A Novel Route to Multinuclear d^8 Metal−Chalcogen Compounds with Nuclearity Control

Rubén Mas-Ballesté,[a] William Clegg,[b] Agustí Lledós,*[a] and Pilar González-Duarte*[a]

Keywords: Cluster compounds / Platinum / Metalloligands / Self-assembly / Sulfur

We have designed a new synthetic procedure to obtain multinuclear aggregates containing a $\{Pt_2S_2\}_n$ core. The synthetic strategy involves the reaction of $[(dppp)Pt(\mu\text{-}S)_2Pt(dppp)]$ with $[PtCl_2(PhCN)_2]$ and thus the expansion of the $\{Pt_2S_2\}$ ring to a $[\{Pt_2S_2\}PtCl_2]$ fragment. The lability of the chloride anions allows their replacement by bridging sulfide ligands, thus affording a new $[\{Pt_2(\mu_3\text{-}S)_2\}\{Pt_2(\mu\text{-}S)_2\}\{Pt_2(\mu_3\text{-}S)_2\}]$ core. Its subsequent evolution to $[\{Pt_2S_2\}_3PtCl_2]$ lays the foundation for a new cycle.

Introduction

Preparation of novel structures in good yields by systematic approaches is relevant in transition-metal sulfide chemistry in view of the current interest and economic importance of these compounds in industrial uses.[1] Although novel approaches to the synthesis of high nuclearity platinum complexes have been reported recently,[2] the chemistry of noble-metal−sulfido clusters has been neglected compared with that of aggregates containing the first transition series metals and molybdenum.[3] Here we report a novel synthetic route based on the behavior of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds as metalloligands, which leads to multinuclear aggregates containing a $\{Pt_2S_2\}_n$ core. The synthetic strategy allows control of the nuclearity of the cluster and can be extended to other metals with square-planar coordination.

The outstanding nucleophilicity of the sulfur atoms in the $\{Pt_2S_2\}$ core accounts for the significant number of known homo- and heterometallic derivatives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L = phosphane) identified to date,[4] as well as for its reaction with organic electrophiles[5] and protons.[6] On the basis of the ability of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ to act as a ligand to metal centers, we now address the use of these compounds for building up multinuclear aggregates containing a $\{Pt_2S_2\}_n$ core. The synthetic strategy involves first expansion of the $\{Pt_2S_2\}$ rings to $[\{Pt_2S_2\}PtL'_2]$ fragments containing labile terminal L′ ligands, which are then replaced by bridging sulfide ligands. As a result, the PtL'_2 fragment evolves to a $\{Pt_2S_2\}$ linking unit between two $\{Pt_2S_2\}$ rings, thus affording a new $[\{Pt_2S_2\}_2\{Pt_2S_2\}]$ core. Its subsequent evolution to $[\{Pt_2S_2\}_3PtL'_2]$ lays the foundation for a new cycle. In this work we present the synthesis and characterization of three complexes derived from $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**1**; Scheme 1) and provide evidence for the lability of chloride ligands in the $[\{Pt_2S_2\}PtCl_2]$ fragment.

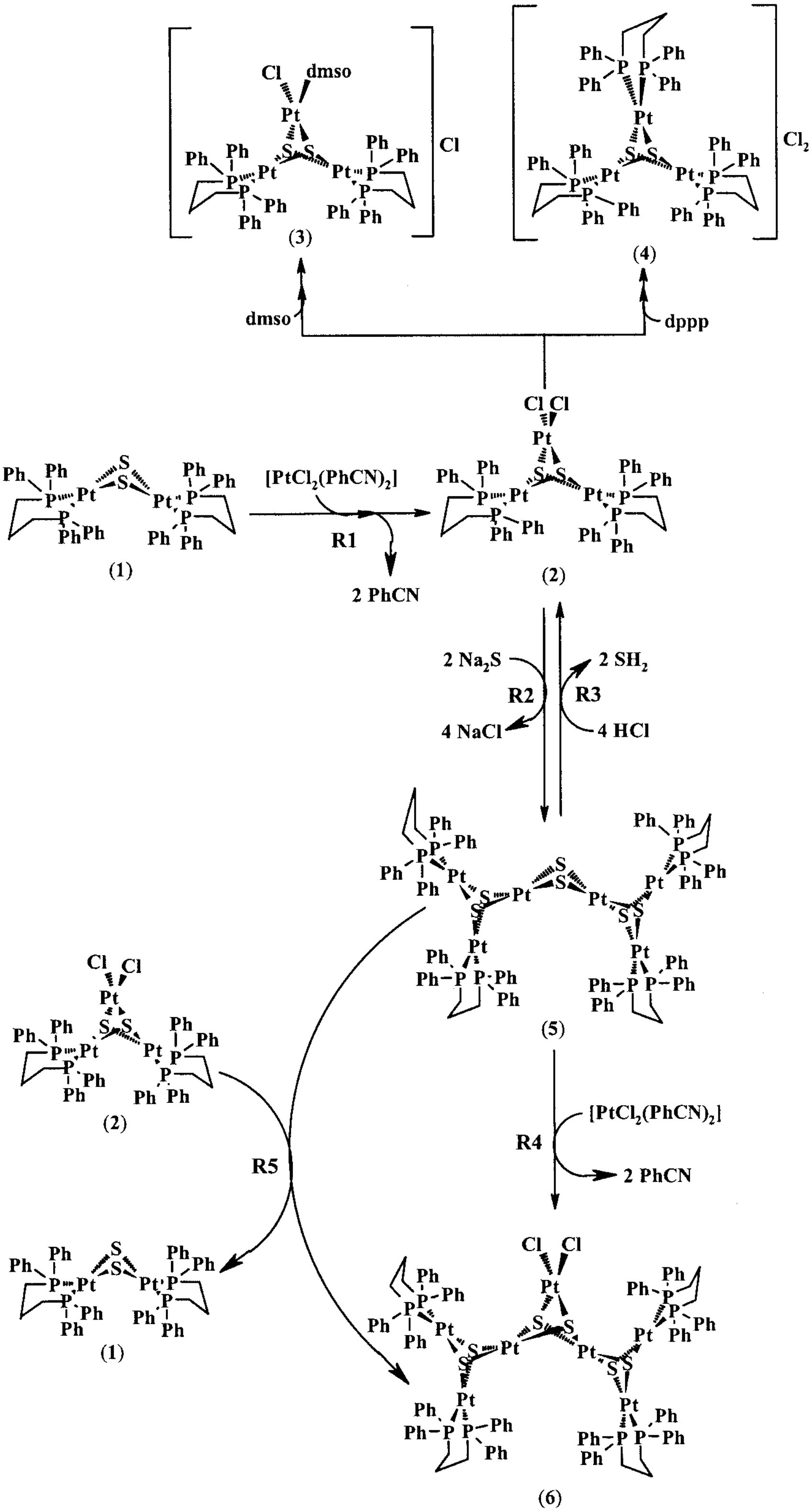
Results and Discussion

The reaction of equimolar quantities of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**1**) and $[PtCl_2(PhCN)_2]$ gave the compound $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl_2]$ (**2**) in good yield. The X-ray crystal structure of this complex consists of discrete trinuclear species and solvent molecules. Although the latter show disorder, the structure of the complex (Figure 1) has been unequivocally determined. Thus, the central Pt_3S_2 unit consists of a nonequilateral triangle of platinum atoms capped above and below by two sulfur atoms, thus forming a trigonal bipyramid. Each platinum atom has approximate square-planar coordination. Significantly, among the wide family of derivatives obtained from $[L_2Pt(\mu\text{-}S)_2PtL_2]$ metalloligands (L = phosphane) no previous example of the $P_4Cl_2Pt_3S_2$ core observed in **2** has been observed by X-ray diffraction. Thus, in the absence of X-ray data, three different alternatives have been proposed as a result of synthetic strategies similar to that followed for the synthesis of **2** (reaction R1). These are: formation of a mixture of hexanuclear $[\{Pt_2(\mu_3\text{-}S)_2[P(tolyl)_3]_4\}M_2(\mu\text{-}Cl)_2\{Pt_2(\mu_3\text{-}S)_2[P(tolyl)_3]_4\}]^{2+}$ and trinuclear $[\{Pt_2(\mu_3\text{-}S)_2[P(tolyl)_3]_4\}MCl_2]$ (M = Pd, Pt) species,[7] or formation of only a hexanuclear $[\{Pt_2(\mu_3\text{-}S)_2(PPh_3)_4\}Pd_2(\mu\text{-}Cl)_2\{Pt_2(\mu_3\text{-}S)_2(PPh_3)_4\}]^{2+}$,[8] or a trinuclear $[\{Pt_2(\mu_3\text{-}S)_2(PPh_3)_4\}PtCl_2]$[9] complex. The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ shows only one signal centered at $\delta = -8.08$ ppm with $^1J_{Pt,P} = 2978$ Hz, thus indicating that the ^{31}P nuclei are equivalent in solution, in agreement with the solid-state structure.

---

[a] Departament de Química, Universitat Autònoma de Barcelona,
08193 Bellaterra, Barcelona, Spain
Fax: (internat.) + 34-935-813-101
E-mail: Pilar.Gonzalez.Duarte@uab.es
[b] School of Natural Sciences (Chemistry), University of Newcastle,
Newcastle upon Tyne NE1 7RU, UK

DOI: 10.1002/ejic.200400257



Scheme 1

The lability of the chloro ligands in **2** becomes apparent in the characterization of this compound by ESI-MS. Thus, depending on the recording conditions and on the solvent used to obtain mass data, the following cationic species have been identified: $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl]^+$ (*m*/*z* = 1509.5), $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl(CH_3CN)]^+$ (*m*/*z* = 1550.8), $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(CH_3CN)_2]^{2+}$ (*m*/*z* = 778.2), or $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl(CH_3OH)]^+$ (*m*/*z* = 1541.6).

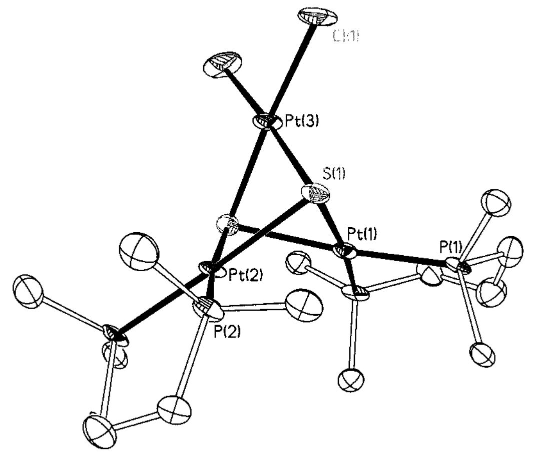


Figure 1. Molecular structure of **2** with the key atoms labeled and 50% probability ellipsoids; H atoms, phenyl rings and CH_2Cl_2 solvent molecules have been omitted; selected structural parameters [Å, °]: Pt−Cl 2.330(7), Pt(1)−S 2.381(7), Pt(2)−S 2.357(6), Pt(3)−S 2.287(6), Pt(1)−P(1) 2.237(7), Pt(2)−P(2) 2.256(7), Pt(1)···Pt(2) 3.124(2), Pt(1)···Pt(3) 2.942(2), Pt(2)···Pt(3) 3.277(2), S···S 2.981; Cl−Pt(3)−Cl 91.1(4), P−Pt(1)−P 93.6(4), P−Pt(2)−P 93.1(3), S−Pt(1)−S 77.5(3), S−Pt(2)−S 78.5(3), S−Pt(3)−S 81.4(3); dihedral (hinge) angles between PtS_2 planes: Pt(1)/Pt(2) 116.0, Pt(1)/Pt(3) 110.1, Pt(2)/Pt(3) 134.0

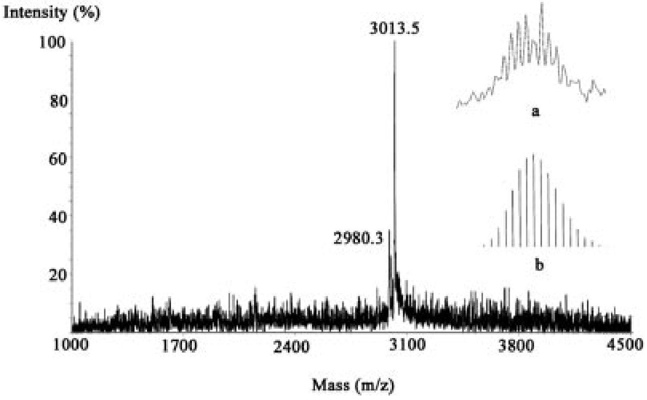


Figure 2. MALDI-TOF spectrum of **5** showing the major intensity peak at m/z = 3013.5 corresponding to $[\mathbf{5} + H]^+$; experimental (a) and simulated (b) isotope-distribution patterns are included; the peak at m/z = 2980 corresponds to $[\mathbf{5} - S]^+$

For the three species a good match between experimental and theoretical isotope distribution has been observed, the above m/z values corresponding to the major intensity peak. Additional evidence for this lability is provided by the fact that a solution of **2** in DMSO yields the unprecedented complex $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl(dmso)]Cl$ (**3**), whose synthesis and characterization is reported here. Moreover, the addition of a stoichiometric amount of dppp to **2** affords complex $[Pt_3(\mu_3\text{-}S)_2(dppp)_3]Cl_2$ (**4**), already obtained from a different synthetic procedure.[6a]

On the basis of its ability to exchange the chloride ions, the synthesis of $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}_2\{Pt_2(\mu\text{-}S)_2\}]$ (**5**) was carried out by treating complex **2** with a stoichiometric amount of $Na_2S{\cdot}9H_2O$. The $^{31}P\{^1H\}$ NMR spectrum of **5** in $[D_6]$DMSO shows a broad signal centered at δ = −7.9 ppm with a $^1J_{Pt,P}$ value of ca. 3000 Hz, and the ^{195}Pt NMR spectrum in the same solvent consists of two signals, one singlet at δ = −3524 ppm (PtS_4) and one triplet centered at δ = −4425 ppm (S_2PtP_2) with $^1J_{Pt,P}$ = 3002 Hz. Further evidence for the hexanuclear nature of **5** was provided by the MALDI-TOF mass spectrum, which shows a complex isotope-pattern distribution with a major peak at m/z = 3013.5. As shown in Figure 2, both features are consistent with the molecular mass of the cation $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(\mu\text{-}S)(\mu\text{-}SH)Pt\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}]^+$, and thus with the nature of complex **5**.

Comparison of the nucleophilicity of the $\{Pt_2S_2\}$ core in complexes **5** and **1** was established by determination of their basic character. Thus, titration of **1** and **5** with HCl was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The addition of a stoichiometric amount of HCl to **5** leads to **2** quantitatively, while formation of $[PtCl_2(dppp)]$ from **1** requires a significant excess of HCl.[6a] Additional evidence for the greater basicity of the $\{Pt_2S_2\}$ core in **5** than in **1** comes from the ability of the former to displace the $\{PtCl_2\}$ fragment from **2** to afford **1** and $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt_2(\mu_3\text{-}S)_2PtCl_2\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}]$ (**6**), as indicated in Scheme 1. An alternative way to obtain **6** is by treating **5** with a stoichiometric amount of $[PtCl_2(PhCN)_2]$.

Complex **6** was characterized by mass spectrometry and NMR spectroscopy. The MALDI-TOF spectrum has a major signal at m/z = 1640.2, which can be assigned to the $[\mathbf{6} + 2\ H]^{2+}$ cation (for the major peak, theoretical m/z = 1640). Comparison of the experimental and theoretical isotope-distribution patterns is given in Figure 3. $^{31}P\{^1H\}$ NMR measurements of **6** in $[D_6]$DMSO show a broad signal centered at δ = −9.3 ppm with $^1J_{Pt,P}$ of about 3000 Hz. The broadness of this signal, which does not allow us to distinguish the nonequivalence of the phosphorus nuclei, can be attributed to the high number of possible couplings between magnetically active platinum and phosphorus nuclei in **6**. The ^{195}Pt NMR spectrum consists of two singlets (δ = −3519, −3418 ppm) corresponding to the platinum nuclei in the PtS_4 and $PtCl_2S_2$ fragments, respectively, and

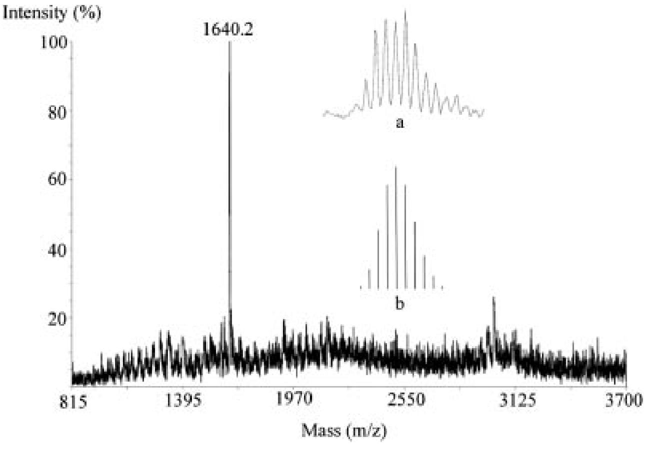


Figure 3. MALDI-TOF spectrum of **6** showing the major intensity peak at m/z = 1640.3 corresponding to $[\mathbf{6} + 2\ H]^{2+}$; experimental (a) and simulated (b) isotope-distribution patterns are included

two triplets — $\delta = -4403$ ppm ($^1J_{\mathrm{Pt,P}} = 2997$ Hz) and $\delta = -4420$ ppm ($^1J_{\mathrm{Pt,P}} = 2970$ Hz) — which can be assigned to the two different platinum nuclei present as S_2PtP_2 in **6**.

The thermodynamic feasibility of the reactions given in Scheme 1 has been corroborated by means of density functional calculations performed for complexes **1**, **2**, **5** and **6**, where dppp is modeled by two PH_3 ligands. The calculated reaction energies are given in Table 1. Geometry optimization of **1t**, **2t**, **5t** and **6t** affords their structural data, that of **2t** being in good agreement with the crystallographically determined data for **2**. As regards the HOMO orbitals of **1t** and **5t**, they essentially consist of an antibonding combination of p_π orbitals of the sulfur atoms pointing outwards from the hinged $\{Pt_2S_2\}$ ring, thus accounting for the observed coordinating ability of the sulfur atoms. Interestingly, the energy level of the HOMO for **5t** (−2.46 eV) is 1.95 eV higher than for **1t** (−4.41 eV), which is in agreement with the greater basicity found experimentally for the $\{Pt_2S_2\}$ core in **5** than in **1**.

Table 1. B3LYP reaction energies in the gas phase

Reaction	R1	R3	R4	R5
Energy [kcal/mol]	−8.3	−41.2	−49.7	−40.4

Conclusion

In this work, we have provided a new insight into the chemistry of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds that goes beyond their usual behavior as metalloligands towards a wide range of transition metals. The synthetic route used demonstrates that the nucleophilicity of the $\{Pt_2S_2\}$ core can be driven to build nuclearity-controlled multinuclear aggregates containing a $\{Pt_2S_2\}_n$ core. This strategy requires replacement of the terminal X ligands in $[\{Pt_2S_2\}_nPtX_2]$ fragments. For X = Cl, this has been achieved by reaction with sodium sulfide.

Characterization of the high nuclearity complexes here obtained has required several spectroscopic techniques, among which MALDI-TOF mass spectrometry has proved very valuable despite its scarce use in coordination chemistry studies.

Finally, on the basis of these results it can be concluded that a similar reaction scheme should be suitable for obtaining macromolecular complexes containing a $\{M_2(\mu\text{-}S)_2\}_n$ core provided M has a preference for square-planar coordination environments.

Experimental Section

General Remarks: All reactions were carried out under pure dinitrogen, and conventionally dried and degassed solvents were used throughout. Complex $[PtCl_2(dppp)]$ was prepared according to published methods.[10] The synthesis of $[(dppp)Pt(\mu\text{-}S)_2Pt(dppp)]$ has already been reported.[5] ^{1}H, ^{13}C{^{1}H} ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded from samples in $(CD_3)_2SO$ solution at room temperature, using a Bruker 250 spectrometer. ^{1}H and ^{13}C chemical shifts are relative to $SiMe_4$, ^{31}P chemical shifts to external 85% H_3PO_4 and ^{195}Pt chemical shifts to external H_2PtCl_6. The ESI-MS measurements were performed with a VG Quattro Micromass Instrument. Experimental conditions are given elsewhere.[5] MALDI mass spectra were obtained with a Voyager DE-RP (PerSeptive Biosystems, Framighan) time-of-flight (TOF) mass spectrometer equipped with a nitrogen laser (337 nm, 3 ns pulse). The accelerating voltage in the ion source was 20 kV. Data were acquired in the reflector mode operation with a delay time of 60 ns. Experiments were performed using the matrix 2,5-dihydroxybenzoic acid (DHB; Aldrich). Matrix solutions were prepared by dissolving 10 mg of DHB in 10 mL of CH_3CN/H_2O 50% (v/v). Equal volumes (1 μL + 1 μL) of matrix solution and diluted samples (10^{-2} M in CH_3CN) were mixed and spotted onto the stainless-steel sample plate. The mixture was dried in air before being introduced into the mass spectrometer. Microanalytical data have been omitted because those referring to the carbon content were unsatisfactory, as already reported in some related (phosphane)platinum complexes.[5][6a][6b]

Synthesis of $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl_2]$ (2): The reaction of equimolar quantities of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (**1**; 500 mg, 0.39 mmol) and $[PtCl_2(PhCN)_2]$ (184 mg, 0.39 mmol) in benzene (80 mL) at room temperature for 6 h gave $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl_2]$ (**2**) as an orange solid, which was filtered off and washed with diethyl ether (532 mg, yield 82%). Slow evaporation of the solvent from a solution of **2** in CH_2Cl_2 afforded yellow X-ray-quality crystals. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = -8.1$ ppm ($^1J_{\mathrm{Pt,P}} = 2978$ Hz). ESI-MS: *m/z* = 1509.5 $[M - Cl]^+$.

Synthesis of $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}PtCl(dmso)]Cl$ (3): Complex **2** (300 mg, 0.19 mmol) was dissolved in the minimum amount of DMSO (1 mL). Addition of diethyl ether caused precipitation of complex **3** as a yellowish solid, which was filtered off and washed with diethyl ether (206 mg, yield 67%). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta_A = -7.1$ ppm ($^1J_{\mathrm{Pt,P_A}} = 3022$ Hz); $\delta_B = -7.8$ ppm ($^1J_{\mathrm{Pt,P_B}} = 3051$ Hz). ^{1}H NMR ($CDCl_3$): $\delta = 2.85$ ppm (coordinated dmso). ^{13}C NMR ($CDCl_3$): $\delta = 44.4$ ppm (coordinated dmso). ESI-MS: *m/z* = 1587.7 $[M]^+$.

Synthesis of $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt_2(\mu\text{-}S)_2\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}]$ (5): A suspension of complex **2** (400 mg, 0.25 mmol) in methanol (50 mL) was allowed to react with a stoichiometric amount of $Na_2S{\cdot}9H_2O$ (61 mg, 0.25 mmol) at room temperature for 1 h. Concentration of the filtered orange solution thus obtained, followed by addition of diethyl ether, allowed isolation and characterization of the title compound (229 mg, yield 61%). ^{31}P{^{1}H} NMR ([D$_6$]DMSO): $\delta = -7.9$ ppm. ^{195}Pt NMR ([D$_6$]DMSO): $\delta = -3524, -4425$ ppm ($^1J_{\mathrm{Pt,P}} = 3000$ Hz). MALDI: *m/z* = 3013.5 $[M + H]^+$.

Synthesis of $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt_2(\mu_3\text{-}S)_2PtCl_2\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}]$ (6): A solution of **5** (200 mg, 0.07 mmol) in acetonitrile (50 mL) containing a stoichiometric amount of $[PtCl_2(PhCN)_2]$ (32 mg, 0.07 mmol) was left to react at room temperature for 3 h. The red solution was filtered and the resulting filtrate concentrated. The title compound was isolated after addition of diethyl ether (123 mg, yield 54%). ^{31}P{^{1}H} NMR ([D$_6$]DMSO): $\delta = -9.3$ ppm. ^{195}Pt NMR ([D$_6$]DMSO): $\delta = -3519, -3418, -4403$ ppm ($^1J_{\mathrm{Pt,P}} = 2997$ Hz), -4420 ($^1J_{\mathrm{Pt,P}} = 2970$ Hz) ppm; MALDI: *m/z* = 1640.2 $[M + 2\,H]^{2+}$.

X-ray Crystallographic Study of Complex 2: $C_{54}H_{52}Cl_2P_4Pt_3S_2 \cdot 6CH_2Cl_2$, $M = 2054.7$, orthorhombic, *Pnma*, $a = 19.982(3)$, $b = 18.607(2)$, $c = 19.372(2)$ Å, $V = 7202.5(16)$ Å^3, $Z = 4$, $T = 160$ K, $R = 0.091$. The molecule lies in a crystallographic mirror plane, as do some of the chloroform solvent molecules, while others are in general positions. High displacement parameters suggest possible disorder of the solvent molecules, but this could be resolved only for one, in which one chlorine atom occupies alternative sites on either side of a mirror plane while the carbon atom and the other chlorine atom are in the plane. Restraints on geometry and displacement parameters were used to aid the refinement. The crystallographic analysis was further complicated by the probable occurrence of multiple twinning by exchange among the unit cell axes, all three of which are similar in length; this was indicated by an analysis of the agreement of observed and calculated intensities, but it was not possible to find a simple model for the twinning. This leads to the relatively high *R* factor. CCDC-221226 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: Gas-phase DFT calculations with the B3LYP functional were carried out using the Gaussian 98 suite of programs.[11] Effective core potentials and their related double-ζ basis set known as LANL2DZ were used for Pt, P, Cl and S atoms, supplemented with polarization functions for P, Cl and S atoms. The 6-31G basis set was used for H, C and N atoms with the addition of polarization functions for the N atom. A thermodynamic consideration for the R2 reaction requires taking into account the solvent effects. However, PCM calculation for compound **5** was hindered by the size of the system and thus the reaction energy for R2 could not be obtained.

Acknowledgments

Thanks are due to Prof. O. Rossell and I. Angurell for their assistance in the recording of the ^{195}Pt NMR spectra. Financial support from the Ministerio de Ciencia y Tecnología of Spain (projects BQU2001-1976 and BQU2002-04110-CO2-02) and the EPSRC (UK) is gratefully acknowledged. R. M. B. is indebted to the Universitat Autònoma de Barcelona for a pre-doctoral scholarship.

---

[1] E. I. Stiefel, *ACS Symp. Ser.* **1996**, *653*, 2.

[2] [2a] C. H. Tao, K. M.-C. Wong, N. Y. Zhu, V. W.-W. Yam, *New J. Chem.* **2003**, *27*, 150. [2b] C.-K. Hui, B. W.-K. Chu, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2002**, *41*, 6178. [2c] B. T. Sterenberg, R. Ramachandran, R. J. Puddephatt, *J. Cluster Sci.* **2001**, *12*, 49. [2d] W. Schuh, G. Wachtler, G. Laschober, H. Kopacka, K. Wurst, P. Peringer, *Chem. Commun.* **2000**, 1181.

[3] M. Hidai, S. Kuwata, Y. Mizobe, *Acc. Chem. Res.* **2000**, *33*, 46.

[4] [4a] Z. Li, W. Zheng, H. Liu, K. F. Mok, T. S. A. Hor, *Inorg. Chem.* **2003**, *42*, 8481. [4b] X. Xu, S.-W. A. Fong, Z. Li, Z.-H. Loh, F. Zhao, J. J. Vittal, W. Henderson, S.-B. Khoo, T. S. A. Hor, *Inorg. Chem.* **2002**, *41*, 6838. [4c] M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. González-Duarte, A. Lledós, J. A. Ramírez, *J. Chem. Soc., Dalton Trans.* **1999**, 3103. [4d] S.-W. A. Fong, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1999**, 639 and references cited therein. [4e] V. W.-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 739.

[5] R. Mas-Ballesté, M. Capdevila, P. A. Champkin, W. Clegg, R. A. Coxall, A. Lledós, C. Mégret, P. González-Duarte, *Inorg. Chem.* **2002**, *41*, 3218.

[6] [6a] R. Mas-Ballesté, G. Aullón, P. A. Champkin, W. Clegg, C. Mégret, P. González-Duarte, A. Lledós, *Chem. Eur. J.* **2003**, *9*, 5023. [6b] G. Aullón, M. Capdevila, W. Clegg, P. González-Duarte, A. Lledós, R. Mas-Ballesté, *Angew. Chem. Int. Ed.* **2002**, *41*, 2776. [6c] S.-W. A. Fong, W. T. Yap, J. J. Vittal, T. S. A. Hor, W. Henderson, A. G. Oliver, C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.* **2001**, 1986. [6d] S.-W. A. Fong, J. J. Vittal, W. Henderson, T. S. A. Hor, A. G. Oliver, C. E. F. Rickard, *Chem. Commun.* **2001**, 421.

[7] S. Narayan, V. K. Jain, *Trans. Met. Chem.* **2000**, *25*, 400.

[8] C. E. Briant, T. S. A. Hor, N. D. Howells, D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.* **1983**, 1118.

[9] B. H. Aw, K. K. Looh, H. S. O. Chan, K. L. Tan, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1994**, 3177.

[10] M. P. Brown, R. J. Puddephatt, M. Rashidi, K. R. Seddon, *J. Chem. Soc., Dalton Trans.* **1977**, 951.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb., J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revission A.7, Gaussian Inc., Pittsburgh, PA, **1998**.

Received March 30, 2004