

Transition-Metal Complexes with Sulfur Ligands. 132.¹ Electron-Rich Fe and Ru Complexes with [MN₂S₃] Cores Containing the New Pentadentate Ligand 'N₂H₂S₃'²⁻ (= 2,2'-Bis(2-mercaptophenylamino)diethyl Sulfide(2-))

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The new pentadentate amine thioether thiolate ligand 'N₂H₂S₃'-H₂ (= 2,2'-bis(2-mercaptophenylamino)diethyl sulfide) (**3**) was synthesized in order to obtain iron and ruthenium complexes with high electron densities at the metal centers. The reaction of 'N₂H₂S₃'²⁻ with Fe²⁺ yielded the dinuclear high-spin complex [Fe('N₂H₂S₃')]₂ (**5**). Complex **5** added CO to give the low-spin complex [Fe(CO)('N₂H₂S₃')] (**6**) whose low frequency $\nu(\text{CO})$ (1932 cm⁻¹) indicates a high electron density at the iron center and a strong Fe–CO bond. However, **6** is labile and readily dissociates CO in solution. Treatment of suitable ruthenium precursor complexes with 'N₂H₂S₃'²⁻ yielded [Ru(CO)(PCy₃)('N₂H₂S₃')] (**7**), [Ru(PPR₃)₂('N₂H₂S₃')] (**8**), [Ru(PR₃)('N₂H₂S₃')] (R = Pr (**9**), Ph (**10**)), and [Ru(NO)('N₂HS₃')] (**13**). In complexes **7** and **8**, 'N₂H₂S₃'²⁻ acts as a tetradentate ligand. When heated in solution, complex **8** dissociates one PPR₃ ligand to give **9**. Complex **13** contains the trisanionic 'N₂HS₃'³⁻ resulting from deprotonation of one amine NH function. All [Ru(L)('N₂H₂S₃')] complexes proved inert toward dissociation of the Ru–L bonds. The NH functions of [M(L)('N₂H₂S₃')] complexes are acidic and show H⁺/D⁺ exchange reactions with D₂O. Methylation of the thiolate donors in **10** yielded the thioether derivative [Ru(PPh₃)('N₂H₂S₃'-Me₂)]₂ (**11**) whose PPh₃ ligand is as inert to substitution as that of **10**. Complex **11** can reversibly be deprotonated to give [Ru(PPh₃)('N₂HS₃'-Me₂)]I (**12**). NMR spectroscopic investigations showed that the deprotonation/protonation reactions of **11** and **12** are stereoselective. In contrast, protonation of **13** with HBF₄ gives two diastereomers of the corresponding [Ru(NO)('N₂H₂S₃')]BF₄ salt (**14**). X-ray structure analyses of **5**, **6**, **9**, and **11** and NMR spectra showed that the 'N₂H₂S₃'²⁻ ligand and its derivatives bind to the metal centers in the same fashion which combines fac and mer coordination of the donor atoms. The [MN₂S₃] cores of all complexes have an analogous C₁ symmetrical structure in which both the two N and the two terminal S donors assume cis positions.

Introduction

The metal oxidation state, the type and number of donor atoms, and the core structure are major factors determining structure–function relationships of metal complexes.² In the quest for complexes that model structural and functional features of the transition metal sulfur centers in enzymes such as nitrogenases, hydrogenases, and CO dehydrogenases, our interest focuses on transition-metal complexes with multidentate ligands containing thiolate, thioether, and amine donors. When these complexes bind biologically relevant molecules and catalyze enzyme-related reactions, they model structural (metal sulfur sites) and functional (reactivity) features of the active centers in the enzymes.³ One ultimate goal in this area of research are complexes with enzymelike activity, which can be termed “competitive” catalysts.⁴

In our search for nitrogenase-related complexes, the [Fe('NHS₄') fragment ('NHS₄'²⁻ = 2,2'-bis(2-mercaptophenylthio)diethylamine(2-)) was found to bind the key molecules of N₂ fixation, N₂H₂, N₂H₄, and NH₃,⁵ but not N₂.

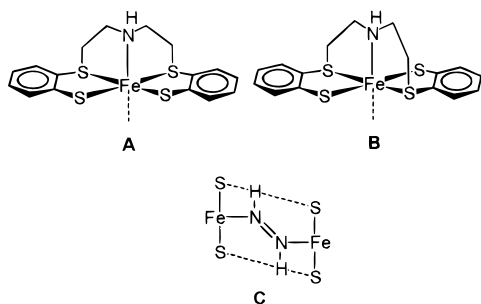
The [Fe('NHS₄') fragment demonstrated the importance of the core structures for binding and/or stabilization of the coligands. The [Fe('NHS₄') fragment exists in the two diastereomeric forms **A** and **B**. While **A** binds only σ ligands such as NH₃, N₂H₄, or MeOH, **B** binds only σ – π ligands such as CO, PMe₃, or diazene, N₂H₂.^{5,6} In the diazene complex, the trans coordination of the thiolate donors in **B** proved pivotal for the stabilization of N₂H₂, because it renders possible strong bifurcated N–H \cdots (S)₂ bridges in the [FeN₂H₂Fe] unit of the binuclear [μ -N₂H₂{Fe('NHS₄')}]₂ according to **C**.

Because almost all stable N₂ complexes exhibit electron-rich metal centers,⁷ a major factor for the binding of N₂ can be considered a high electron density at the metal center. Whereas the $\nu(\text{CO})$ frequency of [Fe(CO)('NHS₄')] (1960 cm⁻¹) indicates

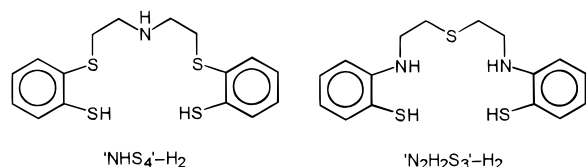
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a relatively high electron density of the Fe(II) center, it is possibly not high enough to enable the coordination of N_2 . For this reason, we have started a systematic study aiming at the stepwise substitution of the potentially π -accepting thioether sulfur donors in the $'NHS_4'^{2-}$ ligand by amine functions which act as σ donors only. Our first target ligand in this context was $'N_2H_2S_3'-H_2$ (= 2,2'-bis(2-mercaptophenylamino)diethyl sulfide).



$'N_2H_2S_3'-H_2$ relates to $'NHS_4'-H_2$ by having one more amine donor and one less thioether donor. $'N_2H_2S_3'-H_2$ further maintains terminal thiol functions which are necessary for the trans coordination of thiolate donors as found in the form **B** of $[Fe('NHS_4')]$.

The notation $'N_2H_2S_3'-H_2$ has been chosen in order to allow a facile designation of the varying sets of donor atoms and of deprotonation states of the $'N_2H_2S_3'-H_2$ or related ligands. The synthesis of the $'N_2H_2S_3'-H_2$ ligand and a couple of characteristic Fe and Ru complexes will be described here.

Experimental Section

General Methods. Unless noted otherwise, all procedures were carried out under an atmosphere of dinitrogen at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments: IR, Perkin-Elmer 16 PC FT-IR; NMR, JEOL JNM-GX 270 and JNM-EX 270; mass spectra, Varian MAT 212 and JEOL JMS-700. Bis(2-bromoethyl)sulfide,⁸ $[RuCl_3(NO)(PPh_3)_2]$,⁹ $[RuCl_2(PPh_3)_3]$,¹⁰ $[Ru(H)(Cl)(CO)(PCy_3)_2]$ ¹¹, and 2(3*H*)-benzothiazolone¹² were prepared by literature methods. Hydrazine was obtained by 2-fold distillation of $N_2H_4 \cdot H_2O$ over solid potassium hydroxide under reduced pressure.

Alkylation of 2(3*H*)-Benzothiazolone (1) to give 2. *n*-BuLi (130.8 mmol, 52.3 mL of a 2.5 M solution in *n*-hexane) was added dropwise to a solution of 2(3*H*)-benzothiazolone (**1**) (19.74 g, 130.6 mmol) in THF (100 mL) at $-78^\circ C$. The reaction mixture was warmed to room temperature, and bis(2-bromoethyl)sulfide (16.19 g, 65.3 mmol) was added. The resulting yellow solution was refluxed for 14 h and then evaporated to dryness, yielding a foamy residue which was redissolved in boiling EtOH (80 mL). Addition of H_2O (120 mL) led to precipitation of a white powder, which was separated, digested two times with EtOH

(80 mL), and dried in vacuo to yield 15.2 g (60%) of **2**: IR (KBr, cm^{-1}) 1678 vs $\nu(CO)$; 1H NMR ($CDCl_3$, ppm, 269.6 MHz) δ 7.42 (d, 2 H, C_6H_4), 7.32 (t, 2 H, C_6H_4), 7.15 (t, 2 H, C_6H_4), 7.09 (d, 2 H, C_6H_4), 4.14 (t, 4 H, NCH_2), 2.92 (t, 4 H, SCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 67.7 MHz) δ 169.9 (CO), 136.4, 126.5, 123.3, 122.7, 122.6, 110.4 (C_6H_4), 41.9 (NCH_2), 28.9 (SCH_2); MS (FD, DMSO) m/z 388 [$'N_2S_3O_2'$] $^+$. Anal. Calcd for $C_{18}H_{16}N_2O_2S_3$ (388.54): C, 55.64; H, 4.15; N, 7.21; S, 24.76. Found: C, 55.49; H, 4.22; N, 7.24; S, 24.74.

$'N_2H_2S_3'-H_2$ (3). A solution of NaOH (14.4 g, 360 mmol) in H_2O (150 mL) was added to a suspension of **2** (14.0 g, 36.0 mmol) in EtOH (150 mL). The mixture was refluxed for 14 h and cooled to room temperature and concentrated hydrochloric acid was added (ca. 25 mL) until pH 3 was reached. The resulting solution was evaporated in vacuo to one-half of its original volume, diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (150 mL). The combined CH_2Cl_2 phases were dried with anhydrous Na_2SO_4 and evaporated to dryness, yielding 12.0 g (99%) of **3** as a yellow, highly viscous oil: 1H NMR ($CDCl_3$, ppm, 269.6 MHz): δ 7.41 (d, 2 H, C_6H_4), 7.19 (t, 2 H, C_6H_4), 6.64 (m, 4 H, C_6H_4), 5.00 (s, br, 2 H, NH), 3.41 (t, 4 H, NCH_2), 2.88 (t, 6 H, SCH_2 and SH superimposed); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 67.7 MHz) δ 136.8, 135.3, 128.7, 128.1, 123.1 (C_6H_4), 48.3 (NCH_2), 27.6 (SCH_2); MS (FD, $CDCl_3$) m/z 336 [$'N_2H_2S_3'-H_2'$] $^+$. Anal. Calcd for $C_{16}H_{20}N_2S_3$ (336.55): C, 57.10; H, 5.99; N, 8.32; S, 28.58. Found: C, 55.89; H, 6.26; N, 8.67; S, 27.79.

$'N_2H_2S_3'-H_2 \cdot 2HCl$ (3·2HCl). Concentrated hydrochloric acid (0.75 mL, 9.0 mmol) was added to a solution of $'N_2H_2S_3'-H_2$ (**3**) (0.50 g, 1.50 mmol) in MeOH (20 mL). Removal of the solvents gave a white residue, which was digested three times with CH_2Cl_2 (15 mL) and dried in vacuo, yielding 0.56 g (91%) of **3·2HCl**: 1H NMR (CD_3OD , ppm, 269.6 MHz): δ 7.61 (d, 2 H, C_6H_4), 7.45–7.25 (m, 6 H, C_6H_4), 3.68 (t, 4 H, NCH_2), 3.03 (t, 4 H, SCH_2); $^{13}C\{^1H\}$ NMR (CD_3OD , ppm, 67.7 MHz) δ 137.7, 136.5, 129.9, 129.8, 124.7, 123.7 (C_6H_4), 50.0 (NCH_2), 28.5 (SCH_2); MS (FD, MeOH) m/z 338 [$'N_2H_2S_3'-H_2'$] $^+$. Anal. Calcd for $C_{16}H_{22}Cl_2N_2S_3$ (409.47): C, 46.93; H, 5.42; N, 6.84; S, 23.49. Found: C, 47.16; H, 5.53; N, 6.86; S 23.63.

$'N_2H_2S_3'-Me_2$ (4). MeI (0.75 mL, 11.7 mmol) was added to a solution of $'N_2H_2S_3'-H_2$ (**3**) (0.99 g, 2.9 mmol) and LiOMe (6.2 mmol, 6.2 mL of a 1 M solution in MeOH) in THF (20 mL). The reaction mixture was stirred for 16 h and then evaporated to dryness. The residue was redissolved in 80 mL of a 1:1 mixture of H_2O and CH_2Cl_2 , the CH_2Cl_2 phase was separated, dried with anhydrous Na_2SO_4 , and evaporated to dryness yielding 1.00 g (95%) of **4** as a yellow oil: 1H NMR ($CDCl_3$, ppm, 269.6 MHz) δ 7.35 (d, 2 H, C_6H_4), 7.13 (t, 2 H, C_6H_4), 6.63 (t, 2 H, C_6H_4), 6.54 (d, 2 H, C_6H_4), 5.24 (t, 2 H, NH), 3.33 (dt, 4 H, NCH_2), 2.78 (t, 4 H, SCH_2), 2.27 (s, 6 H, SCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm, 67.7 MHz) δ 147.3, 133.7, 129.1, 120.0, 117.1, 109.8 (C_6H_4), 42.6 (NCH_2), 31.1 (SCH_2), 17.9 (SCH_3); MS (FD, CH_2Cl_2) m/z 364 [$'N_2H_2S_3'-Me_2'$] $^+$.

$'N_2H_2S_3'-Me_2 \cdot 2HCl$ (4·2HCl). Concentrated hydrochloric acid (0.20 mL, 2.40 mmol) was added to a solution of $'N_2H_2S_3'-Me_2$ (**4**) (0.20 g, 0.55 mmol) in MeOH (20 mL). Removal of the solvents gave a bright yellow residue, which was digested with CH_2Cl_2 (15 mL) and dried in vacuo yielding 0.22 g (91%) of **4·2HCl**: 1H NMR (CD_3OD , ppm, 269.6 MHz) δ 7.70–7.38 (m, 8 H, C_6H_4), 5.11 (s, br, 4 H, NH), 3.68 (t, 4 H, NCH_2), 3.08 (t, 4 H, SCH_2), 2.58 (s, 8 H, SCH_3); $^{13}C\{^1H\}$ NMR (CD_3OD , ppm, 67.7 MHz) δ 136.2, 133.5, 133.1, 131.0, 129.4, 124.2 (C_6H_4), 51.1 (NCH_2), 28.2 (SCH_2), 18.5 (SCH_3); MS (FD, MeOH) m/z 364 [$'N_2H_2S_3'-Me_2'$] $^+$. Anal. Calcd for $C_{18}H_{26}Cl_2N_2S_3$ (437.52): C, 49.41; H, 5.99; N, 6.40; S, 21.99. Found: C, 49.79; H, 6.19; N, 6.45; S, 22.18.

$[Fe('N_2H_2S_3')]_2$ (5). A light green solution of $FeCl_2 \cdot 4H_2O$ (0.19 g, 0.95 mmol) in MeOH (10 mL) was added to a yellow solution of $'N_2H_2S_3'-H_2$ (**3**) (0.32 g, 0.95 mmol) and LiOMe (1.9 mmol, 1.9 mL of a 1 M solution in MeOH) in MeOH (20 mL). The color of the solution changed to orange, and an orange solid precipitated. The solid was separated, washed with MeOH (20 mL), and dried in vacuo. During drying, the color of the solid changed from orange to green, yield 0.30 g (81%) of **5**: IR (KBr, cm^{-1}) 3240 w, br $\nu(NH)$; MS (FD, DMSO) m/z 334 [$'(N_2H_2S_3)'$] $^+$, 390 [$[Fe('N_2H_2S_3')]_2'$] $^+$; μ_{eff} (293 K) 4.14 μ_B . Anal. Calcd for $C_{32}H_{36}Fe_2N_4S_6$ (780.76): C, 49.23; H, 4.65; N, 7.18; S, 24.64. Found: C, 49.05; H, 4.60; N, 7.13; S, 24.53.

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[Fe(CO)(N₂H₂S₃')] (6). CO was bubbled through a suspension of [Fe(N₂H₂S₃')]₂ (**5**) (0.38 g, 0.49 mmol) in THF (30 mL) for 2 h. A green solid resulted which was separated, washed with THF (20 mL), and dried in vacuo yielding 0.42 g (97%) of **6**·0.33THF (**6** was obtained in equally high yields when the reaction mixture resulting in the synthesis of **5** is directly treated with CO for 2 h): IR (KBr, cm⁻¹) 3229 w, 3166 w ν(NH), 1932 vs ν(CO); ¹H NMR (DMSO-*d*₆, ppm, 269.6 MHz) δ 8.06 (s, br, 1 H, NH), 7.50–6.34 (m, 8 H, C₆H₄), 5.10 (d, 1 H, NH), 4.25–1.90 (m, 8 H, C₂H₄); ¹³C{¹H} NMR (DMSO-*d*₆, ppm, 67.7 MHz) δ 221.0 (CO), 152.9, 151.3, 148.0, 146.4, 129.1, 128.3, 125.3, 125.2, 120.8, 120.6, 119.5 (C₆H₄), 52.8, 52.1 (NCH₂), 35.2, 33.0 (SCH₂); MS (FD, DMSO) *m/z* 334 [(N₂H₂S₃')]⁺, 390 [Fe(N₂H₂S₃')]⁺, 780 [[Fe(N₂H₂S₃')]₂]⁺. Anal. Calcd for C₁₇H₁₈FeN₂O₃·0.33C₄H₈O (442.43): C, 49.77; H, 4.71; N, 6.33; S, 21.74. Found: C, 49.86; H, 4.74; N, 6.32; S, 21.60.

[Ru(CO)(PCy₃)(N₂H₂S₃')] (7). [Ru(H)(Cl)(CO)(PCy₃)₂] (1.08 g, 1.49 mmol) was added to a solution of N₂H₂S₃'-H₂ (**3**) (0.50 g, 1.49 mmol) and LiOMe (1.5 mmol, 1.5 mL of a 1 M solution in MeOH) in THF (40 mL). The reaction mixture was stirred for 3 d and yielded a green suspension. The gray-green solid was separated, washed with THF (10 mL), and dried in vacuo yielding 0.75 g (65%) of **7**·MeOH. IR (KBr, cm⁻¹) 3213, 3203 w ν(NH), 1935 s ν(CO); ¹H NMR (DMF-*d*₇, ppm, 269.6 MHz) δ 9.12 (s, 1 H, NH), 7.67–6.54 (m, 8 H, C₆H₄), 5.41 (s, 1 H, NH), 4.30–0.97 (m, 41 H, C₂H₄ and P(C₆H₁₁)₃ superimposed); ¹³C{¹H} NMR (DMSO-*d*₆, ppm, 67.7 MHz) δ 160.3, 160.0, 146.7, 131.6, 129.6, 126.2, 125.9, 125.3, 118.9, 118.7, 117.3 (C₆H₄), 51.8, 48.9 (NCH₂), 38.0, 37.7 (SCH₂), 29.3, 28.9, 27.3, 26.3 (br, P(C₆H₁₁)); ³¹P{¹H} NMR (DMF-*d*₇, ppm, 109.38 MHz) δ 47.8 (s, P(C₆H₁₁)); MS (FD, DMSO, ¹⁰²Ru) *m/z* 716 [Ru(PCy₃)(N₂H₂S₃')]⁺. Anal. Calcd for C₃₅H₅₁N₂PORuS₃·CH₃OH (776.09): C, 55.72; H, 7.14; N, 3.61; S, 12.40. Found: C, 55.45; H, 7.18; N, 3.62; S, 12.27.

[Ru(PPr₃)₂(N₂H₂S₃')] (8). [RuCl₂(PPr₃)₃] was synthesized in situ by treating a suspension of [RuCl₂(PPh₃)₃] (3.18 g, 3.32 mmol) in *n*-hexane (50 mL) with PPr₃ (4.0 mL, 20.0 mmol) for 20 h. The resulting green solution was filtered and evaporated to dryness. The green residue was suspended in MeOH (30 mL), combined with a solution of N₂H₂S₃'-H₂ (**3**) (1.12 g, 3.32 mmol) and LiOMe (6.65 mmol, 6.65 mL of a 1 M solution in MeOH) in MeOH (30 mL), and stirred for 3 d to yield a red suspension. The orange solid was separated, washed with MeOH and *n*-hexane (30 mL each), and dried in vacuo to yield 1.46 g (58%) of **8**: IR (KBr, cm⁻¹) 3289 w, 3227 w ν(NH); ¹H NMR (CD₂-Cl₂, ppm, 269.6 MHz): δ 7.60–6.50 (m, 8 H, C₆H₄), 5.88 (dd, 1 H, NH), 5.09 (s, br, 1 H, NH), 3.68–2.20 (m, 7 H, C₂H₄), 1.94–1.37 (m, 25 H, P(C₃H₇) and C₂H₄ superimposed), 0.95 (dt, 18 H, P(C₃H₇)); ¹³C{¹H} NMR (CD₂-Cl₂, ppm, 67.7 MHz) δ 155.3, 151.9, 148.6, 135.8, 135.7, 130.3, 126.5, 124.8, 124.7, 121.3, 118.9, 114.7 (C₆H₄), 59.6, 44.8 (NCH₂), 38.6, 31.8 (SCH₂), 32.3, 28.3 (d, P(CH₂CH₂CH₃)), 19.2, 18.0 (d, P(CH₂CH₂CH₃)), 16.4, 16.3 (d, P(CH₂CH₂CH₃)); ³¹P{¹H} NMR (CD₂-Cl₂, ppm, 109.38 MHz) δ 22.0 (d, 1 P, P(C₃H₇)), 17.3 (d, 1 P, P(C₃H₇)); MS (FD, DMSO, ¹⁰²Ru) *m/z* 756 [Ru(PPr₃)₂(N₂H₂S₃')]⁺, 596 [Ru(PPr₃)(N₂H₂S₃')]⁺. Anal. Calcd for C₃₄H₆₀N₂P₂RuS₃ (756.08): C, 54.01; H, 8.00; N, 3.71. Found: C, 54.20; H, 7.86; N, 3.50.

[Ru(PPr₃)(N₂H₂S₃')] (9). A red solution of [Ru(PPr₃)₂(N₂H₂S₃')] (**8**) (1.30 g, 1.72 mmol) in THF (40 mL) was refluxed for 4 h in the course of which the color changed to green-brown. The solution was cooled to room temperature and layered with *n*-hexane (40 mL). Green-brown crystals precipitated which were separated after 5 d, washed with THF (5 mL, 0 °C), and dried in vacuo to yield 0.46 g (42%) of **9**·0.5THF: IR (KBr, cm⁻¹) 3251 w ν(NH); ¹H NMR (CD₂-Cl₂, ppm, 269.6 MHz) δ 7.38–6.64 (m, 8 H, C₆H₄), 5.55 (s, 1 H, NH), 4.44 (s, 1 H, NH), 3.85–2.37 (m, 8 H, C₂H₄), 1.88–1.26 (m, 12 H, P(CH₂CH₂-CH₃)); 0.94 (t, 9 H, P(CH₂CH₂CH₃)); ³¹P{¹H} NMR (THF-*d*₈, ppm, 109.38 MHz) δ 31.6 ppm (s, P(C₃H₇)); MS (FD, CH₂Cl₂, ¹⁰²Ru) *m/z* 596 [Ru(PPr₃)(N₂H₂S₃')]⁺. Anal. Calcd for C₂₅H₃₉N₂PRuS₃·0.5C₄H₈O (631.90): C, 51.32; H, 6.86; N, 4.43. Found: C, 51.12; H, 7.09; N, 4.13.

[Ru(PPh₃)(N₂H₂S₃')] (10). [RuCl₂(PPh₃)₃] (0.65 g, 0.68 mmol) was added to a solution of N₂H₂S₃'-H₂ (**3**) (0.23 g, 0.68 mmol) and LiOMe (1.3 mmol, 1.3 mL of a 1 M solution in MeOH) in THF (20 mL). The reaction mixture was refluxed for 4 h to yield a green suspension, from which a yellow solid precipitated. The yellow precipitate was separated

at 20 °C, washed with THF and MeOH (20 mL each), and dried in vacuo yielding 0.25 g (50%) of **10**·0.5THF. IR (KBr, cm⁻¹) 3202 m, 3178 m ν(NH); ¹H NMR (CD₂-Cl₂, ppm, 269.6 MHz) δ 7.84–6.57 (m, 23 H, C₆H₄ and P(C₆H₅) superimposed), 5.36 (s, br, 1 H, NH), 4.46 (dd, 1 H, NH), 3.30–2.08 (m, 8 H, C₂H₄); ¹³C{¹H} NMR (CD₂-Cl₂, ppm, 67.7 MHz) δ 155.1, 148.3, 144.0, 136.9, 136.3 (C₆H₄), 134.0 (d, P(C₆H₅)), 133.9, 132.5, 130.6 (C₆H₄), 129.5 (s, br, P(C₆H₅)), 128.4 (d, P(C₆H₅)), 126.5, 126.4, 125.6, 121.6 (C₆H₄), 120.6 (d, P(C₆H₅)), 59.0, 51.1 (NCH₂), 42.5, 40.7 (SCH₂); ³¹P{¹H} NMR (CD₂-Cl₂, ppm, 109.38 MHz) δ 63.8 (s, P(C₆H₅)); MS (FD, CH₂Cl₂, ¹⁰²Ru) *m/z* 697 [Ru(PPh₃)(N₂H₂S₃')]⁺. Anal. Calcd for C₃₄H₃₃N₂PRuS₃·0.5C₄H₈O (733.95): C, 58.91; H, 5.08; N, 3.82; S, 13.11. Found: C, 58.92; H, 5.22; N, 3.81; S, 12.94.

[Ru(PPh₃)(N₂D₂S₃')] (10a). (a) A suspension of [Ru(PPh₃)(N₂H₂S₃')]·0.5THF (**10**·0.5THF) (0.09 g, 0.12 mmol) and D₂O (2.0 mL) in THF (20 mL) was refluxed for 5 h. After removal of the solvents, the yellow residue was characterized by IR spectroscopy (KBr) to be a mixture of **10** and [Ru(PPh₃)(N₂D₂S₃')] (**10a**).

(b) LiOMe (0.24 mmol, 0.24 mL of a 1 M solution in MeOH) and D₂O (1.0 mL) were added to a suspension of [Ru(PPh₃)(N₂H₂S₃')]·0.5THF (**10**·0.5THF) (0.09 g, 0.12 mmol) in THF (20 mL). The reaction mixture was refluxed for 1 h and then evaporated to dryness. The residue was redissolved in CH₂Cl₂ and the resulting green solution was filtered over filter pulp and evaporated to dryness to give 0.09 g (100%) of **10a**·0.5THF as a yellow powder: IR (KBr, cm⁻¹) 2385 m, br ν(ND); ¹H NMR (CD₂-Cl₂, ppm, 269.6 MHz) δ 7.84–6.57 (m, 23 H, C₆H₄ and P(C₆H₅) superimposed), 3.25–2.08 (m, 8 H, C₂H₄).

[Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂ (11). Under stirring, MeI (1.0 mL, 16 mmol) was added to a suspension of [Ru(PPh₃)(N₂H₂S₃')]·0.5THF (**10**·0.5THF) (0.27 g, 0.37 mmol) in THF (30 mL). The color of the suspension slowly changed from yellow to beige. The resulting beige solid was separated after 3 d, washed with THF (10 mL), and dried in vacuo to yield 0.32 g (82%) of **11**·THF: IR (KBr, cm⁻¹) 3180 w ν(NH); ¹H NMR (CD₂-Cl₂, ppm, 269.6 MHz) δ 8.95 (m, 2 H, NH), 7.88–7.13 (m, 23 H, C₆H₄ and P(C₆H₅) superimposed), 4.41 (m, 1 H, C₂H₄), 3.74–2.86 (m, 6 H, C₂H₄), 2.33 (s, 3 H, SCH₃), 1.92 (s, 3 H, SCH₃), 1.40 (m, 1 H, C₂H₄); ¹³C{¹H} NMR (CD₂-Cl₂, ppm, 67.7 MHz) δ 149.6, 149.2, 135.2, 134.1 (d), 133.6 (d), 133.0, 132.6, 131.4, 130.8, 130.2, 129.4, 129.1 (d), 126.9, 124.7 (C(aryl)), 54.1, 47.5 (NCH₂), 39.4 (d), 36.2 (SCH₂), 27.2, 26.4 (SCH₃); ³¹P{¹H} NMR (CD₂-Cl₂, ppm, 109.38 MHz) δ 33.8 (s, P(C₆H₅)); MS (FD, CH₂Cl₂, ¹⁰²Ru) *m/z* 727 [Ru(PPh₃)(N₂H₂S₃'-Me₂)]⁺, 712 [Ru(PPh₃)(N₂H₂S₃'-Me)]⁺, 697 [Ru(PPh₃)(N₂HS₃')]⁺. Anal. Calcd for C₃₆H₃₉I₂N₂PRuS₃·C₄H₈O (1053.88): C, 45.59; H, 4.50; N, 2.66; S, 9.13. Found: C, 45.74; H, 4.41; N, 2.64; S, 9.01.

[Ru(PPh₃)(N₂HS₃'-Me₂)]₂ (12). [Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂·THF (**11**·THF) (0.62 g, 0.59 mmol) was dissolved in N₂H₄ (5.0 mL). The yellow reaction mixture was stirred for 4 h and evaporated to dryness. The yellow residue was redissolved in CH₂Cl₂ (50 mL) and the CH₂-Cl₂ solution was filtered over filter pulp and evaporated to dryness. The resulting yellow powder was digested with MeOH (10 mL) and dried in vacuo to yield 0.47 g (90%) of **12**·MeOH: IR (KBr, cm⁻¹) 3124 w, br ν(NH); ¹H NMR (DMSO-*d*₆, ppm, 269.6 MHz) δ 7.80 (dd, 1 H, CH(aryl)), 7.71 (d, 1 H, CH(aryl)), 7.58 (s, 1 H, NH), 7.50–7.08 (m, 17 H, CH(aryl)), 6.94 (dt, 1 H, CH(aryl)), 6.85 (dd, 1 H, CH(aryl)), 6.23 (d, 1 H, CH(aryl)), 6.09 (t, 1 H, CH(aryl)), 3.41–2.76 (m, 6 H, C₂H₄), 2.37–2.20 (m, 1 H, C₂H₄), 2.16, 1.97 (s, 3 H each, CH₃), 1.94–1.79 (m, 1 H, C₂H₄); ¹³C{¹H} NMR (DMSO-*d*₆, ppm, 67.7 MHz) δ 158.9, 146.9, 136.1 (d) (C₆H₄), 133.1, 132.3 (d, P(C₆H₅)), 131.5, 131.2, 130.6 (C₆H₄), 130.2 (s, br, P(C₆H₅)), 129.3, 128.7 (C₆H₄), 128.2 (d, P(C₆H₅)), 127.2, 119.6, 111.4, 110.3 (C₆H₄), 57.5, 48.4 (NCH₂), 40.5, 34.2 (SCH₂), 27.4, 21.9 (d) (SCH₃); ³¹P{¹H} NMR (DMSO-*d*₆, ppm, 109.38 MHz) δ 43.7 (s, P(C₆H₅)); MS (FD, DMSO, ¹⁰²Ru) *m/z* 727 [Ru(PPh₃)(N₂HS₃'-Me₂)]⁺, 712 [Ru(PPh₃)(N₂HS₃'-Me)]⁺, 698 [Ru(PPh₃)(N₂H₂S₃')]⁺. Anal. Calcd for C₃₆H₃₈I₂N₂PRuS₃·CH₃OH (885.91): C, 50.16; H, 4.78; N, 3.16; S, 10.86. Found: C, 50.42; H, 4.94; N, 3.18; S, 10.52.

[Ru(PPh₃)(N₂H₂S₃'-Me₂)](I)(Cl) from 12 and HCl. Hydrochloric acid (0.50 mmol, 5 mL of a 0.1 M solution of HCl in H₂O) was added to a solution of [Ru(PPh₃)(N₂HS₃'-Me₂)]₂·MeOH (**12**·MeOH) (0.048 g, 0.054 mmol) in CH₂Cl₂ (15 mL). The reaction mixture was stirred

Table 1. Selected Crystallographic Data for [Fe(N₂H₂S₃')₂·4MeOH (5·4MeOH), [Fe(CO)(N₂H₂S₃') (6), [Ru(PPr₃)(N₂H₂S₃')·2THF (9·2THF), and [Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂·2CH₂Cl₂ (11·2CH₂Cl₂)

compd	5·4MeOH	6	9·2THF	11·2CH ₂ Cl ₂
formula	C ₃₆ H ₅₂ Fe ₂ N ₄ O ₄ S ₆	C ₁₇ H ₁₈ FeN ₂ OS ₃	C ₃₃ H ₅₅ N ₂ O ₂ PRuS ₃	C ₃₈ H ₄₃ Cl ₄ I ₂ N ₂ PRuS ₃
fw	908.88	418.36	740.01	1151.56
crystal size, mm ³	0.5 × 0.5 × 0.5	0.8 × 0.4 × 0.2	0.4 × 0.4 × 0.2	0.5 × 0.4 × 0.4
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , pm	976.3(3)	813.6(8)	1053.7(3)	3313(1)
<i>b</i> , pm	1025.5(4)	1141(2)	2443.7(7)	1625.2(5)
<i>c</i> , pm	1160.7(6)	1987(2)	1453.1(7)	1718.5(7)
α , deg	114.01(4)	90	90	90
β , deg	95.03(3)	95.36(7)	102.35(3)	109.24(5)
γ , deg	95.23(3)	90	90	90
<i>V</i> , nm ³	1.0471(8)	1.836(3)	3.655(2)	8.736(6)
<i>Z</i>	1	4	4	8
λ , pm	71.073	71.073	71.073	71.073
<i>d</i> _{calc} , g/cm ⁻³	1.441	1.514	1.345	1.751
μ , mm ⁻¹	1.034	1.169	0.675	2.227
2 θ range, deg	4 ≤ 2 θ ≤ 48	4 < 2 θ < 54	4 ≤ 2 θ ≤ 54	4 < 2 θ < 48
meas reflections	4287	5010	12031	18249
indep reflections	3291	4030	8036	6895
obsd reflections	2677	2741	3914	5063
refined parameters	339	217	535	460
<i>R</i> ₁ (w <i>R</i> ₂), ^{a,b} %	3.60 (10.52)	4.15 (14.24)	4.29 (8.89)	3.61 (9.04)
<i>q</i> ^b	0.0693	0.0639	0.0246	0.0515
<i>r</i> ^b		1.0635		

^a $R_1 = [\sum ||F_o| - |F_c|| / \sum |F_o|]$ for $F > 4\sigma(F)$. ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (qP)^2 + rP]$ and $P = (F_o^2 + 2F_c^2)/3$.

for 5 min. Removal of the solvents yielded a yellow powder, which was identified by ¹H NMR spectroscopy as [Ru(PPh₃)(N₂H₂S₃'-Me₂)](Cl) (I)(Cl).

[Ru(NO)(N₂HS₃') (13). [RuCl₃(NO)(PPh₃)₂] (0.648 g, 0.85 mmol) was added to a solution of N₂H₂S₃'-H₂ (3) (0.285 g, 0.85 mmol) and LiOMe (2.55 mmol, 2.55 mL of a 1 M solution in MeOH) in THF (25 mL). The reaction mixture was stirred for 14 h to yield a green suspension. The deep green opalescent precipitate was separated, washed with MeOH and THF (20 mL each), and dried in vacuo to yield 0.287 g (67%) of 13·0.5THF: IR (KBr, cm⁻¹) 3228 m ν (NH), 1799 vs ν (NO); ¹H NMR (DMSO-*d*₆, ppm, 269.6 MHz) δ 7.20 (d, 1 H, C₆H₄), 7.00–6.73 (m, 6 H, C₆H₄ and NH), 6.49 (d, 1 H, C₆H₄), 6.39 (t, 1 H, C₆H₄), 4.15–2.64 (m, 8 H, C₂H₄); ¹³C{¹H} NMR (DMSO-*d*₆, ppm, 67.7 MHz) δ 159.2, 145.6, 145.4, 137.7, 128.9, 127.1, 126.5, 125.0, 122.8, 122.0, 115.7, 110.0 (C₆H₄), 58.5, 54.8 (NCH₂), 39.2, 34.7 (SCH₂); MS (FD, DMSO, ¹⁰²Ru) *m/z* 465 [Ru(NO)(N₂HS₃')⁺. Anal. Calcd for C₁₆H₁₇N₃ORuS₃·0.5C₄H₈O (500.65): C, 43.18; H, 4.23; N, 8.39; S, 19.21. Found: C, 43.22; H, 4.27; N, 8.26; S, 18.94.

[Ru(NO)(N₂H₂S₃')BF₄ (14). HBF₄ (1.63 mmol, 0.225 mL of a 54% solution in Et₂O) was added to a green suspension of [Ru(NO)(N₂HS₃')·0.5THF (13·0.5THF) (0.816 g, 1.63 mmol) in Et₂O (40 mL) and stirred for 14 h. A red solid precipitated, which was separated, washed with Et₂O (40 mL), and dried in vacuo to yield 0.890 g (99%) of 14. ¹³C{¹H} and ¹H NMR spectra showed that the red solid contained a 1:1 mixture of two diastereomers of 14. IR (KBr, cm⁻¹) 3202 w, br, 3169 w ν (NH), 1856 vs ν (NO), 1084 s ν (BF₄); ¹H NMR (DMSO-*d*₆, ppm, 269.6 MHz) δ 9.97 (d, 0.5 H, NH), 8.64 (s, 0.5 H, NH), 7.99 (d, 0.5 H, NH), 7.39 (s, 0.5 H, NH), 7.70–6.90 (m, 8 H, C₆H₄), 4.80–2.70 (m, 8 H, C₂H₄); ¹³C{¹H} NMR (DMSO-*d*₆, ppm, 67.7 MHz) δ 150.0, 147.2, 146.7, 145.2, 145.1, 142.6, 141.5, 141.1, 129.5, 129.3, 128.8, 128.7, 128.4, 128.3, 128.0, 127.7, 127.0, 125.4, 124.0, 123.9, 123.7, 122.7 (C₆H₄), 63.6, 59.3, 57.1, 51.5 (NCH₂), 39.3, 37.0, 36.2, 36.0 (SCH₂); MS (FD, DMSO, ¹⁰²Ru) *m/z* 465 [Ru(NO)(N₂HS₃')⁺. Anal. Calcd for C₁₆H₁₈BF₄N₃ORuS₃ (552.41): C, 34.79; H, 3.28; N, 7.61; S, 17.41. Found: C, 34.75; H, 3.31; N, 7.38; S, 17.34.

X-ray Structure Analyses of [Fe(N₂H₂S₃')₂·4MeOH (5·4MeOH), [Fe(CO)(N₂H₂S₃') (6), [Ru(PPr₃)(N₂H₂S₃')·2THF (9·2THF), and [Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂·2CH₂Cl₂ (11·2CH₂Cl₂). Black columns of [Fe(N₂H₂S₃')₂·4MeOH (5·4MeOH) were obtained by layering a solution of N₂H₂S₃'-H₂ (3) (0.16 g, 0.48 mmol) and LiOMe (0.95 mmol, 0.95 mL of a 1 M solution in MeOH) in MeOH (80 mL) with a solution

of FeCl₂·4H₂O (0.95 g, 0.48 mmol) in MeOH (80 mL). Brown columns of [Fe(CO)(N₂H₂S₃') (6) formed when a saturated solution of 6 in a 1:1 mixture of MeOH and THF was layered with Et₂O under an atmosphere of CO. Brown plates of [Ru(PPr₃)(N₂H₂S₃')·2THF (9·2THF) crystallized from a saturated THF solution of 9 which was layered with *n*-hexane. Yellow plates of [Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂·2CH₂Cl₂ (11·2CH₂Cl₂) were grown from a saturated solution of 11 in CH₂Cl₂ by slowly evaporating the solvent. Suitable single crystals were sealed under N₂ in glass capillaries and data were collected with a Siemens P4 diffractometer at 200 K. The structures were solved by direct methods (SHELXTL-PLUS).¹³ Full-matrix least-squares refinement was carried out on *F*² values (SHELXL-93).¹⁴ The hydrogen atoms were located in a difference Fourier synthesis and either restricted during refinement (6, 11) or isotropically refined (5, 9). Complex 5 crystallizes with four molecules of MeOH, 11 with two molecules of CH₂Cl₂, and 9 with two molecules of THF per unit. The hydrogen atoms of the THF molecules in 9·2THF and of the CH₂Cl₂ molecules of 11·2CH₂Cl₂ were calculated for ideal geometries. Their isotropic temperature factors were fixed at 1.5 times the *U*_{eq} value of the preceding carbon atom. Table 1 contains selected crystallographic data of [Fe(N₂H₂S₃')₂·4MeOH (5·4MeOH), [Fe(CO)(N₂H₂S₃') (6), [Ru(PPr₃)(N₂H₂S₃')·2THF (9·2THF), and [Ru(PPh₃)(N₂H₂S₃'-Me₂)]₂·2CH₂Cl₂ (11·2CH₂Cl₂).

Results and Discussion

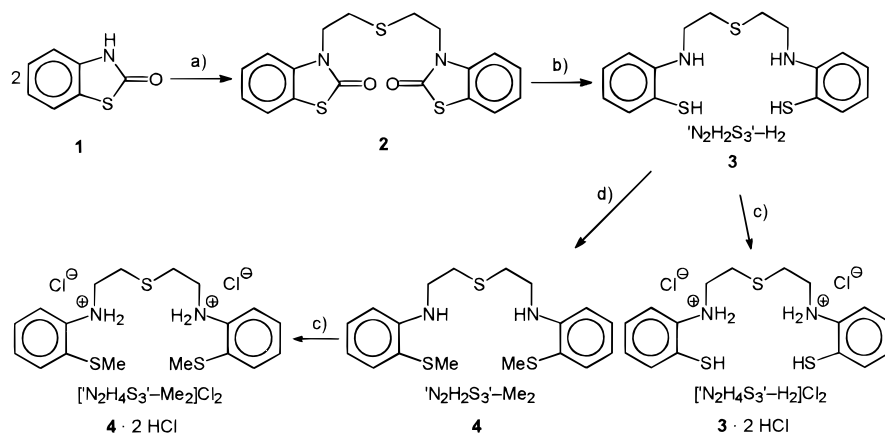
Syntheses of Ligands. The requirement of having terminal thiolate functions in the target ligand N₂H₂S₃'²⁻ necessitated the development of the synthesis route shown in Scheme 1.

Deprotonation of 2(3*H*)-benzothiazolone (1) by *n*-BuLi and subsequent treatment with bis(2-bromoethyl)sulfide yielded 2 as the major product. The ¹H NMR spectrum of the crude product indicated that byproducts resulting from O-alkylation of 1 had also formed.¹⁵ These byproducts could readily be removed by extraction with EtOH. The remaining 2 proved

(13) SHELXTL-PLUS for Siemens Crystallographic Research Systems, Release 4 21/V, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.

(14) Sheldrick, G. M. SHELXL-93, Program for crystal structure refinement, Universität Göttingen, 1993.

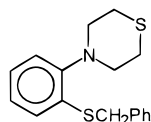
(15) Klein, G.; Priejs, B. *Helv. Chim. Acta* **1954**, *37*, 2057.

Scheme 1. Synthesis of $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ and Its Derivatives^a

^a Key: (a) $+2n\text{-BuLi}$, $+\text{S}(\text{C}_2\text{H}_4\text{Br})_2$, THF, reflux, 14 h; (b) (1) $+\text{NaOH}$, EtOH/H₂O, reflux, 14 h, (2) $+\text{HCl}$; (c) $+\text{HCl}$, MeOH; (d) $+2\text{LiOMe}$, $+\text{exc. MeI}$, 16 h.

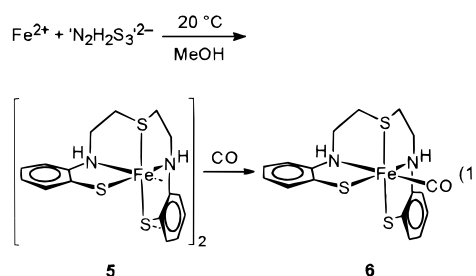
soluble in CH_2Cl_2 and THF and was characterized by spectroscopic methods and elemental analysis. The CO group ^{13}C NMR signal ($\delta = 169.9$ ppm) and the $\nu(\text{CO})$ IR band (1678 cm^{-1}) proved particularly suitable to confirm the N-alkylation of 1. Alkaline hydrolysis of 2 and subsequent acidification yielded 3 as a highly viscous yellow oil which could be purified via the white dihydrochloride $[\text{'N}_2\text{H}_4\text{S}_3\text{'-H}_2]\text{Cl}_2$ (3 · 2HCl). For the syntheses of complexes, 3 could be used without further purification. Successive treatment of 3 with LiOMe and MeI yielded the dimethyl derivative $\text{'N}_2\text{H}_2\text{S}_3\text{'-Me}_2$ (4).

The facile alkylation of the thiol functions of 3 illustrates the necessity to provide an efficient protective group for the sulfur functions, which are to become thiol groups in the synthesis of 3. Accordingly, numerous attempts to obtain the target ligand 3 via other routes remained unsuccessful. For example, template alkylations of doubly deprotonated 2-aminothiophenol bound to $[\text{Fe}(\text{CO})_2]^{2+}$ fragments yielded untractable materials. Benzylation of the thiol function in 2-aminothiophenol and subsequent treatment of the resulting 2-benzylthioaniline with $\text{S}(\text{C}_2\text{H}_4\text{Br})_2$ led to 2-fold alkylation of the NH_2 group and formation of 4-(2-benzylthiophenyl)-thiomorpholine.¹⁶



Syntheses of Complexes. The reaction between Fe(II) salts and the $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ anion obtained by deprotonation of 3 with LiOMe yielded green $[\text{Fe}(\text{'N}_2\text{H}_2\text{S}_3\text{'})_2]$ (5) (eq 1). In solid state, 5 is dinuclear (X-ray diffraction) and paramagnetic (μ_{eff} (293 K) = $4.14\ \mu_{\text{B}}$). The paramagnetism of 5 is compatible with four unpaired electrons at the Fe centers, whose spins partially couple via Fe–S–Fe bridges. In solution (THF or MeOH), 5 proved unreactive toward N_2H_4 , NEt_3 , PMe_3 , and also N_2 , but readily added CO to give diamagnetic green $[\text{Fe}(\text{CO})(\text{'N}_2\text{H}_2\text{S}_3\text{'})]$ (6). The molecular structure of 6 was determined by X-ray diffraction.

The low frequency $\nu(\text{CO})$ IR band of 6 (1932 cm^{-1} in KBr) indicates strong Fe–CO π -back bonding, and solid 6 is indeed stable at room temperature for unlimited periods of time. Therefore, it was surprising to observe that 6 is labile in solution and slowly loses CO to regenerate 5.



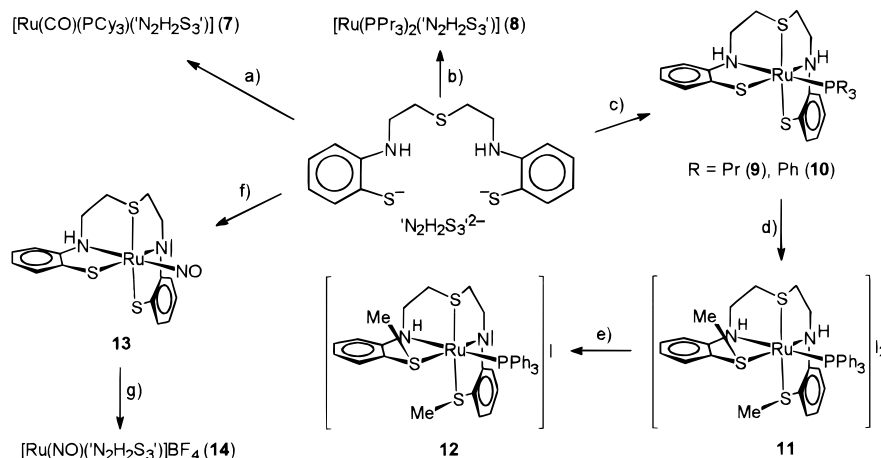
The unexpected lability of 6 prompted us to search for less labile ruthenium complexes of 3 (Scheme 2). All efforts to obtain the ruthenium analogue of 6, $[\text{Ru}(\text{CO})(\text{'N}_2\text{H}_2\text{S}_3\text{'})]$, from ruthenium carbonyl precursor complexes and $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ remained as yet unsuccessful. Precursor complexes such as $[\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PCy}_3)_2]$ or $[\text{RuCl}_2(\text{CO})_3(\text{THF})]$ ^{17,18} proved too inert to exchange all ligands except one CO for the $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ donors. For example, the reaction of $[\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PCy}_3)_2]$ with $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ yielded green $[\text{Ru}(\text{CO})(\text{PCy}_3)(\text{'N}_2\text{H}_2\text{S}_3\text{'})]$ (7), whose composition suggests that $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ acts as tetradentate ligand only. Complex 7 proved so stable that it did not lose PCy_3 or CO even when heated for 14 h in refluxing THF.

Phosphine complexes such as $[\text{RuCl}_2(\text{PR}_3)_3]$ ($\text{R} = \text{Pr}, \text{Ph}$) proved more reactive toward $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$. At room temperature, the reaction of $[\text{RuCl}_2(\text{PPr}_3)_3]$ with $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ yielded orange $[\text{Ru}(\text{PPr}_3)_2(\text{'N}_2\text{H}_2\text{S}_3\text{'})]$ (8), in which the $\text{'N}_2\text{H}_2\text{S}_3\text{'-H}_2$ ligand again probably utilizes only four of its five donors. However, 8 is readily converted into green-brown $[\text{Ru}(\text{PPr}_3)(\text{'N}_2\text{H}_2\text{S}_3\text{'})]$ (9) in boiling THF. The C_1 symmetrical structure of 9 and 10 indicated in Scheme 2 was concluded from NMR spectra and could be confirmed for 9 by X-ray structure analysis. Complexes 9 and 10 proved inert toward substitution of the remaining PR_3 ligands with CO, N_2H_4 , N_2 , or other PR_3 ligands. In an attempt to labilize the Ru– PR_3 bonds via alkylation of the thiolate donors, 10 was treated with MeI and yielded beige $[\text{Ru}(\text{PPh}_3)(\text{'N}_2\text{H}_2\text{S}_3\text{'-Me}_2)]_2$ (11). The molecular structure of 11 could be elucidated by X-ray structure determination, but the PPh_3 ligand in 11 proved as inert to substitution as that in 10. In the respective experiments, however, it was observed that Brønsted bases such as N_2H_4 caused deprotonation of one amine function of the $\text{'N}_2\text{H}_2\text{S}_3\text{'-Me}_2$ ligand of 11. The monoiodide $[\text{Ru}(\text{PPh}_3)(\text{'N}_2\text{HS}_3\text{'-Me}_2)]\text{I}$ (12) resulted which contains one amide donor (Scheme 2, reaction e). A similar deprotonation of amine functions was

(16) Cf.: Helfrich, O. B.; Reid, E. E. *J. Am. Chem. Soc.* **1920**, *42*, 1226.

(17) Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1967**, 1238.

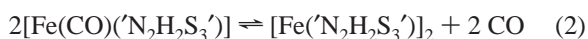
(18) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466.

Scheme 2. Synthesis of [Ru('N₂H₂S₃') Complexes^a

^a Key: (a) + [Ru(H)(Cl)(CO)(PCy₃)₂], THF, 3 d; (b) + [RuCl₂(PPR₃)₃], MeOH, 3 d; (c) + [RuCl₂(PR₃)₃] (R = Pr, Ph), THF, reflux, 4 h; (d) + exc. MeI, THF, 3 d; (e) + N₂H₄; (f) + [RuCl₃(NO)(PPh₃)₂], + LiOMe, MeOH/THF, 14 h; (g) + HBF₄, Et₂O.

observed when the nitrosyl complex [RuCl₃(NO)(PPh₃)₂] was treated with 'N₂H₂S₃'-H₂ in the presence of 3 equiv of LiOMe. Deep green [Ru(NO)('N₂HS₃') (13) ($\nu(\text{NO}) = 1799 \text{ cm}^{-1}$) formed, which is neutral and diamagnetic and contains the trianionic 'N₂HS₃'³⁻ ligand. Subsequent treatment of 13 with HBF₄ yielded red [Ru(NO)('N₂H₂S₃')BF₄ (14) ($\nu(\text{NO}) = 1856 \text{ cm}^{-1}$) and showed that the amine deprotonation is reversible. In accordance with expectations, the protonation of 13 to yield 14 shifts the $\nu(\text{NO})$ band to higher frequencies.

Substitution and Acid–Base Reactions. The lability of [Fe(CO)('N₂H₂S₃') (6) toward CO dissociation and the resulting formation of the dinuclear [Fe('N₂H₂S₃')₂ (5) can be regarded as substitution of CO by thiolate ligands. This reaction is plausibly explained by the equilibrium according to eq 2. The formation of the sparingly soluble dinuclear 5 most likely serves as driving force. It precipitates from solution and shifts the equilibrium to the right side. The favored formation of the dinuclear 5 could also explain why the attempts to obtain [Fe(L)('N₂H₂S₃') derivatives with L = N₂H₄, NH₃, N₃⁻ remained unsuccessful.



In contrast to the labile [Fe(CO)('N₂H₂S₃')], the ruthenium complexes [Ru(PR₃)('N₂H₂S₃') (R = Pr (9), Ph (10)) and [Ru(NO)('N₂HS₃') (13) proved extremely inert to substitution. The PPh₃ ligand in 10 could be substituted by CO neither under elevated pressure (50 bar, 20 °C, 2 d) nor by treatment with hydrazine as solvent (40 °C, 1 d). Attempts to nucleophilically attack the NO ligand in [Ru(NO)('N₂HS₃') (13) with N₂H₄ or NEt₄N₃ in boiling THF or MeOH also remained unsuccessful. A possible reason for this inertness to substitution is, in addition to the inherent kinetic stability of ruthenium complexes, the Brønsted acidity of the 'N₂H₂S₃'²⁻ amine functions. The NH Brønsted acidity was indicated by the deprotonation of the 'N₂H₂S₃'-Me₂ ligand, when 11 was treated with N₂H₄, and it could subsequently be observed for 'N₂H₂S₃'²⁻ in the formation of the NO complex 13.

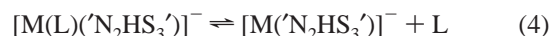
The Brønsted acid–base reactions could further be established by H⁺/D⁺ exchange reactions. Addition of D₂O to THF solutions of [Fe(CO)('N₂H₂S₃') (6) spontaneously yielded [Fe(CO)('N₂D₂S₃') (6a). The H⁺/D⁺ exchange of the ruthenium complex [Ru(PPh₃)('N₂H₂S₃') (10) was rather slow with neutral D₂O (in THF), but highly accelerated by addition of base (LiOMe) and yielded [Ru(PPh₃)('N₂D₂S₃') (10a). [Ru(PPh₃)-

('N₂H₂S₃'-Me₂)]₂ (11) and [Ru(NO)('N₂H₂S₃')BF₄ (14) spontaneously exchanged with D⁺ from D₂O. In these two cases, the corresponding amide complexes could also be isolated. Addition of Brønsted bases such as N₂H₄ and NEt₄N₃ to solutions of 11 and 14 gave [Ru(PPh₃)('N₂HS₃'-Me₂)]I (12) and [Ru(NO)('N₂HS₃') (13), respectively.

These results show that the amine NH donors of [M(L)-('N₂H₂S₃') complexes can be reversibly deprotonated to give amide donors according to the equilibrium of eq 3.



The formation of the amide species [M(L)('N₂HS₃')⁻ can have two opposite consequences with respect to the M–L bond: (1) The M–L bond can be labilized because the amide donor stabilizes a coordinatively unsaturated species via π donation, resulting from M–L bond dissociation according to eq 4.¹⁹ (2) In the opposite case, and this could be favored when L is a π acceptor, the M–L bond is stabilized by exactly the same effect of π donation from the amide donor.^{6b}



For the complexes described here, apparently the second alternative prevails. It also explains why the NO ligand in [Ru(NO)('N₂H₂S₃')BF₄ (14), which shows a high-frequency $\nu(\text{NO})$ at 1856 cm⁻¹, is unsusceptible to nucleophilic attack by N₂H₄ or azide ions. The primary reaction is a deprotonation of 14 to give 13, whose $\nu(\text{NO})$ of 1799 cm⁻¹ indicates a relatively high electron density at the NO ligand.

The investigation of the protonation/deprotonation reactions of [Ru(PPh₃)('N₂HS₃'-Me₂)]I (12) and [Ru(NO)('N₂HS₃') (13) further revealed that the attack of the amide donors by H⁺ can be influenced by the ligands L so that it occurs in a stereocontrolled manner. ¹³C{¹H} and ¹H NMR spectra (see below) showed that protonation of 12 by HCl yielded only one stereoisomer of [Ru(PPh₃)('N₂H₂S₃'-Me₂)](I)(Cl). However, the protonation of [Ru(NO)('N₂HS₃') (13) (with HBF₄) resulted in a 1:1 mixture of two diastereomers of [Ru(NO)('N₂H₂S₃')]-BF₄. These findings are explained by the chirality of the complexes, which allows the protons to approach the amide donors from two distinguishable ("front" or "back") sides. In 12, which exhibits the sterically demanding PPh₃ ligand and

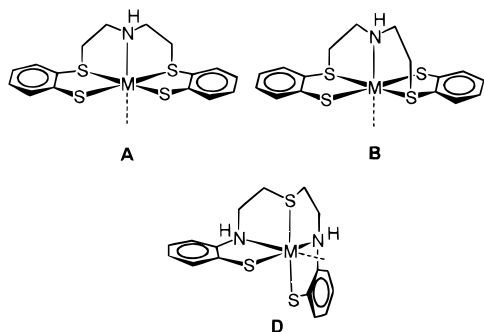
(19) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, 2, 1.

The Ru–N and Ru–S distances of **9** and **11** are in the range expected for Ru(II) complexes. The comparison of **9** with **11**, which contains only thioether S donors, shows that the Ru–S distances do not allow an unambiguous differentiation between Ru–S(thiolate) and Ru–S(thioether) distances. This certainly reflects the electronic flexibility of thiolate and thioether S donors which can exhibit σ -donor, σ -donor– π -acceptor as well as σ -donor– π -donor properties.²⁰ Therefore, the Ru–P distance in **11** (235.6(2) pm), which is markedly longer than that in **9** (225.7(2) pm), may be due not only to a higher steric demand of PPh₃ vs PPr₃ but also to the decreased electron density at the ruthenium center of **11** which carries three potentially π -accepting thioether donors.

Conclusion

The new pentadentate 'N₂H₂S₃'-H₂ ligand has been synthesized, aiming at transition metal complexes which exhibit electron rich-metal centers, possess core configurations with thiolate, thioether, and amine donors relating to the structures of [Fe('NHS₄')] fragments, and bind biologically relevant small molecules.

The goal of increasing the electron density at the metal centers by replacing thioether S by amine N donors in pentadentate thiolate thioether amine ligands could be reached. This is evidenced by the $\nu(\text{CO})$ frequencies of [Fe(CO)('N₂H₂S₃')] (1932 cm⁻¹) vs [Fe(CO)('NHS₄')] (1960 cm⁻¹). However, the metal donor core configurations of [M('NHS₄')] and [M('N₂H₂S₃')] complexes strongly differ. While [M('NHS₄')] complexes exhibit either structure **A** or **B** (cf. introduction), all [M('N₂H₂S₃')] complexes characterized so far invariably show the structure **D**. A major geometric difference between these structures is



the fac–fac coordination of the 'NHS₄'²⁻ ligand versus the fac–mer coordination of the 'N₂H₂S₃'²⁻ ligand. This structural difference complicates direct comparison between [M(L)('NHS₄')] and [M(L)('N₂H₂S₃')] complexes and may explain some unexpected results. For example, [Fe(CO)('N₂H₂S₃')]

(20) Sellmann, D.; Geck, M.; Knoch, F.; Ritter, G.; Dengler, J. *J. Am. Chem. Soc.* **1991**, *113*, 3819.

readily loses its CO ligand though its low frequency $\nu(\text{CO})$ indicates strong Fe–CO π -back bonding, whereas [Fe(CO)('NHS₄')] is practically inert toward loss of CO. With regard to the labile CO binding, it was not unexpected to be found that N₂ could not be coordinated. Another important difference between the [M(L)('N₂H₂S₃')] and [M(L)('NHS₄')] complexes is the relatively high acidity of the (aromatic) NH functions in the [M(L)('N₂H₂S₃')] complexes. The NH acidity was proved by H⁺/D⁺ exchange reactions and isolation of conjugate acid–base complex couples. The NH acidity also influences the substitution properties of the M–L bonds via intermediate formation of amide complexes. For example, when L is a strong electron withdrawing ligand such as NO in [Ru(NO)('N₂H₂S₃')]-BF₄, one NH function is easily deprotonated by bases such as N₂H₄ or by azide ions. As a consequence, the NO ligand in the resulting [Ru(NO)('N₂H₂S₃')] becomes unsusceptible for attack by nucleophiles. Similar effects have been observed with Fe, Ni, and Ru complexes which contain [M('N₂H₂S₂')] fragments ('N₂H₂S₂'²⁻ = 1,2-ethanediamino-*N,N'*-bis(2-benzenethiolato)-(2-)).²¹ The resulting coordination geometry and, in addition, acid–base reactions of the amine functions drastically reduce the versatility of the [Fe('N₂H₂S₃')] or [Ru('N₂H₂S₃')] fragments with respect to coordination and/or substitution of small coligand molecules. In particular, the cis coordination of the thiolate donors in [M('N₂H₂S₃')] fragments is unsuited to effect a stabilization of the unstable diazene molecule via [M⁺⁺–NH[–]–NH[–]–M] four-center/six-electron π bonds and tricentric N–H[–](S)₂ bridges. This stabilization has been observed in complexes such as [μ -N₂H₂{Fe('NHS₄')}]₂⁵ or [μ -N₂H₂{Ru(PPh₃)('S₄')}]₂,²² and it imperatively requires trans-thiolate donors at the metal centers.

Acknowledgment. Support of this work by the Fonds der chemischen Industrie is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data, in CIF format, for compounds **5**·4MeOH, **6**, **9**·2THF, and **11**·2CH₂Cl₂ are available on the Internet. Access information is given on any current masthead page. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as depository nos. 104537 (**5**·4MeOH), 104538 (**6**), 104539 (**9**·2THF), and 104540 (**11**·2CH₂Cl₂). Copies of the data can be obtained free of charge upon application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int.code +44(1223)336–033, e-mail: deposit@chemcris.cam.ac.uk].

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