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Iron Carbene Chemistry

Coupling of an N-Heterocyclic Carbene on Iron with Alkynes to Form η^5-Cyclopentadienyl-Diimine Ligands[**]

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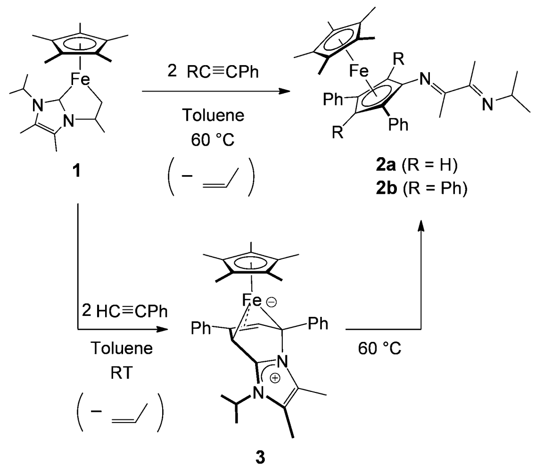
Abstract: *A cyclometalated N-heterocyclic carbene ligand in a half-sandwich iron complex was found to couple with alkynes, leading to a unique type of ring opening of the carbene ligand and the formation of ferrocenyl–diimine complexes. An intermediary iron complex obtained from the reaction with phenylacetylene reveals that the ring opening follows the formation of a fused heterocycle consisting of an imidazole ring and two alkynes.*

N-heterocyclic carbenes (NHCs) are a growing class of ligands for transition metals,[1] and like phosphines they serve as two-electron donors in homogeneous catalysts. An advantage for NHCs is their strong σ-donating ability, which leads to strong bonding to various metals. Whereas this property is useful for preventing the decomposition of the metal complexes, it has been recently demonstrated that NHCs sometimes react with other ligands within the coordination sphere of metals.[2,3] The reported examples involve the migratory insertion of an NHC ligand into metal–carbon bonds,[2b–e] and the migration of alkyl or aryl groups to the carbene carbon of NHC ligands followed by ring opening.[3] The ring opening of NHC ligands has been also demonstrated with a dinuclear ruthenium hydride complex[4] and with main group hydrides.[5] The removal of an N-bound substituent of NHC ligands has been demonstrated with Ni, Ru, and Fe complexes.[6] In this paper, we report an unprecedented type of coupling reaction between a cyclometalated NHC ligand on iron and alkynes at 60 °C, leading to the ring opening of an NHC ligand and the formation of η^5-cyclopentadienyl ligands carrying a diimine moiety. An intermediary iron complex was also obtained from the reaction of the iron complex with phenylacetylene at room temperature.

The titled reaction was discovered during the course of our studies on the reactions of iron-NHC complexes.[7] Treatment of complex **1**[7a] bearing a cyclometalated NHC ligand with two equivalents of phenylacetylene at 60 °C resulted in the formation of a red solution after three days, from which crystals of ferrocenyl–diimine complex **2a**, having two phenyl groups at the 2- and 4-positions of the cyclopentadienyl ring, were isolated in 79 % yield (Scheme 1). Similarly, the reaction of **1** with diphenylacetylene gave an analogous complex **2b**, which was crystallized in 40 % yield. From the difference in formula between **2a** and **1** + **2**(phenylacetylene), one can see the loss of the -$CH(CH_3)CH_2$- group during the reaction. As described below, the lost group was observed as propylene in the ^1H NMR experiment. Whereas complex **2a** may be formed together with its regioisomers, in terms of the positions of Ph groups on the η^5-cyclopentadienyl ring, the ^1H and $^{13}C\{^1H\}$ NMR spectra of the reaction mixture and the high yield of isolated **2a** support its selective formation. Two methyl signals for the *i*Pr group of the diimine moiety in **2a** were observed at $\delta = 1.18$ and 1.16 ppm in the ^1H NMR spectrum and at $\delta = 24.13$ and 24.09 ppm in the $^{13}C\{^1H\}$ NMR spectrum, owing to the asymmetric structure of the η^5-$C_5H_2Ph_2$(diimine) ligand. The cyclic voltammetry of **2a**,**b** showed the reversible Fe^{II}/Fe^{III} redox couple of the ferrocenyl group at $E_{1/2} = -0.11$ V (**2a**) and -0.15 V (**2b**) vs. Ag/Ag$^+$ (in CH_2Cl_2), and these potentials are similar to that of Cp*FeCp (-0.18 V).[8]



Scheme 1. Reactions of **1** with alkynes.

The molecular structures of **2a**,**b** were determined by X-ray crystallographic analysis. As shown on the left in Figure 1, complex **2a** reveals a typical sandwich structure, and one of the η^5-cyclopentadienyl rings carries two phenyl groups and a diimine moiety. Whereas **2a** is a new planar-chiral ferrocene,[9,10] it crystallizes in a centrosymmetric space group (P-1) as a result of the formation of a racemic couple. The composition of the new η^5-cyclopentadienyl ligand suggests that the five-membered ring consists of two phenyl-

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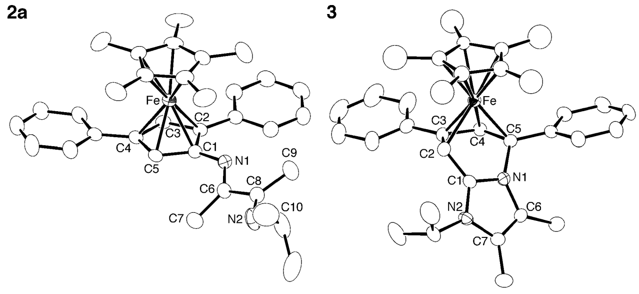

Figure 1. Molecular structures of **2a** and **3**, with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): **2a**, Fe–C(1–5) = 2.041(2)–2.054(2), N1–C6 = 1.281(3), C6–C8 = 1.506(3), C8–N2 = 1.262(3). **3**, Fe–C2 = 2.012(3), Fe–C3 = 1.981(3), Fe–C4 = 1.983(2), Fe–C5 = 2.053(2), C1–C2 = 1.449(3), C2–C3 = 1.484(4), C3–C4 = 1.438(5), C4–C5 = 1.455(4), C5–N1 = 1.483(3), N1–C1 = 1.336(4), C1–N2 = 1.361(3), N1-C1-N2 = 107.6(2).

acetylene molecules and the carbene carbon. The incorporation of the carbene carbon in the new cyclopentadienyl group results in the opening of the ring of the NHC ligand, and the remaining four atoms of the NHC ring provide a diimine moiety. The formation of a diimine moiety is indicated by the short N=C distances (1.262(3) and 1.281(3) Å) and the C6—C8 single bond (1.506(3) Å). Complex **2b** is structurally very similar to **2a**, although its Fe-C(η^5-C_5Ph_4(diimine)) (2.0570(14)–2.0722(15) Å) and Fe-C(Cp*) (2.0657(14)–2.0826(15) Å) distances are longer than the Fe-C(η^5-$C_5H_2Ph_2$(diimine)) (2.041(2)–2.054(2) Å) and Fe-C-(Cp*) (2.039(2)–2.053(2) Å) distances in **2a**, possibly due to the steric congestion caused by the four phenyl groups on the cyclopentadienyl ring.

When the reaction of **1** with phenylacetylene was carried out at room temperature, complex **3**, which has a fused N-containing heterocycle, was formed (Scheme 1, bottom). The -CH(CH_3)CH_2- group of the metallacycle in **1** is already lost at this point as propylene, which was observed in the ^{1}H NMR of the reaction mixture. The metallacycle in **1** is probably important for the C—N bond cleavage to release propylene, as relevant C—N bond cleavage reactions have been reported for nickel and ruthenium complexes having a cyclometalated NHC ligand.[6] Complex **3** was isolated as dark orange crystals in 67% yield, and the molecular structure was determined by X-ray crystallography (Figure 1, right). The fused heterocycle ligand of **3** is made from the NHC ligand and two phenylacetylene molecules, and is bent 48.41(19)° with respect to the C2–C5 axis. The Cp*Fe unit is bound to four carbon atoms (C2–C5) of the heterocycle. The Fe–C(C2–C5) distances of 1.981(3)–2.053(2) Å are slightly shorter than the Fe–C distances in the η^4-1,3-butadiene complexes (2.027(10)–2.282(4) Å),[11] which indicates a strong Fe–C(C2–C5) interaction. The Fe–C2/C5 distances (2.012(3) and 2.053(2) Å) are longer than the Fe–C3/C4 distances (1.981(3) and 1.983(2) Å), and this tendency fits with that of the η^4-1,3-butadiene complexes. On the other hand, the C2–C3 and C4–C5 distances (1.484(4) Å and 1.455(5) Å) are slightly longer than the C3–C4 distance (1.438(5) Å), which is in accordance with the bent η^4-metallacyclo-3-pentene structure. Thus, the Fe–C(C2–C5) interaction may be described as in between the η^4-1,3-butadiene and the bent η^4-metallacyclo-3-pentene structures, although the structure of **3** in Scheme 1 is drawn as the latter. The C1 and N1 atoms, which are from the NHC ligand of **1**, are bound to carbon atoms originated from phenylacetylene, C2 and C5, respectively, and the N-containing five-membered ring has the cationic imidazolium character. Indeed, the C–N and C–C distances of the five-membered ring are comparable to those for pentaalkyl imidazolium cations.[12]

As the formula of **3** is the same as **2a**, we assumed that **3** is an intermediate for the synthesis of **2a**. This hypothesis was supported by the ^{1}H NMR experiment, and heating a C_6D_6 solution of isolated **3** at 60 °C for three days resulted in the formation of **2a** in > 99% yield based on an internal standard (C_6Me_6). On a preparative scale, **2a** was isolated as crystals in 90% yield. Whereas the reaction mechanism remains uncertain, the bond formation between the C1 and C5 atoms of **3** and the cleavage of C1—N2 and C5—N1 bonds are probably involved in this process.

In summary, we have found a unique type of coupling reaction between a cyclometalated NHC ligand and alkynes, producing η^5-cyclopentadienyl ligands with a diimine moiety through the evolution of propylene associated with C—N bond cleavage, followed by ring-opening of the NHC ligand.

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[1] a) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; c) S. D. González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; d) M. J. Ingleson, R. A. Layfield, *Chem. Commun.* **2012**, *48*, 3579–3589; e) D. Bézier, J. B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2013**, *355*, 19–33.

[2] a) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247–2273; b) A. A. Danopoulos, N. Tsoureas, J. C. Green, M. B. Hursthouse, *Chem. Commun.* **2003**, 756–757; c) E. Becker, V. Stingl, G. Dazinger, M. Puchberger, K. Mereiter, K. Kirchner, *J. Am. Chem. Soc.* **2006**, *128*, 6572–6573; d) E. Becker, V. Stingl, G. Dazinger, K. Meteiter, K. Kirchner, *Organometallics* **2007**, *26*, 1531–1535; e) E. P. A. Couzijn, E. Zocher, A. Bach, P. Chen, *Chem. Eur. J.* **2010**, *16*, 5408–5415.

[3] a) A. W. Waltman, T. Ritter, R. H. Grubbs, *Organometallics* **2006**, *25*, 4238–4239; b) D. Pugh, A. Boyle, A. A. Danopoulos, *Dalton Trans.* **2008**, 1087–1094.

[4] A. Kaiho, H. Suzuki, *Angew. Chem.* **2012**, *124*, 1437–1440; *Angew. Chem. Int. Ed.* **2012**, *51*, 1408–1411.

[5] a) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2012**, *124*, 2140–2142; *Angew. Chem. Int. Ed.* **2012**, *51*, 2098–2100; b) D. Schmidt, J. H. J. Berthel, U. Radius, *Angew. Chem.* **2012**, *124*, 9011–9015; *Angew. Chem. Int. Ed.* **2012**, *51*, 8881–8885; c) S. M. I. Al-Rafia, R. McDonald, M. J. Ferguson, E. Rivard, *Chem. Eur. J.* **2012**, *18*, 13810–13820.

[6] a) S. Caddick, F. G. N. Cloke, P. B. Hitchcock, A. K. Lewis, *Angew. Chem.* **2004**, *116*, 5948–5951; *Angew. Chem. Int. Ed.* **2004**, *43*, 5824–5827; b) S. Burling, M. F. Mahon, R. Powell,

M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702 – 13703; c) J. A. Cabeza, I. Rio, D. Miguel, M. G. Sánchez-Vega, *Angew. Chem.* **2008**, *120*, 1946 – 1948; *Angew. Chem. Int. Ed.* **2008**, *47*, 1920 – 1922; d) L. J. L. Häller, M. J. Page, S. Erhardt, S. A. Macgregor, M. F. Mahon, M. A. Naser, A. Vélez, M. K. Whittlesey, *J. Am. Chem. Soc.* **2010**, *132*, 18408 – 18416; e) L. Xiang, J. Xiao, L. Deng, *Organometallics* **2011**, *30*, 2018 – 2025; f) B. M. Day, T. Pugh, D. Hendriks, C. F. Guerra, D. J. Evans, F. M. Bickelhaupt, R. A. Layfield, *J. Am. Chem. Soc.* **2013**, *135*, 13338 – 13341.

[7] a) Y. Ohki, T. Hatanaka, K. Tatsumi, *J. Am. Chem. Soc.* **2008**, *130*, 17174 – 17186; b) T. Hatanaka, Y. Ohki, K. Tatsumi, *Chem. Asian J.* **2010**, *5*, 1657 – 1666; c) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* **2012**, *31*, 4474; d) C. Grohmann, T. Hashimoto, R. Frölich, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* **2012**, *31*, 8047 – 8050; e) T. Hatanaka, Y. Ohki, K. Tatsumi, *Eur. J. Inorg. Chem.* **2013**, 3966 – 3971.

[8] K. L. Cunningham, D. R. McMillin, *Polyhedron* **1996**, *15*, 1673 – 1675.

[9] a) T. J. Colacot, *Chem. Rev.* **2003**, *103*, 3101 – 3118; b) P. Barbaro, C. Bianchini, G. Giambastiani, S. L. Parisel, *Coord. Chem. Rev.* **2004**, *248*, 2131 – 2150; c) R. C. T. Atkinson, V. C. Gibson, N. J. Long, *Chem. Soc. Rev.* **2004**, *33*, 313 – 328; d) R. G. Arrayás, J. Adrio, J. C. Carretero, *Angew. Chem.* **2006**, *118*, 7836 – 7878; *Angew. Chem. Int. Ed.* **2006**, *45*, 7674 – 7715.

[10] B. Bildstein, M. Malaum, H. Kopacka, M. Fontani, P. Zanello, *Inorg. Chim. Acta* **2000**, *300 – 302*, 16 – 22.

[11] a) V. G. Andrianov, V. P. Martynov, Y. T. Struchkov, *Zh. Strukt. Khim.* **1971**, *12*, 866 – 874; b) J. L. Davidson, M. Green, F. G. A. Stone, A. J. Welch, *J. Chem. Soc. Dalton Trans.* **1976**, 2044 – 2053; c) F. McArdle, A. G. Ryder, D. Cunnigham, *Organometallics* **1997**, *16*, 2638 – 2645.

[12] a) N. Kuhn, M. Goehner, M. Steimann, *Z. Naturforsch. B* **2002**, *57*, 631 – 636; b) N. Kuhn, A. Al-Sheikh, S. Schwarz, M. Steimann, *Z. Naturforsch. B* **2005**, *60*, 398 – 402; c) N. Kuhn, A. Kuhn, E. Niquet, M. Steimann, K. Sweidan, *Z. Naturforsch. B* **2005**, *60*, 924 – 928.

[13] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169 – 1204, and references therein.