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

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The reaction of $RuHCl(CO)L_2$ ($L = P^iPr_3$) with NO initially forms a 1:1 adduct, shown by DFT calculations and EPR spectroscopy (including the RuD isotopomer) to contain a bent (∠Ru–N–O = 143.9°) nitrosyl where the majority of the spin density is on the nitrosyl nitrogen. This radical adduct transforms further to give equimolar $RuCl(NO)(CO)L_2$ and $RuHCl(HNO)(CO)L_2$, the latter with hydride trans to the nitroxyl ligand HN=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 $RuHCl(HNO)(CO)L_2$ 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, $N(O)(NO)R^{-1}$, 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.

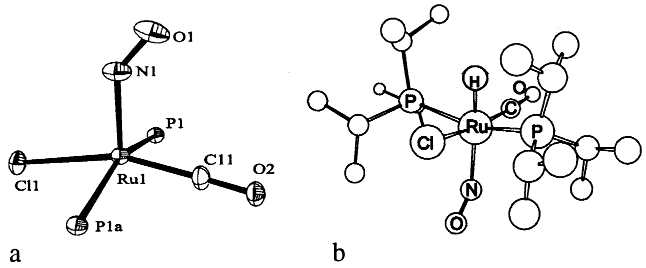
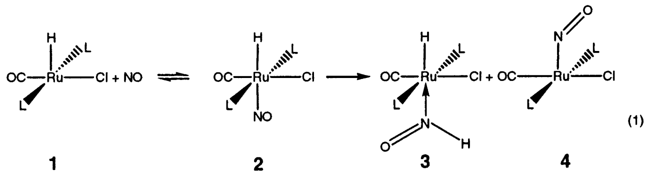


Figure 1. (a) ORTEP drawing (50% probability) of $Ru(NO)Cl(CO)(P^iPr_3)_2$, omitting methyl carbon and hydrogen: Ru1 and N1 lie on a crystallographic C_2 axis, so C11 and the carbonyl are disordered, as in O1. Selected data: Ru1−N1, 1.857(1) Å; Ru−C(11), 1.781(2) Å; Ru−Cl1, 2.4905(5) Å; Ru−P1, 2.4117(2) 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 $RuHCl(CO)(NO)[P(^iPr)_3]_2$, 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.

Reaction of $RuHCl(CO)L_2$ ($L = P^iPr_3$) 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 $Ru(NO)Cl(CO)L_2$ (Figure 1a),[4] a square pyramidal complex with a bent nitrosyl ligand (∠Ru−N−O = 138.8°) 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 (Ru/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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR singlet



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(4) Crystallographic data for $C_{19}H_{42}ClNO_2P_2Ru$ at 120 K: $a = 21.7112(5)$ Å, $b = 8.5601(2)$ Å, $c = 15.0871(4)$ Å, $\beta = 118.9110(10)°$, $Z = 4$ in space group $C2/c$. $R(F) = 0.0236$ for 6942 observed reflections $I > 2\sigma(I)$.

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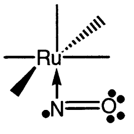
(61.5 ppm) which correlates with a hydride signal at −7.65 ppm, all assigned to **3**. The large downfield shift of this hydride signal compared to that in **1** indicates there is now a ligand trans to this hydride. Compound **3** also has a ^{1}H NMR signal at +20.9 ppm, characteristic[6−8] of the nitroxyl ligand, HNO. As the temperature is raised, **1** is consumed, and **3** and **4** grow concurrently (∼1:1 ratio), although the signal for **3** is always weaker than that for **4**. At −20 °C, the ^{1}H 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 ($J_{\mathrm{P-Ru-H}}$) with unresolved additional structure. These two ^{1}H 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 set[12]), 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 RuHCl(CO)(PMe$_3$)$_2$ is −23.6 kcal/mol, and $\Delta G°_{298}$ is −12.4 kcal/mol.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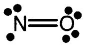
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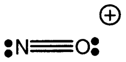
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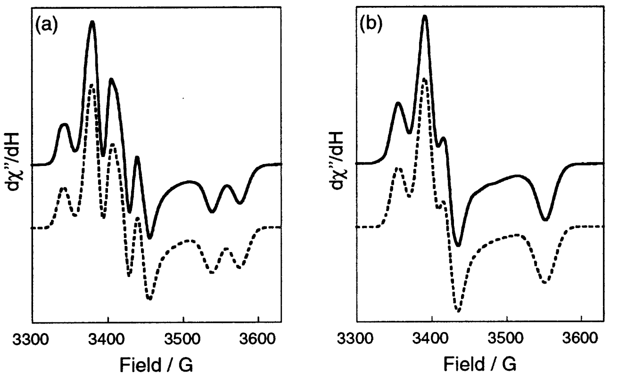

Figure 2. Observed (—) and calculated (···) X-band EPR spectra of **2** (a) and its deuteride analogue (b) in toluene at 77 K. Both spectra show near axial symmetry with the following parameters: (a) $g_x = 2.001$, $g_y = 1.993$, and $g_z = 1.910$; (b) $g_x = 2.001$, $g_y = 1.994$, and $g_z = 1.910$.

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 RuHCl(CO)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 RuHCl(HNO)(CO)L$_2$ and RuCl(NO)(CO)L$_2$, together with 25% unreacted RuHCl(CO)L$_2$ (confirming the intended deficiency of NO). Under these conditions, it is, thus, impossible to trap any metal containing radical.

Combining RuHCl(CO)L$_2$ with l atm (i.e., excess) NO at −198 °C in d_8-toluene shows, at −60 °C, complete consumption of RuHCl(CO)L$_2$ and a 93% yield of RuCl(NO)(CO)L$_2$. Only about 3% of RuHCl(HNO)(CO)L$_2$ is observed at −60 °C, which suggests that excess NO diverts the conversion away from the nitroxyl complex and toward RuCl(NO)(CO)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 Ru(H)Cl(CO)L$_2$, N$_2$O (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 ^{1}H NMR signal at +6.2 ppm is attributed to the proton of HONO.

$$\mathrm{HNO + 2NO \rightarrow HONO + N_2O} \qquad (2)$$

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

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

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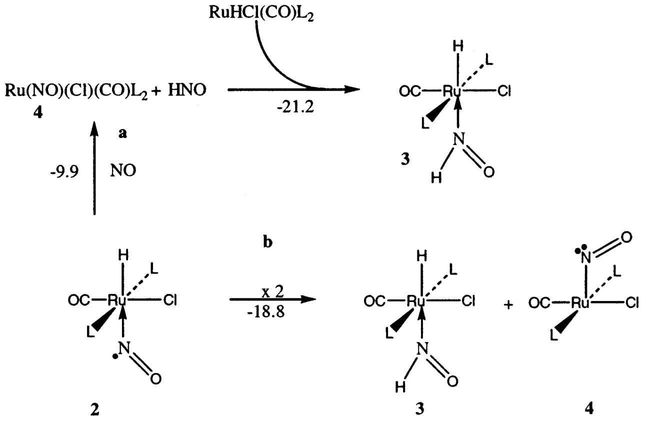
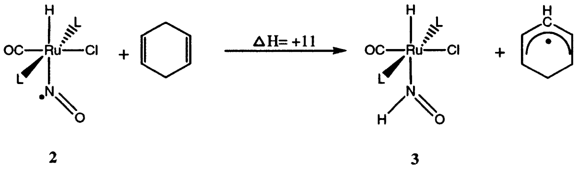
Scheme 1



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 NO$^+$ + e$^-$ → NO, where each N is bound to Fe, Ru, or Os.

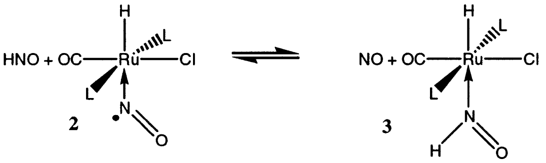
What is the mechanism of H-atom transfer? Scheme 1 (L = PMe$_3$, DFT $\Delta G°_{298}$ values shown in kcal/mol) shows *two* possible mechanisms after 1:1 adduct formation (eq 1). The calculations confirm that each avoids high energy intermediates. Path b is “efficient” in that H-atom transfer between 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)L$_2$ will have less steric repulsion because NO is the hydrogen acceptor[24] rather than another molecule of RuHCl(NO)(CO)L$_2$. We therefore favor path a because of a lower anticipated $\Delta G^{\ddagger}$.

An important verification of the *calculated* energies is that the observed inability of 1,4-cyclohexadiene to trap RuHCl(NO)(CO)L$_2$ 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.



(3)

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)L$_2$ or by RuHCl(NO)(CO)L$_2$ ($\Delta G°_{298} = -9$ 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)L$_2$ both by decreasing the concentration of 5-coordinated RuHCl(CO)L$_2$, 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)L$_2$ by the reverse of eq 4, abstracting H from coordinated HNO.



(4)

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(PPh$_3$)$_3$, RhH(porphyrin), IrHCl$_2$(PR$_3$)$_2$, and PtHClL$_2$.

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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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