

Stepwise Sulfuration of the Terminal Phosphido Complex *trans*-[PtCl(PHCy₂)₂(PCy₂)]: Synthesis of [Pt(κ²S,S'-PS₂Cy₂)(PHCy₂)₂]Cl and [Pt(κ²S,S'-PS₂Cy₂){κP-P(S)Cy₂}(PHCy₂)] and Crystal Structure of [Pt(κ²-S,S-PCy₂S₂)(κ-S-PCy₂S₂)(PHCy₂)]

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The terminal phosphido complex *trans*-[PtCl(PHCy₂)₂(PCy₂)] (**1**) has been prepared, exploiting the reversibility of the reaction with HCl, by action of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) on [PtCl(PHCy₂)₃]Cl, and its reactivity towards elemental sulfur studied. The first product obtained by reaction of **1** with 1 equiv. of sulfur is *trans*-[PtCl(PHCy₂)₂{κP-P(S)Cy₂}] (**2**), which rapidly isomerises in halogenated solvents into *cis*-[PtCl(PHCy₂)₂{κP-P(S)Cy₂}] (**3**). Further addition of sulfur causes the formation of a mixture of [Pt(κ²S,S'-PS₂Cy₂)-

(PHCy₂)₂]Cl (**4**) and [Pt(κ²S,S'-PS₂Cy₂){κP-P(S)Cy₂}(PHCy₂)] (**5**), which could be selectively synthesised; the first upon sulfuration of pure **3** and the second by reaction of **4** with 1 equiv. of sulfur in the presence of DBU. Complex **5** can be further sulfurated to [Pt(κ²S,S'-PCy₂S₂)(κS-PCy₂S₂)(PHCy₂)] (**6**), which is fluxional in solution and was also characterised by single-crystal X-ray diffraction.

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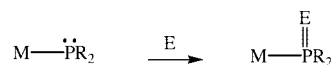
Introduction

Terminal phosphides are interesting albeit rare ligands, the reactivity of which depends mainly on the characteristics of the lone pair on the phosphorus atom. The first terminal phosphido complexes were prepared in 1968 by reaction of CpFe(CO)₂⁻ or CpMo(CO)₃⁻ with P(C₆F₅)₂Cl to give Cp(CO)₂Fe[P(C₆F₅)₂] and Cp(CO)₃Mo[P(C₆F₅)₂], respectively.^[1] From then on, a number of terminal phosphido complexes have been prepared mainly by two routes: (i) the reaction of diorganometal phosphides with a metal species;^[2–16] (ii) the deprotonation of a coordinated phosphane bearing at least a P–H bond by means of an appropriate base {1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),^[17–19] methoxide, OH⁻,^[20–24] *t*BuO⁻,^[25–29] [N(SiMe₃)₂]⁻,^[30–32] NEt₃,^[33] BuLi^[34]} that, in some instances, was previously coordinated onto the metal atom.^[35–39]

The reactivity of terminal phosphido complexes is determined by the presence of the lone pair on the phosphorus atom, which renders such molecules highly nucleophilic.

Such high nucleophilicity has been exploited for the synthesis of phosphido-bridged heterodimetallic species,^[40] and is also responsible for the ease of protonation of the three-coordinate phosphorus atom^[13,20,41–43] as well as for its reactivity with MeI.^[41,43–47]

The typical reaction of coordinated terminal phosphides with chalcogens transforms the trivalent into a pentavalent phosphorus atom bound to the chalcogen as in Scheme 1.



Scheme 1. Typical addition of chalcogens E to coordinated terminal phosphides.

Such reactivity is shown by Ir(CO)(Cl)₂(PEt₃)₂(PF₂) (reaction with O₂, S₈ or Se),^[48] (η⁵-C₅H₅)Ru(PEt₃)₂(PPh₂) (reaction with O₂),^[25] (η⁵-C₅H₅)Re(NO)(PPh₃)₂(PR₂) (R = Ph, *t*Bu, reaction with O₂),^[28] (η⁵-C₅H₅)Fe(CO)₂[P(CF₃)₂] (reaction with S₈),^[49] (η⁵-C₅H₅)M(CO)₃(PCL₂) (M = Cr, reaction with S₈; M = W, reaction with S₈, Se)^[50] and (η⁵-C₅H₅)M(CO)₂(L)(PPh₂) (L = CO or PMe₃, M = Mo, reaction with S₈; M = W, reaction with S₈, Se).^[41,51]

We have recently described the synthesis and characterisation of *trans*-[PtCl(PHCy₂)₂(PCy₂)Cl] (**1**) obtained by reaction of *cis*-PtCl₂(PHCy₂)₂ with LiPCy₂.^[52] Complex **1** is stable under inert gases but reacts promptly with dry dioxygen to give the hydrogen-bound bis(phosphinito) complex [PtCl(PHCy₂)₂{P(O)Cy₂}₂H]^[53] and with hydrogen peroxide to give *trans*-[PtCl(PHCy₂)₂{κP-P(O)Cy₂}Cl].^[54]

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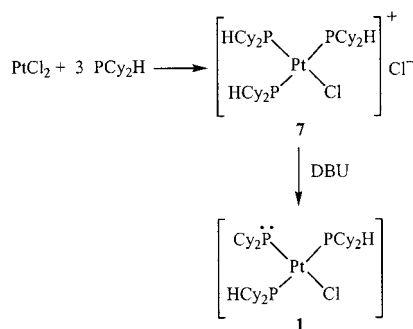
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Herein we describe the stepwise sulfuration of **1** leading to the compounds *trans*-[PtCl(PHCy₂)₂{κ*P*-P(S)Cy₂}] (**2**), *cis*-[PtCl(PHCy₂)₂{κ*P*-P(S)Cy₂}Cl] (**3**), [Pt(κ²*S,S'*-PS₂Cy₂)-(PHCy₂)₂]Cl (**4**), [Pt(κ²*S,S'*-PCy₂S₂)(PHCy₂){κ*P*-P(S)Cy₂}] (**5**) and [Pt(κ²*S,S'*-PCy₂S₂)(κ*S*-PCy₂S₂)(PHCy₂)] (**6**).

Results and Discussion

Reversible Protonation of **1**

Reaction of *trans*-[PtCl(PHCy₂)₂(PCy₂)] (**1**) with gaseous HCl results in the fast and complete protonation of the coordinated terminal phosphide with formation of the cationic Pt^{II} complex [PtCl(PHCy₂)₃]Cl (**7**). In order to test the reversibility of the protonation reaction of **1**, a toluene suspension of **7** was treated with DBU, leading to the quantitative formation of **1** as the only soluble product, so that the reaction sequence shown in Scheme 2 represents the most convenient way for preparing **1**.

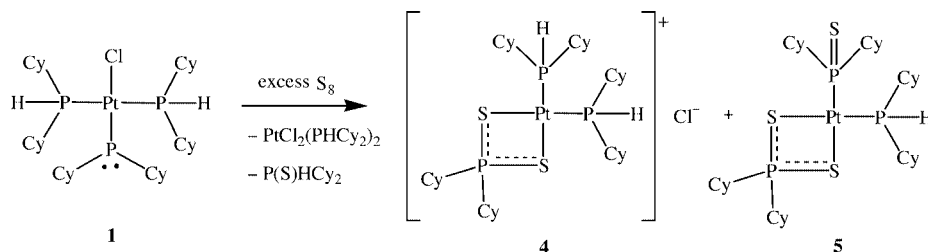


Scheme 2.

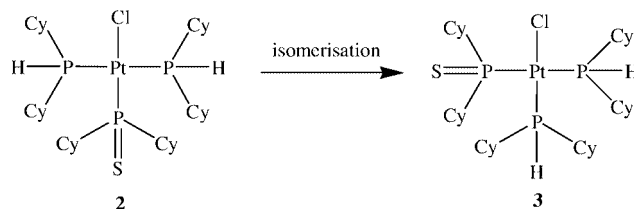
Reaction with S₈

Reaction of **1** with sulfur carried out in toluene at room temperature using an S/Pt molar ratio of 1.0 resulted in the formation of the *P*-bound thiophosphinito complex *trans*-[PtCl(PHCy₂)₂{κ*P*-P(S)Cy₂}] (**2**).^[54] Dissolving **2** in halogenated solvents, the irreversible isomerisation into the thermodynamically favoured *cis* complex **3** took place as indicated in Scheme 3. This isomerisation was completed in 5 min by heating the reaction mixture at 40 °C.

When an excess of sulfur (S/Pt molar ratio of 8) was treated with **1** in toluene, the reaction led, after 1 h, to a mixture of two new sulfur-containing platinum complexes, **4** and **5**, along with *cis*-PtCl₂(PHCy₂)₂ and dicyclohexylphosphane sulfide P(S)HCy₂ (Scheme 4).



Scheme 4.



Scheme 3.

Complex **4**, which incorporates two S atoms, showed two ³¹P{¹H} NMR signals in CDCl₃ at δ = 136.6 (²*J*_{P,Pt} = 151 Hz) and δ = 2.0 (¹*J*_{P,Pt} = 3048 Hz), which support a structure in which the sulfur atoms are bound to the phosphide P atom and chelate the platinum atom. The remaining coordination sites are occupied by two PHCy₂ ligands, mutually *cis*. Accordingly, the ¹⁹⁵Pt{¹H} NMR spectrum in CDCl₃ consists of a triplet (¹*J*_{Pt,P} = 3048 Hz) of doublets (²*J*_{Pt,P} = 151 Hz) centred at δ = −4596 ppm. Compound **4** can be therefore formulated as [Pt(κ²*S,S'*-PS₂Cy₂)-(PHCy₂)₂]Cl, a dithiophosphinato complex of Pt^{II}. ESI-MS analysis confirmed this formulation by comparison of the measured isotope pattern centred at 852.35 Da with that calculated on the basis of the natural abundances.

Recording the ³¹P{¹H} and ¹H NMR spectra of **4** in different solvents, we noticed that the resonance of (PS₂Cy₂) remained almost unchanged (δ = 134–138 ppm), whilst the chemical shift of the coordinated PHCy₂ ligand ranged from δ = −5.9 to 10.0 ppm (³¹P) and from δ = 4.3 to 6.8 ppm (¹H) (Table 1).

Table 1. ³¹P{¹H} and ¹H NMR spectroscopic data of **4** in different solvents.

	PS ₂	PH	PH
C ₆ D ₆	134	−5.9	6.83
CDCl ₃	137	2.0	5.15
CD ₂ Cl ₂	139	9.3	4.32
CD ₃ CN	140	10.0	4.43

Such behaviour could be explained invoking a hydrogen bond interaction between the P–H of the cationic complex and the chloride anion, an interaction already found for [PtCl(PCy₂H)₃]Cl.^[54] In order to confirm such a hypothesis we have compared the ³⁵Cl NMR spectra recorded in CD₂Cl₂ before and after the addition of CD₃OD as a hydrogen bond breaker. No signal could be observed in the ³⁵Cl NMR spectrum recorded in CD₂Cl₂, as expected for a

quadrupolar nucleus surrounded by an asymmetric electron cloud. However, the addition of a few drops of CD_3OD caused the rupture of the ion pairs, leaving the chloride anion in a nearly symmetric solvation sphere, and permitted the observation of a broad ^{35}Cl NMR signal centred at $\delta = -18$ ppm after the same number of scans (Figure 1).

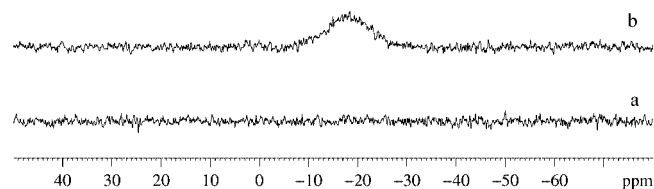


Figure 1. ^{35}Cl NMR spectrum of **4** (39 MHz, 295 K); a) in CD_2Cl_2 ; b) after the addition of a few drops of CD_3OD .

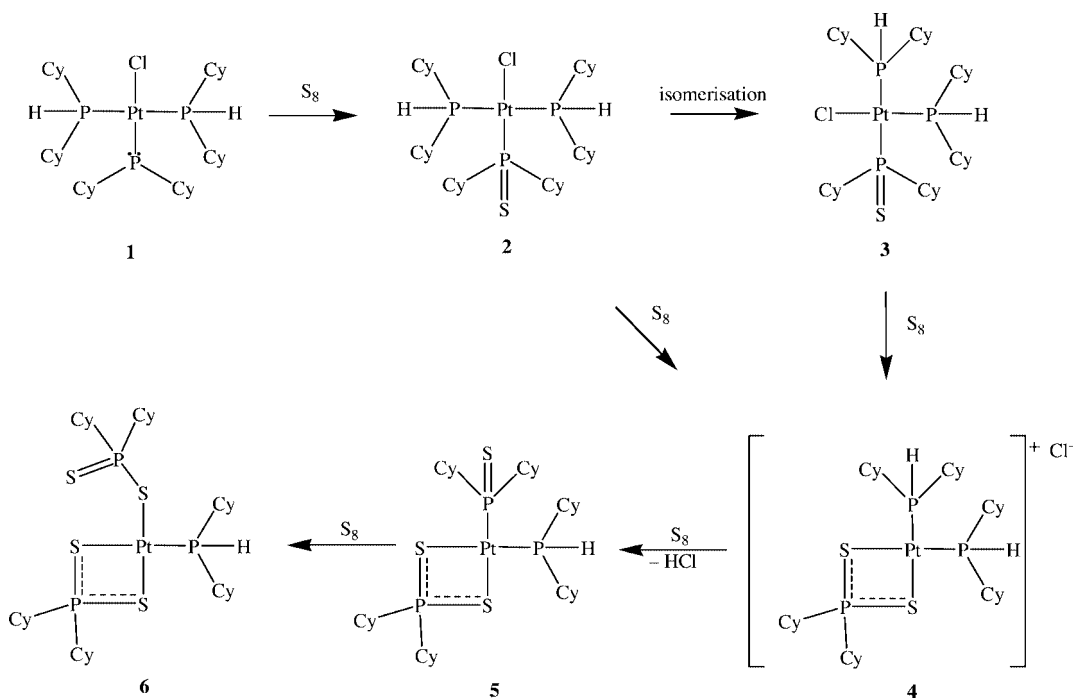
Pure **4** could be isolated from the reaction of **3** with 1 equiv. S_8 in dichloromethane at room temperature and showed IR bands ascribable to PH (2272 cm^{-1}) and PS_2 stretchings (591 , 553 cm^{-1}).

Complex **5** incorporates three atoms of S and gives in C_6D_6 three $^{31}\text{P}\{^1\text{H}\}$ NMR signals flanked by ^{195}Pt satellites

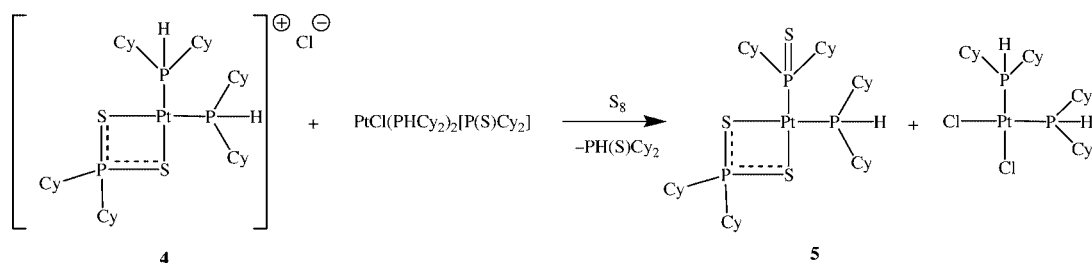
at $\delta = 127.2$, 48.4 and 38.9 ppm. Of these, that at $\delta = 38.9$ ppm can be attributed to a coordinated PHCy_2 ligand (proton-coupled spectrum gave $^1J_{\text{P,H}} = 424\text{ Hz}$) and that at $\delta = 48.4$ ppm can be attributed, on the basis of its chemical shift and $^1J_{\text{P,Pt}}$ value (2977 Hz), to a *P*-bound P(S)Cy_2 ligand *cis* to PHCy_2 . The remaining signal at $\delta = 127.2$ ppm is flanked by satellites from which a $^2J_{\text{P,Pt}}$ value of 137 Hz was extracted and can be attributed to a chelating dithiophosphinate ligand, PS_2Cy_2 . The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum consists of a doublet of doublets of doublets centred at $\delta = -4522$ ppm and the proposed structure for **5** is $[\text{Pt}(\kappa^2\text{S,S'}-\text{PS}_2\text{Cy}_2)\{\kappa\text{P-P(S)Cy}_2\}(\text{PHCy}_2)]$.

Complex **5** could be obtained in high yield by treating **4** with S_8 in the presence of DBU as proton scavenger, and showed P=S (of the thiophosphinite ligand) and PH IR stretchings at 597 and 2366 cm^{-1} respectively. Comparison of the IR features of complexes **2**, **4** and **5** allowed us to assign the νPS_2 bands of **5** at 556 ($\nu_{\text{sym.}}$) and 597 ($\nu_{\text{asym.}}$). Such assignments are consistent with those reported for R_2PS_2 complexes.^[55–57]

A mechanism for the reaction of **1** with excess sulfur in CH_2Cl_2 is depicted in Scheme 5. The initially formed **2** par-



Scheme 5. Stepwise sulfuration of **1**.



Scheme 6.

tially isomerises into **3**. Both **2** and **3** can incorporate one more S atom yielding **4**. The subsequent sulfuration of **4** into **5** requires a proton scavenger, as confirmed by the lack of reaction between **4** and S₈ in the absence of DBU.

In the reaction medium, possible proton scavengers are the thiophosphinite complexes **2** and **3**, whose products of HCl formal addition are P(S)HCy₂ and Pt(PHCy₂)₂Cl₂, effectively found as byproducts (Scheme 6).

Compound **5** reacted slowly (several weeks) with elemental sulfur in toluene solution to give the bis(dithiophosphinato)phosphane product Pt(κ^2 S,S'-PCy₂S₂)(κ S-PCy₂S₂)-(PHCy₂) (**6**, Scheme 5), which precipitated from the reaction medium.

Complex **6** showed IR bands in the PS region (650–500 cm⁻¹) attributable to bidentate (620 and 527 cm⁻¹) and unidentate (598 and 559 cm⁻¹) PCy₂S₂ ligands (Table 2).^[55,58]

Table 2. Characteristic IR bands in the PS region.

Complex	P(S)Cy ₂ ν	PS ₂ Cy ₂ Bidentate		PS ₂ Cy ₂ Monodentate	
		$\nu_{\text{sym.}}$	$\nu_{\text{asym.}}$	$\nu_{\text{sym.}}$	$\nu_{\text{asym.}}$
2	579				
3	577				
4		553	591		
5	597	556	597		
6		559	598	527	620
8		561	595		

The ³¹P{¹H} NMR spectrum of **6** in C₆D₆ showed three resonances at δ = 124.8, 81.8 and 2.5 ppm ascribable to bidentate PCy₂S₂, unidentate PCy₂S₂ and PHCy₂, respectively. Complexes of the general formula M(PS₂)₂(P) (where PS₂ represents a dithiophosphinato and P a tertiary phosphane) have long been known as the reaction products between M(PS₂)₂ and P in polar solvents^[55] and, in fact, we could prepare **6** in high yield also starting from [Pt(κ^2 S,S'-PCy₂S₂)₂] (**8**) and 1 equiv. of PHCy₂ in toluene.

As already noticed for related complexes,^[59–61] dynamic ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR experiments (Figures 2 and

3) demonstrated the existence, for compound **6**, of a rapid interchange of bidentate and unidentate dithiophosphinates (Scheme 7).

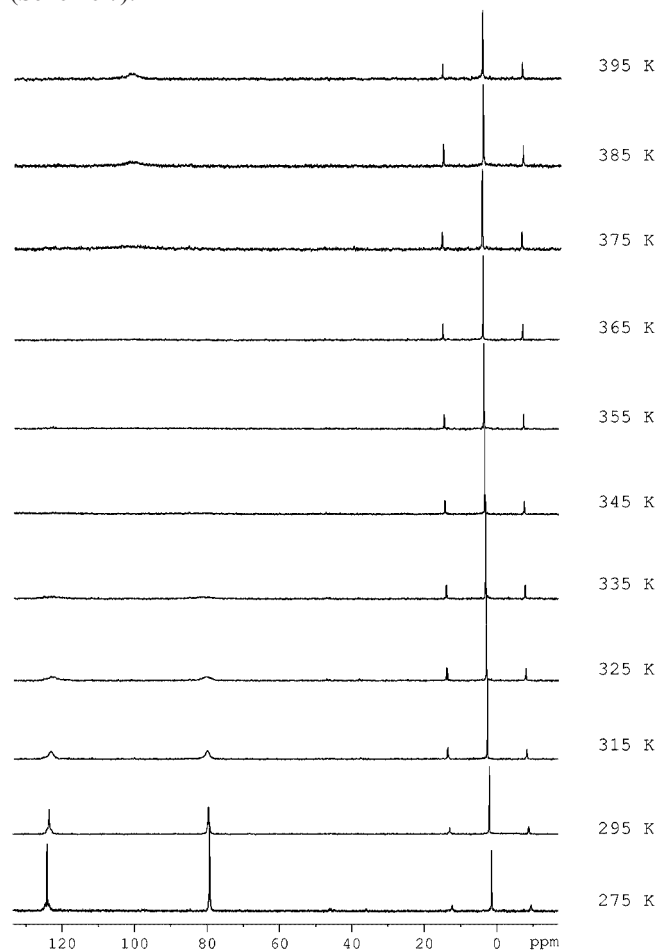


Figure 2. Variable-temperature ³¹P{¹H} NMR spectra of **6** in 1,2-dichlorobenzene.

Accordingly, the ³¹P EXSY experiment showed an intense exchange cross-peak between the signals at δ = 124.8 ppm (bidentate PS₂Cy₂) and δ = 81.8 ppm (uniden-

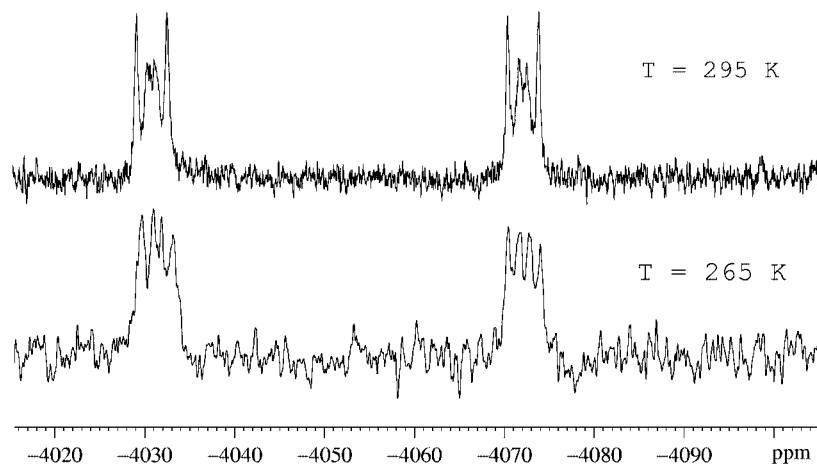
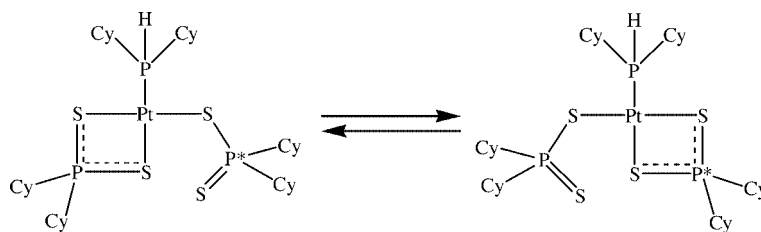
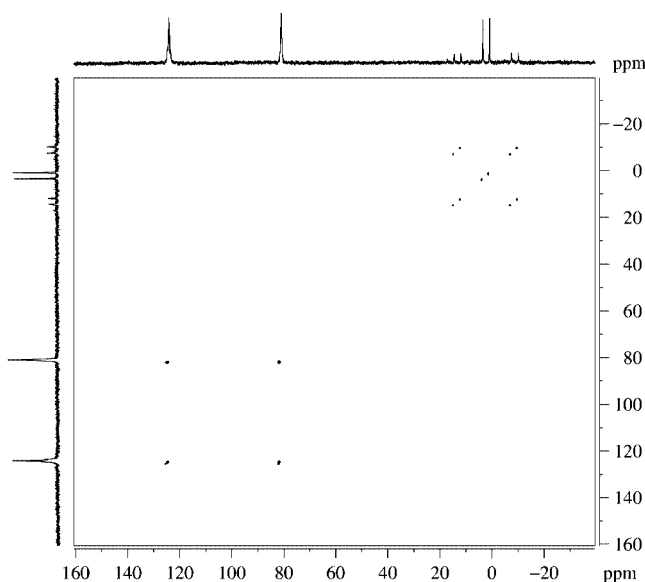


Figure 3. Variable-temperature ¹⁹⁵Pt{¹H} NMR spectra of **6** in CDCl₃.



Scheme 7.

tate PS_2Cy_2) (Figure 4). Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra allowed us to calculate an activation $\Delta G^\ddagger$ value of 59 ± 1 kJ/mol. Such a value is fully consistent with those obtained in the related complexes $\text{Pt}(\text{Me}_2\text{PS}_2)(\text{PPh}_3)$ ($\Delta G^\ddagger = 56$ kJ/mol),^[60,62] $\text{Pt}(\text{Me}_2\text{PS}_2)(\text{PPh}_2\text{C}_6\text{F}_5)$ ($\Delta G^\ddagger = 55$ kJ/mol)^[62] and $\text{Pt}\{(\text{OEt})_2\text{PS}_2\}(\text{PPh}_3)$ ($\Delta G^\ddagger = 52$ kJ/mol).^[60,61]

Figure 4. ^{31}P EXSY spectrum of **6** in C_6D_6 .

Yellow crystals of **6** suitable for single-crystal X-ray diffraction were deposited upon slow concentration of a toluene solution. Complex **6** crystallises in the monoclinic space group $P2_1/c$ with one complex molecule in the asymmetric unit. The molecular structure, depicted in Figure 5, is characterised by a distorted square-planar geometry around the Pt atom. The Pt atom is bound to two PCy_2S_2^- ligands, one of which is chelating whereas the other one is unidentate. The Pt–S(1) [2.3419(16) Å] and Pt–S(3) [2.3024(15) Å] bond lengths are shorter than Pt–S(2) [2.4134(15) Å], as expected on the basis of the different *trans* influences of P and S. The structure of **6** resembles that found for the related complex $\text{Pt}[(\text{OEt})_2\text{PS}_2]_2(\text{PPh}_3)$.^[61] Both complexes show one uncoordinated sulfur atom at a $\text{Pt}\cdots\text{S}$ distance of more than 4 Å. The interaction between H(3) and the sulfur atom S(4) not coordinated to Pt is certainly weak: the interatomic distance amounts to 2.91 Å, to be compared with several intra- and

intermolecular C–H $\cdots$ S contacts in the range between 2.8 and 3.0 Å. Selected bond lengths and angles are listed in Table 3.

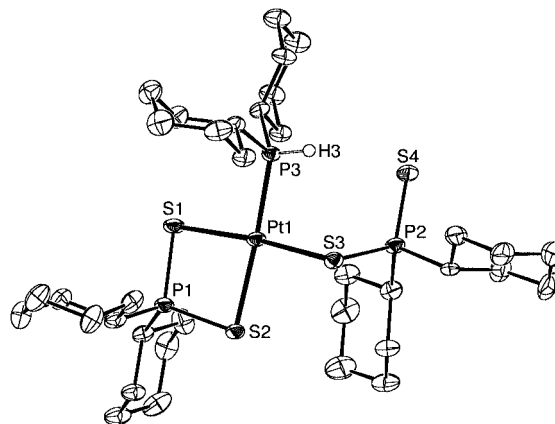


Figure 5. Displacement ellipsoid plot of **6**.^[63] Ellipsoids are scaled to 50% probability. Only the phosphorus-bonded hydrogen atom is shown with arbitrary radius; the other H atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for **6**.

Pt(1)–P(3)	2.2136(15)
Pt(1)–S(3)	2.3024(15)
Pt(1)–S(1)	2.3419(16)
Pt(1)–S(2)	2.4134(15)
S(1)–P(1)	2.024(2)
S(2)–P(1)	2.017(2)
S(3)–P(2)	2.062(2)
S(4)–P(2)	1.964(2)
P(3)–Pt(1)–S(3)	91.20(5)
P(3)–Pt(1)–S(1)	93.89(5)
S(3)–Pt(1)–S(1)	173.92(5)
P(3)–Pt(1)–S(2)	176.44(6)
S(3)–Pt(1)–S(2)	90.58(5)
S(1)–Pt(1)–S(2)	84.16(5)
P(1)–S(1)–Pt(1)	86.17(7)
P(1)–S(2)–Pt(1)	84.44(7)
P(2)–S(3)–Pt(1)	108.61(8)
P(3)–H(3)–S(4)	136

Conclusion

We have demonstrated that the sulfuration of complex **1** occurs stepwise, and involves first the terminal phosphide giving rise to the formation of complexes **2**, **3** and **4** and

subsequently one of the coordinated PHCy₂ ligands with formation of products **5** and **6**.

Experimental Section

General: All manipulations were carried out under pure argon, using freshly distilled and oxygen-free solvents. Dicyclohexylphosphane (Strem) and PtCl₂ (Acros) were used as received. Complexes **2** and **7** were prepared as described elsewhere.^[54] Melting points were determined with Gallenkamp equipment and are uncorrected. C, H and S elemental analyses were carried out with a Eurovector CHNS-O Elemental Analyser. Cl elemental analysis was performed by potentiometric titration using a Metrohm DMS Titrino. Infrared spectra were recorded with a Bruker Vector 22 spectrometer. All the ESI-MS spectra were recorded with an Agilent LC-MS SL series instrument adopting the following general conditions: electrospray, positive ions, flow rate 0.200 mL/min, drying gas flow 4.0 L/min, nebuliser pressure 25 psi, drying gas temperature 300 °C, capillary voltage 4000 V, mass range *m/z* = 400–1400. CH₂Cl₂ solutions of the complexes were infused with a Cole-Parmer syringe pump. The isotopic pattern was calculated by the Isotope Pattern Viewer software available free of charge from the www.surfacespectra.com Web site. NMR spectra were recorded with a BRUKER Avance DRX400 spectrometer; frequencies are referenced to Me₄Si (¹H and ¹³C), 85% H₃PO₄ (³¹P), H₂PtCl₆ (¹⁹⁵Pt) and aqueous 1 M NaCl (³⁵Cl). The reported temperatures of variable-temperature NMR experiments were calibrated from the chemical shift difference of the signals in the ¹H NMR spectrum of a standard sample of methanol. The uncertainty in the Δ*G*[‡]_{Tc} value (±1 kJ/mol) was estimated on the basis of the assumption that there is an error of 5 °C in the determination of the coalescence temperature. 2D ³¹P EXSY spectra were recorded with a gradient-selected NOESY pulse program from Bruker (noesygpph) with a mixing time of 10 or 50 ms and a relaxation delay of 1.0 s. The spectra were phased to give positive peaks along the diagonal.

***trans*-[Pt(PHCy₂)₂(PCy₂)Cl] (**1**):**^[52] DBU (131 μL, 0.86 mmol) was added to a suspension of **7** (0.74 g, 0.86 mmol in 15 mL of toluene) and the mixture stirred at room temperature for 5 min. The resulting yellow suspension was filtered and pure **1** was obtained as a yellow solid after solvent evaporation (0.63 g, 0.77 mmol, 89%).

Isomerisation of *trans*-[Pt(PHCy₂)₂(P(S)Cy₂)Cl] (2**) into *cis*-[Pt(PHCy₂)₂(P(S)Cy₂)Cl] (**3**):** A dichloromethane solution of **2** was stirred at room temperature for 1 h. Pure **3** was obtained after evaporation of the solvent under reduced pressure. The complex is very soluble in halogenated solvents, fairly soluble in toluene, and scarcely soluble in hexane. C₃₆H₆₈ClP₃PtS (856.44): calcd. C 50.49, H 8.00, Cl 4.14, S 3.74; found C 50.92, H 7.85, Cl 4.35, S 3.72. LC-MS: exact mass calcd. for C₃₆H₆₈ClP₃PtS: 855.36 amu; found 856 [M + H]⁺. M.p. 186 °C (dec.). IR (Nujol mull): $\tilde{\nu}_{\max}$ = 2272 (w, PH), 1344 (w), 1297 (m), 1268 (m), 1201 (m), 1176 (m), 1115 (m), 1074 (w), 1005 (s), 918 (m), 895 (m), 870 (m), 848 (m), 819 (w), 736 (s), 577 (s, P=S), 511 (m), 411 (w), 400 (w), 388 (w), 298 (m, Pt–Cl), 227 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 295 K): δ = 5.39 (m, ¹J_{P,H} = 383 Hz, PH *trans* Cl), 5.22 [m, ¹J_{P,H} = 373, ²J_{H,Pt} = 67 Hz, PH *trans* P(S)] ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 295 K): δ = 67.4 [dd, ¹J_{P,Pt} = 1733, ²J_{P,P} = 252, ²J_{P,P} = 16 Hz, P(S)], 11.6 (br. s, ¹J_{P,Pt} = 3540, P *trans* Cl), 10.9 [dd, ¹J_{P,Pt} = 2822, ²J_{P,P} = 252, ²J_{P,P} = 14 Hz, P *trans* P(S)] ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, CDCl₃, 295 K): δ = –5329 (ddd, ¹J_{P,Pt} = 3540, ¹J_{P,Pt} = 2822, ¹J_{P,Pt} = 1733 Hz) ppm.

[Pt(κ²S,S'-PS₂Cy₂)(PHCy₂)₂]Cl (4**):** A dichloromethane solution of sulfur (9.0 mg, in 2 mL) was slowly added to a stirred CH₂Cl₂ solu-

tion of **3** (0.230 g, 0.268 mmol in 5 mL) at room temperature. After 2 h, the solvent was removed under reduced pressure and the residue was treated with toluene (5 mL). Addition of *n*-hexane caused the precipitation of **4** as a yellow solid, which was isolated by filtration, washed with *n*-hexane and dried under vacuum. Yield: 0.170 g (71%). The complex was very soluble in halogenated solvents and toluene and scarcely soluble in *n*-hexane. C₃₆H₆₈ClP₃PtS₂ (888.51): calcd. C 48.66, H 7.71, Cl 3.99, S 7.22; found 48.45, H 7.83, Cl 4.05, S 6.95. LC-MS: exact mass calcd. for the cationic C₃₆H₆₈P₃PtS₂: 852.36 amu; found 852. M.p. 214 °C (dec.). IR (Nujol mull): $\tilde{\nu}_{\max}$ = 2274 (w, P–H), 1345 (w), 1296 (m), 1268 (m), 1201 (w), 1172 (m), 1120 (m), 1074 (w), 1005 (s), 918 (s), 888 (m), 850 (m), 820 (m), 752 (w), 727 (m), 591 (m, νPS₂), 553 (s, νPS₂), 515 (m), 466 (s), 406 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, 295 K): δ = 4.19 (m, ¹J_{P,H} = 402, ²J_{Pt,H} = 88 Hz, PH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 295 K): δ = 136.6 (s, ²J_{P,Pt} = 151 Hz, PS₂Cy₂), 2.0 (s, ¹J_{P,Pt} = 3048 Hz, PHCy₂) ppm. ³⁵Cl NMR (39 MHz, CD₂Cl₂, 295 K): δ = –18 (br.) ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, CDCl₃, 295 K): δ = –4596 (td, ¹J_{P–Pt} = 3048, ²J_{P–Pt} = 151 Hz) ppm.

[Pt(κ²S,S'-PS₂Cy₂)(κP-P(S)Cy₂)(PHCy₂)] (5**):** DBU (30 μL, 0.202 mmol) was added to a stirred dichloromethane solution (5 mL) containing **4** (0.180 g, 0.202 mmol) and sulfur (7.5 mg). After 10 min, the solvent was removed under reduced pressure and the residue was treated with toluene (5 mL). The resulting suspension was filtered and **5** was obtained as a white solid (0.16 g, 89% yield) after evaporation of the filtrate under reduced pressure. The complex is very soluble in toluene and halogenated solvents, and scarcely soluble in hexane and methanol. C₃₆H₆₇P₃PtS₃ (884.11): calcd. C 48.91, H 7.64, S 10.88; found C 48.67, H 7.54, S 11.08. LC-MS: exact mass calcd. for C₃₆H₆₇P₃PtS₃: 883.33 amu; found 884 [M + H]⁺. M.p. 248–250 °C. IR (Nujol mull): $\tilde{\nu}_{\max}$ = 2366 (w, PH), 1342 (w), 1328 (w), 1296 (m), 1175 (m), 1111 (m), 1075 (m), 1025 (s), 1002 (s), 889 (m), 848 (s), 817 (m), 756 (m), 736 (s), 597 (s, νP=S and νPS₂), 556 (s, νPS₂), 510 (m), 467 (w), 403 (m), 400 (m), 352 (w), 316 (m) cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 295 K): δ = 5.24 (br. d, ¹J_{P,H} = 424, ²J_{Pt,H} = 72 Hz) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆, 295 K): δ = 127.2 (br., ²J_{P,Pt} = 137 Hz, PS₂Cy₂), 48.4 [br., ¹J_{P,Pt} = 2977 Hz, P(S)Cy₂], 38.9 (br., ¹J_{P,Pt} = 3977 Hz, PHCy₂) ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, C₆D₆, 295 K): δ = –4522 (ddd, ¹J_{P,Pt} = 3977, ¹J_{P,Pt} = 2977, ²J_{P,Pt} = 137 Hz) ppm.

[Pt(κ²S,S'-PCy₂S₂)(κS-PCy₂S₂)(PHCy₂)] (6**):** A toluene solution of PHCy₂ (0.180 mmol in 2 mL) was slowly added to an orange toluene suspension of **8** (0.133 g, 0.184 mmol in 5 mL). After 10 min, the obtained yellow suspension was filtered, the filtrate was concentrated to dryness and the resulting yellow solid was washed with *n*-hexane (3 × 2 mL). Yield: 0.128 g, 76%. Complex **6** is very soluble in halogenated solvents, slightly soluble in toluene and scarcely soluble in *n*-hexane. C₃₆H₆₇P₃PtS₄ (916.18): calcd. C 47.19, H 7.37, S 14.0; found C 47.25, H 7.45, S 14.4. LC-MS: exact mass calcd. for C₄₈H₉₀OP₄Pt₂: 915.30 amu; found 916 [M + H]⁺, 718 [M – PHCy₂ + H]⁺. M.p. 208–210 °C. IR (Nujol mull): $\tilde{\nu}_{\max}$ = 2367 (w, P–H), 1297 (w), 1267 (w), 1178 (m), 1113 (m), 1075 (w), 999 (m), 919 (w), 885 (m), 849 (m), 819 (m), 748 (m), 620 (s, ν of unidentate PS₂), 598 (m, ν of bidentate PS₂), 559 (s, ν of bidentate PS₂), 527 (m, ν of unidentate PS₂), 473 (w), 356 (w), 310 (w) cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 295 K): δ = 5.94 (br. m, ¹J_{P,H} = 417 Hz, PH) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆, 295 K): δ = 124.8 (br. s, ²J_{P,Pt} = 195 Hz, κ²S,S'-PCy₂S₂), 81.8 (br. s, κS-PCy₂S₂), 2.5 (s, ¹J_{P,Pt} = 3551 Hz, PHCy₂) ppm. ¹⁹⁵Pt{¹H} NMR (86 MHz, CDCl₃, 265 K): δ = –4052 (ddd, ¹J_{P,Pt} = 3551, ²J_{P,Pt} = 184, ²J_{P,Pt} = 116 Hz) ppm.

Pt(κ²S,S'-PCy₂S₂)₂ (8**):** Dicyclohexylphosphane sulfide,^[64] prepared by addition of 1 equiv. of elemental sulfur to a toluene solu-

tion of PHCy_2 at room temperature, was converted into $\text{P}(\text{Cy})_2\text{-S}_2\text{Na}$ by further reaction with 1 equiv. of sulfur and subsequent deprotonation by NaH . $\text{NaP}(\text{Cy}_2\text{S}_2)$ (0.193 g, 0.678 mmol)^[65] was then poured into an ethanol suspension of K_2PtCl_4 (0.141 g, 0.339 mmol in 5 mL) and the mixture was vigorously stirred at room temperature for 24 h. Complex **8** was isolated by filtration as a pale orange solid, washed with *n*-hexane (4 × 2 mL) and dried under vacuum. Yield: 0.181 g, 74%. The complex is fairly soluble in halogenated solvents and insoluble in hexane and ethanol. $\text{C}_{24}\text{H}_{44}\text{P}_2\text{PtS}_4$ (717.90): calcd. C 40.15, H 6.18, S 17.87; found C 40.65, H 6.31, S 18.05. LC-MS: exact mass calcd. for $\text{C}_{24}\text{H}_{44}\text{P}_2\text{PtS}_4$: 717.14 amu; found 718 $[\text{M} + \text{H}]^+$. M.p. 279 °C (dec.). IR (Nujol mull): $\tilde{\nu}_{\text{max}} = 1266$ (w), 1180 (m), 1113 (w), 1078 (w), 1023 (w), 1001 (m), 887 (m), 850 (w), 818 (w), 742 (m), 595 (m, ν of bidentate PS_2), 561 (s, ν of bidentate PS_2), 524 (w), 401 (w), 298 (m) cm^{-1} . ^1H NMR (162 MHz, CDCl_3 , 295 K): $\delta = 134.5$ (s, $^2J_{\text{P-Pt}} = 279$ Hz) ppm. $^{15}\text{Pt}\{^1\text{H}\}$ NMR (86 MHz, CDCl_3 , 295 K): $\delta = -3025$ (t, $^2J_{\text{P-Pt}} = 279$ Hz) ppm.

X-ray Data Collection, Structure Solution and Refinement of **6**:

Crystal data, parameters for intensity data collection and convergence results are compiled in Table 4. A pale yellow platelet of approximate dimensions $0.30 \times 0.20 \times 0.20$ mm was studied at 110 K with a BRUKER-AXS SMART APEX diffractometer. An empirical absorption correction (min. trans. 0.40, max. trans. 0.52) was applied before averaging symmetry-equivalent data [$R(\text{int}) = 0.0815$]. After merging, 11370 independent reflections remained for the structure solution by direct methods.^[66] The structure model was completed by Fourier difference syntheses and refined with full-matrix least squares on F^2 .^[67] CCDC-299582 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for **6**.

Empirical formula	$\text{C}_{36}\text{H}_{67}\text{P}_3\text{PtS}_4$
Formula mass	916.14
Temperature [K]	110(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a [Å]	15.731(2)
b [Å]	11.1000(16)
c [Å]	27.258(3)
β [°]	121.060(5)
V [Å ³]	4077.2(9)
Z	4
$D_{\text{calcd.}}$ [Mg/m ³]	1.492
Absorption coeff. [mm ⁻¹]	3.788
θ range for data coll. [°]	2.25–29.70
Reflections measured	51300
Independent reflections	11370
Observed reflections [$I > 2\sigma(I)$]	8705
Data/parameters	11370/397
Goodness-of-fit on F^2	1.102
$R^{\text{[a]}}$ [$I > 2\sigma(I)$]	0.0581
$wR_2^{\text{[b]}}$ (all data)	0.1208
Largest diff. peak/hole [$\text{e}/\text{Å}^3$]	1.934/–2.962

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of **3**, **4**, **5** and **8**, $^{15}\text{Pt}\{^1\text{H}\}$ NMR spectrum of **8**, ESI-MS spectra of **3**, **4**, **5**, **6** and **8**.

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