Ruthenium Nitrosyl Complexes of Bis(3,5-dimethylpyrazol-1-yl)methane Oxyanions

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New ruthenium(II) mononitrosyl complexes of general composition $[Ru(NO)LCl_2]$, $[Ru(NO)L(en)]Cl_2$ and $[Ru(NO)L_2]Cl$ have been obtained upon treating $Ru(NO)Cl_3$ with potential κ^3-*N*,*N*,O ligands bis(3,5-dimethylpyrazol-1-yl)methanesulfonate (bdmpzsa) and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) in 1:1 and 1:2 molar ratios. These mononitrosyl complexes have a sharp, intense νNO band in the IR spectra within 1874–1851 cm^{-1}, indicating a linear $Ru–NO^+$ coordination. For both $[Ru(NO)L_2]Cl$ compounds, a dynamic switch on-off process occurs between the oxyanionic moieties on the apical position *trans* to NO^+ and the pyrazolic ligands on the equatorial plane. A dynamic ^1H NMR experiment of this process gave $\Delta G^{\#}$= 46–48 kJ·mol^{-1} at 218–228 K for the acetate derivative.

Introduction

In the past decade nitric oxide, NO, has been widely studied since it was found to be an essential component in many physiological processes. The physiological functions of NO are various: a killer of invading microorganisms, primary messenger in regulating blood pressure and neurotransmitter. Dysfunction in NO metabolism has been associated with several disease states, such as epilepsy, arthritis, hypertension and septic shock.[1]

Ruthenium(III) complexes coordinate nitric oxide, NO, to form stable Ru^{II} mononitrosyl complexes. This reaction can occur rapidly in aqueous solution.[1b] It is assumed that, generally, a $Ru^{II}-NO^+$ linear bond is formed. The νNO bands (IR) lie within the range 1789−1960 cm^{-1}.[2,3]

However, when a linear Ru^{II} mononitrosyl complex is submitted to a chemical (or electrochemical) one-electron reduction,[4] the stable low-spin d^6 configuration of Ru^{II} apparently remains unaffected while the electron transferred in the reduction process is accepted by NO, by which it is transformed into a radical, $NO^{\cdot}$. This radical is ESR active with $g_x = 1.995$; $g_y = 2.035$, and $g_z = 1.883$. Under such conditions the $NO^{\cdot}$ radical can easily be released.[4a] The $NO^{\cdot}$ signal can be observed in the ESR spectrum of these Ru^{II} mononitrosyl complexes at 77 K. Some Ru^{II} nitrosyl complexes photochemically dissociate $NO^{\cdot}$.[5]

Different Ru^{III} complexes with polyaminocarboxylic acids have been studied as NO scavengers.[6] Complexes of Ru^{II} coordinated to NO^+, $NO^{\cdot}$ and NO^- have been obtained by the interaction of NO with $[Ru(hedta)Cl]^-$ [hedta: *N*-(hydroxyethyl)ethylenediaminetriacetate] and further electrochemical reduction.[6b]

The first report on ruthenium nitrosyl complexes with pyrazol-1-yl derivatives included the study of $[TpRuNOCl_2]$, $[pzTpRuNOCl_2]$ and $[Tp^*RuNOCl_2]$ (Tp: trispyrazol-1yl borate; Tp*: 3,5-substituted Tp).[7] Ruthenium nitrosyl complexes with 3,5-dimethylpyrazole have also been reported.[8] These complexes were structurally characterized by single-crystal X-ray diffraction and in all cases the Ru−N−O angle lies between 176.2 and 179.6°, while the νNO band (IR) appears within 1894−1790 cm^{-1}.

Recently, we reported different ruthenium(II) complexes with bis(3,5-dimethylpyrazol-1-yl)methane derivatives: Bis(3,5-dimethylpyrazol-1-yl)methanesulfonate (bdmpzsa, **1**), and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza, **2**) (Figure 1).[9] Both ligands lie on the equatorial plane and coordinate as κ^3-*N*,*N*,O scorpionates, but with a weak interaction through the oxyanionic moiety.

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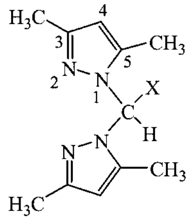

Figure 1. Schematic representation of the studied ligands bis(3,5-dimethylpyrazol-1-yl)methanesulfonate (bdmpzsa, **1**) (X = SO_3^-), and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza, **2**) (X = COO^-)

In this paper, we report on Ru^{II} mononitrosyl complexes with ligands **1** and **2**, prepared by the interaction of the ligands with Ru(NO)Cl$_3$.

Results and Discussion

In the synthesized complexes reported previously,[9] the bis(pyrazolic) ligands lie on the equatorial plane – only one set of signals appear in the NMR spectra. Conversely, NO is assumed to be coordinated on an apical position. In compounds **3** and **4**, one bis(pyrazolic) ligand and the two chloride anions lie on the equatorial plane (Figure 2 for **4**). In **5** and **6** both bis(pyrazolic) ligands lie on the equatorial plane, while in **7** and **8** ethylenediamine (en) and the bis(pyrazolic) ligand lie in this plane.

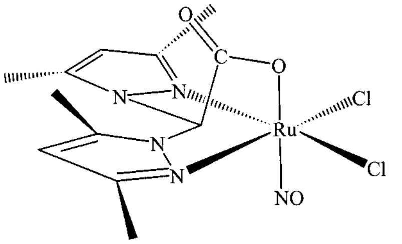

Figure 2. Representation of compound **4**

Very small shifts appear in the NMR signals of the pyrazolic rings upon coordination, as reported previously.[9]

To confirm the earlier ^{1}H and ^{13}C NMR assignments of the pyrazolic rings the ^{1}H,^{15}N gs-HMBC (NMR) two-dimensional spectrum of [Ru(bdmpza)$_2$(NO)]Cl (**6**) was recorded (Figure 3).

This technique permits the correlation of coupling of ^{1}H and ^{15}N signals of atoms 2–3 bonds apart. Two signals of ^{15}N coupled to ^{1}H occur: one at δ = 127.5 ppm (N^1) and another at δ = 212.5 ppm (N^2). The former couples through three bonds to the protons of the CH$_3{}^5$, through two bonds to the methylenic (CH) proton, and through three bonds to the protons of the CH group of the pyrazolic ring. The ^{15}N signal at δ = 212.5 ppm (N^2) ppm couples through three bonds to the protons of CH$_3{}^3$, through three bonds to the proton of the methylenic (CH) and through three bonds to the proton of the CH group of the pyrazolic ring. Small shifts (Δδ = 2 ppm) were now observed for ^{15}N of N^1 and N^2 of the pyrazolic ring upon coordination. These results confirm the previous assignments.

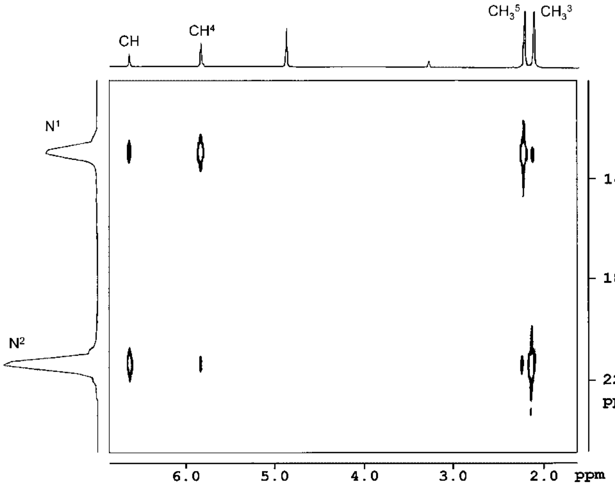

Figure 3. ^{1}H, ^{15}N gs-HMBC spectrum of [Ru(bdmpza)$_2$NO]Cl in CD$_3$OD

Coordinated NO could not be detected by this technique since the neighboring protons are too distal. Nevertheless, the small chemical shifts in the spectra of the obtained Ru^{II} nitrosyl complexes indicate that coordinated NO, with a significant *trans* effect, is on an apical position. Only one set of ^{15}N signals are observed, confirming that the bis(pyrazolic) ligands lie on the equatorial plane.

IR stretching bands of the oxyanionic moieties and the methylenic CH signals (^{1}H and ^{13}C NMR) of the pyrazolic rings shift very slightly upon coordination. This indicates that the oxyanionic moiety is weakly coordinated. In addition, the IR spectra of both [Ru(NO)L$_2$]Cl complexes (**5** and **6**) present only one asymmetric stretching band for the oxyanionic groups: 1647 [$\nu_{as}(COO^-)$] and 1249 cm^{-1} [$\nu_{as}(SO_3^-)$] respectively, indicating that they are equivalent. Conversely, in the ^{1}H NMR spectra, δ_H of methylenic CH at room temperature broadens when two bis(pyrazolic) ligands (**1** or **2**) are coordinated. This can be interpreted as a dynamic switch on-off exchange between both oxyanionic groups to coordinate to Ru^{II} at the only vacant site left, since the four positions on the equatorial plane are occupied by the four N atoms of both bis(pyrazolic) rings, plus NO on an apical position.

A dynamic-^{1}H NMR technique was used to confirm a switch on-off exchange between both groups in [Ru(NO)-L$_2$]Cl (**5**, **6**). With decreasing temperature the proton signal of the methylenic groups of **6** initially broadened further and then, finally, decoalesced into two broad singlets at 193 K (Figure 4).

This latter effect should be because the dynamic exchange is "frozen", such that one oxyanionic group remains near Ru^{II} and the other more distant. From the difference in chemical shifts and the approximately estimated coalescence temperature (218–228 K), the free energy of acti-

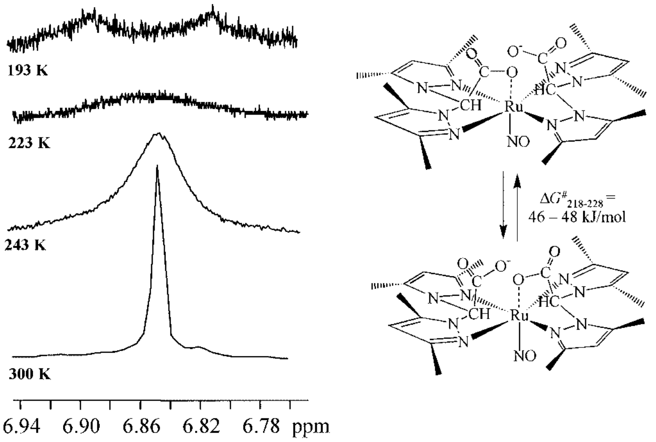

Figure 4. Switch on-off process of carboxylate groups in compound **6** studied by dynamic ^1H NMR spectroscopy

vation ($\Delta G^{\#}$) of the process could be evaluated,[10] corresponding to 46−48 kJ·mol^{-1} for [Ru(NO)(bdmpza)$_2$]Cl (**6**). This low value supports the proposed room-temperature dynamic process that causes the observed equivalency between both methylenic groups. For compound **5**, decoalescence takes place below 193 K, indicating an even weaker coordination of the sulfonate group with respect to the carboxylate.

The switch on-off process was modeled by molecular dynamics for complex **6**. Movement of the bonding oxygen atom of one of the carboxylate groups, as time function, indicates a fast motion to and from the proximity of Ru^{II} (Figure 5, a). The steric effect of the $CH_3{}^3$ groups in the pyrazolic rings is important in this dynamic process since it restricts the complete approach of the carboxylate groups to Ru^{II} (Figure 5, b).

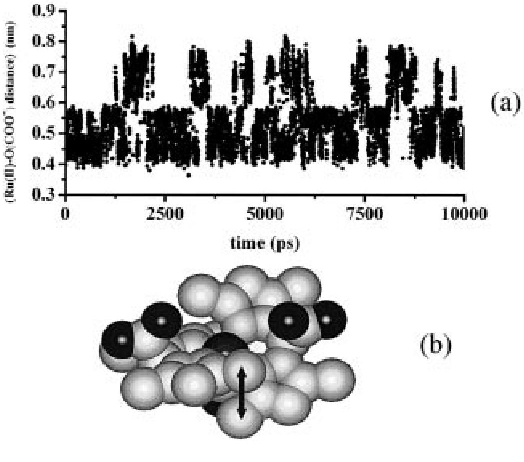

Figure 5. (a) Ru^{II}−OOC− distance as time function obtained by molecular dynamics; (b) schematic representation of complex **6** where both switching oxygen atoms of the carboxylate groups are in black, as is Ru^{II} (a larger sphere); steric repulsion between both $CH_3{}^3$ groups is indicated by a double arrow

This prediction agrees with both the low $\Delta G^{\#}$ obtained from ^1H NMR studies and the very similar chemical shifts (^{13}C NMR) of the carboxylate group in the free ligand (**2**) and in complex **6**.

We earlier reported that for the complex [Ru(NEt$_3$)(bdmpza)$_2$], formed by treating [Ru(bdmpza)$_2$] with NEt$_3$, the COO$^-$ and CH signals in the ^{13}C NMR spectrum are two well-defined singlets, while the $\nu_{as}(COO^-)$ band (IR) appears as two peaks at 1660 and 1647 cm^{-1}. A similar result occurs in the ^{13}C NMR spectrum of [Ru(NEt$_3$)(bdmpzsa)$_2$].[9] Comparing these results with those obtained for **5** and **6**, where the switch on-off process is observed, shows that NO$^+$ evidently weakens the *trans* position much more than NEt$_3$. This can be explained by the strong *trans* effect of NO$^+$, which provokes the observed switch on-off process of the oxyanionic groups.

Coordination of NEt$_3$ was also used here to "freeze" the dynamic exchange of both oxyanionic groups in the obtained nitrosyl complexes. For this, the reaction products of [Ru(NO)L$_2$]Cl (**5**, **6**) and NEt$_3$ (1:1 molar ratio) in methanol were isolated and purified. Once NEt$_3$ was coordinated to Ru^{II} *trans* to NO, leaving both oxyanionic groups free, the methylenic protonic signals became sharp and the ^{13}C NMR spectra gave only one set of signals (Supporting Information, Figure S1; for Supporting Informations see also the footnote on the first page of this article).

As expected, the obtained mononitrosyl complexes are ESR silent and completely diamagnetic according to SQUID determinations, which excludes any possible Ru^{III} impurity.

All IR spectra of the mononitrosyl complexes gave a sharp, intense band at 1874−1851 cm^{-1}, and only very slight differences (0−4 cm^{-1}) were observed between the spectra of samples prepared as KBr tablets and those recorded in CH$_2$Cl$_2$ solutions. The band, assigned as νNO, indicates a linear coordination to Ru^{II}.

Heating KBr tablets of different samples from 200 up to 400 K resulted in no significant loss in intensity and only slight, reversible, shifts to higher frequencies (3−17 cm^{-1}) in the νNO band. These results indicate that NO is characterized by a stable coordination to Ru^{II} in the studied complexes.

Conclusion

Stable Ru^{II} complexes with a typical Ru^{II}−NO$^+$ bond have been obtained by reacting ligands **1** and **2** with Ru(NO)Cl$_3$. Compounds **5** and **6**, with two pyrazolic ligands, are characterized by a switch on-off process between both oxyanionic groups. This process has been studied by dynamic ^1H NMR for complex **6**, for which $\Delta G^{\#}_{218-228K}$ = 46−48 kJ·mol^{-1} was obtained. This process, modeled by molecular dynamics studies, should be enhanced by the *trans* effect of NO over the oxyanionic groups in **5** and **6**.

Experimental Section

Reagents: All chemicals used, including Ru(NO)Cl$_3$, were of high quality and purchased from Aldrich. Solvents were dried and distilled before use.

Spectroscopy: Electronic spectra were recorded with an Ultrospec III spectrophotometer (Pharmacia-LKB) interfaced with a microcomputer for data acquisition. IR spectra were recorded with a Perkin-Elmer 883 FT-IR spectrometer, with samples prepared as KBr tablets and as CH_2Cl_2 solutions in CaF_2 cells. ESR spectra at room temperature were carried out at X-band with a Bruker ESP 300 spectrometer, operating at 100 kHz field modulation. The frequency was measured with a Hewlett−Packard 5352B frequency counter. NMR spectra were obtained with a Bruker AC 250 (62.89 MHz for ^{13}C) equipped with an ASPECT 3000 computer. All samples were dissolved in [D$_4$]methanol (30 mg/0.4 mL) and recorded at 300 K. Chemical shifts (δ) are expressed in ppm and referred to tetramethylsilane (TMS). The nature of each carbon atom was determined using the DEPT technique with proton pulses at $\theta = 135°$. Quantitative measurements were carried out by recording the ^{13}C NMR spectra using the inverse-gated decoupled technique with a relaxation $D_1 = 10$ s, to fulfill the condition $D_1 > 5T_1$ (maximum) for hydrogenated carbon atoms. The ^{1}H NMR dynamic experiment was carried out with a Varian FT-300, using an Oxford Instruments VTC 4 unit, measured by a thermocouple and calibrated with [D$_4$]methanol, within 300 and 193 K, using [D$_6$]acetone as solvent. ^{1}H, ^{15}N gs-HMBC spectra were obtained with a Bruker AV 400 (40.53 MHz for ^{15}N) equipped with a GRASP accessory, using [D$_4$]methanol as solvent. The chemical shifts (δ, ppm)/CH_3NO_2 of the ^{15}N signals have been converted into the liquid ammonia reference scale. Resonances observed upfield of nitromethane were assigned as negative chemical shifts and those downfield as positive chemical shift for the conversion.

Molecular Dynamics: Molecular dynamics calculations were performed using the Gromos 96 program with additional parameters of ab initio calculus and crystallographic data of similar compounds.[11] One solute molecule and 168 solvent molecules of methanol made up the studied system, confined in a truncate octahedral box of 2.8 nm (300 K, 1 atm). Periodic frontier conditions were used; simulation time of 10 ns with a path of 0.002 ps.

Magnetic Susceptibility Determinations: Magnetic susceptibility measurements (1.8−300 K) were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 1 T at high temperature and 100 G at low temperature to avoid any problem of magnetic saturation. The device was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$. Corrections for the diamagnetism were estimated from Pascal constants. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [60 × 106 cm^3·mol^{-1} per copper(II) ion] and the magnetization of the sample holder.

The ligand [{Li(bdmpzsa)(H$_2$O)}$_4$] (**1**) (and, alternatively, the potassium salt) was prepared as reported previously.[9]

[{Li(bdmpza)(H$_2$O)}$_4$] (2): This ligand was prepared as reported previously.[12]

[Ru(NO)(bdmpzsa)(Cl)$_2$] (3): Ru(NO)Cl$_3$ (50 mg, 0.21 mmol) was dissolved in methanol (20 mL) containing ligand **1** (61 mg, 0.21 mmol) and stirred for 12 h in an inert atmosphere. The so-formed brownish-red suspension was roto-evaporated and the product dissolved in dichloromethane to separate LiCl by filtration. The solution was then evaporated to dryness under vacuum, and a brownish red hygroscopic solid was obtained. Yield: 75 mg (73.5%). $C_{11}H_{15}Cl_2N_5O_4RuS$ (485.3): calcd. C 27.21, H 3.09, N 14.43; found C 27.18, H 3.12, N 14.41. IR (KBr): $\tilde{\nu}$ = 1874 ν(NO), 1562 ν(C=N), 1175 $\nu_{as}(SO_3^-)$, 1114 $\nu_s(SO_3^-)$, 334 ν(Ru−Cl) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1874 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 230 (sh) (π → π*), 457 (2.95, d-d) nm. ^{1}H NMR (250 MHz, CD$_3$OD, 298 K): δ = 2.11 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5), 5.85 (s, 2 H, H^4), 6.82 (s, 1 H, CH) ppm. ^{13}C{^{1}H} NMR/DEPT-135° (62.89 MHz, CD$_3$OD, 298 K): δ = 10.9 (+, Me^5), 13.3 (+, Me^3), 75.2 (+, CH), 105.8 (+, C^4), 141.3 (0, C^5), 147.5 (0, C^3) ppm.

[Ru(NO)(bdmpza)(Cl)$_2$] (4): A procedure similar to that described for **3** was used, but with Ru(NO)Cl$_3$ (50.0 mg, 0.21 mmol) and ligand **2** (53.3 mg, 0.21 mmol) to afford a brownish-red hygroscopic solid. Yield: 0.080 g (84.7%). $C_{12}H_{15}Cl_2N_5O_3Ru$ (449.3): calcd. C 32.07, H 3.34, N 15.59; found C 32.04, H 3.37, N 15.61. IR/KBr: $\tilde{\nu}$ = 1872 ν(NO), 1645 $\nu_{as}(CO_2^-)$, 1562 ν(C=N), 1387 $\nu_s(CO_2^-)$, 336 ν(Ru−Cl) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1868 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 234 (sh, π → π*), 400 (2.96, d-d) nm. ^{1}H NMR (250 MHz, CD$_3$OD, 298 K): δ = 2.15 (s, 6 H, Me^3), 2.24 (s, 6 H, Me^5), 5.86 (s, 2 H, H^4), 6.62 (s, 1 H, CH) ppm. ^{13}C{^{1}H} NMR / DEPT-135° (62.89 MHz, CD$_3$OD, 298 K): δ = 11.2 (+, Me^5) 13.3 (+, M3^5), 73.9 (+, CH), 107.3 (+, C^4), 142.4 (0, C^5), 149.5 (0, C^3), 169.7 (0, C=O) ppm.

[Ru(NO)(bdmpzsa)$_2$]Cl (5): A procedure similar to that for **3** was used, but with Ru(NO)Cl$_3$ (50.0 mg, 0.21 mmol) and ligand **1** (122.0 mg, 0.42 mmol) to furnish a brownish red crystalline solid. Yield: 140 mg (91.0%). $C_{22}H_{30}ClN_9O_7RuS_2$ (733.2): calcd. C 36.03, H 4.09, N 17.20; found C 35.99, H 4.12, N 17.18. IR (KBr): $\tilde{\nu}$ = 1865 ν(NO), 1564 ν(C=N), 1249 $\nu_{as}(SO_3^-)$, 1049 $\nu_s(SO_3^-)$ cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1868 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 251 (sh, π → π*), 374 (sh, MLCT), 455 (2.59, d-d) nm. ^{1}H NMR (250 MHz, CD$_3$OD, 298 K): δ = 2.12 (s, 12 H, Me^3), 2.22 (s, 12 H, Me^5), 5.86 (s, 4 H, H^4), 6.67 (s, 2 H, CH) ppm. ^{13}C{^{1}H} NMR/ DEPT 135° (62.89 MHz, CD$_3$OD, 298 K): δ = 11.3 (+, Me^5), 13.2 (+, Me^3), 75.2 (+, CH), 107.4 (+, C^4), 143.0 (0, C^5), 150.1 (0, C^3) ppm.

[Ru(NO)(bdmpza)$_2$]Cl (6): A procedure similar to that for **3** was used, but with Ru(NO)Cl$_3$ (50.0 mg, 0.21 mmol) and ligand **2** (106.6 mg, 0.42 mmol) to give a brownish red crystalline solid. Yield: 134 mg (96.4%). $C_{24}H_{30}ClN_9O_5Ru$ (661.1): calcd. C 43.60, H 4.54, N19.07; found C 43.58, H 4.57, N 19.04. IR (KBr): $\tilde{\nu}$ = 1860 ν(NO), 1647 $\nu_{as}(CO_2^-)$, 1562 ν(C=N), 1385 $\nu_s(CO_2^-)$ cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1862 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 250 (sh, π → π*), 376 (3.52, MLCT), 564 (2.84, d-d) nm. ^{1}H NMR (250 MHz, CD$_3$OD, 298 K): δ = 2.15 (s, 12 H, Me^3), 2.24 (s, 12 H, Me^5), 5.85 (s, 4 H, H^4), 6.61 (s, 2 H, CH) ppm. ^{13}C{^{1}H} NMR/DEPT 135° (62.89 MHz, CD$_3$OD, 298 K): δ = 11.2 (+, Me^5), 13.4 (+, Me^3), 73.9 (+, CH), 107.1 (+, C^4), 142.6 (0, C^5), 149.6 (0, C^3), 169.6 (0, C=O) ppm.

[Ru(NO)(bdmpzsa)(en)]Cl$_2$ (7): A procedure similar to that for **3** was used, but with Ru(NO)Cl$_3$ (50.0 mg, 0.21 mmol), ligand **1** (61.0 mg 0.21 mmol) and ethylenediamine (14 µL, 0.21 mmol) to afford a brownish red crystalline solid. Yield: 105.0 mg (91.3%). $C_{13}H_{23}Cl_2N_7O_4RuS$ (545.4): calcd. C 28.62, H 4.22, N 17.98; found C 28.60, H 4.25, N17.96. IR (KBr): $\tilde{\nu}$ = 3234 $\nu_{as}(NH_2)$, 3135 $\nu_s(NH_2)$, 1855 (1818, sh) ν(NO), 1557 ν(C=N), 1178 $\nu_{as}(SO_3^-)$, 1113 $\nu_s(SO_3^-)$, 328 ν(Ru−Cl) cm^{-1}. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1851 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 252 (sh, π → π*), 308 (sh, MLCT), 455 (2.88, d-d) nm. ^{1}H NMR (250 MHz, CD$_3$OD, 298 K): δ = 2.16 (s, 6 H, Me^3), 2.44 (s, 6 H, Me^5), 2.24 /2.63 [t, 4 H, CH$_2$(en)], 5.95 (s, 2 H, H^4), 6.80 (s, 1 H, CH) ppm. ^{13}C{^{1}H} NMR/NOE suppression, DEPT 135° (62.89 MHz, CD$_3$OD, 298 K): δ = 10.8 (+, 2 C, Me^5), 13.1 (+, 2 C, Me^3), 45.6/45.5 [−, 2 C, CH$_2$(en)], 75.3 (+, 1 C, CH), 106.9 (+, 2 C, C^4), 142.5 (0, 2 C, C^5), 151.3 (0, 2 C, C^3) ppm.

[Ru(NO)(bdmpza)(en)]Cl$_2$ (8): A procedure similar to that for **3** was used, but with Ru(NO)Cl$_3$ (50.0 mg, 0.21 mmol), ligand **2** (53.3 mg, 0.21 mmol) and ethylenediamine (14 µL, 0.21 mmol) to furnish a brownish red crystalline solid. Yield: 97 mg (90.6%).

$C_{14}H_{23}Cl_2N_7O_3Ru$ (509.4): calcd. C 33.00, H 4.52, N 19.25; found C 33.03, H 4.55, N 19.21. IR (KBr): $\tilde{\nu}$ = 3233 $\nu_{as}(NH_2)$, 3130 $\nu_s(NH_2)$, 1867 (1822, sh) ν(NO), 1637 $\nu_{as}(CO_2^-)$, 1560 ν(C=N), 1386 $\nu_s(CO_2^-)$ cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1863 ν(NO) cm^{-1}. UV/Vis: λ (log ε) = 252 (sh, $\pi \rightarrow \pi^*$), 300 (sh, MLCT), 464 (2.96, d-d) nm. ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.13 (s, 6 H, Me^3), 2.27 (s, 6 H, Me^5), 2.31 /2.65 (t, 4 H, CH_2(en)), 5.86 (s, 2 H, H^4), 6.62 (s, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR/NOE suppression, DEPT-135° (62.89 MHz, CD_3OD, 298 K): δ = 11.6 (+, 2 C, Me^5), 13.5 (+, 2 C, Me^3), 46.5/46.4 [−, 2 C, CH_2(en)], 74.8 (+, 1 C, CH), 107.5 (+, 2 C, C^4), 142.8 (0, 2 C, C^5), 149.1 (0, 1 C, C^3), 170.03 (0, 1 C, C=O) ppm.

Supporting Information Available (see also footnote on the first page of this article): ^{13}C NMR spectrum with suppressed NOE of $[Ru(NO)(bdmpza)_2(NEt_3)]$ (Figure S1).

Acknowledgments

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[1] [1a] S. Moncada, R. M. J. Palmer, E. A. Higgs, *Biochem. Pharmacol.* **1989**, *38*, 1709−1715. [1b] A. R. Buttler, D. L. H. Williams, *Chem. Soc. Rev.* **1993**, *22*, 233−241.

[2] B. Mondal, H. Paul, V. G. Puranik, G. K. Lahiri, *J. Chem. Soc., Dalton Trans.* **2001**, 481−487.

[3] G. B. Yi, M. A. Khan, D. R. Powell, G. B. Richter-Addo, *Inorg. Chem.* **1998**, *37*, 208−214.

[4] [4a] D. R. Lang, J. A. Davis, L. G. F. Lopes, A. A. Ferro, L. C. G. Vasconcellos, D. W. Franco, E. Tfouni, A. Wieraszko, M. J. Clarke, *Inorg. Chem.* **2000**, *39*, 2294−2300. [4b] B. R. McGarvey, A. A. Ferro, E. Tfouni, C. W. B. Bezaerra, I. Bagatin, D. W. Franco, *Inorg. Chem.* **2000**, *39*, 3577−3581. [4c] M. Wanner, T. Schreiring, W. Kaim, *Inorg. Chem.* **2001**, *40*, 5704−5707.

[5] [5a] A. K. Patra, P. K. Mascharak, *Inorg. Chem.* **2003**, *42*, 7363−7365. [5b] C. F. Works, C. J. Jocher, G. D. Bart, X. Bu, P. C. Ford, *Inorg. Chem.* **2002**, *41*, 3728−3739. [5c] C. F. Works, P. C. Ford, *J. Am. Chem. Soc.* **2000**, *122*, 7592−7593.

[6] [6a] S. P. Fricker, E. Salde, N. A. Powell, O. J. Vaughan, G. R. Henderson, S. A. Murrer, I. C. Megson, S. K. Bisland, F. W. Flitney, *Br. J. Pharmacol.* **1997**, *122*, 1441. [6b] Y. Chen, F.-T. Lin, R. E. Shepherd, *Inorg. Chem.* **1999**, *38*, 973−983. [6c] J. M. Slocik, M. S. Ward, K. V. Somayajula, R. E. Shepherd, *Trans. Metal Chem.* **2001**, *26*, 351−364.

[7] M. Onishi, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3039−3045.

[8] D. S. Bohle, E. S. Sagan, *Eur. J. Inorg. Chem.* **2000**, 1609−1616.

[9] M. Ortiz, A. Díaz, R. Cao, A. Otero, J. Fernández-Baeza, *Inorg. Chim. Acta* **2003**, *357*, 19−24.

[10] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**.

[11] A. López-Hernández, R. Müller, H. Kopf, N. Burzlaff, *Eur. J. Inorg. Chem.* **2002**, 671−677.

[12] A. Otero, J. Fernández-Baeza, J. Tejeda, A. Antiñolo, F. Carrillo-Hermosilla, E. Díez-Barra, A. Lara-Sánchez, M. Fernández-López, *J. Chem. Soc., Dalton Trans.* **2000**, 2367−2374.

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