# A Facile Approach to a d^4 Ru≡N: Moiety

Amy Walstrom, Maren Pink, Xiaofan Yang, John Tomaszewski, Mu-Hyun Baik, and
Kenneth G. Caulton*

*Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Room A250B,
Bloomington, Indiana 47405-7102*

Received January 19, 2005; E-mail: caulton@indiana.edu

Monatomic ligands multiply bound to transition metals with more than two d electrons are currently rare.[1,2] These will have a multiple M/E bond with electron-rich E and thus interesting reactivity.[3,4] In principle, an attractive synthetic route to such targets is to employ an oxidized form of element E, together with a metal complex reagent that is electron-rich.[5–10] Thus, an oxygen *atom* transfer reagent (e.g., R₃NO) would take L$_n$M^{n+} to L$_n$M^{n+2}=O. In the case of nitride, N³⁻, azide, N₃⁻, represents an attractive source of oxidized nitrogen, but one that is rarely used in the lab even though it is the basis for the entire automotive air bag industry;[11] therefore, it is clearly essential that eq 1 possess a high barrier *against* occurrence. While this method of forming N³⁻ has already been reviewed,[12] it invariably involves a thermolysis step,[13] or photolysis (thus high activation energy),[14–18] and it has been applied primarily to production of d⁰ to d² complexes; at these high oxidation states, the low coordinate metals then often adopt oligomeric forms with bridging, not terminal, nitrides. We report here some dramatic exceptions to these principles.[19]

$$N_3^- + 2e^- \rightarrow N^{3-} + N_2 \qquad (1)$$
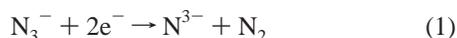
The reaction of paramagnetic ($S = 1$) unsaturated and planar (PNP)RuCl,[20] where PNP is N(SiMe₂CH₂P^{t}Bu₂)₂, with NaN₃ or (faster) with Me₃SiN₃ in THF at room temperature proceeds to completion to furnish a single product **1** that is diamagnetic, judged by ¹H NMR chemical shifts in the normal 0–10 ppm range. The two phosphorus nuclei are equivalent, and there is one ¹H NMR signal each for CH₂, SiMe₂, and ^{t}Bu groups.[21] The conclusion is that this species has effective C_{2v} symmetry.

We struggled to understand the observed diamagnetism in terms of various geometries (linear, bent, η^1 and η^2 azide) of an anticipated product, the [(H₂PCH₂SiH₂)₂N]RuN₃ monomer, using DFT (B3LYP) geometry optimizations.[21] Triplet states were invariably[21] more stable than singlets by 6.3 kcal/mol, and the starting geometries always converged to the same geometry, **A**. In search of diamagnetism, we considered dimeric species **B**, and in fact these calculations showed minima for these dimers, but their enthalpy of dimerization (−8.1 kcal/mol) is weaker than $T\Delta S$ at 273 K (+20.9 kcal/mol), and thus dimerization is not favorable.
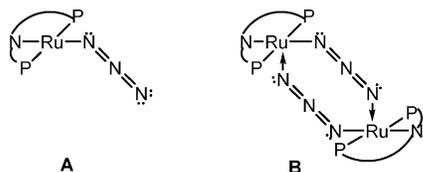
A crystal of **1** grown from pentane was shown by [21] X-ray diffraction (Figure 1) to be in fact the monomeric *nitride* (PNP)-RuN, which was confirmed for the bulk sample by ESI mass spectrometry. Because the coordination geometry is not planar
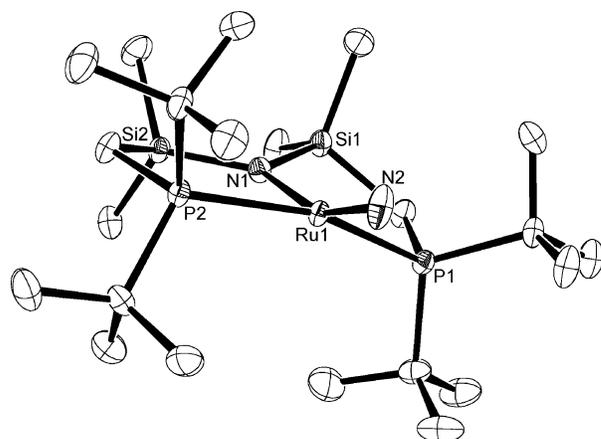

Figure 1. ORTEP view (50% probability, −150 °C) of the non-hydrogen atoms of one of two independent molecules of [(^{t}Bu₂PCH₂SiMe₂)₂N]RuN, showing selected atom labeling. Selected structural parameters (second independent molecule in parentheses): Ru1−N2, 1.627(2)(1.629(2)); Ru1−N1, 2.137(2) (2.128(2)); Ru−P1, 2.401(1) (2.437(1)); −N1−Ru1−N2, 155.86(13)(156.11(12)); −P1−Ru1−P2, 160.96(2) (162.77(2)).

(∠NRuN = 156°), the simplicity of the ¹H NMR requires fluxionality, with a low barrier to "wagging" of the nitride from above to below the (PNP)Ru plane. The Ru/nitride bond length, 1.627(2) A°, is consistent with a triple bond[22] and thus Ru⁴⁺−N³⁻ oxidation state assignments and a d⁴ electron configuration. The structure also shows (Figure 1) a nonlinear P−Ru−P angle. The latter may reflect that hypothetical L₂ClRuN would prefer[23] a pseudotetrahedral geometry to optimize Ru−nitride multiple bonding (Figure S3).[21] The nitride in *both* independent molecules in the X-ray study has its largest vibrational amplitude in the N−Ru−N bending direction, a conclusion consistent with the DFT results discussed later. A sample of (PNP)Ru¹⁵N shows an ¹⁵N NMR signal for the nitride center at 848 ppm. No coupling to P is resolved in the ¹⁵N signal, whose full width at half-height was 1.7 Hz. This sample has an infrared band at 990 cm⁻¹, which is shifted to energy lower than that in (PNP)Ru¹⁴N, 1030 cm⁻¹. The expected isotopic shift is 32 cm⁻¹.

Since N₂ loss has already occurred in the synthetic reaction executed at 22 °C, we combined equimolar Me₃SiN₃ with (PNP)-RuCl in d_8-toluene at −196 °C, thawed and mixed the solution very briefly, and monitored the evolution of the ¹H and ³¹P NMR spectra as the temperature was incremented by 10 °C amounts from −60 °C.[21] First observed is minor conversion ((PNP)RuCl is abundant by ¹H NMR) to a diamagnetic species (³¹P{¹H} singlet at 48 ppm), which grows at −50 and −40 °C but converts to the 77 ppm signal of (PNP)RuN beginning at −30 °C. Already at −20 °C the 48 ppm signal of the intermediate is essentially absent and (PNP)RuN is the dominant product. The observed intermediate thus is diamagnetic (hence five-coordinate and therefore not simply

(PNP)RuN$_3$). We have characterized (PNP)RuCl as a very bulky Lewis acid (e.g., binds two PhCN), which is nevertheless electron-rich.[20,24] The formation of an "adduct" with Me$_3$SiN$_3$ is thus indicated, with candidate geometries **C** and **D**. The atom connectivity in structure **D** is clearly preferable in terms of facile N$_2$ extrusion, while Ru−N multiple bonding develops at the expense of Ru−Cl scission. The possibility that the 48 ppm species is the N$_2$ adduct (PNP)Ru(N)(N$_2$) was ruled out by equilibrating (PNP)RuN with 1 atm N$_2$ in toluene at −60 °C and finding no ^{1}H or ^{31}P NMR spectroscopic features at −40 °C other than those of (PNP)RuN. We therefore suggest that the mechanism involves a low conversion pre-equilibrium to form **D** (which may or may not have an Si−Cl interaction) and rate-determining loss of N$_2$ and Me$_3$SiCl; if instead (PNP)RuN$_3$ is first formed from the observed intermediate, its rate of loss of N$_2$ at −30 °C must be faster than its rate of formation. The production of (PNP)RuN from NaN$_3$ suggests that authentic (PNP)Ru(N$_3$) does indeed easily lose N$_2$. Although steric bulk can result in **C** being favored,[25] structure **D** is the one established[26] for the Lewis acid/base adduct Me$_3$SiN$_3$·GaCl$_3$, whose crystal structure shows lengthening of the N$_\alpha$−N$_\beta$ bond and shortening of the N$_\beta$−N$_\gamma$ bond, which is along the path to N$_2$ loss. Remarkably, there is no reaction between (PNP)RuCl and Me$_3$SiNCO(i.e., no (PNP)-RuN and released CO); even after heating at 70 °C for 2 h in benzene, the reagents are recovered unchanged.

C   **D**
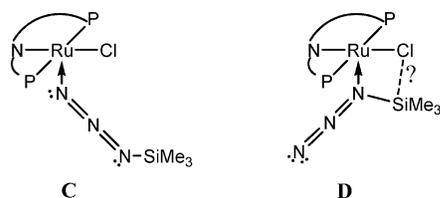
DFT geometry optimization[21] of the full species [(^{t}Bu$_2$PCH$_2$-SiMe$_2$)$_2$N]RuN gave a nonplanar ground state in good agreement with the experimental bond lengths and angles. Both Ru−N distances in the planar structure are longer than those in the nonplanar. A step scan of the energy profile along the N−Ru−N′ angle, with other geometric parameters optimized freely, shows that the PES is very flat (varying only 0.6 kcal/mol) around 180° ± 20°, and the 180° value lies only 1.6 kcal/mol above the global minimum, 140°. Consistent with this, the ^{1}H NMR shows no decoalescence at −40 °C. The calculated ΔH for N$_2$ loss from triplet (PNP)Ru(N$_3$) is −20.8 kcal/mol, consistent with the nitride being a thermodynamic product. The release of N$_2$ from triplet (PNP)-RuN$_3$ to singlet nitride is of course a spin-forbidden reaction,[27] but our observed reactions at 20 °C are nevertheless found to have a half-life shorter than the time of mixing. In addition, since triplet (PNP)RuN is calculated to lie about 20 kcal/mol above the singlet, ΔH to form the triplet nitride is thermoneutral. Since the preferred geometry of a four-coordinate Ru^{IV}≡N species is pseudo-tetrahedral (i.e., C_{3v}),[23] the near degeneracy of the "nonplanar" and the planar structures can be attributed to PNP chelate constraint destabilizing the tetrahedral and favoring the latter.

Although an isoelectronic Fe^{IV}N complex has been reported,[28] that tetrahedral species contrasts with (PNP)RuN in undergoing a redox dimerization to form an Fe^I ← N≡N → Fe^I unit. Clearly the +4 oxidation state is uncomfortably high for iron (in that tetrahedral ligand environment and with N^{3-} as the reductant), while Ru(IV) here has the opposite preference. Higher oxidation states and more metal ligand bonds are generally preferred as one goes down a group in the periodic table. Because the calculated[21] triplet state of the ruthenium nitride has spin density on the nitride nitrogen, it is attractive as a participant in the redox dimerization to LM^{I}NNM^{I}L

observed for M = Fe. Spin density on nitride in the triplet not only promotes N−N bonding, but it warrants consideration as a first step in reduction of the metal in the iron case (i.e., the triplet is M^{III}−N^{2-}).

This synthetic approach to terminal nitrides succeeds at least in part because of the low coordination number and the high reducing power of d^6 and Ru(II) in the absence of π acid ligands and augmented by the presence of the π-donor amide ligand. These generalizations also suffice to explain the recent synthesis of terminal imide (NR) complexes of Fe and Co from RN$_3$ (R = hydrocarbyl) where the C−N bond is retained as N$_2$ is released.[6,9] However, the method has its limits. For example,[29] [(C$_6$Me$_6$)-RuCl$_2$]$_2$, a molecule devoid of strong π-acid ligands, reacts with NaN$_3$ to give [(C$_6$Me$_6$)Ru(N$_3$)$_2$]$_2$ with no spontaneous loss of N$_2$. There are thus subtle aspects of the energetics of intramolecular electron transfer required to tame eq 1 as a reliable route to the nitride ligand.

Supporting Information Available: Full synthetic, spectroscopic, and crystallographic information, together with DFT-optimized geometries on molecules described in the text (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA050361K