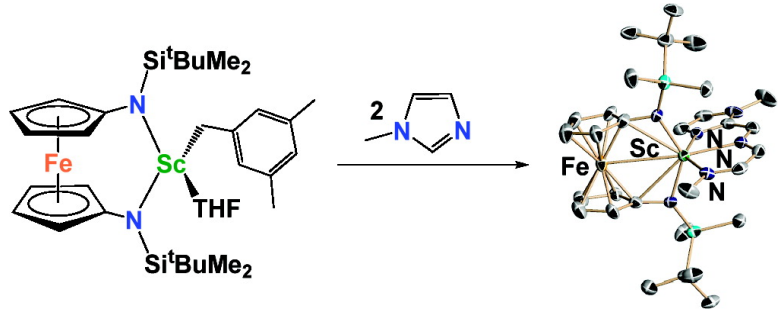
Communication

Ring-Opening Reactions of Aromatic N-Heterocycles by Scandium and Yttrium Alkyl Complexes

Colin T. Carver, and Paula L. Diaconescu

J. Am. Chem. Soc., **2008**, 130 (24), 7558-7559 • DOI: 10.1021/ja802728k • Publication Date (Web): 21 May 2008



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 05/21/2008

Ring-Opening Reactions of Aromatic N-Heterocycles by Scandium and Yttrium Alkyl Complexes

Colin T. Carver and Paula L. Diaconescu*

Department of Chemistry & Biochemistry, University of California, Los Angeles, California 90095

Received April 14, 2008; E-mail: pld@chem.ucla.edu

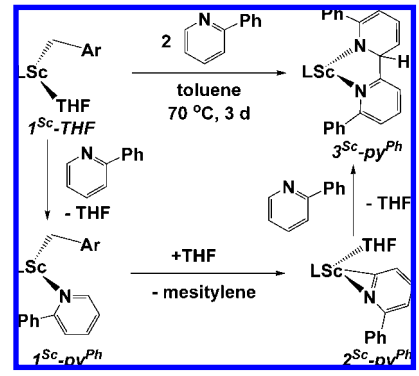
Understanding C−N bond breaking processes in the presence of transition metals, especially ring opening of aromatic heterocycles, is significant in establishing heterogeneous mechanisms and assessing whether mild conditions are viable for hydro-denitrogenation processes.[1] In this context, the reactivity of early transition metal−ligand bonds[2,3] toward aromatic heterocycles falls within one of two major categories: reactions involving metal−element σ bonds, where σ-bond metathesis and migratory insertions predominate, and reactions involving metal−element π bonds, where [2 + 2] cycloadditions are the norm. Reactions that involve only σ bonds are found in ortho-metalation and functionalization of heterocycles, while reactions involving multiple bonds lead to the ring opening of aromatic heterocycles.

In some cases, metal complexes employing only σ bonds are able to ring-open oxygen or sulfur-containing heterocycles.[4] However, to date,[5] the most difficult case of ring opening, the cleavage of the C−N bonds in aromatic heterocycles, has been restricted to the involvement of metal−element multiple bonds. Given the strength of the C−N bond in aromatic heterocycles (133 kcal/mol estimated in pyridine),[6] it is not surprising that only isolated examples of homogeneous metal-mediated C−N bond cleavage exist. These examples are limited to tantalum,[7,8] niobium,[9−11] and titanium[12,13] and all involve metal−element multiple bonds. Herein we report on examples of aromatic N-heterocycle ring-opening reactions mediated by scandium and yttrium alkyl complexes. In these reactions, only σ bonds are formed and broken at the metal center.

Initial reactions between the ferrocene 1,1′-diamide scandium benzyl complex, Sc(fc[NSi^{t}BuMe$_2$]$_2$)(CH$_2$Xy-3,5)(THF) (**1^{Sc}-THF**),[14] and pyridine or 2-picoline gave mixtures of compounds. Investigation of these mixtures by ^{1}H NMR spectroscopy indicated the presence of olefinic peaks, which we interpreted to arise from either dearomatization or the ring opening of the heterocycle. This reactivity stands in contrast to that reported by Bercaw et al., who showed that Cp$_2$ScMe reacts with pyridine to form a scandium η^2-*N*,*C*-pyridyl complex.[15]

In a screening of several pyridines, we noticed that the reaction of a yellow toluene solution of **1^{Sc}-THF** with 2-phenylpyridine could be driven until it showed a dark green color. We attribute the dark green color to the presence of a conjugated structure formed by C−N cleavage (see below) of the pyridine ring. Using ^{1}H NMR spectroscopy, we identified that the first step was THF displacement and coordination of 2-phenylpyridine to form **1^{Sc}-py^{Ph}**, followed by ortho-metalation of the pyridine ring to give **2^{Sc}-py^{Ph}**. When the reaction was stopped at that stage, **2^{Sc}-py^{Ph}** contained a coordinated THF molecule, as opposed to coordinated 2-phenylpyridine. However, heating the **2^{Sc}-py^{Ph}** THF adduct in the presence of 1−2 equiv of 2-phenylpyridine (Scheme 1) allowed the isolation of a brown product, **3^{Sc}-py^{Ph}**. The X-ray crystal structure of **3^{Sc}-py^{Ph}** (Figure 1) shows two C−C coupled[16] pyridine rings, in which one ring is dearomatized. Although heating of **3^{Sc}-py^{Ph}** led to the

Scheme 1. Reactions of 2-Phenylpyridine and Scandium Benzyl Complex **1^{Sc}-THF** (L = fc[NSi^{t}BuMe$_2$]$_2$, Ar = 3,5-Dimethylphenyl)



observation of a dark green color, we have been unable to isolate and structurally characterize it due to decomposition before its formation was completed.

A similar transformation was proposed by Teuben et al. to explain the formation of 2,2′-bipy from Cp*$_2$Y(η^2-*N*,*C*-pyridyl) and excess pyridine.[17] In their case, hydrolytic workup was thought to induce elimination of H_2 from a dearomatized coupling product (no characterization reported). When we performed the analogous experiment with **1^{Sc}-THF**, we observed transfer of the benzyl group to pyridine (GC−MS and ^{1}H NMR characterization, see Supporting Information), with very little 2,2′-bipy formation. However, hydrolysis of a pyridyl coupling product (see Supporting Information for details) showed formation of the corresponding aromatic bipyridyl, so it is possible that **1^{Sc}-THF** and Cp*$_2$Y(η^2-*N*,*C*-pyridyl) share a mechanistic pathway in their reactions with pyridines.

In order to determine whether this transformation is general, we turned to 1-methylimidazole; Jordan et al. reported that [Cp$_2$ZrMe(THF)]$^+$ did not promote C−H activation of 1-methylimidazole.[18] The reaction of a yellow toluene solution of **1^{Sc}-**

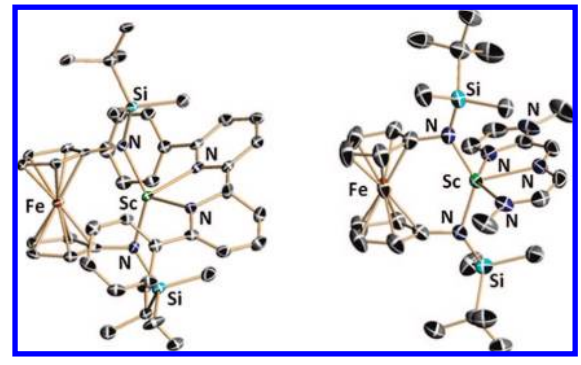
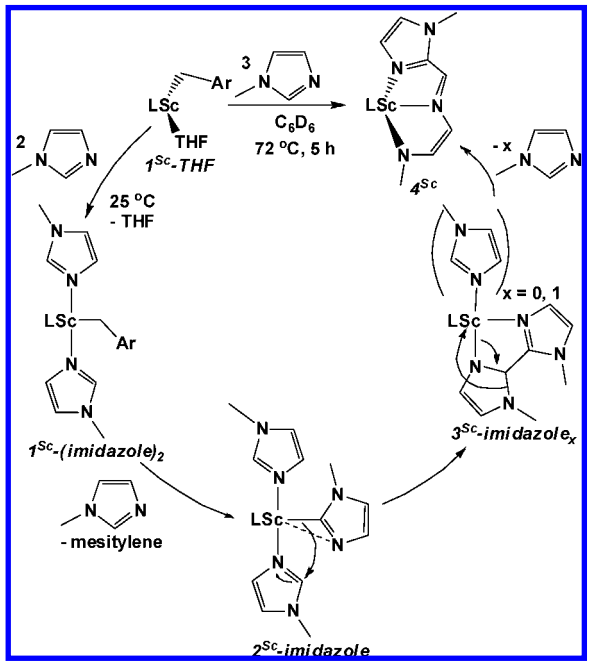


Figure 1. ORTEP representations of **3^{Sc}-py^{Ph}** (left) and **4^{Sc}** (right) with thermal ellipsoids at 50% probability (H atoms and solvent molecules were omitted for clarity).

10.1021/ja802728k CCC: $40.75

Scheme 2. Proposed Mechanism for the Ring Opening of 1-Methylimidazole by Scandium Benzyl Complex **1^{Sc}-THF** (L = fc[NSi^{t}BuMe$_2$]$_2$, Ar = 3,5-Dimethylphenyl)



THF with 3 equiv of 1-methylimidazole (Scheme 2) resulted in the formation of a dark purple mixture after heating for 5 h at 70 °C. After workup, a crystalline material was isolated and its X-ray crystal was structure determined (Figure 1). That study revealed that the product (**4^{Sc}**) contained an imidazole−imine−amide fragment, in which one imidazole molecule was ring-opened. The solid-state structure is preserved in solution, as confirmed by ^{1}H NMR spectroscopy. An analogous product was isolated from the reaction of the yttrium benzyl complex Y(fc[NSi^{t}BuMe$_2$]$_2$)(CH$_2$Ph)(THF) (**1^{Y}-THF**) and 1-methylimidazole, although the formation of the ring-opened product was slower than that in the scandium case.

Since ring opening of aromatic N-heterocycles by early transition metal σ bonds is unprecedented, we decided to investigate the mechanism by which such a transformation took place. After mixing of **1^{Sc}-THF** and 1-methylimidazole, displacement of THF was observed immediately. On the basis of ^{1}H NMR integrations, a scandium benzyl complex with two coordinated imidazoles, **1^{Sc}-(imidazole)$_2$**, was formed (Scheme 2). Transformation of **1^{Sc}-(imidazole)$_2$** to the final product **4^{Sc}** was rapid and did not allow the observation of other intermediates. However, the analogous yttrium reaction allowed the isolation of the imidazole C−H activation product, **2^{Y}-imidazole**. In the X-ray crystal structure of **2^{Y}-imidazole**, the η^2-*N*,*C*-imidazolyl ligand was disordered, but connectivity information could still be gathered (see Supporting Information for details), and two additional molecules of imidazole were found to coordinate to the yttrium center. The coordination of two as opposed to one molecule of 1-methylimidazole is important; heating of **1^{Sc}-(imidazole)$_2$** solutions (a total of 2 equiv of 1-methylimidazole) to give the ring-opened product was not completed in 1 week. It is likely that the steric pressure exerted by the third imidazole molecule accelerates the reaction. After the C−H activation step took place, transformation to the ring-opened product **4^{Y}** was also fast for the yttrium complex and no intermediates (i.e., **3^{Y}-imidazole$_x$**, $x = 0, 1$) could be observed.

We propose that following the C−H activation step, C−C coupling occurs between the η^2-*N*,*C*-bond and one of the coordinated imidazoles accompanied by the dearomatization of one of the rings to give **3^{Sc}-imidazole$_x$**. Such a transformation is analogous to that observed in the case of pyridines (Scheme 1). This intermediate was not observed and transformed very rapidly into the final product, which is likely stabilized by the extended conjugation present.

In conclusion, we have shown that ring opening of aromatic N-heterocycles can be initiated by metal−carbon σ-bonded fragments. We are looking into computational studies that might explain the driving force for the C−C coupling reaction. We are currently investigating the reactions of modified systems containing highly electrophilic metal centers with other N-heterocycles in order to determine the generality of the observations presented here.

Acknowledgment. The authors thank Prof. Ohyun Kwon for discussions and Dr. Saeed Khan for help with crystallography. This work was supported by the UCLA and the UC Energy Institute (EST grant).

Supporting Information Available: Experimental details for compound syntheses and characterization, full crystallographic descriptions, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Furimsky, E.; Massoth, F. E. *Catal. Rev.-Sci. Eng.* **2005**, *47*, 297–489, and references therein.
(2) Piers, W.; Shapiro, P.; Bunel, E.; Bercaw, J. *Synlett* **1990**, 74–84.
(3) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233−234*, 131–155.
(4) Hitzbleck, J.; Okuda, J. *Organometallics* **2007**, *26*, 3227–3235, and references therein.
(5) Huertos, M. A.; Perez, J.; Riera, L. *J. Am. Chem. Soc.* **2008**, *130*, 5662–5663.
(6) Priyakumar, U. D.; Dinadayalane, T. C.; Sastry, G. N. *Chem. Phys. Lett.* **2001**, *337*, 361–367, and references therein.
(7) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678–10693.
(8) Weller, K. J.; Fox, P. A.; Gray, S. D.; Wigley, D. E. *Polyhedron* **1997**, *16*, 3139–3163, and references therein.
(9) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247–248.
(10) Bonanno, J. B.; Veige, A. S.; Wolczanski, P. T.; Lobkovsky, E. B. *Inorg. Chim. Acta* **2003**, *345*, 173–184.
(11) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421–4423.
(12) Fout, A. R.; Bailey, B. C.; Tomaszewski, J.; Mindiola, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 12640–12641.
(13) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M. H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 6798–6799.
(14) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363–370.
(15) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219.
(16) Soo, H. S.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2004**, *23*, 498–503.
(17) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881–3891.
(18) Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116–2123.

JA802728K