N-Heterocyclic Nitrenium Ligands

DOI: 10.1002/anie.201104868

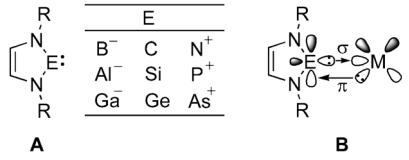
N-Heterocyclic Nitrenium Ligands: A Missing Link Explored**

*Joyanta Choudhury**

N-heterocyclic carbene analogues · ligand design · pincer · transition metals · π acceptor

Ligands are at the heart of coordination chemistry, organometallic chemistry, and homogeneous catalysis. The chemistry community is well aware of the immense importance of phosphine ligands in the above fields. In continuation with chemists' curiosities for the development of new as well as improvement of existing chemical properties and processes, the demand for new ligands always remains a major research avenue to explore.

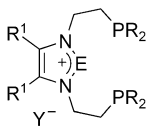
The initial discovery of stable N-heterocyclic carbenes[1] has triggered an upswing in the investigation of their ligand properties in fundamental as well as application-oriented transition-metal chemistry in the past few years.[2] N-heterocyclic carbene(NHC)-based ligands (**A**, E = C, Scheme 1) possess strong σ-electron-donating properties, thereby forming strong and stable bonds to wide varieties of transition-metal centers. Moreover, they entertain some extra advantageous characteristics as ligands, namely, 1) the σ-electron-withdrawing and π-electron-donating character of the nitrogen center(s) of the heterocyclic ring, 2) steric protection from the exocyclic nitrogen substitutents, and 3) simple and extensive structural modification. Owing to the above superior features, these compounds have been recognized as excellent ligands and have been utilized extensively in various fields including catalysis[3] and materials chemistry.[4] The rapid development of NHC-based transition-metal chemistry has influenced the organometallic chemists to discover and explore the ligation behavior of the isovalent NHC-analogues of other Group 13–15 p-block elements (**A**, Scheme 1).[5]



Scheme 1. N-Heterocyclic carbene-type ligands of Group 13–15 p-block elements E (**A**) and their most likely bonding picture with transition metals M (**B**).

All of these main-group carbene analogues possess one unshared lone pair of electrons at the carbenoid center (in their singlet states) and a vacant *p*-orbital with monoanionic (Group 13), neutral (Group 14), or monocationic (Group 15) charge (Scheme 1). Hence these species can be considered as potential σ-donor and π-acceptor ligands for transition metals (**B**, Scheme 1). Considering the electronegativity and charge effects, the nature and strengths of the σ-donor and π-acceptor abilities of these ligands differ. Accordingly, due to weak σ-donor and strong π-acceptor properties, Group 15 cationic ligands are electrophilic in nature and very much susceptible to nucleophilic attack, in contrast to the nucleophilic Group 13 and Group 14 congeners. To explore this diverse electronic nature, chemists have utilized almost all of these species (e.g., boron, gallium, silicon, germanium, phosphorus, arsenic analogues) as ligands for transition metals.[5] However, the nitrogen counterpart, that is, N-heterocyclic nitrenium ions, were, until very recently, unknown to behave as ligand for metals.

In transition-metal chemistry, a commonly followed strategy for the modification of a reactive species to give a potential ligand is to incorporate it into a pincer framework that imparts stability to the generated metal complex by virtue of providing a sterically and electronically protected metal-ligating site through desired pendant design.[6] Very recently, Gandelman and co-workers have utilized this concept for exploring the unprecedented ligand behavior of nitrenium cations and have found the missing link in the series of main-group N-heterocyclic carbene-type ligands (Scheme 2).[7] Attaching the phosphorus chelating arms to the two nitrogen atoms (at the 1- and 3-position) of the core 1,2,3-triazolium heterocyclic ring, they designed and synthesized the new ligands **1**–**3** (Scheme 2) to investigate the coordination ability of the central nitrenium nitrogen atom to



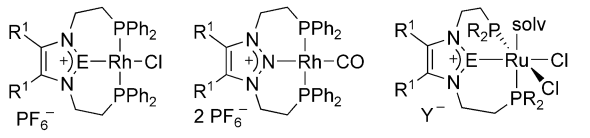
1a (R^1 = -$(CH)_2$-, R = Ph, E = N, Y = PF_6)
1b (R^1 = -$(CH)_2$-, R = Ph, E = ^{15}N, Y = PF_6)
2 (R^1 = H, R = *i*Pr, E = N, Y = Br)
3 (R^1 = H, R = Ph, E = N, Y = PF_6)

Scheme 2. N-Heterocyclic nitrenium ligands based on tridentate pincer framework.

[*] Dr. J. Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research Bhopal
Bhopal 462 023, M.P. (India)
E-mail: joyanta@iiserbhopal.ac.in
Homepage: http://home.iiserbhopal.ac.in/~joyanta/

[**] Financial support and infrastructure from IISER Bhopal are gratefully acknowledged.

different metal centers. Thus unambiguous formation of stable Rh^{I} and Ru^{II} complexes (**4**–**6**, Scheme 3) with the novel N-heterocyclic nitrenium ligands in a tridentate bonding fashion was proved both in solution and in the solid state by multinuclear NMR spectral studies including selective ^{15}N-labeling experiments and X-ray crystallography, respectively.



4a (R^1 = –$(CH)_2$–, E = N)

4b (R^1 = –$(CH)_2$–, E = ^{15}N)

5a (R^1 = –$(CH)_2$–)

5b (R^1 = H)

6a (R^1 = H, R = *i*Pr, E = N, Y = Br)

6b (R^1 = –$(CH)_2$–, R = Ph, E = ^{15}N, Y = PF_6)

Scheme 3. Complexes **4**–**6** derived from the nitrenium ligands **1**–**3**; solv = solvent.

The ^{15}N NMR spectroscopy of complexes **4b** and **6b** showed significant upfield shifts of $\delta = 62.9$ ppm and 41.9 ppm relative to the free ligand **2b**, thus indicating its coordination to rhodium and ruthenium centers, respectively. Moreover, for **4b**, the ^{15}N signal appeared as a doublet of triplets caused by both ^{15}N–^{103}Rh and ^{15}N–^{31}P couplings; for **6b**, the signal was a triplet caused by ^{15}N–^{31}P coupling. The remarkably large $^{1}J_{N-Rh}$ value (29 Hz) was attributed to an increase in the carbene-like character of the triazolium nitrogen atom of **1b** upon coordination to the metal atom. X-ray crystallographic analyses of the molecular structures of **4a** and **6a** established long N–N bonds, hence again confirming an increased nitrenium character of the central nitrogen atom of the coordinated ligand. The N-heterocyclic nitrenium ligand was also suggested to be weaker *trans* influencing than trialkylphosphine based on the different Ru–Cl bond lengths in **6a**. A longer Rh–N bond in **5a** (2.151(6) Å) compared to **4a** (1.991(7) Å) revealed weak σ-donor and reasonable π-acceptor abilities of the nitrenium ion ligands that are in line with related Group 15 ligands. The weaker σ-donating properties of these ligands compared to NHCs and pyridines were also evident from significantly higher CO stretching frequency values in **5a** ($\nu_{CO} = 2024\ cm^{-1}$) and **5b** ($\nu_{CO} = 2019\ cm^{-1}$) than in similar NHC- and pyridine-based rhodium complexes.[8] Density functional theory (DFT) calculations explained that metal-to-ligand π-back-donation is the dominant bonding parameter in nitrenium and related phosphenium complexes, whereas ligand-to-metal σ donation has a stronger influence in NHC- and pyridine-complexes. Therefore, these new ligands are found to be electronically similar to the other cationic congeners of Group 15 elements, but they differ from the neutral and anionic NHC analogues.

The above development of the ligand properties of N-heterocyclic nitrenium cations within a tridentate pincer scaffold is remarkable in the field of organometallic chemistry. However, there remains ample scope to investigate whether other binding modes of these ligands, for instance, monodentate and chelating bidentate, to different metal centers, can be made feasible to find broader application in exploring basic organometallic reactions. In this respect, a greater control over their electronic nature through judicious modification of the heterocyclic core (that is to say, 1,3-*N*-substituents of the triazolium system) is necessary. Any potential non-innocent behavior of this type of ligands under certain conditions would also be interesting. Nevertheless, the key of the inspiring results reported by Gandelman and co-workers is that they established the long-standing nitrenium ions[9] as potential ligands for catalytically important transition metals. Moreover, they pave the way for opening new avenues toward exploring their reasonable π-acceptor and weak σ-donor properties in both stabilizing electron-rich metal centers, for example, Pd^0 in many organometallic reactions and in increasing the electrophilic properties of metal centers during catalysis. The above electronic feature in combination with a vast library of pincer frameworks remains to be exploited in the near future to make this novel class of N-heterocyclic nitrenium ligands not only an academically interesting but also a potentially useful and versatile reagent in transition-metal chemistry.

Received: July 12, 2011
Published online: September 28, 2011

[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363.

[2] a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992 – 9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810 – 8849; b) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862 – 892; c) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166 – 3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122 – 3172; d) *Coord. Chem. Rev.* **2007**, *251*, 595 – 896 (Ed.: R. H. Crabtree).

[3] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612 – 3676; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342 – 1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290 – 1309.

[4] a) L. Mercs, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 5570 – 5576; b) F. E. Hahn, C. Radloff, T. Pape, A. Hepp, *Organometallics* **2008**, *27*, 6408 – 6410; c) A. Rit, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2010**, *132*, 4572 – 4573; d) F. M. Conrady, R. Fröhlich, C. S. to Brinke, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 11496 – 11499; e) A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2011**, *30*, 334 – 347.

[5] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113 – 115; b) Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201 – 9203; c) E. S. Schmidt, A. Jockisch, H. Schmidbaur, *J. Am. Chem. Soc.* **1999**, *121*, 9758 – 9759; d) R. J. Baker, R. D. Farley, C. Jones, M. Kloth, D. M. Murphy, *J. Chem. Soc. Dalton Trans.* **2002**, 3844 – 3850; e) R. J. Baker, J. Cameron, J. A. Platts, *J. Am. Chem. Soc.* **2003**, *125*, 10534 – 10535; f) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691 – 2692; g) H. Yoo, P. J. Carroll, D. H. Berry, *J. Am. Chem. Soc.* **2006**, *128*, 6038 – 6039; h) N. J. Hill, R. West, *J. Organomet. Chem.* **2004**, *689*, 4165 – 4183; i) W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489 – 1492; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485 – 1488; j) F. Ullah, O. Kühl, G. Bajor, T. Veszprémi, P. G. Jones, J. Heinicke, *Eur. J. Inorg. Chem.* **2009**, 221 – 229; k) A. V. Zabula, F. E. Hahn, *Eur. J. Inorg. Chem.* **2008**, 5165 – 5179; l) S. Burck, J. Daniels, T. Gans-Eichler, D. Gudat, K.

Nättinen, M. Nieger, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1403 – 1412; m) C. A. Caputo, A. L. Brazeau, Z. Hynes, J. T. Price, H. M. Tuononen, N. D. Jones, *Organometallics* **2009**, *28*, 5261 – 5265; n) G. S. Day, B. Pan, D. L. Kellenberger, B. M. Foxman, C. M. Thomas, *Chem. Commun.* **2011**, *47*, 3634 – 3636; o) D. Heitmann, T. Pape, A. Hepp, C. Mück-Lichtenfeld, S. Grimme, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 11 118 – 11 120.

[6] a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866 – 3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750 – 3781; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759 – 1792.

[7] Y. Tulchinsky, M. A. Iron, M. Botoshansky, M. Gandelman, *Nat. Chem.* **2011**, *3*, 525 – 531.

[8] a) J. Y. Zeng, M.-H. Hsieh, H. M. Lee, *J. Organomet. Chem.* **2005**, *690*, 5662 – 5671; b) G. Vasapollo, P. Giannoccaro, C. F. Nobile, A. Sacco, *Inorg. Chim. Acta* **1981**, *48*, 125 – 128.

[9] G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek, C. Willeke, *J. Am. Chem. Soc.* **1996**, *118*, 4925 – 4930.

