Synthesis and Reactivity of Trinuclear Complexes of Platinum containing the Single Bridging Ligand SC_4H_8. Molecular Structure of $[NBu_4]_2[\textit{trans}\text{-}PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ *

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Trinuclear complexes of the type $[NBu_4]_2[\textit{trans}\text{-}PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ (X = Cl, Br, I, or C_6F_5; SC_4H_8 = tetrahydrothiophene) (**1**)—(**4**) have been prepared from *trans*-$[PtX_2(SC_4H_8)_2]$ and $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ (molar ratio 1 : 2). The SC_4H_8 ligands act as the single bridge between the central platinum atom and the two terminal ones. Attempts to prepare similar trinuclear complexes with singly bridging halide ligands failed since the reaction between *trans*-$[PtCl_2(py)_2]$ (py = pyridine) and $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ (molar ratio 1 : 2) does not take place, while *trans*-$[PtI_2(py)_2]$ or $[PtBr_2(cod)]$ (cod = cyclo-octa-1,5-diene), under similar conditions, yield *cis*-$[Pt(C_6F_5)_2(py)_2]$ and $[NBu_4]_2[Pt_2(\mu\text{-}I)_2(C_6F_5)_4]$ or $[Pt(C_6F_5)_2(cod)]$ and $[NBu_4]_2[Pt_2(\mu\text{-}Br)_2(C_6F_5)_4]$ respectively. The trinuclear derivatives (**1**) and (**3**) react with neutral ligands L to give different mononuclear complexes, depending on the ligand L: when L = PPh_3, $NBu_4[Pt(C_6F_5)_3(SC_4H_8)]$ and *cis*-$[PtX_2(PPh_3)_2]$; when L = CO, $NBu_4[Pt(C_6F_5)_3(CO)]$ and *trans*-$[PtCl_2(SC_4H_8)_2]$. The molecular structure of $[NBu_4]_2[\textit{trans}\text{-}PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ has been established by a single-crystal *X*-ray diffraction study. The compound forms triclinic crystals in the space group $P\bar{1}$, with $Z = 1$ and unit-cell dimensions $a = 12.463(3)$, $b = 12.487(3)$, $c = 15.137(3)$ Å, $\alpha = 85.68(15)$, $\beta = 66.04(2)$, and $\gamma = 87.04(1)°$. The structure was refined to $R = 0.048$ and $R' = 0.048$. The central platinum atom in the trinuclear anion $[\textit{trans}\text{-}PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]^{2-}$ lies on a crystallographic centre of symmetry and is bonded to two Cl atoms and two S atoms (from two SC_4H_8 ligands), the latter acting as bridging ligands between the central and the terminal Pt atoms.

Platinum complexes containing weakly co-ordinating ligands are of interest[1] both as regards the homogeneous activation of organic substrates and as useful intermediates for the synthesis of unusual types of compounds which are inaccessible from other more conventional starting compounds; for instance, we have recently reported the synthesis of neutral *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ (M = Pd or Pt; X = F or Cl; OC_4H_8 = tetrahydrofuran) containing two weakly bonded molecules of OC_4H_8 which can readily be displaced by carbon monoxide, diphenylacetylene, and *cis*-dihalogeno complexes to give the unusual complexes *cis*-$[M(C_6X_5)_2(CO)_2]$,[2,3] *cis*-$[M(C_6F_5)_2(PhC{\equiv}CPh)_2]$,[4] tetrameric $[(C_6X_5)_2M(\mu\text{-}X')M'(cod)(\mu\text{-}X')M(C_6X_5)_2(\mu\text{-}X')M'(cod)(\mu\text{-}X')]$,[5] and trimeric $[NBu_4]_2[(C_6X_5)_2M(\mu\text{-}X')_2M'(\mu\text{-}X')_2M(C_6X_5)_2]$ (M, M' = Pd or Pt; X = F or Cl; X' = Cl, Br, or I; cod = cyclo-octa-1,5-diene).[6]

Another promising precursor would be the complex $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and more so since $OCMe_2$ is a weaker donor than OC_4H_8 and could therefore be more readily displaced. The synthesis of this complex can be accomplished by chloride abstraction from $[NBu_4]_2[PtCl(C_6F_5)_3]$ with $AgClO_4$ (1 : 1) in acetone solution.

Attempts to isolate the complex by vacuum evaporation of the acetone solutions failed, since the co-ordinated acetone is given off and the binuclear C_6F_5-bridged complex $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ is obtained. This complex has been described elsewhere.[7] Notwithstanding, the acetone solutions behave as if they contain $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and we have used them to prepare trinuclear platinum complexes of stoicheiometry $[NBu_4]_2[\textit{trans}\text{-}PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ (X = Cl, Br, I, or C_6F_5) containing two single-bridging SC_4H_8 ligands. The molecular structure of one of these complexes (X = Cl) has been established by single-crystal *X*-ray studies and the reactivity of the complexes has been studied.

Results and Discussion

(*a*) *Preparation of Acetone Solutions of* $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$.—The 1 : 1 reaction between $[NBu_4]_2[PtCl(C_6F_5)_3]$ and $AgClO_4$ in acetone results in the precipitation of AgCl. Upon partial evaporation and addition of n-hexane the colourless solution, which presumably contains $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$, renders only oily residues and if the solution is evaporated to dryness a yellow solid, identified as $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ is obtained[7] (80% yield). The bridging system (two C_6F_5 groups) persists in the yellow dichloromethane solution but is lost in the colourless acetone solution. Equation (1) summarizes the above observations.

$$\begin{aligned}2\,[NBu_4]_2[PtCl(C_6F_5)_3] + 2\,AgClO_4 &\xrightarrow{\text{acetone}} 2\,AgCl\,+\\ 2\,NBu_4ClO_4 + 2\,NBu_4[Pt(C_6F_5)_3(OCMe_2)] &\xrightarrow{\text{evaporation}}\\ [NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] &+ 2\,OCMe_2 \qquad (1)\end{aligned}$$

Therefore, for our purposes we have used the colourless acetone solution, after filtering off the silver chloride precipitate. The solution also contains NBu_4ClO_4 which does not interfere in the subsequent reactions.

(*b*) *Reaction of* $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ *with trans*-$[PtX_2(SC_4H_8)_2]$ (X = Cl, Br, or I).—In the *trans*-$[PtX_2(SC_4H_8)_2]$

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* Bis(tetrabutylammonium) *trans*-2,2-dichloro-1,1,1,3,3,3-hexakis(pentafluorophenyl)-1,2;2,3-bis(μ-tetrahydrothiophene-*S*)-triplatinate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xiii—xx.

Table 1. Analytical results, melting points, and yields

	Complex	Analysis*/%				M.p. (°C)	Yield (%)
		C	H	N	X		
(1)	$[NBu_4]_2[$*trans*-$PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}]$	39.10 (39.35)	3.80 (3.80)	1.10 (1.20)	3.65 (3.05)	158	93
(2)	$[NBu_4]_2[$*trans*-$PtBr_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}]$	37.55 (37.90)	3.65 (3.65)	1.05 (1.15)	6.30 (6.65)	143	71
(3)	$[NBu_4]_2[$*trans*-$PtI_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}]$	36.80 (36.45)	3.55 (3.50)	1.15 (1.10)	—	135	75
(4)	$[NBu_4]_2[$*trans*-$Pt(C_6F_5)_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}]$	40.70 (40.90)	3.50 (3.40)	0.85 (1.10)	—	165	87

* Calculated values in parentheses.

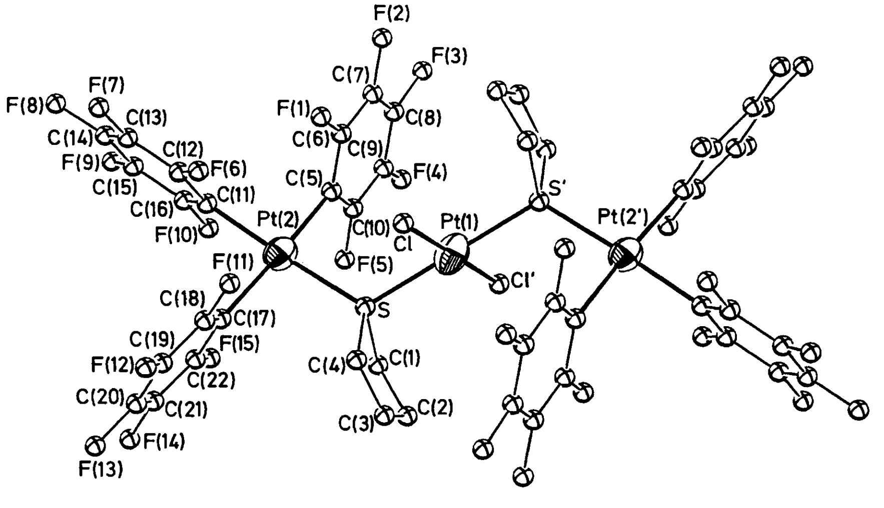

Figure. ORTEP drawing of the anion $[$*trans*-$PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]^{2-}$. All non-metallic atoms are represented by arbitrarily small circles for clarity

complexes we have two pairs of potentially bridging ligands, *i.e.* the halide ions and the neutral SC_4H_8 ligands. Whilst halide-bridged complexes are numerous, SC_4H_8-bridged complexes are scarce and none has hitherto been reported for platinum. Moreover, most of the reported complexes $[Fe_3(CO)_8(SC_4H_8)_2]$,[8] $[Ta_2Cl_6(SC_4H_8)_3]$,[9] $[Ta_2Br_6(SC_4H_8)_3]$,[10] and $[Mn_2(CO)_8(SC_4H_8)]$[11] also have other bridging ligands and/or metal–metal bonds and only the silver complex $[Ag(SC_4H_8)_2]BF_4$[12] contains chains of silver atoms singly bridged by SC_4H_8 along with another SC_4H_8 molecule linked to each silver atom as a terminal ligand.

When acetone solutions of $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and *trans*-$[PtX_2(SC_4H_8)_2]$ (molar ratio 2:1) are evaporated to dryness the trinuclear derivatives $[NBu_4]_2[$*trans*-$PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ are obtained [equation (2)]. If the

$$\textit{trans-}[PtX_2(SC_4H_8)_2] + 2\,NBu_4[Pt(C_6F_5)_3(OCMe_2)] \longrightarrow [NBu_4]_2[\textit{trans-}PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2] + 2\,OCMe_2 \quad (2)$$

$$X = Cl\ (\mathbf{1}),\ Br\ (\mathbf{2}),\ \text{or}\ I\ (\mathbf{3})$$

reaction is carried out in a 1:1 molar ratio the same trinuclear complexes are obtained, albeit mixed with unreacted *trans*-$[PtX_2(SC_4H_8)_2]$. On the other hand *trans*-$[Pt(C_6F_5)_2(SC_4H_8)_2]$ reacts with $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ yielding the trinuclear $[NBu_4]_2[$*trans*-$Pt(C_6F_5)_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ (**4**). Analytical data and melting points for complexes (**1**)—(**4**) are collected in Table 1. Acetone solutions of these complexes are highly conducting but their ^1H n.m.r. spectra in $(CD_3)_2CO$, for the SC_4H_8 signals, coincide with the spectra of *trans*-$[PtX_2(SC_4H_8)_2]$ indicating the existence of an equilibrium (2) which is totally displaced to the left in the presence of the solvent. Thus the latter must be totally eliminated (evaporating to dryness) in order to displace the equilibrium to the right.

(*c*) *Structure of* $[NBu_4]_2[$*trans*-$PtCl_2\{(SC_4H_8)Pt(C_6F_5)_3\}_2]$ (**1**).—To establish the structure of complex (**1**) by *X*-ray diffraction, single crystals were grown (at −25 °C) by slow diffusion (*ca.* 2 weeks) of n-hexane into a CH_2Cl_2 solution of the complex. Table 2 lists atomic co-ordinates. The compound consists of discrete trinuclear anions and NBu_4^+ cations in a 1:2 ratio.

The structure of the $[$*trans*-$PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]^{2-}$ anion is showed in the Figure. Selected bond distances and angles are collected in Table 3. The central platinum atoms sits on a crystallographic centre of symmetry.

The central platinum atom [Pt(1)] is bonded to two terminal chlorine atoms and two bridging SC_4H_8 ligands in a *trans*-square-planar environment as in the starting material *trans*-$[PtCl_2(SC_4H_8)_2]$. The Pt(1)–Cl distance is 2.285(5) Å and Pt(1)–S is 2.295(5) Å. The Pt(1)–Cl distances are in the usual

Table 2. Fractional atomic co-ordinates (× 10^4) and estimated standard deviations for $[\mathrm{NBu_4}]_2[\mathit{trans}\text{-}\mathrm{PtCl_2}\{(\mu\text{-}\mathrm{SC_4H_8})\mathrm{Pt}(\mathrm{C_6F_5})_3\}_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	0(0)	10 000(0)	0(0)	C(10)	1 896(12)	7 277(10)	290(8)
Pt(2)	−82(1)	7 920(1)	2 124(1)	C(11)	−439(10)	6 406(8)	2 719(8)
S	222(4)	9 643(4)	1 427(3)	C(12)	−1 612(10)	6 108(8)	3 122(8)
Cl(1)	1 960(4)	10 232(6)	−905(4)	C(13)	−1 915(10)	5 079(8)	3 555(8)
F(1)	−1 141(10)	6 795(11)	794(9)	C(14)	−1 044(10)	4 347(8)	3 585(8)
F(2)	−80(12)	5 866(11)	−928(9)	C(15)	129(10)	4 645(8)	3 182(8)
F(3)	2 310(15)	5 832(13)	−1 864(9)	C(16)	432(10)	5 674(8)	2 749(8)
F(4)	3 611(12)	6 703(13)	−1 058(11)	C(17)	−653(10)	8 421(9)	3 538(7)
F(5)	2 593(9)	7 665(11)	626(9)	C(18)	−1 817(10)	8 743(9)	4 058(7)
F(6)	−2 467(8)	6 700(9)	3 111(9)	C(19)	−2 183(10)	9 023(9)	5 013(7)
F(7)	−3 018(9)	4 733(10)	3 961(10)	C(20)	−1 386(10)	8 981(9)	5 449(7)
F(8)	−1 341(12)	3 347(9)	4 014(12)	C(21)	−222(10)	8 659(9)	4 928(7)
F(9)	929(12)	3 918(11)	3 206(14)	C(22)	145(10)	8 379(9)	3 973(7)
F(10)	1 541(9)	5 919(9)	2 371(10)	C(23)	4 166(16)	8 308(16)	2 330(13)
F(11)	−2 640(8)	8 852(9)	3 681(8)	C(24)	4 934(20)	9 278(19)	2 067(16)
F(12)	−3 280(10)	9 365(11)	5 527(9)	C(25)	4 364(24)	10 166(24)	1 633(20)
F(13)	−1 718(12)	9 253(11)	6 375(8)	C(26)	5 014(32)	11 166(32)	1 408(26)
F(14)	525(12)	8 619(11)	5 341(9)	C(27)	5 873(16)	6 931(16)	1 801(14)
F(15)	1 215(9)	8 087(10)	3 499(9)	C(28)	5 626(22)	6 613(21)	897(18)
N	4 705(12)	7 282(11)	2 658(10)	C(29)	6 733(22)	6 230(21)	163(19)
C(1)	1 620(17)	10 113(16)	1 353(16)	C(30)	6 606(24)	5 911(23)	−739(20)
C(2)	1 366(35)	11 341(24)	1 488(22)	C(31)	5 076(15)	7 495(14)	3 493(12)
C(3)	105(47)	11 551(32)	2 107(34)	C(32)	4 035(16)	7 829(15)	4 422(14)
C(4)	−683(26)	10 708(17)	2 211(16)	C(33)	4 542(22)	7 995(21)	5 174(19)
C(5)	674(12)	7 279(10)	764(8)	C(34)	3 568(22)	8 303(20)	6 174(18)
C(6)	8(12)	6 804(10)	355(8)	C(35)	3 736(17)	6 417(16)	2 972(14)
C(7)	564(12)	6 328(10)	−529(8)	C(36)	4 154(21)	5 353(20)	3 329(17)
C(8)	1 786(12)	6 326(10)	−1 003(8)	C(37)	3 063(28)	4 643(28)	3 588(23)
C(9)	2 452(12)	6 800(10)	−594(8)	C(38)	3 436(34)	3 571(35)	3 841(30)

Table 3. Bond distances (Å) and angles (°) and their estimated standard deviations for $[\mathrm{NBu_4}]_2[\mathit{trans}\text{-}\mathrm{PtCl_2}\{(\mu\text{-}\mathrm{SC_4H_8})\mathrm{Pt}(\mathrm{C_6F_5})_3\}_2]$

S–Pt(1)	2.295(5)	C(22)–F(15)	1.280(14)	Cl(1)–Pt(1)	2.285(5)	C(23)–N	1.558(22)
S–Pt(2)	2.303(4)	C(27)–N	1.574(21)	C(5)–Pt(2)	2.089(10)	C(31)–N	1.555(20)
C(11)–Pt(2)	2.023(9)	C(35)–N	1.562(23)	C(17)–Pt(2)	2.097(9)	C(2)–C(1)	1.562(36)
C(1)–S	1.825(17)	C(3)–C(2)	1.488(46)	C(4)–S	1.856(21)	C(4)–C(3)	1.433(48)
C(6)–F(1)	1.312(17)	C(24)–C(23)	1.509(28)	C(7)–F(2)	1.354(18)	C(25)–C(24)	1.535(32)
C(8)–F(3)	1.377(15)	C(26)–C(25)	1.465(41)	C(9)–F(4)	1.329(18)	C(28)–C(27)	1.600(28)
C(10)–F(5)	1.300(18)	C(29)–C(28)	1.461(30)	C(12)–F(6)	1.270(14)	C(30)–C(29)	1.519(32)
C(13)–F(7)	1.338(15)	C(32)–C(31)	1.545(23)	C(14)–F(8)	1.359(13)	C(33)–C(32)	1.540(29)
C(15)–F(9)	1.322(16)	C(34)–C(33)	1.567(31)	C(16)–F(10)	1.306(15)	C(36)–C(35)	1.542(28)
C(18)–F(11)	1.358(15)	C(37)–C(36)	1.558(36)	C(19)–F(12)	1.334(15)	C(38)–C(37)	1.468(44)
C(20)–F(13)	1.357(13)			C(21)–F(14)	1.313(16)		

Cl(1)–Pt(1)–S	94.2(2)	C(16)–C(11)–Pt(2)	122.7(3)	C(5)–Pt(2)–S	91.1(4)	C(13)–C(12)–F(6)	114.8(6)
C(11)–Pt(2)–S	176.5(3)	C(11)–C(12)–F(6)	125.1(6)	C(11)–Pt(2)–C(5)	88.3(5)	C(12)–C(13)–F(7)	123.7(7)
C(17)–Pt(2)–S	93.8(3)	C(14)–C(13)–F(7)	116.3(7)	C(17)–Pt(2)–C(5)	171.4(5)	C(14)–C(15)–F(9)	118.0(7)
C(17)–Pt(2)–C(11)	87.2(4)	C(13)–C(14)–F(8)	120.0(7)	Pt(2)–S–Pt(1)	118.4(2)	C(15)–C(16)–F(10)	118.2(7)
C(1)–S–Pt(1)	111.9(7)	C(16)–C(15)–F(9)	122.0(7)	C(1)–S–Pt(2)	109.7(6)	C(18)–C(17)–Pt(2)	121.3(3)
C(4)–S–Pt(1)	103.9(8)	C(11)–C(16)–F(10)	121.8(7)	C(4)–S–Pt(2)	115.4(7)	C(19)–C(18)–F(11)	115.9(5)
C(4)–S–C(1)	95.1(13)	C(22)–C(17)–Pt(2)	118.6(3)	C(27)–N–C(23)	109.8(13)	C(18)–C(19)–F(12)	121.9(7)
C(31)–N–C(23)	111.9(13)	C(17)–C(18)–F(11)	124.1(5)	C(31)–N–C(27)	105.1(12)	C(21)–C(20)–F(13)	118.8(8)
C(35)–N–C(23)	105.5(13)	C(20)–C(19)–F(12)	118.1(7)	C(35)–N–C(27)	112.7(13)	C(21)–C(22)–F(15)	119.7(7)
C(35)–N–C(31)	112.0(13)	C(19)–C(20)–F(13)	121.2(8)	C(2)–C(1)–S	102.3(17)	C(24)–C(23)–N	114.1(16)
C(3)–C(2)–C(1)	110.8(26)	C(22)–C(21)–F(14)	120.2(7)	C(4)–C(3)–C(2)	116.2(29)	C(26)–C(25)–C(24)	111.5(26)
C(3)–C(4)–S	106.1(24)	C(17)–C(22)–F(15)	120.3(7)	C(6)–C(5)–Pt(2)	122.4(4)	C(29)–C(28)–C(27)	108.0(20)
C(10)–C(5)–Pt(2)	117.5(4)	C(25)–C(24)–C(23)	107.6(19)	C(7)–C(6)–F(1)	119.3(7)	C(32)–C(31)–N	113.2(13)
C(5)–C(6)–F(1)	120.7(7)	C(28)–C(27)–N	111.3(15)	C(6)–C(7)–F(2)	120.2(7)	C(34)–C(33)–C(32)	112.4(20)
C(8)–C(7)–F(2)	119.8(7)	C(30)–C(29)–C(28)	112.7(22)	C(9)–C(8)–F(3)	121.4(10)	C(37)–C(36)–C(35)	101.1(21)
C(7)–C(8)–F(3)	118.6(10)	C(33)–C(32)–C(31)	106.8(16)	C(8)–C(9)–F(4)	116.3(9)	C(38)–C(37)–C(36)	104.6(28)
C(10)–C(9)–F(4)	123.6(9)	C(36)–C(35)–N	110.9(16)	C(9)–C(10)–F(5)	115.4(6)		
C(5)–C(10)–F(5)	124.6(6)			C(12)–C(11)–Pt(2)	117.3(3)		

range for $\mathrm{Pt^{II}}$–Cl (terminal).[13] The Cl–Pt(1)–S angle is 94.2(2)°. The terminal Pt(2) and Pt(2′) are located in identical square-planar environments formed by three C_6F_5 groups and a SC_4H_8 bridging ligand. The Pt–C distances of the C_6F_5 groups in mutually *trans* position are identical within the experimental error [2.089(10) and 2.097(9) Å], while the Pt–C distance corresponding to the C_6F_5 *trans* to the SC_4H_8 is shorter [2.023(9) Å]. Angles between Pt(2)–*cis* ligand bonds are in the range 87.2(4)—93.8(3)° and the angles C(11)–Pt(2)–S and C(17)–Pt(2)–C(5) are 176.5(3) and 171.4(5)° respectively. Atom

Table 4. Some relevant i.r. absorptions (cm^{-1})

Complex	X-sensitive[a]		Others	SC_4H_8	NBu_4
(**1**)[b]	802s, 788m, 774s	958vs	1 634w, 1 607w, 1 495vs, 1 056vs, 1 044s	1 278w, 1 255vw, 1 247w, 517w	885m
(**2**)	803s, 790m, 773s	958vs	1 634w, 1 606w, 1 495vs, 1 056vs, 1 045s	1 277w, 1 255vw, 1 247w, 516w	885m
(**3**)	803s, 790m, 773s	957vs	1 634w, 1 606w, 1 495vs, 1 055vs, 1 044s	1 277w, 1 255vw, 1 247w, 517w	884m
(**4**)	804s, 776s, 771s	959vs	1 633m, 1 605m, 1 498vs, 1 055vs	1 271m, 1 259w, 1 255m, 512w	884m

[a] E. Maslowsky, jun., 'Vibrational Spectra of Organometallic Compounds,' Wiley, New York, 1977, p. 437 and refs. therein. [b] ν(Pt–Cl) 345w cm^{-1}; *cf.* 346 cm^{-1} for *trans*-$[PtCl_2(SC_4H_8)_2]$.

Pt(1) is linked to Pt(2) and Pt(2′) by two single bridging SC_4H_8 ligands. The angle Pt(2)–S–Pt(1) is 118.4(2)° similar to the Ag–S–Ag angle [126.59(7)°] found in $[Ag(SC_4H_8)_2]BF_4$.[12] Smaller M–S–M angles have been found in other complexes containing bridging SC_4H_8 or SR_2 groups, *e.g.* $[Ta_2Cl_6(SMe_2)_3]$ [68.9(2)],[9] $[Pt_2Br_4(SEt_2)_2]$ [98.1(5)],[14] and $[Fe_3(CO)_8(SC_4H_8)_2]$ (73.8)[8] although in these complexes there are metal–metal bonds and/or other bridging ligands.

The co-ordination planes around Pt(2) and Pt(1) form an angle of 93.05(25)°.

The Pt–S distances are the same within the experimental error [Pt(1)–S 2.295(5), Pt(2)–S 2.303(4) Å] and slightly longer than analogous distances found in $[\{PtBr_2(\mu\text{-}SEt_2)\}_2]$ [2.21(1) and 2.25(1) Å].[14] It should be noted that these Pt–S bridging distances are slightly shorter than the Pt–S terminal one found in $[(C_6F_5)_3(SC_4H_8)PtAg(PPh_3)]$ [Pt–S 2.328(3) Å][15] which can be considered unusual (for instance the reverse is the case with bridging and terminal halide ligands) but not unique, since shorter bridging than terminal M–S distances have also been reported in other cases: $[\{PtBr_2(\mu\text{-}SEt_2)\}_2]$, and $[Pd(\mu\text{-}Br)Br(SMe_2)]_2$,[14] $[Ta_2Cl_6(SC_4H_8)_3]$ and $[Ta_2Cl_6(SMe_2)_3]$,[9] $[Ta_2Br_6(SC_4H_8)_3]$,[10] $[Mn_2(CO)_9(SC_4H_8)]$, and $[Mn_2(CO)_8(SC_4H_8)]$.[11]

(*d*) *I.r. and N.M.R. Spectra.*—Table 4 collects some relevant i.r. absorptions. Although complex (**4**) should present four absorptions due to the X-sensitive modes of the C_6F_5 groups [three for C_6F_5 groups bonded to the terminal platinum atoms and one for the C_6F_5 (*trans*) bonded to the central platinum atom], only three strong absorptions are observed in our i.r. spectrum. Probably one of the absorptions due to the C_6F_5 bonded to the terminal platinum atoms which appear for complexes (**1**)—(**3**) as a medium-intensity band at 788—790 cm^{-1} is overlapped with that due to the C_6F_5 group bonded to the central platinum atom. The three absorptions of (**4**) are strong, while complexes (**1**)—(**3**) show two strong and one medium absorption in this region. In the region 1 300—1 250 cm^{-1} absorptions due to the SC_4H_8 are present. The mononuclear derivatives *trans*-$[PtX_2(SC_4H_8)_2]$ show in this region a very similar pattern of two strong and very close absorptions, located at 1 269 and 1 253 cm^{-1}, while the trinuclear complexes also show two absorptions although more separated and of medium intensity (see Table 4). These data suggest that complexes (**1**)—(**4**) have the same structure with bridging SC_4H_8 ligands. Their very low solubility in $CDCl_3$ prevents ^1H n.m.r. studies in this solvent. The ^{19}F n.m.r. spectrum of (**4**) in $CDCl_3$–CH_2Cl_2 shows a very complicated pattern due to the presence in the complex of many inequivalent C_6F_5 groups; since no signals appear in the region corresponding to bridging C_6F_5 groups,[7] the complex only contains terminal ones.

(*e*) *Reactivity of the Trinuclear Complexes* (**1**)—(**3**).—If a weak donor such as acetone causes splitting of the bridge system in the trinuclear complexes, it is expected that stronger ligands will also destroy the polynuclear structure. This expectation was fulfilled in all the cases studied, but two extreme behaviours have been observed: (*i*) splitting of the Pt(central)–SC_4H_8 bonds with simultaneous isomerisation and, (*ii*) splitting of the Pt(terminal)-SC_4H_8 bonds. The former behaviour is illustrated by the reaction (3) (X = Cl or I) with PPh_3 in CH_2Cl_2, the latter by the reaction (4) with CO. As may be seen, PPh_3 acts upon the

$$[NBu_4]_2[PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2] + 2\ PPh_3 \longrightarrow \\ cis\text{-}[PtX_2(PPh_3)_2] + 2\ NBu_4[Pt(C_6F_5)_3(SC_4H_8)] \quad (3)$$

$$[NBu_4]_2[PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2] + 2CO \longrightarrow \\ trans\text{-}[PtCl_2(SC_4H_8)_2] + 2\ NBu_4[Pt(C_6F_5)_3(CO)] \quad (4)$$

central platinum atom which is the less electron-rich metal centre, since it is bonded to only two anionic σ-donor ligands whilst CO attacks the terminal platinum atoms, which being bonded to three anionic σ-donor ligands are electron-richer metal centres. Probably the poorer σ-donor and the better π-acceptor abilities of the CO ligand are responsible for its different behaviour. The carbonyl and phosphine complexes have previously been described.[7,16]

(*f*) *Attempts to prepare Halide-bridged Trinuclear Complexes.*—We have discussed above (*b*) that the reaction between $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and *trans*-$[PtX_2(SC_4H_8)_2]$, containing two pairs of potentially bridging ligands, could give S-bridged or X-bridged polynuclear derivatives. Since the former, and rarer, possibility has been demonstrated, it was tempting to see whether the second one could be verified by using a similar reagent containing neutral ligands with donor atoms unable to act as a bridge, *e.g.* *trans*-$[PtX_2(py)_2]$ (py = pyridine) or $[PtBr_2(cod)]$ thereby forcing the halide ligands to act as a bridging ligand. Surprisingly, under similar conditions (stirring, for 1 h, room temperature) as above [equation (2)] no reaction occurred between $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and *trans*-$[PtCl_2(py)_2]$ and upon evaporation of the solutions unreacted starting materials were recovered. By substituting *trans*-$[PtI_2(py)_2]$ for the dichloro derivative reaction (5) takes place but the

$$2\ NBu_4[Pt(C_6F_5)_3(OCMe_2)] + trans\text{-}[PtI_2(py)_2] \longrightarrow \\ cis\text{-}[Pt(C_6F_5)_2(py)_2] + [NBu_4]_2[Pt_2(\mu\text{-}I)_2(C_6F_5)_4] \quad (5)$$

isolated products are the result of ligand rearrangement. An analogous rearrangement has been observed in the reaction between $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and $[PtBr_2(cod)]$ which yields $[NBu_4]_2[Pt_2(\mu\text{-}Br)_2(C_6F_5)_4]$ and $[Pt(C_6F_5)_2(cod)]$.

Experimental

The C, H, and N analyses were carried out with a Perkin-Elmer 240-B micronanalyzer. Chlorine and bromine analyses were made as described by White,[17] a few milligrams of sucrose being added to facilitate combustion.[18] I.r. spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates). Molar conductivities were determined in 5×10^{-4} mol dm^{-3} acetone solutions. Proton n.m.r. spectra were recorded on a Varian XL 200 spectrometer (200 MHz for ^1H) in $(CD_3)_2CO$ or $CDCl_3$–CH_2Cl_2.

Literature methods were used to prepare *trans*-$[PtCl_2(SC_4H_8)_2]$,[16] *trans*-$[PtCl_2(py)_2]$,[19] and $[NBu_4]_2[PtCl(C_6F_5)_3]$.[20]

trans-$[PtI_2(SC_4H_8)_2]$.—To a suspension of PtI_2[21] (0.2 g, 4.45×10^{-4} mol) in CH_2Cl_2 (25 cm^3), SC_4H_8 (78.55 µl, 8.9×10^{-4} mol) was added and the mixture was stirred at room temperature for 24 h. After filtration, the resulting solution was evaporated to dryness and the orange residue was washed with n-hexane. Yield 95%.

trans-$[PtI_2(py)_2]$.—To PtI_2 (0.3 g, 6.7×10^{-4} mol) suspended in CH_2Cl_2 (30 cm^3), py (106 µl, 13.36×10^{-4} mol) was added and the mixture was stirred at room temperature for 5 h. After filtration, the resulting yellow-orange solution was evaporated to dryness and the residue was treated with Pr^{i}OH (10 cm^3) yielding a yellow solid, which consisted of a mixture of *cis*- and *trans*-$[PtI_2(py)_2]$. This was dissolved in acetone (*ca.* 3 cm^3) and water (*ca.* 30 cm^3) and py (0.5 cm^3) were added. After refluxing for 3 h, the yellow precipitate formed, *trans*-$[PtI_2(py)_2]$, was filtered off and washed with Pr^{i}OH. Yield 72%.

trans-$[PtBr_2(SC_4H_8)_2]$.—To a CH_2Cl_2 (25 cm^3) solution of *trans*-$[PtI_2(SC_4H_8)_2]$ (0.5 g, 7.99×10^{-4} mol), AgBr (0.30 g, 1.59×10^{-3} mol) was added and the mixture, protected from the light, was stirred at room temperature for 48 h. After filtration, the solution obtained was evaporated to dryness and the residue was washed with Pr^{i}OH, yielding a yellow solid. Yield 93%.

$[NBu_4]_2$[*trans*-$PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2$] [X = Cl (**1**), Br (**2**), I (**3**), or C_6F_5 (**4**)].—A typical preparation was as follows. To a CH_2Cl_2–acetone (6:1) (35 cm^3) solution of $[NBu_4]_2[PtCl(C_6F_5)_3]$ (0.5 g, 4.11×10^{-4} mol), $AgClO_4$ (0.0852 g, 4.11×10^{-4} mol) was added and the mixture, protected from the light, was stirred for 30 min. To the resulting colourless solution, after filtration of the AgCl formed, *trans*-$[PtCl_2(SC_4H_8)_2]$ (0.0908 g, 2.05×10^{-4} mol) was added, the solution was stirred at room temperature for 1 h and then evaporated to dryness. The residue was washed with isopropyl alcohol yielding a pale yellow solid which was filtered off and washed with n-hexane.

Complexes (**2**)—(**4**) were prepared similarly, using the same amounts of $[NBu_4]_2[PtCl(C_6F_5)_3]$ and $AgClO_4$ as for (**1**), and *trans*-$[PtBr_2(SC_4H_8)_2]$ (0.1089 g, 2.05×10^{-4} mol) for (**2**), *trans*-$[PtI_2(SC_4H_8)_2]$ (0.1281 g, 2.05×10^{-4} mol) for (**3**), and *trans*-$[Pt(C_6F_5)_2(SC_4H_8)_2]$ (0.145 g, 2.05×10^{-4} mol) for (**4**). Yields are reported in Table 1.

Reaction of $[NBu_4]_2[Pt(C_6F_5)_3(OCMe_2)]$ *with trans*-$[PtX_2(py)_2]$ (X = Cl or I) *or* $[PtBr_2(cod)]$.—To a CH_2Cl_2–acetone (2:1) solution (30 cm^3) of $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ (0.2055 mmol), *trans*-$[PtCl_2(py)_2]$ (0.0436 g, 0.1028 mmol) was added and the mixture was stirred for 1 h. The resulting solution was evaporated to dryness and the pale yellow residue washed with isopropyl alcohol. By washing this residue with diethyl ether, a white residue, identified as a mixture of *trans*-$[PtCl_2(py)_2]$ and NBu_4ClO_4, and a yellow solution were obtained. When the yellow solution was evaporated to dryness and treated with Pr^{i}OH–hexane, $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[7] (yield 58%) was obtained.

The reaction between $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ and *trans*-$[PtI_2(py)_2]$ under similar conditions renders a mixture of *trans*-$[Pt(C_6F_5)_2(py)_2]$[22] and $[NBu_4]_2[Pt_2(\mu\text{-}I)_2(C_6F_5)_4]$[16] which was separated with MeOH in which the neutral complex is insoluble and the anionic one is soluble.

The complex $NBu_4[Pt(C_6F_5)_3(OCMe_2)]$ reacted with $[PtBr_2(cod)]$ under similar conditions yielding a mixture of $[Pt(C_6F_5)_2(cod)]$ and $NBu_4[Pt_2(\mu\text{-}Br)_2(C_6F_5)_4]$[16] which was separated with MeOH.

Reaction of $[NBu_4]_2$[*trans*-$PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2$] (X = Cl *or* I) *with* PPh_3.—To a CH_2Cl_2 solution of complex (**1**) (0.15 g, 6.46×10^{-5} mol), PPh_3 (0.034 g, 1.129×10^{-4} mol) was added; the solution was stirred at room temperature for 1 h and then evaporated to dryness. The residue was treated with Et_2O (15 cm^3) and the resulting white solid was treated with MeOH (10 cm^3) to give a white residue of *cis*-$[PtCl_2(PPh_3)_2]$ (identified by C and H analyses and its i.r. spectrum) and a colourless solution. From the solution $NBu_4[Pt(C_6F_5)_3(SC_4H_8)]$[16] was obtained by evaporating almost to dryness.

When $[NBu_4]_2$[*trans*-$PtI_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2$] (**3**)[16] was used, under similar conditions, *cis*-$[PtI_2(PPh_3)_2]$ and $NBu_4[Pt(C_6F_5)_3(SC_4H_8)]$ were obtained.

Reaction of $[NBu_4]_2$[*trans*-$PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2$] *with* CO.—Through a CH_2Cl_2 (25 cm^3) solution of complex (**1**) (0.15 g), CO was bubbled for 15 min and the resulting solution was evaporated to dryness. The residue was treated with diethyl ether, yielding a pale yellow solid identified as *trans*-$[PtCl_2(SC_4H_8)_2]$. The ether solution was evaporated to dryness and the resulting solid was treated with MeOH. The insoluble residue was identified as *trans*-$[PtCl_2(SC_4H_8)_2]$ and the MeOH solution was evaporated to dryness yielding $NBu_4[Pt(C_6F_5)_3(CO)]$[7] (yield 72%).

X-Ray Structure Analysis.—Crystal data. $C_{76}H_{88}Cl_2F_{30}N_2Pt_3S_2$, $M = 2\,319.8$, triclinic, $a = 12.463(3)$, $b = 12.487(3)$, $c = 15.137(3)$ Å, $\alpha = 85.68(15)$, $\beta = 66.04(2)$, $\gamma = 87.04(1)°$, $U = 2\,146$ Å^3 (by refinement of 2θ values for 70 reflections including Friedel pairs, in the range 25—36°), space group $P\bar{1}$, $Z = 1$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,112$, size $0.25 \times 0.04 \times 0.3$ mm, $\mu(\text{Mo-}K_\alpha) = 48.7$ cm^{-1}.

Data collection and processing. Siemens/Stoe AED2 four-circle diffractometer, monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å), scan range $4 \leqslant 2\theta \leqslant 45°$. Index range: two sets ($\pm h$, $\pm k$, $+l$; $\pm h$, $\pm k$, $-l$), total number of reflections 11 210, unique reflections 5 315, 3 069 with $F_0 \geqslant 5\sigma(F_0)$ used for all calculations. Scan method ω—2θ. Room temperature. Three check reflections were measured every 45 min. They showed an average loss of intensity of 19% during the data collection. An interpolative decay correction was applied. Absorption correction (6ψ scans, with transmission factors 0.249—0.565).

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.048, R' 0.048. All atoms of the anionic part of the compound were treated as anisotropic, the remaining atoms as isotropic. Phenyl rings were regarded as idealised rigid groups with C–C 1.395 Å. Weighting scheme $w = K/[\sigma^2(F_0) + gF_0^2]$ *with* $K = 1.1996$ and $g = 0.0017$. Maximum shift/error 0.011; highest peak in difference map 0.8 e Å^{-3}; 399 parameters. Program system SHELX 76.[23]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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