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N-Methylhydroxylamido(1−)- and Nitrosomethaneruthenium Complexes Derived from Nitrosyl Complexes: Reversible N-Protonation of an N-Coordinated Nitrosoalkane[**]

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Nitric oxide (NO), nitroxyl (HNO), and hydroxylamine have been invoked as key intermediates in the biological multielectron reduction of nitrite to ammonia, which is a fundamental process in the inorganic nitrogen cycle in nature. The reaction is catalyzed by a certain type of nitrite reductase that contains heme moieties at its active site.[1] Within this context,

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the electrochemical reduction of nitrite to ammonia by coordination compounds of iron and its congeners ruthenium and osmium has been studied extensively.[2] In these systems, however, the exact formulation and coordination mode of the intermediary nitroxyl and hydroxylamine complexes are not known. Indeed, interconversion of these partially reduced nitrogenous species, including their organic derivatives such as nitrosoalkanes (RNO), on late transition-metal centers remains unexplored[3–8] compared with that on the early transition metals.[9,10] In an early example, Roper and co-workers[3] reported the reversible protonation of the nitrosyl complex $[Ir(NO)\{P(C_6H_5)_3\}_3]$ by HCl to afford the hydroxylamine complex $[IrCl_3(NH_2OH)\{P(C_6H_5)_3\}_2]$. Although the nitroxyl complex $[IrCl(HNO\text{-}\kappa N)\{P(C_6H_5)_3\}_3]$ has recently been characterized as an initial protonation product in this transformation,[4] the second protonation site of the nitroxyl complex, for example, is still unclear. We now describe the stepwise transformation of nitrosylruthenium complexes to nitrosoalkane and *N*-alkylhydroxylamido(1−) complexes, as well as the facile interconversion of the latter two species.

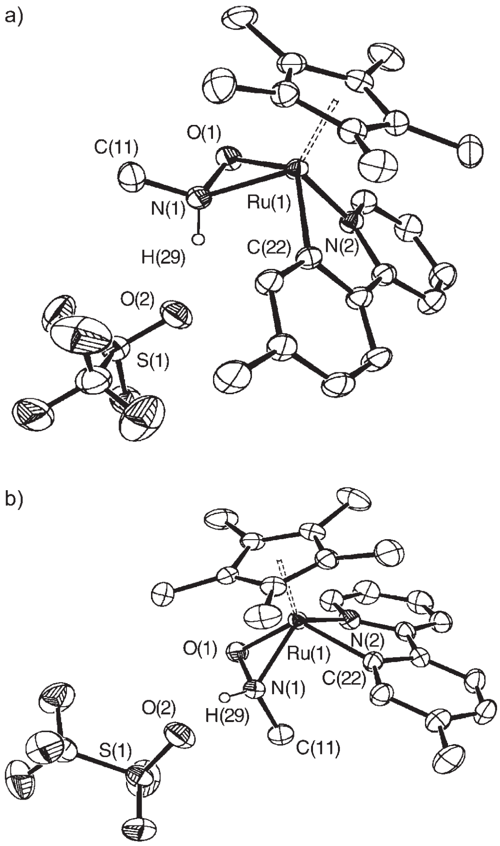
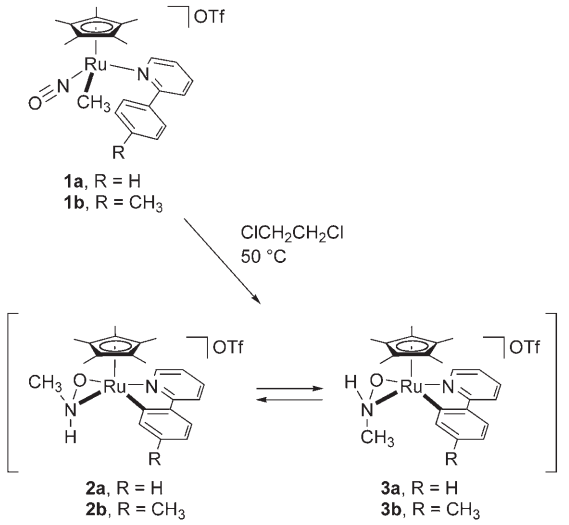


Figure 1. Structures of a) **2b** and b) **3b** with 30% ellipsoids. Hydrogen atoms except that for the hydroxylamido group are omitted for clarity. Selected interatomic distances [Å] for **2b**: Ru(1)–O(1) 2.042(3), Ru(1)–N(1) 2.057(3), Ru(1)–N(2) 2.081(3), Ru(1)–C(22) 2.075(4), N(1)–O(1) 1.379(4), N(1)–O(2) 2.869(5). For **3b**: Ru(1)–O(1) 2.040(2), Ru(1)–N(1) 2.042(2), Ru(1)–N(2) 2.087(3), Ru(1)–C(22) 2.073(3), N(1)–O(1) 1.370(3), N(1)–O(2) 2.982(4).

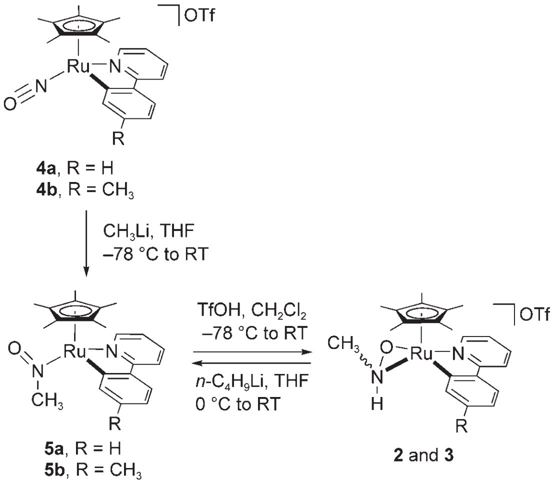


Scheme 1. Synthesis of **2** and **3**.

The thermolysis of the linear nitrosyl complexes $[Cp^*Ru(NO)(CH_3)(NC_5H_4Ar\text{-}2)](OTf)$ (**1a**, Ar = C_6H_5; **1b**, Ar = 4-$CH_3C_6H_4$; Cp* = C_5Me_5)[11] gave mixtures of the two isomeric *N*-methylhydroxylamido(1−)-κ^2N,O complexes **2** and **3** (Scheme 1). Fortunately, all of these isomers, except for the phenylpyridine derivative **3a**, could be isolated by adjusting the reaction conditions and subsequent workup procedure. The solid-state structures of the tolylpyridine derivatives **2b** and **3b** are depicted in Figure 1.[12] The two isomers **2b** and **3b** have the same stereochemistry around the Ru atom but are differentiated by the relative orientation of the Cp* and methyl groups with respect to the three-membered RuNO ring; these groups lie on the same side of the RuNO plane in **2** and on the opposite side in **3**. The N–O distances (1.380(5) and 1.377(4) Å) are unexceptional for hydroxylamido(1−) complexes.[9,14,15] Although the hydroxylamido(1−) H atom could not be located in the difference Fourier map, close contacts (ca. 2.9 Å) of the N atom and the triflate O atom in both crystals clearly indicate the presence of an amine proton hydrogen-bonded to the OTf^- counterion. The presence of the amine proton was also deduced from the IR spectra, which display an NH stretching band around 3140 cm^{-1}. In the ^1H NMR spectra, the amine proton in **3** is observed at around $\delta = 8.6$ ppm as a quartet split by the *N*-methyl protons with a $^3J_{H,H}$ coupling constant of 4.4 Hz;[16] the corresponding signal of **2** is overlapped by the aryl resonances around $\delta = 7.8$ ppm. These observations confirm the formulation of the Ru^{IV} hydroxylamido(1−) complexes **2** and **3**. To the best of our knowledge, **2** and **3** are the first fully characterized hydroxylamido(1−) complexes of a late transition metal.[5,7]

It should be noted that samples of isolated **2** and **3** undergo slow isomerization to give mixtures of **2** and **3**. The disappearance of the ^1H NMR signal of the amine proton upon treatment of **2** or **3** with D_2O suggests that the isomerization takes place by a deprotonation–protonation sequence that involves the amine proton. Dissociation of the M–N bond followed by inversion at the N atom[17] seems less plausible because **2** and **3** were found to be inert towards various two-electron donor ligands such as CO, phosphanes, and alkynes at room temperature.

In the formation of **2** and **3** from **1**, the nitrosyl ligand undergoes an intramolecular methylation and protonation coupled with the cyclometalation of the coordinated arylpyridine. Evidence for the stepwise transformation of the nitrosyl ligand was obtained from separate experiments. Treatment of the ruthenacyclic complexes $[Cp^*Ru(NO)(C_6H_3R\text{-}C_5H_4N\text{-}\kappa^2N,C)](OTf)$ (**4a**, R = H; **4b**, R = CH_3)[11] with an equimolar amount of CH_3Li afforded the Ru^{II} nitrosomethane-κN complexes **5** as the main product, although the yields of isolated product were unsatisfactory due to the difficulty in separating them from small amounts of uncharacterized by-products (Scheme 2). The X-ray crystal structure analysis of the phenylpyridine derivative **5a** revealed the N-coordination of the nitrosomethane ligand (Figure 2).[12] The N–O distance of 1.264(13) Å is much shorter than those in the hydroxylamido(1−) complexes **2b** and **3b**. The nitrosomethane ligand, the Ru atom, and the centroid of the Cp* ligand are coplanar to maximize the π back-donation to the nitrosomethane ligand, as observed in the isoelectronic complex $[Cp^*Ru(C_6H_5)(C_2H_5NO\text{-}\kappa N)\{P(CH_3)_2(C_6H_5)\}]$.[18]



Scheme 2. Transformation of **4** into **2** and **3** via **5**.

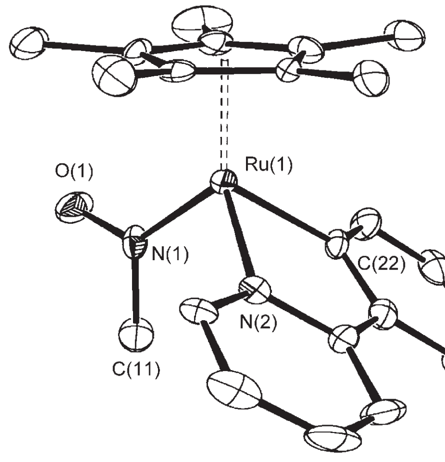
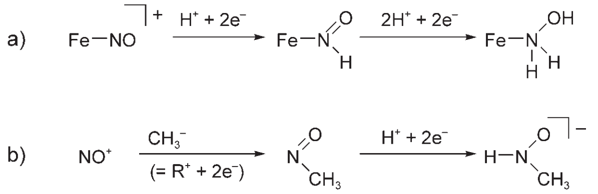


Figure 2. Structure of **5a** with 30% ellipsoids. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ru(1)–N(1) 1.914(7), Ru(1)–N(2) 2.067(7), Ru(1)–C(22) 2.068(7), N(1)–O(1) 1.27(1), N(1)–C(11) 1.47(1); Ru(1)–N(1)–O(1) 125.2(6), Ru(1)–N(1)–C(11) 124.0(6), O(1)–N(1)–C(11) 110.7(7).

As expected, subsequent protonation of the nitrosomethane complexes **5** with a slight excess of triflic acid gave isomeric mixtures of the hydroxylamido(1−) complexes **2** and **3**. Despite the rich coordination chemistry of nitrosoalkane,[19] protonation of well-defined nitrosoalkane (or nitroxyl) ligands on late transition-metal centers is extremely rare. The only precedent we are aware of is the *O*-protonation of the nitrosobenzene complex $[Os(NO)Cl(C_6H_5NO\text{-}\kappa^2N,O)\{P(C_6H_5)_3\}_2]$, the product of which was characterized only by IR spectroscopy.[7] Furthermore, the reverse reaction, namely deprotonation of isomeric mixtures of **2** and **3**, regenerated the nitrosomethane-κN complexes **5**. The formation of the nitroxyl-κN derivatives **5** contrasts sharply with the deprotonation of the hydroxylamido(1−)molybdenum complex $[Mo(NO)(terpy)(H_2O)(H_2NO\text{-}\kappa^2N,O)]^{2+}$, which forms a nitroxyl-κ^2N,O complex.[20]

The overall transformation shown in Scheme 2 has close relevance to the biological reduction of nitrite (Scheme 3). In the biological system, alternating proton and electron transfer is thought to convert the nitrosyl intermediate into the heme-bound nitroxyl and hydroxylamine.[1c] On the other hand, the nitrosyl ligand on the ruthenium complexes **4** is reduced upon methylation and subsequent protonation. The electrons for this reduction are formally supplied by the methyl anion in the first step, and by the Ru^{II} center in the nitrosomethane complexes **5** in the second step, to give the hydroxylamido(1−) ligand in the Ru^{IV} complexes **2** and **3**. Similarly, the reaction in Scheme 1 can be considered as the migratory insertion of the nitrosyl ligand in **1** into the $Ru–CH_3$ bond[10,21] followed by an aromatic C–H bond activation and subsequent proton migration to the resultant nitrosomethane ligand. It should be emphasized that related electron–proton chemistry of the nitrosyl ligand has been observed only in some early transition-metal complexes.[14,22]



Scheme 3. a) Consecutive proton and electron transfer to the nitrosyl intermediate proposed for the mechanism of cytochrome *c* nitrite reductase. b) Sequential reduction of the nitrosyl ligand at the $\{Cp^*Ru(C_6H_3R\text{-}C_5H_4N\text{-}\kappa^2N,C)\}$ chromophore.

In summary, we have demonstrated that organic derivatives of the possible intermediates in the inorganic nitrogen cycle, with various formal oxidation states of nitrogen ranging from +3 (NO^+) and +1 (RNO) to −1 ($RNHO^-$), can be stabilized, structurally characterized, and converted into each other on an organometallic platform. Reversible *N*-protonation of the nitrosoalkane ligand, which results in the formation of the unprecedented hydroxylamido(1−)ruthenium complexes **2** and **3**, is particularly noteworthy because it sheds light on the detailed mechanism of the biological nitrite–ammonia conversion at a late transition-metal center. The reactions described herein also feature a facile aromatic C$-$H bond activation in **1** to give the high-valent, yet stable, Ru^{IV} center in **2** and **3**, and the isomerism of the novel *N*-methylhydroxylamido(1$-$) complexes of a late transition metal.

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Keywords: bioinorganic chemistry · C$-$H activation · N,O ligands · nitrogen oxides · ruthenium

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[11] The detailed synthetic procedures and spectroscopic data for all the novel complexes **1**–**5** are provided as Supporting Information.

[12] Crystal data for **2b**: monoclinic, $P2_1/c$, $a = 8.783(3)$, $b = 15.029(5)$, $c = 19.833(7)$ Å, $\beta = 99.106(6)°$, $V = 2585.0(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.541$ g cm^{-3}, $F_{000} = 1224$, $\mu = 7.41$ cm^{-1}, transmission factors: 0.8592–1.0000, reflections measured 20196, independent reflections 5702, $R1 = 0.045$ $[I > 2\sigma(I)]$, $wR2 = 0.116$ (all data), residual electron density 1.27/$-$0.57 e Å^{-3}. For **3b**: monoclinic, $P2_1/n$, $a = 8.287(4)$, $b = 15.301(6)$, $c = 21.140(9)$ Å, $\beta = 105.085(6)°$, $V = 2588.1(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.539$ g cm^{-3}, $F_{000} = 1224$, $\mu = 7.40$ cm^{-1}, transmission factors: 0.7399–1.0000, reflections measured 20240, independent reflections 5868, $R1 = 0.036$ $[I > 2\sigma(I)]$, $wR2 = 0.092$ (all data), residual electron density 0.57/$-$0.50 e Å^{-3}. For **5a**: orthorhombic, $Pna2_1$, $a = 17.493(3)$, $b = 8.510(2)$, $c = 13.009(2)$ Å, $V = 1936.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.494$ g cm^{-3}, $F_{000} = 896$, $\mu = 8.23$ cm^{-1}, transmission factors: 0.7993–1.0000, reflections measured 15411, independent reflections 4410, $R1 = 0.040$ $[I > 2\sigma(I)]$, $wR2 = 0.143$ (all data), residual electron density 2.25/$-$2.22 e Å^{-3}. Data were collected at 193 K using a Rigaku Saturn CCD area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å) to a maximum 2θ value of 55°. Intensity data were corrected for Lorentz-polarization effects and for absorption. Structure solution and refinements were performed with the CrystalStructure program package.[13] The structures were refined against F^2 with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC-265939 (**2b**), -265939 (**3b**), and -265940 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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