

A Cheap Metal for a “Noble” Task: Preparative and Mechanistic Aspects of Cycloisomerization and Cycloaddition Reactions Catalyzed by Low-Valent Iron Complexes

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Abstract: Reaction of ferrocene with lithium in the presence of either ethylene or COD allows the Fe(0)-ate complexes **1** and **4** to be prepared on a large scale, which turned out to be excellent catalysts for a variety of Alder-ene, [4+2], [5+2], and [2+2+2] cycloaddition and cycloisomerization reactions of polyunsaturated substrates. The structures of ferrates **1** and **4** in the solid-state reveal the capacity of the reduced iron center to share electron density with the ligand sphere. This feature, coupled with the kinetic lability of the bound olefins, is thought to be responsible for the ease with which different enyne or diyne substrates undergo oxidative cyclization as the triggering event of the observed skeletal reorganizations. This mechanistic proposal is corroborated by highly indicative deuterium labeling experiments. Moreover, it was possible to intercept two different products of an oxidative cyclization manifold with the aid of the Fe(+1) complex **6**, which, despite its 17-electron count, also turned out to be catalytically competent in certain cases. The unusual cyclobutadiene complex **38** derived from **6** and tolane was characterized by X-ray crystallography.

Introduction

Late transition metals, and in particular the noble ones among them, dominate a very significant part of contemporary catalysis research. Their ability to maintain reversible redox cycles, the excellent tunability of their steric and electronic characteristics by a host of ligand sets, the pronounced affinity to π -systems, and an outstanding compatibility with many functional groups are just the most elementary of the many factors that contribute to this privileged status.^{1,2} Yet, noble metals in general are (very) expensive, whereas other commonly used late transition metals are either toxic and/or require special treatment of the waste stream due to serious environmental concerns (cobalt, nickel, copper). Therefore, it is a worthwhile endeavor to search for possible alternatives in a quest for more affordable and sustainable methodology.

Iron catalysis seems to provide many opportunities in this regard, because salts of this metal are cheap, generally nontoxic, benign, and readily available. Despite these a priori favorable attributes and the pre-eminent role of iron in biological catalysis,³ applications in organic synthesis were largely confined, for a long time, to Lewis acid chemistry as well as to the stoichiometric use of iron templates stabilized by strongly bound

ancillary ligands.⁴ More recently, however, a rapidly growing number of examples highlights how iron catalysis may fertilize fields not commonly associated with this particular metal,⁵ such as olefin oligo- and polymerization,⁶ cross coupling chemistry,^{7–16}

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allylations,¹⁷ carbometalations,¹⁸ cycloadditions,^{19,20} cycloisomerizations,²¹ or hydrogenations,²² to name just a few.²³ Despite these important advances, the field is still in its infancy, not least because the exact nature of the catalytically competent iron species is often unknown and/or subject to somewhat controversial debate.

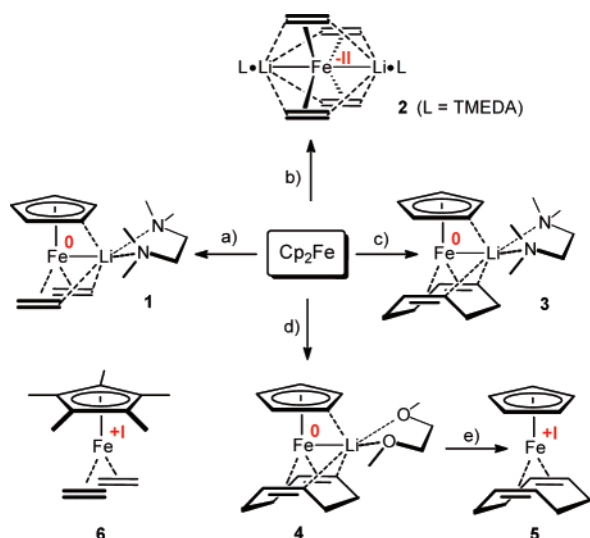
Convinced of the relevance of this emerging field, we launched a program aiming at a more systematic investigation of the potential of iron catalysis for preparative purposes. So far, this venture has successfully borne out in the cross coupling arena,^{7,10,11,14} including various applications to the total synthesis of bioactive natural products.^{24,25} Though highly efficacious in many cases, such C–C bond formations are mechanistically exceedingly complex and may occur along more than one pathway.²⁶ In an attempt to gain a better mechanistic under-

standing, we became interested in structurally well-defined low-valent iron complexes as potential mimics for the actual catalysts generated in situ from FeX₃ and RMgX. In fact, the rather unusual but structurally well-defined olefin complexes **1** and **2** turned out to be highly relevant in this context, because they even allow one to effect the particularly difficult cross coupling of alkyl halides and Grignard reagents with exceptional ease.^{27,28} Encouraged by these results, we started to investigate the yet largely unexplored chemical behavior of such "bare" ferrate species in more detail, which led to the discovery of their remarkable potential as catalysts for various cycloisomerization and cycloaddition reactions of polyunsaturated substrates. Outlined below is a summary of our investigations in this field.²⁹

Results and Discussion

Low-Valent Ferrate Complexes. Under the premise that iron complexes of suitable oxidation state, spin configuration, and coordination geometry might qualify as substitutes for precious noble metal catalysts, we became interested in the pioneering work of Jonas et al. who showed that the individual Cp-rings of ferrocene can be successively removed under reducing conditions.^{30,31} When performed under ethylene atmosphere, the reductive cleavage primarily results in formation of the Fe(0) half-sandwich complex **1**, which reacts further on prolonged stirring at ambient temperature to give the rather unusual tetraethylene ferrate **2** of the formal oxidation state –2 (Scheme 1). Both compounds can be isolated in respectable yields on a multigram scale as air-sensitive but nicely crystalline and indefinitely storable materials upon complexation of the escorting lithium counterions with TMEDA. If ethylene is replaced by 1,5-cyclooctadiene (COD), complex **3** or the TMEDA-free

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Scheme 1^a

^a (a) (i) Li, ethylene (1 bar), THF, $-50\text{ }^{\circ}\text{C} \rightarrow 0\text{ }^{\circ}\text{C}$, (ii) N,N,N',N' -tetramethylethylenediamine (TMEDA), $-30\text{ }^{\circ}\text{C}$, 45% (23 g scale); (b) (i) Li, THF, ethylene (5 bar), $-80\text{ }^{\circ}\text{C} \rightarrow \text{RT}$; (ii) TMEDA, Et_2O , $0\text{ }^{\circ}\text{C}$, 43% (12 g scale); (c) (i) Li, COD, THF, $-50\text{ }^{\circ}\text{C}$; (ii) TMEDA, Et_2O , RT, 75%; (d) Li, COD, DME, $-50\text{ }^{\circ}\text{C} \rightarrow \text{RT}$, 97% (85 g scale) [50% after recrystallization, 11 g scale]; (e) Ph_3CCl , pentane, $-35\text{ }^{\circ}\text{C} \rightarrow \text{RT}$, 70%.

DME adduct **4** become available. On treatment with 1,2-dichloroethane or trityl chloride, complex **4** undergoes a remarkably clean one-electron oxidation to give the formal $\text{Fe}(+1)$ complex **5** with a 17 electron count.³² The corresponding half-sandwich complexes bearing Cp^* ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$) rather than Cp ligands are also accessible as exemplified by compound **6**.³² Detailed procedures for the large-scale preparation of ferrates **1** and **4**, serving as the preferred catalysts in this study, are given in the Experimental Section of this paper.

A look at the spectroscopic data and X-ray structures of representative ferrate complexes is highly informative. Thus, the ^{13}C NMR spectrum of **3** in toluene- d_8 at low temperature shows two signals each for the olefins ($\delta = 52.5$ (d), 41.6 (d) ppm) and the methylene groups ($\delta = 35.5$ (t), 32.9 (t) ppm) of the COD ligand, which coalesce if the spectrum is recorded at $+80\text{ }^{\circ}\text{C}$ ($\delta = 47.9$ (d), 34.1 (t) ppm). This behavior is deemed to reflect the increasing mobility of the Li cation on the anionic $[\text{Fe}]$ template, which is in accordance with the observed conductivity of THF solutions of **3** at ambient temperature.³⁰ It is also interesting to note that formal replacement of the TMEDA ligand on the lithium counterion by DME markedly increases the intrinsic motion, because complex **4** shows only one set of signals even at $-78\text{ }^{\circ}\text{C}$.

The structure of **4** in the solid state (Figure 1) is composed of four crystallographically independent molecules, which show almost identical molecular conformations.³³ Small but significant differences of the lithium and iron coordination spheres are revealed only upon closer inspection. All four independent molecules are characterized by a remarkably close contact between the iron center and the lithium atom which averages $2.493(4)\text{ \AA}$ and is significantly shorter than the $\text{Fe}\cdots\text{Li}$ distance

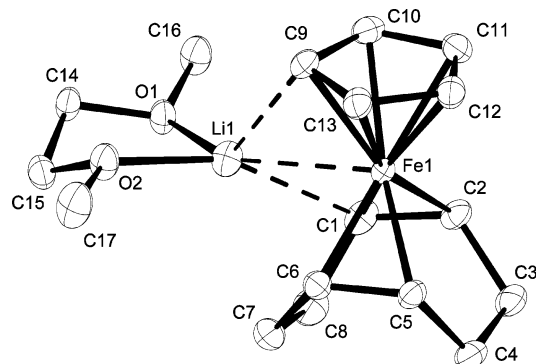


Figure 1. Molecular structure of **4** in the solid state (only one of the four crystallographically independent molecules is depicted).³³ Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity.

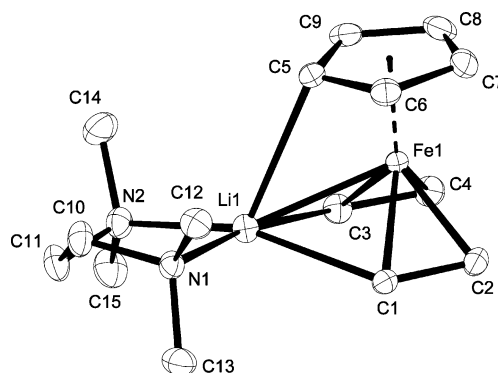


Figure 2. Molecular structure of **1** in the solid state. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity.

in the related TMEDA complex **3** ($2.530\text{ \AA}$).³⁰ Further short contacts are observed between the lithium atom and one of the Cp -ring carbon atoms ($2.466(13)\text{ \AA}$) as well as one of the two proximal olefinic sites of the COD ligand ($2.33(4)\text{ \AA}$); the distance to the other double bond is substantially longer ($2.73(6)\text{ \AA}$). These features indicate substantial back-bonding of electron density from the central metal into the π^* orbital of the alkenes, which is also evident from the considerable elongation of the $\text{C}=\text{C}$ bond from a theoretical value of $1.34\text{ \AA}$ in free COD to an average of $1.436(10)\text{ \AA}$ in **4**.³³

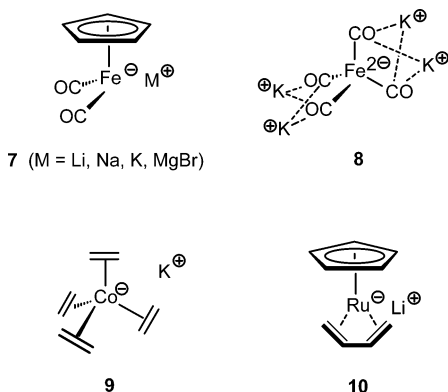
Although the global structure of the corresponding ethylene complex **1**³⁴ in the solid state is similar, the interactions between the lithium atom and the bound olefins become even more prominent (Figure 2). Specifically, the lithium center resides even closer to the ethylene moieties, with which it entertains now almost equidistant contacts at $2.354(2)$ and $2.368(2)\text{ \AA}$; thereby, the $\text{Fe}\cdots\text{Li}$ distance remains virtually unchanged ($2.5097(19)\text{ \AA}$). Transpiring from these structural details is the eminent role of the olefins for the stabilization of the electron rich iron center in **1** and **4**; yet, they can be readily displaced by other ligands such as CO, which leads to the known half sandwich complex **7** ($\text{M} = \text{Li}$)³⁵ in good yield.

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(33) For a depiction of the four independent molecules in the unit cell and a more detailed discussion of the structure, see the Supporting Information.

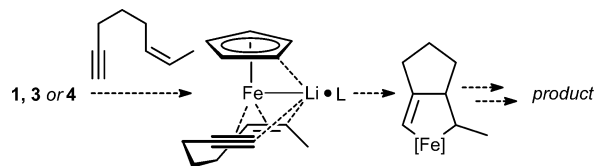
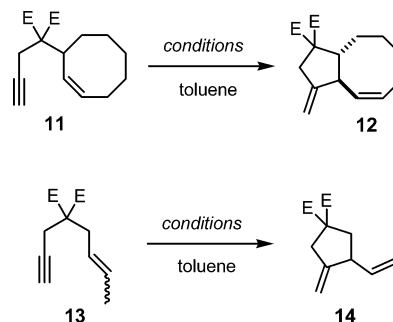
(34) The structure of **1** was briefly discussed in the following review, but no data have been deposited: Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 237.

(35) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (b) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417. (c) Burlitch, J. M.; Ulmer, S. W. *J. Organomet. Chem.* **1969**, *19*, P21. (d) Theys, R. D.; Vargas, R. M.; Wang, Q.; Hossain, M. M. *Organometallics* **1998**, *17*, 1333 and literature cited therein.

Scheme 2. Related Metalate Complexes

The even more highly reduced tetraethyleneferrate(−2) species **2**³⁰ is reminiscent of Collman's reagent [M₂Fe(CO)₄] (**8**, M = Li, Na, K),^{36,37} formally, the tightly bound and strongly backbonding CO ligands of **8** are replaced by four ethylene units. The olefins in **2**, however, remain kinetically labile, thus imparting a somewhat "bare" character onto the exceptionally nucleophilic iron center of this complex. In structural terms, however, complexes **2** and **8** show distinct differences: whereas there is a substantial direct interaction of the Fe and the Li centers in **2** according to the published crystal structure,³⁰ **8** consists of discrete [Fe(CO)₄]^{2−} fragments held together in the solid state by a three-dimensional network of remote interactions with the K⁺ counterions (Scheme 2).³⁸

Iron Catalyzed Alder-Ene Reactions. The known propensity of **1–4** to undergo ligand exchange spurred our efforts to use such complexes as catalysts for cycloisomerization and cycloaddition reactions.^{29,39} A recent investigation has shown that alkynes bind significantly more tightly than alkenes to low-valent iron centers.⁴⁰ Therefore, we reasoned that the alkene ligands in **1**, **3**, or **4** might be replaced by chelating substrates containing at least one alkyne unit. If such an exchange process allows one to bring, for example, 1,6-enynes into the coordination sphere of the electron rich lithium ferrate unit, an oxidative cyclization might ensue (Scheme 3). As the metal center in **1** or **4** is isoelectronic with Rh(+1), the resulting metallacycle might possibly evolve via a β -hydride elimination/reductive elimination sequence, resulting in a net Alder-ene type cycloisomerization of the substrate. Apart from a few remarkable exceptions,^{21,41} Alder-ene reactions are commonly performed with

Scheme 3. Envisaged Role of Ferrate Complexes as Catalysts for the Cycloisomerization of Enynes**Table 1.** Screening of Various Ferrate Complexes and Related Catalysts; E = COOEt

entry	substrate	catalyst (5%)	conditions	t (h)	yield
1	11	1	0.1 M, 90 °C	6	83%
2	11	2	0.1 M, 90 °C	12	0%
3	11	3	0.1 M, 90 °C	12	82%
4	11	4	0.1 M, 90 °C	12	80%
5	11	5	0.1 M, 90 °C	12	<20%
6	11	CpFe(CO) ₂ I	0.1 M, 95 °C	12	0%
7	11	[CpFe(CO) ₂] ₂	0.1 M, 95 °C	12	0%
8	11	7	0.1 M, 90 °C	12	0%
9	11	9	0.1 M, 20 °C	30	72%
10	11	10	0.1 M, 90 °C	12	0%
11	13	1	0.1 M, 90 °C	18	0%
12	13	4	0.1 M, 90 °C	18	53%
13	13	4	0.08 M, reflux	4	60%
14	13	4	0.02 M, reflux	4	80%
15	13	4	0.01 M, reflux	20	83%

noble metal catalysts;^{39,42–44} if the hypothesis sketched in Scheme 3 can be successfully reduced to practice, however, the iron complexes in question might qualify as cheap,⁴⁵ nontoxic, benign, and structurally well-defined alternatives that are available in quantity.

Compounds **11** and **13** were chosen as model substrates to optimize the reaction conditions. As shown in Table 1, the Alder-ene product **12** was obtained in high yield after 6 h reaction time in the presence of ferrate **1** (5 mol %) in toluene at 80–90 °C. The analogous COD complexes **3** and **4** performed

(36) (a) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342. (b) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.

(37) For other structurally defined iron ate complexes see the following for leading references: (a) Brennessel, W. W.; Jilek, R. E.; Ellis, J. E. *Angew. Chem. Int. Ed.* **2007**, *46*, 6132. (b) Döring, M.; Uhlig, E. Z. *Chem.* **1986**, *26*, 449. (c) Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P.; Jean, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1251. (d) Ellis, J. E.; Chen, Y. S. *Organometallics* **1989**, *8*, 1350.

(38) Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. J. *Am. Chem. Soc.* **1977**, *99*, 1104.

(39) Authoritative reviews: (a) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (b) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813. (c) Trost, B. M.; Krische, M. J. *Synlett* **1998**, *1*. (d) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38. (e) Fairlamb, I. J. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1048. (f) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (g) Wender, P. A.; Bi, F. C.; Gamber, G. G.; Gosselin, F.; Hubbard, R. D.; Scania, M. J. C.; Sun, R.; Williams, T. J.; Zhang, L. *Pure Appl. Chem.* **2002**, *74*, 25.

(40) Yu, Y.; Smith, J. M.; Flaschenriem, C. J.; Holland, P. L. *Inorg. Chem.* **2006**, *45*, 5742.

(41) Low valent titanium: (a) Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976. (b) Sato, F.; Urabe, H.; Okamoto, S. *Pure Appl. Chem.* **1999**, *71*, 1511. (c) Takayama, Y.; Okamoto, S.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3559.

(42) Leading references on Pd-based catalysts: (a) Review: Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34 and literature cited therein. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. (c) Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 249.

(43) Leading references on Ru-based catalysts: (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025. (b) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 9728. (c) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714. (d) Trost, B. M.; Surivet, J.-P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15592. (e) Trost, B. M.; Dong, L.; Schroeder, G. M. *J. Am. Chem. Soc.* **2005**, *127*, 10259. (f) Chen, H.; Li, S. *Organometallics* **2005**, *24*, 872.

(44) Leading references on Rh-based catalysts: (a) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198. (b) Oppolzer, W.; Fürstner, A. *Helv. Chim. Acta* **1993**, *76*, 2329.

(45) According to the current 2007–2008 Aldrich price list, 500 g of Cp₂Fe costs 132 Euros; if purchased on a larger scale, it may actually be significantly cheaper because ferrocene is a bulk chemical used as fuel additive in certain countries. For a very cost effective and scaleable synthesis, see: Eisenbach, W.; Lehmkuhl, H. *Chem. Ing. Tech.* **1982**, *54*, 690. For comparison, 1 g of Pd(OAc)₂ as the cheapest palladium salt presently costs 108 Euros, whereas 1 g of (Ph₃P)₃RhCl amounts to 112 Euros.

similarly well, although a somewhat longer reaction time was necessary (12 h). This rate difference is deemed to reflect the more facile and irreversible substitution of the ethylene ligands in **1** by the enyne, whereas the chelating COD in **3** or **4** is arguably more difficult to replace, remains in solution and might therefore compete with substrate binding. Although this kinetic retardation may seem undesirable at first sight, the presence of COD in the reaction medium actually turns out to be advantageous with somewhat more demanding substrates. For example, compound **13** would not cyclize with ferrate **1** (entry 11), whereas the COD complex **4** furnished the desired product **14** in up to 83% yield. This striking difference is tentatively ascribed to a stabilizing effect of COD, which may serve as ancillary ligand to protect the catalyst in the resting state. As evident from entries 12–15, Alder-ene reactions of acyclic substrates such as **13** are best performed in more dilute solution (0.01–0.05 M).

In line with the notion that the olefins in precatalysts **1** or **4** are initially replaced by the enyne substrate when entering the catalytic cycle, formal exchange of these ligands by strongly bound CO (complex **7**, M = Na, entry 8) results in complete loss of catalytic activity. The neutral iron carbonyl precursors [CpFe(CO)₂I] and [CpFe(CO)₂]₂ were equally unsuitable (entries 6–7). The fact that the more highly reduced tetraethylene ferrate **2** failed to afford the desired product **12** is tentatively ascribed to the lability of this complex at higher temperatures (entry 2). It is interesting to note, however, that the corresponding ethylene cobaltate complex [(C₂H₄)₄Co]K (**9**)^{31,46} is catalytically competent even at ambient temperature, although the reaction needed 30 h to go to completion (entry 9).

Another noteworthy observation concerns the analogous ruthenate complex **10**,⁴⁷ which was found inactive (entry 10). Even though this species contains a 1,3-diene rather than a 1,5-diene ligand, the comparison with the closely related iron complex **4** showcases the much higher catalytic competence of low valent iron in the present context. The failure of the nucleophilic Ru(0) species **10** is somewhat surprising if one considers the exceptional utility of electrophilic complexes of ruthenium in higher oxidation states as catalysts for Alder-ene reactions and related processes.^{39,43,48}

The two optimized reaction conditions (**A**: **1** cat., toluene 0.1 M, 90 °C; **B**: **4** cat., toluene, 0.01 M, reflux) were then applied to a host of different substrates to investigate the scope and limitations of this new iron catalyzed Alder-ene protocol. Several observations deserve comment: Although the formation of bicyclic products by Alder-ene processes is rare, the iron-based method is particularly well suited for such annulation reactions (Table 2). The pre-existing ring of the starting material, however, determines the stereochemistry at the ring junction (see below) and exerts a distinct influence on the reaction rate, with larger cycloalkenes usually rendering the transformation more facile. This is evident from the fact that the [3.3.0]bicyclo-octene derivative (entry 1) was the most difficult to form among all products compiled in Table 2. It is believed that the strain in the metalla-tricyclic intermediate peaks for this particular compound (see below).

Except for the decaline product derived from a 1,7-enyne (entry 4), which is formed as a *cis/trans*-mixture, all compounds shown in Table 2 were obtained as single isomers. Thereby, the exocyclic alkene is invariably (*E*)-configured as expected for an Alder-ene pathway. The newly generated endocyclic olefin must be (*Z*)-configured when part of a 5–8 membered ring (entries 1–18), whereas it is the corresponding (*E*)-isomer that is exclusively formed wherever the ring size allows to (≥10, entries 19–30).⁴⁹

Although one might be concerned about the potential basicity of ferrate complexes in general, enynes containing terminal acetylene units posed no problems (entries 6, 19, 24). Likewise, different substituents on the alkyne are well accommodated, including electron-withdrawing substituents, cyclopropyl- and silyl groups. The latter result is remarkable because silylated enynes are unsuitable for Alder-ene reactions catalyzed by low-valent titanium reagents.^{41a} If the alkyne carries an aryl substituent, the electronic characteristics of this ring are largely inconsequential. Particularly significant is the compatibility of the iron catalyst with various tethers and functional groups, including esters, ketones, acetals, ethers, silyl ethers, sulfonamides, pyrroles, cyclopropanes, and remote alkenes; even a tertiary amine does not interfere, indicating a moderate Lewis acidity of the chosen catalyst system, if any (entry 13). The fact that aryl halides also remain untouched shows that the oxidative cyclization of the enyne must be favored over a conceivable oxidative insertion of the low-valent iron center into such C–X bonds (entries 14, 27).

Table 3 compiles representative examples of iron-catalyzed Alder-ene reactions of acyclic enynes according to Scheme 4. As already mentioned above, the substitution pattern of such substrates has a pronounced effect on their reactivity. Specifically, enynes with R² = H failed to react with the bis-ethylene complex **1** under the standard conditions, whereas they were cleanly converted to the desired Alder-ene products with the aid of the analogous COD complex **4** (conditions **B**) (cf. entries 1/2, 3/4, 5/6). This superior performance of **4**, which also transpires upon comparison of entries 8/9 and 20/21, is thought to reflect the stabilizing influence of the ancillary COD ligand remaining in solution, which was also noticed during our investigations on the [5+2] cycloaddition processes (vide infra). In striking contrast, conformationally more biased enynes with R² ≠ H react with both catalysts, affording the corresponding *trans*-disubstituted products as the major isomers in all cases investigated.⁵⁰ As in the annulation mode discussed above, the reaction applies to 1,6- as well as 1,7-enynes, tolerates various kinds of tethers, and is compatible with basic amine functions as well as various potentially reducible functional groups.

The major limitation encountered during our investigation concerns enynes bearing a trisubstituted alkene moiety that failed to react under the chosen conditions. Representative examples of such unreactive substrates are compiled in Chart 1.

Stereochemical Aspects and Mechanistic Investigation. A striking aspect of the Alder-ene annulation process concerns

(46) See also: Jonas, K.; Mynott, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 767.

(47) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.

(48) Review: Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 6630.

(49) The endocyclic olefin was invariably (*E*)-configured even though the substrates used were *E/Z*-mixtures. Moreover, GC investigations show that the (*E*)-isomer does not result from equilibration but is the primary product of the reaction.

(50) The stereochemical assignment is based on NOESY data [Table 2: entry 1 (*cis*), entry 2 (*cis*), entry 4 (*trans*), entry 6 (*trans*), entry 27 (*trans*); Table 3: entry 16 (*trans*), entry 28 (*trans*)] all other products were assigned by analogy.

Table 2. Iron Catalyzed Alder-ene Annulation Reactions;^a E = COOEt

Entry	Product	Yield	Entry	Product	Yield
1		50% ^b	2		93% (X = CE ₂) 60% (X = NTs) ^b
4		68% ^{b,c}	5		63%
6		83%	7		93%
8		96%	9		70%
10		95% (X = CE ₂) 94% (X = NTs) ^b 70% (X = O) ^b	13		93% ^b
11			15		68%
12			18		96%
14		97%	20		86% (X = NTs) ^b 55% (X = O) ^b
16		84% (R = Ac) 86% (R = TIPS)	21		
17			23		85%
19		76%	25		98% (X = NTs) ^b 86% (X = O) ^d
22		89%	26		
24		81%	28		96%
27		95%	30		94%
29		79%			

^a All reactions were performed with complex **1** (5 mol %) in toluene at 90 °C, unless stated otherwise. ^b Using 10 mol % of catalyst. ^c dr ≈ 2.5:1. ^d Using 20 mol % of catalyst.

its stereodivergent course with regard to the ring junction. Whereas enynes containing a cyclopentene- or cyclohexene ring exclusively form the corresponding *cis*-annulated ring systems (Table 2, entries 1–3) as evident from the pertinent ³J_{H3,H4} coupling constants and the strong NOE effects between these protons (Scheme 5), all substrates incorporating larger cycloalkenes uniformly lead to the corresponding *trans*-adducts (Table 2, entries 5–30).⁵¹

This assignment is based on the observed large coupling constant (³J_{H3,H4} ≈ 11 Hz) and the analysis of the entire NOE pattern indicated in Scheme 5. It is important to note, however,

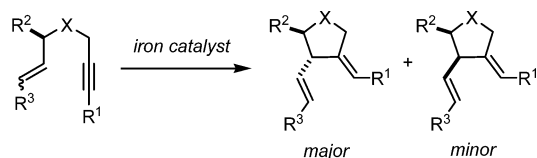
that a feeble yet non-negligible NOE is recorded between the protons at the ring junction even though they are *trans* disposed. Although the overall NMR data set leaves no doubt with regard to the stereochemical assignment, the *trans*-ring fusion was independently confirmed for sulfonamide **15** (Table 2, entry 11) by X-ray structure analysis to avoid any ambiguity in this regard (Figure 3).

(51) Some precedence for a related stereochemical switch from *cis* to *trans* on going to larger ring sizes is found in organopalladium chemistry, cf.: Trost, B. M.; Grese, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 7363.

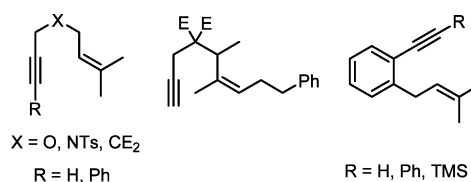
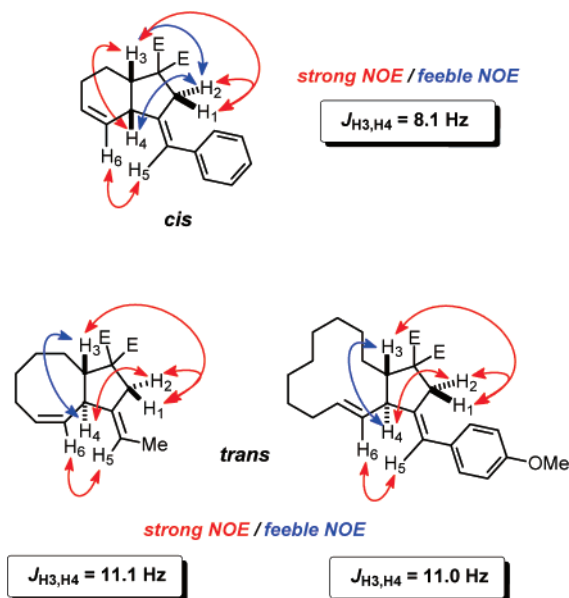
Table 3. Iron Catalyzed Alder-ene Type Reactions of Acyclic Enynes; ^a E = COOEt

Entry	Product ^b	Method	Yield	d.r.
1		A	0% (R = H)	
2		B	80% (R = H)	
3		A	0% (R = Ph)	
4		B	88% (R = Ph)	
5		A	0% (R = H)	
6		B	79% (R = H)	
7		A	65% (R = Me) ^d	3.9:1
8		A	60% (R = propyl) ^d	5:1
9		B	90% (R = propyl)	7.9:1
10		A	60% (R=cyclopropyl) ^c	2:1
11		A	93% (R = Me)	5.8:1
12		A	78% (R = Ph)	9:1
13		A	48% (R = Pr) ^d	20:1
14		A	68% (R = <i>i</i> Pr) ^d	20:1
15		A	97%	6.7:1
16		A	97% (X = OMe)	6.3:1
17		A	96% (X = CF ₃)	4.8:1
18		A	91% (X = C(O)CH ₃)	4.1:1
19		A	98%	
20		A	0%	
21		B	81% ^e	
22		A	98% (X = H) ^c	4.2:1
23		A	84% (X = OMe) ^c	3:1
24		A	90% (X = F) ^c	3:1
25		A	53% (R = H) ^c	2.3:1
26		A	74% (R = Ph) ^c	1.3:1
27		A	70% (R = Me) ^d	9.8:1
28		A	82% (R = propyl) ^d	20:1
29		A	54% (R = <i>i</i> Pr) ^d	20:1

^a Conditions: A: complex **1** (5 mol %), toluene (0.1 M), 90 °C; B: complex **4** (5 mol %), toluene (0.02 M), reflux. ^b Only the major isomer is depicted. ^c Using 10 mol % of catalyst. ^d Using 20 mol % of catalyst. ^e Using 15 mol % of catalyst.

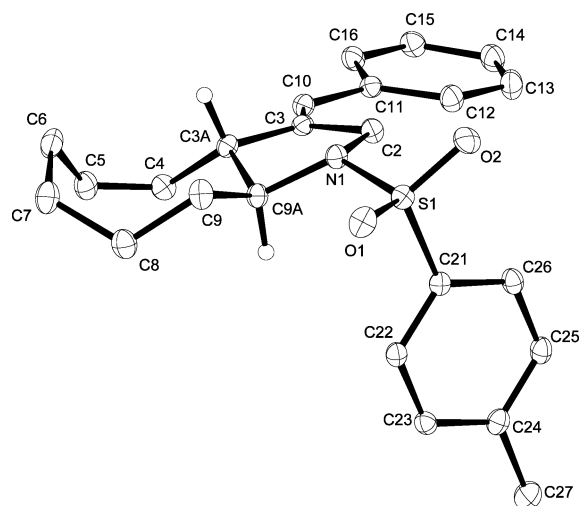
Scheme 4. Iron-catalyzed Reactions of Acyclic Enynes

This stereodivergent course of the reaction likely reflects distinct conformational preferences of the different ring sizes. We assume that substrates of type **16** adopt a transition state placing the tether in a pseudoequatorial position on the fairly rigid cyclohexenyl scaffold; an ensuing axial attack then generates metallacycle **18** and hence nicely explains the formation of the *cis*-annulated bicycle **19** as the only product (Scheme 6). In contrast, transannular interactions dominate the behavior of medium rings, which strongly disfavor such a

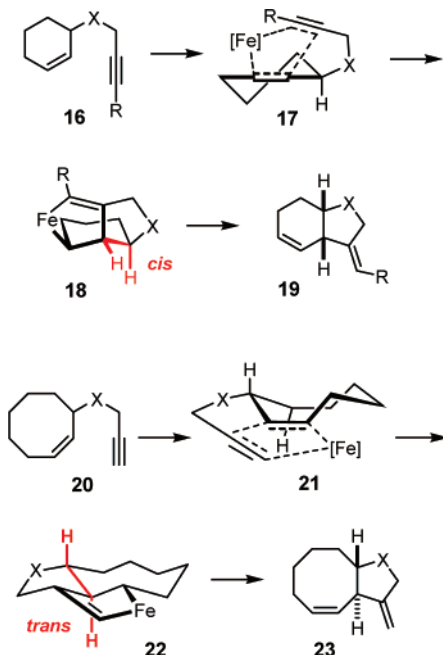
Chart 1**Scheme 5.** Stereochemical Assignment of Representative *cis*- and *trans*-fused Alder-ene Products

trajectory as exemplified for the substrate class **20** incorporating a cyclooctenyl entity (Scheme 6, bottom). To avoid a clash with the hydrogen in transannular proximity, the alkyne in the tether approaches the olefin in a pseudo-equatorial fashion, which readily explains the experimentally observed *trans*-annulation mode in this and related cases.

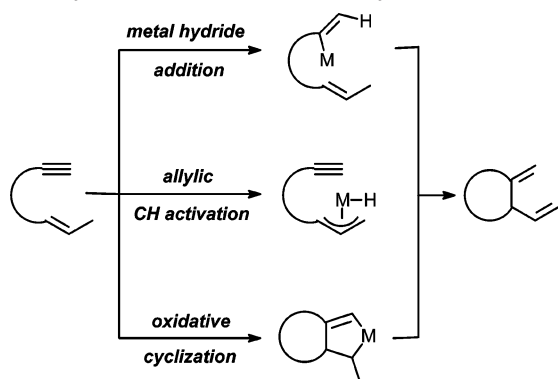
This interpretation tacitly assumes metallacycles as the key reactive intermediates, which, however, is by no means the only conceivable pathway. Metal-catalyzed Alder-ene reactions in general may occur by one of three different scenarios which

**Figure 3.** Molecular structure of **15** (Table 2, entry 11) in the solid state. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity, except those at the ring junction.

Scheme 6. Tentative Explanation for the Stereodivergent Course of the Alder-ene Annulation Process as a Function of the Size of the Pre-existing Ring



Scheme 7. Conceivable Mechanistic Scenarios of Metal-Catalyzed Alder-ene Reactions of Enynes



can be classified according to the initial step as follows (Scheme 7):^{39,52} (1) addition of a metal hydride species formed in situ or ex situ to the alkyne generates a vinyl metal reagent which adds to the double bond in a "Heck type" manner and thereby leads to the final product; (2) activation of the allylic CH-bond by the catalyst generates an allylmetal species which undergoes a "metallo-ene" type reaction with the alkyne; (3) oxidative cyclization of the enyne generates a metallacyclopentene, which affords the product via a subsequent β -hydride elimination/reductive elimination process.

A priori, it is very difficult to rigorously distinguish between these scenarios,⁵³ and direct spectroscopic evidence is usually lacking due to the very limited lifetimes of the putative intermediates.³⁹ Whereas the metal hydride mechanism can likely be ruled out in our case, since no proton source is present

to generate the required metal hydride initiator, the available data do not allow for a clear-cut choice between the two remaining options. We reasoned, however, that the stereodivergent course of the iron-catalyzed Alder-ene annulation process may provide a unique opportunity to gather indirect evidence via labeling experiments.

If the reaction of the stereospecifically labeled cyclooctenyl derivative **24** commences with allylic CH activation, the iron catalyst will insert into the C–H as well as into the C–D bond with similar ease (Scheme 8, right).^{54–56} Activation of the C–D bond affords the allyliron species **1a** which transfers the label to the exocyclic alkene of *trans*-annulated bicycle as the only observed product (**24** $\rightarrow$ **25a**).⁵⁷ However, the isomeric allyliron complex **1c**, generated by activation of the allylic C–H rather than C–D bond, can also lead to the *trans*-annulated product if an allyl-interconversion to **1d** intervenes. Such a process may be triggered by π - σ - π hapticity changes or result from intermolecular metal exchange, which are well preceded phenomena in allyliron chemistry.^{58–60} Because a course via **1c,d** transmits hydrogen but leaves the label intact at its original site, it delivers isotopomer **25b**. One may hence anticipate that a mechanism based on CH-activation—overall—likely results in *some degree of scrambling* of the deuterium in the product (**25a/25b**).

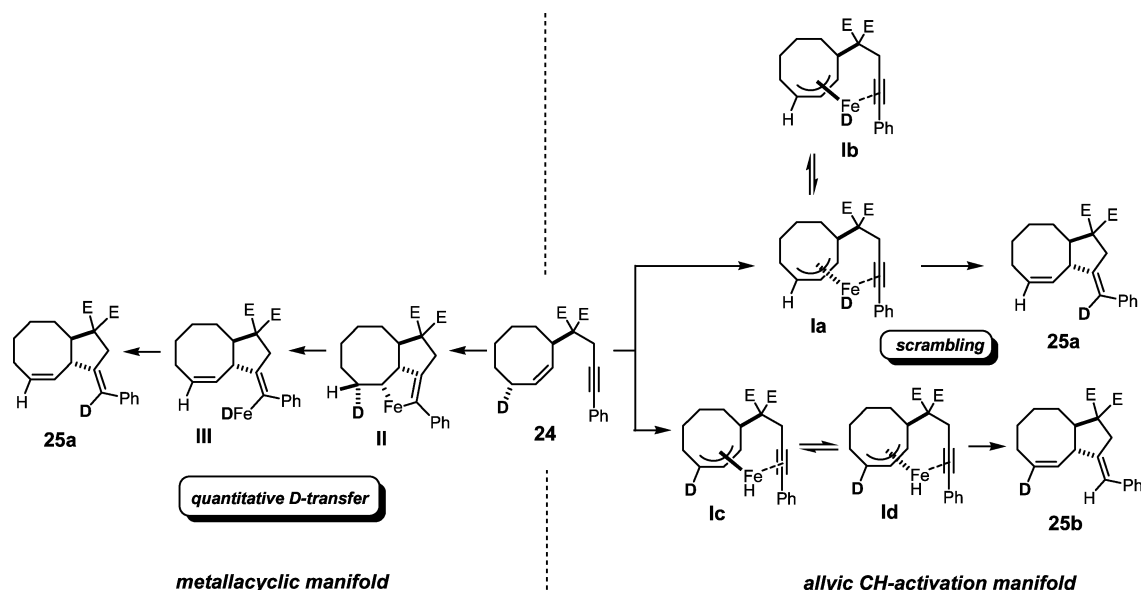
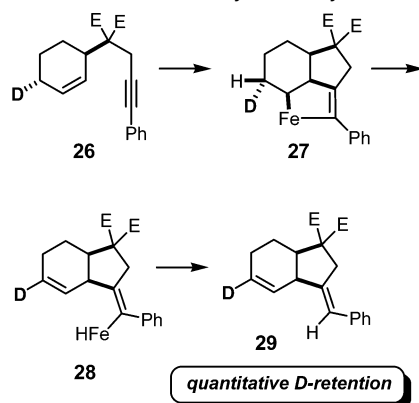
In contrast, a metallacyclic pathway can afford the experimentally observed *trans*-annulated product only via an intermediate of type **II** as a consequence of the geometrical constraints inherent to a tricyclic scaffold (Scheme 8, left). In this case, β -elimination exclusively activates the deuterium label in *cis*-disposition relative to the C–Fe bond. Hence, a metallacyclic scenario must engender a *complete transmission of the label* to the exocyclic olefin (**II** $\rightarrow$ **III** $\rightarrow$ **25a** only).

The same arguments apply to the formation of the *cis*-annulated product **29** derived from the labeled cyclohexenyl

- (54) Even if one assumes that this step is rate determining and hence a kinetic isotope effect comes into play, the probabilities for activation of the C–H and the C–D bonds are of the same order of magnitude.
- (55) For the facile formation of allyl- and pentadienyliron complexes by allylic CH activation, see the following for a leading reference: Angermund, K.; Geier, S.; Jolly, P. W.; Kessler, M.; Krüger, C.; Lutz, F. *Organometallics* **1998**, *17*, 2399.
- (56) For evidence for fast allylic CH activation by low valent iron in the gas phase as the first step of a formal Alder-ene type process, see: Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 1682.
- (57) Note that reductive elimination from **1b** would afford the *cis*-adduct which is not observed; therefore, putative **1b** must be outside the productive pathway.
- (58) (a) The $\pi \rightarrow \sigma$ hapticity change is particularly fast upon coordination of an extra ligand to a π -allyliron species; the alkyne could play such a role in the present case, see: (a) Gabor, B.; Holle, S.; Jolly, P. W.; Mynott, R. *J. Organomet. Chem.* **1994**, *466*, 201. (b) Cardaci, G.; Foffani, A. *J. Chem. Soc., Dalton Trans.* **1974**, 1808. (c) Hapticity change accompanied by an *exo/endo* rearrangement: Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71.
- (59) Reviews: (a) π -allyliron complexes: Moss, J. R.; Smith, G. S.; Kaschula, C. H. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Eds.; Elsevier: Amsterdam, 2007; Vol. 6, pp 127. (b) σ -Allyliron complexes: Knorr, M. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Eds.; Elsevier: Amsterdam, 2007; Vol. 6; pp 77.
- (60) Less common than π -allyliron complexes, σ -allyliron species are well known and have been isolated and fully characterized in certain cases. Additionally, there is strong evidence for various reactions to proceed via σ -allyliron complexes as the key intermediates. For leading references see ref. 17 and the following, together with literature cited therein: (a) Akita, M.; Shirasawa, N. *Chem. Commun.* **1998**, 973. (b) Akita, M. *J. Organomet. Chem.* **2004**, *689*, 4540. (c) Eberhardt, U.; Mattern, G. *Chem. Ber.* **1988**, *121*, 1531. (d) Stereochemical arguments for σ -allyliron: Xu, Y.; Zhou, B. *J. Org. Chem.* **1987**, *52*, 974. (e) Benn, R.; Brenneke, H.; Frings, A.; Lehmkühl, H.; Mehler, G.; Rufinska, A.; Wildt, T. *J. Am. Chem. Soc.* **1988**, *110*, 5661. (f) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (g) Dey, K.; Koner, D.; Bhattacharyya, P. K.; Gangopadhyay, A.; Bhasin, K. K.; Verma, R. D. *Polyhedron* **1986**, *5*, 1201. (h) Bassett, J.-M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1779.

(52) Review on mechanisms of cycloisomerization reactions of enynes: Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215.

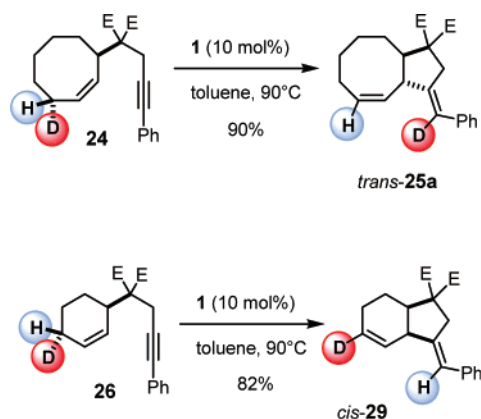
(53) (a) In this context, it is interesting to note that most Ru-catalyzed Alder-ene reaction were analyzed on the basis of metallacyclic intermediates; however, a mechanistic switch to a CH activation pathway was proposed to explain certain outcomes, cf. ref 43. (b) A CH activation process was also invoked in closely related cobalt-catalyzed Alder-ene processes, cf.: Ajamian, A.; Gleason, J. L. *Org. Lett.* **2003**, *5*, 2409.

Scheme 8. Deuterium Labeling Experiments as Possible Probes for the Mechanism of the Iron Catalyzed Alder-ene Reaction of Substrate **24****Scheme 9.** Stereochemical Implication of a Metallacyclic Pathway for the Alder-ene Reaction of the Cyclohexenyl Derivative **26**

derivative **26**. An allylic CH-activation pathway will again likely engender some degree of scrambling. It is of special note, however, that a metallacyclic intermediate—in striking contrast to the cyclooctenyl case discussed above—necessarily invokes a quantitative *preservation of the deuterium atom* at the original site as evident from Scheme 9.

The experimental results are highly informative (Scheme 10). Specifically, reaction of **24**⁶¹ with catalytic amounts of complex **1** in toluene at 90 °C gave **25a** as the only product in 90% isolated yield, in which the deuterium label has quantitatively migrated to the exocyclic alkene. Under the exact same conditions, the smaller homologue **26**, in contrast, exclusively affords compound **29** (82%) in which the deuterium atom is completely retained at the original site. Within the limits of detection, no sign of scrambling of the label was observed in either case. Even though these opposite labeling patterns cannot be taken as an ultimate proof for a metallacyclic pathway, they do provide strong evidence for such a scenario.

Iron Catalyzed [4+2] Cycloadditions. Diene-yne derivatives such as **30** were previously shown to undergo unusual Alder-ene reactions to give ene-allenes of type **31** in the presence of low valent titanium.^{41a,21} When reacted with catalytic amounts of **4** under the usual conditions, however, only the Diels–Alder

Scheme 10

product **32** was obtained.⁶² This outcome is general, although the yields of the cycloadducts were only moderate (54–67%). Control experiments confirmed the catalytic role of the iron species, which accelerates the [4+2] cycloaddition over the thermal background reaction (Table 4). Because metal-catalyzed Diels–Alder reactions of unactivated alkynes as dienophiles are thought to proceed via metallacyclic intermediates,^{39,63} this behavior is consistent with the mechanistic conclusions reached above.

Iron Catalyzed [5+2] Cycloaddition Reactions. The success of the iron-catalyzed Alder-ene and Diels–Alder reactions encouraged us to extend our program to other skeletal reorganization processes. Given the fact that [5+2] cycloadditions are not only exceedingly useful for the construction of variously substituted seven-membered rings but also dominated by noble metal catalysis,^{48,64–66} such transformations constitute another

(61) The deuterated cycloalkenes were prepared as described in: (a) Franzén, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2003**, *125*, 6056. (b) Bäckvall, J.-E.; Nyström, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676; for details, see the Supporting Information.

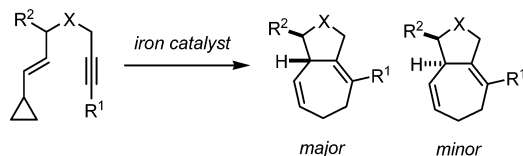
(62) For precedence on Diels–Alder reactions catalyzed by structurally unknown low-valent iron species generated *in situ*, see ref 19a.

(63) For alternative mechanisms allowing [4+2] cycloadditions of diene-yne to proceed, see: Füßner, A.; Stimson, C. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 8845.

Table 4. Intramolecular [4+2] Cycloadditions of Unactivated Diene-yne Complexes Catalyzed by the Iron-ate Complex **4**; ^a E = COOEt

entry	X	R	catalyst	t (h)	conversion	yield ^b
1	NTs	H	—	1.5	23%	
2	H	H	4 (10%)	1.5	>90%	54%
3	CE ₂	H	—	7	25%	
4	H	H	4 (10%)	7	85%	67%
5	Me	H	—	16	10%	
6	Me	H	4 (20%)	16	100%	57%
7	SiMe ₃	H	—	6	25%	
8	SiMe ₃	H	4 (10%)	6	100%	66%

^a All reactions were performed in toluene at 80–90 °C. ^b After work up in air, the products contain variable amounts of the fully aromatized compounds.

Scheme 11. Iron-Catalyzed [5+2] Cycloadditions

attractive testing ground for the cheap ferrate complexes discussed herein (Scheme 11).

In line with our expectations, a set of representative vinyl-cyclopropane derivatives were converted into the corresponding cycloheptadiene derivatives on exposure to the Fe(0) complexes **1** or **4** under the established conditions (Table 5). Like in the Alder-ene case, the COD-containing species **4** turned out to be more generally applicable, allowing conformationally less biased substrates with R² = H to be transformed to the corresponding cycloadducts, whereas the ethylene complex **1** failed in such cases. The products are obtained with good to excellent diastereoselectivity, invariably favoring the 1,2-*trans*-disubsti-

Table 5. [5+2] Cycloaddition Reactions Catalyzed by Ferrate(0) Complexes; ^a E = COOEt

Entry	Product ^b	Method	Yield	d.r.
1		B	66% (R = H) ^{c,e}	
2		B	66% (R = SiMe ₃)	
3		B	75% (X = H)	
4		B	58% (X = OMe)	
5		B	69% (X = F)	
6		B	62% (R = Ac)	
7		B	73% (R = TBS)	
8		B	54% ^f	
9		A	56% ^d	5.5:1
10		B	70%	5.7:1
11		A	91% ^e	6.7:1
12		A	92% (R = Me) ^d	9.4:1
13		A	76% (R = COOEt) ^d	2.3:1
14		A	99% (R = SiMe ₃)	15:1
15		A	98% (X = H)	6.2:1
16		A	98% (X = OMe)	7.3:1
17		A	97% (X = F)	6.6:1

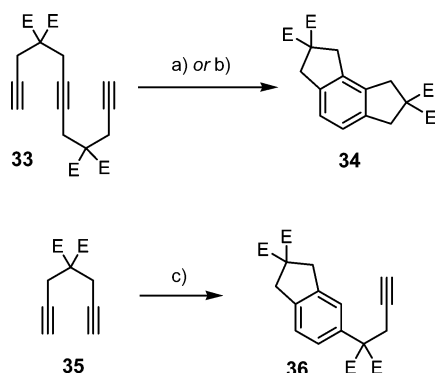
^a Conditions: **A**: complex **1** (10 mol %), toluene (0.1 M), 90 °C; **B**: complex **4** (10 mol %), toluene (0.02 M), reflux. ^b Only the major isomer is depicted. ^c No product was obtained under conditions **A**. ^d Using 20 mol % of catalyst. ^e Using 5 mol % of catalyst. ^f Using 15 mol % of catalyst.

tuted isomer.⁶⁷ Terminal and differently end-capped alkynes participate with similar ease (R¹ = H, Me, SiMe₃, COOEt, aryl), independent of the electronic variations that such substituents impose. Entry 8 shows that a [5.4.0] bicyclic product can also be formed by this methodology. As in the Alder-ene regimen, the only serious limitation concerns substrates with trisubstituted olefins which remain unchanged under the chosen conditions.

Iron Catalyzed [2+2+2] Cycloadditions and Additional Mechanistic Insights. Finally, the applicability of ferrate complexes to catalytic [2+2+2] cycloadditions was briefly surveyed. Such transformations are effected by a host of transition metal catalysts, among which CpCoL₂ (L = CO, C₂H₄) and various Rh(+1) complexes are arguably most widely used.^{39,68,69} Because the ferrate complexes **1** and **4** are isoelectronic with such templates, one might expect them to be competent catalysts for such purposes too.

- (64) Rhodium catalysis: (a) Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. (b) Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 9154. (c) Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164. (d) Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442. (e) Wender, P. A.; Dyckman, A. *J. Org. Lett.* **1999**, *1*, 2089. (f) Wender, P. A.; Williams, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4550. (g) Wender, P. A.; Haustedt, L. O.; Lim, J.; Love, J. A.; Williams, T. J.; Yoon, J.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 6302. (h) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348. (i) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940. (j) Ashfeld, B. L.; Martin, S. F. *Tetrahedron* **2006**, *62*, 10497. (k) Wender, P. A.; Rieck, H.; Fujii, M. *J. Am. Chem. Soc.* **1998**, *120*, 10976. (l) Wender, P. A.; Bi, F. C.; Brodney, M. A.; Gosselin, F. *Org. Lett.* **2001**, *3*, 2105. (m) Saito, A.; Ono, T.; Hanzawa, Y. *J. Org. Chem.* **2006**, *71*, 6437. (n) Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem.* **2006**, *71*, 91. (65) For a C-H activation/[5+2] tandem, see: Aissa, C.; Fürstner, A. *J. Am. Chem. Soc.* **2007**, *129*, 14836. (66) Ruthenium catalysis: (a) Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc.* **2000**, *122*, 2379. (b) Trost, B. M.; Shen, H. *C. Org. Lett.* **2000**, *2*, 2523. (c) Trost, B. M.; Shen, H. C.; Schulz, T.; Koradin, C.; Schirok, H. *Org. Lett.* **2003**, *5*, 4149. (d) Trost, B. M.; Shen, H. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2313. (e) Trost, B. M.; Toste, F. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1114 and literature cited therein.

- (67) The stereochemical assignment is based on NOESY data for compounds shown in entries 9 and 11; all other products were assigned by analogy. (68) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Bönemann, H.; Brijoux, W. *Adv. Heterocycl. Chem.* **1990**, *48*, 177. (c) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787. (d) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503. (e) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307.

Scheme 12^a

^a Reagents and conditions: (a) complex **4** (10 mol %), toluene (0.08 M), reflux, 2 h, 89%; (b) complex **6** (20 mol %), toluene (0.08 M), reflux, 21 h, 80%; (c) complex **4** (5 mol %), toluene (0.1 M), 90 °C, 24 h, 70%; E = COOEt.

In fact, triyne **33** was smoothly converted into product **34** on exposure to catalytic amounts of **4** in refluxing toluene; analogously, diyne **35** underwent a clean dimerization to give **36** in respectable yield (Scheme 12). Interestingly, the Fe(+1) complex **6** was also active, although a higher loading and a longer reaction time were needed. In each case, addition of the substrate to the solution of the iron species was accompanied by an instantaneous and very characteristic color change from red to bright green. Although similar observations were made with the other types of substrates discussed above, it was particularly pronounced in this series. Speculating that this effect might either reflect the exchange of the COD ligand for the substrate or even the formation of the putative metallacyclic intermediate on the reaction coordinate, attempts were made to isolate and characterize the new species formed in situ.

To this end, the different iron complexes were reacted with stoichiometric amounts of 1,2-diphenylacetylene (tolane) as the model substrate. Although all attempts to characterize the corresponding complexes derived from this alkyne and **1** or **4** have so far been unsuccessful, the Fe(+1) complex **6** allowed us to obtain a stable product in analytically pure form in 77% yield. Spectroscopic data and elemental analysis showed that two equivalents of tolane must have reacted with **6**,^{30d} but the identity of this new compound could only be revealed by X-ray structure analysis. As can be seen from Figure 4, it turned out to be the Fe(+1) cyclobutadiene complex **38**, a remarkable compound given the odd electron count of the central metal.⁷⁰ This 17-electron iron species is somewhat reminiscent of the closed shell (CO)₃Fe(0)(cyclobutadiene) complexes formed by oxidative insertion of Collman's reagent into *cis*-3,4-carbonyldioxycyclobutenes, which, however, benefit from additional

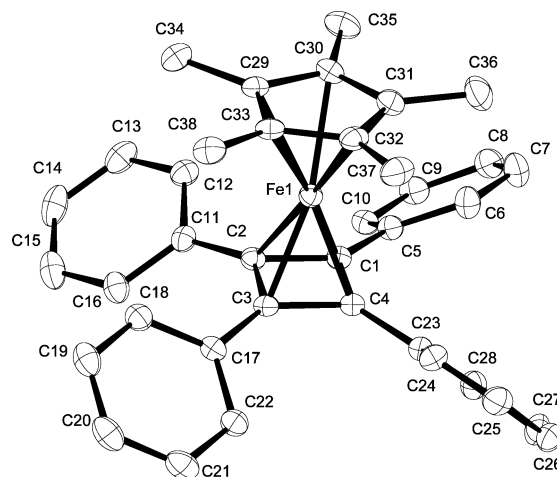
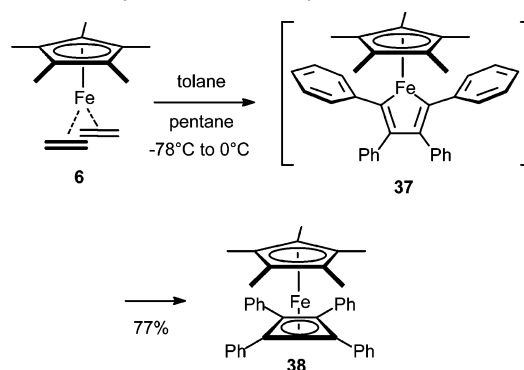


Figure 4. Molecular structure of **38** in the solid state. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity.

Scheme 13. Possible Pathway for the Formation of the 17-electron Fe–Cyclobutadiene Complex **38**



stabilization by the strongly backbonding carbonyl ligands.⁷¹ Moreover, the formation of **38** from **6** parallels the behavior of [Cp*Co(C₂H₄)₂], which is a particularly effective catalyst for [2+2+2] cycloadditions of various alkynes, yet transforms toluene into the cyclobutadiene complex [Cp*Co(η⁴-C₄Ph₄)].^{72,73}

The formation of **38** is best explained by assuming an oxidative cyclization with formation of metallacycle **37** as the primary product, which, upon reductive elimination, generates the butadiene entity that remains bound to the regenerated Fe(+1) template (Scheme 13). As the latter step is likely driven by the release of strain caused by the clash of the bulky Cp* ligand with the adjacent phenyl rings in **37**, we suspected that smaller substituents on the alkyne might allow one to intercept other intermediates. Therefore, **6** was reacted with a slight excess of 2-butyne which also resulted in the formation of an iron complex that could be isolated in analytically pure form, even though it is much more labile. Although no crystals suitable for X-ray structure analysis could be obtained, all available data suggest that the new iron complex **41** is the product of the [2+2+2] cycloaddition between two molecules of butyne and one ethene ligand derived from the starting complex itself, which

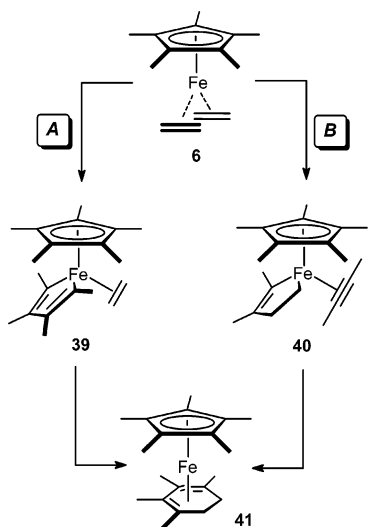
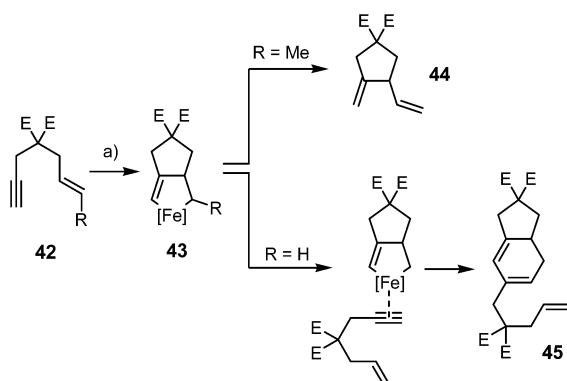
(69) For previous examples of iron-catalyzed cyclotrimerizations, see the following for leading references and literature cited therein: (a) Breschi, C.; Piparo, L.; Pertici, P.; Caporusso, A. M.; Vitulli, G. *J. Organomet. Chem.* **2000**, 607, 57. (b) Funhoff, A.; Schäufele, H.; Zenneck, U. *J. Organomet. Chem.* **1988**, 345, 331. (c) Usieli, V.; Victor, R.; Sarel, S. *Tetrahedron Lett.* **1976**, 17, 2705. (d) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, 93, 103. (e) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, 33, 3948. (f) Weber, S. R.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, 127, 45. (g) Simons, L. H.; Lagowski, J. J. *J. Organomet. Chem.* **1983**, 249, 195. (h) Saino, N.; Kogure, D.; Okamoto, S. *Org. Lett.* **2005**, 7, 3065.

(70) The geometry of this Cp*Fe(C₄Ph₄) radical differs only slightly from that of the anion [Cp*Fe(C₄Ph₄)][−] [Li(thf)₄]⁺, whose structure was briefly reported in the following publication: Krüger, C.; Sekutowski, J. C.; Tsay, Y.-H. *Z. Kristallogr.* **1979**, 149, 109. Despite the higher uncertainty associated with the earlier measurement, the tendency of the ligands to be closer to the Fe atom in the anionic complex is evident.

(71) (a) Grubbs, R. H. *J. Am. Chem. Soc.* **1970**, 92, 6693. (b) Grubbs, R. H.; Grey, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 76.

(72) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, 221, C25–C27.

(73) Crystallographic investigation on the mechanism of Co-catalyzed, cyclo-trimerizations: Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, 120, 8247.

Scheme 14. Participation of an Ethylene Ligand of the 17-electron Fe(+1) Complex **6** in a Mixed [2+2+2] Cycloaddition**Scheme 15**^a

^a Reagents and conditions: (a) complex **4** (10%), toluene (0.1 M), 90 °C, 80% (**44**), 63% (**45**); E = COOEt.

has been intercepted in the coordination sphere of the 17e Fe(+1) center (Scheme 14).^{30d} It cannot be decided at this stage whether **41** forms via an initial oxidative cyclization of two butynes followed by insertion of the (coordinated) ethylene (path **A**), or, conversely, implies an initial mixed oxidative cyclization mode between butyne and ethene followed by insertion of the second alkyne (path **B**); as the latter corresponds to the initial steps of the Alder-ene manifold (e.g., **42** (R = Me) → **43** → **44**), we are inclined to favor this pathway (Scheme 15). It will also explain why substrate **42** (R = H) dimerizes to the [2+2+2] cycloadduct **45**, which is formed as a single isomer.

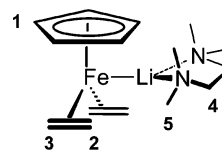
In any case, the rather unusual complexes **38** and **41** corroborate the competence of highly electron-rich—neutral as well as charged—iron half-sandwich complexes in oxidative cyclization processes and hence stimulate further investigations into this still fairly unexplored terrain of organometallic chemistry. The fact that even an Fe(+1) template with an odd electron count is catalytically relevant and well behaved is a hitherto largely unrecognized aspect that deserves particular attention.

Conclusions. Ferrocene serves as a convenient and very cheap starting material for the preparation of a family of low valent iron olefin complexes of the formal oxidation states −2, 0 and +1. The structures of the ferrate complexes **1** and **4** in

the solid state are reported, which reveal the capacity of the metal center to share electron density with the ligand environment and hence explains the capacity of such catalysts to induce oxidative cyclization reactions of polyunsaturated compounds. As a result, these complexes effect a variety of cycloaddition and cycloisomerization reactions of the Alder-ene, [4+2], [5+2], and [2+2+2] type. These transformations are compatible with a variety of substitution patterns, potentially reducible functional groups, basic sites, and even fairly CH-acidic terminal alkyne units. Labeling experiments together with the isolation of two novel Fe(+1) complexes, which incorporate different primary cycloadducts, provide compelling evidence for the proposed mechanism. Although additional investigations are warranted to expand the scope and upgrade the catalytic performance of the catalysts even further, we believe that this study constitutes an important step toward a more prolific use of inexpensive, readily available, nontoxic, and benign iron complexes as powerful alternatives to the commonly used noble metal catalysts in the realm of cycloaddition and cycloisomerization chemistry.

Experimental Section

The complete experimental section is found in the Supporting Information. Outlined below is the preparation of the ferrate complexes used as catalysts herein, as well as the synthesis of the novel 17-electron iron cyclobutadiene complex **38**.



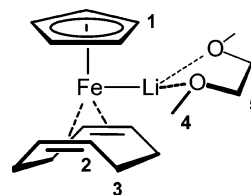
Preparation of [CpFe(C₂H₄)₂][Li(tmeda)] (1**).** A flame-dried three-necked round-bottom flask equipped with a magnetic stirbar, a gas inlet, a glass stopper, and a stopcock connected to the vacuum line is charged under Ar with lithium sand (2.40 g, 346 mmol) and THF (200 mL). The suspension is cooled to −50 °C and vacuum is applied until gentle boiling of the solvent is observed. At that stage, the flask is back-filled with ethene (from a gas burette to monitor the uptake) and the evacuation/back-filling cycle is repeated three times. Ferrocene (32.1 g, 173 mmol) is then added in portions under a gentle stream of ethene and the resulting orange–brown suspension is vigorously stirred for 20 h at −50 °C. During the first 2–3 h, a fast uptake of ethylene can be observed, which slowly ceases. The resulting mixture is allowed to warm to 0 °C before it is filtered under Ar through a cooled funnel (cooling jacket) at 0 °C. The filtrate is evaporated under reduced pressure to ca. 1/2 of the original volume before freshly distilled *N,N,N',N'*-tetramethyl-ethylenediamine (TMEDA, 100 mL) is added. Storing of the resulting solution at −30 °C overnight causes the precipitation of orange–red crystals, which are filtered off, washed with cold Et₂O (0 °C, 200 mL in two portions), and dried at ambient temperature under vacuum (10^{−3} Torr). The resulting air-sensitive orange–red crystals of complex **1** (23.5 g, 45%) can be handled at ambient temperature without noticeable decomposition and can be stored at −20 °C for extended periods of time (>1 year). Although the signals in the ¹H NMR spectrum are broad, the ¹³C NMR recorded at 193 K shows characteristic sharp lines. ¹³C NMR (100 MHz, THF-d₈, 193K, arbitrary numbering scheme as shown in the insert): δ = 77.4 (C-1, d), 58.5 (C-4, t, *J*_{CH} = 133 Hz), 46.4 (C-5, q, *J*_{CH} = 132 Hz), 28.3 (C-3, t, *J*_{CH} = 150 Hz), 18.1 (broad, C-2, t, *J*_{CH} = 141 Hz).

Preparation of [CpFe(cod)][Li(dme)] (4**).** A flame-dried three-necked round-bottom flask equipped with a magnetic stirbar, a gas inlet, a glass stopper and a stopcock connected to the vacuum line is charged

under Ar with ferrocene (50.0 g, 268 mmol), freshly distilled 1,5-cyclooctadiene (COD, 75 mL, 611 mmol) and DME (350 mL). The resulting suspension is cooled to $-50\text{ }^{\circ}\text{C}$ before lithium sand (4.7 g, 680 mmol) is introduced. Stirring is continued at $-20\text{ }^{\circ}\text{C}$ for 4 h, during which time a characteristic color change from orange to red indicates the progress of the reaction. The resulting suspension, which hardly settles, is allowed to stir for another hour at ambient temperature before all insoluble materials are filtered off under Ar. The dark red filtrate is stored at $-30\text{ }^{\circ}\text{C}$ for ca. 20 h, causing the formation of orange-red crystals which are collected, washed with cold Et_2O ($2 \times 100\text{ mL}$), and dried under vacuum (10^{-3} Torr) giving crude **4** as an orange-red powder (85 g, 97%).

Analytically pure samples are obtained by recrystallization as follows: COD (1 mL) is added to a suspension of a fraction of the crude product (23.1 g) in toluene (100 mL) and the resulting mixture is heated to reflux with stirring. Remaining undissolved materials are filtered off while hot, and the resulting dark red, clear filtrate is kept at $0\text{ }^{\circ}\text{C}$ causing the precipitation of analytically pure **4** in form of dark orange-red crystals which are filtered off and dried under vacuum (10^{-3} Torr) (11.6 g, 50%). The air- and moisture sensitive product can be handled at ambient temperature without noticeable decomposition and can be stored under Ar at $-20\text{ }^{\circ}\text{C}$ for extended periods of time (>1 year). ^{13}C NMR (100 MHz, THF-d_8 , 193 K, arbitrary numbering scheme as shown in the insert): $\delta = 75.2$ (C-1), 72.6 (C-5), 58.9 (C-4), 32.6 (C-3) ppm; The signal of the olefinic carbons is not detected under these conditions; however, it is visible as a broad signal in the spectrum of **4** recorded in toluene at 353 K: ^{13}C NMR (100 MHz, toluene- d_8): $\delta = 75.8$ (C-1), 72.3 (C-5), 58.9 (C-4), 48.0 (br, C-2), 34.0 (C-3) ppm.

Preparation of $\text{Cp}^*\text{Fe}(\text{tetraphenylcyclobutadiene})$ (38**).** Tolane (367 mg, 2.06 mmol) is added to a red solution of complex **6** (246 mg, 0.995 mmol)³² in pentane (5 mL) at $-78\text{ }^{\circ}\text{C}$. After stirring for 5 min,



the mixture is allowed to reach ambient temperature, during which time a characteristic color change to dark brown and the evolution of gas is noticed. After stirring for 1 h, the mustard-colored precipitate is filtered off under Ar, the crude product is recrystallized from toluene, the crystals are rinsed with cold ($0\text{ }^{\circ}\text{C}$) pentane and dried in vacuo to give complex **38** as a brown solid (420 mg, 77%). MS (EI): m/z (%): 548 (42), 547 (100) [M^+], 412 (4), 369 (5), 133 (7); elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{35}\text{Fe}$ (547.57): C 83.35, H 6.44; found: C 83.17, H 6.36.

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Supporting Information Available: Experimental part including spectroscopic data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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