Carbene Ligands

An N-Heterocyclic Carbene/Iridium Hydride Complex from the Oxidative Addition of a Ferrocenyl–Bisimidazolium Salt: Implications for Synthesis**

Mónica Viciano, Elena Mas-Marzá, Macarena Poyatos,
Mercedes Sanaú, Robert H. Crabtree, and
*Eduardo Peris**

Despite the increasing recent use of N-heterocyclic carbenes (NHCs) in the preparation of new homogeneous catalysts, catalytic applications of NHC-based complexes have already been extended to a surprisingly wide range of synthetic organic reactions. The large number of reviews published in the last five years[1–5] shows the rapid development of NHC ligands in catalyst design.

Unlike phosphines, the coordination of NHCs to metal centers requires the activation or deprotonation of a precursor, which makes NHC-based complexes relatively less accessible than the analogous phosphine compounds. Several activation strategies have been used to prepare NHC–metal complexes: 1) insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene)-containing olefins (Lappert method);[6–8] 2) generation of a free carbene by deprotonation of the corresponding imidazolium precursor with a strong base (for example, NaH, *t*BuOK, *n*ButLi) and addition to the metal fragment;[9–13] 3) transmetalation from a silver–NHC complex prepared by direct reaction of an imidazolium precursor and Ag_2O;[14–17] 4) in situ deprotonation of an imidazolium salt with a weak base (for example, NEt_3, NaOAc, Cs_2CO_3),[18–24] and 5) oxidative addition by activation of the C2−X (X = Me, I, H) bond of an imidazolium cation.[25–31] We have found that methods 3 and 4 afford good results in the preparation of several Rh, Ir, Ru, and Pd complexes under very mild reaction conditions. Methods 2–5 all use imidazolium cations as precursors to the NHC ligands.

---

[*] M. Viciano, E. Mas-Marzá, M. Poyatos, Dr. E. Peris
Departamento de Química Inorgánica y Orgánica
Universitat Jaume I
12071 Castellón (Spain)
Fax: (+34) 964-728-214
E-mail: eperis@qio.uji.es

Dr. M. Sanaú
Departamento de Química Inorgánica
Universitat de València
46100 Burjassot (Spain)

Prof. R. H. Crabtree
Chemistry Department, Yale University
225 Prospect Street, New Haven
CT 06520-8127 (USA)

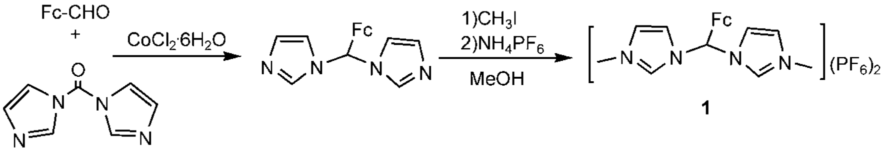
[**] We gratefully acknowledge financial support from the DGESIC (MAT2002-04421-C02-01) and Bancaixa (P1.1B2001-03). We would also like to thank the Spanish MEC for a fellowship (E.M.-M.).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200461918

Experimental and theoretical studies have shown that a σ interaction is the main contribution to the NHC–M bond, with limited π backdonation. As regards the mechanistic aspects of the metalation, most experimental results seem to point to the direct formation of a M–C bond from free carbenes in those cases when an imidazolium precursor and a base are used (strategies 2 and 4), but deprotonation of an agostic CH group cannot be excluded in some cases. Some mechanistic aspects of the oxidative addition of C2–X bonds (X = Me, I, H; method 5) have been studied experimentally[25–29,31] and theoretically,[30] but this reaction has so far been limited to low-valent electron-rich coordinatively unsaturated Group 10 metal complexes. We now report the synthesis of a stable [Ir^{III}(H)(biscarbene)] complex by C2–H oxidative addition of a ferrocenyl–bisimidazolium precursor.

The reaction of bis(imidazolyl)ketone and ferrocene carboxaldehyde at 80 °C in the presence of $CoCl_2{\cdot}6H_2O$ affords bisimidazolylferrocenylmethane (Scheme 1). This compound can be methylated with CH_3I in the presence of NH_4PF_6 to yield the corresponding bis(methylimidazolium) salt **1**. We thought that the introduction of the ferrocenyl moiety could significantly modify the electronic and steric properties of the resulting biscarbene complexes.



1

Scheme 1. Preparation of bis(imidazolylferrocenylmethane) **1**. Fc = ferrocenyl.

The reaction of **1** with [{M(cod)Cl}$_2$] (cod = 1,5-cyclooctadiene; M = Rh, Ir) in the presence of NEt_3 at room temperature yields two different types of ligand coordination depending on the metal used (Scheme 2). For rhodium, the reaction gives the monometalated complex **2b**, where the ligand adopts a monodentate coordination mode. Compound **2b** was unambiguously characterized by NMR spectroscopic and mass spectrometric analysis. The ^{1}H NMR spectrum reveals that the twofold symmetry of the ligand is lost upon coordination. The downfield shift of the proton in the 2′-position of the imidazolium functionality ($\delta = 8.8$ ppm) shows that one of the rings remains unbound. The signals of the protons of the bound imidazolylidene ring appear at higher field than those of the unbound ring, thus indicating its coordination, as we have previously described for other similar systems.[18,20,23,32] A doublet at $\delta = 185$ ppm ($^1J_{\mathrm{Rh,C}} = 49$ Hz) in the ^{13}C NMR spectrum confirms that metalation has occurred. Similar NMR patterns have been observed for related ligands in the monometalated form.[23]

The reaction of **1** with [{Ir(cod)Cl}$_2$] under the same conditions affords the compound **3a**. The NMR spectra confirm that the twofold symmetry of the ligand is maintained upon coordination. The ^{1}H NMR spectrum shows a hydride signal at $\delta = -14.7$ ppm. The two metalated carbon atoms appear as a singlet at $\delta = 145$ ppm. This compound represents the first example of a (NHC)-Ir-hydride complex. Compound **3a** is indefinitely stable in solution at room temperature. The failure of **3a** to reductively eliminate may be related to the chelating character of the bis-NHC, as it keeps the imidazole ring from achieving the rotameric conformation required for reductive elimination with Ir–H normal to the ring plane.

The molecular structure of **3a** was confirmed by single-crystal X-ray diffraction analysis. Figure 1 shows the ORTEP diagram and the more relevant bond lengths and angles. The Ir atom adopts a distorted octahedral geometry with a biscarbene bite angle C-Ir-C of 83.5°. The Ir–C bond lengths of 2.056 and 2.043 Å lie in the range of previously reported Ir–C bond

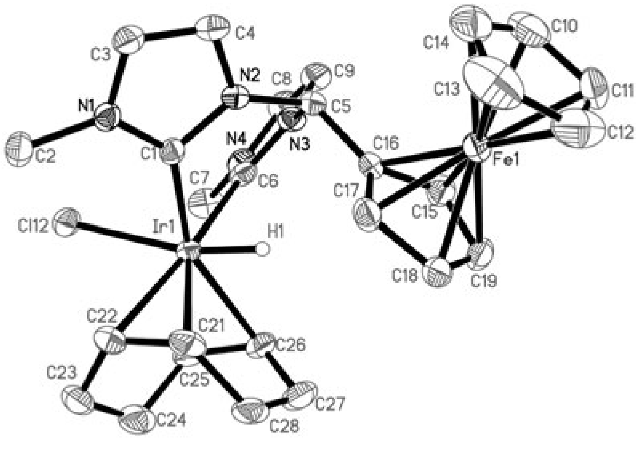
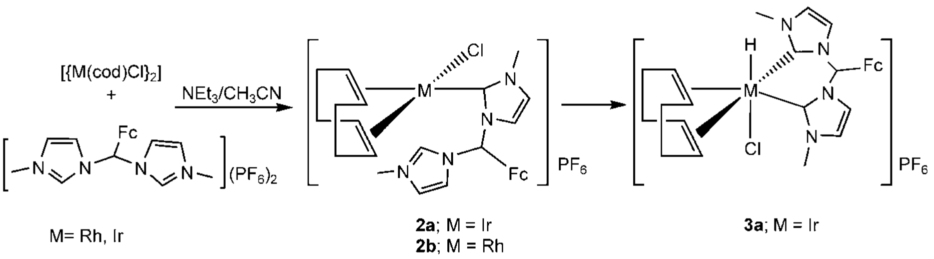


Figure 1. Molecular diagram of **3a**. Hydrogen atoms and the PF_6 anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1-C1 2.056(5), Ir1-C6 2.043(5), Ir1-H1 1.35 (6), H1-Cp$_c$ 2.83(7), C6-Ir1-C1 83.4(2), H1-Ir1-Cl12 166(3), H1-Ir1-C1 81(3), H1-Ir1-C6 78(3).

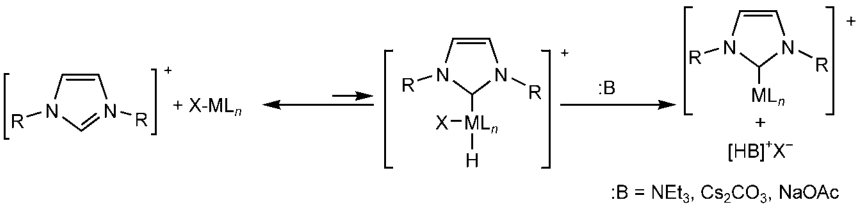


Scheme 2. Different ligand coordination modes produced after reaction of bisimidazolylferrocenylmethane **1** with [{M(cod)Cl}$_2$].

lengths for NHC ligands.[17,32–34] The Ir–H bond length is 1.35 Å. Interestingly, the ferrocenyl group points towards at the hydride ligand, and so provides a high steric hindrance, which may partially explain the stability of this metal hydride. This steric hindrance is illustrated by the short IrH···Cp_c (Cp_c = centroid of the Cp (C_5H_5) ring) distance of 2.83 Å. This short distance can also be detected in solution by NOE experiments.

To elucidate the mechanism of the metalation process, we performed several reactions to test the reversibility of the last step in the formation of **3a**. We thought that the reaction of **3a** with CO to substitute the cod ligand would likely promote reductive elimination of the carbene and hydride to yield the carbonyl analogue of **2a**. However, the chelate carbene hydride in **3a** was extremely stable and resisted conversion under all the reaction conditions tried. Addition of a weak base (NEt_3, NaOAc) also failed to give the deprotonated compound by reductive elimination of HCl. On the other hand, attempts to metalate **2b** to obtain the rhodium analogue of **3a** failed under a variety of reaction conditions, such as refluxing in CH_3CN, addition of a weak base (NEt_3, NaOAc), or addition of phosphine. However, we were able to obtain the monodentate compound **2a** by treating **1** with [{Ir(cod)Cl}$_2$] in the presence of NEt_3 in CH_3CN for 10 minutes at room temperature. Unfortunately, **2a** could not be quantitatively separated from **3**-Ir, and only 70:30 mixtures of **2a**/**3a** could be isolated. The identification of **2a** was made by NMR spectroscopic and mass spectrometric analysis. The NMR spectrum of **2a** is virtually identical to that of **2b**.

Complex **2a** evolves to give **3a** quantitatively on standing for two hours at room temperature in an NMR tube ($CDCl_3$, [D_6]acetone, [D_6]DMSO) in the absence of an external base. This result now explains why we could not obtain **2a** in a quantitative form, since it spontaneously evolves to give **3a**. This result suggests that the metalation of the imidazolium ring proceeds through oxidative addition of the C2–H bond. If the metalation of the imidazolium precursor takes place in the absence of a base, could the overall reaction proceed without a base? To verify this point we performed the reaction of **1** and [{Ir(cod)Cl}$_2$] in CH_3CN at a range of temperatures (from room temperature to reflux). The reaction mixtures did not show any metalated species even after three days, so the base seems to be a key factor in the formation of the metalated products. Given this result, why should the base be important for the first step of the metalation (formation of compounds **2a** and **2b**) and not for the second one (formation of **3a**)? Previously, we have shown that the addition of a weak base facilitates the activation of the imidazolium precursor to yield the corresponding NHC compounds.[18–23] The p*K* values of the species involved make us think that NEt_3 is not strong enough to deprotonate the bisimidazolium salt. We originally rationalized this result on the grounds that the addition of an excess of the base (10:1), together with the rapid coordination of the carbene to the metal center, may displace the equilibrium towards the desired species.[20] We now see that smaller amounts of base (2:1) and milder reaction conditions (room temperature) yield the same desired product, so the role of the base needs to be reconsidered. We now believe that the role of the base can be explained by the reaction mechanism shown in Scheme 3.



Scheme 3. Proposed reaction mechanism explaining the role of the base.

The reaction of the imidazolium precursor with the metal complex may lead to an oxidative addition/reductive elimination equilibrium in which the starting materials are clearly favored over the oxidative addition product. In the absence of a base, only the starting compounds are detectable. In fact, this could also explain why NHC-metal-hydrides are so scarce, since reductive elimination to the imidazolium ions should be very favorable. If a base is now added to the reaction medium, the oxidative addition product can eliminate HX (X = halide) by reaction with the base. The overall process has the same effect as if the imidazolium salt had first been deprotonated and the resulting carbene had then replaced the halide in the coordination sphere of the metal. The result is the same, but the pathway is different, and has important implications in the design of synthetic procedures to NHC–metal compounds. In any case, while Scheme 3 is applicable to 16e d^8 complexes (Rh^I, Ir^I), further work is needed to see how far it applies to 18e d^6 complexes (for example, Ru^{II}/Ru^{IV}).

The ferrocenyl group may be a key factor in the stability of **3a**. We believe that the ferrocene group may be sterically protecting the hydride in the molecular structure of **3a**. Another key point in the preparation of **3a** is the use of a PF_6 salt of the imidazolium precursor instead of the corresponding halide salt. The reaction of the dichloride analogue of **1** with [{Ir(cod)Cl}$_2$] yields a mixture of compounds that we could not characterize, but no hydrides were detected. We believe that the introduction of the chloride into the reaction medium may favor other pathways.

We believe that our results may have important implications for NHC chemistry, in that oxidative addition may be a more useful general method to synthesize NHC–metal complexes than previously thought. Even if the process is endothermic, it can be driven by base and the overall reaction may be mistaken for a simple deprotonation of the azolium precursor. Although more detailed study is needed, we believe that our observations may modify current mechanistic concepts in the formation of an NHC–M bond, especially when a weak base is used to promote the metalation. Our synthetic procedure provides a method to obtain a highly stable NHC–Ir–H complex, thus challenging the idea that such complexes are usually unstable. It has also been pointed out that ionic liquids may not be "innocent" solvents with low-valent Group 10 metal complexes because of their capability to undergo oxidation addition.[27]

Received: September 8, 2004

Keywords: C–H activation · carbene ligands · hydrides · iridium · rhodium

---

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

[2] K. J. Cavell, D. S. McGuinness, *Coord. Chem. Rev.* **2004**, *248*, 671.

[3] E. Peris, R. H. Crabtree, *C. R. Chim.* **2003**, *6*, 33.

[4] W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1291.

[5] A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913.

[6] P. B. Hitchcock, M. F. Lappert, P. Terreros, *J. Organomet. Chem.* **1982**, *239*, C26.

[7] M. J. Doyle, M. F. Lappert, P. L. Pye, P. Terreros, *J. Chem. Soc. Dalton Trans.* **1984**, 2355.

[8] P. B. Hitchcock, M. F. Lappert, P. Terreros, K. P. Wainwright, *J. Chem. Soc. Chem. Commun.* **1980**, 1180.

[9] A. A. Danopoulos, S. Winston, W. B. Motherwell, *Chem. Commun.* **2002**, 1376.

[10] S. Burling, L. D. Field, H. L. Li, B. A. Messerle, P. Turner, *Eur. J. Inorg. Chem.* **2003**, 3179.

[11] W. A. Herrmann, L. J. Goossen, M. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357.

[12] U. Kernbach, M. Ramm, P. Luger, W. P. Fehlhammer, *Angew. Chem.* **1996**, *108*, 333; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 310.

[13] R. E. Douthwaite, M. L. H. Green, P. J. Silcock, P. T. Gomes, *J. Chem. Soc. Dalton Trans.* **2002**, 1386.

[14] K. M. Lee, H. M. J. Wang, I. J. B. Lin, *J. Chem. Soc. Dalton Trans.* **2002**, 2852.

[15] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972.

[16] R. S. Simons, P. Custer, C. A. Tessier, W. J. Youngs, *Organometallics* **2003**, *22*, 1979.

[17] A. R. Chianese, X. W. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663.

[18] M. Poyatos, E. Mas-Marza, J. A. Mata, M. Sanau, E. Peris, *Eur. J. Inorg. Chem.* **2003**, 1215.

[19] M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, *Organometallics* **2003**, *22*, 1110.

[20] M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* **2003**, *42*, 2572.

[21] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, *Organometallics* **2004**, *23*, 323.

[22] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* **2004**, *43*, 2213.

[23] M. Poyatos, E. Mas-Marza, M. Sanau, E. Peris, *Inorg. Chem.* **2004**, *43*, 1793.

[24] B. Cetinkaya, S. Demir, I. Ozdemir, L. Toupet, D. Semeril, C. Bruneau, P. H. Dixneuf, *Chem. Eur. J.* **2003**, *9*, 2323.

[25] D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **2001**, *123*, 8317.

[26] M. A. Duin, N. D. Clement, K. J. Cavell, C. J. Elsevier, *Chem. Commun.* **2003**, 400.

[27] N. D. Clement, K. J. Cavell, C. Jones, C. J. Elsevier, *Angew. Chem.* **2004**, *116*, 1297; *Angew. Chem. Int. Ed.* **2004**, *43*, 1277.

[28] A. Furstner, G. Seidel, D. Kremzow, C. W. Lehmann, *Organometallics* **2003**, *22*, 907.

[29] M. S. Viciu, G. A. Grasa, S. P. Nolan, *Organometallics* **2001**, *20*, 3607.

[30] D. S. McGuinness, K. J. Cavell, B. F. Yates, *Chem. Commun.* **2001**, 355.

[31] S. Grundemann, M. Albrecht, A. Kovacevic, J. W. Faller, R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2002**, 2163.

[32] M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596.

[33] J. R. Miecznikowski, R. H. Crabtree, *Organometallics* **2004**, *23*, 629.

[34] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461.