt(1)–Pt(2) 2.899(1) Å]. The geometry of the $Pt(2)(\mu\text{-}PPh_2)Pt(3)$ unit in **A** is consequently highly distorted. The Pt_2P_2 fragment is non-planar [interplanar angle between Pt(2)–P(1)–P(3) and Pt(2)–P(2)–Pt(3) 23.8(1)°] and the Pt(2)–Pt(3) distance [2.772(1) Å] is at the high end of the range of bond distances in such species.[6] Most striking is the angular distortion at P(1) caused by the Pt(1)–P(1) interaction and the η^2-coordination of one phenyl group on P(1) to Pt(3) [Pt(3)–C(37) 2.401(10) and Pt(3)–C(38) 2.543(10) Å]. While the P–C and C–C distances within this group are not perceptibly affected by this distortion the Pt(3)–P(1) bond length that results [2.466(2) Å] is clearly longer than those of the other Pt–Pt bonds here [Pt(1)–P(1) 2.290(3), Pt(2)–P(1) 2.317(3), Pt(2)–P(2) 2.188(3), Pt(3)–P(2) 2.205(3) Å]. Finally one C_6F_5 ligand on Pt(1) is apparently semi-bridging to Pt(2) [Pt(2)···C(13) 2.621(10), Pt(1)–C(13) 2.108(10) Å]. While this is an unusual geometry a similarly distorted mode of coordination has been observed for an aryl ligand in $[Zn_2Ph_2(\mu\text{-}Ph)_2]$[7] and semi-bridging is of course familiar in carbonyl ligand chemistry.[8] An alternative view of the structure of the anion in **1** is that it contains $[Pt(1)(C_6F_5)_3(PPh_2)]^{2-}$ **C** and Pt–Pt bonded $[Pt(2)(C_6F_5)(\mu\text{-}PPh_2)Pt(3)(C_6F_5)]^+$ **D** units. In fragment **C** the phosphide ligand would have a phosphorus lone pair available to donate to **D**. The coordination requirements of fragments **D** are then completed by the η^2-phenyl interaction and a dative Pt(1)–Pt(2) bond. The geometry of the unusual μ_3-PPh_2 ligand in **1** might serve as a model for an intermediate on the pathway for P–Ph cleavage at a polynuclear metal centre, a reaction often observed in cluster chemistry (see *e.g.* ref. 9).

The ^{31}P NMR spectrum of **1** at 183 K, in CD_2Cl_2, is in accord with the solid-state structure. It shows two doublets at higher chemical shifts (δ *ca.* 180 and 80) than the signal due to the starting material (δ −146.9).[3a] These low-field chemical shifts point to the presence of PPh_2 ligands supporting metal–metal bonds in **1**.[1–3] The signal located at δ 179.5 {[*J*(PP)] 60.5 Hz} is assigned to P(2) and shows two pairs of ^{195}Pt satellites with

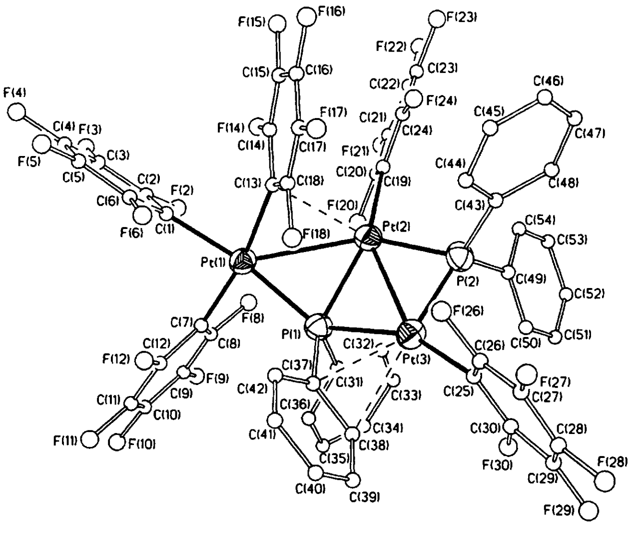
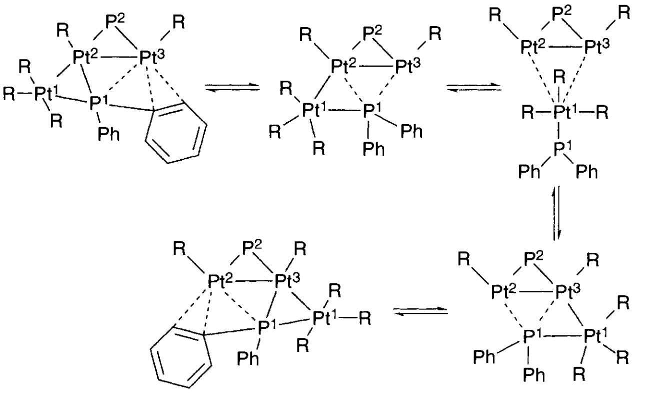


Fig. 1 Molecular structure of the anion in crystals of $\mathbf{1}\cdot CH_2Cl_2$. Some other bond lengths (Å) and angles (°): Pt(1)–C(7) 2.058(11), Pt(1)–C(1) 2.070(10), Pt(1)–C(13) 2.108(10), Pt(2)–C(19) 2.072(10), Pt(2)–P(2) 2.188(3), Pt(3)–C(25) 2.035(9), C(19)–Pt(2)–P(2) 100.1(3), Pt(1)–Pt(2)–P(1) 50.60(6), Pt(1)–Pt(2)–C(19) 108.1(3), C(25)–Pt(3)–P(2) 104.5(3), C(25)–Pt(3)–midpoint of the C(37)–C(38) bond 99.8(4), Pt(1)–P(1)–Pt(2) 77.97(8), Pt(2)–P(1)–Pt(3) 70.77(7), Pt(2)–P(2)–Pt(3) 78.28(9).



Scheme 1 R = C_6F_5

large coupling constant values {4095.1 and 3679.9 Hz, ^1J[PtP(2)]} and another pair with a lower coupling constant value (129.2 Hz) due to ^2J[Pt(1)P(2)]. The doublet that appears at δ 79.6 [J(PP) 60.5 Hz], due to P(1), shows only two pairs of platinum satellites due to coupling with Pt(1) and Pt(2) {^1J[Pt(1)P(1)] 1868.2 and ^1J[Pt(2)P(1)] 1387.8 Hz}.

The NMR spectrum at room temperature indicates a dynamic behaviour of **1** in CD_2Cl_2 solution. It shows two doublets in the same region as that at low temperature (*i.e.* inequivalence of the P atoms). The signal due to P(2) [δ 175.6, J(PP) 60.1 Hz] shows two pairs of ^{195}Pt satellites, one of them with a very low value of the coupling constant {^2J[Pt(1)P(2)] 134.5 Hz} and the other pair shows a separation of 3915.9 Hz {intermediate between ^1J[Pt(2)P(2)] and ^2J[Pt(3)P(2)] in the spectrum at low temperature} and are of higher intensity. This indicates that at room temperature, Pt(2) and Pt(3) are equivalent. In addition the signal due to P(1) appears as a doublet [δ 71.0, J(PP) 60.1 Hz] and shows only one pair of ^{195}Pt satellites {^1J[Pt(1)P(1)] 1877.9 Hz}. A plausible mechanism which could explain these observations is represented in Scheme 1.

Studies on the reactivity of this unusual trinuclear compound are in progress.

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Footnotes

Experimental details for **1**. To a colourless CH_2Cl_2 (15 cm^3) solution of $[NBu_4]_2[Pt_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ (1.250 g, 0.653 mmol) were added 0.880 g (1.307 mmol) of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (under N_2 and at room temp.) and the resulting solution, which almost immediately turns orange, was stirred for 1 h and then evaporated to dryness. The residue was treated twice with 3 cm^3 of $CHCl_3$ and evaporated to dryness and the resulting solid was dissolved in 2 cm^3 of $CHCl_3$ and kept overnight in a refrigerator. The orange solid obtained was filtered and washed (2 × 0.5 cm^3) with cold $CHCl_3$. **1**, 0.730 g, 55% yield. $C_{70}H_{56}F_{25}NP_2Pt_3$: calc. C 41.35, H 2.78, N 0.69; found C 41.47 H 2.97, N 0.73%. By treating the mother-liquor with *n*-hexane, $[NBu_4]_2[Pt_2(C_6F_5)_6]$ (identified by ^{19}F NMR and IR) can be obtained.

‡ *Crystal data* for **1**·CH_2Cl_2. Suitable crystals of **1**·CH_2Cl_2 were obtained by recrystallization from CH_2Cl_2–*n*-hexane at −18 °C. $C_{71}H_{58}Cl_2F_{25}NP_2Pt_3$, $M_r = 2118.29$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.454(2)$, $b = 40.578(8)$, $c = 15.748(2)$ Å, $\beta = 93.490(10)°$, $U = 7306(2)$ Å^3, $Z = 4$, $D_c = 1.93$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 59.5 cm^{-1}, $F(000) = 4056$, $T = 293$ K, crystal size 0.40 × 0.30 × 0.20 mm. All diffraction measurements were made at room temperature on a Siemens P3m diffractometer, using graphite-monochromated Mo-Kα X-radiation. Unit-cell dimensions were determined from 30 centred reflections ($15.6 < 2\theta < 29.6°$). Diffracted intensities were measured in a unique quadrant of reciprocal space for $3.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections remeasured after every 100 ordinary data showed no decay and variation of ±3%. 20455 intensity data (other than checks) collected, 12867 unique (R_{int} 0.073), of these, 8689 had $I > 2\sigma(I)$. An absorption correction was applied based on 504 azimuthal scan data (maximum and minimum transmission coefficients were 1.000 and 0.470). Lorentz and polarisation corrections were applied. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to idealised geometries. Full-matrix least-squares refinement on F^2 of this model using the SHELXL-93 program[10] (938 parameters) converged to final residual indices $R1 = 0.047$, $wR2 = 0.102$, $S = 1.06$. Final difference electron density maps showed no features outside the range +1.64 to −0.72 e Å^{-3}, the largest of these being close to the platinum atoms (< 1.2 Å). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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