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Single and unsupported Ru–H–Ru bond: preparation and crystal structure of $\{Ru_2H(\mu\text{-}H)Cl(syn\text{-}Me_4[14]aneS_4)_2\}Cl$ ($Me_4[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane) *

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Abstract

Treatment of *cis*-$RuCl_2Me_4[14]aneS_4$ with an excess of $NaBH_4$ in EtOH gave $\{Ru_2H(\mu\text{-}H)Cl(Me_4[14]aneS_4)_2\}Cl$ (**1**) together with *trans*-$RuH(Cl)(syn\text{-}Me_4[14]aneS_4)$ (**2**). Compound **1** represents a novel example of a single μ_2-hydrido complex of crown thioether without any supporting bridged ligands or metal–metal bond. The molecular structure of **1** was elucidated by an X-ray diffraction study.

Most M–H–M three center two electron bonds (3c–2e) of transition metals so far reported are supported by additional bridging ligands and/or metal–metal bonds and single, unsupported μ_2-hydrido complexes still remain a rarity. $[M_2(\mu\text{-}H)(CO)_{10}]^-$ (M = Cr, Mo, W) [1], $[W_2(\mu\text{-}H)(CO)_9(NO)]$ [2], $(\eta^5\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}H)M(\eta^5\text{-}C_5H_5)(CO)_3$ (M = Nb, V) [3], and $\{(\eta^5\text{-}C_5H_5)_2WH(\mu\text{-}H)PtPh(PEt_3)_2\}^+$ [4] may be such complexes bearing no definite metal–metal bond. The compounds were characterized by X-ray and neutron diffraction studies. Here we present the preparation and crystal structure of $\{Ru_2H(\mu\text{-}H)Cl(Me_4[14]aneS_4)\}_2Cl$ (**1**), which represents a novel example of a single μ_2-hydrido crown thioether complex containing no supporting ligands or metal–metal bond.

A reaction of *cis*-$RuCl_2Me_4[14]aneS_4$ [5] with a large excess of $NaBH_4$ in EtOH at room temperature gave compound **1** as brown crystals together with *trans*-$RuH(Cl)(syn\text{-}Me_4[14]aneS_4)$ (**2**) in 54 and 16% yield, respectively. The choice

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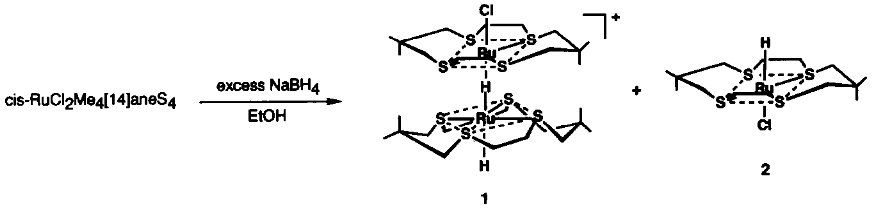
of the reaction solvent is critical for the formation of **1** since a similar reaction carried out in MeOH afforded the mononuclear complex **2** selectively [6]. The reaction is also highly dependent on the ring size of crown thioethers. Thus, treatment of 15- and 16-membered crown thioether complexes *cis*-$RuCl_2L$ (L = Me_6[15]aneS_4, Me_8[16]aneS_4) with a stoichiometric amount and a large excess of $NaBH_4$ in EtOH under similar conditions gave *trans*-RuH(Cl)L and *trans*-RuH(η^1-BH_4)L as the sole product, respectively [6,7]. The ionic character of **1** was readily confirmed by the facile precipitation of {$Ru_2H(\mu$-H)Cl(Me_4[14]ane$S_4)_2$}-BPh_4 on addition of $NaBPh_4$ into the MeOH solution.



The ^{1}H NMR spectrum of **1** measured in CD_2Cl_2 at room temperature shows two hydrido signals at δ −20.8 (d, J = 13.9 Hz) and −33.3 (d, J = 13.9 Hz). The chemical shift of the former is comparable with the terminal hydride (δ −23.1) of **2** [6], while the extensive shielding of the latter may be assigned to a bridging hydrido ligand (H_b) [8]. The observation of four Me singlets [δ 1.03 (3H), 1.04 (3H), 1.07 (3H), and 1.10 (3H)] and four CH_2 doublets [δ 1.91 (2H, J = 9.9 Hz), 2.44 (2H, J = 9.9 Hz), 3.09 (2H, J = 10.9 Hz), and 3.78 (2H, J = 10.9 Hz) of the $SCH_2CMe_2CH_2S$ moieties along with three multiplets [δ ~ 2.3 (2H), ~ 2.8 (2H), and ~ 3.0 (4H)] owing to the CH_2 protons of SCH_2CH_2S groups indicates the presence of two inequivalent Me_4[14]aneS_4 ligands both adopting a *syn* conformation. The IR spectrum shows a single and very strong ν(Ru–H_t) band (H_t = terminal hydride) at 1820 cm^{-1}, but a ν(Ru–H_b–Ru) band was not detected in the expected region. The lower ν(Ru–H_t) frequency compared with that (1958 cm^{-1}) of **2** [6] suggests that the hydride of strong *trans* influence rather than the chloro ligand is located as a bridging ligand at the opposite axial site of the terminal hydride. Consistent with this, two hydrido ligands, mutually in *trans*, couple strongly (see above). The single crystal X-ray diffraction of **1** [9*] unequivocally confirmed the structural features thus proposed on the basis of the spectral data.

The molecular structure of **1** is shown in Fig. 1 together with the selected bond distances and angles. The molecule possesses C_2 symmetry with a face to face disposition of the RuH(*syn*-Me_4[14]aneS_4) and RuCl(*syn*-Me_4[14]aneS_4) moieties. Both the H_t and Cl ligands in these moieties are located at the congested axial site surrounded by ring C atoms of *syn*-Me_4[14]aneS_4. These two fragments are connected together by the H_b ligand, thus the geometry about the two Ru atoms is essentially octahedral. The Cl, Ru1, and Ru2 atoms are exactly colinear. The least-squares plane defined by the four S atoms [±0.019(5) Å] of the RuCl(*syn*-Me_4[14]aneS_4) fragment is also strictly parallel with the corresponding plane [±0.040(4) Å)] of the other moiety. The long separation between the two Ru

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

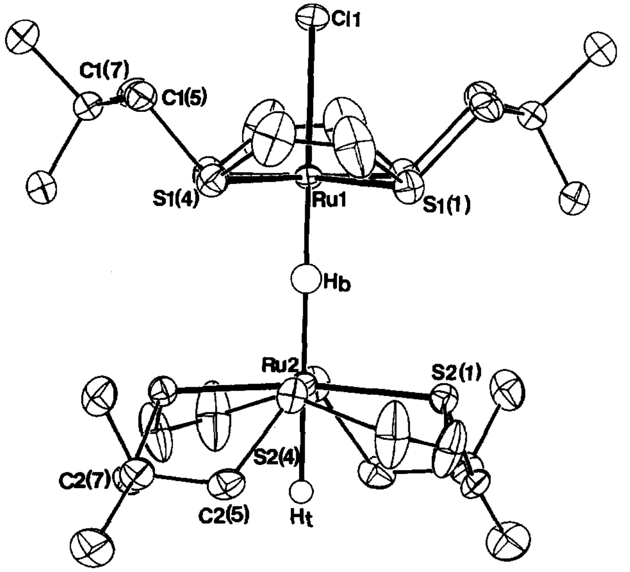

Fig. 1. ORTEP drawing of the cation $\{Ru_2H(\mu\text{-}H)Cl(Me_4[14]aneS_4)_2\}^+$ in **1** with thermal ellipsoids at the 50% probability level. The selected molecular dimensions are: Ru1–S1(1) 2.292(3), Ru1–S1(4) 2.293(3), Ru2–S2(1) 2.299(3), Ru2–S2(4) 2.299(3) Å; S2(1)–Ru2–H_t 85.9(1), S2(4)–Ru2–H_t 87.8(1), S1(1)–Ru1–H_b 89.4(1), S1(4)–Ru1–H_b 88.4(1), S2(1)–Ru2–H_b 94.1(1), S2(4)–Ru2–H_b 92.2(1), Cl–Ru1–S1(1) 90.6(1), Cl–Ru1–S1(4) 91.6(1), S1(1)–Ru1–S1(4) 87.7(1), S1(1)–Ru1–S1(4′) 92.3(1), S1(1)–Ru1–S1(1′) 178.8(2), S1(4)–Ru1–S1(4′) 176.9(2), S2(1)–Ru2–S2(4) 87.4(1), S2(1)–Ru2–S2(4′) 92.3(1), S2(1)–Ru2–S2(1′) 171.7(1), S2(4)–Ru2–S2(4′) 175.7(2)°.

atoms [3.410(2) Å] clearly indicates that the Ru–Ru bonding interaction is negligibly small if any. The Ru1–H_b, Ru2–H_b, and Ru2–H_t distances are 1.82(15), 1.60(15), and 1.69(13) Å, respectively. The average Ru1–S [2.292(3) Å] and Ru2–S distances [2.299(3) Å] are very similar to the corresponding mean separation found in **2** (2.297(2) Å) [6]. Th equatorial S atoms of the two moieties are mutually staggered with the torsion angle S1(1)–Ru1–Ru2–S2(4) of 54.3(1)°. This configuration, where the free lone pair orbitals of the S atoms in two equatorial planes are interlocked, seems to be favorable in reducing the electrostatic repulsions between the lone pair electrons.

The RuH(*syn*-Me_4[14]aneS_4) and RuCl(*syn*-Me_4[14]aneS_4) fragments differ in their direction of Ru atom deviation from the 4S plane, the Ru1 atom by 0.043(2) Å toward the Cl atom surrounded by the ring C atoms, while the Ru2 atom by 0.126(2) Å toward the H_b ligand located at the uncongested axial site. This probably arises from the difference in steric demands of the axial H_t and Cl ligands. The molecular structure of **2** suggested that the cavity surrounded by the ring C atoms in *syn*-Me_4[14]aneS_4 has the volume just to accommodate a hydrido ligand [6]. Therefore, to admit the more bulky Cl ligand into the congested axial side, the room should be dilated by bending down the S–C vectors toward the equatorial plane. Such a deformation of the *syn*-Me_4[14]aneS_4 ligand may be accompanied by displacement of the Ru atom from the 4S plane toward the congested side along the C_2 axis, while an upright deformation of the C–S vectors could induce the deviation toward the opposite and uncongested axial side.

Indeed, the dihedral angle [47.4(6)°] between the 4S plane and the least-squares plane defined by the S1(1), S1(4), C1(5), and C1(7) atoms of the $\overline{\mathrm{RuSCH_2CMe_2CH_2S}}$ ring is more acute than the corresponding angle [53.9(4)°] of the RuH(*syn*-$\mathrm{Me_4}$[14]ane$\mathrm{S_4}$) moiety. Despite the dilation of the cavity, the non-bonded distances between the Cl and axial H atoms bonded at the C1(5) and C1(7) [2.61(1) and 2.73(1) Å, respectively] is still significantly shorter than the sum of corresponding van der Waals radii. To reduce the stereochemical repulsions between these atoms as much as possible, the Ru1–Cl bond [2.589(4) Å] is considerably elongated compared with those of **2** (2.559(2) Å) [6] and *trans*-RuH(Cl)(diop)$_2$ (2.549(1) Å) [11]. By contrast, the $\mathrm{H_t}$ ligand in the RuH(*syn*-$\mathrm{Me_4}$[14]ane$\mathrm{S_4}$) moiety shows van der Waals contacts with the axial H atoms of the ring C2(5) and C2(7) atoms (2.51(3) and 2.45(4) Å, respectively).

The single and unsupported M–H–M bond of transition metals is known to be inherently bent [1,12,13] and this is also the case observed for a Cr–H–Cr linkage [158.9(1)°] in $[\mathrm{Cr_2(\mu\text{-}H)(CO)_{10}}]^-$ possessing a D_{4h} non-hydrido framework $[\mathrm{Cr_2(CO)_{10}}]$ [14]. Therefore, the C_2 geometry of **1** does not warrant a linearity of the Ru–H–Ru bond. The poor quality of the bond parameters of the $\mathrm{H_b}$ ligand in **1** [15*] and the limitations of the X-ray diffraction method to determine the accurate positions of hydrido ligand [13] prevent delineation of the nature of the Ru–H–Ru bond. However, it is worth recalling here that the $\mathrm{H_b}$ ligand is completely surrounded by the free lone pair orbitals of eight S atoms. Should the Ru–H–Ru linkage bend, a severe electrostatic repulsion would appear between the lone pair and Ru–$\mathrm{H_b}$ bonding electrons. We are now carrying out extended Hückel MO calculations to estimate the effect of these lone pair orbitals on the geometry of the Ru–H–Ru 3c-2e bond. Finally it is to be noted that the single and unsupported Ru–H–Ru bond in **1** is stable even in solution and there exists no equilibrium between **1** and **2**.

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9 Crystal data of **1**: $\mathrm{C_{28}H_{58}Cl_2S_8Ru_2 \cdot 1/2(CH_3)_2CO \cdot H_2O}$ (from acetone), FW = 971.2, trigonal, space group $R\bar{3}c$ (No. 167), $a = 18.615(6)$, $c = 64.937(13)$ Å, $V = 19487(11)$ Å^3, $Z = 18$, $D_c = 1.49$ g cm^{-3}, μ(Mo-K_α) = 17.3 cm^{-1}. 5204 unique reflections ($5 \le 2\theta \le 55°$) were collected on a Rigaku AFC-6 diffractometer using graphite monochromated Mo-K_α radiation; 1975 reflections with $|F_o| \ge 6\sigma(F_o)$ were used in the structure determination by the Patterson method and by block-diagonal least-squares refinements for 225 parameters to converge to R (R_w) = 0.055 (0.063), GOF = 1.42. Refinement was carried out with anisotropic thermal parameters for non-hydrogen atoms and

with fixed thermal and positional parameters ($B_{iso} = 4.0$ Å^2) for non-hydrido hydrogen atoms. The H_t and H_b atoms were found in the difference Fourier maps and were refined isotropically by the low-angle method ($\sin \theta / \lambda < 0.40$ Å^{-1}) [10]. The difference Fourier map using all reflection data failed to reveal the positions of the hydrido ligands. Atomic coordinates, bond lengths and angles, the thermal parameters, and $F_o - F_c$ tables are available from the authors.

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