Transition Metal Complexes with Sulfur Ligands. 130.[1] Synthesis, Structure, and Reactivity of the Sulfur-Rich Ruthenium Hydride Complexes [Ru(H)(PR_3)('S_4')]$^-$ and the η^2-H_2 Complex [Ru(H_2)(PCy_3)('S_4')] (R = Ph, ^{i}Pr, Cy; 'S_4'$^{2-}$ = 1,2-Bis((2-mercaptophenyl)thio)ethane(2−))

Dieter Sellmann,* Torsten Gottschalk-Gaudig, and Frank W. Heinemann

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-91058 Erlangen, Germany

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Hydride and η^2-H_2 ruthenium complexes with sulfur-rich coordination spheres were synthesized. Substitution of either DMSO or PPh_3 in [Ru(DMSO)(PR_3)('S_4')] and [Ru(PPh_3)$_2$('S_4')] by hydride anions from $LiAlH_4$ or $NaBEt_3H$ yielded [Ru(H)(PR_3)('S_4')]$^-$ complexes (R = ^{i}Pr, Ph, Cy; 'S_4'$^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethane(2−)). They were isolated as [Li(THF)(Et_2O)][Ru(H)(PR_3)('S_4')] (R = ^{i}Pr (**1a**), Cy (**1b**), Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (**2a**), and the solvent-free Na[Ru(H)(PPh_3)('S_4')]·2BEt_3 (**2b**). X-ray structure determinations of **1a**·0.5Et_2O and **1b**·Et_2O showed that in both complexes pseudooctahedral [Ru(H)(PR_3)('S_4')]$^-$ anions are bridged to pseudotetrahedral [Li(THF)(Et_2O)] cations via the hydride ligand and one thiolate donor of the 'S_4'$^{2-}$ ligand (crystal data: **1a**, monoclinic, $P2_1/n$, a = 1401.6(2) pm, b = 1045.2(3) pm, c = 2590.6(4) pm, β = 95.04(1)°, V = 3.780(1) nm^3, Z = 4; **1b**, triclinic, $P\bar{1}$, a = 1264.2(1) pm, b = 1322.9(3) pm, c = 1569.5(2) pm, α = 88.96(1)°, β = 83.48(1)°, γ = 62.16(1)°, V = 2.3042(6) nm^3, Z = 2). Short intramolecular C−H···H−Ru contacts (≈230 pm) between the hydride ligands, phosphine substituents, and lithium-coordinated Et_2O molecules indicate "unconventional" hydrogen bonds. They potentially help to decrease the hydridic character of the hydride ligand to such an extent that no structural hydride trans influence can be observed in the solid state. In solution at room temperature, all hydride complexes **1a**−**2b** rapidly release H_2 or HD, when treated with CH_3OH or CD_3OD. Low-temperature ^{1}H and ^{2}H NMR spectroscopy between −20 and −80 °C showed that initially η^2-H_2 or η^2-HD complexes form. Their formation explains the observed scrambling between protons and hydride ligands, which requires a heterolytic cleavage of dihydrogen. A 1:1:1 triplet at δ = −6.5 ppm (^1J(HD) = 32 Hz, ^2J(PH) = 5 Hz) and a relaxation time of T_1(min) = 4 ms (−60 °C, 270 MHz) firmly established the formation of the η^2-dihydrogen complexes. The reversibility of H_2 release and uptake by [Ru(PCy_3)('S_4')] fragments and the heterolytic cleavage of H_2 in [Ru(η^2-H_2)(PCy_3)('S_4')] was further ascertained by the reaction of [Ru(DMSO)(PCy_3)('S_4')] with H_2 in the presence of NaOMe, yielding the [Ru(H)(PCy_3)('S_4')]$^-$ anion. The relevance of the complexes and their reactions for the heterolytic H_2 activation at the transition metal sulfur sites of hydrogenases is discussed.

Introduction

The activation of molecular hydrogen at transition metal sulfur sites is a key feature of metal sulfur enzymes such as hydrogenases[2] and nitrogenases[3] and of heterogeneous catalysts for the hydrotreatment of petroleum.[4] In all three types of metal hydrogenases, [Ni,Fe,S], [Ni,Fe,S,Se], or [Fe,S], the metal centers exhibit sulfur-rich coordination spheres which are believed to be the H_2 binding sites.[5] X-ray structure analysis revealed that the active site of hydrogenase isolated from *Desulfovibrio gigas* contains a binuclear nickel iron center in which the nickel is surrounded by four cysteine thiolate donors and bridged via two of them to the iron.[6] On the basis of electrochemical and spectroscopic investigations, e.g., redox titrations and EPR spectra, it has been suggested that in [NiFe] hydrogenases the nickel atom is the H_2 binding site.[7] In the nickel-free "iron-only" hydrogenases,[5c] however, iron sulfur

* To whom correspondence should be addressed.

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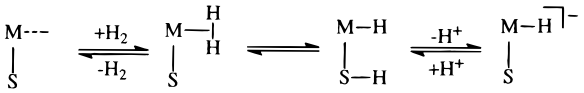
centers must be considered the H_2 binding site[5c,2b] and the question remains how H_2 is molecularly activated at transition metal sulfur sites.

Hydrogenases catalyze the redox equilibrium and the heterolytic cleavage of H_2 according to eq 1a,b.[8]

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (1a)$$

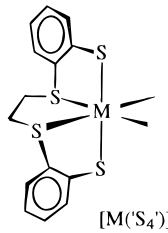
$$H_2 + D_2O \rightleftharpoons HD + HDO \quad (1b)$$

The catalysis of reaction 1b has proved an important criterion for hydrogenase activity, and it has been suggested that it occurs via formation of η^2-H_2 and thiol hydride species according to eq 2.[9]



(2)

Our investigations aim at model complexes which combine structural *and* functional features of the hydrogenase centers.[10] For these reasons, the model complexes should (1) exhibit transition metals with sulfur-dominated coordination spheres, (2) allow the proof of key intermediates such as coordinatively unsaturated species, η^2-H_2, hydride thiol, and/or hydride derivatives upon reaction with H_2, and (3) catalyze reaction 1b. Such complexes are extremely rare. For example, nickel hydride complexes with sulfur donors such as $[Ni(H)\{N(C_2H_4SR)_3\}]^+$ [11] or $[Ni(H)(PMe_3)(C_6H_4S_2)]^-$ [12] have been synthesized but could not be proved to catalyze reaction 1b. As a matter of fact, transition metal hydride[13] and, likewise, η^2-H_2[14] complexes rarely exhibit sulfur-rich coordination spheres. The dominant coligands of hydride or η^2-H_2 ligands preferably are phosphines, carbon ligands such as cyclopentadienyl or CO, and/or "hard" ligands, e.g., halides or amines.[13−15] There are only a very few hydride[16] or η^2-H_2[17] complexes that exhibit at least one sulfur donor in their coordination sphere. Some of these complexes, e.g., $[Os(\eta^2\text{-}H_2)(CO)(quS)(PPh_3)_2]^+$ (quS^- = quinoline-8-thiolate),[17b] $[Ir(H)_2(HS(CH_2)_3SH)(PCy_3)_2]BF_4$,[16o] and $[Os(\eta^2\text{-}H_2)(CO)(S_2COEt)(P^iPr_3)_2]$,[17c] allowed us to observe equilibria between hydride thiol and η^2-H_2 species, the scrambling between hydride ligands and thiol protons, and the heterolytic splitting of H_2. Our search for sulfur-rich transition metal hydride complexes has resulted in [Rh(H)(L)('S_4')] complexes (L = CO, PR_3; 'S_4'$^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethane(2−)).[18] These complexes have [M('S_4')] cores and thus exhibit predominantly sulfur donors in their coordination sphere.



[M('S_4')]

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Nickel[19] and, in particular, iron[20] hydride complexes with 'S_4'$^{2-}$ ligands have remained inaccessible as yet. Anticipating that ruthenium may yield less labile species than iron, we have now extended our efforts to ruthenium complexes with [M('S_4')] cores and could isolate hydride complexes of the type M[Ru(H)(PR_3)('S_4')] (M = Li, Na; R = ^{i}Pr, Ph, Cy) which give η^2-H_2 complexes upon protonation. Prerequisite for these investigations have been the recently reported Ru(II) complexes [Ru(DMSO)(PR_3)('S_4')] (R = ^{i}Pr, Cy)[21] and [Ru(PPh_3)$_2$('S_4')][22] that contain a labile DMSO ligand or PPh_3 ligand, respectively.

Experimental Section

General Procedures. Unless noted otherwise, all manipulations were performed under argon, using standard Schlenk techniques. Solvents were freshly dried, distilled, and saturated with argon before use. As far as possible, reactions were monitored by NMR spectroscopy. The NMR spectra were recorded on JEOL FT-JNM-GX 270, EX 270, and Lambda LA 400 spectrometers with the protio-solvent signal used as a reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. The T_1 measurements were carried out at 270 MHz using the standard inversion−recovery pulse sequence, 180°−τ−90°.

[Ru(DMSO)(PR_3)('S_4')] (R = ^{i}Pr, Cy)[21] and [Ru(PPh_3)$_2$('S_4')][22] were prepared by literature methods. $LiAlH_4$, $LiAlD_4$, and $NaBEt_3H$ (1 M in toluene) were purchased from Aldrich, and HBF_4 (54% in Et_2O) was purchased from Merck.

[Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')] (1a). $LiAlH_4$ (112 mg, 3.0 mmol) was added to a yellow-green suspension of [Ru(DMSO)(P^iPr_3)('S_4')] (385 mg, 0.59 mmol) in THF (15 mL) at −55 °C. Warming the mixture to room temperature yielded a cloudy orange solution which was filtered. Removal of all volatile material resulted in a red oil that was redissolved in Et_2O (10 mL). Insoluble material was filtered off, and the filtrate was stored at −25 °C for 1 year. Yellow crystals that had precipitated were separated, washed with Et_2O (4 mL), and dried for 5 min in vacuo; yield 34% (145 mg). ^{1}H NMR (269.60 MHz, ppm, CD_2Cl_2): δ 7.60 (m, 1 H, C_6H_4), 7.40 (m, 2 H, C_6H_4), 6.95−6.70 (m, 4 H, C_6H_4), 2.80 (m, 1 H, CH_2), 2.40 (m, 4 H, CH_2, CH), 1.30−1.00 (m, 20 H, CH_2, CH_3), −12.20 (d (^2J(HP) = 27.0 Hz), 1 H, RuH).

[Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')] (1b). Addition of $LiAlH_4$ (155 mg, 4.1 mmol) to a yellow-green suspension of [Ru(DMSO)(PCy_3)('S_4')] (633 mg, 0.82 mmol) in THF (10 mL) at −65 °C and warming up the mixture to room temperature gave a cloudy orange solution. The solution was filtered, the filtrate was stripped from all volatile material in vacuo, and the remaining red oil was redissolved in Et_2O (10 mL) and stirred for 30 min. The solution was concentrated in volume to 3 mL and stored at −25 °C. Precipitated yellow crystals were separated after 14 d, washed with cold Et_2O (4 mL), and dried in vacuo at −78 °C for 5 h; yield 33% (229 mg). ^{1}H NMR (269.60 MHz, ppm, THF-d_8): δ 7.50 (m, 1 H, C_6H_4), 7.40 (m, 3 H, C_6H_4), 6.75−6.55 (m, 4 H, C_6H_4), 2.80 (m, 1 H, CH_2), 2.65 (m, 1 H, CH_2), 2.40−0.95 (m, 35 H, CH_2, C_6H_{11}), −10.60 (d (^2J(HP) = 25.4 Hz), 1 H, RuH). ^{31}P{^{1}H} NMR (109.38 MHz, ppm THF-d_8): δ +59.50 (s).

[Li(THF)(Et_2O)][Ru(D)(PCy_3)('S_4')] (**1c**) was obtained in an analogous way by using $LiAlD_4$. ^{2}H NMR (41.25 MHz, ppm, THF-d_8): δ −10.90 (s, RuD).

Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (2a). $NaBEt_3H$ (2.5 mL, 2.5 mmol) was added to a yellow-green suspension of [Ru(DMSO)(PCy_3)('S_4')] (372 mg, 0.48 mmol) in toluene (7.5 mL). In the course of 4 h a yellow solid precipitated, which was separated, washed with toluene (10 mL) and pentane (10 mL), and dried in vacuo; yield 60% (272 mg). ^{1}H NMR (269.60 MHz, ppm, THF-d_8): δ 7.45−7.05 (m, 4 H, C_6H_4), 6.70−6.40 (m, 4 H, C_6H_4), 2.80 (m, 1 H, CH_2), 2.65 (m, 1 H, CH_2), 2.50 (s, 3 H, DMSO), 2.35−0.90 (m, 35 H, CH_2, C_6H_{11}), 0.74 (br, 18 H, BCH$_2$CH_3), 0.04 (br, 12 H, BCH_2CH$_3$), −11.35 (d (^2J(HP) = 25.6 Hz), 1 H, RuH). ^{31}P{^{1}H} NMR (109.38 MHz, ppm, THF-d_8): δ +60.00 (s). ^{11}B NMR (86.47 MHz, ppm, THF-d_8): δ −9.0 (s).

Na[Ru(H)(PPh_3)('S_4')]·2BEt_3 (2b). $NaBEt_3H$ (2.0 mL, 2.0 mmol) was added to a yellow suspension of [Ru(PPh_3)$_2$('S_4')] (281 mg, 0.3 mmol) in toluene (10 mL), and the mixture was stirred for 4 d. A clear yellow solution resulted, which was cooled to −20 °C after addition of pentane (20 mL). A yellow solid precipitated that was separated after 1d, washed with pentane (30 mL), and dried in vacuo; yield 37% (100 mg). ^{1}H NMR (269.60 MHz, ppm, THF-d_8): δ 7.55 (m, 6 H, H [aryl]), 7.40−6.95 (m, 13 H, H [aryl]), 6.75−6.55 (m, 3 H, H [aryl]), 6.45 (m, 1 H, H [aryl]), 2.75 (m, 1 H, CH_2), 2.55 (m, 1 H, CH_2), 1.60 (m, 1 H, CH_2), 1.35 (m, 1 H, CH_2), 0.70 (m, 18 H, BCH$_2$CH_3), 0.00 (m, 12 H, BCH_2CH$_3$), −11.15 (d (^2J(HP) = 25.8 Hz), 1 H, RuH). ^{31}P{^{1}H} NMR (109.38 MHz, ppm, THF-d_8): δ +59.50 (s).

General Procedure for the Protonation of [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')] (1b). In a NMR tube fitted with a rubber septum, an orange THF-d_8 (0.7 mL) solution of [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')] (**1b**) was combined at −78 °C with CD_3OH (10 equiv) and HBF_4 (1 equiv) by means of a syringe. The resulting green solution was investigated NMR spectroscopically at −80 °C.

Reaction of [Ru(DMSO)(PCy_3)('S_4')] with H_2 in the Presence of NaOMe. H_2 was bubbled through a yellow green suspension of [Ru(DMSO)(PCy_3)('S_4')] (330 mg, 0.43 mmol) and NaOMe (230 mg, 4.3 mmol) in THF (20 mL). In the course of 3 h an orange solution formed, which was filtered, and the filtrate was stripped from all volatile material in vacuo. The formation of the [Ru(H)(PCy_3)('S_4')]$^-$ anion was established via its hydride signal (δ = −11.3 ppm; THF-d_8) in the ^{1}H NMR spectrum.

X-ray Crystallography and Structure Solution. Yellow single crystals (cubes) of [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) and [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')]·Et_2O (**1b**·Et_2O) were obtained from the reaction mixtures which contained the applied excess of $LiAlH_4$ as described above. The crystal growth of **1a** was extremely slow, and crystals suitable for X-ray analysis were obtained only after keeping the glass stopper sealed Schlenk tube at −25 °C for 1 year. Crystals of **1a**·0.5Et_2O and **1b**·Et_2O were coated with an inert perfluorinated polyether in a stream of dry argon at −78 °C,[23] mounted on a glass capillary, and transferred into the nitrogen stream of the low-temperature device of the Siemens P4 diffractometer. Data collection parameters are summarized in Table 1. For all complexes, crystal systems were determined photographically, and space groups were assigned by systematic absences; further refinement confirmed the space group assignments. No correction was made for absorption. The structures were solved by direct methods (SHELXTL-PLUS[24] for **1a**·0.5Et_2O; SHELXTL 5.03[25] for **1b**·Et_2O); refinement on F^2 was carried out by full-matrix least-squares procedures (SHELXTL 5.03). All non-hydrogen atoms were refined anisotropically with exception of the non-hydrogen atoms of the solvent molecule in **1a**·0.5Et_2O that were refined isotropically. The hydrogen atom positions were determined from difference Fourier maps with exception of the H atoms of the solvent molecule in **1a**·0.5Et_2O. In the case of **1a**·0.5Et_2O, the atomic coordinates of the hydrogen atoms were refined with a fixed isotropic thermal parameter. For **1b**·Et_2O, the hydrogen atoms were refined isotropically with exception of the H atoms H73A, B, and

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(25) *SHELXTL 5.03 for Siemens Crystallographic Research Systems*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

Table 1. Crystallographic Data for [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) and [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')]·Et_2O (**1b**·Et_2O)

	1a·0.5Et_2O	**1b**·Et_2O
formula[a]	$C_{33}H_{57}LiO_{2.5}PRuS_4$	$C_{44}H_{74}LiO_3PRuS_4$
fw	761.01	918.25
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, pm	1401.6(2)	1264.2(1)
b, pm	1045.2(3)	1322.9(3)
c, pm	2590.6(4)	1569.5(2)
α, deg	90	88.96(1)
β, deg	95.04(1)	83.48(1)
γ, deg	90	62.16(1)
V, nm^3	3.780(1)	2.3042(6)
Z	4	2
ρ_{calc}, g/cm^3	1.337	1.323
μ, mm^{-1}	0.706	0.593
λ, pm	Mo Kα (λ = 71.073)	Mo Kα (λ = 71.073)
T, K	175	153
R_1;[b] wR_2,[c] %	2.94, 9.06	4.81, 12.49

[a] Including solvent molecule. [b] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$ for $F > 4\sigma(F)$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, $P = (F_o^2 + 2F_c^2)/3$, and $a = 0.0493$ (**1a**·0.5Et_2O) or 0.0586 (**1b**·Et_2O).

H74A,B,C, where groupwise isotropic thermal parameters were refined with fixed atomic coordinates.

Results

The reactions according to eq 3 yielded the ruthenium hydride complexes $[Ru(H)(PR_3)('S_4')]^-$ that were isolated as [Li(THF)-(Et_2O)][Ru(H)(PR_3)('S_4')] (R = ^{i}Pr (**1a**), Cy (**1b**)). The deuterium derivative [Li(THF)(Et_2O)][Ru(D)(PCy_3)('S_4')] (**1c**) was obtained by using $LiAlD_4$.

$$[Ru(DMSO)(PR_3)('S_4')] + \text{exc. } LiAlH_4 \xrightarrow[\text{r.t.}]{THF/Et_2O} [Li(THF)(Et_2O)][Ru(H)(PR_3)('S_4')] \quad (3)$$

R = ^{i}Pr **1a**, Cy **1b**

The complexes **1a**−**c** are yellow, thermolabile, and extremely sensitive toward air and moisture such that no elemental analyses could be carried out. In the solid state, the complexes can be stored for longer periods of time at −78 °C only.

The formation of the hydride complex anions $[Ru(H)(PR_3)('S_4')]^-$ in **1a**,**b** could be conclusively deduced from the ^{1}H and ^{31}P NMR spectra. The NMR spectra further indicated the overall composition of **1a**,**b** that was unambiguously confirmed by X-ray structure analysis.

A likewise extremely air and moisture sensitive, but thermally more stable hydride complex was obtained according to eq 4.

$$[Ru(DMSO)(PCy_3)('S_4')] + \text{exc. } NaBEt_3H \xrightarrow[5\text{ h/ r.t.}]{\text{toluene}} Na[Ru(H)(PCy_3)('S_4')]\cdot 2BEt_3\cdot 0.5DMSO \quad (4)$$

2a

As in the case of complexes **1a**−**c**, no elemental analyses could be carried out, and the composition of **2a** was concluded from NMR spectra (^{1}H, ^{11}B, ^{31}P). The DMSO of **2a** probably serves as solvate only, because the reaction according to eq 5

$$[Ru(PPh_3)_2('S_4')] + \text{exc. } NaBEt_3H \xrightarrow[4\text{ d/ r.t.}]{\text{toluene}} Na[Ru(H)(PPh_3)('S_4')]\cdot 2BEt_3 \quad (5)$$

2b

yielded the solvate-free analogue Na[Ru(H)(PPh_3)('S_4')]·2BEt_3 (**2b**·2BEt_3). In this case, longer reaction times of up to 4 days were required because the precursor complex [Ru(PPh_3)$_2$('S_4')] is much less substitution labile than [Ru(DMSO)(PCy_3)('S_4')]. Complexes **2a**,**b** both contain two BEt_3 molecules that could not be removed even by prolonged drying in vacuo.

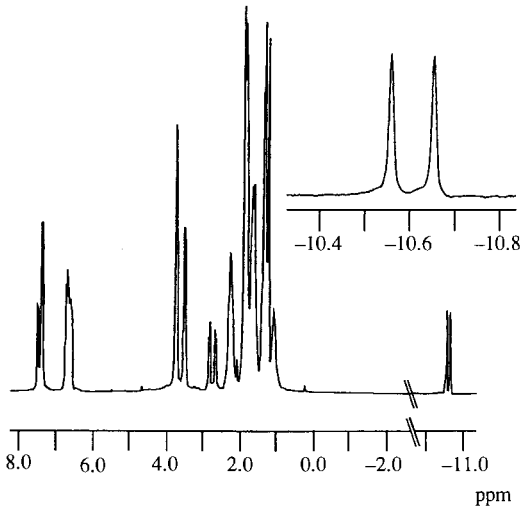


Figure 1. ^{1}H NMR spectrum of **1b** in THF-d_8 at 20 °C.

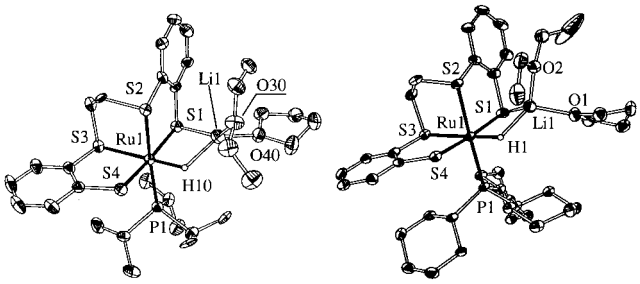


Figure 2. Molecular structures of [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) (left) and [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')]·Et_2O (**1b**·Et_2O) (right) (50% probability ellipsoids, hydrogen atoms with the exception of the hydrides omitted for clarity).

Spectroscopic and X-ray Structural Characterization. The ^{1}H NMR spectra of the complexes **1a**,**b** and **2a**,**b** each exhibit a characteristic hydride doublet in the region of −10.0 to −11.5 ppm. The coupling constants ^2J(PH) ∼ 25 Hz indicate cis positions of the phosphine and hydride ligands.[13a] Figure 1 depicts the ^{1}H NMR spectrum of **1b**. It shows, in addition to the hydride doublet, the 'S_4'$^{2-}$ ligand multiplet which are typical of C_1-symmetric [Ru(L_1)(L_2)('S_4')] complexes.[21] The signals at 3.75, 3.58, and 3.40 ppm indicate free and coordinated THF and Et_2O. (The other signals of THF and Et_2O overlap with the PCy_3 signals in the region of 2.5−0.9 ppm.)

The ^{1}H NMR spectra of the BEt_3 adducts **2a**,**b** each reveal two slightly broadened singlets (**2a**) or two narrow multiplets (**2b**) for the C_2H_5 groups. Their intensities prove the presence of two BEt_3 groups in both **2a**,**b**, which were also confirmed by ^{11}B NMR spectra.

The molecular structures of [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)-('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) and [Li(THF)(Et_2O)][Ru(H)(PCy_3)-('S_4')]·Et_2O (**1b**·Et_2O) have been elucidated by X-ray structure determination. Figure 2 shows a view of the molecular structures, Table 2 lists selected distances and angles.

The hydride ligands were located in the difference Fourier synthesis. In both complexes, the Ru centers are pseudooctahedrally surrounded by one H, one P, and four S donors. The thiolate donors of the 'S_4'$^{2-}$ ligand occupy trans positions, and hydride and phosphine donors occupy cis positions. In both

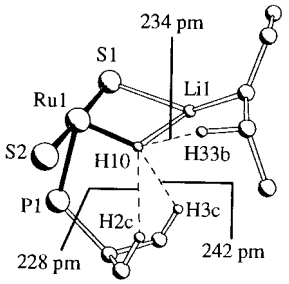


Figure 3. Intramolecular interactions in the M−H···H−C units of **1a**·0.5Et_2O.

Table 2. Selected Distances (pm) and Angles (deg) of [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) and [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')]·Et_2O (**1b**·Et_2O)

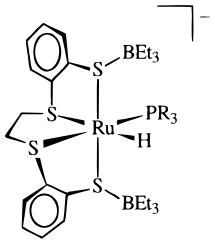
	1a·0.5Et_2O	**1b**·Et_2O
Ru1−S1	240.51(8)	241.03(13)
Ru1−S2	234.19(8)	235.31(11)
Ru1−S3	237.11(9)	237.11(11)
Ru1−S4	237.42(8)	238.43(13)
Ru1−P1	231.92(9)	232.93(11)
Ru1−H10	164(4)	
Ru1−H1		161(5)
Li1−S1	247.2(6)	248.6(8)
Li1−H10	187(4)	184(5)
S1−Ru1−S4	173.36(3)	173.64(4)
S2−Ru1−S3	86.94(3)	86.41(4)
S2−Ru1−P1	174.09(3)	177.26(4)
S1−Ru1−H10	89.4(14)	88(2)
S1−Li1−H10	82.4(12)	81(2)

complexes, the lithium cations are bound to the [Ru(H)(PR_3)('S_4')]$^-$ anions via one thiolate and the hydride ligand. One coordinated THF and Et_2O molecule each complete the pseudotetrahedral coordination sphere of the Li ions.

Angles and distances are in the range usually found in [Ru('S_4')] complexes.[21,26] This is insofar remarkable as even the Ru−S3 distances trans to the hydride ligands do not show a significant elongation; i.e., the hydride ligand appears to exert no structural trans influence. This missing trans influence signaling a reduced hydridic character of the hydride ligand could be due to three reasons. (1) The hydride ligand functions as a bridge between the ruthenium and lithium metal centers. (2) The chelating 'S_4'$^{2-}$ ligand exerts sterical constraints upon the trans S3 donor. (3) Finally, the conformations of the phosphine alkyl substituents are eclipsed with regard to the hydride, which leads to short intramolecular C−H···H(hydride) contacts that indicate "unconventional" hydrogen bridges.[27] These eclipsed conformations of the phosphine ligands are sterically rather disfavored than favored and have been observed for the first time in the molecular structure of [Rh(H)(PCy_3)('$^{bu}S_4$')] ('$^{bu}S_4$' = 1,2- bis((2-mercapto-3,5-di-*tert*-butylphenyl)-thio)ethane(2−))[18c] and recently been described by Crabtree et al.[27] In the structures discussed here, for instance, the distances H2c−H10 (228 pm) in **1a** (Figure 3) and H35b−H1 (231 pm) in **1b** are smaller than twice the van der Waals radius of hydrogen (r = 120 pm).[28] Likewise short contacts are observed between hydrogen atoms of the lithium-coordinated Et_2O molecules and the hydride ligand in **1a** (d(H33b−H10) = 234 pm), and in **1b** (d(H72b−H1) = 248 pm). The fact that the C−H···H−M distances described here involve hydride ligands bridging two metals may cause that the C−H···H−M distances are marginally larger than the limiting distance of 220 pm given by Crabtree et al. for such interactions in complexes with terminal hydride ligands.[27]

In summary, the bridging coordination of the hydride ligand plus "unconventional" C−H···H−M interactions potentially decrease the hydridic character of the hydride ligand to such an extent that no structural hydride trans influence can be observed. This does not rule out that **1a**,**b** dissociate in solution yielding THF- and Et_2O-coordinated lithium cations and ruthenium hydride complex anions.

The solid-state structures and the coordination of the sodium cations in **2a**,**b** remain open to question. However, it can plausibly be assumed that the Lewis acidic BEt_3 entities bind to the Lewis basic thiolate donors of the [Ru(H)(PR_3)('S_4')]$^-$ anions yielding structures such as shown in the following formula:



Reactions of the Hydride Complexes, Proof of the η^2-H_2 Complex [Ru(H_2)(PCy_3)('S_4')], and the Heterolytic Activation of H_2. The extreme moisture sensitivity of complexes **1a**,**b** and **2a**,**b** became evident in recording their NMR spectra. Even when the solvents had carefully been dried and freshly distilled, the ^{1}H NMR spectra of the complexes showed a small signal at 4.6 ppm that indicated the formation of free dihydrogen[17e] resulting from protonation of the hydride ligand and subsequent release of H_2. This effect was investigated in detail by systematically treating complexes **1b** and **2a** at ambient or low temperatures with either CH_3OH or CD_3OD and recording the resultant ^{1}H and ^{2}H NMR spectra.

At room temperature, treatment of THF-d_8 solutions of Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (**2a**) with CH_3OH resulted in a significant increase of the δ = 4.60 ppm signal and a decrease of the hydride doublet at δ = −11.35 ppm. The identity of the δ = 4.60 ppm signal was established by the 1:1:1 triplet of HD that resulted upon treatment with CD_3OD. A ^{2}H NMR spectrum revealed that simultaneously the deuteride derivative [Ru(D)(PCy_3)('S_4')]$^-$ formed, showing a ^{2}H NMR singlet at δ = −10.90 ppm.

The analogous experiments with [Li(THF)(Et_2O)][Ru(H)(PR_3)('S_4')] (**1b**) were carried out at low temperatures between −80 and −20 °C. Treatment of THF solutions of **1b** with CD_3OD at −20 °C gave rise to [Ru(D)(PCy_3)('S_4')]$^-$ as shown by the ^{2}H NMR signal at δ = −10.90 ppm (Figure 4). When an analogous experiment was carried out at −50 °C, the ^{1}H NMR spectrum (at −50 °C) revealed a decreased hydride signal and the simultaneous appearance of a 1:1:1 triplet at δ = −6.5 ppm (Figure 5a). This signal indicated the formation of the η^2-HD complex [Ru(η^2-HD)(PCy_3)('S_4')]. The large ^1J(HD) = 32 Hz, the ^2J(PH) = 5 Hz, and T_1 measurements further corroborated the presence of a η^2-HD ligand in this complex.

The T_1 measurements were carried out with [Ru(H_2)(PCy_3)('S_4')] obtained by treatment of **1b** with CD_3OH and HBF_4 at −80 °C. The resultant ^{1}H NMR spectrum showed a broad singlet at −6.5 ppm (Figure 5b), and the relaxation time

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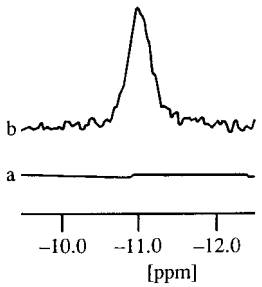


Figure 4. ^{2}H NMR spectra of [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')] (**1b**) in THF (−20 °C) before (trace a) and after (trace b) addition of CD_3OD.

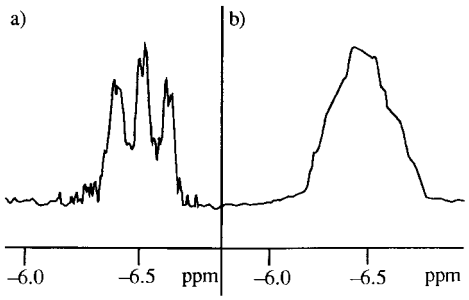


Figure 5. Hydride region of the ^{1}H NMR spectrum of [Li(THF)(Et_2O)]-[Ru(H)(PCy_3)('S_4')] (**1b**) in THF-d_8 after addition of (a) CD_3OD (−50 °C) and (b) CD_3OH (−80 °C).

determination yielded T_1(min) = 4 ms (−60 °C). The η^2-H_2 complex [Ru(H_2)(PCy_3)('S_4')] proved too thermolabile to be isolated at room temperature. In one experiment, for example, Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (**2a**) was dissolved in an excess of CH_3OH at ambient temperature. A yellow solution resulted and rapid evolution of H_2 gas took place. The yellow complex that precipitated was identified as [Ru(DMSO)(PCy_3)-('S_4')] by comparison with authentic samples.[21] In a further experiment, the uptake of H_2 and the reversibility of the H_2 release could be ascertained. When a solution of [Ru(DMSO)-(PCy_3)('S_4')] was treated with H_2 in the presence of NaOMe at ambient temperature, the ^{1}H NMR spectrum of the reaction solution revealed the hydride doublet of [Ru(H)(PCy_3)('S_4')]$^-$. This result is explained by the initial formation of the η^2-H_2 complex and its subsequent deprotonation by the NaOMe being present.

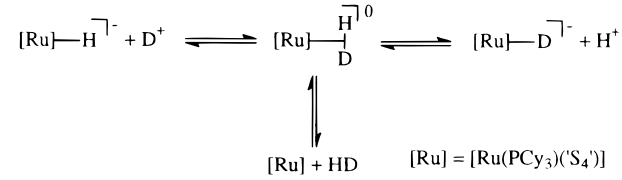
Concluding Discussion

Aiming at sulfur-rich transition metal hydride complexes as model compounds for hydrogenases, the ruthenium hydride complexes [Li(THF)(Et_2O)][Ru(H)(PR_3)('S_4')] (R = ^{i}Pr (**1a**), Cy (**1b**)), Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (**2a**), and Na-[Ru(H)(PPh_3)('S_4')]·2BEt_3 (**2b**) have been synthesized and characterized. All complexes are thermolabile and extremely reactive toward protons (or deuterons). Monitoring the reactions of **1b** or **2a** with CH_3OH or CD_3OD by NMR spectroscopy revealed the simultaneous formation of free H_2 or HD and of the deuteride complex [Ru(D)(PCy_3)('S_4')]$^-$ when CD_3OD was applied. This result rules out that the formation of the deuteride complex is due to a simple Ru−H dissociation according to eq 6.

$$[\{Ru\}\text{—}H]^- \rightleftharpoons [\{Ru\}]^{2-} + H^+ \qquad (6)$$

In the quest of potential intermediates, low-temperature NMR investigations yielded proof of the η^2-H_2 complex [Ru(η^2-H_2)-(PCy_3)('S_4')] and its η^2-HD derivative. The ^1J(HD) coupling

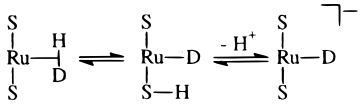
Scheme 1. Deuteration Reactions of **1b**



constant of 32 Hz[14,29] and a relaxation time of T_1 = 4 ms (−60 °C)[14,30] corroborated the presence of η^2-dihydrogen ligands in these complexes. The large ^1J(HD) of 32 Hz lies at the upper end of the range commonly found for HD complexes.[14] [Ru-(η^2-HD)(PCy_3)('S_4')] further is one of the rare examples for which ^2J(HP) coupling constants (5 Hz) could be observed.[15g,31]

These results are summarized in Scheme 1 showing the sequences of the deuteration reactions. The reversibility of the protonation/deprotonation reactions explains the formation of the deuteride ligands from deuterons. Release of HD from the η^2-HD complex yields a coordinatively unsaturated species. The vacant site in these species can be occupied by donor molecules such as DMSO and explains the formation of [Ru(DMSO)-(PCy_3)('S_4')] when Na[Ru(H)(PCy_3)('S_4')]·2BEt_3·0.5DMSO (**2a**) is treated with an excess of CH_3OH.

Finally, also the reversibility of the H_2 release and uptake by [Ru(PCy_3)('S_4')] fragments could be proved by the formation of [Ru(H)(PCy_3)('S_4')]$^-$ anions when [Ru(DMSO)(PCy_3)('S_4')] was treated with H_2 in the presence of NaOMe. This reaction also shows that H_2 can heterolytically be cleaved at ruthenium sulfur sites. A detailed mechanism for the heterolytic H_2 cleavage at transition metal sulfur sites has recently been elucidated with [Rh(H)(PCy_3)('$^{bu}S_4$')] and [Rh(PCy_3)('$^{bu}S_4$')]$^+$ complexes, respectively.[32] In this case, the Lewis acidic Rh center and the Bronsted basic thiolate donors of the [Rh(PCy_3)-('$^{bu}S_4$')]$^+$ fragment concertedly attack the H_2 molecule. The resultant thiol hydride species [Rh(H)(PCy_3)('$^{bu}S_4$'-H)]$^+$ could unambiguously be identified. The close similarity between the [Rh(PCy_3)('$^{bu}S_4$')]$^+$ and the [Ru(PCy_3)('S_4')] fragments suggests that the η^2-HD ligand in [Ru(η^2-HD)(PCy_3)('S_4')] is intramolecularly cleaved in an analogous manner according to eq 7.



(7)

In the case of the ruthenium complexes, however, thiol hydride species could not yet be detected, and [Rh(H)(PCy_3)-('$^{bu}S_4$')] and [Ru(H)(PCy_3)('S_4')]$^-$ thus differ with respect to the detectable intermediate or transitory species. In the case of the rhodium complexes, η^2-H_2 complexes could not be detected and probably are transitory species only which immediately give thiol hydride derivatives. Vice versa, in the case of the

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ruthenium complexes, thiol hydride complexes appear to be transitory and immediately yield η^2-H_2 intermediates. However, the rhodium and ruthenium complexes both demonstrate that H_2 is readily cleaved heterolytically at sulfur-rich transition metal sites under very mild conditions. In this regard they yield model compounds that combine structural and functional features of the active centers in hydrogenases.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for compounds **1a**·0.5Et_2O and **1b**·Et_2O are available on the Internet. Access information is given on any masthead page. Details of the X-ray crystallography have also been deposited at the Fachinformationzentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, and can be obtained by citing the depository numbers, CSD 408047 for [Li(THF)(Et_2O)][Ru(H)(P^iPr_3)('S_4')]·0.5Et_2O (**1a**·0.5Et_2O) and CSD 408048 for [Li(THF)(Et_2O)][Ru(H)(PCy_3)('S_4')]·Et_2O (**1b**·Et_2O), the authors, and the reference.

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