Isomerisation of [{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$]: ^{1}H Nuclear Magnetic Resonance and Electrochemical Studies and the *X*-Ray Crystal Structure of [*anti*-{Rh(μ-SPh)(η-C$_5$H$_5$)}$_2$]

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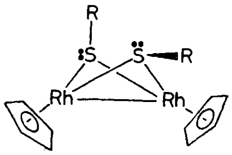
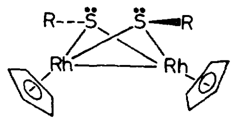
Summary The isomerisation of [*syn*-{Rh(μ-SR^1)(η-C$_5$H$_4$R^2}$_2$] to the *anti*-isomer, the structure of which (R^1 = Ph, R^2 = H) has been elucidated by *X*-ray crystallography, involves opening of the Rh$_2$S$_2$ ring; insertion into the metal–metal bond to give [Rh$_2$(μ-SR^1)$_2$(μ-X)(η-C$_5$H$_4$R^2)$_2$]$^+$ (X = SR^1 or Cl) is initiated by one-electron oxidation.

It was shown in the preceding communication[1] that complexes [{Rh(μ-SR)L}$_2$] (R = alkyl or Ph, L = cyclo-octatetraene or cyclo-octadiene) can undergo two intramolecular dynamic processes, Rh$_2$S$_2$ ring-inversion and rotation of the olefin. We now show that the metal–metal bond in [{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$] prevents ring inversion and allows only isomerisation, *via* Rh$_2$S$_2$ ring-opening. In addition, insertion into the metal–metal bond is initiated by one-electron oxidation.

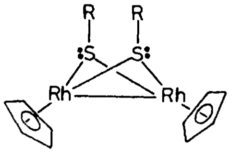
The complex [Rh(CO)$_2$(η-C$_5$H$_5$)] with R^{1}SSR^1, or [{Rh(CO)$_2$(μ-SR^1)}$_2$] with C$_5$H$_4$R^2,[2] in refluxing toluene afford a mixture of two isomers of [{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$] (R^1 = Ph or C$_6$H$_4$Me-*p*, R^2 = H or Me). For R^1 = C$_6$H$_4$Me-*p* and R^2 = H, the hexane-soluble isomer has a temperature-invariant (+120 to −40 °C in C$_6$H$_5$Cl) ^{1}H n.m.r. spectrum [τ (CDCl$_3$ 7·75 (6H, s, Me), 4·70 (10H, s, C$_5$H$_5$), 3·14 (2H, d,



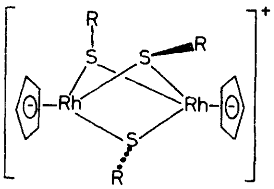
(I)



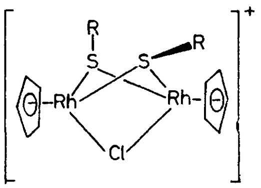
(II)



(III)



(IV)



(V)

$|J_o + J_p|$ 8 Hz, m-C_6H_4), 3·12 (2H, d, $|J_o + J_p|$ 8 Hz, m-C_6H_4), 2·69 (2H, d, $|J_o + J_p|$ 8 Hz, o-C_6H_4), and 2·66 (2H, d, $|J_o + J_p|$ 8 Hz, o-C_6H_4)] which can only arise from a static *anti*-isomer with structure (I). The ^1H n.m.r. spectrum of the hexane-insoluble isomer [τ ($CDCl_3$) 7·70 (6H, s, Me), 4·88 (10H, s, C_5H_5), 3·05 (4H, d, $|J_o + J_p|$ 8 Hz, m-C_6H_4), and 2·48 (4H, d, $|J_o + J_p|$ 8 Hz, o-C_6H_4)] is due to either one of the two symmetrical isomers (II) or (III), or a rapidly equilibrating mixture of the two. As (I) is static we rule out the last possibility and on steric grounds assign structure (II) to the hexane-insoluble isomer. *X*-Ray diffraction studies have elucidated the structure of (I) and confirm the presence of the metal–metal bond which prevents Rh_2S_2 ring-inversion.

Crystal data: Crystals of [{Rh(μ-SPh)(η-C_5H_5)}$_2$] are orthorhombic, space group *Pcmn*, $Z = 4$, $a = 10{\cdot}198(6)$, $b = 10{\cdot}306(6)$, $c = 19{\cdot}140(12)$ Å. The structure was solved by conventional heavy-atom methods from data collected to $2\theta = 50°$ on a Syntex $P2_1$ four-circle diffractometer with monochromatised Mo-K_α X-radiation. For the 1331 observed reflections, $R = 0{\cdot}070$.†

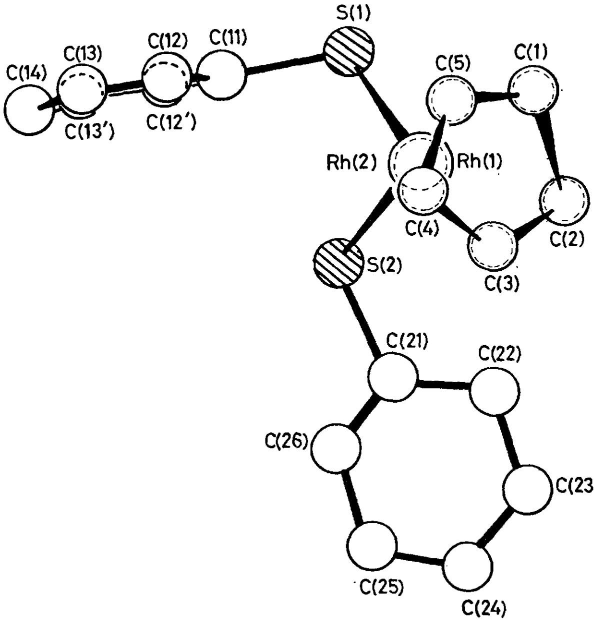


FIGURE. Molecular structure of [{Rh(μ-SPh)(η-C_5H_5)}$_2$]. Rh–Rh, 2·644(2); Rh–S (mean), 2·306(3) Å; interplanar angle between Rh–S–Rh bridges, 110°.

The diffraction study (Figure) shows that the two Rh atoms are bonded together (Rh–Rh 2·64 Å) and bridged (∠S–Rh–S 82·0°) by two SPh ligands in an *anti*-relationship. The planes of the phenyl groups are constrained crystallographically to be mutually perpendicular, and the bond angles at the S atoms are close to the ideal tetrahedral value.

Although both (I) and (II) are static, the isomerisation of (II) to (I) may be followed by visible and ^1H n.m.r. spectroscopy. A deep blue solution of [(II); $R^1 = C_6H_4Me$-p, $R^2 = H$] [λ_{max}(CH_2Cl_2) 563 nm] becomes deep purple (λ_{max} 551 nm) in *ca.* 10 min while the ^1H n.m.r. spectrum shows conversion of (II) into (I). Such a conversion can only involve cleavage of one of the Rh–S–Rh bridges, rotation about the resulting terminal Rh–S bond, and regeneration of the Rh_2S_2 ring. Previous studies[3] have shown the energy barrier to such an isomerisation in [{Fe(CO)$_3$(μ-ER^{1}R^2)}$_2$] (E = P or As, $R^1 \neq R^2$) to be high owing to the requirement that inversion at E must occur before reformation of the Fe_2E_2 ring. Our results show that since no inversion at S is necessary the isomerisation of (II) to (I) can occur readily at room temperature.

The conversion of (II) into (I) may also be studied electrochemically. Cyclic voltammetric studies‡ show that (I) undergoes an irreversible one-electron oxidation [$R^1 = C_6H_4Me$-p, $R^2 = H$, $(E_p)_{ox}$ 0·24 V, $(i_p)_{ox}$ 4·0 μA] whereas a deep blue solution of (II) shows two waves [$(E_p)^1_{ox}$ 0·11 V, $(i_p)^1_{ox}$ 3·5 μA; $(E_p)^2_{ox}$ 0·24 V, $(i_p)^2_{ox}$ 0·5 μA], the relative heights of which change as the solution becomes purple [after 10 min $(i_p)^1_{ox}$ 1·5 μA, $(i_p)^2_{ox}$ 2·5 μA]. Complex (I) ($R^1 = C_6H_4Me$-p, $R^2 = H$) reacts rapidly at room temperature with di-p-tolyl disulphide and [NO][PF_6], as oxidising agent, to give orange [Rh_2(μ-SC_6H_4Me-p)$_3$(η-C_5H_5)$_2$][PF_6] of structure (IV) [τ{(CD_3)$_2$CO} 7·56 (9H, s, Me), 4·29 (10H, s, C_5H_5), 2·80 (6H, d, $|J_o + J_p|$ 8 Hz, m-C_6H_4), and 2·23 (6H, d, $|J_o + J_p|$ 8 Hz, o-C_6H_4)], and with [(C_6H_4Br-p)$_3$N][$SbCl_6$] to give orange-brown [Rh_2(μ-SC_6H_4Me-p)$_2$(μ-Cl)(η-C_5H_5)$_2$][$SbCl_6$] of structure (V) [τ{(CD_3)$_2$CO} 7·64 (3H, s, Me), 7·62 (3H, s, Me), 4·17 (10H, s, C_5H_5), 2·78 (4H, d, $|J_o + J_p|$ 8 Hz, m-C_6H_4), 2·33 (2H, d, $|J_o + J_p|$ 8 Hz, o-C_6H_4), and 2·03 (2H, d. $|J_o + J_p|$ 8 Hz, o-C_6H_4)]. The electrochemical and chemical studies show that formation of (IV) or (V) from (I) involves an initial one-electron oxidation followed by insertion of RS• or Cl• into the metal–metal bond of the radical cation [{Rh(μ-SR^1)(η-$C_5H_4R^2$)}$_2$]$^+$. Current bonding theories[4] on bridged bimetallic species suggest that the H.O.M.O. for [{Rh(μ-SR^1)(η-$C_5H_4R^2$)}$_2$] will have considerable metal–metal bonding character. A comparison of the relative orientations of the sulphur substituents in (I) with those in (IV) or (V) shows that the insertion step occurs before the intermediate radical cation (which formally has a one-electron metal–metal bond) can isomerise.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ At Pt wire electrode in CH_2Cl_2, scan rate 100 mV s^{-1}, potentials are *vs.* a calomel electrode (1M in LiCl).

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[2] R. Hill and S. A. R. Knox, unpublished results.
[3] R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter, and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395.
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