First platinum clusters containing a direct Pt–Si bond: molecular structure of $[Pt_3\{Si(OSiMe_3)_3\}(\mu\text{-}PPh_2)_3(PPh_3)_2]$ and electrochemical studies

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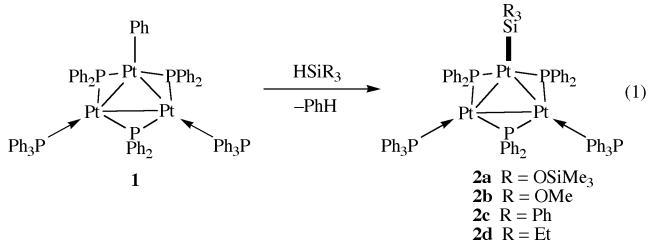
The reaction of $[Pt_3Ph(\mu\text{-}PPh_2)_3(PPh_3)_2]$ (1) with various silanes and siloxanes afforded the first platinum clusters containing a direct Pt–Si bond that could be characterized by X-ray diffraction, in the case of $[Pt_3\{Si(OSiMe_3)_3\}(\mu\text{-}PPh_2)_3(PPh_3)_2]$ (2a): the redox properties of the 44-electron clusters 1 and $[Pt_3\{Si(OMe)_3\}(\mu\text{-}PPh_2)_3(PPh_3)_2]$ (2b) have been studied by cyclic voltammetry.

Silicon forms bonds with most transition metals, generally in mononuclear complexes and only to a lesser extent in polynuclear complexes.[1] Research continues to be very active in this area owing to the fundamental interest and catalytic relevance of such complexes.[2] Despite the well-known catalytic properties of platinum complexes and colloids in silicon chemistry,[3] there appears to be no crystal structure reported of a platinum cluster containing a direct Pt–Si bond, although such species are likely to be involved as intermediates in a number of transformations. Furthermore, metallasiloxane complexes are attracting considerable interest,[4a–c] recently enhanced by the discovery of the lability of the –SiO → Pd bond in heterometallic complexes containing a Fe–Si–O → Pd ring.[4d,e] Here we present the synthesis and the first crystal structure of a platinum cluster containing a siloxy ligand.

Refluxing a chlorobenzene solution of $[Pt_3Ph(\mu\text{-}PPh_2)_3(PPh_3)_2]$, **1**, with an excess of $HSi(OSiMe_3)_3$ for 24 h afforded a red solution from which $[Pt_3\{Si(OSiMe_3)_3\}(\mu\text{-}PPh_2)_3(PPh_3)_2]$, **2a**, was isolated in 47% yield.† Reactions with $HSi(OMe)_3$, $HSiPh_3$ or $HSiEt_3$ yielded the analogous clusters **2b**–**d** in *ca.* 40–55% isolated yield, after refluxing for 5 h, 1 d and 4 d, respectively [eqn. (1)].

Deep red crystals of **2a** could be grown from a 1 : 1 mixture of chlorobenzene–hexane and the molecular structure of this cluster has been determined by X-ray diffraction (see Fig. 1 and Table 1). Although the quality of the structure does not allow a detailed discussion, it allowed the basic features to be established. The cluster is built on a quasi-equilateral triangle of Pt atoms, with a mean Pt–Pt distance of 2.975 Å. The longest of the three Pt–Pt distances in **1** (in the "open" as well as in the "closed" forms, see Scheme 1) was that of the edge opposite to the phenyl group. In **2a**‡ however, the longest



1

2a R = $OSiMe_3$
2b R = OMe
2c R = Ph
2d R = Et

(1)

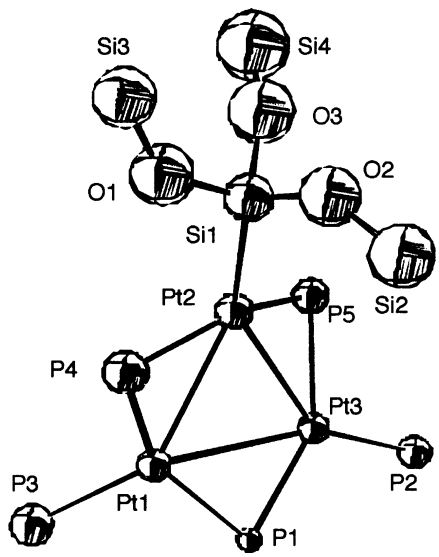
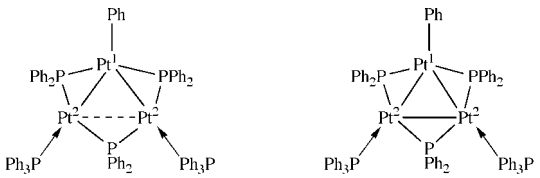


Fig. 1 ORTEP view of the molecular structure of **2a** with partial labelling scheme. Ellipsoids are scaled to enclose 50% of the electron density. All the phenyl rings attached to the P atoms and the methyl groups attached to the Si atoms have been omitted for clarity.



Scheme 1

Table 1 Selected bond distances (Å) and angles (°) of **2a**

Pt(1)–Pt(2)	2.969(2)	Pt(3)–P(2)	2.22(1)
Pt(2)–Pt(3)	3.007(3)	Pt(3)–P(5)	2.34(1)
Pt(1)–Pt(3)	2.948(3)	Pt(2)–Si(1)	2.27(1)
Pt(1)–P(1)	2.25(1)	Si(1)–O(1)	1.63(5)
Pt(1)–P(3)	2.25(1)	Si(1)–O(2)	1.57(4)
Pt(1)–P(4)	2.32(1)	Si(1)–O(3)	1.71(4)
Pt(2)–P(4)	2.23(2)	Si(2)–O(2)	1.67(4)
Pt(2)–P(5)	2.27(1)	Si(3)–O(1)	1.69(4)
Pt(3)–P(1)	2.24(1)	Si(4)–O(3)	1.47(5)
Pt(1)–Pt(2)–Pt(3)	59.11(6)	P(4)–Pt(2)–P(5)	150.9(4)
Pt(1)–Pt(3)–Pt(2)	59.81(6)	P(1)–Pt(3)–P(5)	149.0(5)
Pt(2)–Pt(1)–Pt(3)	61.07(6)	P(4)–Pt(2)–Si(1)	99.1(5)
Pt(1)–P(1)–Pt(3)	82.0(3)	P(5)–Pt(2)–Si(1)	108.6(5)
Pt(1)–P(4)–Pt(2)	81.5(5)	Pt(2)–Si(1)–O(1)	115.1(1)
Pt(2)–P(5)–Pt(3)	81.6(4)	Pt(2)–Si(1)–O(2)	114(1)
Pt(1)–Pt(2)–Si(1)	149.5(5)	Pt(2)–Si(1)–O(3)	116(2)
Pt(3)–Pt(2)–Si(1)	147.4(4)	Si(1)–O(1)–Si(3)	146(2)
Pt(3)–Pt(1)–P(3)	151.5(4)	Si(1)–O(2)–Si(2)	139(2)
Pt(1)–Pt(3)–P(2)	154.2(3)	Si(1)–O(3)–Si(4)	167(3)
Pt(2)–Pt(1)–P(3)	142.8(3)	O(1)–Si(1)–O(2)	105(2)
Pt(2)–Pt(3)–P(2)	146.0(3)	O(2)–Si(1)–O(3)	104(2)
P(1)–Pt(1)–P(4)	144.4(4)	O(1)–Si(1)–O(3)	102(2)

Pt–Pt bond is adjacent to the $Si(OSiMe_3)_3$ group, while the shortest is opposite this group. Each Pt–Pt edge is bridged by a PPh_2 group and the coordination sphere of the platinum atoms is completed by PPh_3 ligands for Pt(1) and Pt(3) and a $Si(OSiMe_3)_3$ group for Pt(2). The various Pt–P distances lie in the usual range and the length of the Pt–Si single bond is comparable to those in the mononuclear complexes $[HPt(SiH_3)(PCy_3)_2]$ [2.382(3) Å][6a] or $[Pt(SiMe_2Ph)Cl(PMe_2Ph)_2]$ (2.29 Å),[6b] or in the dinuclear complex $[(OC)_4Fe(\mu\text{-}PPh_2)Pt\{Si(OMe)_3\}(PPh_3)]$ [2.288(1) Å].[6c] The P(2) atom is located approximately in the plane of the metallic skeleton ($d = +0.033$ Å), while P(1), P(4) and Si(1) are distant from this plane by +0.513, +0.504 and +0.453 Å and P(3) and P(5) by −0.494 and −1.025 Å, respectively. This deformation away from planarity appears to be due to steric factors, at least in part because of the asymmetric disposition of the bulky $Si(OSiMe_3)_3$ moiety. This ligand deviates slightly away from the Pt(2)–P(1) axis and, while the geometry around Si(1) is regular, the Si–O–$SiMe_3$ branches are not symmetrically disposed around the Si(1)–Pt(2) vector, with only O(2)–Si(2)Me_3 being oriented towards the metal core. However, the O(2) atom lies too far away (>3.2 Å) from the Pt atoms to interact with any of them.

Like their precursor **1**, clusters **2** have an overall 44 electron count and contain two Pt(I) and one Pt(II) centres in a 4e-3c metal-metal system. Their formation could be explained by an oxidative addition of the silane to **1**, followed by reductive elimination of benzene or, alternatively, by σ-bond metathesis. The latter mechanism would have the advantage of avoiding formal oxidation of the Pt(II) centre in the mixed-valence cluster **1**. We have shown that the latter cluster exhibits a remarkable skeletal isomerism in the solid state, which depends on the crystallization solvent and results in considerable variations (>0.5 Å!) in the separation between the two formally Pt(I) centres (Scheme 1).[7] Cluster **2a** is related to the "closed" isomer of **1**: both were crystallized from the same solvent and have a deep red colour. Unfortunately, recrystallization in solvents like acetone, toluene or benzene, which afforded the "open", bright red isomer of **1**[7] did not afford crystals of **2a** suitable for X-ray diffraction. Thus, the possibility of finding other structural isomers of **2a** still exists in this series of triangular clusters.

The $^{31}P\{^1H\}$ NMR spectrum of **2a** in chlorobenzene resembles that of **1** in the same solvent where the latter probably adopts a "closed" structure, although slightly more open than in CH_2Cl_2.[7] It contains three signals, corresponding to the terminal phosphines P(2) and P(3) (singlet at δ 9.9) and to the chemically different phosphido bridges [doublet at δ 100.2 for P(4) and P(5) and triplet at δ 116.7 for P(1)]. All these signals are flanked by satellites due to $^{1\text{ or }2}J_{PPt}$(^{195}Pt, $I = 1/2$, natural abundance 33.7%). An analogous spectrum was found for **2b**. However, in the case of **2d**, the signals of the phosphido bridges are more separated and show singlets without coupling. This could result from a lengthening of the Pt(1)–Pt(3) distance towards a more open form of **2d**, which would induce a high field shift of the P(1) signal and bring the phosphido groups P(1) and P(4) and P(1) and P(5), respectively, into a more cisoid relationship. For **2c**, these signals draw nearer and present a complicated multiplet formed by an AB_2 system for the phosphido nuclei, which is superimposed with their ^{195}Pt satellites.

We have previously observed that selective oxidation of **1** by iodine induces reductive coupling of the terminal phenyl ligand and a μ-PPh_2 group to give a PPh_3 ligand.[8] This triggered our interest in the redox behaviour of these triplatinum clusters. Fig. 2 illustrates the cyclic voltammogram exhibited by complexes **1** and **2b** in dichloromethane solution.§ In spite of apparent similarities, the electrode mechanisms governing the anodic processes are quite different. Controlled potential coulometry corresponding to the first anodic peak of both complexes ($E_w = 0.1$ V) revealed that: (*i*) in the case of **1**, two electrons per molecule are exchanged and a cyclic voltammogram recorded on the exhaustively oxidized solution showed no trace of the original profile; (*ii*) in the case of **2b**, one electron per molecule is consumed and the final cyclic voltammetric test displays a profile quite complementary to the original one. Taking into account that in both complexes the oxidation of the phosphine ligands occurs irreversibly at potential values around + 1 V, it is reasonable to assume that in both cases the actual two-electron oxidations are centred on the two Pt(I) centres. In the case of **1**, the simultaneous two-electron removal ($E^{\circ\prime} = -0.06$ V *vs.* SCE) almost immediately destroys the triangular framework (at 0.1 V s^{-1} the i_{pc}/i_{pa} ratio is 0.4) to afford fragments that in turn undergo irreversible oxidation at $E_p = +0.20$ V. In the case of **2b**, removal of the first electron ($E^{\circ\prime} = -0.05$ V) generates the stable monocation $\mathbf{2b}^+$, which loses a second electron

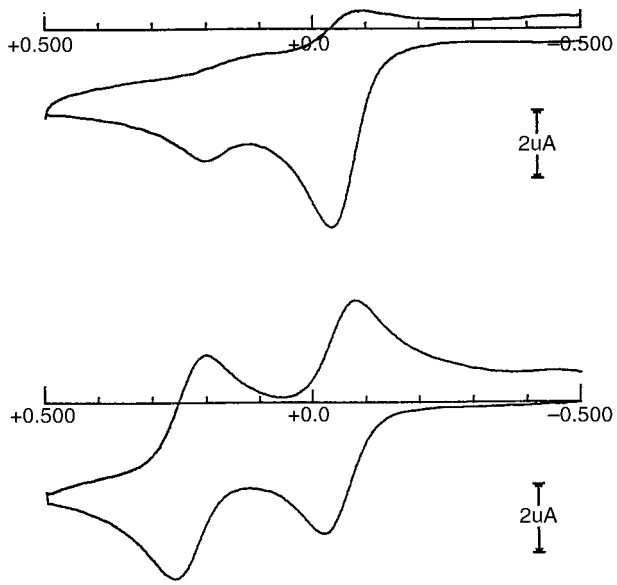


Fig. 2 Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing NBu_4PF_6 (0.2 mol dm^{-3}) and (top) **1** (0.4×10^{-3} mol dm^{-3}); (bottom) **2b** (0.4×10^{-3} mol dm^{-3}). Scan rate 0.1 V s^{-1}.

($E^{\circ\prime} = +0.23$ V) to afford the dication $\mathbf{2b}^{2+}$. The latter was stable on the cyclic voltammetric timescale, but unstable on the longer timescale of macroelectrolysis ($E_w = +0.5$ V). Based on the peak separation of the $\mathbf{2b}/\mathbf{2b}^{+}/\mathbf{2b}^{2+}$ sequence, a K_{com} of 5×10^4 was calculated, which allows us to classify $\mathbf{2b}^{+}$ as a $Pt^{I}Pt^{II}_2$ derivative at the limit between a slightly delocalized (Class II) and a completely delocalized (Class III) mixed-valent species. In conclusion, the replacement of the phenyl group in **1** for the siloxane group in **2**, even if maintaining unaltered the total cluster electron count, dramatically changes the redox properties of the two complexes.

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Notes and references

† All operations were carried out in an inert atmosphere of purified nitrogen and in distilled solvents. Synthesis of **2a**. A suspension of **1** (0.175 g, 0.10 mmol) and $HSi(OSiMe_3)_3$ (1 mL, 2.9 mmol) in chlorobenzene (20 mL) was refluxed for 24 h. Evaporation of the solvent to *ca.* 5 mL afforded a dark red solid, which was filtered off and washed with pentane. Recrystallization from a minimum amount of a 1 : 1 mixture of chlorobenzene–hexane afforded crystals of **2a** (0.092 g, 47% yield). Found: C, 49.47; H, 4.27%. $C_{81}H_{87}O_3P_5Pt_3Si_4$ requires C, 49.61; H, 4.48%.

Selected $^{31}P\{^{1}H\}$-NMR (81.02 MHz, chlorobenzene–C_6D_6) data: complex **2a**: δ 9.9 (s, PPh_3, $^{1}J_{PPt}$ 4393, $^{2}J_{PPt}$ 298, $^{3}J_{PP}$ 125 Hz), 100.2 (d, μ-PPh_2, $^{1}J_{PPt}$ 2275 and 1942, $^{2}J_{PP}$ 186 Hz), 116.7 (t, μ-PPh_2, $^{1}J_{PPt}$ 2608, $^{2}J_{PP}$ 186 Hz); complex **2b**: 11.07 (s, PPh_3, $^{1}J_{PPt}$ 4572, $^{2}J_{PPt}$ 275, $^{3}J_{PP}$ 122 Hz), 82.3 (t, μ-PPh_2, $^{1}J_{PPt}$ 2357, $^{2}J_{PP}$ 190 Hz), 103.3 (d, μ-PPh_2, $^{1}J_{PPt}$ 2152 and 2080, $^{2}J_{PPt}$ 322, $^{2}J_{PP}$ 190 Hz); complex **2c**: 10.16 (s, PPh_3, $^{1}J_{PPt}$ 4483, $^{2}J_{PPt}$ 290, $^{3}J_{PP}$ 120 Hz), complex multiplet between 85 and 115 ppm; complex **2d**: 12.44 (s, PPh_3, $^{1}J_{PPt}$ 5078, $^{2}J_{PPt}$ 162, $^{3}J_{PP}$ 65 Hz), 54.7 (s, μ-PPh_2, $^{1}J_{PPt}$ 3940 Hz), 98.74 (s, μ-PPh_2, $^{1}J_{PPt}$ 2443 and 2042 Hz).

‡ Crystal data for **2a**: $C_{81}H_{87}O_3P_5Pt_3Si_4$, $M = 1812.61$; triclinic; space group $P\bar{1}$; $\mu = 49.318$ cm^{-1}, $R = 0.082$, $R_w = 0.081$, $a = 14.1242(1)$, $b = 14.6598(1)$, $c = 23.1135(1)$ Å, $\alpha = 79.124(1)$, $\beta = 79.107(1)$, $\gamma = 74.303(1)^\circ$, $U = 4776.2$ Å^3, $T = 297$ K, $Z = 2$. Measurements: Enraf-Nonius CAD4-F, $\theta/2\theta$ scans, Mo-Kα graphite monochromated radiation ($\lambda = 0.7107$ Å), 12 659 unique reflections ($\pm h$, $\pm k$, $-l$), of which 3322 with $I > 3\sigma(I)$ were used for structure solution (heavy atom) and refinement (full-matrix least squares). Owing to the small number of reflections used with respect to the number of non-hydrogen atoms, only the Pt, P and Si atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions [d(C–H) = 0.95 Å, $B_H = 1.3B_{eqv}$ for the carbon to which it was attached]. For all computations, the Nonius Molen/Vax package was used.[5]

§ Material and apparatus for electrochemistry have been described elsewhere.[9] Under the present experimental conditions the one-electron oxidation of ferrocene occurs at +0.38 V *vs.* SCE.

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