Transition Metal Complexes with Sulfur Ligands. 95.[1] N_2H_2, N_2H_4, NH_3, and N_3^- Complexes with Sulfur Dominated [Ru(PPh$_3$)('^{bu}S$_4$')] Fragments ('^{bu}S$_4$'$^{2-}$ = 1,2-Bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethanato(2-))

Dieter Sellmann,* Joachim Käppler, Matthias Moll, and Falk Knoch

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, Germany

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[Ru(ClH)(PPh$_3$)('^{bu}S$_4$')] (**1**) ('^{bu}S$_4$'$^{2-}$ = 1,2-bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethane(2-)) was obtained by *one-pot synthesis* from [RuCl$_2$(PPh$_3$)$_3$], '^{bu}S$_4$'-Li$_2$, and HCl gas. Elimination of HCl from **1** by reaction with bases gave [Ru(PPh$_3$)('^{bu}S$_4$')] (**2**). **2** formally contains a coordinatively unsaturated Ru center and reacted with *Lewis bases* such as N_3^-, NH_3, and N_2H_4, yielding very soluble [Ru(L)(PPh$_3$)('^{bu}S$_4$')] complexes (L = N_3^- (**3**), NH_3 (**4**), N_2H_4 (**5**)). Oxidation of the hydrazine complex **5** led to the dinuclear diazene complex [μ-N_2H_2{Ru(PPh$_3$)('^{bu}S$_4$')}$_2$] (**6**), which was characterized by an X-ray structure analysis. Crystals of **6**·4CH_2Cl_2 are monoclinic, space group $C2/c$, with a = 2870.0(16) pm, b = 1380.4(4) pm, c = 2849.2(13) pm, β = 93.65(4)°, V = 11 265(9) × 10^6 pm^3, Z = 4, and R (R_w) = 0.075 (0.072) for 5801 reflections. The diazene (HN=NH) ligand of **6** is stabilized by intramolecular N-H···(S)$_2$ hydrogen bonds, steric protection, and a Ru⌢N⌢N⌢Ru 4c-6e$^-$ π bond, but according to NMR experiments, **6** is still highly reactive in solution. **4-6** can be regarded as model compounds for the active centers of nitrogenases, because they contain intermediates of N_2 fixation bound to transition metal centers in a coordination sphere dominated by sulfur donors.

Introduction

Diazene, HN=NH, is regarded a key intermediate of enzymatic N_2 reduction,[2] although it is extremely unstable in free state and decomposes above -180 °C.[3] Stabilization of N_2H_2 at standard conditions could be achieved in a few cases by coordination to transition metals, but the resulting diazene complexes, e.g., [μ-N_2H_2{CpM(CO)$_2$}$_2$] (M = Mn, Re),[4,5] [μ-N_2H_2{M'(CO)$_5$}$_2$] (M' = Cr, Mo, W),[6-8] and [Cr(CO)$_5$-N_2H_2-CpMn(CO)$_2$],[9] are still rare and usually contain metalorganic complex fragments. The same holds for the mononuclear [W(N_2H_2)(CO)$_2$(NO)(PCy$_3$)$_2$].[10] Recently the Ru complex [μ-N_2H_2Ru$_2$(L*)$_2$DPB] was reported[11] (DPB = biphenylenediporphyrinato(4-), L* = 1-*tert*-butyl-5-phenylimidazole), in which N_2H_2 bridges two cofacial ruthenium porphyrins. Of particular interest are [μ-N_2H_2{Ru(PPh$_3$)('S$_4$')}$_2$][12] ('S$_4$'$^{2-}$ = 1,2-bis((2-mercaptophenyl)thio)ethane(2-)) and [μ-N_2H_2{Fe('N_HS$_4$')}$_2$][13] ('N_HS$_4$'$^{2-}$ = 2,2'-bis((2-mercaptophenyl)thio)diethylamine(2-)), because they contain iron or the homologous ruthenium and sulfur dominated coordination spheres as it is assumed for the metals in nitrogenases.

All nitrogenases isolated so far contain iron[14] and most of them in addition either molybdenum[15] or vanadium.[16] The discovery of a nitrogenase containing exclusively iron[17] suggests that in all nitrogenases coordination, activation, and reduction of N_2 take place at the iron centers. For this reason, iron complexes with sulfur ligands and vacant coordination sites for binding N_2 or its reduction products N_2H_2, N_2H_4, and NH_3, can be regarded model compounds for nitrogenases with respect to structure *and* function, and ruthenium complexes become of interest, if analogous iron complexes are too labile to be isolated and characterized.

X-ray diffraction studies of [μ-N_2H_2{Ru(PPh$_3$)('S$_4$')}$_2$][12] and [μ-N_2H_2{Fe('N_HS$_4$')}$_2$][13] gave first evidence that stabilization of N_2H_2 is not only due to steric protection and 4c-6e$^-$ π M⌢N⌢N⌢M bonds, but can additionally be promoted in [MS] complexes by formation of strong tricentric N-H···(S)$_2$ bridges between diazene protons and thiolate donors. However, the low solubility of these complexes prevented detailed studies of their reactivity. For this reason, we have been searching for better soluble derivatives and obtained now the very soluble [μ-N_2H_2-{Ru(PPh$_3$)('^{bu}S$_4$')}]. The synthesis of this complex and of related compounds will be reported here.

Experimental Section

General Procedures. Unless noted otherwise, all preparations were carried out under argon atmosphere at room temperature by using Schlenk techniques. Solvents were freshly distilled and argon-saturated. As far as possible, the reactions were monitored by IR spectroscopy. Compounds which crystallized below room temperature were separated at the same temperature and washed with cold solvents. Spectra were recorded on the following instruments: IR (KBr disks or CaF_2 cuvettes, solvent bands were compensated), Perkin Elmer 983 or 1620 FT-IR; NMR, JEOL

* Author to whom correspondence should be addressed.

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FT-JNM-GX 270 or EX 270; mass spectra, Varian MAT 212; UV, Shimadzu UV-3101 PC.

NEt_4N_3 and NMe_4OH were purchased from Fluka; *n*-BuLi (in *n*-hexane) was obtained from Aldrich and titrated according to Gilman's double titration method.[18] $[RuCl_2(PPh_3)_3]$[19] and $^{tbu}S_4'$-H_2[20] were prepared as described in the literature; N_2H_4 was obtained by 2-fold distillation from $N_2H_4 \cdot H_2O$ over solid KOH under reduced pressure.[21]

Caution! Hydrazine may cause cancer, and anhydrous hydrazine can explode when heated under standard pressure. Distillations should be carried out in a well-ventilated hood behind a safety shield.

Syntheses. **[Ru(ClH)(PPh$_3$)(^{tbu}S$_4$')] (1).** *n*-BuLi in *n*-hexane (7.75 mL, 1.77 M solution, 13.7 mol) was added to $^{tbu}S_4'$-H_2 (3.67 g, 6.86 mmol) in 75 mL of THF at −78 °C. The solution was warmed to room temperature and added dropwise from a dropping funnel to $[RuCl_2(PPh_3)_3]$ (6.58 g, 6.86 mmol) in 250 mL of THF, and the mixture was heated to reflux for 2.5 h. The brown reaction mixture was cooled to room temperature and evaporated to dryness. The resulting residue was suspended in 175 mL of CH_2Cl_2, and HCl gas was bubbled through the suspension, whose color turned from yellowish-green to blackish-brown within 10 min. The mixture was stirred under an atmosphere of HCl for another 20 h, precipitated $PHPh_3Cl$ and LiCl were removed by filtration, and the filtrate was reduced to 10 mL in volume and kept at −78 °C for 4 d. Yellow **1** precipitated, was separated, washed with CH_2Cl_2 (30 mL) and Et_2O (10 mL), and dried in vacuo. Yield: 4.71 g (74%). Anal. Calcd for $C_{48}ClH_{60}PRuS_4$ (MW = 932.7): C, 61.8; H, 6.5; S, 13.7. Found: C, 61.8; H, 6.7; S, 13.5.

IR (KBr, [cm^{-1}]): 2171 broad, ν_{SHCl}. ^{1}H NMR (270 MHz, CD_2Cl_2, δ [ppm]): 1.22 (s, 9H, C_4H_9), 1.35 (s, 9H, C_4H_9), 1.47 (s, 9H, C_4H_9), 1.59 (s, 9H, C_4H_9), 2.13–2.84 (m, 4H, C_2H_4), 4.57 (s, 1H, S*H*Cl), 6.52–7.86 (m, 19H, C_6H_2 and $P(C_6H_5)_3$, overlapped). $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, δ [ppm]): 29.6, 30.9, 31.3, 31.4, 34.4, 35.3, 37.6, 39.8, 46.3, 46.4 (C_{alkyl}); 124.4, 126.0, 126.5, 126.6, 127.6, 128.5, 129.0, 129.3, 134.1, 134.4, 135.4, 135.5, 135.6, 136.0, 149.1, 152.7 (C_{aryl}). $^{31}P\{^1H\}$ NMR (109.4 MHz, CD_2Cl_2, δ [ppm]): 28.8 (s, *P*Ph$_3$). FD mass spectrum (CH_2Cl_2, [*m*/*z*]): 932 ([Ru(ClH)(PPh$_3$)(^{tbu}S$_4$')]$^+$).

[Ru(PPh$_3$)(^{tbu}S$_4$')] (2). To a suspension of **1** (456 mg, 0.489 mmol) in 15 mL of MeOH was added NMe_4OH (0.20 mL, 2.41 M solution, 0.49 mmol). The suspension was stirred for 1 h, and its yellow color slightly deepened. The solid was separated, washed with MeOH (15 mL) in order to remove NMe_4Cl, and dried in vacuo (8 h), in the course of which it turned brown on the surface. Yield: 382 mg (87%). Anal. Calcd for $C_{48}H_{59}PRuS_4$ (MW = 896.3): C, 64.3; H, 6.6; S, 14.3. Found: C, 63.2; H, 6.7; S, 13.1. Since **2** is extremely sensitive both in solution and in the solid state, it could not be further purified.

^{1}H NMR (270 MHz, acetone-d_6, δ [ppm]): 1.16 (s, 9H, C_4H_9), 1.28 (s, 9H, C_4H_9), 1.60 (s, 9H, C_4H_9), 1.63 (s, 9H, C_4H_9), 1.86–2.82 (m, 4H, C_2H_4), 6.42–7.88 (m, 19H, C_6H_2 and $P(C_6H_5)_3$, overlapped). $^{31}P\{^1H\}$ NMR (109.4 MHz, CD_2Cl_2, δ [ppm]): 39.5 (s, *P*Ph$_3$). The spectra showed also peaks of decomposition products; ^{13}C NMR and mass spectra could not be obtained.

NEt$_4$[Ru(N$_3$)(PPh$_3$)(^{tbu}S$_4$')] (3). To a suspension of **1** (1.47 g, 1.58 mmol) in 100 mL of acetone were added methanolic NMe_4OH (0.66 mL, 2.51 M solution, 1.6 mmol) and NEt_4N_3 (272 mg, 1.58 mmol) in 50 mL of acetone. The resulting orange suspension was stirred for 1 h and filtered and the filtrate slowly concentrated to about 15 mL and cooled to −78 °C. Precipitated golden-yellow **3** was separated after 3 d, washed with acetone (15 mL), and dried in vacuo (2 h). Yield: 1.07 g (63%). Anal. Calcd for $C_{56}H_{79}N_4PRuS_4$ (MW = 1068.5): C, 62.9; H, 7.5; N, 5.2; S, 12.0. Found: C, 62.7; H, 7.4; N, 4.9; S, 11.6.

IR (acetone, [cm^{-1}]): 2033 vs, ν_{N3}. IR (KBr, [cm^{-1}]): 2034 vs, ν_{N3}. ^{1}H NMR (270 MHz, dmf-d_7, δ [ppm]): 1.21 (s, 9H, C_4H_9), 1.31 (s, 9H, C_4H_9), 1.35 (m, 12H, $N(CH_2CH_3)_4^+$, $^2J(^1H^1H)$ = 7.5 Hz), 1.55 (s, 9H, C_4H_9), 1.66 (s, 9H, C_4H_9), 1.85–2.84 (m, 4H, C_2H_4), 3.46 (m, 8H, $N(CH_2CH_3)_4^+$, $^2J(^1H^1H)$ = 7.5 Hz), 6.60–7.88 (m, 19H, C_6H_2 and $P(C_6H_5)_3$, overlapped). $^{31}P\{^1H\}$ NMR (109.4 MHz, dmf-d_7, δ [ppm]): 41.0 (s, *P*Ph$_3$). ^{13}C NMR and mass spectra could not be obtained.

[RuCl(PPh$_3$)(^{tbu}S$_4$')]. A small, thin-walled vial was filled with a methanolic NMe_4OH solution (0.62 mL, 2.51 M, 1.6 mmol), closed with a rubber stopper, and put into the glass insert of a laboratory autoclave which then was filled with argon and sealed with a septum. **1** (489 mg, 0.524 mmol) in 10 mL of CH_2Cl_2 was injected with a syringe, and the cannula was left in the septum for pressure balancing. The glass insert was transferred into the autoclave which was filled with N_2 (150 bar). The NMe_4OH phial crushed at a pressure of about 40 bar. After 16 h of stirring the resulting solution was transferred into a Schlenk tube and evaporated to dryness. The residue was suspended in CH_2Cl_2 (4 mL) and filtered, the filtrate evaporated to dryness again, and the yellowish-brown residue dried in vacuo (14 h). Yield: 330 mg (68%). Anal. Calcd for $C_{48}ClH_{59}PRuS_4$ (MW = 931.7): C, 61.9; H, 6.4. Found: C, 62.0; H, 6.5.

[Ru(NH$_3$)(PPh$_3$)(^{tbu}S$_4$')] (4). NH_3 gas was bubbled through a solution of **1** (1.80 g, 1.93 mmol) in THF (50 mL) for 3 min. The resulting yellowish-green solution was stirred under NH_3 atmosphere for 6 h and filtered, and the filtrate was concentrated to about 10 mL in a stream of NH_3 gas at 30 °C and cooled to −30 °C (1 d). Precipitated yellow **4** was separated and washed with THF (10 mL) and Et_2O (3 mL). When it was dried in vacuo (2.5 h) under exclusion of light, it turned green on the surface. Yield: 1.12 g (64%). Anal. Calcd for $C_{48}H_{62}NPRuS_4$ (MW = 913.3): C, 63.1; H, 6.8; N, 1.5; S, 14.0. Found: C, 63.3; H, 7.4; N, 1.4; S, 13.6.

Recrystallization from CH_2Cl_2/MeOH (2:1) (+20 °C to −30 °C) gave yellow crystals of **4**·CH_2Cl_2. Anal. Calcd for $C_{49}Cl_2H_{64}NPRuS_4$ (MW = 998.2): C, 59.0; H, 6.5; N, 1.4; S, 12.8. Found: C, 59.8; H, 6.8; N, 1.5; S, 13.0.

IR (KBr, [cm^{-1}]): 3138 w, 3178 vw, 3234 vw, 3304 w, 3358 w. ^{1}H NMR (270 MHz, CD_2Cl_2, δ [ppm]): 1.25 (s, 9H, C_4H_9), 1.31 (s, 9H, C_4H_9), 1.58 (s, 9H, C_4H_9), 1.64 (s, 3H, NH_3), 1.68 (s, 9H, C_4H_9), 1.79–2.88 (m, 4H, C_2H_4), 6.97–7.71 (m, 19H, C_6H_2 and $P(C_6H_5)_3$, overlapped). $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, δ [ppm]): 29.5, 29.7, 31.5, 31.6, 34.4, 34.5, 37.6, 37.9, 44.7, 45.1 (C_{alkyl}); 123.8, 124.4, 126.4 (d), 126.5, 127.8 (d), 129.2, 134.1 (d), 134.5, 134.7, 135.3, 136.6, 143.8, 144.2, 148.4, 149.7, 151.2 (C_{aryl}). $^{31}P\{^1H\}$ NMR (109.4 MHz, CD_2Cl_2, δ [ppm]): 43.1 (s, *P*Ph$_3$). No M^+ ion could be detected in the FD mass spectrum.

[Ru(N$_2$H$_4$)(PPh$_3$)(^{tbu}S$_4$')] (5). In a Schlenk tube that had been flame dried in vacuo, **1** (3.44 g, 3.69 mmol) was dissolved in 100 mL of THF, and N_2H_4 (1.0 mL, 30 mmol) was added dropwise. The resulting deep orange emulsion was stirred for 1 h and cooled to −78 °C (1 d), precipitated N_2H_5Cl was removed by filtration, and the filtrate was evaporated to dryness. When the yellow residue was dried in vacuo (1 h) under exclusion of light, it turned green on the surface. Yield: 3.72 g of **5**·2THF (94%, raw product). Anal. Calcd for $C_{56}H_{79}N_2O_2PRuS_4$ (MW = 1072.5): C, 62.7; H, 7.4; N, 2.6. Found: C, 63.3; H, 7.4; N, 2.4.

Recrystallization from CH_2Cl_2 (20 °C to 7 °C) gave yellow crystals of **5**·2CH_2Cl_2. Anal. Calcd for $C_{50}Cl_4H_{67}N_2PRuS_4$ (MW = 1098.2): C, 54.7; H, 6.1; N, 2.5; S, 11.7. Found: C, 54.5; H, 5.8; N, 2.2; S, 12.4.

IR (KBr, [cm^{-1}]): 3345 sh, 3300 w, 3245 sh, 3165 vw. ^{1}H NMR (270 MHz, CD_2Cl_2, δ [ppm]): 1.26 (s, 9H, C_4H_9), 1.32 (s, 9H, C_4H_9), 1.60 (s, 9H, C_4H_9), 1.68 (s, 9H, C_4H_9), 1.80–2.95 (m, 4H, C_2H_4), 3.48 (s, 2H, Ru–NH_2–NH_2), 4.01 (d, 1H, Ru–NH_2–NH_2, $^2J(^1H^1H)$ = 10.8 Hz), 4.29 (d, 1H, Ru–NH_2–NH_2, $^2J(^1H^1H)$ = 10.8 Hz), 6.93–7.80 (m, 19H, C_6H_2 and $P(C_6H_5)_3$, overlapped). FD mass spectrum (CH_2Cl_2, [*m*/*z*]: 928 ([Ru(N$_2$H$_4$)(PPh$_3$)(^{tbu}S$_4$')]$^+$), 900 ([Ru(N$_2$H$_4$)(PPh$_3$)(^{tbu}S$_2$')$_2$]$^+$), 896 ([Ru(PPh$_3$)(^{tbu}S$_4$')]$^+$).

[μ-N$_2$H$_2${Ru(PPh$_3$)(^{tbu}S$_4$')}$_2$] (6). **5**·2THF (3.50 g, 3.28 mmol) was dissolved in the minimum volume of THF (about 30 mL) in a 1-L flask that was closed by a septum. The solution was rapidly stirred, and air (260 mL, 2.45 mmol O_2) was injected in several portions. In the course of 2–3 h the color of the solution turned from orange to deep green and **6** began to precipitate. Cooling down to −78 °C completed the deposition of the product, which was separated, washed with THF (10 mL), and dried in vacuo (8 h). Yield: 950 mg of **6**·THF (31%). Anal. Calcd for $C_{100}H_{128}N_2OP_2Ru_2S_8$ (MW = 1894.7): C, 63.4; H, 6.8; N, 1.5. Found: C, 63.5; H, 7.2; N, 1.1.

Recrystallization from CH_2Cl_2 (+20 °C to −78 °C) gave blackish-green crystals of **6**·CH_2Cl_2. Anal. Calcd for $C_{97}Cl_2H_{122}N_2P_2Ru_2S_8$ (MW = 1907.5): C, 61.1; H, 6.4; N, 1.5; S, 13.4. Found: C, 61.3; H, 6.4; N, 1.2; S, 13.4.

^{1}H NMR (270 MHz, CD_2Cl_2, δ [ppm]): 1.19 (s, 18H, C_4H_9), 1.25 (s, 18H, C_4H_9), 1.48 (s, 18H, C_4H_9), 1.77 (s, 18H, C_4H_9), 1.25–2.60 (m, 8H, C_2H_4), 6.65–7.48 (m, 38H, C_6H_2 and $P(C_6H_5)_3$, overlapped), 14.9 (s, 2H, N_2H_2). $^{13}C\{^1H\}$ NMR (67.9 MHz, CS_2, δ [ppm]): 29.4, 29.7, 31.2, 31.3, 33.4, 33.7, 36.8, 37.2, 43.3, 43.5 (C_{alkyl}); 123.4 (d), 124.6, 125.5, 126.8, 127.0, 127.2 (d), 128.3, 132.3, 133.6 (d), 134.1, 135.6, 142.0, 143.2, 148.0, 149.0, 151.1 (C_{aryl}). $^{31}P\{^1H\}$ NMR (109.4 MHz, CD_2Cl_2, δ [ppm]): 37.5 (s, *P*Ph$_3$). FD mass spectrum (CH_2Cl_2, [*m*/*z*]): 1822 ([μ-N$_2$H$_2${Ru(PPh$_3$)(^{tbu}S$_4$')}$_2$]$^+$). UV (2.17×10^{-4} M solution, CH_2Cl_2, λ [nm]/ϵ [L mol^{-1} cm^{-1}]): 630/5400, 478/15500.

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Table I. Summary of Crystallographic Data and Data Collection Procedures of $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{tbu}S_4')\}_2]\cdot 4CH_2Cl_2$

formula	$C_{100}Cl_8H_{128}N_2P_2Ru_2S_8$
fw	2162.4
space group	$C2/c$
cryst syst	monoclinic
a (pm)	2870.0(16)
b (pm)	1380.4(4)
c (pm)	2849.2 (13)
β (deg)	93.65 (4)
V (pm^3)	11265(9) × 10^6
Z	4
D_{calc} (g/cm^3)	1.270
μ (cm^{-1})	6.76
diffractometer	Siemens P4
radiation (pm)	Mo Kα (λ = 71.073 pm)
monochromator	graphite
temp. of meas (K)	200
scan technique	ω-scan
2θ Range (deg)	$3.0 \le 2\theta \le 50.0$
scan speed (deg/min)	3.00–30.00
no. of reflcns collcd	10 636
no. of indep reflcns	9229
no. of obsd reflcns	5801
σ criterion	$F > 4.0\sigma(F)$
R/R_w (%)	7.5/7.2
weight	$1/\sigma^2$
no. of params refined	497

Table II. Selected Distances (pm) and Angles (deg) for $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{tbu}S_4')\}_2]$ (**6**)

	Distances		
N(1)–N(1a)	127.9(14)	Ru(1)–S(1)	237.7(3)
N(1)–H(1)	97[a]	Ru(1)–S(2)	230.7(3)
H(1)–S(1)	288[a]	Ru(1)–S(3)	235.5(3)
H(1)–S(4a)	257[a]	Ru(1)–S(4)	239.1(3)
Ru(1)–N(1)	200.9(8)	Ru(1)–P(1)	233.2(3)
		S(1)–H(1)	288[a]
		S(4a)–H(1)	257[a]
	Angles		
Ru(1)–N(1)–N(1a)	131.9(8)	S(2)–Ru(1)–N(1)	172.6(2)
Ru(1)–N(1)–H(1)	121[a]	S(1)–Ru(1)–S(4)	169.3(1)
N(1)–Ru(1)–S(1)	86.2(2)	S(1)–Ru(1)–S(3)	85.0(1)
N(1)–Ru(1)–S(3)	90.5(2)	S(3)–Ru(1)–S(4)	84.7(1)
S(2)–Ru(1)–S(4)	96.0(1)	S(4)–Ru(1)–P(1)	95.0(1)
		P(1)–Ru(1)–S(1)	95.4(1)

[a] No standard deviations are given for the diazene H atoms (and angles), because they were located by difference Fourier synthesis and fixed during refinement.

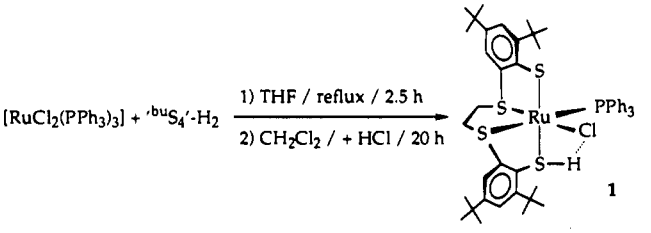
X-ray Structure Determination of 6·4CH$_2$Cl$_2$. Blackish-green single crystals of hexagonal shape (0.70 × 0.60 × 0.60 mm^3) were obtained by cooling a saturated CH_2Cl_2 solution from 20 to 7 °C. They were sealed in glass capillaries under argon atmosphere.

The structure was solved by direct methods (SHELXTL-PLUS). Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the phenyl groups were placed at calculated positions and refined as rigid groups; the hydrogen atoms of methyl and methylene groups were placed in ideal tetrahedral positions and allowed to rotate around their central carbon atom during refinement. The diazene hydrogen atoms were located by difference Fourier synthesis and fixed at this position. Hydrogen atoms were refined with a common temperature factor. The crystal contained CH_2Cl_2 at several positions that were filled only partially. Two of these molecules were determined, refined isotropically, and fixed during the last refinement. Their positions, temperature coefficients, and large residual electron densities in their vicinity indicate disorder. Another position of high electron density might indicate a third CH_2Cl_2 molecule which could not be localized and refined exactly.

Selected crystallographic data are summarized in Table I; Table II lists selected bond distances and angles.

Results

Synthesis, Characterization, and Reactions of [Ru(L)(PPh$_3$)(^{tbu}S$_4$')] Complexes (L = N$_3^-$, NH$_3$, N$_2$H$_4$). [Ru(ClH)(PPh$_3$)(^{tbu}S$_4$')] (**1**) is the most suitable starting material for synthesis of [Ru(L)(PPh$_3$)(^{tbu}S$_4$')] complexes, since its HCl ligand can be easily removed by reaction with bases and replaced by other ligands. However, **1** had been accessible in low yields only;[22] therefore an improved *one-pot synthesis* was developed according to eq 1. This method circumvents tedious separation and



(1)

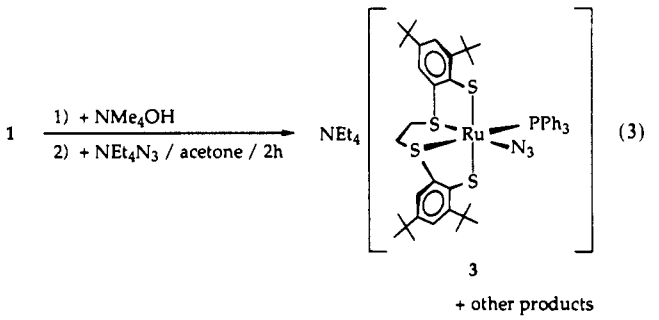
purification of [Ru(PPh$_3$)$_2$(^{tbu}S$_4$')], which forms as primary product, and yields analytically pure **1** on a 5-g scale.

When reacted with NMe$_4$OH according to eq 2, **1** instantaneously gave a precipitate of [Ru(PPh$_3$)(^{tbu}S$_4$')] (**2**) and NMe$_4$Cl. The latter could be easily removed by extraction with MeOH.

$$\mathbf{1} + NMe_4OH \xrightarrow[-NMe_4Cl,\ -H_2O]{MeOH/1\ h} \underset{\mathbf{2}}{[Ru(PPh_3)(^{tbu}S_4')]} \qquad (2)$$

2 formed as yellow powder which is extremely sensitive and turns greenish-brown in a few days even when kept at −30 °C under argon. Isolation of **2** was only possible from methanol solutions, because in all other solvents it rapidly decomposed, giving brown solutions that were not further characterized.

1 or **2** rendered possible the synthesis of the azido complex [Ru(N$_3$)(PPh$_3$)(^{tbu}S$_4$')]$^-$ that was obtained as an NEt$_4^+$ salt (**3**) according to eq 3. In this reaction, **2** needs not be isolated but



(3)

is generated in situ only. The reaction can be monitored by IR spectroscopy showing that the $\nu(N_3)$ band of free N_3^- ions at 2000 cm^{-1} quickly disappears while the $\nu(N_3)$ band of **3** at 2033 cm^{-1} emerges.

Yellow **3** is very soluble in acetone, MeOH, THF, and DMF and shows a characteristic $\nu(N_3)$ band at 2034 cm^{-1} in its KBr IR spectrum and four *tert*-butyl singlets in its ^{1}H NMR spectrum. The number of *tert*-butyl singlets indicates C_1 symmetry and the structure of the complex anion is schematically shown in eq 3. This structure is supported by the number of signals observed in the ^{13}C and ^{31}P NMR spectra.

When dissolved in CH_2Cl_2 at room temperature, **3** quickly gave [Ru(N$_3$)(PPh$_3$)(^{tbu}S$_4$'-CH$_2$Cl)] in which one thiolate donor has become chloromethylated. In boiling CH_2Cl_2 this complex went on reacting to form [Ru(CN)(PPh$_3$)(^{tbu}S$_4$'-CH$_2$Cl)]. Both compounds were only identified by their IR bands at 2043 and 2096 cm^{-1}, because analogous reactions had been previously observed with the parent [Ru(N$_3$)(PPh$_3$)('S$_4$'-CH$_2$Cl)][23] complex.

The good solubility of **1** in CH_2Cl_2 allowed attempts to coordinate N_2 to the [Ru(PPh$_3$)(^{tbu}S$_4$')] fragment. For this

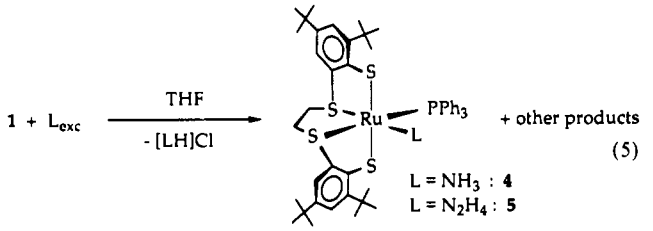
(22) Sellmann, D.; Barth, I.; Moll, M. *Inorg. Chem.* **1990**, *29*, 176.
(23) Sellmann, D.; Waeber, M.; Binder, H.; Boese, R. *Z. Naturforsch.* **1986**, *41B*, 1541.

purpose, **2** was generated in situ in the presence of N_2 pressure according to eq 4. Nevertheless, formation of a dinitrogen complex

$$\mathbf{1} \xrightarrow[CH_2Cl_2/16\ h]{(1)\ 150\ bar\ N_2;\ (2)\ +NMe_4OH} [Ru(Cl)(PPh_3)(^{bu}S_4')] \quad (4)$$

could not be observed. Instead, the isolated product was identified to be the Ru(III) complex $[Ru(Cl)(PPh_3)(^{bu}S_4')]$ which we had previously obtained in a different way.[24]

When ligands that can act as *Brönstedt bases* are to be coordinated to the $[Ru(PPh_3)(^{bu}S_4')]$ fragment, no isolated **2** is needed as starting material, but **1** can be used directly. Accordingly, with an excess of ammonia or hydrazine, $[Ru(NH_3)(PPh_3)(^{bu}S_4')]$ (**4**) and $[Ru(N_2H_4)(PPh_3)(^{bu}S_4')]$ (**5**) form (eq 5). First evidence of the formation of **4** and **5** had previously

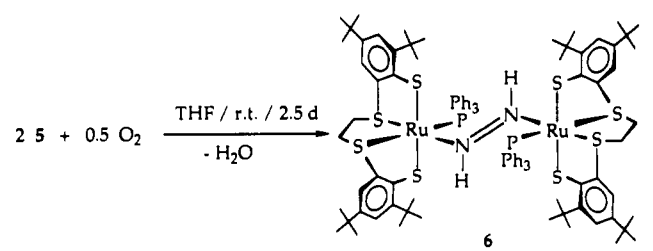


been obtained when $[Ru(PPh_3)_2(^{bu}S_4')]$ was reacted with NH_3 and N_2H_4, but it had not been possible to isolate pure complexes from the reaction mixtures.[25] This was certainly due to the properties of **4** and **5** which proved to be very labile and already decomposed when dried in vacuo. They are also extremely air sensitive, and for example, when NMR spectra are recorded, air is to be excluded meticulously and freshly distilled, argon-saturated solvents are to be used.

4 and **5** are yellow, are extremely soluble in CH_2Cl_2, $CHCl_3$, THF, and CS_2, and could be fully characterized. The ^1H, ^{13}C, and ^{31}P NMR spectra of **4** and **5** show the typical patterns of C_1 symmetrical $[Ru(L)(PPh_3)(^{bu}S_4')]$ complexes. In the ^1H NMR spectrum, the NH_3 protons of **4** gave a characteristic singlet at 1.64 ppm; the N_2H_4 protons of **5** gave rise to two doublets at 4.01 and 4.29 ppm that are attributed to the Ru-bound NH_2 group and a broad singlet at 3.48 ppm which is assigned to the terminal NH_2 group. Due to the C_1 symmetry of **5**, all NH protons are magnetically inequivalent. The different splitting of metal bound and terminal NH_2 groups and the equivalence of terminal NH_2 protons can be attributed to rotation of the NH_2 groups around the N–N bond.

When yellow **5** comes into contact with traces of air, its color spontaneously turns green both in the solid state and in solution. This indicated that **5** can be oxidized to a diazene complex.[4,12]

This complex was obtained by the reaction according to eq 6. Treatment of a highly concentrated orange THF solution of **5**



with stoichiometric amounts of air gave a dark-green solution, from which the dinuclear diazene complex $[\mu\text{-}N_2H_2\text{-}\{Ru(PPh_3)(^{bu}S_4')\}_2]$ (**6**) precipitated as dark green solid in the course of 2–3 days.

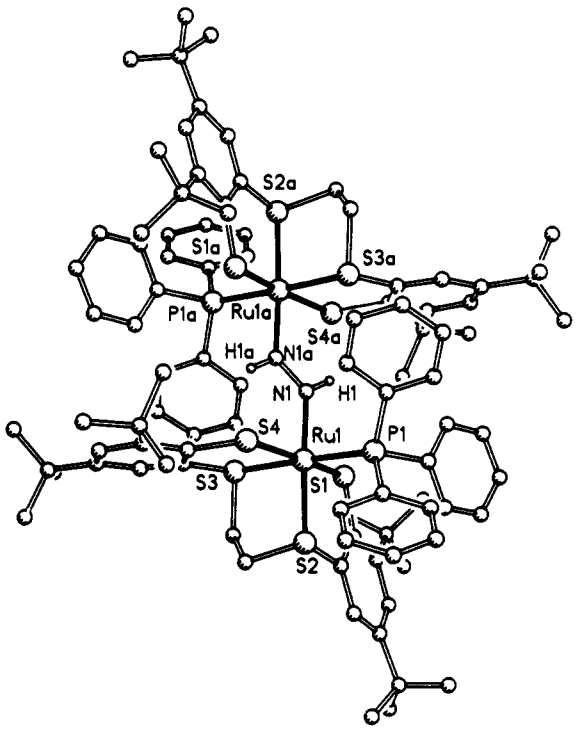


Figure 1. Molecular structure of $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{bu}S_4')\}_2]$ (**6**). C bound H atoms and thermal ellipsoids are omitted for sake of clarity.

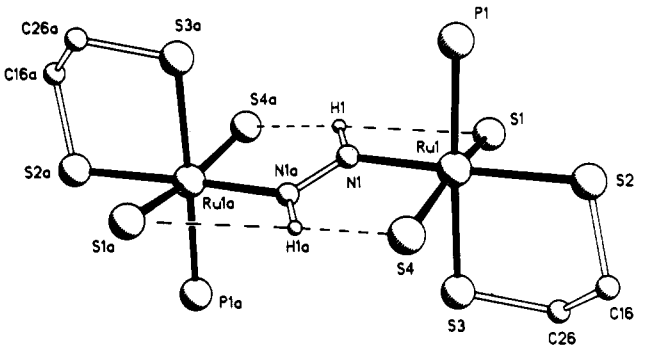


Figure 2. $[Ru_2N_2P_2S_8]$ core of **6** including N_2H_2 protons and C_2H_4 bridges.

6 is very soluble in CH_2Cl_2, $CHCl_3$, and CS_2. It was obtained in single crystals as the solvate **6**·$4CH_2Cl_2$ from CH_2Cl_2 solutions and could be characterized by X-ray structure determination.

X-ray Structure Analysis of $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{bu}S_4')\}_2]\cdot 4CH_2Cl_2$ (6·$4CH_2Cl_2$). Figure 1 shows the molecular structure of **6**, and Figure 2, the $[Ru_2N_2P_2S_8]$ core including the diazene protons and C_2H_4 bridges of the $^{bu}S_4'$ ligand in order to allow distinction of thiolate and thioether donors. Selected distances and angles are listed in Table II.

6 has a crystallographically imposed inversion center in the middle of the N–N unit that connects two enantiomeric $[Ru(PPh_3)(^{bu}S_4')]$ fragments. Each Ru center is pseudooctahedrally coordinated by one nitrogen, one phosphorous, and four sulfur atoms. As is shown in Figure 2, the Ru centers, diazene atoms, and four thiolate S-atoms approximately form a plane. The thiolate–H(N) distances (288, 257 pm) indicate intramolecular tricentric hydrogen bonds between diazene-N and thiolate-S atoms as had been found in $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{S}S_4')\}_2]$[12] and $[\mu\text{-}N_2H_2\{Fe(^{N_H}S_4')\}_2]$[13] before.

If the N–N distance in azomethane (124.3(3) pm)[26] is taken as reference, the N–N distance of **6** (127.9(14) ppm) corresponds with a slightly elongated N=N double bond. Comparable

(24) Sellmann, D.; Lechner, P.; Knoch, F. *Z. Naturforsch.* **1991**, *46B*, 1585.
(25) Sellmann, D.; Barth, I. *Z. Anorg. Allg. Chem.* **1989**, *577*, 234.
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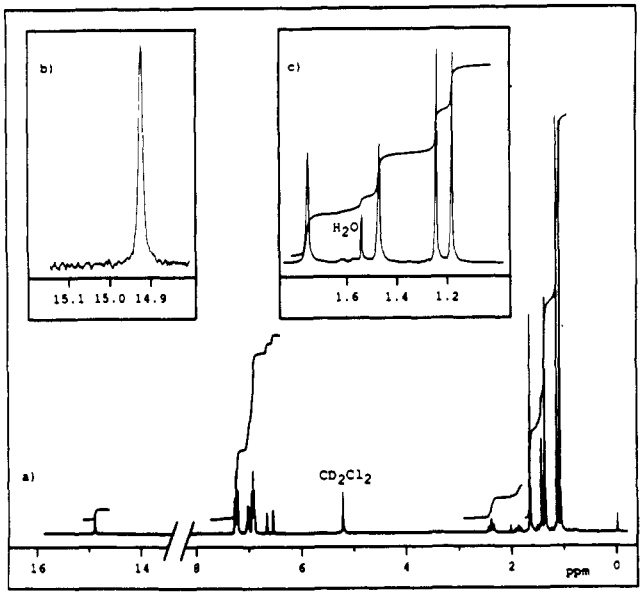

Figure 3. (a) ^{1}H NMR spectrum (270 MHz, CD_2Cl_2) of $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{tbu}S_4')\}_2]$ (**6**). (b) Diazene and (c) *tert*-butyl regions of the spectrum.

distances had been observed in $[\mu\text{-}N_2H_2\{Cr(CO)_5\}_2]\cdot 2THF$ (125.0(25) pm),[27] $[\mu\text{-}N_2H_2\{Ru(PPh_3)('S_4')\}_2]$ (130.1(14) pm),[12] and $[\mu\text{-}N_2H_2\{Fe('N_HS_4')\}_2]$ (130.0(7) pm).[13]

The Ru–S and Ru–P distances show no anomalies; the Ru–N distances (200.9(8) pm), however, are relatively short and indicate partial Ru=N double bond character. Ru–N single bonds in Ru(II) complexes such as $[Ru(NH_3)_6]^{2+}$ usually exhibit distances in the range 214–217 pm.[28]

Elongation of N–N and shortening of Ru–N bonds of **6** indicate a 4c–6e$^-$ π bond in the Ru⌢N⌢N⌢Ru fragment. Such a bond can further be deduced from intense absorptions in the UV/vis spectrum at 478 and 630 nm (ϵ = 15500, 5400 L mol^{-1} cm^{-1}, respectively). Comparable bands also occur in other diazene complexes[12,13] but are not found in the UV/vis spectra of **3** and **5**.

In conclusion, the stabilization of diazene in **6** can be attributed to three factors: (1) formation of tricentric N–H···(S)$_2$ hydrogen bonds; (2) steric protection by the bulky $^{tbu}S_4'$ and PPh_3 ligands; (3) the Ru⌢N⌢N⌢Ru 4c–6e$^-$ π bond.

NMR Spectra of 6. ^{1}H NMR spectra are the best criterion to judge the purity of **6**. In order to obtain the ^{1}H NMR spectrum shown in Figure 3, it was necessary to dissolve single crystals of **6** in CD_2Cl_2 at 0 °C and to record the spectrum immediately afterward.

Only if these precautions are taken does the ^{1}H NMR spectrum of **6** exhibit the characteristic pattern of a centrosymmetric complex containing enantiomeric $[Ru(PPh_3)(^{tbu}S_4')]$ fragments of C_1 symmetry, which is indicated by four singlets for the *tert*-butyl groups. The spectrum also confirms that the centrosymmetric structure of **6** which had been found in the solid state is retained in solution, because the two diazene protons give rise to only one singlet at 14.9 ppm. The number of signals observed in the ^{13}C and ^{31}P NMR spectra further corroborate this conclusion. The large downfield shift of the diazene protons is typical of protons bound to sp^2-hybridized N-atoms[29] and was also observed in other diazene complexes.[4,6-9,12]

If the solution which gave the spectrum of Figure 3 was kept at room temperature for 1 d, it did not undergo any visible changes, but in its ^{1}H NMR spectrum new signals appeared. The *tert*-butyl singlets split, the intensity of the original N_2H_2 signal decreased, and a second signal at 15.1 ppm appeared. New peaks could also be observed in the ^{31}P NMR spectrum, particularly a singlet at 43.1 ppm that is tentatively assigned to the NH_3 complex $[Ru(NH_3)(PPh_3)(^{tbu}S_4')]$ (**4**).

Two diazene signals at 14.9 and 15.1 ppm also occurred in the ^{1}H NMR spectrum of the THF solvate **6**·THF which crystallized from the reaction mixture. This indicates that **6** can form diastereomers resulting from the combination of two $[Ru(PPh_3)(^{tbu}S_4')]$ fragments both exhibiting either *R* or *S* configurations.

Discussion and Conclusion

$[Ru(ClH)(PPh_3)(^{tbu}S_4')]$ (**1**) was obtained by a convenient *one-pot synthesis* on a 5-g scale. Elimination of HCl by reaction with NMe_4OH yielded $[Ru(PPh_3)(^{tbu}S_4')]$ (**2**), which formally contains a coordinatively unsaturated Ru center. Reaction of **2** with azide ions gave an azide complex anion that was isolated as $NEt_4[Ru(N_3)(PPh_3)(^{tbu}S_4')]$ (**3**). **3** is a potential precursor for dinitrogen complexes which are not accessible via direct coordination of gaseous nitrogen.[30] All attempts in the past to synthesize the corresponding parent $[Ru(N_3)(PPh_3)('S_4')]^-$ complex had been unsuccessful. With ligands which have *Brönstedt* base character such as NH_3 and N_2H_4, **1** can be reacted directly. The resulting $[Ru(NH_3)(PPh_3)(^{tbu}S_4')]$ (**4**) and $[Ru(N_2H_4)(PPh_3)(^{tbu}S_4')]$ (**5**) complexes had not been accessible by other routes, because they are extremely labile. This can be attributed to the softness of the Ru center in $[Ru(PPh_3)(^{tbu}S_4')]$ fragments which exhibit high electron density because their coordination spheres are dominated by thiolate and thioether donors.

In agreement with these considerations, the *trans*-diazene complex $[\mu\text{-}N_2H_2\{Ru(PPh_3)(^{tbu}S_4')\}_2]$ (**6**) is considerably less sensitive toward temperature or oxidation, because *trans*-diazene can act as a σ-donor π-acceptor ligand. In **6**, HN=NH which is extremely unstable in the free state, is stabilized by a 4c–6e$^-$ Ru⌢N⌢N⌢Ru π bond, by steric shielding, and, in addition, by strong tricentric N–H···(S)$_2$ hydrogen bridges between diazene protons and thiolate donors. Despite of this stabilization of the diazene ligand, the NMR results indicate that **6** is highly reactive in solution and can also form diastereomers due to the chirality of the $[Ru(PPh_3)(^{tbu}S_4')]$ fragments. These exist as *R* and *S* enantiomers and, as was discussed previously,[31] yield diastereomers when combined in dinuclear complexes. Such observations had not been possible with the parent complex $[\mu\text{-}N_2H_2\{Ru(PPh_3)('S_4')\}_2]$ due to its insolubility.[32]

With respect to the active centers of nitrogenases, the Ru compounds $[Ru(L)(PPh_3)(^{tbu}S_4')]$ (L = $(N_2H_2)_{1/2}$, N_2H_4, NH_3) may be regarded as model complexes, because they contain key intermediates of N_2 fixation bound to transition metal centers in a coordination sphere dominated by sulfur donors.

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Supplementary Material Available: Figures showing the ^{1}H and ^{31}P NMR spectra of **6**, complete listings of bond distances and angles, and listings of anisotropic thermal parameters and fractional coordinates of atoms (9 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analysis have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Germany, by citing Deposition No. CSD-320509, the authors, and the reference.

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