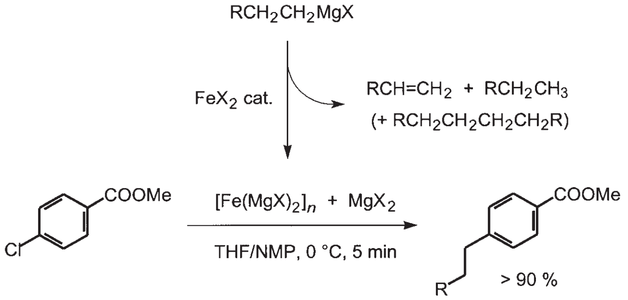
Synthetic Methods

DOI: 10.1002/anie.200502859

Unusual Structure and Reactivity of a Homoleptic "Super-Ate" Complex of Iron: Implications for Grignard Additions, Cross-Coupling Reactions, and the Kharasch Deconjugation**

Alois Fürstner, Helga Krause, and*
Christian W. Lehmann

Our recent investigations on iron-catalyzed cross-coupling reactions of organomagnesium reagents with various electrophiles were guided by the perception that bare, low-valent iron clusters formed in situ according to Scheme 1 might account for the observed turnover.[1–5] Since the analysis of the released gas suggests that this reduction process involves a β-hydride elimination/reductive coupling event,[6] it should proceed only with Grignard reagents containing at least two



Scheme 1. Proposed formation of low-valent, intermetallic iron clusters serving as the actual catalysts in cross-coupling reactions of aryl chlorides and alkyl Grignard reagents with two or more carbon atoms. NMP = *N*-methylpyrrolidone.

---

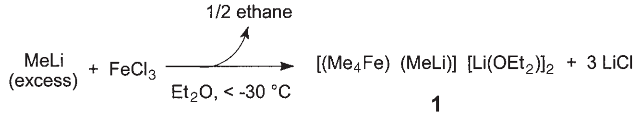
[*] Prof. A. Fürstner, H. Krause, Dr. C. W. Lehmann
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
Fax: (+49) 208-306-2994
E-mail: fuerstner@mpi-muelheim.mpg.de

[**] Generous financial support by the MPG and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. B. Scheiper for performing the reaction of enol triflate **8**.

carbon atoms. In line with this notion, MeMgBr essentially *fails* to react with methyl 4-chlorobenzoate in the presence of [Fe(acac)$_3$] (acac = acetylacetone) or FeCl$_n$ ($n = 2$, 3) as precatalysts, whereas all higher alkyl Grignard reagents are cross-coupled with exceptional ease under these conditions (Scheme 1).[1] This strikingly different behavior is general; in fact, methyl groups are transferred only to highly activated substrates such as enol triflates, acid chlorides, and very electron-deficient heteroarenes.[7,8]

To confirm this dichotomy in the proposed mechanism further, we set out to elucidate the structure of the reagent derived from FeX$_n$ and MeMgBr. It was previously proposed that a host of homoleptic non-stabilized alkyl-iron species and/or iron-ate complexes of different composition is formed depending on the chosen stoichiometry, although none of these putative intermediates has ever been confirmed by spectroscopic or structural data.[9,10] Only the rapid reduction of FeCl$_3$ to FeCl$_2$ on treatment with the first equivalent of MeLi or MeMgBr is formally secured.[11]

Reaction of an anhydrous ethereal solution of FeCl$_3$ with MeLi at low temperature (< -30 °C), removal of the precipitated LiCl, and evaporation of the solvent at -78 °C afforded a red solid **1**, which dissolves in THF to give bright yellow colored solutions (Scheme 2). This material was previously thought to consist of [Me$_4$Fe][Li(OEt$_2$)]$_2$.[12] Although the reported protonolysis data roughly matched this composition,[12] all previous attempts to further characterize this compound remained unsuccessful.[13] Gratifyingly, however, we managed to obtain crystalline samples suitable for crystal structure analysis upon slow cooling of saturated solutions of **1** in Et$_2$O from about -40 °C to -78 °C. Greatest possible care has to be taken due to the *exceptional* sensitivity of this product, which ignites in air and rapidly decomposes both in solution and in solid form at ≥ 0 °C.



Scheme 2. Formation of the iron "super-ate" complex **1** from FeCl$_3$ and MeLi.

The remarkable structure of the resulting complex **1**[14] comprises a homoleptic ferrate moiety in which four methyl groups surround the Fe^{II} atom in an almost ideal tetrahedral arrangement (Figure 1).[15] The molecule possesses crystallographic mirror symmetry with the iron atom, one lithium, and two methyl groups situated in special positions. The average of the four independent C-Fe-C angles is 109(3)°. For three (only two are crystallographically independent) of the four methyl groups the average Fe–C distance is 2.185(4) Å, whereas the distance to the fourth methyl group is shortened to 2.095(4) Å. The three former methyl groups each exhibit two further short distances to three lithium atoms (2.279(4)–2.321(5) Å). These lithium atoms form an equilateral triangle[16] and, together with the iron atom, a tetrahedral metal framework that shows T_d symmetry. Three of the four sides of this cluster are capped in a μ^3-fashion by the already mentioned methyl groups, the fourth face is capped symmetrically by a fourth methyl group (av Li–C distance 2.186(6) Å) *devoid* of any direct contact to the iron center. The coordination sphere of two of the lithium atoms is completed by O-ether contacts (Li2 and Li2*), whereas Li1 forms a close contact of 2.301(6) Å to the carbon atom of the terminal Fe-methyl group of a neighboring molecule.

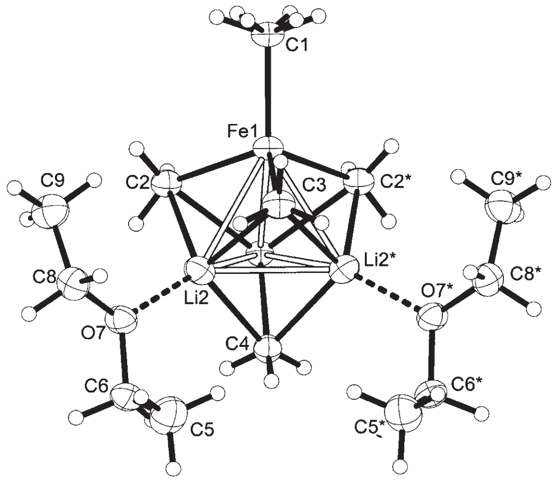
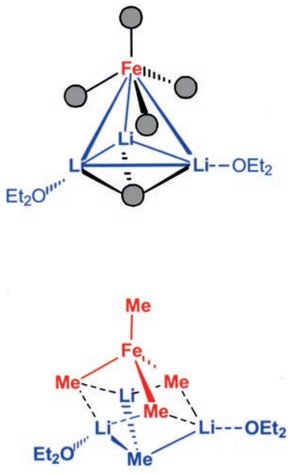


Figure 1. Structure of the iron "super-ate" complex **1** in the solid state. Li1 is the unlabeled ellipsoid in the back of the tetrahedral metallic frame. Selected bond lengths [Å]: Fe1–C1 2.095(4), Fe1–C2 2.188(3), Fe1–C3 2.182(4), Li1–C2 2.279(4), Li1–C4 2.181(7), Li2–C3 2.298(5), Li2–C4 2.190(6). The hydrogen atoms of methyl group C1 are disordered. Anisotropic displacement parameter ellipsoids are drawn at the 50% probability level.

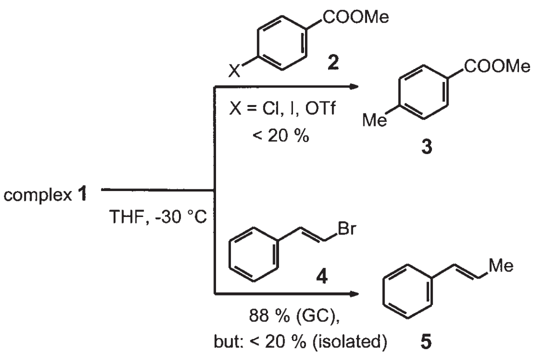
Overall, the structure of **1** shows a striking similarity to the solid-state structure of the methyllithium tetramer.[17] The structure of (MeLi)$_4$ has crystallographic T_d or $\bar{4}3m$ symmetry, resulting in only one independent Li–Li distance (2.68(5) Å), which is within one standard uncertainty of the average length of the tetrahedral edge in **1**. The comparison between the Li–C distances in (MeLi)$_4$ and **1** underlines this similarity further.[18]

Based only on interatomic distances, it is difficult to deduce a "simple" model for the chemical bonding in **1**. Graphical representations emphasizing either the ferrate substructure with its "intertwined" lithium cap or the tetrahedral metallic frame are depicted in Scheme 3. Overall, the product derived from FeCl$_3$ and excess MeLi analyzes as [(Me$_4$Fe)(MeLi)][Li(OEt$_2$)]$_2$ (**1**). As such, **1** represents the first *alkyl*-ate complex of iron devoid of any stabilizing ligands that has been structurally characterized and adds one more example to the very small family of homoleptic iron complexes with η^1-bound carbon entities other than CO.[19,20]

Next, the reactivity of **1** was checked in a set of prototype transformations. As expected, this compound essentially fails to alkylate p-XC$_6$H$_4$COOMe (**2**; X = Cl, I, OTf; Scheme 4), thus corroborating the notion that ate-complexes play no role in the iron-catalyzed cross-coupling reactions of higher alkyl Grignard reagents mentioned above (cf. Scheme 1).[1] Likewise, alkenyl halides such as **4** were found to be rather poor substrates; this result is in striking contrast to previous reports that an iron-ate complex of the putative composition



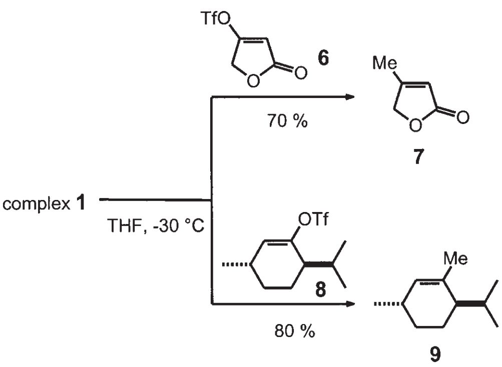
Scheme 3. Two different representations of the structure of the Fe^{II}-ate complex **1**: Top: Graphical illustration of the metal cluster forming the inner core; the methyl units are represented as balls, four of which reside over the faces of this tetrahedron. Bottom: The ferrate unit is color-coded in red; its negative charges are counterbalanced by the intertwined lithium "cap" carrying an extra methyl group.



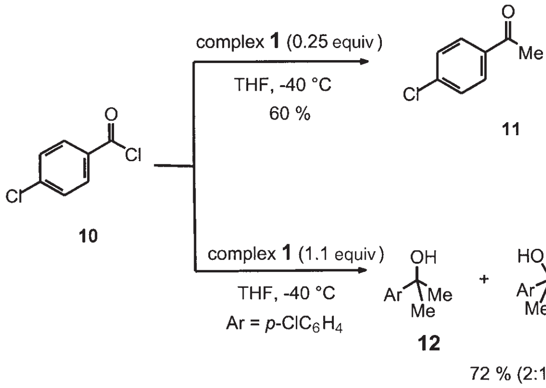
Scheme 4.

"Me_4FeLi_2" formed in situ methylates bromide **4** in high yield and selectivity.[9,21] Moreover, the claimed stability of the in situ species up to 40 °C[9] is inconsistent with our data.

Complex **1**, however, transfers its methyl groups to more activated electrophiles such as enol triflates, as previously communicated (Scheme 5).[7] Along the same lines, acid chloride **10** affords the corresponding acetophenone derivative **11**, again without any competing side reaction of the aryl chloride moiety interfering (Scheme 6). When **1** is used in excess, the reaction proceeds further to give the carbonyl addition product **12** and the corresponding pinacol **13**, suggesting that the ate-complex also acts as a single-electron transfer (SET) agent towards the ketone initially formed. This result is highly reminiscent of early work of Ashby et al. who found that the amount of pinacol produced in attempted additions of MeMgBr to aromatic ketones is *directly proportional to the iron impurities of the magnesium metal* used to form the Grignard reagent.[22] Our results, therefore, suggest that the reagent responsible for this striking correlation is an ate-complex of the type described herein.[23] More generally speaking, this finding sheds light into the well established but hardly understood "alchemistic" effects exerted by certain transition-metal residues on the course of Grignard reactions.[24]

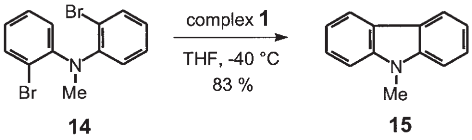


Scheme 5.



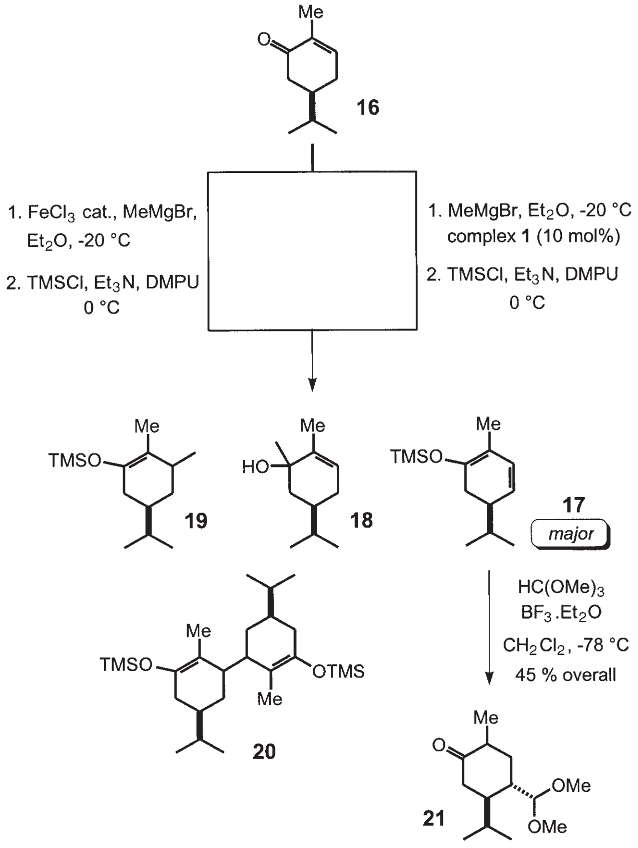
Scheme 6.

The SET potential of complex **1** is also responsible for the conversion of dibromide **14** to carbazole **15** (Scheme 7). This Ullmann-type coupling was recently effected with the putative complex "Me_4FeLi_2" formed in situ.[25] Since the defined metalate **1** provides the same result, it seems reasonable to assume that it constitutes the actual intermediate operative under the in situ conditions.



Scheme 7.

Finally, we propose that ate-complexes similar to **1** also play a vital role in the deconjugation of α,β-unsaturated enones pioneered by Kharasch et al. using catalytic amounts of $FeCl_3$ and excess MeMgBr.[26] A modified version of this process allows the formation of thermodynamic silyl enol ethers that are difficult to obtain otherwise.[27] Although this method has undergone significant empirical optimization,[27,28] the identity of the active species remained obscure, except for the vague statement that it might consist of a "mixture of activated zero-valent iron and Grignard reagent".[27] To check whether ate-complexes play any significant role in this transformation, we treated dihydrocarvone **16**[29] according to the original recipe ($FeCl_3$ cat., MeMgX)[30] as well as with complex **1** as the catalyst (Scheme 8). The crude product spectrum obtained after quenching of the reaction with $TMSCl/Et_3N$ is virtually identical for both cases. The silyl enol ether **17** is the major compound accompanied by the corresponding 1,2- and 1,4-addition products **18** and **19** as well as dimer **20** (diastereomeric mixture) formed again by an SET event. Compound **17** can be further elaborated into product **21**, which served as a key intermediate for the preparation of the cytotoxic diterpenoids of the sarcodictyin family.[30] These comparative experiments strongly suggest that iron "super-ate" complexes constitute the actual "Kharasch reagent", at least in those optimized cases where the reaction is performed at low temperature.



Scheme 8. Conversion of dihydrocarvone **16** to the silyl enol ether **17**, the corresponding 1,2- and 1,4-addition products **18** and **19**, and the dimer **20**. TMSCl = trimethylsilyl chloride, DMPU = *N,N'*-dimethyl-*N,N'*-propylene urea.

In summary, we disclosed the first structurally characterized ate-complex of Fe^{II} bearing only alkyl substituents without any further stabilizing ligands; the fact that **1** incorporates an additional molecule of methyllithium represents a particularly remarkable structural feature. Since defined homoleptic complexes of iron, in contrast to those of the neighboring elements in the periodic table, are extremely scarce,[20] we hope that our data will help to unravel the as of yet largely unknown chemistry and catalytic potential of such species. Concerning its reactivity profile, compound **1** obviously combines many different facets including nucleophilic behavior, a prominent electron-transfer capacity, as well as a significant basicity. With this in mind, we like to express a "caveat" concerning selectivity claims for reactions invoking putative iron-ate complexes of different "formal" compositions found in the early literature,[9] notably in those cases where the reactions have been performed at higher temperatures.

Received: August 11, 2005

Keywords: ate complexes · cross-coupling · Grignard reaction · iron · single-electron transfer

---

[1] a) A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863; b) A. Fürstner, A. Leitner, *Angew. Chem.* **2002**, *114*, 632–635; *Angew. Chem. Int. Ed.* **2002**, *41*, 609–612; c) A. Fürstner, A. Leitner, G. Seidel, *Org. Synth.* **2005**, *81*, 33–42.

[2] a) A. Fürstner, A. Leitner, *Angew. Chem.* **2003**, *115*, 320–323; *Angew. Chem. Int. Ed.* **2003**, *42*, 308–311; b) G. Seidel, D. Laurich, A. Fürstner, *J. Org. Chem.* **2004**, *69*, 3950–3952; c) A. Fürstner, D. De Souza, L. Parra-Rapado, J. T. Jensen, *Angew. Chem.* **2003**, *115*, 5516–5518; *Angew. Chem. Int. Ed.* **2003**, *42*, 5358–5360; d) A. Fürstner, L. Turet, *Angew. Chem.* **2005**, *117*, 3528–3532; *Angew. Chem. Int. Ed.* **2005**, *44*, 3462–3466; e) A. Fürstner, M. Méndez, *Angew. Chem.* **2003**, *115*, 5513–5515; *Angew. Chem. Int. Ed.* **2003**, *42*, 5355–5357; f) B. Scheiper, F. Glorius, A. Leitner, A. Fürstner, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 11960–11965; g) A. Fürstner, D. Kirk, M. D. B. Fenster, C. Aïssa, D. De Souza, O. Müller, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 8103–8108; h) O. Lepage, E. Kattnig, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 15970–15971; i) R. Martin, A. Fürstner, *Angew. Chem.* **2004**, *116*, 4045–4047; *Angew. Chem. Int. Ed.* **2004**, *43*, 3955–3957; j) A. Fürstner, R. Martin, K. Majima, *J. Am. Chem. Soc.* **2005**, *127*, 12236–12237.

[3] Reviews: a) H. Shinokubo, K. Oshima, *Eur. J. Org. Chem.*, **2004**, 2081–2091; b) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; c) A. Fürstner, R. Martin, *Chem. Lett.* **2005**, *34*, 624–629.

[4] Pioneering studies on the use of iron for cross-couplings: a) M. Tamura, J. K. Kochi, *J. Am. Chem. Soc.* **1971**, *93*, 1487–1489; b) J. K. Kochi, *Acc. Chem. Res.* **1974**, *7*, 351–360; c) G. Cahiez, H. Avedissian, *Synthesis* **1998**, 1199–1205; d) G. A. Molander, B. J. Rahn, D. C. Shubert, S. E. Bonde, *Tetrahedron Lett.* **1983**, *24*, 5449–5452; e) C. K. Reddy, P. Knochel, *Angew. Chem.* **1996**, *108*, 1812–1813; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1700–1701; f) A. Fürstner, H. Brunner, *Tetrahedron Lett.* **1996**, *37*, 7009–7012; g) J.-L. Fabre, M. Julia, J.-N. Verpeaux, *Tetrahedron Lett.* **1982**, *23*, 2469–2472; h) A. Yanagisawa, N. Nomura, H. Yamamoto, *Tetrahedron* **1994**, *50*, 6017–6028.

[5] Recent contributions from other groups: a) B. Hölzer, R. W. Hoffmann, *Chem. Commun.* **2003**, 732–733; b) W. Dohle, F. Kopp, G. Cahiez, P. Knochel, *Synlett* **2001**, 1901–1904; c) M. Hojo, Y. Murakami, H. Aihara, R. Sakuragi, Y. Baba, A. Hosomi, *Angew. Chem.* **2001**, *113*, 641–643; *Angew. Chem. Int. Ed.* **2001**, *40*, 621–623; d) M. A. Fakhfakh, X. Franck, R. Hocquemiller, B. Figadère, *J. Organomet. Chem.* **2001**, *624*,

131–135; e) M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 3686–3687; f) T. Nagano, T. Hayashi, *Org. Lett.* **2004**, *6*, 1297–1299; g) M. Nakamura, S. Ito, K. Matsuo, E. Nakamura, *Synlett* **2005**, 1794–1798; h) K. Itami, S. Higashi, M. Mineno, J. Yoshida, *Org. Lett.* **2005**, *7*, 1219–1222; i) I. Sapountzis, W. Lin, C. C. Kofink, C. Despotopoulou, P. Knochel, *Angew. Chem.* **2005**, *117*, 1682–1685; *Angew. Chem. Int. Ed.* **2005**, *44*, 1654–1658; j) R. B. Bedford, D. W. Bruce, R. M. Frost, J. W. Goodby, M. Hird, *Chem. Commun.* **2004**, 2822–2823.

[6] B. Bogdanovic, M. Schwickardi, *Angew. Chem.* **2000**, *112*, 4788–4790; *Angew. Chem. Int. Ed.* **2000**, *39*, 4610–4612.

[7] a) B. Scheiper, M. Bonnekessel, H. Krause, A. Fürstner, *J. Org. Chem.* **2004**, *69*, 3943–3949; b) see also: C. Duplais, F. Bures, I. Sapountzis, T. J. Korn, G. Cahiez, P. Knochel, *Angew. Chem.* **2004**, *116*, 3028–3030; *Angew. Chem. Int. Ed.* **2004**, *43*, 2968–2970.

[8] Recent applications: a) M. Hocek, H. Dvoráková, *J. Org. Chem.* **2003**, *68*, 5773–5776; b) N. Maulide, J.-C. Vanherck, I. E. Markó, *Eur. J. Org. Chem.* **2004**, 3962–3967; c) M. Hocek, R. Pohl, I. Cisarová, *Eur. J. Org. Chem.* **2005**, 3026–3030.

[9] Review: T. Kauffmann, *Angew. Chem.* **1996**, *108*, 401–418; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 386–403.

[10] Leading references: a) E. J. Corey, G. H. Posner, *Tetrahedron Lett.* **1970**, *11*, 315–318; b) E. J. Corey, H. Yamamoto, D. K. Herron, K. Achiwa, *J. Am. Chem. Soc.* **1970**, *92*, 6635–6636; c) T. Kauffmann, B. Laarmann, D. Menges, G. Neiteler, *Chem. Ber.* **1992**, *125*, 163–169; d) T. Kauffmann, K.-U. Voß, G. Neiteler, *Chem. Ber.* **1993**, *126*, 1453–1459.

[11] H. J. Berthold, H. J. Spiegl, *Z. Anorg. Allg. Chem.* **1972**, *391*, 193–202.

[12] H. J. Spiegl, G. Groth, H. J. Berthold, *Z. Anorg. Allg. Chem.* **1973**, *398*, 225–230.

[13] Attempted crystallizations are reported in ref. [9].

[14] X-ray crystal structure analysis of **1:** $C_{13}H_{35}FeLi_3O_2$, $M_r = 300.08\ \mathrm{g\,mol^{-1}}$, yellow-orange plate, crystal size $0.08 \times 0.06 \times 0.05\ \mathrm{mm^3}$, orthorhombic, space group *Pnma*, $a = 12.3527(5)$ Å, $b = 15.9319(8)$ Å, $c = 9.9546(5)$ Å, $V = 1959.08(16)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd} = 1.017\ \mathrm{g\,cm^{-3}}$, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 0.762\ \mathrm{mm^{-1}}$, Nonius Kappa CCD diffractometer, $3.30 < \theta < 27.08°$, 17506 measured reflections, 2231 independent reflections, 1601 reflections with $I > 2\sigma(I)$, structure solved by direct methods and refined by full matrix least-squares on F_o^2 to $R_1 = 0.050$ $[I > 2\sigma(I)]$, $wR_2 = 0.114$, 116 parameters, H atoms mixed, $S = 1.038$, residual electron density $+0.5/-0.3$ e Å^{-3}. CCDC-279956 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] The four independent C-Fe-C angles are 113.67(15), 109.24(9), 109.28(9), and 105.83(15)°.

[16] The standard uncertainty of the average edge is within three times the average standard uncertainties of each individual edge.

[17] a) E. Weiss, G. Hencken, *J. Organomet. Chem.* **1970**, *21*, 265–268; b) for a review on the structure of organolithium compounds, see: W. N. Setzer, P. v. R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353–451; c) A. Streitweiser, S. M. Bachrach, A. Dorigo, P. von R. Schleyer in *Lithium Chemistry* (Eds.: A.-M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, pp. 1–43.

[18] The C–Li distance in Me_4Li_4 is 2.31(5) Å, the average C–Li distance in **1** is 2.25(6) Å.

[19] Reviews: a) R. C. Kerber in *Comprehensive Organometallic Chemistry II, Vol. 7*, 2nd ed. (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 101–229; b) J. R. Green, W. A. Donaldson in *Encyclopedia of Inorganic Chemistry, Vol. 4* (Ed.: R. B. King), Wiley, Chichester, **1994**, pp. 1735–1784; c) A. Segnitz in *Methoden der Organischen Chemie (Houben-Weyl), Vol. 13/9a*, 4th ed. (Ed.: A. Segnitz), Thieme, Stuttgart, **1986**, pp. 175–523; d) for a review on iron-alkyl species carrying extra stabilizing ligands, see: A. Yamamoto, *J. Organomet. Chem.* **1986**, *300*, 347–367.

[20] a) T. A. Bazhenova, R. M. Lobkovskaya, R. P. Shibaeva, A. K. Shilova, M. Gruselle, G. Leny, E. Deschamps, *J. Organomet. Chem.* **1983**, *244*, 375–382; b) T. A. Bazhenova, L. M. Kachapina, A. E. Shilov, M. Y. Antipin, Y. T. Struchkov, *J. Organomet. Chem.* **1992**, *428*, 107–123; c) H. Müller, W. Seidel, H. Görls, *J. Organomet. Chem.* **1993**, *445*, 133–136; d) H. Müller, W. Seidel, H. Görls, *Z. Anorg. Allg. Chem.* **1996**, *622*, 756–758; e) W. Seidel, K.-J. Lattermann, *Z. Anorg. Allg. Chem.* **1982**, *488*, 69–74; f) T. A. Bazhenova, R. M. Lobkovskaya, R. P. Shibaeva, A. E. Shilov, A. K. Shilova, M. Gruselle, G. Leny, B. Tchoubar, *J. Organomet. Chem.* **1983**, *244*, 265–272; g) A. Klose, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, *J. Am. Chem. Soc.* **1994**, *116*, 9123–9135.

[21] Although GC shows seemingly clean conversions, the isolated yields of **5** remained disappointingly low using either defined **1** or the in situ system, see Scheme 4.

[22] a) E. C. Ashby, T. L. Wiesemann, *J. Am. Chem. Soc.* **1978**, *100*, 189–199; b) E. C. Ashby, J. D. Buhler, I. G. Lopp, T. L. Wiesemann, J. S. Bowers, Jr., J. T. Laemmle, *J. Am. Chem. Soc.* **1976**, *98*, 6561–6570.

[23] Complex **1**, however, seems to be unable to transfer electrons to dialkyl ketones as evident from the clean addition to 4-*tert*-butylcyclohexanone. This result is again in excellent agreement with the report by Ashby et al. who showed that the iron content in the magnesium has no effect in Grignard additions to aliphatic carbonyl compounds. Moreover, they are in line with the finding that certain iron salts beneficially effect the stereoselective course of addition of cyclic ketones as reported by Reetz et al., see: M. T. Reetz, S. Stanchev, *J. Chem. Soc. Chem. Commun.* **1993**, 328–330.

[24] M. S. Kharasch, O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Constable, London, **1954**.

[25] a) M. Uchiyama, Y. Matsumoto, S. Nakamura, T. Ohwada, N. Kobayashi, N. Yamashita, A. Matsumiya, T. Sakamoto, *J. Am. Chem. Soc.* **2004**, *126*, 8755–8759; b) short review: R. W. Hoffmann, *Angew. Chem.* **2005**, *117*, 6433–6435; *Angew. Chem. Int. Ed.* **2005**, *44*, 6277–6279.

[26] M. S. Kharasch, P. O. Tawney, *J. Am. Chem. Soc.* **1941**, *63*, 2308–2315.

[27] a) M. E. Krafft, R. A. Holton, *J. Am. Chem. Soc.* **1984**, *106*, 7619–7621; b) M. E. Krafft, R. A. Holton, *J. Org. Chem.* **1984**, *49*, 3669–3670.

[28] a) J. Meinwald, L. Hendry, *J. Org. Chem.* **1971**, *36*, 1446–1447; b) N. Ito, T. Etoh, *J. Chem. Soc. Perkin Trans. 1* **1996**, 2397–2405.

[29] Dihydrocarvone was prepared as described in ref. [30]. The reported ^{13}C NMR data of this compound, however, are incorrect; compound **16** analyzes as follows: ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.5$, 145.2, 142.0, 141.9, 135.2, 31.9, 29.7, 19.5, 19.4, 15.5 ppm.

[30] S. M. Ceccarelli, U. Piarulli, C. Gennari, *Tetrahedron* **2001**, *57*, 8531–8542.