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## COMMUNICATION

# Straightforward synthesis of iron cyclopentadienone *N*-heterocyclic carbene complexes

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**Novel iron complexes bearing both cyclopentadienone and *N*-heterocyclic carbene ancillary ligands have been obtained by a straightforward synthesis from Fe<sub>2</sub>(CO)<sub>9</sub>. The preparation represent a rare example of silver transmetalation involving iron. The reaction is general and occurs in the presence of variously functionalized NHC and cyclopentadienones.**

Iron is the most abundant transition metal in Earth's crust; it is cost effective and environmentally benign. Furthermore, its low toxicity is vouched for its involvement in several biological processes that make iron as one of the most important elements in nature.<sup>1</sup> For a long time noble metals such as Pd, Rh, Ir, Ru have dominated the field of homogeneous catalysis and only in the last decade the use of iron complexes in catalysis has witnessed a strong acceleration.<sup>2</sup> In particular iron cyclopentadienone complexes have recently received a special attention due to their easy preparation from simple and cheap materials, air–water stability and, most important, their unique catalytic features arising from the presence of a non-innocent ligand able to trigger powerful redox properties.<sup>3</sup> Furthermore, in addition to the economic benefits, developing iron-based complexes produces an opportunity to access complementary chemoselectivities and discover new reactivity.

One important aspect in coordination chemistry is the control and fine-tuning of electronic and steric properties of the ligand sphere. Good candidates for this job are *N*-heterocyclic carbenes (NHC), universal ligands for coordination compounds and catalysis.<sup>4</sup> NHC ligands are easily prepared and, due to the robust bond formed with most metal centers, are highly resistant toward decomposition. Easy accessibility and

steric/electronic tunability are further important features of NHCs. Indeed, a series of reports in the last few years have shown that, in addition to the intrinsic interest in iron-NHC chemistry, such compounds do have considerable potential for unique and wide-ranging applications including: novel coordination chemistry, homogeneous catalysis, and bio-mimetic chemistry.<sup>5</sup> Developments in homogeneous catalysis involving iron-NHC complexes are represented by cross-coupling Kochi reactions, C–C bond formation reactions, hydrosilylation,<sup>6</sup> allylic alkylation, C–X bond formation (X = B, N, Mg, S), reduction reactions, transfer hydrogenation<sup>7</sup> and cyclization reactions.<sup>1</sup>

In principle by combining NHC and cyclopentadienone ligands on transition metal complexes the properties of both ligands can be exploited allowing the design of novel metal/cyclopentadienone bifunctional catalysts in which steric and electronic properties, solubility and the introduction of substituents suitable for heterogenization can be finely tuned on the NHC ancillary ligand. Furthermore by choosing a proper substituent, the NHC ligand itself could cooperate with the metal as non-innocent species.

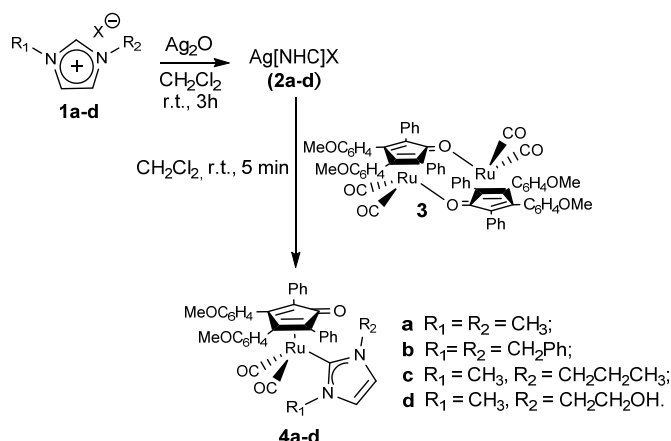
With this aim in mind, a straightforward approach towards Ru(0)-NHC complexes has been recently communicated by our group,<sup>8</sup> based on a dimeric Ru(0) cyclopentadienone dicarbonyl dimer (**3**). Cleavage of **3** in the presence of the silver carbene precursor **2** provided access to a new class of ruthenium complexes (Scheme 1).

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Supplementary Information (ESI) available: experimental details for complexes **5**, **6**, **7a-f**, **8**, **9** and **10a,b,c,e** (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR, ESI-MS, elemental analyses, X-Ray diffraction CCDC: 1416717-1416721).

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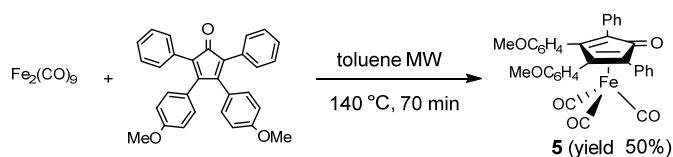


**Scheme 1.** Synthesis of dicarbonyl-cyclopentadienone-N-heterocyclic carbene ruthenium complexes (**4a-d**).

The reaction, clean and quantitative, can be also performed in one pot by generating the silver-NHC complex *in situ*. The same procedure has been successively extended to triazolylidene ligands and the corresponding complexes showed to be active in transfer hydrogenation and in oxidation of alcohol in the presence of additives such as cerium ammonium nitrate (CAN).<sup>9</sup>

In order to expand the scope of this reaction to iron, a cyclopentadienone tricarbonyl iron complex was chosen as precursor. We herein present a novel synthesis of cyclopentadienone NHC complexes suitable for catalytic reactions such as those verified on ruthenium analogues. To the best of our knowledge this is the first report in which iron complexes containing both a cyclopentadienone and a NHC ligand are reported.

Inspired by our previous work on ruthenium,<sup>10</sup> we tried to take advantage of microwave irradiation for the synthesis of the tricarbonyl cyclopentadienone precursor (**5**) with significant reduction of the reaction time. Indeed, after screening different temperatures and times, best reaction conditions have been found at 140 °C, with a reaction time of 70 minutes. Under these conditions a yield of 50% was reached which is identical to the yield reached by the classical protocol (heating under reflux for 18 h).<sup>11</sup>



**Scheme 2.** Microwave assisted synthesis of tricarbonyl-( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**).

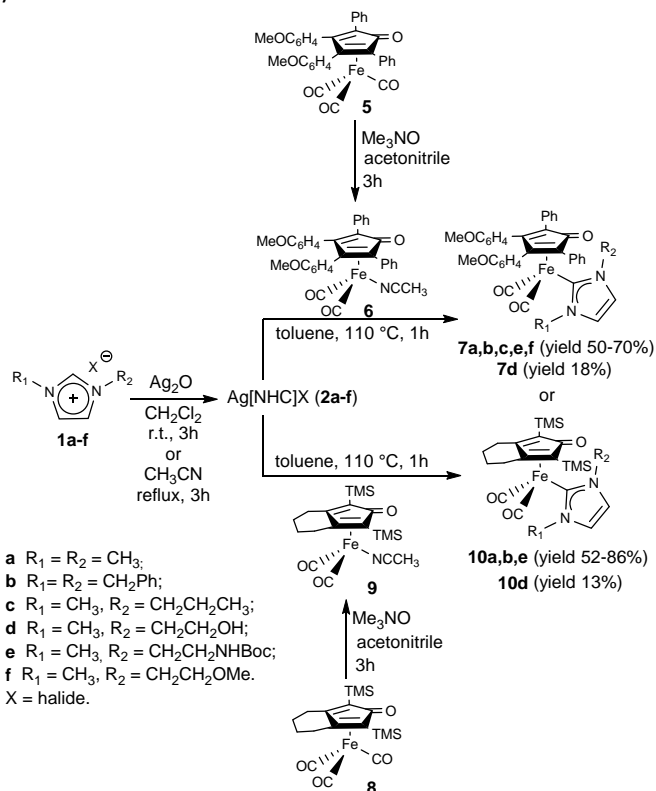
Suitable crystals of **5** have been obtained with the double layer technique (dichloromethane/hexane). The structure of **5** is described in the ESI.

After having optimized the preparation of **5**, one of the terminal carbonyls has been replaced upon reaction with  $\text{Me}_3\text{NO}$  in acetonitrile, with the more labile acetonitrile ligand, leading to the formation of biscarbonyl-acetonitrile( $\eta^4$ -3,4-

bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**6**). Complex **6** has been treated with silver-NHC complexes, obtained *in situ* by reaction of imidazolium salts **1** and  $\text{Ag}_2\text{O}$ .<sup>8</sup> The latter reaction, performed in refluxing toluene, leads to the formation of the desired NHC complexes **7a-f** generally in good or excellent yields (50-80%, Scheme 3). The low yield (18%) observed for **7d** can be probably ascribed to the presence of an -OH group in the NHC side chain which could interact with the C=O group of cyclopentadienone and/or with the metal center with a detrimental influence on transmetalation.

Indeed, indication of an intramolecular hydrogen bond between the cyclopentadienone and -OH group in complex **7d** can be inferred from IR and  $^{13}\text{C}$  NMR spectra. In the IR spectra the low-energy shift of the carbonyl band of **7d** [ $\nu(\text{CO}) = 1576 \text{ cm}^{-1}$ ] compared with those of **7a-7c**, **7e,f** [ $\nu(\text{CO}) = 1584\text{-}1587 \text{ cm}^{-1}$ ] suggests a  $\eta^4$  to an  $\eta^5$  coordination change of cyclopentadienone. Furthermore the  $^{13}\text{C}$ -NMR shift of the C=O signal (**7a-7c**, **7e,f**: 166-167 ppm vs. **7d**: 163 ppm) and the broadness of  $\text{CH}_2$  signals in  $^1\text{H}$ -NMR are in agreement with H-bond formation.

The same behaviour was observed for a similar ruthenium complex for which the H-bond formation was also confirmed by X-Ray diffraction.<sup>8</sup> To further confirm the role of -OH group in conditioning transmetalation to iron complexes the corresponding silver complex of the -OMe functionalized imidazolium salt **1f** has been reacted with **6** affording **7f** in 55% yield.

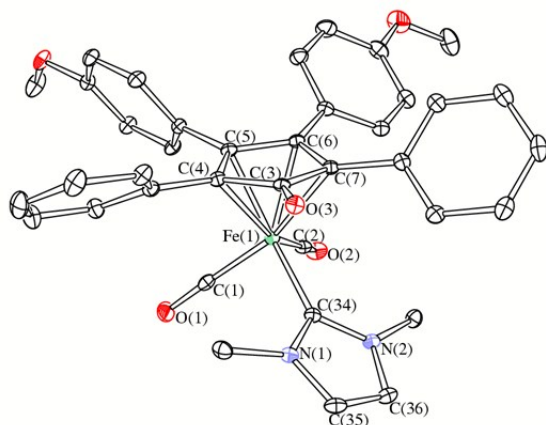


**Scheme 3.** Synthesis of dicarbonyl-cyclopentadienone-N-heterocyclic carbene iron complexes (**7a-e** and **10a,b,d,e**).

The reaction is general with non-bulky NHCs and tolerant of functional groups: in fact it occurs in the presence of a primary alcohol and amide in the lateral chain (**1d,e** to **7d,e**). The synthesis of **7a-f** has been followed by IR spectroscopy observing in all cases a lowering in the CO stretching frequencies (e.g. **7a**:  $\nu(\text{CO}) = 1988, 1930 \text{ cm}^{-1}$  vs. **5**:  $2008, 1954 \text{ cm}^{-1}$ ) due to the strong NHC  $\sigma$  donor properties.  $^{13}\text{C}$ -NMRs show a diagnostic signal for the  $\text{Fe-C}_{\text{carbene}}$  within the range 182–185 ppm and molecular ions of complexes **7a-f** are detectable by ESI-MS. Complexes **7a-f** are air- and moisture-stable both in solid state and in solution and are soluble in the most common organic solvents.

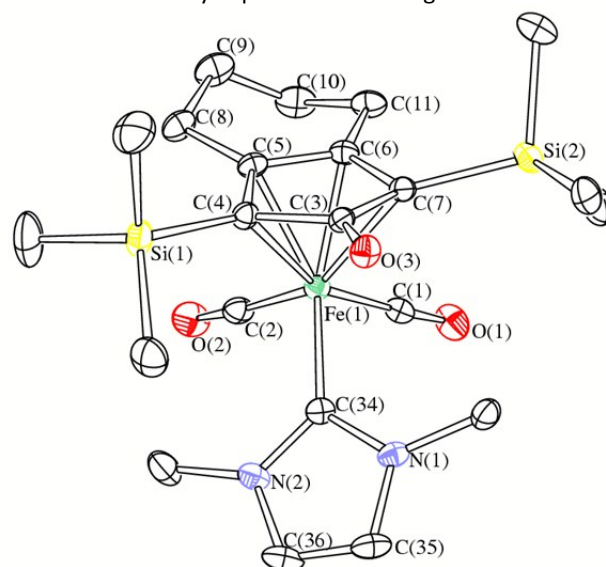
In order to further extent the ligand scope, the Knölker's cyclopentadienone triscarbonyl complex,<sup>12</sup> has been obtained, exploiting microwave irradiation (ESI, Scheme S1). Likewise what previously observed for **5**, the synthesis is by far faster than that reported in the literature affording **8** in good yield (83%). By treating **8** with  $\text{Me}_3\text{NO}$  in  $\text{CH}_3\text{CN}$ , the intermediate **9** has been obtained and employed as precursor for the synthesis of NHC complexes **10** by transmetalation with silver-NHC complexes prepared *in situ* (Scheme 3). Complexes **10a,b,d,e** have been completely characterized (ESI). Noteworthy  $-\text{OH}$  functionalized complex **10d** ( $y = 13 \%$ ) resembles the behavior of the congener **7d** further confirming an influence of the hydroxyl group on the reactivity of these complexes.

Complexes **7a**, **7b** and **7c** and **10a** have been also characterized by X-Ray diffraction studies. The molecular structure of **7a** is reported in Figure 1, whereas those of **7b** and **7c** are given in the ESI (Figures S2 and S3). Their structures are similar to those previously reported for analogous Ru-complexes.<sup>8</sup> In particular, the  $\text{Fe(1)-C(3)}$  distance [ $2.348(3) \text{ \AA}$  in **7a**] is significantly longer than  $\text{Fe(1)-C(4-7)}$  [ $2.053(3)$ – $2.162(3) \text{ \AA}$ , average  $2.118(6) \text{ \AA}$  in **7a**] and  $\text{C(3)-O(3)}$  [ $1.246(4) \text{ \AA}$  in **7a**] is essentially a double bond,<sup>13</sup> in agreement with  $\text{C=O}$  bond, absorptions around  $1585 \text{ cm}^{-1}$  were found in the IR spectra of complexes **7a-f**. The  $\text{Fe(1)-C(34)}$  contact [ $1.980(3) \text{ \AA}$  in **7a**] is in the typical range for the interaction between  $\text{Fe(0)}$  and a *N*-heterocyclic carbene.<sup>7a</sup>



**Figure 1.** ORTEP drawing of **7a**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ):  $\text{Fe(1)-C(1)}$   $1.754(3)$ ,  $\text{Fe(1)-C(2)}$   $1.765(3)$ ,  $\text{Fe(1)-C(3)}$   $2.348(3)$ ,  $\text{Fe(1)-C(4)}$   $2.162(3)$ ,  $\text{Fe(1)-C(5)}$   $2.053(3)$ ,  $\text{Fe(1)-C(6)}$   $2.099(3)$ ,  $\text{Fe(1)-C(7)}$   $2.156(3)$ ,  $\text{Fe(1)-C(34)}$   $1.980(3)$ ,  $\text{C(3)-O(3)}$   $1.246(4)$ .

The structure of **10a** is similar to **7a** apart from the different substituents on the cyclopentadienone ring.



**Figure 2.** ORTEP drawing of **10a**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ):  $\text{Fe(1)-C(1)}$   $1.747(3)$ ,  $\text{Fe(1)-C(2)}$   $1.754(3)$ ,  $\text{Fe(1)-C(3)}$   $2.359(2)$ ,  $\text{Fe(1)-C(4)}$   $2.153(3)$ ,  $\text{Fe(1)-C(5)}$   $2.091(3)$ ,  $\text{Fe(1)-C(6)}$   $2.067(2)$ ,  $\text{Fe(1)-C(7)}$   $2.177(2)$ ,  $\text{Fe(1)-C(34)}$   $1.996(3)$ ,  $\text{C(3)-O(3)}$   $1.250(3)$ .

The reaction reported in Scheme 3 is one of the rare examples of transmetalation from silver complexes to first row transition metals, such as iron<sup>1,14–17</sup> and the first example in which transmetalation is employed in the synthesis of piano stool complexes. Such complexes were initially obtained upon reaction of diamines with mononuclear ( $[\text{FeCp}(\text{SnPh}_3)(\text{CO})(\text{CS})]$ ) or dinuclear ( $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-C}(\text{SMe}_2)(\text{CN}))^+]$ ) thiocarbonyl complexes.<sup>18</sup> Later on the procedure consisting in the deprotonation of the imidazolium salts followed by reaction of the resulting carbene with an iron halide precursor (e.g.  $[\text{FeCp}(\text{CO})_2\text{I}]$ ) was introduced.<sup>19</sup> Finally, an elegant synthetic approach, was described by Royo et al.<sup>20</sup> based on the formation of bidentate cyclopentadienyl functionalized iron(II)-NHC by direct reaction of the imidazolium proligands with  $\text{Fe}_3(\text{CO})_{12}$ .

The disadvantage of the deprotonation method is that the generation of a free, often unstable, carbene intermediate requires special bases, rigorous air and moisture-free conditions and generally deliver the corresponding complexes with scarcely reproducible yields. On the other hand, transmetalation with silver complexes does not require any particular reaction conditions and can be applied to a broad range of imidazolium salts bearing various *N*-substituents.

In our case transmetalation might be favored by the presence of the non-innocent cyclopentadienone ligand, which can interact with silver<sup>8</sup> and labilize the silver-carbene bond. The valence of the iron center might also have an influence on the reactivity, as suggested by the related complex  $[\text{FeCp}(\text{CO})_2(\text{CH}_3\text{CN})]\text{BF}_4$ , obtained reacting  $[\text{FeCp}(\text{CO})_2]_2$  with  $\text{AgBF}_4$ , that does not undergo transmetalation with silver-NHC complexes. Furthermore, a possible role of the NHCs donor



properties in addition to steric effects should not be excluded (complex **6** is unreactive towards hindered silver-NHC such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride). Indeed, NHCs with bulky substituents generally display better donor properties, as evaluated by TEP values (Tolman Electronic Parameters). A combination of these steric and electronic effects might increase both stability and inertness of the silver complexes intermediates and consequently disfavor carbene transmetalation.<sup>22</sup>

In summary a very efficient and rapid synthetic route for obtaining a new class of Fe(0) complexes, which contain both *N*-heterocyclic carbenes and cyclopentadienone ligands has been developed. The synthetic approach takes advantage of transmetalation from silver-NHC complexes, which is a method rarely exploited in the case of iron-NHC complexes. Transmetalation could be favored either by non-innocent cyclopentadienone ligand or by iron valence. Donor and steric properties of NHCs can also play a role. The novel synthetic method for the preparation of complexes of type **7** and **10** is general and pave the way for future developments in iron mediated redox homogeneous catalysis.

## Notes and references

- K. Riener, S. Haslinger, A. Raba, M. P. Hogerl, M. Cokoja, W. A. Herrmann and F. E. Kuhn, *Chem. Rev.*, 2014, **114**, 5215.
- (a) C. Bolm, J. Legros, J. Le Paih, and L. Zani, *Chem. Rev.* 2004, **104**, 6217; (b) B. D. Sherry and A. Fürstner, *Acc. Chem. Res.*, 2008, **41**, 1500; (c) A. Correa, O. Garcia Mancheño and C. Bolm, *Chem. Soc. Rev.*, 2008, **37**, 1108; (d) S. Gaillard and J.-L. Renaud, *ChemSusChem*, 2008, **1**, 505; (e) S. Enthaler, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2008, **47**, 3317; (f) W. M. Czaplik, M. Mayer, J. Cvengroš and A. J. von Wangelin, *ChemSusChem*, 2009, **2**, 396; (g) R. H. Morris, *Chem. Soc. Rev.*, 2009, **38**, 2282; (h) A. Fürstner, *Angew. Chem., Int. Ed.*, 2009, **48**, 1364; (i) B. A. F. Le Bailly and S. P. Thomas, *RSC Adv.*, 2011, **1**, 1435; (j) K. Junge, K. Schröder and M. Beller, *Chem. Commun.*, 2011, **47**, 4849; (m) K. Gopalaiah, *Chem. Rev.*, 2013, **113**, 3248.
- (a) A. Quintard and J. Rodriguez, *Angew. Chem. Int. Ed.*, 2014, **53**, 4044; (b) C. P. Casey and H. Guan, *J. Am. Chem. Soc.* 2007, **129**, 5816; (c) S. Fleischer, S. S. Zhou, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 5120; (d) C. P. Casey and H. Guan, *Organometallics*, 2012, **31**, 2631; (e) C. P. Casey and H. Guan, *J. Am. Chem. Soc.*, 2009, **131**, 2499.
- For selected reviews on NHC: (a) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (b) R. H. Crabtree, *J. Organomet. Chem.*, 2005, **690**, 5451; (c) S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, 2007, **251**, 874; (d) O. Kühl, *Chem. Soc. Rev.*, 2007, **36**, 592; (e) S. T. Liddle, I. S. Edworthy and P. L. Arnold, *Chem. Soc. Rev.*, 2007, **36**, 1732; (f) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (g) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (h) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687; (i) O. Kühl, *Coord. Chem. Rev.*, 2009, **253**, 2481; (j) L. A. Schaper, S. J. Hock, W. A. Herrmann and F. E. Kuhn, *Angew. Chem., Int. Ed.*, 2013, **52**, 270; (m) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723; (n) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485; (o) S. P. Nolan, *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*, Wiley VCH, 2014.
- M. J. Ingleson and R. A. Layfield, *Chem. Commun.*, 2012, **48**, 3579.
- (a) D. Bezier, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19; (b) S. Warratz, L. Postigo, and B. Royo, *Organometallics*, 2013, **32**, 893; (c) J. M. S. Cardoso, A. Fernandes, B. de P. Cardoso, M. D. Carvalho, L. P. Ferreira, M. J. Calhorda and B. Royo, *Organometallics*, 2014, **33**, 5670; (d) R. Lopes, J. M. S. Cardoso, L. Postigo and B. Royo, *Catal Lett*, 2013, **143**, 1061; (e) J. M. S. Cardoso, R. Lopes and B. Royo, *J. Organomet. Chem.*, 2015, **775**, 173.
- (a) V. V. K. M. Kandepi, J. M. S. Cardoso, E. Peris, and B. Royo, *Organometallics*, 2010, **29**, 2777; (b) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tsumumi and F. Glorius, *Organometallics*, 2012, **31**, 4474.
- C. Cesari, S. Conti, S. Zacchini, V. Zanotti, M. C. Cassani and R. Mazzoni, *Dalton Trans.*, 2014, **43**, 17240.
- C. Cesari, R. Mazzoni, H. Müller-Bunz and M. Albrecht, *J. Organomet. Chem.*, 2015, **793**, 256.
- (a) C. Cesari, L. Sambri, S. Zacchini, V. Zanotti and R. Mazzoni, *Organometallics*, 2014, **33**, 2814;
- S. Moulin, H. Dentel, A. Pagnoux-Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J.-F. Lohier, and J.-L. Renaud, *Chem. Eur. J.*, 2013, **19**, 17881.
- (a) H.-J. Knölker, J. Heber and C. H. Mahler, *Synlett*, 1992, 1002; (b) H.-J. Knölker and J. Heber, *Synlett*, 1993, 924; (c) H.-J. Knölker, E. Baum and R. Klaus, *Tetrahedron Lett.*, 1995, **36**, 7647; (d) H.-J. Knölker, H. Goesmann and R. Klaus, *Angew. Chem. Int. Ed.*, 1999, **38**, 702.
- H. Allen, O. Kennard, D. G. Watson, L. Brammer A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, 1987, **2**, S1-S19.
- Require electrochemical conditions: B. Liu, Y. Zhang, D. Xu and W. Chen, *Chem. Commun.*, 2011, **47**, 2883.
- Polydentate ligands: B. Liu, Q. Xia and W. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 5513. Such findings were later questioned in ref. 17
- Polydentate ligands: Z. Lu, S. A. Cramer and D. M. Jenkins, *Chem. Sci.*, 2012, **3**, 3081.
- A. Raba, M. Cokoja, S. Ewald, K. Riener, E. Herdtweck, A. Pothig, W. A. Herrmann and F. E. Kuhn, *Organometallics*, 2012, **31**, 2793.
- Dinuclear piano stool iron complexes: V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V. G. Albano, M. Monari and F. Prestopino, *Organometallics*, 1995, **14**, 5232; first mononuclear piano stool complex: M. H. Quick and R. J. Angelici, *J. Organomet. Chem.*, 1978, **160**, 231.
- (a) P. Buchgraber, L. Toupet, and V. Guerchais, *Organometallics*, 2003, **22**, 5144; (b) L. Mercs, G. Labat, A. Neels, A. Ehlers, and M. Albrecht, *Organometallics*, 2006, **25**, 5648; (c) L. Mercs, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Dalton Trans.*, 2009, 7168.
- J. M. S. Cardoso and B. Royo, *Chem. Commun.*, 2012, **48**, 4944.
- B. L. Conley, M. K. Pennington-Boggio, E. Boz, and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294.
- (a) D. G. Gusev, *Organometallics*, 2009, **28**, 6458; (b) R. Tonner and G. Frenking, *Organometallics*, 2009, **28**, 3901; (c) A. Fürstner, M. Alcarazo, H. Krause and C. W. Lehmann, *J. Am. Chem. Soc.*, 2007, **129**, 12676.

**Graphical abstract**

Silver-NHC transmetallation to iron complexes lead to a novel class of easily prepared iron NHC complexes.

