Oxidatively induced reductive coupling of PPh_2 and Ph groups mediated by a platinum cluster: synthesis and crystal structure of the butterfly cluster $[Pt_3(\mu_3\text{-}AgO_2CCF_3)(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]\cdot C_6H_6$

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Recombination of a PPh_2 bridge and a terminal Ph group, originally produced by P–C bond breaking of PPh_3 in a Pt complex, is achieved by the two-electron oxidation of the cluster $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ 1 with I_2, followed by reductive coupling of both fragments, thus restoring a PPh_3 ligand in the cationic cluster $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]I$ 2; the electron-rich character of 1 is evidenced by its reaction with AgO_2CCF_3 which leads to the formation of the structurally characterized $[Pt_3(\mu_3\text{-}AgO_2CCF_3)(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ 3.

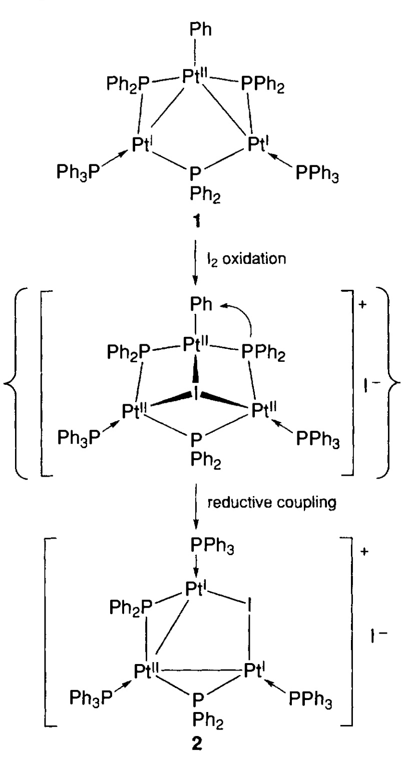
It is well known that tertiary phosphine ligands can be converted thermally to phosphido bridges or orthometallated species as a result of P–C or C–H bond breaking and formation of new M–P or M–C bonds.[1,2] While studying the reactivity of the triplatinum 44-electron cluster $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ **1**[2] with electrophiles in thf‡ we have observed that a coupling reaction between a PPh_2 bridge and the phenyl group, to give a PPh_3 ligand, can be induced by oxidation while the integrity of the cluster is preserved. We present here the reactivity of complex **1** with I_2, AgO_2CCF_3 and H^+.

Reaction of **1** with 1 equiv. of I_2 afforded, in spectroscopically quantitative yield, the cationic complex $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]I$ **2**.‡ Both its valence electron count (VEC) and the oxidation numbers of the Pt atoms are as in **1**. A tentative mechanistic rationale for this reaction is presented in Scheme 1.

Oxidation of **1** by I_2 would oxidise the two Pt^I centres to Pt^{II} and give an intermediate 48 VEC cluster containing no metal–metal bonds. This unstable species transforms immediately into **2** by reductive coupling of the terminal Ph group with a *cis*-PPh_2 bridge, forming a PPh_3 ligand and restoring two Pt^I and one Pt^{II} centre. This P–C bond coupling reaction which restores a PPh_3 ligand represents the reverse of the thermally induced P–C bond breaking which led to the formation of **1** from $[Pt(C_2H_4)(PPh_3)_2]$ ($PPh_3 \rightarrow \mu\text{-}PPh_2 + Ph$).[2] Examples of reductive coupling between a phosphido group and a one-electron donor ligand to afford a tertiary phosphine are rather rare.[3] The cluster mediated conversion of a M–C into a P–C bond reported here appears unprecedented.

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows the resonances for three types of chemically different phosphorus nuclei which are flanked by satellites due to ^{195}Pt–P couplings (Fig. 1).‡ The signal for the phosphido bridges, characteristic of two symmetrical phosphorus nuclei bridging two Pt–Pt bonds in a Pt_3 triangle,[4] is centred at δ 147.4 (s) and those for the phosphines at δ 26.7 (d) and 10.0 (m).

With the hope of gaining some insight into possible intermediates leading to the formation of **2**, we treated **1** with 1 or 2 equiv. of the one-electron oxidant AgO_2CCF_3. This resulted in the formation of the 1 : 1 adduct $[Pt_3(\mu_3\text{-}AgO_2CCF_3)(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ **3**.‡ In contrast to the tetrahedral structure of the only other structurally characterized Pt_3Ag cluster[5] (and more generally of Group 11 Pt_3 clusters),[6] the metal core of **3**·C_6H_6 was found to consist of a butterfly with an Ag–Pt hinge (Fig. 2).§ The silver atom is linked to the three Pt atoms and to one oxygen atom of the O_2CCF_3 group. The bent chain arrangement of the Pt atoms is similar to that in the



Scheme 1

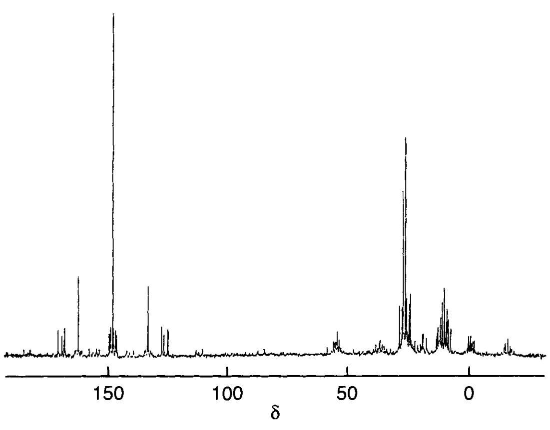


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum of $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]I$ **2**

open form of **1**:[2] there are two short metal–metal distances [2.8606(6), 2.8662(6) Å] whereas the Pt(1)···Pt(3) separation of 3.3247(7) Å is too long to represent a significant bonding interaction. Compared to **1**, the shorter distances have increased by 0.05 and 0.1 Å, whereas the longer has decreased by 0.25 Å. The planarity of the skeleton in the open form of **1** is broken in **2**: P(3) and P(4) are now slightly out of the Pt_3 plane [+0.234(4), +0.273(3) Å, respectively], leaning towards the Ag atom, while P(2) remains in this plane [−0.053(3) Å] and P(1) and C(73) are below the Pt_3 plane [−0.671(3), −0.511(2) Å, respectively].

The $^{31}P\{^1H\}$ NMR spectrum of **3** in thf (Fig. 3) shows the signals of five phosphorus atoms, their couplings with the ^{107}Ag (51.84%) and ^{109}Ag (48.16%) nuclei, and their satellites due the ^{195}Pt–P couplings. The triplet at δ 7.6 and the doublet at δ 52.3 are assigned to the μ-PPh_2 bridges P(1) and P(3) and P(4), respectively. These two types of bridges are coupled with $^2J_{PP}$ 209 Hz. The two phosphines appear as a doublet of doublets at δ 16.6, with little change compared to **1**, and the phosphido bridges are shifted towards higher field in a different manner: P(1) from δ 73.6 in **1** to 7.6 in **3**, and P(3) and P(4) from δ 97.9 in **1** to 52.3 in **3**.

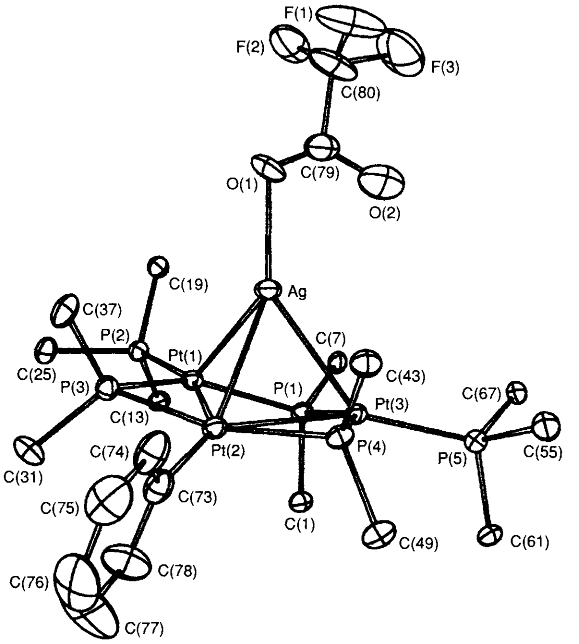


Fig. 2 ORTEP view of the molecular structure of **3** with partial labelling scheme. Ellipsoids are scaled to enclose 30% of the electronic density. For all phenyl rings attached to P atoms only the *ipso* carbon atoms are shown. Hydrogen atoms are omitted. Selected distances (Å) and angles (°): Pt(1)–Pt(2) 2.8606(6), Pt(1)–Pt(3) 3.3247(6), Pt(2)–Pt(3) 2.8662(6), Pt(1)–Ag 2.755(1), Pt(2)–Ag 2.802(1), Pt(3)–Ag 2.785(1), O(1)–Ag 2.21(1), O(2)–Ag 2.860(1), C(73)–Pt(2) 2.05(1), P(1)–Pt(1) 2.310(3), P(1)–Pt(3) 2.297(3), P(3)–Pt(1) 2.265(3), P(3)–Pt(2) 2.281(3), P(4)–Pt(2) 2.277(3), P(4)–Pt(3) 2.281(3), P(2)–Pt(1) 2.245(3), P(5)–Pt(3) 2.246(3); Pt(2)–Pt(1)–Pt(3) 54.59(1), Pt(1)–Pt(2)–Pt(3) 70.98(2), Pt(1)–Pt(3)–Pt(2) 54.43(1).

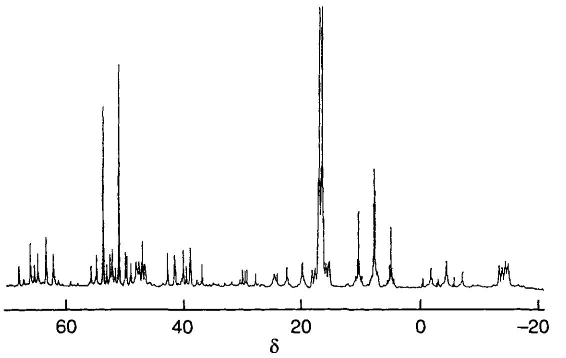


Fig. 3 $^{31}P\{^1H\}$ NMR of $[Pt_3(\mu_3\text{-}AgO_2CCF_3)(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$ **3**

The cationic cluster $[Pt_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PPh_3)_3]PF_6$ **4**, analogous to **2**, was obtained when a thf solution of **1** was treated with an aqueous solution of HPF_6 and the product was recrystallized from CH_2Cl_2.‡ An adduct is probably first formed, which we formulate as $[Pt_3(\mu_3\text{-}H)(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]PF_6$ by comparison with its isolobal analogue **3**. The $^{31}P\{^1H\}$ NMR spectrum of this compound is comparable to that of **3**, but shows only broad peaks, even at low temperature, and the bridging proton could not be detected by ^1H NMR, indicating a dynamic process in solution. Contact with CH_2Cl_2 transforms this complex into **4**, whose $^{31}P\{^1H\}$ NMR spectrum is analogous to that of **2**.

These results illustrate the ability of electrophiles (I_2, Ag^+, H^+) to interact in a multicentre fashion with electron-rich (although only 44 VEC) Pt clusters, leading to the formation of adducts which can eventually induce selective ligand reductive coupling reactions, while the trinuclear nature of the original cluster is retained.

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Footnotes

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‡ All operations were carried out in an inert atmosphere of purified nitrogen and in absolute solvents.

§ *Crystal data* for $\mathbf{3}\cdot C_6H_6$: brown crystals from toluene–benzene–hexane. $C_{86}H_{71}AgF_3O_2P_5Pt_3$, M = 2041.5; triclinic, space group $P\bar{1}$; a = 14.727(4), b = 19.279(5), c = 13.970(4) Å, α = 93.42(2), β = 98.50(2), γ = 89.69(2), U = 3915.5 $Å^3$, Z = 2, D_c = 1.731 g cm^{-3}, μ = 57.955 cm^{-1}. Measurements: Enraf-Nonius CAD4-F, θ–2θ scans. Mo-Kα graphite-monochromated radiation (λ = 0.7107 Å), T = 293 K. 10 188 unique reflections (θ = 2–22°), of which 9952 with $I > 3\sigma(I)$ were used for structure solution (heavy atom) and refinement (full-matrix least squares); R = 0.028, R_w = 0.040. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions [d(C–H) = 0.95 Å, $B_H = 1.3\,B_{equiv.}$ for the carbon to which it was attached] with the exception of the benzene protons not introduced. For all computations, the Nonius Molen/Vax package was used.[7]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/294.

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