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Synthesis, Molecular Structure, Fluxional Behavior, and Tricarbonyliron Transfer Reactions of (η^4-1-Azabuta-1,3-diene)tricarbonyliron Complexes

Hans-Joachim Knölker*[a], Gerhard Baum[b], Norbert Foitzik[a], Helmut Goesmann[b], Peter Gonser[a], Peter G. Jones[c], and Herbert Röttele[a]

Institut für Organische Chemie der Universität Karlsruhe[a],
Richard-Willstätter-Allee, D-76131 Karlsruhe, Germany
Fax: +49 (0) 721/698529
E-mail: knoe@ochhades.chemie.uni-karlsruhe.de

Institut für Anorganische Chemie der Universität Karlsruhe[b],
Engesserstraße, D-76128 Karlsruhe, Germany

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig[c],
Hagenring 30, D-38106 Braunschweig, Germany

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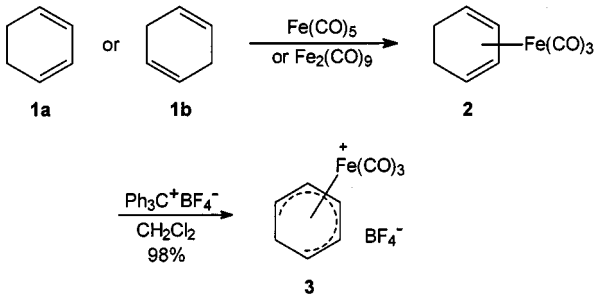
The (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** are easily prepared in high yield by condensation of the corresponding arylamines **7** with the cinnamaldehydes **8** and subsequent ultrasound-promoted complexation of the resulting 1-azabuta-1,3-dienes **9** with nonacarbonyldiiron. The complexes **10** are shown to represent excellent reagents for the transfer of the tricarbonyliron fragment onto cyclohexa-1,3-diene (**1a**). The structural characterization for the complexes **10** is achieved by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, as well as X-ray crystallography of **10b**, **10c**, and **10l**. Using variable temperature ^{13}C-NMR spectroscopy the fluxionality of the complexes **10a**, **10b**, **10c**, **10e**, and **2** is investigated and the activation barrier for the turnstile rotation of the tricarbonyliron fragment is determined. The transfer reaction and the structural factors influencing the transfer of the tricarbonyliron fragment are extensively investigated.

Introduction

Tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes have found many useful applications in synthetic organic chemistry and have been shown to represent excellent starting materials for the stereoselective synthesis of natural products.[1] The parent complex, tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**), was prepared first in 1958 by Pauson via complexation of cyclohexa-1,3-diene (**1a**) with pentacarbonyliron under thermal reaction conditions (yield: 21%).[2] The yield of this complexation was later improved by photolytic reaction of cyclohexa-1,4-diene (**1b**) with pentacarbonyliron in benzene (yield: 56%),[3] by reaction of cyclohexa-1,4-diene (**1b**) with pentacarbonyliron in di-*n*-butyl ether at reflux (yield: 46%),[4] by reaction of cyclohexa-1,3-diene (**1a**) with nonacarbonyldiiron in tetrahydrofuran at reflux (yield: 43%),[5] and by photolytic reaction of cyclohexa-1,3-diene (**1a**) with pentacarbonyliron in hexane (yield: 77%)[5] (Scheme 1).

The high synthetic potential of tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) became evident in 1960, when E. O. Fischer found the possibility of hydride abstraction using triphenylmethyl tetrafluoroborate.[6] The reactivity of the resulting tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate (**3**) can be utilized for regio- and stereoselective bond formation with a broad range of nucleophiles.[1] Projected synthetic applications of the complex salt **3** require an access to the iron complex **2** in large scale and high yield. However, the methods described above, involving either thermally or photochemically induced direct complexation of the cyclohexadienes **1a** or **1b** with pentacarbonyliron or nonacarbonyldiiron, afford complex **2** in only 21−77% yield. Moreover, these procedures lead to the formation of pyrophoric iron which is hazardous during

Scheme 1. Complexation of cyclohexa-1,3-diene (**1a**) and cyclohexa-1,4-diene (**1b**) with $Fe(CO)_5$ or $Fe_2(CO)_9$ and preparation of the complex salt **3**



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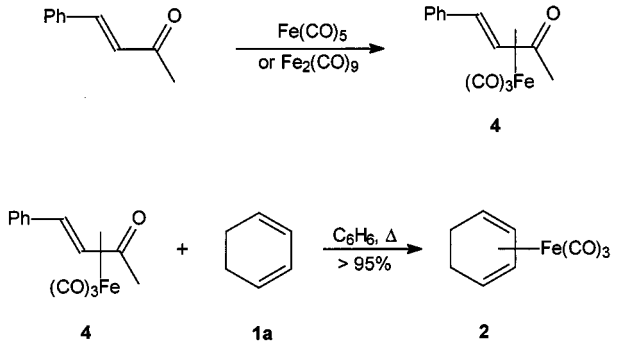
workup, especially on large scale complexations. This problem can be circumvented by using labile tricarbonyliron complexes in order to transfer the tricarbonyliron fragment from the weakly bound ligand to cyclohexa-1,3-dienes or buta-1,3-dienes under mild reaction conditions. The development of such tricarbonyliron transfer reagents for the efficient complexation of 1,3-dienes has been extensively investigated over the last 25 years.[7]

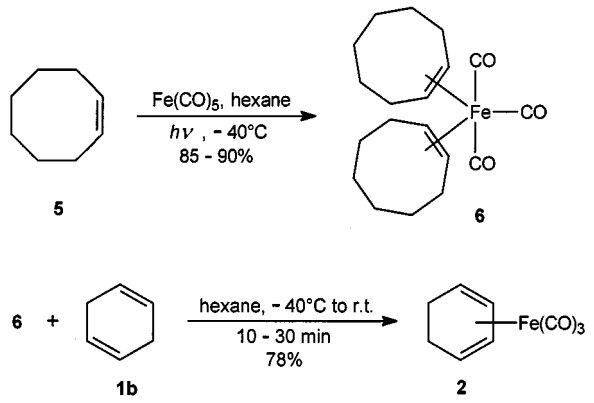
The ability of tricarbonyl(η^4-1-oxabuta-1,3-diene)iron complexes to serve as a mild source of the tricarbonyliron fragment was first described by Lewis in 1972.[8] The (η^4-benzylideneacetone)tricarbonyliron (**4**) was found to represent an especially efficient transfer reagent. Brookhart reported the transfer of the tricarbonyliron fragment of **4** to cyclohexa-1,3-diene (**1a**) in a thermal reaction that affords the iron complex **2** in over 95% yield (Scheme 2).[9]

Scheme 2. Complexation of benzylideneacetone to **4** and tricarbonyliron transfer to cyclohexa-1,3-diene (**1a**) using the complex **4**



However, the problematic step of this reaction sequence is the preparation of the transfer reagent **4**. The original procedure described by Lewis involved complexation of benzylideneacetone with 1 equivalent of nonacarbonyldiiron in toluene at 60°C and afforded complex **4** in only 32% yield.[8] Brookhart improved this yield to 60% by a photolytic and subsequent thermal reaction of benzylideneacetone with pentacarbonyliron.[9] Only by heating a solution of benzylideneacetone with an excess of nonacarbonyldiiron in diethyl ether at reflux, as reported by Thomas, the tricarbonyliron complex **4** was obtained in reasonable yields (74–81%).[10]

Scheme 3. Complexation of cyclohexa-1,4-diene (**1b**) to **2** using Grevels′ reagent **6**



A further tricarbonyliron transfer reagent was developed by Grevels in 1984. Photolytic reaction of pentacarbonyliron with an excess of *cis*-cyclooctene (**5**) in hexane at −40°C afforded tricarbonylbis(η^2-*cis*-cyclooctene)iron (*Grevels′ reagent*) (**6**), which can be isolated as yellow crystals in 85–90% yield (Scheme 3).[11] While the solid compound can be handled at room temperature, complex **6** is labile in solution at temperatures above −35°C. The advantage of Grevels′ reagent is that the transfer of the tricarbonyliron fragment to 1,3-dienes occurs under extremely mild reaction conditions at temperatures below 0°C. Moreover, using Grevels′ reagent **6** also non-conjugated 1,4-dienes can be complexed with concomitant migration of the double bond, e.g. the transfer of the tricarbonyliron fragment of Grevels′ reagent **6** to cyclohexa-1,4-diene (**1b**) provides tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) in 78% yield (Scheme 3).

The high lability of the tricarbonyl(η^4-1-oxabuta-1,3-diene)iron complex **4** and the Grevels′ reagent **6** in solution at room temperature and in the air induced our search for alternative tricarbonyliron transfer reagents, whose higher stability should make them useful for a wider range of applications in synthetic organometallic chemistry.

Results and Discussion

Our investigations led us to the (η^4-1-azabuta-1,3-diene)-tricarbonyliron complexes **10** as efficient and selective tricarbonyliron transfer reagents of high stability (Scheme 4).[12][13] (η^4-1-Azabuta-1,3-diene)tricarbonyliron complexes were first described by Otsuka[14] and Lewis[15] and have been applied to the synthesis of dicarbonyl(η^4-styrene)iron carbene complexes,[16] substituted pyrroles,[17] and to the preparation of labile Schiff bases in the form of their metal complexes.[18] The following methods were previously used for the preparation of the complexes **10**: 1. condensation of amines with tetracarbonyl(η^2-1-oxabuta-1,3-diene)-iron complexes;[14a][18] 2. thermal reaction of the 1-azabuta-1,3-dienes **9** with nonacarbonyldiiron;[14][17] and 3. aza-Wittig reaction of tetracarbonyl(η^2-1-oxabuta-1,3-diene)iron complexes.[19] We found that the yields of the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** are considerably improved by an ultrasound-promoted complexation[20] of 1-azabuta-1,3-dienes **9** with nonacarbonyldiiron at room temperature.[12][13] In the present paper we describe an extensive investigation of the transfer reaction of the tricarbonyliron fragment from the complexes **10** to cyclohexa-1,3-diene (**1a**) as well as the structural factors influencing the transfer of the metal fragment.

The synthesis of the 1-azabuta-1,3-dienes **9** was achieved by adaptation of standard literature procedures for the imine condensation of the arylamines **7** with the cinnamaldehydes **8**. Reaction of 1 equivalent of the freshly distilled or sublimated arylamine **7** and 1 equivalent of the cinnamaldehyde **8** in an inert solvent, generally with addition of a drying agent, afforded the 1-azabuta-1,3-dienes **9** in high yields (Scheme 4, Table 1). Most of the arylamines **7** and the cinnamaldehydes **8** are commercially available. 2,4,6-Trimethoxyaniline (**7i**) was prepared in 88% yield by hydrogen-

Scheme 4. Synthesis of the azadienes **9**, complexation of **9** to the iron complexes **10** with nonacarbonyldiiron, and the tricarbonyliron transfer to cyclohexa-1,3-diene (**1a**)

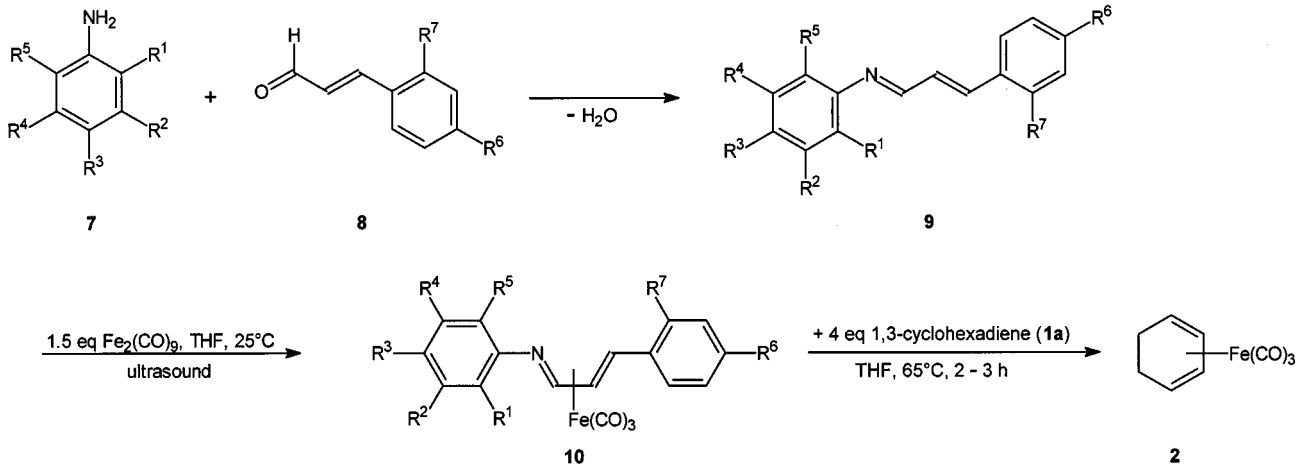


Table 1. Synthesis and characteristic ^{1}H-NMR data of the 1-azabuta-1,3-dienes **9** and their iron complexes **10** and transfer of the tricarbonyliron fragment to cyclohexa-1,3-diene (**1a**)

	R^1	R^2	R^3	R^4	R^5	R^6	R^7	**9**, Yield [%]	δ [ppm][a]	**10**, Yield [%]	δ [ppm][a]	**2**, Yield [%]
a	H	H	H	H	H	H	H	82	8.27	82	6.95	88
b	H	H	OMe	H	H	H	H	100	8.30	88	6.99	95
c	OMe	H	H	H	H	H	H	87	8.28	80	7.10	74
d	H	H	NMe_2	H	H	H	H	40	8.35	55	7.06	45
e	H	H	CF_3	H	H	H	H	72	8.24	59	6.84	78
f	H	NO_2	H	H	H	H	H	56	8.30	0	–	–
g	OMe	H	OMe	H	H	H	H	81	8.31	43	7.15	80
h	H	OMe	OMe	OMe	H	H	H	79	8.30	40	6.97	87
i	OMe	H	OMe	H	OMe	H	H	73	8.51	56	7.94	74
j	H	H	H	H	H	OMe	H	88	8.21	73	–[b]	93
k	H	H	OMe	H	H	OMe	H	95	8.26	41	6.95	90
l	OMe	H	H	H	H	OMe	H	79	8.24	82	–[b]	83
m	H	H	CF_3	H	H	OMe	H	59	8.20	64	6.83	88
n	OMe	H	OMe	H	H	OMe	H	80	8.26	79	7.10	78
o	H	H	OMe	H	H	H	OMe	86	8.31	81	6.95	92
p	H	H	H	H	H	CN	H	78	8.47	57	7.04	69
q	OMe	H	OMe	H	H	CN	H	99	8.36	61	7.23	60
r	H	H	OMe	H	H	NMe_2	H	85	8.24	62	6.89	74
s	H	H	OMe	H	H	NO_2	H	75	8.34	0	–	–

[a] Chemical shift of the H-C2 signal in the ^{1}H-NMR spectrum. – [b] No assignment possible, due to coincidental overlap of signals.

ation of 2,4,6-trimethoxynitrobenzene.[21] The synthesis of 4-cyanocinnamaldehyde (**8p** = **8q**; R^6 = CN, R^7 = H) was achieved in 78% yield by Wittig reaction of 4-cyanobenzaldehyde and (formylmethylene)triphenylphosphorane in toluene at reflux.

As shown below, the electron density at the nitrogen of the 1-azabuta-1,3-dienes **9** is crucial for the efficiency of the tricarbonyliron transfer from the corresponding complexes **10** and for the catalytic complexation[12][13] of cyclohexa-1,3-diene (**1a**) using **9** and nonacarbonyldiiron or pentacarbonyliron. The chemical shift of the imine proton (H-C2) in the ^{1}H-NMR spectra of the 1-azabuta-1,3-dienes **9** is a measure of the electron density at the imine nitrogen atom. A larger downfield shift of H-C2 correlates with a higher electron density at the nitrogen. Thus, this value can be used to estimate the activity of the 1-azabuta-1,3-dienes **9** for catalytic complexations and the transfer ability of the corresponding complexes **10**. Donor substituents in the *ortho* and *para* positions of the 1-aryl ring (R^1, R^3, R^5) cause a downfield shift of the signal of the imine proton relative to the value obtained for the parent compound **9a** (δ = 8.27). The maximum is observed for the 2,4,6-trimethoxy derivative **9i** with a chemical shift of δ = 8.51, which can be at least partly ascribed to the influence of the anisotropy of the oxygen atoms. In contrast, a highfield shift is found with donor substituents in the *para* position of the 4-aryl ring (R^6). Exactly the opposite effects on the chemical shift of H-C2 are observed with acceptor substituents in these positions. In a few cases steric effects are overriding, since substituents in the *ortho* positions of the aryl ring cause larger torsion angles between the aryl ring and the 1-azabuta-1,3-diene plane, resulting in decreased π-overlap.

The complexation of the 1-azabuta-1,3-dienes **9** to the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** was conveniently achieved by reaction with nonacarbonyldiiron under sonication in tetrahydrofuran at room temperature

(Scheme 4, Table 1). The ultrasound-promoted tricarbonyliron complexation, previously applied by Ley and coworkers to buta-1,3-dienes and cyclohexa-1,3-dienes,[20] was found to be superior to the thermal complexation of the 1-azabuta-1,3-dienes **9**. With respect to the diastereoselectivity of the complexation of chiral 1-azabuta-1,3-dienes,[22] the ultrasound procedure also provides better results than the thermal reaction, since it does not require elevated temperatures, which were shown to cause epimerization of the planar chirality.[23]

The red crystalline (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** are stable in the air for months and therefore appeared to represent appropriate potential transfer reagents for our purposes. The IR spectra of the iron complexes **10** in KBr exhibit intense broad bands in the region of 1960−2060 cm^{-1}, which are typical of carbonyl ligands of tricarbonyliron−diene complexes (Table 2). The wave number of the CO stretching vibration represents an indirect measure of the strength of the bonding between the metal and the organic ligand. A shift to lower wave numbers relative to the value for the parent compound **10a** is observed by donor substituents in the *para* position of the 1-aryl ring (e.g. **10b**: R^3 = OMe, **10d**: R^3 = NMe_2) indicating a reduced back bonding from the iron atom to the azadiene ligand in these complexes, which is explained by an increase in energy of the π* orbitals of the 1-azabutadiene.

The ^{1}H-NMR spectra of the η^4-tricarbonyliron-complexed 1-azabuta-1,3-dienes **10** exhibit the characteristic high field shifts for the protons at the carbon atoms which are coordinated to the metal (C2 to C4). A closer inspection of the chemical shifts which are found for the signals of the imine protons (H-C2) of the complexes **10** reveals that generally a highfield shift of about 1.3−1.4 ppm relative to the value for the corresponding free ligand **9** is observed (Table 1). For those derivatives of **10** having one methoxy substituent in the *ortho* position of the 1-aryl ring (R^1 = OMe; **10c**, **10g**, **10n**, and **10q**) this highfield shift relative to **9** is decreased to 1.13−1.18 ppm, which is ascribed partly to a steric effect of the *ortho* substituent (increase of the torsion angle) leading to reduced π-overlap and partly to the anisotropy of the oxygen atom. For complex **10i** with two *ortho* methoxy substituents in the 1-aryl ring (R^1 = R^5 = OMe) the highfield shift of the imine proton relative to the value observed for **9i** drops to 0.57 ppm.

Almost all of the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** described in this paper show no or at best three very broad signals for the carbon atoms of the carbonyl ligands in their ^{13}C-NMR spectra when taken in deuterochloroform at room temperature, although the IR spectra in KBr exhibit the typical three bands for the carbonyl ligands at 1960−2060 cm^{-1}. The trifluoromethyl-substituted compounds **10e** and **10m** are exceptions and exhibit three only slightly broadened signals in their ^{13}C-NMR spectra under these conditions (**10e**: δ = 204.77, 208.30, 211.49; **10m**: δ = 205.07, 208.94, 211.97). The ^{13}C-NMR spectra of (η^4-carba-1,3-diene)tricarbonyliron complexes show in most cases only one singlet at δ = 210−213 for the three carbonyl ligands at room temperature. The fluxionality of these complexes leading to equivalency of the three carbonyl ligands is caused by the turnstile rotation of the tricarbonyliron fragment. This dynamic process is sufficiently slow on the NMR time scale at low temperatures to allow the observation of two peaks for the three carbonyl ligands with an intensity ratio of 2:1 in the case of symmetrical diene ligands or three peaks of equal height for unsymmetrical diene ligands.[24] Previous investigations of the fluxional behavior of tricarbonyliron-diene complexes have demonstrated that the activation barriers for this intramolecular basal-apical exchange of the carbonyl groups for complexes with carbadiene ligands are significantly lower than those of 1-heterodiene ligands.[25] Takats concluded that the variations in the activation barrier for the turnstile rotation of the tricarbonyliron fragment can be rationalized by the metal-carbonyl back bonding, however steric factors also contribute to this value.[25c]

We determined precisely the activation barrier for the intramolecular carbonyl ligand exchange of four (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes (**10a−c** and **10e**) and for tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) by dynamic ^{13}C-NMR spectroscopy at 125 MHz in deuterated toluene (Figure 1a−e, Table 2). The stepwise increase of the temperature up to 373 K during the measurement of the ^{13}C-NMR spectra of the complexes **10** provided a single signal for the three carbonyl ligands, which still showed some line broadening. As expected the low temperature spectra of the 1-azadiene complexes **10** at 233 K exhibited three sharp singlets for the carbonyl ligands. The coalescence temperature T_C of the dynamic process was clearly above room temperature for all four cases investigated. This was already indicated by the fact that the signals for the carbonyl ligands were missing in the ^{13}C-NMR spectra in deuterochloroform at room temperature for most of the 1-azadiene complexes **10** prepared in the present work. For the cyclohexadiene complex **2** one sharp singlet for the three carbonyl ligands is observed at room temperature, while the ^{13}C-NMR spectrum at 185 K exhibits two singlets at δ = 211.32 and 216.05 in a ratio of 2:1. The coalescence temperatures could be determined with a tolerance of ±5 K. With the value for δν taken from the low temperature spectrum, the free enthalpy of activation for the intramolecular exchange of carbonyl ligands could be calculated in good approximation by using the formula $\Delta G^{\neq} = R \cdot T_C [22.96 + \ln(T_C/\delta\nu)]$.[26] The activation barrier for this turnstile rotation of the tricarbonyliron fragment in the 1-*p*-anisyl-substituted 1-azadiene complex **10b** is 13.5 ± 0.3 kcal/mol. For the other 1-azadiene complexes that were investigated by dynamic ^{13}C-NMR spectroscopy (**10a**, **10c**, and **10e**), the value was found to be increased by about 1 kcal/mol (Table 2). Thus the intramolecular ligand exchange of the carbonyl groups is facilitated by a donor substituent in the *para* position of the 1-aryl ring (complex **10b**) as compared to the parent compound **10a**. This finding is again in agreement with the assumption of reduced back bonding from the iron atom to the 1-azadiene ligand in complex **10b** relative to **10a**. The opposite effect is observed with an acceptor group in this position (complex **10e**) and also with

Figure 1a. Dynamic ^{13}C-NMR spectra of complex **10a** in the metal carbonyl region (125 MHz, [D$_8$]toluene)

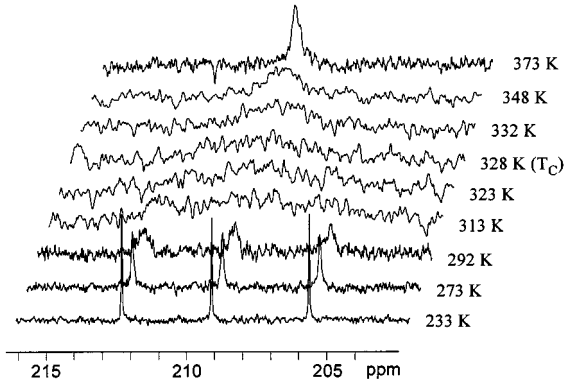


Figure 1b. Dynamic ^{13}C-NMR spectra of complex **10b** in the metal carbonyl region (125 MHz, [D$_8$]toluene)

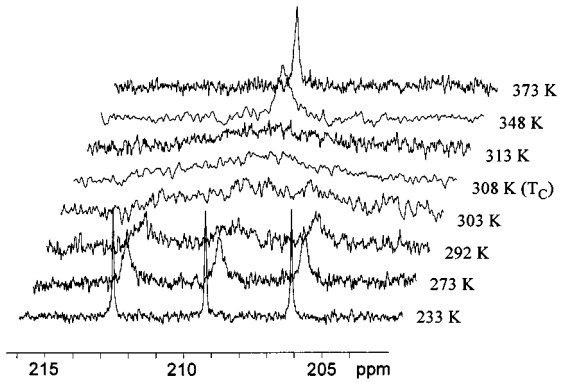


Figure 1c. Dynamic ^{13}C-NMR spectra of complex **10c** in the metal carbonyl region (125 MHz, [D$_8$]toluene)

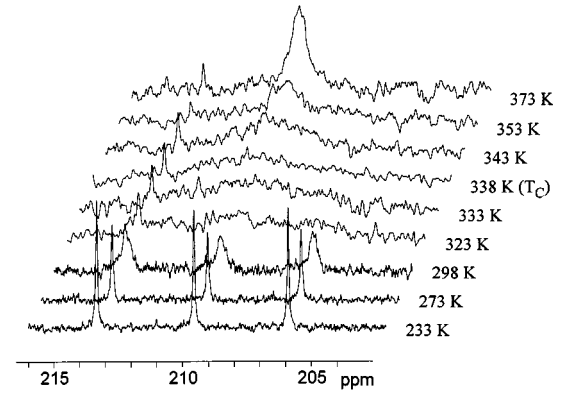


Figure 1d. Dynamic ^{13}C-NMR spectra of complex **10e** in the metal carbonyl region (125 MHz, [D$_8$]toluene)

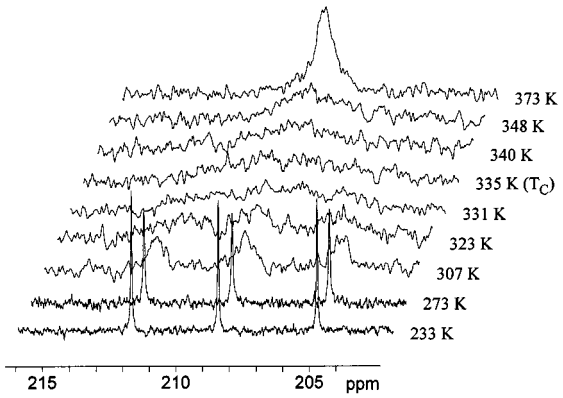
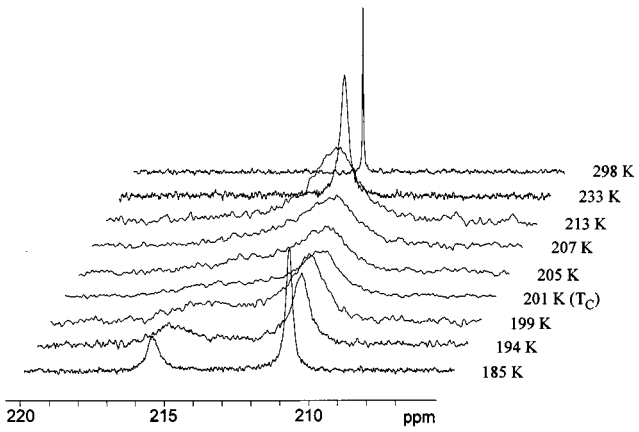


Figure 1e. Dynamic ^{13}C-NMR spectra of complex **2** in the metal carbonyl region (125 MHz, [D$_8$]toluene)



a donor group in the *ortho* position of the 1-aryl ring, because of the increased torsion angle (compound **10c**). For the cyclohexa-1,3-diene complex **2** the activation barrier for the rotation of the tricarbonyliron fragment has been determined as 8.7 ± 0.3 kcal/mol, which is in good agreement with the value of 8.8 ± 0.5 kcal/mol obtained earlier by Takats et al. in [D$_6$]DMSO/CS$_2$.[25c] For the related (η^4-buta-1,3-diene)tricarbonyliron complex activation barriers of 9.5 kcal/mol[24] and 10.5 ± 0.5 kcal/mol[25c] have been reported. These findings emphasize that the free enthalpy of activation for the turnstile rotation of the tricarbonyliron fragment for the complexes of 1-hetero-1,3-dienes is generally about 4−5 kcal/mol higher than for the corresponding complexes of carba-1,3-dienes, no matter whether they are cyclic or acyclic. The data are in agreement with decreased back donation of electrons from filled iron d-orbitals into the LUMO of the carbonyl group for the tricarbonyliron

Table 2. Characteristic IR and ^{13}C-NMR data for the carbonyl ligands of selected tricarbonyliron complexes[a]

	$\tilde{\nu}_{CO}$ [cm^{-1}]	δ_{CO} (233 K) [ppm]	δ_{CO} (373 K) [ppm]	T_C [K]	$\delta\nu$ [Hz]	$\Delta G^{\neq}$ [kcal/mol]
10a	2055, 1988, 1977	206.02, 209.49, 212.70	209.53	328 ± 5	840.79	14.3 ± 0.3
10b	2049, 1987, 1963	206.60, 209.71, 213.03	209.81	308 ± 5	809.65	13.5 ± 0.3
10c	2058, 2000, 1970	206.41, 210.06, 213.84	210.02	338 ± 5	934.21	14.7 ± 0.3
10e	2059, 2002, 1983	205.19, 208.90, 212.16	208.79	335 ± 5	876.08	14.6 ± 0.3
2	2042, 1957	211.32, 216.05[b]	212.56[c]	201 ± 5	594.79	8.7 ± 0.3

[a] IR spectra: Drift at room temp.; ^{13}C-NMR spectra: 125 MHz in [D$_8$]toluene. − [b] This spectrum was recorded at 185 K. − [c] This spectrum was recorded at 298 K.

complexes of 1-hetero-1,3-dienes, as compared to 1-carba-1,3-dienes. This is confirmed by the higher stretching frequencies for the carbonyl bands in the IR spectra of 1-hetero-1,3-diene complexes. In consequence the averaged chemical shifts in the ^{13}C-NMR spectra observed at high temperatures are shifted to higher field and the activation barrier for the rotation of the tricarbonyliron fragment is higher for the 1-heterodiene complexes.

Figure 2. Molecular structure of **10b** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [A]: Fe−N 2.075(3), Fe−C2 2.074(4), Fe−C3 2.068(4), Fe−C4 2.167(4). Torsion angle: C2,N−C11,C16: 10.8°

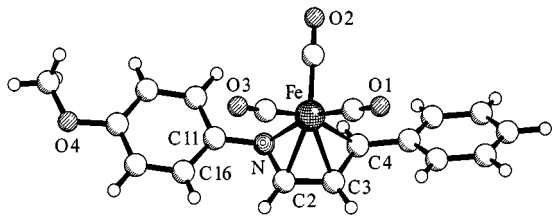


Figure 3. Molecular structure of **10c** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [A]: Fe−N 2.074(2), Fe−C2 2.064(2), Fe−C3 2.050(2), Fe−C4 2.132(3). Torsion angle: C2,N−C11,C16: 13.4°. Distance Fe−O4: 3.62 A

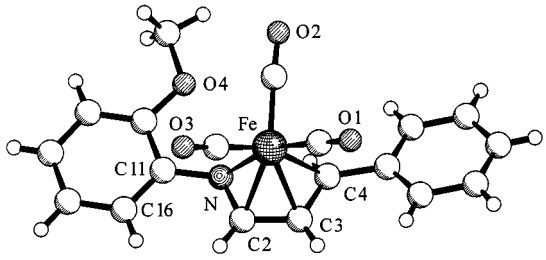
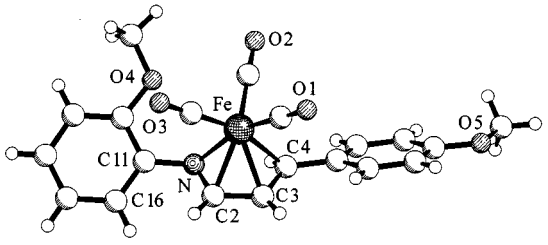


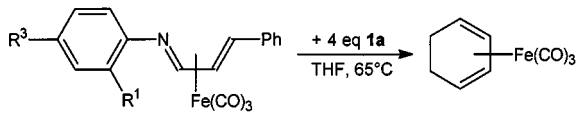
Figure 4. Molecular structure of **10l** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [A]: Fe−N 2.070(2), Fe−C2 2.068(2), Fe−C3 2.062(2), Fe−C4 2.155(2). Torsion angle: C2,N−C11,C16: 37.4°. Distance Fe−O4: 3.35 A



The X-ray crystal structure determinations of the (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10b**, **10c**, and **10l** confirm the tetragonal pyramidal coordination of the iron atom (Figure 2−4, Table 4). Two basal positions are occupied by the two π bonds, the two others by carbonyl ligands. The third carbonyl ligand adopts the apical position of these complexes. Similar arrangements were previously found for tricarbonyliron complexes of buta-1,3-dienes and cyclohexa-1,3-dienes and also for the parent complex **10a**.[14b] The bond lengths found in the tricarbonyliron complexes of 1-azabuta-1,3-dienes, compared to those of cyclohexa-1,3-dienes and buta-1,3-dienes, correlate very well with the concept of increased back bonding from the filled iron d-orbitals into the π* orbitals of the organic ligand for the heterodiene complexes. This is emphasized by the IR, ^{1}H-NMR, and ^{13}C-NMR data described above. Some anomalies in the spectral data of the 1-azabuta-1,3-diene complexes presented above were ascribed to steric factors, especially for those cases of 1-azabuta-1,3-dienes resulting from an *ortho*-substituted arylamine. The X-ray crystal structures reveal an increased torsion angle for the complexes with an *ortho*-methoxy substituent. It is noteworthy that the out-of-plane arrangement of the 1-aryl ring relative to the 1-azabuta-1,3-diene plane in these complexes proceeds in a way that the oxygen atom of the methoxy group is oriented towards the iron atom. For electronic reasons this arrangement becomes most evident for complex **10l** with an *ortho*-methoxy substituent in the 1-aryl ring and a *para*-methoxy substituent in the 4-aryl ring. The torsional angle between the 1-aryl ring and the 1-azabuta-1,3-diene plane of **10l** is 37.4° and the distance Fe−O4 is only 3.35 A, suggesting the possibility of chelation of the tricarbonyliron fragment by coordination of the oxygen to the iron atom on haptotropic $\eta^4 \rightarrow \eta^1$ migration during the transfer of the metal fragment (see below).

The transfer of the tricarbonyliron fragment from the (1-azabuta-1,3-diene)tricarbonyliron complexes **10** to cyclohexa-1,3-diene (**1a**) was extensively investigated. It was shown that a smooth transfer of the metal fragment from all 1-azabuta-1,3-diene complexes described in this study was achieved simply by heating the reaction mixture of complex **10** and **1a** in tetrahydrofuran at reflux (Scheme 4, Table 1). The variation of the reaction time for the transfer of the tricarbonyliron fragment to cyclohexa-1,3-diene (**1a**) was investigated for the complexes **10b**, **10c**, and **10g** (Table 3). At all three different reaction times the transfer reagent **10b** was superior. Complex **10b** transfers the metal fragment faster and provides the best yield after 2 h. With increasing turnover, the transfer of the tricarbonyliron fragment from complex **10** to already generated corresponding free 1-azabuta-1,3-diene ligand **9** can compete with the desired transfer to **1a** and finally becomes dominant if only a 1:1 ratio

Table 3. Variation of the reaction time for the tricarbonyliron transfer to **1a** using the complexes **10b**, **c**, **g**



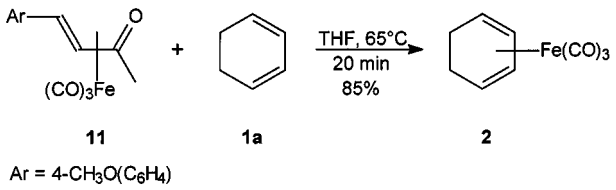
10b, c, g **2**

Transfer Reagent	R^1	R^3	Reaction Time **2**, Yield (%) 30 min	60 min	120 min
10b	H	OCH_3	61	83	95
10c	OCH_3	H	31	47	74
10g	OCH_3	OCH_3	50	67	80

of complex **10** and **1a** is employed. Therefore, an excess of cyclohexa-1,3-diene (**1a**) is used in order to bring the reaction to completion.

Using a standard set of reaction conditions, the transfer of the metal fragment to cyclohexa-1,3-diene (**1a**) was compared for the various (1-azabuta-1,3-diene)tricarbonyliron complexes **10** (Table 1, Scheme 4). By far the best overall result was achieved using tricarbonyl[(1-4-η)-1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10b**) as transfer reagent. First, the free 1-azabuta-1,3-diene **9b** can be prepared quantitatively and crystallizes very easily. Secondly, the complexation of **9b** with nonacarbonyldiiron promoted by ultrasound provided the tricarbonyliron complex **10b** in a yield of 88%. Thirdly, the reaction of **10b** with cyclohexa-1,3-diene (**1a**) afforded tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) in 95% yield. Thus, the complexation of **1a** using this 3-step sequence could be realized in an overall yield of 84%. Moreover, the free 1-azadiene **9b** can be recovered from the reaction mixture by simple crystallization in more than 95% yield.

Scheme 5. Transfer of the tricarbonyliron fragment from the 4-methoxybenzylideneacetone complex **11** to cyclohexa-1,3-diene (**1a**)

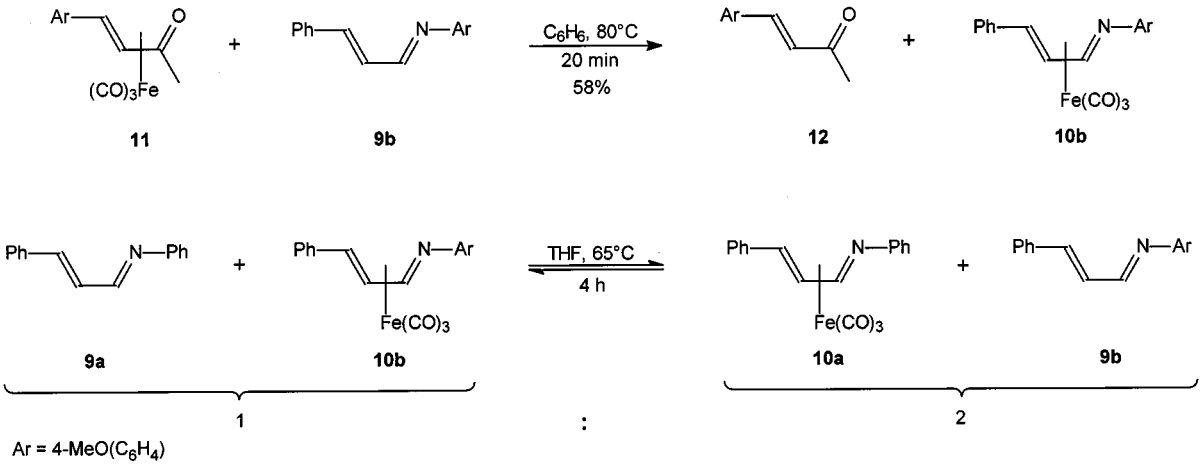


Some information on the relative reactivities of various tricarbonyliron transfer reagents was provided by competition experiments. For this purpose we prepared the tricarbonyliron complex **11** containing the more electron-rich 4-methoxybenzylideneacetone ligand. Complex **11** was reported to be more reactive in transfer reactions than the tricarbonyliron complex **4** with unsubstituted benzylideneacetone as ligand.[27] A smooth transfer of the metal fragment was observed on reaction of complex **11** with cyclohexa-1,3-diene (**1a**) in tetrahydrofuran at reflux and afforded the iron complex **2** after 20 min in 85% yield (Scheme 5). Thus, the required reaction time for comparable yields of **2** with the 1-oxabuta-1,3-diene complex **11** as transfer reagent is significantly shorter than with the 1-azabuta-1,3-diene complexes **10** (cf. Table 3). On direct comparison of the transfer reagents **11** and **10b** this difference in reactivity becomes even more evident (Scheme 6). The transfer of the tricarbonyliron fragment from the tricarbonyl(4-methoxybenzylideneacetone)iron complex **11** to the free 1-azadiene **9b** by heating in benzene at reflux for 20 min afforded exclusively the (1-azabuta-1,3-diene)tricarbonyliron complex **10b** along with the free 1-oxabuta-1,3-diene **12**. However, a transfer of the metal fragment from complex **10b** to the free ligand **12** could not be achieved. This result confirmed the higher reactivity of the 1-oxabuta-1,3-diene complexes for the transfer of the tricarbonyliron fragment.

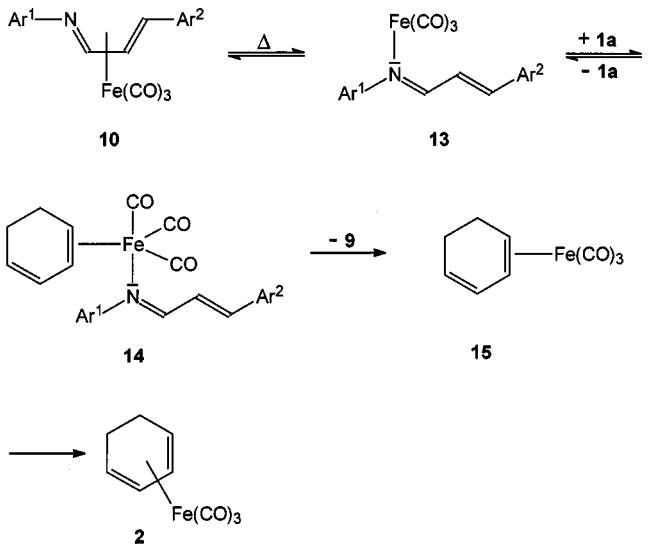
A direct comparison of the (η^4-1-azabuta-1,3-diene)-tricarbonyliron complexes **10a** and **10b** demonstrated the higher transfer reactivity of the latter reagent. Reaction of either equimolar amounts of the free 1-azabuta-1,3-diene **9a** with the iron complex **10b** of the free ligand **9b** with the iron complex **10a** in tetrahydrofuran at reflux led within 4 h to an equilibrium with a 2:1 ratio of the iron complexes **10a** and **10b**. This result confirms again that the transfer of the tricarbonyliron fragment is facilitated by the donor substituent in the *para* position of the 1-aryl ring.

Based on previous kinetic studies on ligand exchange reactions at complex **10a**[28] and our own mechanistic investigations,[23][29] the following mechanism is proposed for the transfer of the tricarbonyliron fragment using (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes **10** (Scheme 7). Complex **10** generates, by a thermally induced haptotropic migration, the 16-electron tricarbonyl(η^1-imine)iron complex **13**. This type of 16-electron η^1-imine complex is also considered as the intermediate in the thermal epimerization of tricarbonyliron complexes of chiral 1-azabuta-1,3-dienes[23] and was obtained on matrix photolysis studies of (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes.[30] The vacant coordination site of complex **13** is filled by η^2-coor-

Scheme 6. Competition experiments between various tricarbonyliron transfer reagents



Scheme 7. Proposed mechanism of the tricarbonyliron transfer from 1,4-diaryl-1-azabuta-1,3-diene complexes **10** to cyclohexa-1,3-diene (**1a**)



dination of cyclohexa-1,3-diene (**1a**) to provide complex **14**. This 18-electron complex, which could not be isolated, represents the crucial intermediate of the transfer reaction. Based on X-ray crystal structure determinations of (η^1-1-azabuta-1,3-diene)tetracarbonyliron complexes[29][31] and additional experimental evidence,[29][32] complex **14** is proposed to have a trigonal-bipyramidal structure with the η^2-coordinated 1,3-diene in equatorial and the η^1-coordinated α,β-unsaturated imine in an axial position. Disengagement of the 1-azabuta-1,3-diene **9** from complex **14** leads to the 16-electron complex **15**, which affords the tricarbonyliron complex **2** by haptotropic ($\eta^2 \rightarrow \eta^4$) migration of the metal fragment.

Conclusion

We have shown that the tricarbonyliron complexes of 1,4-diaryl-substituted 1-azabuta-1,3-dienes serve as highly efficient tricarbonyliron transfer reagents for the complexation of cyclohexa-1,3-diene. Complexation using these transfer reagents can also be applied to a broad range of other 1,3-dienes.[12] After the transfer of the metal fragment the 1-azabuta-1,3-dienes **9** are recovered almost quantitatively by simple crystallization. This fact has been exploited for the development of a complexation of 1,3-dienes using only catalytic amounts of the 1-azabuta-1,3-dienes **9**.[12][13] Most importantly, it has been demonstrated that high asymmetric inductions are achieved on the catalytic complexation of prochiral 1,3-dienes using chiral 1-azabuta-1,3-dienes.[32]

This work was supported by the *Deutsche Forschungsgemeinschaft* (Gerhard-Hess award) and the *Fonds der Chemischen Industrie*.

Experimental Section

General: All reactions were carried out using anhydrous and degassed solvents under an argon atmosphere. − Flash chromatography: Baker or Merck silica gel (0.03−0.06 mm). − Ultrasound: Bandelin Sonorex-TK52H cleaning bath; frequency: 35 kHz, used at 50% power. − Melting points: Leitz hot stage and Büchi 535. − IR spectra: Bruker IFS-88, Perkin-Elmer 882 and 1710. − ^{1}H-NMR and ^{13}C-NMR spectra: Bruker WP-200, AC-250, AM-400, and 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. Bulb-to-bulb distillation: Büchi glass tube oven GKR-51. − X-ray analyses: The data were collected on a STOE STADI-4 diffractometer using Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86) and refined anisotropically by full-matrix least squares based on all unique F^2 (SHELXL-93); the program SCHAKAL-92 was used for the graphical representation of the crystal structures (E. Keller, a computer program for the graphic representation of molecular and crystallographic models, Universität Freiburg, Germany, 1992).

2,4,6-Trimethoxyaniline (**7i**): A mixture of 2,4,6-trimethoxynitrobenzene[21] (500 mg, 2.35 mmol) and Pd/C (100 mg) in EtOH (30 ml) was stirred under a hydrogen atmosphere (1.1 bar) for 20 h. The reaction mixture was filtered through a short path of Celite/Alox B and the solvent was removed under reduced pressure. Bulb-to-bulb distillation (120°C, 0.1 mbar) of the residue afforded **7i** (380 mg, 88%). Pale yellow solid. M.p. 33−35°C. − IR (drift): ν = 3449, 3362, 2939, 2837, 1611, 1512, 1164 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (br s, 2 H), 3.74 (s, 3 H), 3.81 (s, 6 H), 6.15 (s, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.91 (3 CH_3), 91.40 (2 CH), 118.97 (C), 148.13 (2 C), 152.62 (C). − MS (30°C): *m/z* (%) = 183 (100) [M$^+$], 168 (87), 140 (39), 125 (28); HRMS: 183.0910 ($C_9H_{13}NO_3$, calcd. 183.0895).

4-Cyanocinnamaldehyde (**8**; R^6 = CN, R^7 = H): A solution of 4-cyanobenzaldehyde (823 mg, 6.28 mmol) and (formylmethylene)triphenylphosphorane (2.10 g, 6.90 mmol) in toluene (40 ml) was stirred at 80°C for 24 h. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (gradient elution, first with Et_2O/pentane, 1:3 and then elution with Et_2O) on silica gel. Evaporation of the solvent afforded a crude product, which was dissolved in Et_2O (30 ml). Recrystallization at −30°C provided the aldehyde **8** (R^6 = CN, R^7 = H) as a mixture of diastereoisomers (771 mg, 78%, (*E*)/(*Z*) ≥ 10:1). Yellow solid. M.p. 132°C. − IR (drift): ν = 2228, 1685, 1627, 1420, 1293, 1129, 987, 817 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$) [(*E*)-isomer]: δ = 6.78 (dd, *J* = 16.1, 7.5 Hz, 1 H), 7.49 (d, *J* = 16.1 Hz, 1 H), 7.67 (d, *J* = 8.5 Hz, 2 H), 7.74 (d, *J* = 8.5 Hz, 2 H), 9.78 (d, *J* = 7.5 Hz, 1 H). − MS (25°C): *m/z* (%) = 157 (100) [M$^+$], 156 (92), 129 (57), 128 (46), 103 (14), 102 (20), 101 (17); HRMS: 157.0516 ($C_{10}H_7NO$, calcd. 157.0528).

1,4-Diphenyl-1-azabuta-1,3-diene (**9a**): Na_2SO_4 (3 g) was added to a solution of cinnamaldehyde (**8**; R^6 = R^7 = H) (1.91 ml, 2.00 g, 15.1 mmol) and freshly distilled aniline (**7a**) (1.38 ml, 1.41 g, 15.1 mmol) in Et_2O (30 ml). The reaction mixture was stirred at room temp. for 1 h, then filtered, and the residue was washed with Et_2O (20 ml). Crystallization from the filtrate at −20°C afforded the product **9a** (2.56 g, 82%). Pale yellow needles. − IR (drift): ν = 2958, 2839, 1630, 1605, 1505, 1295, 1251, 1032, 986, 720 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (m, 5 H), 7.38 (m, 5 H), 7.54 (m, 2 H), 8.27 (dd, *J* = 7.2, 1.0 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 120.87 (2 CH), 126.07 (CH), 127.44 (2 CH), 128.52 (CH), 128.87 (2 CH), 129.13 (2 CH), 129.55 (CH), 135.50 (C), 143.98 (CH), 151.64 (C), 161.60 (CH). − MS (35°C): *m/z* (%) = 207 (40) [M$^+$], 206 (100), 130 (3), 115 (7), 77 (22); HRMS: 207.1062 ($C_{15}H_{13}N$, calcd. 207.1048).

Table 4. Crystallographic data, summary of data collection, and refinement of **10b**, **10c**, and **10l**

	10b	**10c**	**10l**
empirical formula	$C_{19}H_{15}FeNO_4$	$C_{19}H_{15}FeNO_4$	$C_{20}H_{17}FeNO_5$
formula weight	377.17	377.17	407.20
crystal color	red	red	red
crystal size [mm]	0.54 x 0.12 x 0.12	0.4 × 0.3 × 0.3	0.80 × 0.60 × 0.55
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	*Pbca*	*P*1
a [A]	11.975(5)	18.5970(10)	6.549(3)
b [A]	15.735(8)	7.938(3)	10.400(5)
c [A]	9.439(4)	23.483(3)	14.618(6)
α [°]	90	90	106.71(3)
β [°]	101.07(3)	90	96.30(3)
γ [°]	90	90	103.07(3)
V [A^3]	1745.5(14)	3466.6(14)	912.4(7)
Z	4	8	2
$\rho_{calcd.}$ [g cm^{-3}]	1.435	1.445	1.482
absorption coefficient [mm^{-1}]	0.862	0.893	0.858
F (θ00)	776	1552	420
λ [A]	0.71073	0.71073	0.71073
T [K]	293(2)	200(2)	173(2)
θ range [°]	5.20−28.15	1.73−25.03	3.04−25.00
reflections collected	9737	6121	3202
independent reflections	4111	3063	3202
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
data / restraints / parameters	4106 / 0 / 251	3062 / 0 / 286	3200 / 3 / 255
final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0583$; w$R_2 = 0.1376$	$R_1 = 0.0317$; w$R_2 = 0.0772$	$R_1 = 0.0317$; w$R_2 = 0.0805$
max. residual electron density [e A^{-3}]	0.467	0.274	0.395
CSD number[a]	59410	408182	58301

[a] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe D-76344 Eggenstein-Leopoldshafen on quoting the CSD numbers given.

1-(4-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**9b**): Cinnamaldehyde (**8**; $R^6 = R^7 = H$) (10 ml, 10.5 g, 79.3 mmol) was added to a solution of freshly sublimated *p*-anisidine (**7b**) (9.77 g, 79.3 mmol) in EtOAc (150 ml). $MgSO_4$ (4 g) was added and the mixture was stirred for 1 h at room temp. The solution was separated and the residue was washed with EtOAc. The solutions were combined and the solvent was evaporated slowly at 40°C until crystallization could be observed. Then pentane (100 ml) was added to the warm solution. Recrystallization at −20°C afforded the azadiene **9b** (18.8 g, 100%). Yellow-green crystals. M.p. 122°C. − IR (drift): ν = 3060, 1625, 1600, 1576, 1150, 999, 994, 753 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.92 (br d, *J* = 9.0 Hz, 2 H), 7.11 (m, 2 H), 7.21 (br d, *J* = 9.0 Hz, 2 H), 7.38 (m, 3 H), 7.53 (m, 2 H), 8.30 (dd, *J* = 4.5, 3.8 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 55.29 (CH_3), 114.27 (2 CH), 122.11 (2 CH), 127.24 (2 CH), 128.61 (CH), 128.75 (2 CH), 129.23 (CH), 135.60 (C), 142.85 (CH), 144.37 (C), 158.25 (C), 159.29 (CH). − MS (55°C): *m/z* (%) = 237 (63) [M$^+$], 236 (100), 115 (17); HRMS: 237.1137 ($C_{16}H_{15}NO$, calcd. 237.1154). − $C_{16}H_{15}NO$: C 80.98, H 6.37, N 5.90; found: C 81.14, H 6.35, N 6.35.

1-(2-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**9c**): Na_2SO_4 (1.5 g) was added to a solution of cinnamaldehyde (**8**; $R^6 = R^7 =$ H) (1.91 ml, 2.00 g, 15.1 mmol) and freshly distilled *o*-anisidine (**7c**) (1.70 ml, 1.86 g, 15.1 mmol) in Et_2O (30 ml). The reaction mixture was stirred at room temp. for 3 h. The solution was separated and the residue was washed with Et_2O. The solution of the combined organic layers was evaporated in vacuo to a volume of 5 ml. Crystallization from the filtrate at −20°C provided the product **9c** (3.11 g, 87%). Yellow crystals. M.p. 67°C. − IR (drift): ν = 1627, 1602, 1581, 1493, 1447, 1296, 1247, 1115, 1027, 1001, 754, 747 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3 H), 6.95 (m, 2 H), 7.00 (dd, *J* = 7.7, 2.0 Hz, 1 H), 7.12 (d, *J* = 16.0 Hz, 1 H), 7.19 (m, 1 H), 7.23 (dd, *J* = 16.0, 8.7 Hz, 1 H), 7.33−7.41 (m, 3 H), 7.53 (m, 2 H), 8.28 (d, *J* = 8.7 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.75 (CH_3), 111.22 (CH), 119.41 (CH), 120.93 (CH), 126.99 (CH), 127.47 (2 CH), 128.89 (2 CH), 129.06 (CH), 129.47 (CH), 135.66 (C), 141.21 (C), 143.66 (CH), 152.73 (C), 162.01 (CH). − MS (45°C): *m/z* (%) = 237 (100) [M$^+$], 236 (81), 220 (21), 130 (12), 115 (17); HRMS: 237.1140 ($C_{16}H_{15}NO$, calcd. 237.1154). −$C_{16}H_{15}NO$: C 80.98, H 6.37, N 5.90; found: C 80.46, H 6.37, N 6.30.

1-(4-N,N-Dimethylaminophenyl)-4-phenyl-1-azabuta-1,3-diene (**9d**): A solution of cinnamaldehyde (**8**; $R^6 = R^7 =$ H) (0.95 ml, 1.00 g, 7.57 mmol) and freshly sublimated 4-*N*,*N*-dimethylaminoaniline (**7d**) (1.03 g, 7.57 mmol) in Et_2O (30 ml) was stirred at room temp. for 1 h. Na_2SO_4 (2 g) was added and the reaction mixture was stirred at room temp. for additionally 2 h. The solution was separated and evaporated in vacuo to a volume of 15 ml. Crystallization at −20°C provided the product **9d** (760 mg, 40%). Yellow crystals. M.p. 146°C. − IR (drift): ν = 1625, 1605, 1512, 1448, 1349, 1220, 1169, 955, 821, 752, 693 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.99 (s, 6 H), 6.75 (br d, *J* = 9.0 Hz, 2 H), 7.07 (d, *J* = 15.9 Hz, 1 H), 7.14 (dd, *J* = 15.9, 8.2 Hz, 1 H), 7.25 (br d, *J* = 9.0 Hz, 2 H), 7.33 (m, 1 H), 7.39 (m, 2 H), 7.53 (m, 2 H), 8.35 (d, *J* = 8.2 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 40.68 (2 CH_3), 112.76 (2 CH), 122.33 (2 CH), 127.25 (2 CH), 128.86 (2 CH), 129.07 (CH), 129.15 (CH), 136.03 (C), 140.31 (C), 141.63 (CH), 149.58 (C), 156.94 (CH). − MS (65°C): *m/z* (%) = 250 (84) [M$^+$], 249 (100), 233 (12), 124 (4); HRMS: 250.1450 ($C_{17}H_{18}N_2$, calcd. 250.1470).

1-(4-Trifluoromethylphenyl)-4-phenyl-1-azabuta-1,3-diene (**9e**): A solution of cinnamaldehyde (**8**; $R^6 = R^7 =$ H) (1.26 ml, 1.32 g, 10.0 mmol) and freshly sublimated 4-trifluoromethylaniline (**7e**) (1.61 g,

10.0 mmol) in Et_2O (30 ml) was stirred at room temp. for 2 h. The mixture was subsequently dried over Na_2SO_4. The solution was separated and the residue was washed with Et_2O. The solution of the combined organic layers was evaporated to a volume of 20 ml. Crystallization at −20°C provided a crude product, which was washed with a mixture of cold Et_2O/pentane (1:7) to afford **9e** (1.97 g, 72%). Yellow crystals. − IR (drift): ν = 1628, 1611, 1586, 1333, 1313, 1156, 1109, 1073, 841, 753 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 15.9, 8.7 Hz, 1 H), 7.22 (d, *J* = 15.9 Hz, 1 H), 7.22 (d, *J* = 8.2 Hz, 2 H), 7.40 (m, 3 H), 7.56 (m, 2 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 8.24 (d, *J* = 8.7 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 121.03 (2 CH), 124.51 (CF_3, q, $^1J_{CF}$ = 276 Hz), 126.38 (2 CH, q, $^3J_{CF}$ = 3.4 Hz), 127.67 (2 CH), 128.08 (CH), 129.00 (2 CH), 129.99 (CH), 135.25 (C), 145.51 (CH), 154.87 (C), 163.30 (CH), the signal of one carbon atom is missing. − MS (35°C): *m/z* (%) = 275 (34) [M^+], 274 (100), 145 (7), 115 (4); HRMS: 275.0907 ($C_{16}H_{12}F_3N$, calcd. 275.0922).

1-(3-Nitrophenyl)-4-phenyl-1-azabuta-1,3-diene (**9f**): A solution of cinnamaldehyde (**8**; $R^6 = R^7$ = H) (0.95 ml, 1.00 g, 7.57 mmol) and freshly sublimated 3-nitroaniline (**7f**) (1.05 g, 7.57 mmol) in C_6H_6 (30 ml) was stirred with activated molecular sieves (4 A, 5 g) at room temp. for 17 h. The reaction mixture was filtered over a short path of Celite. The solvent was evaporated and the residue dissolved in EtOAc (15 ml). The crude product was crystallized by addition of pentane (80 ml). The solid was recrystallized twice from EtOAc/pentane (1:10) to afford the product **9f** (1.07 g, 56%). Yellow needles. − ^1H NMR (200 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 16.0, 8.4 Hz, 1 H), 7.27 (d, *J* = 16.0 Hz, 1 H), 7.38−7.59 (m, 7 H), 8.00 (m, 1 H), 8.07 (dt, *J* = 7.2, 2.1 Hz, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H).

1-(2,4-Dimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**9g**): Na_2SO_4 (5 g) was added to a solution of cinnamaldehyde (**8**; $R^6 = R^7$ = H) (2.86 ml, 3.00 g, 22.7 mmol) and freshly distilled 2,4-dimethoxyaniline (**7g**) (3.24 ml, 3.48 g, 22.7 mmol) in Et_2O (50 ml) and the reaction mixture was stirred at room temp. for 2 h. The mixture was filtered and the residue was washed with Et_2O. The solution of the combined ethereal layers was evaporated in vacuo to a volume of 25 ml. Crystallization at −20°C provided the product **9g** (4.91 g, 81%). Yellow crystals. M.p. 75°C. − IR (drift): ν = 1628, 1602, 1588, 1497, 1280, 1259, 1206, 1157, 966, 824, 754 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 3.89 (s, 3 H), 6.48 (dd, *J* = 8.5, 2.6 Hz, 1 H), 6.53 (d, *J* = 2.6 Hz, 1 H), 7.01 (d, *J* = 8.5 Hz, 1 H), 7.07 (d, *J* = 16.0 Hz, 1 H), 7.22 (dd, *J* = 16.0, 8.6 Hz, 1 H), 7.35 (m, 3 H), 7.50 (m, 2 H), 8.31 (d, *J* = 8.6 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 55.50 (CH_3), 55.82 (CH_3), 99.24 (CH), 104.33 (CH), 119.53 (CH), 127.36 (2 CH), 128.87 (2 CH), 129.25 (CH), 129.39 (CH), 134.50 (C), 135.90 (C), 142.59 (CH), 154.21 (C), 159.37 (C), 159.90 (CH). − MS (50°C): *m/z* (%) = 267 (93) [M^+], 266 (100), 130 (6), 115 (13); HRMS: 267.1254 ($C_{17}H_{17}NO_2$, calcd. 267.1259).

1-(3,4,5-Trimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**9h**): Na_2SO_4 (5 g) was added to a solution of cinnamaldehyde (**8**; $R^6 = R^7$ = H) (2.86 ml, 3.00 g, 22.7 mmol) and freshly sublimated 3,4,5-trimethoxyaniline (**7h**) (4.16 g, 22.7 mmol) in Et_2O (50 ml) and the reaction mixture was stirred at room temp. for 2 h. The mixture was filtered and the residue was washed with Et_2O. The solution of the combined organic layers was evaporated in vacuo to a volume of 25 ml. Crystallization at −20°C provided the product **9h** (5.33 g, 79%). Yellow needles. M.p. 88−91°C. − IR (drift): ν = 1627, 1584, 1503, 1446, 1417, 1243, 1232, 1008, 991, 838, 753, 693 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 3.90 (s, 6 H), 6.48 (s, 2 H), 7.09 (dd, *J* = 15.9, 7.9 Hz, 1 H), 7.19 (d, *J* = 15.9 Hz, 1 H), 7.39 (m, 3 H), 7.55 (m, 2 H), 8.30 (d, *J* = 7.9 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 56.09 (2 CH_3), 60.97 (CH_3), 98.29 (2 CH), 127.46 (2 CH), 128.41 (CH), 128.93 (2 CH), 129.60 (CH), 135.57 (C), 136.67 (C), 143.97 (CH), 147.42 (C), 153.58 (2 C), 160.70 (CH). − MS (70°C): *m/z* (%) = 297 (100) [M^+], 296 (84), 282 (52), 115 (19), 74 (68), 59 (91); HRMS: 297.1347 ($C_{18}H_{19}NO_3$, calcd. 297.1365).

1-(2,4,6-Trimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**9i**): A solution of cinnamaldehyde (**8**; $R^6 = R^7$ = H) (195 µl, 204 mg, 1.54 mmol) and freshly sublimated 2,4,6-trimethoxyaniline (**7i**) (282 mg, 1.54 mmol) in Et_2O (20 ml) was stirred at room temp. for 2 h. The solvent was evaporated and the residue was dissolved in Et_2O (5 ml). Crystallization at −20°C provided the product **9i** (336 mg, 73%). Yellow crystals. M.p. 114°C. − IR (drift): ν = 1628, 1607, 1579, 1468, 1449, 1334, 1228, 1201, 1149, 1121, 812 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 3.83 (s, 6 H), 6.21 (s, 2 H), 7.02 (d, *J* = 16.0 Hz, 1 H), 7.20 (dd, *J* = 16.0, 8.9 Hz, 1 H), 7.35 (m, 3 H), 7.51 (m, 2 H), 8.51 (d, *J* = 8.9 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.45 (CH_3), 56.12 (2 CH_3), 91.43 (2 CH), 123.64 (C), 127.34 (2 CH), 128.81 (2 CH), 129.02 (CH), 130.19 (CH), 136.15 (C), 142.04 (CH), 153.22 (2 C), 158.09 (C), 165.18 (CH). − MS (75°C): *m/z* (%) = 297 (100) [M^+], 296 (99.7), 266 (9), 130 (12), 115 (17); HRMS: 297.1351 ($C_{18}H_{19}NO_3$, calcd. 297.1365).

4-(4-Methoxyphenyl)-1-phenyl-1-azabuta-1,3-diene (**9j**): Na_2SO_4 (3 g) was added to a solution of 4-methoxycinnamaldehyde (**8**; R^6 = OMe, R^7 = H) (2.00 g, 12.3 mmol) and freshly distilled aniline (**7j**) (1.12 ml, 1.15 g, 12.3 mmol) in Et_2O (30 ml). The mixture was stirred for 3 h at room temp. and then filtered. The residue was washed with Et_2O and the solvent of the combined organic layers was evaporated. The crude product was dissolved in a mixture of Et_2O (80 ml) and EtOAc (10 ml). Recrystallization afforded the azadiene **9j** (2.58 g, 88%). Light yellow crystals. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 6.98 (dd, *J* = 15.9, 8.5 Hz, 1 H), 7.07 (d, *J* = 15.9 Hz, 1 H), 7.18 (m, 3 H), 7.36 (t, *J* = 7.5 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 8.21 (d, *J* = 8.5 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.37 (CH_3), 114.40 (2 CH), 120.95 (2 CH), 125.91 (CH), 126.46 (CH), 128.40 (C), 129.07 (2 CH), 129.18 (2 CH), 143.85 (CH), 151.90 (C), 160.86 (C), 161.92 (CH).

1,4-Di-(4-methoxyphenyl)-1-azabuta-1,3-diene (**9k**): 4-Methoxycinnamaldehyde (**8**; R^6 = OMe, R^7 = H) (1.62 g, 10.0 mmol) and freshly sublimated *p*-anisidine (**7k**) (1.23 g, 10.0 mmol) were dissolved in a mixture of Et_2O (30 ml) and THF (15 ml). On cooling the reaction mixture to 5°C for 15 h, the azadiene **9k** crystallized (1.03 g, 39%). The solvent of the mother liquor was evaporated and the residue was dissolved in EtOAc (200 ml) at 65°C. Recrystallization at −20°C afforded **9k** (1.50 g, 56%). Total yield of the azadiene **9k**: 2.53 g (95%). Light yellow crystals. M.p. 182°C. − IR (drift): ν = 1900, 1627, 1602, 1576, 1504, 1441, 1307, 1290, 1245, 1178, 1031, 864, 816 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 3.84 (s, 3 H), 6.91 (br d, *J* = 8.8 Hz, 4 H), 6.98 (dd, *J* = 15.9, 8.4 Hz, 1 H), 7.07 (d, *J* = 15.9 Hz, 1 H), 7.19 (br d, *J* = 8.8 Hz, 2 H), 7.47 (br d, *J* = 8.8 Hz, 2 H), 8.26 (d, *J* = 8.4 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 55.74 (CH_3), 55.86 (CH_3), 114.75 (2 CH), 114.78 (2 CH), 122.53 (2 CH), 127.08 (CH), 128.99 (C), 129.28 (2 CH), 143.19 (CH), 145.17 (C), 158.59 (C), 160.24 (CH), 161.07 (C). − MS (80°C): *m/z* (%) = 267 (34) [M^+], 266 (100), 252 (12), 145 (6); HRMS: 267.1264 ($C_{17}H_{17}NO_2$, calcd. 267.1259).

1-(2-Methoxyphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene (**9l**): A solution of 4-methoxycinnamaldehyde (**8**; R^6 = OMe, R^7 =

H) (1.62 g, 10.0 mmol) and freshly distilled *o*-anisidine (**7l**) (1.13 ml, 1.23 g, 10.0 mmol) in Et_2O (30 ml) was stirred at room temp. for 2 h. Subsequently, the reaction mixture was dried over Na_2SO_4. The solution was separated and the residue was washed with Et_2O. The solution of the combined organic layers was evaporated in vacuo to a volume of 20 ml. Crystallization at −30°C afforded **9l** (2.11 g, 79%). Light yellow needles. M.p. 105°C. − IR (drift): ν = 1626, 1580, 1492, 1307, 1246, 1025, 810, 754 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 3.90 (s, 3 H), 6.90−7.00 (m, 5 H), 7.04−7.20 (m, 3 H), 7.47 (br d, *J* = 8.8 Hz, 2 H), 8.24 (dd, *J* = 7.5, 0.8 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.30 (CH_3), 55.70 (CH_3), 111.12 (CH), 114.30 (2 CH), 119.34 (CH), 120.88 (CH), 126.69 (CH), 126.95 (CH), 128.46 (C), 128.96 (2 CH), 141.38 (C), 143.40 (CH), 152.69 (C), 160.69 (C), 162.21 (CH). − MS (50°C): *m/z* (%) = 267 (40) [M^+], 266 (100), 252 (24), 250 (8), 236 (6); HRMS: 267.1249 ($C_{17}H_{17}NO_2$, calcd. 267.1259).

1-(4-Trifluoromethylphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene (**9m**): 4-Methoxycinnamaldehyde (**8**; R^6 = OMe, R^7 = H) (1.62 g, 10.0 mmol) and freshly distilled 4-trifluoromethylaniline (**7m**) (1.25 ml, 1.61 g, 10.0 mmol) were dissolved in a mixture of Et_2O (50 ml) and THF (15 ml). The reaction mixture was cooled to 5°C for 15 h and was dried over Na_2SO_4. After filtration the solvent was evaporated and the residue was crystallized from Et_2O/EtOAc (3:1, 80 ml) to afford the azadiene **9m** (1.81 g, 59%). Yellow crystals. M.p. 121°C. − IR (drift): ν = 1628, 1588, 1513, 1330, 1270, 1130, 1011, 850 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.94 (br d, *J* = 8.8 Hz, 2 H), 6.99 (dd, *J* = 15.9, 8.9 Hz, 1 H), 7.16 (d, *J* = 15.9 Hz, 1 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.50 (br d, *J* = 8.8 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 8.20 (d, *J* = 8.9 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.39 (CH_3), 114.44 (2 CH), 121.02 (2 CH), 124.30 (CF_3, q, $^1J_{CF}$ = 272 Hz), 125.93 (CH), 126.35 (2 CH, q, $^3J_{CF}$ = 3.5 Hz), 127.53 (C, q, $^2J_{CF}$ = 32.5 Hz), 128.06 (C), 129.27 (2 CH), 145.33 (CH), 155.04 (C), 161.15 (C), 163.54 (CH). − MS (40°C): *m/z* (%) = 305 (25) [M^+], 304 (100), 290 (13), 261 (7), 145 (7); HRMS: 305.1006 ($C_{17}H_{14}F_3NO$, calcd. 305.1027).

1-(2,4-Dimethoxyphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene (**9n**): A solution of 4-methoxycinnamaldehyde (**8**; R^6 = OMe, R^7 = H) (1.00 g, 6.17 mmol) and freshly distilled 2,4-dimethoxyaniline (**7n**) (0.88 ml, 945 mg, 6.17 mmol) in THF (30 ml) was stirred at 40°C for 1 h. The solvent was evaporated and the residue was crystallized from a mixture of Et_2O (200 ml) and EtOAc (30 ml) at −20°C to provide the product **9n** (1.46 g, 80%). Yellow solid. M.p. 123°C. − IR (drift): ν = 1625, 1603, 1587, 1509, 1497, 1259, 1246, 1206, 1176, 1157, 1128, 1025, 824 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 3.81 (s, 3 H), 3.88 (s, 3 H), 6.46 (dd, *J* = 8.6, 2.5 Hz, 1 H), 6.52 (d, *J* = 2.5 Hz, 1 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 1 H), 7.02 (d, *J* = 15.9 Hz, 1 H), 7.09 (dd, *J* = 15.9, 8.3 Hz, 1 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 8.26 (d, *J* = 8.3 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.33 (CH_3), 55.49 (CH_3), 55.80 (CH_3), 99.20 (CH), 104.26 (CH), 114.33 (2 CH), 119.41 (CH), 127.30 (CH), 128.72 (C), 128.85 (2 CH), 134.72 (C), 142.40 (CH), 154.13 (C), 159.14 (C), 160.22 (CH), 160.57 (C). − MS (85°C): *m/z* (%) = 297 (56) [M^+], 296 (100), 282 (22), 145 (5); HRMS: 297.1354 ($C_{18}H_{19}NO_3$, calcd. 297.1365).

1-(4-Methoxyphenyl)-4-(2-methoxyphenyl)-1-azabuta-1,3-diene (**9o**): Na_2SO_4 (5 g) was added to a solution of 2-methoxycinnamaldehyde (**8**; R^6 = H, R^7 = OMe) (2.00 g, 12.3 mmol) and freshly sublimated *p*-anisidine (**7o**) (1.52 g, 12.3 mmol) in Et_2O (100 ml). The reaction mixture was stirred at room temp. for 2 h. The solution was separated and the residue was washed with Et_2O. The solvent of the combined organic solutions was evaporated and the residue was dissolved in Et_2O/pentane (2:1, 100 ml). Precipitation of the product was completed by cooling this solution to −78°C and subsequent warming to 40°C. Repetition of this procedure several times afforded the product **9o** (2.82 g, 86%). Yellow solid. M.p. 62°C. − IR (drift): ν = 2839, 1620, 1596, 1504, 1484, 1467, 1244, 1028, 990, 956, 756 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 3.89 (s, 3 H), 6.88−7.01 (m, 2 H), 6.91 (br d, *J* = 8.9 Hz, 2 H), 7.11−7.23 (m, 2 H), 7.17 (dd, *J* = 16.1, 9.0 Hz, 1 H), 7.32 (m, 1 H), 7.48 (d, *J* = 16.1 Hz, 1 H), 7.57 (dd, *J* = 7.7, 1.6 Hz, 1 H), 8.31 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 56.13 (2 CH_3), 111.72 (CH), 115.04 (2 CH), 121.51 (CH), 122.85 (2 CH), 125.38 (C), 128.30 (CH), 129.90 (CH), 131.24 (CH), 138.96 (CH), 145.43 (C), 158.12 (C), 158.90 (C), 161.24 (CH). − MS (70°C): *m/z* (%) = 267 (32) [M^+], 266 (24), 252 (16), 237 (16), 236 (100), 115 (6); HRMS: 267.1237 ($C_{17}H_{17}NO_2$, calcd. 267.1259).

4-(4-Cyanophenyl)-1-phenyl-1-azabuta-1,3-diene (**9p**): A solution of 4-cyanocinnamaldehyde (**8**; R^6 = CN, R^7 = H) (157 mg, 1.00 mmol) and freshly distilled aniline (**7p**) (182 µl, 186 mg, 2.00 mmol) in THF (10 ml) was stirred at room temp. for 1.5 h. After addition of pentane (30 ml) the product was crystallized at −30°C to afford the azadiene **9p** (181 mg, 78%). Yellow crystals. M.p. 104°C. − IR (drift): ν = 3049, 2221, 1627, 1608, 1583, 1488, 1413, 1156, 983, 954, 816, 764 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.32−7.47 (m, 5 H), 7.58 (m, 2 H), 7.77 (d, *J* = 7.9 Hz, 2 H), 7.83 (d, *J* = 7.9 Hz, 2 H), 8.47 (d, *J* = 7.0 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 112.93 (C), 119.11 (C≡N), 121.48 (2 CH), 127.22 (CH), 128.27 (2 CH), 129.79 (2 CH), 132.27 (CH), 133.14 (2 CH), 140.35 (C), 141.68 (CH), 151.70 (C), 161.00 (CH). − MS (60°C): *m/z* (%) = 232 (53) [M^+], 231 (100), 77 (21); HRMS: 232.1015 ($C_{16}H_{12}N_2$, calcd. 232.1000).

4-(4-Cyanophenyl)-1-(2,4-dimethoxyphenyl)-1-azabuta-1,3-diene (**9q**): A solution of freshly distilled 2,4-dimethoxyaniline (**7q**) (141 µl, 153 mg, 1.00 mmol) in Et_2O (14 ml) was added to a solution of 4-cyanocinnamaldehyde (**8**; R^6 = CN, R^7 = H) (157 mg, 1.00 mmol) in Et_2O (20 ml). The reaction mixture was stirred for 10 min at room temp. and then cooled to −20°C for 15 h without stirring. Evaporation of the solvent afforded the product **9q** (289 mg, 99%). Orange solid. M.p. 121°C. − IR (drift): ν = 2223, 1623, 1604, 1585, 1498, 1311, 1258, 1210, 1161, 1130, 1047, 843, 827 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 3.90 (s, 3 H), 6.49 (dd, *J* = 8.6, 2.6 Hz, 1 H), 6.54 (d, *J* = 2.6 Hz, 1 H), 7.05 (d, *J* = 8.6 Hz, 1 H), 7.06 (d, *J* = 16.0 Hz, 1 H), 7.28 (dd, *J* = 16.0, 8.9 Hz, 1 H), 7.58 (br d, *J* = 8.4 Hz, 2 H), 7.65 (br d, *J* = 8.4 Hz, 2 H), 8.36 (d, *J* = 8.9 Hz, 1 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.54 (CH_3), 55.86 (CH_3), 99.23 (CH), 104.49 (CH), 112.06 (C), 118.69 (C≡N), 119.73 (CH), 127.59 (2 CH), 132.63 (2 CH), 132.69 (CH), 133.80 (C), 139.62 (CH), 140.27 (C), 154.45 (C), 158.43 (CH), 159.92 (C). − MS (85°C): *m/z* (%) = 292 (43) [M^+], 291 (42), 157 (100), 156 (82), 153 (25), 138 (28), 129 (51), 128 (43); HRMS: 292.1203 ($C_{18}H_{16}N_2$, calcd. 292.1212).

1-(4-Methoxyphenyl)-4-(4-N,N-dimethylaminophenyl)-1-azabuta-1,3-diene (**9r**): A solution of 4-*N*,*N*-dimethylaminocinnamaldehyde (**8**; R^6 = NMe_2, R^7 = H) (1.00 g, 5.71 mmol) and freshly sublimated *p*-anisidine (**7r**) (703 mg, 5.71 mmol) in CH_2Cl_2 (30 ml) was stirred at room temp. for 1 h. Na_2SO_4 (2 g) was added and the reaction mixture was stirred at room temp. for an additional 2 h. The solution was separated and by addition of Et_2O/pentane (1:7, 50 ml) the product **9r** was precipitated (1.36 g, 85%). Green crystals. M.p. 146−150°C. − IR (drift): ν = 2540, 2057, 2006, 1887,

1609, 1575, 1503, 1248, 1156, 836, 810 cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.01 (s, 6 H), 3.82 (s, 3 H), 6.63–6.76 (m, 2 H), 6.87–6.94 (m, 2 H), 6.92 (dd, *J* = 15.7, 8.5 Hz, 1 H), 7.05 (d, *J* = 15.7 Hz, 1 H), 7.18 (br d, *J* = 8.9 Hz, 2 H), 7.42 (br d, *J* = 8.9 Hz, 2 H), 8.24 (d, *J* = 8.5 Hz, 1 H). – ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 40.11 (2 CH_3), 55.40 (CH_3), 111.96 (2 CH), 114.30 (2 CH), 122.02 (2 CH), 123.74 (C), 124.08 (CH), 128.87 (2 CH), 143.90 (CH), 145.05 (C), 151.11 (C), 157.86 (C), 160.35 (CH). – MS (110°C): *m/z* (%) = 280 (45) [M^+], 279 (100), 265 (3), 158 (7); HRMS: 280.1563 ($C_{18}H_{20}N_2O$, calcd. 280.1576).

1-(4-Methoxyphenyl)-4-(4-nitrophenyl)-1-azabuta-1,3-diene (**9s**): A solution of 4-nitrocinnamaldehyde (**8**; R^6 = NO_2, R^7 = H) (713 mg, 4.02 mmol) in THF (20 ml) was added to a solution of freshly sublimated *p*-anisidine (**7s**) (495 mg, 4.02 mmol) in THF (20 ml). The reaction mixture was stirred at room temp. for 1 h. The solvent was evaporated and the residue was recrystallized from EtOAc (60 ml) to afford the azadiene **9s** (848 mg, 75%). Yellow needles. M.p. 164°C. – IR (drift): ν = 1622, 1608, 1595, 1441, 1415, 1300, 953, 758 cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.94 (br d, *J* = 8.9 Hz, 2 H), 7.14 (d, *J* = 16.1 Hz, 1 H), 7.23 (dd, *J* = 16.1, 8.3 Hz, 1 H), 7.24 (br d, *J* = 8.9 Hz, 2 H), 7.66 (br d, *J* = 8.8 Hz, 2 H), 8.25 (br d, *J* = 8.8 Hz, 2 H), 8.34 (d, *J* = 8.3 Hz, 1 H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.51 (CH_3), 114.52 (2 CH), 122.46 (2 CH), 124.25 (2 CH), 127.78 (2 CH), 132.86 (CH), 139.45 (CH), 142.02 (C), 143.95 (C), 147.76 (C), 157.90 (CH), 158.98 (C). – MS (100°C): *m/z* (%) = 282 (100) [M^+], 281 (74), 235 (65), 192 (9); HRMS: 282.0998 ($C_{16}H_{14}N_2O_3$, calcd. 282.1004).

Preparation of the (η⁴-1-Azabuta-1,3-diene)tricarbonyliron Complexes **10** *by Sonochemical Reaction of the 1-Azabuta-1,3-dienes* **9** *with Nonacarbonyldiiron at Room Temperature – General Procedure:* A solution of the 1-azabuta-1,3-dienes **9** (1 eq.) and $Fe_2(CO)_9$ (1.5 eq.) in THF (15 ml) was sonicated at room temp. for 16 h. Removal of the solvent by evaporation and flash chromatography (Et_2O/pentane) of the residue on silica gel afforded the tricarbonyliron complexes **10** as red crystals (Table 5).

Table 5. Sonochemical complexation of the 1-azabuta-1,3-dienes **9** and yield of the iron complexes **10**

Entry	**9**		$Fe_2(CO)_9$		Eluent[b]	Yield **10**	
	[g]	[mmol]	[g]	[mmol]	Et_2O/pentane	[g]	[%]
a	0.500	2.41	1.10	3.03[a]	1:10	0.682	82
b	0.500	2.11	0.960	2.64[a]	1:10	0.701	88
c	1.78	7.50	4.11	11.3	1:10	2.25	80
d	0.500	2.00	1.09	3.00	1:7 to 1:3	0.428	55
e[c]	1.00	3.63	1.98	5.45	1:10	0.882	59
g	1.50	5.61	3.06	8.42	1:10	0.990	43
h	1.50	5.04	2.75	7.56	1:10	0.890	40
i	1.00	3.36	1.83	5.04	10:1 to 5:1	0.819	56
j[c]	1.00	4.21	2.30	6.32	0:1 to 1:4	1.16	73
k	1.00	3.74	2.04	5.61	1:10 to 1:2	0.626	41
l	1.50	5.61	3.06	8.42	1:7	1.88	82
m	1.00	3.28	1.79	4.92	0:1 to 1:3	0.935	64
n	0.500	1.68	0.917	2.52	1:10 to 1:5	0.578	79
o	1.00	3.74	2.04	5.61	1:10	1.24	81
p	0.450	1.94	1.06	2.91	1:7 to 1:1	0.410	57
q	0.846	2.89	1.58	4.34	1:10 to 2:1	0.760	61
r	0.500	1.78	0.971	2.67	1:7 to 1:0	0.463	62

[a] 1.25 Equivalents of $Fe_2(CO)_9$. – [b] Gradient elution by entry **d**, **i**, **j**, **k**, **m**, **n**, **p**, and **q**. – [c] Reaction time (sonication) of entry **e** was 18 h and of entry **j** 17 h.

Tricarbonyl[(1-4-η)-1,4-diphenyl-1-azabuta-1,3-diene]iron (**10a**): Mp ≥ 132°C (dec). – IR (drift): ν = 2055, 1988, 1977, 1593, 1486, 1450, 1290, 1155, 761 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.38 (d, *J* = 9.4 Hz, 1 H), 5.72 (dd, *J* = 9.4, 2.8 Hz, 1 H), 6.92 (m, 3 H), 6.95 (d, *J* = 2.8 Hz, 1 H), 7.19 (m, 3 H), 7.30 (m, 4 H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ (*T* = 298 K) = 62.17 (CH), 74.45 (CH), 103.86 (CH), 121.86 (2 CH), 122.56 (CH), 126.61 (2 CH), 126.93 (CH), 128.80 (2 CH), 128.99 (2 CH), 138.81 (C), 153.38 (C), 205.79 (CO, very br), 208.77 (CO, very br), 211.90 (CO, very br); ^{13}C NMR (125 MHz, [D_8]toluene): δ (*T* = 233 K) = 62.31 (CH), 74.20 (CH), 104.37 (CH), 122.09 (2 CH), 122.63 (CH), 126.67 (2 CH), 127.08 (CH), 128.93 (2 CH), 129.16 (2 CH), 138.91 (C), 153.90 (C), 206.02 (CO), 209.49 (CO), 212.70 (CO); δ (*T* = 292 K) = 62.63 (CH), 74.29 (CH), 104.43 (CH), 122.16 (2 CH), 122.79 (CH), 126.81 (2 CH), 127.12 (CH), 128.96 (2 CH), 129.19 (2 CH), 138.13 (C), 153.96 (C), 206.04 (CO, br), 209.42 (CO, br), 212.66 (CO, br); δ (*T* = 373 K) = 63.21 (CH), 74.51 (CH), 104.75 (CH), 122.37 (2 CH), 123.13 (CH), 127.15 (2 CH), 127.30 (CH), 129.11 (2 CH), 129.34 (2 CH), 139.61 (C), 154.15 (C), 209.53 (3 CO, br). – MS (75°C): *m/z* (%) = 347 (3) [M^+], 319 (8), 291 (12), 263 (100), 207 (10), 206 (31), 56 (18); HRMS: 347.0217 ($C_{18}H_{13}FeNO_3$, calcd. 347.0245). – $C_{18}H_{13}FeNO_3$: C 62.28, H 3.77, N 4.03; found: C 62.33, H 4.08, N 4.22.

Tricarbonyl[(1-4-η)-1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10b**): Mp ≥ 140°C (dec). – IR (drift): ν = 2049, 1987, 1963, 1507, 1250, 1040, 832 cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 3.37 (d, *J* = 9.4 Hz, 1 H), 3.75 (s, 3 H), 5.68 (dd, *J* = 9.4, 2.9 Hz, 1 H), 6.73 (d, *J* = 8.9 Hz, 2 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 6.99 (d, *J* = 2.9 Hz, 1 H), 7.19–7.34 (m, 5 H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ (*T* = 298 K) = 55.42 (CH_3), 61.89 (CH), 73.95 (CH), 104.28 (CH), 114.28 (2 CH), 122.55 (2 CH), 126.59 (2 CH), 126.84 (CH), 128.77 (2 CH), 138.97 (C), 146.55 (C), 155.37 (C); ^{13}C NMR (125 MHz, [D_8]toluene): δ (*T* = 233 K) = 54.44 (CH_3), 62.10 (CH), 73.71 (CH), 104.82 (CH), 114.20 (2 CH), 122.76 (2 CH), 126.69 (2 CH), 127.00 (CH), 128.93 (2 CH), 139.12 (C), 146.74 (C), 155.59 (C), 206.60 (CO), 209.71 (CO), 213.03 (CO); δ (*T* = 298 K) = 54.85 (CH_3), 62.48 (CH), 73.81 (CH), 105.03 (CH), 114.65 (2 CH), 122.94 (2 CH), 126.92 (2 CH), 127.12 (CH), 129.03 (2 CH), 139.46 (C), 147.00 (C), 156.17 (C), 206.91 (CO, very br), 209.80 (CO, very br), 212.84 (CO, very br); δ (*T* = 373 K) = 55.31 (CH_3), 62.89 (CH), 73.90 (CH), 105.32 (CH), 115.17 (2 CH), 123.09 (2 CH), 127.15 (2 CH), 127.19 (CH), 129.08 (2 CH), 139.80 (C), 147.27 (C), 156.75 (C), 209.81 (3 CO). – MS (90°C): *m/z* (%) = 377 (3) [M^+], 349 (6), 321 (8), 293 (100), 237 (29), 236 (54), 115 (16); HRMS: 377.0339 ($C_{19}H_{15}FeNO_4$, calcd. 377.0350). – $C_{19}H_{15}FeNO_4$: C 60.50, H 4.01, N 3.71; found: C 60.51, H 4.05, N 3.94.

Tricarbonyl[(1-4-η)-1-(2-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10c**): Mp ≥ 123°C (dec). – IR (drift): ν = 2058, 2000, 1970, 1497, 1455, 1297, 1245, 1031, 749, 695 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.33 (d, *J* = 9.5 Hz, 1 H), 3.97 (s, 3 H), 5.80 (dd, *J* = 9.5, 3.0 Hz, 1 H), 6.81 (m, 2 H), 6.98 (br dt, *J* = 1.5, 7.8 Hz, 1 H), 7.04 (m, 1 H), 7.10 (br d, *J* = 3.0 Hz, 1 H), 7.19 (m, 1 H), 7.28 (m, 2 H), 7.34 (m, 2 H). – ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ (*T* = 298 K) = 54.79 (CH_3), 62.08 (CH), 76.09 (CH), 101.99 (CH), 110.99 (CH), 118.96 (CH), 120.51 (CH), 123.57 (CH), 126.53 (2 CH), 126.75 (CH), 128.76 (2 CH), 139.11 (C), 141.38 (C), 150.88 (C), 205.70 (CO, very br), 209.33 (CO, very br), 212.82 (CO, very br); ^{13}C NMR (125 MHz, [D_8]toluene): δ (*T* = 233 K) = 53.90 (CH_3), 62.58 (CH), 76.24 (CH), 101.97 (CH), 110.90 (CH), 118.41 (CH), 120.39 (CH), 123.59 (CH), 126.61 (2 CH), 126.86 (CH), 128.91 (2 CH), 139.33 (C), 141.70 (C), 150.86 (C), 206.41 (CO), 210.06 (CO), 213.84 (CO); δ (*T* = 298 K) = 54.33 (CH_3), 62.85 (CH), 76.00 (CH), 102.71 (CH), 111.47 (CH), 119.17 (CH), 120.73 (CH), 123.64 (CH), 126.79 (2 CH),

126.93 (CH), 128.93 (2 CH), 139.54 (C), 142.14 (C), 151.44 (C), 206.46 (CO, br), 210.04 (CO, br), 213.75 (CO, br); δ (T = 373 K) = 55.01 (CH_3), 63.27 (CH), 75.85 (CH), 103.64 (CH), 112.50 (CH), 120.21 (CH), 121.27 (CH), 123.82 (CH), 127.10 (3 CH), 129.05 (2 CH), 139.93 (C), 142.73 (C), 152.26 (C), 210.02 (3 CO, br). − MS (75°C): *m/z* (%) = 377 (3) [M^+], 349 (12), 321 (23), 293 (58), 278 (100), 237 (11), 236 (11), 139 (12), 56 (6).

Tricarbonyl[(1-4-η)-1-(4-N,N-dimethylaminophenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10d**): Mp ≥ 136°C (dec). − IR (drift): ν = 2047, 1987, 1965, 1607, 1515, 1283, 1154, 822, 765, 698 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.88 (s, 6 H), 3.37 (d, J = 9.3 Hz, 1 H), 5.63 (dd, J = 9.3, 2.9 Hz, 1 H), 6.58 (br d, J = 9.0 Hz, 2 H), 6.93 (br d, J = 9.0 Hz, 2 H), 7.06 (dd, J = 2.9, 0.8 Hz, 1 H), 7.17−7.34 (m, 5 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 40.91 (2 CH_3), 61.34 (CH), 73.43 (CH), 104.40 (CH), 113.28 (2 CH), 122.45 (2 CH), 126.56 (2 CH), 126.64 (CH), 128.69 (2 CH), 139.29 (C), 143.14 (C), 146.96 (C). − MS (105°C): *m/z* (%) = 390 (5) [M^+], 362 (1), 334 (7), 306 (100), 250 (69), 249 (89), 233 (15); HRMS: 390.0671 ($C_{20}H_{18}FeN_2O_3$, calcd. 390.0667).

Tricarbonyl[(1-4-η)-1-(4-trifluoromethylphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10e**): Mp ≥ 151°C (dec). − IR (drift): ν = 3061, 2059, 2002, 1983, 1611, 1329, 1288, 1166, 1123, 1110, 842, 768, 698 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.41 (d, J = 9.5 Hz, 1 H), 5.75 (dd, J = 9.5, 2.9 Hz, 1 H), 6.84 (dd, J = 2.9, 0.7 Hz, 1 H), 6.92 (d, J = 8.3 Hz, 2 H), 7.22 (m, 1 H), 7.31 (m, 4 H), 7.41 (d, J = 8.3 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ (T = 298 K) = 63.04 (CH), 75.65 (CH), 102.01 (CH), 121.77 (2 CH), 123.98 (C, q, $^2J_{CF}$ = 32.6 Hz), 124.45 (CF_3, q, $^1J_{CF}$ = 271 Hz), 126.24 (2 CH, q, $^3J_{CF}$ = 3.5 Hz), 126.67 (2 CH), 127.26 (CH), 128.93 (2 CH), 138.34 (C), 156.70 (C), 204.77 (CO, br), 208.30 (CO, br), 211.49 (CO, br); ^{13}C NMR (125 MHz, [D_8]toluene): δ (T = 233 K) = 62.95 (CH), 75.33 (CH), 102.36 (CH), 121.94 (2 CH), 123.56 (C, q, $^2J_{CF}$ = 32.2 Hz), 125.22 (CF_3, q, $^1J_{CF}$ = 271 Hz), 126.32 (2 CH, br), 126.68 (2 CH), 127.41 (CH), 129.04 (2 CH), 138.38 (C), 156.97 (C), 205.19 (CO), 208.90 (CO), 212.16 (CO); δ (T = 307 K) = 63.49 (CH), 75.54 (CH), 102.50 (CH), 122.05 (2 CH), 124.31 (C, q, $^2J_{CF}$ = 33 Hz), 126.46 (2 CH, br), 126.89 (2 CH), 127.51 (CH), 129.08 (2 CH), 138.66 (C), 157.10 (C), 205.44 (CO, br), 208.89 (CO, br), 212.16 (CO, br), the signal of the CF_3 carbon atom is missing due to overlapping; δ (T = 373 K) = 64.02 (CH), 75.80 (CH), 102.74 (CH), 122.22 (2 CH), 125.35 (CF_3, q, $^1J_{CF}$ = 273 Hz), 126.63 (2 CH, br), 127.16 (2 CH), 127.66 (CH), 129.20 (2 CH), 139.01 (C), 157.25 (C), 208.79 (3 CO, br), the signal of the aromatic carbon atom α to the CF_3 group is missing due to overlapping. − MS (90°C): *m/z* (%) = 415 (1) [M^+], 387 (6), 359 (7), 331 (73), 275 (24), 274 (100), 256 (17), 145 (13), 115 (29); HRMS: 415.0085 ($C_{19}H_{12}F_3FeNO_3$, calcd. 415.0119).

Tricarbonyl[(1-4-η)-1-(2,4-dimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10g**): Mp ≥95°C (dec). − IR (drift): ν = 2048, 1994, 1970, 1503, 1456, 1285, 1259, 1205, 1030, 823 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.30 (d, J = 9.4 Hz, 1 H), 3.77 (s, 3 H), 3.96 (s, 3 H), 5.77 (dd, J = 9.4, 2.9 Hz, 1 H), 6.34 (dd, J = 8.7, 2.6 Hz, 1 H), 6.41 (d, J = 2.6 Hz, 1 H), 6.99 (d, J = 8.7 Hz, 1 H), 7.15 (d, J = 2.9 Hz, 1 H), 7.19 (m, 1 H), 7.28 (t, J = 7.4 Hz, 2 H), 7.34 (m, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 54.93 (CH_3), 55.43 (CH_3), 61.66 (CH), 75.59 (CH), 99.25 (CH), 102.30 (CH), 103.60 (CH), 118.53 (CH), 126.53 (2 CH), 126.66 (CH), 128.74 (2 CH), 135.03 (C), 139.29 (C), 152.27 (C), 156.67 (C). − MS (70°C): *m/z* (%) = 407 (1) [M^+], 379 (5), 351 (18), 323 (78), 308 (100), 267 (74), 266 (82), 154 (15), 115 (16); HRMS: 407.0447 ($C_{20}H_{17}FeNO_5$, calcd. 407.0456).

Tricarbonyl[(1-4-η)-1-(3,4,5-trimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10h**): Mp ≥ 147°C (dec). − IR (drift): ν = 2054, 1995, 1980, 1580, 1501, 1451, 1251, 1128, 1011, 770 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.38 (d, J = 9.4 Hz, 1 H), 3.78 (s, 3 H), 3.86 (s, 6 H), 5.70 (dd, J = 9.4, 2.9 Hz, 1 H), 6.18 (s, 2 H), 6.97 (dd, J = 2.9, 0.8 Hz, 1 H), 7.17−7.35 (m, 5 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 56.00 (2 CH_3), 60.92 (CH_3), 62.30 (CH), 74.11 (CH), 99.26 (2 CH), 103.91 (CH), 126.61 (2 CH), 126.99 (CH), 128.81 (2 CH), 134.03 (C), 138.74 (C), 149.43 (C), 153.22 (2 C). − MS (90°C): *m/z* (%) = 437 (3) [M^+], 409 (9), 381 (6), 353 (100), 297 (51), 296 (45), 282 (28), 177 (8); HRMS: 437.0575 ($C_{21}H_{19}FeNO_6$, calcd. 437.0562).

Tricarbonyl[(1-4-η)-1-(2,4,6-trimethoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]iron (**10i**): Mp ≥103°C (dec). − IR (drift): ν = 2052, 2038, 1992, 1978, 1968, 1597, 1578, 1465, 1337, 1205, 1131 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.23 (d, J = 9.4 Hz, 1 H), 3.77 (s, 3 H), 3.91 (s, 6 H), 5.65 (dd, J = 9.4, 3.0 Hz, 1 H), 6.09 (s, 2 H), 7.17 (m, 1 H), 7.30 (m, 4 H), 7.94 (dd, J = 3.0, 0.8 Hz, 1 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 55.25 (CH_3), 55.44 (2 CH_3), 60.79 (CH), 74.06 (CH), 91.18 (2 CH), 106.17 (CH), 122.93 (C), 126.33 (CH), 126.43 (2 CH), 128.56 (2 CH), 139.62 (C), 153.60 (2 C), 156.00 (C). − MS (120°C): *m/z* (%) = 437 (0.2) [M^+], 409 (2), 381 (9), 353 (72), 338 (100), 297 (43), 296 (31), 115 (20); HRMS: 437.0546 ($C_{21}H_{19}FeNO_6$, calcd. 437.0562).

Tricarbonyl[(1-4-η)-4-(4-methoxyphenyl)-1-phenyl-1-azabuta-1,3-diene]iron (**10j**): Mp ≥136°C (dec). − IR (drift): ν = 2054, 1981, 1607, 1515, 1485, 1475, 1278, 1249, 1032, 835, 762 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.43 (d, J = 9.5 Hz, 1 H), 3.80 (s, 3 H), 5.65 (dd , J = 9.5, 2.9 Hz, 1 H), 6.84 (br d, J = 8.8 Hz, 2 H), 6.92 (m, 4 H), 7.17 (m, 2 H), 7.27 (br d, J = 8.8 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.27 (CH_3), 63.15 (CH), 74.28 (CH), 103.03 (CH), 114.31 (2 CH), 121.86 (2 CH), 122.44 (CH), 127.83 (2 CH), 128.96 (2 CH), 130.89 (C), 153.51 (C), 158.71 (C). − MS (85°C): *m/z* (%) = 377 (2) [M^+], 349 (7), 321 (11), 293 (100), 237 (19), 236 (73), 222 (12); HRMS: 377.0360 ($C_{19}H_{15}FeNO_4$, calcd. 377.0350).

Tricarbonyl[(1-4-η)-1,4-di-(4-methoxyphenyl)-1-azabuta-1,3-diene]iron (**10k**): Mp ≥132°C (dec). − IR (drift): ν = 2049, 1985, 1974, 1607, 1518, 1506, 1274, 1252, 1179, 1031, 839 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.41 (d, J = 9.5 Hz, 1 H), 3.75 (s, 3 H), 3.79 (s, 3 H), 5.61 (dd, J = 9.5, 2.9 Hz, 1 H), 6.72 (br d, J = 8.9 Hz, 2 H), 6.83 (br d, J = 8.8 Hz, 2 H), 6.90 (br d, J = 8.9 Hz, 2 H), 6.95 (br d, J = 2.9 Hz, 1 H), 7.26 (br d, J = 8.8 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.27 (CH_3), 55.42 (CH_3), 62.83 (CH), 73.77 (CH), 103.48 (CH), 114.23 (2 CH), 114.27 (2 CH), 122.52 (2 CH), 127.79 (2 CH), 131.05 (C), 146.68 (C), 155.27 (C), 158.64 (C). − MS (115°C): *m/z* (%) = 407 (0.4) [M^+], 379 (1), 351 (2), 323 (32), 267 (20), 266 (100), 252 (14), 145 (10); HRMS: 407.0473 ($C_{20}H_{17}FeNO_5$, calcd. 407.0456).

Tricarbonyl[(1-4-η)-1-(2-methoxyphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene]iron (**10l**): Mp ≥ 134−136°C (dec). − IR (drift): ν = 2054, 1989, 1972, 1516, 1495, 1274, 1253, 1023, 831 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.38 (d, J = 9.5 Hz, 1 H), 3.80 (s, 3 H), 3.98 (s, 3 H), 5.74 (dd, J = 9.5, 3.0 Hz, 1 H), 6.78−6.87 (m, 2 H), 6.84 (br d, J = 8.8 Hz, 2 H), 6.95−7.07 (m, 3 H), 7.29 (br d, J = 8.8 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 54.80 (CH_3), 55.28 (CH_3), 63.00 (CH), 75.88 (CH), 101.18 (CH), 110.92 (CH), 114.27 (2 CH), 118.94 (CH), 120.48 (CH), 123.44 (CH), 127.72 (2 CH), 131.21 (C), 141.50 (C), 150.86 (C), 158.57 (C). − MS (110°C): *m/z* (%) = 379 (2) [M^+ − 28), 351 (13), 323 (42), 308 (100), 267 (11), 266 (28), 252 (10), 56 (11); HRMS: 379.0484 ($C_{19}H_{17}FeNO_4$ [M^+ − CO]), calcd. 379.0507).

Tricarbonyl[(1-4-η)-1-(4-trifluoromethylphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene]iron (**10m**): Mp 124°C. − IR (drift): ν = 2066, 2001, 1982, 1610, 1517, 1443, 1325, 1312, 1172, 1129, 831 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (d, *J* = 9.6 Hz, 1 H), 3.81 (s, 3 H), 5.71 (dd, *J* = 9.6, 2.9 Hz, 1 H), 6.83 (dd, *J* = 2.9, 0.8 Hz, 1 H), 6.85 (br d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 7.29 (br d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.33 (CH_3), 64.14 (CH), 75.49 (CH), 101.19 (CH), 114.48 (2 CH), 121.80 (2 CH), 123.86 (C, q, $^2J_{CF}$ = 32.6 Hz), 124.49 (CF_3, q, $^1J_{CF}$ = 271 Hz), 126.24 (2 CH, q, $^3J_{CF}$ = 3.8 Hz), 127.97 (2 CH), 130.42 (C), 156.87 (C), 159.01 (C), 205.07 (CO, br), 208.94 (CO, br), 211.97 (CO, br). − MS (90°C): *m/z* (%) = 445 (2) [M^+], 417 (6), 389 (11), 361 (100), 304 (52), 286 (16), 145 (17); HRMS: 445.0214 ($C_{20}H_{14}F_3FeNO_4$, calcd. 445.0224).

Tricarbonyl[(1-4-η)-1-(2,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-1-azabuta-1,3-diene]iron (**10n**): Mp ≥116°C (dec). − IR (drift): ν = 2051, 2043, 1992, 1984, 1964, 1518, 1443, 1285, 1255, 1034, 837 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.34 (d, *J* = 9.5 Hz, 1 H), 3.76 (s, 3 H), 3.79 (s, 3 H), 3.96 (s, 3 H), 5.70 (dd, *J* = 9.5, 2.8 Hz, 1 H), 6.33 (dd, *J* = 8.6, 2.5 Hz, 1 H), 6.41 (d, *J* = 2.5 Hz, 1 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 6.99 (d, *J* = 8.6 Hz, 1 H), 7.10 (d, *J* = 2.8 Hz, 1 H), 7.28 (d, *J* = 8.7 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 54.91 (CH_3), 55.28 (CH_3), 55.40 (CH_3), 62.52 (CH), 75.40 (CH), 99.14 (CH), 101.42 (CH), 103.44 (CH), 114.22 (2 CH), 118.39 (CH), 127.69 (2 CH), 131.35 (C), 135.10 (C), 152.18 (C), 156.52 (C), 158.48 (C). − MS (135°C): *m/z* (%) = 437 (0.2) [M^+], 409 (2), 381 (13), 353 (49), 338 (81), 310 (11), 299 (16), 297 (59), 296 (100), 282 (28), 153 (35), 138 (40), 84 (30), 56 (28); HRMS: 437.0583 ($C_{21}H_{19}FeNO_6$, calcd. 437.0562).

Tricarbonyl[(1-4-η)-1-(4-methoxyphenyl)-4-(2-methoxyphenyl)-1-azabuta-1,3-diene]iron (**10o**): Mp ≥121°C (dec). − IR (drift): ν = 2049, 1994, 1975, 1604, 1595, 1503, 1441, 1293, 1242, 1100, 1031, 1024, 836, 754 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.71 (d, *J* = 9.8 Hz, 1 H), 3.75 (s, 3 H), 3.92 (s, 3 H), 5.81 (dd, *J* = 9.8, 3.0 Hz, 1 H), 6.72 (br d, *J* = 8.9 Hz, 2 H), 6.85 (d, *J* = 7.9 Hz, 2 H), 6.92 (br d, *J* = 8.9 Hz, 2 H), 6.95 (br d, *J* = 3.0 Hz, 1 H), 7.15−7.24 (m, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.11 (CH_3), 55.44 (CH_3), 56.33 (CH), 73.73 (CH), 104.51 (CH), 110.46 (CH), 114.18 (2 CH), 120.30 (CH), 122.57 (2 CH), 125.27 (CH), 127.37 (C), 127.81 (CH), 147.01 (C), 155.14 (C), 157.14 (C). − MS (100°C): *m/z* (%) = 407 (1) [M^+], 379 (1), 351 (5), 323 (32), 267 (21), 266 (16), 252 (11), 236 (100); HRMS: 407.0455 ($C_{20}H_{17}FeNO_5$, calcd. 407.0456). − $C_{20}H_{17}FeNO_5$: C 58.99, H 4.21, N 3.44; found: C 58.80, H 4.26, N 3.65.

Tricarbonyl[(1-4-η)-4-(4-cyanophenyl)-1-phenyl-1-azabuta-1,3-diene]iron (**10p**): Mp ≥143°C (dec). − IR (drift): ν = 2224, 2057, 1997, 1991, 1485, 1439, 1295, 836, 764 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.24 (d, *J* = 9.2 Hz, 1 H), 5.70 (dd, *J* = 9.2, 2.9 Hz, 1 H), 6.94 (m, 3 H), 7.04 (dd, *J* = 2.9, 0.8 Hz, 1 H), 7.20 (m, 2 H), 7.37 (br d, *J* = 8.4 Hz, 2 H), 7.56 (br d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 58.69 (CH), 73.70 (CH), 105.71 (CH), 109.80 (C), 118.95 (C≡N), 121.82 (2 CH), 123.04 (CH), 126.85 (2 CH), 129.12 (2 CH), 132.57 (2 CH), 144.86 (C), 152.81 (C). − MS (95°C): *m/z* (%) = 372 (1) [M^+], 344 (2), 316 (5), 288 (32), 232 (51), 231 (100), 77 (24); HRMS: 372.0204 ($C_{19}H_{12}FeN_2O_3$, calcd. 372.0197).

Tricarbonyl[(1-4-η)-4-(4-cyanophenyl)-1-(2,4-dimethoxyphenyl)-1-azabuta-1,3-diene]iron (**10q**): Mp ≥118°C (dec). − IR (drift): ν = 2226, 2057, 2004, 1995, 1970, 1602, 1503, 1311, 1214, 843, 791 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15 (d, *J* = 9.2 Hz, 1 H), 3.77 (s, 3 H), 3.97 (s, 3 H), 5.74 (dd, *J* = 9.2, 3.0 Hz, 1 H), 6.35 (dd, *J* = 8.7, 2.6 Hz, 1 H), 6.43 (d, *J* = 2.6 Hz, 1 H), 7.01 (d, *J* = 8.7 Hz, 1 H), 7.23 (br d, *J* = 3.0 Hz, 1 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 54.91 (CH_3), 55.43 (CH_3), 58.19 (CH), 74.87 (CH), 99.27 (CH), 103.70 (CH), 103.93 (CH), 109.43 (C), 118.54 (CH), 119.10 (C≡N), 126.72 (2 CH), 132.51 (2 CH), 134.37 (C), 145.36 (C), 152.30 (C), 157.04 (C).

Tricarbonyl[(1-4-η)-1-(4-methoxyphenyl)-4-(4-N,N-dimethylaminophenyl)-1-azabuta-1,3-diene]iron (**10r**): Mp ≥125°C (dec). − IR (drift): ν = 2045, 2041, 1989, 1971, 1964, 1605, 1502, 1243, 1035, 836, 823 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.95 (s, 6 H), 3.50 (d, *J* = 9.6 Hz, 1 H), 3.75 (s, 3 H), 5.61 (dd, *J* = 9.6, 2.9 Hz, 1 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.89 (br d, *J* = 2.9 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.22 (d, *J* = 8.8 Hz, 2 H). − ^{13}C NMR and DEPT (63 MHz, $CDCl_3$): δ = 40.36 (2 CH_3), 55.44 (CH_3), 65.36 (CH), 73.60 (CH), 102.53 (CH), 112.46 (2 CH), 114.22 (2 CH), 122.53 (2 CH), 126.06 (C), 127.80 (2 CH), 147.01 (C), 149.52 (C), 155.15 (C). − MS (130°C): *m/z* (%) = 420 (0.1) [M^+], 392 (0.2), 364 (1), 336 (9), 280 (43), 279 (100), 158 (10); HRMS: 420.0795 ($C_{21}H_{20}FeN_2O_4$, calcd. 420.0772).

Preparation of Tricarbonyl(η⁴-cyclohexa-1,3-diene)iron (**2**) *by Transfer of the Fe(CO)₃-Fragment of the (η⁴-1-Azabuta-1,3-diene)-tricarbonyliron Complexes* **10** *to Cyclohexa-1,3-diene* (**1a**) − *General Procedure:* Dry THF (10 ml) and cyclohexa-1,3-diene (**1a**) (0.37 ml, 3.88 mmol) were added to the azadiene complex **10** (1.00 mmol) and the reaction mixture was stirred at reflux (reaction time, see Table 6). The mixture was cooled to room temp. and the solvent was evaporated in vacuo to a volume of 1 ml. The residue was subjected to flash chromatography (pentane) on silica gel and afforded the iron complex **2** as a yellow oil (Table 6).

Table 6. Transfer reagent **10**, reaction time, and yield of the iron complex **2**

Entry	Iron Complex **10** [mg]	Reaction time [min]	**2**, Yield [mg]	[%]
a[a]	250	180	140	88
b	377	30	134	61
	377	60	183	83
[b]	200	120	111	95
c	377	30	68	31
	377	60	103	47
	377	120	163	74
d[c]	200	120	98	45
e	415	120	171	78
g	407	30	109	50
	407	60	148	67
	407	120	177	80
h	437	120	192	87
i	437	120	163	74
j	377	120	205	93
k	407	120	199	90
l	407	120	183	83
m	445	120	194	88
n	437	120	172	78
o	407	120	203	92
p	372	120	152	69
q	432	120	131	60
r	420	120	162	74

The following reactions were run on a different scale: [a] Cyclohexa-1,3-diene **1a** (0.20 ml, 168 mg, 2.10 mmol) and azadiene complex **10a** (250 mg, 0.720 mmol). − [b] Cyclohexa-1,3-diene **1a** (0.20 ml, 168 mg, 2.10 mmol) and azadiene complex **10b** (200 mg, 0.531 mmol). − [c] Cyclohexa-1,3-diene **1a** (0.25 ml, 210 mg, 2.62 mmol) and azadiene complex **10d** (200 mg, 0.513 mmol).

Preparation of Tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) *by Direct Complexation of Cyclohexa-1,3-diene* (**1a**) *with Nonacarbonyldiiron:* Cyclohexa-1,3-diene (**1a**) (13.9 ml, 146 mmol) was added to a suspension of nonacarbonyldiiron (44.2 g, 121.5 mmol) in THF (250 ml) and the heterogeneous mixture was stirred at reflux for 6 h. The mixture was cooled to room temp., filtered through a short path of Celite, and the solvent was removed. The residue was dissolved in light petroleum and filtered through a short path of Alox B. Evaporation of the solvent in vacuo afforded the iron complex **2** (11.5 g, 43%), which could be subjected directly to hydride abstraction. Yellow oil. − IR (film): ν = 3009, 2926, 2907, 2887, 2850, 2042, 1957, 1467, 1333, 1180, 1029, 1007, 938, 879, 865, 642, 623 cm^{-1}. − ^1H NMR (400 MHz, C_6D_6): δ = 1.18 (br d, *J* = 12 Hz, 2 H), 1.45 (br dt, *J* = 12, 2 Hz, 2 H), 2.74 (dd, *J* = 5, 2 Hz, 2 H), 4.63 (dd, *J* = 5, 3 Hz, 2 H). − ^{13}C NMR and DEPT (100 MHz, C_6D_6): δ (*T* = 298 K) = 23.82 (2 CH_2), 62.52 (2 CH), 85.37 (2 CH), 212.63 (3 CO); ^{13}C NMR (125 MHz, [D_8]toluene): δ (*T* = 185 K) = 23.45 (2 CH_2), 62.30 (2 CH), 85.09 (2 CH), 211.32 (2 CO), 216.05 (CO); δ (*T* = 298 K) = 23.89 (2 CH_2), 62.47 (2 CH), 85.41 (2 CH), 212.56 (3 CO). − MS (20°C): *m*/*z* (%) = 220 (9) [M^+], 192 (32), 164 (5), 162 (10), 134 (100), 56 (33); HRMS: 219.9834 ($C_9H_8FeO_3$, calcd. 219.9823).

Synthesis of the Tricarbonyl(η^5-cyclohexadienylium)iron Tetrafluoroborate (**3**) *by Hydride Abstraction of the Iron Complex* **2**: A solution of tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**2**) (11.5 g, 52.4 mmol) in CH_2Cl_2 (70 ml) was added to a solution of triphenylmethyl tetrafluoroborate (20.8 g, 62.9 mmol) in CH_2Cl_2 (70 ml). The reaction mixture was stirred for 40 min at room temp. and then poured into wet Et_2O (700 ml). The resulting yellow precipitate was washed twice with Et_2O (150 ml) and dried in vacuo to provide pure tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate (**3**) (15.7 g, 98%). Yellow crystals. − IR (KBr): ν = 2118, 2060, 1455, 1410, 1311, 1062, 603, 589, 558 cm^{-1}. − ^1H NMR (200 MHz, CD_3CN): δ = 1.91 (d, *J* = 15.7 Hz, 1 H), 2.92 (dt, *J* = 15.7, 6.3 Hz, 1 H), 4.24 (t, *J* = 6.3 Hz, 2 H), 5.83 (t, *J* = 6.3 Hz, 2 H), 7.16 (t, *J* = 6.3 Hz, 1 H).

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