Transition Metal Complexes with Sulfur Ligands, 135[+]

Electron-Rich Fe and Ru Complexes with the New Trisamine Dithiolate Ligand $'N_3H_3S_2'$-H_2 [2,2′-Bis(2-mercaptophenylamino)diethylamine]

Dieter Sellmann,*[a] Jürgen Utz,[a] and Frank W. Heinemann[a]

Keywords: N ligands / S ligands / Iron / Ruthenium / Pentadentate ligands

In order to obtain iron and ruthenium complexes which are analogous to [M(L)($'NHS_4'$)] and [M(L)($'N_2H_2S_3'$)] complexes [$'NHS_4'^{2-}$ = 2,2′-bis(2-mercaptophenylthio)diethylamine(2–), $'N_2H_2S_3'^{2-}$ = 2,2′-bis(2-mercaptophenylamino)diethylsulfide-(2–)] but have electron-richer metal centers, the new pentadentate amine thiolate ligand $'N_3H_3S_2'$-H_2 [= 2,2′-bis(2-mercaptophenylamino)diethylamine] (**4**) was synthesized. The dianion $'N_3H_3S_2'^{2-}$ reacted with Fe^{II} salts to give high-spin [Fe($'N_3H_3S_2'$)] (**5**) [μ_{eff} (293 K) = 3.94 μ_B], which yielded diamagnetic [Fe(CO)($'N_3H_3S_2'$)] (**6**) upon reaction with CO. Complex **6** exhibits a low-frequency ν(CO) band (1934 cm^{-1} in THF) indicating an electron-rich Fe center and a strong Fe–CO bond. In spite of this, **6** readily dissociated in solution to **5** and CO. The reaction of $[RuCl_2(PPh_3)_3]$ with $'N_3H_3S_2'^{2-}$ yielded [Ru(PPh_3)($'N_3H_3S_2'$)] (**7**), which proved inert with respect to PPh_3 substitution but could be methylated at the thiolate donors. The resulting [Ru(PPh_3)($'N_3H_3S_2'$-Me_2)]I_2 (**8**) proved as inert towards substitution as **7**. Complex **8** could reversibly be deprotonated to give [Ru(PPh_3)($'N_3H_2S_2'$-Me_2)]I (**11**), in the course of which the $[RuPN_3S_2]$ cores rearrange from C_S to C_1 symmetry. Reversible protonation/deprotonation was also found with [Ru(NO)($'N_3H_2S_2'$)] (**9**) which formed from $[RuCl_3(NO)(PPh_3)_2]$ and $'N_3H_3S_2'^{2-}$ in the presence of one additional equivalent of LiOMe. Protonation of **9** with HBF_4 gave [Ru(NO)($'N_3H_3S_2'$)]BF_4 (**10**). The NMR spectra and the X-ray structure analysis of **8** proved that the $[RuPN_3S_2]$ cores of **7** and **8** exhibit a C_S-symmetrical *meso* structure. In all other complexes, however, the $[MLN_3S_2]$ cores exhibit a C_1-symmetrical structure. It results from the *fac-mer* coordination mode of the $'N_3H_3S_2'^{2-}$ ligand and favors the planarization of amide donors when NH functions are reversibly deprotonated.

Structure−function relationships of transition metal complexes are primarily determined by the metal oxidation state, type and number of the donor atoms, and the structure of the metal ligand core.[1] In quest of metal complexes that combine structural (metal sulfur sites) and functional (reactivity) features of nitrogenase centers, our interest focusses on complexes with multidentate ligands which contain amine N, thioether S, and thiolate S donors. In this search the [Fe($'NHS_4'$)] fragment (Scheme 1) was found to exist in the diastereomeric forms **A** and **B** and to bind N_2H_2, N_2H_4, NH_3, and CO, but not N_2.[2] As high electron densities at the metal centers usually favor the coordination of N_2,[3] we tried to increase the iron electron density in the [Fe($'NHS_4'$)] cores through a systematic substitution of σ-donor−π-acceptor thioether functions by σ-donor amine functions.

The first target ligand $'N_2H_2S_3'$-H_2[4] yielded the CO complex [Fe(CO)($'N_2H_2S_3'$)], whose ν(CO) frequency of 1932 cm^{-1} indicated a higher Fe electron density when compared with to that of [Fe(CO)($'NHS_4'$)] (1960 cm^{-1}). However, despite the low-frequency ν(CO) indicating strong Fe−CO π-back-bonding, [Fe(CO)($'N_2H_2S_3'$)] proved much more labile than [Fe(CO)($'NHS_4'$)], and neither N_2 nor N_2H_2, N_2H_4, or NH_3 complexes could be obtained with the [Fe($'N_2H_2S_3'$)] fragment. Beyond that all [Fe(L)($'N_2H_2S_3'$)] and corresponding [Ru(L)($'N_2H_2S_3'$)] complexes were shown to exhibit the core structure **C** having thiolate donor atoms in *cis* positions. The core structure **C** distinctly differs from the [Fe($'NHS_4'$)] core structure **B** having *trans*-thiolate donors. *trans*-Thiolate donors, however, proved to be essential for the stabilization of molecules such as N_2H_2 in [μ-N_2H_2{Fe($'NHS_4'$)}$_2$], because only a *trans* coordination of thiolate donors allows the formation of strong N−H···$(S)_2$ bridges.[2a,2c]

In the series of systematically varied ligands, our next target ligand was $'N_3H_3S_2'$-H_2. It is comparable with the $'NHS_4'^{2-}$ ligand in so far as all thioether donors are exchanged for amine donors. Simultaneously, the terminal thiolate donors are maintained in a coordination mode that enables them to occupy, at least in principle, *trans* positions in six-coordinate metal complexes.

Results

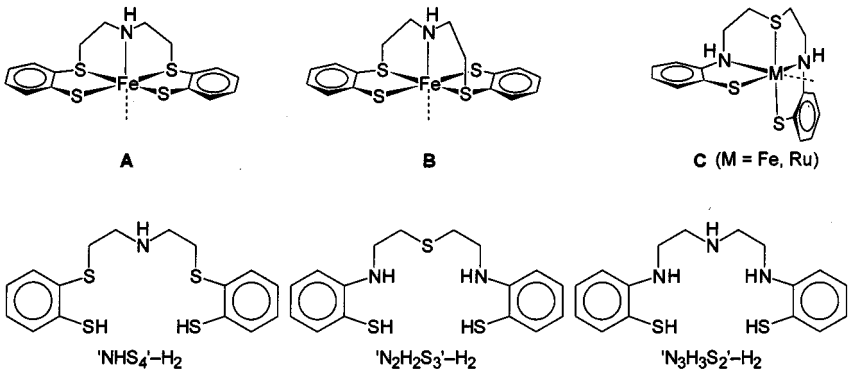
Ligand Synthesis

As in the case of the $'N_2H_2S_3'^{2-}$ ligand synthesis, the requirement of terminal thiolate functions in the target ligand $'N_3H_3S_2'^{2-}$ necessitated a specific synthetic route (Scheme 2).

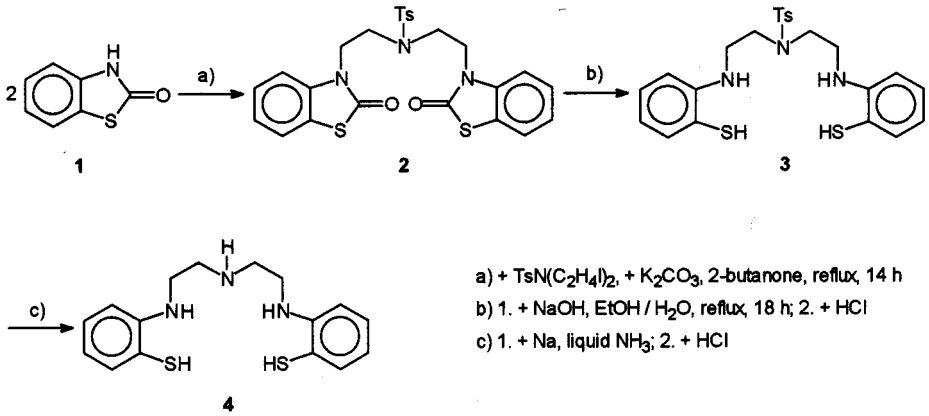
[+] Part 134: D. Sellmann, K. Engl, T. Gottschalk-Gaudig, F. W. Heinemann, *Eur. J. Inorg. Chem.* **1999**, 333−339

[a] Institut für Anorganische Chemie der Universität Egerlandstraße 1, D-91058 Erlangen, Germany
Fax: (internat.) + 49(0)9131/8527367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

  1434−1948/99/0202−0341 $ 17.50+.50/0



Scheme 1. Ligands and core structures of metal complex fragments



Scheme 2. Synthesis of $'N_3H_3S_2'$-H_2 (**4**)

Alkylation of 2(3*H*)-benzothiazolone (**1**) with TsN-$(C_2H_4I)_2$ in the presence of K_2CO_3 yielded **2** as major product. The rather unusual N-lost derivative $TsN(C_2H_4I)_2$ had to be applied because all other and more common alkylation reagents such as $NH(C_2H_4Br)_2$ or amides of the type $R(CO)N(C_2H_4Br)_2$ failed. For example, $NH(C_2H_4Br)_2$ gave piperazine derivatives[5] instead of alkylating **1**, the amides $R(CO)N(C_2H_4Br)_2$ rearranged.[6] From the crude product of **2**, traces of by-products resulting from oxygen alkylation of **1**[7] could readily be removed by extraction with EtOH. Compound **2** is soluble in CH_2Cl_2 and THF and moderately soluble in EtOH or MeOH; it was characterized by the usual spectroscopic methods and by elemental analysis. The $^{13}C\{^1H\}$-NMR CO signal (δ = 170.6) and the IR ν(CO) band (1678 cm^{-1} in KBr) are particularly suited to confirm alkylation of the N atom in **1** and to identify **2**.

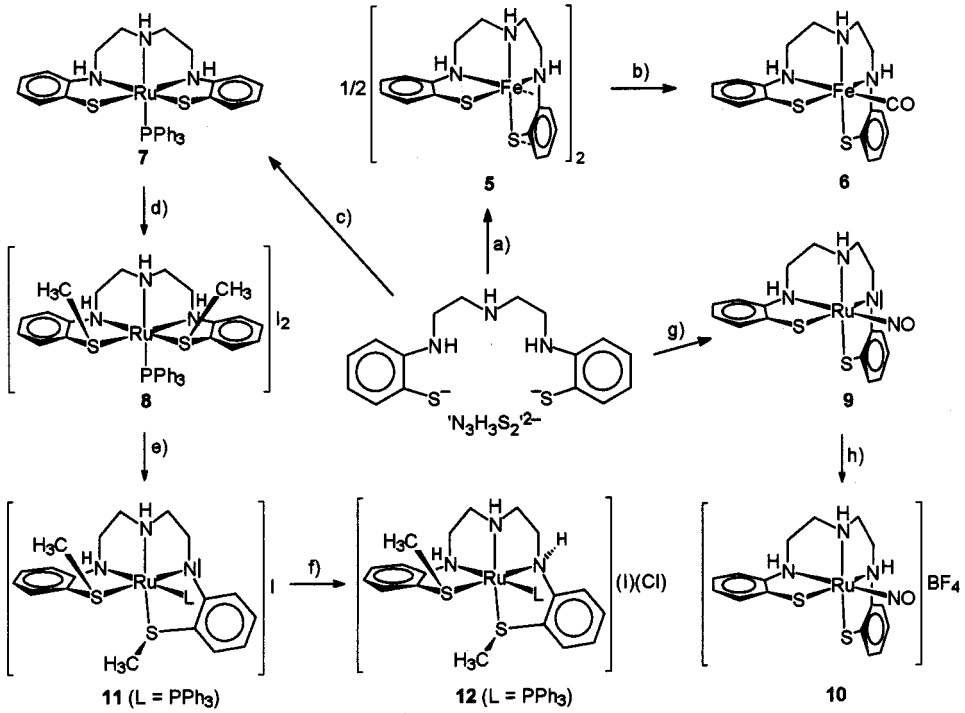
Alkaline hydrolysis of **2** by aqueous NaOH in EtOH and subsequent acidification with hydrochloric acid yielded **3** as yellow powder in nearly quantitative amounts. The final step, the reductive detosylation of the central N atom in **3** with sodium in liquid NH_3 gave **4**, which was isolated after recrystallization from EtOH in form of beige needles.

Syntheses of Fe and Ru Complexes

Scheme 3 summarizes the syntheses and reactions of $[M('N_3H_3S_2')]$ complexes.

The reaction a) of Fe^{II} salts with $'N_3H_3S_2'^{2-}$, which was routinely obtained from $'N_3H_3S_2'$-H_2 and two equivalents of LiOMe, gave grey-white $[Fe('N_3H_3S_2')]$ (**5**). The structure of **5** remains unknown, but in analogy to the closely related dinuclear $[Fe('N_2H_2S_3')]_2$ complex, **5** is suggested to exhibit a dinuclear structure resulting from thiolate bridging. In solid state, **5** is paramagnetic [μ_{eff} (293 K) = 3.94 μ_B]. The μ_{eff} value is compatible with four unpaired electrons per Fe center, which are partially coupled antiferromagnetically through Fe−S−Fe bridges.

All attempts to obtain $[Fe(L)('N_3H_3S_2')]$ derivatives by treating **5** with N_2H_4, NEt_4N_3, or PMe_3 in MeOH or THF solutions remained unsuccessful and yielded only the starting complex **5**. Exclusively CO could be added to give red $[Fe(CO)('N_3H_3S_2')]$ (**6**) (Scheme 3, reaction b). Complex **6** is diamagnetic and probably exhibits the C_1-symmetric structure indicated in Scheme 3. The C_1 symmetry is concluded from the NMR spectra of **6** (see below), and it corresponds with that of the related $[Fe(CO)('N_2H_2S_3')]$ whose structure has been determined by X-ray diffraction. Complex **6** exhibits a low-frequency ν(CO) IR band at 1934 cm^{-1} (in THF) indicating strong Fe−CO π-back-bonding. In accordance with this, solid **6** is stable at room temperature for unlimited periods of time. In solution, however, **6** rather unexpectedly readily loses CO within a few hours and yields the starting complex **5**. In this respect, the properties of **6** resemble very closely those of the related



Scheme 3. Syntheses and reactions of [M('$N_3H_3S_2$')] complexes (M = Fe, Ru)

[Fe(CO)('$N_2H_2S_3$')]. For this reason, we tried to obtain the kinetically less labile ruthenium homologue of **6**. As in the case of the '$N_2H_2S_3$'$^{2-}$ ligand, all efforts to obtain the corresponding monocarbonyl complex [Ru(CO)('$N_3H_3S_2$')] remained unsuccessful. The composition of the complexes resulting from reactions of precursors such as $[Ru(H)(Cl)(CO)(PCy_3)_2]$[8] or $[Ru(Cl)_2(CO)_3(THF)]$[9] with '$N_3H_3S_2$'$^{2-}$ suggested that only four of the five '$N_3H_3S_2$'$^{2-}$ donors had become coordinated.

However, coordination of all five '$N_3H_3S_2$'$^{2-}$ donors could be achieved when $[RuCl_2(PPh_3)_3]$ was treated with '$N_3H_3S_2$'$^{2-}$ in refluxing THF (Scheme 3, reaction c). Yellow [Ru(PPh$_3$)('$N_3H_3S_2$')] (**7**) resulted, which interestingly also formed when $[RuCl_2(PPh_3)_3]$ was treated with the *N*-tosylated ligand '$^{Ts}N_3H_2S_2$'$^{2-}$ (**3**). This indicates that coordination of **3** facilitates its detosylation. Detosylation of amides normally needs much more drastic reaction conditions.[10] The C_S symmetry of **7** indicated in Scheme 3 is concluded from the ^{1}H-NMR signal pattern of the aliphatic '$N_3H_3S_2$'$^{2-}$ protons. It consists of two pseudo triplets and a multiplet and characteristically differs from the pattern observed consisting of two pseudo triplets. This signal pattern characteristically differs from that observed for the aliphatic protons in C_1-symmetrical [Fe(CO)('$N_3H_3S_2$')]. A ^{13}C-NMR spectrum confirming this conclusion could not be recorded due to insufficient solubility of **7**. However, the C_S symmetry assumed for **7** is further supported by the C_S-symmetrical structure of the *S*-methylated derivative of **7**. Alkylation of **7** by CH_3I yielded [Ru(PPh$_3$)('$N_3H_3S_2$'-Me_2)]I_2 (**8**) (reaction d), whose molecular structure could be determined by X-ray structure analysis.

Coordination of the '$N_3H_3S_2$'$^{2-}$ ligand to (nitrosyl)ruthenium complexes resulted in deprotonation of one aromatic amine function. Treatment of $[RuCl_3(NO)(PPh_3)_2]$ with '$N_3H_3S_2$'$^{2-}$ and LiOMe yielded neutral, deep green [Ru(NO)('$N_3H_2S_2$')] (**9**), which exhibits one amide donor (reaction g). The formation of the amide could further be substantiated by protonation of **9** with HBF_4 (reaction h). It yielded red [Ru(NO)('$N_3H_3S_2$')]BF_4 (**10**). The protonation is accompanied by a shift of the ν(NO) band from 1779 cm^{-1} in **9** to 1855 cm^{-1} in **10**. The ^{1}H- and ^{13}C-NMR spectra indicate that **10** exists in two diastereomeric forms (see below).

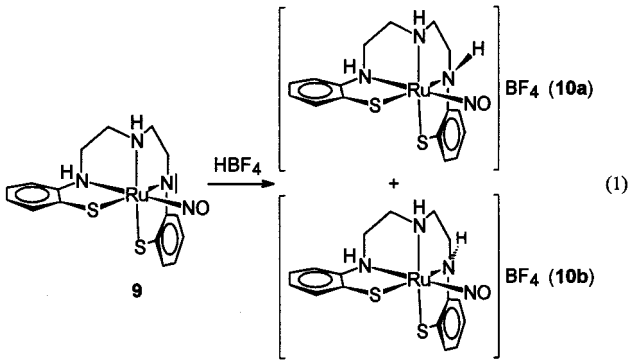
Substitution and Acid−Base Reactions

The reactivity of the complexes containing [M('$N_3H_3S_2$')] or [M('$N_3H_2S_2$')] cores paralleled that of complexes with [M('$N_2H_2S_3$')] or [M('N_2HS_3')] cores. The [Fe(CO)('$N_3H_3S_2$')] complex proved unexpectedly labile with respect to CO loss.

The ruthenium complexes proved extremely inert towards substitution. For example, the PPh_3 ligand in [Ru(PPh$_3$)('$N_3H_3S_2$')] (**7**) could neither be substituted by CO (50 bar, 2 d, THF) nor by N_2H_4 which was used as solvent (40°C, 1 d). With the intention to labilize the Ru−PPh_3 bond by converting the thiolate into thioether

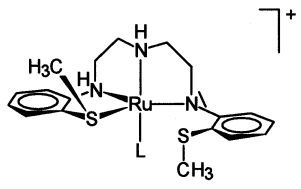
functions, **7** was alkylated. The resulting [Ru(PPh$_3$)-('N$_3$H$_3$S$_2$'-Me$_2$)]I$_2$ (**8**) proved to be as inert towards substitution as **7**.

As in the case of [M('N$_2$H$_2$S$_3$')] complexes, protonation−deprotonation reactions of the [M('N$_3$H$_3$S$_2$')] cores could be observed. Protonation of the amide donor in [Ru(NO)('N$_3$H$_2$S$_2$')] yielded two diastereomers of [Ru(NO)('N$_3$H$_3$S$_2$')]BF$_4$. The formation of two diastereomers could be concluded from the $^{13}C\{^1H\}$-NMR spectrum and is explained by the stereogenicity of the amine function that results from either a "front"- or a "back"-side attack of the proton upon the prochiral amide donor (Equation 1).



The protonation−deprotonation reactions of [Ru(PPh$_3$)('N$_3$H$_3$S$_2$'-Me$_2$)]I$_2$ (**8**) differ from those of the analogous [Ru(PPh$_3$)('N$_2$H$_2$S$_3$'-Me$_2$)]I$_2$. The ^{1}H-NMR spectrum and X-ray structure determination established that **8** formed in isomerically pure form as C_S-symmetrical species when synthesized from **7** and CH$_3$I. Complex **8** can be deprotonated by bases such as N$_2$H$_4$ to give [Ru(PPh$_3$)('N$_3$H$_2$S$_2$'-Me$_2$)]I (**11**), which is converted into [Ru(PPh$_3$)('N$_3$H$_3$S$_2$'-Me$_2$)](I)(Cl) (**12**) when treated with HCl. The ^{1}H- and ^{13}C-NMR spectra unambiguously show that **11** and **12** have C_1 symmetry only. Thus, the deprotonation−protonation reactions [steps e) and f) in Scheme 3] lead to a configurational rearrangement of **8**.

The rearrangement could occur via the five-coordinate intermediate [Ru(PPh$_3$)('N$_3$H$_2$S$_2$'-Me$_2$)]$^+$ in which one thioether donor has dissociated. Driving force of this rearrangement probably is the planarization tendency of amide N atoms[11] and, in addition, the capability of amide donors to stabilize five-coordinate intermediates by π donation.[2e] The rearrangement further indicates that, like [M('N$_2$H$_2$S$_3$')] cores, also [M('N$_3$H$_3$S$_2$')] cores prefer the C_1-symmetrical configuration. It is noteworthy that the protonation of **11** yields only one diastereomer of **12** (cf. ref.[4]).



Characterization of Complexes

All complexes except [Fe('N$_3$H$_3$S$_2$')]$_2$ (**5**) are diamagnetic and exhibit similar solubilities. They are soluble in DMF and DMSO, moderately soluble in CH$_2$Cl$_2$, THF, and acetone, and virtually insoluble in all other common organic solvents. The phosphane complex [Ru(PPh$_3$)('N$_3$H$_3$S$_2$')] (**7**) is only very moderately soluble even in DMSO. All complexes have been characterized by elemental analysis, IR, NMR, and mass spectra. The FD mass spectra of the complexes showed the molecular ions except in the case of **6** in which only the decarbonylated species [Fe('N$_3$H$_3$S$_2$')]$^+$ could be observed. As expected the IR (KBr) spectra show numerous bands. One broad or up to three weak- to medium-intensity ν(NH) bands in the region of 3293 to 3102 cm^{-1} can be used as an IR probe for the complexes containing [M('N$_3$H$_3$S$_2$')] cores. In contrast, [Ru(NO)('N$_3$H$_2$S$_2$')] (**9**) containing one amide donor gives rise to two medium ν(NH) bands at 3245 and 3224 cm^{-1}. The complexes **6**, **9**, and **10** can further readily be identified by their strong ν(CO), ν(NO), and ν(BF$_4$) bands which appear at 1934 cm^{-1} (**6** in THF), 1779 cm^{-1} (**9** in KBr), and 1855 and 1084 cm^{-1}, respectively (**10** in KBr). $^{13}C\{^1H\}$-NMR spectra are the most suitable probe for distinguishing between C_1 or C_S symmetry of the complexes[4][12]. Twelve aromatic ^{13}C-NMR signals in the range δ = 160−108 and four aliphatic ^{13}C-NMR signals of the *N*-bonded C atoms in the range δ = 65−45 indicate C_1 symmetry of the complexes **6** and **9** containing [M('N$_3$H$_3$S$_2$')] or [M('N$_3$H$_2$S$_2$')] cores. Two sets of this signal pattern in the $^{13}C\{^1H\}$-NMR spectrum of **10** suggest the presence of two diastereomers. Only six aromatic and two aliphatic (*N*-bonded C$_2$H$_4$ groups) ^{13}C-NMR signals for the [M('N$_3$H$_3$S$_2$')] core indicate the C_S symmetry of **8**, which was confirmed by X-ray structure analysis. The C_S symmetry of **8** is also reflected in the appearance of only one SCH$_3$ singlet in the ^{1}H-NMR spectrum.

X-ray Structure Analysis of [Ru(PPh$_3$)('N$_3$H$_3$S$_2$'-Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (**8** · 2 CH$_2$Cl$_2$)

The molecular structure of [Ru(PPh$_3$)('N$_3$H$_3$S$_2$'−Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (**8** · 2 CH$_2$Cl$_2$) (Figure 1) was determined by X-ray structure analysis. Table 1 lists selected distances and angles.

The ruthenium center of **8** is pseudo-octahedrally surrounded by the phosphane and the 'N$_3$H$_3$S$_2$'-Me$_2$ donors. Both the aromatic amine and the thioether donor atoms assume *cis* positions, and the aliphatic amine donor N3 and the phosphane donor occupy *trans* positions such that **8** exhibits approximate C_S symmetry. Distances and angles show no anomalies and are typical for this type of Ru^{II} complexes.[4,13] Within the crystal, the complex cations, iodide anions, and CH$_2$Cl$_2$ solvate molecules are connected by hydrogen bonds. The shortest interionic contact is observed between the N2, H2, and I2 atoms [N2−H2···I2: N2−H2 86(6), N2···I2 352.8(4), H2···I2 274(5) pm; N2−H2···I2 153(4)°].

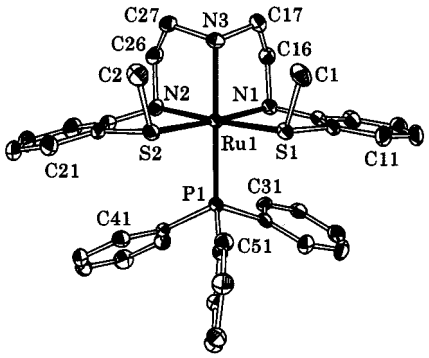


Figure 1. Molecular structure of the cation of $[Ru(PPh_3)('N_3H_3S_2'\text{-}Me_2)]I_2 \cdot 2\ CH_2Cl_2$ (**8** · 2 CH_2Cl_2) (50% probability ellipsoids, H atoms and solvate molecules omitted)

Table 1. Selected distances [pm] and angles [°] of $[Ru(PPh_3)('N_3H_3S_2'\text{-}Me_2)]I_2 \cdot 2\ CH_2Cl_2$ (**8** · 2 CH_2Cl_2)

Ru1−N1	217.6(3)	N1−Ru1−N3	80.5(1)
Ru1−N2	215.9(3)	N2−Ru1−N3	80.6(1)
Ru1−N3	216.4(3)	P1−Ru1−N3	173.4(1)
Ru1−P1	234.3(1)	S1−Ru1−N3	96.0(1)
Ru1−S1	231.5(1)	S2−Ru1−N3	96.2(1)
Ru1−S2	231.3(1)	N1−Ru1−N2	96.0(1)

Concluding Discussion

In the course of a study aiming at the series of $'NHS_4'^{2-}$, $'N_2H_2S_3'^{2-}$, and $'N_3H_3S_2'^{2-}$ ligands and transition metal complexes with increasing electron density at the transition metal centers, the new pentadentate ligand $'N_3H_3S_2'\text{-}H_2$ was prepared.

A special synthetic route which warranted the NH and the terminal thiolate donors of $'N_3H_3S_2'\text{-}H_2$ was developed. The low-frequency ν(CO) of $[Fe(CO)('N_3H_3S_2')]$ (**6**) (1934 cm^{-1}) shows that the iron center indeed exhibits a high electron density. However, the Fe electron density is not higher than in the related $[Fe(CO)('N_2H_2S_3')]$ (1932 cm^{-1}), the CO ligand is very labile and no small molecules other than CO could be coordinated to the $[Fe('N_3H_3S_2')]$ fragment. With respect to $[Fe('NHS_4')]$ fragments, a further serious shortcoming of $[M(L)('N_3H_3S_2')]$ complexes is their core structure. Like $[M(L)('N_2H_2S_3')]$ complexes, $[M(L)('N_3H_3S_2')]$ complexes appear to prefer C_1-symmetrical structures and thiolate donors in *cis* position. Only $[Ru(PPh_3)('N_3H_3S_2')]$ (**7**) and its *S*-methylated derivative $[Ru(PPh_3)('N_3H_3S_2'\text{-}Me_2)]I_2$ (**8**) exhibit C_S-symmetrical structures which are comparable with the C_S-symmetrical diastereomer of the $[Fe('NHS_4')]$ fragment. However, the deprotonation−protonation reactions of **8** lead to the C_1-symmetrical diastereomer **12** and indicate that also the $[Ru('N_3H_3S_2')]$ fragment prefers the C_1-symmetrical core structure. Thus, with respect to structure, $[M(L)('N_3H_3S_2')]$ and $[M(L)('N_2H_2S_3')]$ complexes show largely similar properties. The same holds for the electronic and reactivity features. The corresponding carbonyliron complexes exhibit high electron density at the metal centers, but are labile. The ruthenium complexes are virtually substitution inert. The reversible deprotonation of one amine NH function to give an amide donor is their only significant reaction. It has previously been discussed in detail that this formation of π-donor amides can lead to either labilization or stabilization of *trans*-metal−ligand bonds.[4,14]

Experimental Section

General: Unless noted otherwise, all procedures were carried out under N_2 at room temperature by using Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. − Spectra were recorded with the following instruments: IR: Perkin Elmer 16 PC FT-IR. − NMR: JEOL JNM-GX 270 and JNM-EX 270 [^{1}H NMR (269.6 MHz) and ^{13}C NMR (67.7 MHz): The protio-solvent signal was used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane; ^{31}P NMR (109.38 MHz): external standard H_3PO_4]. − Mass spectra: Varian MAT 212 and JEOL JMS 700. − Magnetic moments: Johnson Matthey magnetic susceptibility balance (293K). − $[RuCl_3(NO)(PPh_3)_2]$,[15] $[RuCl_2(PPh_3)_3]$,[16] *N,N*-bis[2-(*p*-tolylsulfonyloxy)ethyl]-*p*-toluolsulfonamide,[17] and 2(3*H*)-benzothiazolone[18] were prepared by literature methods. *N,N*-bis(2-iodoethyl)-*p*-toluenesulfonamide[19] was prepared in situ and directly used afterwards. Hydrazine was obtained by twofold distillation of $N_2H_4 \cdot H_2O$ over solid potassium hydroxide under reduced pressure.

Alkylation of 2(3*H*)-Benzothiazolone (1) with *N,N*-Bis(2-iodoethyl)-*p*-toluenesulfonamide To Give 2: A solution of *N,N*-bis[2-(*p*-tolylsulfonyloxy)ethyl]-*p*-toluenesulfonamide (2.03 g, 3.58 mmol) and NaI (2.50 g, 10.68 mmol) in acetone (40 mL) was refluxed for 14 h and concentrated to dryness. The resulting residue was dissolved in CH_2Cl_2 (30 mL), insoluble material was removed by filtration, and the filtrate was concentrated to dryness, yielding *N,N*-bis(2-iodoethyl)-*p*-toluenesulfonamide (1.52 g, 89%). − A suspension of 2(3*H*)-benzothiazolone (0.96 g, 6.35 mmol) and K_2CO_3 (0.88 g, 6.37 mmol) in 2-butanone (20 mL) was refluxed for 30 min and then combined with a solution of *N,N*-bis(2-iodoethyl)-*p*-toluenesulfonamide (1.52 g, 3.17 mmol) in 2-butanone (10 mL). The resulting white suspension was refluxed for 14 h and concentrated to dryness to give a foamy white residue. It was redissolved in EtOH (30 mL). Addition of water (50 mL) precipitated a white powder, which was separated, digested with EtOH (30 mL), and dried in vacuo. Yield: 1.39 g (74%). − $C_{25}H_{23}N_3O_4S_3$ (525.67): calcd. C 57.12, H 4.41, N 7.99, S 18.30; found C 56.71, H 4.47, N 7.98, S 18.11. − IR (KBr): $\tilde{\nu}$ = 1678 vs ν(CO), 1327, 1153 w ν(SO_2) cm^{-1}. − MS (FD, CH_2Cl_2); *m/z*: 525 [**2**]$^+$. − ^{1}H NMR ($CDCl_3$): δ = 7.59 (d, 2 H, C_6H_4), 7.40 (d, 2 H, C_6H_4), 7.34 (d, 2 H, C_6H_4), 7.25−7.10 (m, 6 H, C_6H_4), 4.14 (t, 4 H, C_2H_4), 3.50 (t, 4 H, C_2H_4), 2.35 (s, 3 H, CH_3, Ts). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 170.6 (CO), 144.6, 137.3, 135.8, 130.6, 127.7, 127.4, 124.0, 123.4, 123.3, 111.3 (C, aryl), 46.9, 42.2 (C_2H_4), 22.2 (CH_3, Ts).

$'^{Ts}N_3H_2S_2'\text{-}H_2$ (3): A suspension of **2** (1.83 g, 3.48 mmol) in EtOH (20 mL) was combined with a solution of NaOH (1.39 g, 34.8 mmol) in H_2O (20 mL) and refluxed for 18 h. Concentrated hydrochloric acid was added until pH = 3 was reached, the solution was concentrated in volume to one half, diluted with H_2O (60 mL), and extracted with CH_2Cl_2 (60 mL). The combined CH_2Cl_2 phases were dried with anhydrous Na_2SO_4 and concentrated to dryness, yielding **3** as a yellow powder. Yield: 1.60 g (97%). − $C_{23}H_{27}N_3O_2S_3$ (473.69): calcd. C 58.32, H 5.75, N 8.87, S 20.31; found: C 58.10, H 5.90, N 8.91, S 19.99. − IR (KBr): $\tilde{\nu}$ = 3385, 3364 w ν(NH), 2522 w ν(SH), 1323 s, 1159 vs ν(SO_2) cm^{-1}. − MS (FD, CH_2Cl_2);

m/z: 474 [$'^{Ts}N_3H_2S_2'$-H_2]$^+$. – ^{1}H NMR ($CDCl_3$): δ = 7.62 (d, 2 H, C_6H_4, Ts, *ortho* to SO_2), 7.23 (d, 2 H, C_6H_4, *ortho* to SH), 7.17 (d, 2 H, C_6H_4, Ts, *meta* to SO_2), 7.03 (dd, 2 H, C_6H_4, *para* to SH), 6.50 (dd, 2 H, C_6H_4, *para* to NH), 6.42 (d, 2 H, C_6H_4, *ortho* to NH), 4.80 (s, br., 2 H, NH), 3.27 (s, 8 H, C_2H_4), 2.70 (s, br., 2 H, SH), 2.30 (s, 3 H, CH_3, Ts). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 147.6, 143.7, 135.5, 135.2, 129.8, 129.4, 127.1, 117.2, 111.6, 109.8 (C, aryl), 48.8, 42.9 (C_2H_4), 21.4 (CH_3, Ts).

$'N_3H_3S_2'$-H_2 (4): Metallic sodium was added in small portions to a solution of $'^{Ts}N_3H_2S_2'$-H_2 (**3**) (1.0 g, 2.1 mmol) in refluxing liquid NH_3 (100 mL) until the blue color of dissolved sodium persisted for 10 min. Ammonium chloride was added until the blue color disappeared, and the liquid NH_3 was allowed to evaporate. The resulting beige residue was dissolved in aqueous NaOH (0.4 g NaOH in 100 mL H_2O). The resulting H_2O solution was extracted with CH_2Cl_2 (70 mL) and filtered through filter pulp. Concentrated hydrochloric acid was added to the H_2O filtrate. When pH = 8 was reached, a white solid precipitated which was separated and washed with H_2O (40 mL). Recrystallization from EtOH yielded beige needles of **4**. The pH = 8 proved critical, because further lowering of the pH led to formation of yellow material, which had a gummy consistency, proved insoluble in all common organic solvents, and was not characterized in detail. Yield: 0.51 g (66%) of **4** · EtOH. – $C_{18}H_{27}N_3OS_2$ (365.57): calcd. C 59.14, H 7.44, N 11.49, S 17.54; found C 58.86, H 7.61, N 11.74, S 17.69. – IR (KBr): $\tilde{\nu}$ = 3376, 3317 m ν(NH), 2588 w, br. ν(SH) cm^{-1}. – MS (FD, CH_2Cl_2); *m/z*: 319 [$'N_3H_3S_2'$-H_2]$^+$. – ^{1}H NMR (CD_2Cl_2): δ = 7.35 (d, 2 H, C_6H_4), 7.15 (t, 2 H, C_6H_4), 6.68–6.53 (m, 4 H, C_6H_4), 3.50–3.10 (s, br., superimposed by t, 9 H, SH, NH, C_2H_4), 2.97 (t, 4 H, C_2H_4). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 148.8, 135.1, 129.3, 117.3, 110.8, 110.8 (C_6H_4), 48.4, 43.6 (C_2H_4).

[Fe($'N_3H_3S_2'$)]$_2$ (5): A yellow solution of $'N_3H_3S_2'$-H_2 · EtOH (**4** · EtOH) (0.22 g, 0.60 mmol) and LiOMe (1.20 mmol, 1.20 mL of a 1 M solution in MeOH) in THF (10 mL) was combined with a solution of $FeCl_2 \cdot 4\ H_2O$ (0.12 g, 0.60 mmol) in MeOH (10 mL). A white solid precipitated which was separated, washed with MeOH (15 mL), and dried in vacuo, in the course of which the color of the solid changed from white to grey. Yield: 0.20 g (89%). – $C_{32}H_{38}Fe_2N_6S_4$ (746.66): calcd. C 51.48, H 5.13, N 11.26, S 17.18; found C 51.19, H 5.29, N 11.17, S 16.98. – IR (KBr): $\tilde{\nu}$ = 3145 m, br. ν(NH) cm^{-1}. – MS (FD, DMSO); *m/z*: 373 [Fe($'N_3H_3S_2'$)]$^+$. – μ_{eff} (293 K) = 3.94 μ_B.

[Fe(CO)($'N_3H_3S_2'$)] (6): CO was continuously bubbled through a solution of $'N_3H_3S_2'$-H_2 · EtOH (**4** · EtOH) (0.135 g, 0.37 mmol) and LiOMe (0.75 mmol, 0.75 mL of a 1 M solution in MeOH) in MeOH (15 mL). A solution of $FeCl_2 \cdot 4\ H_2O$ (0.074 g, 0.37 mmol) in MeOH (15 mL) was added and a red suspension formed. After 15 min, the resulting red solid was separated, washed with MeOH (20 mL), and dried in vacuo. Yield: 0.15 g (97%) **6** · 0.5 MeOH. – $C_{17.5}H_{21}FeN_3O_{1.5}S_2$ (417.36): calcd. C 50.36, H 5.07, N 10.07, S 15.37; found C 50.35, H 4.88, N 10.27, S 15.59. – IR (KBr): $\tilde{\nu}$ = 3241, 3157, 3102 w ν(NH), 1930 s, 1910 vs ν(CO) cm^{-1}. – IR (THF): $\tilde{\nu}$ = 1934 vs ν(CO) cm^{-1}. – MS (FD, DMSO); *m/z*: 373 [Fe($'N_3H_3S_2'$)]$^+$, 317 [($'N_3H_3S_2'$)]$^+$. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.26–6.50 (m, 9 H, C_6H_4 and NH superimposed), 5.86 (s, br., 1 H, NH), 5.78 (s, br., 1 H, NH), 3.70–2.20 (m, 8 H, C_2H_4). – ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 221.3 (CO), 153.6, 152.1, 151.1, 149.1, 129.0, 128.2, 124.7, 124.5, 122.4, 119.5, 119.4, 119.0 (C_6H_4), 62.2, 58.9, 46.2, 45.0 (C_2H_4).

[Ru(PPh$_3$)($'N_3H_3S_2'$)] (7): [$RuCl_2(PPh_3)_3$] (0.79 g, 0.82 mmol) was added to a solution of $'N_3H_3S_2'$-H_2 · EtOH (**4** · EtOH) (0.30 g, 0.82 mmol) and LiOMe (1.65 mmol, 1.65 mL of a 1 M solution in MeOH) in THF (30 mL). The reaction mixture was stirred for 24 h and then refluxed for 3 h. The yellow solid precipitating from the green solution was separated, washed with THF (15 mL) and MeOH (60 mL), and dried in vacuo. [Compound **7** was obtained in equally high yields, when instead of **4** · EtOH the ligand $'^{Ts}N_3H_2S_2'$-H_2 (**3**) was used]. Yield: 0.18 g (32%). – $C_{34}H_{34}N_3PRuS_2$ (680.84): calcd. C 59.98, H 5.03, N 6.17, S 9.42; found C 59.63, H 5.19, N 6.29, S 9.34. – IR (KBr): $\tilde{\nu}$ = 3288 w, 3258, 3247 m ν(NH) cm^{-1}. – MS (FD, DMSO, ^{102}Ru); *m/z*: 681 [Ru(PPh$_3$)($'N_3H_3S_2'$)]$^+$. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.35–6.17 [m, 23 H, C_6H_4 and P(C_6H_5) superimposed], 5.77 (d, 2 H, NH), 4.41 (s, br., 1 H, NH), 3.75 (pseudo-t, 2 H, C_2H_4), 2.90 (pseudo-t, 2 H, C_2H_4), 2.75–2.20 (m, 4 H, C_2H_4). – ^{31}P{^{1}H} NMR ([D$_6$]DMSO): δ = 52.6 [s, P(C_6H_5)].

[Ru(PPh$_3$)($'N_3H_3S_2'$-Me$_2$)]I$_2$ (8): Addition of MeI (0.50 mL, 8.0 mmol) to a yellow suspension of [Ru(PPh$_3$)($'N_3H_3S_2'$)] (**7**) (0.13 g, 0.19 mmol) in THF (20 mL) yielded a beige suspension. The beige solid was separated after 2 d, washed with THF (10 mL), and dried in vacuo. Yield: 0.19 g (96%) **8** · THF. – $C_{40}H_{48}I_2N_3OPRuS_2$ (1036.83): calcd. C 46.34, H 4.67, N 4.05, S 6.19; found C 46.18, H 4.85, N 3.92, S 6.48. – IR (KBr): $\tilde{\nu}$ = 3284 w, br. ν(NH) cm^{-1}. – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z*: 838 {[Ru(PPh$_3$)-($'N_3H_3S_2'$–Me$_2$)](I)}$^+$, 711 [Ru(PPh$_3$)($'N_3H_3S_2'$-Me$_2$)]$^+$. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.73–6.96 [m, 23 H, C_6H_4 and P(C_6H_5) superimposed], 6.85 (d, 2 H, NH arom.), 6.46 (s, br., 1 H, NH aliphat.), 4.06 (m, 2 H, C_2H_4), 2.92 (s, 6 H, SCH_3), 2.87–2.72 (m, 6 H, C_2H_4). – ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 148.3 (C_6H_4), 133.2, 132.7 [d, P(C_6H_5)], 131.7, 131.2, 130.6 (C_6H_4), 129.8 [s, br., P(C_6H_5)], 128.2 (C_6H_4), 127.8 [d, P(C_6H_5)], 126.4 (C_6H_4), 60.0, 51.8 (C_2H_4), 25.3 (d, SCH_3). – ^{31}P{^{1}H} NMR ([D$_6$]DMSO): δ = 37.5 [s, P(C_6H_5)].

[Ru(PPh$_3$)($'N_3H_2S_2'$-Me$_2$)]I (11): [Ru(PPh$_3$)($'N_3H_3S_2'$-Me$_2$)]I$_2$ · THF (**8** · THF) (0.10 g, 0.10 mmol) was suspended in N_2H_4 (1.0 mL). The yellow reaction mixture was stirred for 4 h and then concentrated to dryness. The resulting yellow residue was dissolved in CH_2Cl_2 (5 mL), insoluble material was removed by filtration, and the filtrate was concentrated to dryness yielding a yellow powder. Yield: 0.07 g (84%). – IR (KBr): $\tilde{\nu}$ = 3275 m ν(NH) cm^{-1}. – MS (FD, DMSO, ^{102}Ru); *m/z*: 694 [Ru(PPh$_3$)($'N_3H_2S_2'$-CH$_2$)]$^+$. – ^{1}H NMR (CD_2Cl_2): δ = 7.57 [t, 2 H, CH(aryl)], 7.47–7.19 [m, 17 H, CH(aryl)], 6.97 [t, 1 H, CH(aryl)], 6.75 [d, 1 H, CH(aryl)], 6.31 [d, 1 H, CH(aryl)], 6.09 [t, 1 H, CH(aryl)], 5.72 (t, br., 1 H, NH), 5.46 (t, br., 1 H, NH), 3.46–2.60 (m, 8 H, C_2H_4), 2.36 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 158.6, 147.3, 138.1 (d) (C_6H_4), 133.8, 133.6 [d, P(C_6H_5)], 131.9, 131.3, 131.0 (C_6H_4), 130.1 [s, br., P(C_6H_5)], 130.0, 129.6 (C_6H_4), 129.2 [d, P(C_6H_5)], 127.2, 120.0, 111.4, 110.7 (C_6H_4), 58.7, 57.4, 55.8, 49.2 (C_2H_4), 28.2, 23.1 (d) (SCH_3). – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 43.7 [s, P(C_6H_5)].

[Ru(PPh$_3$)($'N_3H_3S_2'$-Me$_2$)](I)(Cl) (12) by Protonation of 11: Hydrochloric acid (0.50 mmol, 5 mL of a 0.1 M solution of HCl in H_2O) was added to a yellow suspension of [Ru(PPh$_3$)($'N_3H_2S_2'$-Me$_2$)]I (**11**) (0.04 g, 0.05 mmol) in MeOH (15 mL). The reaction mixture was stirred for 5 min. Removal of the solvents yielded a yellow powder (0.04 g). – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z*: 711 [Ru(PPh$_3$)($'N_3H_3S_2'$-Me$_2$)]$^+$, 695 [Ru(PPh$_3$)($'N_3H_2S_2'$-Me)]$^+$, 681 [Ru(PPh$_3$)($'N_3H_3S_2'$)]$^+$. – ^{1}H NMR (CD_2Cl_2): δ = 9.57 (t, br., 1 H, NH arom.), 9.37 (s, br., 1 H, NH arom.), 7.80–7.04 [m, 24 H, C_6H_4, P(C_6H_5) and NH superimposed], 3.96–2.82 (m, 8 H, C_2H_4), 2.29 (s, 3 H, SCH_3), 1.84 (s, 3 H, SCH_3). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 151.9, 151.4, 136.8, 134.3, 134.1 (d), 133.5 (d), 132.1, 131.9, 131.8, 131.2, 130.9, 129.6 (d), 129.2 (d), 128.8, 125.4, 125.1

Table 2. Selected crystallographic data of [Ru(PPh$_3$)('$N_3H_3S_2$'-Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (**8** · 2 CH$_2$Cl$_2$)

Compound	**8**·2 CH$_2$Cl$_2$
Formula	$C_{38}H_{44}Cl_4I_2N_3PRuS_2$
M_r [g/mol]	1134.52
Crystal size [mm]	0.7 × 0.5 × 0.4
F(000)	2232
Space group	$P2_1/c$
Cryst. system	monoclinic
a [pm]	1602.7(4)
b [pm]	1738.8(4)
c [pm]	1695.5(4)
β [°]	110.67(2)
Z	4
V [nm^3]	4.421(2)
$d_{calcd.}$ [g/cm^{-3}]	1.705
μ [mm^{-1}]	2.154
Diffractometer	Siemens P4
Radiation [pm]	Mo-K_α (λ = 71.073)
Temperature [K]	163
Scan technique	ω scan
2θ range [°]	4.6−54.2
Scan speed [°/min]	3.0−30.0
Meas. reflections	13956
Indep. reflections	9702
Obsd. reflections	7037
σ criterion	$F \geq 4\sigma(F)$
Refined parameters	620
R_1, wR_2 (%)	3.34, 9.18

(C, aryl), 59.1, 54.4, 53.6, 46.3 (NCH$_2$), 28.4, 26.4 (d) (SCH$_3$). − ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 36.0 [s, P(C$_6$H$_5$)].

[Ru(NO)('$N_3H_2S_2$')] (9): [RuCl$_3$(NO)(PPh$_3$)$_2$] (0.42 g, 0.55 mmol) was added to a solution of '$N_3H_3S_2$'-H$_2$ · EtOH (**4** · EtOH) (0.20 g, 0.55 mmol) and LiOMe (1.64 mmol, 1.64 mL of a 1 M solution in MeOH) in THF (20 mL). The resulting black solution was stirred for 48 h, during which time a green solid precipitated. The solid was separated, washed with MeOH and THF (20 mL each), and dried in vacuo. Yield: 0.14 g (57%). − $C_{16}H_{18}N_4ORuS_2$ (447.55): calcd. C 42.94, H 4.05, N 12.52, S 14.33; found C 42.96, H 4.22, N 12.37, S 14.09. − IR (KBr): $\tilde{\nu}$ = 3245, 3224 m ν(NH), 1779 vs ν(NO) cm^{-1}. − MS (FD, DMSO, ^{102}Ru); *m/z*: 448 [Ru(NO)('$N_3H_2S_2$')]$^+$. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.83 (s, br., 1 H, NH), 7.20 (d, 1 H, C$_6$H$_4$), 6.97−6.29 (m, 8 H, C$_6$H$_4$ and NH superimposed), 3.89−2.77 (m, 8 H, C$_2$H$_4$). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 158.5, 146.6, 146.1, 137.9, 129.0, 127.0, 126.3, 125.0, 122.6, 121.7, 114.7, 108.3 (C$_6$H$_4$), 59.0, 57.7, 52.5, 50.5 (C$_2$H$_4$).

[Ru(NO)('$N_3H_3S_2$')]BF$_4$ (10): Addition of HBF$_4$ (0.30 mL of a 54% solution in Et$_2$O) to a green suspension of [Ru(NO)('$N_3H_2S_2$')] (**9**) (0.94 g, 2.12 mmol) in a 1:1 mixture (20 mL) of MeOH and Et$_2$O yielded a red suspension. The resulting red solid was separated after 3 h, washed with MeOH (5 mL), and dried in vacuo. Yield: 0.67 g (59%). − $C_{16}H_{19}BF_4N_4ORuS_2$ (535.36): calcd. C 35.90, H 3.58, N 10.47, S 11.98; found C 36.12, H 3.56, N 10.42, S 11.69. − IR (KBr): $\tilde{\nu}$ = 3293, 3238, 3219 w ν(NH), 1855 vs ν(NO), 1084 s ν(BF$_4$) cm^{-1}. − MS (FD, DMSO, ^{102}Ru); *m/z*: 448 [Ru(NO)('$N_3H_2S_2$')]$^+$. − ^{1}H NMR ([D$_6$]DMSO): δ = 10.04 (m, 0.6 H, NH arom.), 8.42 (m, 0.3 H, NH arom.), 8.24 (s, br., 0.3 H, NH arom.), 8.05 (s, br., 0.6 H, NH arom.), 7.67−6.87 (m, 8 H, C$_6$H$_4$), 4.41 (m, 0.3 H, NH aliphat.), 4.10 (m, 0.6 H, NH aliphat.), 3.94−2.95 (m, 8 H, C$_2$H$_4$). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 150.9, 148.5, 147.4, 147.3, 145.0, 143.1, 142.2, 141.3, 129.7, 129.2, 129.1, 128.0, 127.6, 127.0, 125.2, 124.3, 123.8, 123.7, 123.6, 123.4, 122.5 (C$_6$H$_4$), 62.5, 58.5, 57.6, 57.1, 54.2, 52.0, 51.7, 51.4 (C$_2$H$_4$).

X-ray Structure Analysis of [Ru(PPh$_3$)('$N_3H_3S_2$'-Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (8 · 2 CH$_2$Cl$_2$): Bright green columns of [Ru(PPh$_3$)('$N_3H_3S_2$'-Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (**8** · 2 CH$_2$Cl$_2$) were grown from a saturated CH$_2$Cl$_2$ solution of **8** which was layered with *n*-hexane. A suitable single crystal was sealed under N$_2$ in a glass capillary, and data were collected with a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXTL-PLUS).[20] Full-matrix least-squares refinement was carried out on F^2 values (SHELXL-93).[21] The hydrogen atoms were located in a difference Fourier synthesis and isotropically refined. The hydrogen atoms of the CH$_2$Cl$_2$ solvate molecules were calculated for ideal geometries. Their isotropic temperature factors were fixed at 1.5 times the value for the C atoms attached to them. For the atom Cl41, an obvious alternative position exists, which, however, could not be refined. Table 2 contains selected crystallographic data for [Ru(PPh$_3$)('$N_3H_3S_2$'-Me$_2$)]I$_2$ · 2 CH$_2$Cl$_2$ (**8** · 2 CH$_2$Cl$_2$).[22]

Acknowledgments

Support of these investigations by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

[1] [1a] D. P. Mellor in *Chelating Agents and Metal Chelates* (Eds.: F. P. Dwyer, D. P. Mellor), Academic Press, New York, London, **1964**, p. 44. − [1b] K. Burger, in *Biocoordination Chemistry* (Ed.: K. Burger), Ellis Horwood, New York, **1990**, p. 11.
[2] [2a] D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460−469. − [2b] D. Sellmann, W. Soglowek, F. Knoch, G. Ritter, J. Dengler, *Inorg. Chem.* **1992**, *31*, 3711−3717. − [2c] D. Sellmann, W. Soglowek, F. Knoch, M. Moll, *Angew. Chem.* **1989**, *101*, 1244−1245; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1271−1272. − [2d] D. Sellmann, H. Kunstmann, F. Knoch, M. Moll, *Inorg. Chem.* **1988**, *27*, 4183−4190. − [2e] D. Sellmann, T. Hofmann, F. Knoch, *Inorg. Chim. Acta* **1994**, *224*, 61−71.
[3] R. A. Henderson, G. J. Leigh, C. J. Picket, *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 245.
[4] D. Sellmann, J. Utz, F. W. Heinemann, *Inorg. Chem.*, submitted.
[5] Cf.: A. F. Childs, L. J. Goldsworthy, G. F. Harding, F. E. King, A. W. Nineham, W. L. Norris, S. G. P. Plant, B. Selton, A. L. L. Tompsett, *J. Chem. Soc.* **1948**, 2174−2177.
[6] Cf.: W. C. J. Ross, J. G. Wilson, *J. Chem. Soc.* **1959**, 3616−3622.
[7] Cf.: G. Klein, B. Prijs, *Helv. Chim. Acta* **1954**, *37*, 2057−2067.
[8] D. Sellmann, R. Ruf, F. Knoch, M. Moll, *Inorg. Chem.* **1995**, *34*, 4745−4755.
[9] M. I. Bruce, F. G. A. Stone, *J. Chem. Soc. A* **1967**, 1238−1241.
[10] R. C. Roemmele, H. Rapoport, *J. Org. Chem.* **1988**, *53*, 2367−2371.
[11] B. R. Cameron, D. A. House, A. McAuley, *J. Chem. Soc., Dalton Trans.* **1993**, 1019−1022.
[12] [12a] D. Sellmann, H. Kunstmann, F. Knoch, M. Moll, *Inorg. Chem.* **1988**, *27*, 4183−4190. − [12b] D. Sellmann, C. Rohm, M. Moll, F. Knoch, *Z. Naturforsch.* **1995**, *50b*, 1229−1244.
[13] [13a] D. Sellmann, R. Ruf, F. Knoch, M. Moll, *Inorg. Chem.* **1995**, *34*, 5963−5972. − [13b] D. Sellmann, O. Käppler, F. Knoch, M. Moll, *Z. Naturforsch.* **1990**, *45b*, 803−816.
[14] M. L. Tobe, *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1.
[15] J. J. Levison, S. D. Robinson, *J. Chem. Soc. A* **1970**, 2947−2954.
[16] T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1966**, *28*, 945−956.
[17] L. Qian, Z. Sun, M. P. Mertes, K. Bowman Mertes, *J. Org. Chem.* **1991**, *56*, 4904−4907.
[18] R. F. Hunter, *J. Chem. Soc.* **1930**, 125−147.
[19] F. P. Schmidtchen, *Chem. Ber.* **1980**, *113*, 2175−2182.
[20] *SHELXTL-PLUS for Siemens Crystallographic Research Systems, Release 4 21/V*, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1990**.

[21] G. M. Sheldrick, *SHELXL-93, Program for crystal structure refinement*, Universität Göttingen, **1993**.
[22] Crystallographic data (excluding structure factors) for the structure of $[Ru(PPh_3)('N_3H_3S_2'\text{-}Me_2)]I_2 \cdot 2\ CH_2Cl_2$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100956. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int.code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received August 7, 1998
[I98278]