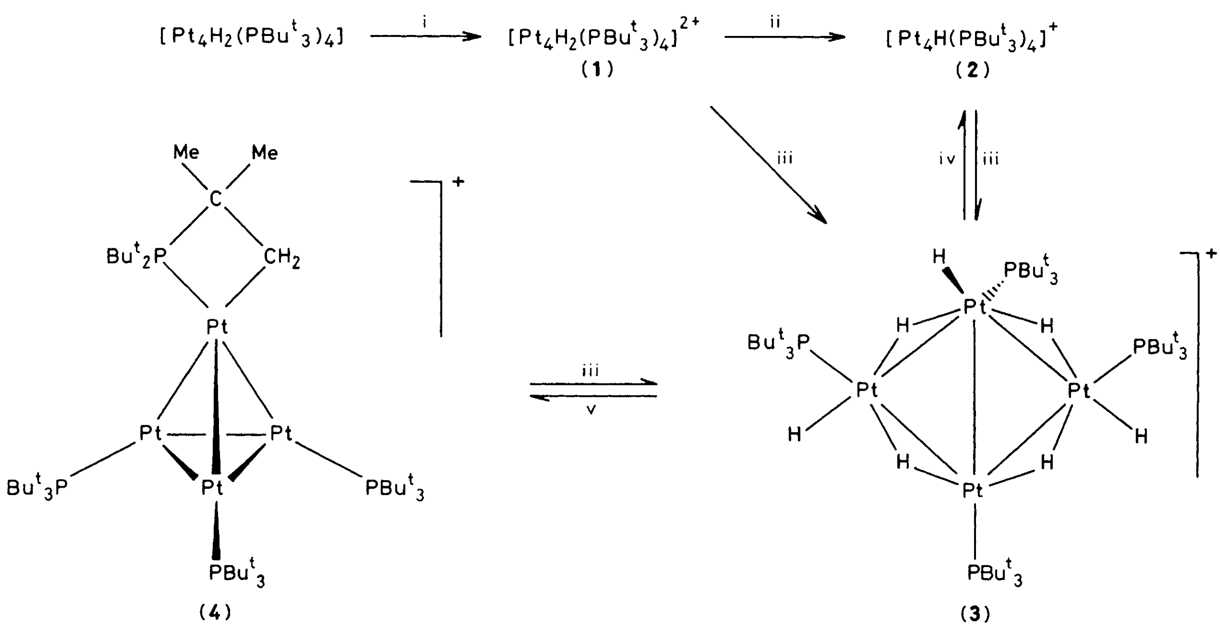
Cationic Platinum Hydride Clusters: *X*-Ray Crystal Structures of $[Pt_4H_2(PBu^t_3)_4][BF_4]_2[HBF_4]_2$ and $[Pt_4H_7(PBu^t_3)_4][BPh_4]$

Robin J. Goodfellow, Elaine M. Hamon, Judith A. K. Howard, John L. Spencer, and David G. Turner
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Reaction of $[Pt_4H_2(PBu^t_3)_4]$ with strong acid affords the cationic hydrido clusters $[Pt_4H_2(PBu^t_3)_4]^{2+}$ and $[Pt_4H(PBu^t_3)_4]^+$, both of which react rapidly with H_2 to give the heptahydrido cluster $[Pt_4H_7(PBu^t_3)_4]^+$ shown by *X*-ray crystallography to have a 'butterfly' core of platinum atoms.

The relationship between the structure of metal clusters and the formal number of cluster bonding electrons is of current interest.[1] We have previously described[2] a series of neutral hydrido-platinum clusters $[Pt_xH_y(PR_3)_x]$ ($x = 3, y = 6; x = 4, y = 2$ or $8; x = 5, y = 8$) and report herein a related series of tetranuclear cationic hydrido clusters which differ markedly in the number of cluster-bonding electrons and in the core geometries.

Addition of excess of $HBF_4 \cdot OEt_2$ to a red-brown toluene solution of $[Pt_4H_2(PBu^t_3)_4]$ resulted in the precipitation of $[Pt_4H_2(PBu^t_3)_4][BF_4]_2[HBF_4]_2$ (**1**) and recrystallization from acetone afforded dark green crystals suitable for a single-



Scheme 1. i, $HBF_4{\cdot}OEt_2$; ii, $-H^+$; iii, H_2 (1 atm); iv, C_2H_4 (1 atm); v, air. Hydride positions in (**3**) are tentative.

crystal *X*-ray diffraction study.† The structure of the dication (Figure 1) is that of a flattened tetrahedron with the PBu^t_3 ligands each arranged to lie approximately *trans* to one Pt–Pt bond (Pt_4P_4 core of S_4 symmetry). The structure is reminiscent of $[Pt_4H_8(PPr^i_2Ph)_4]$[2b] (a 56-electron cluster) although the Pt–Pt distances are approximately 0.25 Å shorter in the 48-electron cluster (**1**). At −100 °C, the ^{31}P n.m.r. spectrum showed two different values for ^2J(PtP) (776 and 205 Hz) as well as one value of ^1J(PtP), consistent with the solid-state geometry.

In acetone, complex (**1**) slowly deprotonated to form $[Pt_4H(PBu^t_3)_4]^+$ (**2**). The number of hydride ligands in (**1**) and (**2**) was determined from a comparison of the ^{195}Pt n.m.r. spectra recorded with and without ^1H decoupling.

Both (**1**) and (**2**) reacted rapidly with H_2 (1 atm; 25 °C) affording the deep red-brown cationic cluster $[Pt_4H_7(PBu^t_3)_4]^+$ (**3**) which was isolated as the crystalline† tetraphenylborate salt. The structure of the cation (**3**) (Figure 2) is of the 'butterfly' type with a distinct head and tail (approximate C_s symmetry). Hydride stoicheiometry was determined by ^1H n.m.r. spectroscopy (400 MHz; CD_3COCD_3; −90 °C) which revealed four complex patterns at δ −0.37, −1.91, −8.22, and −13.47, with relative intensities 1 : 2 : 2 : 2. The ^{31}P n.m.r. spectrum at −90 °C shows three signals with their attendant satellites at δ 112.3 [^1J(PtP) 2 903 Hz], 87.4 [^1J(PtP) 3 711, ^2J(PtP) 562 Hz], and 87.0 p.p.m. [^1J(PtP) 4 036, ^2J(PtP) 337 Hz] with relative intensities 1 : 1 : 2, consistent with the observed solid-state structure.

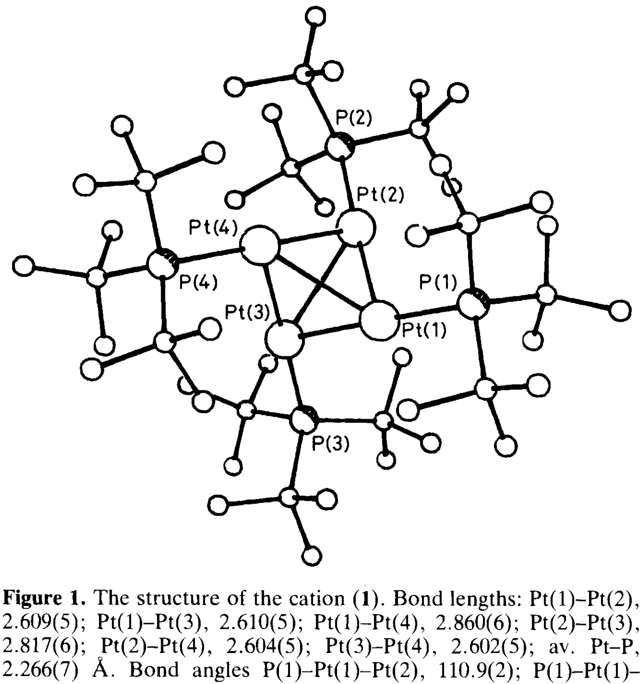


Figure 1. The structure of the cation (**1**). Bond lengths: Pt(1)–Pt(2), 2.609(5); Pt(1)–Pt(3), 2.610(5); Pt(1)–Pt(4), 2.860(6); Pt(2)–Pt(3), 2.817(6); Pt(2)–Pt(4), 2.604(5); Pt(3)–Pt(4), 2.602(5); av. Pt–P, 2.266(7) Å. Bond angles P(1)–Pt(1)–Pt(2), 110.9(2); P(1)–Pt(1)–Pt(3), 173.2(2); P(1)–Pt(1)–Pt(4), 126.8(2); Pt(2)–Pt(1)–Pt(4), 56.6(1); Pt(2)–Pt(1)–Pt(3), 65.3°.

At room temperature, or above, the hydride ligands of (**1**), (**2**), and (**3**) show the single symmetrical ^1H n.m.r. multiplets expected if they migrate rapidly over the Pt_4 skeleton [(**1**) δ −30.1, av. *J*(PtH) 538, av. *J*(PH) 0 Hz; (**2**) δ −33.7, av. *J*(PtH) 506, av. *J*(PH) 0 Hz; (**3**) (80 °C) δ −7.7, av. *J*(PtH) 314, av. *J*(PH) 8 Hz]. At 30 °C, the ^{31}P n.m.r. spectra of (**1**), (**2**), and (**3**) consist of single symmetrical patterns suggesting rapid skeletal rearrangement [(**1**) δ 81.2 p.p.m., ^1J(PtP) 4 202,

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† *Crystal data for* (**1**): $C_{48}H_{114}B_4F_{16}P_4Pt_4$, $M = 1\,942.88$, monoclinic, space group $P2_1/a$, $a = 23.97(4)$, $b = 17.21(2)$, $c = 17.23(1)$ Å, $\beta = 109.9(1)°$, $U = 6\,674(14)$ Å^3 (190 K), $Z = 4$, $D_x = 1.94$ g cm^{-3}, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 86.2 cm^{-1}, $R(R') = 0.058(0.056)$ for 6 963 unique reflections [$I > 3\sigma(I)$].

Crystal data for (**3**): $C_{72}H_{135}BP_4Pt_4$, $M = 1\,915.94$, monoclinic, space group $C2$, $a = 25.14(3)$, $b = 24.27(1)$, $c = 17.97(2)$ Å, $\beta = 135.26(6)°$, $U = 7\,717(12)$ Å^3 (200 K), $Z = 4$, $D_x = 1.66$ g cm^{-3}, $\bar{\lambda} = 0.710\,69$ Å μ(Mo-K_α) = 74.2 cm^{-1}, $R(R') = 0.078(0.081)$ for 5 422 unique reflections [$I > 3.5\sigma(I)$].

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

av. ^{2}J(PtP) 344 Hz; (**2**) δ 66.3 p.p.m., ^{1}J(PtP) 4793 Hz, ^{2}J(PtP) 396 Hz; (**3**) δ 93.4 p.p.m., av. ^{1}J(PtP) 3717, av. ^{2}J(PtP) 105 Hz]. The value of ^{1}J(PtPt) in (**2**) (5289 Hz) is *double that* in (**1**) (2638 Hz).

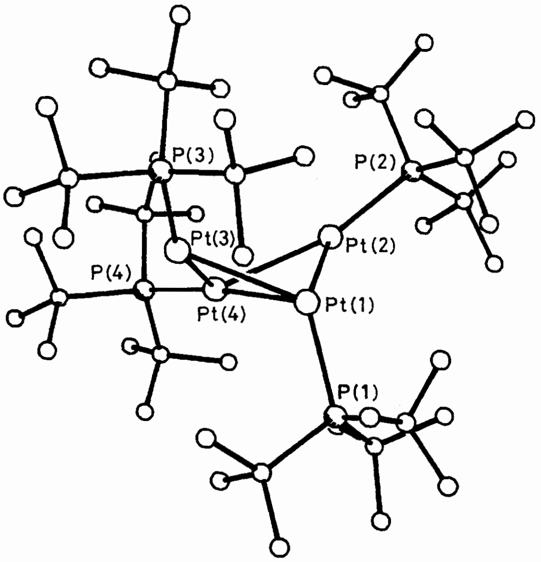

Figure 2. The structure of the cation (**3**). Bond lengths: Pt(1)–Pt(2), 2.862(3); Pt(1)–Pt(3), 2.870(2); Pt(1)–Pt(4), 2.636(2); Pt(2)–Pt(4), 2.780(3); Pt(3)–Pt(4), 2.734(3); Pt(1)–P(1), 2.381(9); Pt(2)–P(2), 2.273(11); Pt(3)–P(3), 2.242(10); Pt(4)–P(4), 2.236(8) Å. Bond angles: Pt(2)–Pt(1)–Pt(3), 102.8(1); Pt(2)–Pt(1)–Pt(4), 60.6(1); Pt(1)–Pt(2)–Pt(4), 55.7(1); Pt(2)–Pt(4)–Pt(3), 108.6(1); P(1)–Pt(1)–Pt(2), 125.5(3); P(1)–Pt(1)–Pt(4), 113.3(2); P(2)–Pt(2)–Pt(1), 120.2; P(2)–Pt(2)–Pt(4), 162.7(3); P(4)–Pt(4)–Pt(1), 173.9; P(4)–Pt(4)–Pt(2), 118.7(4)°.

The cation (**3**) reacts with ethene in acetone at 40 °C to regenerate the cation (**2**) *via* an intermediate hydrido cluster. In contrast, atmospheric oxidation of (**3**), either in solution or in the solid state, affords the non-hydride cluster (**4**) in which one of the t-butyl groups has been metallated[3] {n.m.r. data for (**4**) (CD_3COCD_3): ^{1}H δ 2.89 [d with ^{195}Pt satellites, 2H, $\overline{PtBu^{t}_{2}CMe_{2}C}H_{2}$, ^{2}J(PtH) 107, ^{3}J(PH) 6.1 Hz], ^{31}P, δ 55.1 [3P, ^{1}J(PtP) 4546, ^{2}J(PtP) 555 Hz] and −15.5 p.p.m. [1P, ^{1}J(PtP) 3345, ^{2}J(PtP) 422 Hz]}.

Brief exposure of the cation (**4**) to H_2 (1 atm; 20 °C) in solution or in the solid state rapidly, and cleanly, regenerates (**3**). This reaction cycle which involves the transfer of eight hydrogen atoms and a difference of six cluster bonding electrons between (**3**) and (**4**), demonstrates the extraordinary flexibility of these tetraplatinum clusters.

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