4238 *Organometallics* **2006,** *25,* 4238−4239

Rearrangement of N-Heterocylic Carbenes Involving Heterocycle Cleavage

Andrew W. Waltman, Tobias Ritter, and Robert H. Grubbs*

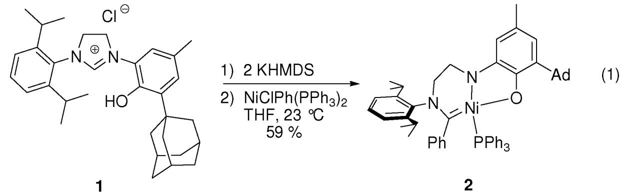
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received June 16, 2006

Summary: In two similar but unrelated cases, a novel type of ring-opening reaction of N-heterocyclic carbenes (NHCs) was observed. These compounds may represent a general class of hitherto unknown decomposition products of NHCs.

N-Heterocyclic carbenes (NHCs) are a class of stable carbenes that have found increasing use as ligands for transition metals in a role analogous to that of phosphines and other neutral two-electron donors.[1] The distinctive electronic properties of NHCs—namely their high σ-basicity and low π-acidity—can provide enhanced reactivity to transition-metal catalysts that feature NHCs as ligands.[2] Recently, however, it has been demonstrated that NHCs do not always act simply as spectator ligands and are occasionally found to participate in unanticipated side reactions. These include ligand C−C and C−H insertion[3] and entry into abnormal binding modes.[4] Because these reactions can be detrimental to catalyst function, understanding them is of fundamental importance to the design of stable transition-metal catalysts with NHC ligands. In this communication, we report a novel type of ring-expansion reaction of NHCs involving heterocyclic N−C bond cleavage that has been observed in two unrelated systems. Unlike the processes described above, this new type of reaction is unique because it modifies the heterocycle itself.

We recently reported a series of unsymmetrically substituted NHC ligands, e.g., **1**, that feature a chelating phenoxide moiety appended to one of the NHC N atoms.[5] Treatment of **1** with 2 equiv of potassium hexamethyldisilazide (KHMDS), followed by $NiClPh(PPh_3)_2$, gave a dark green solid (eq 1). X-ray crystallography of this compound provided a surprising structure (**2**, Figure 1).



(1)

1 **2**

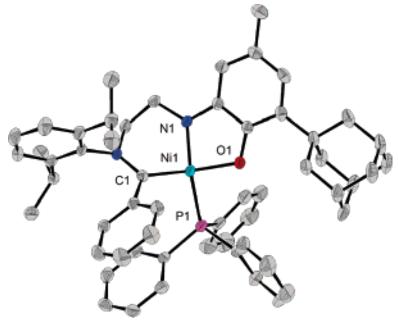
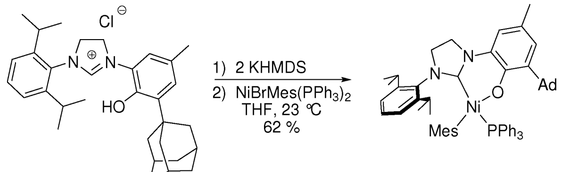


Figure 1. ORTEP drawing of **2**. Atoms are represented by ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C−Ni, 1.8506(16); N−Ni, 1.8448(13); P−Ni, 2.1836(5); O−Ni, 1.881(10); C−Ni−N, 93.74(6); N−Ni−O, 85.59(5); O−Ni−P, 91.78(4); P−Ni−C, 99.69(5).

Complex **2** features a six-membered nickelacycle apparently derived from N−C cleavage of the NHC ring and ring expansion of the heterocycle. This produces a tridentate ligand on Ni with Fischer carbene, amide, and phenoxide moieties. The phenyl group originally bound to Ni has migrated to the former NHC carbon atom. The attack of a metal-bound alkyl group on a monodentate NHC ligand has been observed before in complexes of Ni and Pd.[6] This process appears to occur via intramolecular alkyl attack on the empty orbital of the NHC and results, unlike in our case, in the reductive elimination of a 2-alkylimidazolium salt.[7] We reasoned that metal complexes of our novel ligands would not be as prone to this type of rearrangement, since chelation should hinder rotation of the NHC into the necessary conformation for attack by the aryl group.[8] However, it appears that the chelating nature of ligand **1** does not prevent alkyl attack in the formation of **2**.

If the ring-opening reaction leading to the formation of **2** occurs following phenyl group migration, replacement of the phenyl with a bulkier aryl group incapable of migration would therefore prevent ring opening. Treatment of KHMDS-activated **1** with $NiBrMes(PPh_3)_2$ (eq 2) and X-ray crystallography of the resulting yellow solid confirmed this (**3**; Figure 2). The ortho methyl groups of the mesityl ligand of complex **3** prevent migration of the mesityl group to the carbene carbon atom,



(2)

1 **3**

---

* To whom correspondence should be addressed. E-mail: rhg@caltech.edu.

[1] Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−92.

[2] (a) Chatterjee, A. K.; Morgan, J. P.; Scholl. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783−3784. (b) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 4053−4056. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

[3] (a) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944−4945. (b) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054−5055.

[4] (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *Chem. Commun.* **2001**, 2274−2275. (b) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473−10481. (c) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046−5047.

[5] Waltman, A. W.; Grubbs, R. H. *Organometallics* **2004**, *23*, 3105−3107.

10.1021/om060528y CCC: $33.50

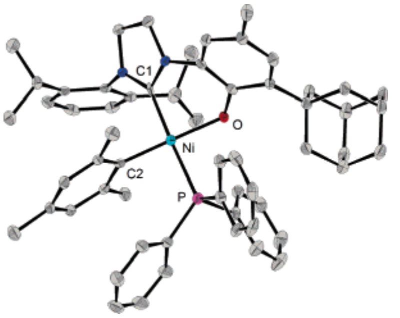
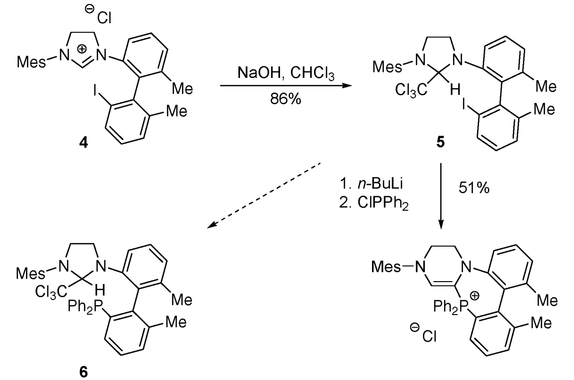


Figure 2. ORTEP drawing of **3**. Atoms are represented by ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−Ni, 1.874(2); C(2)−Ni, 1.905(2); P−Ni, 2.2274(7); O−Ni, 1.9544(15); C(1)−Ni−O, 87.85(8); O−Ni−P, 89.54(5); P−Ni−C(2), 89.17(7); C(1)−Ni−C(2), 93.11(10).

Scheme 1. Rearrangement to Phosphonium Salt 7



6
Expected, not observed

7

which apparently accounts for the stability of **3** as a "normal" NHC complex.[9]

To the best of our knowledge, this NHC-ring-expansion reaction has not been reported before. However, in the course of independent research we have observed a similar ring expansion. During the attempted development of a new family of neutral bidentate phosphine/NHC ligands for Ru-catalyzed olefin metathesis, biphenyl iodide **4** was prepared (Scheme 1). The latent carbene of **4** was protected as its chloroform adduct (**5**). Such adducts have been used for the in situ generation of NHCs upon thermolytic loss of chloroform.[10] We intended to further functionalize this protected carbene by phosphination of the aryl iodide to provide NHC precursor **6**.

However, lithiation of **5** and subsequent reaction with chlorodiphenylphosphine provided phosphonium salt **7**, the structure of which was established through spectroscopic and X-ray crystallographic analysis (Figure 3).[11] In this compound the NHC heterocycle has been expanded by a single carbon atom, to which the phosphine is now appended, giving a 6,7-heterobicycle.[12]

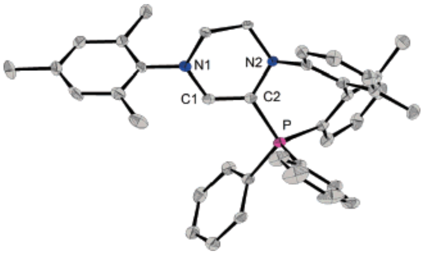


Figure 3. ORTEP drawing of **7**. Atoms represented by ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−C(1), 1.352(2); C(1)−C(2), 1.364(3); C(2)−N(2), 1.420(2); C(2)−P, 1.7743(19); N(1)−C(1)−C(2), 122.75(18); C(1)−C(2)−N(2), 122.73(17); N(2)−C(2)−P, 116.32(14).

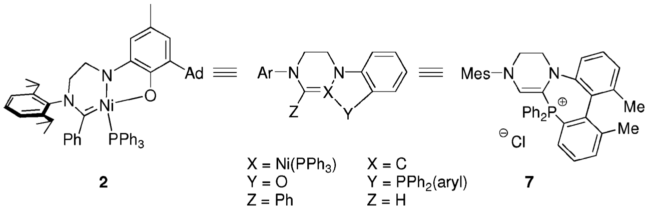


Figure 4. Generic representations of **2** and **7**.

Interestingly, Ni compound **2** and phosphonium salt **7** can be represented generically, even though the identities of the atoms participating in the rearrangements differ significantly (Figure 4). The central Ni(PPh$_3$) unit of **2** is substituted by a carbon atom in **7**, and the phenoxide moiety of **2** is replaced by a phosphine in **7**. Although the pathways by which compounds **2** and **7** arise from their respective precursors are currently unclear, their structural similarities, along with their mutual origins as NHC-related compounds, suggest that their formation may represent a general process in carbene chemistry which has not yet been well noted, possibly due to the instability of the byproducts.[13] This reaction type is an excellent example of the unexpected reactivity possible when NHCs are used in place of traditional ligands.

Acknowledgment. We thank Mr. Larry Henling and Dr. Mike Day for X-ray crystallographic analysis. A.W.W. thanks the Rohm and Haas Corporation for funding. T.R. thanks the German Academic Exchange Service (DAAD) for a postdoctoral fellowship.

Supporting Information Available: Text and figures giving detailed synthetic procedures and characterization data for ligands and metal compounds, as well as crystallographic data; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 600387 (**2**), 600389 (**3**), and 267284 (**7**).

OM060528Y

---

(6) (a) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596−1605. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918−4920.

(7) (a) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029−4040. (b) Nielsen, D. J.; Magill, A. M.; Yates, B. F.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **2002**, 2500−2501. (c) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756−757.

(8) Indeed, this seems to be the case for a palladium complex of **1**, the ^{1}H NMR spectrum of which is unchanged after 1 week at room temperature.

(9) Ortho methyl groups have been used before to stabilize arylnickel complexes of NHCs.[6a]

(10) (a) Arduengo, A. J., III; Calabrese, J. C.; Davidson, F.; Rasika Dias, H. V.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348−2364. (b) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. L.; Ding, S. D.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558.

(11) The corresponding dicyclohexylphosphonium product was also prepared (71% yield).

(12) The use of ^{13}C-labeled chloroform leads to incorporation of the chloroform-derived carbon atom in the 2- and 3-positions of the new heterocycle of **7** in a 1:2 ratio.

(13) Following submission of this paper, another NHC-derived compound with a structure similar to those of **2** and **7** was reported: Pelegri, A. S.; Elsegood, M. R. J.; McKee, V.; Weaver, G. W. *Org. Lett.* **2006**, *8*, 3049−3051.