

An Electron-Excessive Nitrosyl Complex: Reactivity of a Ligand-Centered Radical Leading to Coordinated HNO

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The reaction of $\text{RuHCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{P}^i\text{Pr}_3$) with NO initially forms a 1:1 adduct, shown by DFT calculations and EPR spectroscopy (including the RuD isotopomer) to contain a bent ($\angle\text{Ru}-\text{N}-\text{O} = 143.9^\circ$) nitrosyl where the majority of the spin density is on the nitrosyl nitrogen. This radical adduct transforms further to give equimolar $\text{RuCl}(\text{NO})(\text{CO})\text{L}_2$ and $\text{RuHCl}(\text{HNO})(\text{CO})\text{L}_2$, the latter with hydride trans to the nitroxyl ligand $\text{HN}=\text{O}$. This is the first observation of the synthesis of coordinated HNO from NO itself. DFT calculations lead to the proposal that this H-atom transfer is effected by free NO, and the lifetime of $\text{RuHCl}(\text{HNO})(\text{CO})\text{L}_2$ is indeed qualitatively dependent on the presence of free NO.

Nitric oxide^{1,2} is a reagent that is not immediately compatible with a 16-valence electron complex; the radical character of NO would appear to lead to a radical coordination complex, so the advantage of forming an *adduct* to the unsaturated reagent complex is not evident. In the event that an alkyl ligand is present, a single insertion into the M–R bond still leaves a radical product, the observed reaction for a metal alkyl often involves *two* NO molecules, and a bidentate *N*-alkyl-*N*-nitrosohydroxylaminato ligand, $\text{N}(\text{O})(\text{NO})\text{R}^-$, results.³ For a hydride ligand, no NO insertion has ever been observed. We report here a 1:1 reaction of the type introduced above, together with mechanistic information on how the reaction may proceed from radicals to even-electron products.

Reaction of $\text{RuHCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{P}^i\text{Pr}_3$) with *excess* NO in benzene proceeds over 10 min at 23 °C to one major product which was characterized by spectroscopic methods and single-crystal X-ray diffraction as $\text{Ru}(\text{NO})\text{Cl}(\text{CO})\text{L}_2$ (Figure 1a),⁴ a square pyramidal complex with a bent nitrosyl ligand

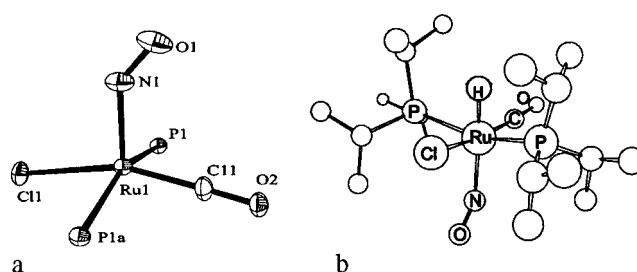
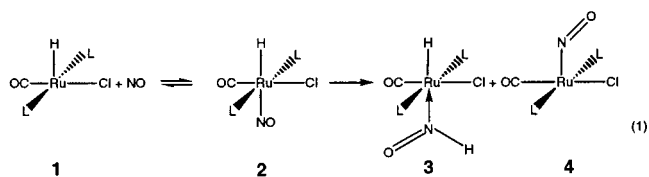


Figure 1. (a) ORTEP drawing (50% probability) of $\text{Ru}(\text{NO})\text{Cl}(\text{CO})-(\text{P}^i\text{Pr}_3)_2$, omitting methyl carbon and hydrogen: Ru1 and N1 lie on a crystallographic C_2 axis, so C11 and the carbonyl are disordered, as in O1. Selected data: Ru1–N1, 1.857(1) Å; Ru–C(11), 1.781(2) Å; Ru–Cl1, 2.4905(5) Å; Ru–P1, 2.4117(2) Å; N1–O1, 1.139(2) Å; Ru1–N1–O1, 138.8(1)°; Cl1–Ru1–C(11), 160.3(1)°; N1–Ru1–Cl1, 100.80(1)°; N1–Ru1–C(11), 98.9(1)°. (b) DFT geometry-optimized structure of $\text{RuHCl}(\text{CO})(\text{NO})[\text{P}^i\text{Pr}_3]_2$, with methyl hydrogens omitted. Selected structural parameters: Ru–H, 1.634 Å; Ru–N, 2.015 Å; N–O, 1.187 Å; H–Ru–N, 174.1°; Ru–N–O, 143.9°. This structure was confirmed as a true minimum by frequency analysis.

($\angle\text{Ru}-\text{N}-\text{O} = 138.8^\circ$) in the apical position. This 16-valence electron product gives the appearance of “replacement” of H by NO, which only raises the question of the fate of the lost H. The reaction (eq 1) was therefore carried out with a *deficiency* of NO ($\text{Ru}/\text{NO} = 2:1$), and the reagents were combined below -70°C in d_8 -toluene, followed by progressive warming in 10° increments and monitoring by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. At -60°C , the strongest ^{31}P NMR signal is that of **1**, but it is ~ 1 ppm broad and shifted 1 ppm downfield from the chemical shift of pure **1**. The hydride signal of **1** is also (~ 0.4 ppm) broad (J_{PH} is not resolved, which is *not* true of pure **1**). This suggests some



slow exchange, by adduct **2** formation, and that the (paramagnetic) adduct **2** is NMR silent.⁵ Also present already at -60°C are weak signals due to **4** and a $^{31}\text{P}\{^1\text{H}\}$ NMR singlet

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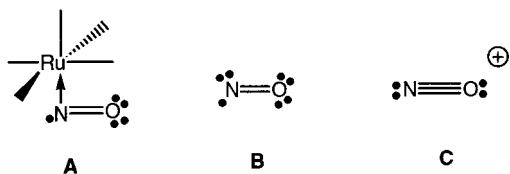
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(4) Crystallographic data for $\text{C}_{19}\text{H}_{42}\text{ClNO}_2\text{P}_2\text{Ru}$ at 120 K: $a = 21.7112(5)$ Å, $b = 8.5601(2)$ Å, $c = 15.0871(4)$ Å, $\beta = 118.9110(10)^\circ$, $Z = 4$ in space group $\text{C}2/c$. $R(F) = 0.0236$ for 6942 observed reflections $I > 2\sigma(I)$.

(61.5 ppm) which correlates with a hydride signal at -7.65 ppm, all assigned to **3**. The large downfield shift of this hydride signal compared to that in **1** indicates there is now a ligand trans to this hydride. Compound **3** also has a ^1H NMR signal at $+20.9$ ppm, characteristic^{6–8} of the nitroxyl ligand, HNO. As the temperature is raised, **1** is consumed, and **3** and **4** grow concurrently ($\sim 1:1$ ratio), although the signal for **3** is always weaker than that for **4**. At -20 °C, the ^1H NMR resolution has improved to the point where the HNO signal is observed as a 9.8 Hz doublet, and the hydride signal of **3** is observed as a triplet ($J_{\text{P-Ru-H}}$) with unresolved additional structure. These two ^1H NMR signals are thus clearly in the same molecule, and the 9.8 Hz coupling is the first observation of a coupling between hydride and nitroxyl H. This supports the proposed mutually trans stereochemistry of these groups in **3**, because the only other known H–M–N(H)O complexes have no resolved J_{HH} , and there these ligands are mutually cis.⁹ An HNO ligand has never before been formed from NO.

Because there is no deuterium in **3** when the reaction is run in d_8 -toluene, it appears that equimolar **3** and **4** are linked by reaction mechanism and that the material balance of eq 1 fully accounts for the hydrogen. The actual structure of **2**, available through geometry optimization with a DFT method (Priroda program package,¹⁰ PBE functional,¹¹ SBK basis set¹²), is shown in Figure 1b. The Ru–N–O angle (143.9°) and the single bond Ru–N distance (2.02 Å) are consistent with Lewis structure **A**. Spin densities are Ru, 0.04; N, 0.69; O, 0.27, establishing this as a ligand-centered radical.

It thus appears from drawing **A** that **B** is a very useful representation of the effective reactivity of NO toward 16-electron complexes which are resistant to 1-electron reduction by NO (to give NO^+ , **C**). Although **B** lacks an octet at N, it



does have the advantage of no formal charge on either atom. The calculated (DFT) reaction enthalpy for binding NO to $\text{RuHCl}(\text{CO})(\text{PMe}_3)_2$ is -23.6 kcal/mol, and ΔG°_{298} is -12.4 kcal/mol.

- (5) By $+20$ °C, the $^{31}\text{P}\{^1\text{H}\}$ signal of $\text{RuHCl}(\text{CO})\text{L}_2$ is even broader (2 Hz) but still within 0.5 ppm of its actual value. This increased broadening further confirms the presence of a dynamic process (eq 1), together with a small contribution from paramagnetism.
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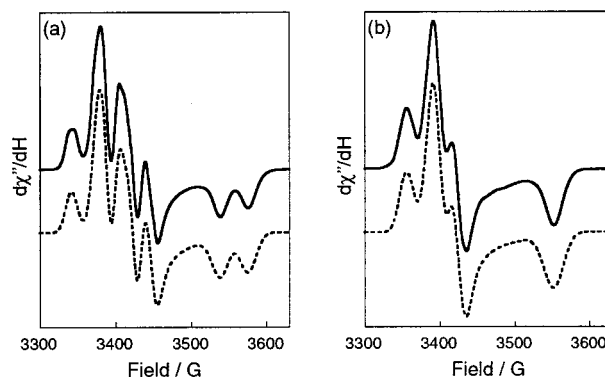


Figure 2. Observed (—) and calculated (···) X-band EPR spectra of **2** (a) and its deuteride analogue (b) in toluene at 77 K. Both spectra show near axial symmetry with the following parameters: (a) $g_x = 2.001$, $g_y = 1.993$, and $g_z = 1.910$; (b) $g_x = 2.001$, $g_y = 1.994$, and $g_z = 1.910$.

If **2** is indeed a good H-atom acceptor (i.e., based on **A**, and to form **3**), it should be possible to intercept it with a H-atom donor and, thus, divert the product from **4** (a hydrogen-loss product) toward **3**. Reaction of $\text{RuHCl}(\text{CO})\text{L}_2$ with NO (1:0.66 mole ratio) at 20 °C in neat 1,4-cyclohexadiene as a H-atom donor shows, within 5 min of combining the reagents, the formation of equimolar $\text{RuHCl}(\text{HNO})(\text{CO})\text{L}_2$ and $\text{RuCl}(\text{NO})(\text{CO})\text{L}_2$, together with 25% unreacted $\text{RuHCl}(\text{CO})\text{L}_2$ (confirming the intended deficiency of NO). Under these conditions, it is, thus, impossible to trap any metal containing radical.

Combining $\text{RuHCl}(\text{CO})\text{L}_2$ with 1 atm (i.e., excess) NO at -198 °C in d_8 -toluene shows, at -60 °C, complete consumption of $\text{RuHCl}(\text{CO})\text{L}_2$ and a 93% yield of $\text{RuCl}(\text{NO})(\text{CO})\text{L}_2$. Only about 3% of $\text{RuHCl}(\text{HNO})(\text{CO})\text{L}_2$ is observed at -60 °C, which suggests that excess NO diverts the conversion away from the nitroxyl complex and toward $\text{RuCl}(\text{NO})(\text{CO})\text{L}_2$. Compound **3** is persistent at 23 °C for more than 12 h when [NO] is low; however, even then, it slowly evolves further in toluene solvent to give (NMR and IR evidence) mainly $\text{Ru}(\text{H})\text{Cl}(\text{CO})\text{L}_2$, N_2O (2210 cm^{-1}), and HONO (3642 cm^{-1}). The latter two are the products^{13,14} of decomposition of free HNO by NO (eq 2). A broad ^1H NMR signal at $+6.2$ ppm is attributed to the proton of HONO.

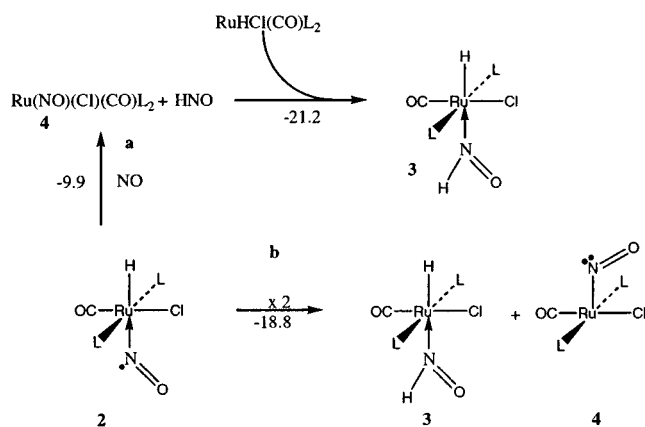


Attempts were made to directly observe **2**. The 77 K EPR spectrum of a toluene solution formed by adding <1 equiv of NO to $\text{RuHCl}(\text{CO})\text{L}_2$ shows (Figure 2a) a pattern with $g_x = 2.001$, $g_y = 1.993$, and $g_z = 1.910$. The large doublet splitting on the g_z signal is absent when $\text{RuCl}(\text{CO})\text{L}_2$ is the reagent (Figure 2b), thereby identifying this as a^{H}_z , so the signal is due to a monohydride. The simulated spectrum yields $a^{\text{N}}_x = 34.4$ G, $a^{\text{N}}_y = 4.4$ G, $a^{\text{N}}_z = 5.4$ G, $a^{\text{H}}_x = 36.7$ G, $a^{\text{H}}_y = 35.0$ G, $a^{\text{H}}_z = 35.5$ G. In fact, these EPR g values resemble closely those of a number of $\text{L}_5(\text{RuNO}^{2+})$ species (and Fe and Os analogues),^{15–23} and all of these (uniformly made by 1 e^- reduction of $(\text{RuNO})^{3+}$) have been interpreted

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Scheme 1

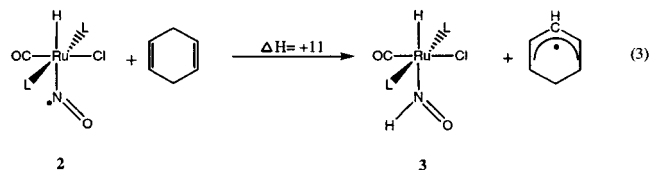


as having a bent Ru–N–O unit. Those workers have represented the bent, ligand-centered radical character as that of a d^6 divalent metal, with appended *neutral* NO (not NO^+ and not NO^-), which is precisely the Lewis structure represented here as **A**. Indeed, these authors represent their reduction reactions as $\text{NO}^+ + \text{e}^- \rightarrow \text{NO}$, where each N is bound to Fe, Ru, or Os.

What is the mechanism of H-atom transfer? Scheme 1 (L = PMe_3 , DFT ΔG°_{298} values shown in kcal/mol) shows *two* possible mechanisms after 1:1 adduct formation (eq 1). The calculations confirm that each avoids high energy intermediates. Path b is “efficient” in that H-atom transfer between two adduct complexes simultaneously produces *both* products. One reagent molecule is the H-atom donor, while the other is the H-atom acceptor. Path a, however, has the advantage that the transition state for H-atom abstraction from RuHCl(NO)(CO)L₂ will have less steric repulsion because NO is the hydrogen acceptor²⁴ rather than another molecule of RuHCl(NO)(CO)L₂. We therefore favor path a because of a lower anticipated ΔG^\ddagger .

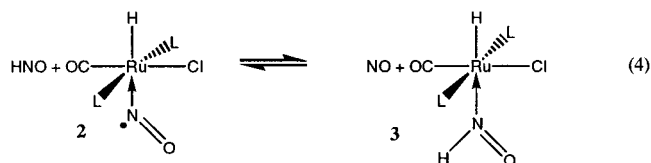
An important verification of the *calculated* energies is that the observed inability of 1,4-cyclohexadiene to trap RuHCl-

(NO)(CO)L₂ is *thermodynamic* in origin; eq 3 is not calculated to be exergonic even with this reagent because the new H–N bond is no stronger than the C–H bond broken. At the same time, factors favoring stability of the



cyclohexadienyl radical (spin delocalization and expansion of the conjugated system) contribute only at later stages of the H-atom transfer, so the activation barrier will be high.

The failure to observe nitroxyl complex **3** under the condition of higher [NO] is due to HNO *not* being produced within the protection of the metal coordination sphere but, rather, as a free triatomic (Scheme 1, path a), where bimolecular trapping by RuHCl(CO)L₂ or by RuHCl(NO)(CO)L₂ ($\Delta G^\circ_{298} = -9$ kcal/mol for eq 4, which is thus another source of **3**) competes with other decays, via bimolecular reaction with free NO (eq 2). Higher initial [NO]



suppresses the yield of RuHCl(CO)(HNO)L₂ both by decreasing the concentration of 5-coordinated RuHCl(CO)L₂, and also by increasing the frequency of collisions of free HNO with NO or (NO)₂. Alternatively, the reversibility of eq 4 under *standard* conditions could permit high NO concentration conditions to consume RuHCl(HNO)(CO)L₂ by the reverse of eq 4, abstracting H from coordinated HNO.

We have presented here some *general* principles for how a radical reagent like nitric oxide reacts with an unsaturated transition metal monohydride “functionality”. To avoid a 19-valence electron configuration at the metal, the “surplus” electron is forced to reside primarily on the ligands (i.e., neutral NO, not NO^+), requiring RuNO bending; H-atom transfer ultimately occurs. This provides an unprecedented, even if quite rational, synthesis of the nitroxyl ligand. Other candidate complexes for displaying this same behavior are RuHCl(PPh₃)₃, RhH(porphyrin), IrHCl₂(PR₃)₂, and PtHClL₂.

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Supporting Information Available: Full crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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