J|A|C|S
COMMUNICATIONS

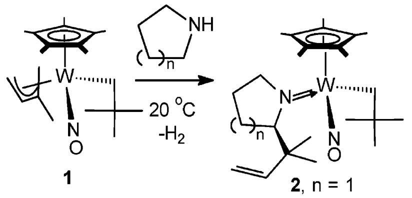
Concurrent N−H and α-C−H Bond Activations of Pyrrolidine and Piperidine under Ambient Conditions by 18e Tungsten Allyl Nitrosyl Complexes

Jenkins Y. K. Tsang, Chikako Fujita-Takayama, Miriam S. A. Buschhaus, Brian O. Patrick, and Peter Legdzins*

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

Received August 4, 2006; E-mail: legzdins@chem.ubc.ca

The search for complexes that exhibit selective C−H bond activation is the focus of considerable research in organometallic chemistry at the present time, primarily because of the potential for functionalization of readily available hydrocarbons into more desirable products.[1] One of our previous contributions to this area involved the development of the 16e allene nitrosyl complex of tungsten, $Cp^*W(NO)(\eta^2\text{-}H_2C{=}C{=}CMe_2)$, that effects single and triple intermolecular C−H bond activations of hydrocarbon substrates under thermal conditions.[2] This allene complex is generated virtually quantitatively by thermolysis of the 18e precursor, $Cp^*W(NO)(CH_2CMe_3)(\eta^3\text{-}H_2CCHCMe_2)$ (**1**), at 50 °C to induce the evolution of neopentane. While extending this C−H activation chemistry to encompass various heteroatom-containing organic substrates, we discovered that **1** and related allyl nitrosyl complexes effect the concurrent activation of N−H and α-C−H bonds of pyrrolidine and piperidine without thermal activation (i.e., under ambient conditions). It is these unprecedented transformations that we now wish to communicate.



(1)

1

2, n = 1
3, n = 2

The new chemical reactions that we have discovered are presented in eq 1 with complex **1** being the prototypical reactant. Thus, treatment of racemic **1** with neat pyrrolidine at room-temperature results in the quantitative formation of a racemic mixture of the alkyl amido complex, **2**. This compound is very soluble in common organic solvents, but it can be isolated as an orange air-stable solid in 52% yield by chromatography of the final reaction mixture on alumina with pentane as eluant and crystallization from the concentrated eluate at −30 °C.[3] The solid-state molecular structure of **2** (Figure 1)[4] exhibits metrical parameters that are consistent with solution NMR data and reflect loss of hydrogen atoms from the pyrrolidine nitrogen atom, N(2), and a carbon atom α to it, C(9). The W(1)−N(2) bond length of 1.940(2) Å and the coplanarity of W(1), N(2), C(6), and C(9) in **2** are indicative of this linkage being a slightly elongated W=N double bond,[5] the tungsten center thereby attaining the favored 18e configuration. The original allyl ligand in **1** has become a vinylalkyl substituent at C(9) of the newly formed pyrrolide ligand in **2**. Once formed, complex **2** (mp 115 °C) is thermally stable and undergoes no detectable changes when maintained at 120 °C for 1 h.

As summarized in eq 2, other related allyl nitrosyl complexes react with pyrrolidine under ambient conditions in a similar manner. Full details of these reactions and the characterization data for the new complexes produced in this manner (including a single-crystal X-ray crystallographic analysis of **5**) are provided in the Supporting Information. Interestingly, the ^{1}H NMR spectrum of the volatiles resulting from the reaction of pyrrolidine with **4** contains a small singlet at 4.80 ppm indicative of the production of H_2 during the course of the reaction.

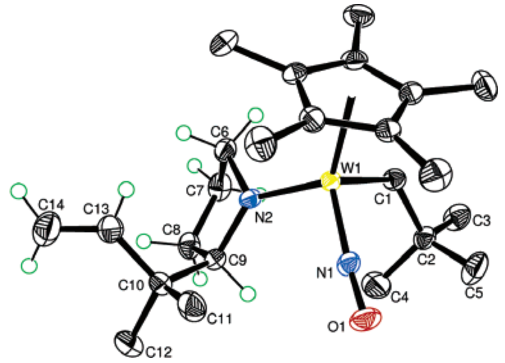
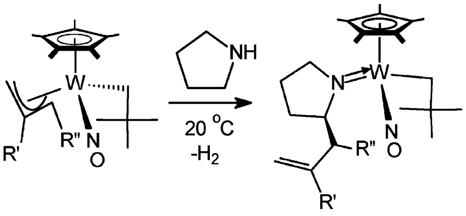


Figure 1. Solid-state molecular structure of **2** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−N(2) = 1.940(2), N(2)−C(6) = 1.485(3), N(2)−C(9) = 1.496(4), C(9)−C(10) = 1.560(4), C(10)−C(13) = 1.510(4), C(13)−C(14) = 1.316(4), W(1)−N(1) = 1.761(2), N(1)−O(1) = 1.239(3), W(1)−N(1)−O(1) = 169.4(2), C(10)−C(13)−C(14) = 127.4(3), C(9)−C(10)−C(13) = 111.2(2), N(1)−W(1)−N(2) = 98.61(10), N(1)−W(1)−C(1) = 98.41(11), W(1)−N(2)−C(6) = 119.91(18), C(6)−N(2)−C(9) = 106.1(2), W(1)−N(2)−C(9) = 132.32(17).



(2)

4, R' = Me, R'' = H
6, R' = H, R'' = Me
8, R' = H, R'' = Ph

5, R' = Me, R'' = H
7, R' = H, R'' = Me
9, R' = H, R'' = Ph

Since all the product complexes are formed at room temperature, it is unlikely that the allyl reactants convert to allene intermediates or that the pyrrolidine is dehydrogenated to pyrroline prior to reacting.[6] Nevertheless, a number of possible mechanisms can be envisaged for these conversions, and more studies will be required to evaluate the various possibilities. Particularly intriguing in this regard is the fact that the allyl and not the neopentyl group migrates with such selectivity.

This type of reactivity with cyclic saturated amines appears to be general for these allyl nitrosyl complexes of tungsten. Thus, treatment of **1** with piperidine under ambient conditions affords a

10.1021/ja065663g CCC: $33.50 © 2006 American Chemical Society

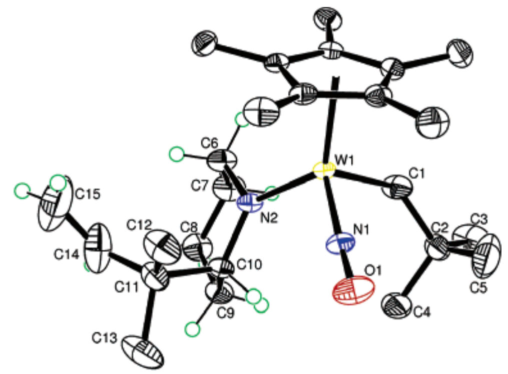


Figure 2. Solid-state molecular structure of **3** with 50% probability thermal ellipsoids shown. Selected interatomic distances (Å) and angles (deg): W(1)−N(2) = 1.937(2), N(2)−C(6) = 1.482(3), N(2)−C(10) = 1.480(3), C(10)−C(11) = 1.573(4), C(11)−C(14) = 1.494(5), C(14)−C(15) = 1.306(6), W(1)−N(1) = 1.753(2), N(1)−O(1) = 1.229(3), W(1)−N(1)−O(1) = 169.3(2), C(11)−C(14)−C(15) = 127.8(5), C(10)−C(11)−C(14) = 114.1(3), N(1)−W(1)−N(2) = 97.76(9), N(1)−W(1)−C(1) = 97.38(10), W(1)−N(2)−C(6) = 118.38(16), C(6)−N(2)−C(10) = 113.9(2), W(1)−N(2)−C(10) = 127.64(16).

racemic mixture of orange complex **3**, the product analogous to **2**, as the principal organometallic complex. However, the reaction proceeds more slowly than with pyrrolidine,[3] and so it is accompanied by some thermal decomposition of the reactant **1**. Workup of the final reaction mixture in a manner analogous to that employed for the isolation of **2** (vide supra) affords **3** in 16.9% yield. Complex **3** is also very soluble in common organic solvents. The solid-state molecular structure of **3** (Figure 2)[7] bears a striking resemblance to that exhibited by **2**, and its spectroscopic properties confirm that this structure persists in solutions. ^{1}H NMR spectroscopic monitoring indicates that the other allyl nitrosyl complexes **4**, **6**, and **8** react with piperidine in a similar manner.

To the best of our knowledge, these reactions of the saturated cyclic amines constitute the first unambiguous examples of concurrent N−H and C−H bond activations of organic substrates by transition-metal complexes. Our studies of the thermal reactions of these tungsten allyl nitrosyl complexes with other heteroatom-containing organic molecules are continuing, and the results of these investigations will be reported in due course.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P. L. We also thank the reviewers for their insightful comments.

Supporting Information Available: Experimental procedures and complete characterization data for complexes **2**−**9** and full details of the crystal structure analyses including associated tables for **2**, **3**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Activation and Functionalization of C-H Bonds;* Goldberg, K. I., Goldman, A. S., Eds.; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004.
(2) Ng, S. H. K.; Adams, C. S.; Hayton, T. W.; Legzdins, P.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 15210.
(3) Complete experimental details and characterization data are provided in the Supporting Information.
(4) Crystal data for **2**: monoclinic, space group $P2_1/n$, $a = 11.732(3)$ Å, $b = 13.594(2)$ Å, $c = 15.641(3)$ Å, $\beta = 104.1618(8)°$, $V = 2418.6(8)$ Å^3, $Z = 4$, $R_1 = 0.043$, $wR_2 = 0.067$, and GOF(F^2) = 0.94 for 12520 reflections and 264 variables.
(5) A search of the Cambridge Structural Database reveals that typical W═N distances fall between 1.70 and 1.80 Å.
(6) For a review of methods for the synthesis of Δ^1-pyrrolines, see Shvekhgeimer, M.-G. A. *Chem. Heterocycl. Comp.* **2003**, *39*, 405.
(7) Crystal data for **3**: monoclinic, space group $P2_1/n$, $a = 10.7760(10)$ Å, $b = 18.681(2)$ Å, $c = 13.0480(10)$ Å, $\beta = 98.560(5)°$, $V = 2597.4(4)$ Å^3, $Z = 4$, $R_1 = 0.0201$, $wR_2 = 0.0472$, and GOF(F^2) = 1.065 for 6277 reflections and 272 variables.

JA065663G