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Inorganica Chimica Acta 357 (2004) 2134-2142

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Thiolato-bridged "Linear" trinuclear platinum complexes $[Pt_3(\mu-SR)_4(dppm)_2]^{2+ r/2}$

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Received 25 November 2003; accepted 20 December 2003

Abstract

Thiolato-bridged tri- and dinuclear platinum complexes of the types $[Pt_3(\mu-SR)_4(dppm)_2]^{2+}$ (1) and $[Pt_2(\mu-ER)_2(dppm)_2]^{2+}$ (2) (E = S or Se; R = alkyl or aryl; dppm = bis(diphenylphosphino)methane) have been prepared using the mononuclear precursors $[Pt(ER)_2(dppm)]$. The complexes have been characterized by NMR (¹H, ¹³C, ³¹P, ¹⁹⁵Pt), FT-IR and FAB mass spectral data. The structure of $[Pt_3(\mu-SC_6H_4CH_3-4)_4(dppm)_2][CF_3SO_3]_2 \cdot 6CH_2Cl_2$ (1d), has been established through X-ray crystallography, revealing a *zig-zag* arrangement of the three coordination spheres around the platinum atoms.

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Keywords: Crystal structure; NMR spectroscopy; Platinum compounds; Thiolato ligands; Trinuclear complexes

1. Introduction

There is a growing interest in the chemistry of highnuclearity platinum group metal complexes stabilized by bridging ligands [1–12]. In contrast to the large number of dinuclear platinum derivatives [13–15], investigations on trinuclear and higher nuclearity compounds are limited and primarily deal with low-valent metal clusters [16]. The interest in high-nuclearity complexes is manifold: (i) they may serve as molecular precursors for the preparation of inorganic materials under mild conditions [11,17], (ii) they represent possible conceptual bridges between homogeneous and heterogeneous catalysis [13d,18], (iii) they may act as models for redoxactive metalloproteins [8,9,19], and (iv) they offer several synthetic challenges and structural diversity. For instance, structures adopted by this class of molecules include (a) triangular clusters such as $[M_3E_2(dppe)_2]^{2+}$ (M = Ni, Pd, Pt; E = S, Se, Te) [2], $[Pd_3(\mu-E)_2\{S_2P(OR)_2\}_2(PPh_3)_2]$ [6], or $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ (Th = thienyl) [10b], (b) linear chain species such as $[Pd_3(OAc)_6]$ [20] or $[Pd_3(\eta^3-2\text{-methylallyl})_2(\mu-Cl)_4]$ [21], or (c) non-planar framework structures such as $[Pd_3Cl_3(\mu-SeCH_2CH_2NMe_2)_3]$ [11] or $[\{Pd_3\{\mu-S(c-Hx)\}_4Cl_2(PMe_3)_2]$ [22]. There may be weak metal-metal bonding interactions, as postulated in the case of $[Pt_4(OAc)_8]$ [23,24], or such interactions may be absent altogether.

We have been active in the synthesis of platinum group metal complexes containing bridging organochalcogenido ligands [6,7b,11,25,26] and have demonstrated their use as molecular precursors for the synthesis of metal chalcogenides relevant to applications in electronics. Complexes of the type $[Pd_2(\mu-ER)_2(\eta^3-C_4H_7)_2]$ show interesting thermal behaviour and yield metal-rich chalcogenides at moderately low temperatures [7b]. Thermolysis [11] of $[PdCl(SeCH_2CH_2NMe_2)]_3$ yields $Pd_{17}Se_{15}$ whereas $[Pd(TeC_5H_4NMe-3)Cl(PPh_3)]$ affords PdTe. We have earlier employed monomeric palladium

 $^{^{\}star}$ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2003.12.024.

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and platinum complexes containing bis(diphenylphosphino)alkanes as precursors for the synthesis of dinuclear complexes [25,26]. In the present study we report the use of mononuclear platinum(II) complexes of the type [Pt(SR)₂(dppm)] in synthesizing bridged dinuclear and linear trinuclear platinum complexes, $[Pt_2(\mu ER)_2(dppm)_2]^{2+}$ and $[Pt_3(\mu-SR)_4(dppm)_2]^{2+}$.

2. Results and discussion

2.1. Preparation and spectroscopic properties

The treatment of $[PtCl_2(RCN)_2]$ (R = Me or Ph) with two equivalents of $[Pt(SR)_2(dppm)]$ in the presence of NaBF₄ or Tl(CF₃SO₃) gave thiolato-bridged trinuclear platinum(II) complexes, $[Pt_3(\mu-SR)_4(dppm)_2][X]_2$ (1) (X = BF₄⁻ or CF₃SO₃⁻) (1). The reaction between $[PtCl_2-(dppm)]$ and $[Pt(ER)_2(dppm)]$, E = S or Se, in 1:1 molar ratio in the presence of Tl(CF₃SO₃) afforded the dinuclear complexes $[Pt_2(\mu-ER)_2(dppm)_2][CF_3SO_3]_2$ (2) (2).



(2)

The elemental analyses of the complexes 1 and 2 are consistent with tri- and dinuclear formulations. The NMR (¹H, ³¹P, ¹⁹⁵Pt) data of the dinuclear complexes are well in agreement with those reported for analogous complexes [25,26]. The ³¹P NMR spectra of 1 and 2 display a single resonance with ¹⁹⁵Pt satellites. The signal is deshielded from the corresponding resonance for [Pt(SR)₂(dppm)], the deshielding being greater for complexes 2. The magnitudes of ${}^{1}J(Pt-P)$ for 1 and 2 are increased with respect to the corresponding mononuclear complex, the coupling constants increasing from mononuclear via trinuclear to the dinuclear compounds. This indicates that the electron density at the sulphur atom is reduced as a result of the coordination to another platinum center. The ¹H NMR spectra exhibit a triplet for the CH₂ protons bound to phosphorus with $^{2}J(P-H) \sim 12$ Hz, however, the platinum satellites were broadened. Such broadening of ¹⁹⁵Pt satellites is not uncommon for platinum complexes in ¹H NMR spectra recorded at high field [5]. The IR spectra of complexes containing the trifluoromethanesulfonate anion [3c]



Fig. 1. FAB mass spectrum of [Pt₃(µ-SC₆H₄Cl-4)₄(dppm)₂][CF₃SO₃]₂.

showed absorptions attributable to the CF_3SO_3 group at 1281, 1247 and 1223 cm⁻¹.

The FAB mass spectra of some representative trinuclear complexes were recorded. The spectra (Fig. 1) displayed peaks assignable to $M-X^+$, $M-2X^+$, $[Pt_3(S)(SR)_3(dppm)_2]^+$ and $[Pt(SR)(dppm)]^+$. However, in the FAB mass spectrum of $[Pt_3(\mu-SPh)_4-(dppm)_2][BF_4]_2$ peaks due to higher masses $(m/e\ 2282\ ([Pt_4(SPh)_6(dppm)_2][BF_4]^+)$ and 2197 $([Pt_4(SPh)_6-(dppm)_2]^+))$ were also observed. They appear to be formed by recombination of smaller fragments. The existence of these peaks suggests that tetra- and higher-nuclearity complexes can also be prepared. A thiolato-bridged tetranuclear palladium complex anion $[Pd_4(SC_6F_5)_6(C_6F_5)_4]^{2-}$ has been reported earlier [3c].

2.2. Crystal and molecular structure of $[Pt_3(\mu - SC_6H_4CH_3-4)_4(dppm)_2][CF_3SO_3]_2 \cdot 6CH_2Cl_2$ (1d) $(\cdot 6CH_2Cl_2)$

The structure of $1d(-6CH_2Cl_2)$ was solved in the triclinic $P\bar{1}$ space group with the results summarized in Tables 1 and 2. Attempts to obtain higher symmetry solutions failed. Two independent dications were found together with each two CF₃SO₃⁻ anions and each six cocrystallized CH₂Cl₂ molecules in the unit cell. The shortest intermolecular contacts were found between the O atoms of the trifluoromethanesulfonate anions and the solvent molecule protons (2.38(3) Å) and the ortho-H of the dppm aryl substituents (2.45(3) A), respectively. They are far too long to be classified as notable H-bridges. The molecules are oriented along the *a*-axis and also pack in this direction, leaving a huge space between the stacks which is occupied by the co-crystallized CH₂Cl₂, the anions, and phenyl groups of the dppm ligand as can be seen in Fig. 2.

The overall quality of the structure is low due to a poor data set. The reason may be that solvent molecules have evaporated during storage of the crystals. We shall thus discuss only the unequivocal findings for this structure.

Table 1			
Crystal data	and structure	refinement for	$1d\cdot 6CH_2Cl_2$

Empirical formula/formula weight	$C_{86}H_{84}Cl_{12}F_6O_6P_4Pt_3S_6/2654.44 \text{ g mol}^{-1}$
Crystal system/space group	monoclinic/P1
Unit cell dimensions	$a = 15.475(3)$ Å, $\alpha = 88.265(10)^{\circ}$
	$b = 15.773(2)$ Å, $\beta = 77.685(12)^{\circ}$
	$c = 23.632(3)$ Å, $\gamma = 71.982(12)^{\circ}$
Volume/Z/Density (calculated)	5355.1(13) Å ³ /2/1.646 g dm ⁻³
Absorption coefficient/ $F(000)$	$4.441 \text{ mm}^{-1}/2592$
θ range for data collection	2.19–24.00°
Limiting indices	-17 < h < 17, -18 < k < 18, 0 < l < 27
Reflections collected (R_{int})	17317 ($R_{\rm int} = 0.0816$)
Independent data/restraints/parameters	16611/183/610
Goodness-of-fit on F^2	1.151
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0982, wR_2 = 0.2137$
R indices (all data)	$R_1 = 0.1954, wR_2 = 0.2562$
Largest diffraction peak and hole	3.086 and $-3.282 \text{ e} \text{ Å}^{-3}$

Table 2

Selected structural parameters for $1d \cdot 6CH_2Cl_2$

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
Pt(1)-S(2)2.311(6) $Pt(2)-P(1)$ 2.265(7) $Pt(4)-P(3)$ 2.254(6) $Pt(3)-S(4)$ 2.292(6) $Pt(2)-S(2)$ 2.360(6) $Pt(4)-S(3)$ 2.351(6) $Pt(3)-S(2)$ $Pt(2)-S(2)$ $Pt(2)-S(2)$ $Pt(2)-S(3)$ $Pt(3)-S(3)$ $Pt(3)-S(3)$	
Pt(3)–S(4) 2.292(6) Pt(2)–S(2) 2.360(6) Pt(4)–S(3) 2.351(6)	
$\mathbf{D}_{1}(0) = \mathbf{C}_{1}(0) = \mathbf{D}_{2}(0) = \mathbf{D}_{1}(0) = \mathbf{D}_{2}(0) = \mathbf{D}$	
Pt(3)-S(3) 2.325(5) $Pt(2)-S(1)$ 2.364(6) $Pt(4)-S(4)$ 2.353(6)	
$Pt(1) \cdots Pt(2)$ 3.315(3) $Pt(3) \cdots Pt(4)$ 3.264(3)	
$X1A\cdots X1B^{a}$ 3.648(8) $X1A\cdots X1C^{a}$ 3.965(9) $X1C\cdots X1D^{a}$ 3.679(8)	
$X1E\cdots X1F^{a}$ 3.667(8) $X1E\cdots X1G^{a}$ 3.769(9) $X1G\cdots X1H^{a}$ 3.907(9)	
Angles (°)	
S(2)–Pt(1)–S(1) 80.9(2) P(2)–Pt(2)–P(1) 73.6(2) P(4)–Pt(4)–P(3) 73.8(2)	
S(2A)-Pt(1)-S(1) 99.1(2) P(2)-Pt(2)-S(2) 102.7(2) P(4)-Pt(4)-S(3) 177.5(2)	
$Pt(1)-S(1)-Pt(2) \qquad 89.9(2) \qquad P(1)-Pt(2)-S(2) \qquad 172.7(2) \qquad P(3)-Pt(4)-S(3) \qquad 103.7(2)$	
Pt(1)-S(2)-Pt(2) 90.4(2) P(2)-Pt(2)-S(1) 178.1(2) P(4)-Pt(4)-S(4) 103.0(2)	
S(4A)-Pt(3)-S(3) 98.7(2) P(1)-Pt(2)-S(1) 104.6(2) P(3)-Pt(4)-S(4) 174.0(2)	
S(4)–Pt(3)–S(3) 81.3(2) S(2)–Pt(2)–S(1) 79.2(2) S(3)–Pt(4)–S(4) 79.47(19)	
Pt(3)-S(3)-Pt(4) 88.53(19)	
Pt(3)–S(4)–Pt(4) 89.3(2) P(2)–C(20)–P(1) 93.4(11) P(3)–C(59)–P(4) 92.7(10)	
Tilt angles (°)	
$[C(8)]/[C(1)]^{b}$ 9.5(2) $[C(40A)]/[C(47A)]^{b}$ 7.3(2)	
$[C(33A)/[C(1)]^b$ 8.1(2) $[C(40A)]/[C(72)]^b$ 8.7(2)	
$[C(33A)]/[C(27A)]^{b}$ 6.0(2) $[C(72)]/[C(66)]^{b}$ 8.7(2)	

^a The centromers correspond to the following C₆-planes (see Fig. 2): X1A = [C(1)], X1B = [C(8)], X1C = [C(33A)], X1D = [C(27A)], X1E = [C(40A)], X1F = [C(47A)], X1G = [C(72)], X1H = [C(66)].

^b The parentheses [] represent the C₆-planes numbered according to their α -C-atom as shown in Fig. 2.

The molecular structure confirms the analytical composition of **1d** to contain three platinum(II) atoms. The central ones (Pt(1) or Pt(3), respectively) are coordinated by an S₄-core, and the peripheral platinum atoms (Pt(2), Pt(2A), Pt(4) and Pt(4A)) have a S₂P₂ ligand set (Fig. 3). The three platinum coordination spheres are almost planar. The tilt-angles between the planes PPtP vs. SPtS are 5.1° and 6.4°, respectively, the S₂PtS₂ cores are perfectly planar due to the symmetry centre at the Pt atom. These two coordination spheres are tilted towards each other by 42.9° and 45.4°, respectively, giving the molecule a *zig-zag* shape (Fig. 4) which could also be described as the *anti*-form. The same was observed in the tetranuclear complex [NMe₄]₂[R₂Pd(μ -SR)₂Pt(μ -SR)₂PtR₂] (R = C₆F₅) [3c].

Two of the dppm phenyl substituents are oriented parallel to the neighbouring tolyl groups (Fig. 4). The distances between the planes as listed in Table 2 are not significant for strong π - π interaction. The perspective view in Fig. 5 reveals that on one side the two aryl rings are eclipsed (P1S1 and P3S3), whereas on the other side a graphite-like stacking is observed (P2S2 and P4S4). In the related mononuclear complexes [(dppm)Pt(EC₆H₅)₂] (E=S or Se) [27] one of the two thio- or selenophenyl substituents also approach one of the phenyl groups on the dppm ligand, however, the distances are around 4 Å and the two planes are tilted by about 20°. For the "stacking" in the present compound we can note markedly shorter distances and flattened tilt angles. The tolyl groups of neighbouring thiolates do not exhibit



Fig. 2. Unit cell of 1d showing the orientation along the a-axis.

such stacking, they only approach by their α - and β -C atoms and their interplanar distance is much longer. Thus they prevent interaction of the two methyl groups. Passing through the structures of a number of dppm Pt complexes [28] we found that the phenyl groups show very flexible orientation, e.g., they *bent* away upon steric stress (for details see Table S6). In view of the latter we conclude that the observed stacking between the phenyl groups on the dppm ligand and the tolyl thiolate ligands is likely due to a real π - π interaction and not the result of steric optimization within the molecule.



Fig. 4. Perspective view of molecule 2 of 1d showing the *anti* arrangement.



Fig. 5. Perspective view of molecule 2 of 1d along the molecular axis.

Bond lengths and angles around the platinum atoms are in the range observed for related structures. Very similar values are obtained in the mononuclear complexes [(dppm)Pt(EC₆H₅)₂] (E = S or Se) [27] for the



Fig. 3. Numbering of the molecules 1 (left) and 2 (right) of 1d. The aryl substituents are numbered according to the first C atom in the corresponding ring.

P–Pt–P angles (73.7°) and also for the P–C–P angles in the dppm ligand (ca. 94°). Due to the formation of the central S₂PtS₂ core, the S–Pt–S angles for the P₂PtS₂ unit are reduced from 91.6° in the mononuclear complex to 79.2° and 79.5°. We can therefore conclude that the (dppm)Pt(II) building block does not show any peculiarities other than a weak to medium π – π -stacking of two phenyl groups with neighbouring tolyl thiolates.

Furthermore, we could not find any evidence of metal-metal interaction. The formal +II oxidation state of all platinum atoms is confirmed by the stoichiometry with two $CF_3SO_3^-$ anions, the Pt···Pt distances are 3.315(3) and 3.264(3) Å, respectively.

Comparison with other linear chain oligonuclear complexes with such S_2PtS_2 (or S_2PdS_2) cores lacks from the fact that many of these compounds like $[NMe_4]_2[R_2Pt(\mu-SR)_2Pt(\mu-SR)_2PtR_2]$ (R = C₆F₅) [3c] or $[Pt_3(AET)_4]^{2+}$ (AET = 2-aminoethanethiolate) [8b] have not been structurally characterized, while in others the bridging S (or Se) groups have not the same chemical character as our thiolate bridges. They are either sulphides as in the heterometallic $[{Pt_2(\mu-S)_2(PPh_3)_4}_2Pd]$ [1c] or the thiolate group is part of a chelate ligand like in [(PPh₃)₂Pt(µ-SNC(Ph)NS)Pt(µ-SNC(Ph)NS)- $Pt(PPh_3)_2$ [1g], [Pd₄(phbt-C,N,S)₄] (phbt = 2-(phenylmethyleneamino)benzenethiolate [4a] or $[Pt_6(AET)_8]^{4+}$ (AET = 2-aminoethanethiolate) [8b]. Therefore, to our knowledge, we present here for the first time the crystal and molecular structure of such a trimeric complex with a linear chain arrangement of the metal atoms.

3. Experimental

3.1. General

[PtCl₂(dppm)] [29], [Pb(ER)₂] [30] and [Pt(ER)₂dppm] [26] were prepared by published methods. All reactions were carried out under a nitrogen atmosphere in dry, distilled and degassed solvents. IR spectra were recorded as Nujol mulls between polyethylene sheets in the range 4000-200 cm⁻¹ on a Bomem MB-series FT-IR spectrophotometer. Microanalyses (C, H, S) were carried on a Carlo Erba 1106 microanalyzer. Unless otherwise stated ${}^{1}H, {}^{13}C{}^{1}H, {}^{31}P{}^{1}H$ and ${}^{195}Pt{}^{1}H$ spectra were recorded on a Bruker DPX-300 NMR spectrometer. Chemical shifts are referenced to the internal chloroform peak (¹H and ¹³C), to external phosphoric acid (³¹P), or Na₂PtCl₆ in D₂O (for ¹⁹⁵Pt). Most of the carbon resonances have not been assigned but signals corresponding to quaternary and ternary carbons are indicated as C or CH with the help of DEPT experiments. ${}^{13}C{}^{1}H$ data for dppm (75 MHz, CDCl₃): 28.3 (t, 24 Hz, PCH₂), 128.4 (br, C-3,5, PPh₂), 128.6 (s, C-4, PPh₂); 132.9 (t, 10 Hz, C-2,6, PPh₂), 139.1 (br, C-1, PPh₂).

3.2. Synthesis

The mononuclear complexes $[Pt(ER)_2(dppm)]$ were prepared by a method previously published [25,26], the physical, analytical and NMR (¹H, ³¹P{¹H}) data are included here for comparison.

3.2.1. Synthesis of [Pt(SPh)₂(dppm)]

Yield: 78%. Mp: 201 °C. *Anal.* Calc. for $C_{37}H_{32}P_2PtS_2$: C, 55.7; H, 4.0. Found: C, 55.6; H, 4.0%. IR (cm⁻¹): 1103 (s), 1024 (w), 998 (w), 546 (s), 490 (m), 480 (m), 352 (m), 279 (s), 266 (w), 247 (s), 224 (s). ¹H NMR (500 MHz, CDCl₃): 4.10 (t, 10 Hz, CH₂); 6.50–7.55 (m, Ph). ¹³C{¹H} (75 MHz, CDCl₃): 49.3 (t, *J*(P–C) = 31 Hz, PCH₂–), 123.7 (CH, SPh), 126.9 (CH, SPh), 128.1 (d, *J*(P–C) = 26 Hz, C-1, PPh₂), 128.9 (CH, PPh₂), 131.4 (CH, PPh₂), 133.4 (CH, PPh₂), 134.9 (CH, SPh), 142.6 (C–S). ³¹P{¹H} (202 MHz, CDCl₃): δ (¹*J*(Pt–P)): -48.8 ppm (2500 Hz).

3.2.2. Synthesis of $[Pt(STol)_2(dppm)]$

Yield: 78%. Mp: 264 °C. Anal. Calc. for $C_{39}H_{36}P_2PtS_2$: C, 56.7; H, 4.4. Found: C, 55.6; H, 4.5%. IR (cm⁻¹): 1102 (s), 1088 (m), 806 (m), 548 (s), 501 (m), 479 (m), 352 (m), 325 (w), 302 (w), 279 (s), 247 (s), 226 (s). ¹H NMR (300 MHz, CDCl₃): 2.06 (s, 6H, CH₃), 4.13 (t, 10 Hz, 2H, CH₂); 6.36, 7.11 (each d, 8 Hz, 8H, C₆H₄), 7.30–7.35 (m, 8H), 7.41–7.46 (m, 4H), 7.57–7.62 (m, 8H) [Ph]. ¹³C{¹H} (75 MHz, CDCl₃): 20.7 (s, CH₃), 49.9 (br, PCH₂–), 127.7 (CH, STol), 128.7 (CH, PPh₂), 129.7 (C-1, PPh₂), 131.1 (CH, PPh₂), 133.0 (CH, STol) 133.4 (CH, PPh₂), 134.9 (CH, STol), 138.8 (C–S). ³¹P{¹H} (121 MHz, CDCl₃): δ (¹J(Pt–P)): –47.9 ppm (2505 Hz).

3.2.3. Synthesis of $[Pt(SC_6H_4Cl-4)_2(dppm)]$

Yield: 84%. Mp: 243–245 °C. *Anal.* Calc. for $C_{37}H_{30}Cl_2P_2PtS_2$: C, 51.3; H, 3.5. Found: C, 51.9; H, 3.3%. IR (cm⁻¹): 1092 (s), 1012 (m), 813 (m), 805 (m), 547 (s), 501 (s), 356 (m), 325 (w), 302 (m), 279 (s), 247 (m). ¹H NMR (300 MHz, CDCl₃): 4.21 (t, 10 Hz, PCH₂); 6.52, 7.13 (each d, 8 Hz, C₆H₄), 7.35–7.64 (m, Ph)]. ¹³C{¹H} (75 MHz, CDCl₃): 49.2 (t, 31 Hz, PCH₂-), 126.9 (CH, SAr), 128.0 (t, 26 Hz, C-1, PPh₂), 129.0 (CH, PPh₂), 129.7 (C-4, SAr), 131.6 (CH, PPh₂), 133.3 (CH, PPh₂), 135.9 (br, CH, SAr), 141.5 (C–S, ²*J*(Pt–C) = 29 Hz). ³¹P{¹H} (75 MHz, CDCl₃): δ (¹*J*(Pt–P)): -48.2 ppm (2506 Hz).

3.2.4. Synthesis of [Pt(SePh)₂(dppm)]

Yield: 82%. Mp: 230 °C. *Anal.* Calc. for $C_{37}H_{32}P_2PtSe_2$: C, 49.8; H, 3.6. Found: C, 49.9; H, 3.7%. IR (cm⁻¹): 1098 (s), 1020 (m), 546 (s), 502 (s), 473 (s), 351 (m), 279 (s), 266 (w), 247 (s), 224 (m). ¹H NMR (500 MHz, CDCl₃): 4.17 (t, 10 Hz, CH₂); 6.50–7.55 (m, Ph)]. ¹³C{¹H} (75 MHz, CDCl₃): 51.6 (t, PCH₂–), 124.6

(CH, SePh), 127.0 (CH, SePh), 128.3 (C-1, PPh₂), 128.7 (CH, PPh₂), 131.2 (CH, PPh₂), 133.2 (CH, PPh₂), 137.0 (CH, SePh), 143.8 (C–Se). ³¹P{¹H} (202 MHz, CDCl₃): δ (¹*J*(Pt–P)): -51.7 ppm (2530 Hz).

3.2.5. Synthesis of $[Pt_3(\mu-SEt)_4(dppm)_2][BF_4]_2$ (1a)

Prepared in a manner similar to **1b** described below in 70% yield. Mp: 219–220 °C. *Anal.* Calc. for $C_{58}H_{64}B_2F_8P_4Pt_3S_4$: C, 39.3; H, 3.6. Found: C, 38.7; H, 3.8%. ¹H NMR (500 MHz, dmso-d_6): 1.09 (t, 7 Hz, SCH₂Me), 2.50 (CH₂ merged with dmso signal), 5.49 (t, 12 Hz, PCH₂–), 7.55–7.78 (m, Ph). ³¹P{¹H} (202 MHz, dmso-d_6): δ (¹*J*(Pt–P)): -47.3 (2551 Hz). FAB Mass (*m*/*z*): 1684 [M–BF₄], 1596 [M–2BF₄], 1568 [Pt₃(S)(SEt)₃(dppm)₂]²⁺, 798.

3.2.6. Synthesis of $[Pt_3(\mu-SPh)_4(dppm)_2][BF_4]_2$ (1b)

To a suspension of [PtCl₂(PhCN)₂] (0.021 g, 0.045 mmol) in methanol (5 ml) was added a solution of NaBF₄ (0.011 g, 0.098 mmol) in methanol (2 ml) and the mixture was stirred for 15 min at room temperature. To this a dichloromethane (5 ml) solution of [Pt(SPh)₂-(dppm)] (0.070 g, 0.088 mmol) was added and the reactants were further stirred for 2 h. The solvents were removed in vacuo. The residue was extracted with dichloromethane $(2 \times 5 \text{ ml})$ and filtered to remove NaCl. The filtrate was again evaporated to dryness and the residue so obtained was recrystallized from dichloromethane-methanol mixture to give yellow crystalline solid (yield: 0.058 g, 67%). Mp: 220-222 °C. Anal. Calc. for C₇₄H₆₄B₂F₈P₄Pt₃S₄: C, 45.3; H, 3.3. Found: C, 45.3; H, 3.3%. ¹H NMR (500 MHz, dmso-d₆): 5.08 (t, 12 Hz, PCH₂-), 6.70-7.55 (m, Ph). ³¹P{¹H} (202 MHz, dmsod₆): δ (¹J(Pt-P)): -44.7 (2641 Hz). FAB mass (m/z): 1875 [M-BF₄], 1787 [M-2BF₄], 1461, 1374, 1298, 1266, 687 [Pt(SPh)(dppm)], 2282, 2197.

3.2.7. Synthesis of $[Pt_3(\mu-SPh)_4(dppm)_2][CF_3SO_3]_2$ (1c)

Solid Tl(CF₃SO₃)(40 mg, 0.113 mmol) was added to a solution of [PtCl₂(MeCN)₂] (18 mg, 0.052 mmol) in acetonitrile (15 ml). After 2 h of stirring the above suspension, [Pt(SPh)₂(dppm)] (73 mg, 0.091 mmol) was added and the resulting mixture stirred overnight (12 h). The suspension so obtained was filtered to remove TlCl and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from an aceto-nitrile/diethyl ether mixture to give the title complex as yellow solid (yield 52 mg, 55%). Mp: 258–260 °C. *Anal.* Calc. for C₇₆H₆₄F₆O₆S₆P₄Pt₃: C, 43.7; H, 3.1; S, 9.2. Found: C,43.5; H, 3.0; S, 9.2%. ¹H NMR: 4.76 (t, 11 Hz, CH²₂), 6.61 (t, 7.5 Hz), 6.80 (t, 7 Hz), 7.00 (d, 7.5 Hz) [SPh], 7.17–7.45 (m, PPh₂). ¹³C{¹H} (75 MHz, CH₃CN + CDCl₃): 44.9 (t, 33 Hz, PCH₂), 123.4 (t, 30

Hz, C-1, PPh₂), 127.4 (CH, SPh), 127.8 (CH, SPh), 128.8 (CH, PPh₂), 129.5 (CH, PPh₂), 132.2 (CH, PPh₂), 132.8 (CH, SPh). (C-1 of SPh ligand was not detected). ${}^{31}P{}^{1}H{}$ (121 MHz, CDCl₃): δ (${}^{1}J(Pt-P)$): -46.6 (2638 Hz). # Platinum satellites broadening.

3.2.8. Synthesis of $[Pt_3(\mu-SC_6H_4CH_3-4)_4(dppm)_2] [CF_3SO_3]_2$ (1d)

Prepared in a manner similar to 1c above in 76% vield: Mp.: 298-302 °C. Anal. Calc. for C₈₀H₇₂F₆O₆P₄Pt₃S₆: C, 44.8; H, 3.4; S, 8.9. Found: C, 44.1; H, 3.4; S, 8.6%. IR (cm⁻¹): 1281 (s), 1247 (s), 1223 (m), 1160 (br), 1027 (s), 803 (m), 637 (s), 548 (s), 279 (w), 255 (w), 228 (w). ¹H NMR: 2.09 (s, 12H, CH₃) 4.78 (t, 11 Hz, 4H, $CH_2^{\#}$); 6.34, 6.84 (each d, 8 Hz, 16 H, C_6H_4); 7.28–7.29 (m, 30 H), 7.40–7.44 (m, 10H, PPh₂). ¹³C{¹H} (75 MHz, CDCl₃): 20.9 (s, CH₃), 46.0 (t, PCH₂), 124.7 (t, 30 Hz, C-1, PPh2); 126.9 (C-4, STol), 128.7 (CH, PPh₂), 129.5 (br, CH, PPh₂), 132.4 (CH, STol), 133.3 (CH, PPh₂), 133.5 (CH, STol), 138.4 (C-1, STol). ³¹P{¹H} (121 MHz, CDCl₃): δ (¹J(Pt-P)): -46.9 (2630 Hz). FAB mass (m/z): 1994 [M-CF₃SO₃H], 1844 [M-2CF₃SO₃H], 1723, 923, 702 [Pt(STol)(dppm)], 641, 577. UV/vis (in MeCN) λ (nm): 365sh, 323sh, 282sh, 259sh. # Platinum satellites broadening.

3.2.9. Synthesis of $[Pt_3(\mu - SC_6H_4Cl-4)_4(dppm)_2] - [CF_3SO_3]_2$ (1e)

Prepared in a manner similar to 1c in 87% yield. Mp.: 286-288 °C. Anal. Calc. for C76H60Cl4F6O6P4Pt3S6: C, 40.9; H, 2.7; S, 8.6. Found: C, 40.6; H, 2.7; S, 8.4%. IR (cm⁻¹): 1287 (s), 1241 (s), 1223 (s), 1168 (m, br), 1027 (s), 821 (m), 637 (s), 548 (s), 504 (s), 479 (s), 279 (m), 255 (w). ¹H NMR (300 MHz, CD₃CN): 4.70 (t, 10 Hz, 4H, CH[#]₂); 6.53, 6.98 (each d, 8 Hz, 16H, C₆H₄); 7.34-7.38 (m), 7.47–7.56 (m). ${}^{13}C{}^{1}H{}$ (75 MHz, CD₃CN): 46.9 (br, CH₂), 124.9 (t, 29 Hz, C-1, PPh₂), 129.2 (CH, PPh₂), 129.5 (CH, SAr), 130.7 (CH, PPh₂), 134.2 (CH, PPh₂), 136.0 (CH, SAr), (C-1 of SC₆H₄Cl-4 group was not observed due to low signal to noise ratio). ${}^{31}P{}^{1}H{}$ (121 MHz, CD₃CN): δ (¹*J*(Pt–P)): -47.4 (2663 Hz). FAB mass (m/z): 2079 [M-CF₃SO₃H], 1927 [M-2CF₃SO₃H], 1785, 964, 723 [Pt(SC₆H₄Cl-4)(dppm)]. # Platinum satellites broadening.

3.2.10. Synthesis of $[Pt_2(\mu-SC_6H_4CH_3-4)_2(dppm)_2]-$ [CF₃SO₃]₂ (**2a**)

To a suspension of $[PtCl_2(dppm)]$ (52 mg, 0.08 mmol) in acetonitrile (20 ml) was added solid Tl(CF₃SO₃) (62 mg, 0.17 mmol). After 2 h of stirring $[Pt(SC_6H_4CH_3-4)_2(dppm)]$ (60 mg, 0.073 mmol) was added to the above reaction mixture and the reactants were further stirred for 8 h at room temperature. The resulting suspension so obtained was filtered and the filtrate was evaporated to dryness in vacuo. The residue was recrystallized from acetonitrile/diethyl ether mixture to give the title complex as an off-white solid, (yield: 98 mg, 78%). Mp: 226-228 °C. Anal. Calc. for C₆₆H₅₈F₆O₆P₄Pt₂S₄: C, 46.5; H, 3.4; S, 7.5. Found: C, 45.9; H, 3.4; S, 6.9%. IR (cm⁻¹): 1281 (s), 1248 (s), 1223 (s), 1163 (s), 1102 (s), 1027 (s), 814 (m), 637 (s), 549 (m), 504 (s), 279 (w). ¹H NMR: 1.93 (s, 6H, CH₃); 4.82 (t, 11Hz, 4H, CH[#]₂); 6.11, 7.09 (each d, 8 Hz, 8H, C_6H_4); 7.28–7.47 (m) [Ph]. ¹³C{¹H} (75 MHz, CDCl₃): 20.9 (s, Me); 45.2 (br, PCH₂); 124.3 (t, 30 Hz, C-1, PPh₂); 126.1 (C-4, STol), 129.2 (CH, STol); 129.6 (CH, PPh₂); 132.4 (CH, PPh₂); 133.4 (CH, PPh₂); 134.2 (CH, STol), 138.7 (C-1, STol). ³¹P{¹H} (121 MHz, CDCl₃): δ (¹*J*(Pt–P)): –44.8 ppm (2743 Hz). ¹⁹⁵Pt{¹H} (64 MHz, CDCl₃): -3813 ppm (t, ¹*J*(Pt–P) = 2700 Hz). # Platinum satellites broadening.

3.2.11. Synthesis of $[Pt_2(\mu-SC_6H_4Cl-4)_2(dppm)_2]-$ [CF₃SO₃]₂ (**2b**)

Prepared in a manner similar to **2a** in 67% yield. Mp: 226–228 °C. *Anal.* Calc. for $C_{64}H_{52}Cl_2F_6O_6P_4Pt_2S_4$: C, 44.0; H, 3.00; S, 7.3. Found: C, 43.6; H, 3.0; S, 6.7. IR (cm⁻¹): 1279 (s), 1246 (s), 1223 (s), 1160 (s) 1102 (s) 816 (s, br), 573 (w), 548 (s), 504 (s), 364 (m), 278 (m), 255 (w). ¹H NMR: 4.78 (br, m, 4H, CH²/₂); 6.14 (d, 8Hz, 4H, C₆H₄); 7.23–7.42 (m, Ph+C₆H₄). ¹³C{¹H} (75 MHz, CDCl₃): 45.5 (m, CH₂), 123.8 (t, C-1, PPh₂), 127.5 (C-4, SAr), 128.5 (CH, SAr), 129.8 (CH, PPh₂), 132.7 (CH, PPh₂), 133.4 (CH, PPh₂), 135.4 (C-1, SAr), 135.6 (CH, SAr). ³¹P{¹H} (121 MHz, CDCl₃): δ (¹*J*(Pt–P)): -43.9 ppm (2780 Hz). ¹⁹⁵Pt{¹H} (64 MHz, dmso-d₆): -3811 ppm (t, ¹*J*(Pt–P)=2677 Hz). # Platinum satellites broadening.

3.2.12. Synthesis of [*Pt*₂(μ-Se*Ph*)₂(*dppm*)₂][*CF*₃SO₃]₂ (2c)

Prepared in a manner similar to **2a** in 74% yield. Mp: 226–228 °C. *Anal.* Calc. for C₆₄H₅₄F₆O₆P₄Pt₂S₂Se₂: C, 43.5; H, 3.0; S, 3.6. Found: C, 43.0; H, 2.9; S, 3.5%. IR (cm⁻¹): 1281 (s, br), 1158 (s, br), 1102 (s, br), 1027 (s), 801 (m), 637 (s), 549 (s) 505 (s), 368 (w), 279 (w), 255 (w), 225 (w). ¹H NMR: 4.99 (t, 11 Hz, 4H, CH[#]₂); 6.57 (t, 4H, Ph), 6.75 (t, 2H, Ph); 7.15 (d, 3H) [SePh]; 7.29–7.47 (m, PPh₂). ¹³C{1H} (75 MHz, CDCl₃): 45.2 (m, CH₂), 124.6 (t, C-1, PPh₂), 128.6 (CH, SePh), 128.8 (CH, SePh), 129.4 (CH, PPh₂), 132.6 (CH, PPh₂), 133.0 (CH, PPh₂), 135.0 (CH, SePh); C-1 of the SePh ligand not detected. ³¹P{¹H} (121 MHz, CDCl₃): δ ¹J(Pt–P)): -45.7 ppm (2708 Hz). ¹⁹⁵Pt{¹H} (64.52 MHz, CH₂Cl₂ + CDCl₃): δ: -4085 ppm (t, ¹J(Pt–P)=2693 Hz). # Platinum satellites broadening.

3.3. Structure determination

Single crystals of $[Pt_3(\mu-SC_6H_4CH_3-4)_4(dppm)_2]$ -[CF₃SO₃]₂ · 6CH₂Cl₂ were obtained as yellow blocks

from a saturated CH₂Cl₂/methanol solution. Data collection was performed at 173(2) K on a Siemens P3 diffractometer with Mo K α radiation ($\lambda = 0.71073$ A) employing Wyckoff scans. The structure was solved by the Patterson method using the SHELXTL package [31] and refinement was carried out with SHELXL97 employing full-matrix least-squares methods on F^2 with $F_0^2 \ge -2\sigma(F_0^2)$. From the non-hydrogen atoms only the core atoms Pt, S, P and the bridging C atoms of the dppm ligands were refined anisotropically as well as the trifluoromethanesulfonate anions and the solvent molecules. The aryl carbon atoms were constrained to regular hexagons. Subsequent anisotropic treatment did not yield better results. Hydrogen atoms were included using appropriate riding models. The disordered solvent molecules had to be refined with SADI restraints for the C-Cl distances.

4. Supplementary material

Six tables giving structural details of $[Pt_3(\mu-SC_6H_4CH_3-4)_4(dppm)_2][CF_3SO_3]_2 \cdot 6CH_2Cl_2$ are available. Full structural information has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 226419. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax: +44-1223-336-033, or Email: deposit@ccdc.cam.ac.uk.

Table S6 compares essential structural parameters of $[Pt_3(\mu-SC_6H_4CH_3-4)_4(dppm)_2][CF_3SO_3]_2 \cdot 6CH_2Cl_2$ with those of related dppm platinum complexes. Three figures are provided showing packing of the molecules within the unit cell viewed along the *b* axis or the *a* axis and a figure of molecule 2 showing 50% thermal ellipsoids.

Acknowledgements

We thank Drs. J.P. Mittal and S.K. Kulshreshtha for encouragement of this work. The help of Prof. Dr. M.T. Chicote in recording FAB mass spectra and in analyses of the samples is gratefully acknowledged. This work was carried out in the framework of the indo-german bilateral agreement (BMBF, project IND 99/060).

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