Fluxional Dirhodium Complexes: Crystal and Molecular Structure of $[Rh_2(CO)_2(\mu\text{-}SPh)_2(C_8H_8)]$

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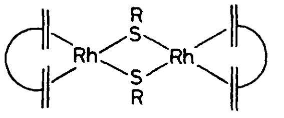
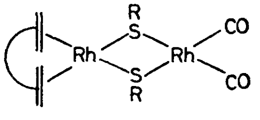
Summary Variable temperature n.m.r. studies of complexes $[Rh_2(CO)_2(\mu\text{-}SPh)_2L]$ and $[Rh_2(\mu\text{-}SR)_2L_2]$ (R = Me, Et, Pr^i, Bu^t, or Ph; L = cyclo-octatetraene or cyclo-octa-1,5-diene) reveal the existence of both an olefin rotation and an inversion of non-planar Rh_2S_2 rings; this non-planarity is established by an *X*-ray diffraction study of $[Rh_2(CO)_2(\mu\text{-}SPh)_2(C_8H_8)]$.

There have been many studies[1] in recent years of complexes containing two transition metals bridged by two ligands (*e.g.*, RS, R_2Ge, or R_2As) such that a non-planar four-atom ring system is present. Interest has centred on the capacity of these complexes for intramolecular environmental exchange of R groups, and whether this is a consequence of ring-inversion or ring-opening. We describe here complexes $[Rh_2(\mu\text{-}SR)_2L_2]$ (**1**) and $[Rh_2(CO)_2(\mu\text{-}SR)_2L]$ (**2**; L = cyclo-octatetraene or cyclo-octa-1,5-diene) which are ideally suited for a study of this phenomenon in that the n.m.r. signals of the co-ordinated olefinic protons are sensitive both to conformational changes of the Rh_2S_2 ring and to the dispositions of the R groups. Variable temperature studies reveal a low energy ring-inversion process for complexes with an *anti* orientation of R groups, and an unprecedented higher energy rotation of the olefin ligand for all complexes.

The yellow-to-red crystalline complexes (**1**; R = Me, Et, Pr^i, Bu^t, or Ph) are obtained in good yield on heating together the appropriate olefin with $[Rh_2(\mu\text{-}SR)_2(CO)_4]$ in heptane; only for R = Ph can intermediate complex (**2**) be isolated. An *X*-ray diffraction study of the orange cyclo-octatetraene complex $[Rh_2(CO)_2(\mu\text{-}SPh)_2(C_8H_8)]$ (**2**; R = Ph) has established the existence of a non-planar Rh_2S_2 ring, a feature apparently general to complexes (**1**) and (**2**).



(1)



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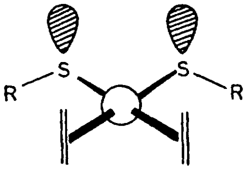

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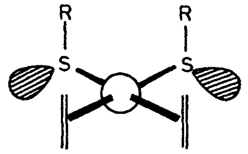

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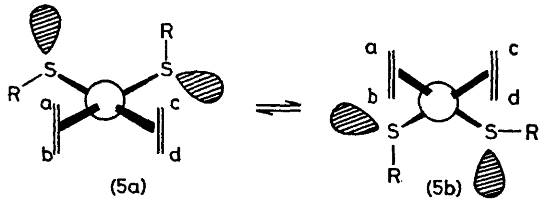
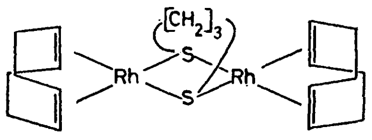


(5a) (5b)



(6)

Crystal data: Crystals of $[Rh_2(CO)_2(\mu\text{-}SPh)_2(C_8H_8)]$ are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8{\cdot}206(5)$, $b = 11{\cdot}053(7)$, $c = 12{\cdot}299(13)$ Å, $\alpha = 95{\cdot}00(7)$, $\beta = 103{\cdot}04(7)$, $\gamma = 99{\cdot}42(5)°$. The structure was solved by conventional heavy-atom methods from data collected to $2\theta = 55°$ on a Syntex $P2_1$ four-circle diffractometer with monochromatized Mo-K_α X-radiation. For the 4012 observed reflections $R = 0{\cdot}055$.†

The X-ray study reveals (Figure 1) the presence of two rhodium atoms in essentially square-planar configurations, one bearing two carbonyl ligands and the other a cyclo-octatetraene bonded in 1,5-diene (tub) fashion. The metals are not directly bonded to one another (Rh · · · Rh = 3·12 Å), but are bridged by two SPh ligands such that their co-ordination planes are folded along the S · · · S vector at a dihedral angle of 135°. The phenyl groups adopt a *syn* orientation, represented as (**3**; R = Ph) when viewed along the Rh · · · Rh axis.

Variable temperature n.m.r. studies show that each of the complexes (**1**) and (**2**) is fluxional to some extent. The ^1H n.m.r. spectrum of $[Rh_2(\mu\text{-}SBu^t)_2(C_8H_8)_2]$ at various temperatures displays all of the features shown by the other complexes in whole or in part and is exemplary (Figure 2). Thus, the inequivalence at −95 °C of the four co-ordinated olefinic protons (τ 4·5—6·5) of each cyclo-octatetraene and of the two Bu^t groups (τ *ca.* 8·5) clearly demands a rigid *anti* isomer (**5**) with a non-planar Rh_2S_2 ring. Moreover, the spectral changes brought about on warming are compatible only with the occurrence of two dynamic intramolecular processes, neither of which requires ring-opening: (a) a low energy degenerate ring-inversion (**5a**)$\rightleftharpoons$ (**5b**) which effects pair-wise averaging (a/d and b/c) of co-ordinated olefinic protons, generating the AB quartet observed in the range −30 to 0 °C, and (b) a relatively higher energy rotation of the olefins which completes total averaging of co-ordinated

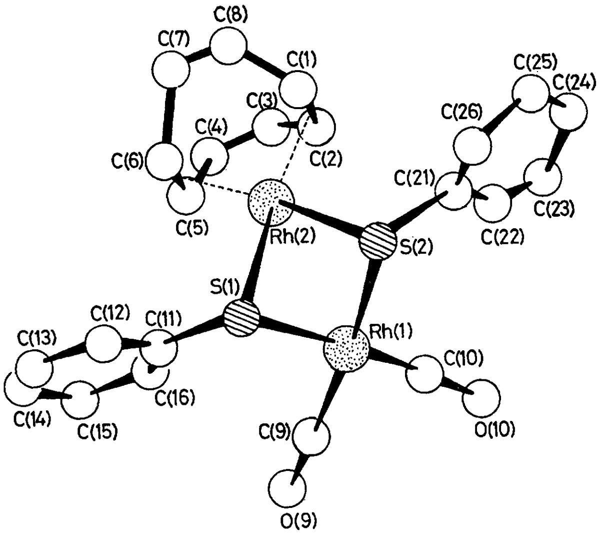


FIGURE 1. Molecular structure of $[Rh_2(CO)_2(\mu\text{-}SPh)_2(C_8H_8)]$.

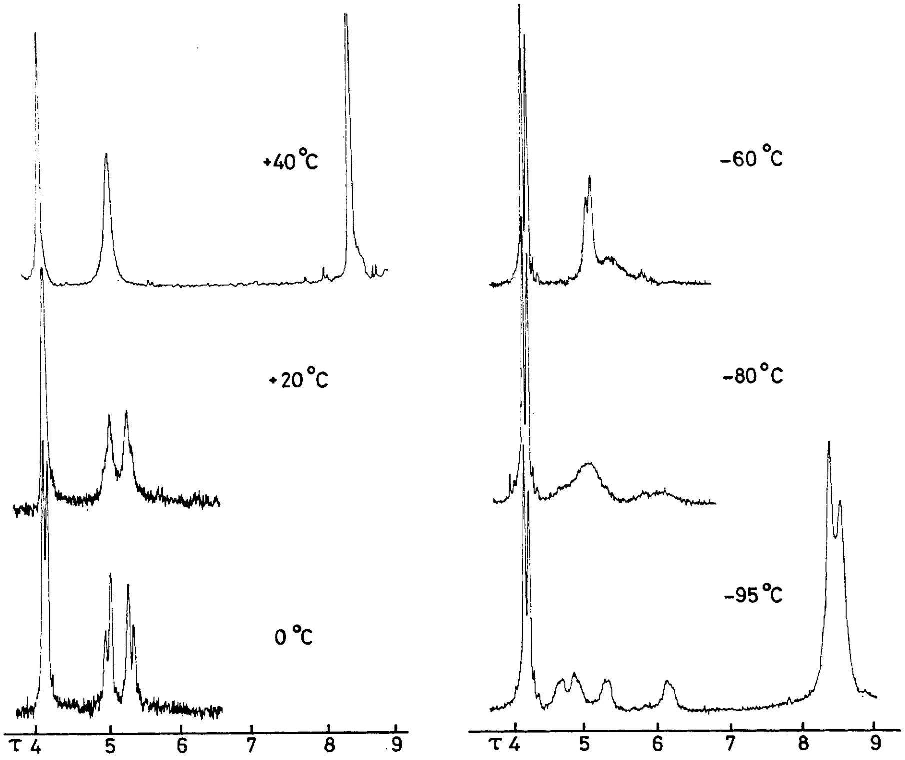


FIGURE 2. ^1H N.m.r. spectrum of $[Rh_2(\mu\text{-}SBu^t)_2(C_8H_8)_2]$ in $CFCl_3$ (−95 to +20 °C) and PhCl (+40 °C).

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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.

olefinic proton environments at +40 °C. Time-averaged signals are also observed for the unco-ordinated olefinic protons and for the SBu^t groups at this temperature, as required.

Confirmation of the nature of the high temperature process was achieved by synthesis and study of complex (**6**). Neither ring-inversion nor any isomerism of the type (**3**) $\rightleftharpoons$ (**4**) $\rightleftharpoons$ (**5**) is possible for (**6**), yet between −30 and +60 °C the ^1H n.m.r. spectrum of the co-ordinated olefinic protons changes analogously to that of $[Rh_2(SBu^t)_2(C_8H_8)_2]$ in the same range. Only a rotation of the olefins can be responsible, such that the two co-ordinated bonds exchange co-ordination sites.

The dynamic behaviour of SPr^i and SBu^t complexes is analogous; complexes (**1**; R = Me or Et) and (**2**; R = Ph) behave differently, however, in having ^1H n.m.r. spectra at −90 °C typical of static *syn* isomers (**3**), and higher temperature spectra reflecting only the onset of olefin rotation. Ring-inversion serves to generate *syn* isomer (**4**), which molecular model construction indicates to be sterically most unfavourable. Complexes $[Rh_2(\mu\text{-}SPh)_2L_2]$ are anomalous in apparently undergoing rapid olefin rotation even at −90 °C, at which temperature only one co-ordinated olefinic proton signal is observed.

Calculations based on spectral changes provide free energies of activation of 9·0—10·5 kcal mol^{-1} for ring-inversion and 10·5—15·0 kcal mol^{-1} for olefin rotation, depending on complex type, the nature of R and olefin, and also on solvent. The sixteen-electron character of rhodium in these complexes no doubt accounts for the solvent dependency. It should be noted that the olefin rotation implies a relatively easy traversal of tetrahedral stereochemistry for Rh^I in these complexes, and that ring-inversion *via* a planar Rh_2S_2 transition state does not demand an inversion at sulphur. Ring-inversion extends the Rh · · · Rh separation and is therefore favoured by the lack of a direct metal–metal bond. The constraining effect of such bonding is shown by the resistance to ring inversion of $[Rh_2(\mu\text{-}SR)_2(\eta\text{-}C_5H_5)_2]$,[2] described in the following communication.

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[1] R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter, and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395, and references therein.

[2] N. G. Connelly, G. A. Johnson, B. A. Kelly, and P. Woodward, following communication.