Transition Metal Complexes with Sulfur Ligands, 142[‡]

Inert and Labile [Ru(L)('pyS_4')] Complexes with Rigid [$RuNS_4$] Cores and *trans*-Thiolate Donors [L = PPh_3, PEt_3, DMSO, CO, NO^+, N_2H_4; 'pyS_4'$^{2-}$ = 2,6-Bis(2-mercaptophenylthio)dimethylpyridine(2–)]

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Dedicated to Professor Wilhelm Preetz on the occasion of his 65th birthday

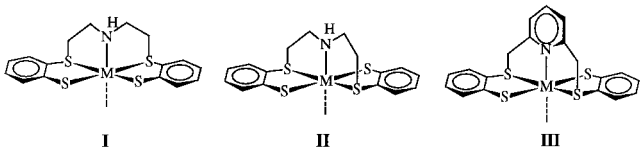
Keywords: Ruthenium / Sulfur ligands / Exchange reactions

In a quest for ruthenium complexes having [$RuNS_4$] cores, a non-fluxional configuration, *trans*-thiolate donors, and exchangeable coligands L, [Ru(L)('pyS_4')] complexes have been synthesized ['pyS_4'$^{2-}$ = 2,6-bis(2-mercaptophenylthio)dimethylpyridine(2–)]. Treatment of [$RuCl_2(PPh_3)_3$] with 'pyS_4'$^{2-}$ gave [Ru(PPh_3)('pyS_4')] (**1**). Alkylation of **1** with excess MeI yielded [Ru(PPh_3)('pyS_4'–Me_2)]I_2 (**2**). [Ru(DMSO)('pyS_4')] (**3**) was obtained from [$RuCl_2(DMSO)_4$] and 'pyS_4'$^{2-}$. The PPh_3 or DMSO coligands in **1**, **2**, and **3** proved to be very inert to substitution. Only the DMSO could be displaced by CO under drastic conditions yielding [Ru(CO)('pyS_4')] (**4**). Treatment of [$RuCl_2(CH_3CN)_4$] with 'pyS_4'$^{2-}$ yielded [Ru('pyS_4')]$_2$ (**5**); in the presence of PEt_3 or N_2H_4 mononuclear [Ru(PEt_3)('pyS_4')] (**6**) and [Ru(N_2H_4)('pyS_4')] (**7**) were formed. Template alkylation of NBu_4[Ru(NO)($S_2C_6H_4$)$_2$] with 2,6-bis(tosyloxymethyl)pyridine gave [Ru(NO)('pyS_4')]Tos (**8**). Complex **8** proved to be the best suited precursor for L exchange reactions. Under reducing conditions, **8** releases its NO ligand and the resulting [Ru('pyS_4')] fragments can combine either with each other to give **5**, or with PEt_3 and N_2H_4 to yield **6** and **7**, respectively. All complexes have been characterized by spectroscopic methods and elemental analysis; **1**, **2**, **3**, and **4** have also been submitted to X-ray structure analysis.

Introduction

Transition metals in sulfur-dominated coordination spheres form the active centers of numerous oxidoreductases, e.g. of nitrogenases, hydrogenases, and CO dehydrogenases.[1] Efforts to elucidate the molecular mechanisms of the enzyme reactions and to find competitive catalysts with enzyme-like activity are a major impetus in the search for low molecular weight complexes that combine structure and reactivity features of the enzyme metal–sulfur [MS] centers.[2] An important aspect of this search is the design of new ligands that meet specific requirements with regard to donor atom sets, configurations, stability, and reactivity of the resulting complexes.[3]

In this respect, the 'N_HS_4'$^{2-}$ [= 2,2'-bis(2-mercaptophenylthio)diethylamine(2–)] ligand has proved particularly versatile.[4] It has yielded a large number of [Fe(L)('N_HS_4')] complexes with L comprising the nitrogenase-relevant molecules CO, NO, N_2H_2, N_2H_4, and NH_3, although not N_2. This prompted us to investigate the coordination behaviour of 'N_HS_4'$^{2-}$ towards ruthenium as well; it was anticipated that with the kinetically more inert ruthenium, species that are labile with iron would become isolable. However, practically all our experiments in this area proved unsuccessful. Besides the problem of finding [Ru(L)('N_HS_4')] complexes with exchangeable coligands L, the diastereoisomerism of the [M('N_HS_4')] fragments led to the formation of inseparable mixtures of diastereomeric [Ru(L)('N_HS_4')] species. In [M(L)('N_HS_4')] complexes, the [M('N_HS_4')] fragments can exist in two diastereomeric forms, indicated by formulae I and II (Scheme 1).



Scheme 1. Configurations of [MNS_4] complexes

While in the case of iron these diastereomers isomerize via five-coordinate intermediates to yield, depending on the coligand L, either I or II,[4,5] the ruthenium analogues do not isomerize, due to the inert nature of the ruthenium donor bonds. In order to eliminate this problem, we replaced the flexible $N(C_2H_4)_2$ bridge of the 'N_HS_4'$^{2-}$ ligand by the rigid 2,6-bis(methylene)pyridine bridge and synthesized the ligand 'pyS_4'$^{2-}$ [= 2,6-bis(2-mercaptophenylthio)-dimethylpyridine(2–)].[6] This 'pyS_4'$^{2-}$ ligand indeed yielded iron complexes consistently containing the fragment III.[6,7] It is also noteworthy that the hydrazine complex [Fe(N_2H_4)('pyS_4')] contains a low-spin Fe^{II} center,[7] in con-

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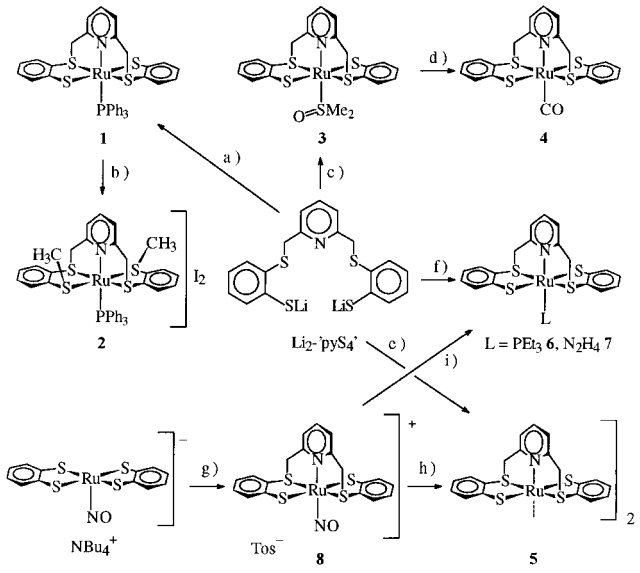
trast to the [Fe(N_2H_4)('N_HS_4')] complex, which has the core structure I and a high-spin Fe^{II} center.

In this paper we report our efforts to synthesize [Ru(L)('pyS_4')] complexes and to find species in which the L coligands may be displaced by nitrogenase-relevant small molecules. The exchange of L proved to be the major problem.

Results

The HCl adduct ('pyS_4'–H_2) · HCl served as the starting material for preparing the ligand. It was routinely deprotonated with three equivalents of LiOMe to give Li_2'pyS_4'. The subsequent reactions of Li_2'pyS_4' with suitable Ru precursor complexes are summarized in Scheme 2.



Scheme 2. Syntheses and reactions of [Ru('pyS_4')] complexes; (a) + [$RuCl_2(PPh_3)_3$]/MeOH/15 h/room temp.; (b) + exc. CH_3I/THF/2 d/room temp.; (c) + [$RuCl_2(DMSO)_4$]/MeOH/15 h/room temp.; (d) + CO, 120 bar/THF/110 °C/3 d; (e) + [$RuCl_2(CH_3CN)_4$]/MeOH/4 h reflux; (f) + [$RuCl_2(CH_3CN)_4$]/exc. L (L = PEt_3, N_2H_4)/MeOH/4 h reflux; (g) + 'pyTos'/THF/4 h reflux; (h) + 2.5 $LiBEt_3H$/THF/2.5 d room temp.; (i) + exc. L (L = PEt_3, N_2H_4)/THF/room temp.

The PPh_3 complex [Ru(PPh_3)('pyS_4')] (**1**) was found to be readily soluble in CH_2Cl_2 or THF. Although PPh_3 is a relatively bulky ligand, it proved practically inert to substitution. As yet, we have not been able to exchange it by N_2H_4 or even CO, neither under standard conditions nor at elevated temperatures. Attempts to labilize the Ru–PPh_3 bond of **1** by alkylation of the thiolate donors using excess CH_3I gave [Ru(PPh_3)('pyS_4'–Me_2)]I_2 (**2**), which contains the 'pyS_4'–Me_2 ligand. Complex **2** was formed in diastereomerically pure form. The PPh_3 ligand in **2** has proved to be as substitution inert as that in **1**. Our next target complex was [Ru(DMSO)('pyS_4')] (**3**) as we anticipated that the DMSO ligand would be as labile as that in the related [Ru(DMSO)(PR_3)('S_4')] complexes with R = Cy, *i*Pr; 'S_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2–).[8a] However, the DMSO ligand in **3** also proved very inert and could not be exchanged for CO at room temperature at pressures ranging from 1–100 bar. Only under very drastic conditions in an autoclave (120 bar CO, 110 °C, THF) did a slow reaction (3 d) take place to give [Ru(CO)('pyS_4')] (**4**). Another potentially labile target complex was [Ru(CH_3CN)('pyS_4')]. Its synthesis was attempted starting from [$RuCl_2(CH_3CN)_4$] and Li_2'pyS_4'. However, heating in MeOH proved necessary in order to observe a reaction, and the resulting product was found not to contain CH_3CN. A red-brown solid precipitated, which was found to be practically insoluble in all common solvents. Its IR spectrum, elemental analysis, and mass spectrum, which featured an ion peak at m/z = 973, were compatible with the dinuclear [Ru('pyS_4')]$_2$ (**5**). Complex **5** was found not to react with boiling DMSO, pyridine, or with CO in these solvents. The reaction of [$RuCl_2(CH_3CN)_4$] with Li_2'pyS_4' took a different course when potential ligands such as PEt_3 or N_2H_4 were present. In these cases, the mononuclear complexes [Ru(PEt_3)('pyS_4')] (**6**) and [Ru(N_2H_4)('pyS_4')] (**7**) were formed. This might be indicative of the formation of a labile [Ru(CH_3CN)('pyS_4')] intermediate, which loses CH_3CN in boiling MeOH and either dimerizes to give **5** or adds PEt_3 and N_2H_4 to yield **6** and **7**, respectively. Complex **6** proved as inert to substitution as the PPh_3 complex **1**. Complex **7** demonstrates that the [Ru('pyS_4')] fragment can bind "hard" σ coligands. The purification of complexes **6** and **7** synthesized by this method proved troublesome. They were more easily obtained from reactions of the nitrosyl complex [Ru(NO)('pyS_4')]Tos (**8**). Complex **8** was obtained by template alkylation of NBu_4[Ru(NO)($S_2C_6H_4$)$_2$] with 2,6-bis(tosyloxymethyl)pyridine ('pyTos') in boiling THF. Pure **8** was precipitated from the reaction solution in good yield. It was found to be soluble in MeOH, DMF, and DMSO, but insoluble in THF, CH_2Cl_2, Et_2O, and *n*-hexane. The relatively high frequency of the ν(NO) absorption of **8** (1892 cm^{-1}) suggested that nucleophiles could be added to the NO ligand.[9] Indeed, rapid reactions occurred upon treatment of **8** with equimolar amounts of NH_3 or LiOMe in MeOH. Green-brown solids were immediately precipitated, which exhibited strong bands in their IR spectra at around 1800 cm^{-1}, consistent with the formation of ligands derived from NO. However, these products were so insoluble in all common solvents that they could not be adequately characterized.

In order to probe the reducibility of **8**, a cyclic voltammogram was recorded (Figure 1). The quasi-reversible (–275 mV) and irreversible (–1200 mV) redox waves in the cathodic region could tentatively be assigned to the formation of neutral [Ru(NO)('pyS_4')]^0 and anionic [Ru(NO)('pyS_4')]$^-$ complexes, which formally represent 19 and 20 valence electron [VE] species.

In order to achieve chemical reductions, **8** was treated with $LiBEt_3H$ and N_2H_4. On addition of $LiBEt_3H$ to a red-brown suspension of **8** in THF, gas was evolved and a deep-red solution was produced, from which red [Ru('pyS_4')]$_2$ (**5**) precipitated. The IR spectrum of the deep-red solution did not feature any bands attributable to an NO ligand. When a red-brown THF suspension of **8** was treated with an excess of N_2H_4, gas was again evolved and a deep-red solu-

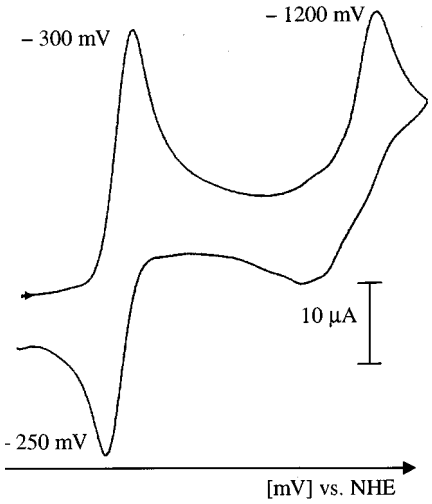


Figure 1. Cyclic voltammogram of [Ru(NO)('pyS$_4$')]Tos (**8**) in DMF (10^{-3} M **8**, 10^{-1} M NBu_4PF_6, $v = 0.02$ Vs^{-1})

tion was produced. Red microcrystals of the hydrazine complex **7** were precipitated upon addition of MeOH and Et_2O. In another experiment, a THF suspension of **8** was treated with excess PEt_3. A red-orange solid formed, which was characterized as the pure PEt_3 complex **6**. Phosphanes frequently act as reductants[10] and hence these results suggest that reduction of **8** gives a substitution labile species that releases NO to yield [Ru('pyS$_4$')] fragments. In the absence of suitable ligands, these fragments dimerize to give [Ru('pyS$_4$')]$_2$ (**5**), while in the presence of such ligands the corresponding [Ru(L)('pyS$_4$')] derivatives are formed.

Characterization and General Properties of the Complexes

As far as possible, all the complexes have been characterized by standard spectroscopic methods and by elemental analysis. The molecular structures of **1**, **2**, **3**, and **4** have been determined by X-ray diffraction analysis. All complexes are colored yellow-red to deep-red. The neutral complexes **1**, **3**, **4**, **6**, and **7** show moderate to good solubility in CH_2Cl_2 and THF, while the ionic complexes **2** and **8** are soluble in DMSO and DMF. The dinuclear species [Ru('pyS$_4$')]$_2$ (**5**) was found to be insoluble in all common solvents. Consequently, no NMR spectra of **5** could be recorded, and this complex could only be characterized by its IR and mass spectra and elemental analysis.

In the FD mass spectra, either the respective molecular ions or the [Ru('pyS$_4$')]$_2^+$ ion arising from dissociation of the coligand L and dimerization of the resulting [Ru('pyS$_4$')] fragments could be observed. The FD mass spectrum of [Ru(PPh$_3$)('pyS$_4$'–Me$_2$)]I$_2$ (**2**) exhibited only fragment ions resulting from demethylation, e.g. [Ru(PPh$_3$)('pyS$_4$'–Me)]$^+$ and [Ru(PPh$_3$)('pyS$_4$')]$^+$. The IR spectra in KBr featured the typical bands attributable to the [Ru('pyS$_4$')] fragment besides the characteristic bands of the coligands. For example, the ν(SO) band at 1015 cm^{-1} indicates *S*-coordination of the DMSO ligand in [Ru(DMSO)('pyS$_4$')] (**3**). Characteristic strong ν(CO) and ν(NO) bands are seen for **4** (1954 cm^{-1}) and **8** (1892 cm^{-1}), respectively, while ν(NH) bands at 3335, 3207, and 3042 cm^{-1} give evidence of the coordination of N_2H_4 in [Ru(N_2H_4)('pyS$_4$')] (**7**).

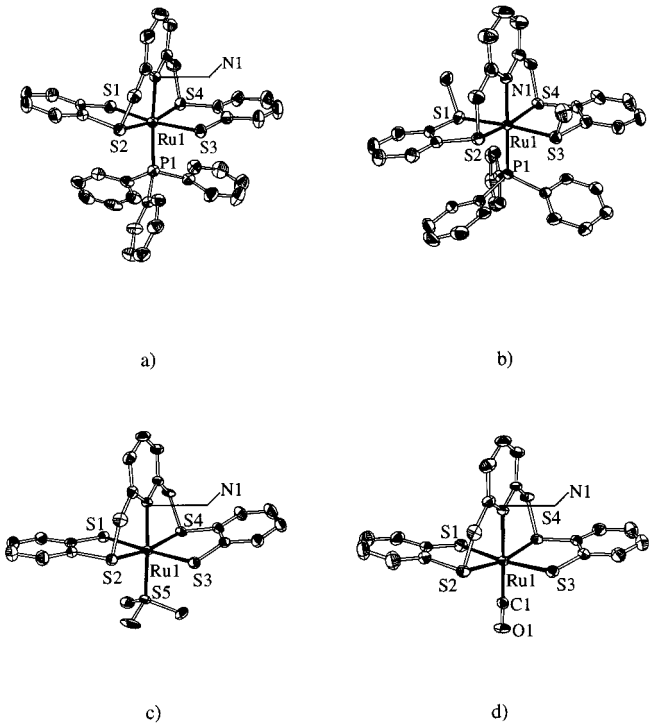


Figure 2. Molecular structures of [Ru(PPh$_3$)('pyS$_4$')] (**1**), [Ru(PPh$_3$)('pyS$_4$'-Me$_2$)]I$_2$ · 2 CH_2Cl_2 (**2** · 2 CH_2Cl_2), [Ru(DMSO)-('pyS$_4$')] · MeOH (**3** · MeOH), and [Ru(CO)('pyS$_4$')] · MeOH (**4** · MeOH) (50% probability ellipsoids; H atoms and solvent molecules omitted for clarity)

The $^{13}C\{^1H\}$-NMR spectra proved particularly helpful in establishing the diastereomeric purity of the complexes and the twofold symmetry of the [Ru('pyS$_4$')] fragments. The seventeen aromatic and two aliphatic C atoms of the [Ru('pyS$_4$')] fragments give rise to only ten ^{13}C signals. This is compatible with C_2 or C_S symmetry of the fragments. Steric considerations and the X-ray structure analyses show that in all cases the C_2-symmetric [Ru('pyS$_4$')] configuration with *trans*-thiolate donors is adopted. The singlet ^{13}C-NMR signal due to the two SCH_3 groups in [Ru(PPh$_3$)('pyS$_4$'–Me$_2$)]I$_2$ (**2**) proves that the thiolate alkylation of **1** yields only one diastereomer of **2**.

The AB splitting of the diastereotopic CH_2 protons, giving rise to two pseudo doublets is a characteristic feature of the [Ru('pyS$_4$')] pattern in the ^1H-NMR spectra. In some cases, a triplet due to the pyridine H_γ proton can also be observed. Usually, this triplet is superimposed by the signals of either the pyridine H_β, benzenedithiolate, or PPh_3 protons. Two DMSO methyl group singlets are seen for the DMSO complex **3**, while two N_2H_4 singlets are seen in the spectrum of the hydrazine complex **7**.

Table 1. Selected distances (pm) and angles (°) in [Ru(PPh_3)('pyS_4')] (**1**), [Ru(PPh_3)('pyS_4'–Me_2)]$I_2 \cdot 2\ CH_2Cl_2$ (**2** · 2 CH_2Cl_2), [Ru(DMSO)('pyS_4')] · MeOH (**3** · MeOH), and [Ru(CO)('pyS_4')] · MeOH (**4** · MeOH)

Complex (L)	**1** (PPh_3)	**2** · 2 CH_2Cl_2 (PPh_3)	**3** · MeOH (DMSO)	**4** · MeOH (CO)
Ru1–N1	211.1(4)	211.8(4)	208.8(3)	212.0(4)
Ru1–S1	238.8(1)	238.5(1)	239.1(1)	240.1(1)
Ru1–S2	231.0(1)	232.4(1)	230.3(1)	231.7(1)
Ru1–S3	239.8(1)	234.7(1)	239.3(1)	237.5(1)
Ru1–S4	231.4(1)	234.1(1)	231.7(1)	232.0(1)
Ru1–L	231.0(1)	234.9(1)	225.6(1)	185.3(5)
S1–Ru1–S2	87.46(4)	86.08(5)	87.18(4)	87.58(5)
S1–Ru1–S4	88.33(4)	99.43(5)	94.77(4)	94.10(5)
S3–Ru1–S4	86.85(4)	86.72(5)	87.08(4)	87.94(5)
S2–Ru1–S3	95.69(4)	88.37(5)	90.25(4)	89.06(5)
N1–Ru1–S1	86.57(10)	90.31(12)	85.62(9)	87.08(11)
N1–Ru1–S2	83.41(10)	84.19(12)	84.17(9)	83.43(12)
N1–Ru1–L	174.37(10)	178.18(11)	177.05(9)	178.6(2)

X-ray Structure Analysis

X-ray structure analyses of **1**, **2**, **3**, and **4** corroborated the spectroscopic conclusions with regard to the structures. Figure 2 depicts the molecular structures of [Ru(PPh_3)('pyS_4')] (**1**), [Ru(PPh_3)('pyS_4'–Me_2)]$I_2 \cdot 2\ CH_2Cl_2$ (**2** · 2 CH_2Cl_2), [Ru(DMSO)('pyS_4')] · MeOH (**3** · MeOH), and [Ru(CO)('pyS_4')] · MeOH (**4** · MeOH). Table 1 lists selected distances and angles.

In all the complexes, the ruthenium centers exhibit pseudo-octahedral coordination. The [Ru('pyS_4')] fragments are pseudo-C_2 symmetrical. The thiolate donors occupy positions *trans* to one another, and the coligands L occupy the positions *trans* to the pyridine N donor. Distances and angles show no anomalies.[8] The Ru–S(thiolate) distances are usually slightly longer than the Ru–S(thioether) distances. The Ru–N(pyridine) distances in all four complexes are almost identical. The molecular structure of **3** proves the *S*-coordination of the DMSO ligand, as had been concluded from the IR spectrum.

The results further indicate that the [Ru('pyS_4')] core is structurally very robust. This is also evidenced by a direct comparison of **1** and **2**. The Ru–N distances and the average Ru–S distances in **1** (235.3 pm) and the twofold methylated derivative **2** (234.9 pm) are practically identical. This demonstrates that the [$RuNS_4$] cores remain unaffected even when the electronic situation changes, as must occur upon alkylation of the thiolate donors. These results support the structure–function relationship of metal–sulfur complexes described in several previous papers.[2,11]

Discussion and Conclusion

The results reported herein demonstrate that the 'pyS_4'$^{2-}$ ligand forms ruthenium complexes possessing [Ru('pyS_4')] cores that (i) exhibit the desired configuration, having *trans*-thiolate donors, and (ii) are structurally robust. The new complexes were obtained either by direct reaction of 'pyS_4'$^{2-}$ with suitable Ru precursor complexes or by template alkylation of [Ru(NO)($S_2C_6H_4$)$_2$]$^-$ yielding [Ru(NO)('pyS_4')]Tos (**8**). In comparison with analogous [Fe(L)('pyS_4')] complexes, which are usually synthesized at room temperature, the synthesis of the corresponding [Ru(L)('pyS_4')] complexes has in many cases been found to require heating or very drastic conditions as, for example, in the case of the CO complex **4**. This reflects the more inert nature of Ru complexes as compared to their Fe counterparts. It also accounts for the fact that it is difficult to find complexes with labile L ligands that can serve as precursors for other [Ru(L)('pyS_4')] complexes. For example, the PPh_3 ligand in **1** is inert and could not be labilized by thiolate methylation, which can be expected to withdraw electron density from the Ru center and to weaken the Ru–PPh_3 bond.[11] Even the DMSO complex **3** proved virtually inert; only under very drastic conditions could a DMSO/CO exchange be achieved. Attempts to obtain labile [Ru(CH_3CN)('pyS_4')] complexes were unsuccessful, yielding only insoluble [Ru('pyS_4')]$_2$ (**5**) or, in the presence of PEt_3 or N_2H_4, the corresponding [Ru(L)('pyS_4')] complexes with L = PEt_3 (**6**) and N_2H_4 (**7**). Complexes **6** and **7** obtained by this method proved difficult to purify, probably due to the formation of side-products as a result of the drastic reaction conditions.

The best suited precursor complex for exchange reactions was ultimately found to be [Ru(NO)('pyS_4')]Tos (**8**). Cyclic voltammetry demonstrated the reducibility of **8**. The resulting 19 or even 20 valence electron species can be expected to be labile as antibonding orbitals must be populated.[4] Indeed, reduction of **8** with $LiBEt_3H$ leads to loss of the NO ligand with the formation of [Ru('pyS_4')]$_2$ (**5**). Reduction of **8** with excess N_2H_4 likewise releases NO, but the excess N_2H_4 adds as a ligand and the hydrazine complex **7** can be isolated in high yield in analytically pure form.

The potential of this method for the synthesis of [Ru(L)('pyS_4')] complexes with nitrogenase-relevant L ligands is currently being investigated.

Experimental Section

General Methods: Unless noted otherwise, all reactions and operations were carried out at room temperature under nitrogen using standard Schlenk techniques. Solvents were dried and distilled

prior to use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded with the following instruments: IR (KBr discs or CaF_2 cuvettes; solvent bands were compensated): Perkin–Elmer 983, 1620 FT-IR, and 16PC FT-IR. – NMR: Jeol FT-JNM-GX 270, EX 270, and Lambda LA 400; spectra were referenced to residual protio-solvent signals; chemical shifts are quoted on the δ scale (downfield shifts are positive) with respect to tetramethylsilane (^1H, $^{13}C\{^1H\}$ NMR) or 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR); spectra were recorded at 25 °C. – Mass spectra: Jeol MSTATION 700 spectrometer. – Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. – Cyclic voltammetry was performed with a PAR 264A potentiostat using a three-electrode cell with a glassy carbon ROTEL A working electrode and Pt reference and counterelectrodes. Solutions were 10^{-3} M in the substance under investigation; TBA[PF_6] (10^{-1} M) was used as the supporting electrolyte. Potentials were referenced to the normal hydrogen electrode (NHE) using Fc/Fc^+ as an internal standard ($E_{Fc/Fc+} = +0.4$ V vs. NHE).[12]

$[RuCl_2(PPh_3)_3]$,[13] $[RuCl_2(DMSO)_4]$,[14] $[RuCl_2(CH_3CN)_4]$,[15] $NBu_4[Ru(NO)(S_2C_6H_4)_2]$,[16] 'pyTos' = 2,6-bis(tosyloxymethyl)pyridine),[17] and 'pyS_4'-H_2HCl[6] were prepared as described in the literature; LiOMe was purchased from Aldrich.

[Ru(PPh_3)('pyS_4')] (1): Solid $[RuCl_2(PPh_3)_3]$ (959 mg, 1.0 mmol) was added to a stirred MeOH solution (20 mL) of 'pyS_4'–$H_2 \cdot HCl$ (424 mg, 1.0 mmol) and LiOMe (3.0 mL of a 1 M solution in MeOH, 3.0 mmol). In the course of 15 h, a red-brown suspension was produced. The red-brown solid was separated, washed with MeOH (20 mL) and Et_2O (40 mL), dried, and dissolved in hot pyridine (40 mL). The resulting solution was cooled to room temperature and layered with MeOH (100 mL). Orange crystals precipitated, which were separated after 1 d, washed with MeOH (20 mL) and Et_2O (30 mL), and dried in vacuo. Yield: 615 mg of **1** (82%). – $C_{37}H_{30}NPRuS_4$ (748.94): calcd. C 59.34, H 4.04, N 1.87, S 17.12; found C 59.25, H 4.08, N 1.94, S 17.16. – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z* = 749 [Ru(PPh_3)('pyS_4')]$^+$. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.46–7.01 [m, 22 H, C_6H_4, P(C_6H_5) and pyridine], 6.87–6.76 (m, 4 H, C_6H_4), 4.94 (d, 2 H, CH_2), 4.46 (d, 2 H, CH_2). – $^{13}C\{^1H\}$ NMR (67.8 MHz, CD_2Cl_2): δ = 157.69, 157.45, 137.42, 136.81, 134.59 (arom. C), 133.85 [d, P(C_6H_5)], 132.40, 131.60, 130.87 (arom. C), 129.10 [d, P(C_6H_5)], 128.06 (arom. C), 127.71 [d, P(C_6H_5)], 121.31 [d, P(C_6H_5)], 58.68 (d, CH_2). – $^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2): δ = 49.0 (s).

[Ru(PPh_3)('pyS_4'–Me_2)]I_2 (2): 2 mL (32.13 mmol) of CH_3I was added to a stirred orange THF suspension (30 mL) of [Ru(PPh_3)('pyS_4')] (**1**) (350 mg, 0.47 mmol). A beige solid formed, which was separated after 2 d, washed with THF (80 mL) and Et_2O (40 mL), and dried in vacuo. Recrystallization from CH_2Cl_2/Et_2O yielded yellow crystals, which were separated, washed with Et_2O (20 mL), and dried in vacuo. Yield: 395 mg of **2** · 2 CH_2Cl_2 (70%). – $C_{41}H_{40}Cl_4I_2NPRuS_4$ (1202.68): calcd. C 40.95, H 3.35, N 1.16, S 10.66; found C 41.07, H 3.17, N 1.20, S 10.78. – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z* = 749 [Ru(PPh_3)('pyS_4')]$^+$. – ^1H NMR (269.6 MHz, [D_6]DMSO): δ = 8.00 (d, 2 H, C_6H_4), 7.92 (t, 1 H, H_γ, pyridine), 7.83 (d, 2 H, C_6H_4), 7.64–7.52 [m, 6 H, C_6H_4, P(C_6H_5)], 7.30–7.17 [m, 15 H, C_6H_4, P(C_6H_5), H_β, pyridine], 5.80 (d, 2 H, CH_2), 5.23 (d, 2 H, CH_2), 2.12 (s, 6 H, CH_3). – $^{13}C\{^1H\}$ NMR (67.8 MHz, [D_6]DMSO): δ = 158.67, 138.06, 135.78, 133.78, 133.12 (arom. C), 132.76 [d, P(C_6H_5)], 131.99 [t, P(C_6H_5)], 130.96, 130.57, 130.27 (arom. C), 128.37 [d, P(C_6H_5)], 123.23, (arom. C), 55.54 (CH_2), 24.36 (CH_3). – $^{31}P\{^1H\}$ NMR (109.38 MHz, [D_6]DMSO): δ = 36.0 (s).

[Ru(DMSO)('pyS_4')] (3): Solid $[RuCl_2(DMSO)_4]$ (485 mg, 1.0 mmol) was added to a stirred MeOH solution (20 mL) of 'pyS_4'–$H_2 \cdot HCl$ (424 mg, 1.0 mmol) and LiOMe (3.0 mL of a 1 M solution in MeOH, 3.0 mmol). In the course of 15 h, a yellow suspension resulted. The yellow solid was separated, washed with MeOH (20 mL), dried, and dissolved in hot DMSO (20 mL). The resulting solution was cooled to room temperature and layered with MeOH (60 mL). Yellow crystals precipitated, which were separated after 2 d, washed with MeOH (20 mL) and Et_2O (30 mL), and dried in vacuo. Yield: 325 mg of **3** · MeOH (54%). – $C_{22}H_{25}NO_2RuS_5$ (596.82): calcd. C 44.28, H 4.22, N 2.35, S 26.86; found C 44.16, H 4.40, N 2.37, S 26.86. – IR (KBr): $\tilde{\nu}$ = 1015 cm^{-1} ν(SO). – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z* = 565 [Ru(DMSO)('pyS_4')]$^+$. – ^1H NMR (269.6 MHz, [D_6]DMSO): δ = 7.70 (d, 2 H, C_6H_4), 7.45 (t, 1 H, H_γ, pyridine), 7.35 (d, 2 H, C_6H_4), 7.25 (d, 2 H, H_β, pyridine), 6.95–6.85 (m, 4 H, C_6H_4), 4.7 (s, 4 H, CH_2), 3.05 [s, 3 H, $CH_3S(O)CH_3$], 2.8 [s, 3 H, $CH_3S(O)CH_3$]. – $^{13}C\{^1H\}$ NMR (67.8 MHz, [D_6]DMSO): δ = 157.40, 155.60, 135.30, 132.60, 130.60, 130.10, 128.00, 121.50, 121.30, (arom. C), 55.70 (CH_2), 46.80, 46.30 (CH_3).

[Ru(CO)('pyS_4')] (4): In an autoclave, a yellow suspension of [Ru(DMSO)('pyS_4')] · MeOH (**3**) (330 mg, 0.55 mmol) in 30 mL of THF was exposed to CO gas (120 bar) for 3 d at 110 °C. The resulting yellow solution was then concentrated to dryness, the yellow residue was digested with MeOH (60 mL) and Et_2O (20 mL), and the product was dried in vacuo. Yield: 170 mg of **4** · MeOH (57%). – $C_{21}H_{19}NO_2RuS_4$ (546.70): calcd. C 46.14, H 3.50, N 2.56, S 23.46; found C 45.92, H 3.72, N 2.59, S 23.60. – IR (KBr): $\tilde{\nu}$ = 1954 cm^{-1} ν(CO). – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z* = 515 [Ru(CO)('pyS_4')]$^+$. – ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 7.63–7.60 (m, 2 H, C_6H_4), 7.46–7.43 (m, 3 H, C_6H_4, H_γ, pyridine), 7.19 (d, 2 H, H_β, pyridine), 7.02–6.91 (m, 4 H, C_6H_4), 5.07 (d, 2 H, CH_2), 4.59 (d, 2 H, CH_2). – $^{13}C\{^1H\}$ NMR (100.40 MHz, CD_2Cl_2): δ = 201.62 (CO), 156.23, 155.91, 136.76, 132.48, 131.02, 129.12, 122.60, 121.99 (arom. C), 58.11 (CH_2).

['pyS_4')]$_2$ (5): $LiBEt_3H$ (1.375 mL of a 1 M solution in THF, 1.375 mmol) was added to a red-brown suspension of [Ru(NO)('pyS_4')]Tos (**8**) (380 mg, 0.55 mmol) in 15 mL of THF. Gas was evolved and a deep-red solution was produced, from which a red-brown solid precipitated in the course of 2.5 d. This solid was separated, washed with MeOH (10 mL), THF (10 mL), and Et_2O (10 mL), and dried in vacuo. Yield: 120 mg of **5** · MeOH (43%). – $C_{39}H_{34}N_2ORu_2S_8$ (1005.33): calcd. C 46.59, H 3.41, N 2.79, S 25.51; found C 46.20, H 3.20, N 2.89, S 25.42. – MS (FD, DMSO, ^{102}Ru); *m/z* = 973 [Ru('pyS_4')]$_2^+$.

[Ru(PEt_3)('pyS_4')] (6): PEt_3 (0.5 mL, 3.40 mmol) was added to a red-brown suspension of [Ru(NO)('pyS_4')]Tos (**8**) (300 mg, 0.44 mmol) in 12 mL of THF. In the course of 20 h, an orange solid precipitated, which was separated, washed with MeOH (20 mL) and *n*-hexane (25 mL), and dried in vacuo. Yield: 100 mg of **6** (38%). – $C_{25}H_{30}NPRuS_4$ (604.80): calcd. C 49.65, H 5.00, N 2.32, S 21.20; found C 49.89, H 5.03, N 2.42, S 21.20. – MS (FD, CH_2Cl_2, ^{102}Ru); *m/z* = 605 [Ru(PEt_3)('pyS_4')]$^+$. – ^1H NMR (399.65 MHz, CD_2Cl_2): δ = 7.63–7.61 (m, 2 H, C_6H_4), 7.42–7.40 (m, 2 H, C_6H_4), 7.27 (t, 1 H, H_γ, pyridine), 7.10 (d, 2 H, H_β, pyridine), 6.90–6.82 (m, 4 H, C_6H_4), 4.78 (d, 2 H, CH_2), 4.42 (d, 2 H, CH_2), 1.90–1.79 (m, 3 H, P-CH_2CH_3), 1.57–1.46 (m, 3 H, P-CH_2CH_3), 0.97–0.89 (m, 9 H, P-CH_2CH_3). – $^{13}C\{^1H\}$ NMR (67.8 MHz, CD_2Cl_2): δ = 157.87, 156.39, 133.85, 132.34, 131.98, 130.69, 127.81, 120.90, 120.85 (arom. C), 59.26 (d, CH_2), 18.34 (d, P-CH_2CH_3), 7.70 (d, P-CH_2CH_3). – $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2): δ = 34.7 (s).

Table 2. Selected crystallographic data for [Ru(PPh_3)('pyS_4')] (**1**), [Ru(PPh_3)('pyS_4'–Me_2)]$I_2 \cdot 2\,CH_2Cl_2$ (**2** · 2 CH_2Cl_2), [Ru(DMSO)('pyS_4')] · MeOH (**3** · MeOH), and [Ru(CO)('pyS_4')] · MeOH (**4** · MeOH)

Compound	**1**	**2** · 2 CH_2Cl_2	**3** · MeOH	**4** · MeOH
Formula	$C_{37}H_{30}NPRuS_4$	$C_{41}H_{40}Cl_4I_2NPRuS_4$	$C_{22}H_{24}NO_2RuS_5$	$C_{21}H_{19}NO_2RuS_4$
M_r [g/mol]	748.90	1202.62	595.79	546.68
Crystal size [mm]	0.50 × 0.30 × 0.12	0.60 × 0.54 × 0.38	0.35 × 0.20 × 0.10	0.50 × 0.20 × 0.10
F(000)	1528	1180	606	552
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [pm]	1315.8(3)	1136.9(1)	921.3(2)	837.7(2)
b [pm]	1381.2(3)	1143.2(2)	1113.5(1)	1132.3(2)
c [pm]	1868.3(4)	1783.2(2)	1247.9(2)	1220.3(2)
α [°]	83.98(2)	94.13(1)	90.35(1)	68.05(1)
β [°]	81.80(2)	96.38(1)	102.92(1)	84.18(2)
γ [°]	78.42(2)	94.83(1)	106.64(1)	87.79(2)
V [nm^3]	3.2821(12)	2.2873(5)	1.1921(3)	1.0680(4)
Z	4	2	2	2
$d_{calcd.}$ [g/cm^3]	1.516	1.746	1.660	1.700
μ [mm^{-1}]	0.809	2.174	1.116	1.143
Diffractometer	Nicolet R3m/V	Siemens P4	Siemens P4	Siemens P4
Radiation [pm]		Mo-K_α (λ = 71.073)		
Temperature [K]	293(2)	200(2)	200(2)	200(2)
Scan technique	ω scan	ω scan	ω scan	ω scan
2Θ range [°]	3.6–54.0	3.6–54.0	3.8–54.0	3.6–56.0
Scan speed [°/min]	10	8.0	4.0–40.0	5.0
Meas. reflections	15392	11544	6196	5949
Indep. reflections	14316	10003	5207	4958
R_{int} [%]	9.46	19.24	3.70	5.69
Obsd. reflections	8063	7518	3925	3602
σ criterion	$F_o \geq 4\sigma(F)$	$F_o \geq 4\sigma(F)$	$F_o \geq 4\sigma(F)$	$F_o \geq 4\sigma(F)$
$R1$; $wR2$ [%]	4.24, 9.06	4.86, 13.82	4.22, 11.15	4.92, 12.20
ref. parameters	973	607	352	319

[Ru(N_2H_4)('pyS_4')] (7): N_2H_4 (1.0 mL, 31.86 mmol) was added to a red-brown suspension of [Ru(NO)('pyS_4')]Tos (**8**) (200 mg, 0.29 mmol) in 20 mL of THF. Gas was evolved and a red solution was produced, from which a red oil separated. It was redissolved by the addition of MeOH (20 mL). Subsequent addition of Et_2O (40 mL) led to the precipitation of a microcrystalline red solid, which was separated, washed with MeOH (20 mL), THF (15 mL), and Et_2O (20 mL), and dried in vacuo. Yield: 50 mg of **7** (33%). – $C_{19}H_{19}N_3RuS_4$ (518.69): calcd. C 44.00, H 3.69, N 8.10, S 24.72; found C 43.97, H 3.70, N 7.56, S 24.53. – IR (KBr): $\tilde{\nu}$ = 3335, 3208, 3105 cm^{-1} ν(NH). – MS (FD, DMF, ^{102}Ru); *m/z* = 973 [Ru('pyS_4')]$_2^+$. – ^{1}H NMR (269.6 MHz, [D_7]DMF): δ = 7.75–7.72 (m, 2 H, C_6H_4), 7.46–7.42 (m, 2 H, C_6H_4), 7.12–7.07 (m, 3 H, pyridine), 6.92–6.81 (m, 4 H, C_6H_4), 4.86 (s, 2 H, –NH_2NH$_2$), 4.73 (d, 2 H, CH_2), 4.52 (d, 2 H, CH_2), 3.62 (s, 2 H, –NH$_2$NH_2). – ^{13}C{^{1}H} NMR (67.8 MHz, [D_7]DMF): δ = 159.60, 158.03, 133.09, 132.90, 131.85, 131.23, 127.86, 121.19, 120.77 (arom. C), 56.32 (CH_2).

[Ru(NO)('pyS_4')]Tos (8): A solution of 'pyTos' (2.27 g, 5.07 mmol) in 60 mL of THF was added dropwise to a stirred green solution of NBu_4[Ru(NO)($S_2C_6H_4)_2$] (3.32 g, 5.08 mmol) in 30 mL of THF and the resulting mixture was heated under reflux for 4 h. After cooling to room temperature, the precipitated red-brown solid was separated, washed with THF (60 mL) and Et_2O (30 mL), and dried in vacuo. Yield 1.96 g of **8** (56%). – $C_{26}H_{22}N_2O_4RuS_5$ (687.87): calcd. C 45.40, H 3.22, N 4.07, S 23.31; found C 45.45, H 3.38, N 4.04, S 22.98. – IR (KBr): $\tilde{\nu}$ = 1892 cm^{-1} ν(NO). – MS (FD, DMSO, ^{102}Ru); *m/z* = 517 [Ru(NO)('pyS_4')]$^+$. – ^{1}H NMR (269.6 MHz, [D_6]DMSO): δ = 8.01 (d, 2 H, C_6H_4), 7.79 (t, 1 H, H_γ, pyridine), 7.55 (d, 2 H, H_β, pyridine), 7.50–7.45 (m, 4 H, C_6H_4), 7.31–7.21 (m, 4 H, C_6H_4), 7.08 (d, 2 H, C_6H_4), 5.50 (d, 2 H CH_2), 5.29 (d, 2 H, CH_2), 2.25 (s, 3 H, CH_3). – ^{13}C{^{1}H} NMR (67.8 MHz, [D_6]DMSO): δ = 157.90, 149.12, 145.67, 140.22, 137.64, 132.95, 130.81, 129.58, 128.68, 128.07, 125.49, 125.24, 124.29 (arom. C), 55.22 (CH_2), 20.80 (CH_3).

X-ray Structure Analyses of [Ru(PPh_3)('pyS_4')] (1), [Ru(PPh_3)('pyS_4'-Me_2)]$I_2 \cdot 2\,CH_2Cl_2$ (2 · 2 CH_2Cl_2), [Ru(DMSO)('pyS_4')] · MeOH (3 · MeOH), and [Ru(CO)('pyS_4')] · MeOH (4 · MeOH): Orange platelets of [Ru(PPh_3)('pyS_4')] (**1**) were grown by layering a hot pyridine solution (8 mL) of **1** (110 mg, 0.15 mmol) with MeOH. Yellow rhombs of **2** · 2 CH_2Cl_2 formed upon layering a saturated CH_2Cl_2 solution of **2** with Et_2O. Yellow block-shaped crystals of **3** · MeOH were deposited from a saturated DMSO/MeOH solution at –30 °C. Yellow-orange needles of **4** · MeOH crystallized from a saturated CH_2Cl_2 solution of **4** upon layering with MeOH. Suitable single crystals were either sealed under N_2 in glass capillaries (**1**) or coated with inert perfluoropolyalkyl ether (**2** · CH_2Cl_2, **3** · MeOH, and **4** · MeOH). Data were corrected for Lorentz and polarization effects. An absorption correction was applied for **2** · CH_2Cl_2 using ΔF^2 methods (XABS2, T_{min} = 0.0644, T_{max} = 0.1740),[18] as well as for **3** · MeOH (T_{min} = 0.5690, T_{max} = 0.6561), and **4** · MeOH (T_{min} = 0.5707, T_{max} = 0.7288) on the basis of psi-scans.[19] The structures were solved by direct methods and refined using full-matrix least-squares procedures on F^2 (SHELXTL 5.03).[20] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were taken from difference Fourier maps and their positional parameters were refined. Complex **1** was found to contain two crystallographically independent molecules in the asymmetric unit. Selected crystallographic data are summarized in Table .[21]

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[1] [1a] J. Reedijk (Ed.), *Bioinorganic Chemistry*, 2nd edition, M. Dekker, New York, **1999**. – [1b] J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965–2982. – [1c] R. K. Thauer, A. R. Klein, G. C. Hartmann, *Chem. Rev.* **1996**, *96*, 3031–3042. – [1d] S. W. Ragsdale, M. Kumar, *Chem. Rev.* **1996**, *96*, 2515–2539.
[2] D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460–469.
[3] D. Sellmann, J. Sutter, in: *Molybdenum Enzymes, Cofactors and Model Systems* (Eds.: E. I. Stiefel, D. Coucouvanis, W. E. Newton), A.C.S. Symp. Ser. **1993**, *535*, 332–345.
[4] D. Sellmann, W. Soglowek, F. Knoch, G. Ritter, J. Dengler, *Inorg. Chem.* **1992**, *31*, 3711–3717.
[5] D. Sellmann, Th. Hofmann, F. Knoch, *Inorg. Chim. Acta* **1994**, *224*, 61–71.
[6] D. Sellmann, J. Utz, F. W. Heinemann, *Inorg. Chem.*, **1999**, *38*, 5314–5322.
[7] N. Blum, Diploma Thesis, University of Erlangen-Nürnberg, **1997**.
[8] [8a] D. Sellmann, T. Gottschalk-Gaudig, F. W. Heinemann, F. Knoch, *Chem. Ber.* **1997**, *130*, 571–579. – [8b] D. Sellmann, T. Gottschalk-Gaudig, F. W. Heinemann, *Inorg. Chem.* **1998**, *37*, 3982–3988.
[9] F. Bottomley, *Acc. Chem. Res.* **1978**, *11*, 158–163.
[10] [10a] J. Chatt, in: *Homogeneous Catalysis with Metal Phosphine Complexes* (Ed.: L. H. Pignolet), Plenum Press, New York, **1983**, 1–11. – [10b] A. Cahours, H. Gal, *Compt. Rend.* **1870**, *70*, 897–903. – [10c] A. Cahours, H. Gal, *Jahresber.* **1870**, 808–814.
[11] D. Sellmann, Th. Becker, F. Knoch, *Chem. Eur. J.* **1996**, *2*, 1092–1098.
[12] H. M. Koepp, H. Wendt, H. Strehlow, *Z. Elektrochem.* **1960**, *64*, 483–491.
[13] T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1966**, *28*, 945–956.
[14] I. P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 204–209.
[15] J. D. Gilbert, D. Rose, G. Wilkinson, *J. Chem. Soc. (A)* **1970**, 2765–2769.
[16] D. Sellmann, G. Binker, *Z. Naturforsch.* **1987**, *42b*, 341–347.
[17] J. S. Bradshaw, P. Huszthy, C. W. McDaniel, J. Y. Zhu, N. K. Dalley, R. M. Izatt, *J. Org. Chem.* **1990**, *55*, 3129–3137.
[18] S. Parkin, B. Moezzi, H. Hope, *J. Appl. Cryst.* **1995**, *28*, 53–56.
[19] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Cryst.* **1968**, *A24*, 351–359.
[20] SHELXTL 5.03 *for Siemens Crystallographic Research Systems*, Copyright **1995** by Siemens Analytical X-ray Instruments Inc., Madison WI.
[21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC-119398 (**1**), 119399 (**2** · 2 CH_2Cl_2), 119400 (**3** · MeOH), and 119401 (**4** · MeOH). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@chemcrys.cam.ac.uk].

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