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Organoiron Complexes

Elementary Steps of Iron Catalysis: Exploring the Links between Iron Alkyl and Iron Olefin Complexes for their Relevance in C–H Activation and C–C Bond Formation[**]

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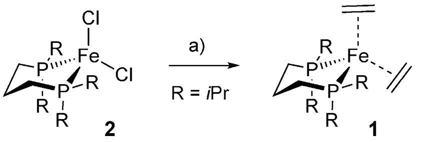
Abstract: *The alkylation of complexes **2** and **7** with Grignard reagents containing β-hydrogen atoms is a process of considerable relevance for the understanding of C–H activation as well as C–C bond formation mediated by low-valent iron species. Specifically, reaction of **2** with EtMgBr under an ethylene atmosphere affords the bis-ethylene complex **1** which is an active precatalyst for prototype [2+2+2] cycloaddition reactions and a valuable probe for mechanistic studies. This aspect is illustrated by its conversion into the bis-alkyne complex **6** as an unprecedented representation of a cycloaddition catalyst loaded with two substrates molecules. On the other hand, alkylation of **2** with 1 equivalent of cyclohexylmagnesium bromide furnished the unique iron alkyl species **11** with a 14-electron count, which has no less than four β-H atoms but is nevertheless stable at low temperature against β-hydride elimination. In contrast, the exhaustive alkylation of **1** with cyclohexylmagnesium bromide triggers two consecutive C–H activation reactions mediated by a single iron center. The resulting complex has a diene dihydride character in solution (**15**), whereas its structure in the solid state is more consistent with an η^3-allyl iron hydride rendition featuring an additional agostic interaction (**14**). Finally, the preparation of the cyclopentadienyl iron complex **25** illustrates how an iron-mediated C–H activation cascade can be coaxed to induce a stereoselective C–C bond formation. The structures of all relevant new iron complexes in the solid state are presented.*

The reduction of complexes of type [L_2FeX_2] (L = phosphine, X = Cl, Br) with magnesium in the presence of alkenes (dienes) is a gateway to coordinatively unsaturated 16-electron iron(0) bis-olefin (diene) complexes of the general types [$L_2Fe(alkene)_2$] and [$L_2Fe(diene)$].[1–5] Although several members of these series have been well characterized, their reactivity patterns remain somewhat opaque.[6] For example, 1,5-diene substrates may or may not get isomerized to the corresponding 1,3-dienes upon complexation;[7] small changes in the structure of the bidentate phosphorus ligand framework seem to switch this isomerization process on and off. Owing to this enigmatic behavior, we conjectured that this system provides an opportunity to study and eventually control iron-mediated C–H activation processes which may be of more general interest.[8] Furthermore, complexes of the general type [$L_2Fe(alkene)_2$] are also expected to be catalysts for other transformations upon replacement of the olefinic ligands by more reactive substrates. In any case, they should serve as valuable mechanistic probes for reactions in which low-valent iron species of unknown constitution are generated in situ by empirically optimized recipes.[9]

In this context, we planned to use the bis-ethylene complex **1** for further mechanistic investigations into iron catalysis (Scheme 1).[10–13] The bis(diisopropylphosphino)propane ligand (dippp) was chosen in accordance with literature to ensure the necessary solubility of **1** and its precursor complex **2**;[2–7,14,15] at the same time, dippp is thought to balance the steric shielding of and the accessibility to the unsaturated iron center in **1**. However, initial attempts to reduce complex **2** with activated magnesium or lithium sand in the presence of ethylene in analogy to the literature[2–7] gave erratic results. Gratifyingly, we found EtMgBr to be a much more reliable reducing agent. The structure of **1** in the solid state suggests that backbonding from the metal center into the π* orbitals of the ligated olefins must be substantial.[14,16]



Scheme 1. a) EtMgBr, THF, ethylene, −5 °C, 77–97 %.

Despite their apparent stabilizing function,[17] it seemed plausible that the olefins in **1** can be replaced by either 1,3-dienes or by acetylenes which tend to bind low-valent iron centers more tightly.[10,18] As such substrates are potentially more reactive too,[19] it met with our expectation that **1** catalyzes the [2+2+2] cycloaddition of prototype alkynes or alkyne/nitrile combinations (Scheme 2).[20] Although we do not pretend that the bulky and electron-rich dippp is the optimal ligand, we note the close analogy of complex **1** to a recent report in which a structurally undefined cyclotrimerization catalyst was generated in situ by reduction of FeI_2 with zinc dust in the presence of diphenylphosphinopropane.[21] This congruence corroborates the notion that complex **1** is a valuable source of [L_2Fe^0] fragments for use in catalysis and (mechanistic) organometallic chemistry.[22]

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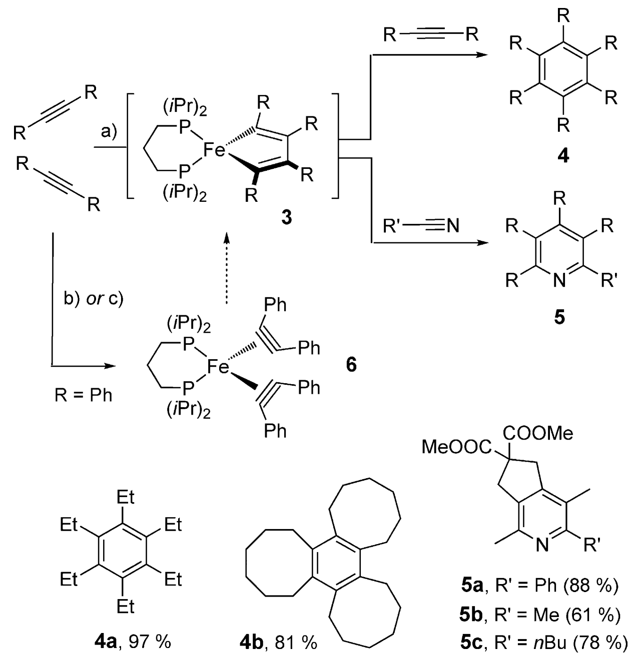

Scheme 2. a) **1** (10 mol%), THF, −50°C→RT; b) **1**, −5°C, then PhC≡CPh, 70%; c) FeBr$_2$, dippp, PhC≡CPh, Mg, THF, 0°C, 53%.

The iron-catalyzed cyclotrimerization of diarylalkynes is known to be considerably more difficult than that of aliphatic alkynes.[23] Therefore it was hoped that the reaction of **1** with tolane would allow reactive intermediates to be studied.[24] Despite the electron-rich nature of **1**, however, the formation of the expected metallacycle of type **3** (or a descendent thereof) was not observed;[25,26] rather, treatment of **1** with tolane furnished the bis(alkyne) Fe^0 complex **6**, which seems to be without precedent.[27,28] Massive electron back-donation from the metal center into the π^* orbitals of the acetylenic ligands can be inferred from the very elongated $C\equiv C$ bonds (1.286(2)/1.290(2) Å in **6** versus 1.198(3) Å in free tolane)[29] and the high degree of rehybridization expressed in the bending of the phenyl rings away from linearity with the former triple bond (the bond angles $C\equiv C$-C(ipso) are 138.9(1)/140.9(1)° and 141.6(2)/144.6(2)°) (Figure 1). Moreover, the two ligated alkynes are twisted against each other, a geometry that is likely enforced by the sterically demanding propellers of the forward-pointing P-*i*Pr groups. This particular geometry, however, obstructs significant orbital overlap between the ligand π bonds and hence prevents metallacycle formation. Complex **6** is therefore thought to represent the loaded catalyst ready to enter into the catalytic cycle of a [2+2+2] cycloaddition reaction, but which is "locked" in a pre-reactive state on steric grounds.

As mentioned above, the use of EtMgBr opens a convenient and reliable entry into the iron ethylene complex **1**. This result in itself is nontrivial, since alkylation of the closely related precursor complex **7** (X = Br) with dialkylmagnesium reagents devoid of β-hydrogen atoms had been previously shown to give isolable 14-electron Fe^{II} alkyl complexes **8** (Scheme 3).[30] Their *meta* stability implies that reductive ligand coupling is slow in this particular coordination environment. The very fast reduction of **2** to **1** via complex **9** as the presumed intermediate must therefore proceed by a different mechanism, most likely by means of β-hydride elimination (**9**→**10**→**1**).[31] This pathway, however, is by no means obvious because the tetrahedral Fe^{II} phosphine complexes **8** were previously shown to be paramagnetic high-spin species with four unpaired electrons ($\mu_{eff} = 4.9\ \mu_B$); as a result, all metal orbitals are at least singly occupied.[30,32] If an analogous diethyl complex **9** is passed through en route to **1**,[33] which likely shares this geometrical and electronic configuration, spin crossover (most probably associated with a rearrangement from tetrahedral to square-planar coordination geometry) must first vacate an empty orbital before β-hydride elimination can actually take place.[34–36]

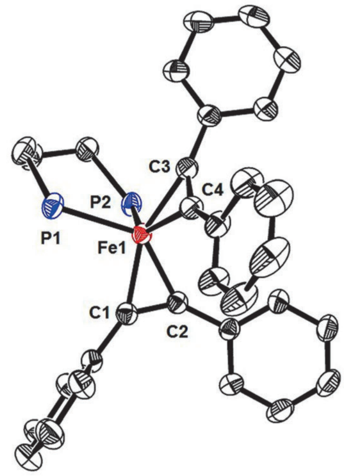

Figure 1. Structure of complex **6** in the solid state; for clarity, the isopropyl groups at both P atoms were removed (the full structure is contained in the Supporting Information).

Under the premise of such a "two-state reactivity",[37] it is tempting to speculate that iron(II) phosphine complexes might exist with alkyl substituents amenable to β-hydride elimination that are sufficiently long lived in the tetrahedral high-spin state to be isolated and characterized. Although we have not yet managed to obtain a dialkyl variant of such an elusive species, reaction of **2** with cyclohexylmagnesium chloride at −45°C delivered the unorthodox iron(II) monoalkyl complex **11**. Its structure in the solid state shows a 14-electron diphosphine iron(II) compound bearing an alkyl residue with no less than four hydrogen atoms amenable to β-hydride elimination, which is nonetheless stable at low temperature for extended periods of time (Figure 2). This pattern seems to be unprecedented;[35,36] complex **11** can therefore be regarded as the missing link between the known dialkyliron complexes **8**[30] and the transient diethyliron intermediate **9** invoked in the formation of the iron(0) bis-ethylene complex **1** outlined above.

Attempts at isolating the analogous bis-cyclohexyl complex **12** have so far met with failure. Rather than decomposing to the corresponding bis(cyclohexene) complex **13** (L = cyclohexene) as a sibling of the ethylene complex **1**, this fleeting intermediate evolves into another remarkable species. Single-crystal X-ray diffraction showed that the resulting

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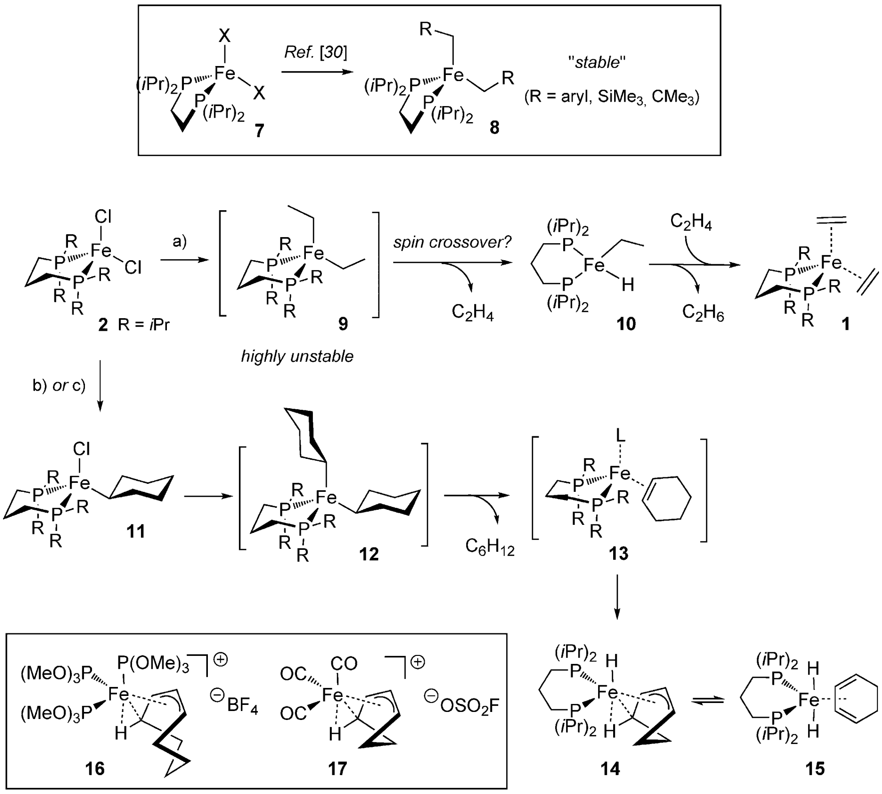

Scheme 3. a) EtMgBr, THF, ethylene, −5 °C, 77–97 %; b) $C_6H_{11}MgCl$ (1 equiv), THF, −35 °C, 51 % (**11**); c) $C_6H_{11}MgCl$ (2 equiv), THF, cyclohexene (5 equiv), −30 °C, 79 % (**14**/**15**).

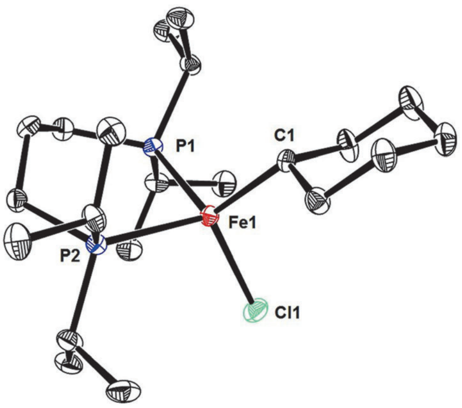

Figure 2. Structure of complex **11** in the solid state; cocrystallized THF was removed for clarity; for the entire structure, see the Supporting Information.

product **14** is an η^3-allyliron hydride complex formed by activation of the allylic C–H bond of what originally must have been a cyclohexene ligand in a transient complex of type **13** (L = neutral ligand).[38] For the iron center in **14** to gain an 18-electron count, it engages in a second C–H activation that has not yet progressed much beyond the agostic state (Figure 3). However, the recorded 1.66(3) Å for the Fe···H bond length occurs at the very low end of such agostic interactions (usually between 1.8 and 2.3 Å), whereas the H-C-Fe bond angle (101(1)°) in **14** is in the typical range (90–140°).[39] The Fe–H bond length is 1.39(3) Å, and the H···Fe–H bond angle is close to linearity (171(2)°).

The notion of a rather "advanced" agostic state in **14** is corroborated by the NMR data of this diamagnetic species. When the NMR spectrum is recorded at −80 °C, the presence of a single signal in the hydride region at $\delta_H = -19.37$ ppm with an integral of 2 H suggests that the complex in THF solution features a diene dihydride character **15** on the NMR timescale; all other ^1H, ^{13}C, and ^{31}P NMR data are in line with the proposed symmetric structure, which is reached by fully breaking the formerly agostic C–H bond. Complex **14** is reminiscent of the classical species **16**$[BF_4]$[40] and **17**$[SO_3F]$,[41] which provided early illustrations for the peculiar three-center/two-electron bonding mode that later became commonly known as "agostic" interaction.[39] It is of note, however, that the duality of the new species **14**/**15** is a distinctive feature, as is the preparation of this neutral complex by C–H activation; we recall that the cationic complexes **16** and **17** were prepared by protonation of a diene iron precursor in strongly acidic or even superacidic media.[40,41]

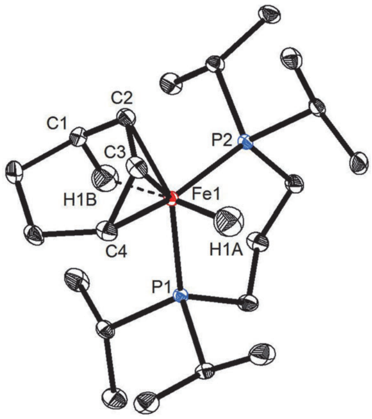

Figure 3. Structure of complex **14** in the solid state; the two explicitly shown H atoms interacting with the Fe center have been localized in a difference Fourier map and their positions refined.

The ready formation of **14** at low temperature infers that allylic C–H activation of an alkene ligand by the low-valent iron center can be very facile.[42] Therefore, it was no surprise that treatment of **18**[15] with cyclopentadiene gives the cyclopentadienyl iron ethyl complex **20**,[14] which is apparently formed by initial C–H activation and migratory insertion of the remaining ethylene ligand into the transient iron hydride bond (Scheme 4). Even more involved is the formation of

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compound **25**, which was obtained from **1** and 1,3-cyclohexadiene.[2] In this case, the ethyl and the cyclohexadienyl groups of the presumed intermediate **23**, generated by an initial C–H activation, undergo reductive ligand coupling with formation of a substituted iron(0) diene intermediate of type **24**, which is set up for a second C–H activation that positions the ethyl substituent *endo* relative to the iron center and forms the observed Fe–H bond (1.40(4) Å). This transformation is a striking case of two consecutive C–H activations intimately coupled with a stereoselective C–C bond formation, all of which are mediated by a single iron center. Although complex **25** and close analogues have previously been described in the literature, they are either difficult to retrieve and/or have not been fully delineated.[2,7b,c,43] Therefore the structure of this noteworthy product in the solid state is displayed in Figure 4.

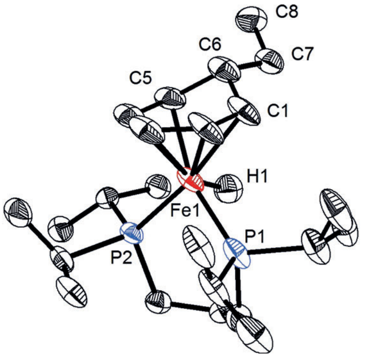
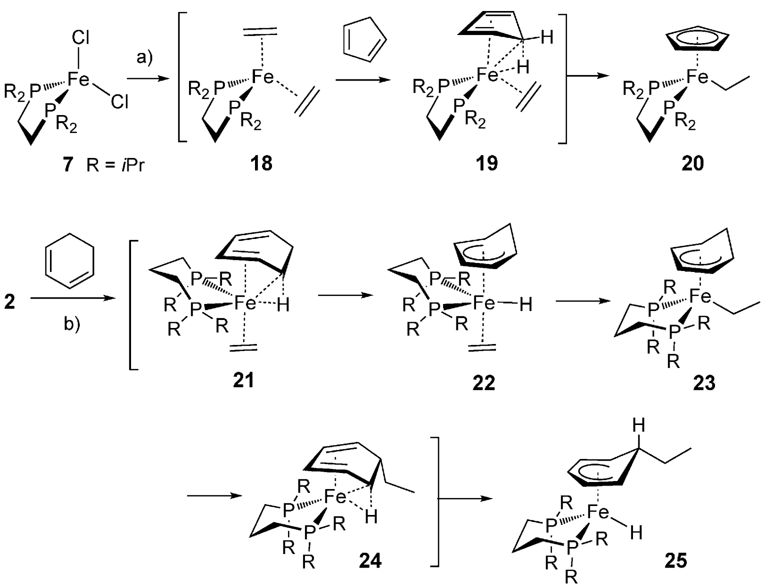


Figure 4. Structure of complex **25** in the solid state; the hydrogen atom of the Fe–H bond has been localized in a difference Fourier map and its position refined.



Scheme 4. a) EtMgBr, THF, ethylene, −20 °C, then cyclopentadiene, −20°→RT, 65 %; b) EtMgBr, THF, ethylene, −5 °C, then 1,3-cyclohexadiene, −5 °C→RT, 40 %.

To summarize, alkylation of diphosphine iron complexes **2** and **7** with alkyl Grignard reagents is an intriguing process. On the one hand, it provides access to Fe^0 diethylene complexes such as **1** and **18**, which are valuable starting points for investigations into iron catalysis and the organometallic chemistry of this element. This aspect is illustrated by the use of **1** as a catalyst for prototype [2+2+2] cycloaddition reactions and by the preparation of an unprecedented Fe^0 bis(alkyne) complex that mimics the loaded catalyst of such transformations. On the other hand, alkylation of **1** with cyclohexylmagnesium chloride furnished the unique Fe^{II} cyclohexyl complex **11**. Despite its 14-electron count and four H atoms at appropriate positions, **11** is surprisingly resistant to β-hydride elimination. In contrast, treatment of **1** with an excess of cyclohexylmagnesium chloride gave a remarkable complex with a chameleon nature, which transmutes from a η^3-allyliron hydride bonding mode in **14** with an additional agostic interaction in the solid state to a true diene dihydride complex **15** in solution. Finally, a prototype reaction cascade outlines how to combine C–H activation with stereoselective C–C bond formation. Attempts to generalize these unusual observations, to characterize the new complexes in more electronic detail, and to explore the obvious links of this chemistry to iron catalysis[44] are subject to ongoing studies in this laboratory.[45]

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[15] The analogous complex **18** with a dippe ligand prepared from **7** and EtMgBr is less stable but well behaved when used immediately after formation, see Scheme 4.

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[34] Spin crossover was recently proposed to explain β-hydride elimination of trigonal high-spin Fe^{II} alkyl complexes bearing diketoiminato ligands; for an in-depth discussion, see: S. M. Bellows, T. R. Cundari, P. L. Holland, *Organometallics* **2013**, *32*, 4741 – 4751.

[35] If the formation of square-planar complexes is geometrically prohibited, alkyl iron complexes become thermally robust, cf. Ref. [34] and the following: N. Shirasawa, T. T. Nguyet, S. Hikichi, Y. Moro-oka, M. Akita, *Organometallics* **2001**, *20*, 3582 – 3598.

[36] For metastable iron complexes with other ligand sets and coordination geometries which contain alkyl ligands with β-H atoms, see: a) J. Vela, S. Vaddadi, T. R. Cundari, J. M. Smith, E. A. Gregory, R. J. Lachiotte, C. J. Flaschenriem, P. L. Holland, *Organometallics* **2004**, *23*, 5226 – 5239; b) R. J. Trovitch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 11631 – 11640.

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