

A novel binuclear rhodium complex with two mercapto bridges and two terminal thioether groups

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The cyclic thioether–thioester ligand $[7,8-\mu\text{-SCH}_2\text{C(O)S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$, $[\text{L1}]^-$, is a source of strongly co-ordinating mercapto and thioether groups. Upon reaction with complexes with metal ions in oxidation state higher than + 1, $[\text{L1}]^-$ modifies to the dianionic ligand $[7,8-\mu\text{-SCH}_2\text{C(O)OMe-7,8-C}_2\text{B}_9\text{H}_{10}]^{2-}$, $[\text{L2}]^{2-}$. Reaction of $[\text{NMe}_4][\text{L1}]$ with $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ ($\text{M} = \text{Rh}^{\text{III}}$ or Ir^{III}) in MeOH produces $[\text{M}_2(\text{C}_5\text{Me}_5)_2(\text{L2})_2]$, a molecule with an earmuff shape.

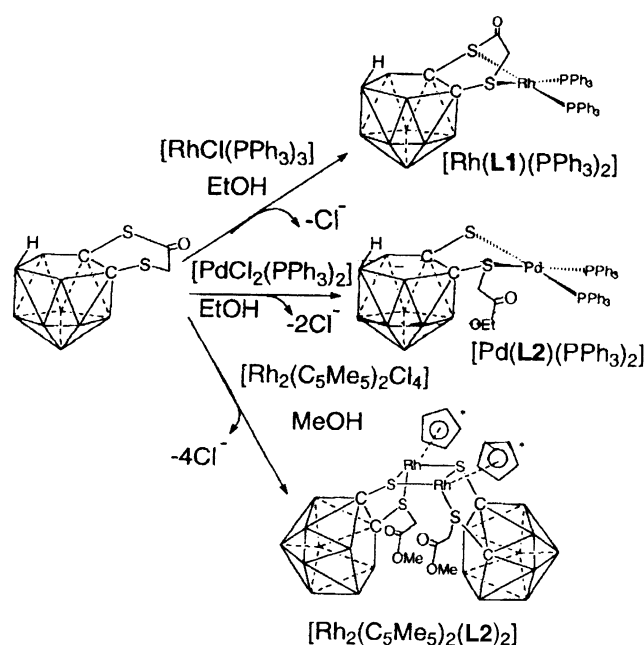
In earlier publications we have proven that the bonding capacity of monothioether ligands is dramatically improved when the thioether is bonded to the cluster carbon of a $[\text{C}_2\text{B}_9\text{H}_{10}]^-$ residue,¹ which is interpreted as if the negative charge of the cluster partly resides on the thioether, thus enhancing its donor capacity.² An example is the ready substitution of Cl^- by these ligands. Recently the synthesis of a cyclic thioether–thioester ligand, $[\text{NMe}_4][7,8-\mu\text{-SCH}_2\text{C(O)S-7,8-C}_2\text{B}_9\text{H}_{10}]$ or $[\text{NMe}_4][\text{L1}]$,³ and its reactivity towards $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{PdCl}_2(\text{PPh}_3)_2]$ has been reported. A preliminary interpretation of the bonding behaviour of $[\text{L1}]^-$

was that the exo-cycle was retained if bonding to a monovalent cation took place,³ while $[\text{L1}]^-$ modified to $[\text{L2}]^{2-}$ by an opening transesterification proven for divalent metal ions, see Scheme 1.

In an attempt to know more on the complex behaviour of ligand $[\text{L1}]^-$, the reactions of the binuclear trivalent metal complexes $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ ($\text{M} = \text{Rh}^{\text{III}}$ or Ir^{III}), with $[\text{NMe}_4][\text{L1}]$ have been examined. We report herein the results of these studies and, in particular, the X-ray structural analysis of the binuclear compound $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L2})_2] \cdot \text{MeCN}$ which represents the first example of a binuclear complex incorporating C_5Me_5 rings and both bridging mercapto and terminal thioether groups. Reaction of $[\text{NMe}_4][\text{L1}]$ with $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ in boiling methanol in the ratio 2 : 1 for 2 h yields an orange-red solid product. The ^{11}B NMR spectrum displayed a 1 : 1 : 3 : 2 : 1 : 1 pattern not coincident with $[\text{L1}]^-$. The ^1H NMR spectrum displayed one resonance at -2.5 ppm corresponding to B-H-B and another at 3.8 ppm attributable to a methoxy group. The $\nu(\text{CO})$ absorption in the IR shifted from 1630 cm^{-1} in $[\text{L1}]^-$ to 1734 cm^{-1} in the complex indicating that the initial $-\text{C(O)SR}$ group had modified to $-\text{C(O)OMe}$ by a transesterification process and that, consequently, the initial carborane exo-cycle had been broken to produce $-\text{S}^-$ and $-\text{SR}$ co-ordinating groups. Furthermore the chemical analyses were in agreement with the formula $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{L2})]$. The absence of B-H-M interactions suggested a bidentate carborane ligand, in which case the Rh would be pentacoordinated if the mononuclear complex had been obtained. A similar reaction was found for $[\text{Ir}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ whose spectroscopic and analytical data are consistent with $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{L2})]$.

Although rare, some examples of pentacoordinated Ir^{III} such as $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{SC}_6\text{F}_5)_2]$ are reported,⁴ however binuclear Rh^{III} and Ir^{III} structures with bridging mercapto groups are well known too,⁵ and these could represent better the structures of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{L2})]$ and $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{L2})]$. In order to determine the structure of this compound unambiguously, good quality X-ray red needle crystals were grown from acetonitrile by slow evaporation.

A binuclear complex unit of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L2})_2] \cdot \text{MeCN}$ is



Scheme 1 Reactivity of $[\text{NMe}_4][\text{L1}]$

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presented in Fig. 1. The complex unit has a two-fold symmetry with the symmetry axis perpendicular to the plane of the Rh_2S_2 moiety and going through the midpoint of this moiety. In the binuclear complex unit the $\text{SCH}_2\text{C}(\text{O})\text{OMe}$ substituent connected to C(8) has two orientations (A and B). The disordered forms A and B are almost equally populated. The acetonitrile molecule is disordered over a two-fold axis. In the binuclear unit each Rh has a three-legged piano-stool coordination. The two C_5Me_5 ligands occupy a *cis* position while in the starting complex $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ they are *trans* to each other. The dihedral angle between the two C_2B_3 open faces is $19.3(3)^\circ$. Overall the two $[\text{L}_2]^{2-}$ ligands have removed the four initial chloride atoms of the starting complex $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$. The thioether groups occupy the positions initially occupied by the terminal chlorides while the mercapto groups occupy the initial chloride bridging positions. Remarkably the two carborane cages dispose their open faces in a face to face orientation overall producing an earmuff-like molecule.

Interestingly, it is found that the geometrical characteristics of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ are retained in $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L}_2)_2]$. If the dihedral angle values, RhCl_2Rh and RhS_2Rh , the $\text{Rh}-\text{Rh}$ distances and the $\text{Rh}-\text{Cl}-\text{Rh}$ ($\text{Rh}-\text{S}-\text{Rh}$) angles are compared between $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L}_2)_2]$, the following values are found $0.00(2)^\circ$ [$2.9(2)^\circ$]; $3.7191(6)$ Å [$3.636(1)$ Å] and $98.29(3)^\circ$ [$100.35(6)^\circ$], respectively.

Ligand $[\text{L}_1]^-$ has been altered upon reaction to M^{III} ($\text{M} = \text{Rh}$ or Ir) to produce a new ligand, $[\text{L}_2]^{2-}$, containing both mercapto and thioether groups. Both are able to substitute halogens from the co-ordination sphere of the metal, the mercapto because of its negative charge and the thioether due to the neighbouring anionic negative cluster. Owing to the $-\text{S}^-$, $-\text{SR}$ rigid disposition induced by the *nido*-carborane, and their distance, ligand $[\text{L}_2]^{2-}$ and analogues represent a unique class of compounds ready to produce $\text{M}-\text{M}$ dimercapto-bridged complexes with strong terminal thioether groups.

§ *Crystal data*: $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L}_2)_2] \cdot \text{MeCN}$, $\text{C}_{32}\text{H}_{63}\text{B}_{18}\text{NO}_4\text{Rh}_2\text{S}_4$, $M_r = 1054.4$. Trigonal, space group $P3_221$ (no. 154), $a = 19.830(3)$, $c = 11.967(5)$ Å, $U = 4075(2)$ Å³, $Z = 3$, $D_c = 1.289$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 7.94$ cm⁻¹, $F(000) = 1614$. The data were collected on a Rigaku AFC5S diffractometer using Mo-K α radiation ($\lambda = 0.71069$ Å) at 294 K. The intensities were corrected for Lorentz and polarization effects and for absorption (ψ -scans, transmission coefficient 0.806–1.000). The structure was solved by direct methods⁶ and refined⁷ on F^2 by least-squares techniques to $R_1 = 0.0506$ ($wR_2 = 0.1192$) and $\text{g.o.f.} = 1.031$ for 3878 independent reflections having $I > 2\sigma(I)$. The structure is also disordered in the lower symmetry space group $P3_2$. Disordered carbon atoms and the non-hydrogen atoms of MeCN solvent were refined with isotropic but the rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms, except the bridging H atom at the open face of the cage and those of the solvent molecule, were placed at fixed distances from their host atoms.

CCDC reference number 440/034.

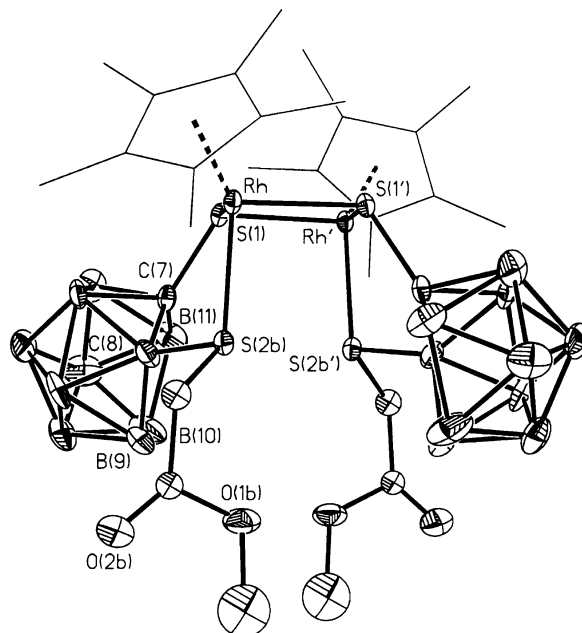


Fig. 1 Crystal structure of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{L}_2)_2] \cdot \text{MeCN}$. A simplified structure of the complex unit showing the $\text{SCH}_2\text{C}(\text{O})\text{OMe}$ substituent in the B orientation. Only skeletons of C_5Me_5 ligands are shown. Selected intramolecular distances (Å) and angles ($^\circ$): $\text{Rh}-\text{S}(1)$ 2.367(2), $\text{Rh}-\text{S}(1')$ 2.368(2), $\text{Rh}-\text{S}(2b)$ 2.416(2), $\text{S}(1)-\text{C}(7)$ 1.813(7), $\text{C}(7)-\text{C}(8)$ 1.580(8); $\text{S}(1)-\text{Rh}-\text{S}(1')$ $79.62(6)$, $\text{Rh}-\text{S}(1)-\text{Rh}'$ $100.35(6)$, $\text{S}(1)-\text{Rh}-\text{S}(2b)$ $78.43(8)$. Prime indicates equivalent position $y, x, -z$.

Acknowledgements

This work was supported in part by projects PB94-0226 and QF 95-4721.

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Received in Basel, Switzerland, 5th January 1998;
Letter 8/03026J