# Tri- and Tetra-nuclear Palladium(II) and/or Platinum(II) Compounds with Double Thiolato Bridges. Crystal Structure of $[P(CH_2Ph)Ph_3]_2[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$†

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The complexes *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt, thf = tetrahydrofuran) react (2:1) with $[NMe_4]_2[M'(SC_6F_5)_4]$ [M' = Pd or Pt] or $Q_2[M'_2(SC_6F_5)_6]$ [M' = Pd, Q = $NBu_4$; M' = Pt, Q = $NMe_4$ or $P(CH_2Ph)Ph_3$] to give homo- or hetero-metallic tri- or, respectively, tetra-nuclear dianions. The structure of the tetranuclear complex $[P(CH_2Ph)Ph_3]_2[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ has been established by single-crystal X-ray crystallography: the dianion possesses a crystallographic inversion centre; space group $P\bar{1}$, $a = 12.247(2)$, $b = 12.901(2)$, $c = 17.942(3)$ Å, $\alpha = 84.47(2)$, $\beta = 78.20(2)$, $\gamma = 77.21(2)°$, $Z = 1$, and $R = 0.0454$. The co-ordination at the metal atoms is planar. The outer (palladium) planes form an angle of 28.20(11)° with the inner ones.

Polynuclear palladium(II) or platinum(II) compounds with double halide or pseudohalide bridges are commonly encountered.[1] Most of them are binuclear species, although complexes of higher nuclearity[1] have been known for some time {*e.g.*, the α form of palladium dichloride is a chain polymer $(PdCl_2)_n$ and the β form of platinum(II) chloride is a hexanuclear ring $[Pt_6Cl_{12}]$}.

We have recently described[2] the synthesis of the compounds $[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt, thf = tetrahydrofuran) which have proven[3] to be excellent precursors for the synthesis of tri- or tetra-nuclear palladium or platinum complexes with double halide bridges. Moreover, the reactions between $[M(C_6F_5)_2(thf)_2]$ and neutral bis(thiolato) compounds of the type *cis*-$[M'L_2(SC_6F_5)_2]$ (M' = Ni, Pd or Pt; $L_2$ = diphosphine or L = $PPh_3$) afford[4] neutral homo- and hetero-binuclear complexes of the general formula *gem*-$[L_2M'(\mu\text{-}SC_6F_5)_2M(C_6F_5)_2]$.

In the present paper, we report the synthesis of anionic homo- and hetero-nuclear palladium(II) and/or platinum(II) compounds, containing three or four metal centres doubly bridged by pentafluorobenzenethiolato ligands.

## Results and Discussion

*Trinuclear Complexes.*—The reaction (2:1) between a palladium(II) or platinum(II) complex containing two substitution-labile groups, *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) and $[NMe_4]_2[M'(SC_6F_5)_4]$ (M' = Pd or Pt) leads immediately to the corresponding dianionic trinuclear compound, with two double pentafluorobenzenethiolato bridges between the metal centres, equation (1) [M' = Pd, M = Pd **1** or Pt **2**; M' = Pt, M = Pd **3** or Pt **4**]. Elemental analysis, molar conductivity and yield for complexes **1**–**4** are listed in Table 1.

$$2\,cis\text{-}[M(C_6F_5)_2(thf)_2] + [NMe_4]_2[M'(SC_6F_5)_4] \longrightarrow [NMe_4]_2[(C_6F_5)_2M(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2\text{-}M(C_6F_5)_2] + 4\,thf \quad (1)$$

The IR spectra of the solids (see Table 2) show, along with the typical absorptions of the $C_6F_5$ rings of both the pentafluorobenzenethiolato[5] and the pentafluorophenyl ligands[6] and those due to the cations, a strong, slightly broad band at 850–860 cm$^{-1}$ assignable[5] to the ν(C–S) stretching vibrations of the thiolato groups and two absorptions in the 760–805 cm$^{-1}$ region corresponding[6] to the X-sensitive mode of the pentafluorophenyl ligands, indicative[7] of the *cis* geometry of the $C_6F_5$ groups.

The room-temperature $^{19}F$ NMR spectra of these complexes (see Tables 3 and 4) display two groups of signals (with equal integrals): a doublet (along with the expected $^{195}Pt$ satellites for complexes **2** and **4**), in the region assigned[4,8] to the *ortho*-fluorine nuclei of pentafluorophenyl groups (δ −110 to −122), and a broad resonance between δ −125 and −135 (*ortho*-fluorine region of the pentafluorobenzenethiolate ligands).

The broadness of the signal at lower frequency must be due to a dynamic process, with a low rate at room temperature, as has previously been found for many other thiolato bridged systems,[9,10] arising from the equilibria between the *syn* and *anti* planar (or, alternatively, the *syn–exo*, *syn–endo* and *anti*) geometries of each double bridge, through inversion at the sulfur centres.

In previous work,[4] we found that such dynamic processes took place in hexadeuterioacetone solution, but were absent when deuteriochloroform was used as the solvent, even when 4% (v/v) of acetone was added. The negligible solubility of complexes **1**–**4** in chloroform (no $^{19}F$ signal was observed even after 14 h) has prevented a check on this extreme.

Since the trinuclear complexes contain two double thiolato bridges, even in the simplest case of a planar '$M_3(SR)_4$' geometry five diastereoisomers can be proposed, two of them with a non-superimposable mirror image. In one, neither the four pentafluorobenzenethiolato groups nor the four pentafluorophenyl groups are equivalent. In addition rotation around M–C and/or M–S bonds could be restricted, breaking down the equivalence of the *ortho* (and the *meta*) fluorine nuclei.

The spectra recorded between +50 (where the fast-exchange limit is reached for the $C_6F_5$ but not for the $SC_6F_5$ groups) and −50 °C (slow exchange is not attained) show the dynamic

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† *Supplementary data available* (No. SUP 56981, 5 pp.): mass spectral data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

**Table 1** Elemental analyses, molar conductivities and yields of complexes **1**–**8**; calculated values are given in parentheses; $R = C_6F_5$

| Compound | Analysis (%) C | H | N | $\Lambda_M$/S cm$^2$ mol$^{-1}$ | Yield (%) |
|---|---|---|---|---|---|
| **1** $[NMe_4]_2[R_2Pd(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2PdR_2]$ | 35.4 (34.8) | 1.0 (1.3) | 1.3 (1.4) | 240.7 | 72.0 |
| **2** $[NMe_4]_2[R_2Pt(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2PtR_2]$ | 32.1 (31.9) | 1.0 (1.1) | 1.3 (1.4) | 232.5 | 64.1 |
| **3** $[NMe_4]_2[R_2Pd(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2PdR_2]$ | 33.5 (33.3) | 1.1 (1.2) | 1.2 (1.4) | 244.3 | 74.5 |
| **4** $[NMe_4]_2[R_2Pt(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2PtR_2]$ | 31.0 (30.6) | 0.9 (1.1) | 1.2 (1.3) | 246.3 | 79.6 |
| **5** $[NBu_4]_2[R_2Pd(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2PdR_2]$ | 40.5 (39.8) | 2.5 (2.6) | 1.0 (1.0) | 193.4 | 83.4 |
| **6** $[NBu_4]_2[R_2Pt(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2Pd(\mu\text{-}SR)_2PtR_2]$ | 37.6 (37.4) | 2.5 (2.5) | 0.8 (0.9) | 193.5 | 79.6 |
| **7** $[NMe_4]_2[R_2Pd(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2PdR_2]$ | 31.1 (31.2) | 0.8 (0.9) | 1.0 (1.1) | 247.2 | 77.8 |
| **8** $[NMe_4]_2[R_2Pt(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2Pt(\mu\text{-}SR)_2PtR_2]$ | 29.1 (29.3) | 0.8 (0.9) | 0.9 (1.0) | 247.5 | 82.3 |

**Table 2** Characteristic IR absorptions (cm$^{-1}$)

| Complex | ν(C–S) | X-sensitive | ν(C–F) |
|---|---|---|---|
| **1** | 854s | 788s, 779s | 1397s, 1359s, 1347s, 1283m, 1253m, 1138m, 1087s, 1056s, 1010s, 978s, 955s |
| **2** | 853s | 803s, 793s | 1397s, 1367s, 1285m, 1271m, 1258m, 1139m, 1087s, 1064s, 1011s, 977s, 957s |
| **3** | 852s | 789s, 780s | 1397s, 1366s, 1283m, 1254m, 1139m, 1088s, 1060s, 1010s, 975s, 947s |
| **4** | 849m | 803m, 793m | 1397s, 1365s, 1285m, 1270m, 1140m, 1087s, 1058s, 1011s, 981s, 957s |
| **5** | 857s | 788s, 778s | 1397s, 1365s, 1347s, 1287m, 1275m, 1256m, 1141m, 1089s, 1055s, 1010m, 978s, 956s |
| **6** | 854s | 802s, 793s | 1397s, 1366s, 1287m, 1269m, 1142m, 1087s, 1059s, 1011m, 979s, 958s |
| **7** | 851s | 789s, 779s | 1398m, 1368s, 1288m, 1142m, 1089s, 1056s, 1010m, 979s, 955s |
| **8** | 850m | 803s, 793s | 1397s, 1367s, 1288m, 1270m, 1143m, 1089s, 1058s, 1012m, 981s, 958s |

**Table 3** Fluorine-19 NMR data (*ortho*-fluorine region) for complexes **1**–**8**

| | $C_6F_5$ | | | $SC_6F_5$ | | $SC_6F_5'$ | |
|---|---|---|---|---|---|---|---|
| Complex | $\delta_o$ | $J_{o-m}$/Hz | $J_{Pt-F}$/Hz | $\delta_o$ | $J_{o-m}$/Hz | $\delta_o$ | $J_{o-m}$/Hz |
| **1** | −114.0 | *a* | — | −127.5 | *a* | | |
| **2** | −118.9 | *a* | 438 | −129.1 | *a* | | |
| **3** | −116.0 | 25 | — | −129.6 | *a* | | |
| **4** | −117.9 | *a* | 434 | −128.5 | *a* | | |
| **5** | −114.6 | *a* | — | −127.6 | *a* | −139.5 | *a* |
| **6** | −119.2 | *a* | *a* | −129.4 | *a* | −140.8 | *a* |
| **7** | −114.9 | *a* | — | −128.1 | *a* | *b* | *b* |
| **8** | −119.9 | *a* | 430 | −130.4 | *a* | *b* | *b* |

[a] Broad. [b] Not observed (signal coalesces at room temperature, see text).

**Table 4** Fluorine-19 NMR data (*meta*- and *para*-fluorine regions) for complexes **1**–**8**

| Complex | $\delta_m$ | $\delta_p$ | $J_{m-p}$/Hz | $\delta_m$ | $\delta_p$ | $J_{m-p}$/Hz | $\delta_m$ | $\delta_p$ | $J_{m-p}$/Hz |
|---|---|---|---|---|---|---|---|---|---|
| **1** | −165.3 | −160.2 | 21 | −164.9 | −163.3 | 20 | | | |
| **2** | −167.9 | −159.1 | 20 | *a* | *a* | *a* | | | |
| **3** | −166.8 | −159.9 | 20 | −166.3 | −164.9 | 19 | | | |
| **4** | −166.3 | −157.3 | 21 | −164.4 | −164.8 | 19 | | | |
| **5** | −164.9 | −156.9 | 21 | −164.0 | −162.7 | 20 | −160.5 | −154.0 | 20 |
| **6** | −167.7 | −157.5 | 21 | −165.5 | −165.7 | 19 | −161.9 | −155.3 | 20 |
| **7** | −164.9 | −156.5 | 20 | −163.7 | −162.7 | 19 | −162.4 | −153.0 | *b* |
| **8** | −167.6 | −157.2 | 19 | −165.1 | −165.8 | 19 | −163.6 | −154.3 | *b* |

[a] Superimposing signals. [b] Broad.

behaviour of the trinuclear complexes **1**–**4** in acetone solution, but the complexity of the dynamic system makes it impossible to ascertain which conformers are possibly involved.

The trinuclear complexes behave as 2:1 electrolytes in acetone solution,[11] as expected.

A noteworthy feature of the mass spectra (FAB technique) of complexes **1**–**4** is a series of peaks at higher *m*/*z* than that of the parent ion. In particular an intense peak is observed due to the tetranuclear $M_2M'_2(SC_6F_5)_6(C_6F_5)_4$ ion, which corresponds to an ion–molecule association [the spectrum of **1** even shows a peak for $Pd_5(SC_6F_5)_8(C_6F_5)_4$, indicative of the stability of higher oligomeric species].

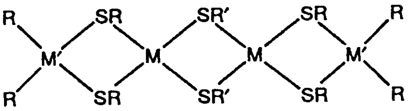
*Tetranuclear Complexes*.—When the binuclear complexes $Q_2[M'_2(SC_6F_5)_6]$ (M′ = Pd, Q = NBu$_4$; M′ = Pt, Q = NEt$_4$) are treated (1:2) with *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) the corresponding dianionic tetranuclear compounds, with three double pentafluorobenzenethiolato bridges between the metal centres, are obtained [equation (2); M′ = Pd,

$$2\ cis\text{-}[M(C_6F_5)_2(thf)_2] + Q_2[M'_2(SC_6F_5)_6] \longrightarrow Q_2[(C_6F_5)_2M(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M(C_6F_5)_2] + 4\ thf \quad (2)$$

Q = NBu$_4$, M = Pd **5** or Pt **6**; M′ = Pt, Q = NMe$_4$,

M = Pd **7** or Pt **8**]. Elemental analyses, molar conductivities and yields for complexes **5**–**8** are listed in Table 1.

The IR spectra of the solids (see Table 2) show bands assignable to the $C_6F_5$ rings of both the pentafluorobenzenethiolato[5] and the pentafluorophenyl ligands.[6] In addition, two absorptions in the 760–805 $cm^{-1}$ region (X-sensitive mode of the pentafluorophenyl ligands), which are characteristic[7] of the mutually *cis* geometry of the pentafluorophenyl groups and a strong, slightly broad band at 850–860 $cm^{-1}$ which corresponds[3] to the ν(C–S) stretching vibrations of the thiolato ligands are observed.



The tetranuclear complexes contain three double thiolato bridges so that [in the simplest case of a planar geometry and ignoring any restriction to rotation around the M–C and/or M–S bonds, which would make the *ortho* (and *meta*) fluorine nuclei inequivalent] 14 diastereoisomers can be proposed, two with a non-superimposable mirror image. In some not all the pentafluorobenzenethiolato and pentafluorophenyl groups would be equivalent.

At room temperature the $^{19}F$ NMR spectra (see Tables 3 and 4) of complexes **5**–**8** display three groups of signals (which integrate as 2:2:1): a doublet (along with the expected $^{195}Pt$ satellites for complexes **6** and **8**) in the region assigned[2,6] to the *ortho*-fluorine nuclei of the four pentafluorophenyl groups, and two broad resonances at higher fields, one arising from the four outer (SR) groups [in the characteristic region[4,8] for the *ortho*-fluorine nuclei of pentafluorobenzenethiolate ligands] and the other due to the two inner (SR′) moieties (at even lower frequencies, around δ −140). For complexes **7** and **8** the peak at higher field coalesces at room temperature but can still be integrated.

Although at low temperatures (−50 °C) the dynamic process approaches the slow-exchange limit, the complexity of the system makes it impossible to ascertain which conformers could possibly be involved.

An X-ray diffraction study (see Fig. 1) was therefore undertaken, which confirms the connectivity in complexes **5**–**8** (and correspondingly in **1**–**4**). However it should be noted that the solid-state structure need not correspond to the most stable one in solution.

Single crystals were grown by slow diffusion of hexane into a dichloromethane solution of $[P(CH_2Ph)Ph_3]_2[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ **7′**. (Crystals of the tetraalkylammonium salts **1**–**8**, which could only be grown from acetone solutions, decayed very easily even in the mother-liquor.)

The tetranuclear dianion lies on a crystallographic inversion centre and each metal atom is in a slightly distorted square-planar environment [S(1)–Pt(1)–S(1a) 83.7(1), S(2)–Pt(1)–S(3) 82.6(1), S(2)–Pd(1)–S(3) 79.6(1)°]. The central part of the anion (formed by both platinum and the six sulfur atoms) is planar (r.m.s. deviation[12] 0.040 Å) as a consequence of the centre of symmetry and the planarity of the environment around the platinum centres; the double thiolato bridge linking them adopts an *anti*-planar conformation. The co-ordination plane around Pd(1) forms a dihedral angle[12] of 28.20(11)° to the central part of the anion and the double bridge shows a *syn*–*endo* geometry (Fig. 2).

The platinum–sulfur bonds of the inner and outer bridges are essentially equal [$d_{Pt-S}$ = 2.315(3)–2.329(3) Å] and slightly shorter than the palladium–sulfur bonds [2.387(3) and 2.391(2) Å].

As expected, the tetranuclear complexes behave as 2:1 electrolytes in acetone solution.[11]

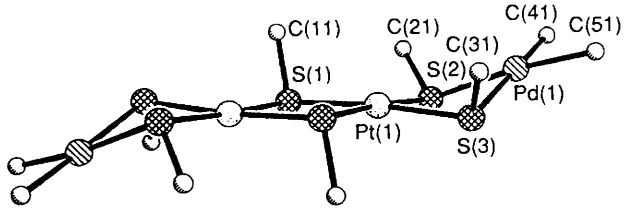


**Fig. 2** The skeleton of the anion in **7′**, showing the conformation of the bridging thiolato ligands

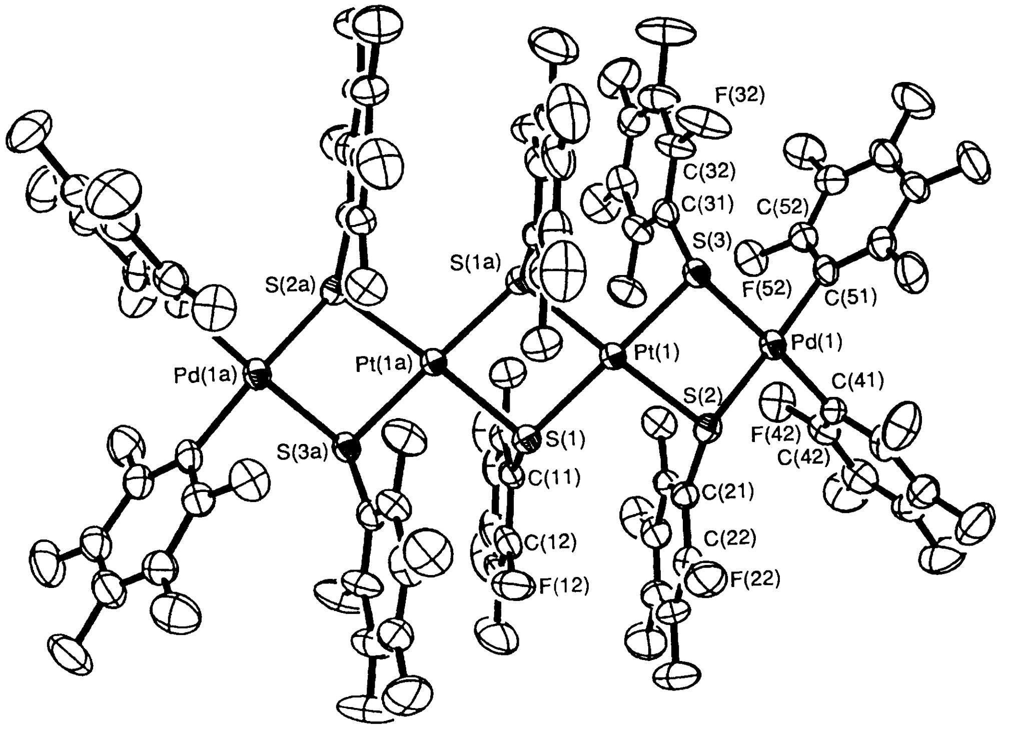


**Fig. 1** Numbering scheme for the anion of compound **7′**, $[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]^{2-}$. Ellipsoids are represented with 30% probability

## Experimental

All reactions were carried out at room temperature in purified solvents. The compounds $Q_2[M'(SC_6F_5)_4]$ (M′ = Pd or Pt; Q = $NMe_4$),[6] $Q_2[M'_2(SC_6F_5)_6]$ [M′ = Pd, Q = $NBu_4$; M′ = Pt, Q = $NMe_4$ or $P(CH_2Ph)Ph_3$][6] and *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt)[2] were prepared according to published procedures.

**Table 5** Selected bond lengths (Å) and angles (°) for compound **7′**

| | | | |
|---|---|---|---|
| Pt(1)–S(1) | 2.329(3) | Pt(1)–S(2) | 2.319(2) |
| Pt(1)–S(3) | 2.315(3) | Pt(1)–S(1a) | 2.331(2) |
| Pd(1)–S(2) | 2.387(3) | Pd(1)–S(3) | 2.391(2) |
| Pd(1)–C(41) | 2.032(8) | Pd(1)–C(51) | 2.034(11) |
| S(1)–C(11) | 1.789(9) | S(2)–C(21) | 1.780(9) |
| S(3)–C(31) | 1.784(11) | | |
| S(1)–Pt(1)–S(2) | 98.6(1) | S(1)–Pt(1)–S(3) | 175.0(1) |
| S(2)–Pt(1)–S(3) | 82.6(1) | S(1)–Pt(1)–S(1a) | 83.7(1) |
| S(2)–Pt(1)–S(1a) | 176.3(1) | S(3)–Pt(1)–S(1a) | 94.9(1) |
| S(2)–Pd(1)–S(3) | 79.6(1) | S(2)–Pd(1)–C(41) | 95.4(3) |
| S(3)–Pd(1)–C(41) | 174.3(3) | S(2)–Pd(1)–C(51) | 172.3(3) |
| S(3)–Pd(1)–C(51) | 94.8(2) | C(41)–Pd(1)–C(51) | 89.9(4) |
| Pt(1)–S(1)–C(11) | 107.7(3) | Pt(1)–S(1)–Pt(1a) | 96.3(1) |
| C(11)–S(1)–Pt(1a) | 103.7(3) | Pt(1)–S(2)–Pd(1) | 93.4(1) |
| Pt(1)–S(2)–C(21) | 109.8(3) | Pd(1)–S(2)–C(21) | 112.0(3) |
| Pt(1)–S(3)–Pd(1) | 93.4(1) | Pt(1)–S(3)–C(31) | 108.1(3) |
| Pd(1)–S(3)–C(31) | 107.5(3) | | |

Atoms labelled a are generated by inversion about 0,0,0.

Carbon, H and N analyses were performed with a Perkin Elmer 240 B microanalyser. IR spectra were recorded (over the range 4000–250 $cm^{-1}$) on a Perkin Elmer 833 spectrophotometer, using Nujol mulls between polyethylene sheets. The $^{19}F$ NMR spectra of hexadeuterioacetone solutions of the compounds were run at various temperatures on a Varian XL-200 or UNITY 300 spectrometer; chemical shifts are relative to $CFCl_3$.

The conductivities of acetone solutions of compounds **1**–**8** were measured with a Philips PW 9509 apparatus, using a PW 9550/60 cell.

Mass spectrometric data were obtained using FAB techniques on a VG Autospec apparatus. The matrix was 3-nitrobenzyl alcohol and the samples were dissolved in acetone.

*General Procedure for the Synthesis of Compounds of the Type* $Q_2[(C_6F_5)_2M(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M(C_6F_5)_2]$.—In each case, the appropriate tetrakis(pentafluorobenzenethiolato)metalate(II) complex was treated (2:1) in dichloromethane with the corresponding $[M(C_6F_5)_2(thf)_2]$ species. The solvent was removed and the residue washed with diethyl ether. A standard preparation is described below.

To a suspension of $[NMe_4]_2[Pd(SC_6F_5)_4]$ (0.095 mmol,

**Table 6** Atomic coordinates ( × $10^4$)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt(1) | 698(1) | −219(1) | −933(1) |
| Pd(1) | 2 002(1) | −1 197(1) | −2 675(1) |
| S(1) | 1 163(2) | −60(2) | 240(1) |
| S(2) | 2 509(2) | −408(2) | −1 679(1) |
| S(3) | 174(2) | −219(2) | −2 102(1) |
| C(11) | 1 799(9) | −1 360(7) | 574(5) |
| C(12) | 2 782(10) | −1 481(9) | 855(5) |
| F(12) | 3 246(5) | −654(6) | 896(4) |
| C(13) | 3 350(12) | −2 461(13) | 1 110(6) |
| F(13) | 4 319(7) | −2 573(7) | 1 364(4) |
| C(14) | 2 892(14) | −3 343(11) | 1 072(7) |
| F(14) | 3 446(7) | −4 316(6) | 1 291(4) |
| C(15) | 1 918(12) | −3 250(9) | 801(6) |
| F(15) | 1 472(7) | −4 093(5) | 771(4) |
| C(16) | 1 350(9) | −2 263(8) | 567(6) |
| F(16) | 416(5) | −2 196(4) | 296(3) |
| C(21) | 3 503(8) | −1 323(7) | −1 212(5) |
| C(22) | 4 403(10) | −999(9) | −1 014(6) |
| F(22) | 4 508(5) | −12(5) | −1 146(4) |
| C(23) | 5 185(9) | −1 728(12) | −679(7) |
| F(23) | 6 061(6) | −1 419(7) | −501(5) |
| C(24) | 5 105(10) | −2 785(11) | −549(7) |
| F(24) | 5 898(6) | −3 466(6) | −241(4) |
| C(25) | 4 246(10) | −3 106(9) | −751(6) |
| F(25) | 4 125(6) | −4 125(5) | −598(4) |
| C(26) | 3 425(9) | −2 378(8) | −1 057(5) |
| F(26) | 2 532(5) | −2 720(4) | −1 189(3) |
| C(31) | −814(8) | −1 076(7) | −2 004(5) |
| C(32) | −1 746(9) | −754(9) | −2 336(6) |
| F(32) | −1 963(6) | 212(5) | −2 679(4) |
| C(33) | −2 507(11) | −1 396(11) | −2 345(7) |
| F(33) | −3 452(7) | −1 037(6) | −2 639(5) |
| C(34) | −2 317(11) | −2 388(11) | −2 011(7) |
| F(34) | −3 031(6) | −3 059(6) | −2 019(4) |
| C(35) | −1 417(11) | −2 748(8) | −1 661(6) |
| F(35) | −1 197(6) | −3 730(5) | −1 348(4) |
| C(36) | −669(9) | −2 085(8) | −1 659(6) |
| F(36) | 218(5) | −2 457(4) | −1 317(3) |
| C(41) | 3 622(8) | −1 915(8) | −3 128(5) |
| C(42) | 4 070(10) | −2 962(8) | −3 004(6) |
| F(42) | 3 417(6) | −3 628(4) | −2 607(4) |
| C(43) | 5 210(12) | −3 413(9) | −3 257(7) |
| F(43) | 5 608(6) | −4 459(6) | −3 095(5) |
| C(44) | 5 914(10) | −2 784(12) | −3 652(7) |
| F(44) | 7 035(6) | −3 202(7) | −3 879(5) |
| C(45) | 5 494(11) | −1 731(11) | −3 804(6) |
| F(45) | 6 192(6) | −1 120(6) | −4 200(4) |
| C(46) | 4 353(10) | −1 324(8) | −3 530(6) |
| F(46) | 3 983(6) | −277(5) | −3 710(4) |
| C(51) | 1 436(8) | −1 676(8) | −3 548(5) |
| C(52) | 896(9) | −2 512(8) | −3 471(6) |
| F(52) | 883(5) | −3 192(4) | −2 842(3) |
| C(53) | 307(9) | −2 728(9) | −4 013(7) |
| F(53) | −247(6) | −3 548(5) | −3 873(4) |
| C(54) | 306(11) | −2 123(11) | −4 659(7) |
| F(54) | −248(7) | −2 333(6) | −5 189(4) |
| C(55) | 888(9) | −1 312(9) | −4 790(6) |
| F(55) | 901(6) | −699(6) | −5 442(3) |
| C(56) | 1 392(9) | −1 073(8) | −4 209(6) |
| F(56) | 1 880(6) | −216(5) | −4 352(3) |
| P(1) | 8 261(2) | 6 742(2) | 3 017(1) |
| C(60) | 7 429(8) | 8 042(6) | 3 278(5) |
| C(61) | 6 175(8) | 8 044(7) | 3 478(6) |
| C(62) | 5 525(10) | 8 231(8) | 2 937(6) |
| C(63) | 4 391(11) | 8 269(10) | 3 118(8) |
| C(64) | 3 862(12) | 8 145(10) | 3 863(9) |
| C(65) | 4 490(11) | 7 964(10) | 4 418(7) |
| C(66) | 5 671(10) | 7 900(8) | 4 227(6) |
| C(71) | 8 116(7) | 6 450(6) | 2 092(5) |
| C(72) | 8 014(8) | 7 263(8) | 1 531(6) |
| C(73) | 7 998(9) | 7 041(9) | 802(6) |
| C(74) | 8 054(10) | 6 012(10) | 638(6) |
| C(75) | 8 157(11) | 5 213(9) | 1 179(7) |
| C(76) | 8 157(9) | 5 427(8) | 1 913(6) |
| C(81) | 7 795(9) | 5 797(7) | 3 744(5) |
| C(82) | 8 319(9) | 5 585(7) | 4 368(6) |
| C(83) | 7 906(11) | 4 940(9) | 4 972(6) |
| C(84) | 6 979(13) | 4 523(9) | 4 946(8) |
| C(85) | 6 444(11) | 4 730(9) | 4 331(7) |
| C(86) | 6 871(9) | 5 365(8) | 3 735(6) |
| C(91) | 9 751(7) | 6 681(7) | 2 979(4) |
| C(92) | 10 165(9) | 7 555(8) | 3 095(6) |
| C(93) | 11 329(10) | 7 428(9) | 3 074(6) |
| C(94) | 12 043(10) | 6 469(10) | 2 964(6) |
| C(95) | 11 639(10) | 5 612(9) | 2 849(6) |
| C(96) | 10 482(9) | 5 726(8) | 2 857(6) |

0.0999 g) in dichloromethane (20 $cm^3$) was added [Pd($C_6F_5$)$_2$(thf)$_2$] (0.190 mmol, 0.1111 g). The colour turned from red to orange in 30 min. After stirring for 20 h, the solvent was removed and diethyl ether (6 $cm^3$) was added. The solid was filtered off, washed with $Et_2O$ (10 × 1 $cm^3$) and dried *in vacuo* over $P_2O_5$.

*General Procedure for the Synthesis of Compounds of the Type* $Q_2[(C_6F_5)_2M(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M(C_6F_5)_2]$.—In each case the appropriate $[(SC_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M'(SC_6F_5)_2]^{2-}$ anion was treated (1:2) in dichloromethane with the corresponding $[M(C_6F_5)_2(thf)_2]$ species. The solution was evaporated to dryness and the residue was washed repeatedly with diethyl ether. A typical preparation was as follows.

After addition of $[Pd(C_6F_5)_2(thf)_2]$ (0.14 mmol, 0.0819 g) to a dichloromethane (20 $cm^3$) solution of $[NBu_4]_2[(SC_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pd(SC_6F_5)_2]$ (0.07 mmol, 0.1324 g), a red precipitate formed slowly. The reaction mixture was stirred for 20 h and the solvent then removed. The crude red solid was stirred with diethyl ether (4 $cm^3$), filtered off, washed with diethyl ether (2 × 1 $cm^3$) and dried *in vacuo* over $P_2O_5$.

*Crystal-structure Determination of Complex* **7′**.—*Crystal data.* $C_{110}H_{44}F_{50}P_2Pd_2Pt_2S_6$, $M = 3172.7$, triclinic, $a$ = 12.247(2), $b$ = 12.901(2), $c$ = 17.942(3) Å, $\alpha$ = 84.47(2), $\beta$ = 78.20(2), $\gamma$ = 77.21(2)°, $U$ = 2702.3(7) Å$^3$ (by refinement of $2\theta$ values for 40 reflections in the range 21 < $2\theta$ < 29°, 20 °C), $\lambda$(Mo-K$\alpha$) = 0.71073 Å, space group $P\bar{1}$, $Z$ = 1, $D_c$ = 1.950 g cm$^{-3}$, $F(000)$ = 1528. Yellow parallelepipeds, 0.17 × 0.19 × 0.27 mm; $\mu$(Mo-K$\alpha$) = 31.90 cm$^{-1}$.

*Data collection and reduction.* Stoe-Siemens four-circle diffractometer, $\omega/\theta$ scan with $\omega$ scan width = 1.05°, variable $\omega$ scan speed 3.60–10.80° min$^{-1}$, graphite-monochromated Mo-K$\alpha$ radiation. 9239 Reflections measured (4 < $2\theta$ < 49°, $+h, \pm k, \pm l$) of which 8784 ($R_{int}$ = 0.0264) unique, 5587 with $F > 4\sigma(F)$ used for all calculations. Absorption correction, based on 7 $\psi$-scans, with transmission factors 0.5362–0.6246; three standard reflections, no decay.

*Structure solution and refinement.* Heavy-atom method, full-matrix least-squares refinement on $F$ to $R$ = 0.0454; $R'$ = 0.0365. All non-H atoms anisotropic; riding H atoms (C–H 0.96 Å), common isotropic $U$(H) = 0.0767 Å$^2$. Weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0001\,F_o^2$; 776 parameters. Program system SHELXTL PLUS,[13] scattering factors from ref. 14. Selected bond lengths and angles are given in Table 5, final atom coordinates of the anion in Table 6.

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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