Transition-Metal Complexes with Sulfur Ligands. 132.[1] Electron-Rich Fe and Ru Complexes with [MN_2S_3] Cores Containing the New Pentadentate Ligand $'N_2H_2S_3'^{2-}$ (= 2,2′-Bis(2-mercaptophenylamino)diethyl Sulfide(2−))

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The new pentadentate amine thioether thiolate ligand $'N_2H_2S_3'$-H_2 (= 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 $'N_2H_2S_3'^{2-}$ with Fe^{2+} yielded the dinuclear high-spin complex [Fe($'N_2H_2S_3'$)]$_2$ (**5**). Complex **5** added CO to give the low-spin complex [Fe(CO)($'N_2H_2S_3'$)] (**6**) whose low frequency ν(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 $'N_2H_2S_3'^{2-}$ yielded [Ru(CO)(PCy_3)($'N_2H_2S_3'$)] (**7**), [Ru(PPr_3)$_2$($'N_2H_2S_3'$)] (**8**), [Ru(PR_3)($'N_2H_2S_3'$)] (R = Pr (**9**), Ph (**10**)), and [Ru(NO)($'N_2HS_3'$)] (**13**). In complexes **7** and **8**, $'N_2H_2S_3'^{2-}$ acts as a tetradentate ligand. When heated in solution, complex **8** dissociates one PPr_3 ligand to give **9**. Complex **13** contains the trisanionic $'N_2HS_3'^{3-}$ resulting from deprotonation of one amine NH function. All [Ru(L)($'N_2H_2S_3'$)] complexes proved inert toward dissociation of the Ru−L bonds. The NH functions of [M(L)($'N_2H_2S_3'$)] complexes are acidic and show H^+/D^+ exchange reactions with D_2O. Methylation of the thiolate donors in **10** yielded the thioether derivative [Ru(PPh_3)($'N_2H_2S_3'$-Me_2)]I_2 (**11**) whose PPh_3 ligand is as inert to substitution as that of **10**. Complex **11** can reversibly be deprotonated to give [Ru(PPh_3)($'N_2HS_3'$-Me_2)]I (**12**). NMR spectroscopic investigations showed that the deprotonation/protonation reactions of **11** and **12** are stereoselective. In contrast, protonation of **13** with HBF_4 gives two diastereomers of the corresponding [Ru(NO)($'N_2H_2S_3'$)]BF_4 salt (**14**). X-ray structure analyses of **5**, **6**, **9**, and **11** and NMR spectra showed that the $'N_2H_2S_3'^{2-}$ ligand and its derivatives bind to the metal centers in the same fashion which combines fac and mer coordination of the donor atoms. The [MN_2S_3] cores of all complexes have an analogous C_1 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($'NHS_4'$)] fragment ($'NHS_4'^{2-}$ = 2,2′-bis(2-mercaptophenylthio)-diethylamine(2−)) was found to bind the key molecules of N_2 fixation, N_2H_2, N_2H_4, and NH_3,[5] but not N_2.

The [Fe($'NHS_4'$)] fragment demonstrated the importance of the core structures for binding and/or stabilization of the coligands. The [Fe($'NHS_4'$)] fragment exists in the two diastereomeric forms **A** and **B**. While **A** binds only σ ligands such as NH_3, N_2H_4, or MeOH, **B** binds only $\sigma-\pi$ ligands such as CO, PMe_3, or diazene, N_2H_2.[5,6] In the diazene complex, the trans coordination of the thiolate donors in **B** proved pivotal for the stabilization of N_2H_2, because it renders possible strong bifurcated N−H···(S)$_2$ bridges in the [FeN_2H_2Fe] unit of the binuclear [μ-N_2H_2{Fe($'NHS_4'$)}$_2$] according to **C**.

Because almost all stable N_2 complexes exhibit electron-rich metal centers,[7] a major factor for the binding of N_2 can be considered a high electron density at the metal center. Whereas the ν(CO) frequency of [Fe(CO)($'NHS_4'$)] (1960 cm^{-1}) indicates

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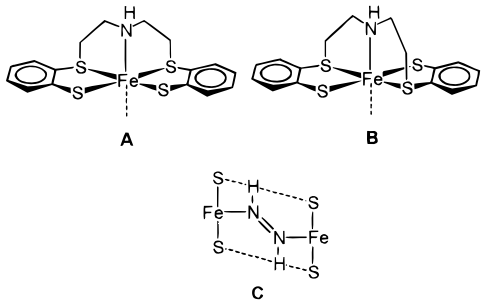
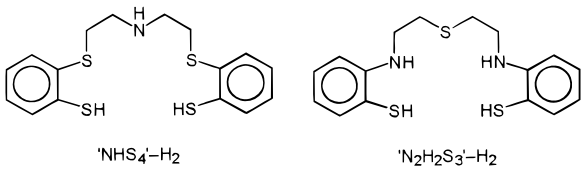


a relatively high electron density of the Fe(II) center, it is possibly not high enough to enable the coordination of N_2. For this reason, we have started a systematic study aiming at the stepwise substitution of the potentially π-accepting thioether sulfur donors in the 'NHS$_4$'$^{2-}$ ligand by amine functions which act as σ donors only. Our first target ligand in this context was 'N$_2$H$_2$S$_3$'-H$_2$ (= 2,2'-bis(2-mercaptophenylamino)diethyl sulfide).



'N$_2$H$_2$S$_3$'-H$_2$ relates to 'NHS$_4$'-H$_2$ by having one more amine donor and one less thioether donor. 'N$_2$H$_2$S$_3$'-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$_2$H$_2$S$_3$'-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$_2$H$_2$S$_3$'-H$_2$ or related ligands. The synthesis of the 'N$_2$H$_2$S$_3$'-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*)-benzothiazolone[12] were prepared by literature methods. Hydrazine was obtained by 2-fold distillation of N$_2$H$_4$·H$_2$O 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 °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$_2$O (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 ν(CO); ^{1}H NMR (CDCl$_3$, ppm, 269.6 MHz) δ 7.42 (d, 2 H, C$_6$*H*$_4$), 7.32 (t, 2 H, C$_6$*H*$_4$), 7.15 (t, 2 H, C$_6$*H*$_4$), 7.09 (d, 2 H, C$_6$*H*$_4$), 4.14 (t, 4 H, NCH$_2$), 2.92 (t, 4 H, SC*H*$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm, 67.7 MHz) δ 169.9 (*C*O), 136.4, 126.5, 123.3, 122.7, 122.6, 110.4 (*C*$_6$H$_4$), 41.9 (N*C*H$_2$), 28.9 (S*C*H$_2$); MS (FD, DMSO) *m*/*z* 388 ['N$_2$S$_3$O$_2$']$^+$. Anal. Calcd for C$_{18}$H$_{16}$N$_2$O$_2$S$_3$ (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$_2$H$_2$S$_3$'-H$_2$ (3). A solution of NaOH (14.4 g, 360 mmol) in H$_2$O (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$_2$O (100 mL) and extracted with CH$_2$Cl$_2$ (150 mL). The combined CH$_2$Cl$_2$ phases were dried with anhydrous Na$_2$SO$_4$ and evaporated to dryness, yielding 12.0 g (99%) of **3** as a yellow, highly viscous oil: ^{1}H NMR (CDCl$_3$, ppm, 269.6 MHz): δ 7.41 (d, 2 H, C$_6$*H*$_4$), 7.19 (t, 2 H, C$_6$*H*$_4$), 6.64 (m, 4 H, C$_6$*H*$_4$), 5.00 (s, br, 2 H, N*H*), 3.41 (t, 4 H, NC*H*$_2$), 2.88 (t, 6 H, SC*H*$_2$ and S*H* superimposed); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm, 67.7 MHz) δ 136.8, 135.3, 128.7, 128.1, 123.1 (*C*$_6$H$_4$), 48.3 (N*C*H$_2$), 27.6 (S*C*H$_2$); MS (FD, CDCl$_3$) *m*/*z* 336 ['N$_2$H$_2$S$_3$'-H$_2$]$^+$. Anal. Calcd for C$_{16}$H$_{20}$N$_2$S$_3$ (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$_2$H$_2$S$_3$'-H$_2$·2HCl (3·2HCl). Concentrated hydrochloric acid (0.75 mL, 9.0 mmol) was added to a solution of 'N$_2$H$_2$S$_3$'-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$_2$Cl$_2$ (15 mL) and dried in vacuo, yielding 0.56 g (91%) of **3**·2HCl: ^{1}H NMR (CD$_3$OD, ppm, 269.6 MHz): δ 7.61 (d, 2 H, C$_6$*H*$_4$), 7.45−7.25 (m, 6 H, C$_6$*H*$_4$), 3.68 (t, 4 H, NC*H*$_2$), 3.03 (t, 4 H, SC*H*$_2$); ^{13}C{^{1}H} NMR (CD$_3$OD, ppm, 67.7 MHz) δ 137.7, 136.5, 129.9, 129.8, 124.7, 123.7 (*C*$_6$H$_4$), 50.0 (N*C*H$_2$), 28.5 (S*C*H$_2$); MS (FD, MeOH) *m*/*z* 338 ['N$_2$H$_4$S$_3$'-H$_2$]$^+$. Anal. Calcd for C$_{16}$H$_{22}$Cl$_2$N$_2$S$_3$ (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$_2$H$_2$S$_3$'-Me$_2$ (4). MeI (0.75 mL, 11.7 mmol) was added to a solution of 'N$_2$H$_2$S$_3$'-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$_2$O and CH$_2$Cl$_2$, the CH$_2$Cl$_2$ phase was separated, dried with anhydrous Na$_2$SO$_4$, and evaporated to dryness yielding 1.00 g (95%) of **4** as a yellow oil: ^{1}H NMR (CDCl$_3$, ppm, 269.6 MHz) δ 7.35 (d, 2 H, C$_6$*H*$_4$), 7.13 (t, 2 H, C$_6$*H*$_4$), 6.63 (t, 2 H, C$_6$*H*$_4$), 6.54 (d, 2 H, C$_6$*H*$_4$), 5.24 (t, 2 H, N*H*), 3.33 (dt, 4 H, NC*H*$_2$), 2.78 (t, 4 H, SC*H*$_2$), 2.27 (s, 6 H, SC*H*$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm, 67.7 MHz) δ 147.3, 133.7, 129.1, 120.0, 117.1, 109.8 (*C*$_6$H$_4$), 42.6 (N*C*H$_2$), 31.1 (S*C*H$_2$), 17.9 (S*C*H$_3$); MS (FD, CH$_2$Cl$_2$) *m*/*z* 364 ['N$_2$H$_2$S$_3$'-Me$_2$]$^+$.

'N$_2$H$_2$S$_3$'-Me$_2$·2HCl (4·2HCl). Concentrated hydrochloric acid (0.20 mL, 2.40 mmol) was added to a solution of 'N$_2$H$_2$S$_3$'-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$_2$Cl$_2$ (15 mL) and dried in vacuo yielding 0.22 g (91%) of **4·2HCl**: ^{1}H NMR (CD$_3$OD, ppm, 269.6 MHz) δ 7.70−7.38 (m, 8 H, C$_6$*H*$_4$), 5.11 (s, br, 4 H, N*H*), 3.68 (t, 4 H, NC*H*$_2$), 3.08 (t, 4 H, SC*H*$_2$), 2.58 (s, 8 H, SC*H*$_3$); ^{13}C{^{1}H} NMR (CD$_3$OD, ppm, 67.7 MHz) δ 136.2, 133.5, 133.1, 131.0, 129.4, 124.2 (*C*$_6$H$_4$), 51.1 (N*C*H$_2$), 28.2 (S*C*H$_2$), 18.5 (S*C*H$_3$); MS (FD, MeOH) *m*/*z* 364 [('N$_2$H$_2$S$_3$'-Me$_2$)]$^+$. Anal. Calcd for C$_{18}$H$_{26}$Cl$_2$N$_2$S$_3$ (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$_2$H$_2$S$_3$')]$_2$ (5). A light green solution of FeCl$_2$·4H$_2$O (0.19 g, 0.95 mmol) in MeOH (10 mL) was added to a yellow solution of 'N$_2$H$_2$S$_3$'-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 ν(NH); MS (FD, DMSO) *m*/*z* 334 [('N$_2$H$_2$S$_3$')]$^+$, 390 [Fe('N$_2$H$_2$S$_3$')]$^+$; μ_{eff}(293 K) 4.14 μ_B. Anal. Calcd for C$_{32}$H$_{36}$Fe$_2$N$_4$S$_6$ (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)(′$N_2H_2S_3$′)] (6). CO was bubbled through a suspension of [Fe(′$N_2H_2S_3$′)]$_2$ (**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); ^{1}H NMR (DMSO-d_6, ppm, 269.6 MHz) ν 8.06 (s, br, 1 H, N*H*), 7.50−6.34 (m, 8 H, C_6H_4), 5.10 (d, 1 H, N*H*), 4.25−1.90 (m, 8 H, C_2H_4); ^{13}C{^{1}H} NMR (DMSO-d_6, ppm, 67.7 MHz) ν 221.0 (*C*O), 152.9, 151.3, 148.0, 146.4, 129.1, 128.3, 125.3, 125.2, 120.8, 120.6, 119.5 (C_6H_4), 52.8, 52.1 (NCH_2), 35.2, 33.0 (SCH_2); MS (FD, DMSO) *m*/*z* 334 [(′$N_2H_2S_3$′)]$^+$, 390 [Fe(′$N_2H_2S_3$′)]$^+$, 780 {[Fe(′$N_2H_2S_3$′)]$_2$}$^+$. Anal. Calcd for $C_{17}H_{18}FeN_2OS_3$·0.33C_4H_8O (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)(PCy$_3$)(′$N_2H_2S_3$′)] (7). [Ru(H)(Cl)(CO)(PCy$_3$)$_2$] (1.08 g, 1.49 mmol) was added to a solution of ′$N_2H_2S_3$′-H_2 (**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); ^{1}H NMR (DMF-d_7, ppm, 269.6 MHz) δ 9.12 (s, 1 H, N*H*), 7.67−6.54 (m, 8 H, C_6H_4), 5.41 (s, 1 H, N*H*), 4.30−0.97 (m, 41 H, C_2H_4 and P(C_6H_{11})$_3$ superimposed); ^{13}C{^{1}H} 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 (C_6H_4), 51.8, 48.9 (NCH_2), 38.0, 37.7 (SCH_2), 29.3, 28.9, 27.3, 26.3 (br, P(C_6H_{11})); ^{31}P{^{1}H} NMR (DMF-d_7, ppm, 109.38 MHz) δ 47.8 (s, *P*(C_6H_{11})); MS (FD, DMSO, ^{102}Ru) *m*/*z* 716 [Ru(PCy$_3$)(′$N_2H_2S_3$′)]$^+$. Anal. Calcd for $C_{35}H_{51}N_2PORuS_3$·CH_3OH (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(PPr$_3$)$_2$(′$N_2H_2S_3$′)] (8). [RuCl$_2$(PPr$_3$)$_3$] was synthesized in situ by treating a suspension of [RuCl$_2$(PPh$_3$)$_3$] (3.18 g, 3.32 mmol) in *n*-hexane (50 mL) with PPr$_3$ (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 ′$N_2H_2S_3$′-H_2 (**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); ^{1}H NMR (CD_2Cl_2, ppm, 269.6 MHz): δ 7.60−6.50 (m, 8 H, C_6H_4), 5.88 (dd, 1 H, N*H*), 5.09 (s, br, 1 H, N*H*), 3.68−2.20 (m, 7 H, C_2H_4), 1.94−1.37 (m, 25 H, P(C_3H_7) and C_2H_4 superimposed), 0.95 (dt, 18 H, P(C_3H_7)); ^{13}C{^{1}H} NMR (CD_2Cl_2, 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 (C_6H_4), 59.6, 44.8 (NCH_2), 38.6, 31.8 (SCH_2), 32.3, 28.3 (d, P(*C*H_2CH$_2$CH$_3$)), 19.2, 18.0 (d, P(CH$_2$*C*H$_2$CH$_3$)), 16.4, 16.3 (d, P(CH$_2$CH$_2$*C*H$_3$)); ^{31}P{^{1}H} NMR (CD_2Cl_2, ppm, 109.38 MHz) δ 22.0 (d, 1 P, *P*(C_3H_7)), 17.3 (d, 1 P, *P*(C_3H_7)); MS (FD, DMSO, ^{102}Ru) *m*/*z* 756 [Ru(PPr$_3$)$_2$(′$N_2H_2S_3$′)]$^+$, 596 [Ru(PPr$_3$)(′$N_2H_2S_3$′)]$^+$. Anal. Calcd for $C_{34}H_{60}N_2P_2RuS_3$ (756.08): C, 54.01; H, 8.00; N, 3.71. Found: C, 54.20; H, 7.86; N, 3.50.

[Ru(PPr$_3$)(′$N_2H_2S_3$′)] (9). A red solution of [Ru(PPr$_3$)$_2$(′$N_2H_2S_3$′)] (**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); ^{1}H NMR (CD_2Cl_2, ppm, 269.6 MHz) δ 7.38−6.64 (m, 8 H, C_6H_4), 5.55 (s, 1 H, N*H*), 4.44 (s, 1 H, N*H*), 3.85−2.37 (m, 8 H, C_2H_4), 1.88−1.26 (m, 12 H, P(CH_2CH_2-CH$_3$)$_3$), 0.94 (t, 9 H, P(CH$_2$CH$_2$CH_3)$_3$); ^{31}P{^{1}H} NMR (THF-d_8, ppm, 109.38 MHz) δ 31.6 ppm (s, *P*(C_3H_7)); MS (FD, CH_2Cl_2, ^{102}Ru) *m*/*z* 596 [Ru(PPr$_3$)(′$N_2H_2S_3$′)]$^+$. Anal. Calcd for $C_{25}H_{39}N_2PRuS_3$·0.5C_4H_8O (631.90): C, 51.32; H, 6.86; N, 4.43. Found: C, 51.12; H, 7.09; N, 4.13.

[Ru(PPh$_3$)(′$N_2H_2S_3$′)] (10). [RuCl$_2$(PPh$_3$)$_3$] (0.65 g, 0.68 mmol) was added to a solution of ′$N_2H_2S_3$′-H_2 (**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); ^{1}H NMR (CD_2Cl_2, ppm, 269.6 MHz) δ 7.84−6.57 (m, 23 H, C_6H_4 and P(C_6H_5) superimposed), 5.36 (s, br, 1 H, N*H*), 4.46 (dd, 1 H, N*H*), 3.30−2.08 (m, 8 H, C_2H_4); ^{13}C{^{1}H} NMR (CD_2Cl_2, ppm, 67.7 MHz) δ 155.1, 148.3, 144.0, 136.9, 136.3 (C_6H_4), 134.0 (d, P(C_6H_5)), 133.9, 132.5, 130.6 (C_6H_4), 129.5 (s, br, P(C_6H_5)), 128.4 (d, P(C_6H_5)), 126.5, 126.4, 125.6, 121.6 (C_6H_4), 120.6 (d, P(C_6H_5)), 59.0, 51.1 (NCH_2), 42.5, 40.7 (SCH_2); ^{31}P{^{1}H} NMR (CD_2Cl_2, ppm, 109.38 MHz) δ 63.8 (s, *P*(C_6H_5)); MS (FD, CH_2Cl_2, ^{102}Ru) *m*/*z* 697 [Ru(PPh$_3$)(′N_2HS_3′)]$^+$. Anal. Calcd for $C_{34}H_{33}N_2PRuS_3$·0.5C_4H_8O (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(PPh$_3$)(′$N_2D_2S_3$′)] (10a). (a) A suspension of [Ru(PPh$_3$)(′$N_2H_2S_3$′)]·0.5THF (**10**·0.5THF) (0.09 g, 0.12 mmol) and D_2O (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(PPh$_3$)(′$N_2D_2S_3$′)] (**10a**).

(b) LiOMe (0.24 mmol, 0.24 mL of a 1 M solution in MeOH) and D_2O (1.0 mL) were added to a suspension of [Ru(PPh$_3$)(′$N_2H_2S_3$′)]·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 CH_2Cl_2 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); ^{1}H NMR (CD_2Cl_2, ppm, 269.6 MHz) δ 7.84−6.57 (m, 23 H, C_6H_4 and P(C_6H_5) superimposed), 3.25−2.08 (m, 8 H, C_2H_4).

[Ru(PPh$_3$)(′$N_2H_2S_3$′-Me$_2$)]I$_2$ (11). Under stirring, MeI (1.0 mL, 16 mmol) was added to a suspension of [Ru(PPh$_3$)(′$N_2H_2S_3$′)]·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); ^{1}H NMR (CD_2Cl_2, ppm, 269.6 MHz) δ 8.95 (m, 2 H, N*H*), 7.88−7.13 (m, 23 H, C_6H_4 and P(C_6H_5) superimposed), 4.41 (m, 1 H, C_2H_4), 3.74−2.86 (m, 6 H, C_2H_4), 2.33 (s, 3 H, SCH_3), 1.92 (s, 3 H, SCH_3), 1.40 (m, 1 H, C_2H_4); ^{13}C{^{1}H} NMR (CD_2Cl_2, 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 (NCH_2), 39.4 (d), 36.2 (SCH_2), 27.2, 26.4 (SCH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, ppm, 109.38 MHz) δ 33.8 (s, *P*(C_6H_5)); MS (FD, CH_2Cl_2, ^{102}Ru) *m*/*z* 727 [Ru(PPh$_3$)(′N_2HS_3′-Me$_2$)]$^+$, 712 [Ru(PPh$_3$)(′N_2HS_3′-Me)]$^+$, 697 [Ru(PPh$_3$)(′N_2HS_3′)]$^+$. Anal. Calcd for $C_{36}H_{39}I_2N_2PRuS_3$·C_4H_8O (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(PPh$_3$)(′N_2HS_3′-Me$_2$)]I (12). [Ru(PPh$_3$)(′$N_2H_2S_3$′-Me$_2$)]I$_2$·THF (**11**·THF) (0.62 g, 0.59 mmol) was dissolved in N_2H_4 (5.0 mL). The yellow reaction mixture was stirred for 4 h and evaporated to dryness. The yellow residue was redissolved in CH_2Cl_2 (50 mL) and the CH_2Cl_2 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); ^{1}H NMR (DMSO-d_6, ppm, 269.6 MHz) δ 7.80 (dd, 1 H, C*H*(aryl)), 7.71 (d, 1 H, C*H*(aryl)), 7.58 (s, 1 H, N*H*), 7.50−7.08 (m, 17 H, C*H*(aryl)), 6.94 (dt, 1 H, C*H*(aryl)), 6.85 (dd, 1 H, C*H*(aryl)), 6.23 (d, 1 H, C*H*(aryl)), 6.09 (t, 1 H, C*H*(aryl)), 3.41−2.76 (m, 6 H, C_2H_4), 2.37−2.20 (m, 1 H, C_2H_4), 2.16, 1.97 (s, 3 H each, CH_3), 1.94−1.79 (m, 1 H, C_2H_4); ^{13}C{^{1}H} NMR (DMSO-d_6, ppm, 67.7 MHz) δ 158.9, 146.9, 136.1 (d) (C_6H_4), 133.1, 132.3 (d, P(C_6H_5)), 131.5, 131.2, 130.6 (C_6H_4), 130.2 (s, br, P(C_6H_5)), 129.3, 128.7 (C_6H_4), 128.2 (d, P(C_6H_5)), 127.2, 119.6, 111.4, 110.3 (C_6H_4), 57.5, 48.4 (NCH_2), 40.5, 34.2 (SCH_2), 27.4, 21.9 (d) (SCH_3); ^{31}P{^{1}H} NMR (DMSO-d_6, ppm, 109.38 MHz) δ 43.7 (s, *P*(C_6H_5)); MS (FD, DMSO, ^{102}Ru) *m*/*z* 727 [Ru(PPh$_3$)(′N_2HS_3′-Me$_2$)]$^+$, 712 [Ru(PPh$_3$)(′N_2HS_3′-Me)]$^+$, 698 [Ru(PPh$_3$)(′$N_2H_2S_3$′)]$^+$. Anal. Calcd for $C_{36}H_{38}IN_2PRuS_3$·CH_3OH (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(PPh$_3$)(′$N_2H_2S_3$′-Me$_2$)](I)(Cl) from 12 and HCl. Hydrochloric acid (0.50 mmol, 5 mL of a 0.1 M solution of HCl in H_2O) was added to a solution of [Ru(PPh$_3$)(′N_2HS_3′-Me$_2$)]I·MeOH (**12**·MeOH) (0.048 g, 0.054 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred

Table 1. Selected Crystallographic Data for [Fe(′$N_2H_2S_3$′)]$_2$·4MeOH (**5**·4MeOH), [Fe(CO)(′$N_2H_2S_3$′)] (**6**), [Ru(PPr_3)(′$N_2H_2S_3$′)]·2THF (**9**·2THF), and [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (**11**·2CH_2Cl_2)

compd	**5**·4MeOH	**6**	**9**·2THF	**11**·2CH_2Cl_2
formula	$C_{36}H_{52}Fe_2N_4O_4S_6$	$C_{17}H_{18}FeN_2OS_3$	$C_{33}H_{55}N_2O_2PRuS_3$	$C_{38}H_{43}Cl_4I_2N_2PRuS_3$
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	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/c$
a, pm	976.3(3)	813.6(8)	1053.7(3)	3313(1)
b, pm	1025.5(4)	1141(2)	2443.7(7)	1625.2(5)
c, 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
V, nm^3	1.0471(8)	1.836(3)	3.655(2)	8.736(6)
Z	1	4	4	8
λ, pm	71.073	71.073	71.073	71.073
d_{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	$4 \le 2\theta \le 48$	$4 < 2\theta < 54$	$4 \le 2\theta \le 54$	$4 < 2\theta < 48$
meas reflections	4287	5010	12031	18249
indep reflections	3291	4030	8036	6895
obsd reflections	2677	2741	3914	5063
refined parameters	339	217	535	460
R_1 (wR_2),[a,b] %	3.60 (10.52)	4.15 (14.24)	4.29 (8.89)	3.61 (9.04)
q[b]	0.0693	0.0639	0.0246	0.0515
r[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 ^{1}H NMR spectroscopy as [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]-(I)(Cl).

[Ru(NO)(′N_2HS_3′)] (13). [$RuCl_3$(NO)(PPh_3)$_2$] (0.648 g, 0.85 mmol) was added to a solution of ′$N_2H_2S_3$′-H_2 (**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); ^{1}H NMR (DMSO-d_6, ppm, 269.6 MHz) *δ* 7.20 (d, 1 H, C_6H_4), 7.00−6.73 (m, 6 H, C_6H_4 and N*H*), 6.49 (d, 1 H, C_6H_4), 6.39 (t, 1 H, C_6H_4), 4.15−2.64 (m, 8 H, C_2H_4); ^{13}C{^{1}H} 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 (C_6H_4), 58.5, 54.8 (NCH_2), 39.2, 34.7 (SCH_2); MS (FD, DMSO, ^{102}Ru) *m*/*z* 465 [Ru(NO)(′N_2HS_3′)]$^+$. Anal. Calcd for $C_{16}H_{17}N_3ORuS_3$·0.5C_4H_8O (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)(′$N_2H_2S_3$′)]BF_4 (14). HBF_4 (1.63 mmol, 0.225 mL of a 54% solution in Et_2O) was added to a green suspension of [Ru(NO)(′N_2-HS_3′)]·0.5THF (**13**·0.5THF) (0.816 g, 1.63 mmol) in Et_2O (40 mL) and stirred for 14 h. A red solid precipitated, which was separated, washed with Et_2O (40 mL), and dried in vacuo to yield 0.890 g (99%) of **14**. ^{13}C{^{1}H} and ^{1}H 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*(BF_4); ^{1}H NMR (DMSO-d_6, ppm, 269.6 MHz) *δ* 9.97 (d, 0.5 H, N*H*), 8.64 (s, 0.5 H, N*H*), 7.99 (d, 0.5 H, N*H*), 7.39 (s, 0.5 H, N*H*), 7.70−6.90 (m, 8 H, C_6H_4), 4.80−2.70 (m, 8 H, C_2H_4); ^{13}C{^{1}H} 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 (C_6H_4), 63.6, 59.3, 57.1, 51.5 (NCH_2), 39.3, 37.0, 36.2, 36.0 (SCH_2); MS (FD, DMSO, ^{102}Ru) *m*/*z* 465 [Ru(NO)(′N_2HS_3′)]$^+$. Anal. Calcd for $C_{16}H_{18}BF_4N_3ORuS_3$ (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(′$N_2H_2S_3$′)]$_2$·4MeOH (5·4MeOH), [Fe(CO)(′$N_2H_2S_3$′)] (6), [Ru(PPr_3)(′$N_2H_2S_3$′)]·2THF (9·2THF), and [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (11·2CH_2Cl_2). Black columns of [Fe(′$N_2H_2S_3$′)]$_2$·4MeOH (**5**·4MeOH) were obtained by layering a solution of ′$N_2H_2S_3$′-H_2 (**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 $FeCl_2$·4H_2O (0.95 g, 0.48 mmol) in MeOH (80 mL). Brown columns of [Fe(CO)(′$N_2H_2S_3$′)] (**6**) formed when a saturated solution of **6** in a 1:1 mixture of MeOH and THF was layered with Et_2O under an atmosphere of CO. Brown plates of [Ru(PPr_3)(′$N_2H_2S_3$′)]·2THF (**9**·2THF) crystallized from a saturated THF solution of **9** which was layered with *n*-hexane. Yellow plates of [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (**11**·2CH_2Cl_2) were grown from a saturated solution of **11** in CH_2Cl_2 by slowly evaporating the solvent. Suitable single crystals were sealed under N_2 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 CH_2Cl_2, and **9** with two molecules of THF per unit. The hydrogen atoms of the THF molecules in **9**·2THF and of the CH_2Cl_2 molecules of **11**·2CH_2-Cl_2 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(′$N_2H_2S_3$′)]$_2$·4MeOH (**5**·4MeOH), [Fe(CO)(′$N_2H_2S_3$′)] (**6**), [Ru(PPr_3)(′$N_2H_2S_3$′)]·2THF (**9**·2THF), and [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (**11**·2CH_2-Cl_2).

Results and Discussion

Syntheses of Ligands. The requirement of having terminal thiolate functions in the target ligand ′$N_2H_2S_3$′$^{2-}$ 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 ^{1}H 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

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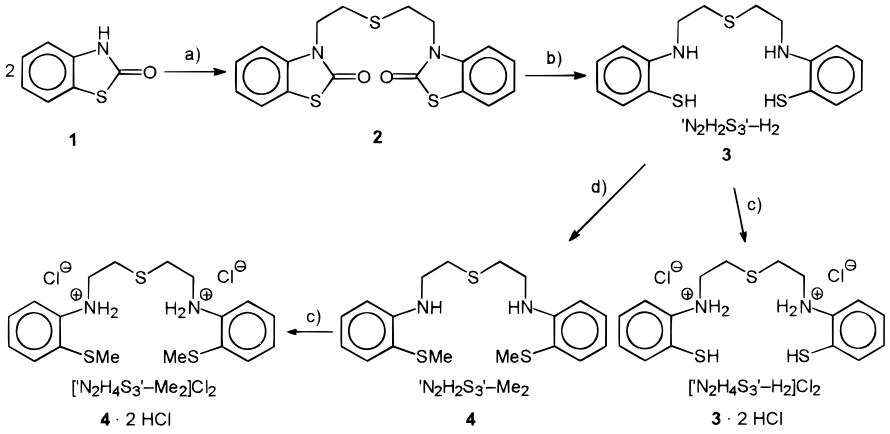
(15) Klein, G.; Prijs, B. *Helv. Chim. Acta* **1954**, *37*, 2057.

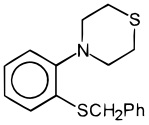
Scheme 1. Synthesis of ′$N_2H_2S_3$′-H_2 and Its Derivatives[a]



[a] Key: (a) +2n-BuLi, + $S(C_2H_4Br)_2$, THF, reflux, 14 h; (b) (1) + NaOH, EtOH/H_2O, reflux, 14 h, (2) + HCl; (c) + HCl, MeOH; (d) + 2LiOMe, + exc. MeI, 16 h.

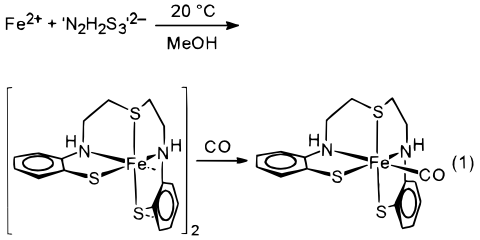
soluble in CH_2Cl_2 and THF and was characterized by spectroscopic methods and elemental analysis. The CO group ^{13}C NMR signal (δ = 169.9 ppm) and the ν(CO) IR band (1678 cm^{-1}) proved particularly suitable to confirm the N-alkylation of **1**. Alkaline hydrolysis of **2** and subsequent acidification yielded **3** as a highly viscous yellow oil which could be purified via the white dihydrochloride [′$N_2H_4S_3$′-H_2]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 ′$N_2H_2S_3$′-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 $[Fe(CO)_2]^{2+}$ fragments yielded untractable materials. Benzylation of the thiol function in 2-aminothiophenol and subsequent treatment of the resulting 2-benzylthioaniline with $S(C_2H_4Br)_2$ 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 ′$N_2H_2S_3$′$^{2-}$ anion obtained by deprotonation of **3** with LiOMe yielded green [Fe(′$N_2H_2S_3$′)]$_2$ (**5**) (eq 1). In solid state, **5** is dinuclear (X-ray diffraction) and paramagnetic (μ_{eff} (293 K) = 4.14 μ_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_4N_3, PMe_3, and also N_2, but readily added CO to give diamagnetic green [Fe(CO)(′$N_2H_2S_3$′)] (**6**). The molecular structure of **6** was determined by X-ray diffraction.

The low frequency ν(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**, [Ru(CO)(′$N_2H_2S_3$′)], from ruthenium carbonyl precursor complexes and ′$N_2H_2S_3$′$^{2-}$ remained as yet unsuccessful. Precursor complexes such as [Ru(H)(Cl)(CO)(PCy_3)$_2$] or [$RuCl_2$(CO)$_3$(THF)][17,18] proved too inert to exchange all ligands except one CO for the ′$N_2H_2S_3$′$^{2-}$ donors. For example, the reaction of [Ru(H)(Cl)(CO)(PCy_3)$_2$] with ′$N_2H_2S_3$′$^{2-}$ yielded green [Ru(CO)(PCy_3)(′$N_2H_2S_3$′)] (**7**), whose composition suggests that ′$N_2H_2S_3$′$^{2-}$ acts as tetradentate ligand only. Complex **7** proved so stable that it did not loose PCy_3 or CO even when heated for 14 h in refluxing THF.

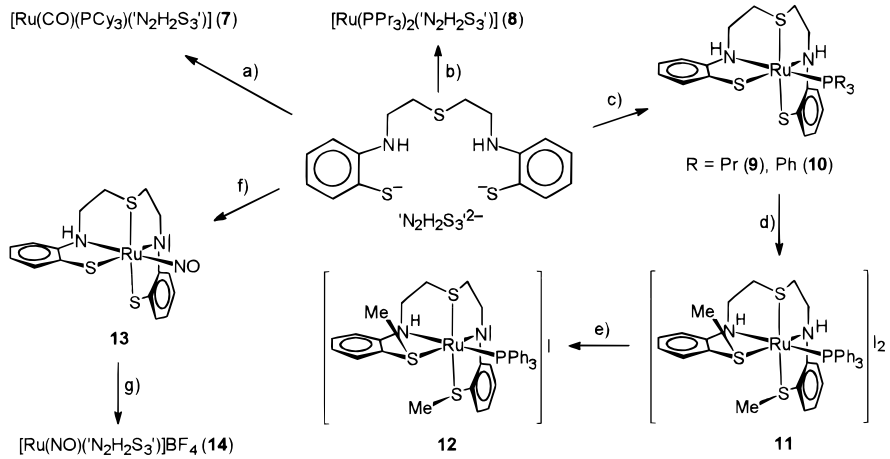
Phosphine complexes such as [$RuCl_2(PR_3)_3$] (R = Pr, Ph) proved more reactive toward ′$N_2H_2S_3$′$^{2-}$. At room temperature, the reaction of [$RuCl_2(PPr_3)_3$] with ′$N_2H_2S_3$′$^{2-}$ yielded orange [Ru(PPr_3)$_2$(′$N_2H_2S_3$′)] (**8**), in which the ′$N_2H_2S_3$′$^{2-}$ ligand again probably utilizes only four of its five donors. However, **8** is readily converted into green-brown [Ru(PPr_3)(′$N_2H_2S_3$′)] (**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 [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_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 ′$N_2H_2S_3$′-Me_2 ligand of **11**. The monoiodide [Ru(PPh_3)(′N_2HS_3′-Me_2)]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(′$N_2H_2S_3$′)] Complexes[a]



[a] Key: (a) + [Ru(H)(Cl)(CO)(PCy_3)$_2$], THF, 3 d; (b) + [$RuCl_2$(PPr_3)$_3$], MeOH, 3 d; (c) + [$RuCl_2$(PR_3)$_3$] (R = Pr, Ph), THF, reflux, 4 h; (d) + exc. MeI, THF, 3 d; (e) + N_2H_4; (f) + [$RuCl_3$(NO)(PPh_3)$_2$], + LiOMe, MeOH/THF, 14 h; (g) + HBF_4, Et_2O.

observed when the nitrosyl complex [$RuCl_3$(NO)(PPh_3)$_2$] was treated with ′$N_2H_2S_3$′-H_2 in the presence of 3 equiv of LiOMe. Deep green [Ru(NO)(′N_2HS_3′)] (**13**) (ν(NO) = 1799 cm^{-1}) formed, which is neutral and diamagnetic and contains the trisanionic ′N_2HS_3′$^{3-}$ ligand. Subsequent treatment of **13** with HBF_4 yielded red [Ru(NO)(′$N_2H_2S_3$′)]BF_4 (**14**) (ν(NO) = 1856 cm^{-1}) and showed that the amine deprotonation is reversible. In accordance with expectations, the protonation of **13** to yield **14** shifts the ν(NO) band to higher frequencies.

Substitution and Acid−Base Reactions. The lability of [Fe(CO)(′$N_2H_2S_3$′)] (**6**) toward CO dissociation and the resulting formation of the dinuclear [Fe(′$N_2H_2S_3$′)]$_2$ (**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)(′$N_2H_2S_3$′)] derivatives with L = N_2H_4, NH_3, N_3^- remained unsuccessful.

$$2[\mathrm{Fe(CO)}(′\mathrm{N_2H_2S_3}′)] \rightleftharpoons [\mathrm{Fe}(′\mathrm{N_2H_2S_3}′)]_2 + 2\ \mathrm{CO} \quad (2)$$

In contrast to the labile [Fe(CO)(′$N_2H_2S_3$′)], the ruthenium complexes [Ru(PR_3)(′$N_2H_2S_3$′)] (R = Pr (**9**), Ph (**10**)) and [Ru(NO)(′N_2HS_3′)] (**13**) proved extremely inert to substitution. The PPh_3 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)(′N_2HS_3′)] (**13**) with N_2H_4 or NEt_4N_3 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 ′$N_2H_2S_3$′$^{2-}$ amine functions. The NH Brønsted acidity was indicated by the deprotonation of the ′$N_2H_2S_3$′-Me_2 ligand, when **11** was treated with N_2H_4, and it could subsequently be observed for ′$N_2H_2S_3$′$^{2-}$ in the formation of the NO complex **13**.

The Brønsted acid−base reactions could further be established by H^+/D^+ exchange reactions. Addition of D_2O to THF solutions of [Fe(CO)(′$N_2H_2S_3$′)] (**6**) spontaneously yielded [Fe(CO)(′$N_2D_2S_3$′)] (**6a**). The H^+/D^+ exchange of the ruthenium complex [Ru(PPh_3)(′$N_2H_2S_3$′)] (**10**) was rather slow with neutral D_2O (in THF), but highly accelerated by addition of base (LiOMe) and yielded [Ru(PPh_3)(′$N_2D_2S_3$′)] (**10a**). [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)]I_2 (**11**) and [Ru(NO)(′$N_2H_2S_3$′)]BF_4 (**14**) spontaneously exchanged with D^+ from D_2O. In these two cases, the corresponding amide complexes could also be isolated. Addition of Brønsted bases such as N_2H_4 and NEt_4N_3 to solutions of **11** and **14** gave [Ru(PPh_3)(′N_2HS_3′-Me_2)]I (**12**) and [Ru(NO)(′N_2HS_3′)] (**13**), respectively.

These results show that the amine NH donors of [M(L)(′$N_2H_2S_3$′)] complexes can be reversibly deprotonated to give amide donors according to the equilibrium of eq 3.

$$[\mathrm{M(L)}(′\mathrm{N_2H_2S_3}′)] \rightleftharpoons [\mathrm{M(L)}(′\mathrm{N_2HS_3}′)]^- + \mathrm{H}^+ \quad (3)$$

The formation of the amide species [M(L)(′N_2HS_3′)]$^-$ 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]

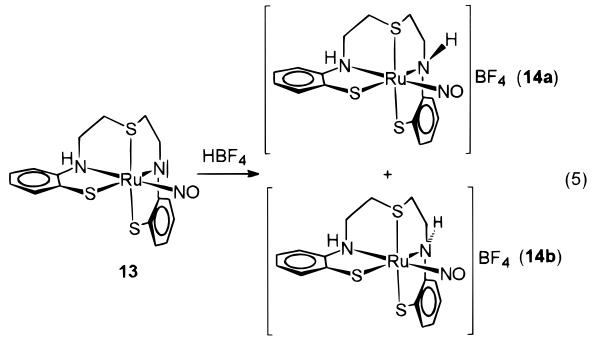
$$[\mathrm{M(L)}(′\mathrm{N_2HS_3}′)]^- \rightleftharpoons [\mathrm{M}(′\mathrm{N_2HS_3}′)]^- + \mathrm{L} \quad (4)$$

For the complexes described here, apparently the second alternative prevails. It also explains why the NO ligand in [Ru(NO)(′$N_2H_2S_3$′)]BF_4 (**14**), which shows a high-frequency ν(NO) at 1856 cm^{-1}, is insusceptible to nucleophilic attack by N_2H_4 or azide ions. The primary reaction is a deprotonation of **14** to give **13**, whose ν(NO) of 1799 cm^{-1} indicates a relatively high electron density at the NO ligand.

The investigation of the protonation/deprotonation reactions of [Ru(PPh_3)(′N_2HS_3′-Me_2)]I (**12**) and [Ru(NO)(′N_2HS_3′)] (**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. $^{13}C\{^1H\}$ and ^1H NMR spectra (see below) showed that protonation of **12** by HCl yielded only one stereoisomer of [Ru(PPh_3)(′$N_2H_2S_3$′-Me_2)](I)(Cl). However, the protonation of [Ru(NO)(′N_2HS_3′)] (**13**) (with HBF_4) resulted in a 1:1 mixture of two diastereomers of [Ru(NO)(′$N_2H_2S_3$′)]BF_4. 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 PPh_3 ligand and

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

two methyl groups at the terminal sulfur atoms, one of these two sides is evidently blocked. In **13**, which carries the small NO ligand, both sides are accessible so that protons can attack the amide function from the front as well as from the back side as indicated in eq 5.



Characterization of Complexes. All complexes but [Fe(′$N_2H_2S_3$′)]$_2$ (**5**) proved to be diamagnetic and exhibit similar solubilities. The neutral CO, NO, and phosphine complexes are soluble in DMF, DMSO, CH_2Cl_2, THF, and acetone but virtually insoluble in all other common organic solvents. The salt **14** is soluble only in DMF and DMSO and is sparingly soluble in MeOH. All complexes have been characterized by elemental analyses, IR, NMR, and mass spectra. The FD mass spectra showed the molecular ions or ions resulting from loss of CO (**6**, **7**). Characteristic IR bands of the complexes containing [M(′$N_2H_2S_3$′)] cores are either one, unresolved, broad or two, weak-to-medium ν(NH) absorptions in the region of 3290 to 3160 cm^{-1} (in KBr). The complexes containing [Ru(′N_2HS_3′)] cores display one medium ν(NH) IR band at 3124 cm^{-1} (**12**) or 3228 cm^{-1} (**13**). The strong ν(CO) or ν(NO) IR bands of **6** (1932 cm^{-1}), **7** (1935 cm^{-1}), **13** (1799 cm^{-1}), and **14** (1856 cm^{-1}) are suited to monitor reactions by IR spectroscopy. All mononuclear complexes possess only C_1 symmetry. This is clearly displayed by the $^{13}C\{^1H\}$ NMR spectra. The [M(′$N_2H_nS_3$′)] cores (n = 1 or 2) of the respective complexes give rise to 12 aromatic ^{13}C signals in the range of 160−110 ppm and two signals each for the N-bonded (63−44 ppm) and S-bonded (42−31 ppm) aliphatic C atoms. The $^{13}C\{^1H\}$ NMR spectrum of [Ru(NO)(′$N_2H_2S_3$′)]BF_4 (**14**) displays two sets of this signal pattern, which indicates that **14** exists in two diastereomeric forms.

X-ray Structure Analyses of [Fe(′$N_2H_2S_3$′)]$_2$·4MeOH (5·4MeOH), [Fe(CO)(′$N_2H_2S_3$′)] (6), [Ru(PPr$_3$)(′$N_2H_2S_3$′)]·2THF (9·2THF), and [Ru(PPh$_3$)(′$N_2H_2S_3$′-Me$_2$)]I_2·2CH_2Cl_2 (11·2CH_2Cl_2). The molecular structures of four complexes could be elucidated by X-ray structure determination. Figures 1 and 2 show views of the molecular structures, and Tables 2 and 3 list selected distances and angles.

In all four complexes, the metal centers exhibit pseudo-octahedral coordination. The ′$N_2H_2S_3$′$^{2-}$ ligand and its ′$N_2H_2S_3$′-Me_2 derivative bind to the metals in the same characteristic fashion which combines mer and fac coordination of the donor atoms. For the ′$N_2H_2S_3$′$^{2-}$ ligand, cis positions of both the two amine and the two thiolate donors result. A further result of this coordination is that all [M(′N_2S_3′)] cores exhibit C_1 symmetry only. Bond distances and angles show no anomalies. The distances of **5** and **6** are typical for high-spin and low-spin Fe(II) complexes, respectively, which contain thiolate−thioether−amine ligands.[5,6] They correspond with distances found in high-spin/low-spin [Fe(L)(′NHS_4′)] complexes. The low-spin complexes always show markedly shorter distances than the high-spin complexes. Worth being noted are the very similar Fe−S(thiolate) and Fe−S(thioether) distances of **6**, which are found in the narrow range of 227.9(2)−231.5(2) pm. In the high-spin Fe(II) complex **5** which possesses crystallographically imposed inversion symmetry, Fe−S(thiolate) and Fe−S(thioether) distances differ more from each other (∼15 pm). It is also noted that the Fe1−S2a and Fe1a−S2 distances (251.7(2) pm) in the Fe−S(thiolate)−Fe bridges are distinctly longer than the Fe−S(thiolate) distances (242.71(12), 244.66(13) pm) within the two [Fe(′$N_2H_2S_3$′)] halves. This certainly reflects the ability of **5** to dissociate into [Fe(′$N_2H_2S_3$′)] monomers in solution.

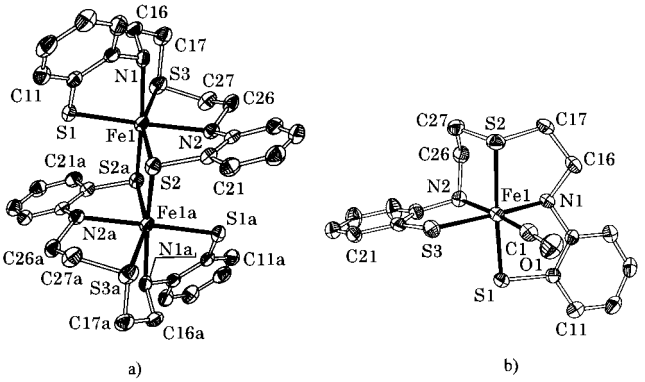


Figure 1. ORTEP diagrams of (a) [Fe(′$N_2H_2S_3$′)]$_2$·4MeOH (**5**·4MeOH) and (b) [Fe(CO)(′$N_2H_2S_3$′)] (**6**) (50% probability ellipsoids; H atoms and solvate molecules omitted).

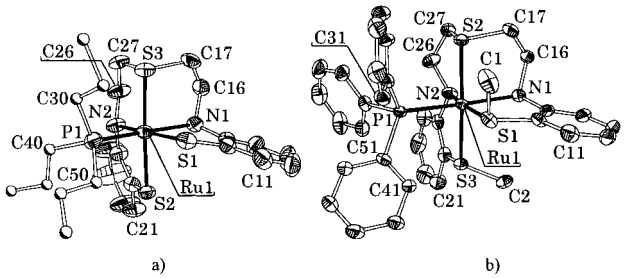


Figure 2. ORTEP diagrams of (a) [Ru(PPr$_3$)(′$N_2H_2S_3$′)]·2THF (**9**·2THF) and (b) the cation of [Ru(PPh$_3$)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (**11**·2CH_2Cl_2) (50% probability ellipsoids; H atoms and solvate molecules omitted).

Table 2. Selected Distances (pm) and Angles (deg) of [Fe(′$N_2H_2S_3$′)]$_2$·4MeOH (**5**·4MeOH) and [Fe(CO)(′$N_2H_2S_3$′)] (**6**)

complex	**5**·4MeOH	**6**	complex	**5**·4MeOH	**6**
Fe1−S1	242.7(1)	229.9(2)	N1−Fe1−S1	79.79(9)	86.8(1)
Fe1−S2	244.7(1)	227.9(2)	N1−Fe1−N2	94.9(1)	89.8(1)
Fe1−S3	257.2(1)	231.5(2)	S2−Fe1−S3	158.70(3)	92.21(8)
Fe1−N1	225.4(3)	207.5(3)	N1−Fe1−S3	79.41(8)	175.76(9)
Fe1−N2	232.1(3)	210.2(3)	N2−Fe1−S3	80.37(7)	85.9(1)
Fe1−S2a	251.7(2)		N2−Fe1−S2a	88.84(8)	
Fe1−C1		175.6(4)	C1−Fe1−N1		93.8(2)

Table 3. Selected Distances (pm) and Angles (deg) of [Ru(PPr$_3$)(′$N_2H_2S_3$′)]·2THF (**9**·2THF) and [Ru(PPh$_3$)(′$N_2H_2S_3$′-Me_2)]I_2·2CH_2Cl_2 (**11**·2CH_2Cl_2)

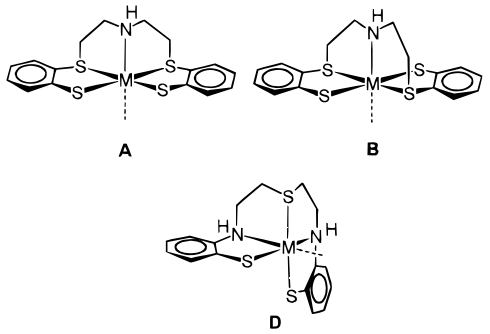
complex	**9**·2THF	**11**·2CH_2Cl_2	complex	**9**·2THF	**11**·2CH_2Cl_2
Ru1−S1	236.9(2)	233.2(2)	N1−Ru1−S1	83.0(1)	83.0(1)
Ru1−S2	236.2(2)	233.6(2)	N1−Ru1−N2	90.8(2)	86.3(2)
Ru1−S3	229.1(2)	234.3(2)	N2−Ru1−P1	95.0(2)	98.4(1)
Ru1−N1	223.2(4)	220.5(4)	N1−Ru1−S3	84.4(1)	94.2(1)
Ru1−N2	214.2(5)	213.9(5)	N2−Ru1−S3	86.9(1)	83.4(1)
Ru1−P1	225.7(2)	235.6(2)	S2−Ru1−S3	167.35(5)	168.12(5)

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 PPh_3 vs PPr_3 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 $'N_2H_2S_3'$-H_2 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($'NHS_4'$)] 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 ν(CO) frequencies of [Fe(CO)($'N_2H_2S_3'$)] (1932 cm^{-1}) vs [Fe(CO)($'NHS_4'$)] (1960 cm^{-1}). However, the metal donor core configurations of [M($'NHS_4'$)] and [M($'N_2H_2S_3'$)] complexes strongly differ. While [M($'NHS_4'$)] complexes exhibit either structure **A** or **B** (cf. introduction), all [M($'N_2H_2S_3'$)] complexes characterized so far invariably show the structure **D**. A major geometric difference between these structures is



the fac−fac coordination of the $'NHS_4'^{2-}$ ligand versus the fac−mer coordination of the $'N_2H_2S_3'^{2-}$ ligand. This structural difference complicates direct comparison between [M(L)($'NHS_4'$)] and [M(L)($'N_2H_2S_3'$)] complexes and may explain some unexpected results. For example, [Fe(CO)($'N_2H_2S_3'$)] readily loses its CO ligand though its low frequency ν(CO) indicates strong Fe−CO π-back bonding, whereas [Fe(CO)($'NHS_4'$)] is practically inert toward loss of CO. With regard to the labile CO binding, it was not unexpected to be found that N_2 could not be coordinated. Another important difference between the [M(L)($'N_2H_2S_3'$)] and [M(L)($'NHS_4'$)] complexes is the relatively high acidity of the (aromatic) NH functions in the [M(L)($'N_2H_2S_3'$)] 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)($'N_2H_2S_3'$)]-BF_4, one NH function is easily deprotonated by bases such as N_2H_4 or by azide ions. As a consequence, the NO ligand in the resulting [Ru(NO)($'N_2HS_3'$)] becomes insusceptible for attack by nucleophiles. Similar effects have been observed with Fe, Ni, and Ru complexes which contain [M($'N_2H_2S_2'$)] fragments ($'N_2H_2S_2'^{2-}$ = 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($'N_2H_2S_3'$)] or [Ru($'N_2H_2S_3'$)] fragments with respect to coordination and/or substitution of small coligand molecules. In particular, the cis coordination of the thiolate donors in [M($'N_2H_2S_3'$)] 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-N_2H_2{Fe($'NHS_4'$)}$_2$][5] or [μ-N_2H_2{Ru(PPh_3)($'S_4'$)}$_2$],[22] and it imperatively requires trans-thiolate donors at the metal centers.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for compounds **5**·4MeOH, **6**, **9**·2THF, and **11**·2CH_2Cl_2 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**·2CH_2Cl_2). 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@chemcrys.cam.ac.uk].

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