H_2 Activation Mechanism

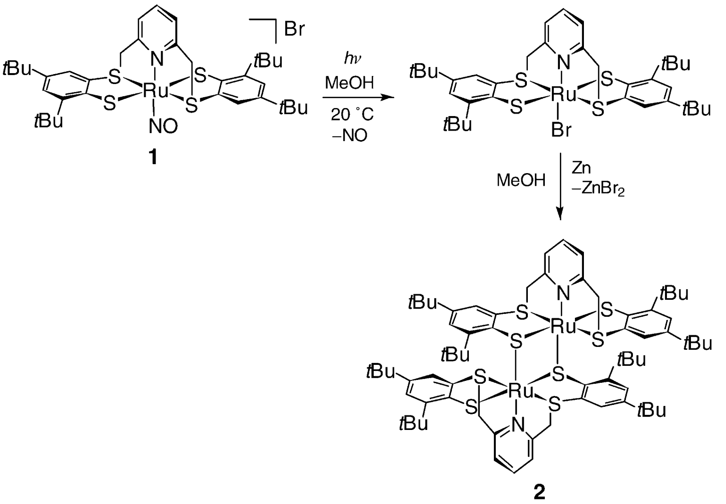
Heterolytic Cleavage of H_2 at a Sulfur-Bridged Dinuclear Ruthenium Center[**]

Dieter Sellmann, Raju Prakash, Frank W. Heinemann, Matthias Moll, and Maria Klimowicz*

Activation of H_2 is a vital process in hydrogen metabolism,[1] nitrogen fixation,[2] and fossil-fuel desulfurization.[3] Dihydrogen activation mediated by transition-metal complexes proceeds either homolytically or heterolytically.[4] There is ample evidence that metal hydrides derived from heterolytic cleavage of H_2 are among the key intermediates in the reactions of hydrogenases,[5] the active sites of which consist of thiolate-bridged dinuclear metal centers.[6] In recent years, intensive research in this area has been further motivated by the fact that the metal hydrides can act as convenient sources of hydrogen and may therefore have potential application in the hydrogen economy.[7]

Heterolytic cleavage of the H–H bond is well-documented only in the case of mononuclear complexes.[8] There are a few soluble dinuclear complexes that bring about this reaction, but they usually contain sulfido bridges.[9] Even though many thiolate-bridged dinuclear[10] and trinuclear[11] complexes are known, reports on their activity in heterolytic H–H cleavage are rare. One such example, which contains iron, catalyzes the light-induced heterolytic cleavage of H_2, and a metal-bound hydride is postulated to be the basic site for the H_2 heterolysis.[10a] We describe herein the synthesis of $[Ru(py^{bu}S_4)]_2$ (**2**) ($py^{bu}S_4^{2-}$ = 2,6-bis(2-sulfanyl-3,5-di-*tert*-butylphenylthio)dimethylpyridine(2−)) and its remarkable reactivity towards H_2 to afford a protonated thiolate hydride with unusual reactivity.

UV irradiation of the 18-valence-electron complex $[Ru(NO)(py^{bu}S_4)]Br$ (**1**)[12] dissolved in MeOH proceeds with the extrusion of NO and subsequent coordination of bromide ion to afford $[Ru^{III}(Br)(py^{bu}S_4)]$, which may be reduced with an equimolar amount of zinc to give **2** according to [Eq. (1)].



(1)

Compound **2** is diamagnetic, highly stable, and sparingly soluble in most common solvents. ^1H and ^{13}C NMR spectra recorded in $[D_8]THF$ are typical for a complex having C_1 symmetry, which has also been confirmed by an X-ray structure determination (Figure 1).[13] Each ruthenium center (Ru1, Ru2) is surrounded by one N and five S atoms in a pseudooctahedral geometry. The thioether and thiolate donors are *trans* to each other, and one of the thiolate donors forms a bridge to the other ruthenium center. The distances and angles around ruthenium are in the range usually found for diamagnetic six-coordinate Ru^{II} thiolate complexes.[12] The Ru–S(thioether) distances are shorter than the Ru–S(thiolate) distances. The bridging Ru–S(thiolate) distances (243.0(2) pm) are, however, distinctly longer than the terminal Ru–S (thiolate) distances (239.2(2) and 238.1(2) pm), suggesting that a dissociation into the $[Ru(py^{bu}S_4)]$ monomers may be feasible. The Ru···Ru distance of **2** (354.0(2) pm) excludes a direct Ru–Ru bond. The four-membered ring [Ru1-S1-S5-Ru2] has a dihedral angle of 155.7° along the S1–S5 line.

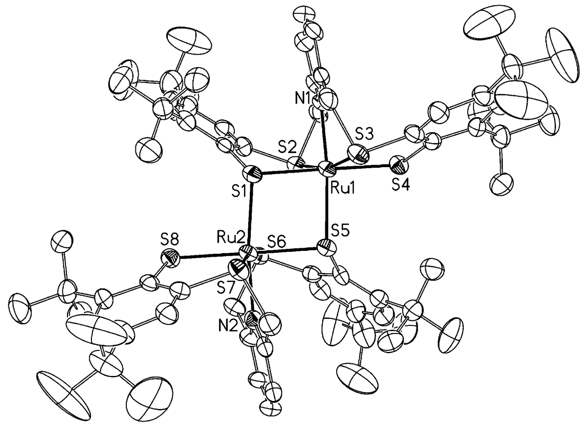


Figure 1. Molecular structure of **2** (50% probability ellipsoids; H atoms omitted). Selected distances [pm] and angles [°]: Ru1-N1 204.1 (6), Ru1-S1 239.1(2), Ru1-S2 234.1(2), Ru1-S3 227.7(2), Ru1-S4 239.1(2), Ru1-S5 243.0(2), Ru1···Ru2 354.0(2), S1-Ru1-N1 89.5(2), S1-Ru1-S2 84.24(7), S1-Ru1-S3 95.71(7), S1-Ru1-S4 178.09(7), S1-Ru1-S5 82.58(6), S2-Ru1-S3 165.75(7), S2-Ru1-S4 94.04(6), S2-Ru1-S5 102.69(6), S2-Ru1-N1 82.3(2), N1-Ru1-S5 170.1(2), Ru1-S1-Ru2 94.53(6).

The diruthenium complex **2** reacts with H_2 (15 bar) at room temperature to give the mononuclear protonated thiolate hydride $[Ru(H)(py^{bu}S_4\text{-}H)]$ (**3**)[14] presumably via a

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[*] Prof. Dr. D. Sellmann,[+] Dr. R. Prakash, Dr. F. W. Heinemann, Dr. M. Moll, Dr. M. Klimowicz
Institut für Anorganische Chemie
Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax: (+49) 9131-85-27367
E-mail: prakash@anorganik.chemie.uni-erlangen.de

[+] Deceased

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transient η^2-H_2 species and subsequent H_2 heterolysis. In the course of the reaction, the pink suspension of **2** in THF changes to a clear red solution. The ^{1}H NMR spectrum shows a sharp hydride resonance at $\delta = -14.54$ ppm in the region typical for terminal RuH protons, and a broad resonance at $\delta = 4.69$ ppm (integration: 1 H) is assigned to the SH proton of compound **3**. When the same reaction is performed with D_2, the corresponding RuD and SD resonances appear in the ^{2}H NMR spectra over the course of 48 h (Figure 2 a, b). The new RuH and SH resonances disappear, and the spectrum of **2** reappears when H_2 pressure is released, showing this conversion to be reversible.

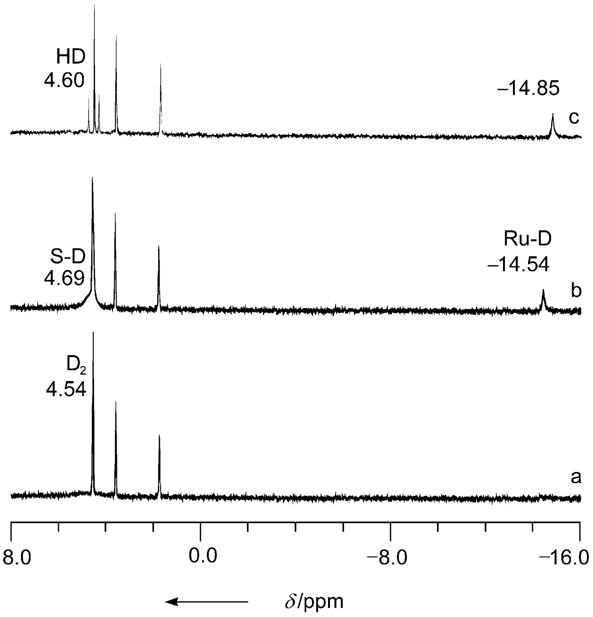


Figure 2. ^{2}H NMR spectra of **2** in THF under D_2 (20 bar) after a) 1 h and b) 48 h. c) ^{2}H NMR spectrum of **4** in THF at D_2 atmosphere, 1 h at 20 °C.

With a view to stabilizing the hydride species by abstracting the proton with an external base, we performed suitable NMR experiments. With one equivalent of NaOMe per Ru the complex Na[Ru(H)(py^{bu}S$_4$)] (**4**) and MeOH were obtained. ^{1}H NMR monitoring of this reaction revealed a sharp singlet for RuH at $\delta = -14.85$ ppm, and a weak resonance at $\delta = 4.89$ ppm, which presumably is due to the OH proton of MeOH, apart from the signals of the [Ru(py^{bu}S$_4$)] fragment. The number and pattern of ^{1}H NMR signals are characteristic of complexes with C_2 symmetry. Complex **4** can be isolated in the solid state.[15] Figure 3 depicts the molecular structure of **4** as determined by X-ray crystallography.[13] The ruthenium center is coordinated in a pseudooctahedral fashion by one N, one H, and four S atoms. The thioether and thiolate donors adopt *trans* positions, and the hydride ligand occupies the position *trans* to the N atom. The Na^+ ion is bound to the [Ru(H)(py^{bu}S$_4$)]$^-$ moiety through thiolate and hydride ligands. One THF molecule completes the coordination of the Na^+ ion. In the solid state, there is a crystallographic inversion center between two units of **4**, which assemble by means of S···Na···S(thiolate) and S···Na···H bridges.

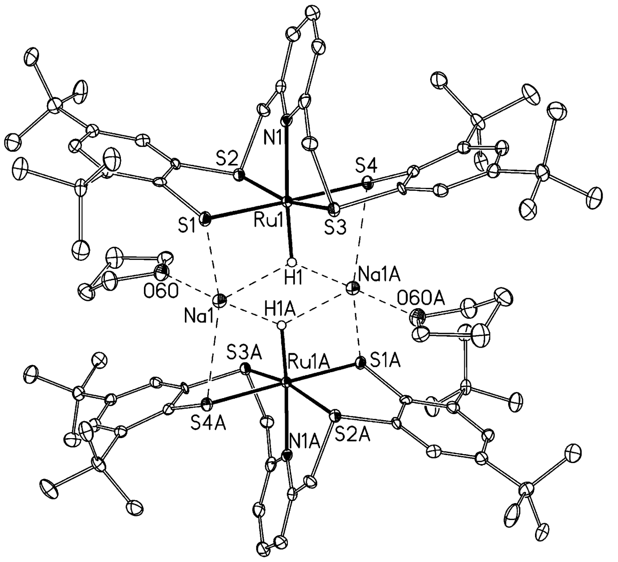
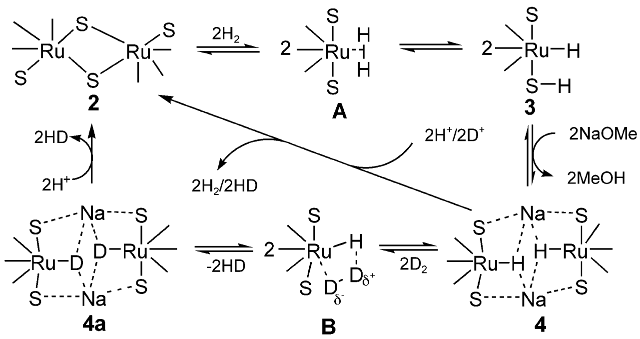


Figure 3. Molecular structure of **4** (50 % probability ellipsoids; H atoms (except H1) omitted). Selected distances [pm] and angles [°]: Ru1-N1 210.2(3), Ru1-S1 236.4(2), Ru1-S2 230.5(2), Ru1-S3 227.5(2), Ru1-S4 239.7(2), Ru1-H1 161(5), H1···Na1 221(5), S1···Na1 293.5(2), S4···Na1A 286.4(2), Na1···O60 228.6(3), S1-Ru1-N1 94.3(1), S1-Ru1-S2 85.96(4), S1-Ru1-S3 91.81(4), S1-Ru1-S4 177.69(4), S1-Ru1-H1 90(2), S2-Ru1-S3 165.97(4), S2-Ru1-S4 95.42(4), S2-Ru1-N1 82.0(1), S2-Ru1-H1 100(2), S3-Ru1-H1 95(2), S4-Ru1-N1 84.1(1), N1-Ru1-H1 176(2).

In the presence of both CO (1 bar) and H_2 (15 bar), **2** reacts exclusively with CO to give the carbonyl complex [Ru(CO)(py^{bu}S$_4$)]. A ^{13}C NMR experiment with **2** in [D$_8$]THF, in the presence of ^{13}CO (1 bar) and H_2 (15 bar), confirms the formation of [Ru(^{13}CO)(py^{bu}S$_4$)], as inferred from the appearance of a new resonance at $\delta = 202.8$ ppm after 12 h, well separated from the resonance of dissolved ^{13}CO at $\delta = 184.5$ ppm. No RuH or SH resonances were observed in ^{1}H NMR spectra even after four days. This indicates that CO competes with H_2 for the same coordination site and thus inhibits the reaction.

Interestingly, **4** undergoes D_2/H^- exchange with D_2 to give [Ru(D)(py^{bu}S$_4$)]$^-$ (**4a**) and HD.[16] During ^{1}H NMR monitoring, the RuH resonance at $\delta = -14.85$ ppm disappeared, and a 1:1:1 triplet of HD grew in at $\delta = 4.60$ ppm. The ^{2}H NMR spectrum is complementary with the appearance of a corresponding HD doublet and RuD signals (Figure 2 c).[17] Protonation of **4** and **4a** with HBF_4/CD_3COOD always regenerates **2** by releasing H_2, HD, or D_2.

Taken together, these results demonstrate that complex **2** is capable of heterolyzing H_2. The proposed mechanism (Scheme 1) involves the initial dissociation of Ru–S bridges and subsequent binding of H_2 to the Ru center to form a labile η^2-H_2 species **A**, which undergoes heterolytic cleavage by the concerted action of Lewis acidic Ru and Brønsted basic sulfur centers to give the protonated thiolate hydride complex **3**. An external base (NaOMe) can abstract the proton to form the hydride complex **4**. The D_2/H^- exchange reaction of **4** with D_2 to give **4a** may proceed via transitory intermediate **B**.



Scheme 1. Cyclic mechanism for the heterolytic H_2 activation reaction of **2**.

Protonation of **4** or **4a** regenerates **2** by releasing H_2 or HD and completes the cycle. The identification of **3** and the isolation of **4** unambiguously prove the heterolytic H_2 cleavage at the Ru–S centers of **2**. Salient features are the breaking of Ru–S bridges of **2** by incoming H_2, subsequent cleavage of the H–H bond to give H^+ and H^-, transfer of the proton to the external base, and the D_2/H^- exchange reaction of **4** with D_2. Compound **2** is a rare example of thiolate-bridged dinuclear complex that can heterolyze the H–H bond of dihydrogen. The proposed mechanism of the heterolytic cleavage at the Ru–S centers is intriguing with relevance to the activation of H_2 by hydrogenases. Work to prepare analogous NiFe and FeFe complexes is in progress.

Experimental Section

All reactions and manipulations were carried out in dried and distilled solvents under argon using standard Schlenk techniques.

2: A violet solution of **1** (800 mg, 0.97 mmol) in MeOH (40 mL) was irradiated in a quartz immersion lamp apparatus with a Hg lamp (150 W) for 15 min at 20 °C. The resulting green suspension was treated with zinc powder (32 mg, 049 mmol) to give pink-red microcrystals of **2**. Yield: 640 mg (92 %). Elemental analysis calcd (%) for **2** ($C_{70}H_{94}N_2S_8Ru_2$): C 59.12, H 6.66, N 1.97, S 18.04; found: C 58.85, H 7.00, N 2.10 S 17.76; ^{1}H NMR (269.7 MHz, [D$_8$]THF, 20 °C): $\delta = 7.80$ (d, 2H; C_6H_2), 7.55 (d, 2H; C_6H_2), 7.03 (d, 2H; C_6H_2), 7.01 (d, 2H; C_6H_2), 6.80–6.40 (m, 6H; C_5H_3N), 4.92 (d, 2H; CH_2), 4.58 (d, 2H; CH_2), 4.41 (d, 2H; CH_2), 3.96 (d, 2H; CH_2), 1.42 (s, 18H; *t*Bu), 1.41 (s, 18H; *t*Bu), 1.34 (s, 18H; *t*Bu), 1.05 ppm (s, 18H; *t*Bu); ^{13}C{^{1}H} NMR (67.8 MHz, [D$_8$]THF, 20 °C): $\delta = 160.4$, 159.5, 154.9, 152.7, 150.8, 148.9, 148.4, 142.6, 140.6, 136.8, 134.4, 130.6, 127.1, 126.6, 123.2, 122.9, 119.9, 119.6 (C_6H_2/C_5H_3N), 57.7, 56.5 (CH_2), 38.4, 38.2, 35.4, 34.8, 32.0, 31.8, 30.1, 29.9 ppm (*t*Bu); MS (FD, THF); *m/z* (%): 1422 (100) [M^+].

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[13] X-ray structural analysis of **2** and **4**: Red fragments of **2**·6THF were obtained from a saturated solution of **2** in THF at 5 °C. Red needles of **4**·THF were obtained from a THF/pentane solution after 10 d at −25 °C. Suitable single crystals were embedded in protective perfluoro polyether. Data were collected on either a Siemens P4 diffractometer (**2**) or a Nonius Kappa CCD diffractometer (**4**) using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), and a graphite monochromator. A semiempirical absorption correction using Psi-scans was performed for **2**, and a numerical absorption correction applied to **4**. The structures were solved by direct methods; full-matrix least-squares refinement was carried out on F^2 using SHELXTL NT 5.1. All non-hydrogen atoms were refined anisotropically. The H atoms of **2**·6THF were geometrically positioned while all H-atom positions of **4**·THF were derived from a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter. Selected crystallographic data for **2**: $C_{94}H_{142}N_2O_6Ru_2S_8$, crystal size $0.50 \times 0.40 \times 0.32$ mm, orthorhombic, space group $Pna2_1$, $a = 2997.2(3)$, $b = 1223.6(2)$, $c = 2634.8(2)$ pm, $V = 9.663(2)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.275$ g cm^{-3}, $T = 200$ K, $\mu = 0.536$ mm^{-1}, $(3.6 < 2\theta < 52.0°)$, $T_{min} = 0.522$, $T_{max} = 0.556$, 18561 measured reflections, 17630 unique reflections, 12279 observed reflections($I > 2\sigma(I)$), 1033

parameters, $R1 = 0.0601$ ($I > 2\sigma(I)$), $wR2 = 0.1340$(all data). **4**: $C_{39}H_{56}NNaORuS_4$, crystal size $0.29 \times 0.07 \times 0.06$ mm, triclinic, space group $P\bar{1}$, $a = 1008.4(2)$, $b = 1449.8(1)$, $c = 1464.8(2)$ pm, $\alpha = 88.81(1)$, $\beta = 73.58(1)$, $\gamma = 77.42(1)°$, $V = 2.0029(5)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.338$ g cm^{-3}, $T = 100$ K, $\mu = 0.641$ mm^{-1}, ($6.0 < 2\theta < 54.0°$), $T_{min} = 0.851$, $T_{max} = 0.936$, 36687 measured reflections, 8691 unique reflections, 5870 observed reflections ($I > 2\sigma(I)$), 592 parameters, $R1 = 0.0529$($I > 2\sigma(I)$), $wR2 = 0.1059$ (all data). CCDC 228286 (**2**) and CCDC 228287 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] In a high-pressure NMR tube, a solution of **2** (50 mg) in [D$_8$]THF/THF (0.6 mL) was pressurized with H_2/D_2 (15 bar). The reaction was monitored by recording ^{1}H/^{2}H NMR spectra at various time intervals over 2 d.

[15] **4**: In an autoclave, a mixture of **2** (500 mg, 0.35 mmol) and NaOMe (38.5 mg, 0.71 mmol) in THF (15 mL) was stirred at 20 °C under H_2 (20 bar) for 2 d. The autoclave was cooled to −80 °C, the pressure released, and the solution filtered through a cannula into pentane at −80 °C to give **4** as a red solid. Yield: 236 mg (46 %). ^{1}H NMR (269.7 MHz, [D$_8$]THF, 20 °C): $\delta = 7.51$ (d, 2H; C_6H_2), 6.99 (d, 2H; C_6H_2), 6.90–6.83 (m, 3H; C_5H_3N), 4.65 (d, 2H; CH_2), 4.42 (d, 2H; CH_2), 1.51 (s, 18H; *t*Bu), 1.28 (s, 18H; *t*Bu), −14.85 ppm (s, 1H; Ru-H); ^{13}C{^{1}H} NMR(67.8 MHz, [D$_8$]THF, 20 °C): $\delta = 155.7$, 154.9, 148.9, 142.2, 137.7, 129.7, 127.2, 122.5, 119.1 (C_6H_2/C_5H_3N), 62.4 (CH_2), 38.4, 34.8, 32.0, 30.0 ppm (*t*Bu).

[16] **4a**: A solution of **4** (150 mg, 0.10 mmol) in THF (5 mL) was stirred under a D_2 atmosphere for 2 h at 20 °C. Then the solution was concentrated to dryness. ^{1}H NMR: as **4**, no RuH signal. ^{2}H NMR: $\delta = -14.85$ ppm (RuD).

[17] In a Youngs NMR tube, the reaction of **4** (50 mg) in [D$_8$]THF/THF (0.6 mL) under D_2 atmosphere was monitored by recording ^{1}H/^{2}H NMR spectra at 20 °C.