Di- and Tri-nuclear Platinum Complexes with Double Acetylide Bridges. Molecular Structure of $[NBu_4]_2[Pt_3(C_6F_5)_4(\mu\text{-}C{\equiv}CPh)_4]\cdot4thf$ (thf = tetrahydrofuran)†

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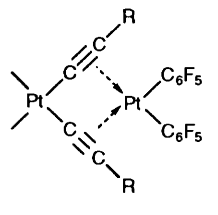
The homoleptic σ-bonded tetrakis(acetylide) complexes $[NBu_4]_2[Pt(C{\equiv}CR)_4]\cdot2H_2O$ (R = Bu^t or $SiMe_3$) reacted with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) in a 1 : 1 molar ratio to give the dinuclear derivatives $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]\cdot H_2O$ (R = Bu^t **1** or $SiMe_3$ **2**). Similar treatment of $[NBu_4]_2[Pt(C{\equiv}CR)_4]\cdot nH_2O$ (R = Ph, $n = 0$; R = Bu^t or $SiMe_3$, $n = 2$) with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in a 1 : 2 molar ratio afforded the trinuclear bridging tetraacetylide complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R = Ph **3**, Bu^t **4** or $SiMe_3$ **5**). Complexes **4** and **5** are also obtained from the reaction of **1** and **2** with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (1 : 1 molar ratio). An unambiguous structural assignment for the trinuclear bridging tetrakis(acetylide) complexes **3**–**5** has been established by an X-ray diffraction study on $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ **3**. The structure of the anion has shown that one of the σ-alkynyl groups of $[Pt(C{\equiv}CPh)_4]^{2-}$ has migrated to one of the two '$Pt(C_6F_5)_2$' fragments yielding a formally dianionic dinuclear fragment $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C{\equiv}CPh)_2]$ which in its turn acts as chelate metallo ligand to the other '$Pt(C_6F_5)_2$' unit.

The chemistry of mononuclear platinum–acetylide complexes has been fairly well developed and a wide range of compounds have been prepared and studied.[1] By contrast, the chemistry of polynuclear platinum–acetylide complexes is scarcely represented;[2] for instance, very few dinuclear platinum complexes stabilised through bridging acetylide μ-C≡CR ligands are presently known,[3] especially when compared with the large variety and vast number of such complexes stabilised by bridging halide, SCN^-, pyrazole, SR, O_2CR, PR_2 *etc*., ligands.[4] On the other hand, although $\eta^2(\sigma,\sigma)$-acetylide polymeric complexes of types $[\text{–}PtL_2(C{\equiv}C\text{–}C{\equiv}C)\text{–}]_n$ and $[\text{–}PtL_2(C{\equiv}CR\text{–}C{\equiv}C)\text{–}]_n$ in which platinum centres are linked by conjugated acetylenes have been described,[5] to our knowledge trinuclear platinum polyacetylide complexes involving the C≡CR ligand have not yet been reported. This relatively late development of polyacetylide platinum complexes is surprising in view of the established value of acetylide complexes as versatile reagents in mechanistic studies and organometallic synthesis.

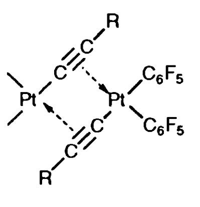
As part of our current research on polynuclear complexes with bridging acetylide groups,[6] we are studying the reactivity of different types of acetylide derivatives towards *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt, thf = tetrahydrofuran) in order to prepare homo- and hetero-polynuclear acetylide-bridged complexes.[3d,7] Here we report the synthesis of a variety of di- and tri-metallic platinum complexes, $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]$ and $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$, obtained by the reaction of $[NBu_4]_2[Pt(C{\equiv}CR)_4]$ (R = Ph, Bu^t or $SiMe_3$) with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in a 1 : 1 or 1 : 2 molar ratio respectively. The molecular structure of one trinuclear (R = Ph) complex has been established by a single-crystal X-ray study. To the best of our knowledge, this is the first example of a trinuclear complex of platinum where the metal centres are doubly bridged by acetylide ligands. To date, only the structurally characterised mixed-valence complex $[Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4]$ has been shown to contain two systems of two acetylide ligands bridging the metal centres.[8]

Results and Discussion

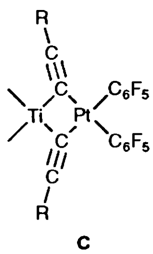
The reactions between neutral *cis*-$[Pt(C_6F_5)_2(thf)_2]$ which contains two very labile thf ligands and bis(σ-alkynyl) complexes have rendered homo- and hetero-dinuclear doubly acetylide-bridging compounds. Moreover, different bonding situations of the two C≡CR groups **A**, **B** and **C** have been observed depending on the bis(alkynyl) derivative used. Thus, the neutral bis(alkynyl) complexes *cis*-$[PtL_2(C{\equiv}CR)_2]$ react with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ to give dinuclear derivatives of type **A**, while similar reactions with the anionic alkynylplatinate(II) complexes $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ (R = Ph, Q = $PMePh_3$; R = Bu^t, Q = NBu_4) give type **B** derivatives, presumably by an overall alkynylating process of the '$Pt(C_6F_5)_2$' fragment *via* intermediate species of type **A**, which have only rarely been isolated.[3d] However, $[Ti(C{\equiv}CR)_2(\eta^5\text{-}C_5H_5)_2]$ reacts with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ to afford a heterodinuclear derivative containing a type **C** system with two asymmetric μ-σ-alkynyl ligands bridging both metal centres.[7] Earlier we reported the successful synthesis of several hexanuclear $[Pt_2M_4(C{\equiv}CR)_8]$ (M = Cu, Ag or Au; R = Ph or Bu^t)



A



B



C

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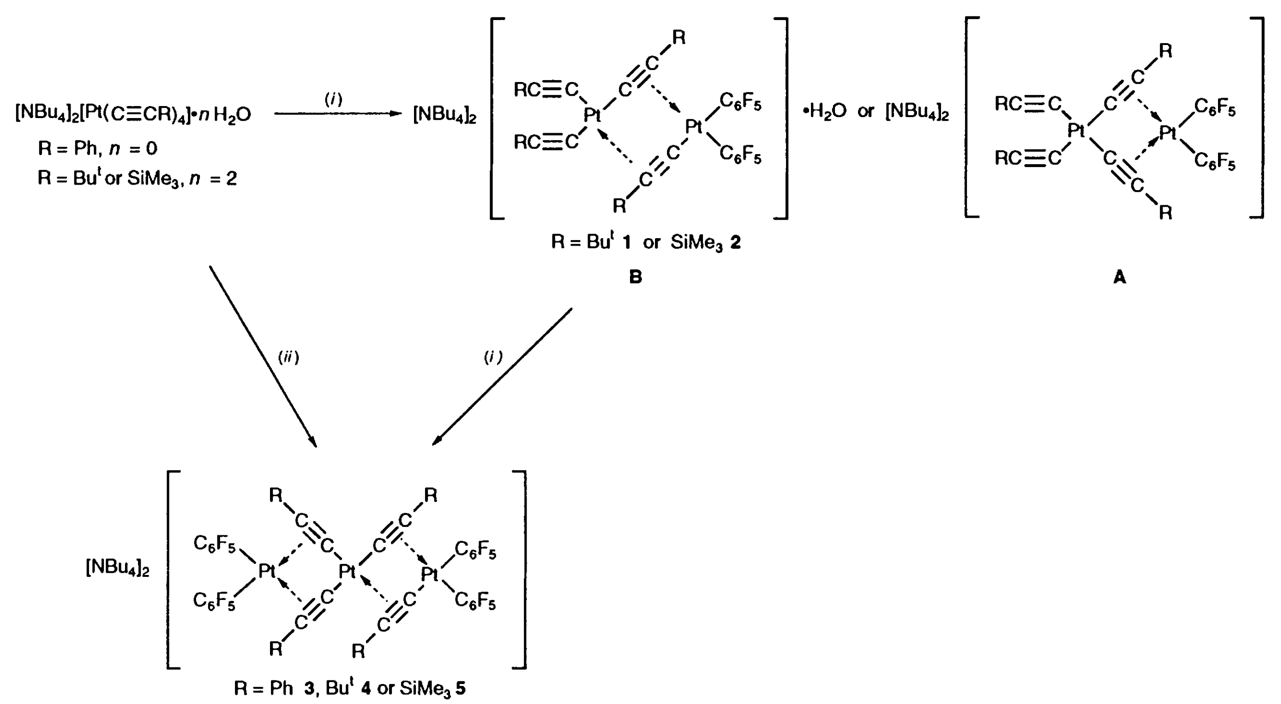
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) 1 equivalent *cis*-$[Pt(C_6F_5)_2(thf)_2]$, R = Bu^t or SiMe$_3$; (*ii*) 2 equivalents *cis*-$[Pt(C_6F_5)_2(thf)_2]$

derivatives by reaction of the $[Pt(C{\equiv}CR)_4]^{2-}$ anionic substrates with adequate transition-metal Lewis acids.[6a] In order to develop further the synthetic potential of these σ-bonded tetraacetylide species, we have studied the reactivity of $[Pt(C{\equiv}CR)_4]^{2-}$ (R = Ph, Bu^t or SiMe$_3$) towards *cis*-$[Pt(C_6F_5)_2(thf)_2]$ and report the synthesis of two di- and three tri-nuclear platinum tetraacetylide complexes.

Synthesis of the Complexes.—A general synthetic route is shown in Scheme 1. The (1:1) low-temperature (−10 °C) reaction between $[NBu_4]_2[Pt(C{\equiv}CR)_4]{\cdot}2H_2O$ (R = Bu^t or SiMe$_3$) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in diethyl ether affords the dinuclear complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]{\cdot}H_2O$ (R = Bu^t **1** or SiMe$_3$ **2**) in moderate yield. Both complexes can be isolated as white solids by evaporating the solution to dryness and subsequently adding cold Pr^{i}OH. Both complexes are moderately stable in the solid state although their acetone, dichloromethane or chloroform solutions darken after 2 or 3 h.

We have also attempted to synthesise the dinuclear derivative $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C{\equiv}CPh)_2]$ by treating $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ with 1 equivalent of *cis*-$[Pt(C_6F_5)_2(thf)_2]$. However, although numerous reaction conditions have been examined, such as the use of different solvents and reaction temperatures or times, we have not succeeded in isolating the desired compound. The reactions afford mixtures of products which have not been investigated further.

Analytical data (C, H and N), molar conductivities and other structural data (IR, ^1H and ^{19}F NMR) for complexes **1** and **2** are given in the Experimental section. Their conductivities in acetone solutions are those expected for 2:1 electrolytes.[9] The structure **B**, depicted in Scheme 1, is tentatively proposed on the basis of their IR spectra. Thus, both complexes show two absorptions in the 797–777 cm^{-1} region due to the X-sensitive mode[10] of the C_6F_5 groups indicating that the *cis* geometry of the '$Pt(C_6F_5)_2$' unit is retained after the reaction. However, they show one (1930 cm^{-1} R = Bu^t **1**) or two (1907 and 1893 cm^{-1} R = SiMe$_3$ **2**) ν(C≡C) bands considerably shifted to lower wavenumbers as compared to those of the σ-acetylide precursors (2081 cm^{-1} R = Bu^t;[6a] 2015 cm^{-1} R = SiMe$_3$) which can be assigned to the $Pt(\mu\text{-}C{\equiv}CR)_2Pt$ moiety. On the basis of these spectroscopic data two reasonable structures **A** and **B** (depicted in Scheme 1) can be postulated. We prefer structure **B** since, as expected, the complexes show additional absorptions at higher frequencies due to the ν(C≡C) stretching vibrations of the two terminal acetylide ligands (2100 cm^{-1} **1**, 2051 and 2037 cm^{-1} **2**). Interestingly, these latter bands are *ca.* 19–36 cm^{-1} higher than those corresponding to the starting materials, suggesting that the platinum atom bonded to the terminal acetylides, probably supports a lower negative charge in the dinuclear derivatives than in the $[Pt(C{\equiv}CR)_4]^{2-}$ precursor species.[1] This fact is in good agreement with the proposed structure **B** which can be formed through an overall alkynylating process of the '$Pt(C_6F_5)_2$' fragment. It should be mentioned that a similar alkynylating process of this fragment has been observed in the reaction of $[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ which renders $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]^{2-}$.[3d] Moreover we will show later that the proposed arrangement of the acetylide ligands seems to be preserved in the trinuclear tetraacetylide–platinum derivatives **3**–**5** which are formed by treating the dinuclear compounds **1** and **2** with an additional equivalent of *cis*-$[Pt(C_6F_5)_2(thf)_2]$.

Due to the two acetylide groups acting as terminal ligands, **1** and **2** are potential synthons for higher nuclearity compounds. The reactivity of **1** and **2** towards *cis*-$[Pt(C_6F_5)_2(thf)_2]$ has therefore been investigated. Treatment of **1** or **2** with 1 equivalent of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in diethyl ether affords, after work up, the trinuclear complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ in moderate (60%, R = Bu^t **4**) or low (20%, R = SiMe$_3$ **5**) yield respectively (Scheme 1). In the latter case, an additional fraction containing **5** and unreacted **2** is also obtained (see Experimental section), so that the total yield of complex **5** should probably be higher. Alternatively **4** and **5** can also be obtained by reacting $[NBu_4]_2[Pt(C{\equiv}CR)_4]{\cdot}2H_2O$ (R = Bu^t or SiMe$_3$) with two equivalents of *cis*-$[Pt(C_6F_5)_2(thf)_2]$. For R = Bu^t the reaction mixture was stirred for 5 min and then the usual work up gives complex **4** only. However for R = SiMe$_3$ a longer reaction time (30 min) is required to achieve completion. Shorter reaction times (*e.g.* 10 min) give first a fraction of **5** (20% yield) and then a fraction containing a mixture of **5** and the dinuclear derivative **2**. These observations indicate that by this route the trinuclear complexes **4** and **5** are also formed through the intermediate dinuclear derivatives **1** and **2**. In addition, by using this alternative route the synthesis of the analogous trinuclear derivative $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ **3** was accomplished. Treatment of $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$ with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (ratio 1:2) in diethyl ether (15 min) gives an orange-brown solution which, after concentrating to a small volume and cooling in the freezer, affords the trinuclear derivative **3** as a pale yellow solid with a moderate yield (40%).

These new compounds are characterised by C, H and N analyses, conductivity measurements, and by IR and NMR (^1H and ^{19}F) spectroscopy. Furthermore, an unambiguous structural assignment for these trinuclear bridging acetylide complexes has been established by an X-ray diffraction study on complex **3**. The IR spectra show $\nu(C{\equiv}C)$ absorptions (2032, 2015 and 1959 cm^{-1} **3**; 2005 and 1938 cm^{-1} **4**; 1950 and 1900 cm^{-1} **5**) in the expected range for carbon–carbon triple bonds co-ordinated side-on to a transition-metal centre.[3a,d,6] The perceptible separation, $\Delta\nu$, between the highest and lowest peak in **3** and between the two observed bands in **4** or **5** seems to indicate that two types of '$Pt(\mu\text{-}C{\equiv}CR)_2Pt$' moieties are probably present in these derivatives. This fact has been confirmed by the X-ray crystal structure of complex **3** which revealed two systems of two asymmetric μ-η^2 acetylide ligands (types **A** and **B**) bridging the central platinum atom with each one of the two other metal centres.

Structure of $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ **3**.—Suitable crystals for the X-ray diffraction study were obtained by the slow diffusion of *n*-hexane into a tetrahydrofuran solution of complex **3** at −40 °C.

Two views of the anion are presented in Fig. 1. Selected bond distances and angles are listed in Table 1 and the atomic coordinates in Table 2.

One of the most interesting features of this structure is the simultaneous presence of two different doubly acetylide-bridging systems of types **A** and **B**. To the best of our knowledge, there is no precedent for an organometallic species having such a specific structure. The most closely reported compound is perhaps the mixed-valence trinuclear tetraacetylide ytterbium complex $[Yb_3(C_5Me_5)_4(\mu\text{-}C{\equiv}CPh)_4]$[8] although in this case the compound is much more symmetric since the two acetylide bridging systems adopt the bonding situation **C**. As can be seen from Fig. 1 the anion in **3** is very asymmetric. Although the three platinum atoms have basically square-planar geometries, their co-ordination environments are clearly different. The Pt(1) atom is σ bonded to three carbon atoms [the two C_{ipso} atoms of two C_6F_5 groups and the C_α atom of one C≡CPh [C(13)≡C(14)–C(15) ligand] and π bonded to the C(21)≡C(22) triple bond of another C≡CPh [C(21)≡C(22)–C(23)] ligand which is σ bonded to Pt(2). The Pt(2) atom is σ bonded to three carbon atoms [the C_α atoms of three C≡CPh, C(21)≡C(22)–C(23), C(29)≡C(30)–C(31) and C(37)≡C(38)–C(39)] and π bonded to the C(13)≡C(14) triple bond of one acetylide group which is σ bonded to Pt(1). Finally Pt(3) is σ bonded to two carbon atoms (the two C_{ipso} atoms of two C_6F_5 groups) and π bonded to two triple bonds of two different C≡CPh ligands [C(29)≡C(30)–C(31) and C(37)≡C(38)–C(39)] which are σ bonded to Pt(2). As is observed in Fig. 1(*b*), the whole anion is not planar, the dihedral angles between the co-ordination planes of each platinum centre (*i.e.* the best least-squares planes including the corresponding platinum centre, the carbon atoms σ bonded to it and the midpoint of the carbon–carbon triple bonds of the acetyline groups π bonded to it) are: Pt(1) plane–Pt(2) plane 133.9°, Pt(2) plane–Pt(3) plane 149.1° and Pt(1) plane–Pt(3) plane 154.7°. The relative disposition of the metal centres is such that the Pt(3) and Pt(1) atoms are displaced 0.814(1) and 1.329(1) Å up and down respectively from the Pt(2) co-ordination plane. Finally, the C(13)≡C(14), C(21)≡C(22), C(29)≡C(30) and C(37)≡C(38) bonds of the acetylide groups form angles of 55.4(4), 56.2(4), 57.8(4) and 52.2(4)° to the perpendicular to the co-ordination plane of each platinum centre [Pt(2), Pt(1), Pt(3) and Pt(3), respectively] to which they are π bonded.

The μ-η^2 bonding mode of the acetylide groups and the bond lengths of the two metallocycles formed are shown in Fig. 2. The C≡C bond distances which vary from 1.219 to 1.241 Å are similar to those reported for other μ-η^2 (σ-π)-acetylide complexes.[3d] A relevant feature is that the platinum acetylide η^2 linkages are rather asymmetric as the Pt–C_α distances are longer than the corresponding Pt–C_β distances. This structural feature contrasts with the symmetrical π linkages found in the $[(Ph_2PCH_2CH_2PPh_2)Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ and $[PMePh_3]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ dinuclear compounds.[3d] Moreover, this type of asymmetry is not usual since it is opposite to the asymmetry generally found in side-on co-ordinated acetylides with longer M–C_β than M–C_α distances.[6] The Pt(1)–C(13), Pt(2)–C(21), Pt(2)–C(29) and Pt(2)–C(37) bond lengths are quite short but they lie within the range found in the literature for σ-acetylide–platinum complexes.[6,11] Each acetylenic skeleton [defined by Pt–C_α–C_β–C(Ph)] is distorted from linearity, adopting a transoidal disposition. The Pt–C_α–C_β angles range from 162.2(6) to 173.2(5)°, whereas the C_α–C_β–C(Ph) angles vary from 150.4(7) to 155.5(7)°. These values

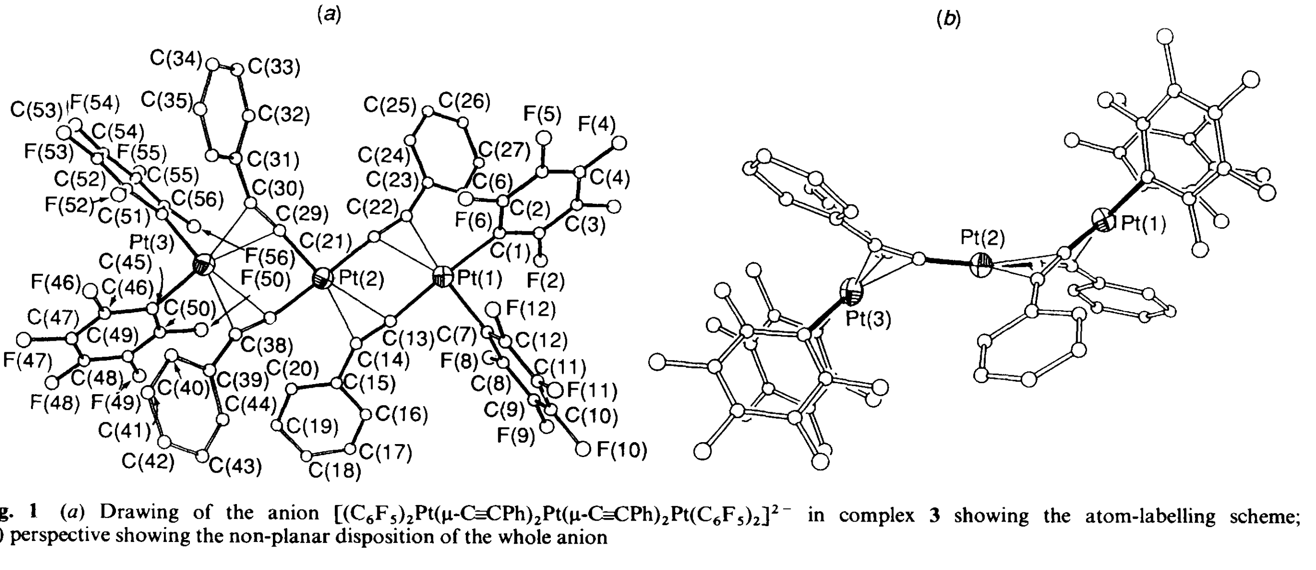


Fig. 1 (*a*) Drawing of the anion $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]^{2-}$ in complex **3** showing the atom-labelling scheme; (*b*) perspective showing the non-planar disposition of the whole anion

Table 1 Selected bond distances (Å) and angles (°) for $[NBu_4]_2[Pt_3(C_6F_5)_4(\mu\text{-}C{\equiv}CPh)_4]\cdot 4thf$

Pt(1)–C(1)	2.052(7)	Pt(3)–C(29)	2.330(6)	Pt(1)–C(7)	2.039(7)	Pt(3)–C(30)	2.286(7)
Pt(1)–C(13)	1.990(7)	Pt(3)–C(37)	2.358(7)	Pt(1)–C(21)	2.328(6)	Pt(3)–C(38)	2.274(6)
Pt(1)–C(22)	2.243(6)	Pt(3)–C(45)	2.035(7)	Pt(2)–C(13)	2.333(7)	Pt(3)–C(51)	2.030(8)
Pt(2)–C(14)	2.252(7)	C(13)–C(14)	1.222(9)	Pt(2)–C(21)	2.008(6)	C(21)–C(22)	1.219(9)
Pt(2)–C(29)	1.942(7)	C(29)–C(30)	1.241(10)	Pt(2)–C(37)	1.987(7)	C(37)–C(38)	1.230(9)
C(1)–Pt(1)–C(7)	86.2(3)	C(30)–Pt(3)–C(37)	90.5(2)	C(1)–Pt(1)–C(13)	178.0(2)	C(37)–Pt(3)–C(38)	30.7(2)
C(7)–Pt(1)–C(13)	91.9(3)	C(30)–Pt(3)–C(38)	106.6(2)	C(1)–Pt(1)–C(21)	112.3(2)	C(30)–Pt(3)–C(45)	167.1(3)
C(7)–Pt(1)–C(21)	159.1(2)	C(29)–Pt(3)–C(45)	159.4(3)	C(7)–Pt(1)–C(22)	169.5(2)	C(38)–Pt(3)–C(45)	84.8(2)
C(1)–Pt(1)–C(22)	86.9(2)	C(37)–Pt(3)–C(45)	102.4(3)	C(21)–Pt(1)–C(22)	30.9(2)	C(30)–Pt(3)–C(51)	83.8(3)
C(13)–Pt(1)–C(22)	95.0(2)	C(29)–Pt(3)–C(51)	104.8(3)	C(13)–Pt(2)–C(21)	69.1(2)	C(38)–Pt(3)–C(51)	166.5(3)
C(13)–Pt(2)–C(14)	30.8(2)	C(37)–Pt(3)–C(51)	161.3(2)	C(13)–Pt(2)–C(29)	162.0(3)	Pt(1)–C(13)–C(14)	173.2(5)
C(14)–Pt(2)–C(21)	95.0(2)	C(45)–Pt(3)–C(51)	84.1(3)	C(21)–Pt(2)–C(29)	96.8(3)	Pt(2)–C(21)–C(22)	172.0(6)
C(13)–Pt(2)–C(29)	167.0(2)	C(13)–C(14)–C(15)	150.4(7)	C(14)–Pt(2)–C(37)	90.6(3)	Pt(2)–C(29)–C(30)	170.6(5)
C(13)–Pt(2)–C(37)	115.0(3)	C(21)–C(22)–C(23)	155.4(6)	C(29)–Pt(2)–C(37)	78.0(3)	Pt(2)–C(37)–C(38)	162.2(6)
C(21)–Pt(2)–C(37)	173.1(3)	C(29)–C(30)–C(31)	155.1(7)	C(29)–Pt(3)–C(37)	63.7(2)		
C(29)–Pt(3)–C(30)	31.2(3)	C(37)–C(38)–C(39)	155.5(7)	C(29)–Pt(3)–C(38)	88.2(2)		

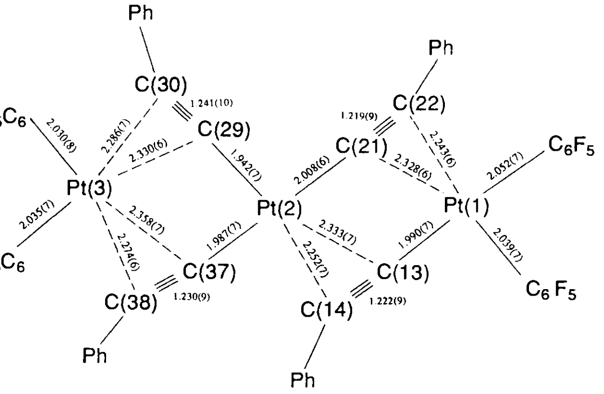


Fig. 2 Schematic view of the μ-η^2-bonded acetylide groups for complex **3** with bonds lengths in Å

are similar to those observed in other platinum η^2-acetylide complexes.[3a,c,d,6] The Pt(1)···Pt(2) and Pt(2)···Pt(3) distances are 3.429(1) and 3.400(1) Å respectively, indicating that there are no metal–metal interactions present.

The structure of complex **3** indicates that the reactions between $[Pt(C{\equiv}CR)_4]^{2-}$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ probably take place in two steps: (*a*) the dianionic substrate $[Pt(C{\equiv}CR)_4]^{2-}$ acts as an alkynylating agent towards *cis*-$[Pt(C_6F_5)_2(thf)_2]$ rendering $[(RC{\equiv}C)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]^{2-}$ and (*b*) these dinuclear derivatives act as chelating metallo ligands towards *cis*-$[Pt(C_6F_5)_2(thf)_2]$ yielding the trinuclear compound by displacing both thf ligands.

NMR Data.—The NMR spectra for complexes **1**–**5** are indicative of fluxional behaviour in solution. Thus, the ^{19}F NMR spectra of complexes **1** and **2** at room temperature show that in solution both C_6F_5 groups are equivalent [δ −112.6 (d, *o*-F), −169.0 (t, *p*-F) and −168.2 (m, *m*-F) **1**; two broad unresolved signals, δ −113.6 (*o*-F) and −167.7 (*m*-F and *p*-F) **2**]. Further indications of the dynamic behaviour of both complexes are observed in their ^1H NMR spectra in which there appear resonances for only one type of C≡CR group (δ 1.13 **1**, δ 0.01 **2**, *i.e.* all the terminal and bridging acetylide ligands are equivalent), together with resonances associated with the NBu_4^+ cation. Since the resonances due to the $SiMe_3$ and NBu_4^+ groups in complex **2** appear well separated, the ^1H NMR spectra of this complex at low temperature were studied. At −80 °C $[(CD_3)_2CO]$, four signals of similar intensity due to $SiMe_3$ (δ 0.11, −0.04, −0.09 and −0.24) were observed. Although this pattern could indicate a static situation (structure **B**, Scheme 1), the ^{19}F NMR spectrum of complex **2** at −85 °C (see Experimental section), does not give any conclusive evidence, for although two resonances (one sharp and the other one broad) appear in the *ortho*-fluorine region, the *meta*- and *para*-fluorine signals appear overlapped as a complex multiplet and it is therefore not possible to infer unambiguously the presence of two inequivalent C_6F_5 groups at this temperature.

In solution, the trinuclear derivatives **3**–**5** also display fluxional behaviour. The ^1H NMR spectrum $[(CD_3)CO]$ of complex **4** at room temperature shows, in addition to the NBu_4^+ pattern, one signal due to the Bu^t group, a singlet at δ 1.11, which remains a singlet even at −85 °C.

At room temperature the ^{19}F NMR spectra of complexes **3** and **4** show only a one signal pattern for the C_6F_5 groups [δ −114.8 (d, *o*-F), −166.4 (t, *p*-F) and −167.04 (m, *m*-F) **3**; δ −112.55 (d, *o*-F) and −167.7 (m, *p*-F and *m*-F) **4**] indicating an apparent D_{2h} symmetry. Unfortunately, on cooling, the ^{19}F NMR spectra were only poorly resolved. Thus, when the temperature was lowered the signals due to the *para*- and *meta*-fluorines in both complexes not only broaden but even at very low temperature (−80 °C for **3** or −85 °C for **4**) they were not resolved. On the other hand, at −50 °C complex **3** exhibits a broad singlet centred at δ −115.1 (Δv = 900 Hz) in the *ortho*-fluorine region, which separates into two broad singlets (δ −116.5 and −117.4) when the temperature is lowered to −80 °C. In complex **4** the signal due to the *ortho*-fluorine is sharp even at 60 °C, but at −85 °C decoalesces into two broad singlets at δ −111.0 and −113.3 respectively. The ^1H and ^{19}F NMR spectra of complex **5** at low temperature (−80 °C) are very complicated. The ^{19}F NMR spectrum exhibits a complex multiplet in the *ortho*-fluorine region and the ^1H NMR spectrum eight peaks of different intensity for the organic $SiMe_3$ group. These data could suggest the presence of several species in solution.

Experimental

All manipulations were carried out under an N_2 atmosphere. Solvents were dried by standard procedures and distilled under dry nitrogen before use.

Carbon, H and N analyses were determined with a Perkin-Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets and ^1H and ^{19}F NMR spectra on a Varian XL-200 or Varian Unity-300 spectrometer. Chemical shifts are given in ppm relative to external standards ($SiMe_4$ and $CFCl_3$). Conductivities were measured in acetone solutions (*ca.* 5×10^{-4} mol dm^{-3}) using a Phillips 9501/01 conductimeter. Literature methods were used to prepare $[NBu_4]_2[Pt(C{\equiv}CPh)_4]$,[6a] $[NBu_4]_2[Pt(C{\equiv}CBu^t)_4]\cdot 2H_2O$[6a] and *cis*-$[Pt(C_6F_5)_2(thf)_2]$.[12]

Syntheses.—$[NBu_4]_2[Pt(C{\equiv}CSiMe_3)_4]\cdot 2H_2O$. *n*-Butyllithium (1.6 mol dm^{-3}; 5 cm^3, 7.913 mmol) in *n*-hexane was added

Table 2 Atomic coordinates (× 10^4) for $[NBu_4]_2[Pt_3(C_6F_5)_4(\mu C{\equiv}CPh)_4]{\cdot}4thf$

Atom	*x*	*y*	*z*
Pt(1)	988(1)	5 770(1)	1 591(1)
Pt(2)	−283(1)	4 580(1)	2 446(1)
Pt(3)	−1 582(1)	3 893(1)	3 358(1)
C(1)	1 036(5)	7 005(5)	1 211(2)
C(2)	1 264(6)	7 065(6)	764(2)
C(3)	1 309(6)	7 896(6)	524(2)
C(4)	1 104(6)	8 741(6)	701(3)
C(5)	939(6)	8 752(6)	1 152(3)
C(6)	886(6)	7 897(5)	1 382(2)
F(2)	1 441(4)	6 268(3)	546(1)
F(3)	1 535(5)	7 905(4)	78(2)
F(4)	1 152(5)	9 566(4)	463(2)
F(5)	762(5)	9 587(4)	1 343(2)
F(6)	728(4)	7 987(3)	1 829(2)
C(7)	2 565(5)	6 062(5)	1 579(2)
C(8)	3 000(5)	5 449(6)	1 323(3)
C(9)	4 054(7)	5 628(7)	1 303(3)
C(10)	4 724(6)	6 439(9)	1 552(4)
C(11)	4 337(6)	7 063(7)	1 797(3)
C(12)	3 272(5)	6 866(6)	1 804(2)
F(8)	2 398(4)	4 617(4)	1 078(2)
F(9)	4 442(4)	4 991(5)	1 052(2)
F(10)	5 772(4)	6 606(5)	1 537(2)
F(11)	4 977(4)	7 865(5)	2 043(2)
F(12)	2 917(3)	7 543(3)	2 053(1)
C(13)	994(5)	4 589(5)	1 967(2)
C(14)	886(5)	3 837(5)	2 187(2)
C(15)	1 144(5)	2 894(5)	2 292(2)
C(16)	1 902(7)	2 629(7)	2 068(3)
C(17)	2 143(7)	1 715(8)	2 130(4)
C(18)	1 714(8)	1 086(7)	2 439(4)
C(19)	950(9)	1 335(7)	2 662(3)
C(20)	661(6)	2 231(5)	2 585(3)
C(21)	−626(5)	5 183(5)	1 851(2)
C(22)	−763(5)	5 479(4)	1 467(2)
C(23)	−1 388(5)	5 624(5)	1 035(2)
C(24)	−2 356(5)	5 859(5)	1 052(2)
C(25)	−2 965(7)	5 938(6)	658(3)
C(26)	−2 651(7)	5 808(6)	229(3)
C(27)	−1 711(7)	5 556(6)	213(3)
C(28)	−1 073(5)	5 471(5)	611(2)
C(29)	−1 321(5)	4 983(5)	2 766(2)
C(30)	−1 862(5)	5 299(5)	3 021(2)
C(31)	−2 489(5)	5 951(5)	3 155(3)
C(32)	−3 289(7)	6 148(7)	2 850(3)
C(33)	−3 839(9)	6 825(11)	2 969(5)
C(34)	−3 591(11)	7 334(10)	3 388(6)
C(35)	−2 785(10)	7 155(10)	3 685(5)
C(36)	−2 235(8)	6 486(8)	3 573(3)
C(37)	37(5)	4 134(5)	3 072(2)
C(38)	184(5)	4 109(5)	3 492(2)
C(39)	804(5)	4 131(5)	3 938(2)
C(40)	522(6)	4 497(6)	4 332(2)
C(41)	1 174(7)	4 569(8)	4 746(3)
C(42)	2 091(7)	4 314(8)	4 763(3)
C(43)	2 370(7)	3 914(8)	4 376(3)
C(44)	1 712(6)	3 805(7)	3 969(3)
C(45)	−1 645(5)	2 630(5)	3 709(2)
C(46)	−1 849(6)	2 500(6)	4 166(2)
C(47)	−1 991(7)	1 628(8)	4 358(3)
C(48)	−1 941(8)	777(8)	4 118(3)
C(49)	−1 775(7)	837(6)	3 670(3)
C(50)	−1 608(6)	1 748(6)	3 486(2)
F(46)	−1 873(4)	3 316(4)	4 427(1)
F(47)	−2 235(5)	1 551(5)	4 796(2)
F(48)	−2 138(6)	−130(5)	4 309(2)
F(49)	−1 723(6)	14(4)	3 423(2)
F(50)	−1 440(4)	1 760(3)	3 045(1)
C(51)	−3 147(6)	3 565(6)	3 386(2)
C(52)	−3 619(8)	3 952(8)	3 724(3)
C(53)	−4 664(10)	3 644(12)	3 755(4)
C(54)	−5 297(9)	2 960(13)	3 443(6)
C(55)	−4 878(8)	2 534(9)	3 100(5)
C(56)	−3 831(6)	2 856(7)	3 076(3)
F(52)	−3 017(6)	4 635(6)	4 055(2)
F(53)	−5 053(7)	4 097(8)	4 086(3)
F(54)	−6 343(5)	2 670(8)	3 479(3)
F(55)	−5 511(5)	1 864(6)	2 806(3)
F(56)	−3 482(4)	2 437(4)	2 743(2)
N(1)	7 536(4)	2 382(4)	1 246(2)
C(57)	7 204(5)	3 169(5)	1 520(2)
C(58)	6 101(6)	2 934(6)	1 610(3)
C(59)	5 896(6)	3 871(6)	1 851(3)
C(60)	4 781(8)	3 697(8)	1 956(4)
C(61)	7 410(6)	1 433(5)	1 496(2)
C(62)	8 056(6)	1 494(6)	1 968(2)
C(63)	7 954(8)	460(6)	2 140(3)
C(64)	6 935(9)	−20(9)	2 277(4)
C(65)	8 667(5)	2 815(5)	1 182(2)
C(66)	9 254(6)	2 113(5)	996(2)
C(67)	10 294(6)	2 701(6)	873(3)
C(68)	10 970(8)	2 050(8)	714(4)
C(69)	6 859(5)	2 084(5)	793(2)
C(70)	6 734(7)	2 941(6)	490(2)
C(71)	5 985(8)	2 473(8)	72(3)
C(72)	5 752(10)	3 212(9)	−276(4)
N(2)	8 226(5)	2 420(4)	6 691(2)
C(73)	8 989(9)	1 785(9)	6 995(4)
C(74)	9 914(8)	2 305(8)	7 203(3)
C(75)	10 652(10)	1 665(10)	7 452(4)
C(76)	11 495(11)	2 182(11)	7 769(5)
C(77)	8 886(9)	2 928(9)	6 310(4)
C(78)	9 312(10)	2 272(11)	6 026(4)
C(79)	9 715(8)	2 829(8)	5 628(3)
C(80)	10 214(12)	2 100(12)	5 369(5)
C(81)	8 042(9)	3 213(8)	7 010(4)
C(82)	7 295(10)	3 795(10)	6 762(5)
C(83)	6 879(12)	4 364(12)	7 121(5)
C(84)	6 266(12)	5 092(12)	6 891(5)
C(85)	7 239(10)	1 622(10)	6 463(4)
C(86)	6 453(11)	1 181(10)	6 784(5)
C(87)	5 612(12)	401(12)	6 544(5)
C(88)	4 734(17)	84(16)	6 750(7)
C(73′)	9 135(19)	2 800(19)	7 059(8)
C(75′)	10 723(22)	2 434(22)	7 407(9)
C(77)	8 527(20)	2 314(20)	6 219(8)
C(78′)	9 565(23)	3 084(22)	6 140(10)
C(81′)	7 641(20)	3 470(20)	6 630(9)
C(82′)	7 231(21)	3 775(21)	7 031(10)
C(83′)	7 026(26)	4 768(26)	6 954(11)
C(84′)	6 335(26)	5 110(26)	7 267(12)
C(85′)	7 329(23)	1 536(22)	6 880(10)
C(86′)	6 312(23)	1 340(22)	6 517(11)
O(1)	5 616(8)	−811(7)	9 070(4)
C(89)	5 700(11)	160(9)	9 225(5)
C(90)	5 956(12)	794(12)	8 812(7)
C(91)	6 219(15)	36(19)	8 461(6)
C(92)	6 297(12)	−820(11)	8 741(6)
O(2)	3 102(16)	633(15)	9 300(7)
O(2′)	3 143(17)	709(15)	9 660(8)
C(93)	2 827(15)	1 275(15)	9 030(6)
C(93′)	2 628(21)	400(19)	9 232(8)
C(94)	1 852(11)	1 173(10)	9 061(5)
C(95)	1 677(12)	1 271(11)	9 515(5)
C(96)	2 460(20)	566(18)	9 718(8)
C(96′)	2 649(19)	1 426(19)	9 876(8)
O(3)	1 743(13)	289(9)	3 881(4)
C(97)	854(17)	710(15)	3 866(7)
C(98)	877(16)	1 091(18)	4 306(7)
C(99)	1 849(18)	1 050(16)	4 573(5)
C(100)	2 443(19)	745(18)	4 213(11)
O(4)	5 942(15)	2 702(16)	5 595(7)
C(101)	5 359(35)	2 026(25)	5 234(12)
C(102)	5 667(34)	2 821(41)	4 937(9)
C(103)	5 034(25)	3 506(24)	5 194(10)
C(104)	5 319(29)	3 291(40)	5 613(8)

to a solution of $\mathrm{HC{\equiv}CSiMe_3}$ (0.78 g, 7.94 mmol) in diethyl ether (40 $\mathrm{cm^3}$, −10 °C). The mixture was stirred at −10 °C for 15 min and then $[\mathrm{PtCl_2(tht)_2}]$ (tht = tetrahydrothiophene) (0.7 g, 1.5825 mmol) was added. The mixture was stirred for 10 min at 0 °C and the resulting solution was evaporated to dryness. Deoxygenated $\mathrm{H_2O}$ (30 $\mathrm{cm^3}$) was added, and the resulting colourless solution filtered and added dropwise to an aqueous solution (10 $\mathrm{cm^3}$) of $\mathrm{NBu_4Br}$ (1.12 g, 3.481 mmol), to yield the complex $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CSiMe_3)_4}]\cdot 2\mathrm{H_2O}$ as a white solid. The solid was filtered off, washed with water and dried over $\mathrm{P_2O_5}$ under vacuum. Yield 70% [Found (calc.): C, 56.55 (56.30); H, 10.20 (10.20); N, 2.55 (2.55)%]. IR: ν(C≡C) 2015s and 1981 (sh), 3453s, 3285m and 1654s $\mathrm{cm^{-1}}$ (due to $\mathrm{H_2O}$[13]); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.02 (s, $\mathrm{SiMe_3}$), 1.00 (t, $\mathrm{CH_3}$ $\mathrm{Bu^n}$), 1.5 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.71 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 3.55 (m, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$) and 4.78 (br s, $\mathrm{H_2O}$). $\Lambda_M(\mathrm{CH_3NO_2})$: 138 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CR})_2\mathrm{Pt(C{\equiv}CR)_2}]\cdot\mathrm{H_2O}$ (R = $\mathrm{Bu^t}$ **1** *or* $\mathrm{SiMe_3}$ **2**). A typical preparation of complex **1** was to add *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.097 g, 0.144 mmol) to a suspension of $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CBu^t)_4}]\cdot 2\mathrm{H_2O}$ (0.150 g, 0.144 mmol) in diethyl ether (10 $\mathrm{cm^3}$). The mixture was stirred at −10 °C for 1 h and the resulting orange-yellow solution was evaporated to dryness. Addition of cold propan-2-ol (*ca.* 2 $\mathrm{cm^3}$) gave a white solid which was washed subsequently with further propan-2-ol (1 $\mathrm{cm^3}$) and *n*-hexane (5 $\mathrm{cm^3}$). Complex **2** (white) was prepared similarly using 0.092 g (0.136 mmol) of *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ and 0.15 g, (0.136 mmol) of $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CSiMe_3)_4}]\cdot 2\mathrm{H_2O}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{Pt(C{\equiv}CBu^t)_2}]\cdot\mathrm{H_2O}$ **1**. Yield 45% [Found (calc.): C, 52.40 (52.65); H, 7.50 (7.15); N, 1.75 (1.80)%]. IR: ν(C≡C) 2100s and 1930m, ν($\mathrm{C_6F_5}$)(X-sens[10]) 794s and 777s, 3453m $\mathrm{cm^{-1}}$ (due to $\mathrm{H_2O}$[13]); NMR($\mathrm{CDCl_3}$): ^{1}H, δ 1.13 (s, $\mathrm{Bu^t}$), 0.95 (t, $\mathrm{CH_3}$ $\mathrm{Bu^n}$), 1.48 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.69 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$) and 3.44 (m, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$), no signal due to water is detected, suggesting that it is very broad due to exchange; ^{19}F, δ −112.6 [^3J(Pt–*o*-F) = 417 Hz, *o*-F], −169.0 (t, *p*-F) and −168.2 (m, *m*-F). $\Lambda_M(\mathrm{Me_2CO})$: 156 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CSiMe_3})_2\mathrm{Pt(C{\equiv}CSiMe_3)_2}]\cdot\mathrm{H_2O}$ **2**. Yield 61% [Found (calc.): C, 47.90 (47.55); H, 7.20 (6.85); N, 1.85 (1.75)%]. IR: ν(C≡C) 2051s, 2037s, 1907s and 1893 (sh), ν($\mathrm{C_6F_5}$) (X-sens[10]) 797s and 780s, 3485m $\mathrm{cm^{-1}}$ (due to $\mathrm{H_2O}$[13]). For low temperature (−80 °C) ^{1}H NMR data, see text. NMR [20 °C, $(\mathrm{CD_3})_2\mathrm{CO}$]: ^{1}H, δ 0.01 (s, $\mathrm{SiMe_3}$), 0.96 (t, $\mathrm{CH_3}$ $\mathrm{Bu^n}$), 1.47 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.8 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$) and 3.56 (m, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$); ^{19}F, δ −114.1 (s, *o*-F) and −168.2 (m, *p*-F and *m*-F); at −85 °C, δ −113.2 (d), −114.3 (br, *o*-F), −165.9, −166.2 and −166.6 (m, *p*-F and *m*-F). $\Lambda_M(\mathrm{Me_2CO})$: 152 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CPh})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CPh})_2\mathrm{Pt(C_6F_5)_2}]$ **3**. To a suspension of $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CPh)_4}]$ (0.111 g, 0.102 mmol) in diethyl ether (20 $\mathrm{cm^3}$), was added *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.178 g, 0.204 mmol). The original white suspension turned to an orange-brown solution within a few minutes. After stirring at room temperature for 15 min, evaporation of the solvent to a small volume (*ca.* 1 $\mathrm{cm^3}$) and cooling in the freezer afforded complex **3** as a pale yellow solid, which was washed with cold propan-2-ol. Yield 40% [Found (calc.): C, 49.10 (49.30); H, 4.40 (4.35); N, 1.35 (1.30)%]. IR: ν(C≡C) 2032m, 2015m and 1959s, ν($\mathrm{C_6F_5}$)(X-sens[10]) 802s, 792s and 780s $\mathrm{cm^{-1}}$; NMR: ^{1}H ($\mathrm{CDCl_3}$), δ 7.3 (m, Ph), 7.1 (m, Ph), 3.24 (m, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$), 1.49 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.26 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$) and 0.76 (t, $\mathrm{CH_3}$ $\mathrm{Bu^n}$); ^{19}F[$(\mathrm{CD_3})_2\mathrm{CO}$]: at 10 °C, δ −114.8 [d, ^3J(^{195}Pt–*o*-F) = 415 Hz, *o*-F], −166.4 (t, *p*-F) and −167.04 (m, *m*-F); at −20 °C, δ −114.9 [d, ^3J(^{195}Pt–*o*-F) = 412 Hz, *o*-F], −165.9 (t, *p*-F) and −166.6 (m, *m*-F); at −50 °C, δ −115.1 (br s, *o*-F), −165.3 (br s, *p*-F) and −166.2 (br m, *m*-F); at −80 °C, δ −116.5 and −117.4 (2 × br s, *o*-F), −166.05, −166.5, −166.9, −167.3 and −167.6 (complex multiplet, *p*-F and *m*-F). $\Lambda_M(\mathrm{Me_2CO})$: 210 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{Pt(C_6F_5)_2}]$ **4**. To a stirred suspension of $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CBu^t)_4}]\cdot 2\mathrm{H_2O}$ (0.360 g, 0.346 mmol) in diethyl ether (10 $\mathrm{cm^3}$) was added *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.466 g, 0.692 mmol). Immediately a colourless solution was formed but after a few minutes a white solid began to precipitate. The mixture was stirred at room temperature for 1 h and then the white solid **4** was filtered off and washed with diethyl ether (yield 53%).

Alternatively, complex **4** was prepared from complex **1**. To a solution of complex **1** (0.080 g, 0.052 mmol) in diethyl ether (10 $\mathrm{cm^3}$), *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.035 g, 0.052 mmol) was added. The mixture was stirred at room temperature for 1 h and then the resulting white solid **4**, was filtered off and washed with diethyl ether (2 $\mathrm{cm^3}$) (Yield 60%) [Found (calc.): C, 46.15 (46.60); H, 5.60 (5.25); N, 1.25 (1.35)%]. IR: ν(C≡C) 2005m and 1938m, ν($\mathrm{C_6F_5}$) (X-sens[10]) 793s and 778 (sh) $\mathrm{cm^{-1}}$; NMR [$(\mathrm{CD_3})_2\mathrm{CO}$]: ^{1}H (20 °C), δ 1.11 (s, $\mathrm{Bu^t}$), 0.97 (t, $\mathrm{CH_3}$ $\mathrm{Bu^n}$), 1.4 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.8 (m, $\mathrm{CH_2}$ $\mathrm{Bu^n}$) and 3.5 (m, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$); the same pattern is observed at −30 and −85 °C (where the signals are broad); ^{19}F (20 °C), δ −112.5 [d, ^3J(Pt–*o*-F) = 427 Hz, *o*-F] and −167.7 (m, *p*-F and *m*-F). The same pattern is observed at −30 and −60 °C; at −85 °C, δ −111.0 and −113.3 (2 × vbr, *o*-F, no platinum satellites), −165.2 and −166 (m, *p*-F and *m*-F). $\Lambda_M(\mathrm{Me_2CO})$: 212 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

$[\mathrm{NBu_4}]_2[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CSiMe_3})_2\mathrm{Pt}(\mu\text{-}\mathrm{C{\equiv}CSiMe_3})_2\mathrm{Pt(C_6F_5)_2}]$ **5**. To a suspension of $[\mathrm{NBu_4}]_2[\mathrm{Pt(C{\equiv}CSiMe_3)_4}]\cdot 2\mathrm{H_2O}$ (0.150 g, 0.136 mmol) in diethyl ether (10 $\mathrm{cm^3}$) was added *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.183 g, 0.271 mmol) and the mixture was stirred at room temperature for 10 min. The resulting orange solution was evaporated to a small volume (*ca.* 3 $\mathrm{cm^3}$) and then cooled in the freezer for 24 h to give a white microcrystalline solid which was collected by filtration and washed with cold diethyl ether (yield 0.058 g, 20%). Evaporation of the mother-liquors to dryness and addition of *n*-hexane afforded a white solid (0.1 g) which was identified by IR spectroscopy as a mixture of the dinuclear and trinuclear derivatives **2** and **5** respectively.

If the initial mixture was stirred for 30 min, the orange solution turned brown. After removal of the solvent, addition of propan-2-ol gave complex **5** as an analytically pure material (0.022 g). The filtrate was evaporated to dryness and the resulting residue triturated with *n*-hexane, filtered and air-dried to give additional complex **5** as a brown impure material (0.156 g) (IR spectroscopy) [Found (calc.): C, 42.55 (42.90); H, 5.00 (5.10); N, 1.50 (1.30)%]. IR: ν(C≡C) 1950s and 1900s; ν($\mathrm{C_6F_5}$)-(X-sens) 797s and 777 (sh) $\mathrm{cm^{-1}}$; NMR[$(\mathrm{CD_3})_2\mathrm{CO}$]: ^{1}H (−80 °C), δ 0.9 (br, s, $\mathrm{CH_3}$ $\mathrm{Bu^n}$), 1.3 (br s, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 1.7 (br s, $\mathrm{CH_2}$ $\mathrm{Bu^n}$), 3.4 (br s, $\mathrm{NCH_2}$ $\mathrm{Bu^n}$) and 0.15, 0.07, −0.05, −0.10, −0.16, −0.19, −0.22 and −0.26 (varying intensity, $\mathrm{SiMe_3}$); ^{19}F, δ −114.6 (*o*-F) and −165.6 (m, *p*-F and *m*-F). $\Lambda_M(\mathrm{Me_2CO})$: 181 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$.

Alternatively, complex **5** could be prepared from complex **2**. To a solution of complex **2** (0.072 g, 0.045 mmol) in diethyl ether (10 $\mathrm{cm^3}$) was added *cis*-$[\mathrm{Pt(C_6F_5)_2(thf)_2}]$ (0.030 g, 0.045 mmol) and the mixture was stirred at room temperature for 2 h. The resulting orange-brown solution was evaporated to a small volume (*ca.* 1 $\mathrm{cm^3}$) and cooled in the freezer to give **5** (yield 20%). The mother-liquors were removed under vacuum and the residue treated with *n*-hexane to give an additional fraction (0.03 g) which was identified by IR spectroscopy as a mixture of **2** and **5**.

Crystal Structure Determination of Complex **3**.—*Crystal data.* $\mathrm{C_{88}H_{92}F_{20}N_2Pt_3\cdot 4C_4H_8O}$, M = 2431.39, triclinic, space group $P\bar{1}$, a = 13.292(3), b = 13.751(3), c = 29.434(8) Å, α = 91.54(2), β = 97.09(3), γ = 104.28(3)°, U = 5164(2) Å^3, Z = 2, D_c = 1.56 g $\mathrm{cm^{-3}}$; λ(Mo-Kα) = 0.710 73 Å, μ = 41.4 $\mathrm{cm^{-1}}$, $F(000)$ = 2280, T = 233 K, crystal dimensions 0.85 × 0.76 × 0.76 mm.

Crystallographic data were collected on a Siemens–Stoe AED2 four-circle diffractometer, $4 < 2\theta < 47°$ (ω–θ scan); 15 281 independent reflections, 13 180 with $I > 3\sigma(I)$ were used for all calculations (program system SHELXTL PLUS[14]). Cell constants were refined from 2θ values of 70 reflections including Friedel pairs ($25 < 2\theta < 31°$). An absorption correction based on ψ scans was applied (transmission factors: 1.000–0.711). Three standard reflections were measured every 240 min but showed no decay. The structure was solved by direct methods and refined on $|F_o|$ to $R = 0.039$ and $R' = 0.062$ for 1136 variables [weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0030F_o^2$], highest shift/error 0.004. Ten atoms of one of the NBu_4^+ cations and three atoms of one of the C_4H_8O molecules are disordered over two sites each. All non-hydrogen atoms, except for those of the disordered NBu_4^+ cation and C_4H_8O molecule, were refined anisotropically.

Owing to the number of variables involved in the model the final refinement was conducted in blocks. The three platinum atoms were refined in all cycles, and the remaining atoms were refined in two groups: first the remainder of the anion, and secondly the NBu_4^+ cation and the interstitial C_4H_8O molecules. All hydrogen atoms of the anion and the (non-disordered) NBu_4^+ were included in calculated positions (C–H 0.96 Å, $U = 0.10187$ Å^2).

A difference map following convergence showed nine peaks higher than 1 e Å^{-3} (1.66–1.00). All these peaks lay within 1.0 Å of the platinum atoms (minimum difference density −1.47 e Å^{-3}).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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