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Transition Metal Complexes in Organic Synthesis. Part 57:[1] Synthesis of 1-Azabuta-1,3-dienes and Application to Catalytic Complexation of Buta-1,3-dienes and Cycloalkadienes by the Tricarbonyliron Fragment

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Abstract—The 1-azabuta-1,3-dienes **5a**–**g** were prepared and transformed to the corresponding tricarbonyliron complexes **6**. The efficiency of **6** as tricarbonyliron transfer reagents and the activity of **5a**–**g** for the catalytic complexation with either nonacarbonyldiiron or pentacarbonyliron was investigated. It was shown that the catalytic complexation with pentacarbonyliron using the azadiene **5b** as catalyst in dioxane at reflux can be applied to 1-methoxycyclohexa-1,4-diene.

Introduction

Tricarbonyliron complexes of buta-1,3-dienes and cyclohexa-1,3-dienes represent versatile starting materials for modern synthesis.[2] The reactivity of the free conjugated diene is reduced by coordination to the tricarbonyliron fragment, which therefore may be regarded as a protecting group. The metal fragment stabilizes cations in the allylic positions of the 1,3-diene via the η^5-coordinated dienyl systems and thus enables the addition of nucleophiles at these positions. The stereoselectivity of reactions at tricarbonyliron complexes is controlled by the steric demand of the bulky metal fragment.[2]

Using classical procedures for the preparation of tricarbonyliron–diene complexes the 1,3- or the 1,4-diene is treated with pentacarbonyliron or nonacarbonyldiiron under either thermal or photolytic reaction conditions.[3] However, these methods very often have the drawback that in order to get good yields a large excess of the carbonyliron complex has to be applied, thus leading to the formation of pyrophoric iron, which is hazardous on workup. Considerably milder conditions leading to a more selective reaction for the coordination of the diene to the metal fragment can be applied by using tricarbonyliron transfer reagents.[4] These are labile tricarbonyliron complexes that transfer the metal fragment from the weakly bound ligand to a buta-1,3-diene or a cyclohexa-1,3-diene, thus forming a thermodynamically more stable complex. The tricarbonyl-(η^4-1-oxabuta-1,3-diene) iron complexes with the (η^4-benzylideneacetone)tricarbonyliron as parent compound were the first class of such transfer reagents to be reported.[5,6] A further tricarbonyliron transfer reagent is the tricarbonyl-bis(η^2-*cis*-cyclooctene)iron developed by Grevels.[7] In contrast to the former reagent, Grevels' reagent can be used for the complexation of 1,4-dienes by the tricarbonyliron fragment with concomitant conjugation to the 1,3-diene.

We recently described (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes as a novel class of highly efficient tricarbonyliron transfer reagents.[8–11] Tricarbonyliron complexes of 1-azabuta-1,3-dienes were first reported by Otsuka and Lewis three decades ago,[12] but have found only few applications to synthesis.[13,14] We found that for several reasons they are superior to the two former reagents as tricarbonyliron transfer reagents. The red crystalline (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes are stable in air and can be prepared in high yields (70–90%) by an ultrasound-promoted complexation of the 1-azabuta-1,3-dienes with nonacarbonyldiiron at room temperature.[8–11] The metal fragment of the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes is easily transferred to 1,3-dienes at elevated temperature (THF, reflux) and following the transfer, the free 1-azabuta-1,3-dienes are almost completely recovered by crystallization. This observation led us to develop a highly efficient catalytic complexation of 1,3-dienes with either nonacarbonyldiiron or pentacarbonyliron in the presence of a 1-azabuta-1,3-diene.[8,15] Moreover, using

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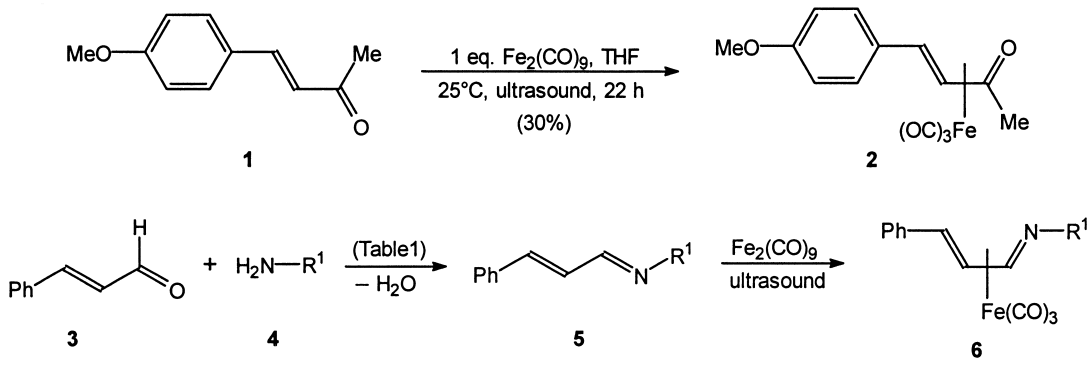


Scheme 1.

Table 1. Yields of the 1-azabuta-1,3-dienes **5** and the complexes **6**

4	R^1	**5**, Yield [%]	**6**, Yield [%]
a	Ph	82[11]	82[11]
b	*p*-MeO(C_6H_4)	100[11]	88[11]
c	CH_2Ph	80[13c]	76
d	(*S*)-CH(Me)Ph	92	80[a]
e	Bu	79	–
f	NMe_2	99	16
g	SO_2Ph	40	73

[a] The complexation of (*S*)-**5d** afforded a 1.2:1 mixture of diastereoisomers (*Rp*/*Sp*,*S*)-**6d**

chiral 1-azabuta-1,3-diene catalysts we achieved an asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes to the corresponding planar–chiral tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes with high asymmetric inductions (up to 85% ee).[16]

The extensive early studies directed towards the development of an efficient catalytic complexation by the tricarbonyliron fragment were accomplished with 1,4-diaryl-1-azabuta-1,3-dienes and cyclohexa-1,3-diene.[11,15] Alternative 1-substituted 4-aryl-1-azabuta-1,3-dienes for the synthesis of novel transfer reagents and the complexation of other 1,3-dienes were described only in preliminary studies.[8a,9] Several 4-phenyl-1-azabuta-1,3-dienes which derive from cinnamaldehyde and a chiral alkylamine were successfully applied to the asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes.[16a,c,d] We now report full details of the synthesis of novel 1-substituted 4-aryl-1-azabuta-1,3-dienes, the synthesis of the corresponding tricarbonyliron complexes as transfer reagents, and applications to catalytic complexation. Moreover, the method is extended to the complexation of cyclohepta-1,3-diene, buta-1,3-dienes, 1-methoxycyclohexa-1,3-diene and -1,4-diene.

Results and Discussion

For comparison of the reactivities of the various tricarbonyliron transfer reagents we prepared the tricarbonyliron complex of *p*-methoxybenzylideneacetone **1**.[6] The 1-oxadiene **1** is prepared by aldol condensation of *p*-methoxybenzaldehyde and acetone.[17] The complexation of **1** by reaction with $Fe_2(CO)_9$ under sonication[18] in THF at room temperature afforded tricarbonyl(η^4-*p*-methoxybenzylideneacetone)iron **2** in 30% yield (Scheme 1), which is about the same yield as obtained by the thermal procedure.[6] In contrast to the ultrasound-promoted complexation of the 1-azabuta-1,3-dienes[11] the reaction of the 1-oxabuta-1,3-diene **1** under the same conditions led to the formation of large amounts of dodecacarbonyltriiron (confirmed by IR spectroscopy). A similar formation of dodecacarbonyltriiron as by-product was observed in the ultrasound-promoted complexation of cyclohexa-1,3-diene with $Fe_2(CO)_9$ which provided tricarbonyl(η^4-cyclohexa-1,3-diene)iron in only 31% yield. Imine condensation of cinnamaldehyde **3** and the amino compounds **4** afforded the corresponding 1-azabuta-1,3-dienes **5** in high yields (80–100%) except for the reaction with benzenesulfonamide **4g**, which gave the 1-phenylsulfonyl derivative **5g**[19] in only 40% yield (Scheme 1, Table 1). Reaction of the 1-azabuta-1,3-dienes **5** with nonacarbonyldiiron at room temperature under sonication for 15–18 h provided the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **6** generally in excellent yields (73–88%). The α,β-unsaturated *N*,*N*-dimethylhydrazone **5f** led to the 1-(*N*,*N*-dimethylamino)-substituted tricarbonyliron complex **6f** in only 16% yield.

The 1,4-diaryl-1-azabuta-1,3-diene tricarbonyliron complexes **6a** and **6b** represent two of the previously established standard reagents for the transfer of the metal fragment[11] and were used as a measure to evaluate the novel 1-azadiene complexes. The ultrasound-promoted complexation of the 1-azadienes with $Fe_2(CO)_9$ led once again to better results than the previously used thermally induced reaction.[12,13] The 1-benzyl complex **6c** was obtained in 76% yield as a red, highly viscid oil, which is stable under inert gas atmosphere and therefore could be purified and fully characterized for the first time (compare Ref. 13c). The 1-(*S*)-α-phenylethyl complex **6d**, previously prepared only in its racemic form (52% yield),[13c] was isolated in 80% yield as a 1.2:1 mixture of the two enantiopure diastereoisomers. The method of Otsuka,[12a] reaction of the tetracarbonyl(η^2-cinnamaldehyde)iron complex with (*S*)-α-phenylethylamine, gave the same diastereoisomeric ratio for **6d** although in only 34% yield. The spectroscopic data of the novel 1-*N*,*N*-dimethylamino complex **6f** are substantially different from those of the 1-aryl complexes **6a** and **6b**.[11] The chemical shift of the imine proton (H–C2) in the ^{1}H NMR spectrum of complex **6f** is δ_{H-C2}=6.70, which

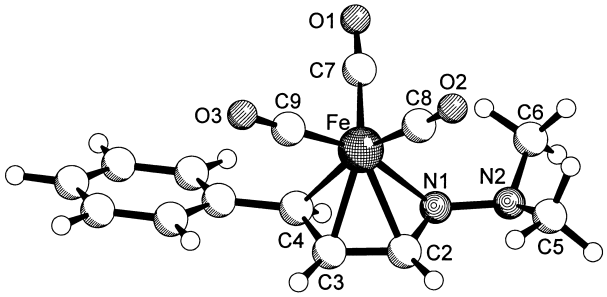


Figure 1. Molecular structure of **6f** in the crystal (arbitrary numbering). Selected bond lengths [Å]: Fe–N1 2.177(2), Fe–C2 2.097(2), Fe–C3 2.038(2), Fe–C4 2.154(2), N1–N2 1.383(2).

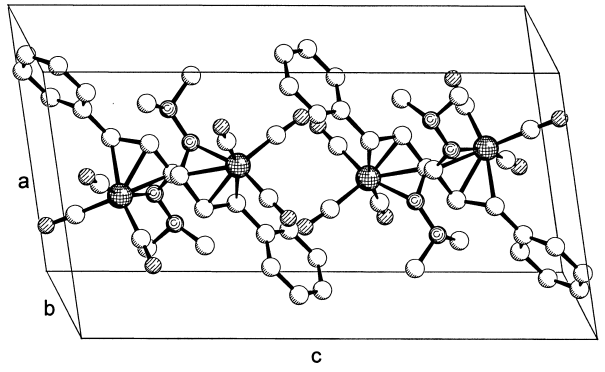


Figure 2. Crystal packing of complex **6f**.

corresponds to a highfield shift of $\Delta\delta$=0.43 relative to the chemical shift found for the imine proton of the free ligand **5f** (δ_{H-C2}=7.13). This value is smaller than observed for all of the 1-aryl complexes so far investigated (e.g. **6a**: $\Delta\delta$=1.32, **6b**: $\Delta\delta$=1.31).[11] The wave numbers of the stretching vibration of the carbonyl ligands in the IR spectrum of complex **6f** (2032, 1972 and 1932 cm^{-1}) are significantly lower than those of the 1-aryl complexes,[11] indicating a reduced back bonding from the iron atom to the 1-azabutadiene ligand for **6f** because of the increase in energy of the π^* orbitals of the ligand. In the ^{13}C NMR spectrum of complex **6f** the signals for the iron-coordinated carbon atoms of the 1-azadiene (C2, C3 and C4) appear at 100.78, 66.89, and 57.67 ppm, respectively and are shifted to higher field as compared to the 1-phenyl complex **6a** (δ_{C2-4}=103.86, 74.45 and 62.17). Most remarkable, the ^{13}C NMR spectrum of **6f** at 100 MHz in deuterochloroform at room temperature exhibits one sharp signal at δ=211.83 for the carbonyl ligands. The 1-aryl-1-azabutadiene complexes show under these conditions in their ^{13}C NMR spectra for the carbonyl ligands in most cases no (as complex **6b**) or three very broad signals (e.g. **6a**). Obviously, the activation barrier for the turnstile rotation of the tricarbonyliron fragment of the 1-*N*,*N*-dimethylamino complex **6f** is much lower than for the 1-aryl complexes. The average value for the 3 signals of the carbonyl ligands of complex **6a** in deuterochloroform is δ=208.77. This spectroscopic finding is in agreement with the results of Takats, who reported for tricarbonyliron–carbadiene complexes that the free enthalpy of activation for the intramolecular carbonyl ligand exchange is inversely proportional to the chemical shift of the carbonyl ligands.[20] Thus, the ^{13}C NMR data support an increased back donation of electrons from the filled iron d-orbitals into the LUMO of the carbonyl ligands for the 1-*N*,*N*-dimethylamino complex **6f** as compared to the 1-aryl complexes **6a** and **6b**.

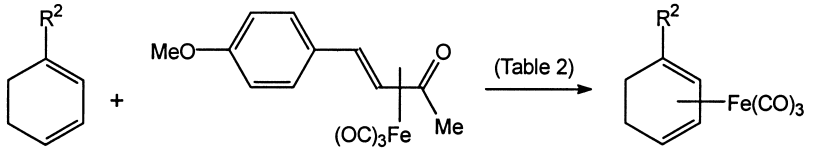
We determined the structure of complex **6f** by an X-ray crystal structure analysis (Fig. 1), which confirmed the η^4-bonding mode of the tricarbonyliron fragment to the 1-(*N*,*N*-dimethylamino)-4-phenyl-1-azabuta-1,3-diene ligand. However, the bond lengths differ significantly from those found for the tricarbonyl(η^4-1,4-diaryl-1-azabuta-1,3-diene)iron complexes.[11] Compared to the crystal structure of complex **6b** the Fe–N bond in complex **6f** is significantly longer by 0.102 Å, the Fe–C2 bond is only 0.023 Å longer, while the Fe–C3 bond is 0.030 Å and the Fe–C4 bond is 0.013 Å shorter. Thus, the strong dimethylamino donor substituent weakens the coordination of the iron atom to the C=N double bond. Fig. 2 shows the arrangment of **6f** in the unit cell.

The 1-phenylsulfonyl complex **6g** differs from the red 1-aryl complexes by its orange color and is air-stable even in solution. The high stretching frequencies for the carbonyl ligands in the IR spectrum of complex **6g** (2071, 2013 and 1998 cm^{-1}) indicate a strong metal–azadiene bond due to the high π-acceptor ability of the electron-poor ligand. This interpretation derives further support by the 100 MHz ^{13}C NMR spectrum of **6g** which exhibits (in deuterochloroform at room temperature) three signals for the carbonyl ligands at 202.19, 207.27 and 209.05 ppm. The signal for the imine proton in the ^1H NMR spectrum of **6g** (δ_{H-C2}=6.95) is shifted strongly to higher field ($\Delta\delta$=1.86) relative to the value for **5g** (δ_{H-C2}=8.81).

Table 2. Complexation of the cyclohexa-1,3-dienes **7a** and **7b** by the tricarbonyliron-fragment using complex **2** as transfer reagent

7	R^2	Solvent	T [°C]	t [min]	**8**, Yield [%]
a	H	THF	65	20	85
b	OMe	Benzene	80	30	58[a]

[a] Mixture of 1- **8b** and 2-methoxycyclohexa-1,3-diene complex **8b′**.

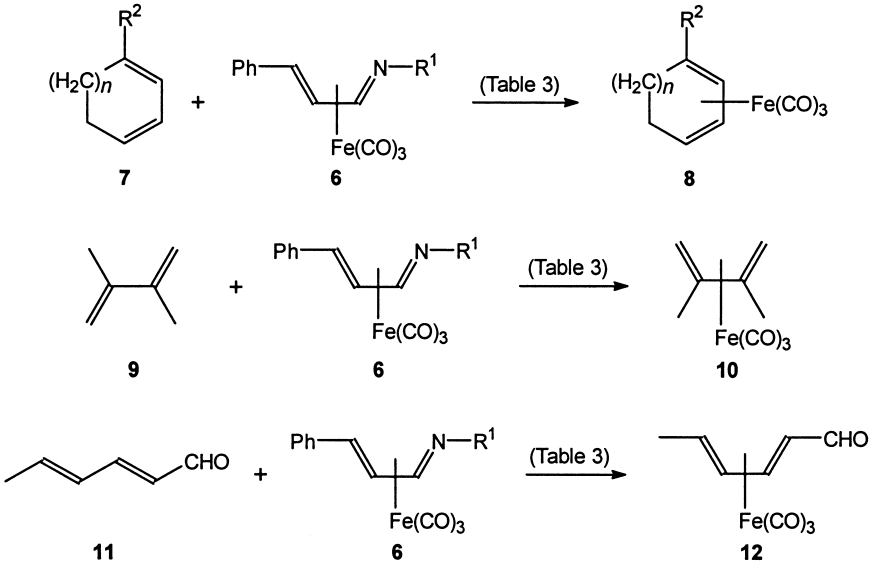


Scheme 2.

Reaction of the *p*-methoxybenzylideneacetone complex **2** with cyclohexa-1,3-diene **7a** in THF at reflux for 20 min led to a smooth transfer of the tricarbonyliron fragment and provided complex **8a** in 85% yield (Scheme 2, Table 2). Thus, this reaction time is considerably shorter than reported by Brookhart for the reaction of the (η^4-benzylideneacetone)tricarbonyliron complex with **7a** (benzene, 60°C, 24 h, >95% yield),[5b,c] which probably can be ascribed to the *p*-methoxy group. The transfer of the metal fragment from complex **2** to 1-methoxycyclohexa-1,3-diene **7b** by heating in benzene at reflux for 30 min afforded a mixture of the 1-methoxycyclohexa-1,3-diene complex **8b** and the 2-methoxycyclohexa-1,3-diene complex **8b′**.

Firstly we wished to establish the influence of the aryl-substituent in the 1-position of the standard reagents **6a** and **6b** on their reactivity as tricarbonyliron transfer reagents. Therefore, we applied the easily available 1-benzyl complex **6c** and its chiral homologue, the 1-(*S*)-α-phenylethyl complex **6d**, to the tricarbonyliron transfer reactions of the cycloalka-1,3-dienes **7a–c** and the buta-1,3-dienes **9** and **11** (Scheme 3, Table 3). The complex **6d** was always used as the 1.2:1 diastereoisomeric mixture of (R_P,*S*)-**6d** and (S_P,*S*)-**6d**, which was obtained by the ultrasound-promoted complexation. The results of the transfer reactions using the complexes **6c** and **6d** show that there is no fundamental difference in reactivity as compared to the 1,4-diaryl-substituted complexes **6a** and **6b**. However, the disadvantage is the lower stability not only of the complexes **6c** and **6d** but also of their corresponding free ligands **5c** and (*S*)-**5d**. Therefore, the yields for the recovery of the free azadienes **5c** and **5d** after the transfer of the metal fragment is much lower than for the recovery of **5b** (>95% yield[11]).

The transfer of the tricarbonyliron fragment from the complexes **6c** and (R_P/S_P,*S*)-**6d** to the 1-methoxycyclohexa-1,3-diene **7b** afforded the 1-methoxy complex **8b** and the 2-methoxy complex **8b′** in a ratio of 2:1. The reaction product from the transfer of (R_P/S_P,*S*)-**6d** was separated by flash chromatography with pentane on silica gel into the complexes **8b′** (less polar fraction) and **8b** (more polar fraction). For the 1-methoxycyclohexa-1,3-diene complex **8b** it was shown that no asymmetric induction occurred (specific rotation, chiral HPLC[16b]). This result contrasts with the asymmetric catalytic complexation of **7b** with pentacarbonyliron in benzene at reflux using catalytic amounts of (*S*)-**5d**, which provided **8b** in 69% yield with 6% ee of the *R* enantiomer.[16a] The complexation of sorbic aldehyde **11** with (R_P/S_P,*S*)-**6d** in THF at reflux provided complex **12** in 59% yield. Condensation of this

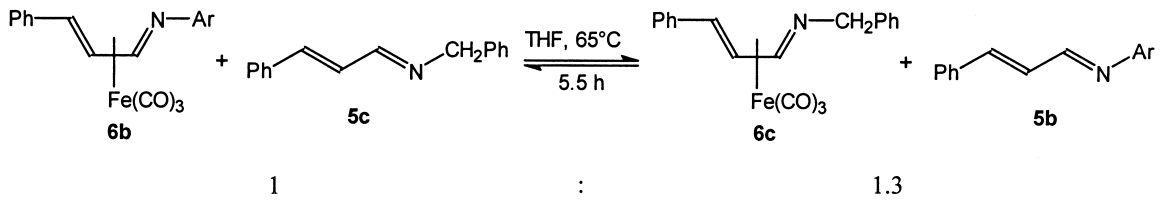


Scheme 3.

Table 3. Complexation of 1,3-dienes by the tricarbonyliron-fragment using the complexes **6a–d**, **6f** and **6g** as transfer reagents

	n	R^2	Solvent	*T* [°C]	Product	Yield [%]					
						6a	**6b**	**6c**	(*R*p/*S*p,*S*)-**6d**	**6f**	**6g**
7a	1	H	THF	65	**8a**	88	95	73	70	83	83[c]
7b	1	OMe	C_6H_6	80	**8b**	67[a]	64[a]	64[b]	86[b]	–	–
7c	2	H	C_6H_6	80	**8c**	73	84	86	65	–	–
9	–	–	C_6H_6	80	**10**	77	71	72[d]	–	–	–
11	–	–	Toluene	110	**12**	–	69	–	59[d]	–	–

[a] Mixture of the regioisomers 1-methoxy- **8b** and 2-methoxycyclohexa-1,3-diene complex **8b′** (1:1).
[b] Mixture of the regioisomers **8b** and **8b′** (2:1.)
[c] For this reaction benzene was used as solvent, *T*=80°C.
[d] For this reaction THF was used as solvent, *T*=65°C.



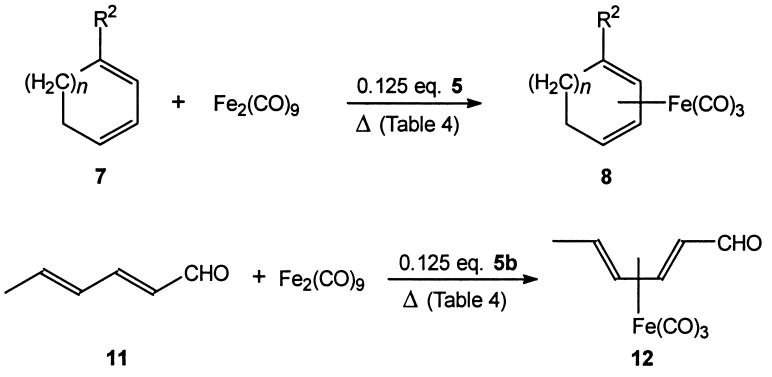
Scheme 4. Ar=4-MeO–C_6H_4.

product with either (*S*)-α-phenylethylamine or RAMP[21] afforded quantitatively the corresponding imine and hydrazone as a 1:1 mixture of diastereoisomers in each case as shown by the ^{1}H NMR spectra in benzene-d_6. Thus, complex **12** was also formed as a racemic mixture.

The 1-*N*,*N*-dimethylamino complex **6f** exhibited a surprisingly slow transfer of the tricarbonyliron fragment. On heating the complex **6f** with cyclohexa-1,3-diene **7a** in THF at reflux, complex **8a** was finally obtained in 83% yield but only after a reaction time of 19 h. The 1-phenylsulfonyl complex **6g** is even less reactive, because of the electron-poor azadiene ligand, and shows only a small turnover on reaction with **7a** in THF at reflux even with extended reaction times. Heating complex **6g** with **7a** in benzene at 80°C for 16 h provided complex **8a** in 83% yield. In conclusion, the transfer reagents **6f** and **6g**, as compared to **6a**–**d**, show a considerably decreased reactivity for the transfer of the tricarbonyliron fragment on reaction with cyclohexa-1,3-diene **7a**.

A direct comparison of the reactivity of the transfer reagents **6b** and **6c** was obtained from a competition experiment (Scheme 4). Reaction of equimolar amounts of the 1-benzyl azadiene **5c** with the 1-aryl complex **6b** in THF at reflux afforded after 5.5 h the tricarbonyliron complexes **6b** and **6c** in a ratio of 1:1.3. However, the total yield of the complexes **6b** and **6c** was only 65%. This is ascribed to the decomposition of **6c** under these conditions, which thus also had an effect on the observed ratio. The corresponding reaction of either **5a** with **6b** or **5b** with **6a** provided quantitatively an equilibrium of the complexes **6a** and **6b** in a ratio of 2:1.[11]

A transfer of the tricarbonyliron fragment from an (η^4-1-azabuta-1,3-diene)tricarbonyliron complex to a deconjugated diene with formation of the tricarbonyl(η^4-1,3-diene)iron complex is obviously not feasible. The attempted transfer of the metal fragment of the 1-(*p*-anisyl)-1-azadiene complex **6b** to cyclohexa-1,4-diene led even under drastic conditions (toluene, 110°C, 24 h) only to the reisolation of the starting complex **6b**. Also the reaction of the 1-benzyl complex **6c** with cyclohexa-1,4-diene did not afford the tricarbonyliron complex **8a**. Thus, the 1-azabuta-1,3-diene complexes **6**, like the 1-oxabuta-1,3-diene complexes,[5c]

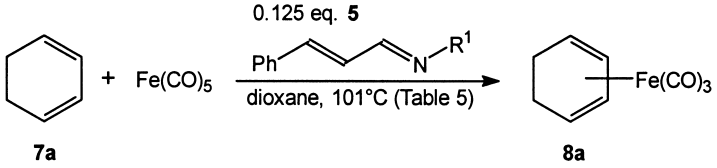


Scheme 5.

Table 4. Results of the thermally induced complexation of the dienes **7a**–**c** and **11** with $Fe_2(CO)_9$ without catalyst in comparison with those of the complexation using catalytic amounts of the heterodienes **1**, **5b**, **5f** and **5g** (all yields are calculated based on the tricarbonyliron equivalents)

	n	R^2	Product	Yield [%][a]	Catalyst	Reaction conditions	Yield [%]
7a	1	H	**8a**	22	**1**	THF, 65°C, 19 h	16
7a	1	H	**8a**	22	**5b**	DME, 85°C, 16.5 h	98
7a	1	H	**8a**	22	**5f**	DME, 85°C, 16 h	30
7a	1	H	**8a**	22	**5g**	Benzene, 80°C, 17.5 h	60
7b	1	OMe	**8b**	32[b,c]	**5b**	DME, 85°C, 17 h	86[c]
7c	2	H	**8c**	23	**5b**	Dioxane, 101°C, 17 h	67
11	–	–	**12**	41	**5b**	DME, 85°C, 16 h	72

[a] Complexation without catalyst: THF, 65°C, 6–19 h.
[b] 1-Methoxycyclohexa-1,4-diene (**13**) was used as starting material.
[c] Mixture of the 1-methoxy- **8b** and 2-methoxycyclohexa-1,3-diene complex **8b′**.



Scheme 6.

Table 5. Catalytic complexation of cyclohexa-1,3-diene (**7a**) with $Fe(CO)_5$—variation of catalyst **5** and reaction time (all reactions were carried out in dioxane at 101°C)

Catalyst	R^1	**8a**, Yield [%]		
		5 h	14 h	37 h
5a	Ph	–	41	–
5b	*p*-MeO(C_6H_4)	21	50	91
5c	CH_2Ph	16	47	80
(*S*)-**5d**	MeCHPh	20	41	64
5e	Bu	–	39	–

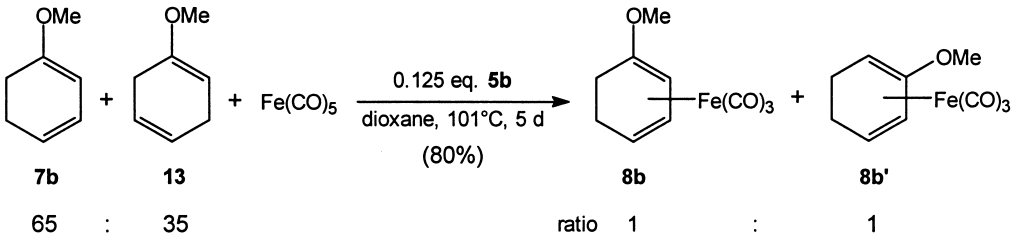
cannot be applied for the complexation of 1,4-dienes to the tricarbonyl(η^4-1,3-diene)iron complexes, in contrast to Grevels' reagent.[7]

We next investigated the catalytic complexation of the dienes **7a–c** and **11** by using nonacarbonyldiiron as the tricarbonyliron source and the various azadienes **5** as catalysts (Scheme 5, Table 4). The results of the catalytic complexation were compared with the thermally induced uncatalyzed complexation of the dienes. The uncatalyzed complexation of cyclohexa-1,3-diene **7a** by heating with nonacarbonyldiiron in tetrahydrofuran at reflux for 6 h afforded complex **8a** in 22% yield (the yields are based on the iron equivalents). The yield for this reaction is in the same range when catalytic amounts of *p*-methoxybenzylideneacetone **1** are added. This result demonstrates, in contrast to the report in Ref. 6, that the 1-oxabuta-1,3-dienes have no catalytic effect on the complexation of cyclohexadienes with nonacarbonyldiiron. The catalytic complexation of **7a** with nonacarbonyldiiron using 12.5 mol% the 1-(*p*-anisyl)-1-azadiene **5b** as catalyst provided under optimized reaction conditions (1,2-dimethoxyethane, 85°C, 16.5 h) the complex **8a** in 98% yield. This result emphasizes that both tricarbonyliron fragments of nonacarbonyldiiron may be transferred quantitatively to the diene by the 1-azadiene-catalyzed complexation. Using the 1-(*N*,*N*-dimethylamino)-1-azadiene **5f** as catalyst under the same reaction conditions, complex **8a** was obtained in only 30% yield. In agreement with the results of the stoichiometric transfer reaction with complex **6g**, the 1-phenylsulfonyl-1-azadiene **5g** shows no catalytic activity in tetrahydrofuran at reflux. However, in benzene at reflux, catalyst **5g** provided almost the result which was obtained with the azadiene **5b** under the same reaction conditions (catalytic complexation of **7a** in benzene at reflux, with **5g** as catalyst: 60% yield of **8a**, and with **5b** as catalyst: 66% yield of **8a**[15]).

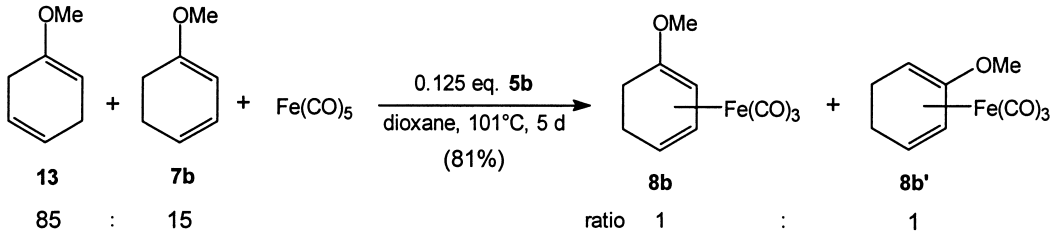
The results of the catalytic complexation of the 1,3-dienes **7b**, **7c**, and **11** with nonacarbonyldiiron using the 1-azadiene **5b** as catalyst emphasize that the exploitation of both tricarbonyliron fragments is not restricted to the catalytic complexation of **7a**. The reaction conditions (amount of catalyst **5b**, solvent and reaction time) are the same as for the catalytic complexation of **7a**, except for the catalytic complexation of cyclohepta-1,3-diene **7c**, which was performed in dioxane as solvent. A comparison with the conventional thermally induced uncatalyzed complexation shows again a remarkable increase of the yields based on the tricarbonyliron equivalents.

We also compared the catalytic activity of the 1-azadienes **5a–e** on the complexation of cyclohexa-1,3-diene **7a** using pentacarbonyliron under the standard reaction conditions (dioxane, 101°C) at different reaction times (Scheme 6, Table 5). The blank experiment (reaction in dioxane at reflux without catalyst) afforded complex **8a** after 14 h in 0.7% yield (see Experimental). With 12.5 mol% of *p*-methoxybenzylideneacetone **1** the complex **8a** was obtained after 14 h in 4% yield (see Experimental), which is ascribed to an in situ generation of a tricarbonyl(η^4-1-oxabuta-1,3-diene)iron complex and transfer of the metal fragment. However, a catalytic effect of the 1-oxadiene **1** on the complexation of **7a** with pentacarbonyliron was not found. Catalytic complexation of **7a** in the presence of 12.5 mol% of the 1-aryl-1-azadienes **5a** and **5b** provided after 14 h complex **8a** in 41 and 50% yield, respectively. A comparison of the results obtained for the catalytic complexation of **7a** after a reaction time of 14 h using the novel catalysts **5c–e** with those obtained by the 1-aryl-1-azadienes **5a** and **5b** leads to the following conclusion. The yield of complex **8a** that was achieved using the 1-benzyl-1-azadiene **5c** as catalyst comes closest to the one achieved with catalyst **5b**, while the turnovers obtained with the catalysts 1-(*S*-α-phenyethyl)-1-azadiene (*S*)-**5d** and 1-butyl-1-azadiene **5e** are in the same range as with the 1-phenyl-1-azadiene **5a**. The catalytic activity of the 1-benzyl-1-azadiene **5c** strongly depends on the aging of this catalyst. The catalytic complexation of **7a** using aged azadiene **5c** with a brownish color afforded complex **8a** in only 39% yield, although the ^1H NMR spectrum of this catalyst showed no impurities. Using a one day old, yellow-colored azadiene **5c** as catalyst, complex **8a** was obtained in 43% yield. The best result (47% yield of **8a**) was provided by using a freshly recrystallized azadiene **5c** which was dried over barium oxide. The lower stability of the azadienes **5c** and (*S*)-**5d** was already observed in the stoichiometric complexation of **7a** using the corresponding complexes **6c** and (R_P/S_P,*S*)-**6d** as transfer reagent (see above). By extension of the reaction time to 37 h the difference of the turnovers obtained with the catalysts **5c** and (*S*)-**5d** as compared to the result using the standard catalyst **5b** becomes even larger, which is probably due to the increasing decomposition of the former azadienes.

The uncatalyzed thermally induced complexation of 1-methoxycyclohexa-1,4-diene **13** with pentacarbonyliron



Scheme 7.



Scheme 8.

in di-*n*-butylether at reflux provides a 1:1 mixture of the complexes **8b** and **8b′** in about 20–30% yield (single-stage procedure).[3e,f] We described above the catalytic complexation of 1-methoxycyclohexa-1,3-diene **7b** with nonacarbonyldiiron and using the azadiene **5b** as catalyst, which afforded in dimethoxyethane at reflux the mixture of the complexes **8b** and **8b′** in 86% yield. For comparison, using the same reaction conditions for the complexation but without catalyst provided the mixture of **8b** and **8b′** in 24% yield (see Experimental). We now wanted to devise reaction conditions for the catalytic complexation of 1-methoxycyclohexa-1,3-diene **7b** and 1-methoxycyclohexa-1,4-diene **13** to the mixture of **8b** and **8b′** by using pentacarbonyliron as starting material. Pentacarbonyliron is the much cheaper source for tricarbonyliron fragments as compared to $Fe_2(CO)_9$ and therefore, such a procedure would be of importance for the large-scale preparation of **8b** and **8b′**. Based on the previous results for the catalytic complexation of cyclohexa-1,3-diene **7a** with pentacarbonyliron,[15] we developed an optimized large-scale preparation for **8b** and **8b′** by using 12.5 mol% of the azadiene **5b** as catalyst in dioxane at reflux. Catalytic complexation of commercial 1-methoxycyclohexa-1,3-diene **7b** (containing about 35% of the 1,4-diene **13**) using these reaction conditions for 5 d afforded a 1:1 mixture of the complexes **8b** and **8b′** in 80% yield (=15.2 g) based on 14.9 g (=10 mL) pentacarbonyliron (Scheme 7).

A further large-scale synthesis starting from the commercial 1-methoxycyclohexa-1,4-diene **13** (containing about 15% of the 1,3-diene **7b**) provided by the same reaction conditions the 1:1 mixture of the complexes **8b** and **8b′** in 81% yield based on 13.3 g pentacarbonyliron (Scheme 8).

Conclusion

In the stoichiometric transfer of the tricarbonyliron fragment using the tricarbonyl(η^4-1-azabuta-1,3-diene)iron complexes **6**, the 1-benzyl derivatives **6c** and **6d** show a similar reactivity to the 1-aryl derivatives **6a** and **6b**. The 1-(*N*,*N*-dimethylamino) derivative **6f** and the 1-phenylsulfonyl derivative **6g** provide comparable yields for the transfer only after prolonged reaction times. The corresponding free ligands, the 1-azadienes **5f** and **5g**, exhibit also a decreased activity for the catalytic complexation of cyclohexa-1,3-diene with nonacarbonyldiiron. It was shown that both the stoichiometric and the catalytic complexation using 1-azadienes can be applied to the synthesis of the tricarbonyliron complexes of methoxycyclohexa-1,3-dienes, cyclohepta-1,3-diene, and various buta-1,3-dienes. For the catalytic complexation of cyclohexa-1,3-diene with pentacarbonyliron the catalyst **5b** is superior to the catalysts **5c**–**e**, because the novel 1-azadienes and their tricarbonyliron complexes show a slow decomposition under the reaction conditions. Finally, we elaborated a large-scale preparation of the tricarbonyliron complexes of 1-methoxy- and 2-methoxycyclohexa-1,3-diene **8b** and **8b′** by catalytic complexation of either 1-methoxycyclohexa-1,3-diene **7b** or 1-methoxycyclohexa-1,4-diene **13** with pentacarbonyliron using the 1-azadiene **5b** as catalyst in dioxane at reflux. Thus, we could show for the first time that under these reaction conditions the azadiene-catalyzed complexation can be used for the transformation of 1,4-dienes with concomitant conjugation to the tricarbonyl(η^4-1,3-diene) iron complexes. This result is in contrast to our observation that a transfer of the tricarbonyliron fragment from (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes to a deconjugated diene does not occur.

Experimental

All reactions were carried out using anhydrous and degassed solvents under an inert gas atmosphere. Flash chromatography: Baker or Merck silica gel (0.03–0.06 mm). Bulb-to-bulb distillation: Büchi glass tube oven GKR-51. Specific rotation: Perkin–Elmer 241 Polarimeter. Ultrasound: Bandelin Sonorex-TK52H; frequency: 35 kHz, used at 50% power. Melting points: Leitz hot stage and Büchi

535. IR: Bruker IFS-88, Perkin–Elmer 882 and 1710. ^{1}H NMR and ^{13}C NMR spectra: Bruker WP-200, AC-250, AM-400, DRX-500; internal standard: tetramethylsilane or the signal of the deuterated solvent; coupling constants in Hz. Mass spectra: Finnigan MAT-312 and MAT-90: ionization potential: 70 eV. Elemental analysis: Heraeus CHN-Rapid.

4-(4-Methoxyphenyl)-2-methyl-1-oxabuta-1,3-diene (1). Acetone (40.5 mL, 32.0 g, 551 mmol) and a solution of sodium hydroxide (15.0 g, 375 mmol) in distilled water (150 mL) was added quickly to a suspension of 4-methoxybenzaldehyde (13.4 mL, 15.0 g, 110 mmol) in distilled water (550 mL). The reaction mixture was stirred at 40°C for 15 h. The precipitate was separated, washed with water, dried in the air, and recrystallized twice from ether to afford the oxabutadiene **1** as pale yellow crystals, yield: 15.3 g (79%). Mp 68°C. IR (KBr): $\tilde{\nu}$=2964, 2840, 1657, 1634, 1602, 1575, 1511, 1424, 1360, 1313, 1270, 1245, 1209, 1178, 1030, 1003, 974, 834, 808, 550, 512 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.36 (s, 3H), 3.85 (s, 3H), 6.61 (d, J=16.4 Hz, 1H), 6.92 (d, J=8.9 Hz, 2H), 7.48 (d, J=16.4 Hz, 1H), 7.50 (d, J=8.9 Hz, 2H). MS (25°C): m/z (%)=176 (M^+, 55), 161 (100), 145 (6), 133 (31), 118 (10). HRMS: calcd for $C_{11}H_{12}O_2$ (M^+): 176.0837. Found: 176.0837.

Tricarbonyl[(1-4-η)-4-(4-methoxyphenyl)-2-methyl-1-oxabuta-1,3-diene]iron (2). A solution of 4-(4-methoxyphenyl)but-3-en-2-one (**1**) (1.45 g, 8.24 mmol) and nonacarbonyldiiron (3.00 g, 8.24 mmol) in THF (15 mL) was sonicated at room temperature for 22 h. Removal of the solvent by evaporation and flash chromatography (Et_2O/pentane, 1:1) of the residue on silica gel afforded the tricarbonyliron complex **2** as a red solid, yield: 780 mg (30%). Mp>95°C (dec.). IR (KBr): $\tilde{\nu}$=3070, 3010, 2958, 2838, 2078, 1997, 1988, 1607, 1519, 1489, 1382, 1295, 1255, 1179, 1039, 935, 835 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.51 (s, 3H), 3.15 (d, J=9.1 Hz, 1H), 3.76 (s, 3H), 5.98 (d, J=9.1 Hz, 1H), 6.81 (d, J=8.7 Hz, 2H), 7.23 (d, J=8.7 Hz, 2H). ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ=20.95 (CH_3), 55.17 (CH_3), 61.69 (CH), 78.02 (CH), 114.28 (2 CH), 127.94 (2 CH), 130.62 (C), 141.51 (C), 158.68 (C=O), 203.71 (CO, br), 209.65 (2 CO, br). MS (50°C): m/z (%)=316 (M^+, 2), 288 (3), 260 (4), 232 (23), 176 (53), 161 (100), 145 (6), 133 (33), 118 (10). HRMS: calcd for $C_{14}H_{12}O_5Fe$ (M^+): 316.0034. Found: 316.0034.

1,4-Diphenyl-1-azabuta-1,3-diene (5a). For the synthesis and the spectral data, see Ref. 11.

1-(4-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (5b). For the synthesis and the spectral data, see Ref. 11.

1-Benzyl-4-phenyl-1-azabuta-1,3-diene (5c). The azadiene **5c** was prepared according to the procedure described by Thomas.[13c] For spectral data, see Ref. 13c.

4-Phenyl-1-((1*S*)-1-phenylethyl)-1-azabuta-1,3-diene ((*S*)-5d). The azadiene (*S*)-**5d** was prepared as described by Thomas[13c] for the racemic compound by using (*S*)-α-phenylethylamine (*S*)-**4d**. The crude product was crystallized from Et_2O/pentane (1:10) to provide the azadiene (*S*)-**5d** as pale yellow crystals, yield 92%. $[\alpha]_D^{20}$=−0.58 (c=13 in MeOH). For further spectral data, see Ref. 13c.

1-Butyl-4-phenyl-1-azabuta-1,3-diene (5e). Cinnamaldehyde (**3**) (0.95 mL, 1.00 g, 7.57 mmol) and butylamine (**4e**) (5.0 mL, 3.73 g, 51 mmol) were stirred at room temperature for 1 h. The excess of butylamine was removed in vacuo (30°C/0.1 mbar) and the product **5e** was obtained by bulb-to-bulb distillation at 125°C/0.1 mbar as a pale yellow oil, yield: 1.12 g (79%). IR (film): $\tilde{\nu}$=2957, 2930, 1637, 1449, 1166, 986, 750, 691 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.94 (t, J=7 Hz, 3H), 1.37 (sext., J=7 Hz, 2H), 1.65 (quint., J=7 Hz, 2H), 3.51 (dt, J=1, 7 Hz, 2H), 6.91 (m, 2H), 7.34 (m, 3H), 7.46 (m, 2H), 8.01 (m, 1H).

1-(*N*,*N*-Dimethylamino)-4-phenyl-1-azabuta-1,3-diene (5f). A solution of cinnamaldehyde (**3**) (1.91 mL, 2.00 g, 15.1 mmol) and 1,1-dimethylhydrazine (**4f**) (1.26 mL, 1.00 g, 16.6 mmol) in ethyl acetate (15 mL) was stirred at room temperature for 30 min. The mixture was dried over magnesium sulfate, then filtered, and the solvent was evaporated. After drying of the residue in vacuo the azabutadiene **5f** was obtained as a yellow oil, yield: 2.62 g (100%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.92 (s, 6H), 6.61 (d, J=16 Hz, 1H), 6.94 (dd, J=16, 9 Hz, 1H), 7.13 (d, J=9 Hz, 1H), 7.18–7.43 (m, 5H). MS (25°C): m/z (%)=174 (M^+, 100), 173 (34), 159 (11), 130 (32), 115 (28), 104 (20), 103 (16), 91 (17), 77 (22).

4-Phenyl-1-phenylsulfonyl-1-azabuta-1,3-diene (5g). A solution of cinnamaldehyde (**3**) (2.86 mL, 3.00 g, 22.7 mmol), benzenesulfonamide (**4g**) (3.57 g, 22.7 mmol), and triethylamine (9.49 mL, 6.89 g, 68.1 mmol) in CH_2Cl_2 (50 mL) was cooled to 0°C and then $TiCl_4$ (1.25 mL, 2.16 g, 11.4 mmol) in CH_2Cl_2 (10 mL) was added slowly. The resulting suspension was stirred for 30 min at room temperature, a saturated aqueous solution of $NaHCO_3$ (5 mL) was added, and the mixture was filtered over a short path of Celite (eluent: EtOAc). After evaporation of the solvent the residue was dissolved with ethyl acetate and the solution was washed twice with brine. The organic layer was dried over sodium sulfate and the solvent was removed. After addition of EtOH (50 mL) **5f** was crystallized at −20°C. Recrystallization of the yellow-brown crystals from Et_2O/EtOH (5:1, 150 mL) provided the product **5f** as bright yellow crystals, yield: 2.43 g (40%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.00 (dd, J=15.8, 9.4 Hz, 1H), 7.40–7.68 (m, 9H), 7.98 (m, 2H), 8.81 (d, J=9.4 Hz, 1H). For further spectral data, see Ref. 19.

Preparation of the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes 6 via complexation of the 1-azabuta-1,3-dienes 5 with $Fe_2(CO)_9$ by sonication at room temperature: general procedure

A solution of the 1-azabuta-1,3-dienes **5** and nonacarbonyldiiron in THF (15 mL) [entry **c**: toluene (10 mL)] was sonicated at room temperature for 15–18 h. Removal of the solvent and flash chromatography (Et_2O/pentane) of the residue on silica gel afforded the tricarbonyliron complexes **10**, unless stated otherwise (Table 6).

Table 6. Complexation of the 1-azabuta-1,3-dienes **5**

Entry	**5**		$Fe_2(CO)_9$		Eluent (Et_2O/pentane)	Yield of **6**	
	[g]	[mmol]	[g]	[mmol]		[g]	[%]
a	0.50	2.41	1.10	3.03	1:10	0.682	82
b	0.50	2.11	0.960	2.64	1:10	0.701	88
c	0.50	2.26	0.824	2.26	1:10	0.619	76
d	2.00	8.51	4.03	11.1	1:10	2.56	80
f	1.00	5.75	2.51	6.90	1:20	0.287	16
g	2.00	7.38	3.22	8.86	—	2.22	73

Tricarbonyl[(1-4-η)-1,4-diphenyl-1-azabuta-1,3-diene]-iron (6a). For the synthesis and the spectral data, see Ref. 11.

Tricarbonyl[(1-4-η)-1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (6b). For the synthesis and the spectral data, see Ref. 11.

[(1-4-η)-1-Benzyl-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron (6c). Red, highly viscid oil. IR (KBr): $\tilde{\nu}$=2044, 1984, 1963, 1497, 1477, 1448, 1434, 1254, 765, 710, 695, 632, 616, 600, 581, 558, 549 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ=3.12 (d, J=9 Hz, 1H), 3.14 (d, J=14 Hz, 1H), 3.56 (d, J=14 Hz, 1H), 4.90 (dd, J=9, 2 Hz, 1H), 5.94 (d, J=2 Hz, 1H), 6.85–7.35 (m, 10H). ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ=61.21 (CH), 63.56 (CH_2), 72.63 (CH), 111.74 (CH), 126.50 (3 CH), 127.09 (CH), 127.69 (2 CH), 128.32 (2 CH), 128.59 (2 CH), 139.18 (C), 140.58 (C), 202.86 (CO, very br), 209.64 (CO, very br), 216.07 (CO, very br). MS (55°C): m/z (%)=361 (M^+, 1), 333 (6), 305 (57), 277 (100), 221 (30), 220 (23), 186 (18), 185 (68), 159 (22), 91 (93). HRMS: calcd for $C_{19}H_{15}FeNO_3$ (M^+): 361.0401. Found: 361.0420.

(R_P/S_P)-Tricarbonyl[(1-4-η)-4-phenyl-1-((1*S*)-1-phenylethyl)-1-azabuta-1,3-diene]iron ((R_P/S_P,*S*)-6d). Red crystals. Diastereoisomeric mixture of (R_P/*S*)-**6d** and (S_P,*S*)-**6d** (ratio: 1.2:1). ^1H NMR (200 MHz, C_6D_6): major diastereoisomer: δ=1.25 (d, J=6.5 Hz, 3H), 2.81 (q, J=6.5 Hz, 1H), 3.16 (d, J=9.5 Hz, 1H), 4.97 (dd, J=9.5, 2.5 Hz, 1H), 6.00 (d, J=2.5 Hz, 1H), 6.87–7.43 (m, 10H); minor diastereoisomer: δ=1.42 (d, J=6.5 Hz, 3H), 2.93 (q, J=6.5 Hz, 1H), 3.22 (d, J=9.5 Hz, 1H), 4.82 (dd, J=9.5, 2.5 Hz, 1H), 5.95 (d, J=2.5 Hz, 1H), 6.87–7.43 (m, 10H). Anal. calcd for $C_{20}H_{17}FeNO_3$: C, 64.02; H, 4.57; N, 3.73. Found: C, 63.99; H, 4.59; N, 3.93. For the spectral data of the racemic compounds, see Ref. 13c.

Tricarbonyl[(1-4-η)-1-(*N*,*N*-dimethylamino)-4-phenyl-1-azabuta-1,3-diene]iron (6f). Red crystals. Mp 48°C. IR (KBr): $\tilde{\nu}$=2032, 1972, 1932, 1592, 1457, 1418, 1221, 1124, 1097, 1005, 865, 756, 696, 619 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ=2.39 (s, 6H), 2.70 (d, J=9.3 Hz, 1H), 5.42 (dd, J=9.3, 3.3 Hz, 1H), 6.70 (d, J=3.3 Hz, 1H), 7.14 (m, 1H), 7.25 (m, 4H). ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ=44.22 (2 CH_3), 57.67 (CH), 66.89 (CH), 100.78 (CH), 126.28 (CH), 126.44 (2 CH), 128.55 (2 CH), 139.87 (C), 211.83 (3 CO). MS (30°C): m/z (%)=314 (M^+, 3), 286 (10), 258 (19), 230 (28), 187 (100), 186 (17), 185 (35), 174 (19), 159 (9), 133 (11), 130 (10). HRMS: calcd for $C_{14}H_{14}FeN_2O_3$ (M^+): 314.0354. Found: 314.0344.

X-Ray crystal structure analysis of 6f. Crystal data: empirical formula $C_{14}H_{14}FeN_2O_3$, crystal size: 0.60×0.60×0.40 mm, M=314.12, monoclinic, space group $P2_1/c$, a=9.561(2) Å, b=8.650(2) Å, c=17.605(4) Å, β=100.11(2)°, V=1433.4(6) $Å^3$, Z=4, ρ_{calcd}=1.456 g cm^{-3}, μ=1.059 mm^{-1}, $F(000)$=648. Data collection: λ=0.71073 Å, T=163(2) K, θ-range: 3.20–27.56°, reflections collected: 3530, independent reflections: 3306. The data were collected on a STOE STADI-4 diffractometer. Refinement: the structure was solved by direct methods (SHELXS-86) and refined anisotropically by full-matrix least-squares on all unique F^2 (SHELXL-93); data-to-parameter ratio 17.2:1; final R indices: R_1 [$I > 2\sigma(I)$] = 0.0293, wR_2 (all data)=0.0787; maximal residual electron density: 0.265 e$Å^{-3}$. The program SCHAKAL-97 was used for the graphical representation (E. Keller, A Computer Program for the Graphic Representation of Molecular and Crystallographic Models, Freiburg, Germany, 1997) (Table 7).

Complete crystallographic details (excluding structure factors) for this structure have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136042, and may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033).

Table 7. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$×10^3) for **6f**. U(equiv.) is defined as the third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(equiv.)
Fe	3803.7(2)	6149.7(3)	1437.9(1)	27.3(1)
N(1)	3413(2)	8018(2)	2202.9(9)	33.5(3)
N(2)	2220(2)	8290(2)	2526.7(10)	40.7(4)
C(2)	4406(2)	7028(2)	2557.6(11)	35.9(4)
C(3)	5580(2)	6822(2)	2181.7(10)	33.9(4)
C(4)	5594(2)	7684(2)	1498.2(11)	32.0(4)
C(5)	1707(3)	7097(3)	2989(2)	64.7(7)
C(6)	1135(2)	8993(3)	1957(14)	59.2(6)
C(7)	2872(2)	7043(2)	566.9(11)	32.7(4)
O(1)	2327(2)	7567(2)	1.4(8)	47.0(4)
C(8)	2544(2)	4767(2)	1659.4(10)	33.1(4)
O(2)	1771(2)	3822(2)	1770.3(9)	47.7(4)
C(9)	4629(2)	4618(2)	1007.1(10)	30.7(4)
O(3)	5138.7(14)	3629(15)	725.8(8)	39.8(3)
C(10)	6704(2)	7541(2)	1021.2(10)	32.1(4)
C(11)	7639(2)	6290(2)	1072.2(12)	36.9(4)
C(12)	8665(2)	6210(2)	606.1(13)	43.7(5)
C(13)	8774(2)	7370(3)	82.0(13)	47.0(5)
C(14)	7873(2)	8618(3)	30.5(13)	47.5(5)
C(15)	6847(2)	8708(2)	495.4(12)	39.5(4)

Tricarbonyl[(1-4-η)-4-phenyl-1-phenylsulfonyl-1-aza-buta-1,3-diene]iron (6g). The red–brown crude product was crystallized from EtOAc at −20°C to provide the azadiene **6g** as orange crystals, mp≥145°C (dec.). IR (drift): $\tilde{\nu}$=3045, 2071, 2013, 1998, 1447, 1318, 1154, 901, 822, 766, 724, 696, 686, 666 cm^{-1}. IR ($CHCl_3$): $\tilde{\nu}$=2080, 2026, 2006, 1322, 1155, 598 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ=3.35 (dd, J=9.7, 0.9 Hz, 1H), 5.82 (dd, J=9.7, 3.1 Hz, 1H), 6.95 (dd, J=3.1, 0.9 Hz, 1H), 7.26 (m, 5H), 7.50 (m, 2H), 7.57 (m, 1H), 7.89 (m, 2H). ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ=64.38 (CH), 78.27 (CH), 97.76 (CH), 126.78 (2CH), 127.05 (2 CH), 127.74 (CH), 129.00 (2 CH), 129.04 (2 CH), 132.83 (CH), 137.22 (C), 140.22 (C), 202.19 (CO), 207.27 (CO), 209.05 (CO). MS (115°C): m/z (%)=411 (M^+, 1), 383 (10), 355 (27), 327 (23), 326 (23), 262 (52), 202 (100), 185 (25), 133 (60). HRMS: calcd for $C_{18}H_{13}FeNO_5S$ (M^+): 410.9864. Found: 410.9841.

Transfer of the tricarbonyliron fragment to the dienes 7a and 7b using the oxadiene complex 2

Transfer to cyclohexa-1,3-diene (7a). A solution of the diene **7a** (105 μL, 88 mg, 1.10 mmol) and the iron complex **2** (200 mg, 0.633 mmol) in THF (15 mL) was stirred at reflux for 20 min. The cold mixture was filtered through a short path of Celite and the solvent was evaporated. The residue was dissolved in a small amount of pentane and the oxadiene **1** was crystallized. The solution was subjected to flash chromatography (pentane) on silica gel to provide the complex **8a** as a yellow oil, yield: 118 mg (85%). For the spectral data, see Ref. 11.

Transfer to 1-methoxycyclohexa-1,3-diene (7b). A solution of methoxycyclohexadiene (0.20 mL, content of **7b**: 65%; 121 mg, 1.1 mmol of 1,3-diene **7b**) and the iron complex **2** (200 mg, 0.633 mmol) in benzene (15 mL) was stirred at reflux for 30 min. After filtration of the mixture through a short path of Celite, the solvent was removed in vacuo. Flash chromatography (EtOAc/pentane, 1:20) on silica gel afforded a mixture of the regioisomers **8b** (1-methoxy-substituted complex) and **8b′** (2-methoxy-substituted complex) as a yellow oil, yield: 91 mg (58%). The two regioisomers can be separated by flash chromatography (pentane) on silica gel, which affords the 2-methoxy-substituted complex **8b′** as the less polar and the 1-methoxy-substituted complex **8b** as the more polar fraction.

8b. IR (drift): $\tilde{\nu}$=3046, 3003, 2961, 2935, 2860, 2834, 2031, 1974, 1948, 1460, 1387, 1335, 1211, 1156, 1036, 717, 611 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=1.66–1.72 (m, 2H), 1.75–1.84 (m, 1H), 2.24 (m, 1H), 2.95 (m, 1H), 3.46 (s, 3H), 5.04 (dd, J=6.3, 4.5 Hz, 1H), 5.32 (d, J=4.5 Hz, 1H). ^1H NMR (200 MHz, C_6D_6): δ=1.08–1.50 (m, 3H), 1.86 (m, 1H), 2.42 (m, 1H), 3.06 (s, 3H), 4.30 (dd, J=6.5, 4.5 Hz, 1H), 4.85 (dd, J=4.5, 1.0 Hz, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=23.25 (CH_2), 25.09 (CH_2), 56.71 (CH_3), 58.36 (CH), 77.58 (CH), 78.52 (CH), 117.15 (C), 212.76 (3 CO). MS (25°C): m/z (%)=250 (M^+, 3), 222 (26), 192 (12), 164 (100), 149 (10). HRMS: calcd for $C_{10}H_{10}FeO_4$ (M^+): 249.9928. Found: 249.9939.

8b′. ^1H NMR (250 MHz, $CDCl_3$): δ=1.39–1.77 (m, 4H), 2.76 (m, 1H), 3.45 (m, 1H), 3.61 (s, 3H), 5.10 (dd, J=6.5, 2.5 Hz, 1H). ^1H NMR (400 MHz, C_6D_6): δ=1.12 (m, 1H), 1.31 (m, 2H), 1.48 (m, 1H), 2.35 (m, 1H), 2.99 (s, 3H), 3.23 (m, 1H), 4.47 (dd, J=6.5, 2.5 Hz, 1H). For further spectral data, see Ref. 3c,e,f.

Transfer of the tricarbonyliron fragment to the dienes 7a–c, 9 and 11 using the azadiene complexes 6

Transfer to cyclohexa-1,3-diene (7a). *General procedure:* A solution of the azadiene complex **6** and cyclohexa-1,3-diene (**7a**) in THF [for **6g** in benzene] (15 mL) was heated at reflux. After the reaction time given, the solvent was evaporated in vacuo and the residue was subjected to flash chromatography (pentane) on silica gel to afford the tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex (**8a**) as a yellow oil. For the spectral data, see Ref. 11 (Table 8).

Table 8. Complexation of cyclohexa-1,3-diene (**7a**) using the azadiene complexes **6**

	Transfer reagent		Cyclohexa-1,3-diene (**7a**)			Reaction time	Yield of **8a**	
	[mg]	[mmol]	[μL]	[mg]	[mmol]	[h]	[mg]	[%]
6a	250	0.720	200	168	2.10	3.0	140	88
6b	200	0.531	200	168	2.10	2.0	111	95
6c	240	0.664	500	421	5.25	2.5	106	73
6d	250	0.666	200	168	2.10	4.0	103	70
6f	150	0.478	90	76	0.948	19.0	87	83
6g	300	0.730	139	117	1.46	16.0	133	83

Table 9. Complexation of 1-methoxycyclohexa-1,3-diene (**7b**) using the azadiene complexes **6**

	Transfer reagent		C_6H_6	Reaction time	Yield of **8b/8b′**		Ratio
	[mg]	[mmol]	[mL]	[h]	[mg]	[%]	**8b/8b′**
6a	250	0.720	15	5.5	121	67	1:1
6b	250	0.663	15	4.0	106	64	1:1
6c	250	0.692	12	3.0	110	64	2:1
6d	250	0.666	12	4.25	143	86	2:1

Transfer to 1-methoxycyclohexa-1,3-diene (7b). *General procedure:* A solution of methoxycyclohexadiene (0.50 mL, content of **7b**: 65%; 302 mg, 2.74 mmol of 1,3-diene **7b**) and the azadiene complex **6** in benzene was stirred at reflux for the time given. After filtration of the mixture through a short path of Celite, the solvent was removed in vacuo. Flash chromatography (EtOAc/pentane, 1:20) on silica gel afforded a mixture of the two regioisomers **8b** and **8b′** as a yellow oil. For spectral data, see above (Table 9).

Transfer to cyclohepta-1,3-diene (7c). *General procedure:* A solution of the azadiene complex **6** and cyclohepta-1,3-diene (**7c**) in benzene (15 mL) was heated at reflux. After the time given the reaction mixture was filtered through a short path of Celite, the solvent was evaporated in vacuo, and the residue was subjected to flash chromatography (pentane) on silica gel to afford tricarbonyl(η^4-cyclohepta-1,3-diene)iron (**8c**) as a yellow oil. IR (film): $\tilde{\nu}$=3031, 2981, 2928, 2890, 2869, 2845, 2039, 1958, 1459, 1441, 1404, 1347, 1338, 1161, 1089, 1058, 957, 860, 791, 630, 607 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ=1.20–1.31 (m, 1H), 1.38–1.44 (m, 1H), 1.84–1.92 (m, 2H), 1.98–2.07 (m, 2H), 3.04 (m, 2H), 5.27 (dd, J=6.0, 2.7 Hz, 2H). ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ=23.94 (CH_2), 28.07 (2 CH_2), 59.51 (2 CH), 87.96 (2 CH), 211.90 (3 CO). MS (25°C): m/z (%)=234 (M^+, 1), 206 (32), 178 (10), 176 (7), 150 (25), 148 (100), 122 (14), 91 (9). HRMS: calcd for $C_{10}H_{10}FeO_3$ (M^+): 233.9979. Found: 234.0008 (Table 10).

Transfer to 2,3-dimethylbuta-1,3-diene (9). *General procedure:* A solution of the azadiene complex **6** and 2,3-dimethylbuta-1,3-diene (**9**) in benzene [for **6c** in THF] (15 mL) was heated at reflux. After the reaction time given the solvent was evaporated in vacuo and the residue was subjected to flash chromatography (pentane) on silica gel to afford tricarbonyl([1-4-η]-2,3-dimethylbuta-1,3-diene)iron (**10**) as a yellow oil. ^1H NMR (200 MHz, C_6D_6): δ=−0.18 (d, J=2.0 Hz, 2H), 1.39 (d, J=2.0 Hz, 2H), 1.67 (s, 6H). For further spectral data, see Ref. 5c,22 (Table 11).

Transfer to hexa-2,4-dienal (11). *(a) Using the azadiene complex **6b**:* A solution of the complex **6b** (250 mg, 0.663 mmol) and hexa-2,4-dienal (**11**) (0.11 mL, 96 mg, 1.00 mmol) in toluene (15 mL) was heated at reflux for 1 h. The solvent was evaporated and the residue was subjected to flash chromatography (EtOAc/pentane, 1:7) on silica gel to afford tricarbonyl([2-5-η]-hexa-2,4-dienal)-iron (**12**) as a yellow oil, yield: 107 mg (69%). ^1H NMR (250 MHz, $CDCl_3$): δ=1.27 (m, 1H), 1.50 (d, J=7.5 Hz, 3H), 1.72 (m, 1H), 5.31 (m, 1H), 5.77 (m, 1H), 9.25 (d, J=5.0 Hz, 1H). For further spectral data, see Ref. 23.

*(b) Using the azadiene complex (R_P/S_P,S)-**6d**:* A solution of the complex (R_P/S_P,S)-**6d** (300 mg, 0.800 mmol) and hexa-2,4-dienal (**11**) (0.18 mL, 154 mg, 1.60 mmol) in THF (15 mL) was heated at reflux for 36 h. The solvent was evaporated and the residue was subjected to flash chromatography (Et_2O/pentane, 1:7) on silica gel. The crude product was purified by bulb-to-bulb distillation (50°C/0.01 mbar)

Table 10. Complexation of cyclohepta-1,3-diene (**7c**) using the azadiene complexes **6**

Transfer reagent			Cyclohepta-1,3-diene (**7c**)			Reaction time	Yield of **8c**	
	[mg]	[mmol]	[mL]	[mg]	[mmol]	[h]	[mg]	[%]
6a	250	0.720	0.20	174	1.85	2.0	123	73
6b	250	0.663	0.20	174	1.85	4.5	130	84
6c	280	0.775	0.30	260	2.76	18.0	156	86
6d	250	0.666	0.20	174	1.85	7.0	102	65

Table 11. Complexation of 2,3-dimethylbuta-1,3-diene (**9**) using the azadiene complexes **6**

Transfer reagent			2,3-Dimethylbuta-1,3-diene (**9**)			Reaction time	Yield of **10**	
	[mg]	[mmol]	[mL]	[mg]	[mmol]	[h]	[mg]	[%]
6a	250	0.720	0.35	254	3.09	18.0	123	77
6b	200	0.531	0.30	218	2.65	25.0	84	71
6c	250	0.692	0.32	232	2.83	20.0	110	72

Table 12. Thermally induced complexation of **7a**, **7c**, **11** and **13** with $Fe_2(CO)_9$

$Fe_2(CO)_9$		Solvent	Diene				Reaction time	Product	Yield	
[g]	[mmol]	[mL]		[mL]	[g]	[mmol]	[h]		[g]	[%][a]
44.2	121.5	THF, 250	**7a**	13.9	11.7	146	6	**8a**	11.5	22
0.500	1.37	DME, 15	**7a**	0.39	0.328	4.09	16	**8a**	0.127	21
20.0	55.0	THF, 120	**13**	9.67	9.09	82.5	15	**8b/8b′**	8.78	32
11.6	31.8	DME, 85	**13**	7.45	7.00	63.6	15	**8b/8b′**	3.83	24
0.560	1.54	THF, 15	**7c**	0.20	0.174	1.85	19	**8c**	0.165	23
0.250	0.687	THF, 15	**11**	0.23	0.200	2.08	18	**12**	0.133	41

[a] The yield is calculated based on the tricarbonyliron equivalents.

to provide tricarbonyl([2-5-η]-hexa-2,4-dienal)iron (**12**) as a yellow oil, yield: 112 mg (59%). For spectral data, see above.

Thermally induced complexation of the dienes 7a, 7c, 11 and 13 with $Fe_2(CO)_9$: general procedure

A solution of $Fe_2(CO)_9$ and the dienes **7a**, **7c**, **11**, and **13** in the solvent given was heated at reflux for 6–19 h. The solvent was evaporated and the residue was subjected to flash chromatography (pentane; for **11**: EtOAc/pentane, 1:7) on silica gel to provide the iron complexes as yellow oils. For spectral data, see above (Table 12).

Catalytic complexation of the dienes 7a–c and 11 with $Fe_2(CO)_9$ using the heterodienes 1, 5b, 5f and 5g: general procedure

A solution of $Fe_2(CO)_9$, the diene, and a catalytic amount of the heterodiene (see below) in a dry solvent was heated at reflux. After the reaction time given the solvent was evaporated and the residue was subjected to flash chromatography (eluent, see below) on silica gel to provide the diene complexes as yellow oils. All yields are calculated based on the tricarbonyliron equivalents.

Complexation of cyclohexa-1,3-diene (7a) with $Fe_2(CO)_9$ using catalytic amounts of the oxadiene 1. $Fe_2(CO)_9$ (1.26 g, 3.46 mmol); cyclohexa-1,3-diene (**7a**) (0.38 mL, 321 mg, 4.00 mmol); *p*-methoxybenzylideneacetone (**1**) (30 mg, 0.170 mmol); THF (15 mL); reaction time: 19 h; eluent: pentane; yield of **8a**: 240 mg (16%). For spectral data, see Ref. 11.

Catalytic complexation of cyclohexa-1,3-diene (7a) with $Fe_2(CO)_9$ using the azadiene 5b. $Fe_2(CO)_9$ (10.0 g, 27.5 mmol); cyclohexa-1,3-diene (**7a**) (7.86 mL, 6.61 g, 82.5 mmol); 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (1.63 g, 6.87 mmol); DME (50 mL); reaction time: 16.5 h; eluent: pentane; yield of **8a**: 11.9 g (98%). For spectral data, see Ref. 11.

Catalytic complexation of cyclohexa-1,3-diene (7a) with $Fe_2(CO)_9$ using the azadiene 5f. $Fe_2(CO)_9$ (500 mg, 1.37 mmol); cyclohexa-1,3-diene (**7a**) (0.33 mL, 275 mg, 3.43 mmol); 1-(*N*,*N*-dimethylamino)-4-phenyl-1-azabuta-1,3-diene (**5f**) (60 mg, 0.344 mmol); DME (15 mL); reaction time: 16 h; eluent: pentane; yield of **8a**: 178 mg (30%). For spectral data, see Ref. 11.

Catalytic complexation of cyclohexa-1,3-diene (7a) with $Fe_2(CO)_9$ using the azadiene 5g. $Fe_2(CO)_9$ (1.00 g, 2.75 mmol); cyclohexa-1,3-diene (**7a**) (0.65 mL, 550 mg, 6.86 mmol); 4-phenyl-1-phenylsulfonyl-1-azabuta-1,3-diene (**5g**) (189 mg, 0.697 mmol); benzene (15 mL); reaction time: 17.5 h; eluent: pentane; yield of **8a**: 730 mg (60%). For spectral data, see Ref. 11.

Catalytic complexation of 1-methoxycyclohexa-1,3-diene (7b) with $Fe_2(CO)_9$ using the azadiene 5b. $Fe_2(CO)_9$ (500 mg, 1.37 mmol); methoxycyclohexadiene (0.62 mL, content of **7b**: 65%; 376 mg, 3.41 mmol of 1,3-diene **7b**); 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (81 mg, 0.341 mmol); DME (15 mL); reaction time: 17 h; eluent: Et_2O/pentane 1:10; yield of **8b** and **8b′**: 587 mg (86%). For spectral data, see above.

Catalytic complexation of cyclohepta-1,3-diene (7c) with $Fe_2(CO)_9$ using the azadiene 5b. $Fe_2(CO)_9$ (500 mg, 1.37 mmol); cyclohepta-1,3-diene (**7c**) (0.37 mL, 321 mg, 3.41 mmol); 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (81 mg, 0.341 mmol); dioxane (15 mL); reaction time: 17 h; eluent: pentane; yield of **8c**: 432 mg (67%). For spectral data, see above.

Catalytic complexation of hexa-2,4-dienal (11) with $Fe_2(CO)_9$ using the azadiene 5b. $Fe_2(CO)_9$ (500 mg, 1.37 mmol); hexa-2,4-dienal (**11**) (0.38 mL, 328 mg, 3.41 mmol); 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (81 mg, 0.341 mmol); DME (15 mL); reaction time: 16 h; eluent: EtOAc/pentane, 1:7; yield of **12**: 465 mg (72%). For spectral data, see above.

Catalytic complexation of cyclohexa-1,3-diene (7a) with $Fe(CO)_5$ using the heterodienes 1 and 5a–e —variation of the reaction time: general procedure

A solution of pentacarbonyliron (0.60 mL, 891 mg, 4.55 mmol), cyclohexa-1,3-diene (**7a**) (0.65 mL, 547 mg, 6.83 mmol), and the heterodiene (0.569 mmol) in dioxane (15 mL) was heated at reflux for the reaction time given. The solvent was evaporated and the residue was subjected to flash chromatography (pentane) on silica gel to afford tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**8a**) as a yellow oil. For spectral data, see Ref. 11 (Table 13).

Catalytic complexation of 1-methoxycyclohexa-1,3-diene (7b) with $Fe(CO)_5$ using the catalyst 5b

A solution of pentacarbonyliron (10.0 mL, 14.9 g, 76.1 mmol), methoxycyclohexadiene (20.2 mL, 18.8 g, 170 mmol, content: 65% of the 1,3-diene **7b** and 35% of the 1,4-diene **13**), and 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (2.19 g, 9.23 mmol) in dioxane (50 mL) was stirred at reflux for 5 days. The solvent was evaporated and the residue was subjected to flash chromatography (Et_2O/pentane, 1:10) on silica gel to afford a mixture

Table 13. Complexation of cyclohexa-1,3-diene (**7a**) with $Fe(CO)_5$ using catalytic amounts of **1** and **5a–e**

Catalyst		Reaction time [h]	Yield of **8a**	
	[mg]		[mg]	[%]
–	–	14	7	0.7
1	100	14	42	4
5a	118	14	413	41
5b	135	5	210	21
5b	135	14	496	50
5b	135	37	910	91
5c	126	5	160	16
5c	126	14	472	47
5c	126	37	798	80
(*S*)-**5d**	134	5	204	20
(*S*)-**5d**	134	14	406	41
(*S*)-**5d**	134	37	642	64
5e	107	14	390	39

of **8b** and **8b′** as a yellow oil, yield: 15.2 g (80%), ratio of **8b/8b′**=1:1. For spectral data, see above.

Catalytic complexation of 1-methoxycyclohexa-1,4-diene (13) with $Fe(CO)_5$ using the catalyst 5b

Pentacarbonyliron (8.93 mL, 13.3 g, 67.9 mmol) was added to a solution of 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**5b**) (2.00 g, 8.43 mmol) in dioxane (100 mL) at room temperature and the mixture was stirred for 30 min. Methoxycyclohexadiene (11.9 mL, 11.2 g, 101.6 mmol, content: 85% of the 1,4-diene **13** and 15% of the 1,3-diene **7b**) and dioxane (150 mL) were added and the reaction mixture was heated at reflux for 5 days. The black suspension was filtered through a short path of Celite and the solvent of the filtrate was evaporated. Flash chromatography (pentane) of the residue on silica gel afforded a mixture of the regioisomers **8b** and **8b′** as a yellow oil, yield: 13.8 g (81%), ratio of **8b/8b′**≈1:1. Flash chromatography (pentane) on silica gel afforded the 2-methoxy-substituted complex **8b′** as the less polar and the 1-methoxy-substituted complex **8b** as the more polar fraction. For spectral data, see above.

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