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μ-Methylene rhodium complexes with SH ligand: synthesis and structures of $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]BPh_4$ and *trans*-$[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(SH)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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Abstract

The μ-methylene rhodium complex with a hydrosulphide ligand, $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]BPh_4$ (**2b**), has been isolated from the reaction of *trans*-$[Rh_2Cp^*_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**) with H_2S in CH_3OH and readily converted to *trans*-$[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(SH)_2]$ (**3**) in the presence of NEt_3 and H_2S; **2b** and **3** have been characterized crystallographically.

H_2S, SH^- and S^{2-} metal complexes have received considerable attention recently with reference to hydro-desulphurization of organosulphur compounds on the surface of transition metal sulphides [1]. In a pathway of the hydro-desulphurization, complete decomposition occurs resulting in surface sulphur, carbon and hydrocarbon fragments which contain carbyne, carbene and other hydrocarbyl species [1b,1d]. In order to understand this surface by using model compounds containing sulphur and carbene ligands, we have begun to synthesize μ-methylene rhodium complexes with sulphur ligands. Here we report the first stable μ-methylene rhodium complexes with a bridged SH ligand, $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]BPh_4$, and with two terminal SH ligands, *trans*-$[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(SH)_2]$.

The reaction of $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2Cl_2]$ (**1**) [2*] with excess H_2S gas in $CHCl_3$ or CH_2Cl_2 did not proceed at all, but in methanol (suspension) led to the formation of a clear solution containing the product, $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]Cl$ (**2a** **); the solution showed a single methyl of C_5Me_5 resonance at δ 1.937 (at 22°C) in ^1H NMR and at δ 8.27 (at 21°C) in ^{13}C NMR, and a single ^{103}Rh resonance at $\delta + 315$. Furthermore, the SH signal appeared at δ -1.925 in a

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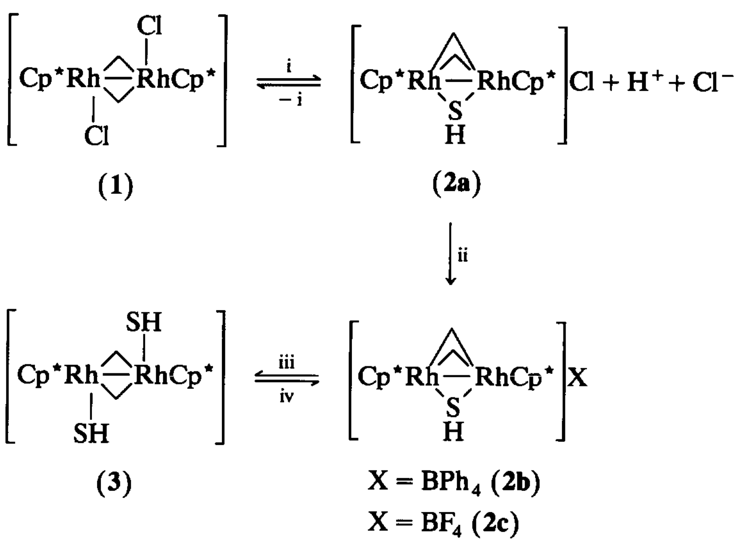
* Reference numbers with asterisk indicates a note in the list of references.



Scheme 1. Reagents and conditions: (i) H_2S, CH_3OH, 20°C; (ii) NaX (X = BPh_4, BF_4), CH_3OH, 20°C; (iii) H_2S, NEt_3, CH_3OH, 20°C; (iv) HBF_4, CH_2Cl_2, 20°C. ∧ denotes the μ-CH_2 ligand.

reduced intensity owing to a H–D exchange in CD_3OD. The product **2a** in the reaction system reverts easily to the starting dichloro complex on removal of the solvent. Although attempts to isolate **2a** were unsuccessful, the addition of a non-nucleophilic anion, for example, BPh_4^- and BF_4^- enables isolation of **2b** ** (90% yield) and **2c** ** (85% yield) even in an acid media (Scheme 1). We were not able to observe formation of any H_2S complex in the system with ^1H NMR spectroscopy.

** All compounds other than **2a** were isolated as analytically pure samples. The ^1H and ^{13}C NMR spectra of **2a** in CD_3OD are very close to those of **2c** in CD_3OD (*vide infra*) and show temperature dependence similar to **2b** and **2c** (see text). Selected spectroscopic data for new compounds are as follows. Complex **2a**: ^1H NMR (CD_3OD, 22°C): 8.697 (s(br), μ-CH_2, 1H); 8.377 (s(br), μ-CH_2, 1H); 8.256 (s(br), μ-CH_2, 1H); 7.902 (s(br), μ-CH_2, 1H); 1.937 (s, C_5Me_5, 30H); −1.925 (br, SH, 0.2H) ppm. ^{13}C NMR (CD_3OD, 21°C): 165.94 (br, μ-CH_2); 160.31 (br, μ-CH_2); 101.38 (s, $C_5$$Me_5$); 8.27 (s, C_5*Me*$_5$) ppm. Complex **2b**: IR (mineral oil): 2496 (w, ν(SH)) cm^{-1}. ^1H NMR (CD_2Cl_2, 21°C): 8.327 (s(br), μ-CH_2, 2H); 7.977 (s(br), μ-CH_2, 1H); 7.705 (s(br), μ-CH_2, 1H); 1.798 (s, C_5Me_5, 30H); −2.730 (s(br), SH, 1H) ppm. ^{13}C NMR (CD_2Cl_2, 21°C): 165.82 (br, μ-CH_2); 161.69 (br, μ-CH_2); 102.43 (d, $C_5$$Me_5$, *J*(Rh–C) = 3 Hz); 10.10 (s, C_5*Me*$_5$) ppm. Complex **2c**: IR (mineral oil): 2501 (w, ν(SH)) cm^{-1}. ^1H NMR (CD_2Cl_2, 21°C): 8.385 (s(br), μ-CH_2, 1H); 8.326 (s(br), μ-CH_2, 1H); 8.033 (s(br), μ-CH_2, 1H); 7.735 (s(br) μ-CH_2, 1H); 1.814 (s, C_5Me_5, 30H); −2.682 (s(br), SH, 1H) ppm. (CD_3OD, 22°C): 8.668 (s(br), μ-CH_2, 1H); 8.392 (s(br), μ-CH_2, 1H); 8.258 (s(br), μ-CH_2, 1H); 7.912 (s(br) μ-CH_2, 1H); 1.934 (s, C_5Me_5, 30H); −1.926 (br, SH, 0.1H) ppm. ^{13}C NMR (CD_2Cl_2, 20°C): 166.15 (t(br), μ-CH_2, *J*(Rh–C) ≈ 10 Hz); 161.63 (t(br), μ-CH_2, *J*(Rh–C) ≈ 10 Hz); 102.42 (s, $C_5$$Me_5$); 10.04 (s, C_5*Me*$_5$) ppm. Complex **3**: IR (mineral oil): 2550 (w, ν(SH)) cm^{-1}. ^1H NMR ($CDCl_3$, 20°C): 9.527 (t, μ-CH_2, 4H, *J*(Rh–H) = 1.5 Hz); 1.694 (s, C_5Me_5, 30H); −3.317 (t, SH, 2H, *J*(Rh–H) < 1Hz) ppm. ^{13}C NMR ($CDCl_3$, 20°C): 172.81 (t, μ-CH_2; *J*(Rh–C) = 26 Hz); 102.59 (s, $C_5$$Me_5$); 10.19 (s, C_5*Me*$_5$) ppm. A mixture (1:2) of *cis* and *trans* isomer. IR (mineral oil): 2550 cm^{-1} (w, ν(SH), *trans*): 2480 (w, ν(SH), *cis*) cm^{-1}. ^1H NMR ($CDCl_3$, 20°C): 9.601 (b, μ-CH_2, *cis*); 9.527 (t, μ-CH_2, *J*(Rh–H) = 1.5 Hz, *trans*); 9.130 (b, μ-CH_2, *cis*); 1.697 (s, C_5Me_5, *cis*); 1.694 (s, C_5Me_5, *trans*); −3.320 (b, SH, *trans* and *cis*).

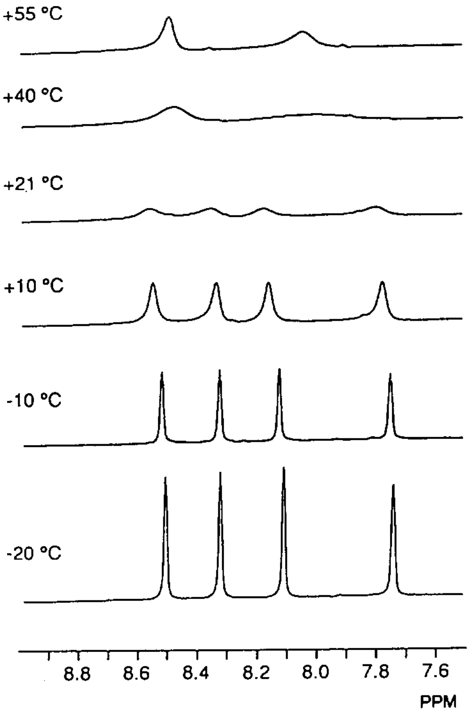


Fig. 1. Variable temperature ^1H NMR spectra of the μ-CH_2 protons in $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]BF_4$ (**2c**) in $CDCl_3$.

Compounds **2b** and **2c** showed the SH proton signal at δ approx. -2.7 and the characteristic signals of the CH_2 protons between δ 8.3 and 7.7 in ^1H NMR spectra in CD_2Cl_2. The four protons of the μ-CH_2 groups are in different chemical environments due to the stereochemistry of the lone pair of electrons on the S atom as shown in the molecular structure (*vide infra*). The chemical shifts vary considerably (max $\approx$ 0.5 ppm for the lowest peak) with solvent and counter anions. Complex **2** in solution shows fluxionality resulting from an inversion [3] at the S atom. The dynamic process sets in around -10°C, and it becomes faster around 55°C where the two highest field and the two lowest field signals owing to the CH_2 groups have coalesced into two signals (Fig. 1). The activation energy was estimated to be approx. 15 kcal/mol by means of a line shape analysis. This is the first example of an inversion process at the μ-SH ligand.

In the molecular structure of **2b** from single-crystal X-ray analysis *** each rhodium atom of the dinuclear cation is coordinated by two μ-CH_2, one μ-SH, and one Cp* ligand to give a slightly puckered Rh_2C_2 ring and has a quite short single Rh–Rh bond distance of 2.554(1) Å (Fig. 2). The two Rh–S distances 2.394(4) and 2.407(4) Å compare well with those in the two other μ-SH rhodium complexes which have been characterized by single-crystal X-ray analysis, but the intriguing structural feature of **2b** is the very small Rh–S–Rh angle (64.3(1)°) which is attributable to the short Rh–Rh distance [4]. (By comparison, $[RhCl(H)(\mu\text{-}SH)(PPh_3)_2]_2$ [5]; Rh–S, 2.383(1), 2.385(1) Å, Rh$\cdots$Rh, 3.637(1),

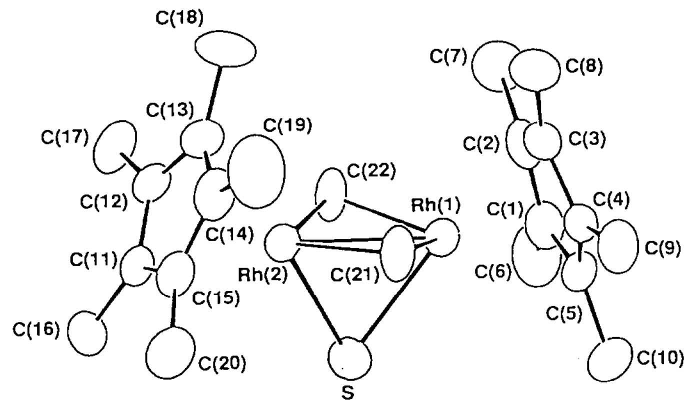


Fig. 2. ORTEP diagram $[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$ in **2b** with the atom numbering scheme. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.554(1), Rh(1)–S 2.407(4), Rh(2)–S 2.394(4), Rh(1)–C(21) 2.06(1), Rh(1)–C(22) 2.04(1), Rh(2)–C(21) 2.03(1), Rh(2)–C(22) 2.06(1), Rh(1)–S–Rh(2) 64.3(1), Rh(1)–C(21)–Rh(2) 77.1(3), Rh(1)–C(22)–Rh(2) 77.1(4), C(21)–Rh(1)–C(22) 100.6(4), C(21)–Rh(2)–C(22) 101.1(4).

Rh–S–Rh, 99.43(4)°, $[(\text{triphos})HRh(\mu\text{-}SH)]_2^{2+}$ [6]; Rh–S, 2.395(3), 2.390(3) Å, Rh ··· Rh, 3.617(2), Rh–S–Rh, 98.2(2)°).

The μ-SH complex **2** reacts with more H_2S gas in the presence of Et_3N to yield *trans*-$[Rh_2Cp^*_2(\mu\text{-}CH_2)_2(SH)_2]$ (**3** **) at 25°C. At −20°C a mixture of *cis* and *trans* isomer (1 : 2 molar ratio) ** was isolated, but the *cis* isomer changed quickly to the *trans* isomer in CH_2Cl_2 upon raising the temperature to 25°C. The formation of the dihydrosulphido complex **3** needs more basic reaction conditions than that of **2**. The SH proton signal of the *trans* isomer **3** resonates at δ −3.317 (t, $J(\text{Rh–H}) < 1$ Hz) and the CH_2 protons at δ 9.527 (t, $J(\text{Rh–H}) = 1.5$ Hz). X-Ray structure analysis of **3** confirmed a *trans* configuration and all hydrogen atoms were located and refined (Fig. 3). The Rh_2C_2 ring is planar and the two Rh–S bonds lie almost perpendicular to the plane in a trans position with each other. The Rh–S bond length (2.3591(8) Å [7*] is slightly shorter but the Rh–Rh bond is longer (2.6487(3) Å) than those of **2b**, separately. The *trans* isomer **3** reacted with HBF_4 to lose 1 mol of H_2S and transformed quantitatively into **2c**.

*** Crystal data for complex **2b**: $C_{46}H_{55}BRh_2S$, $M = 856.62$, monoclinic, space group $P2_1/c$, $a = 12.835(3)$ Å, $b = 17.960(5)$ Å, $c = 18.343(9)$ Å, $\beta = 93.83(6)°$, $Z = 4$, $V = 4129(6)$ Å^3, $D_x = 1.35$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.47$ cm^{-1}, $F(000) = 1768$. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation $\lambda = 0.71073$ in $2\theta \leq 55°$ range. The structure was solved and refined by a block-diagonal least-squares technique. The current R value is 0.052 ($R_w = 0.075$) for 3790 independent absorption-corrected reflections. Complex **3**: $C_{22}H_{36}Rh_2S_2$, $M = 570.46$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.147(1)$ Å, $b = 14.899(1)$ Å, $c = 8.011(1)$ Å, $\beta = 107.39(1)°$, $Z = 2$, $V = 1155.8(2)$ Å^3, $D_x = 1.639$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 15.850$ cm^{-1}, $F(000) = 580$. Intensity data were collected ($2\theta \leq 60°$ range) and the structure was solved by the similar method as mentioned above. All hydrogen atoms, including those in the SH ligands, were found on a difference map and refined. The final R value is 0.022 ($R_w = 0.029$) for 2775 independent absorption-corrected reflections.

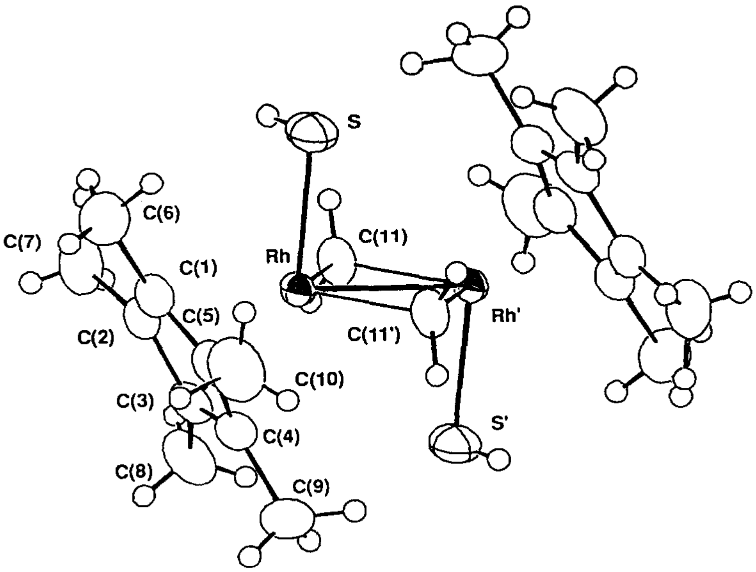


Fig. 3. ORTEP diagram for *trans*-[$Rh_2Cp^*_2(\mu\text{-}CH_2)_2(SH)_2$] (3) with the atom numbering scheme. Selected bond lengths (Å) and angles (°): Rh–Rh' 2.6487(3), Rh–S 2.3591(8), Rh–C(11) 2.039(2), Rh–C(11)' 2.032(3), S–Rh–Rh' 90.28(2), C(11)–Rh–C(11)' 98.82(9), Rh–C(11)–Rh' 81.18(8), Rh–S–H(S) 91(2). (Primed atoms have equivalent coordinates $-x$, $-y$, $-z$.)

In connection with the hydrodesulphurization on the metal surfaces, we are now studying the oxidation and decomposition of **2** and **3** to see what transformation of the μ-CH_2 and SH ligands takes place.

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