[Ru(HNO)('py^{bu}S$_4$')], the First HNO Complex Resulting from Hydride Addition to a NO Complex ('py^{bu}S$_4$'$^{2-}$ = 2,6-Bis(2-mercapto-3,5-di-*tert*-butylphenylthio)dimethylpyridine(2 –))**

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Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday

Abstract: Treatment of the nitrosyl complex [Ru(NO)('py^{bu}S$_4$')]Br (**1a**) with $NaBH_4$ in CH_3OH yielded [Ru(HNO)('py^{bu}S$_4$')](**2**), which could be completely characterized. The X-ray structure determination of **2** confirmed the N coordination of the HNO ligand. Density functional theory calculations enabled us to assign the ν(NO) IR band of **2**, which appears in KBr at 1358 cm^{-1} and in THF at 1378 cm^{-1}. The unprecedented hydride addition to nitrosyl complexes yielding HNO complexes fills a white spot on the map of chemical reactions, represents the as yet unknown counterpart to the well-established formyl complex formation from CO complexes and hydrides, and distinctly differs from the formation reaction of [Os(HNO)(CO)Cl$_2$(PPh$_3$)$_2$], the only other HNO complex characterized structurally. The HNO complex **2** is oxidized stepwise by [Cp$_2$Fe]PF$_6$ in the presence of NEt_3 and directly by Brønsted acids to give [Ru(NO)('py^{bu}S$_4$')]$^+$ in 2e$^-$ oxidations. H$^+$/D$^+$ exchange indicates acidity of the HNO proton.

Keywords: density functional calculations · hydrogenation · nitrogen oxides · ruthenium · S ligands

Introduction

The activation of stable molecules and the stabilization of unstable intermediates through bonding to metals are key features of numerous industrial and biological catalyses. Identification of the unstable intermediates has enabled in numerous cases the elucidation of reaction pathways and mechanisms. A textbook example is the hydride reduction of CO to give formyl (HCO) complexes, considered important intermediates in the Fischer – Tropsch and other industrial CO processes.[1] The analogous reduction of NO to HNO complexes, although isoelectronic and frequently postulated has remained unknown. In addition, HNO complexes are extremely rare and only one example has ever been characterized structurally.[2]

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HNO, termed nitroxyl, nitroso hydrogen, nitrosyl hydride, or monomeric hyponitrous acid, is extremely unstable in the free state. It has spectroscopically been detected as a reactive intermediate in gas-phase radical and photochemical reactions.[3a–d] The formation and decomposition of intermediary HNO have been discussed for the combustion of nitrogen-containing fuels,[3a] the oxidation of atmospheric nitrogen,[4a] the reduction of HNO_2[4b] and metal – NO_2 complexes,[4c] the biological nitrate reduction to N_2 or NH_3,[4d] the rich biological chemistry of NO,[3e–f] and the hydride addition to [CpRe(NO)(CO)(PR$_3$)]$^+$[5] which yields the formyl complex [CpRe(NO)(HCO)(PR$_3$)]. Recently, the HNO adduct of myoglobin (Mb-HNO), formed by electrochemical or chemical reduction of Mb-NO, was identified spectroscopically.[6]

However, all attempts to trap and to characterize unambigously HNO as a hydride reduction product of NO complexes have remained unsuccessful. Herein we report the first example of such a reaction which occurred during chemical reactions of the nitrosyl complexes [Ru(NO)('py^{R}S$_4$')]Br (**1**) and (**1a**).[7]

These complexes contain hexacoordinate 18-valence-electron Ru centers and strongly bound NO ligands which are substitution inert under normal conditions. To study the binding properties of the coordinatively unsaturated [Ru('py^{R}S$_4$')] cores towards small molecules such as N_2, H_2, and other nitrogenase-relevant substrates, methods were needed

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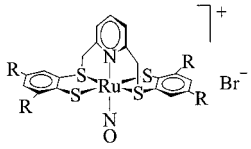
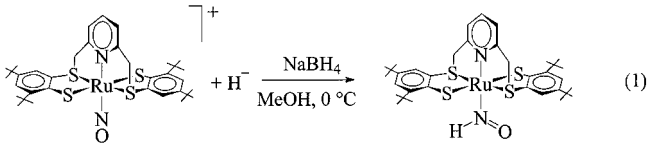


R = H [Ru(NO)(pyS$_4$)]Br (**1**)
R = *t*Bu [Ru(NO)(py^{bu}S$_4$)]Br (**1a**)

to remove the NO ligands in **1** and **1a**. Substitution of ligands in hexacoordinate 18-valence-electron Ru^{II} complexes is notoriously difficult, however, a couple of experiments indicated that the NO ligands of **1** and **1a** could be removed under reducing conditions.[7] For example, when **1** was treated with $LiBEt_3H$, dinuclear [{Ru(′pyS$_4$′)}$_2$] formed. The latter contains thiolate-bridged [Ru(′pyS$_4$′)] fragments, is practically insoluble in all common solvents, and is inert toward cleavage reactions. Since [{Ru(′pyS$_4$′)}$_2$] clearly could not result from a one-step reaction but had to be formed via coordinatively unsaturated and potentially highly reactive [Ru(′pyS$_4$′)] monomers, we carried out detailed investigations of the reactions of hydrides with **1a**, which proved to be more soluble than those of **1**.

Results

The reduction of [Ru(NO)(′py^{bu}S$_4$′)]Br (**1a**) with $LiBEt_3H$ in THF under standard conditions always yielded a mixture of products which could not be separated as yet. Replacing the solvent THF by MeOH and the hydride reagent $LiBEt_3H$ by $NaBH_4$, however, led to a different result. When the red solution of **1a** in MeOH was treated with $NaBH_4$, dark green crystals immediately precipitated from the reaction mixture. They could be isolated in analytically pure form, proved soluble in THF, CH_2Cl_2, and DMF, and their elemental analyses and spectroscopic data (IR, ^{1}H, ^{13}C, NMR, mass spectra) were compatible with the formation of [Ru(HNO)(′py^{bu}S$_4$′)] (**2**) according to Equation (1).



(1)

For example, the ^{1}H NMR spectrum of **2** in [D$_8$]THF exhibited the typical pattern of the C_2-symmetrical [Ru(′py^{bu}S$_4$′)] fragments[7b] and, in addition, a strongly down-field shifted singlet at $\delta = 19.56$, which indicated the presence of a HNO ligand.[2, 8]

The X-ray structure analysis of **2** confirmed the spectroscopic results. Figure 1a depicts the molecular structure of **2**·2 CH_2Cl_2·MeOH. Figure 1b illustrates the hydrogen bonds between two molecules of **2** and the CH_3OH solvate molecules in the unit cell. The Ru center of **2** is surrounded pseudo-octahedrally by four sulfur and two nitrogen donor atoms. The thioether, thiolate, and N-donor atoms pairwise adopt *trans* positions. Distances and angles within the

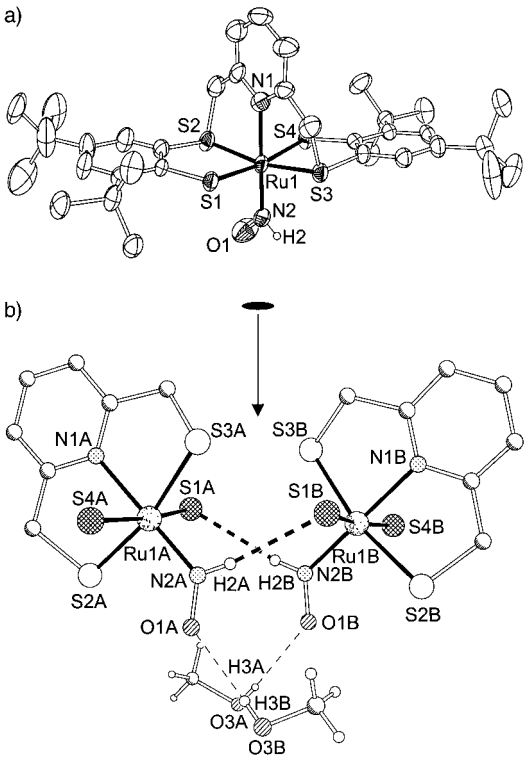


Figure 1. a) Molecular structure of **2**·2 CH_2Cl_2·MeOH (50% thermal probablility ellipsoids; solvate molecules and C-bound H atoms omitted). b) Hydrogen bonds between two molecules of **2** and the MeOH solvate molecules (3,5-ditertiarylbutyl-*o*-phenylene units and C-bound H atoms omitted). Selected distances [pm] and angles [°]: Ru1–N1 212.9(7), Ru1–N2 187.5(7), Ru1–S1 238.2(2), Ru1–S2 232.0(2), Ru1–S3 232.7(2), Ru1–S4 235.8(2), N2–O1 124.2(9), H2A···S1B^a 262, H3A···O1B^b 216, N2A···S1B^a 347.0(8), O3A···O1B^b 290(1); S1-Ru1-S2 86.36(7), S2-Ru1-S4 91.10(7), S4-Ru1-S3 86.97(8), N1-Ru1-N2 179.5(3), Ru1-N2-O1 130.0(6), N2A-H2A···S1B^a 172, O3A–H3A···O1B^b 149; a: $-x-1, y, -z-3/2$; b: $-x-1, y-1, -z-3/2$.

[Ru(′py^{bu}S$_4$′)] core exhibit no anomalies and are comparable with those in previously characterized [Ru(L)(′py^{R}S$_4$′)] complexes.[7] The Ru1–N2 and N2–O1 distances of **2** (187.5(7) and 124.2(9) pm, respectively) are distinctly longer than the corresponding distances in the linear RuNO moiety of **1a** (172.1(6) and 115.6(6) pm, respectively).[7b] The Ru1-N2-O1 angle of 130.0(6)° and likewise the N2–O1 distance of 124.2(9) pm indicate the sp^2 hybridization of the N atom and a N=O double bond in the HNO ligand. Similar values had been observed for the M(HNO) entity in [Os(HNO)(CO)Cl$_2$(PPh$_3$)$_2$].[2]

The position of the HNO proton could be determined from the difference Fourier synthesis. The bonding of the HNO proton to the N atom is further corroborated by the hydrogen bonds found in **2**·2 CH_2Cl_2·MeOH. In the solid state, two molecules of **2** form a dimer through N–H···S(thiolate) bridges (d(H2···S1) = 262 pm). The dimer possesses crystallographically imposed C_2 symmetry. Additional hydrogen bonds exist between the O atoms of the HNO ligands and the OH protons of the two CH_3OH solvate molecules. Hydrogen bonds between the HNO ligand and solvent molecules presumably also form in polar solvents. The major reason for the extreme down-field shift of the HNO signal in the ^{1}H NMR spectrum, however, is presumably the nitrogen sp^2

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hybridization. Comparably large proton shifts have previously been observed for diazene and ketimine complexes.[9]

Density functional theory (DFT) calculations enabled the identification of the ν(NO) IR band of **2**, which appears in KBr at 1358 cm^{-1} and in THF at 1378 cm^{-1}. The unambigous assignment of ν(NO) bands in X–NO compounds is difficult because their frequencies cover a large range from, for example, 1410 cm^{-1} in $[Os(HNO)Cl_2(CO)(PPh_3)_2]$,[2, 8] to 1570 cm^{-1} in matrix-isolated HNO,[3b] up to 1844 cm^{-1} in FNO.[10a] In particular, the ν(NO) bands of large molecules are frequently discussed controversially.[10b]

The DFT calculations for **2** in the gas phase yielded a ν(NO) frequency of 1513 cm^{-1}. Hydrogen bonds to the HNO ligand of **2** led to a drastic change in this frequency. Association of one methanol molecule by a $CH_3O–H\cdots ONH$ bond decreased the ν(NO) frequency to 1397 cm^{-1}, whereas association of a THF molecule through a $C_4H_8O\cdots HNO$ bond decreased the ν(NO) frequency to 1420 cm^{-1}. The simultaneous formation of both hydrogen bonds resulted in a ν(NO) frequency of 1377 cm^{-1}. In all cases, the ν(NO) vibration yielded the most intensive band of the IR spectrum (see Experimental Section).

Reactions of [Ru(HNO)(′py^{bu}S$_4$′)] (2)

Although the HNO ligand in [Ru(HNO)(′py^{bu}S$_4$′)] (**2**) is stabilized by coordination, it is still highly reactive. In the solid state, **2** can be stored at −20 °C for a couple of weeks. However, in THF or CH_2Cl_2 solutions at room temperature, **2** decomposes in the course of 24 h, yielding a mixture of products. To gain more insight into these decomposition reactions, the deuterium derivative [Ru(DNO)(′py^{bu}S$_4$′)] (**3**) was synthesized from [Ru(NO)(′py^{bu}S$_4$′)]Br (**1a**) and $NaBD_4$ in CD_3OD, and its decomposition was monitored by NMR spectroscopy. With the exception of the lack of the HNO signal, the ^{1}H NMR spectrum of **3** proved identical with that of **2**. In the course of 12 h, however, the appearance of a signal at $\delta = 19.56$ indicated the formation of **2**. This formation of **2** can plausibly be traced back to a D^+/H^+ exchange of **3** with traces of H_2O in the solution. This indicates slight acidity of the HNO or DNO protons and deuterons, respectively. (The ^{2}H-NMR spectrum of **3** dissolved in THF showed only the DNO signal at $\delta = 19.56$.)

Attempts to deprotonate **2** with Brønsted bases to obtain the $[Ru(NO)(′py^{bu}S_4′)]^-$ ion were unsuccessful, similarly no reaction was observed when **2** was treated with NEt_3, and treatment of **2** with LiOMe or BuLi gave only mixtures of decomposition products which have so far proved uncharacterizable.

Treatment of [Ru(HNO)(′py^{bu}S$_4$′)] (**2**) with Brønsted acids HX ($X = H_2PO_3^-$, Br^-, $CF_3SO_3^-$) led to oxidation of **2** and the formation of $[Ru(NO)(′py^{bu}S_4′)]^+$. When **2** in THF was treated at −80 °C with one equivalent of HX, the dark green color of the solution turned bright green. Upon warming up to room temperature, the color changed to red, and the formation of the $[Ru(NO)(′py^{bu}S_4′)]^+$ ion was established by ^{1}H NMR and IR spectroscopy. The reaction can be described as a $2e^-/H^+$ oxidation of **2**, the reversal of the formation reaction of **2**, and is probably accompanied by the formation of H_2.

The $2e^-$ oxidation of **2** to give $[Ru(NO)(′py^{bu}S_4′)]^+$ could be divided into two separate steps by using the $1e^-$ oxidant $[Cp_2Fe]PF_6$ ($FcPF_6$) and NEt_3 as proton acceptor. Addition of one equivalent each of $FcPF_6$ and NEt_3 to solutions of **2** in THF resulted in a color change from green to red. The IR spectrum of the solution showed a strong band at 1610 cm^{-1} (Figure 2) which can be assigned to the formation of the 19-

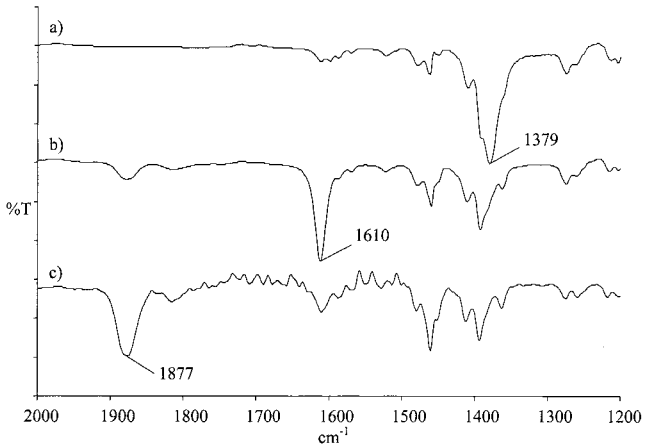


Figure 2. Monitoring the oxidation of **2** in solution by IR spectroscopy: a) Complex **2** in THF (ν(NO): 1379 cm^{-1}), b) after addition of one equivalent of $FcPF_6$, indicating the formation of $[Ru(NO)(′py^{bu}S_4′)]^0$ (ν(NO): 1600 cm^{-1}), and c) after addition of a second equivalent of $FcPF_6$ or direct addition of one equivalent of HX (ν(NO): 1877 cm^{-1}; $X = H_2PO_3^-$, Br^-, $CF_3SO_3^-$).

valence-electron nitrosyl complex [Ru(NO)(′py^{bu}S$_4$′)]. This complex proved too labile to be isolated. Upon the subsequent addition of a second equivalent of $FcPF_6$, the band at 1610 cm^{-1} disappeared and was replaced by the ν(NO) band of $[Ru(NO)(′py^{bu}S_4′)]^+$ at 1877 cm^{-1} (Figure 2c).

These findings could be corroborated by the cyclic voltammograms of [Ru(NO)(′py^{bu}S$_4$′)]Br (**1a**) and [Ru(HNO)(′py^{bu}S$_4$′)] (**2**) (Figure 3). The cyclic voltammogram of **1a** shows three redox waves (A–C). The redox waves A and B become reversible when the current is reversed between 0.86 V and −0.50 V. They indicate that in analogy to related nitrosyl complexes, the neutral 19-valence-electron species [Ru(NO)(′py^{bu}S$_4$′)] is present in solution at 0.0 V. The anodic wave A at 0.52 V can be assigned to the $[Ru(NO)(′py^{bu}S_4′)]^{0/+1}$ couple and the cathodic wave B at −0.32 V to the $[Ru(NO)(′py^{bu}S_4′)]^{0/-1}$ redox couple. The $[Ru(NO)(′py^{bu}S_4′)]^-$ species corresponds with the anion resulting from deprotonation of **2** and is irreversibly reduced at −1.30 V (redox wave C).

At first sight, the cyclic voltammogram of **2** looks very much different from that of **1a**. However, it can be rationalized when the irreversible wave E in the anodic region is assigned to the oxidation of **2** yielding $[Ru(HNO)(′py^{bu}S_4′)]^+$, which subsequently loses a proton to give the 19-valence-electron species $[Ru(NO)(′py^{bu}S_4′)]^0$. This 19-valence-electron complex is reversibly oxidized at +0.77 V (redox wave D) and reduced at −0.43 V (redox wave F) to give $[Ru(NO)(′py^{bu}S_4′)]^+$ and $[Ru(NO)(′py^{bu}S_4′)]^-$, respectively. The irreversible cathodic wave G at −1.70 V can be assigned

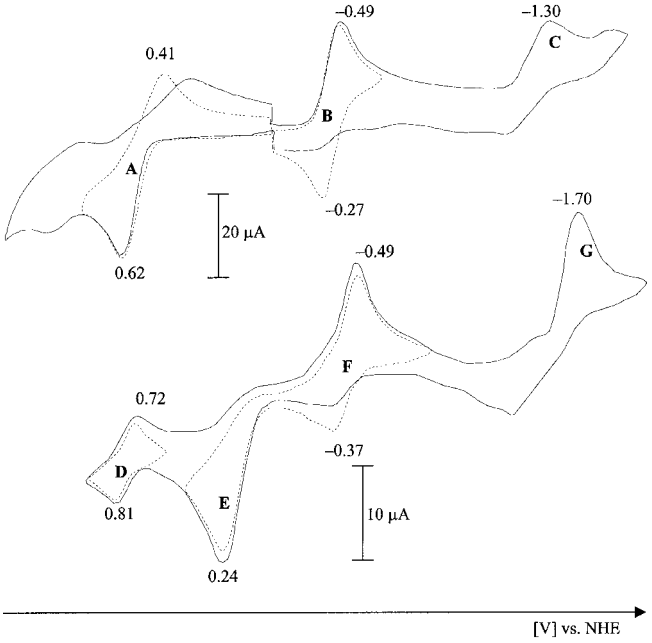


Figure 3. Cyclic voltammograms of a) **1a** in DMF and b)**2** in THF.

to the reduction of **2** yielding $[Ru(HNO)('py^{bu}S_4')]^-$, which decomposes.

Taken into account that for solubility reasons the cyclic voltammogram of **1a** and **2** had to be recorded in different solvents (DMF and THF), the redox potentials of the $[Ru(NO)('py^{bu}S_4')]^{+1/0/-1}$ couples resulting from **1a** on the one and from **2** on the other hand are in good agreement.

Discussion and Conclusion

$[Ru(HNO)('py^{bu}S_4')]$ (**2**) has been synthesized and completely characterized. Complex **2** is only the second example of a HNO nitroxyl complex whose structure has been elucidated by X-ray structure analysis. The formation of **2** is, to the best of our knowledge, the first conversion of a metal nitrosyl into a metal HNO complex by hydride addition and represents the as yet unknown counterpart to the well-established hydride addition to metal carbonyl complexes yielding metal formyl species.

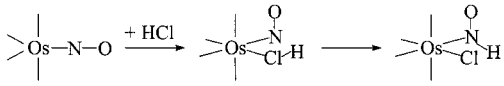
The $[M(NO)]^+ \rightarrow [M(HNO)]$ conversion corresponds with a $1H^+/2e^-$ reduction and clearly differs from the previously reported two methods that yielded HNO complexes. These methods comprise the oxidation of NH_2OH complexes and the HX addition to coordinatively unsaturated NO complexes. Hillhouse et al. showed that oxidation of $[Re(NH_2OH)(CO)_3(PPh_3)_2]OTf$ ($OTf = OSO_2CF_3$) yields $[Re(HNO)(CO)_3(PPh_3)_2]OTf$.[11] Roper et al. achieved the addition of HCl to $[Os(NO)(CO)Cl(PPh_3)_2]$ yielding $[Os(HNO)(CO)Cl_2(PPh_3)_2]$,[8] which represents the as yet only HNO complex characterized by X-ray structure determination.[2]

Since the formation reactions of both **2** and $[Os(HNO)(CO)Cl_2(PPh_3)_2]$ involve the conversion of NO into HNO ligands, their principal differences need to be discussed briefly. Complex **2** is the result of a hydride addition to a (coordinatively saturated) six-coordinate nitrosyl complex, the formation of $[Os(HNO)(CO)Cl_2(PPh_3)_2]$ comprises coordination of an additional ligand to the Os center, an increase of the formal Os oxidation state, and the 'hydrogenation' of the NO ligand. It can be taken for granted that the formation of the HNO ligand in this case requires the addition of chloride as a sixth ligand to the Os center, because the reaction of $[Os(NO)(CO)(Cl)(PPh_3)_2]$ with HX acids such as HBF_4 containing only weakly coordinating X^- ions did not yield a HNO complex.[2]

The essentiality of coordinating additional ligands to the metal center in HX conversions of NO ligands is further underlined by the reactions of $[Ir(NO)(PPh_3)_3]$, which is closely related to $[Os(NO)(CO)Cl(PPh_3)_2]$. $[Ir(NO)(PPh_3)_2]$ reacts with HCl to give the hydroxylamine complex $[Ir(NH_2OH)Cl_3(PPh_3)_2]$,[8] with HPF_6, however, the Ir center is protonated to give $[Ir(H)(NO)(PPh_3)_3]PF_6$.[12]

These findings strongly suggest that the formation of $[Os(HNO)(CO)Cl_2(PPh_3)_2]$ involves the well-established conversion of linear into bent MNO entities, when additional ligands coordinate to the metal centers of nitrosyl complexes which obey the 18-valence-electron rule.[13] One example, substantiated by X-ray crystallography, is the addition of $X^- = NCS^-$, Cl^-, Br^-, I^- to the electronically saturated (but coordinatively unsaturated) 18-valence-electron complex $[Co(NO)(das)_2]^{2+}$, which has linear CoNO groups (das = *o*-phenylenebis(dimethylarsane)). The resulting $[Co(NO)X(das)_2]^+$ complexes exhibit bent CoNO entities.[14] This MNO bending corresponds with a change of the NO ligand from a three-electron into a one-electron donor, or, from a different point of view, with an intramolecular metal to NO electron transfer and $NO^+ \rightarrow NO^-$ reduction.[13]

When applied to the formation of $[Os(HNO)(CO)Cl_2(PPh_3)_2]$ from $[Os(NO)(CO)Cl(PPh_3)_2]$, these considerations suggest the (simplified) reaction pathway according to Equation (2),[8] which had been suggested as one possibility also by Roper et al.



(2)

Addition of HX acids containing nucleophilic X^- ions to nitrosyl complexes also yielded the very few other HNO complexes reported, for example, $[Rh(HNO)Cl_3(PPh_3)_2]$,[15a] $[Mo(HNO)F(dppe)_2]PF_6$ (dppe = 1,2-bis(diphenylphosphanyl)ethane),[15b] $[Re(HNO)(NO)Cl_2(PPh_3)_2]$,[15c] and $[Co(HNO)Br(das)_2](ClO_4)_4$.[14] In most cases, these complexes could be characterized by spectroscopic methods only. Formally related to these complexes is [Mo(HNO)(NO)(terpy)(CN)] (terpy = 2,2′:6′,2″-terpyridine). It forms by deprotonation of $[Mo(H_2NO)(NO)(H_2O)(terpy)]^{2+}$ in the presence of CN^- and contains the η^2-hydroxylamido(2 −) ligand.[16]

While the formation of $[Os(HNO)(CO)Cl_2(PPh_3)_2]$ cannot be considered a hydrogenation of a nitrosyl complex, the formation reactions of both $[Ru(HNO)('py^{bu}S_4')]$ and Mb-HNO represent such hydrogenations. Also these two hydrogenations, however, are distinctly different from each other.

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Cyclic voltammetry indicates that Mb-HNO forms by a $1H^+/1e^-$ reduction of Mb-NO.[6] In contrast, [Ru(HNO)('py^{bu}S$_4$')] clearly results from a (formal) $1H^+/2e^-$ reduction of [Ru(NO)('py^{bu}S$_4$')]$^+$.

Experimental Section

General methods: Unless noted otherwise, all reactions and spectroscopic measurements were carried out at room temperature under argon using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR, UV/Vis, and NMR spectroscopy. Spectra were recorded on the following instruments: IR (KBr discs or CaF_2 cuvettes with compensation of the solvent bands): Perkin Elmer 983, 1620 FT IR; NMR: JEOL-JNM-GX 280, EX 270 with the protio-solvent signal used as an internal reference. Chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane. 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 working electrode and Pt reference and counter electrodes. Solutions were 10^{-3} M in the substance under investigation; $NBu_4[PF_6]$ (10^{-1} M) was used as the supporting electrolyte. Potentials were referenced to the normal hydrogen electrode (NHE) using Fc/Fc^+ as internal standard ($E_{Fc/Fc^+} = 0.4$ V vs. NHE).[17] [Ru(NO)('py^{bu}S$_4$')]Br (**1a**) was prepared as described in the literature.[7b]

Syntheses and reactions

Synthesis of 2: Solid $NaBH_4$ (0.78 mg, 2.06 mmol) was added to a red solution of **1a** (337 mg, 0.41 mmol) in methanol (15 mL) at 0 °C. Vigorous evolution of gas occurred, and green microcrystals precipitated. After the mixture had been stirred for 30 min at 0 °C, the microcrystals were separated by filtration at −5 °C, washed with cold MeOH (30 mL), and dried in vacuo at room temperature. Yield: 255 mg (82 %). The compound can be stored under argon at −20 °C for several weeks without decomposition. ^{1}H NMR (269.6 MHz, [D$_8$]THF, 20 °C): $\delta = 19.56$ (s, 1H; HNO), 7.62 (d, $^4J = 2$ Hz, 2H; C_6H_2), 7.35 (m, 1H; H4-C_5H_3N), 7.24 (d, $^4J = 2$ Hz, 2H; C_6H_2), 7.10 (m, 2H, H3; H5-C_5H_3N), 4.79 (d, $^2J = 16$ Hz, 2H; CH_2), 4.57 (d, $^2J = 16$ Hz, 2H; CH_2), 1.48 (s, 18H; CH_3), 1.33 (s, 18H; CH_3); ^{13}C{^{1}H} NMR (67.8 MHz, [D$_8$]THF, 20 °C): $\delta = 157.7$, 151.1, 149.3, 145.7, 136.8, 134.6, 128.1, 125.0, 121.7 (C_{ar}), 57.2 (CH_2), 38.2, 35.0 (Cq), 31.8, 29.9 (CH_3); IR (KBr): $\tilde{\nu} = 1358$ cm^{-1} (N=O); MS (FD, CH_2Cl_2): m/z: 742 $[M]^+$; elemental analysis calcd for $\mathbf{2}\cdot 0.5$ MeOH ($C_{35.5}H_{50}N_2O_{1.5}RuS_4$)(%): C 56.24, H 6.65, N 3.70, S 16.92; found: C 56.21, H 7.05, N 3.74, S 16.91.

DFT calculations: The density functional and frequency calculations were carried out with the programs TURBOMOLE[18] and NUMFREQ.[19] The BP86 density functional[20] in RI approximation (resolution of the identity[21]) with a triple-zeta-valence basis including a polarization function (TZVP[22]) was used. All structures considered were characterized as minima on the respective potential hypersurface. Unscaled frequencies were given.

X-ray structure analysis of $\mathbf{2\cdot 2CH_2Cl_2\cdot MeOH}$: A suitable green-black single crystal ($0.62 \times 0.40 \times 0.12$ mm^3) was grown from a CH_2Cl_2 solution of **2**, which was layered with MeOH at −80 °C and stored at −40 °C for seven days. The crystal was embedded in perfluoropolyalkylether oil. Data were collected on a Siemens P4 diffractometer at $T = 200$ K. $C_{38}H_{56}Cl_4N_2O_2RuS_4$: monoclinic, space group $C2/c$, $a = 3.429.3(4)$, $b = 996.8(1)$, $c = 2858.1(4)$ pm, $\beta = 112.99(1)°$, $V = 8.994(2)$ nm^3, $Z = 8$, $\rho_{calcd} = 1.394$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.806$ mm^{-1}, graphite monochromator, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), ω scan 4.0° min^{-1}, 10095 measured reflections ($4.2° \le 2\theta \le 52.0°$), 8593 independent reflections, 4527 observed reflections ($F_o \ge 4.0\sigma(F)$). The structure was solved by direct methods (SHELXTL NT 5.10) and refined using full-matrix least-squares procedures on F^2 (SHELXTL 5.10). All non-hydrogen atoms were refined anisotropically. One of the *tert*-butyl groups (C44–C47) and one of the CH_2Cl_2 solvate molecules are disordered. The position of the hydrogen atom at N2 was located in a difference Fourier synthesis. Because not all hydrogen atom positions could be determined unambiguously, geometry-optimized positions for all hydrogen atoms were used in the final refinement cycles. The hydrogen atoms were allowed to ride on their carrier atoms during refinement; their isotropic diplacement parameters were tied to those of the adjacent atoms by a factor of 1.2 or 1.5. For 500 parameters the refinement converged at $wR_2 = 0.1924$, $R_1 = 0.0734$ for $[F_o \ge 4.0\sigma(F)]$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-143363. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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