J|A|C|S
COMMUNICATIONS

Aryl C−H Bond Amination by an Electrophilic Diruthenium Nitride

Amanda Kae Musch Long, Renyuan Pony Yu, George H. Timmer, and John F. Berry*

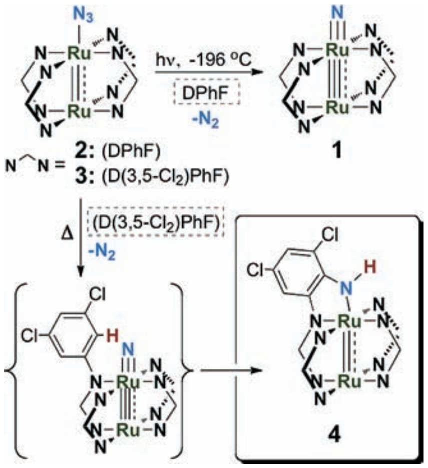
Department of Chemistry, University of Wisconsin−Madison, 1101 University Avenue, Madison, Wisconsin 53706

Received July 15, 2010; E-mail: berry@chem.wisc.edu

Abstract: Thermolysis of the terminal azido $Ru_2(D(3,5\text{-}Cl_2)PhF)_3N_3$ (**3**, $D(3,5\text{-}Cl_2)PhF$ = *N*,*N′*-bis(3,5-dichlorophenyl) formamidinate) cleanly produces $Ru_2[(D(3,5\text{-}Cl_2)PhF)_3(D(3,5\text{-}Cl_2\text{-}2\text{-}NH)PhF)]$ (**4**), which is proposed to result from insertion of a nitrido N atom into a ligand aryl C−H bond. This mechanism is supported by differential scanning calorimetry and thermogravimetric analysis results, which show the two-step reaction to be exothermic by −215 kJ mol^{-1}, in agreement with results from density functional theory calculations. This is the first example of electrophilic insertion of a terminal nitride into an aromatic C−H bond.

One of the features of metal−metal bonded Rh_2 and Ru_2 dimers is their ability to catalyze group transfer reactions that insert an electrophilic carbene or nitrene moiety into a C−H bond.[1] These catalytic reactions are of increasing widespread utility in organic synthesis, and yet few of the mechanistic details of the reaction are known. Metal−metal/metal−ligand multiply bonded carbenoid or nitrenoid species have been proposed as the key intermediates responsible for C−H insertion, though direct evidence for these species is currently lacking.

Scheme 1. Formation of Proposed Nitrido Intermediate **1** and Isolated Amido Product **4**



We have recently reported the metal−metal/metal−ligand multiply bonded Ru_2 nitride, $Ru_2(DPhF)_4N$ (**1**, DPhF = *N*,*N′*-diphenylformamidinate, Scheme 1), as a model for the catalytically relevant dirhodium nitrenoid species. This unstable compound was generated by photolysis of $Ru_2(DPhF)_4N_3$ (**2**) in frozen solution at −196 °C.[2] Compound **1** is well characterized, but study of its reactivity has been severely limited by the fact that it can only be handled in dilute frozen solutions. However, inspired by the solid-state preparation of the first iridium nitrido compound, which was synthesized by thermolysis of the corresponding azido precursor,[3] we decided to investigate the thermolysis of the diruthenium formamidinate azido compound $Ru_2(D(3,5\text{-}Cl_2)PhF)_4N_3$ (**3**),[4] in hopes of synthesizing a solid sample of the corresponding nitride.

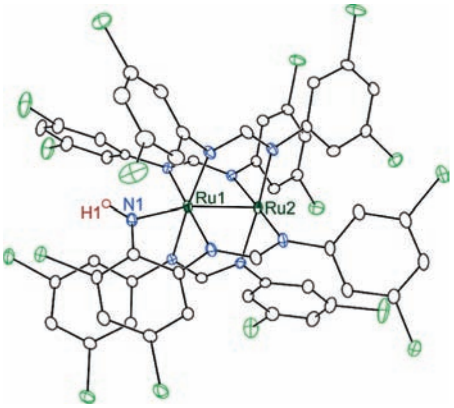


Figure 1. Thermal ellipsoid plot of amido compound **4** from **4**•C_6H_{14} with ellipsoids drawn at the 30% probability level, with non-amido hydrogen atoms omitted for clarity.

We decided to use the 3,5-dichlorophenyl analogue $D(3,5\text{-}Cl_2)PhF$ in this work for two main reasons. First, substitution of the formamidinate aryl rings has been shown to drastically modify the electron density of the Ru_2 unit.[5] We reasoned that the electron-withdrawing 3,5-dichloro substitution might enhance the electrophilicity of the nitride. Second, chlorine atoms are well-known *ortho-*/*para-* directors in electrophilic aromatic substitution reactions,[6] so it was reasonable to expect the enhanced reactivity of the ligand hydrogen atoms.

The thermolysis of **3** led not to an isolable nitrido compound, but instead to the amido complex $Ru_2[(D(3,5\text{-}Cl_2)PhF)_3(D(3,5\text{-}Cl_2\text{-}2\text{-}NH)PhF)]$, **4**, formed via intramolecular insertion of a nitrogen atom into a proximal aryl C−H bond of one of the $D(3,5\text{-}Cl_2)PhF$ ligands. Examples of the electrophilic reactivity of transition metal nitrido compounds are known,[7] but this is to our knowledge the first report of the insertion of an electrophilic nitride into an aryl C−H bond.[8]

The purple diruthenium azido complex $Ru_2(D(3,5\text{-}Cl_2)PhF)_4N_3$, **3**, was prepared as described by Ren et al.[4] and was heated at 100 °C *in vacuo* for 24 h yielding a dark violet solid that was recrystallized from dichloromethane and hexane to yield dark violet crystals (space group *C*2/*c*) of **4**•C_6H_{14}. Monitoring the thermolytic conversion of **3** to **4** by infrared spectroscopy clearly demonstrates the loss of the N_3 azide stretch at 2040 cm^{-1} during this process.

In the X-ray crystal structure of **4** (Figure 1), the Ru_2^{5+} core is surrounded by four $D(3,5\text{-}Cl_2)PhF$ ligands bridging the metal centers in a classical paddlewheel-type arrangement, with one of these four ligands having a modification of one aryl ring at the 2-position with an NH group. This NH nitrogen atom wraps around to bind axially to Ru(1), resulting in a bridging/chelating tridentate

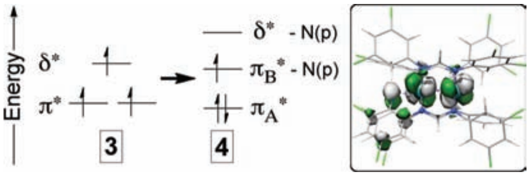
10.1021/ja1062955

coordination of the modified ligand. The effective 4-fold symmetry of the azide precursor **3** is therefore lost in the isolated amido product **4**. The two Ru atoms in **4** are related by a crystallographic 2-fold axis perpendicular to the Ru−Ru bond. The axial nitrogen atom is therefore disordered at either end of the molecule. Interestingly, there is no disorder in the aryl rings of the D(3,5-Cl_2)PhF ligands, suggesting that the aryl C−H bonds in **3** are nearly ideally poised to undergo reaction with the nitrido group.

Prior to this work, diruthenium complexes with axial amido ligands were unknown, so its structural features are of interest. The Ru−Ru distance of 2.4096(4) Å in **4** is comparable to that published by Ren et al. for (Ru_2(D(3,5-Cl_2)PhF)$_4$)(CCPh) with the strongly σ-donating axial phenylethynide, where the Ru−Ru distance is 2.429(1) Å.[9] Notably, these Ru−Ru distances are both longer than values for analogous compounds with axially bound chloride ligands, which range from 2.319(1) to 2.396(1) Å.[10] The amido ligand can therefore be considered to have an intermediate σ-donating ability between chloride and acetylide. The Ru−$N_{(amido)}$ bond distance, 2.070(5) Å, is similar to the Ru−N distances in the formamidinate ligands, consistent with sp^2 hybridization of the amido N atom. The Ru−Ru−$N_{(amido)}$ angle (164.1(2)°) deviates significantly from linearity as a result of the metallocyclic five-membered ring, suggesting that the Ru−$N_{(amido)}$ bonding is not idealized.

EPR spectroscopy has revealed distinct electronic differences between **3** and **4**. The X-band EPR spectrum of **3** at 3.4 K features signals at $g_{\perp,\mathrm{eff}} = 4.28$ and $g_{\|,\mathrm{eff}} = 1.95$, consistent with a spin quartet ground state with large axial zero-field splitting. The spectrum of the thermolyzed product **4** shows rhombic symmetry consistent with the lack of the 4-fold axis with $g_1 = 2.35$, $g_2 = 2.14$, and $g_3 = 1.91$ indicating an $S = {}^1/_2$ ground state. The assignment of a doublet ground state for **4** was confirmed by variable temperature magnetic susceptibility (χ) measurements which are consistent with the existence of one unpaired electron ($\chi \cdot T = 0.53$ emu K mol^{-1}).

Scheme 2. Proposed Ground State Electronic Configurations for **3** and **4** (left); Singly Occupied π^*_B Orbital from DFT Calculations (right)



The loss of symmetry upon formation of **4**, along with the elongated Ru−Ru bond distance, suggests a ground state electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi_A{}^*)^2(\pi^*{}_B)^1$ for **4** in which the degeneracy of the π^* orbitals is lifted, reflecting an axial π interaction of an amido lone pair with one of the Ru_2 π^* orbitals. Results from density functional theory (DFT, BP86) calculations confirm this qualitative result, and the π^*_B orbital is depicted in Scheme 2. The calculations also indicate significant antibonding interactions with δ^*, resulting in destabilization of this orbital. A full molecular orbital analysis of the DFT results may be found in the supporting information.

To gain insight into the mechanism of the formation of **4** from **3**, ΔH of the bulk thermolytic process was measured using differential scanning calorimetry, DSC (Figure 2a). The two-peaked DSC curve indicates the presence of an observable intermediate prior to the formation of the stable product **4**. Step 1 of this irreversible reaction begins at 104 °C and crests at 138 °C, overlapping persistently with the second exothermic step peaking at 141 °C. These inseparable signals result in a combined enthalpic value of $\Delta H = -215.2$ kJ mol^{-1} (-51.42 kcal mol^{-1}) for this net two-step exothermic reaction, consistent with a mechanism involving the formation of the nitride intermediate and then subsequent intramolecular insertion of the electrophilic nitride into the aryl C−H bond. Preliminary DFT calculations on this proposed reaction pathway yield a computed ΔH of -213 kJ mol^{-1}, consistent with experimental results. The fact that two distinct DSC peaks are observed strongly indicates that the second process is slow, relative to the time scale of the DSC experiment.

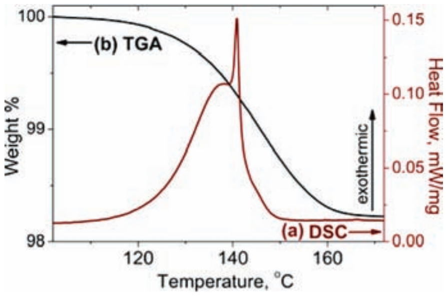


Figure 2. Red: DSC measurement on **3** (a) as a function of temperature. Black: TGA monitoring thermal formation of **4** from **3** consistent with N_2 extrusion (b).

To further support the intermediacy of the diruthenium nitride prior to aryl C−H insertion, thermal gravimetric analysis (TGA) was performed on a sample of **3** (Figure 2b), and the sample was observed to undergo a weight loss of 1.79%. This reduction in bulk sample weight directly corresponds to the extrusion of dinitrogen and begins upon heating above 104 °C coinciding exactly with the first step observed by DSC.

The electrophilicity of the putative nitride Ru_2(D(3,5-Cl_2)PhF_4)N is demonstrated by isolation of the stable product, **4**, with an amido moiety resulting from nitride insertion into the proximal C−H bond. This is consistent with the Ru−Ru≡N electronic structure that we have previously reported in that the LUMO of the nitrido molecule is a Ru−Ru≡N π^* orbital with considerable N(p) character.[2] This is, to our knowledge, the first example of the direct insertion of a nitride into an aryl C−H bond, and we suggest that the feasibility of this reaction is in part due to the unique Ru−Ru≡N structure, which has been shown to lead to an unusually long and weak Ru≡N bond.[2] The results reported here now also indicate this bond to be unusually reactive.

Acknowledgment. We thank the University of Wisconsin for support and Prof. M. Shatruk at Florida State University for collecting SQUID measurements on **4**.

Supporting Information Available: Synthetic procedures, computational and crystallographic information, MALDI data, IR spectra of **3** and **4**, and SQUID measurements of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424. (b) Espino, C. G.; Du Bois, J. Rhodium(II)-Catalyzed Oxidative Amination. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005.
(2) Pap, J. S.; DeBeer, S.; Berry, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 10102–10105.
(3) Schöffel, J.; Rogachev, A. Y.; DeBeer, S.; Burger, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 4734–4738.
(4) (a) Lin, C.; Protasiewicz, J. D.; Ren, T. *Inorg. Chem.* **1996**, *35*, 7455–7458. (b) Chen, W.-Z.; De Silva, V.; Lin, C.; Abellard, J.; Marcus, D. M.;

Ren, T. *J. Cluster Sci.* **2005**, *16*, 151–165. (c) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675–3679.

(5) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D.; Smith, E. T. *Chem. Lett.* **1997**, 753–754.

(6) Fryhle, C. B.; Solomons, T. W. G. *Organic Chemistry*, 9th ed.; John Wiley: Danvers, MA, 2008; pp 651−652.

(7) (a) Berry, J. F. *Comments Inorg. Chem.* **2009**, *30*, 28–66. (b) Silvia, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 446–447. (c) Eikey, R. A.; Abu-Omar, M. M. *Coord. Chem. Rev.* **2003**, *243*, 83–124. (d) Scepaniak, J. J.; Fulton, M. D.; Bontchev, R. P.; Duesler, E. N.; Kirk, M. L.; Smith, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 10515–10517. (e) Schröder, D.; Schwarz, H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18114–18119. (f) Schlangen, M.; Neugebauer, J.; Reiher, M.; Schröder, D.; López, J. P.; Haryono, M.; Heinemann, F. W.; Grohmann, A.; Schwarz, H. *J. Am. Chem. Soc.* **2008**, *130*, 4285–4294. (g) Buschhorn, D.; Pink, M.; Fan, H.; Caulton, K. G. *Inorg. Chem.* **2008**, *47*, 5129–5135. (h) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059–1071. (i) Man, W.-L.; Tang, T.-M.; Wong, T.-W.; Lau, T.-C.; Peng, S.-M.; Wong, W.-T. *J. Am. Chem. Soc.* **2004**, *126*, 478–479.

(8) Insertion of a putative nickel nitrido group into aliphatic C−H bonds has been proposed. See: Hennig, H.; Hofbauer, K.; Handke, K.; Stich, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 408–410.

(9) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Organomet. Chem.* **1999**, *579*, 114–121.

(10) Cotton, F. A.; Murillo, C. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 3rd ed.; Springer: New York, NY, 2005; pp 381−382.

JA1062955