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Structure, Reactivity, and Computational Studies of a Novel Ruthenium Hydrogen Sulfide Dihydride Complex

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Addition of 1 atm of H_2S to $[Ru(IMes)_2(CO)(EtOH)H_2]$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) affords the air-stable hydrogen sulfide dihydride complex, $[Ru(IMes)_2(CO)(H_2S)H_2]$ **2**. Treatment of **2** with excess H_2S leads to formation of the 16-electron bis-hydrosulfido complex, $[Ru(IMes)_2(CO)(SH)_2]$ **3**. Preliminary studies show that **3** reacts with both H_2 and CO in solution as well as in the solid state. Both **2** and **3** have been structurally characterized

Transition metal complexes of hydrogen sulfide are remarkably rare. A recent review has highlighted the existence of just four structurally characterized H_2S complexes, all of them with ruthenium as the central metal atom.[1] Considering the importance of metal−sulfur interactions in metalloenzymes such as nitrogenase and hydrogenase[2] with the alternative group 8 metal, iron, and the relevance of metal−sulfur linkages to catalytic hydrodesulfurization chemistry,[3] characterization of new $M-H_2S$ complexes remains an area of widespread interest.

We have recently reported the synthesis and reactivity of the N-heterocyclic carbene stabilized ruthenium solvent complexes $[Ru(IMes)_2(CO)(sol)H_2]$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; sol = H_2O, EtOH), which provide a route to new Ru−heteroatom Ru−X (X = N, O, S) species, including the thiol and thiolate species $[Ru(IMes)_2(CO)(HS^nPr)H_2]$ and $[Ru(IMes)_2(CO)_2(S^nPr)H]$.[4] On the basis of this success in generating Ru−S bonds, the ethanol complex $[Ru(IMes)_2(CO)(EtOH)H_2]$ (**1**) was treated with 1 atm of H_2S at room temperature to give $[Ru(IMes)_2(CO)(H_2S)H_2]$ (**2**) as an orange microcrystalline solid in 79% yield. Remarkably, **2** appears to be completely air-stable, in direct contrast to other reported H_2S complexes; a solid sample left on the bench in air for 4 days showed no change by IR spectroscopy. The ^1H NMR spectrum of **2** in C_6D_6 displayed equivalent H_2S protons at δ −0.58, while a high-field singlet at δ −24.47 is consistent with retention of the same *trans*-H−Ru−H geometry found in the starting material. The appearance of both of these resonances was unchanged over a +80 to −80 °C temperature range.[5]

The X-ray crystal structure of **2** determined from data recorded at 30 K is shown in Figure 1.[6] The asymmetric unit in this structure was seen to consist of two independent halves of the organometallic species based on Ru1 and Ru2, respectively, plus some solvent fragments. The first of these molecular fragments is positioned such that the central metal along with the CO and sulfur from the H_2S are located on a crystallographic 2-fold rotation axis, with said ligands disordered in a 1:1 ratio along this symmetry element. Nonethe-

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(5) ^1H NMR (300 MHz, C_6D_6, 298 K): δ 6.80 (br s, 4H, $C_6H_2Me_3$), 6.77 (br s, 4H, $C_6H_2Me_3$), 6.20 (s, 4H, CNCH═CHN), 2.32 (s, 12H, CH_3), 2.16 (s, 12H, CH_3), 2.08 (s, 12H, CH_3), −0.58 (s, 2H, SH_2), −24.47 (s, 2H, RuH). $^{13}C\{^1H\}$: δ 202.6 (s, Ru−CO), 197.3 (s, Ru−C), 137.6 (s, N−C), 136.8 (s, *C*−*p*-CH_3), 136.0 (s, *C*−*o*-CH_3), 135.7 (s, *C*−*o*-CH_3), 129.1 (s, *m*-CH), 121.8 (s, NCH═CHN), 21.2 (s, *p*-CH_3), 19.3 (s, *o*-CH_3), 19.2 (s, *o*-CH_3). IR (Nujol): 1879 cm^{-1} (ν_{CO}).

(6) Crystal data for **2**, $[Ru(IMes)_2(CO)(SH_2)H_2]\cdot 0.25C_6H_6$: $C_{44.5}H_{53.5}N_4OSRu$, $M = 459.47$, monoclinic, $a = 20.8470(2)$ Å, $b = 20.8400(2)$ Å, $c = 19.4180(3)$ Å, $\beta = 109.018(1)°$, $V = 7975.70(16)$ Å^3, $T = 30$ K, space group $C2/c$, $Z = 8$, $\mu(Mo\ K\alpha) = 0.71073\ mm^{-1}$, 85360 data were collected of which 14861 were unique ($R_{int} = 0.0750$), 3938 had $F_o > 4\sigma(F_o)$, $7.24° < 2\theta < 66.632°$, no absorption correction was applied. $R1 = 0.0365$ (for 4σ data), $wR2 = 0.0748$, $S = 1.013$ (for all data). Crystal data for **3**, $[Ru(IMes)_2(CO)(SH)_2]$: $C_{49}H_{50}N_4OS_2Ru$, $M = 886.20$, triclinic, $a = 10.1760(3)$ Å, $b = 14.1930(3)$ Å, $c = 16.8530(4)$ Å, $\alpha = 69.3120(10)°$, $\beta = 79.8090(10)°$, $\gamma = 83.1810(10)°$, $V = 2236.99(10)$ Å^3, $T = 20$ K, space group $P1$, $Z = 2$, $\mu(Mo\ K\alpha) = 0.71073\ mm^{-1}$, 37703 data were collected of which 12634 were unique ($R_{int} = 0.0591$), 9702 had $F_o > 4\sigma(F_o)$, $7.10° < 2\theta < 60.40°$, no absorption correction was applied. $R1 = 0.0388$ (for 4σ data), $wR2 = 0.0750$, $S = 1.004$ (for all data). Both structures were solved by direct methods using SHELXS, and all non-hydrogen atoms refined anisotropically using full-matrix least-squares on F^2 (SHELXL-93).[16] Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 209671 for compound **2** and 209672 for compound **3**.

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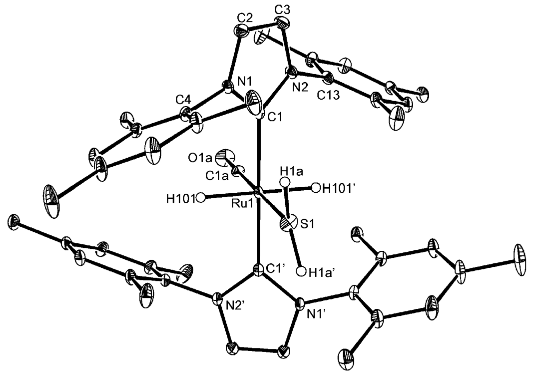
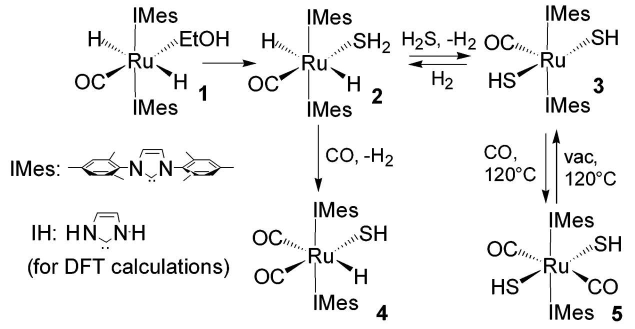


Figure 1. ORTEX view of the molecular structure of **2**. Ellipsoids are shown at the 30% level. Principal bond lengths (Å) and angles (deg), with computed values, averaged where appropriate, in parentheses: Ru−C(1) 2.0739(17) (2.092), Ru−C(1a) 1.797(7) (1.830), Ru−S(1) 2.400(2) (2.453), C(1)−Ru−C(1′) 178.71(9) (178.2).

less the partial hydrogens on Ru−SH_2 were readily located, as was the hydride hydrogen on the metal (H101). The second bis carbene molecule was also seen to be located on a 2-fold rotation axis, although in this instance, it is the metal plus the two hydrides which are located on the symmetry element. As in the previous fragment, the CO and H_2S ligands displayed 1:1 positional disorder. In both molecules, the geometry at ruthenium is close to octahedral with two trans IMes ligands. Disorder in the sulfur position of the two ruthenium fragments implies that the Ru−S bond length is closer to the value of 2.402(2) Å found for Ru−S(1); this distance is in line with the values reported for [(“S_4”)Ru(PPh_3)(SH_2)] (2.399(5) Å; “S_4” = 1,2-bis[(2-mercaptophenol)thio]ethane)[7] and [Ru(PPh_3)(*o*-$Ph_2PC_6H_4NMe_2$)(SH_2)X_2] (X = Cl, 2.333(1) Å; X = Br, 2.3503(3) Å).[8]

In addition to being a rare example of a complex containing a coordinated H_2S group and the first example of one with hydride ligands, **2** is remarkable as it features a *trans* arrangement of the hydrides,[4,9] and we have undertaken a computational study to rationalize this feature.[10] Initial density functional (DF) calculations on both *cis*- and *trans*-**2** using the small 4-imidazol-2-ylidene (IH) model ligand yielded an energetic preference for the *cis* isomer of 5.5 kcal/mol. Incorporation of the full IMes ligands via a QM/MM approach makes *trans*-**2** the more stable form by 0.5 kcal/mol.[11] The stabilization of the *trans* dihydride arrangement in **2** is therefore a response to the large steric strain imposed by the bulky IMes ligands. Both the DF and QM/MM calculations reproduce the immediate metal coordination sphere of *trans*-**2** reasonably well (see caption of Figure 1 and Supporting Information); however, the orientation of the carbene ligands is only well represented when the bulky mesityl groups are included. In [Ru$(IH)_2$(CO)(H_2S)H_2] they lie directly over the H−Ru−H axis whereas in [Ru$(IMes)_2$(CO)(H_2S)H_2] they are slightly staggered with respect to this axis. For *cis*-**2** the lowest energy structure places the IMes ligands over the more sterically demanding OC−Ru−H axis. Our calculations suggest that *cis*-**2** is a viable synthetic target, however, with *trans*-**2** being the favored kinetic product in the current case.

Scheme 1



Complex **2** reacted further upon treatment with additional H_2S (Scheme 1) to afford the purple, 16-electron bis-hydrosulfido complex [Ru$(IMes)_2$(CO)$(SH)_2$] (**3**), which was characterized by the appearance of a distinctive singlet in the ^1H NMR spectrum at δ −1.00.[12] The IR spectrum of **3** showed one carbonyl band at 1925 cm^{-1}, significantly higher in frequency relative to that for **2** (1879 cm^{-1}). The low-temperature (20 K) X-ray structure determination of the bis-SH complex (Figure 2) shows the 5-coordinate ruthenium

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(10) Calculations used Gaussian 98 and employed the BP86 functional. Ruthenium and sulfur were represented with the relativistic core potential of the Stuttgart group with the associated basis sets (Andrae, D.; Häusserman, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123). For sulfur, a d polarization function was added (Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237). H, C, N, and O atoms were represented with a 6-31G** basis set (Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213). All structures were characterized as minima via analytical frequency calculations, and energies incorporate a correction for zero point energies. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.2; Gaussian, Inc.: Pittsburgh, PA, 2001.

(11) We have considered two aspects of the conformations of the IMes ligand in our calculations. Test calculations on *trans*-**2** varying the orientation of the mesityl *o*-CH_3 groups showed that the lowest energy structures were obtained in which the C−H bond coplanar with the aryl group was *syn* to Ru. Subsequent calculations therefore started with this arrangement. Energy differences associated with the orientation of the *p*-CH_3 groups were found to be insignificant. Different conformations of the two IMes ligands relative to the {Ru$(H)_2$(H_2S)} plane were also tested, and for *trans*-**2** all four converged to the same geometry. For *cis*-**2**, eight starting geometries were explored resulting in only two conformations, the second being 4.8 kcal/mol higher than that reported in the text.

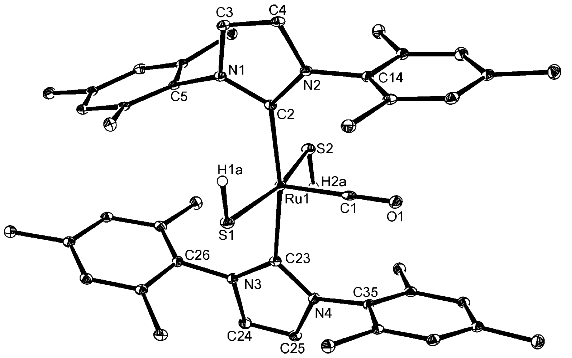

Figure 2. ORTEX view of the molecular structure of **3**. Ellipsoids are shown at the 30% level. Principal bond lengths (Å) and angles (deg) with computed values, averaged where appropriate, in parentheses: Ru−C(1) 1.773(2) (1.769), Ru−C(2) 2.1097(18), Ru−C(23) 2.1086(18) (2.124), Ru−S(1) 2.3764(5), Ru−S(2) 2.3693(5) (2.390); C(2)−Ru−C(23) 169.86(7) (170.2), S(1)−Ru−S(2) 166.203(19) (161.7).

atom with a strained *trans* arrangement of the IMes ligands (∠C−Ru−C, 169.86(7)°).[6] The most prominent feature of the structure is the highly obtuse S−Ru−S angle (166.203(19)°). The Ru−S distances (2.3693(5), 2.3764(5) Å) are quite short compared to other (although coordinatively saturated) Ru hydrosulfido complexes.[13] DF calculations on the model complex $[Ru(IH)_2(CO)(SH)_2]$ provide good agreement with these experimental data, with the exception of the carbene ligand orientations which lie almost parallel to the Ru−S bonds in a C_2 arrangement. Only upon inclusion of the bulky mesityl groups via QM/MM calculations could the correct orientation of the carbene ligands be reproduced. Thus, in this respect, for both *trans*-**2** and **3**, IH appears to be a poor model for the much bulkier IMes ligand. To date only one computational study has systematically considered the effect of the bulky mesityl group on the structure and reactivity of N-heterocyclic carbene complexes,[14] and this and the present study suggest that this factor is important.

Surprisingly, addition of 1 atm of H_2 to a C_6D_6 solution of **3** led to slow, but complete, re-formation of **2** at room temperature. We propose that the interconversion of **2** and **3** takes place by a hydrogen transfer process, analogous to that described for **1**.[4] Thus, H-transfer from the (acidic) Ru−SH_2 moiety to Ru−H in **2** affords the dihydrogen complex $[Ru(IMes)_2(CO)(\eta^2\text{-}H_2)(SH)H]$, which substitutes H_2 for H_2S and then undergoes a second H-transfer to give **3**. The conversion of **3** back to **2** involves two H-transfers from Ru(η^2-H_2) to Ru−SH. Such intramolecular H-atom transfer has precedence in other M−SH systems.[15]

Preliminary studies on the reactivity of **2** and **3** toward other small molecules reveal that both react readily with CO (Scheme 1). Under 1 atm of CO, **2** affords *tcc*-$[Ru(IMes)_2(CO)_2(SH)H]$ (**4**) in time of mixing. Addition of CO to a C_6D_6 solution of **3** gives *all-trans*-$[Ru(IMes)_2(CO)_2(SH)_2]$ (**5**) in quantitative yield. The ^1H NMR spectrum of **5** exhibits a Ru−SH resonance at δ −3.59. More revealing is the IR spectrum, which contains a single ν(CO) band at 1978 cm^{-1}, to higher frequency than recorded for **2** or **3** as expected for a *trans* CO geometry. Complex **4** is unstable in solution in the absence of CO and reverts back to **3**. Remarkably, reactions of **1**, **3**, and **5** can be conducted in the solid state. Complex **5** loses CO under vacuum at 120 °C to regenerate **3** (indicated by a color change from yellow to purple). Placing solid **3** under CO and heating to 120 °C re-forms **4**. Similarly, **3** reacts with H_2 at 120 °C to yield **2** over 3 days.

In summary, $[Ru(IMes)_2(CO)(H_2S)H_2]$ (**2**) is a rare hydrogen sulfide complex and the first such species to feature hydride as a coligand. Computational studies indicate that the unusual *trans* hydride geometry of **2** is stabilized by the bulky N-heterocyclic carbene IMes ligands. Complex **2** reacts reversibly with H_2S to form $[Ru(IMes)_2(CO)(SH)_2]$ (**3**), and the reactivity of **2** and **3** with CO both in solution and in the solid state has been described.

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Supporting Information Available: Synthetic information for compounds **2**−**5**. Cartesian coordinates for *cis*/*trans*-$Ru(IH)_2(CO)(H_2S)H_2$, *cis*/*trans*-**2**, and **3**. Crystallographic information for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) ^1H NMR (300 MHz, C_6D_6, 298K): δ 6.61 (br s, 8H, $C_6H_2Me_3$), 5.99 (s, 4H, NCH=CHN), 2.25 (br s, 36H, CH_3), −1.00 (s, 2H, SH). $^{13}C\{^1H\}$: δ 202.8 (s, Ru−CO), 192.7 (s, Ru−C), 137.6 (br s, N−C), 136.8 (br s, *C*−*p*-CH_3), 136.4 (br s, *C*−*o*-CH_3), 129.6 (s, *m*-CH), 124.2 (s, NCH=CHN), 21.1 (s, *p*-CH_3), 19.8 (br s, *o*-CH_3). IR (Nujol): 1925 cm^{-1} (ν_{CO}).

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