# ORGANOMETALLICS

# Synthesis of Iron(0) Complexes Bearing Protic NHC Ligands: Synthesis and Catalytic Activity

Christoph Mühlen,<sup>†</sup> Jenny Linde,<sup>†</sup> Lena Rakers,<sup>‡</sup> Tristan T. Y. Tan,<sup>†</sup> Florian Kampert,<sup>†</sup> Frank Glorius,\*<sup>,‡</sup><sup>®</sup> and F. Ekkehardt Hahn\*<sup>,†</sup><sup>®</sup>

<sup>†</sup>Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28-30, 48149 Münster, Germany

<sup>‡</sup>Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

#### **S** Supporting Information

ABSTRACT: Preparation of iron(0) pNHC complexes by oxidative addition of N-phosphine-tethered azoles to  $[Fe_3(CO)_{12}]$  is described. Phosphine-tethered imidazoles 1 and 2 react with  $[Fe_3(CO)_{12}]$  to give mononuclear iron(0) complexes of type  $[Fe(CO)_3(C_{pNHC}^PR_2)]$  ([5]: R = Ph; [6]: R = Cy) bearing a  $C_{pNHC}$  phosphine chelate ligand. In addition, the phosphine-tethered imidazolium salt 4-Br was C2-deprotonated and reacted with  $[Fe(bda)(CO)_3]$  (bda = benzylidene acetone) to give the iron(0) chelate complex  $[Fe(\eta^2-4)(CO)_3]$  (7). Complexes [5], [6], and [7] act as moderate to good catalysts in the hydrogenation of acetophenone with elemental hydrogen. The N-H group of the protic NHC ligands in [5] and **[6]** is insignificant to the catalytic outcome.



I solation of the first stable N-heterocyclic carbene (NHC) by Arduengo et al.<sup>1</sup> in 1991 initiated intense research on NHCs. Over the last two decades, NHCs and their metal complexes have gained attention, and various types of NHCs are known today.<sup>2</sup> Due to their useful electronic and steric properties,<sup>3</sup> NHCs have found numerous applications as ligands in catalytically active complexes,<sup>4</sup> as organocatalysts<sup>5</sup> in different fields of coordination chemistry,<sup>6</sup> or as building blocks for metalosupramolecular complexes.

NHC complexes of transition metals, including iron complexes, are generally synthesized either by the Ag<sub>2</sub>O method,<sup>8</sup> by the in situ deprotonation of azolium cations followed by coordination of the NHC ligand to a metal center<sup>2a,9a-c</sup> or by cleavage of entetramines and coordination of the free NHC ligand to the metal center.<sup>9d-f</sup> These methods lead to classical NHC complexes bearing NR,NR-substituted NHC ligands.

Complexes bearing protic NHC ligands (NH,NR-NHC ligands, pNHCs) were initially obtained by the templatecontrolled cyclization of  $\beta$ -functionalized isocyanides.<sup>10</sup> This methodology is significantly influenced by the template metal<sup>10a,d</sup> and therefore not generally applicable. More recently, it was found that neutral 2-halogenoazoles react with low-valent metals in an oxidative addition to give C2metalated intermediates, which upon subsequent protonation yield complexes with pNHC ligands.11 For the challenging oxidative addition of the C2-H bond of neutral azoles, a donor function tethered to one of the ring nitrogen atoms is required. Such azoles are assumed to coordinate first with the N1-tethered donor function followed by the oxidative addition

of the C2-H bond. The hydrido complex generated this way is often not stable and reductively eliminates a proton which protonates the ring-nitrogen atom of the azolato ring, leading to complexes with protic NH,NR-NHC (pNHC) ligands. Such pNHC^donor chelate complexes have been described for Ru,<sup>12</sup> Rh,<sup>13</sup> and Ir.<sup>14</sup> The N–H unit of the NH,NR-NHC donor can be deprotonated<sup>12-14</sup> and has been shown to function as a molecular recognition unit.15

Iron NHC complexes have received attention due to the low cost of iron and its nontoxic and environmentally benign properties. Apart from iron(II) and iron(III) NHC complexes,<sup>91</sup> only a few examples for iron(0) NHC complexes have been reported. The known Fe<sup>0</sup> complexes were obtained by treatment of  $[Fe(CO)_5]$  with a free  $NHC^{16}$  in the presence of an Fe<sup>I</sup> catalyst or by reaction of imidazolium halides with  $[Fe_3(CO)_{12}]^{17}$  proceeding via a currently unknown mechanism. All known Fe<sup>0</sup> NHC complexes bear classical NR,NR-NHC ligands.

We became interested in the synthesis of the currently unknown iron(0) complexes bearing bidentate pNHC^donor chelate ligands. The stability of such complexes might benefit from the chelating coordination while they feature an N-H recognition unit. Herein, we describe the preparation of two new iron(0) complexes bearing imidazole-phosphine-derived pNHC^PR<sub>2</sub> chelate ligands. In addition, the iron(0) chelate complex bearing a phosphine-tethered classical NR,NR-NHC

Received: April 23, 2019

ligand is described, and the catalytic activity of all three complexes in the hydrogenation of acetophenone is discussed.

Neutral proligands N-[2-(diphenylphosphino)ethyl]imidazole 1 and N-[2-(dicyclohexylphosphino)ethyl]imidazole 2 (Scheme 1) were prepared from 1-vinylimidazole<sup>18</sup> following

Scheme 1. Synthesis of Iron(0) pNHC^PR<sub>2</sub> Chelate Complexes [5] and [6]



published procedures (see the Supporting Information for experimental details).<sup>13,14</sup> Alternatively, N3-alkylation of 1-vinylimidazole followed by reaction with diphenyl phosphine/KOtBu yielded the phosphine-tethered imidazolium salt 4-Br (Scheme 2; see the Supporting Information for experimental details).



The phosphine-substituted imidazoles 1 and 2 react with 1/3 equiv of  $[Fe_3(CO)_{12}]$  in refluxing THF over 2 h under cleavage of the trinuclear iron cluster and formation of the mononuclear iron(0) complexes [5] and [6] bearing bidentate pNHC^phosphine chelate ligands. Standard workup procedures yielded [5] and [6] as reddish brown, air-sensitive solids in reproducibly low yields of 28 and 31%, respectively (Scheme 1).

Various reaction conditions such as changing the solvent, the reaction temperature, the reaction time, or the addition of Me<sub>3</sub>NO were tested to improve the yield of [5] and [6], but no improvement was observed. Based on previous studies,<sup>12–14</sup> we assume that the chelate complexes formed by an initial coordination of the phosphine donors of 1 and 2 to the iron atoms of  $[Fe_3(CO)_{12}]$ . In the absence of a base for the imidazole C2-deprotonation, the next step is presumably the loss of a CO ligand followed by the oxidative addition of the C2–H bond to the iron(0) center. Reductive elimination of a proton from the Fe<sup>II</sup> center with concurrent protonation of the azolato-ring nitrogen atom leads to the complexes [5] and [6]. This reaction sequence has been observed multiple times for the formation of pNHC complexes from donor-functionalized azoles.<sup>12–14</sup>

Analyzing the reaction mixtures containing complexes [5] and [6], we noted by NMR spectroscopy the presence of a large amount (up to 60%) of a side product. Upon workup of the reaction mixture leading to [6], the side product was isolated by crystallization and identified as the  $[Fe(CO)_4(PR_2-imidazole)]$  complex [6a]. We observed that complex [6a] once formed did not react further to give [6], thus leading to the conclusion that it is a side product and not an intermediate

in the reaction. Complex [6a] was characterized by an X-ray diffraction study (see the Supporting Information for a molecular plot of [6a]).

Formation of the diamagnetic chelate complexes [5] and [6] was confirmed by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, mass spectrometry, IR spectroscopy, and X-ray diffraction studies (see the Supporting Information). Small amounts of paramagnetic impurities were previously removed by filtration of the reaction solution. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra indicate coordination of the phosphorus donor. Whereas the proligands exhibit resonances at  $\delta$  -21.9 ppm (1) and  $\delta$  -9.4 ppm (2), the equivalent resonances for complexes [5] and [6] were recorded at  $\delta$  51.3 and  $\delta$  60.7 ppm, respectively. In addition, characteristic resonances at  $\delta$ 185.8 (d,  ${}^{2}J_{CP}$  = 30.3 Hz) and  $\delta$  189.0 (d,  ${}^{2}J_{CP}$  = 31.5 Hz) were recorded in the  ${}^{13}C{}^{1}H$  NMR spectra for the carbon atoms of complexes [5] and  $\tilde{[6]}$ . The observation of  ${}^{2}J_{CP}$ coupling for both complexes confirms that the NHC and the phosphine donor are coordinated to the same metal center. The IR spectra of complexes [5] and [6] show the characteristic carbonyl stretching absorptions at  $\nu = 1968$ , 1895, and 1878  $cm^{-1}$  for [5] and at slightly lower wavenumbers at  $\nu = 1963$ , 1882, and 1858 cm<sup>-1</sup> for [6]. This observation is in good agreement with the higher basicity of the dicyclohexyl phosphine donor, resulting in an increased  $\pi$ -backbonding for [6].

The conclusions drawn from the spectroscopic investigations have been confirmed by X-ray diffraction studies with crystals of [5] and [6] $\cdot 0.25$ CH<sub>2</sub>Cl<sub>2</sub> (see the Supporting Information). Molecular plots of [5] and [6] are depicted in Figure 1. The iron centers in [5] and [6] are surrounded in a trigonal-bipyramidal fashion. The pNHC^PR<sub>2</sub> chelate ligand occupies an equatorial (-PR<sub>2</sub>) and an axial (-NHC)



Figure 1. Molecular structures of complex [5] and [6] in [6]. 0.25CH<sub>2</sub>Cl<sub>2</sub> (50% probability ellipsoids; hydrogen atoms except for H3 have been omitted for clarity, and only one of the two essentially identical molecules of [6] in the asymmetric unit is depicted).

coordination site. The axial C2–Fe–C8 angles ([5]: 176.09(5)°, [6]: 173.83(8)°) are almost linear with the larger deviation from linearity observed for complex [6] with the bulkier –PCy<sub>2</sub> donor. The Fe–C<sub>NHC</sub> bond length in [5] (Fe–C2 1.9901(11) Å) is slightly longer than that in [6] (Fe–C2 1.978(2) Å).

To evaluate the influence of the N-substituent (H or alkyl) at the NHC ligand on the catalytic properties of iron(0)NHC<sup>^</sup>phosphine complexes, we have prepared proligand 4-Br and complex [7] (Scheme 2; see the Supporting Information). For the synthesis of complex [7], a preparative method different to than that used for the synthesis of [5] and [6] was employed. Imidazolium salt 4-Br was first deprotonated with KHMDS and then reacted with  $[Fe(bda)(CO)_3]$  (bda = benzylideneacetone<sup>19</sup>). Complex [7] bearing a classical phosphine-tethered NHC ligand was isolated as a yellow, airsensitive solid in 63% yield. Formation of complex [7] was confirmed by NMR spectroscopy and mass spectrometry (see the Supporting Information). As seen for complexes [5] and [6], metalation of the proligand 4-Br leads to a significant downfield shift of the phosphorus resonance ( $\delta$  –22.05 ppm in 4-Br,  $\delta$  54.6 ppm in [7]) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum features the characteristic resonance for the C<sub>NHC</sub> carbon atom at  $\delta$  185.4 ppm (d, <sup>2</sup>*J*<sub>CP</sub> = 27.4 Hz), at a chemical shift almost identical to that of [5].

The N–H moiety of complexes [5] and [6] potentially plays an important role in catalytic transformations either via substrate recognition through N–H···substrate hydrogen bonding<sup>15</sup> or as part of a Noyori-type bifunctional catalyst.<sup>20</sup> Therefore, we evaluated the catalytic activity of complexes [5] and [6] in the hydrogenation of acetophenone and compared the results to those obtained with complex [7] (Table 1; also see the Supporting Information).

The catalytic activity of [5] and [6] in the hydrogenation of acetophenone depends on the polarity of the solvent (entries 1-6). Only low yields were observed in *n*-hexane (entries 1) and 2), whereas the use of solvents with higher polarity such as THF (entries 3 and 4) and EtOH (entries 5 and 6) resulted in moderate to good yields, respectively. The complex with the less basic PPh<sub>2</sub> donor [5] always gave yields lower than those of [6] with the PCy<sub>2</sub> donor. Further optimization of the reaction conditions enabled a catalyst loading as low as 2.5 mol % (entries 7 and 8) with consistent yields, whereas a further decrease led to reduced yields (entries 9 and 10). The reaction time could be reduced to 6 h (entry 12). Both the catalyst and the irradiation with UV light proved to be essential for the catalytic process (entries 13-15). When the reaction was performed under argon instead of H<sub>2</sub>, the yield decreased from 97 to 25% (entry 16), indicating that there might be an alternative catalysis pathway that proceeds via transfer hydrogenation instead of direct hydrogenation.

To understand the role of the N–H moiety for the catalytic outcome, the complex bearing the N,N'-dialkylated NHC [7] was also tested as a catalyst for the hydrogenation of acetophenone. No difference in yield was observed for complexes 7 and 5 under identical conditions (compare entry 17 to entry 5). This indicates that the N–H moiety is not involved in the hydrogen transfer process. We propose the following catalytic cycle (Scheme 3). First, the iron(0) complexes have to be activated by UV light, removing one CO ligand. Hydrogen is then oxidatively added to the iron(0) center, resulting in an iron(II) dihydride complex.<sup>21</sup> The next step is the hydride transfer from the catalyst to the substrate,

Table 1. Selected Results of the Catalytic Hydrogenation of Acetophenone with Iron(0) Complexes<sup>*a*</sup>

	cat., H <sub>2</sub>	cat., H <sub>2</sub> (1 bar), KOtBu (11 mol%) solvent, RT, UV-light		
	s			
entry	catalyst	mol %	solvent	yield (%) <sup>b</sup>
1	[5]	10	<i>n</i> -hexane	0
2	[6]	10	<i>n</i> -hexane	10
3	[5]	10	THF	12
4	[6]	10	THF	61
5	[5]	10	EtOH	46
6	[6]	10	EtOH	97
7	[6]	5	EtOH	97
8	[6]	2.5	EtOH	97
9	[6]	1	EtOH	52
10	[6]	0.5	EtOH	33
11 <sup>c</sup>	[6]	10	EtOH	36
12 <sup>d</sup>	[6]	10	EtOH	97
13	none		EtOH	0
14 <sup>e</sup>	[6]	10	EtOH	0
15 <sup>f</sup>	[6]	10	EtOH	0
16 <sup>g</sup>	[6]	10	EtOH	25
17	[7]	10	EtOH	49

<sup>*a*</sup>General conditions: acetophenone (0.2 mmol), iron catalyst, KOtBu (11 mol %), solvent (1 mL), H<sub>2</sub> (1 bar), 25 °C, UV light, 24 h. <sup>*b*</sup>Yields were determined by GC-FID analysis using mesitylene (17  $\mu$ L, 0.2 mmol, 1 equiv) as internal standard. <sup>*c*</sup>Reaction time 3 h. <sup>*d*</sup>Reaction time 6 h. <sup>*e*</sup>No UV light. <sup>*f*</sup>No UV light and addition of Me<sub>3</sub>NO·2H<sub>2</sub>O (1.4 mg, 0.013 mmol, 0.11 equiv). <sup>*g*</sup>Argon atmosphere instead of H<sub>2</sub>.

Scheme 3. Proposed Catalytic Cycle for the Hydrogenation of Acetophenone with Catalysts [5]-[7]



which explains the observed solvent dependency as this is facilitated in more polar solvents.<sup>22</sup> The second hydride is then reductively eliminated, protonating the substrate to 1-phenyl-ethanol and generating back the active four-coordinate iron(0) catalyst.

We have described the reaction of phosphine-functionalized imidazoles with  $[Fe_3(CO)_{12})]$  to give, most likely by an oxidative addition/reductive elimination process, iron(0) complexes [5] and [6] bearing a pNHC^phosphine chelate ligand. The complexes exhibit a good catalytic activity in the direct hydrogenation of acetophenone with molecular hydrogen. However, the N–H moiety of the pNHC ligands has no significance for the catalytic outcome, as was shown in control

experiments. We propose that the catalytic reaction proceeds via the oxidative addition of  $H_2$  to the iron(0) center and successive hydride transfer from the resulting iron(II) dihydride complex to the substrate.

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00260.

Description of experimental procedures and NMR spectra for all compounds (PDF)

#### Accession Codes

CCDC 1901742–1901744 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION

#### Corresponding Authors

\*E-mail: glorius@uni-muenster.de. \*E-mail: fehahn@uni-muenster.de.

# ORCID 0

Tristan T. Y. Tan: 0000-0001-5391-7232 Frank Glorius: 0000-0002-0648-956X F. Ekkehardt Hahn: 0000-0002-2807-7232

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 858 and IRTG 2027) and also thank Tristan Wegner for experimental support during preparation of the revision.

#### REFERENCES

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. J. Am. Chem. Soc. **1991**, 113, 361–363.

(2) (a) Hahn, F. E.; Jahnke, M. C. Heterocyclic Carbenes: Synthesis and Coordination Chemistry. Angew. Chem., Int. Ed. 2008, 47, 3122–3172. (b) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. Beyond Conventional N-Heterocyclic Carbenes: Abnormal, Remote, and Other Classes of NHC Ligands with Reduced Heteroatom Stabilization. Chem. Rev. 2009, 109, 3445–3478. (c) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable Cyclic Carbenes and Related Species beyond Diaminocarbenes. Angew. Chem., Int. Ed. 2010, 49, 8810–8849. (d) Dröge, T.; Glorius, F. The Measure of All Rings – N-Heterocyclic Carbenes. Angew. Chem., Int. Ed. 2010, 49, 6952. (e) Kuwata, S.; Hahn, F. E. Complexes Bearing Protic N-Heterocyclic Carbenes. Chem. Rev. 2018, 118, 9642–9677.

(3) (a) Nelson, D. J.; Nolan, S. P. Quantifying and understanding the electronic properties of N-heterocyclic carbenes. *Chem. Soc. Rev.* **2013**, *42*, 6723–6753. (b) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimentla Determination. *Chem. Rev.* **2018**, *118*, 9457–9492.

(4) (a) Würtz, S.; Glorius, F. Surveying Sterically Demanding N-Heterocyclic Carbene Ligands with Restricted Flexibility for Palladium-catalyzed Cross-Coupling Reactions. *Acc. Chem. Res.* **2008**, *41*, 1523–1533. (b) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612–3676. (c) Poyatos, M.; Mata, J. A.; Peris, E. Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications. *Chem. Rev.* 2009, 109, 3677–3707. (d) Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* 2018, 118, 9988–10031.

(5) Grossmann, A.; Enders, D. N-Heterocyclic Carbene Catalyzed Domino Reactions. *Angew. Chem., Int. Ed.* **2012**, *51*, 314–325.

(6) (a) Arduengo, A. J., III; Bertrand, G. Carbenes Introduction. *Chem. Rev.* 2009, 109, 3209–3210. (b) Hahn, F. E. Introduction to themed issue on N-heterocyclic carbenes. *Dalton Trans* 2009, 6893.
(c) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* 2014, 510, 485–496.
(d) Hahn, F. E. Introduction: Carbene Chemistry. *Chem. Rev.* 2018, 118, 9455–9456.

(7) (a) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. A Nickel(II)-Cornered Molecular Rectangle with Biscarbene and 4,4'-Bipyridine Bridging Groups. Organometallics 2008, 27, 6408-6410. (b) Rit, A.; Pape, T.; Hahn, F. E. Self Assembly of Molecular Cylinders from Polycarbene Ligands and Ag<sup>I</sup> and Au<sup>I</sup>. J. Am. Chem. Soc. 2010, 132, 4572-4573. (c) Conrady, F. M.; Fröhlich, R.; Schulte to Brinke, C.; Pape, T.; Hahn, F. E. Stepwise Formation of a Molecular Square with Bridging NH,O-Substituted Dicarbene Building Blocks. J. Am. Chem. Soc. 2011, 133, 11496-11499. (d) Schmidtendorf, M.; Pape, T.; Hahn, F. E. Stepwise Preparation of a Molecular Square from NR,NRand NH,O-Substituted Dicarbene Building Blocks. Angew. Chem., Int. Ed. 2012, 51, 2195-2198. (e) Sinha, N.; Roelfes, F.; Hepp, A.; Mejuto, C.; Peris, E.; Hahn, F. E. Synthesis of Nanometer-Sized Cylinder-Like Structures from a 1,3,5-Triphenylbenzene-Bridged Tris-NHC Ligand and Ag<sup>I</sup>, Au<sup>I</sup>, and Cu<sup>I</sup>. Organometallics 2014, 33, 6898-6904. (f) Sinha, N.; Hahn, F. E. Metallosupramolecular Architectures Obtained from Poly-N-heterocyclic Carbene Ligands. Acc. Chem. Res. 2017, 50, 2167-2184. (g) Gan, M.-M.; Liu, J.-Q.; Zhang, L.; Wang, Y.-Y.; Hahn, F. E.; Han, Y.-F. Preparation and Post-Assembly Modification of Metallosupramolecular Assemblies from Poly(N-Heterocyclic Carbene) Ligands. Chem. Rev. 2018, 118, 9587-9641. (8) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. Coinage Metal-N-Heterocyclic Carbene Complexes. Chem. Rev. 2009, 109, 3561-3598.

(9) (a) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. N-Heterocyclic Pincer Dicarbene Complexs of Iron(II): C-2 and C-5 Metalated Carbenes on the Same Metal Center. Organometallics 2004, 23, 166-168. (b) Meyer, S.; Orben, C. M.; Demeshko, S.; Dechert, S.; Meyer, F. Synthesis and Characterization of Di- and Tetracarbene Iron(II) Complexes with Chelating N-Heterocyclic Carbene Ligands and Their Application in Aryl Grignard-Alkyl Halide Cross-Coupling. Organometallics 2011, 30, 6692-6702. (c) Hashimoto, T.; Urban, S.; Hoshino, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. Synthesis of Bis(N-heterocyclic carbene) Complexes of Iron(II) and Their Application in Hydrosilylation and Transfer Hydrogenation. Organometallics 2012, 31, 4474-4479. (d) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. Evidence for an Equilibrium between an N-heterocyclic Carbene and Its Dimer in Solution. Angew. Chem., Int. Ed. 2000, 39, 541-544. (e) Lappert, M. F. Contributions to the chemistry of carbenemetal chemistry. J. Organomet. Chem. 2005, 690, 5467-5473. (f) For a review on iron NHC complexes, see: Riener, K.; Haslinger, S.; Raba, A.; Högerl, M. P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. Chemistry of Iron N-Heterocyclic Carbene Complexes: Syntheses, Structures, Reactivities, and Catalytic Applications. Chem. Rev. 2014, 114, 5215-5272.

(10) (a) For a review on the template-controlled cyclization of  $\beta$ -functionalized isocyanides, see: Tamm, M.; Hahn, F. E. Reactions of  $\beta$ -functional phenyl isocyanides. *Coord. Chem. Rev.* **1999**, *182*, 175–209. (b) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P. Template Synthesis of Benzannulated N-Heterocyclic Carbene Ligands. *Chem. - Eur. J.* **2003**, *9*, 704–712. (c) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Le Van, D. Template Synthesis of a Coordinated Tetracarbene Ligand with Crown Ether Topology. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759–3763. (d) Dumke, A. C.; Pape, T.; Kösters, J.; Feldmann, K.-O.; Schulte to

Brinke, C.; Hahn, F. E. Metal-Template-Controlled Stabilization of  $\beta$ -Functionalized Isocyanides. *Organometallics* **2013**, *32*, 289–299.

(11) (a) Kösterke, T.; Pape, T.; Hahn, F. E. Synthesis of NHC Complexes by Oxidative Addition of 2-Chloro-N-methylbenzimidazole. J. Am. Chem. Soc. 2011, 133, 2112-2115. (b) Kösterke, T.; Pape, T.; Hahn, F. E. Synthesis of complexes bearing NH,NMe-substituted NHCs by oxidative addition of 2-halogenato-N-methylbenzimidazoles to Ni<sup>0</sup>. Chem. Commun. 2011, 47, 10773-10775. (c) Kösterke, T.; Kösters, J.; Würthwein, E.-U.; Mück-Lichtenfeld, C.; Schulte to Brinke, C.; Lahoz, F.; Hahn, F. E. Synthesis of Complexes Containing an Anionic NHC Ligand with an Unsubstituted Ring-Nitrogen Atom. Chem. - Eur. J. 2012, 18, 14594-14598. (d) Brackemeyer, D.; Hervé, A.; Schulte to Brinke, C.; Jahnke, M. C.; Hahn, F. E. A Versatile Methodology for the Regioselective C8-Metalation of Purine Bases. J. Am. Chem. Soc. 2014, 136, 7841-7844. (e) Das, R.; Daniliuc, C. G.; Hahn, F. E. Oxidative Addition of 2-Halogenoazoles - Direct Synthesis of Palladium(II) Complexes Bearing Protic NH,NH-Functionalized NHC Ligands. Angew. Chem., Int. Ed. 2014, 53, 1163-1166. (f) For a review on the synthesis of complexes bearing pNHC ligands, see: Jahnke, M. C.; Hahn, F. E. Complexes Bearing Protic N-Heterocyclic Carbenes: Synthesis and Applications. Chem. Lett. 2015, 44, 226-237.

(12) (a) Araki, K.; Kuwata, S.; Ikariya, T. Isolation and Interconversion or Protic N-Heterocyclic Carbene and Imidazolyl Complexes: Application to Catalytic Dehydrative Condensation of *N*-(2-Pyridyl)benzimidazole and Allyl Alcohol. *Organometallics* **2008**, *27*, 2176–2178. (b) Hahn, F. E.; Naziruddin, A. R.; Hepp, A.; Pape, T. Synthesis, Characterization, and H-Bonding Abilities of Ruthenium-(II) Complexes Bearing NR,NH-Carbene/Phosphine Ligands. *Organometallics* **2010**, *29*, 5283–5288. (c) Flowers, S. E.; Cossairt, B. M. Mono- and Dimetalation of a Tridentate Bisimidazole-Phosphine Ligand. *Organometallics* **2014**, *33*, 4341–4344.

(13) Naziruddin, A. R.; Hepp, A.; Pape, T.; Hahn, F. E. Synthesis of Rhodium(I) Complexes Bearing Bidentate NH,NR-NHC/Phosphine Ligands. *Organometallics* **2011**, *30*, 5859–5866.

(14) (a) Miranda-Soto, V.; Grotjahn, D. B.; DiPasquale, A. G.; Rheingold, A. L. Imidazol-2-yl Complexes of Cp\*Ir as Bifunctional Ambidentate Reactands. J. Am. Chem. Soc. 2008, 130, 13200-13201.
(b) Cepa, S.; Schulte to Brinke, C.; Roelfes, F.; Hahn, F. E. Hydrogen Activation by an Iridium(III) Complex Bearing a Bidentate Protic NH,NR-NHC^Phosphine Ligand. Organometallics 2015, 34, 5454-5460.

(15) (a) Meier, N.; Hahn, F. E.; Pape, T.; Siering, C.; Waldvogel, S. R. Molecular Recognition Utilizing Complexes with NH,NR-Stabilized Carbene Ligands. *Eur. J. Inorg. Chem.* **2007**, 1210–1214.

(16) Li, H.; Misal Castro, L. C.; Zheng, J.; Roisnel, T.; Dorcet, V.; Sortais, J.-B.; Darcel, C. Selective Reduction of Esters to Aldehydes under the Catalysis of Well-Defined NHC-Iron Complexes. *Angew. Chem.*, *Int. Ed.* **2013**, *52*, 8045–8049.

(17) Warratz, S.; Postigo, L.; Royo, B. Direct Synthesis of Iron(0) N-Heterocyclic Carbene Complexes by Using  $Fe_3(CO)_{12}$  and Their Application in Reduction of Carbonyl Groups. *Organometallics* **2013**, 32, 893–897.

(18) Kottsieper, K. W.; Stelzer, O.; Wasserscheid, P. 1-Vinylimidazole – a versatile building block for the synthesis of cationic phosphines useful in ionic liquid biphasic catalysis. *J. Mol. Catal. A: Chem.* **2001**, *175*, 285–288.

(19) Alcock, N. W.; Richards, C. J.; Thomas, S. E. Preparation of Tricarbonyl( $\eta^4$ -vinylketene)iron(0) Complexes from Tricarbonyl( $\eta^4$ -vinyl ketone)iron(0) Complexes and Their Subsequent Conversion to Tricarbonyl( $\eta^4$ -vinylketimine)iron(0) Complexes. *Organometallics* **1991**, *10*, 231–238.

(20) Yamakawa, M.; Ito, H.; Noyori, R. The Metal-Ligand Bifunctional Catalysis: A Theoretical Study on the Ruthenium(II)-Catalyzed Hydrogen Transfer between Alcohol and Carbonyl Compounds. J. Am. Chem. Soc. 2000, 122, 1466–1478.

(21) Harvey, J. N.; Poli, R. Computational study of the spin-forbidden  $H_2$  oxidative addition to 16-electron Fe(0) complexes. *Dalton Trans* **2003**, 4100–4106.

(22) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. Highly Efficient and Selective Hydrogenation of Aldehydes: A Well Defined Fe(II) Catalyst Exhibits Noble-Metal Activity. *ACS Catal.* **2016**, *6*, 2664–2672.