Transition Metal Complexes in Organic Synthesis, Part 49.[1] Development of Novel Chiral Catalysts for the Asymmetric Catalytic Complexation of Prochiral Cyclohexa-1,3-dienes by the Tricarbonyliron Fragment - Mechanism of the Asymmetric Catalysis and Involvement of a Dinuclear Iron Cluster

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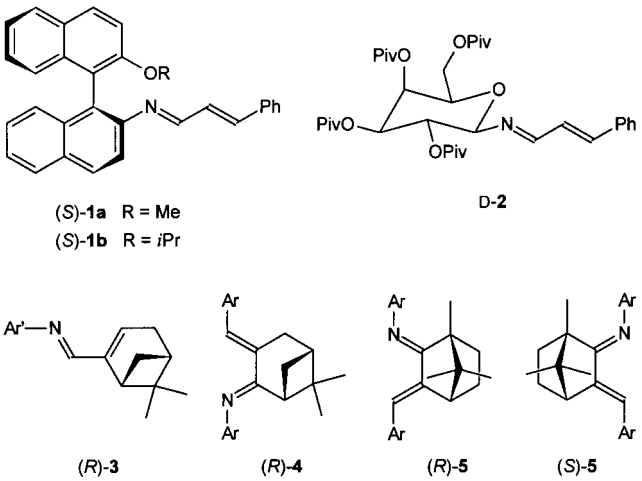
Received 15 January 1999

Abstract: Planar-chiral tricarbonyliron-diene complexes are obtained quantitatively in up to 73% *ee* by asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes. A series of novel chiral 1-azabuta-1,3-diene catalysts is investigated. The mechanism is shown to involve at least in some cases dinuclear iron cluster compounds which lead to a lower asymmetric induction.

Key words: asymmetric catalysis, chirality, cluster, diene complexes, iron compounds

Tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes represent versatile starting materials for stereoselective organic synthesis.[2] For applications to enantioselective synthesis an easy access to enantiopure tricarbonyliron complexes is required. The synthesis of optically active tricarbonyliron complexes was usually achieved by diastereoselective complexation of enantiopure dienes,[3] the separation of racemic complexes by enzymatic reactions[4] or *via* diastereomeric intermediates,[5] and the enantioselective complexation of prochiral dienes by chiral tricarbonyliron transfer reagents.[6] Using tricarbonyliron transfer reagents mild reaction conditions can be employed for the complexation of dienes by the metal fragment.[7] Recently, we reported that (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes represent a novel class of highly efficient tricarbonyliron transfer reagents.[8,9] They offer the special advantage that the free 1-azabuta-1,3-dienes can be used as catalysts for the complexation of dienes with either pentacarbonyliron or nonacarbonyldiiron.[8,10] Using chiral azabutadienes the first asymmetric catalytic complexation of prochiral dienes became feasible.[11] In the present paper we describe the development of novel catalysts and an optimization of the asymmetric catalysis based on mechanistic considerations.

Three different types of chiral azadienes **1**-**5** were synthesized and used as catalysts for the asymmetric complexation (Scheme 1). The first type was obtained by reaction of chiral amines with cinnamaldehyde. Condensation of (*S*)-2-amino-2'-methoxy-1,1'-binaphthyl[12] and of the corresponding 2'-isopropoxy derivative with cinnamaldehyde at room temperature in the presence of 4 Å molecular sieves afforded the axially chiral azadienes (*S*)-**1a** (90% yield) and (*S*)-**1b** (46% yield), respectively. The 1-pyranosylazadiene D-**2** was prepared by acetic acid catalyzed reaction of 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosylamine[13] with cinnamaldehyde in dry isopropanol at room temperature (53% yield). Combination of the chiral α,β-unsaturated aldehyde (1*R*)-(-)-myrtenal with *o*-anisidine provided the second type of chiral azabutadiene catalyst, (*R*)-**3** (75% yield). The third type of chiral azabutadiene was synthesized starting from a chiral bicyclic ketone by a three-component-coupling consisting of aldol condensation with *p*-methoxybenzaldehyde followed by condensation with *p*-anisidine to the unsaturated imine. Thus, (1*R*)-(+)-nopinone provided (*R*)-**4** (76% overall yield) and (1*R*)-(+)- and (1*S*)-(-)camphor gave (*R*)-**5** and (*S*)-**5**, respectively (69% overall yield).



Scheme 1. Structures of the chiral azadiene catalysts employed (Piv = Me_3CCO, Ar' = 2-$MeOC_6H_4$, Ar = 4-$MeOC_6H_4$).

The asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene (**6a**) as the prochiral substrate using the chiral azadiene catalysts (*S*)-**1a** to (*S*)-**5** was performed under a standard set of reactions conditions (4 eq pentacarbonyliron, 0.25 eq of catalyst, benzene, 80°C) (Table 1). The pure enantiomers of complex **7a** are stable under

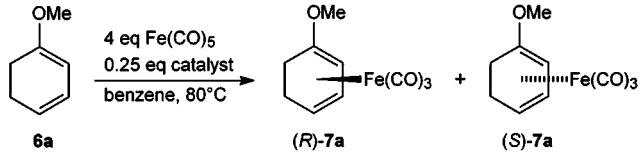


Table 1. Asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene (**6a**) with pentacarbonyliron using the chiral azadiene catalysts (*S*)-**1** to (*S*)-**5**.

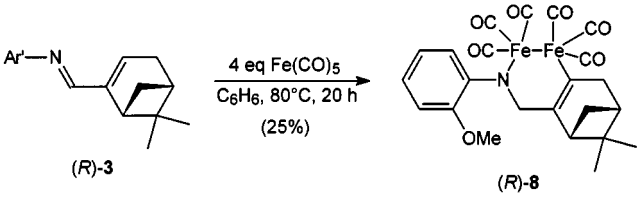
Catalyst	Reaction Time [d]	**7a**, Yield [%]	*ee* [%] [a]
(*S*)-**1a**	1.75	87	25 (*R*)
(*S*)-**1b**	2	81	32 (*R*)
D-**2**	2	38	28 (*R*)
(*R*)-**3**	3	95	33 (*R*)
(*R*)-**8**	2	47	11 (*R*)
(*R*)-**4**	5	97	38 (*S*)
(*R*)-**5**	12	99	73 (*S*)
(*S*)-**5**	12	99	73 (*R*)

[a] Enantiomeric excess as determined by chiral HPLC at a permethylated β-cyclodextrin column (abs. config. of the excess enantiomer).[14]

the reactions conditions.[11] Thus, using a certain amount of catalyst, quantitative yields are obtained in most of the cases by simple extension of the reaction time while the asymmetric induction remains constant. In order to come to reasonable reaction times we applied 25 mol-% of the catalyst, which can be recycled during workup. The enantiomeric excess of the planar chiral tricarbonyliron complex **7a** was determined by separation of the two enantiomers (*S*)-**7a** and (*R*)-**7a** at a permethylated β-cyclodextrin column.[14]

The axially chiral 1-binaphthyl azadienes (*S*)-**1a** and (*S*)-**1b** provided complex **7a** in excellent yields and led preferentially to the formation of the *R* enantiomer in 25% *ee* and 32% *ee*, respectively. From these results we concluded that an increase of the sterical demand of the 2-alkoxy substituent in the binaphthyl moiety leads to a slightly improved asymmetric induction, however at the expense of catalyst activity. A similar degree of asymmetric induction (28% *ee* of the *R* enantiomer) was observed using the 1-pyranosylazadiene D-**2**. In this case the catalyst activity is significantly lower. After the same reaction time of 2 days, the yield of complex **7a** was only 38% and the corresponding (η^4-1-azabuta-1,3-diene)tricarbonyliron complex of D-**2** was isolated in 31% yield as by-product.

In compound (*R*)-**3**, representing the second class of chiral azadiene catalysts investigated for asymmetric induction, the chiral auxiliary is annulated at the 3,4-position of the azadiene. Reaction of **6a** with pentacarbonyliron and catalyst (*R*)-**3** provided complex **7a** after 3 d in 95% yield with 33% *ee* of the *R* enantiomer. As a by-product of this asymmetric catalytic complexation we isolated the dinuclear iron cluster (*R*)-**8** in up to 31% yield dependent on the reaction time and the scale. The chiral hexacarbonyldiiron complex (*R*)-**8** was obtained more easily by direct reaction of (*R*)-**3** with pentacarbonyliron using conditions identical to those of the catalytic complexation (Scheme 2). The structural assignment for (*R*)-**8** is based on spectral data,[15] an elemental analysis,[15] and has been confirmed by an X-ray crystal structure determination.[16]



Scheme 2. Preparation of the hexacarbonyldiiron complex (*R*)-**8**.

In the course of our studies of the catalytic complexation of cyclohexa-1,3-diene we recently described the first synthesis of the hexacarbonyldiiron complex of a cinnamaldehyde imine.[10] Hexacarbonyldiiron complexes of aryl and heteroaryl aldehyde imines were previously reported.[17] We could demonstrate that the dinuclear iron cluster resulting from the reaction of pentacarbonyliron and 1-*p*-anisyl-4-phenyl-1-azabuta-1,3-diene transfers one tricarbonyliron fragment to cyclohexa-1,3-diene in a stoichiometric process, but does not show a catalytic activity in the complexation of cyclohexa-1,3-diene with pentacarbonyliron.[10] In the present case however, the hexacarbonyldiiron complex (*R*)-**8** is a catalyst for the complexation of 1-methoxycyclohexa-1,3-diene (**6a**) with pentacarbonyliron (Table 1). This difference in behavior of the cluster (*R*)-**8** is believed to arise from the *ortho*-methoxy group of the aryl ring which may be capable of stabilizing reactive intermediates of the catalytic cycle by chelation. It was clearly shown that the catalytic activity and the asymmetric induction of the cluster (*R*)-**8** is lower than obtained with the azadiene (*R*)-**3**. Using the cluster (*R*)-**8** as catalyst under the standard reaction conditions for 2 d, complex **7a** was obtained in 47% yield with 11% *ee* of the *R* enantiomer and 70% of (*R*)-**8** was reisolated.

The characteristic structural feature of the third type of chiral azadiene catalysts is a fixed s-*cis* conformation of the azadiene because the bicyclic terpenoid framework is annulated at the 2,3-position. Complexation of **6a** with pentacarbonyliron in the presence of catalytic amounts of (*R*)-**4** led quantitatively to complex **7a** with 38% *ee* of the *S* enantiomer. The camphor-derived chiral azadienes provided the highest asymmetric inductions for the complexation of **6a**. Reaction of **6a** with pentacarbonyliron for 12 days using the (*R*)-camphor derived chiral azadiene (*R*)-**5** afforded quantitatively complex (*S*)-**7a** with 73% *ee*. Catalyst (*S*)-**5** provided complex (*R*)-**7a** in the same *ee* as determined by chiral HPLC.

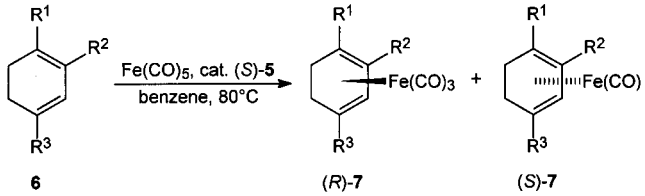


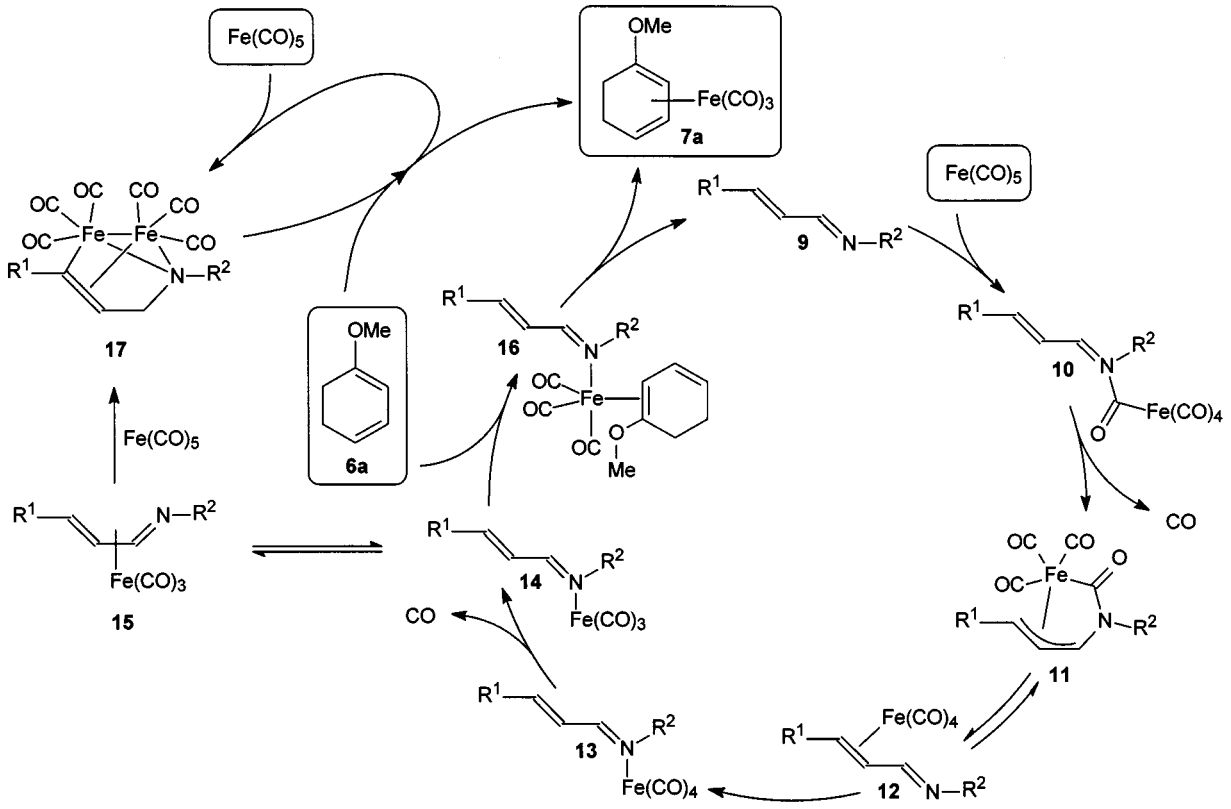
Table 2. Results of the asymmetric catalytic complexation of the prochiral cyclohexa-1,3-dienes **6** using the catalyst (*S*)-**5**.[a]

	R^1	R^2	R^3	Time [d]	**7**, Yield [%]	*ee* [%] [b]
a	OMe	H	H	12	99	73 (*R*)
b	OMe	H	Me	14	57	45 (*R*)
c	OMe	H	CH_2CO_2Me	7	99	24 (*R*)
d	CO_2Me	H	H	7	61	36 (1)
e	H	CO_2Me	H	7	12	45 (2)
f	O*i*Pr	H	H	14	78	62 (2)

[a] Reaction conditions: 1 eq **6**, 2.7-5.3 eq pentacarbonyliron, 0.17-0.33 eq catalyst (*S*)-**5**. [b] Enantiomeric excess and absolute configuration of the excess enantiomer, or respectively, relative polarity of the excess enantiomer (1 = less polar, 2 = more polar peak) on the cyclodextrin column specified below. Determinations of the *ee*: for **7a**, **7c**, **7d**, and **7f** by chiral HPLC at a permethylated β-cyclodextrin column;[14] for **7b** by correlation of the value for optical rotation;[6] for **7e** by chiral HPLC at a non-methylated β-cyclodextrin column.[14]

The azadiene (*S*)-**5** was used for the asymmetric catalytic complexation of a series of prochiral cyclohexa-1,3-dienes **6** with pentacarbonyliron to the tricarbonyliron complexes **7** (Table 2). The asymmetric inductions as determined by chiral HPLC were significant, although no optimization for each single case was executed.

We propose the following mechanism to rationalize the asymmetric catalytic complexation of prochiral cyclohexadienes, *e.g.* **6a**, by using chiral azadienes **9** (Scheme 3). Nucleophilic attack of the imine **9** at a carbonyl ligand of pentacarbonyliron generates the (carbamoyl)tetracarbonyliron complex **10** which is converted to the (η^3-allyl)(carbamoyl)tricarbonyliron complex **11** by intramolecular ligand displacement. Complex **11** isomerizes by a sequence of two haptotropic migrations *via* the intermediate (η^2-olefin)tetracarbonyliron complex **12** to the (η^1-imine)tetracarbonyliron complex **13**. A thermally induced loss of a second carbon monoxide provides the (η^1-imine)tricarbonyliron complex **14**. The 16-electron complex **14** represents the reactive intermediate of the catalytic cycle. The vacant coordination site can be filled in an intramolecular process by haptotropic migration (η^1 to η^4) of the metal fragment generating the (η^4-azadiene)tricarbonyliron complex **15**. Alternatively, one of the double bonds of cyclohexadiene **6a** could bind to the iron atom. This coordination presumably takes place at the more electron-rich double bond and leads to the 18-electron intermediate **16**. We assume for complex **16** a trigonal-bipyramidal structure with the (1-2-η)-1-methoxycyclohexa-



Scheme 3. Mechanism for the Asymmetric Catalytic Complexation.

1,3-diene ligand in equatorial and the (1-η)-1-azabuta-1,3-diene ligand in axial position. At this stage of the catalytic cycle the enantioselection is achieved. The coordination of the metal center to one of the two enantiotopic faces of the methoxy-substituted double bond leads to diastereoisomeric complexes which are differentiated. Loss of the azadiene from this intermediate regenerates the catalyst **9**. A haptotropic migration (η^2 to η^4) of the tricarbonyliron fragment provides complex **7a**. This final isomerization occurs with retention of configuration, since the metal remains bound to the same enantiotopic face of the prochiral ligand. The course of this first catalytic cycle is supported by previous work on (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes[18] and our own mechanistic studies.[8c,10,19]

Reaction of the chiral (η^4-azadiene)tricarbonyliron complex **15** with additional pentacarbonyliron affords the chiral diiron cluster **17**, which also represents a catalyst for the asymmetric complexation of **6a** with pentacarbonyliron. However, our initial results indicate that the asymmetric induction *via* this second catalytic cycle is lower. This observation is of high importance for the future design of novel more efficient chiral catalysts and for optimizing the reaction conditions of the asymmetric catalytic complexation.

Experimental Procedure

A solution of **6a** (220 mg, 2.00 mmol), pentacarbonyliron (1.05 mL, 1.57 g, 8.01 mmol), and (*R*)-**5** or (*S*)-**5** (188 mg, 0.5 mmol) in anhydrous and degassed benzene (30 mL) was heated at reflux for 12 d under an argon atmosphere. The cold reaction mixture was filtered through a short path of Celite, which was subsequently washed several times with diethyl ether. Evaporation of the solvent and flash chromatography (pentane) of the residue on silica gel afforded the complexes (*S*)-**7a** ($[\alpha]_D^{20}$ = +108.0, *c* = 1.00, $CHCl_3$) or (*R*)-**7a** (($[\alpha]_D^{20}$ = -106.2, *c* = 1.07, $CHCl_3$), respectively (498 mg, 99%) as yellow oils. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.66-1.72 (m, 2 H), 1.75-1.84 (m, 1 H), 2.24 (m, 1 H), 2.95 (m, 1 H), 3.46 (s, 3 H), 5.04 (dd, *J* = 6.3, 4.5 Hz, 1 H), 5.32 (d, *J* = 4.5 Hz, 1 H).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (Gerhard-Hess-Förderpreis) and the Fonds der Chemischen Industrie. We are grateful to Professor H. Kunz, Universität Mainz, for a generous gift of 2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosylamine. We thank the BASF AG, Ludwigshafen, for constant supply with pentacarbonyliron.

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(15) (*R*)-**8**: mp 123-124°C; $[\alpha]_D^{20}$ = +1418.4 (*c* = 1.0, $CHCl_3$); IR (drift): = 3000, 2927, 2060, 2021, 2011, 1969, 1590, 1487, 1279, 1253, 1119, 1025 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (d, *J* = 8.6 Hz, 1 H), 1.17 (s, 3 H), 1.35 (s, 3 H), 2.08 (m, 1 H), 2.43 (m, 2 H), 3.21 (d, *J* = 18.0 Hz, 1 H), 3.32 (d, *J* = 18.0 Hz, 1 H), 3.47 (br s, 1 H), 3.83 (s, 3 H), 4.25 (br s, 1 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 6.78 (t, *J* = 8.0 Hz, 1 H), 6.97 (m, 1 H), 7.08 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 22.07 (CH_3), 26.35 (CH_3), 32.66 (CH_2), 41.45 (C), 43.33 (CH), 43.61 (CH_2), 44.72 (CH), 54.48 (CH_3), 78.15 (CH_2), 110.67 (CH), 117.12 (C), 120.26 (CH), 126.18 (CH), 126.78 (CH), 145.75 (C), 153.44 (C), 168.07 (C), 206.48 (CO), 209.79 (CO), 211.92 (CO), 212.01 (CO); analysis calcd. for $C_{23}H_{21}Fe_2NO_7$: C 51.62, H 3.96, N 2.62; found: C 51.50, H 4.09, N 2.97.

(16) X-ray crystal structure analysis of (*R*)-**8**: $C_{46}H_{42}Fe_4N_2O_{14}$, monoclinic (twin), space group *C*2, *a* = 34.426(7), *b* = 8.971(2), *c* = 15.005(3) Å, *V* = 4634.1(16) Å^3, *Z* = 4, *T* = 200(2) K, ρ_{calcd} = 1.534 g cm^{-3}, μ = 1.296 mm^{-1}, λ = 0.71073 Å, *c* range: 2.71-

25.00°; 7662 independent reflections; refinement method: full-matrix least squares on F^2; final R indices [I>2σ(I)]: R_1 = 0.0650, wR_2 = 0.1430, abs. configuration by refinement of the Flack parameter: χ = 0.00(3), maximal residual electron density: 0.905 e Å^{-3}. Programs: G. M. Sheldrick, SHELXS-86 (Göttingen **1986**), SHELXL-93 (Göttingen **1993**); E. Keller, SCHAKAL-97 (Freiburg i.Br., **1997**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112629. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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