An Asymmetric Dinuclear Complex of Rhodium(II) with Bridging Thiolato-ligands Chelated *via* Sulphur and an Alkene Substituent. The *X*-Ray Crystal Structure of $[Rh_2\{\mu_2\text{-}SC_6H_2Pr^i{}_2\text{-}4,6;2\text{-}(\eta^2\text{-}MeC{=}CH_2)\}_2\{SC_6H_2\text{-}2,4,6\text{-}Pr^i{}_3\}_2(NCMe)]$

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The title complex (**1**) was synthesised by reaction of $RhCl_3$ with 2,4,6-tri-isopropylbenzenethiol in MeCN, and it has an asymmetric dinuclear structure with two bridging thiolate ligands with η^2,Rh-bound unsaturated groups formed by dehydrogenation of isopropyl substituents; the Rh–Rh bond distance is 2.756(1) Å with the RhS_2Rh system bent about the S–S vector to give a butterfly configuration.

Previous work has shown the ability of sterically hindered aromatic thiolato-ligands to generate reactive mononuclear complexes of Mo, W, Re, and Fe.[1—4] We are interested in the possibility of synthesising active catalyst systems utilising such thiolato-ligands and here report our preliminary results of their rhodium chemistry. The Ru complexes $[Ru(SAr)_4(NCMe)]$ (Ar = 2,4,6-$Pr^i{}_3C_6H_2S$, or 2,3,5,6-Me_4C_6HS) have recently been reported.[5] The chemistry of Rh is restricted to a series of thiolato-bridged dimeric Rh^I and Ir^I complexes with aliphatic thiols,[6] and some Ir^{III} and Rh^{III} species formed by oxidative addition.[7]

The title complex (**1**) was prepared in about 40% yield by

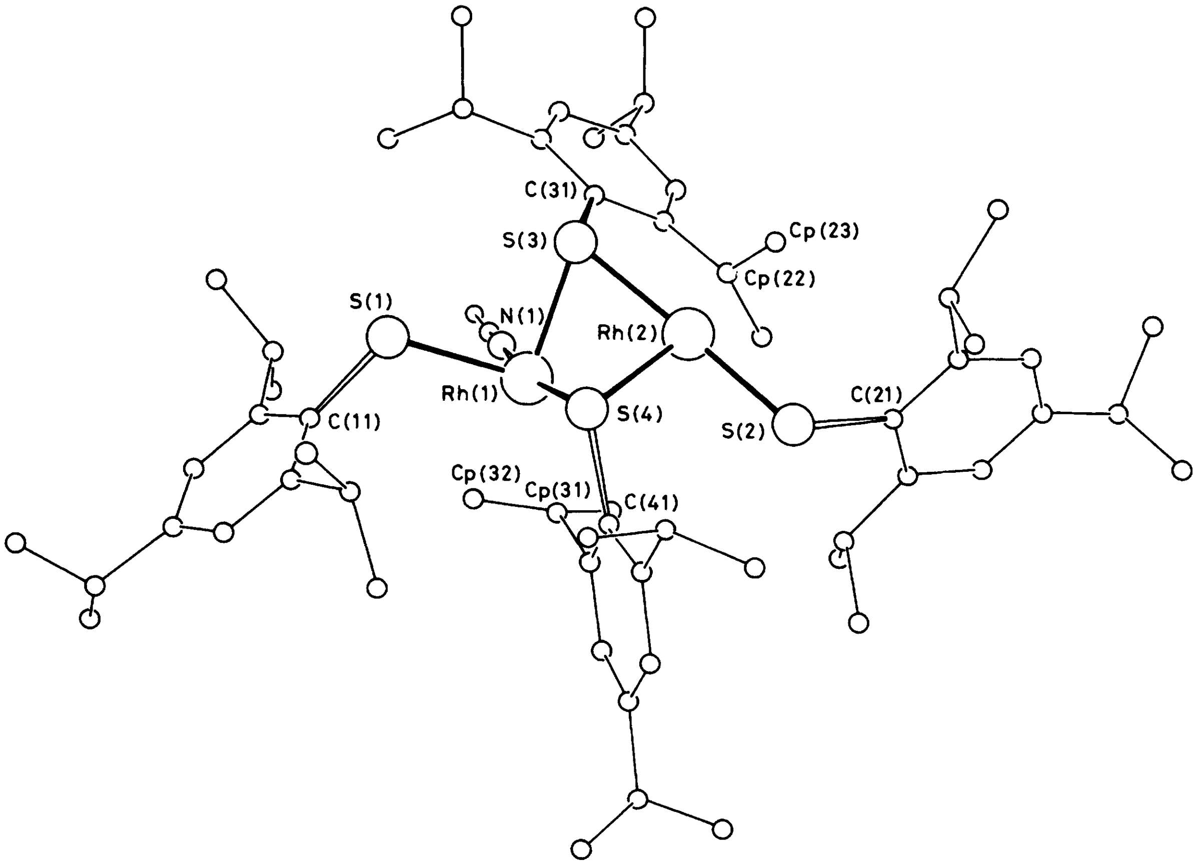

Figure 1. ORTEP view of part of [$Rh_2\{\mu_2\text{-}SC_6H_2Pr^i{}_2\text{-}4,6;\ 2\text{-}(\eta^2\text{-}MeC{=}CH_2)\}_2\{S_6H_2\text{-}2,4,6\text{-}Pr^i{}_3\}_2(NCMe)$] (**1**). Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2), 2.756(1); Rh(1)–S(3), 2.333(2); Rh(2)–S(3), 2.297(3); Rh(1)–S(4), 2.265(3); Rh(2)–S(4), 2.345(3); Rh(1)–S(1), 2.419(2); Rh(2)–S(2), 2.293(3); Rh(1)–N(1), 2.101(8); Rh(1)–Cp(31), 2.139(8); Rh(1)–Cp(32), 2.209(9); Rh(2)–Cp(22), 2.208(9); Rh(2)–Cp(23), 2.173(10); Cp(31)–Cp(23), 1.372(13); Cp(22)–Cp(23), 1.380(14); ∠Rh(1)–S(3)–Rh(2), 73.1(3); S(3)–Rh(1)–S(4), 80.8(1); Rh(1)–S(4)–Rh(2) 73.4(3).

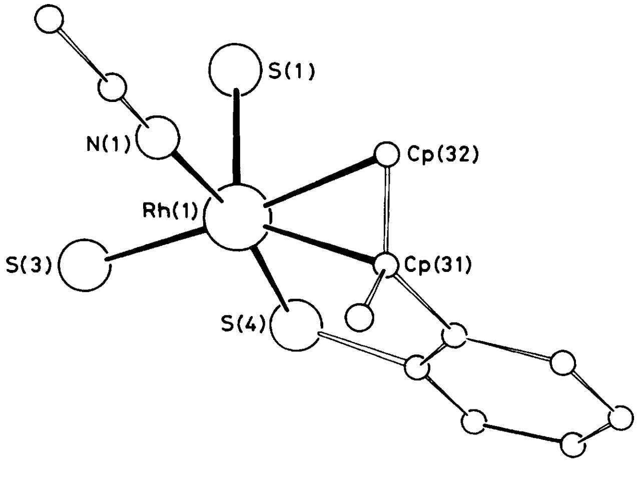

Figure 2. An ORTEP view of the co-ordination sphere of Rh(1) illustrating the interaction of the unsaturated group with the metal.

reaction of $RhCl_3$ with 3 equiv. of $HSC_6H_2Pr^i{}_3$-2,4,6 (Htipt) in dry MeCN at room temperature in the presence of triethylamine. Addition of methanol gave (**1**) as green prisms. The ^1H n.m.r. spectrum was very complex in the aliphatic region and elemental analysis suggested the apparent stoicheiometry $Rh_2(tipt)_4(MeCN)$.† An ORTEP view of the molecule is presented in Figure 1 together with a partial atom-labelling scheme. Pertinent bond lengths and angles are also given. The structure consists of asymmetric dinuclear units with pseudo-octahedral ligation about one Rh atom and pseudo-trigonal bipyramidal geometry for the other. The Rh atoms each have a formal oxidation state of two and are bridged by the thiolato-sulphur atoms S(3) and S(4). The acute Rh–S–Rh angles of 73.1(3) and 73.4(1)° and the Rh–Rh distance of 2.756(1) Å are indicative of an Rh–Rh bond. The Rh_2S_2 system is bent about the S–S vector to impose an overall butterfly-type configuration. The Rh–Rh distance is considerably longer than found in Rh^{II} dimers with four bridging ligands [2.385(5)—2.4861(1) Å].[8] It is, however, comparable with species such as [$Rh_2(O_2CMe)_2(dmg)_2(PPh_3)_2$] (dmg = dimethylglyoximate)[9] [2.618(5) Å], and [$Rh_2(O_2CMe)_2\{Ph_2PC_6H_4\}_2$] [2.556(2) Å][10] which have either only two bridging ligands or two pairs of very different bridging ligands.

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† *Crystal data* for (**1**): triclinic, space group $P\bar{1}$, a = 9.967(2), b = 17.333(3), c = 18.390(3); α = 94.62(3), β = 95.13(3), γ = 102.02(1)°; U = 3169.1(9) Å^3, Z = 2. 8998 reflections were collected and 4320 with $I \geqslant 3\sigma(I)$ used in the structure solution to give a final R value of 0.050 (R_w = 0.048). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

One isopropyl group on each bridging thiolato-ligand has been dehydrogenated to give a $-CMe=CH_2$ unsaturated group η^2-bonded to rhodium (Figure 2). The Rh–C distances lie within the range found for other rhodium–alkene complexes. The dehydrogenation of hydrocarbon substituents has previously been demonstrated for a range of ligands including tertiary phosphines such as 2,2′-bis(diphenylphosphino)-bibenzyl, $Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$.[11]

Cyclic voltammetric studies of the complex in MeCN at a platinum electrode with 0.1 M $[Bu^n{}_4N]BF_4$ as supporting electrolyte revealed a reversible reduction process with $E_{\frac{1}{2}}^{\text{red}} = -0.468$ V (relative to standard calomel electrode, S.C.E.; $\Delta E_p = 80$ mV, $i_p^{\text{red}}/v^{\frac{1}{2}}$ independent of scan rate v 0.2—1 V s^{-1}, $i_p^a/i_p^c \sim 1$). A complex irreversible oxidation process occurs at about +1.1 V. This behaviour contrasts with that of Rh^{II} dimers with quadruple acetato-bridges which exhibit reversible oxidation to Rh(2.5+) radical cations.[8]

The overall asymmetry of the complex is surprising and it is not clear at this stage why Rh(2) is not also ligated by acetonitrile. There is no evidence in the ^1H n.m.r. spectrum for any resonances at high field ascribable to hydride, so it does not appear that the apparently vacant site is occupied by two hydride hydrogens. Reaction of the complex with carbon monoxide gives a thiolato-bridged Rh^I complex $[\{Rh(\mu^2\text{-}SAr)(CO)_2\}_2]$ [ν(CO), 1995 and 2035 cm^{-1}] without evolution of H_2 and with elimination of disulphide. Owing to the complexity of the ^1H n.m.r. spectrum it is not possible to determine if the unsaturated thiol remains co-ordinated or is eliminated as disulphide.

The dinuclear complex is very reactive towards a range of neutral and anionic ligands and studies of this chemistry and the reactions of rhodium and iridium halides with related thiolato-ligands are in progress.

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