Ruthenium Complexes of the Scorpionate Ligand Bis(3,5-dimethylpyrazol-1-yl)-dithioacetate and the Effect of Nitric Oxide Coordination

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Six new ruthenium(II) complexes with the scorpionate ligand bis(3,5-dimethylpyrazol-1-yl)dithio-κ^3N,N,S-acetate (bdmpzdta) were obtained by treatment of the ligand with $RuCl_3$ or $[RuCl_3(NO)]$ in 1:1 or 2:1 molar ratios in the presence or absence of ethylenediamine. In all six complexes the pyrazolic rings lie in the equatorial plane. The mononitrosyl complexes present a sharp ν(NO) band in the range 1864–1859 cm^{-1} for samples prepared either as KBr tablets or dichloromethane solutions. In the case of $[Ru(NO)(bdmpzdta)_2]Cl$ (**7**), the dithiocarboxylate group of one of the ligands is not coordinated (κ^2N,N). In the other five complexes, however, bdmpzdta behaves as a κ^3N,N,S scorpionate ligand. When the complexes obtained from $RuCl_3$ were dissolved in dichloromethane and NO was bubbled through the solution, a high degree of coordination of NO^+ was observed, according to IR, UV and voltammetric studies.
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Introduction

The physiological functions of nitric oxide (NO) have been widely studied in the past decade as dysfunction in NO metabolism has been associated with a great number of diseases.[1,2] When a patient has a severe infection, as in so-called septic shock, the body generates such a large amount of nitric oxide that the patient's blood pressure practically collapses. A specific inhibitor for induced nitric oxide synthase, iNOS, has yet to be found. An alternative to save patients' lives in cases of septic shock involves finding NO scavengers that can be used when NO is produced in relatively large amounts.

Ru^{III} complexes are known to coordinate NO to form stable Ru^{II} mononitrosyl complexes and these can therefore act as efficient NO scavengers. A number of different Ru^{III} complexes with polyaminocarboxylic acids have been studied as NO scavengers.[3–5]

Recently, we reported different ruthenium(II) complexes with the bis(3,5-dimethylpyrazol-1-yl)methane derivatives bis(3,5-dimethylpyrazol-1-yl)methanesulfonate (bdmpzsa) and bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza).[6,7] Both ligands lie in the equatorial plane and coordinate as κ^3N,N,O scorpionates, but with a weak interaction through the oxyanionic moiety. Mononitrosyl complexes of Ru^{II} were also obtained from the same ligands with NO coordinated in the apical position.[7] NO was found to have a strong *trans* influence on the oxyanionic moiety. As a consequence, the mononitrosyl bis(bis-pyrazolic) complexes of Ru^{II} show an on/off switching process of the oxyanionic moiety *trans* to the coordinated NO.

We report here the main results obtained on Ru^{II} complexes with a similar ligand: bis(3,5-dimethylpyrazol-1-yl)-dithioacetate (bdmpzdta; **1**), which is depicted in Figure 1. This ligand is expected to behave as a κ^3N,N,S scorpionate, but with a softer anionic moiety. For this reason, a higher scorpionate affinity for Ru^{II} than the previously studied bdmpza and bdmpzsa ligands is to be expected.

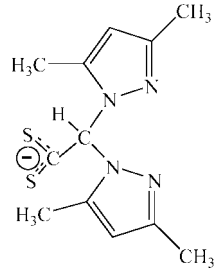

Figure 1. Schematic representation of ligand **1**.

Results and Discussion

In a previous paper,[6] we reported a kinetic study of the interaction of $RuCl_3$ with bis(3,5-dimethylpyrazol-1-yl)ace-

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tate (bdmpza; $k = 1.1 \times 10^{-3}$ s^{-1}), and bis(3,5-dimethylpyrazol-1-yl)methanesulfonate (bdmpzsa; $k = 1.6 \times 10^{-3}$ s^{-1}), in a 1:1 molar ratio in methanol. Coordination of the ligand involves the reduction of Ru^{III} to Ru^{II}. We assumed that the reducing agent was methanol, but could not detect the corresponding oxidation product. After this study was published, a signal at δ = 9.2–9.4 ppm, corresponding to methanal, was detected in the ^{1}H NMR spectra when the reaction was carried out in an NMR tube.

The interaction of $RuCl_3$ with bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzdta; **1**) was studied spectrophotometrically in methanol in an effort to confirm the reduction of Ru^{III}, as observed previously with similar ligands. A decrease in the absorbance of the bdmpzdta band at 350 nm and the appearance and increase in the absorbance of the MLCT band at approximately 300 nm were observed (see Figure 2).

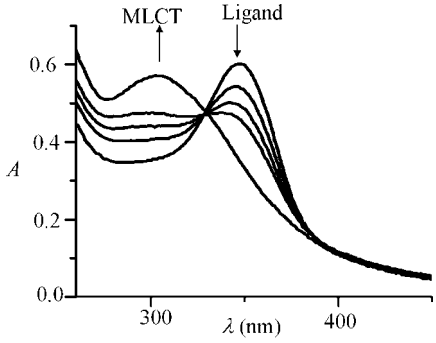

Figure 2. Variations in the UV/Visible spectra with time for the interaction of $RuCl_3$ with bdmpzdta (1:1 molar ratio) in methanol.

This MLCT band corresponds to the transition from Ru^{II} to **1**. A signal at δ = 9.35 ppm (due to methanal) was detected in the ^{1}H NMR spectra when the reaction was carried out in an NMR tube. From the variations observed in the MLCT band, pseudo first-order rate constants of $k = 1.2 \times 10^{-4}$ s^{-1} and 3.4×10^{-4} s^{-1} were obtained for 1:1 and 1:2 Ru^{III}:bdmpzdta molar ratios, respectively. Both values are ten times smaller than those reported previously for similar ligands (bdmpza and bdmpzsa).[6] Furthermore, with these latter ligands the rate constants for 1:2 molar ratios could not be detected using the same procedure.

The complete reduction of Ru^{III} was confirmed by EPR spectroscopy − all the complexes are silent. As one would expect, all NMR spectra contained sharp signals.

The interaction of ligand **1** with $RuCl_3$ gave the complexes $[\{Ru(H_2O)(bdmpzdta)(Cl)\}]_2$ (**2**), [Ru(bdmpzdta)(en)Cl] (**3**) and $[Ru(bdmpzdta)_2]$ (**4**) using procedures similar to those reported for bdmpza and bdmpzsa.[6] Similarly, $[RuNO(bdmpzdta)(Cl)_2]$ (**5**), $[RuNO(bdmpzdta)(en)]Cl_2$ (**6**) and $[RuNO(bdmpzdta)_2]Cl$ (**7**) were synthesised by the interaction of **1** with $[RuCl_3(NO)]$.

The ^{1}H and ^{13}C NMR spectra of **2**, **3**, **4**, **5** and **6** gave only one set of signals for the pyrazolic rings and ethylenediamine (**3**, **6**). In the case of compound **7** (Figure 3) this statement is not completely accurate since the signals of some of the atoms show a slight (or moderate) splitting. The observed equivalence in the NMR signals indicates that the pyrazolic rings of ligand **1** lie in the equatorial plane, as does the ethylenediamine unit in complexes **3** and **6** (Figure 3).

The composition and low solubility of complex **2** in polar organic solvents suggests a dimeric form in which the two chloride ions in the equatorial plane form bridges between the two Ru^{II} centres (Figure 3), similar to a previously reported structure.[8] Under such conditions, and with the water molecule (from $RuCl_3 \cdot xH_2O$) at the apical position *trans* to the coordinated dithiocarboxylate group, the two pyrazolic rings remain equivalent. Each of the two chloride anions in the equatorial plane of compound **5** is coordinated to one Ru^{II} (Figure 3) and the octahedral structure is achieved without the need for bridge formation.

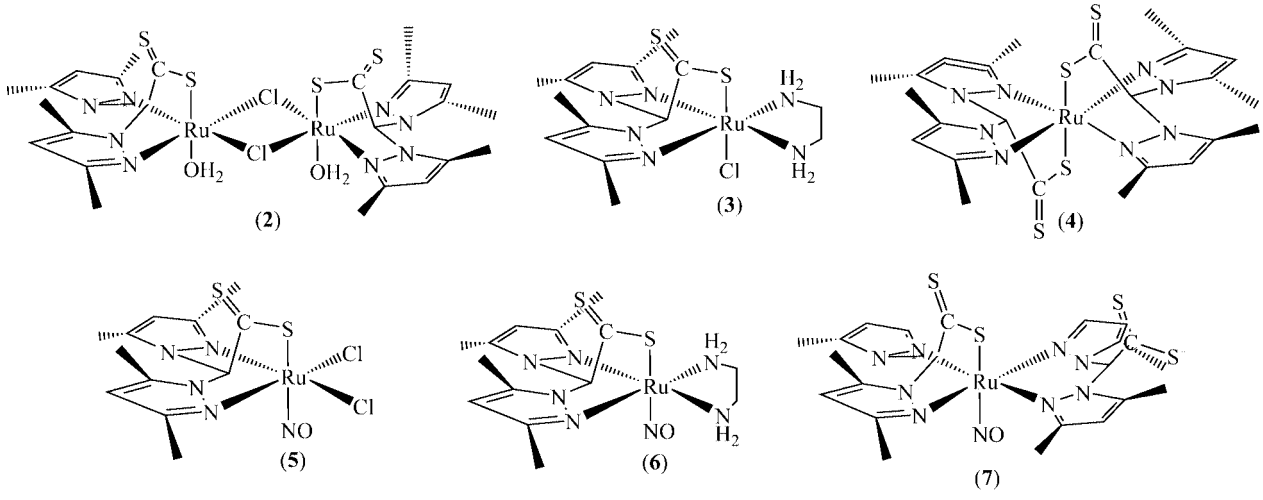

Figure 3. Schematic representation of the synthesised complexes **2**–**7**.

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As expected, the dithiocarboxylate group (a soft base) is very strongly coordinated at an apical position to Ru^{II} (soft acid) through a sulfur atom (Figure 3). Evidence for this structure is provided by the significant shift to higher field of the CS_2^- and aliphatic CH signals in the ^{13}C NMR spectra. Moreover, a significant shift in the $\nu_{C=S}$ and ν_{C-S} stretching bands is observed with respect to the IR spectrum of the free ligand. Coordination of the CS_2^- moiety to Ru^{II} is appreciably stronger than that observed for the CO_2^- moiety of bdmpza and the SO_3^- moiety of bdmpzsa, as reported previously.[6,7,9] Consequently, ligand **1** behaves as a κ^3N,N,S scorpionate ligand.

The strong coordination of the CS_2^- moiety should cause a slight distortion of the two pyrazolic rings in **1**. This distortion takes the rings out of the equatorial plane, although the effect is the same for both rings. This could be the reason why only one set of signals is observed even in the presence of this distortion. In this sense, it is interesting to point out that Otero et al. have investigated Ti^{IV}-bdmpzdta complexes and reported a distortion in the planarity of the pyrazolic rings.[10] In this latter case the soft CS_2^- moiety was coordinated to a hard acid (Ti^{IV}).

The interaction of ligand **1** with Ru^{II} should initially pass through the coordination mode κ^2N,N. The coordination of the CSS^- group should require additional energy and time in order to achieve the formation of the stable Ru^{II}–S bond. This process involves a distortion in the equatorial plane of the pyrazolic rings. Such a situation could explain the kinetically slow coordination of ligand **1** (ten times slower than for bdmpza and bdmpzsa).[6]

The coordination of NO in compounds **5**, **6** and **7** was fully characterised by IR spectroscopy. A sharp and intense band is observed at around 1860 cm^{-1} for all the mononitrosyl complexes, whether the samples were prepared as KBr tablets or CH_2Cl_2 solutions. This band was assigned to the ν(NO) stretching vibration and indicates that in these complexes NO is coordinated in a linear mode, as a $\{RuNO\}^6$ unit according to the Enemark–Feltham formalism.[11] As expected, these ν(NO) values are lower than that for the $[RuCl_3(NO)]$ starting material.

A single set of signals was observed for ligand **1** in the NMR spectra of compounds **5** and **6**, indicating that in the nitrosyl complexes NO is coordinated at the apical position *trans* to the bonded dithiocarboxylate moiety. It is worth pointing out that a single set of signals was also observed for ethylenediamine in compound **6**.

An interesting situation was found for $[Ru(bdmpzdta)_2NO]Cl$ (**7**) as the ^{13}C NMR spectrum (Figure 4) contains two signals for the CS_2^- group (δ = 211.0 and 243.2 ppm). The latter value corresponds to the free CS_2^- group that does not replace NO. In this complex one bdmpzdta is therefore coordinated as a bidentate ligand (κ^2N,N) and the other as a κ^3N,N,S scorpionate ligand. The difference between the two coordinated ligands in compound **7** is that the bidentate one is not distorted from the equatorial plane, while the scorpionate κ^3N,N,S ligand should be. This arrangement explains the observed splitting of the signals in the NMR spectra of **7**, an effect that is particularly significant for the aliphatic CH signal (Figure 4). The signal at δ = 70.3 ppm was assigned to the CH aliphatic group bound to the coordinated CS_2^-, while the signal at δ = 83.4 ppm corresponds to the free CS_2^-.

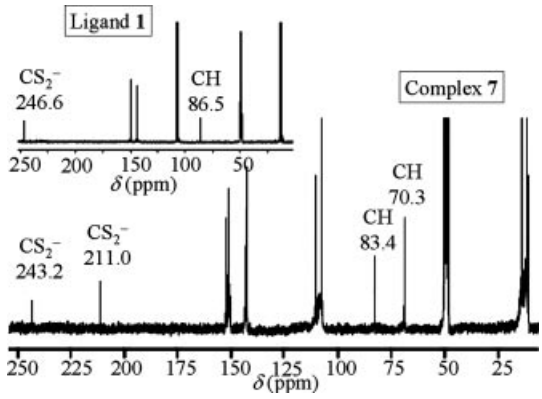

Figure 4. ^{13}C NMR spectra of ligand **1** (inset) and complex **7** in CD_3OD.

In the nitrosyl complexes $[Ru(NO)(L)_2]Cl$ (where L = bdmpza or bdmpzsa), a dynamic on/off switching exchange between the two oxyanionic groups was found to take place in the coordination to Ru^{II} at the only remaining vacant position (*trans* to NO).[7] This process is favoured by the powerful NO *trans* influence over the oxyanionic moiety. In contrast, such an exchange was not observed in complex **7** and the only Ru^{II}–S bond formed was not dissociated by NO in the *trans* position.

The *trans* influence of NO on the dithiocarboxylate group is evidenced by the marked shift observed (about 20 ppm) in the ^{13}C NMR signal relative to that in the corresponding NO-free complex. It appears that the ionic character of this bond is increased when coordinated NO weakens the Ru^{II}–S bond and increases the positive charge on the metal. In this way, the coordinated sulfur atom could increase its electron density with the consequent shielding of the CS_2 carbon atom. The coordination of NO appears to cause a strong electronic shift along the S–Ru^{II}–NO axis, which is also seen in the MLCT band as a hypsochromic shift (by about 10 nm). This change is observed in the UV/Vis spectra when comparing compounds **2**, **3** and **4** with the corresponding mononitrosyl complexes **5**, **6** and **7**, respectively. The mononitrosyl complexes (**5**, **6** and **7**) do not liberate NO under a strong vacuum and in compound **7** the second CS_2^- moiety does not substitute NO. These observations demonstrate the high stability of the Ru^{II}–NO bond. Taking this into consideration, we decided to study the possible interaction of compounds **2**, **3** and **4** with NO in an attempt to obtain the corresponding complexes with coordinated NO^+ ligand. In order to achieve this aim, NO was bubbled through dichloromethane solutions of these complexes under an oxygen-free inert atmosphere. The solutions, which were initially brown, became reddish after 15–20 min. These compounds were isolated and characterised by UV/Vis and IR spectroscopy. The UV/Vis spectra

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Table 1. Spectroscopic properties of the compounds obtained after bubbling NO through CH_2Cl_2 solutions of **2**–**4**.

Compounds	IR ($\tilde{\nu}$, cm^{-1})			UV (λ, nm)
	ν(NO)	ν(C=S)	ν(C–S)	
[{Ru(bdmpzdta)(Cl)(H_2O)}]$_2$ (**2**) + NO(g)	1866	1028	784	286
[Ru(bdmpzdta)(Cl)(en)] (**3**) + NO(g)	1862	1032	782	290
[Ru(bdmpzdta)$_2$] (**4**) + NO(g)	1857	1034	786	292

are very similar (Table 1) to those of complexes obtained from [$RuCl_3$(NO)] (compounds **5**, **6** and **7**). A strong sharp band is observed in the IR spectra of these complexes at around 1860 cm^{-1} and this is assigned to ν(NO). This band was seen when the samples were prepared either as KBr tablets or CH_2Cl_2 solutions (Figure 5 for complex **3** with NO bubbled through). The positions of the ν(NO) bands are very similar to those in **5**, **6** and **7**, respectively, as depicted in Figure 5 for compound **3** (after NO bubbled through) and mononitrosyl complex **6**.

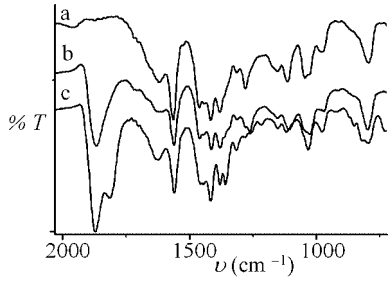

Figure 5. IR spectra of a) compound **3**, b) compound **3** with NO bubbled through and c) compound **6**.

The areas of the ν(NO) bands of the compounds after bubbling NO through were compared with those obtained from [$RuCl_3$(NO)], with the ν(C=S) and ν(C–S) stretching bands taken as references. The areas of the ν(NO) bands of the former compounds correspond to 75–90% of those of the latter. This indicates that a high percentage of Ru^{II} coordinates NO. Possible explanations for the incomplete coordination of NO include unavoidable partial oxidation of NO and its relatively low solubility in CH_2Cl_2. The fact that 100% NO coordination was not achieved in any of these compounds means that they are not pure. Purification of the nitrosyl compound by bubbling NO through solutions of the complexes was not successful.

The ^1H NMR spectra gave an overlap of signals that was not possible to interpret. The ^{13}C NMR spectra of the compounds obtained after bubbling NO through show a double set of signals that are not well resolved in most cases. A well-defined ^{13}C NMR spectrum was obtained only for the product of bubbling NO through a solution of complex **2** (Supporting Information, Figure S1). The differences between the chemical shifts of both set of signals, one of which is much more intense than the other, mainly lie in the range 0.1–1.1 ppm. For the CSS^- signal the observed difference was about 20 ppm. The set of signals with highest intensity is very similar to that of the spectra of the compounds obtained from [$RuCl_3$(NO)] (**5**–**7**), whereas the other set of signals is similar to that of the spectra of the corresponding NO-free complexes (**2**–**4**). Evidently, the compounds obtained by bubbling NO through solutions of complexes **2**–**4** show very similar characteristics (Table 1) to those found for compounds **5**–**7**, respectively, and should therefore be considered as equivalent. This fact should be attributed to the coordination of NO^+ by the bubbled complexes that is assumed to be present in this type of solution.[12]

DMSO solutions of the compounds obtained by bubbling NO through solutions of complexes **2**, **3** and **4** in dichloromethane were studied by voltammetry. The results of these experiments were also similar to those found for compounds **5**, **6** and **7**, respectively. The irreversible cathodic wave assigned to the Ru^{II}–$NO^+ + e^- \rightarrow Ru^{II}$–$NO^0$ reduction[13] is observed in the voltammograms of these six complexes between –700 and –720 mV, as depicted in Figure 6 for complexes **5** and (**2** + NO).

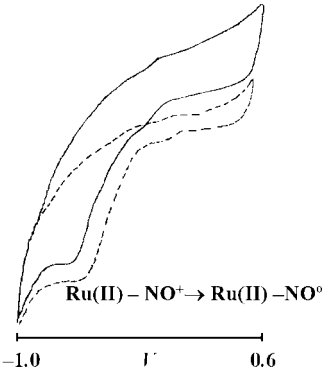

Figure 6. Cyclic voltammograms of complexes **5** (---) and (**2** + NO) (—).

Although the interaction of complexes **2**, **3** and **4** with NO was studied in dichloromethane, it is reasonable to consider the possibility that they could behave as NO scavengers in a biological system. This possibility is currently under investigation.

Conclusions

The interaction of $RuCl_3$ with bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzdta; **1**) in methanol leads to the reduction of Ru^{III} to Ru^{II} with the stabilisation of the latter species. Reaction of compound **1** with [$RuCl_3$(NO)] gives new, stable nitrosyl complexes. In all six complexes the pyrazolic rings of ligand **1** lie in the equatorial plane with the CS_2^- group also coordinated. The ligand therefore behaves as a κ^3N,N,S scorpionate system. One exception to this trend was observed in complex **7**, where the second ligand

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is coordinated in a κ^2N,N manner with its dithiocarboxylate moiety free.

When NO was bubbled through solutions of complexes **2**, **3** and **4** in dichloromethane, a high level of coordination of NO^+ took place to give compounds that are apparently equivalent to complexes **5**, **6** and **7**, respectively. For example, the ν(NO) band of the latter lies in the range 1864–1859 cm^{-1}, while for the former complex the band appears at 1866–1857 cm^{-1}. The irreversible voltammetric wave corresponding to the Ru^{II}–$NO^+ + e^- \rightarrow Ru^{II}$–NO° reduction is observed in the same range (–700 and –720 mV) for both sets of compounds.

Experimental Section

General Remarks: All chemicals used were of high quality and purchased from Aldrich. The solvents were dried and distilled before use.

Spectroscopy: The 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 or as CH_2Cl_2 solutions in CaF_2 cells. NMR spectra were obtained with a Bruker AC 250 (62.89 MHz for ^{13}C) spectrometer equipped with an ASPECT 3000 computer. All samples were dissolved in CD_3OD (30 mg/0.4 mL) and recorded at 300 K. The reported chemical shifts (δ) are expressed in ppm and referenced to tetramethylsilane (TMS). The nature of each carbon atom was determined using the DEPT technique with proton pulses at θ = 135°. X-band EPR spectra of nitrosylruthenium complexes at 120 K were obtained on a Bruker EMX-300 X-band spectrometer operating at a frequency of 9.5 GHz or aBruker ESP 300 spectrometer operating at 100 KHz field modulation for dichloromethane solutions and polycrystalline samples, respectively. The frequencies were measured with a Hewlett–Packard 5352B frequency counter. The temperature was regulated with an Oxford Instruments ESR 900 continuous flow helium cryostate (low temperature) and Bruker RS-232 continuous flow nitrogen thermostat (room temperature).

Techniques for Kinetic Determinations: The UV/Vis kinetic determinations were performed spectrophotometrically at 300 K with the appropriate software. Methanolic solutions containing 5.8×10^{-4} M $RuCl_3$ and corresponding amounts of **1** were studied in 1-cm quartz optical cells.

Electrochemical Measurements: Electrochemical measurements were carried out with a Yanaco P-900 cyclic polarograph coupled to a Graphted WX1000 X-Y recorder using a standard three-holder cell. Glassy carbon, Pt and Ag/AgCl (saturated) were used as working, counter and reference electrodes, respectively. The cyclic voltammograms of the complexes (0.01 M) in DMSO solution, which had been previously deoxygenized, were recorded with tetra-*n*-butylammonium tetrafluoroborate (0.2 M) as supporting electrolyte.

[{Li(bdmpzdta)(H_2O)}$_4$] (1): This ligand was prepared as reported previously.[10,14]

[{Ru(bdmpzdta)(Cl)(H_2O)}]$_2$ (2): $RuCl_3$ (0.050 g, 0.24 mmol) was dissolved in methanol (20 mL) and ligand **1** (0.069 g, 0.24 mmol) was added in two portions. The mixture was stirred for 4 h in an inert atmosphere. The solvent was removed from the resulting brownish suspension, the product was dissolved in dichloromethane, and the LiCl filtered off. The solvent was removed from the filtrate under vacuum to give a brown, hygroscopic solid. Yield: 0.166 g (80%). $C_{12}H_{17}ClN_4ORuS_2$ (433.7): calcd. C 33.21, H 3.92, N 12.92; found C 33.23, H 3.94, N 12.90. IR (KBr): $\tilde{\nu}$ = 1562 ν(C=N), 1027 ν_{as}(C=S), 791 cm^{-1} ν_s(C–S). UV/Vis: λ (log ε) = 295 nm (3.36, MLCT). ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.12 (s, 6 H, Me^3), 2.40 (s, 6 H, Me^5), 5.95 (s, 2 H, H^4), 7.34 (s, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 12.4 (+, Me^5), 13.8 (+, Me^3), 76.4 (+, CH), 105.1 (+, C^4), 143.2 (0, C^5), 152.5 (0, C^3), 240.5 (0, CS_2^-) ppm.

[Ru(bdmpzdta)(Cl)(en)] (3): A procedure similar to that described for **2** was used, but with the addition of ethylenediamine (16 μL, 0.24 mmol) before ligand **1**. A brown crystalline solid was obtained. Yield: 0.097 mg (84%). $C_{14}H_{23}ClN_6RuS_2$ (475.7): calcd. C 35.33, H 4.84, N 17.66; found C 35.36, H 4.87, N 17.64. IR (KBr): $\tilde{\nu}$ = 1562 ν(C=N), 1030 ν_{as}(C=S), 792 ν_s(C–S), 3233 $\nu_{as}(NH_2)$, 3127 cm^{-1} $\nu_s(NH_2)$. UV/Vis: λ (log ε) = 297 nm (3.53, MLCT). ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.10 (s, 6 H, Me^3), 2.31 (s, 6 H, Me^5), 5.86 (s, 2 H, H^4), 7.12 (s, 1 H, CH), 2.24/2.33 [t, 4 H, CH_2(en)] ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 12.4 (+, Me^5), 13.8 (+, Me^3), 76.3 (+, CH), 105.1 (+, C^4), 143.2 (0, C^5), 152.5 (0, C^3), 239.6 (0, CS_2^-) ppm.

[Ru(bdmpzdta)$_2$] (4): A procedure similar to that described for **2** was used, but with the addition of a double quantity of ligand **1** (0.138 g, 0.48 mmol) in four portions. A brown crystalline solid was obtained. Yield: 0.141 g (90%). $C_{24}H_{30}N_8RuS_4$ (659.2): calcd. C 43.70, H 4.55, N 16.99; found C 43.73, H 4.58, N 16.97. IR (KBr): $\tilde{\nu}$ = 1562 ν(C=N), 1029 ν_{as}(C=S), 790 cm^{-1} ν_s(C–S). UV/Vis: λ (log ε) = 298 nm (3.14, MLCT). ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.15 (s, 12 H, Me^3), 2.35 (s, 12 H, Me^5), 6.06 (s, 4 H, H^4), 7.05 (s, 2 H, CH) ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 13.4 (+, Me^5), 12.2 (+, Me^3), 75.7 (+, CH), 103.5 (+, C^4), 144.9 (0, C^5), 157.9 (0, C^3), 230.5 (0, CS_2^-) ppm.

[Ru(bdmpzdta)(Cl)$_2$(NO)] (5): [$RuCl_3$(NO)] (0.050 g, 0.21 mmol) was dissolved in methanol (20 mL) and ligand **1** (0.060 g, 0.21 mmol) was added in two portions. The reaction mixture was stirred for 4 h under an inert atmosphere. The solvent was removed from the resulting reddish suspension, the product was dissolved in dichloromethane, and the LiCl was filtered off. The solvent was removed from the filtrate under vacuum to give a brown hygroscopic solid. Yield: 0.071 mg (70%). $C_{12}H_{15}Cl_2N_5ORuS_2$ (481.2): calcd. C 29.93, H 3.12, N 14.55; found C 29.96, H 3.16, N 14.52. IR (KBr): $\tilde{\nu}$ = 1864 ν(NO), 1560 ν(C=N), 1031 ν_{as}(C=S), 785 cm^{-1} ν_s(C–S). IR (CH_2Cl_2): ν(NO) = 1860 cm^{-1}. UV/Vis: λ (log ε) = 284 nm (3.14, MLCT). ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.11 (s, 6 H, Me^3), 2.42 (s, 6 H, Me^5), 5.93 (s, 2 H, H^4), 7.32 (s, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 10.3 (+, Me^5), 13.0 (+, Me^3), 76.4 (+, CH), 105.2 (+, C^4), 140.4 (0, C^5), 146.8 (0, C^3), 218.1 (0, CS_2^-) ppm.

[Ru(bdmpzdta)(en)(NO)]Cl$_2$ (6): A procedure similar to that described for **5** was used, but with the addition of ethylenediamine (14 μL, 0.21 mmol) before ligand **1**. A brown crystalline solid was obtained. Yield: 0.085 g (75%). $C_{14}H_{23}Cl_2N_7ORuS_2$ (541.2): calcd. C 31.05, H 4.25, N 18.11; found C 31.08, H 4.29, N 18.13. IR (KBr): $\tilde{\nu}$ = 1860 ν(NO), 1562 ν(C=N), 1033 ν_{as}(C=S), 785 ν_s(C–S), 3232 $\nu_{as}(NH_2)$, 3130 cm^{-1} $\nu_s(NH_2)$. IR (CH_2Cl_2): ν(NO) = 1860 cm^{-1}. UV/Vis: λ (log ε) = 288 nm (3.34, MLCT). ^1H NMR (250 MHz, CD_3OD, 298 K): δ = 2.31 (s, 6 H, Me^3), 2.10 (s, 6 H, Me^5), 5.85 (s, 2 H, H^4), 7.15 (s, 1 H, CH), 2.20/2.40 [t, 4 H, CH_2(en)] ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 10.7 (+, Me^5), 13.5 (+, Me^3), 75.2 (+, CH), 106.0 (+, C^4), 140.3 (0, C^5), 147.7 (0, C^3), 220.3 (0, CS_2^-) ppm.

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[Ru(bdmpzdta)$_2$(NO)]Cl (7): A procedure similar to that described for **5** was used, but with the addition of a double quantity of ligand **1** (0.120 g, 0.42 mmol) in four portions. A brown crystalline solid was obtained. Yield: 0.137 g (90%). $C_{24}H_{30}RuN_9OS_4Cl$ (724.7): calcd. C 39.75, H 4.14, N 17.39; found C 39.77, H 4.16, N 17.36. IR (KBr): $\tilde{\nu}$ = 1859 ν(NO), 1560 ν(C=N), 1033 ν_{as}(C=S), 786 cm^{-1} ν_s(C–S). IR (CH_2Cl_2): ν(NO) = 1862 cm^{-1}. UV/Vis: λ (log ε) = 289 nm (3.20, MLCT). ^{1}H NMR (250 MHz, CD_3OD, 298 K): δ = 2.15 (s, 12 H, Me^3), 2.30 (s, 12 H, Me^5), 6.08 (s, 4 H, H^4), 7.07 (s, 2 H, CH) ppm. $^{13}C\{^1H\}$ NMR/DEPT-135 (62.89 MHz, CD_3OD, 298 K): δ = 10.5 (+, Me^5), 13.2 (+, Me^3), 70.3 (+, aliphatic CH of CS_2^- coordinated moiety), 83.4 (+, aliphatic CH of CS_2^- uncoordinated moiety), 105.6/106.2 (+, C^4), 142.8 (0, C^5), 145.7 (0, C^3), 211.0 (0, coordinated CS_2^-), 243.2 (0, uncoordinated CS_2^-) ppm.

Interaction of 2, 3 or 4 with NO in Solution: Nitric oxide was obtained from the reaction between copper and nitric acid (5 M) under a nitrogen atmosphere using Schlenk techniques at 293 K. The gaseous product(s) of this reaction were passed through NaOH(conc) traps to remove nitrogen oxides other than nitric oxide. Compounds **2**, **3** and **4** (0.08–0.11 mmol) were each dissolved in 20 mL of dichloromethane in a Schlenk flask and deoxygenated with oxygen-free nitrogen. These 10^{-3} M solutions had nitric oxide bubbled through them for 20 min and were then stirred for 6 h whilst maintaining anaerobic conditions under nitrogen. The solutions, which were initially brown, became reddish. The corresponding products were isolated by evaporating the solvent under vacuum.

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