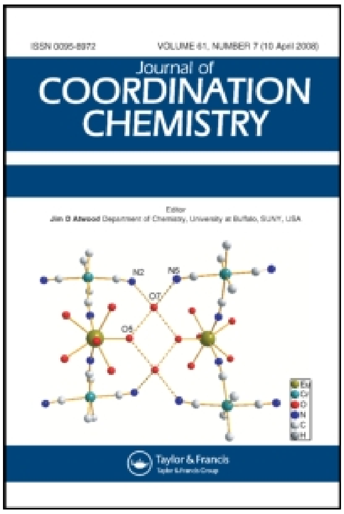

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Binuclear platinum(II) complexes of the type $[Pt_2(ER)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ ($ER = SPr^i$, SBu^t, SPh, $SC_6H_4Cl\text{-}4$, SC_6F_5, SePh) have been prepared and characterized by elemental analysis and NMR spectroscopy. A single-crystal X-ray structure determination of $[Pt_2(SC_6F_5)_4\text{-}(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ has established the binuclear formulation with terminal thiolato groups. The platinum atoms lie in a distorted square planar environment with the sulfur and the phosphine ligands arranged in a *cis* fashion.

Keywords: Platinum; synthesis; NMR; X-ray structure

INTRODUCTION

There is a growing interest in the chemistry of bi- and high-nuclearity platinum group metal complexes which are stabilized through suitable bridging ligands.[1,2] Organochalcogenide anion (RE^-) is a fundamental ligand type which has been extensively used to bridge two metal centers.[3,4] Of late,

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[*] Corresponding author.

mononuclear *cis* complexes, *cis*-$ML_2(SR)_2$, with terminal organochalcogenide groups have proved to be useful precursors for the stepwise synthesis of bi- and polynuclear complexes.[5–10] However, examples of binuclear platinum group metal complexes with terminal organochalcogenide groups are rare.[4] These complexes may be used as synthons for the formation of high nuclearity complexes. As part of our studies on platinum complexes with organochalcogenide ligands, we now report the synthesis of bi-nuclear platinum complexes with terminal organochalcogenide groups.

EXPERIMENTAL

$[Pt_2Cl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$[11] and $Pb(ER)_2$[12] were prepared by published methods. ^1H and ^{31}P NMR (Table I) spectra were recorded on a Varian XLR-300 spectrometer. Chemical shifts are relative to the internal chloroform peak ($\delta = 7.26$) for ^1H and external 85% H_3PO_4 for ^{31}P. Elemental analyses were performed by the Analytical Chemistry Division of this research center.

TABLE I ^1H and $^{31}P\{^1H\}$ NMR data for $[Pt_2(ER)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ in $CDCl_3$

Complex	$^{31}P\{^1H\}$ *NMR data*		^1H *NMR data*
	δ	[$J(Pt\text{–}P)$ *in* Hz]	
$[Pt_2(SPr^i)_4(\mu\text{-}Ph_2C{\equiv}CPPh_2)_2]$	−2.3	[2794]	1.17 (d, 6.8 Hz, $SCMe_2$); 3.83 (m, SCH–); 7.17–7.23 (m), 7.35–7.40 (m), 7.50–7.57 (m) [Ph]
$[Pt_2(SBu^t)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	−8.8	[2773]	1.24 (s, SBu^t); 7.16–7.22 (m), 7.35–7.39 (m), 7.45–7.52 (m) [Ph]
$[Pt_2(SPh)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	−4.6	[2893]	6.76–6.88 (m), 7.10–7.16 (m), 7.23–7.35 (m), 7.48–7.54 (m) [Ph]
$[Pt_2(SC_6H_4Cl\text{-}4)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	−4.6	[2903]	6.74 (d), 7.06 (d) (each 8 Hz, SC_6H_4); 7.15–7.52 (m) [Ph]
$[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$[a]	−5.1	[3020]	7.24–7.28 (m), 7.43–7.56 (m) [Ph]
$[Pt_2(SePh)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	−8.3	[2925]	6.77 (t), 6.91(t), 7.10–7.13 (m), 7.27–7.54 (m), 7.46–7.53 (m) [Ph]

[a] ^{19}F NMR data: $\delta = -138.1$ (d, d; 6, 26 Hz, *m*-F); −165.4 (t, 21 Hz, *p*-F); −169.0 (m, *o*-F) (chemical shifts are relative to external trifluoroacetic acid).

Preparation of $[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$

To an acetone (15 cm^3) suspension of $[Pt_2Cl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ (94 mg, 0.07 mmol) was added an acetone (5 cm^3) solution of $Pb(SC_6F_5)_2$ (92 mg, 0.15 mmol) with vigorous stirring. After 3 h stirring at room temperature, the solvent was stripped off *in vacuo* and the residue extracted with dichloromethane (5 × 3 cm^3) and filtered. The filtrate was concentrated to 3 cm^3 *in vacuo* and then layered with hexane (5 cm^3). Slow evaporation of the resulting solution afforded bright yellow crystals of the title complex in 52% (72 mg) yield. The other complexes were prepared in a similar manner. Pertinent data are summarized in Table II.

Crystallography

All measurements were made at 20 ± 2°C on a Rigaku AFC6S diffractometer using graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal data and data collection details are given in Table III. Data were corrected for Lorentz and polarization effects. Semi-empirical absorption correction was based on Ψ scans of several reflections (maximum and minimum transmission factors: 0.760 and 0.235 respectively). The structure was solved by a combination of Patterson and direct methods[13] and refined by full-matrix least-squares techniques with non-hydrogen atoms refined anisotropically. The maximum and minimum excursions in the final difference Fourier map were 3.026 and -1.826 eÅ^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and

TABLE II Physical and analytical data for $[Pt_2(ER)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ complexes

Complex	*Recry. solvent (% Yield)*	*m.p.* (°C)	*Analysis* (%)[a]	
			C	*H*
$[Pt_2(SPr^i)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	Acetone–hexane (60)	128–130[b]	51.5 (51.9)	4.3 (4.6)
$[Pt_2(SBu^t)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	CH_2Cl_2–MeOH–hexane (64)	157–160[b]	52.9 (53.2)	4.7 (5.0)
$[Pt_2(SPh)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	CH_2Cl_2–hexane (63)	188–190[b]	56.1 (56.5)	3.2 (3.7)
$[Pt_2(SC_6H_4Cl\text{-}4)_4(\mu\text{-}PPh_2C{\equiv}CPPh_2)_2]$	CH_2Cl_2–hexane (62)	203–205[b]	51.9 (52.1)	3.1 (3.2)
$[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	CH_2Cl_2–hexane (52)	220–223[b]	46.3 (46.2)	1.8 (2.0)
$[Pt_2(SePh)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$	CH_2Cl_2–hexane (67)	172–175[b]	50.5 (50.6)	3.6 (3.3)

[a] Required values are given in parentheses. [b] Melts with decomposition.

TABLE III Crystal data and data collection parameters for $[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$

Formula	$C_{76}H_{40}F_{20}P_4S_4Pt_2$
M	1975.4
Temperature (K)	293(2)
Crystal size (mm)	0.41 × 0.38 × 0.27
Symmetry, space group	Monoclinic, $C2/c$
a/Å	12.688(5)
b/Å	19.584(9)
c/Å	32.476(12)
β/°	90.17
Volume/Å^3	8070(6)
Z	4
D_c/g cm^{-3}	1.626
Absorption coefficient/mm^{-1}	3.732
F(000)	3834
Radiation (λ/Å)	0.71073
θ range of data collection/°	2.01–30.00
No. of data collected	12224
No. of independent reflections	11761 ($R_{int} = 0.0824$)
Data/restraints/parameters	11258/0/476
Max. and min. transmission	0.760 and 0.235
Refinement method	Full-matrix least-squares on F^2
Absorption correction	Semi-empirical from φ scans.
Goodness-of-fit on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.068$, $\omega R_2 = 0.125$
R indices (all data)	$R_1 = 0.187$, $\omega R_2 = 0.34$

Waber.[14] Anomalous dispersion effects were included in F_{calc}.[15] The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[16] All calculations were performed using the TEXSAN[17] crystallographic software package of the Molecular Structure Corporation. An ORTEP[18] plot of the molecule with numbering scheme is shown in Figure 1.

RESULTS AND DISCUSSION

Treatment of $[Pt_2Cl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ with $Pb(ER)_2$ in acetone readily gave bis(diphenylphosphino)acetylene-bridged binuclear complexes, $[Pt_2(ER)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ as golden yellow or orange crystalline solids according to (1).

$$Pt_2Cl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2 + 2Pb(ER)_2 \rightarrow [Pt_2(ER)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2] + 2PbCl_2 \qquad (1)$$

$(ER = SPr^i, SBu^t, SPh, SC_6H_4Cl\text{-}4, SC_6F_5, SePh)$

^1H NMR spectra of the complexes showed the expected integration and peak multiplicities. ^{31}P NMR resonances are deshielded as compared to the

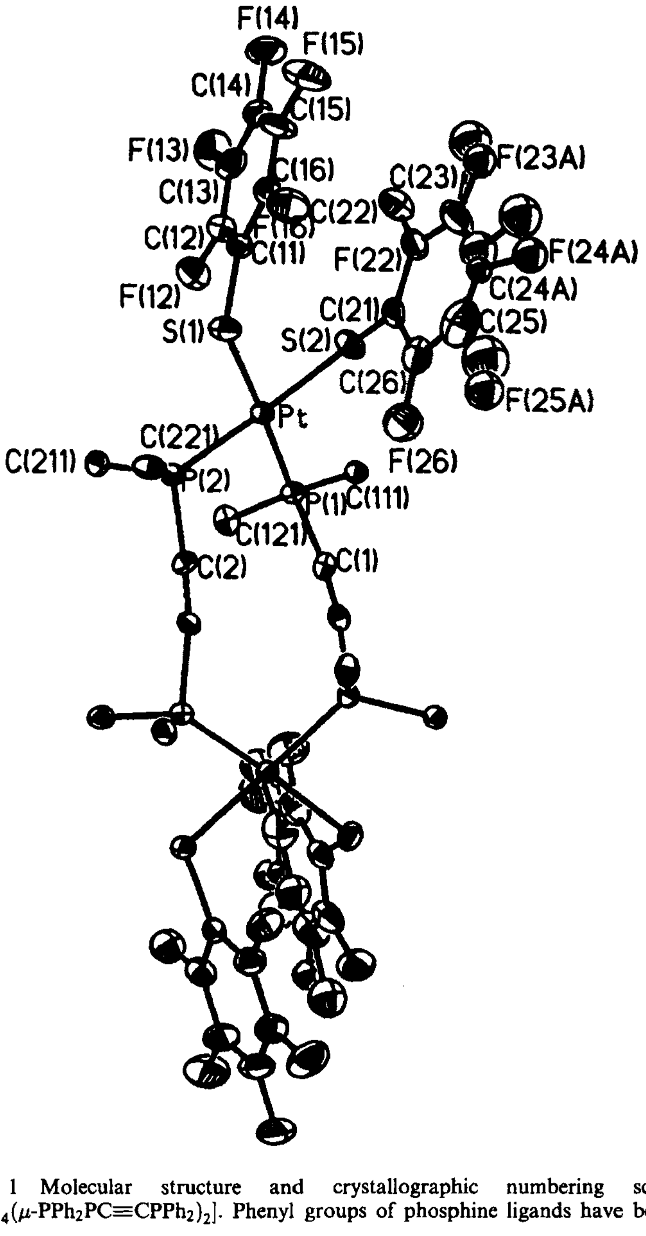

FIGURE 1 Molecular structure and crystallographic numbering scheme for [$Pt_2(SC_6F_5)_4(\mu\text{-}PPh_2PC{\equiv}CPPh_2)_2$]. Phenyl groups of phosphine ligands have been omitted for clarity.

chloro complex $[Pt_2Cl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ ($\delta = -10.9$ ppm, ^1J(Pt–P) = 3668 Hz). The magnitude of ^1J(Pt–P) is reduced significantly, indicating the strong *trans* influence of the ER group *trans* to the phosphine. The magnitude of ^1J(Pt–P) is sensitive to the nature of the R group attached to the chalcogen atom. ^1J(Pt–P) increased in the following order of R substituent: $SBu^t < SPr^i < SPh < SC_6H_4Cl\text{-}4 < SePh < SC_6F_5$. This trend may be explained on the basis of the inductive effect of the R group on the chalcogen atom. Electron withdrawal by the fluorines in the perfluorophenyl group causes weaker Pt–S interactions and consequently strengthens the Pt–P bonds. In the case of SBu^t, the electron release from the methyl groups results in an increase in the electron density at the platinum atom leading to a weaker Pt–P bond.

The molecular structure of $[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ (Figure 1) shows that the platinum atoms lie in a distorted square planar environment with the phosphorus and the sulfur atoms in a *cis* configuration. The Pt–P,[5,9,21] Pt–S,[22] P–C (P–Ph and P–C≡C),[5,19,23] S–C[24] and C≡C[23] bond lengths are in good agreement with those reported earlier. Although the Pt–P distance is in accord with the reported values, it is slightly longer than that in the chloro complex, $[PdPtCl_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$.[23] The lengthening of the Pt–P distance may be attributed to the strong *trans* influence of the SC_6F_5 group. Selected bond lengths and angles are given in Table IV; atomic positions are listed in Table V.

TABLE IV Selected bond distances (Å) and angles (°) for the complex $[Pt_2(SC_6F_5)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$

Pt–S(1)	2.352(3)	P(2)–C(2)	1.754(4)
Pt–S(2)	2.345(3)	P(2)–C(221)	1.809(13)
Pt–P(1)	2.279(3)	P(2)–C(211)	1.815(14)
Pt–P(2)	2.265(3)	C(1)–C(1) #1	1.20(2)
P(1)–C(1)	1.767(12)	C(2)–C(2) #1	1.19(2)
P(1)–C(121)	1.815(13)	S(1)–C(11)	1.753(13)
P(1)–C(111)	1.805(13)	S(2)–C(21)	1.75(2)
P(1)–Pt–P(2)	93.65(11)	C(221)–P(2)–Pt	116.4(5)
P(1)–Pt–S(1)	177.65(13)	C(1)–P(1)–C(111)	102.0(6)
P(1)–Pt–S(2)	89.66(12)	C(111)–P(1)–C(121)	104.2(6)
P(2)–Pt–S(1)	84.23(12)	C(1)–P(1)–C(121)	103.1(6)
P(2)–Pt–S(2)	176.24(12)	C(2)–P(2)–C(221)	95.9(6)
S(1)–Pt–S(2)	92.43(13)	C(221)–P(2)–C(211)	107.7(6)
C(11)–S(1)–Pt	110.3(4)	C(2)–P(2)–C(211)	103.3(6)
C(21)–S(2)–Pt	107.1(5)	C(1) #1–C(1)–P(1)	171.7(4)
C(1)–P(1)–Pt	113.0(4)	C(2) #1–C(2)–P(2)	170.9(10)
C(2)–P(2)–Pt	115.4(4)	C(16)–C(11)–S(1)	121.1(12)
C(121)–P(1)–Pt	114.3(5)	C(12)–C(11)–S(1)	123.8(11)
C(111)–P(1)–Pt	118.4(4)	C(22)–C(21)–S(2)	121(2)
C(211)–P(2)–Pt	115.7(4)	C(26)–C(21)–S(2)	122.4(12)

TABLE V Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for the complex. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Pt	6154(1)	1478(1)	1506(1)	32(1)
P(1)	4809(2)	857(2)	1780(1)	33(1)
S(1)	7500(3)	2160(2)	1227(1)	49(1)
C(1)	4945(9)	727(6)	2316(4)	36(3)
P(2)	5670(3)	2452(2)	1831(1)	35(1)
S(2)	6704(3)	514(2)	1136(1)	53(1)
C(2)	5137(9)	2345(6)	2324(3)	34(3)
C(11)	7782(11)	1902(6)	723(4)	43(3)
F(12)	5985(7)	1883(5)	512(3)	68(2)
C(12)	7018(13)	1800(8)	422(5)	57(4)
F(13)	6499(9)	1546(6)	−261(3)	99(4)
C(13)	7262(15)	1628(8)	24(5)	66(5)
F(14)	8526(10)	1405(6)	−483(3)	101(4)
C(14)	8278(17)	1562(9)	−93(5)	75(5)
F(15)	10076(9)	1595(7)	90(3)	112(4)
C(15)	9067(15)	1656(9)	192(6)	75(5)
F(16)	9589(7)	1919(5)	863(3)	78(3)
C(16)	8815(12)	1826(8)	589(5)	55(4)
C(21)	8068(12)	442(6)	1206(5)	54(4)
F(22)	8282(9)	209(5)	499(4)	95(4)
C(22)	8717(14)	282(8)	878(6)	72(5)
C(23)	9778(17)	156(9)	933(8)	94(7)
F(23A)	10535(26)	57(15)	721(11)	63(10)
C(24A)	10272(36)	252(23)	1393(16)	35(10)
F(24A)	11245(21)	58(13)	1508(11)	68(9)
F(25A)	9919(29)	370(18)	2104(12)	85(11)
F(23B)	10226(16)	−17(9)	518(7)	108(7)
C(24B)	10158(32)	160(21)	1237(14)	85(13)
F(24B)	11253(15)	56(9)	1255(8)	103(7)
F(25B)	10098(25)	349(16)	1943(11)	127(12)
C(25)	9629(21)	339(11)	1608(7)	103(7)
F(26)	7989(9)	589(6)	1928(3)	94(3)
C(26)	8541(14)	471(9)	1594(6)	68(5)
C(111)	4605(9)	−3(6)	1595(4)	36(3)
C(112)	3788(12)	−170(8)	1329(5)	60(4)
C(113)	3662(14)	−852(10)	1193(6)	79(6)
C(114)	4391(16)	−1339(9)	1306(6)	84(6)
C(115)	5189(14)	−1171(8)	1570(5)	69(5)
C(116)	5330(11)	−516(7)	1707(4)	49(3)
C(121)	3524(10)	1256(7)	1735(4)	46(3)
C(122)	3234(12)	1561(8)	1367(5)	62(4)
C(123)	2247(16)	1835(9)	1316(7)	85(6)
C(124)	1531(16)	1822(12)	1610(9)	105(8)
C(125)	1799(13)	1545(11)	1985(7)	91(7)
C(126)	2807(11)	1246(8)	2050(5)	56(4)
C(211)	4685(10)	2964(6)	1567(4)	41(3)
C(212)	4725(12)	3018(7)	1148(4)	52(4)
C(213)	3951(13)	3379(8)	945(5)	67(5)
C(214)	3161(13)	3694(8)	1154(5)	67(5)
C(215)	3131(13)	3648(8)	1571(5)	67(5)
C(216)	3882(11)	3284(7)	1780(5)	53(4)
C(221)	6726(10)	3017(7)	1988(4)	44(3)
C(222)	6576(15)	3733(8)	1980(5)	72(5)
C(223)	7352(19)	4140(11)	2151(6)	93(7)
C(224)	8192(20)	3892(12)	2327(6)	98(8)
C(225)	8351(13)	3204(11)	2346(5)	78(6)
C(226)	7593(13)	2759(9)	2167(4)	64(4)

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Supplementary Data

Full lists of H atom positions, bondlengths and angles, anisotropic temperature factors and observed and calculated structure factors are available from the authors upon request.

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