Extension of the Karplus relationship to vicinal coupling within the P–Ru–S–H moiety of the H_2S complexes *cis*-RuX_2(P–N)(PPh_3)(SH_2) {X = Cl, Br; P–N = [*o*-(*N*,*N*-dimethylamino)phenyl]diphenylphosphine}

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The Ru(II)–H_2S complexes *cis*-RuX_2(P–N)(PPh_3)(SH_2) {X = Cl, Br; P–N = [*o*-(*N*,*N*-dimethylamino)phenyl]diphenylphosphine} are characterised crystallographically and by $^{31}P\{^1H\}$, ^1H and $^1H\{^{31}P\}$ NMR spectroscopies; the ^1H NMR spectra at −50 °C show three-bond coupling of only one H-atom of the coordinated H_2S to the P-atom of the P–N ligand, and this represents an extension of the Karplus relationship to vicinal coupling within a P–Ru–S–H system.

The reactions of H_2S with transition metal complexes are beginning to be explored, the systems having relevance in the biological sulfur cycle, in the formation of ores, in hydrodesulfurisation (HDS) catalysis, and in conversion of H_2S to H_2 and elemental sulfur (or organosulfur compounds).[1]

We recently reported the second structurally characterised transition metal–H_2S complex *cis*-$RuCl_2$(P–N){P(C_6H_4Me-*p*)$_3$}(SH_2) **1** {P–N = [*o*-(*N*,*N*-dimethylamino)phenyl]diphenylphosphine}, formed under ambient conditions from the reaction of the five-coordinate complex $RuCl_2$(P–N){P(C_6H_4Me-*p*)$_3$} with H_2S; unfortunately, although the formulation was unambiguous, only one H atom of the coordinated H_2S was located in the X-ray analysis.[2] We present here the X-ray structures of *cis*-RuX_2(P–N)(PPh_3)(SH_2), (X = Cl **2** or Br **3**), where both H atoms of the H_2S are isotropically refined.

The yellow complex **2** was prepared by adding 1 atm H_2S to $RuCl_2$(P–N)(PPh_3), formed *in situ* from $RuCl_2(PPh_3)_3$ (200 mg, 0.21 mmol) and P–N (64 mg, 0.21 mmol) in acetone (10 mL) at 50 °C.[3] This solution was stirred for 8 h at room temperature, and the resulting precipitate of **2**·Me_2CO was collected and dried *in vacuo* for 1 h (yield: 140 mg, 80%). Complex **3**·Me_2CO was prepared similarly in 72% yield using $RuBr_2$(P–N)(PPh_3) (100 mg, 0.12 mmol) as precursor, this being isolated in 50% yield from a stirred suspension containing an excess of NaBr (1.14 g, 11 mmol), $RuCl_2(PPh_3)_3$ (420 mg, 0.44 mmol) and P–N (136 mg, 0.44 mmol) in acetone (10 mL).

Crystals of **2**·Me_2CO and **3**·C_6H_6 were obtained from saturated acetone and C_6H_6 solutions of the respective complexes left standing under 1 atm H_2S. The ORTEP plots of **2** and **3** (Fig. 1)‡ reveal pseudo-octahedral geometries with *cis* X-atoms, the coordinated H_2S ligand being *cis* to both P-atoms, and the PPh_3 ligand and the –NMe_2 being mutually *trans*. With the exception of the larger Ru–X bonds in **3**, the geometries of **1**–**3** are very similar. The S–H bond lengths (1.20, 1.30 Å in **2**, and 1.25, 1.34 Å in **3**) are generally shorter than those of gaseous H_2S (1.33 Å),[4] but other weak interactions are present and may play a role in stabilising the coordinated H_2S: H-bonding is observed within H(2)···Cl(2) (2.69 Å) and H(1)···Br(1) (2.85 Å), and both H atoms of the H_2S in **2** and **3** point towards phenyl planes. The shortest phenyl···SH distances are 2.80 Å [H(1)···C(9)] and 2.97 Å [H(2)···C(21)] within **2**, and 2.52 Å [H(1)···C(20), phenyl from P–N] and 2.59 Å

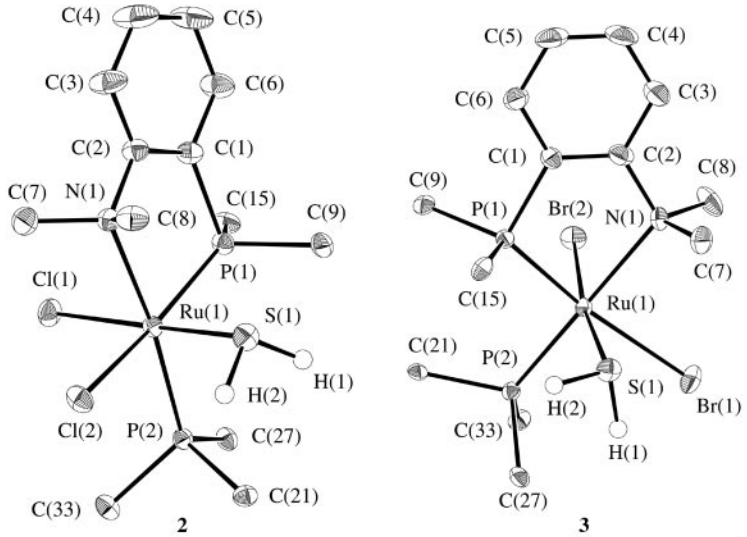

Fig. 1 The ORTEP plots of **2** and **3**. Thermal ellipsoids for non-hydrogen atoms are drawn at 33% probability (some phenyl carbons have been omitted for clarity). Selected bond lengths (Å) and angles (°): for **2**: S(1)–H(1) 1.20(3), S(1)–H(2) 1.30(3), Ru(1)–S(1) 2.3503(3), Ru(1)–P(1) 2.2712(6), Ru(1)–P(2) 2.3110(7), Ru(1)–N(1) 2.338(2), Ru(1)–Cl(1) 2.4238(6), Ru(1)–Cl(2) 2.4721(5); H(1)–S(1)–H(2) 102(2), Ru(1)–S(1)–H(1) 111(1), Ru(1)–S(1)–H(2) 103(1), Cl(1)–Ru(1)–S(1) 175.18(2), Cl(2)–Ru(1)–S(1) 82.63(2), S(1)–Ru(1)–P(1) 90.54(2), S(1)–Ru(1)–P(2) 93.76(2), S(1)–Ru(1)–N(1) 89.18(5). For **3**: S(1)–H(1) 1.25(7), S(1)–H(2) 1.34(6), Ru(1)–S(1) 2.333(1), Ru(1)–P(1) 2.262(1), Ru(1)–P(2) 2.301(1), Ru(1)–N(1) 2.372(3), Ru(1)–Br(1) 2.6343(5), Ru(1)–Br(2) 2.5540(4); H(1)–S(1)–H(2) 98(4), Ru(1)–S(1)–H(1) 101(3), Ru(1)–S(1)–H(2) 115(2), Br(1)–Ru(1)–S(1) 79.77(3), Br(2)–Ru(1)–S(1) 172.31(3), S(1)–Ru(1)–P(1) 93.87(4), S(1)–Ru(1)–P(2) 93.48(4), S(1)–Ru(1)–N(1) 89.43(9).

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† Deceased October 27, 1998.

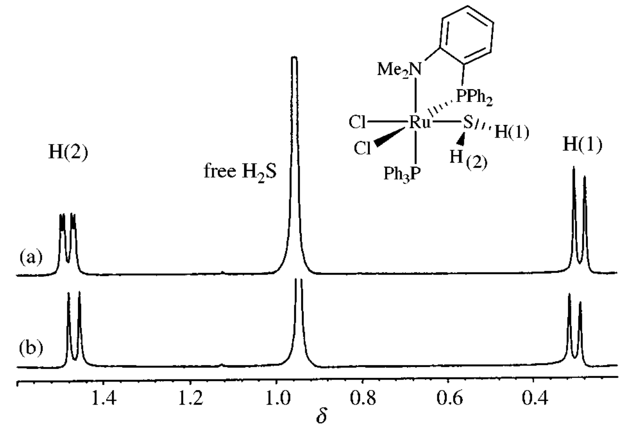
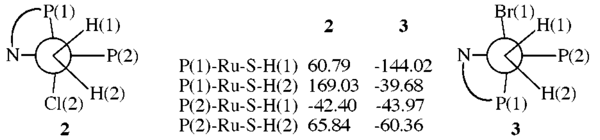


Fig. 2 (a) ^1H NMR spectrum (500 MHz) of **2** in CD_2Cl_2 at −50 °C (under 1 atm H_2S) and (b) the corresponding $^1H\{^{31}P\}$ NMR spectrum.



	2	3
P(1)-Ru-S-H(1)	60.79	-144.02
P(1)-Ru-S-H(2)	169.03	-39.68
P(2)-Ru-S-H(1)	-42.40	-43.97
P(2)-Ru-S-H(2)	65.84	-60.36

Fig. 3 End-on view of the solid state structures of **2** and **3**, with dihedral angles corresponding to P–Ru–S and Ru-S–H planes.

[H(2)···C(28)] within **3** (Fig. 1); related phenyl···mercapto proton interactions have been detected, for example, in $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$,[5] and implicated in HDS mechanisms.[6]

The $^{31}P\{^1H\}$ NMR spectra (200 MHz, 20 °C) of **2** and **3** in CD_2Cl_2 under 1 atm H_2S§ give AX patterns at δ 49.81 (*P*–N) and 43.30 (*P*Ph$_3$) ($^2J_{PP}$ 28.78 Hz) and δ 53.41 (*P*–N) and 44.36 (*P*Ph$_3$) ($^2J_{PP}$ 29.20 Hz), respectively, the coupling constants being characteristic of *cis*-P atoms.[3] Equivalent ^1H signals for the Ru–SH$_2$ resonances of **2** in solution are seen at 20 °C as a broad peak at δ *ca.* 1.0, but at −50 °C in CD_2Cl_2 (500 MHz) this peak is resolved into a doublet at δ 0.30 [H(1)] and doublet of doublets at δ 1.49 [H(2)], when the solution structure approaches that in the solid state [Fig. 2(a)]. The assignments for H(1) and H(2) are based on the observed H-bonding which would deshield the H(2) relative to H(1). The data show that H(1) and H(2) are mutually coupled ($^2J_{HH}$ = 12.3 Hz), while H(2) is coupled to a P-atom ($^3J_{HP}$ 3.50 Hz) and H(1) is not; the $^1H\{^{31}P\}$ NMR spectrum [Fig. 2(b)] shows the H(2) multiplet reduced to a doublet, and by selective ^{31}P decoupling, it was determined that H(2) is coupled to the P-atom of the P–N ligand.

The findings conform nicely to the Karplus relationship, which was initially established for vicinal coupling of protons (^3J, *H*–C–C–*H*),[7] and has been extended to *P*–C–C–*H*, *P*–O–C–*H* and *P*–S–C–*H* systems.[8] For our Ru–H$_2$S systems, the dihedral angles for P–Ru–S–H can be visualised by an end-on view of the Ru–S bond shown in Fig. 3. The absolute dihedral angles (ϕ) for non-coupling P and H atoms in **2** are 60.79, 42.40 and 65.84°, and these correspond to P(1)–H(1), P(2)–H(1) and P(2)–H(2) interactions, respectively, where orbital overlaps are negligible. For P(1)–H(2), ϕ is 169.03° where the $^3J_{HP}$ coupling is observed, consistent with Karplus curves that give maximum coupling when ϕ = 180°; the P(1)–Ru–S–H(2) arrangement likely results from interactions of H(2) with Cl(2) and a phenyl group of PPh$_3$.

Similar findings were obtained for **3**; at −50 °C H(2) appears as a doublet at δ_H 0.48 while H(1), which is H-bonded to Br(1), appears as a doublet of doublets at δ_H 1.23 ($^2J_{HH}$ 12.2, $^3J_{HP}$ 4.3 Hz). Decoupling experiments again show that H(1) is coupled to P(1), where ϕ = 144.02° (Fig. 3). The equivalence of the proton signals of the coordinated H_2S at 20 °C (for **2** and **3**) does not result from exchange with free H_2S,§ and presumably involves inversion at the S atom.

The NMR coupling through a metal centre described should be of quite general application, and provides a further structural probe for any *A*–metal–X–*B*-type system, where A and B are NMR-active nuclei, and X is an appropriate donor atom. To our knowledge, there is no corresponding example involving coordinated water.

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Notes and references

‡ Crystallographic data for both structures were collected on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) at 180 K, solved by heavy-atom Patterson methods and expanded using Fourier techniques with the teXsan crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically; the S–H hydrogens were refined isotropically, the rest were fixed in calculated positions with C–H = 0.98 Å.

Crystal data: for $C_{41}H_{43}Cl_2NOP_2RuS$ **2**·Me$_2$CO: M = 831.78, yellow–brown prisms, crystal size 0.28 × 0.30 × 0.38 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 14.843(2), b = 16.0292(9), c = 16.0099(8) Å, β = 95.286(2)°, V = 3792.8(5) Å^3, Z = 4, D_c = 1.46 g cm^{-3}, $F(000)$ = 1712, μ(Mo-Kα) = 7.27 cm^{-1}, 33910 total reflections, 9547 unique (R_{int} = 0.041), 6176 observed [$I > 3\sigma(I)$], $R(R_w)$ = 0.028(0.025).

For $C_{44}H_{43}Br_2NP_2RuS$ **3**·C$_6$H$_6$: M = 940.72, orange prisms, crystal size 0.15 × 0.20 × 0.25 mm, monoclinic, space group $P2_1$ (no. 4), a = 9.667(1), b = 18.976(2), c = 11.6270(4) Å, β = 110.3292(7)°, V = 2000.0(3) Å^3, Z = 2, D_c = 1.56 g cm^{-3}, $F(000)$ = 948, μ(Mo-Kα) = 25.61 cm^{-1}, 18513 total reflections, 5234 unique (R_{int} = 0.031), 8318 observed [$I > 3\sigma(I)$], $R(R_w)$ = 0.059(0.074). CCDC 182/1473.

§ 1 atm H_2S ensures complete formation of **2** and **3** within equilibria with the respective five-coordinate precursors;[2] the same NMR signals (together with those of the precursors)[3] are observed for solutions of the complexes in the absence of added H_2S.

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