1,4-Diaryl-1-azabuta-1,3-diene-Catalyzed Complexation of Cyclohexa-1,3-diene by the Tricarbonyliron Fragment: Development of Highly Efficient Catalysts, Optimization of Reaction Conditions, and Proposed Mechanism†

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The 1,4-diaryl-1-azabuta-1,3-diene-catalyzed complexation of cyclohexa-1,3-diene with either nonacarbonyldiiron or pentacarbonyliron is reported to provide high yields of the tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex. This procedure enables exploitation of both tricarbonyliron fragments of nonacarbonyldiiron for the complexation of dienes for the first time. Using 12.5 mol % of 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene and optimized reaction conditions (nonacarbonyldiiron, dimethoxyethane, reflux, 16.5 h, or pentacarbonyliron, dioxane, reflux, 45 h), a quantitative catalytic complexation of cyclohexa-1,3-diene is feasible with both reagents. An extensive study with a broad range of 1,4-diaryl-1-azabuta-1,3-dienes shows that the efficiency of the catalysts strongly depends on the substituents of the two aryl rings. Remarkably high activities are found for those catalysts deriving from condensation of cinnamaldehyde and *ortho*-methoxy-substituted arylamines. A hexacarbonyldiiron complex of 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene is obtained as a byproduct of the catalytic complexation and is structurally confirmed by X-ray crystallography. A mechanism supported by the experimental findings is proposed.

Introduction

The tricarbonyliron complexes of conjugated dienes have found a broad range of applications in organic synthesis.[2] The standard procedure for the synthesis of the tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex involves either thermal or photochemical reaction of the diene with pentacarbonyliron, nonacarbonyldiiron, or dodecacarbonyltriiron.[3] Much milder reaction conditions for the complexation step can be employed by using tricarbonyliron transfer reagents.[4] (η^4-Benzylideneacetone)tricarbonyliron investigated by Lewis[5] and Brookhart[6] and tricarbonylbis(η^2-*cis*-cyclooctene)iron developed by Grevels[7] are well-established transfer reagents for complexations of labile diene systems by the tricarbonyliron fragment. We recently found that the (η^4-1,4-diaryl-1-azabuta-1,3-diene)tricarbonyliron complexes[8] represent a novel class of tricarbonyliron transfer reagents.[9−11] The azadiene−tricarbonyliron complexes offer several advantages over the two aforementioned reagents: they can be prepared in high yields (70−90%) by ultrasound-promoted complexation and are stable in the air. Most remarkable is the fact that substoichiometric amounts of the 1,4-diaryl-1-azabuta-

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(1) Part 44: Knölker, H.-J.; Reddy, K. R. *Tetrahedron Lett*. **1998**, *39*, 4007.

(2) For reviews, see: Pearson, A. J. *Acc. Chem. Res*. **1980**, *13*, 463. Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 58. Pearson, A. J. *Metallo-organic Chemistry*; Wiley: Chichester, 1985; Chapters 7 and 8. Grée, R. *Synthesis* **1989**, 341. Knölker, H.-J. In *Organic Synthesis via Organometallics*; Dötz, K. H., Hoffmann, R. W., Eds.; Vieweg: Braunschweig, 1991; p 119. Knölker, H.-J. *Synlett* **1992**, 371. Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: London, 1994; Chapters 4 and 5. Grée, R.; Lellouche, J. P. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, p 129. Knölker, H.-J. In *Advances in Nitrogen Heterocycles*; Moody, C. J., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 1, p 173. Iwata, C.; Takemoto, Y. *Chem. Commun*. **1996**, 2497.

(3) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc*. **1958**, 642. Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332. Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882.

(4) For a brief review on tricarbonyliron transfer reagents, see: Knölker, H.-J. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, 1995; Vol. 1, p 333.

(5) Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Organomet. Chem*. **1972**, *39*, 329. Domingos, A. J. P.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *Inorg. Synth*. **1976**, *16*, 103.

(6) Graham, C. R.; Scholes, G.; Brookhart, M. *J. Am. Chem. Soc*. **1977**, *99*, 1180. Brookhart, M.; Nelson, G. O. *J. Organomet. Chem*. **1979**, *164*, 193.

(7) Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc*. **1984**, *106*, 2027.

(8) Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem*. **1967**, *6*, 20. Brodie, A. M.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Chem. Soc., Dalton Trans*. **1972**, 2031. Yin, J.; Chen, J.; Xu, W.; Zhang, Z.; Tang, Y. *Organometallics* **1988**, *7*, 21. Danks, T. N.; Thomas, S. E. *Tetrahedron Lett*. **1988**, *29*, 1425. Danks, T. N.; Thomas, S. E. *J. Chem. Soc., Perkin Trans. 1* **1990**, 761. Semmelhack, M. F.; Cheng, C. H. *J. Organomet. Chem*. **1990**, *393*, 237.

(9) Knölker, H.-J.; Gonser, P. *Synlett* **1992**, 517.

(10) Knölker, H.-J.; Gonser, P.; Jones, P. G. *Synlett* **1994**, 405.

(11) Knölker, H.-J.; Baum, G.; Foitzik, N.; Goesmann, H.; Gonser, P.; Jones, P. G.; Röttele, H. *Eur. J. Inorg. Chem*. **1998**, 993.

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1,3-dienes can be applied in order to induce the complexation of 1,3-dienes with pentacarbonyliron or nonacarbonyldiiron.[9,10] Thus, catalytic complexations of conjugated dienes by the tricarbonyliron fragment are feasible by using the azadienes as catalysts. Herein, we describe the full details of the development of a highly efficient procedure for the catalytic complexation of cyclohexa-1,3-diene by the tricarbonyliron fragment and preliminary results with respect to the mechanism of this reaction.

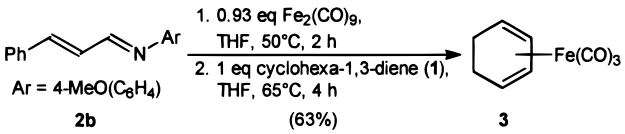
Results and Discussion

Preliminary Investigations. The excellent results which were achieved in the preparation of the (η^4-1,4-diaryl-1-azabuta-1,3-diene)tricarbonyliron complexes and in their application as tricarbonyliron transfer reagents[11] suggest performing both reactions in one pot. Such one-pot procedures for complexations of dienes with tricarbonyliron transfer reagents were used previously for applications of the Grevels' reagent[12] and the benzylideneacetone complexes.[13] The disadvantage of a one-pot procedure using the Grevels' reagent is that the addition of the diene has to take place after the preparation of the reagent because of the photolytical reaction conditions. Performing a one-pot procedure via the (η^4-benzylideneacetone)tricarbonyliron complex suffers from the drawback of a low yield for the preparation of the transfer reagent itself. The thermal reaction conditions required for the transfer of the metal fragment (benzene, 60 °C) are known to afford the benzylideneacetone complex in only 32% yield.[5]

For the complexation of ergosteryl benzoate using nonacarbonyldiiron, a catalytic effect of *p*-methoxybenzylideneacetone was claimed by Barton.[13] However, according to the Experimental Section of that paper,[13] overstoichiometric amounts of *p*-methoxybenzylideneacetone and nonacarbonyldiiron were used. In agreement with an earlier report by Lewis et al. (71% yield),[14] Barton and co-workers reported a yield of 59−69% for the complexation of ergosteryl acetate and ergosteryl benzoate using stoichiometric amounts of either the benzylideneacetone or the *p*-methoxybenzylideneacetone iron complex.[13] We reinvestigated the complexation of ergosteryl benzoate with nonacarbonyldiiron, and it was revealed that similar yields are obtained with or without addition of catalytic amounts of *p*-methoxybenzylideneacetone. In conclusion, there is no catalytic effect of *p*-methoxybenzylideneacetone in this complexation. The beneficial effect (80% yield), observed by adding overstoichiometric amounts of *p*-methoxybenzylideneacetone and nonacarbonyldiiron,[13] has to be ascribed to an in situ generation of the transfer reagent.

The one-pot procedure of the preparation of the azadiene iron complex in stoichiometric amounts and subsequent transfer of the metal fragment was applied to the complexation of cyclohexa-1,3-diene (**1**) (Scheme 1). 1-(4-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene

Scheme 1. In Situ Preparation of the Transfer Reagent



(**2b**) was selected for this in situ generation of the transfer reagent, since the corresponding tricarbonyliron complex provided the best yields in its preparation and in the transfer reaction.[11]

Heating the azadiene **2b** with nonacarbonyldiiron in tetrahydrofuran at 50 °C for 2 h provides a deep red solution, indicating the formation of the (η^4-azadiene)tricarbonyliron complex. After addition of the diene **1**, the solution was refluxed for 4 h and afforded the tricarbonyl(η^4-cyclohexa-1,3-diene)iron (**3**) in 63% yield based on nonacarbonyldiiron. The fact that the formation of the transfer reagent and the transfer of the metal fragment to the diene regenerating the azadiene can be achieved in a one-pot procedure indicated that it should be feasible to develop an azadiene-catalyzed complexation.

Catalytic Complexation with Nonacarbonyldiiron. The direct uncatalyzed complexation of dienes with nonacarbonyldiiron can be performed at lower reaction temperatures than with pentacarbonyliron. Therefore, we started our investigations on catalytic complexations by using nonacarbonyldiiron as the tricarbonyliron source and the azadiene **2b** as the catalyst with the objective of achieving a highly efficient exploitation of the metal fragments. The best results for the uncatalyzed complexation of cyclohexa-1,3-diene with nonacarbonyldiiron are obtained by heating a mixture of the diene and nonacarbonyldiiron (1.2:1) in tetrahydrofuran at reflux for 6 h (43% yield based on nonacarbonyldiiron).[11,15] However, using these reaction conditions, only one tricarbonyliron fragment of nonacarbonyldiiron is exploited for the complexation, since 1 equiv of pentacarbonyliron is formed, which does not react further at this temperature. Thus, the yield based on iron for this complexation is only 21.5%. Better results (referring to higher yields based on cyclohexa-1,3-diene) are obtained by using a large excess of nonacarbonyldiiron. However, this procedure suffers from the drawback that large amounts of pyrophoric iron are formed, which is hazardous during the workup. Therefore, we investigated the catalytic complexation with nonacarbonyldiiron by using a slight excess of cyclohexa-1,3-diene (**1**) (1:1−1.5) and 12.5 mol % of the azadiene **2b** as the catalyst (Scheme 2, Table 1). All specifications of stoichiometry and yields for the azadiene-catalyzed complexation with nonacarbonyldiiron refer to the iron equivalents.

Catalyst **2b** was chosen for our initial studies, since it is easily prepared in large quantities and because the corresponding tricarbonyliron complex was the best transfer reagent for the stoichiometric complexation of cyclohexa-1,3-diene.[11] The variation of solvent and temperature of the catalytic complexation, while carefully controlling the other reaction parameters, showed

(12) Franck-Neumann, M.; Briswalter, C.; Chemla, P.; Martina, D. *Synlett* **1990**, 637. Eilbracht, P.; Hittinger, C.; Kufferath, K.; Schmitz, A.; Gilsing, H.-D. *Chem. Ber.* **1990**, *123*, 1089.

(13) Barton, D. H. R.; Gunatilaka, A. A. L.; Nakanishi, T.; Patin, H.; Widdowson, D. A.; Worth, B. R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 821.

(14) Evans, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1975**, *102*, 507.

(15) Knölker, H.-J.; Pannek, J.-B. Unpublished results. Pannek, J.-B. Diplomarbeit, Universität Hannover, 1989; p 46. Knölker, H.-J. Habilitationsschrift, Universität Hannover, 1989; p 59.

Scheme 2. Catalytic Complexation of Cyclohexa-1,3-diene (1) with $Fe_2(CO)_9$

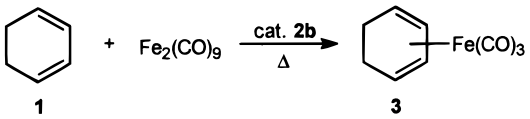


Table 1. Catalytic Complexation of Cyclohexadiene 1 with $Fe_2(CO)_9$ Using 0.125 Equiv of Catalyst 2b: Variation of Solvent, Temperature, and Reaction Time[a]

solvent	*T* [°C]	*t* [h]	**3**, yield [%]
THF	65	16.5	63
cyclohexane	80	16.0	53
benzene	80	16.5	66
DME	85	6.0	93
DME	85	16.5	98

[a] Reaction conditions: 1−1.5 equiv of cyclohexa-1,3-diene (**1**); yield of **3** based on iron.

that working in 1,2-dimethoxyethane (DME) at reflux provided the best results. After a reaction time of 16.5 h, the iron complex **3** could be obtained in a yield of 98% based on the actually available equivalents of iron (the yield refers to a large scale, providing 11.9 g of complex **3**). This result demonstrated for the first time that both tricarbonyliron fragments present in nonacarbonyldiiron can be transferred to the diene in a complexation reaction and that virtually quantitative yields are feasible. For comparison, the uncatalyzed complexation of **1** with nonacarbonyldiiron in dimethoxyethane (reflux, 16 h) afforded complex **3** in a yield of 21% based on iron (Figure 1[15]). Besides the economic advantage of the catalytic method, the safety aspect has to be pointed out. Because of the quantitative transfer of both iron fragments, the formation of pyrophoric iron and pentacarbonyliron does not occur.

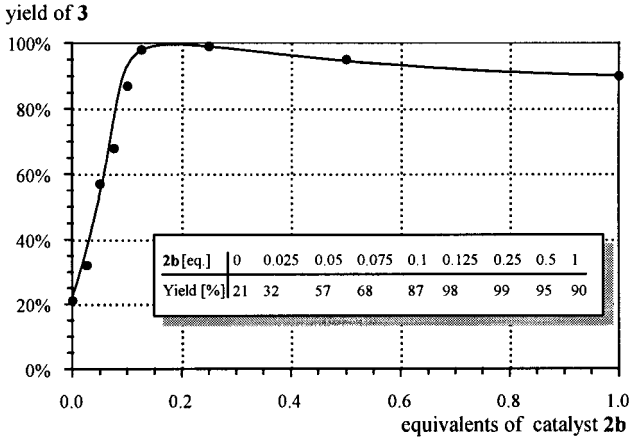


Figure 1. Catalytic complexation of cyclohexa-1,3-diene **(1)** with $Fe_2(CO)_9$ as a function of the amount of catalyst **2b**. Reaction conditions: 1.5 equiv of **1**, DME, 85 °C, 16 h; yield of **3** based on iron.

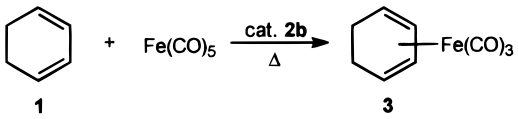
In a further series of experiments, the catalytic complexation of cyclohexadiene **1** with nonacarbonyldiiron was investigated by variation of the amount of catalyst **2b** using the optimized reaction conditions found above (dimethoxyethane, reflux, 16 h) (Figure 1). It was shown that decreasing the amount of catalyst leads to a drastic decrease of the yield as well, down to a value of 21% for the uncatalyzed complexation. Increasing the amount of the catalyst up to a stoichiometric ratio also results in a slight decrease of the yield. In this case, analysis of the reaction mixture shows that the azadiene **2b** is still partly present as the (η^4-azadiene)tricarbonyliron complex. Presumably, a transfer of the tricarbonyliron fragment from this complex to the free azadiene ligand becomes dominant at the end of the reaction, when the concentration of the cyclohexadiene is already very low compared to the concentration of the azadiene. Thus, the intermolecular tricarbonyliron transfer from the azadiene−tricarbonyliron complex to free azadiene prevents the reaction from going to completion if the concentration of the catalyst is too high.

The tricarbonyliron complex of *p*-methoxybenzylideneacetone was shown to transfer the metal fragment much faster to cyclohexa-1,3-diene (**1**) than the (η^4-azadiene)-tricarbonyliron complexes.[11] However, it could be again confirmed that *p*-methoxybenzylideneacetone exhibits no catalytic effect in the complexation of cyclohexadiene **1** with nonacarbonyldiiron. Treatment of **1** with nonacarbonyldiiron in the presence of 2.5 mol % of *p*-methoxybenzylideneacetone in tetrahydrofuran at reflux provided complex **3** in a yield of only 16% based on iron, which is in the same range as for the uncatalyzed complexation.

Catalytic Complexation with Pentacarbonyliron. Pentacarbonyliron is more attractive as a starting material for the complexation because it is much cheaper than nonacarbonyldiiron. However, the standard procedure for the thermal complexation of cyclohexadiene **1** (heating with a large excess of pentacarbonyliron in di-*n*-butyl ether at 142 °C for 18 h) provides the iron complex **3** in only 23% yield (single-stage procedure).[3] Using this method the excess pentacarbonyliron has to be removed from the product and pyrophoric iron is formed. Moreover, only low yields are obtained for the complexation of labile dienes due to the high reaction temperature. Therefore, we tried to develop a catalytic complexation with pentacarbonyliron by using reaction conditions similar to those described above for nonacarbonyldiiron. A slight excess (1.5 equiv) of cyclohexadiene **1** was used in order to ensure that the iron was quantitatively transformed to complex **3**. The efficient azadiene catalyst **2b** should perhaps make it feasible to use considerably lower reaction temperatures than for the uncatalyzed complexation. The reaction conditions leading to quantitative complexation with nonacarbonyldiiron, using catalyst **2b** in dimethoxyethane at reflux, provided complex **3** in 54% yield when applied to the catalytic complexation with pentacarbonyliron (Scheme 3, Table 2). The blank experiment (reaction of **1** with pentacarbonyliron under the same reaction conditions but without catalyst) afforded complex **3** in only 2% yield and indicated the high efficiency of the catalysis, which was already achieved at this stage.

To consume the iron quantitatively for the complexation, we changed the conditions and performed the reaction in dioxane at reflux. Variations of the amount of catalyst and of the reaction time showed again that the use of 12.5 mol % of catalyst **2b** represents the ideal compromise between low catalyst concentration and high turnover. Finally, it was found that the reaction of pentacarbonyliron with the diene **1** in dioxane at

Scheme 3. Catalytic Complexation of Cyclohexa-1,3-diene (1) with $Fe(CO)_5$



1 3

Table 2. Catalytic Complexation of Cyclohexadiene 1 with $Fe(CO)_5$: Variation of Solvent, Temperature, Reaction Time, and Amount of Catalyst 2b[a]

reaction conditions	**1** [equiv]	**2b** [equiv]	**3**, yield [%]
DME, 85 °C, 16.5 h	2.5	0	2
DME, 85 °C, 20 h	2.5	0.25	54
dioxane, 101 °C, 45 h	1.5	0	8
dioxane, 101 °C, 5 h	1.5	0.010	5
dioxane, 101 °C, 5 h	1.5	0.050	11
dioxane, 101 °C, 5 h	1.5	0.125	21
dioxane, 101 °C, 20 h	2.5	0.25	70
dioxane, 101 °C, 63 h	1.5	0.025	67
dioxane, 101 °C, 14 h	1.5	0.125	50
dioxane, 101 °C, 37 h	1.5	0.125	91
dioxane, 101 °C, 45 h	1.5	0.125	99

[a] Reaction conditions: 1.5 equiv of cyclohexa-1,3-diene (**1**); yield of **3** based on iron.

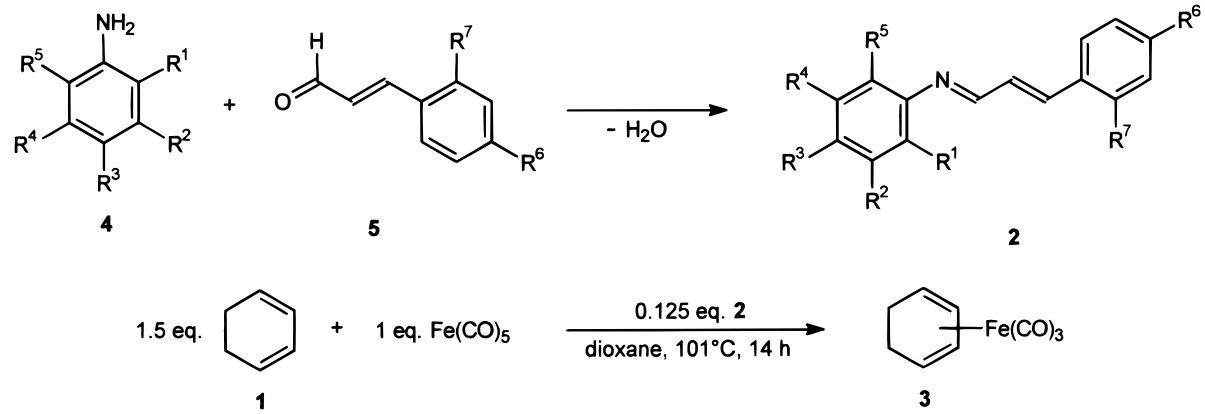
reflux for 45 h in the presence of 12.5 mol % of catalyst **2b** proceeds quantitatively, and the tricarbonyliron complex **3** could be isolated in 99% yield based on pentacarbonyliron. For comparison, the blank experiment (identical conditions without catalyst) provided complex **3** in 8% yield.

All reactions presented in Table 2 were based on a scale of 2.0 g (10.2 mmol) of pentacarbonyliron. The scale of the catalytic complexation of cyclohexadiene **1** using the optimal conditions (dioxane, 101 °C, 0.125 equiv of **2b**) was increased up to 50 g (255 mmol) of pentacarbonyliron (see Experimental Section). On this scale, a large volume of carbon monoxide (more than 11 L) is formed, which mostly displaces the inert gas (argon) using conventional laboratory equipment (flask with reflux condenser). The resulting increase of the partial pressure of carbon monoxide leads to an equilibrium, which stops the catalytic cycle (see proposed mechanism, below) and is responsible for the observed drastic decrease of the turnover. This problem can be simply solved by directing a light flow of argon through the apparatus and increasing the reaction time to 4 days. By using this modified procedure, the complexation of **1** on a scale of 50.0 g (255 mmol) of pentacarbonyliron provided 50.2 g of the tricarbonyliron complex **3** (89% yield), and the catalyst **2b** can be regenerated during the workup by crystallization.

We next investigated the efficiency of the 1,4-diaryl-1-aza-1,3-butadiene catalysts **2** as a function of the substituents of the two aryl rings. The azadienes **2** used as catalysts in the present work were prepared by condensation of the arylamines **4** with the cinnamaldehydes **5** as previously described for the synthesis of (η^4-1-aza-1,3-butadiene)tricarbonyliron complexes.[11] To be able to compare the results, we used a standard set of reaction conditions (dioxane, 101 °C, 14 h, 0.125 equiv of **2**) and the scale of the reaction (4.55 mmol pentacarbonyliron, 1.5 equiv of cyclohexa-1,3-diene **1**) was calculated to afford 1.0 g of complex **3** for 100% yield. The reaction time of 14 h was selected because catalyst **2b** provides complex **3** in a yield of 50% after this time. Thus, the more and the less reactive catalysts can be compared based on this result (Scheme 4, Table 3).

The blank experiment using the reaction conditions described above without catalyst provided complex **3** in 0.7% yield. Performing the complexation in the presence of 12.5 mol % of *p*-methoxybenzylideneacetone afforded complex **3** in 4.2% yield. This outcome confirms again that the oxadiene can be used for an in situ formation of the tricarbonyl(η^4-oxadiene)iron complex followed by transfer of the metal fragment to **1** but shows no catalytic effect in this reaction. In contrast to this result, application of 12.5 mol % of the 1,4-diaryl-1-azabuta-1,3-dienes **2a**−**p** led to a significant increase of the yield. The nitro derivative **2q**, which could not be transformed to the corresponding tricarbonyliron complex for the stoichiometric complexation,[11] exhibited no catalytic effect under the applied reaction conditions. Using the parent compound 1,4-diphenyl-1-azabuta-1,3-diene (**2a**) as the catalyst, the iron complex **3** was obtained in 41% yield. For comparison of the activities of the various catalysts, a standard was required and, therefore, the relative activity of this catalyst was defined as 1.0. It was found that acceptor substituents in the aryl rings generally lead to a drastic decrease of the catalytic activity, e.g., **2e** (0.54), **2l** (0.46), **2o** (0.32), and **2q** (0). The high activity of catalyst **2p** (2.02) is explained by the chelation effect of the *ortho*-methoxy group (see below) which is overriding. On the other hand, donor substituents in positions appropriate to lead to an increase of the electron density at the imine

Scheme 4. Synthesis of the Azadiene Catalysts 2, and Catalytic Complexation of Cyclohexa-1,3-diene (1) with $Fe(CO)_5$ to the Tricarbonyliron Complex 3



4 5 2

1 3

Table 3. Synthesis of the 1-Azabuta-1,3-dienes 2, and Yield of the Catalytic Complexation of Cyclohexa-1,3-diene (1) with Pentacarbonyliron Using 0.125 Equiv of 2[a]

	R^1	R^2	R^3	R^4	R^5	R^6	R^7	**2**, yield [%]	**3**, yield [%]	relative activity[b]
								no catalyst	0.7	
a	H	H	H	H	H	H	H	82	41	≡ 1.00
b	H	H	OMe	H	H	H	H	100	50	1.22
c	OMe	H	H	H	H	H	H	87	83	2.02
d	H	H	NMe_2	H	H	H	H	40	66	1.61
e	H	H	CF_3	H	H	H	H	72	22	0.54
f	OMe	H	OMe	H	H	H	H	81	90	2.20
g	H	OMe	OMe	OMe	H	H	H	79	33	0.80
h	OMe	H	OMe	H	OMe	H	H	73	86	2.10
i	H	H	H	H	H	OMe	H	88	31	0.76
j	H	H	OMe	H	H	OMe	H	95	51	1.24
k	OMe	H	H	H	H	OMe	H	79	91	2.22
l	H	H	CF_3	H	H	OMe	H	59	19	0.46
m	OMe	H	OMe	H	H	OMe	H	80	74	1.80
n	H	H	OMe	H	H	H	OMe	86	71	1.73
o	H	H	H	H	H	CN	H	78	13	0.32
p	OMe	H	OMe	H	H	CN	H	99	83	2.02
q	H	H	OMe	H	H	NO_2	H	75	0	0

[a] Reaction conditions: 1 equiv of pentacarbonyliron, 1.5 equiv of cyclohexadiene **1**, 0.125 equiv of **2**, dioxane, 101 °C, 14 h. [b] Relative activity of the 1-azadiene catalysts **2** as compared to **2a** (≡1.0).

nitrogen atom result in a remarkably increased catalyst activity. Thus, the activity of catalyst **2b** (1.22) with a *para*-methoxy group in the 1-aryl ring is higher compared to **2a** because of the inductive effect of the methoxy group. Stronger donor groups in this position, as the *N*,*N*-dimethylamino substituent in **2d**, lead to an even higher catalyst activity (1.61). The chemical shift of the imine proton (H−C2) in the ^{1}H NMR spectra of the azadienes **2** represents a measure of the electron density at the imine nitrogen atom and, thus, its nucleophilicity.[11] A much more significant increase in catalyst activity is observed with an *ortho*-methoxy group in the 1-aryl ring as for **2c** (2.02). This positive effect on catalyst activity caused by an *ortho*-methoxy group is ascribed to an internal displacement of a carbon monoxide ligand and stabilization of an intermediate 16-electron species due to chelation by coordination of an oxygen lone pair of electrons to iron (see proposed mechanism, below). Similar high activities are also observed for the other catalysts with an *ortho*-methoxy group in the 1-aryl ring: **2f** (2.20), **2h** (2.10), **2k** (2.22), **2m** (1.80), and **2p** (2.02). The high relative catalyst activity of **2f** (2.20), having an *ortho*- and a *para*-methoxy group in the 1-aryl ring, shows that the inductive and the chelation effect on catalyst activity are additive: compare with the relative catalyst activities of **2a** (1.00), **2b** (1.22), and **2c** (2.02). Thus, on catalytic complexation of **1** with catalyst **2f**, complex **3** is already obtained in 90% yield after a reaction time of 14 h.

To emphasize the influence of an *ortho*-methoxy group on the efficiency of the catalyst, the azadiene **2b** was compared with the azadienes **2c**, **2f**, and **2h** using the standard reaction conditions (dioxane, 101 °C, 1.5 equiv of **1**, 0.125 equiv of **2**) at three different reaction times (Table 4).

The higher reactivity of the three latter catalysts is already visible after a reaction time of 5 h and becomes even more evident after 14 h. The results of the catalytic complexation after 37 h demonstrate again that using a certain catalyst, the maximal accessible yield is independent of the turnover, which has been achieved at shorter reaction times.

Mechanism of the Catalytic Complexation. During chromatographic workup of the crude products of catalytic complexations, especially on large scale, it was observed that several orange and red bands of byproducts were formed with only one of them being the (η^4-azadiene)tricarbonyliron complex. We thought that these byproducts might represent important intermediates of the catalytic cycle and that the determination of their structures would perhaps help us to understand the mechanism of the catalytic complexation. Therefore, we attempted a thermal complexation of the azadiene **2b** with pentacarbonyliron using conditions similar to those used for the catalytic complexation of cyclohexadiene **1** (Scheme 5).

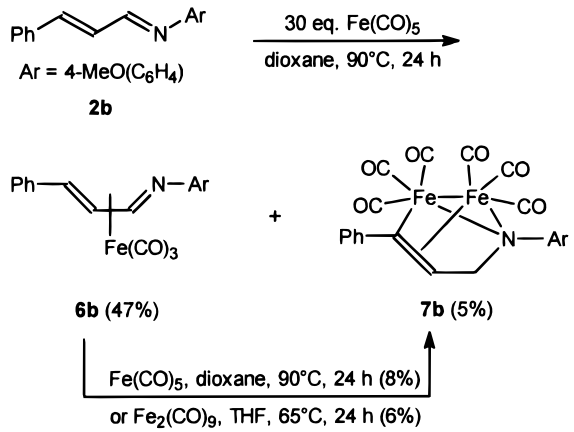
The reaction of catalyst **2b** with an excess of pentacarbonyliron provided the (η^4-azadiene)tricarbonyliron

Table 4. Catalytic Complexation of Cyclohexa-1,3-diene (1) with Pentacarbonyliron (1 Equiv): Variation of Catalyst 2 and Reaction Time[a]

	3, yield [%]		
2	5 h	14 h	37 h
b	21	50	91
c	29	83	92
f	34	90	90
h	46	86	

[a] Reaction conditions: 1.5 equiv of diene **1**, dioxane, 101 °C; 0.125 equiv of **2**.

Scheme 5. Synthesis of the Hexacarbonyldiiron Complex 7b



complex **6b** in 47% yield along with the hexacarbonyldiiron complex **7b** in 5% yield. Both products could be isolated by chromatographic separation in the glovebox. From this result we concluded that the dinuclear iron complex **7b** is possibly formed by complexation of the mononuclear iron complex **6b**. In fact, heating of complex **6b** with pentacarbonyliron in dioxane at 90 °C afforded the hexacarbonyldiiron complex **7b** in 8% yield along with 86% of recovered **6b**. Alternatively, heating of complex **6b** with nonacarbonyldiiron in tetrahydrofuran at reflux provided the dinuclear complex **7b** in 6% yield along with 86% of recovered starting material (Scheme 5).

The (η^4-1-azabuta-1,3-diene)tricarbonyliron complex **6b** was previously described and fully characterized.[11] The structural assignment for the dinuclear complex **7b** is based on the following spectral data. The mass spectrum of **7b** shows the peak for the molecular ion at *m*/*z* 517 followed by sequential loss of six carbon monoxide ligands and two iron atoms. This typical fragmentation pattern and the high resolution of the peak for the molecular ion suggest that **7b** represents a hexacarbonyldiiron complex. The FT-IR spectrum exhibits six bands in the region of 1954−2062 cm^{-1}, which are characteristic of terminal carbonyl ligands. On the other hand, no bands are found in the region of 1700−1900 cm^{-1}, indicating that no bridging carbonyls are present in the complex. In the ^1H NMR spectrum (in C_6D_6), a broad 2-proton singlet at 3.65 ppm and a singlet for 1 proton at 4.26 ppm occur. These signals are assigned to the three protons bound at the two central carbon atoms (C2, C3) of the azadiene moiety. In the ^1H NMR spectrum (in C_6D_6) of the tricarbonyliron complex **6b**, the chemical shifts of the signals for the azadiene protons are significantly different (2-H, δ 6.41; 3-H, δ 5.03; 4-H, δ 3.45). The chemical shifts of the signals for the aromatic protons are almost identical in both complexes. The major change of the signals for the protons at the azadiene unit indicates that the hexacarbonyldiiron fragment is coordinated to the azadiene. A 125 MHz ^{13}C NMR spectrum of the dinuclear complex **7b** in toluene-d_8 at 300 K shows the signals for all 16 carbon atoms of the former azadiene ligand but only one broad singlet at 210.96 ppm for the carbonyl ligands. The signals for the carbon atoms of the two aryl substituents of **7b** show only a slight change of the chemical shift compared to those of the mononuclear complex **6b**.[11] However, a major change of the chemical shift is observed for two of the signals for the azadiene unit of complex **6b**. In the ^{13}C NMR spectrum of complex **6b**, the three CH signals for C2, C3, and C4 appear at 105.03, 73.81, and 62.48 ppm.[11] The ^{13}C NMR and the DEPT spectrum of the dinuclear complex **7b** exhibit a signal at 76.10 ppm for a CH (C3) but also a signal at 75.57 ppm for a CH_2 (C2) and at 188.02 ppm for a C (C4). From these data it was concluded that a 1,3-hydrogen shift from C4 to C2 generating a methylene group at C2 has occurred. The novel hexacarbonyldiiron complex was assigned structure **7b** with a coordination of C4 to both iron atoms. This arrangement rationalizes the drastic downfield shift observed for this carbon atom in the ^{13}C NMR spectrum.

A ^{13}C NMR spectrum of complex **7b** at −60 °C shows the six signals for the six carbonyl ligands (Figure 2).

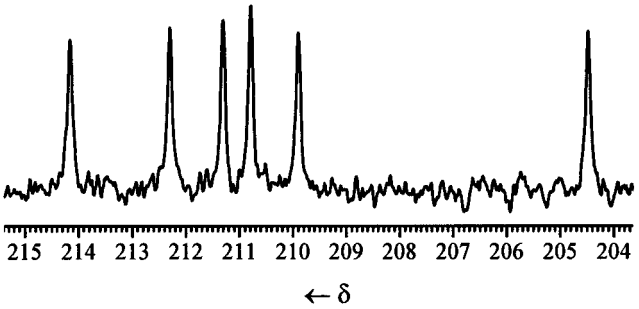


Figure 2. ^{13}C NMR spectrum of **7b** at −60 °C in the metal carbonyl region (125 MHz, toluene-d_8).

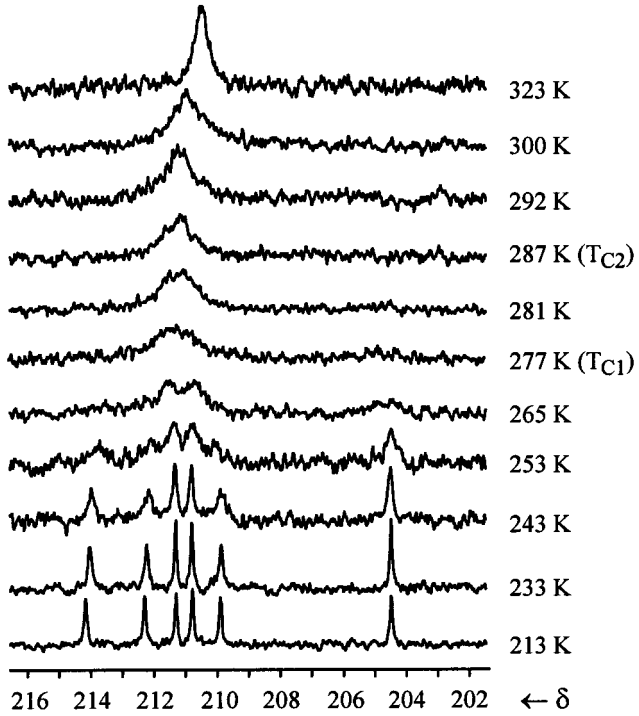


Figure 3. Dynamic ^{13}C NMR spectra of **7b** in the metal carbonyl region (125 MHz, toluene-d_8).

Obviously, the fluxionality of the hexacarbonyldiiron complex **7b** leading to equivalency of all six carbonyl ligands at room temperature is sufficiently slow on the NMR time scale at low temperature, leading to a rigid structure with six distinguishable carbonyl ligands. The variable-temperature NMR spectra reveal that on warming complex **7b** undergoes two successive coalescence events (Figure 3).

We determined the activation barriers for the two fluxional processes of complex **7b** by dynamic ^{13}C NMR spectroscopy at 125 MHz in deuterated toluene. The coalescence temperatures for the low-temperature process (T_{C1} = 277 K) and for the high-temperature process (T_{C2} = 287 K) could be determined from these variable-temperature NMR spectra with a tolerance of ±10 K, and the values for $\delta\nu$ were taken from the low-temperature spectrum at 213 K ($\delta\nu_1$ = 535 Hz and $\delta\nu_2$ = 859 Hz). Using the equation[16] $\Delta G^{\ddagger} = RT_C\,[22.96 + \ln(T_C/\delta\nu)]$, the free enthalpies of activation for the intramolecular exchange of the carbonyl ligands at the two tricarbonyliron fragments could be calculated: $\Delta G_1^{\ddagger}$ = 12.6 ± 0.5 kcal/mol and $\Delta G_2^{\ddagger}$ = 13.1 ± 0.5 kcal/mol. For

(16) Günther, H. *NMR−Spektroskopie*, 3rd ed.; Thieme Verlag: Stuttgart, 1992; p 310.

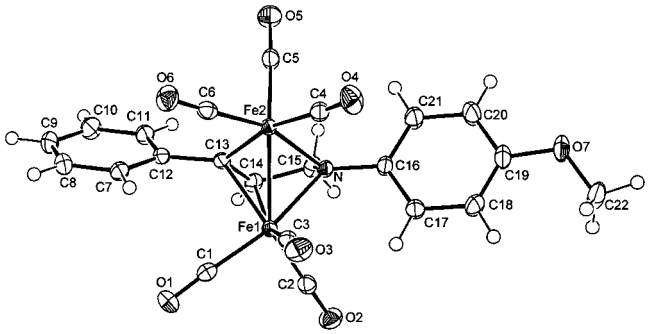


Figure 4. Molecular structure of **7b** (ORTEP plot at the 50% probability level, arbitrary numbering).

comparison, the activation barrier for the turnstile rotation of the tricarbonyliron fragment in complex **6b** was previously determined: $\Delta G^{\ddagger} = 13.5 \pm 0.3$ kcal/mol.[11,17] We propose that the fluxional behavior of the hexacarbonyldiiron complex **7b** is based on two successive coalescence events, similar to the dynamic process reported for related hexacarbonyldiruthenium complexes.[18]

Complex **7b** is the first example of a hexacarbonyldiiron complex of a cinnamaldehyde imine. Related hexacarbonyldiiron complexes of imines from aryl and heteroaryl aldehydes[19] and hexacarbonyldiruthenium complexes of imines from α,β-unsaturated aldehydes were previously reported.[18] The structure for complex **7b** was additionally confirmed by an X-ray crystal structure determination (Figure 4, Tables 5 and 6).[20]

Crystallization of the dinuclear complex **7b** from pentane/ether (15:1) at −30 °C under an argon atmosphere in a glovebox provided red-brown crystals suitable for X-ray analysis. The molecular structure of the cluster **7b**, which crystallizes in the space group $P\bar{1}$, is shown in Figure 4. The Fe−Fe bond length is 2.47 Å and almost the same as that found in nonacarbonyldiiron (2.46 Å). In the X-ray analysis of **7b**, all hydrogen atoms were determined by Fourier difference calculation and refined isotropically. The structure determination confirms the 1,3-hydrogen shift from the β-position of the α,β-unsaturated imine to the carbon atom of the imine group. This hydrogen shift results in a formal reduction of the imine bond. Thus, the dinuclear cluster **7b** could be formally described as follows: Fe1, which has a formal oxidation state of 0, is η^2-coordinated to the carbon−carbon double bond and η^1-coordinated to the nitrogen atom. Fe2 is bound to the vinyl carbon atom C13 and to the nitrogen atom and has a formal oxidation state of +II.

Table 5. Crystal Data and Structure Refinement for 7b

Crystal Data	
empirical formula	$C_{22}H_{15}Fe_2NO_7$
fw	517.04
cryst size [mm]	0.96 × 0.4 × 0.36
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a [Å]	7.8296(11)
b [Å]	11.475(2)
c [Å]	12.929(2)
α [deg]	77.57(2)
β [deg]	73.42(2)
γ [deg]	73.657(13)
vol [Å^3]	1056.7(3)
Z	2
density (calcd) [Mg/m^3]	1.625
abs coeff [mm^{-1}]	1.378
F (000)	524
Data Collection	
diffractometer	STOE STADI-4
radiation	Mo Kα (λ = 0.710 69 Å)
temp [K]	150(1)
monochromator	graphite
θ range for data collection [deg]	1.66−25.00
index ranges	$-8 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 15$
no. of reflns collected	5941
no. of indep reflns	3721 [R(int) = 0.0108]
Solution and Refinement	
solution method	direct methods (SHELXS-86)
refinement method	full-matrix least-squares on F^2 (SHELXL-93)
data/restraints/params	3719/0/350
data:parameter ratio	10.6:1
goodness-of-fit on F^2	1.138
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0250$, w$R_2 = 0.0687$
R indices (all data)	$R_1 = 0.0266$, w$R_2 = 0.0706$
ext coeff	0.0099(10)
largest diff peak and hole [e/Å^3]	0.615 and −0.360

Table 6. Bond Lengths [Å] for 7b

Fe(1)−C(3)	1.791(2)	C(7)−C(12)	1.398(3)
Fe(1)−C(1)	1.802(2)	C(8)−C(9)	1.389(3)
Fe(1)−C(2)	1.812(2)	C(9)−C(10)	1.385(3)
Fe(1)−N	1.979(2)	C(10)−C(11)	1.388(3)
Fe(1)−C(13)	2.132(2)	C(11)−C(12)	1.402(3)
Fe(1)−C(14)	2.169(2)	C(12)−C(13)	1.490(3)
Fe(1)−Fe(2)	2.4704(6)	C(13)−C(14)	1.391(3)
Fe(2)−C(5)	1.778(2)	C(14)−C(15)	1.501(3)
Fe(2)−C(6)	1.790(2)	C(15)−N	1.483(2)
Fe(2)−C(4)	1.834(2)	N−C(16)	1.444(2)
Fe(2)−N	1.971(2)	C(16)−C(17)	1.373(3)
Fe(2)−C(13)	1.975(2)	C(16)−C(21)	1.392(3)
C(1)−O(1)	1.139(3)	C(17)−C(18)	1.391(3)
C(2)−O(2)	1.135(3)	C(18)−C(19)	1.376(3)
C(3)−O(3)	1.145(2)	C(19)−O(7)	1.373(2)
C(4)−O(4)	1.134(2)	C(19)−C(20)	1.389(3)
C(5)−O(5)	1.142(3)	C(20)−C(21)	1.378(3)
C(6)−O(6)	1.141(2)	O(7)−C(22)	1.417(3)
C(7)−C(8)	1.386(3)		

We next examined the question of whether the tricarbonyliron complex **6b** and the hexacarbonyldiiron complex **7b** are intermediates of the catalytic complexation of cyclohexadiene **1** with pentacarbonyliron using **2b** as the catalyst. The (η^4-1-azabuta-1,3-diene)iron complex **6b** was shown to represent a highly efficient tricarbonyliron transfer reagent in the stoichiometric reaction with **1**.[9−11] It was, therefore, expected that complex **6b** is an important intermediate of the catalytic complexation. In fact, a catalytic complexation of **1** to afford **3** could be achieved as well by using the azadiene complex **6b** as the catalyst under conditions identical to those described above for **2b** (Scheme 6).

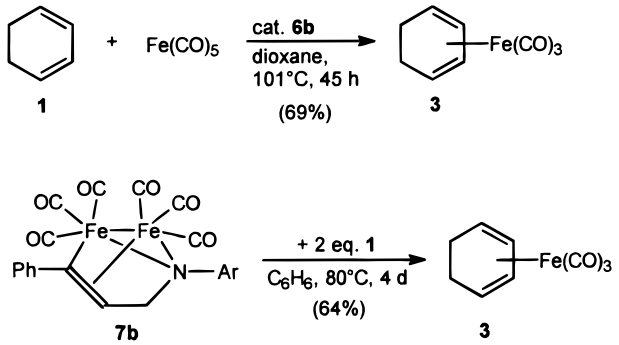
(17) Knölker, H.-J.; Goesmann, H.; Gonser, P. *Tetrahedron Lett.* **1996**, *37*, 6543.

(18) Mul, W. P.; Elsevier, C. J.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1991**, *10*, 2247. Imhof, W. *J. Chem. Soc., Dalton Trans.* **1996**, 1429.

(19) Bagga, M. M.; Pauson, P. L.; Preston, F. J.; Reed, R. I. *J. Chem. Soc., Chem. Commun.* **1965**, 543. Baikie, P. E.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1966**, 707. Nametkin, N. S.; Tyurin, V. D.; Trusov, V. V.; Nekhaev, A. I.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1986**, *302*, 243. Imhof, W. *J. Organomet. Chem.* **1997**, *533*, 31. Imhof, W. *J. Organomet. Chem.* **1997**, *541*, 109. Wang, D.-L.; Hwang, W.-S.; Liang, L.-C.; Wang, L.-I.; Lee, L.; Chiang, M. Y. *Organometallics* **1997**, *16*, 3109.

(20) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223336−033; e-mail deposit@ccdc.cam.ac.uk).

Scheme 6. Complexation of Cyclohexadiene 1 Using Complexes 6b or 7b

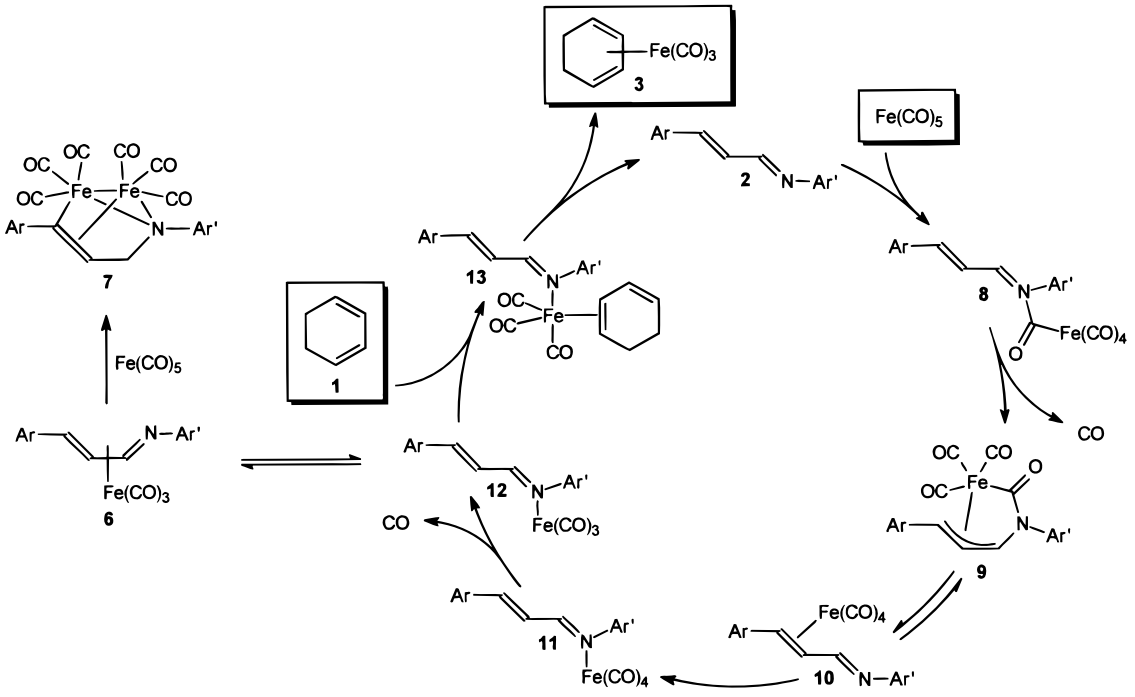


No catalytic activity was detected for the hexacarbonyldiiron complex **7b** in the complexation of cyclohexadiene **1**. However, it was found that complex **7b** acts as a tricarbonyliron transfer reagent in a stoichiometric reaction with **1** in benzene at reflux. In this transfer reaction the hexacarbonyldiiron complex **7b** delivers only one of the two tricarbonyliron fragments to form complex **3** in 64% yield. Obviously, only the tricarbonyliron fragment which is η^2-coordinated to the carbon−carbon double bond and η^1-coordinated to the nitrogen atom can be transferred in this process. Neither the mononuclear tricarbonyliron complex **6b** nor the free azadiene **2b** could be isolated from the reaction mixture after the transfer was completed. The release of one tricarbonyliron fragment is associated with decomposition of the residual iron complex. From these observations it can be concluded that the redox reaction between the imine group and one of the iron atoms is irreversible and that the formation of the hexacarbonyldiiron complex is a side reaction leading to destruction of the catalyst. However, using the optimized reaction conditions for the catalytic complexation described above, this pathway is in general not significant.

On the basis of the experiments described above and additional mechanistic investigations,[21] we propose the following mechanism for the azadiene-catalyzed complexation of cyclohexadiene with pentacarbonyliron (Scheme 7). Nucleophilic attack of the imine nitrogen of the azadiene **2** at one of the carbonyl ligands of pentacarbonyliron generates the (carbamoyl)tetracarbonyliron complex **8**. Subsequent intramolecular displacement of a carbonyl ligand by the carbon−carbon double bond of the azadiene provides the (η^3-allyl)-(carbamoyl)tricarbonyliron complex **9**, which isomerizes to the [(3−4-η)-1-azabuta-1,3-diene]tetracarbonyliron complex **10**.[21,22] Haptotropic migration of the tetracarbonyliron fragment affords the [(1-η)-1-azabuta-1,3-diene]tetracarbonyliron complex **11**.[21,22] Thermally induced loss of a second carbonyl ligand at the stage of complex **11** generates the [(1-η)-1-azabuta-1,3-diene]-tricarbonyliron complex **12**, which represents the reactive 16-electron intermediate of the catalytic cycle. Complex **12** is in equilibrium with the stable 18-electron [(1−4-η)-1-azabuta-1,3-diene]tricarbonyliron complex **6** by haptotropic migration of the tricarbonyliron fragment.[23,24] Further reaction of complex **6** with pentacarbonyliron provides the hexacarbonyldiiron complex **7** and thus, as shown above, leads to loss of catalyst. On the other hand, the vacant coordination site of the 16-electron complex **12** can be occupied by η^2-coordination of cyclohexadiene **1** to afford the [(1-η)-1-azabuta-1,3-diene]tricarbonyl[(1−2-η)cyclohexa-1,3-diene]iron complex **13**, which represents the crucial intermediate of the catalytic complexation. We propose for the 18-electron complex **13** a trigonal-bipyramidal structure with the η^2-coordinated cyclohexa-1,3-diene in an equatorial and the η^1-coordinated 1-azabuta-1,3-diene in an axial position. Loss of the azadiene from complex **13** regenerates the catalyst **2**, and subsequent haptotropic migration of the metal fragment provides the product **3**.

The proposed mechanism is supported by the following experimental observations: (1) The azadiene-catalyzed complexation of cyclohexa-1,3-diene with pen-

Scheme 7. Proposed Mechanism for the Catalytic Complexation



tacarbonyliron occurs quantitatively at a temperature (dioxane, 101 °C) that is 40 °C lower than that used for the conventional uncatalyzed complexation (di-*n*-butyl ether, 143 °C). This fact strongly suggests that the catalytic cycle is started by a nucleophilic attack of the azadiene nitrogen at the carbon monoxide ligand ("associative mechanism") rather than by an initial loss of carbon monoxide and formation of a 16-electron tetracarbonyliron fragment ("dissociative mechanism"). (2) The imine of benzaldehyde and *p*-anisidine does not catalyze the complexation of cyclohexa-1,3-diene with pentacarbonyliron. This result demonstrates that the additional carbon−carbon double bond present in catalyst **2b** is required for the internal displacement of the first carbon monoxide ligand. (3) The turnover of the various azadiene catalysts **2** in the catalytic complexation of **1** (see Table 3) does not correlate with the transfer rate of the corresponding (η^4-azadiene)tricarbonyliron complexes in the stoichiometric reaction with **1** (compare Table 1 in ref 11). In the catalytic complexation, the azadienes **2c**, **2f**, **2h**, **2k**, **2m**, and **2p** resulting from *ortho*-methoxy-substituted arylamines represent the most efficient catalysts. The high activities observed for these catalysts are believed to result from internal displacement of a carbon monoxide ligand by the *ortho*-methoxy group at the stage of the [(1-η)-1-azabuta-1,3-diene]tetracarbonyliron complex **11**. Stabilization of the 16-electron intermediate **12** is possible by coordination of the oxygen to the iron atom, thus forming an 18-electron chelate complex. (4) Previous kinetic studies on ligand exchange reactions at [(1−4-η)-1-azabuta-1,3-diene]tricarbonyliron complexes **6** with triphenylphosphine also suggest a 16-electron [(1-η)-1-azabuta-1,3-diene]tricarbonyliron complex **12** as an intermediate.[25] (5) Asymmetric inductions are feasible in the catalytic complexation of prochiral cyclohexa-1,3-dienes by using chiral azadiene catalysts.[26] This result suggests an intermediate where both the cyclohexa-1,3-diene and the azadiene catalyst are bound to the same metal center as proposed for complex **13**.

A detailed study of the mechanism of the azadiene-catalyzed complexation of cyclohexa-1,3-diene by the tricarbonyliron fragment is under active investigation in our laboratories[21] and will be reported in a forthcoming publication.

Conclusion

The azadiene-catalyzed complexation of cyclohexa-1,3-diene **1** with pentacarbonyliron proceeds quantitatively and represents the most efficient and convient method for the synthesis of the corresponding tricarbonyliron complex **3**. It is environmentally friendly and superior from the safety point of view since no residual pentacarbonyliron is left and no pyrophoric iron is formed. The formation of the hexacarbonyldiiron complex **7b** is shown to represent a potential pathway leading to destruction of catalyst **2b**. An extension of the present method to the catalytic complexation of other 1,3-dienes is feasible.[9] The mechanism which is proposed for the catalytic cycle opens up the way for the development of novel chiral azadienes for more efficient asymmetric catalytic complexations of prochiral cyclohexa-1,3-dienes.

Experimental Section

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). Melting points: Büchi 535. IR spectra: Bruker IFS 88 (FT-IR); $\tilde{\nu}$ in cm^{-1}. ^1H NMR and ^{13}C NMR spectra: Bruker AM-400 and Bruker DRX-500; internal standard, tetramethylsilane or the signal of the deuterated solvent; δ in ppm, coupling constants J in hertz. Mass spectra: MAT-90, at an ionization potential of 70 eV. Elemental analysis: Heraeus CHN-Rapid.

Preparation of Tricarbonyl[(1−4-η)-cyclohexa-1,3-diene]iron (3) by Complexation of Cyclohexa-1,3-diene (1) via in Situ Preparation of Stoichiometric Amounts of the Tricarbonyliron Transfer Reagent 6b. A solution of nonacarbonyldiiron (2.00 g, 5.50 mmol) and 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**2b**) (1.40 g, 5.90 mmol) in tetrahydrofuran (20 mL) was heated at 50 °C for 2 h. Cyclohexa-1,3-diene (**1**) (473 mg, 0.56 mL, 5.9 mmol) was added, and the reaction mixture was stirred for 4 h at reflux. The cold mixture was filtered over a short path of Celite, which was subsequently washed several times with diethyl ether. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane) on silica gel to afford the tricarbonyliron complex **3** (759 mg, 63%) as a yellow oil. ^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). For further spectroscopic data, see ref 11.

Preparation of Tricarbonyl[(1−4-η)-cyclohexa-1,3-diene]iron (3) by Catalytic Complexation of Cyclohexadiene 1 with Nonacarbonyldiiron Using Catalyst 2b. A solution of nonacarbonyldiiron (10.0 g, 27.5 mmol), 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**2b**) (1.63 g, 6.87 mmol), and cyclohexa-1,3-diene (**1**) (6.61 g, 7.86 mL, 82.5 mmol) in DME (50 mL) was heated at reflux for 16.5 h. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane) on silica gel to afford the tricarbonyliron complex **3** (11.9 g, 98%) as a yellow oil. For spectroscopic data, see ref 11.

Preparation of Tricarbonyl[(1−4-η)-cyclohexa-1,3-diene]iron (3) by Catalytic Complexation of Cyclohexadiene 1 with Pentacarbonyliron Using Catalyst 2b. A solution of pentacarbonyliron (2.00 g, 1.34 mL, 10.2 mmol), 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**2b**) (302 mg, 1.27 mmol), and cyclohexa-1,3-diene (**1**) (1.23 g, 1.46 mL, 15.4 mmol) in dioxane (12 mL) was heated at reflux for 45 h. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane) on silica gel to afford the tricarbonyliron complex **3** (2.24 g, 99%) as a yellow oil. For spectroscopic data, see ref 11.

Large-Scale (50 g) Preparation of Tricarbonyl[(1−4-η)-cyclohexa-1,3-diene]iron (3) by Catalytic Complexation of Cyclohexadiene 1 with Pentacarbonyliron Using Catalyst 2b. A solution of pentacarbonyliron (50.0 g, 33.6 mL, 255 mmol), 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**2b**) (7.70 g, 32.4 mmol), and cyclohexa-1,3-diene (**1**) (31.3

(21) Knölker, H.-J.; Gonser, P.; Hermann, H.; Jones, P. G.; Rohde, G.; Schnepf, A. Unpublished results.
(22) Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Gubenko, N. T.; Bokii, N. G.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1978**, *149*, 177. Nesmeyanov, A. N.; Rybin, L. V.; Stelzer, N. A.; Struchkov, Y. T.; Batsanov, A. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1979**, *182*, 399. Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1983**, *248*, 101.
(23) Knölker, H.-J.; Baum, G.; Gonser, P. *Tetrahedron Lett.* **1995**, *36*, 8191.
(24) Kokkes, M. W.; Beentjes, P. C. J.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1986**, *306*, 77.
(25) Bellachioma, G.; Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1977**, 2181. Bellachioma, G.; Reichenbach, G.; Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1980**, 634.
(26) Knölker, H.-J.; Hermann, H. *Angew. Chem.* **1996**, *108*, 363; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 341. Knölker, H.-J.; Gonser, P.; Koegler, T. *Tetrahedron Lett.* **1996**, *37*, 2405.

Table 7. Amount of Catalyst 2, and Yield of the Tricarbonyliron Complex 3

entry	**2** [mg]	**3**, yield [mg]	**3**, yield [%]
	no catalyst	7	0.7
a	118	413	41
b	135	496	50
c	135	834	83
d	142	662	66
e	156	220	22
f	152	902	90
g	169	327	33
h	169	860	86
i	134	54	5
j	135	312	31
k	152	507	51
l	152	914	91
m	173	189	19
n	169	740	74
o	152	709	71
p	132	132	13
q	166	832	83
r	155	0	0

g, 37.2 mL, 391 mmol) in dioxane (200 mL) was heated at reflux for 45 h. During the reaction a light flow of argon was directed through the apparatus. After a reaction time of 72 h, a solution of catalyst **2b** (2.00 g, 8.43 mmol) and diene **1** (4.21 g, 5.0 mL, 52.5 mmol) in dioxane (50 mL) was added. The reaction mixture was stirred at reflux for 24 h. The solvent was evaporated, pentane (200 mL) was added to the residue, and the solution was filtered over Celite to provide, after evaporation of the solvent, the tricarbonyliron complex **3** (50.2 g, 89%) as a yellow oil. For spectroscopic data, see ref 11.

Preparation of Tricarbonyl[(1−4-η)-cyclohexa-1,3-diene]iron (3) by Catalytic Complexation of Cyclohexa-1,3-diene (1) with Pentacarbonyliron Using the Catalysts 2. General Procedure. Pentacarbonyliron (891 mg, 0.60 mL, 4.55 mmol), cyclohexa-1,3-diene (**1**) (547 mg, 0.65 mL, 6.83 mmol), and dioxane (15 mL) were added to the catalyst **2** (0.125 equiv, 0.569 mmol, Table 7). The reaction mixture was heated at reflux for 14 h. The solvent was evaporated in vacuo, and the residue was subjected to flash chromatography (pentane) on silica gel to afford the tricarbonyliron complex **3** (Table 7) as a yellow oil. For spectroscopic data, see ref 11.

Preparation of the Hexacarbonyldiiron Complex 7b. (a) By Direct Complexation of 2b with Pentacarbonyliron. Pentacarbonyliron (1.19 g, 0.80 mL, 6.07 mmol) was added to a solution of 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene (**2b**) (45 mg, 0.190 mmol) in dioxane (10 mL), and the reaction mixture was heated at 90 °C for 24 h. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane/diethyl ether 10:1) on silica gel to afford, first, the hexacarbonyldiiron complex **7b** (5 mg, 5%; brown solid) followed by the more polar fraction, the tricarbonyl(η^4-1-azabuta-1,3-diene)iron complex **6b** (34 mg, 47%; red crystals).

6b: ^{1}H NMR (500 MHz, C_6D_6): δ 3.27 (s, 3 H), 3.45 (d, J = 9.4 Hz, 1 H), 5.03 (dd, J = 9.4, 2.8 Hz, 1 H), 6.41 (d, J = 2.8 Hz, 1 H), 6.64 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.96 (t, J = 7.5 Hz, 1 H), 7.06 (t, J = 7.5 Hz, 2 H), 7.14 (d, J = 7.5 Hz, 2 H). For further spectroscopic data, see ref 11.

7b: Mp ≥ 147 °C (dec). IR (drift): $\bar{\nu}$ 2963, 2898, 2839, 2062, 2045, 2029, 1985, 1973, 1954, 1603, 1504, 1466, 1443, 1416, 1261, 1095, 1023, 864, 800, 764, 706 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 3.18 (s, 3 H), 3.65 (br s, 2 H), 4.26 (s, 1 H), 6.42 (d, J = 8.8 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 7.04 (t, J = 7.6 Hz, 1 H), 7.11 (t, J = 7.6 Hz, 2 H), 7.26 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, toluene-d_8, 300 K): δ 54.78 (CH_3), 75.57 (CH_2), 76.10 (CH), 114.02 (2 CH), 122.48 (2 CH), 128.06 (CH), 128.24 (CH), 129.16 (CH), 129.48 (2 CH), 149.12 (C), 152.09 (C), 157.43 (C), 188.02 (C), 210.96 (6 CO, br). ^{13}C NMR (125 MHz, toluene-d_8, 213 K): δ 54.47 (CH_3), 75.19 (CH_2), 75.25 (CH), 113.55 (2 CH), 122.08 (2 CH), 129.63 (2 CH), 148.67 (C), 151.62 (C), 156.85 (C), 187.34 (C), 204.48 (CO), 209.89 (CO), 210.78 (CO), 211.30 (CO), 212.30 (CO), 214.16 (CO) (the signals of 3 CH groups are missing due to overlapping with signals of the solvent). ^{13}C NMR (125 MHz, toluene-d_8, 323 K): δ 54.91 (CH_3), 75.68 (CH_2), 76.35 (CH), 114.18 (2 CH), 122.61 (2 CH), 128.11 (CH), 128.28 (CH), 129.20 (CH), 129.47 (2 CH), 149.26 (C), 152.25 (C), 157.61 (C), 188.19 (C), 210.46 (6 CO, br). MS (75 °C): m/z 517 (M^+, 4), 489 (6), 461 (11), 433 (1), 405 (18), 377 (16), 349 (39), 293 (14), 238 (10), 237 (38), 236 (100), 115 (16). HRMS calcd for $C_{22}H_{15}Fe_2NO_7$, 516.9547; found, 516.9559. Anal. Calcd for $C_{22}H_{15}Fe_2NO_7$: C, 51.11; H, 2.92; N, 2.71. Found: C, 51.20; H, 3.04; N, 2.42.

(b) By Heating 6b with Pentacarbonyliron in Dioxane. Pentacarbonyliron (596 mg, 0.40 mL, 3.04 mmol) was added to a solution of complex **6b** (72 mg, 0.191 mmol) in dioxane (10 mL), and the reaction mixture was heated at 90 °C for 24 h. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane/diethyl ether 10:1) on silica gel to afford, first, the hexacarbonyldiiron complex **7b** (8 mg, 8%; brown solid, spectroscopic data, see above) followed by the more polar fraction, the tricarbonyliron complex **6b** (62 mg, 86%; red crystals).

(c) By Heating 6b with Nonacarbonyldiiron in THF. Nonacarbonyldiiron (87 mg, 0.24 mmol) was added to a solution of complex **6b** (72 mg, 0.191 mmol) in tetrahydrofuran (10 mL), and the reaction mixture was heated at 65 °C for 24 h. The solvent was evaporated, and the residue was subjected to flash chromatography (pentane/diethyl ether 10:1) on silica gel to afford, first, the hexacarbonyldiiron complex **7b** (6 mg, 6%; brown solid, spectroscopic data, see above) followed by the more polar fraction, the tricarbonyliron complex **6b** (62 mg, 86%; red crystals).

Catalytic Complexation of Cyclohexadiene 1 with Pentacarbonyliron Using the (η^4-1-Azabuta-1,3-diene)-tricarbonyliron Complex 6b as the Catalyst. A solution of pentacarbonyliron (207 mg, 139 μL, 1.06 mmol), the tricarbonyliron complex **6b** (50 mg, 0.13 mmol), and cyclohexadiene **1** (127 mg, 151 μL, 1.58 mmol) in dioxane (15 mL) was heated at reflux for 45 h. Removal of the solvent in vacuo and flash chromatography (pentane) of the residue on silica gel provided the tricarbonyliron complex **3** (181 mg, 69%) as a yellow oil. For spectroscopic data, see ref 11.

Stoichiometric Complexation of Cyclohexadiene 1 Using the Hexacarbonyldiiron Complex 7b as the Transfer Reagent. A solution of the hexacarbonyldiiron complex **7b** (59 mg, 0.114 mmol) and cyclohexadiene **1** (17.4 mg, 20.7 μL, 0.217 mmol) in benzene (15 mL) was heated at 80 °C for 4 days. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (pentane) on silica gel to afford the iron complex **3** (16 mg, 64%) as a yellow oil. For spectroscopic data, see ref 11.

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Supporting Information Available: Tables of atomic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for the crystal structure of **7b** and figures of the ^{1}H NMR spectrum for **6b** and the variable temperature ^{13}C NMR spectra for **7b** (13 pages). Ordering information is given on any current masthead page.

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