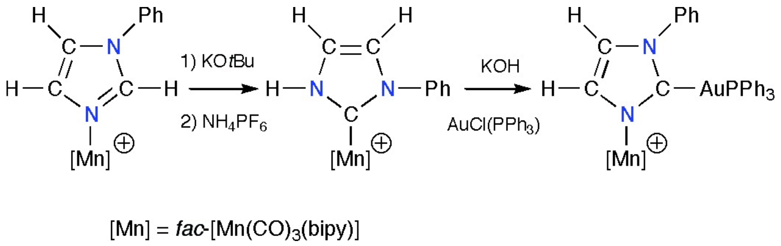
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Base-Promoted Tautomerization of Imidazole Ligands to N-Heterocyclic Carbenes and Subsequent Transmetalation Reaction

Javier Ruiz, and Bernab F. Perandones

J. Am. Chem. Soc., **2007**, 129 (30), 9298-9299• DOI: 10.1021/ja073144n • Publication Date (Web): 04 July 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Base-Promoted Tautomerization of Imidazole Ligands to N-Heterocyclic Carbenes and Subsequent Transmetalation Reaction

Javier Ruiz* and Bernabé F. Perandones

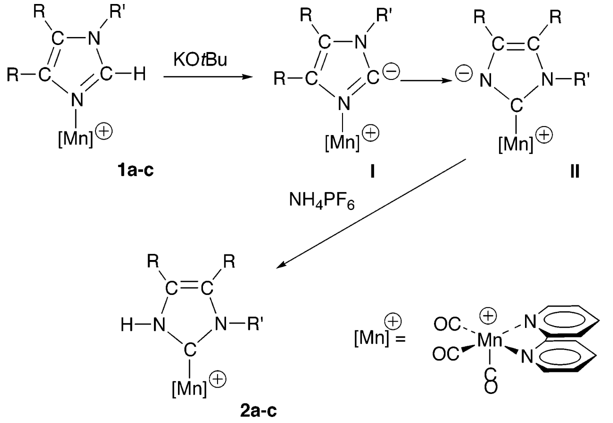
Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo,
33006 Oviedo, Spain

Received May 4, 2007; E-mail: jruiz@fq.uniovi.es

Despite the great interest that the chemistry of N-heterocyclic carbenes (NHC) has awakened within the scientific community in recent years,[1] and the well-established relevance of imidazoles as ligands,[2] it is noteworthy that little is known about the transformation of imidazole complexes to the corresponding imidazole-2-ylidene (Arduengo's carbenes) derivatives. Bergman and Ellman et al. have shown that rhodium-catalyzed arylation[3] and alkene coupling[4] of benzimidazoles proceed through the formation of the corresponding N-heterocyclic carbene complexes, which have been isolated in stoichiometric reactions. In related studies, rhodium-mediated transformation of 3-methyl-3,4-dihydroquinazoline to the Rh−N-heterocyclic carbene complex[5] and metal-induced isomerization of pyridines and quinolines to N-heterocyclic carbenes[6] have been reported. As far as we are aware, in just one case conversion of N-bound to C-bound imidazoles has been seen, allowing the isolation of amino complexes of ruthenium(II) containing NHC ligands, although in very low yield.[7] A single example of tautomerism of a NHC complex to the corresponding imidazole derivative has been described very recently.[8] The preferential C-binding versus N-binding in imidazole has also been investigated by theoretical calculations.[9] In this context, here we report a clean transformation of manganese(I) imidazole complexes to the corresponding N-heterocyclic carbene derivatives and the sequential transmetalation reaction of the NHC ligand to other metallic fragment, promoted by acid−base treatments.

Reaction of the cationic imidazole complexes *fac*-[Mn(L)(CO)$_3$(bipy)]$^+$ (**1a**: L = 1-phenylimidazole, **1b**: L = 1-methylimidazole, **1c**: L = 4,5-dichloro-1-methylimidazole) with KO*t*Bu in THF as solvent readily produces deprotonation of the C^2-H group of the heterocycle to afford somewhat unstable intermediate neutral species (see Scheme 1), which show νCO bands in the IR spectra at frequencies appreciably lower than the starting materials (see Supporting Information). Protonation of these intermediate derivatives with NH$_4$PF$_6$ yields the N-heterocyclic carbene complexes **2a**−**c** (50−67% yield). The presence of a low field N−H signal in the ^{1}H NMR spectrum, together with the appearance of a resonance about 185 ppm in the ^{13}C{^{1}H} NMR spectrum, clearly indicates the carbene nature of the new compounds. The lower νCO frequencies (10 cm^{-1} on average) in the IR spectra of **2a**−**c** with respect to those of **1a**−**c** reflect the stronger donor capability of the NHCs than their corresponding imidazole ligands. At shown in Scheme 1, deprotonation of **1a**−**c** should afford compound **I** at a first step, immediately transforming to **II** in view of the final product on protonation. **I** can be seen as a N-metala-NHC ligand, which is transformed to **II** by a 1,2-migration, a typical reaction for singlet carbenes but very scarcely encountered in NHC molecules, as those containing silyl substituents.[10] An X-ray diffraction study carried out on **1a** and **2a** allows a comparison between the structural parameters of both complexes (Figure 1).

Scheme 1. Isomerization of Imidazole Ligands to N-Heterocyclic Carbenes. **1a**: R = H, R′ = Ph; **1b**: R = H, R′ = Me; **1c**: R = Cl, R′ = Me



The base-promoted transformation of imidazole complexes to carbene derivatives described herein could be a valuable method for the synthesis of N−H containing Arduengo's carbene complexes, as the classical method consisting of deprotonation of the corresponding imidazolium salts can only be applied when both nitrogen atoms are substituted.[11] Furthermore, as can be seen in complexes **1a**−**c**, the methodology can be applied to very differently substituted imidazole molecules.

The formation of intermediate species **II** from **I** implies a preferential C-binding versus N-binding of the imidazolate to Mn(I), but this tendency is inverted when trying to bond a softer

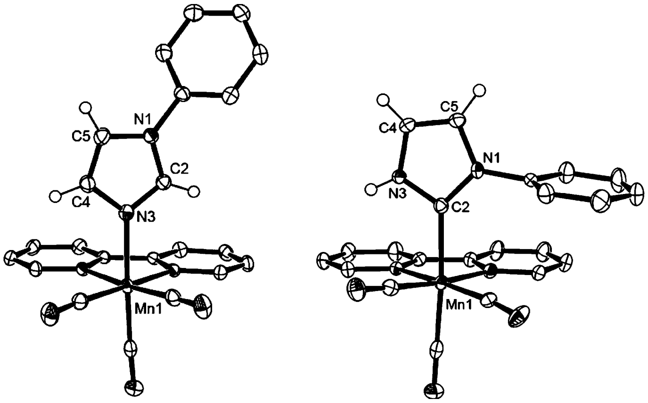
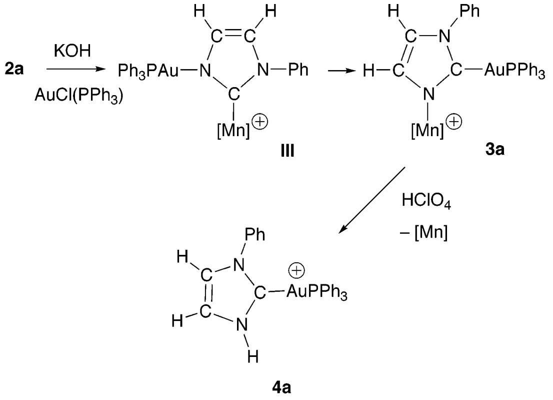


Figure 1. ORTEP diagrams of the structures of the cationic complexes **1a** (left) and **2a** (right). Selected bond distances (Å) and angles (deg): **1a**: Mn1−N3 2.062(2), N3−C2 1.326(3), C2−N1 1.349(3), N1−C5 1.377(3), C5−C4 1.349(3), C4−N3 1.384(3); C4−N3−C2 105.1(2), N3−C2−N1 111.4(2). **2a**: Mn1−C2 2.054(3), N3−C2 1.356(3), C2−N1 1.364(3), N1−C5 1.393(3), C5−C4 1.337(4), C4−N3 1.376(3); C4−N3−C2 113.0(2), N3−C2−N1 102.3(2).

10.1021/ja073144n CCC: $37.00 © 2007 American Chemical Society

Scheme 2. Sequential Transmetalation Reaction of the NHC Ligand



metallic fragment to the negatively charged nitrogen atom of **II**. Thus, with a view to obtain heterometallic complexes containing imidazolate ligands, a dichloromethane solution of **2a** was treated with KOH in the presence of an equivalent of [AuCl(PPh$_3$)]. Compound **3a** was formed in a few minutes and isolated as a yellow solid. The ^{13}C{^{1}H} NMR spectrum of **3a** shows the signal corresponding to the carbene carbon atom shifted downfield with respect to the NHC derivatives **2a**−**c**, suggesting some relevant structural changes other than the expected substitution of the proton by the isolobal [Au(PPh$_3$)]$^+$ fragment (**III** in Scheme 2). An X-ray diffraction study of **3a** (Figure 2) showed that the nitrogen atom of the heterocycle is once again coordinated to manganese, whereas the C^2 carbon atom is bonded to gold.

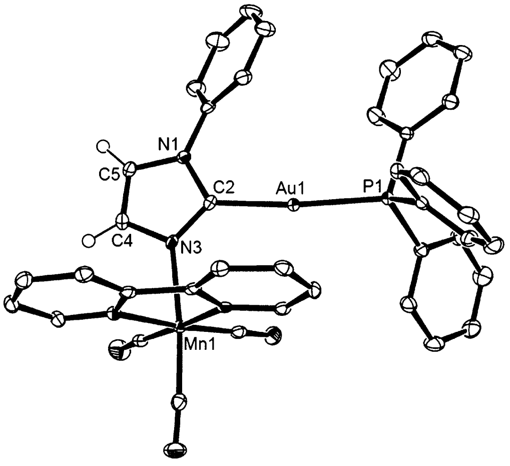


Figure 2. ORTEP diagram of the structure of the cationic complex **3a**. Selected bond distances (Å) and angles (deg): Mn1−N3 2.087(3), N3−C2 1.339(5), C2−N1 1.383(5), N1−C5 1.378(6), C5−C4 1.352(6), C4−N3 1.381(5), C2−Au1 2.035(4), Au1−P1 2.283(1); C4−N3−C2 108.2(4), N3−C2−N1 107.3(4), C2−Au1−P2 173.7(2).

Reaction of **3a** with HClO$_4$ produces the gold carbene complex **4a**, together with *fac*-[Mn(OClO$_3$)(CO)$_3$(bipy)], completing the transmetalation reaction of the NHC ligand (Scheme 2), so that complex **3a** can be considered as an intermediate species in the overall transmetalation process of the carbene from **2a** to **4a**.[12]

In summary, we have found a way to transform imidazole complexes into NHC derivatives and to accomplish subsequent transmetalation reactions through isolable heterometallic species, by means of acid−base treatments. Further studies aiming to extend these results to a variety of metallic complexes are currently in progress.

Acknowledgment. This work was supported by the Spanish Ministerio de Educación y Ciencia (PGE and FEDER funding, Project CTQ2006-10035) and the Principado de Asturias (Project IB05-110). B.F.P. thanks the Universidad de Oviedo for a grant.

Supporting Information Available: Experimental procedures and characterization data for new compounds (PDF), and crystallographic data for **1a**, **2a**, and **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Recent reviews: (a) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) Hermann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (d) Crabtree, R. H. *Coord. Chem. Rev.* **2007**, *251*, 595.
(2) (a) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471. (b) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2; p 73. (c) Haga, M. In *Comprehensive Coordination Chemistry*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2004; Vol. 1, p 125.
(3) Lewis, J. C.; Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 35.
(4) (a) Tan, K. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 3202. (b) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332.
(5) Wiedemann, S. H.; Lewis, J. C.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2006**, *128*, 2452.
(6) (a) Alvarez, E.; Conejero, S.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Serrano, O.; Carmona, E. *J. Am. Chem. Soc.* **2006**, *128*, 13060. (b) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044. (c) Kunz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3405.
(7) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F., Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.
(8) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702.
(9) Sini, G.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2002**, *41*, 602.
(10) Solé, S.; Gornitzka, H.; Guerret, O.; Bertrand, G. *J. Am. Chem. Soc.* **1998**, *120*, 9100.
(11) For the synthesis of other related N−H-containing carbenes, see for instance: (a) Hahn, F. E., Langenhahn, V.; Pape, T. *Chem. Commun.* **2005**, 5390. (b) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P. *Chem.*−*Eur. J.* **2003**, *9*, 704. (c) Hahn, F. E.; Plumed, C. G.; Münder, M.; Lügger, T. *Chem.*−*Eur. J.* **2004**, *10*, 6285. (d) Liu, C.; Chen, D.; Lee, G.; Peng, S.; Liu, S. *Organometallics* **1996**, *15*, 1055. (e) Ruiz, J.; García, G.; Mosquera, M. E. G.; Perandones, B. F.; Gonzalo, M. P.; Vivanco, M. *J. Am. Chem. Soc.* **2005**, *127*, 8584.
(12) Transmetalation reactions are frequently used in the preparation of NHC complexes, notably starting from NHC complexes of Ag(I): Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

JA073144N