Tri- and Tetra-nuclear Homo- or Hetero-metallic Palladium(II) and Platinum(II) Complexes with Double Halide Bridges. Molecular Structure of $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ *

Rafael Usón, Juan Forniés, Milagros Tomás, Babil Menjón, and Javier Carnicer
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain
Alan J. Welch
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

By treating *cis*-$[M(C_6X_5)_2(thf)_2]$ (M = Pd or Pt, X = F or Cl, thf = tetrahydrofuran) with $[M'X'_4]^{2-}$ or $[M'_2(\mu\text{-}X')_2X'_4]^{2-}$ (M′ = Pd or Pt; X′ = Cl or Br) in a 2:1 ratio tri- or tetra-nuclear, homo- or hetero-metallic complexes of the types $[NBu_4]_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2]$ or $[NBu_4]_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2]$ can be obtained. The molecular structure of the trinuclear anion with M = M′ = Pt, X = F, X′ = Cl has been established by single-crystal *X*-ray crystallography. The anion is centrosymmetric, showing a square-planar $PtCl_4$ central unit embraced by two $Pt(C_6F_5)_2$ terminal moieties bonded to the central platinum atom through double chloride bridges.

With the exception of the fluorides, the crystal chemistry of palladium(II) and platinum(II) halide complexes is dominated by square-planar co-ordination,[1] as observed not only in mononuclear derivatives (*e.g.* $[MX_2L_2]$ or $[MX_4]^{2-}$), but also in the simple halides MX_2, for which two different structures are known, one based on the cluster M_6Cl_{12} and the second polymeric in nature. Oligomeric species ranging between these two limits of nuclearity are mostly represented by binuclear derivatives containing the halide doubly bridged moiety $>M(\mu\text{-}X)_2M<$.[1–4] Palladium(II) or platinum(II) halide complexes of higher nuclearity are scarcely represented, *e.g.* ones containing a tetranuclear eight-membered ring $[M(C_6X_5)_2(\mu\text{-}X')M'(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}X')M(C_6X_5)_2(\mu\text{-}X')M'(\eta^4\text{-}1,5\text{-}C_8H_{12})(\mu\text{-}X')]$[5] or the trinuclear halide-bridged complexes which have been suggested to be formed in cyclization and oligomerization reactions of alkynes on palladium or platinum centres.[6] To the best of our knowledge though, only the trinuclear complex containing terminal allyl groups, $[Pd_3(\eta^3\text{-}C_4H_7)_2Cl_4]$ has been structurally characterized.[7]

Here we report a general and straightforward method for the synthesis of a variety of homo- or hetero-metallic palladium(II) trinuclear, $Q_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2]$, or tetranuclear, $Q_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2]$, complexes, where the metal centres are doubly bridged by halide anions. This method is based on the ability of the complex anions $[M'X'_4]^{2-}$ or $[M'_2X'_6]^{2-}$ to act as chelating ligands displacing the labile tetrahydrofuran (thf) ligands in *cis*-$[M(C_6H_5)_2(thf)_2]$.

Results and Discussion

We have recently[8] synthesized the complexes *cis*-$[M(C_6X_5)_2(thf)_2]$ (M = Pd or Pt; X = F or Cl) which are white stable solids. Since the thf ligands are weakly co-ordinating, they can readily be displaced under mild conditions, for instance by CO or acetylenes, to give *cis*-$[M(C_6X_5)_2(CO)_2]$[8,9] or *cis*-$[M(C_6F_5)_2(PhC{\equiv}CPh)_2]$[10] respectively. Even the halide ions in $[M'X'_2(cod)]$ (M′ = Pd or Pt; cod = cyclo-octa-1,5-diene) can displace the thf ligands to give asymmetric homo- or heteronuclear neutral complexes $[\{(C_6X_5)_2M(\mu\text{-}X')_2M'(cod)\}_n]$ (X′ = Cl, Br, or I; M = Pd^{II} or Pt^{II}) which are binuclear (*n* = 1) doubly halide-bridged in solution or tetranuclear (*n* = 2) singly halide-bridged in the solid state.[5]

A general method for the deliberate synthesis of tri- or tetranuclear derivatives has been developed by appropriate choice of reagents: thus, by treating *cis*-$[M(C_6X_5)_2(thf)_2]$ with salts (2:1), either $[M'X'_4]^{2-}$ or $[M'_2(\mu\text{-}X')_2X'_4]^{2-}$, tri- or tetranuclear anionic derivatives, are obtained. Remarkably no rearrangement reactions have been observed.

(*a*) *Synthesis of the Trinuclear Complexes.*—The reactions take place as represented in equation (1) [Q = NEt_4; M =

$$Q_2[M'X'_4] + 2\,cis\text{-}[M(C_6X_5)_2(thf)_2] \longrightarrow Q_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2] + 4\,thf \quad (1)$$

M′ = Pd; X = F, X′ = Cl (**1**); X = Cl, X′ = Cl (**3**); M = Pt, M′ = Pd; X = F, X′ = Cl (**4**); X = Cl, X′ = Cl (**5**); Q = NBu_4; M = M′ = Pt, X = F, X′ = Cl (**2**); M = Pd, M′ = Pt, X = F, X′ = Cl (**6**)]. The salt $[NEt_4]_2[PdCl_4]$ is used as the palladium reagent, $K_2[PtCl_4]$ is the platinum precursor [complexes (**2**) and (**6**)], and NBu_4ClO_4 is added to the reaction mixture to facilitate the isolation of the trinuclear complexes. Complex (**5**) precipitates during the reaction, whereas the isolation of the other compounds requires evaporation to dryness and some working up (see Experimental section). As may be seen from equation (1), suitable choice of M and M′ allows the syntheses of homo- or hetero-metallic derivatives.

Table 1 collects analytical (C, H, and N), conductivity, and relevant i.r. data for these complexes. They behave as 2:1 electrolytes in acetone solutions ($c \approx 5 \times 10^{-4}$ mol dm^{-3}).[11] Two i.r. absorptions due to the X-sensitive modes of the C_6X_5 groups or to $\nu(M\text{-}C)(C_6Cl_5)$ indicate that the *cis* geometry is retained after reaction.[12]

(*b*) *Structure of* $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ (**2**).—The structure of complex (**2**) has been

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* Bis(tetrabutylammonium) 1,2;1,2;2,3;2,3-tetra-μ-chloro-1,1,3,3-tetrakis(pentafluorophenyl)triplatinate(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical results, conductivity, and relevant i.r. data (cm^{-1}) for the complexes

	Analysis^b %				I.r.		
					C_6X_5		
Complex^a	C	H	N	Λ_M/ ohm^{-1} cm^2 mol^{-1}	X-sensitive	ν(M–C)	ν(M–X)
(1) $Q_2[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_5)_2]$	34.1 (34.6)	3.0 (2.9)	2.1 (2.0)	177	798, 782	—	328vs, 267s, 255(sh), 245(sh)
(2) $Q'_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$	35.6 (35.8)	3.6 (3.8)	1.5 (1.5)	198	812, 800	—	330vs, 270m
(3) $Q_2[(C_6Cl_5)_2Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pd(C_6Cl_5)_2]$	27.7 (27.9)	2.4 (2.3)	1.7 (1.6)	209	845, 840	625, 615	330m,br, 260m,br
(4) $Q_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$	30.2 (30.6)	2.6 (2.5)	1.6 (1.8)	193	815, 805	—	335vs, 268s, 240w
(5) $Q_2[(C_6Cl_5)_2Pt(\mu\text{-}Cl)_2Pd(\mu\text{-}Cl)_2Pt(C_6Cl_5)_2]$	25.6 (25.3)	2.1 (2.1)	1.5 (1.5)	*c*	845, 840	630, 620	338vs, 260w, 240w
(6) $Q'_2[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pd(C_6F_5)_2]$	39.7 (39.5)	4.2 (4.2)	1.9 (1.6)	168	798, 785	—	330vs, 270m, 265(sh), 245(sh)
(7) $Q'_2[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(\mu\text{-}Br)_2Pt(C_6F_5)_2]$	34.2 (34.2)	3.6 (3.6)	1.8 (1.4)	*d*	812, 800	—	262w, 255w^e
(8) $Q'_2[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pt(\mu\text{-}Br)_2Pt(\mu\text{-}Br)_2Pt(C_6F_5)_2]$	27.3 (27.9)	3.4 (3.0)	1.3 (1.2)	*d*	810, 798	—	260w, 250w^e
(9) $Q'_2[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(\mu\text{-}Br)_2Pd(\mu\text{-}Br)_2Pt(C_6F_5)_2]$	30.3 (30.1)	3.1 (3.2)	1.4 (1.2)	*d*	810, 798	—	260w, 252w^e
(10) $Q'_2[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pt(\mu\text{-}Br)_2Pt(\mu\text{-}Br)_2Pd(C_6F_5)_2]$	29.5 (30.1)	3.7 (3.2)	1.6 (1.3)	*d*	798, 785	—	260w^e

^{a} Q = NEt_4, Q′ = NBu_4. ^{b} Calculated values in parentheses. ^{c} Not soluble enough in acetone. ^{d} Decomposition takes place. ^{e} The absorptions due to ν(M–Br) might appear below the limit of our apparatus (200 cm^{-1}).

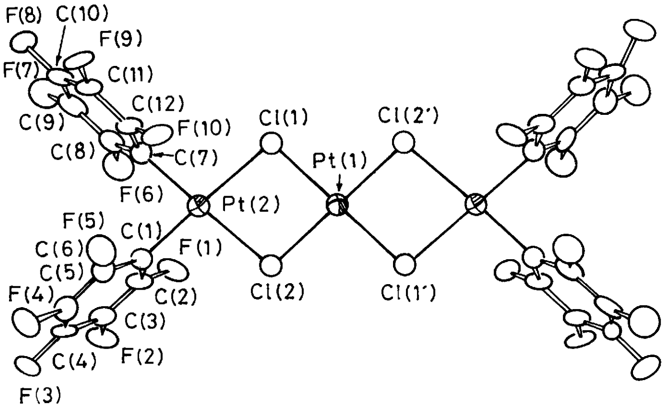

Figure. The geometry of the anion $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]^{2-}$ in complex **(2)**

Table 2. Selected bond distances (Å) and interbond angles (°) in $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ **(2)**

Pt(1)–Cl(1)	2.326(3)	Pt(2)–Cl(2)	2.430(2)
Pt(1)–Cl(2)	2.313(2)	Pt(2)–C(1)	2.017(5)
Pt(2)–Cl(1)	2.441(2)	Pt(2)–C(7)	2.017(5)
Cl(1)–Pt(1)–Cl(2)	87.86(8)	Cl(2)–Pt(2)–C(1)	94.53(16)
Cl(1′)–Pt(1)–Cl(2)	92.14(8)	Cl(2)–Pt(2)–C(7)	174.03(16)
Cl(1)–Pt(2)–Cl(2)	82.73(8)	C(1)–Pt(2)–C(7)	88.53(21)
Cl(1)–Pt(2)–C(1)	174.93(15)	Pt(1)–Cl(1)–Pt(2)	94.23(8)
Cl(1)–Pt(2)–C(7)	94.59(16)	Pt(1)–Cl(2)–Pt(2)	94.86(8)

established by single-crystal *X*-ray crystallography. Single crystals were grown from dichloromethane–hexane at room temperature.

A plan view of the anion, together with the atomic numbering scheme adopted, is presented in the Figure and selected bond distances and angles are listed in Table 2. Table 3 lists the co-ordinates of refined atoms.

The atom Pt(1) lies at the centre of symmetry of the anion, bonded to four chlorine atoms. The bond distances Pt(1)–Cl(1) and Pt(1)–Cl(2) are 2.326(3) and 2.313(2) Å respectively, in the same range as those found in $K_2[PtCl_4]$.[13] Angles around Pt(1) are Cl(1)–Pt(1)–Cl(2) 87.86(8)° and Cl(1)–Pt(1)–Cl(2′) 92.14(8)°. Atoms Pt(2) and Pt(2′) are in approximately *cis*-square-planar environments, formed by one carbon atom of each C_6F_5 group and two bridging chlorine atoms. The Pt(2)–Cl(1) and Pt(2)–Cl(2) distances are respectively 2.441(2) and 2.430(2) Å, longer than Pt(1)–Cl(1) and Pt(1)–Cl(2), thus implying that the Pt(1)–Cl bonds are stronger. A similar feature has been observed in $Pd_3(\eta^3\text{-}C_4H_7)_2Cl_4$,[7] a trinuclear palladium compound with double chloride bridges where the outer Pd–Cl distances are 0.11 Å longer than the inner ones. The Pt(2)–Cl distances are also longer than the corresponding ones in the binuclear pentafluorophenyl derivative $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$[14] [Pt(1)–Cl(1) 2.394(3), Pt(1)–Cl(1′) 2.387(3) Å]. The Pt(2)–C(1) and Pt(2)–C(7) distances are 2.017(5) Å, slightly longer than those in $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ [1.977(10) and 1.991(10) Å]. Angles around Pt(2) are in the range 82.73(8)—94.59(16)°. The angles Pt(2)–Cl(1)–Pt(1) and Pt(2)–Cl(2)–Pt(1) are 94.23(8) and 94.86(8)°, respectively. The distances between the central Pt(1) and the two Pt(2) atoms are 3.494 Å, excluding any direct Pt(1)–Pt(2) bonding interaction.

Since Pt(1) lies on an inversion centre, the central $PtCl_4$ moiety is square planar. The Pt(2),Cl(1),Cl(2),C(1),C(7) unit is essentially planar as well and makes a dihedral angle (6°) with the $PtCl_4$ central plane.

(*c*) *Synthesis of Tetranuclear Complexes*.—The low-temperature (−30, −60 °C) (2:1) reaction between *cis*-$[M(C_6X_5)_2(thf)_2]$ and $[NBu_4]_2[M'_2(\mu\text{-}Br)_2Br_4]$ in dichloromethane solution affords tetranuclear homo- or hetero-metallic com-

Table 3. Fractional atomic co-ordinates for non-hydrogen atoms in $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	0.000 00	0.000 00	0.000 00	C(9)	−0.4441	0.5590	−0.2946
Pt(2)	−0.083 38(4)	0.230 89(2)	−0.201 59(2)	C(10)	−0.5079	0.5187	−0.3443
Cl(1)	−0.206 08(23)	0.143 31(16)	−0.066 63(13)	C(11)	−0.4481	0.3956	−0.3528
Cl(2)	0.126 17(25)	0.067 33(19)	−0.133 32(14)	C(12)	−0.3245	0.3129	−0.3116
F(1)	0.058 1(5)	0.380 7(4)	−0.175 1(3)	N	0.126 9(7)	0.186 5(5)	0.178 5(4)
F(2)	0.200 5(5)	0.482 4(4)	−0.306 4(3)	C(13)	0.061 2(9)	0.104 6(6)	0.227 6(5)
F(3)	0.242 2(5)	0.466 4(4)	−0.505 9(3)	C(14)	−0.035 1(9)	0.138 2(7)	0.326 9(6)
F(4)	0.139 9(5)	0.344 7(4)	−0.572 4(3)	C(15)	−0.105 8(10)	0.057 0(8)	0.361 3(6)
F(5)	−0.001 7(6)	0.239 5(4)	−0.444 6(3)	C(16)	−0.206 0(10)	0.085 8(8)	0.460 1(6)
F(6)	−0.265 8(6)	0.523 1(4)	−0.211 4(4)	C(17)	0.214 9(9)	0.190 3(7)	0.246 9(6)
F(7)	−0.507 7(7)	0.677 0(4)	−0.290 0(5)	C(18)	0.342 6(9)	0.072 0(7)	0.271 8(6)
F(8)	−0.625 8(6)	0.595 5(5)	−0.385 4(5)	C(19)	0.427 4(12)	0.081 1(9)	0.338 9(8)
F(9)	−0.505 4(6)	0.353 9(5)	−0.400 9(4)	C(20)	0.556 4(12)	−0.041 9(12)	0.362 3(8)
F(10)	−0.270 8(5)	0.199 0(4)	−0.319 6(3)	C(21)	0.215 2(8)	0.139 2(6)	0.079 2(5)
C(1)	0.025 4(5)	0.305 0(4)	−0.303 7(3)	C(22)	0.293 8(11)	0.206 8(8)	0.020 0(6)
C(2)	0.0791	0.3676	−0.2700	C(23)	0.374 1(9)	0.156 5(7)	−0.076 6(6)
C(3)	0.1530	0.4214	−0.3388	C(24)	0.445 8(10)	0.225 0(8)	−0.145 2(7)
C(4)	0.1733	0.4128	−0.4412	C(25)	0.007 8(10)	0.314 6(7)	0.156 5(6)
C(5)	0.1197	0.3502	−0.4749	C(26)	−0.102 1(11)	0.323 8(8)	0.098 9(6)
C(6)	0.0457	0.2963	−0.4061	C(27)	0.213 7(15)	−0.455 2(8)	−0.073 5(10)
C(7)	−0.260 7(5)	0.353 2(4)	−0.261 8(4)	C(28)	0.333 4(13)	−0.464 9(10)	−0.033 6(8)
C(8)	−0.3205	0.4763	−0.2533				

plexes, according to equation (2) [M = M′ = Pt (**8**); M = Pt,

$$[NBu_4]_2[M'_2(\mu\text{-}Br)_2Br_4] + 2\ cis\text{-}[M(C_6F_5)_2(thf)_2] \longrightarrow [NBu_4]_2[(C_6F_5)_2M(\mu\text{-}Br)_2M'(\mu\text{-}Br)_2M'(\mu\text{-}Br)_2M(C_6F_5)_2] \qquad (2)$$

M′ = Pd (**9**); M = Pd, M′ = Pt (**10**)]. Complexes (**8**)—(**10**) can be isolated by evaporating the solutions to dryness and subsequent washing of the red-brown solids with Pr^iOH.

At room temperature, dichloromethane solutions of the complexes are not stable and slowly decompose, yielding dark brown precipitates which do not contain C_6F_5 or NBu_4 (i.r. spectra) and are assumed to be $M'Br_2$. When a dichloromethane solution of complex (**9**) was allowed to stand until complete decomposition, $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(\mu\text{-}Br)_2Pt(C_6F_5)_2]$ (**7**) (75% yield) was isolated from the filtrate.

Experimental

Infrared spectra, C, H, and N analyses, and conductance measurements were performed as described elsewhere.[5] The complexes $[NEt_4]_2[PdCl_4]$,[15] $K_2[PtCl_4]$,[15] $[NBu_4]_2[Pd_2Br_6]$,[15] $[NBu_4]_2[Pt_2Br_6]$,[15] *cis*-$[M(C_6F_5)_2(thf)_2]$, and *cis*- $[M(C_6Cl_5)_2(thf)_2]$[8] (M = Pd or Pt) were prepared as reported in the literature.

Preparations—Complexes (**1**), (**3**), (**4**), *and* (**5**). A typical preparation [complex (**1**)] was as follows. To a suspension of $[NEt_4]_2[PdCl_4]$ (0.065 g, 0.13 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.15 g, 0.26 mmol) and the mixture was stirred at room temperature for 10 min. The orange solution obtained was evaporated to dryness and the residue washed with Et_2O and n-hexane. A pale brown solid (**1**) (0.1 g, 73% yield) was obtained. For complexes (**3**)—(**5**) the following reaction conditions were used: (**3**), $[NEt_4]_2[PdCl_4]$ (0.034 g, 0.067 mmol), *cis*-$[Pd(C_6Cl_5)_2(thf)_2]$ (0.1 g, 0.13 mmol), CH_2Cl_2 (20 cm^3), stirring at room temperature for 10 min, 90% yield; (**4**) $[NEt_4]_2[PdCl_4]$ (0.1 g, 0.19 mmol), *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.26 g, 0.39 mmol), CH_2Cl_2 (20 cm^3), stirring at −20 °C for 20 min, 60% yield; (**5**), $[NEt_4]_2[PdCl_4]$ (0.045 g, 0.09 mmol), *cis*-$[Pt(C_6Cl_5)_2(thf)_2]$ (0.15 g, 0.18 mmol), CH_2Cl_2 (20 cm^3); precipitation in 89% yield.

Complex (**2**). To a suspension of $K_2[PtCl_4]$ (0.046 g, 0.11 mmol) in CH_2Cl_2 (20 cm^3) were added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.15 g, 0.22 mmol) and NBu_4ClO_4 (0.085 g, 0.25 mmol) and the mixture was stirred at room temperature for 4 h. The resulting solution was evaporated to dryness and the residue treated with Et_2O (15 cm^3). After further evaporation to dryness the residue (0.1 g, 48% yield; pale brown) was washed with n-hexane.

Complex (**6**). To a suspension of $K_2[PtCl_4]$ (0.053 g, 0.13 mmol) in CH_2Cl_2 (20 cm^3) were added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.15 g, 0.26 mmol) and NBu_4ClO_4 (0.098 g, 0.29 mmol) and the mixture was stirred at room temperature for 2 h. The white solid (mainly $KClO_4$) was eliminated by filtration; the resulting orange solution was evaporated to dryness and the residue was washed with water, then dissolved in CH_2Cl_2 (20 cm^3). This dichloromethane solution was dried with $MgSO_4$ and, after filtration, the filtrate was evaporated to dryness and the residue was washed with n-hexane (0.15 g, 70% yield, orange).

Complex (**8**). To a solution of $[NBu_4]_2[Pt_2Br_6]$ (0.2 g, 0.15 mmol) in CH_2Cl_2 (10 cm^3) was added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.2 g, 0.3 mmol). After stirring for 10 min at −60 °C the red solution was evaporated to dryness at room temperature. The residue was dried under vacuum and the solid was washed with Pr^iOH (brown, 0.23 g, 65% yield).

Complex (**10**) was obtained (0.2 g, 53% yield) in a similar way by using $[NBu_4]_2[Pt_2Br_6]$ (0.23 g, 0.17 mmol) and *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.2 g, 0.34 mmol). Complex (**9**) was obtained from $[NBu_4]_2[Pd_2Br_6]$ (0.175 g, 0.15 mmol) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.2 g, 0.3 mmol) in CH_2Cl_2 at −30 °C. The red residue was washed three times with n-hexane (0.3 g, 90% yield).

Attempts to recrystallize complexes (**8**)—(**10**) from CH_2Cl_2–Et_2O or CH_2Cl_2–hexane resulted in decomposition and precipitation of dark brown solids which do not contain (i.r. spectra) C_6F_5 groups (probably MBr_2). In the case of complex (**9**), after filtering off the brown solid the trinuclear complex (**7**) was obtained (0.22 g, 75% yield) from the filtrate.

X-Ray Crystal Structure of Complex (**2**).—*Crystal data* (*T* = 185 K). $C_{56}H_{72}Cl_4F_{20}N_2Pt_3$, *M* = 1 880, triclinic, space group $P\bar{1}$, $a = 10.936(5)$, $b = 12.792(11)$, $c = 13.744(6)$ Å, $\alpha = 77.61(6)$, $\beta = 76.84(3)$, $\gamma = 60.37(6)°$, $U = 1\,615$ Å^3 (refined from 25 centred reflections, $14 < \theta < 15°$), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $Z = 1$, $D_c = 1.9325$ g cm^{-3}, pale yellow, air-stable. Crystal dimensions $0.2 \times 0.3 \times 0.3$ mm, $\mu = 68$ cm^{-1}, $F(000) = 904$.

Data collection and processing. CAD4 diffractometer with low-temperature device, ω—2θ scans, scan width $0.8 + 0.35 \tan\theta$, 5 934 data measured ($\theta_{\max.}$ 25°, h −13 to 13, k −15 to 15, l 0 to 16), giving 3 800 with $F \geqslant 5\sigma(F)$ for structure solution and refinement. No significant movement or decay over 106 X-ray hours.

Structure solution and refinement. Platinum co-ordinates from Patterson synthesis, all other non-H atoms from ΔF maps. Post-isotropic convergence empirical absorption correction.[16] Weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,038F^2$. All non-H atoms refined with anisotropic thermal parameters. The C_6 rings were idealized as regular, planar hexagons. Hydrogen atoms of the Bu groups were placed in idealized positions, with an overall isotropic thermal parameter, 0.078(11) Å^2. At convergence $R = 0.0364$, $R' = 0.0471$. The computer program SHELX 76[17] was used for all crystallographic work.

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

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