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Dithiolate and diselenolate complexes $[Pt_2(\mu\text{-}ECH_2CH{=}CHCH_2E)(PPh_3)_4]^{2+}$ (E = S, Se); synthesis, characterisation and mass spectrometric formation of the dichalcogenide species $[Pt_2(\mu\text{-}E_2)(PPh_3)_4]^{2+}$

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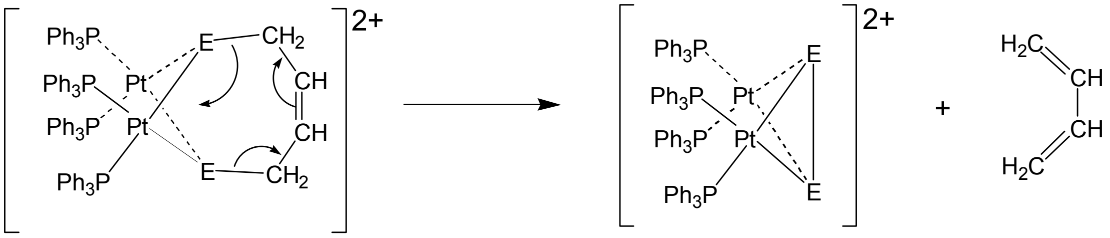
Synopsis

Alkylation reactions of $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ with *cis*-1,4-dichlorobut-2-ene (*cis*-$ClCH_2CH{=}CHCH_2Cl$) gives the complexes $[Pt_2(\mu\text{-}ECH_2CH{=}CHCH_2E)(PPh_3)_4]^{2+}$, which undergo a facile fragmentation reaction in ESI mass spectrometry, *via* a *retro*-Diels-Alder reaction and loss of 1,3-butadiene, giving the dichalcogenide species $[Pt_2(\mu\text{-}E_2)(PPh_3)_4]^{2+}$.



E = S or Se

Abstract

The reactions of $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ (E = S, Se) with *cis*-1,4-dichlorobut-2-ene (*cis*-$ClCH_2CH{=}CHCH_2Cl$) gives the dichalcogenolate complexes $[Pt_2(\mu\text{-}ECH_2CH{=}CHCH_2E)(PPh_3)_4]^{2+}$; an X-ray structure determination on the thiolate complex was carried out. The complexes give the expected dications in ESI mass spectra recorded at very low cone voltages, but at moderate cone voltages undergo facile fragmentation *via* a *retro*-Diels-Alder reaction and loss of 1,3-butadiene, giving the dichalcogenide species $[Pt_2(\mu\text{-}E_2)(PPh_3)_4]^{2+}$. Analogous species containing bidentate phosphine or arsine ligands have been previously generated electrochemically, and studied theoretically.

Keywords: Platinum complexes; Sulfide complexes; Thiolate complexes; Alkylation reactions; Electrospray mass spectrometry

Introduction

Complexes containing the $\{Pt_2S_2\}$ sulfido core continue to attract interest for the diverse reactivity they display.[1,2] Alkylation reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** were originally defined some years ago,[3,4] but have attracted recent interest because of the ease of conversion of bridging sulfido ligands into thiolate ligands containing a diverse range of functionalities.[5,6] This interest has included complexes containing alternative tertiary phosphine ligands.[7,8] The analogous selenide complex $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ **2** has been investigated to a far lesser extent, but appears to undergo similar chemistry.[9,10] Reactions with monoalkylating agents R-X lead to species of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}R)(PPh_3)_4]^+$ and/or $[Pt_2(\mu\text{-}S\text{-}R)_2(PPh_3)_4]^{2+}$ (depending on the strength of the alkylating agent), while dialkylating agents X-R-X form dithiolate bridged complexes $[Pt_2(\mu\text{-}S\text{-}R\text{-}S)(PPh_3)_4]^{2+}$ or linked complexes $[\{Pt_2(\mu\text{-}S)(PPh_3)_4\}_2(\mu\text{-}S\text{-}R\text{-}S)]^{2+}$, *via* intermediates $[Pt_2(\mu\text{-}S)(\mu\text{-}S\text{-}R\text{-}X)(PPh_3)_4]^+$.[11,12] Additional interest in sulfide alkylation chemistry comes from the observation that the use of an excess of a dialkylating agent can lead to a metal-templated synthesis of organosulfur-[13] or organoselenium[9] macrocycles.

In this contribution we describe the reactivity of the complexes $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ (E = S, Se) towards *cis*-1,4-dichlorobut-2-ene ($ClCH_2CH{=}CHCH_2Cl$) which leads to the formation of the dialkylated products $[Pt_2(\mu\text{-}ECH_2CH{=}CHCH_2E)(PPh_3)_4]^{2+}$, previously identified in our mass spectrometric screening study of alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.[5] Here we describe the macroscopic synthesis and characterisation of these complexes, which are also found to display interesting mass spectrometric fragmentation behaviour.

Results and discussion

Complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** reacts readily with an excess of *cis*-$ClCH_2CH=CHCH_2Cl$ in methanol suspension to give a clear pale yellow solution containing $[Pt_2(\mu\text{-}SCH_2CH=CHCH_2S)(PPh_3)_4]^{2+}$ (*m/z* 778.5) as the dominant species in the ESI mass spectrum after 30 minutes of stirring at room temperature. The dication was isolated from the reaction mixture by the addition of excess $NaBPh_4$, giving an off-white solid which was readily identified as $[Pt_2(\mu\text{-}SCH_2CH=CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** by NMR, ESI MS, IR, and elemental microanalysis. The analogous diselenolate complex $[Pt_2(\mu\text{-}SeCH_2CH=CHCH_2Se)(PPh_3)_4](BPh_4)_2$ **4** was similarly prepared from $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ **2** and isolated as a brown powder, though the reaction appeared to proceed rather more slowly than for **3**. The $^{-}SCH_2CH=CHCH_2S^{-}$ ligand has been previously reported in a small number of complexes,[14] but the selenolate ligand $^{-}SeCH_2CH=CHCH_2Se^{-}$ was previously unknown.

The infrared spectrum of complex **3** gave a peak at 1579 cm^{-1} due to the C=C stretch, compared to a value of 1450 cm^{-1} observed for the starting alkylating agent *cis*-$ClCH_2CH=CHCH_2Cl$. The ^{1}H NMR of **3** gave two signals due to the bridging butene group. A broad singlet was observed at 2.46 ppm from the four methylene protons, with ^{195}Pt-H coupling accounting for the broadness, however the ^{3}J(Pt-H) coupling was too small to be resolved. The signal assigned to the two alkene protons was a multiplet at 6.16 ppm, occurring almost as far downfield as the aromatic protons, but was too poorly resolved to be further analysed. The ^{31}P NMR spectrum of **3** gave the expected pattern, with a single central resonance and satellites due to ^{1}J(Pt-P) coupling (3033 Hz), typical of other alkylated derivatives of this general type.

Determination of the structure of **3** by X-ray crystallography confirmed the formation of the dithiolate-bridged species. The molecular structure of complex [Pt_2(μ-$SCH_2CH{=}CHCH_2S$)(PPh_3)$_4$](BPh_4)$_2$ **3** · $3CH_2Cl_2$ is shown in Figure 1, while selected bond lengths and angles are given in Table 1. The asymmetric unit consists of half the cation (lying on a two-fold axis), one BPh_4^- anion, one ordered CH_2Cl_2 molecule and half another disordered CH_2Cl_2. The structure confirms the presence of a diplatinum core bridged by a butenedithiolate (-$SCH_2CH{=}CHCH_2S$-) group, and the expected retention of the hinged structure (fold angle between the two PtS_2 planes, θ = 135.0°). Table 2 provides a comparison between the main structural features of complex **3** and those of the recently structurally characterised analogue, [Pt_2(μ-SC_2H_4S)(PPh_3)$_4$](PF_6)$_2$ **5** · $6CHCl_3$ · H_2O,[11] which contains an ethanedithiolate ($^-SCH_2CH_2S^-$) group, and provides the best comparison among known related structures. The fold angle between the PtS_2 planes in [Pt_2(μ-$SCH_2CH{=}CHCH_2S$)(PPh_3)$_4$](BPh_4)$_2$ **3** · $3CH_2Cl_2$ is 11° larger, and the S···S distance 0.134 Å longer than for **5**, presumably because the unsaturated organic moiety of **3** is more rigid, and pushes the two sulfurs apart. Unfortunately, accurate parameters for the butenedithiolate group could not be obtained, due to the disorder over two crystallographically equivalent sites, and therefore do not merit discussion. Analogous disorder about the S···S axis has been observed in the *ortho*-xylyl derivatives [Pt_2(μ-$ECH_2C_6H_4CH_2E$)(PPh_3)$_4$]$^{2+}$ (E = S[13] and Se[10]).

Complex **3** gave the parent dication as the base peak at *m/z* 778.5 in the ESI mass spectrum at low cone voltages (e.g. 20 V, Figure 2a), together with a very weak ion-pair [Pt_2(μ-$SCH_2CH{=}CHCH_2S$)(PPh_3)$_4BPh_4$]$^+$ at *m/z* 1876 (not illustrated). At higher cone voltages the intensity of the *m/z* 1876 ion increased, and a new dication at *m/z* 751 was formed, this ion having 50% relative intensity at a cone voltage of 50 V (Figure 2b), compared to the base peak of $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4]^{2+}$. Examination of the high resolution isotope pattern of this ion gives excellent agreement for $[Pt_2S_2(PPh_3)_4]^{2+}$ (**6a**) [observed *m/z* 751.121, calculated *m/z* for $C_{72}H_{60}P_4Pt_2S_2$ 751.1186] – clearly distinct from $[Pt_2(SH)_2(PPh_3)_4]^{2+}$, (calculated *m/z* 752.126) that would be formed by *diprotonation* of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.[15] Other weak ions observed at 50 V were $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_3]^{2+}$ (*m/z* 647), $[Pt_2S_2(PPh_3)_3]^{2+}$ (*m/z* 620), $[Pt_2S(PPh_3)_3]^{2+}$ (*m/z* 604) and the frequently-observed[16,17,18] cyclometallated ion $[Pt(C_6H_4PPh_2)(PPh_3)]^+$ (*m/z* 718).

It is proposed that the ion $[Pt_2S_2(PPh_3)_4]^{2+}$ contains a coordinated disulfide (S_2^{2-}) ion **6a**; dinuclear complexes of other metals, containing side-on bridging disulfide ligands are relatively common in the literature.[19,20] The related species containing diphosphine ligands, $[Pt_2(\mu\text{-}S_2)L_2]^{2+}$ [L = $Ph_2P(CH_2)_nPPh_2$; n = 2 or 3] **6b**[21] and diarsine ligand [L = $Ph_2As(CH_2)_2AsPh_2$] **6c**[22] have been observed in electrochemical studies, formed from two consecutive single-electron oxidations of the parent complexes $[Pt_2(\mu\text{-}S)_2L_2]$. Although such oxidised species were unable to be isolated, the electrochemical data were corroborated by means of theoretical investigations. The calculated redox potentials were consistent with the experimental data, and the formation of an S-S bond was predicted to result in pronounced folding of the $\{Pt_2S_2\}$ butterfly core.

The reaction suggests formation of $[Pt_2S_2(PPh_3)_4]^{2+}$ from $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_3]^{2+}$ by a *retro*-Diels-Alder reaction with the elimination of 1,3-butadiene, as shown in Scheme 1. Diels-Alder type [2 + 4] cycloaddition reactions involving metal sulfide complexes have also been reported in the literature.[23] For example the diruthenium complexes $[\{Ru(MeCN)_3L_2\}_2(\mu\text{-}S_2)]^{4+}$ or $[\{Ru(MeCN)L_2\}(\mu\text{-}Cl)_2(\mu\text{-}S_2)]^{2+}$ [L = $P(OMe)_3$] (both containing a bridging disulfide ligand), and related complexes react with 1,3-dienes.[24,25] In these reactions the metal-coordinated disulfide ligand acts as the dienophile (organic disulfides[26] and the sulfur allotrope S_{10}[27] have also been shown to be dienophiles), and this was taken as evidence for significant S-S double bond character in the disulfide ligand. Analogous chemistry has been observed for the diruthenium complex $[\{Ru(MeCN)L_2\}(\mu\text{-}Cl)_2(\mu\text{-}Se_2)]^{2+}$ [L = $P(OMe)_3$], containing a bridging diselenide ligand.[28] We are unaware of any *retro*-Diels-Alder reactions of this general type involving metal-coordinated disulfide or diselenide ligands.

For the selenolate complex **4**, the mass spectrometric fragmentation process was even more facile. Even at the very low cone voltage of 20 V - which in our experience only leads to fragmentation of the most labile systems - the analogous ion $[Pt_2(\mu\text{-}Se_2)(PPh_3)_4]^{2+}$ **7** (observed *m/z* 799.066, calculated *m/z* 799.063) was observed at *ca.* 12% relative intensity, and was the base peak at a slightly higher cone voltage (30 V). Figure 3 shows low resolution ESI mass spectra of **4** at cone voltages of 20 and 30 V, clearly demonstrating the extremely facile fragmentation of the parent ion, favoured in this case by the weaker C-Se bond. Attempts at trapping any $[Pt_2(\mu\text{-}Se_2)(PPh_3)_4]^{2+}$ (generated in solution from **4**) by addition of isoprene (2-methyl-1,3-butadiene) were unsuccessful.

Such a facile fragmentation at extremely low cone voltages has not been previously observed for other platinum-thiolate or -selenolate complexes derived from $\{Pt_2E_2\}$ cores. For example, the known complex $[Pt_2\{\mu\text{-}S(CH_2)_4S\}(PPh_3)_4]^{2+}$ [11] containing a *saturated* dithiolate ligand, gives no $[Pt_2S_2(PPh_3)_4]^{2+}$ at cone voltages up to 70 V, instead the parent cation (*m/z* 779.5) fragments primarily by loss of PPh_3 to give

$[Pt_2\{\mu\text{-}S(CH_2)_4S\}(PPh_3)_3]^{2+}$ (*m/z* 648), or at higher cone voltages, through cyclometallation giving $[Pt(C_6H_4PPh_2)(PPh_3)]^+$ (*m/z* 718). The analogous selenolate complex $[Pt_2\{\mu\text{-}Se(CH_2)_4Se\}(PPh_3)_4]^{2+}$ **[9]** (*m/z* 827.0) begins fragmentation to $[Pt_2\{\mu\text{-}Se(CH_2)_4Se\}(PPh_3)_3]^{2+}$ (*m/z* 696.0) only at cone voltages > 45 V, and only an extremely weak ion was observed at *m/z* 799, whose identity as $[Pt_2Se_2(PPh_3)_4]^{2+}$ could not be confirmed, as an isotope pattern could not be recorded. In systems containing a saturated hydrocarbon bridge, the *retro*-Diels-Alder reaction is precluded.

Experimental

Sodium tetraphenylborate (BDH) and *cis*-1,4-dichlorobut-2-ene (Aldrich) were used as supplied. The complexes $[Pt_2(\mu\text{-}E)_2(PPh_3)_4]$ **1**[3] and **2**[29] were prepared by the literature procedures from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S.9H_2O$ or sodium hydrogen selenide. The complex $[Pt_2\{\mu\text{-}S(CH_2)_4S\}(PPh_3)_4](PF_6)_2$ was synthesised by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $Br(CH_2)_4Br$ in methanol suspension, using a procedure modified from the literature.[11] The complex $[Pt_2\{\mu\text{-}S(CH_2)_4S\}(PPh_3)_4]^{2+}$ was generated in solution for MS analysis by reaction of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ with $Br(CH_2)_4Br$ in methanol.[9] Reactions were carried out without regard for exclusion of air, light or moisture.

Low resolution mass spectra were recorded on a VG Platform II instrument; routine spectra were recorded using a cone voltage of 20 V, while fragmentation processes were investigated by means of higher cone voltages (up to 90 V). High resolution mass spectra were recorded on a Bruker Daltonics MicrOTOF instrument calibrated using a sodium formate solution. Samples (*ca.* 0.1 mg) were dissolved in dichloromethane (1 drop) and diluted with methanol prior to analysis using a methanol mobile phase. NMR spectra were recorded at 300 (^{1}H) and 121.5 (^{31}P) MHz in $CDCl_3$ solution.

Synthesis of $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ 3

To a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (269 mg, 0.179 mmol) in methanol (30 mL) was added *cis*-$ClCH_2CH{=}CHCH_2Cl$ (12 drops, excess) and the reaction mixture stirred at room temperature. The suspension rapidly changed from an orange cloudy colour to a clear yellow solution. After 1 hour stirring, $NaBPh_4$ (200 mg, 0.585 mmol) was added, resulting in the formation of a white precipitate which was filtered, washed successively with distilled water (10 mL), methanol (10 mL), and petroleum spirits (10 mL) and dried under vacuum to give $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** as an off-white powder (299 mg, 76%). Found: C, 67.4; H, 5.1. $C_{124}H_{106}B_2P_4Pt_2S_2$ requires C, 67.8; H 4.9%. M.p. 155-158 °C. IR (KBr disc): ν(C=C), 1579 cm^{-1}. ESI MS: (Cone voltage 20 V) *m/z* 778.6 ($[M]^{2+}$, 100%). ^{31}P-{^{1}H} NMR, δ 20.0 [4P, *s*, ^1J(Pt-P) 3033 Hz]. ^{1}H NMR, δ 7.59-6.75 (80H, *m*, PPh_3), 6.16 (2H, *m*, CH), 2.46 (4H, *s*, br, SCH_2).

Synthesis of $[Pt_2(\mu\text{-}SeCH_2CH{=}CHCH_2Se)(PPh_3)_4](BPh_4)_2$ 4

To a suspension of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ (230 mg, 0.125 mmol) in methanol (30 mL) was added *cis*-$ClCH_2CH{=}CHCH_2Cl$ (10 drops, excess) and the reaction mixture stirred at room temperature for 110 min., giving a deep brown solution. After filtration to remove a small amount of dark insoluble matter, solid $NaBPh_4$ (200 mg, 0.585 mmol) was added to the filtrate, giving a brown precipitate. The solid was filtered, washed with methanol (10 mL), water (10 mL), methanol (10 mL) and diethyl ether (10 mL) and dried *in vacuo* to give **4** as a brown powder (219 mg, 66%). ESI MS: (Cone voltage 20 V) *m/z* 826 ($[M]^{2+}$, 100%). A sample for elemental microanalysis was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution, giving dark brown crystals which analysed as the dichloromethane solvate. Found: C, 63.7; H, 4.9. $C_{125}H_{108}B_2Cl_2P_4Pt_2Se_2$ requires C, 63.2; H, 4.6%.

X-ray structure determination of $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ 3 · $3CH_2Cl_2$

Colourless plates of the dichloromethane solvate were grown by vapour diffusion of diethyl ether into a dichloromethane solution of complex **3**. Intensity data and unit cell dimensions were obtained on a Bruker SMART CCD Diffractometer at the University of Auckland.

The structure was solved by direct methods option of SHELXS-97[30] and refined routinely. The buten-di-yl bridge was disordered over two sites, related by the crystallographic 2-fold axis. There was one well-defined CH_2Cl_2 molecule in the lattice, together with several residual peaks that were associated with disordered solvent (probably another half CH_2Cl_2 and an ether molecule), but these could not be modelled sensibly. Hydrogen atoms were included in calculated positions except for those on the buten-di-yl group and the disordered solvent. Full-matrix least-squares refinement (SHELXL-97[31]) was based on F_o^2 with all non-hydrogen atoms anisotropic converged with $R_1 = 0.0535$ ($I \geq 2\sigma I$), $wR_2 = 0.1376$ (all data), GoF 1.069. A final difference map showed no feature greater than 3.576 and -3.029 e $Å^{-3}$. All calculations were carried out by the SHELXS-97 suite of programmes.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. XXX. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the University of Waikato and the National University of Singapore for financial support of this work, and Pat Gread for assistance with high resolution mass spectrometry. Dr. Tania Groutso (University of Auckland) is thanked for collection of the X-ray data set.

Table 1 Selected bond lengths (Å) and bond angles (°) for [Pt_2(μ-$SCH_2CH=CHCH_2S$)(PPh_3)$_4$](BPh_4)$_2$ **3** · $3CH_2Cl_2$ (Estimated standard deviations are in parentheses)

Bond distances (Å)			
Pt(1)-S(1	2.3700(2)	Pt(1)-S(1)#1	2.3596(2)
Pt(1)-P(1)	2.2971(2)	Pt(1)-P(2)	2.2795(2)
S(1)-C(1)	1.833(1)		
Mean			
P(1)-C(phenyl)	1.826(7)	P(2)-C(phenyl)	1.819(7)
Bond angles (°)			
S(1)-Pt(1)-S(1)#1	81.21(8)	Pt(1)-S(1)-Pt(1)#1	89.06(6)
P(1)-Pt(1)-S(1)	86.83(6)	P(2)-Pt(1)-S(1)	173.96(7)
P(1)-Pt(1)-S(1)#1	168.00(7)	P(2)-Pt(1)-S(1)#1	92.75(7)
P(2)-Pt(1)-P(1)	99.22(6)	C(1)-S(1)-Pt(1)	104.8(4)
C(1)-S(1)-Pt(1)#1	105.8(5)		
Mean			
Pt(1)-P(1)-C(phenyl)	113(2)	Pt(1)-P(2)-C(phenyl)	113(3)

Table 2 Comparison of the geometric parameters [distances (Å) and angles (°)] for $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** · $3CH_2Cl_2$ and $[Pt_2(\mu\text{-}SC_2H_4S)(PPh_3)_4](PF_6)_2$ **5** · $6CHCl_3$ · H_2O

	3[a]	**5**[b]
Mean Pt-SR	2.365(18)	2.365(4)
Mean Pt-P	2.288(18)	2.284(6)
Pt---Pt	3.317	3.265
S---S	3.078	2.944
Mean Pt-S-Pt	89.1(6)	87.3(7)
Mean S-Pt-P	89.8(7)	91.7(2)
Mean S-Pt-S	81.2(8)	76.9(2)
Dihedral angle[c]	135.0	123.8

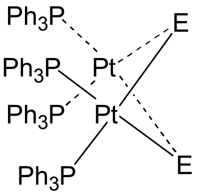
[a] This work

[b] From ref. 11, CSD refcode IVIDOG

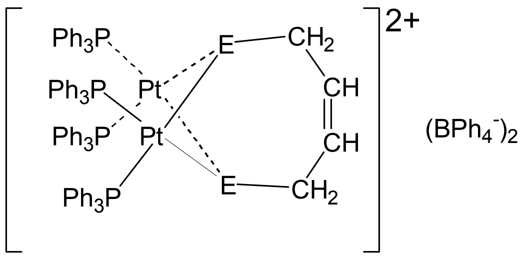
[c] Dihedral angle between the two PtS_2 planes

Table 3 Collection and crystal data for $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** · $3CH_2Cl_2$

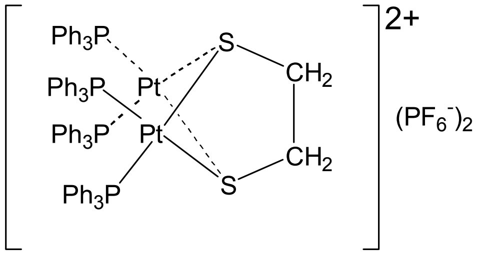
Crystal size	0.28 x 0.22 x 0.10 mm
Total reflections	37516
Unique reflections	10049 [R_{int} = 0.0308]
Range	1.49 to 26.39°
Absorption correction	Empirical
Crystal Data	
Formula	$C_{127}H_{112}B_2Cl_6P_4Pt_2S_2$
M_r	2450.67
Unit cell, space group	Monoclinic, C2/c
Unit cell dimensions	a = 34.3019(4) Å b = 14.8006(1) Å c = 27.8049(4) Å β = 127.129(1)°
Volume (U)	11254.6(2) Å^3
Z	4
Density (D_c)	1.446 g cm^{-3}
F(000)	4936
μ(Mo-Kα)	2.769 mm^{-1}



1, E = S
2, E = Se



3, E = S
4, E = Se



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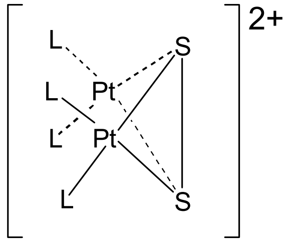
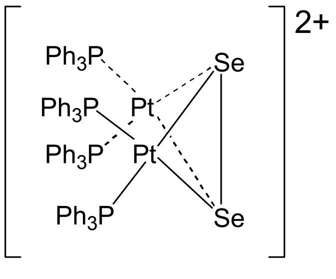


6a, L = PPh_3
6b, L-L= $Ph_2P(CH_2)_nPPh_2$ (n = 2,3)
6c, L-L = $Ph_2As(CH_2)_2AsPh_2$



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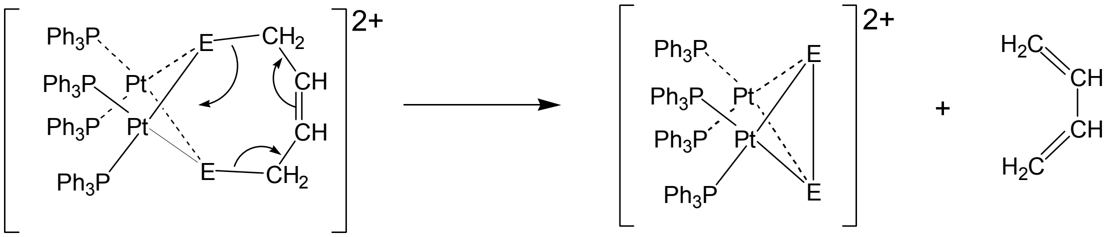

E = S or Se

Scheme 1

Captions for Figures

Figure 1 Molecular structure of the complex $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** · $3CH_2Cl_2$ showing the atom numbering scheme, with only the *ipso* carbon atoms of the PPh_3 ligands shown. The cation is disordered about a 2-fold axis which affects the $CH_2CH{=}CHCH_2$ bridge; only one of the disordered conformations is shown. Thermal ellipsoids are shown at the 50% probability level. The CH_2Cl_2 solvent molecules and the BPh_4^- counterions have been omitted for clarity.

Figure 2 Positive-ion ESI mass spectra of $[Pt_2(\mu\text{-}SCH_2CH{=}CHCH_2S)(PPh_3)_4](BPh_4)_2$ **3** at cone voltages of (a) 20 V and (b) 50 V showing fragment ions formed by loss of 1,3-butadiene and/or triphenylphosphine. The peak marked * at *m/z* 718 is due to $[Pt(C_6H_4PPh_2)(PPh_3)]^+$.

Figure 3 Positive-ion ESI mass spectra of $[Pt_2(\mu\text{-}SeCH_2CH{=}CHCH_2Se)(PPh_3)_4](BPh_4)_2$ **4** at cone voltages of (a) 20 V and (b) 30 V showing facile formation of $[Pt_2(\mu\text{-}Se_2)(PPh_3)_4]^{2+}$ by loss of 1,3-butadiene from $[Pt_2(\mu\text{-}SeCH_2CH{=}CHCH_2Se)(PPh_3)_4]^{2+}$.

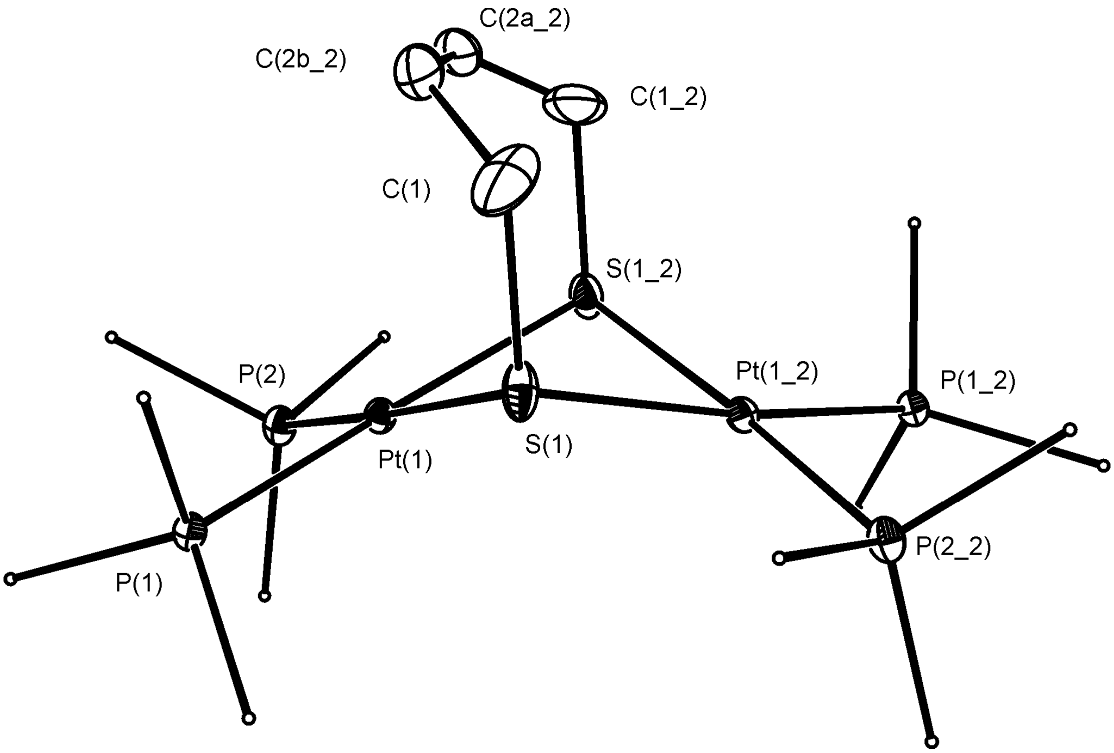

Figure 1

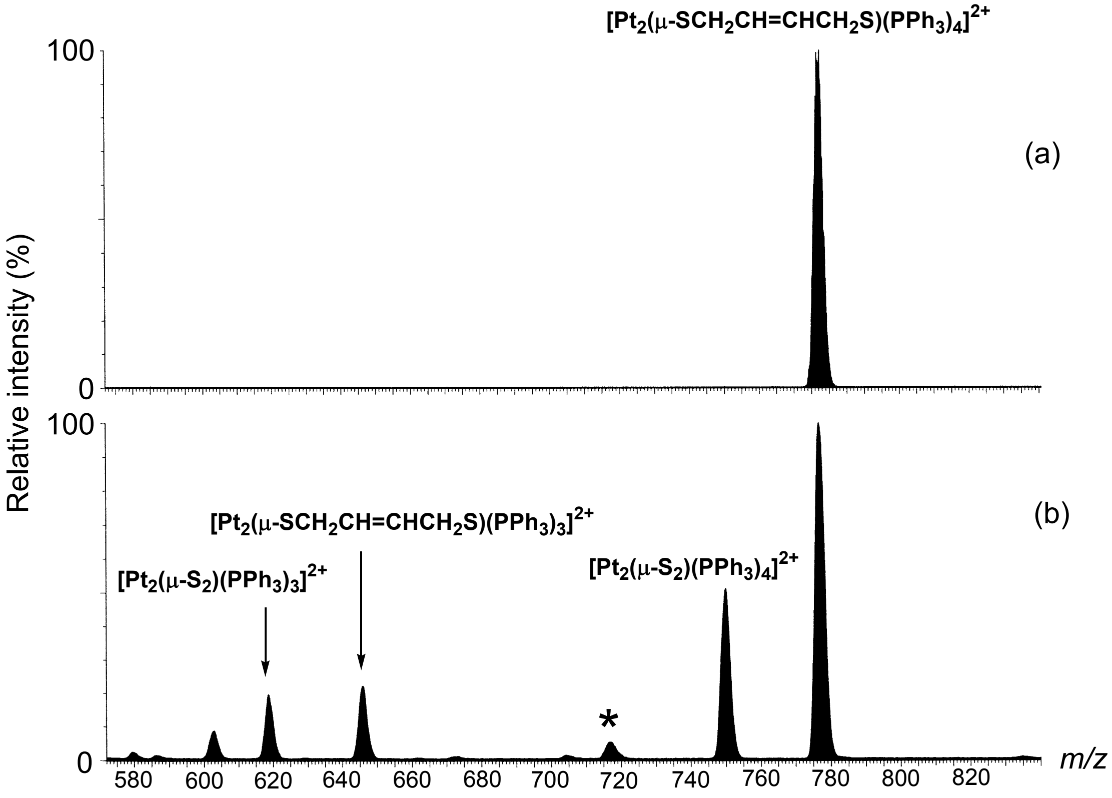
[Pt$_2$(μ-SCH$_2$CH=CHCH$_2$S)(PPh$_3$)$_4$]$^{2+}$
100
(a)
0
Relative intensity (%)
100
(b)
[Pt$_2$(μ-SCH$_2$CH=CHCH$_2$S)(PPh$_3$)$_3$]$^{2+}$
[Pt$_2$(μ-S$_2$)(PPh$_3$)$_3$]$^{2+}$
[Pt$_2$(μ-S$_2$)(PPh$_3$)$_4$]$^{2+}$
*
0
580
600
620
640
660
680
700
720
740
760
780
800
820
m/z

Figure 2

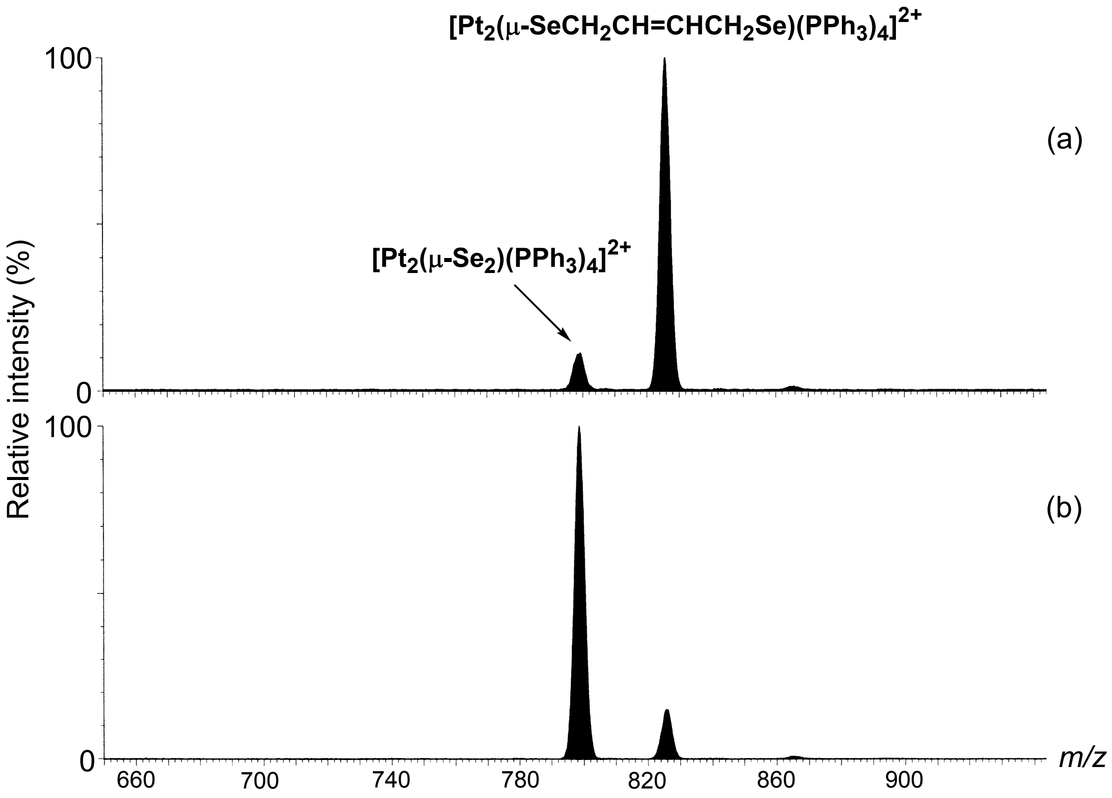
[Pt$_2$(μ-SeCH$_2$CH=CHCH$_2$Se)(PPh$_3$)$_4$]$^{2+}$
[Pt$_2$(μ-Se$_2$)(PPh$_3$)$_4$]$^{2+}$
(a)
(b)
Relative intensity (%)
100
0
100
0
660
700
740
780
820
860
900
m/z

Figure 3

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