[11] a) M. A. Calter, P. M. Sugathapala, C. Zhu, *Tetrahedron Lett.* **1997**, *38*, 3837–3840; b) C. Zhu, M. A. Calter, *J. Org. Chem.* **1999**, *64*, 1415–1419.
[12] a) K. N. Houk, R. W. Strozier, *J. Am. Chem. Soc.* **1973**, *95*, 4094–4096; b) A. Imammura, T. Hirano, *J. Am. Chem. Soc.* **1975**, *97*, 4192–4198; c) A. Dargelos, D. Liotard, M. Chaillet, *Tetrahedron* **1972**, *28*, 5595–5605; d) O. F. Guner, R. M. Ottenbrite, D. D. Shillady, P. V. Alston, *J. Org. Chem.* **1987**, *52*, 391–394; e) R. J. Loncharich, T. R. Schwartz, K. N. Houk, *J. Am. Chem. Soc.* **1987**, *109*, 14–23; f) P. Laszlo, M. Teston, *J. Am. Chem. Soc.* **1990**, *112*, 8750–8754.
[13] For a spectroscopic study on the complexation of $TiCl_4$ and $SnCl_4$ with enones, see: S. E. Denmark, N. G. Almstead, *Tetrahedron*, **1992**, *48*, 5565–5578.
[14] a) L. Brun, *Acta Crystallogr.* **1966**, *20*, 739–749; b) I. W. Bassi, M. Calcaterra, R. Intrito, *J. Organomet. Chem.* **1977**, *127*, 305–313.
[15] S. W. Ng, C. L. Barnes, M. B. Hossain, D. van der Helm, J. J. Zukerman, V. G. Kumer Das, *J. Am. Chem. Soc.* **1982**, *104*, 5359–5364.
[16] For a comprehensive review on α-diazo carbonyl compounds, see: M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**.

First Evidence of Fast S–H···S Proton Transfer in a Transition Metal Complex[**]

Gabriel Aullón, Mercè Capdevila, William Clegg, Pilar González-Duarte,* Agustí Lledós,* and Rubén Mas-Ballesté

In the quest to control noncovalent interactions, S–H···S hydrogen bonds are attracting great interest. Despite the prevalence of the thiol group in cysteine residues and the potential importance of S–H···S bridging bonds in biology, little is known about this interaction.[1] Intermolecular S–H···S chains that play an organizing role in the solid state were found in X-ray structures of several compounds containing S–H groups.[2] The S–H···S hydrogen bonds are typically very weak, but may become moderately strong in particular compounds. Resonance[3] and charge[4] assistances have been put forward as being responsible for strong intramolecular S–H···S bonds. The greater acidity of dithiols relative to their monothiol analogues has been attributed to enhanced stabilization of the thiolate anion by an intramolecular $RS^-\cdots HSR$ hydrogen bond.[5] Evidence of S–H···S interactions in transition metal compounds are scarce,[6] although the acidity of the SH group should be enhanced when the sulfur atom is coordinated to a transition metal. Indeed, Sellmann et al. found strong intermolecular S–H···S bridges in the crystal structure of $[Ru(SH_2)(PPh_3)$"S_4"$]$.[6a] An influence of these bridges on the reactivity of the metal complexes has not been demonstrated, although intramolecular M–SH···hydride interactions have been proposed in the initial stage of the mechanism of hydride protonation.[7] Here we show that a fast S–H···S proton exchange takes place in bimetallic platinum complexes with bridging SH^- and S^{2-} ligands.

Sulfide-bridged aggregates with the Pt_2S_2 core have a rich chemistry.[8, 9] We proved that the reactivity of the Pt_2S_2 core is highly dependent on the nature of the terminal ligands.[9, 10] We have now synthesized of the monoprotonated complexes $[Pt_2\{Ph_2P(CH_2)_nPPh_2\}_2(\mu\text{-S})(\mu\text{-SH})]ClO_4$ ($n = 2$, dppe (**1**); $n = 3$, dppp (**2**)) by adding $HClO_4$ to a solution of the corresponding $[Pt_2(\mu\text{-S})_2P\cap P)_2]$ ($P\cap P$ = dppe or dppp) complex in benzene. The most remarkable spectroscopic feature of **1** and **2** is the equivalence of the four phosphorus nuclei at room temperature according to the ^{31}P NMR spectrum (Figure 1). The only analogous monoprotonated compound previously reported, namely, $[Pt_2(\mu\text{-S})(\mu\text{-SH})(PPh_3)_4]PF_6$, has two distinct environments about the P nuclei, as the SH group is *cis* to two phosphorus atoms and *trans* to the other two. Consequently, at room temperature, it shows two ^{31}P NMR signals with two distinct $^1J_{Pt,P}$ coupling constants.[8b, 11] Surprisingly, each of the monoprotonated complexes **1** and **2** shows only one pseudotriplet with the following apparent spectroscopic parameters in $[D_6]$acetone: $\delta_P = 42.8$ ppm and $^1J_{Pt,P} = 3108$ Hz for **1**, and $\delta_P = -3.3$ ppm and $^1J_{Pt,P} = 2960$ Hz for **2**.

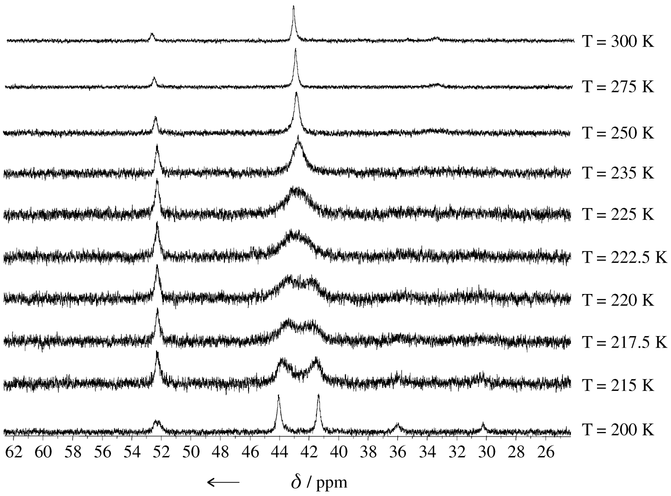

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1**.

We optimized the geometry of the model compounds $[Pt_2\{H_2P(CH_2)_nPH_2\}(\mu\text{-S})(\mu\text{-SH})]^+$ ($n = 2$, dhpe (**1t**); $n = 3$, dhpp (**2t**)) by B3LYP calculations.[12] Two conformations with a hinged Pt_2S_2 skeleton were found as minima in both complexes; they differ in the *endo* (**e**) or *exo* (**x**) orientation of the thiol proton (see Figure 2). As expected, two different Pt–P and two different Pt–S distances were found in all cases (e.g., in **1t(x)** Pt–P(*trans*-S) 2.338, Pt–P(*trans*-SH) 2.279, Pt–S 2.389, Pt–SH 2.465 Å), and this reflects the different *trans* influences of the sulfide and thiol ligands. The *exo* form is slightly more stable than the *endo* form, although the *exo*/

---

[*] Prof. Dr. P. González-Duarte, Prof. Dr. A. Lledós, Dr. G. Aullón, Dr. M. Capdevila, Dipl.-Chem. R. Mas-Ballesté
Departament de Química
Universitat Autònoma de Barcelona
08193 Bellaterra, Barcelona (Spain)
Fax: (+34) 935-812-920
E-mail: Pilar.Gonzalez.Duarte§uab.es, agusti@klingon.uab.es

Prof. Dr. W. Clegg
Department of Chemistry
University of Newcastle
Newcastle upon Tyne NE1 7RU (UK)

[**] Financial support is acknowledged from the Spanish Dirección General de Enseñanza Superior (DGES) under projects PB98-0916-CO2-01 and BQU2001-1976, and from EPSRC (UK).

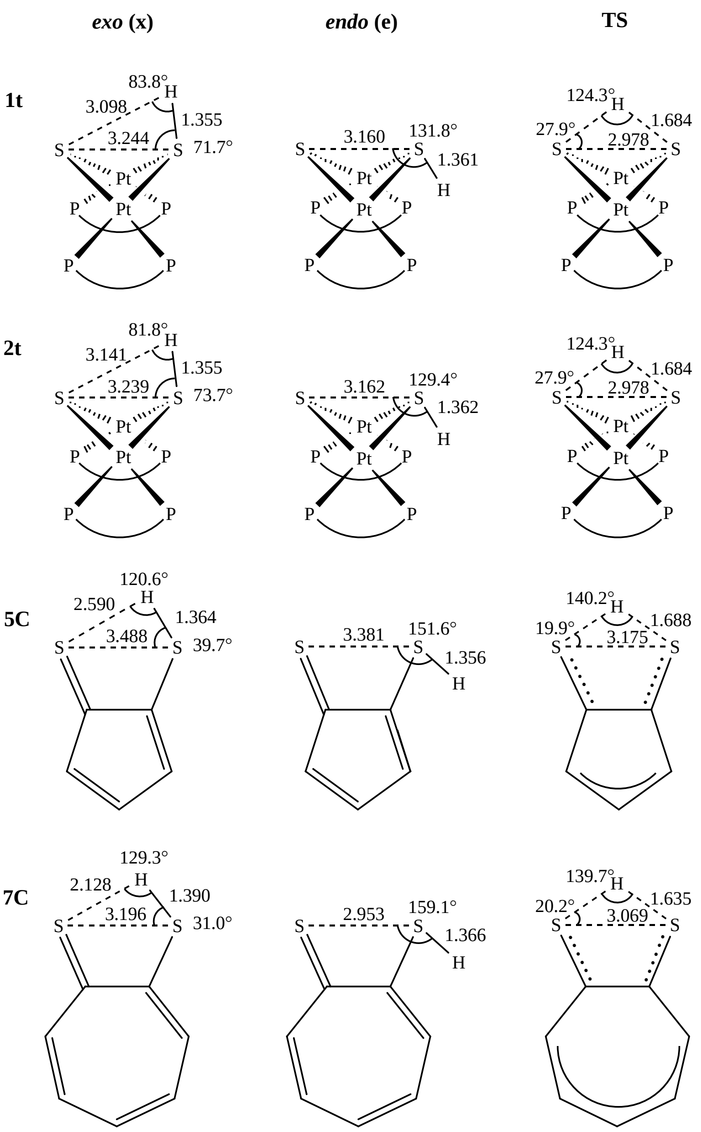

Figure 2. Optimized geometries of the *exo* and *endo* conformations and transition states for proton transfer in **1t**, **2t**, **5C**, and **7C** with bond lengths [Å] and angles [°].

endo interconversion, which takes place through ring inversion,[13] is usually a very fast process. The S–H/S disposition in the *exo* conformations is compatible with the presence of a weak S–H···S hydrogen bond. Comparing the Pt-S-H angle in **1t(x)** (93.3°) with the Pt-S-C angle in the optimized geometry of the methylthiolate analogue (102.1°) reaveals that the S–H proton is tilted towards the sulfide. The energy difference between the *exo* and *endo* forms (Table 1) can be taken as a rough estimate of the hydrogen-bond strength. Similar values (1–2 kcal mol^{-1}) have been reported for weak S–H···S hydrogen bonds.[14]

Table 1. B3LYP relative energies [kcal mol^{-1}] of the *exo* (**x**) and *endo* (**e**) conformations and the transition states (**TS**) for intramolecular proton transfer. In parentheses: MP2 values.

	Gas phase ($\varepsilon = 1$)			Acetone ($\varepsilon = 20.7$)		
	x	**e**	**TS**	**x**	**e**	**TS**
1t	0.0 (0.0)	0.9 (1.5)	19.7 (17.3)	0.0 (0.0)	−0.4 (−0.3)	19.5 (17.2)
2t	0.0 (0.0)	1.5 (2.3)	19.3 (16.1)	0.0 (0.0)	−0.2 (0.8)	18.0 (13.7)
5C	0.0	2.0	11.3	0.0	1.4	11.4
7C	0.0	2.2	2.3	0.0	1.0	1.6

The X-ray crystal structures[15] of **1** and **2** show that the $Pt_2(\mu\text{-}S)(\mu\text{-}SH)$ ring is nonplanar, with a dihedral angle between the two PtS_2 planes of 138.3° in **1** and 127.4° in **2** (Figure 3), and it is comparable to that in the singly protonated complex cation $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SH)]^+$.[11, 16] The H atom attached to S was not directly located in the structures of **1** and **2**, owing to the presence of heavy atoms and actual or possible disorder. Comparison of the Pt_2S_2 cores in **1** and **2** with those of their deprotonated precursors $[Pt_2(\mu\text{-}S)_2(dppe)_2]$[9a] and $[Pt_2(\mu\text{-}S)_2(dppp)_2]$,[10] shows that the S···S distance is shorter (by about 0.1 Å) and the dihedral angle smaller (by ca. 2° (**1**) and 7° (**2**)). However, these distortions do not allow a definite proposal for a unequivocal binding situation of the thiol proton in crystals of **1** or **2**. According to theoretical calculations both *endo* or *exo* conformations are possible, and thus weak interactions may determine the prevalence of one orientation over the other. In fact, an *endo* conformation for the thiol proton in **1** and **2** allows S–H···Ph hydrogen bonding.[17] Regarding the acidity of the S–H group in **1** and **2**, NMR data allowed the corresponding pK_a values to be estimated. Both should be within the range 7–9 on the aqueous scale, as they are deprotonated by 4-aminopyridine (pK_a of the conjugated acid 9.11) but not by 2,4-lutidine (pK_a of the conjugated acid 6.99). This represents a decrease of ten pK_a units from the free SH^- ligand (pK_a = 17–19).

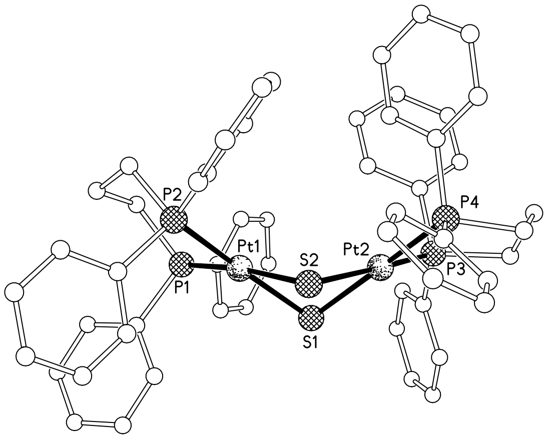

Figure 3. X-ray structure of **2**. Selected bond lengths [Å] and angles [°]: Pt1-S1 2.356(2), Pt1-S2 2.343(2), Pt2-S1 2.350(2), Pt2-S2 2.345(2); S1···S2 3.004, Pt1-S1-Pt2 86.92(7), Pt1-S2-Pt2 87.36(7). Selected bond lengths [Å] and angles [°] for **1**: Pt1-S1 2.374(3), Pt1-S2 2.339(3), Pt2-S1 2.365(3), Pt2-S2 2.343(3); S1···S2 3.057, Pt1-S1-Pt2 89.94(11), Pt1-S2-Pt2 91.37(10).

Hydrogen bonds can be regarded as incipient proton-transfer reactions.[1b] Thus, the equivalence of the phosphorus nuclei in **1** and **2** could be attributed to a fast SH···S proton transfer. To shed light on this process, variable-temperature NMR experiments were carried out (Figure 1). At low temperature, two distinct phosphorus environments were observed for **1** and **2** with the following parameters in $[D_6]$acetone: $\delta_{P(A)} = 44.1$, $\delta_{P(B)} = 41.4$ ppm, $^1J_{Pt,P(A)} = 2626$, $^1J_{Pt,P(B)} = 3608$ Hz for **1**, and $\delta_{P(A)} = -1.8$, $\delta_{P(B)} = -4.9$ ppm, $^1J_{Pt,P(A)} = 3401$, $^1J_{Pt,P(B)} = 2408$ Hz for **2**. Determination of the coalescence temperature allowed an estimation of the energy barrier of the SH ⋯ S proton-transfer process. The values thus obtained are $T_c = 221$ K and $\Delta G^{\neq} = 10.7$ kcal mol^{-1} for **1**, and $T_c = 240$ K and $\Delta G^{\neq} = 10.6$ kcal mol^{-1} for **2**.

We also performed calculations on the intramolecular S–H ⋯ S proton-transfer process. The transition state was located and characterized for both complexes (**TS1** and **TS2**, respectively). Both TSs show a trigonal S-H-S arrangement, in which the partial rupture of the S–H bond is compensated by the partial formation of the new S–H bond (Figure 2). The moderate energy barriers found (Table 1) are consistent with the fast process observed on the NMR timescale. We carried out additional calculations to assess the validity of the theoretical values: 1) single-point MP2 calculations on the B3LYP optimized geometries (Table 1, values in parentheses); 2) inclusion of solvent effects by means of the PCM continuum model.[18] The energy barriers are only slightly modified. Thus, theoretical calculations clearly show that intramolecular S–H ⋯ S proton transfer can occur in **1** and **2** with a low energy barrier. We also considered the possibility of an intermolecular solvent-assisted proton transfer, as defined in Equation (1). The values obtained for the activation energy of this reaction in acetone (32.2 kcal mol^{-1} for **1t** and 32.0 kcal mol^{-1} for **2t**, respectively) rule out this possibility.

$$\begin{aligned} &exo\text{-}[(\mathrm{P}\cap\mathrm{P})_2\mathrm{Pt}_2(\mu\text{-S})(\mu\text{-SH})]^+ + \mathrm{CH_3COCH_3} \rightarrow \\ &\qquad [(\mathrm{P}\cap\mathrm{P})_2\mathrm{Pt}_2(\mu\text{-S})(\mu\text{-S})] + (\mathrm{CH_3})_2\mathrm{COH}^+ \end{aligned} \tag{1}$$

To compare the S–H ⋯ S interaction in **1** and **2** with those in other compounds, in which stereochemical constraints place the S-H-S unit in a similar disposition, we performed calculations on dithiotropolone (**7C**) and the parent species with a five-membered ring **5C** (Figure 2, Table 1). The results obtained show that the structural and energetic parameters of the organic systems are similar to those of the platinum complexes, although the magnitude of the SH ⋯ S interaction decreases in the order **7C** > **5C** > **1** ≈ **2**.

In conclusion, the combined evidence from experimental and theoretical studies demonstrates the potential of a metal-coordinated thiol ligand to transfer its proton to a metal bound sulfide.

Experimental Section

1: $HClO_4$ (20 µL, 11.6 M) was added to a solution of $[Pt_2(\mu\text{-}S)_2(dppe)_2]$ (200 mg, 0.16 mmol) in benzene (50 mL). After 2 h, a pale yellow solid appeared. The solid product was collected by filtration, washed with benzene and water, and dried with diethyl ether. Yield: 146 mg (68%). X-ray quality crystals of **1** were obtained by slow evaporation of a solution in methanol. $^{31}P\{^1H\}$ NMR (162.1 MHz, [D$_6$]acetone, 295 K): δ_P(apparent) = 42.8 ppm, $^1J_{Pt,P}$(apparent) = 3108 Hz. ESI-MS: *m/z*: 1251.

2: The same procedure as for **1** gave a yellow solid from the reaction of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ (200 mg) and of $HClO_4$ (20 µL, 11.6 M) Yield: 70%. Recrystallization of **2** from methanol gave X-ray quality crystals. $^{31}P\{^1H\}$ NMR (162.1 MHz, [D$_6$]acetone, 295 K): δ_P(apparent) = −3.3 ppm, $^1J_{Pt,P}$(apparent) = 2960 Hz. ESI-MS: *m/z*: 1280.

Received: February 14, 2002 [Z18715]

---

[1] a) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, New York, **1999**, pp. 258–263; b) T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

[2] a) J. K. Cockroft, A. N. Fitch, *Z. Kristallogr.* **1990**, *193*, 1; b) C. H. Görbitz, B. Dalhus, *Acta Crystallogr. Sect. C* **1996**, *52*, 1756; c) P. R. Mallinson, D. D. MacNicol, K. L. McCormack, D. S. Yufit, J. H. Gall, R. K. Henderson, *Acta Crystallogr. Sect. C* **1997**, *53*, 90; d) T. Steiner, *Acta Crystallogr. C* **2000**, *56*, 876.

[3] B. Krebs, G. Henkel, W. Stücker, *Z. Naturforsch. B* **1984**, *39*, 43.

[4] P. M. Boorman, X. G. Gao, M. Parvez, *J. Chem. Soc. Chem. Commun.* **1992**, 1656.

[5] J. M. Karty, Y. Wu, J. I. Brauman, *J. Am. Chem. Soc.* **2001**, *123*, 9800.

[6] a) D. Sellmann, P. Lechner, F. Knoch, M. Moll, *J. Am. Chem. Soc.* **1992**, *114*, 922; b) R. J. Pleus, H. Waden, W. Saak, D. Haase, S. Pohl, *J. Chem. Soc. Dalton Trans.* **1999**, 2601.

[7] a) D. Sellmann, J. Käppler, M. Moll, *J. Am. Chem. Soc.* **1993**, *115*, 1830; b) P. G. Jessop, R. H. Morris, *Inorg. Chem.* **1993**, *32*, 2236.

[8] a) S.-W. A. Fong, T. S. A. Hor, *J. Chem. Soc. Dalton Trans.* **1999**, 639, and references therein; b) 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.

[9] a) M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. González-Duarte, A. Lledós, J. Sola, G. Ujaque, *Chem. Commun.* **1998**, 597; b) M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. González-Duarte, A. Lledós, J. A. Ramírez, *J. Chem. Soc. Dalton Trans.* **1999**, 3103.

[10] 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.

[11] S.-W. A. Fong, J. J. Vittal, W. Henderson, T. S. A. Hor, A. G. Oliver, C. E. F. Rickard, *Chem. Commun.* **2001**, 421.

[12] DFT calculations were carried out with the B3LYP functional. The structures were optimized, and transition states were checked by frequency analysis at the B3LYP level of theory. Single-point MP2 calculations were performed on the optimized B3LYP geometries. Effective core potentials and their related double-zeta basis set LANL2DZ were used for Pt, P, and S atoms, supplemented with polarization functions for the P and S atoms, whereas the 6-31G basis set was used for C and H atoms.

[13] G. Aullón, G. Ujaque, A. Lledós, S. Alvarez, *Chem. Eur. J.* **1999**, *5*, 1391, and references therein.

[14] a) J. E. Lowder, L. A. Kennedy, K. G. P. Sulzmann, S. S. Penner, *J. Quantum Spectr. Radiation Transf.* **1994**, *10*, 17; b) E. L. Woodbridge, T.-L. Tso, M. P. McGrath, W. J. Hehre, E. K. C. Lee, *J. Chem. Phys.* **1986**, *85*, 6991.

[15] Crystal data for **1**: $[C_{52}H_{49}P_4Pt_2S_2]ClO_4$, $M_r = 1351.5$, monoclinic, space group $P2_1$, $a = 9.5504(8)$, $b = 14.9721(12)$, $c = 17.6955(14)$ Å, $\beta = 94.202(2)°$, $V = 2523.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.779$ g cm^{-3}, $\mu = 5.84$ mm^{-1}, $T = 160$ K, $R = 0.056$ ($F^2 > 2\sigma$), $R_w = 0.152$ (all F^2) for 10719 data and 586 refined parameters. **2**: $[C_{54}H_{53}P_4Pt_2S_2]ClO_4 \cdot 2\,CH_3OH$, $M_r = 1443.7$, monoclinic, space group $P2_1/c$, $a = 12.5409(8)$, $b = 17.0421(10)$, $c = 26.7036(16)$ Å, $\beta = 98.817(2)°$, $V = 5639.7(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.698$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 5.24$ mm^{-1}), $T = 160$ K, $R = 0.053$ ($F^2 > 2\sigma$), $R_w = 0.117$ (all F^2) for 13082 data and 641 refined parameters. CCDC-177519 (**1**) and CCDC 177518 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[16] Note that the S^{2-} and SH^- bridging ligands in this complex are disordered and indistinguishable by crystallography, because they are symmetry-equivalent, although this is not explicitly stated in the publication.

[17] a) M. S. Rozenberg, T. Nishio, T. Steiner, *New J. Chem.* **1999**, *23*, 585; b) To test the feasibility of S–H ⋯ Ph hydrogen bonding in the *endo* conformer, we took the reported crystal structure of **1** and **2** and located a hydrogen atom on one of the two bridging sulfur atoms with a S–H distance of 1.36 Å and *endo* orientation. Found S–H ⋯ C(phenyl ring) distances range between 2.8 and 3.0 Å, which, according to ref. [17a], are consistent with S–H ⋯ Ph hydrogen bonding.

[18] a) Solvent effects were taken into account in polarized continuum model (PCM) calculations (acetone: $\varepsilon = 20.70$); b) J. Tomasi, M. Persico, *Chem. Rev.* **1994**, *94*, 2027.