# Transition Metal Complexes with Sulfur Ligands. 96.[1] Hydrogenase Model Reactions: $D_2/H^+$ Exchange at Metal Sulfur Centers Catalyzed by [Rh(H)(CO)('$^{bu}S_4$')] ('$^{bu}S_4$'$^{2-}$ = 1,2-Bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethanato(2-))

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**Abstract:** In search of model complexes of hydrogenases, oxidative addition of the tetradentate thioether thiols '$^{bu}S_4$'-$H_2$ ('$^{bu}S_4$'-$H_2$ = 1,2-bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethane) and '$S_4$'-$H_2$ ('$S_4$'-$H_2$ = 1,2-bis((2-mercaptophenyl)thio)ethane) to $[Rh^I(Cl)(CO)_2]_2$ gave $[Rh^{III}(H)(CO)('X_4')]$ ('$X_4$'$^{2-}$ = '$^{bu}S_4$'$^{2-}$ (**1**), '$S_4$'$^{2-}$ (**3**)). **1** exchanges its hydrido ligand for deuterium when reacted with either $D^+$ ions or $D_2$ in the presence of $H^+$. Mechanisms of these reactions are suggested which include heterolytic cleavage of $D_2$ and nonclassical dihydrogen complexes. The reaction with $D_2$ implies a $D_2/H^+$ exchange which is one of the characteristic hydrogenase reactions. This $D_2/H^+$ exchange was further corroborated by the deuteration of EtOH by $D_2$ to give EtOD in the presence of **1** as catalyst. Reactions of other rhodium(I) complexes such as $[Rh(Cl)(cod)]_2$ and $[Rh(Cl)(C_2H_4)_2]_2$ with '$^{bu}S_4$'-$H_2$ yielded $[(\mu$-'$^{bu}S_4$')$\{Rh(cod)\}_2]$ (**4**) and $[Rh(Cl)('^{bu}S_4')]_2$ (**5**). When reacted with $[Rh(Cl)(cod)]_2$, pentadentate '$^{bu}S_5$'-$H_2$ ('$^{bu}S_5$'-$H_2$ = bis(2-((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethyl)sulfide) formed *meso*-[Rh(Cl)('$^{bu}S_5$')] (*meso*-**6**) in addition to a mixture of diastereomers.

## Introduction

Interaction of transition metals with molecular dihydrogen is an elementary reaction of numerous industrial[2] and enzymatic catalyses,[3,4] and activation of $H_2$ has been studied with classical and nonclassical metal hydrogen complexes exhibiting $[M(H)_n]$ or $[M(H_2)]$ entities. The overwhelming majority of these complexes carry phosphines as coligands of the hydrogen.[5-7] In contrast, the nickel, iron, or iron-molybdenum centers of biological hydrogen catalysts such as hydrogenases and nitrogenases are predominantly surrounded by sulfur ligands.[8,9] These enzymes catalyze the $H^+/H_2$ redox equilibrium (eq 1a) and $H_2/D^+$ exchange (eq 1b), which requires heterolytic cleavage of the strong H-H bond.[10]

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

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

Complexes that are intended to serve as structural *and* functional models of the active centers of hydrogenases in order to allow a detailed investigation of the $H_2/D^+$ exchange ought to have at least sulfur-dominated coordination spheres and hydride ligands. Such complexes are relatively rare and usually also contain phosphines, e.g., $[Mo(H)(SR)_3(PMe_2Ph)_2]$ (R = 2,4,6-trimethylthiophenolate(1-), 2,4,6-triisopropylthiophenolate(1-)),[11] $[Ir(H)(CO)(Ph_2PCH_2CH_2SH)(Ph_2PCH_2CH_2S)]^+$,[12] $[Ru(H)(PPh_3)_3(SR)]$,[13] and $[Rh(H)(PPh_3)('^{bu}S_4')]$.[14] The very few exceptions exhibiting exclusively sulfur ligands are $[Ir(H)(1,4,7\text{-trithiacyclononane})_2](PF_6)_2$,[15] $[Rh(H)(1,4,8,11\text{-tetrathiacyclotetradecane})](BF_4)_2$,[16] and $[Li(THF)_4]_3[Mo(H)(S_2C_6H_4)_3]$.[17] No $H_2/D^+$ exchange, however, was observed with these complexes.

Such a reaction taking place at [MS] centers has now been observed with [Rh(H)(CO)('$^{bu}S_4$')] (**1**). The synthesis and properties of **1** and related complexes will be reported here.

## Experimental Section

**General Procedures.** Unless noted otherwise, all reactions were carried out in freshly distilled solvents under an atmosphere of dinitrogen or argon, the Schlenk technique being used. As far as possible, reactions were monitored by IR spectroscopy. Spectra were recorded in $CaF_2$ cuvettes, and solvent bands were compensated. Compounds which had been crystallized below room temperature were isolated at their respective crystallization temperatures and washed with cold solvents. Spectra were recorded on the following instruments: IR, Perkin-Elmer 983 and 1620 FT-IR; NMR, Jeol FT-JNM-GX 270 and EX 270, JNM-PMX 60si; mass, Varian MAT 212.

*n*-BuLi in *n*-hexane was purchased from Aldrich, DCl (37% in $D_2O$) from Fluka, and $D_2$ (99.9%) from Linde. $RhCl_3 \cdot 3H_2O$ was received as a donation from Degussa. $[Rh(Cl)(CO)_2]_2$,[18] $[Rh(Cl)(cod)]_2$,[19] $[Rh(Cl)(C_2H_4)_2]_2$,[20] '$^{bu}S_4$'-$H_2$,[21] '$S_4$'-$H_2$,[22] and '$^{bu}S_5$'-$H_2$[23] were prepared as described in the literature.

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**Synthesis of [Rh(H)(CO)('$^{bu}S_4$')]·THF (1·THF).** A yellow solution of $[Rh(Cl)(CO)_2]_2$ (186 mg, 0.477 mmol) in THF (20 mL) was added dropwise to a solution of '$^{bu}S_4$'–$H_2$ (510 mg, 0.953 mmol) in THF (20 mL). Gas was evolved, and an orange mixture resulted which was instantly concentrated to ca. 5 mL in a stream of $N_2$ gas and kept at −78 °C for 40 h. A yellow solid precipitated that was isolated, washed with THF (15 mL), and dried in vacuo (24 h). Yield: 410 mg of **1**·THF (58%). Anal. Calcd for $C_{35}H_{53}O_2RhS_4$ ($M_r$ = 736.9): C, 57.0; H, 7.2. Found: C, 57.1; H, 7.5.

IR (KBr, $cm^{-1}$): 2009 w, $\nu_{RhH}$; 2069 vs, $\nu_{CO}$. $^1H$ NMR (270 MHz, $CS_2$, $\delta$ (ppm)): −9.12 (d, 1H, Rh–*H*, $^1J(^{103}Rh^1H)$ = 13.5 Hz), 1.25 (s, 9H, $C_4H_9$), 1.26 (s, 9H, $C_4H_9$), 1.51 (s, 9H, $C_4H_9$), 1.54 (s, 9H, $C_4H_9$), 2.03–3.22 (m, 4H, $C_2H_4$), 7.05–7.32 (m, 4H, $C_6H_2$). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 30.1, 30.2, 31.7, 34.7, 38.3, 38.4, 40.5, 46.0 ($C_{alkyl}$); 126.0, 126.2, 126.6, 130.4, 133.0, 146.6, 146.8, 150.7, 150.8, 151.4, 153.0 ($C_{aryl}$); 184.9 (d, *C*O, $^1J(^{103}Rh^{13}C)$ = 62 Hz). FD MS (THF, *m/z*): 664 ([Rh(H)(CO)('$^{bu}S_4$')]$^+$), 635 ([Rh('$^{bu}S_4$')]$^+$), 607 ([Rh('$^{bu}S_2$')$_2$]$^+$).

**Synthesis of [Rh(H)(CO)('$^{bu}S_4$')]·acetone (1·acetone) and [Rh(Cl)(CO)('$^{bu}S_4$')] (2).** $[Rh(Cl)(CO)_2]_2$ (1.14 g, 2.92 mmol) in acetone (50 mL) was added dropwise to a suspension of '$^{bu}S_4$'–$H_2$ (3.12 g, 5.83 mmol) in acetone (100 mL). The mixture was stirred for 1 h at room temperature and kept at −30 °C for 1 h. The resulting yellow precipitate was isolated, washed with acetone (10 mL), and dried in vacuo (16 h). Yield: 2.35 g of **1·acetone** (56%). Anal. Calcd for $C_{34}H_{51}O_2RhS_4$ ($M_r$ = 722.9): C, 56.5; H, 7.1; S, 17.7. Found: C, 56.7; H, 7.4; S, 17.8.

IR (KBr, $cm^{-1}$): 2007 w, $\nu_{RhH}$; 2070 vs, $\nu_{CO}$. $^1H$ NMR (270 MHz, $CS_2$, $\delta$ (ppm)): −9.12 (d, 1H, Rh–*H*, $^1J(^{103}Rh^1H)$ = 13.5 Hz), 1.25 (s, 9H, $C_4H_9$), 1.26 (s, 9H, $C_4H_9$), 1.50 (s, 9H, $C_4H_9$), 1.54 (s, 9H, $C_4H_9$), 2.07–3.25 (m, 4H, $C_2H_4$), 7.07–7.34 (m, 4H, $C_6H_2$).

The mother liquor was reduced in volume to ca. 20 mL and kept at −30 °C for 30 h. Precipitated dark red **2** was isolated, washed with acetone (10 mL), and dried in vacuo (24 h). Yield: 450 mg of **2** (11%). Anal. Calcd for $C_{31}ClH_{44}ORhS_4$ ($M_r$ = 699.3): C, 53.2; H, 6.3; S, 18.3. Found: C, 53.4; H, 6.7; S, 18.6.

IR (KBr, $cm^{-1}$): 318 vw, $\nu_{RhCl}$; 2105 vs, $\nu_{CO}$. $^1H$ NMR (270 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 1.29 (s, 9H, $C_4H_9$), 1.30 (s, 9H, $C_4H_9$), 1.63 (s, 9H, $C_4H_9$), 1.65 (s, 9H, $C_4H_9$), 2.67–3.29 (m, 4H, $C_2H_4$), 7.18 (d, 1H, $C_6H_2$, $^3J(^1H^1H)$ = 2.1 Hz), 7.28 (d, 1H, $C_6H_2$, $^3J(^1H^1H)$ = 2.1 Hz), 7.45 (m, 2H, $C_6H_2$). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 29.7, 29.8, 31.3, 31.4, 34.9, 34.9, 38.0, 38.0, 43.6, 48.9 ($C_{alkyl}$); 125.6, 126.5, 127.1, 127.2, 131.0, 131.8, 147.4, 148.5, 148.9, 150.7, 151.0 ($C_{aryl}$); 178.7 (d, *C*O, $^1J(^{103}Rh^{13}C)$ = 61 Hz). FD MS (THF, *m/z*): 698 ([Rh(Cl)(CO)('$^{bu}S_4$')]$^+$).

The mother liquor that had been obtained after isolation of **2** was evaporated to dryness, and the resulting residue was dried in vacuo (24 h). Its elemental analysis corresponded to [Rh(Cl)('$^{bu}S_4$')]$_2$ (**5**); its $^1H$ NMR spectrum (270 MHz, $CD_2Cl_2$), however, exhibited a triplet at −12.28 ppm, indicating that the chloride was contaminated with a small amount of a binuclear hydride such as [Rh(H)('$^{bu}S_4$')]$_2$. Anal. Calcd for $C_{60}Cl_2H_{88}Rh_2S_8$: C, 53.7; H, 6.6. Found: C, 53.6; H, 6.7.

**Synthesis of [Rh(H)(CO)('$S_4$')] (3).** $[Rh(Cl)(CO)_2]_2$ (196 mg, 0.504 mmol) in THF (30 mL) was added dropwise to a solution of '$S_4$'–$H_2$ (313 mg, 1.01 mmol) in THF (25 mL). Gas was evolved, and an orange solution resulted that was stirred at room temperature for 15 min and evaporated to dryness. The orange residue was dried in vacuo (16 h). Yield: 430 mg (97%). Attempts to recrystallize **3** from mixtures of THF and $Et_2O$ gave decarbonylated products only. Anal. Calcd for $C_{15}H_{13}ORhS_4$ ($M_r$ = 440.4): C, 40.9; H, 3.0; S, 29.1. Found: C, 41.3; H, 2.8; S, 29.1.

IR (THF, $cm^{-1}$): 2014 w, $\nu_{RhH}$; 2075 vs, $\nu_{CO}$. IR (KBr, $cm^{-1}$): 1996 w, $\nu_{RhH}$; 2060 vs, $\nu_{CO}$. $^1H$ NMR (270 MHz, $C_6D_6$, $\delta$ (ppm)): −9.16 (d, 1H, Rh–*H*, $^1J(^{103}Rh^1H)$ = 11.6 Hz), 1.51–2.30 (m, 4H, $C_2H_4$), 6.44–7.62 (m, 8H, $C_6H_4$). No $^{13}C$ NMR spectrum of **3** was obtained due to its low solubility. FD MS (THF, *m/z*): 440 ([Rh(H)(CO)('$S_4$')]$^+$).

**Synthesis of [μ-('$^{bu}S_4$')[Rh(cod)]$_2$] (4).** '$^{bu}S_4$'–$H_2$ (585 mg, 1.09 mmol) in $Et_2O$ (50 mL) was slowly added to a suspension of [Rh(Cl)(cod)]$_2$ (269 mg, 0.545 mmol) in $Et_2O$ (75 mL). A voluminous, pale yellow precipitate formed, which after 1.5 h of stirring was isolated, washed with $Et_2O$ (30 mL), and dried in vacuo (14 h). Yield: 440 mg (42%). Anal. Calcd for $C_{46}H_{68}Rh_2S_4$ ($M_r$ = 955.1): C, 57.8; H, 7.2. Found: C, 58.0; H, 7.5.

IR (KBr, $cm^{-1}$): 2830 m, $\nu_{CH}$; 2873 s, $\nu_{CH}$. $^1H$ NMR (270 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 1.14 (s, 18H, $C_4H_9$), 1.44 (s, 18H, $C_4H_9$), 2.03 (d, 8H, $C_2H_4$ (cod), $^2J(^1H^1H)$ = 8.1 Hz), 2.27 (d, 8H, $C_2H_4$ (cod), $^2J(^1H^1H)$ = 8.1 Hz), 3.12 (s, 4H, $C_2H_4$ ('$^{bu}S_4$'$^{2-}$)), 3.84 (s, 4H, $C_2H_2$ (cod)), 4.88 (s, 4H, $C_2H_2$ (cod)), 6.88 (s, 2H, $C_6H_2$), 7.10 (s, 2H, $C_6H_2$). FD MS ($CS_2$, *m/z*): 674 ([Rh$_2$(cod)$_2$('$^{bu}S_2$')]$^+$).

**Synthesis of [Rh(Cl)('$^{bu}S_4$')]$_2$ (5, Mixture of Diastereomers) from [Rh(Cl)($C_2H_4$)$_2$]$_2$ and '$^{bu}S_4$'–$H_2$.** '$^{bu}S_4$'–$H_2$ (495 mg, 0.926 mmol) in THF (10 mL) was added to [Rh(Cl)($C_2H_4$)$_2$]$_2$ (180 mg, 0.463 mmol) in THF (20 mL). A dark red solution formed that was stirred for 20 min and evaporated to dryness. The resulting black-brown residue was dried in vacuo for another 12 h. Yield: 612 mg (98%). Attempts to separate the mixture of diastereomers by fractional crystallization failed. Anal. Calcd for $C_{60}Cl_2H_{88}Rh_2S_8$ ($M_r$ = 1342.6): C, 53.7; H, 6.6; S, 19.1. Found: C, 53.4; H, 7.0; S, 18.7.

**Isolation of a Pure Stereoisomer of [Rh(Cl)('$^{bu}S_4$')]$_2$ (5) from [Rh(D)(CO)('$^{bu}S_4$')] (7).** An argon-saturated *n*-hexane solution (15 mL) of [Rh(D)(CO)('$^{bu}S_4$')]·THF (7·THF) (246 mg, 0.340 mmol; see below) was combined with 0.027 mL (0.35 mmol) of a DCl/$D_2O$ solution (37%), and the mixture was stirred under an atmopshere of $H_2$ (1 bar) for 50 d. The orange precipitate that had formed was isolated, washed with *n*-hexane (3 mL), and dried in vacuo. Yield: 35 mg (8%). Due to the minor yield, it was only characterized by spectroscopy.

IR (KBr, $cm^{-1}$): 325 vw, $\nu_{RhCl}$. $^1H$ NMR (270 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 1.23 (s, 18H, $C_4H_9$), 1.32 (s, 18H, $C_4H_9$), 1.51 (s, 18H, $C_4H_9$), 1.72 (s, 18H, $C_4H_9$), 1.64–3.22 (m, 8H, $C_2H_4$), 7.08–7.54 (m, 8H, $C_6H_2$). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 29.5, 31.2, 31.4, 33.4, 34.7, 35.4, 37.6, 38.8, 45.4, 47.9 ($C_{alkyl}$); 123.7, 125.7, 125.9, 126.1, 133.2, 137.8, 143.6, 147.0, 148.9, 149.4, 153.4, 154.0 ($C_{aryl}$). FD MS ($CD_2Cl_2$, *m/z*): 1340 ([Rh(Cl)('$^{bu}S_4$')]$_2^+$), 1305 ([Rh$_2$(Cl)('$^{bu}S_4$')$_2$]$^+$), 1270 ([Rh$_2$('$^{bu}S_4$')$_2$]$^+$).

**Synthesis of *meso*-[Rh(Cl)('$^{bu}S_5$')] (*meso*-6). (a) From [Rh(Cl)(cod)]$_2$ and '$^{bu}S_5$'–$H_2$ at Room Temperature.** A THF solution (50 mL) of [Rh(Cl)(cod)]$_2$ (1.03 g, 2.08 mmol) was added dropwise to a THF solution (50 mL) of '$^{bu}S_5$'–$H_2$ (2.47 g, 4.16 mmol) within 2.5 h, and the mixture was stirred at room temperature for 45 h. A black-red suspension formed that was evaporated to dryness. The dry residue was extracted with boiling THF (200 mL) in a Soxhlet apparatus for 2 h. The remaining ochre-yellow residue was dried in vacuo (12 h) and identified as pure *meso*-**6**. Yield: 926 mg (30%).

When the THF extracts were kept at room temperature for 1 d, another 471 mg (15%) of *meso*-**6** crystallized as orange needles, which were collected. Total yield: 1.40 g (45%). Anal. Calcd for $C_{32}ClH_{48}RhS_5$ ($M_r$ = 731.4): C, 52.6; H, 6.6; S, 21.9. Found: C, 52.7; H, 6.6; S, 21.8.

IR (KBr, $cm^{-1}$): 300 vw, $\nu_{RhCl}$. $^1H$ NMR (270 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 1.33 (s, 18H, $C_4H_9$), 1.66 (s, 18H, $C_4H_9$), 2.52–3.28 (m, 8H, $C_2H_4$), 7.34 (d, 2H, $C_6H_2$, $^4J(^1H^1H)$ = 1.9 Hz), 7.42 (d, 2H, $C_6H_2$, $^4J(^1H^1H)$ = 1.9 Hz). $^{13}C\{^1H\}$ NMR (67.9 MHz, $CD_2Cl_2$, $\delta$ (ppm)): 29.8, 31.4, 34.8, 37.9, 42.2, 48.2 ($C_{alkyl}$); 126.5, 127.4, 129.1, 147.6, 148.1, 149.9 ($C_{aryl}$). FD MS ($CD_2Cl_2$, *m/z*): 730 ([Rh(Cl)('$^{bu}S_5$')]$^+$), 695 ([Rh('$^{bu}S_5$')]$^+$).

**(b) From [Rh(Cl)(CO)$_2$]$_2$ and '$^{bu}S_5$'–$H_2$.** $[Rh(Cl)(CO)_2]_2$ (122 mg, 0.314 mmol) in THF (10 mL) was slowly added to '$^{bu}S_5$'–$H_2$ (369 mg, 0.690 mmol) in THF (7 mL), and the solution was stirred at room temperature for 4 h, in the course of which gas was evolved and a dark red suspension formed. The ochre-yellow precipitate was isolated, washed with THF (10 mL), dried in vacuo (24 h), and identified as *meso*-**6** by IR and $^1H$ NMR spectroscopy. Yield: 100 mg of *meso*-**6** (22%).

**(c) From "RhCl$_3$·3H$_2$O" and '$^{bu}S_5$'–Li$_2$.** *n*-BuLi in *n*-hexane (1.25 mL, 1.6 M solution, 2.00 mmol) was added to a THF solution (6 mL) of '$^{bu}S_5$'–$H_2$ (595 mg, 1.00 mmol) at −78 °C. The resulting solution was warmed to room temperature and added dropwise to "$RhCl_3·3H_2O$" (263 mg, 1.00 mmol) in THF/MeOH (50 mL, 1:1), and the mixture was stirred at room temperature for 5 d. The resulting deep red suspension was evaporated to dryness. To remove LiCl, the residue was suspended in $CH_2Cl_2$ (50 mL), the resulting suspension was filtered over filter pulps, and the filtrate was evaporated to dryness again. The residue was extracted with THF (25 mL), the THF extract was filtered, and the filtrate was cooled to −78 °C. Precipitated orange needles of *meso*-**6** were isolated after 7 d, washed with THF (3 mL), and dried in vacuo (24 h). Yield: 65 mg of *meso*-**6** (9%). Anal. Calcd for $C_{32}ClH_{48}RhS_5$ ($M_r$ = 731.4): C, 52.6; H, 6.6; S, 21.9. Found: C, 52.4; H, 7.1; S, 21.4.

**Synthesis of [Rh(D)(CO)('$^{bu}S_4$')]·THF (7·THF).** A THF solution (25 mL) of **1**·THF (510 mg, 0.692 mmol) was combined with DCl/$D_2O$ (37%, 1.0 mL, 12.7 mmol), and the mixture was stirred at room temperature for 1 h and evaporated to dryness. This procedure was repeated, and the product, which had not changed in color, was dried in vacuo (18 h). Yield: 478 mg of **7**·THF (96%). Anal. Calcd for $C_{35}DH_{52}O_2RhS_4$ ($M_r$ = 738.0): C, 56.9; H, 7.1. Found: C, 56.9; H, 7.6.

IR (KBr, $cm^{-1}$): 1445 m, $\nu_{RhD}$; 2070 vs, $\nu_{CO}$. $^1H$ NMR (60 MHz, $CS_2$, $\delta$ (ppm)): 1.24 (s, 18H, $C_4H_9$), 1.48 (s, 9H, $C_4H_9$), 1.52 (s, 9H, $C_4H_9$), 2.00–3.24 (m, 4H, $C_2H_4$), 6.91–7.26 (m, 4H, $C_6H_2$).

**Synthesis of [Rh(H)(CO)('$^{bu}S_4$')] from [Rh(D)(CO)('$^{bu}S_4$')] and $H_2$ in the Presence of D$^+$ under Various Reaction Conditions.** For each experiment, **7**·THF (250 mg, 0.34 mmol) was dissolved in THF (25 mL). When the reaction was carried out in the presence of acid, DCl/$D_2O$ (37%, 0.027 mL, 0.35 mmol) was added.

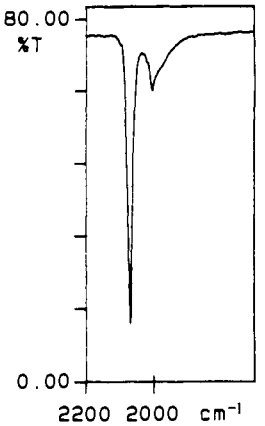



**Figure 1.** KBr IR spectrum of [Rh(H)(CO)('$^{bu}S_4$')] (**1**) ($\nu_{CO}/\nu_{RhH}$ region).

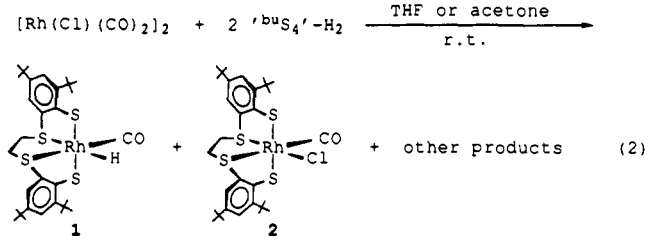
In the reactions at standard pressure, $H_2$ gas was bubbled through the solutions in Schlenk tubes. Evaporated THF was replaced. After the reaction, the solutions, which had not changed in color, were evaporated to dryness, and the resulting residues were characterized by IR and $^1H$ NMR spectroscopy.

In the reactions at high pressures of $H_2$, the solutions were injected into the glass insert of a 250-mL autoclave through a septum, and the cannula was left in the septum for pressure balancing. The autoclave was closed in a stream of argon and filled with $H_2$ of the required pressure. After the end of the reaction, the solution was worked up as described above.

**$D_2/H^+$ Exchange Monitored by the Formation of EtOD from EtOH and $D_2$ in the Presence of [Rh(H)(CO)('$^{bu}S_4$')] and HCl.** In a $^1H$ NMR tube, [Rh(H)(CO)('$^{bu}S_4$')] (22.8 mg, 0.031 mmol) was dissolved in THF (1.1 mL). EtOH (50 μL, 0.85 mmol), $C_6D_6$ (25 μL, 0.28 mmol), and HCl (37%, 3.6 μL, 0.04 mmol) were added, and the NMR tube was kept for 24 h in a micro-autoclave which was filled with $D_2$ gas of 10 or 120 bar. Afterward, the formation of EtOD was established by $^2H$ NMR spectroscopy. Control experiments that were carried out in the absence of [Rh(H)(CO)('$^{bu}S_4$')] under identical conditions gave no EtOD. $C_6D_6$ served as a standard (δ 7.15 ppm). The EtOD signal was observed at 5.18 (120 bar of $D_2$) and 3.34 ppm (10 bar of $D_2$). This shift difference is attributed to the different concentrations of EtOD, being higher in the first case, and to exchange reactions between EtOD and remaining protons of EtOH and $H_2O$. Turnover numbers (TON) were calculated by comparison of the intensities of the $C_6D_6$ and EtOD signals (10 bar of $D_2$, TON ≥ 8; 120 bar of $D_2$, TON ≥ 60). The known concentration of $C_6D_6$ was taken as the reference.

## Results

**Syntheses.** Yellow [Rh(H)(CO)('$^{bu}S_4$')] (**1**) formed as the major product (56%) in the reaction according to eq 2. When




the synthesis was carried out in acetone, the red chloro complex [Rh(Cl)(CO)('$^{bu}S_4$')] (**2**) could be isolated as a byproduct (11%). **1** and **2** are very soluble in THF, acetone, $CH_2Cl_2$, $CS_2$, and benzene. **1** exhibits characteristic $\nu_{CO}$ and $\nu_{RhH}$ bands at 2069 and 2009 $cm^{-1}$ in the KBr IR spectrum (Figure 1). The $\nu_{CO}$ band of **2** appears at 2105 $cm^{-1}$, and a band at 318 $cm^{-1}$ in the KBr IR spectrum of **2** is assignable to the $\nu_{RhCl}$ vibration.

The schematic structures of **1** and **2** depicted in eq 2 are supported by the number of $^1H$ and $^{13}C$ NMR signals which indicate that both complexes have $C_1$ symmetry. For example, the four magnetically nonequivalent *tert*-butyl groups of **1** and **2** give rise to four $^1H$ NMR singlets. Typical of **1** is the hydride signal at −9.12 ppm, which is split into a doublet due to Rh–H coupling ($^1J(^{103}Rh^1H)$ = 13.5 Hz, Figure 2).

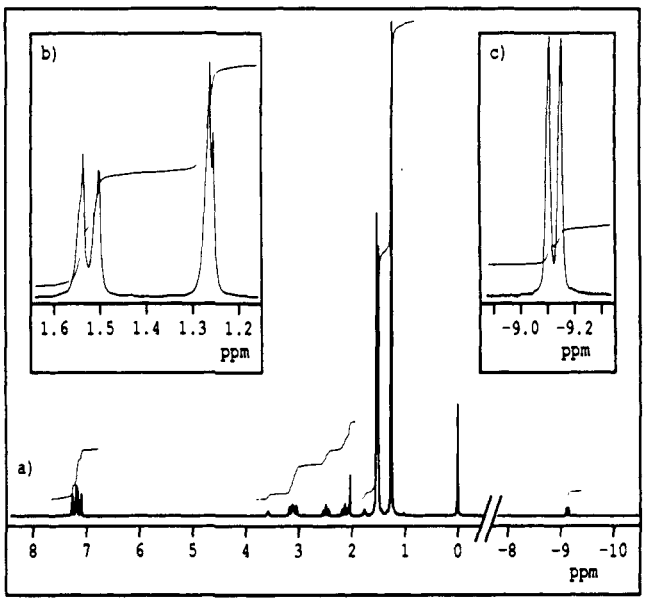
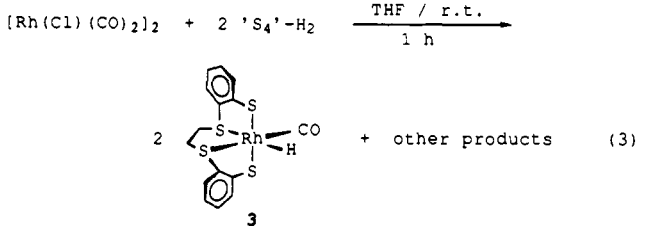



**Figure 2.** $^1H$ NMR spectrum ($CS_2$, 270 MHz) of (a) [Rh(H)(CO)('$^{bu}S_4$')]. Insets: (b) *tert*-butyl region; (c) hydride region.

From the mother liquor of the synthesis according to eq 2 a mixture of products was isolated. The elemental analysis corresponded to [Rh(Cl)('$^{bu}S_4$')]$_2$, but the $^1H$ NMR spectrum exhibited a triplet at −12.3 ppm, which is tentatively assigned to the binuclear hydride complex [(μ-H){Rh('$^{bu}S_4$')}$_2$].

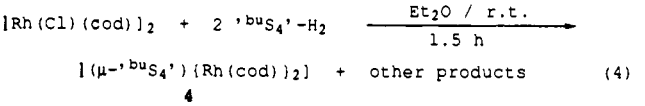
The reaction according to eq 3 gave yellow [Rh(H)(CO)('$S_4$')] (**3**), which is analogous to **1** but contains the parent ligand '$S_4$'$^{2-}$.




This reaction also produced byproducts such as [Rh(Cl)('$S_4$')]$_2$, but they were not isolated and further characterized.

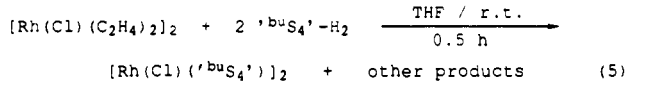
Like **1**, **3** exhibits characteristic $\nu_{CO}$ and $\nu_{RhH}$ bands in its KBr IR spectrum at 2060 and 1996 $cm^{-1}$. The H ligand of **3** appears as a doublet in the $^1H$ NMR spectrum at −9.16 ppm. **3** is considerably less soluble than **1** in all common solvents.

Reactions of '$^{bu}S_4$'–$H_2$ with other Rh(I) complexes yielded no hydride complexes. For instance, the reaction according to eq 4 gave binuclear [(μ-'$^{bu}S_4$'){Rh(cod)}$_2$] (**4**). Light yellow **4** is




soluble in $CH_2Cl_2$, dioxane, and $CS_2$. The symmetrical bridging of two [Rh(cod)] fragments by the '$^{bu}S_4$' ligand is deduced from the $^1H$ NMR spectrum of **4**. In addition to the cod and aromatic proton signals, it exhibits only two sharp *tert*-butyl singlets and one singlet for the $C_2H_4$ bridge of the '$^{bu}S_4$' ligand.

When the labile ethylene complex [Rh(Cl)($C_2H_4$)$_2$]$_2$ was reacted with '$^{bu}S_4$'–$H_2$ according to eq 5, the $C_2H_4$ ligands were




completely removed, and analytically pure binuclear [Rh(Cl)('$^{bu}S_4$')]$_2$ (**5**) formed in nearly quantitative yield. The binuclearity of **5** is concluded from its mass spectrum showing the $M^+$ ion at $m/z$ = 1340 and two fragments at $m/z$ = 1305 and

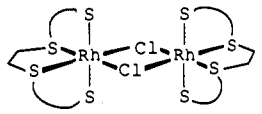
1270 resulting from the consecutive loss of the chloro ligands. The $^1$H NMR spectrum exhibited more than 20 signals in the *tert*-butyl region. This proved that **5** formed as a mixture of several diastereomers. As we had shown previously,[24] dimerization of chiral and coordinatively unsaturated [M(L)('$^{bu}$S$_4$')] fragments can give rise to numerous diastereomers that result not only from the combination of R and S configurations but also from the bridging of R and S fragments via different thiolate S atoms of the '$^{bu}$S$_4$' ligands.

A pure stereoisomer of **5** formed in the very slow reaction according to eq 6. The number of signals which were observed

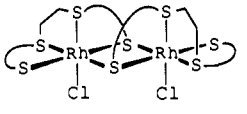
$$2\ [Rh(D)(CO)('^{bu}S_4')] + 2\ HCl \xrightarrow[H_2\ (1\ bar)]{n\text{-hexane / r.t. / 50 d}} [Rh(Cl)('^{bu}S_4')]_2 \ (\mathbf{5}) + \text{other products} \quad (6)$$

in the $^1$H and $^{13}$C NMR spectra indicated that this isomer of **5** has a 2-fold element of symmetry. This could be deduced in particular from the *tert*-butyl region of the $^1$H NMR spectrum, which exhibits only four singlets for the eight *tert*-butyl groups (Figure 3a).

From the large number of possible diastereomers, **5a** and **5b** are compatible with the spectroscopic results. **5a** consists of two



**5a**



**5b**

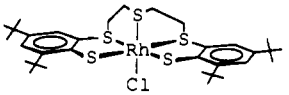
⌒ = (t-bu)$_2$C$_6$H$_2$

enantiomeric [Rh('$^{bu}$S$_4$')] fragments being connected via chloro ligands and possesses a plane of symmetry. In contrast, **5b** contains two homochiral [Rh(Cl)('$^{bu}$S$_4$')] fragments that are connected via thiolate bridges and has a $C_2$ axis.

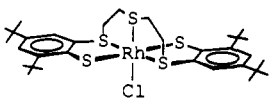
Mixtures of diastereomers also formed in the reaction of Rh(I) complexes with the pentadentate '$^{bu}$S$_5$'–H$_2$ ligand according to eq 7. With regard to the reaction mechanism, it is of interest

$$[Rh(Cl)(cod)]_2 + 2\ '^{bu}S_5'\text{-}H_2 \xrightarrow[45\ h]{THF\ /\ r.t.} 2\ [Rh(Cl)('^{bu}S_5')]\ (\mathbf{6}) + \text{other products} \quad (7)$$

that cyclooctene could be detected in the reaction mixture by mass spectroscopy. The brown solid that was isolated analyzed for [Rh(Cl)('$^{bu}$S$_5$')] (**6**) and gave rise to at least 13 *tert*-butyl signals in the $^1$H NMR spectrum. Among the possible diastereomers, the meso isomer *meso*-[Rh(Cl)('$^{bu}$S$_5$')] (*meso*-**6**) and the racemic



meso-**6**



rac-**6**

isomer *rac*-[Rh(Cl)('$^{bu}$S$_5$')] (*rac*-**6**) have special significance because analogous iron and ruthenium complexes could be isolated and fully characterized.[25-27] *meso*-**6** has $C_s$ symmetry; *rac*-**6**, however, has $C_1$ symmetry only because the $C_2H_4$ bridges of the '$^{bu}$S$_4$' ligand are located asymmetrically on one side of the plane formed by the rhodium center and the three thioether donors.

Due to its minor solubility in THF, *meso*-**6** could be separated by fractional crystallization. Its $^1$H NMR spectrum exhibits only two sharp *tert*-butyl singlets (see Figure 3b), and in the $^{13}$C NMR spectrum, both aromatic and aliphatic C atoms give rise to six signals only.

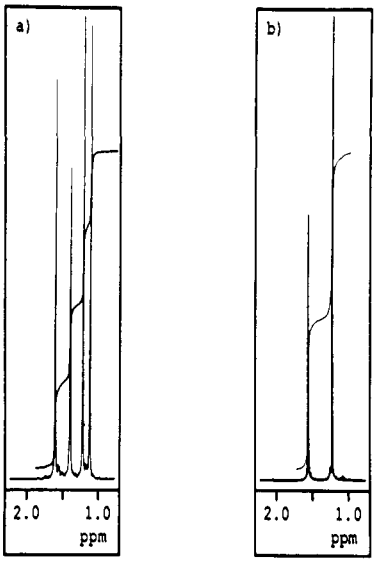



**Figure 3.** *tert*-Butyl region of the $^1$H NMR spectra of (a) [Rh(Cl)('$^{bu}$S$_4$')]$_2$ (**5**), formed according to eq 6 ($CD_2Cl_2$, 270 MHz), and (b) *meso*-[Rh(Cl)('$^{bu}$S$_5$')] (*meso*-**6**, $CD_2Cl_2$, 270 MHz).

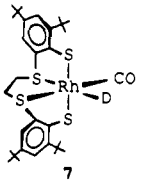
**Table I.** $D^+/H_2$ Exchange of [Rh(D)(CO)('$^{bu}$S$_4$')] (**7**) According to Eq 9 under Various Reaction Conditions

| solvent | $p(H_2)$ (bar) | reacn time (d) | DCl/D$_2$O added | exchange (%) |
|---|---|---|---|---|
| THF | 150 | 1 | yes | 100 |
| THF | 25 | 4.5 | yes | 50 |
| *n*-hexane | 25 | 4.5 | yes | 40 |
| THF | 125 | 1 | no | 0 |
| THF | 1 | 1 | no | 0 |

Mixtures of diastereomers of **6** containing smaller amounts of *meso*-**6** were obtained by reactions of '$^{bu}$S$_5$'–H$_2$ with [Rh(Cl)(norbornadiene)]$_2$, [Rh(Cl)(CO)$_2$]$_2$, or "RhCl$_3$·3H$_2$O" under various reaction conditions. The chloro ligand of *meso*-**6** could not be substituted by hydride ligands when *meso*-**6** was reacted with NaBH$_4$ or LiHBEt$_3$.

**H/D Exchange Reactions of [Rh(H)(CO)('$^{bu}$S$_4$')].** [Rh(H)(CO)('$^{bu}$S$_4$')] (**1**) exchanges its hydride ligand for deuterium when reacted with DCl/D$_2$O according to eq 8. The resulting [Rh-

$$[Rh(H)(CO)('^{bu}S_4')] + DCl/D_2O_{exc} \xrightarrow[2\ h]{THF\ /\ r.t.} \mathbf{7} + \text{other products} \quad (8)$$



(D)(CO)('$^{bu}$S$_4$')] (**7**) was isolated and characterized. In its KBr IR spectrum, **7** does not show the $\nu_{RhH}$ and $\delta_{RhH}$ bands of **1**, but two bands at 1445 and 598 cm$^{-1}$ that are assigned to $\nu_{RhD}$ and $\delta_{RhD}$ vibrations. The observed frequencies are in agreement with the expected $\tilde{\nu}$(RhD)/$\tilde{\nu}$(RhH) ratio of 0.75.[28] The $^1$H NMR spectrum of **7** is identical with the spectrum of **1**, except that it shows no hydride signal.

The exchange of the deuterium ligand of **7** with molecular hydrogen was investigated according to eq 9 and monitored by

$$[Rh(D)(CO)('^{bu}S_4')]\ (\mathbf{7}) + H_2 \xrightarrow{+D^+} [Rh(H)(CO)('^{bu}S_4')]\ (\mathbf{1}) + HD \quad (9)$$

$^1$H NMR spectroscopy via the hydride signal of **1**. Comparison

(24) (a) Sellmann, D.; Weiss, R.; Knoch, F. *Angew. Chem.* **1989**, *101*, 1719; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1703. (b) Sellmann, D.; Weiss, R.; Knoch, F.; Ritter, G.; Dengler, J. *Inorg. Chem.* **1990**, *29*, 4107.

(25) Sellmann, D.; Binker, G.; Moll, M.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *327*, 403.

(26) Sellmann, D.; Kunstmann, H.; Knoch, F.; Moll, M. *Inorg. Chem.* **1988**, *27*, 4183.

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(28) (a) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 189. (b) Krogmann, K.; Binder, W. *J. Organomet. Chem.* **1968**, *11*, 27.

of the relative intensities of the hydride doublet and the $C_6H_2$ multiplet of the '$^{bu}S_4$' ligand rendered possible the determination of the yields of **1**. Table I summarizes the results of several experiments. The results allowed the following conclusions: (1) No exchange occurs in the absence of acid (DCl), neither at low nor at high pressures of $H_2$. (2) Exchange is favored by high $H_2$ pressure. (3) In the presence of acid, exchange rates in THF and *n*-hexane are comparably large. Consequently, solvent polarity might not influence the exchange.

In order to exclude errors due to traces of moisture from, for example, the pressurized $H_2$ gas, the reaction of **1** with $D_2$ gas was investigated according to eq 10 and monitored by the formation of EtOD. EtOH and HCl were added to THF solutions of [Rh(H)(CO)('$^{bu}S_4$')] in $^1$H NMR tubes, the solutions were kept under 10 or 120 bar of $D_2$ pressure for 24 h, and the amount of EtOD which had formed was determined by $^2$H NMR spectroscopy. Control experiments proved that no EtOD formation occurred in the absence of [Rh(H)(CO)('$^{bu}S_4$')]. Turnover numbers ranged between 8 (at 10 bar of $D_2$) and 60 (at 120 bar of $D_2$).

$$\mathrm{EtOH} + \mathrm{D_2} \xrightarrow[\mathrm{HCl}]{[\mathrm{Rh(H)(CO)('^{bu}S_4')}]\ /\ \mathrm{THF}} \mathrm{EtOD} + [\mathrm{HD}] \qquad (10)$$

In preliminary experiments, the reaction between [Rh(H)(CO)('$^{bu}S_4$')] (**1**) and $HBF_4$ under standard pressure of $H_2$ was also monitored by $^1$H NMR spectroscopy. Evidence was obtained of a labile species which exhibited a broad $^1$H NMR singlet at −7.47 ppm and rapidly transformed into another species showing a multiplet at −12.5 ppm. Attempts to isolate and further characterize these species are being carried out.

## Discussion

Oxidative addition of the neutral '$X_4$'–$H_2$ ligands ('$X_4$'–$H_2$ = '$^{bu}S_4$'–$H_2$, '$S_4$'–$H_2$) to $[Rh^I(Cl)(CO)_2]_2$ gave the target hydride complexes $[Rh^{III}(H)(CO)('^{bu}S_4')]$ (**1**) and [Rh(H)(CO)('$S_4$')] (**3**), which have sulfur-dominated coordination spheres and prove that complexes with [MS] centers can bind hydride ligands in the absence of stabilizing phosphines.

Oxidative additions of SH bonds had been previously used for the synthesis of thiolato hydride complexes, but the resulting compounds such as $[Mo(H)(SR)_3(PMe_2Ph)_2]$[11] or [Rh(H)-$(PPh_3)$('$S_4$')][14] usually contained phosphine coligands.

The syntheses of **1** and **3** always yielded the chloro complexes [Rh(Cl)(CO)('$^{bu}S_4$')] (**2**) and [Rh(Cl)(CO)('$S_4$')] as byproducts. Their formation can be explained by the reaction of the hydride complexes with HCl that is released in the first step according to eqs 11a,b. Intermediates of the $H_2$ release might be the same species which are proposed for the acid-catalyzed $D^+/H_2$ exchange (see below).

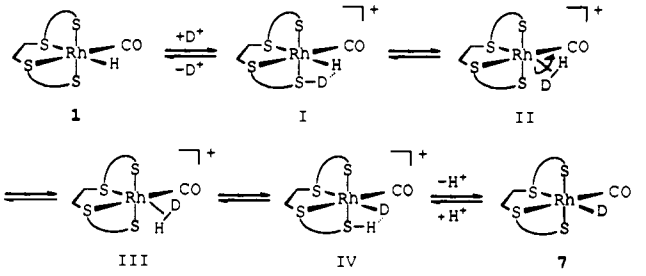
$$[\mathrm{Rh(Cl)(CO)_2}]_2 + 2\ {}'^{\mathrm{bu}}\mathrm{S_4}'\text{–}\mathrm{H_2} \longrightarrow 2\ [\mathrm{Rh(H)(CO)('^{bu}S_4')}] + 2\ \mathrm{HCl} + 2\ \mathrm{CO} \qquad (11a)$$

$$[\mathrm{Rh(H)(CO)('^{bu}S_4')}] + \mathrm{HCl} \longrightarrow [\mathrm{Rh(Cl)(CO)('^{bu}S_4')}] + \mathrm{H_2} \qquad (11b)$$

Other Rh(I) precursor complexes such as $[Rh(Cl)(cod)]_2$ or $[Rh(Cl)(C_2H_4)_2]_2$ did not yield hydride complexes when reacted with '$^{bu}S_4$'–$H_2$. Instead, $[(\mu$-'$^{bu}S_4$')$\{Rh(cod)\}_2]$ (**4**) and [Rh-(Cl)('$^{bu}S_4$')]$_2$ (**5**) were obtained. The formation of **4** can be traced back to the inert coordination of the bidentate cod ligand to the Rh(I) center. **5** possibly forms because the ethylene ligand of an intermediary hydride complex such as $[Rh(H)(C_2H_4)('^{bu}S_4')]$ is hydrogenated via $\beta$-hydrogen transfer and subsequently released as $C_2H_6$ after reaction with protons. The resulting fragments that are coordinatively unsaturated get stabilized by addition of chloride and dimerization.

In an analogous way, it can be explained that all reactions of the pentadentate '$^{bu}S_5$'–$H_2$ ligand with various Rh(I) complexes gave [Rh(Cl)('$^{bu}S_5$')] (**6**). The presence of cyclooctene in the reaction mixture obtained from $[Rh(Cl)(cod)]_2$ and '$^{bu}S_5$'–$H_2$ supports the suggestion of intermediary rhodium hydride olefin complexes which lead to hydrogenation of the diolefin ligand.

**Scheme I.** $H^+/D^+$ Exchange of [Rh(H)(CO)('$^{bu}S_4$')]




Formation of diastereomers which have to be separated is a general problem in the synthesis of [M(L)('$^{bu}S_5$')] complexes. It was also encountered in the synthesis of [Rh(Cl)('$^{bu}S_5$')] (**6**), but the meso isomer could be separated and fully characterized.

With regard to model reactions of hydrogenases, the most significant result is that the H/D exchange of [Rh(H)-(CO)('$^{bu}S_4$')] (**1**) occurs not only with $D^+$ ions (eq 12a) but also with $D_2$ (eq 12b) and that this exchange requires the presence of protons. Equations 12a,b can be summarized by eq 12c, which demonstrates that [Rh(H)(CO)('$^{bu}S_4$')] (**1**) functions as a catalyst for the $D_2/H^+$ exchange which is one of the two characteristic reactions of hydrogenases. The exchange according to eq 12c was definitively established by the formation of EtOD from EtOH and $D_2$ in the presence of **1**.

$$[\mathrm{Rh(H)(CO)('^{bu}S_4')}] + \mathrm{D^+} \longrightarrow [\mathrm{Rh(D)(CO)('^{bu}S_4')}] + \mathrm{H^+} \qquad (12a)$$

$$[\mathrm{Rh(D)(CO)('^{bu}S_4')}] + \mathrm{H_2} \xrightarrow{\mathrm{D^+}} [\mathrm{Rh(H)(CO)('^{bu}S_4')}] + \mathrm{HD} \qquad (12b)$$

$$\mathrm{H_2} + \mathrm{D^+} \xrightarrow{[\mathrm{Rh(H)(CO)('^{bu}S_4')}]} \mathrm{H^+} + \mathrm{HD} \qquad (12c)$$

For these reactions, we suggest the mechanisms outlined in Schemes I and II. The $D^+$ ion primarily attacks a thiolato donor of the '$^{bu}S_4$' ligand such that the monothiol I forms. The SD function is stabilized by an intramolecular S—D···H hydrogen bridge to the hydride ligand. Subsequently, the nonclassical $\eta^2$-HD complex II forms, in which the $\eta^2$-HD ligand rotates such that the reverse cleavage of the HD ligand can take place giving IV and finally the deuterium complex **7**.

Alternatives to this mechanism can be discussed which include intermolecular $H^+/D^+$ exchange steps. This could be, for example, a heterolytic dissociation of the RhH bond of **1** such that $H^+$ and the rhodium(I) complex [Rh(CO)('$^{bu}S_4$')]$^-$ form. Another alternative would be oxidative addition of $D^+$ to **1**, yielding the rhodium(V) complex [Rh(H)(D)(CO)('$^{bu}S_4$')]$^+$ which subsequently loses $H^+$. Although the thiol species I and IV of Scheme I have not yet been observed by NMR spectroscopy, the mechanism of Scheme I appears more plausible because it has to be seen in conjunction with the $H_2/D^+$ exchange requiring the presence of protons and not of bases (Scheme II below) and it takes into account previous findings for other thioether thiolate complexes.

Coordinated thiolato donors exhibit Brönsted base properties, and SH thiol donors are stabilized by intramolecular hydrogen bridges. Comparable hydrogen bridges could be observed in [Ru(ClH)$(PPh_3)$('$^{bu}S_4$')],[29] [Ru$(SH_2)(PPh_3)$('$S_4$')],[30] [Ru(*N*-acetyl-L-cysteine)$(PPh_3)$('$S_4$')],[31] and the diazene complexes $[(\mu\text{-}N_2H_2)\{Fe('N_HS_4')\}_2]$[32] and $[(\mu\text{-}N_2H_2)\{Ru(PPh_3)('S_4')\}_2]$.[33]

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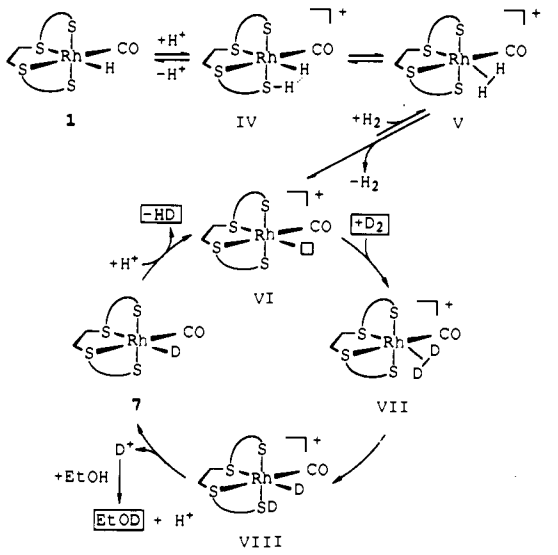
**Scheme II.** $D_2/H^+$ Exchange Catalyzed by [Rh(H)(CO)($^{tbu}S_4$')]




$\eta^2$-$H_2$ complexes that formed upon protonation of hydride complexes are now proved by numerous examples which show that $\eta^2$-$H_2$ ligands can rotate,[34] are relatively acidic,[34d,35] and deprotonate heterolytically upon reaction with bases.[35a,36] The $\eta^2$-HD complex III suggested in Scheme I differs from these examples with respect to the *intra*molecular deprotonation which is due to the Brönsted basicity of the thiolate donors.

The $^1$H NMR signal at −7.47 ppm that is observed when **1** is reacted with $HBF_4$ may be taken as an indication of the formation of the nonclassical $\eta^2$-$H_2$ complex [Rh($\eta^2$-$H_2$)(CO)($^{tbu}S_4$')]$^+$.

The intermediate formation of nonclassical $\eta^2$-$H_2$ complexes is also assumed in order to explain the conversion of the hydrido complex **1** into its deuterium analogue **7** by $D_2$. Essential for this conversion is the presence of protons. Scheme II shows that the function of these protons is to generate a vacant site of coordination at the rhodium center. The steps leading to the $\eta^2$-$H_2$ complex V and the reactions within the cycle are identical to the steps of Scheme I. In addition, a reversible dissociation of V leading to release of $H_2$ and formation of the coordinatively unsaturated VI has to be assumed. In this equilibrium, the $\eta^2$-$H_2$ complex seems to be favored because $D_2/H^+$ exchange can only be observed under increased $D_2$ pressure. Once the $D_2$ complex VII is formed, heterolytic cleavage of $D_2$ gives VIII, which then releases $D^+$. The latter exchanges with EtOH and generates $H^+$ which is used for protonation of the deuterium complex **7** such that a $\eta^2$-HD complex can form. Release of HD finally gives back VI, and the cycle starts again.

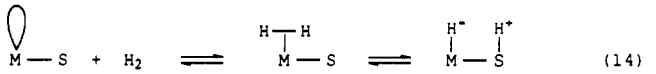
## Conclusion

New rhodium complexes with polydentate thioether thiolate ligands were obtained. Among these, [Rh(H)(CO)($^{tbu}S_4$')] (**1**) is of particular interest because it is one of the few transition metal hydride complexes which have a sulfur-dominated coordination sphere and exhibit no abiological phosphine ligands that possibly stabilize the metal hydride bond. For this reason, such compounds are sought as potential model complexes of the active centers of hydrogenases (and nitrogenases).

Rhodium has not yet been found in oxidoreductases. However, **1** appears to be the first complex with a metal–sulfur core that catalyzes the $H_2/D^+$ exchange according to eq 13, which is one of the two characteristic reactions of hydrogenases.

$$H_2 + D^+ \rightleftharpoons HD + H^+ \qquad (13)$$

The isolation of **1** as well as of its deuterium derivative **7** and the finding that **1** catalyzes the $H_2/D^+$ exchange in the presence of protons suggest a reaction mechanism for the $H_2/D^+$ exchange. Its key feature is the reversible heterolytic cleavage of $H_2$ molecules through joint interaction of vacant metal sites and Brönsted basic thiolate donors with the $H_2$ molecule according to eq 14. Such




(14)

a mechanism was previously proposed for hydrogenase [FeS] centers[37] and, on the basis of theoretical calculations, suggested for hydrogenase [NiS] centers.[38] It was also proposed for the $H_2/D^+$ exchange observed with [Ni(*o*-$C_6H_4$(OH)CH=NNHCS$NH_2$)$_2$]$^{2+}$,[39] but in this case, no intermediate hydride complexes could be isolated. Other examples of heterolytic cleavage of $H_2$ were observed recently with Ru and Os porphyrin complexes[40] and are summarized in several reviews,[41] but the respective complexes did not contain [MS] centers.

In this regard, the results obtained with [Rh(H)(CO)($^{tbu}S_4$')] can be considered the first experimental verification not only of an $H_2/D^+$ exchange at [MS] centers but also of previously suggested reaction mechanisms.

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