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Diazadienes as Controlling Ligands in Catalysis, 5[1)]

Synthesis of Chiral Diazadienes R* – N = CR′ – CR′ = N – R*

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The condensation of glyoxal (as hydrate) or 2,3-butanedione with primary amines is, in principle, a simple reaction. Unfortunately, aliphatic amines with secondary or tertiary α-carbons often give unwanted addition products. Under special reaction conditions the desired diimines (**diazadienes** (dad): R* – N = CR′ – CR′ = N – R*, R′ = H, CH_3) **4**, and **6** – **8** are obtained from (*R*)-1-phenylethylamine (**1**) and (1*S*,2*S*,3*S*,5*R*)-3-(aminomethyl)pinane (**2**). Depending on the dione, a morpholinomorpholine **9** and a bioxazolidine **10** are formed from (*S*)-2-amino-1-butanol (**3**), which are bound by electron-rich metals in their isomeric dad form ((dad)$Mo(CO)_4$ **11** and **12**). The acyclic dad structure is stabilized by *O*-silylation (**14**, **15**). The (dad)iron(0) catalyzed dimerization of butadiene with these controlling ligands to 4-vinyl-1-cyclohexene occurs with an enantiomeric excess up to 16%.

Diazadiene als Steuerliganden in der Katalyse, 5[1)]

Synthese chiraler Diazadiene R* – N = CR′ – CR′ = N – R*

Die im Prinzip einfache Kondensationsreaktion von Glyoxal (als Hydrat) und 2,3-Butandion mit primären Aminen führt leider bei aliphatischen Aminen mit tertiärem bzw. sekundärem α-Kohlenstoff oftmals zu unerwünschten Additionsprodukten. Unter speziellen Synthesebedingungen können mit (*R*)-1-Phenylethylamin (**1**) und (1*S*,2*S*,3*S*,5*R*)-3-(Aminomethyl)pinan die gewünschten Diimine (**Diazadiene** (dad): R* – N = CR′ – CR′ = N – R*, R′ = H, CH_3) **4**, **6** – **8** erhalten werden. Aus (*S*)-2-Amino-1-butanol (**3**) werden je nach Dion-Komponente ein Morpholinomorpholin **9** bzw. ein Bioxazolidin **10** gebildet, die von elektronenreichen Metallen in ihrer isomeren Form als Diazadiene gebunden werden ((dad)$Mo(CO)_4$ **11** und **12**). Die offenkettige dad-Form ist durch *O*-Silylierung (**14**, **15**) stabilisierbar. Die (dad)Eisen(0)-katalysierte Dimerisierung von Butadien zu 4-Vinyl-1-cyclohexen mit diesen dad-Liganden ergibt Enantiomerenüberschüsse e.e. bis zu 16%.

Unsaturated systems of the 1,4-**d**i**aza**-1,3-**d**iene type (dad), R – N = CR′ – CR′ = N – R, show the most versatile coordination behaviour of all known conjugated dienes in metal complexes of low formal oxidation states[2)] and can act as controlling ligands in homogeneously catalyzed reactions[1,3)]. In principle, the condensation reaction of 1,2-dicarbonyl compounds with primary amines is quite simple[4)] and it seemed promising to synthesize dad ligands for enantioselective catalyses from glyoxal or biacetyl and optically active primary amines. We report here on the synthesis of chiral dads

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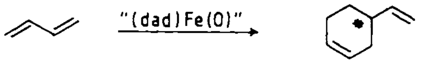
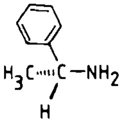
$R^*-N=CR'-CR'=N-R^*$ (R' = H, CH_3). They were successfully used in screening experiments for the enantioselective dimerization of butadiene to 4-vinyl-1-cyclohexene according to eq. (1)[5].



(1)

Synthesis of Chiral Diazadienes

The optically pure primary amines (*R*)-1-phenylethylamine (**1**), (1*S*,2*S*,3*S*,5*R*)-3-(aminomethyl)pinane (**2**) and (*S*)-2-amino-1-butanol (**3**) were chosen for the condensation with aqueous glyoxal and biacetyl.



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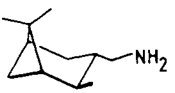

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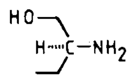

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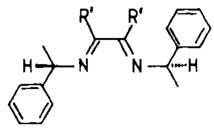
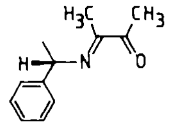
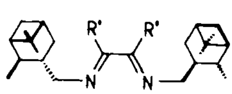


4-*RR*: R' = H
6-*RR*: R' = CH_3



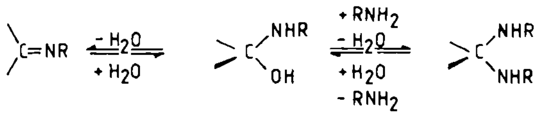
5-*R*



7: R' = H
8: R' = CH_3

Reaction of **1** with glyoxal in solvents such as methanol, chloroform and dichloromethane gave oily products, which, according to their NMR and IR spectra, contained 30–70% of the double condensation product. Unfortunately, purification could neither be accomplished by column chromatography nor by fractional crystallization.

The reaction rate was considerably increased by catalysis with formic acid, and the formation of coloured by-products was suppressed. To avoid the competing addition reaction [eq. (2)] a nonpolar solvent was used and an excess of drying agent (molecular sieve or sodium sulfate) added.



(2)

Under these conditions an 80% yield of *N,N'*-bis[(*R*)-1-phenylethyl]glyoxal diimine (**4-*RR***) is obtained at room temperature. Pure **4-*RR*** shows no tendency to crystallize, while in a similar experiment with racemic **1** a crystalline product **4** (m.p. 68 °C) was obtained. NMR showed that **4** contained the *meso* compound **4-*RS*** in slight excess.

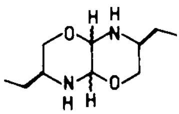
van der Poel and *van Koten* investigated the reaction of **1**-*S* with biacetyl (2,3-butanedione) and described the synthesis of the monocondensation product **5**-*S*. The dad **6**-*S* could only be observed by NMR in solution[6]. **6**-*S* was recently described by *Brunner* et al. without further characterization[7].

The condensation of **1** with biacetyl is indeed sufficiently slow to be easily followed by NMR in solution. The reaction rate increases with temperature, but the equilibrium between **5**-*R* and **6**-*RR* is displaced in favour of the imino-oxo compound **5**-*R*. Under the conditions described for the synthesis of **4** the *N,N'*-bis[(*R*)-1-phenylethyl]biacetyl diimine (**6**-*RR*) was obtained in 66% yield after 6 days stirring at 18 °C. In contrast to **4**-*RR*, **6**-*RR* slowly crystallizes from hexane (m. p. 15 – 20 °C).

The problems encountered for the condensation of **1** also arise for (+)-3-(aminomethyl)pinane (**2**). The presence of the drying agent is absolutely necessary. Without an acid catalyst **7** is formed after a few hours in 75% yield as a viscous, non-crystallizing oil. The preparation of the biacetyl diimine **8** again requires acid catalysis.

Condensation of 2-Amino-1-butanol

β-Amino alcohols like **3** react with carbonyl compounds to give either azomethines (addition + 1,2-elimination) or oxazolidines (addition + 1,5-elimination)[8] with comparable thermodynamic stability[9]. The reaction of glyoxal with **3** affords a product, which shows in the infrared neither the typical ν(C=N) bands of a dad around 1640 cm^{-1} nor typical oxazolidine bands. From mass spectra, ^{1}H and ^{13}C NMR spectra and the infrared spectrum the structure **9** of a morpholinomorpholine is proposed, while with biacetyl the bioxazolidine **10** is formed. Both compounds are isomers of the desired diazadienes; they can be rearranged by thermal reaction with hexacarbonylmolybdenum. Diazadiene complexes (dad)Mo(CO)$_4$ like **11**/**12** exhibit a very characteristic and intense charge transfer absorption in the visible and four infrared active CO stretching vibrations[10].



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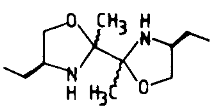

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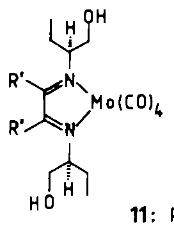


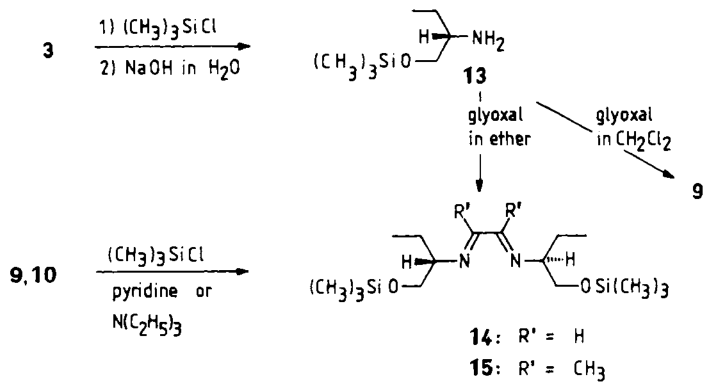
11: R' = H

12: R' = CH$_3$

As the condensation of 2-amino-1-butanol gave only the isomeric compounds **9** and **10** instead of the dads, and metal complexes such as **11** or **12** with free hydroxyl groups might give rise to undesired reactions in catalytic experiments, we tried to prepare *O*-substituted derivatives.

Alkylation of free **3** inevitably yields useless *N*-alkylated products together with the *O*-alkylamine; previous acetylation to protect the amino group, on the other hand, partially gives the *O*-acetylated compound. Alkylation of **9** or **10** with methyl iodide in alkaline medium finally affords, as expected, the *N*-methyl compounds, which do not rearrange thermally to *O*-methylated ligands when reacted with $Mo(CO)_6$ or $FeCl_2$. The alkylation of **9** or **10** with secondary or tertiary alkyl halides, to improve the tendency for alkyl migration, and subsequent reaction with metal compounds, did not result in the desired *O*-alkyl systems[11].

The *O*-trimethylsilyl derivative **13** is formed with chlorotrimethylsilane in ether followed by deprotonation. The protecting silyl group is lost, when **13** is reacted with glyoxal in methanol or dichloromethane; the product being again **9**. In diethyl ether, on the other hand, the *O,O'*-disilylated diazadiene **14** is formed [eq. (3)]. Even in ether **13** reacts with biacetyl to give **10**. However, the oxazolidine **10** can be *O*-silylated with $(CH_3)_3SiCl$ in the presence of triethylamine, yielding the dad **15**. The corresponding reaction **9** → **14** does not proceed with triethylamine but with pyridine.

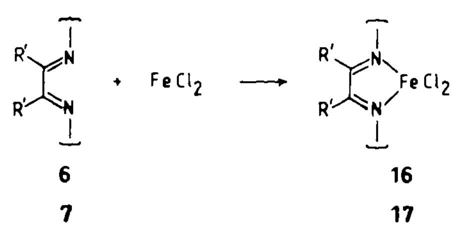


(3)

(4)

Examples for Catalytic Applications

Iron(II) chloride reacts in aprotic solvents like THF with the described diazadienes to give complexes (dad)$FeCl_2$. These violet to blue compounds exhibit two or three absorption bands between 630 – 500 nm with molar extinctions $\varepsilon = 100 - 300\ l \cdot mol^{-1} \cdot cm^{-1}$; they are monomeric non-electrolytes, as was shown for a number of achiral analogues[12].



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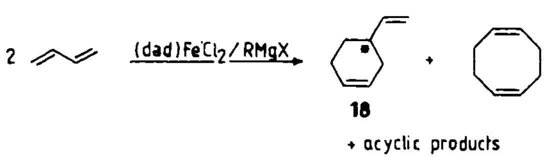

(6)

The iron dichloride adducts **16** and **17**, dissolved in ether, are added to excess butadiene and then treated with a Grignard solution. After the catalytic oligomerization has taken place, the products, mainly 4-vinyl-1-cyclohexene and 1,5-cyclooctadiene, are determined by gas chromatography.

The only chiral product of the dimer fraction is 4-vinyl-1-cyclohexene (**18**). The enantiomeric excess of **18** formed can thus be determined directly from the dimer fraction by polarimetry. The e.e. results, based on the α_D^{22}-value of 113° for **18**[13], in the two test experiments amounted to [**16**]: 9.2% e.e. **18**-*R*; [**17**]: 16.4% e.e. **18**-*S*. Attempts to correlate the absolute configuration of the excess enantiomer with the absolute configuration of the catalyst have to be based on a much wider range of chiral dad-iron catalysts[14].

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Experimental Part

Organic compounds were handled in conventional manner, while all procedures involving metal complexes and catalytic species were performed under an inert gas atmosphere. Electronic spectra were recorded on a Perkin-Elmer spectrometer 554, infrared spectra on a Perkin-Elmer spectrograph 457 or 325, or a Pye-Unicam SP 1100. ^{1}H NMR spectra measured on Varian T 60 or EM 360 spectrometers, ^{13}C NMR spectra on a Bruker HX 90 spectrometer and mass spectra on a Varian MAT CH 7. Polarimetry was performed on a Perkin-Elmer 243 instrument. The composition of mixtures from catalytic butadiene dimerization experiments was determined by gas chromatography with a Hewlett Packard Model 5840 A instrument (column 10 ft 3/8″, 20 % silicon SE 30 on chromosorb A with T-programme 3.5 min at 100 °C and 20 °C/min to 130 °C, with flow rate 25 ml/min).

Aqueous glyoxal and the optically pure amines **1** – **3** were obtained from BASF AG and the latter tested for purity by their specific rotation. Biacetyl was purchased from Merck, Darmstadt. Anhydrous iron dichloride was prepared by thermal reaction of $FeCl_3$ in chlorobenzene.

N,N′-Bis[(R)-1-phenylethyl]-1,2-ethanediimine (**4**-*RR*): 9.15 ml (78 mmol) of aq. glyoxal (40%) were introduced into 150 ml of dichloromethane and vigorously stirred with 40 g of freshly dehydrated sodium sulfate. Following the addition of 0.5 ml (13 mmol) of formic acid (98%) and 22 ml (170 mmol) of **1** the reaction mixture was allowed to stir for 5 min, after which time another 50 g of sodium sulfate were added. During 2.5 h of stirring at room temperature the solution turned slightly yellow. The mixture was then filtered, the residue washed with 50 ml of CH_2Cl_2 and the solvent from the combined filtrates removed in vacuo. The oily product was diluted with 100 ml of petroleum ether (30 – 50 °C), washed five times with 50 ml of water, and dried for 2 d over molecular sieve (3Å). Finally, the solvent was completely removed. Yield 16.6 g (80%). – ^{1}H NMR (CCl_4): δ = 7.88 (s), 7.2 (s), 4.33 (q), 1.47 (d). – ^{13}C NMR ($CDCl_3$): δ = 160.5, 143.6, 128.4, 127.0, 126.5, 69.5, 23.9. – IR (film): 1628 cm^{-1} (C = N).

$C_{18}H_{20}N_2$ (264.4) Calcd. C 81.78 H 7.62 N 10.60 Found C 81.8 H 7.9 N 10.5

N,N′-Bis[(R)-1-phenylethyl]-2,3-butanediimine (**6**-*RR*): To 25 ml (194 mmol) of **1** in 100 ml of dichloromethane 7.8 ml (90 mmol) of biacetyl, 5 drops of 98% formic acid and 30 g of molecular sieve (4 Å) were added and the mixture stirred at ambient temperature for 1 week. After filtration the solvent was evaporated, the residual oil dissolved in 100 ml of *n*-hexane and washed five times with altogether 300 ml of water. The separated organic layer was dried over molecular sieve (4 Å) for 24 h, and then the hexane was removed in vacuo. Yield 18.8 g (66%) yellowish oil. Colourless crystals with m. p. 15 – 20 °C can be obtained after recrystallization from ether (at – 80 °C) or *n*-hexane (at 0 °C). – ^{1}H NMR (CCl_4): δ = 7.2 (m), 4.71 (q), 2.15 (s), 1.42 (d). – ^{13}C NMR ($CDCl_3$): δ = 166.3, 146.0, 128.2, 126.6, 60.3, 24.7, 12.7. – IR (film): 1648 cm^{-1} (C = N).

$C_{20}H_{24}N_2$ (292.4) Calcd. C 82.15 H 8.27 N 9.58 Found C 81.4 H 8.3 N 9.4

N,N'-Bis[(1S, 2S, 3S, 5R)-pinan-3-ylmethyl]-1,2-ethanediimine (7): 4 ml (34 mmol) of 40% aq. glyoxal were stirred in 15 ml of diethyl ether for 15 min with 50 g of sodium sulfate. Then 10.4 g (68 mmol) of (+)-3-(aminomethyl)pinane (2) were added and the stirring was continued for 3 h. The filtered, slightly yellow solution was washed three times with 50 ml of water and dried overnight with molecular sieve (4 Å). 7.5 g (75%) of a viscous yellow oil remained after evaporation of the solvent. – ^{1}H NMR (CCl_4): δ = 7.8 (s), 3.5 (m), 1.9 (m), 1.18 (s), 1.1 (s), 1.0 (s). – IR (film): 1635 cm^{-1} (C = N).

$C_{24}H_{40}N_2$ (356.6) Calcd. C 80.84 H 11.31 N 7.86 Found C 79.4 H 11.5 N 7.36

N,N'-Bis[(1S,2S,3S,5R)-pinan-3-ylmethyl]-2,3-butanediimine (**8**): To 4.3 g (50 mmol) of biacetyl in 120 ml of chloroform, 10 g of molecular sieve (4 Å) and 10 drops of 98% formic acid, 16.5 g (108 mmol) of **2** were added quickly and the mixture, which slowly turned yellow-brown, stirred for 1 d at room temperature. After filtration and evaporation of the solvent, the oily residue was washed twice with methanol, homogenized with ethanol and then kept at – 20 °C. 10.3 g (54%) of yellowish crystals with m. p. 38 – 40 °C were collected. – ^{1}H NMR (CCl_4): δ = 3.4 (m), 2.1 (s), 2.0 (m), 1.22 (s), 1.12 (s), 1.0 (s). – ^{13}C NMR ($CDCl_3$): δ = 168.4, 60.3, 48.3, 41.9, 41.0, 39.1, 37.7, 33.4, 32.7, 28.1, 23.0, 21.7, 12.8.

$C_{26}H_{44}N_2$ (384.6) Calcd. C 81.19 H 11.53 N 7.28 Found C 81.2 H 11.8 N 7.3

4,9-Diethyl-2,7-dioxa-5,10-diazabicyclo[4.4.0]decane (**9**): 2 ml (17 mmol) of aq. glyoxal (40%) were mixed with 3.5 ml (37 mmol) of (+)-2-amino-1-butanol (**3**) and a few drops of 98% formic acid in 50 ml of methanol and stirred at room temperature for 12 h. After evaporating the solvent the residue was dried in vacuo (10^{-2} torr) for 7 h. The colourless oil crystallized after some days (m.p. 41 – 43 °C). Yield 2.9 g (85%). – ^{1}H NMR (CCl_4): δ = 4.0 (s, 2H), 2.9 – 3.7 (several mult., 6H), 2.3 (broad, 2 NH), 1.1 (m, 4H), 0.9 (t, 6H). – ^{13}C NMR ($CDCl_3$): δ = 81.3, 70.2, 48.0, 24.8 and 9.6. – IR (film): 3300 (N – H), 1202, 1100 and 1070 cm^{-1} (C – O). – MS (70eV): *m/e* = 100 ($M/2^+$, 100%), 112 (55), 83 (30), 71 (42), 57 (94), 41 (45).

$C_{10}H_{20}N_2O_2$ (200.3) Calcd. C 59.97 H 10.06 N 13.99 Found C 60.1 H 10.3 N 13.8

4,4'-Diethyl-2,2'-dimethyl-2,2'-bioxazolidine (**10**): 10 ml (106 mmol) of **3** in 100 ml of dichloromethane were stirred for 14 h with 4.66 ml (53 mmol) of biacetyl and 30 g of sodium sulfate. After filtration, evaporation of CH_2Cl_2, redissolution in 100 ml of petroleum ether (30 – 50 °C), the usual washing procedure and drying with molecular sieve (3 Å) and elimination of the solvent, 10.9 g (90%) of a slightly yellow oil remained. – IR (film): 3300 (N – H), 1100 and 1070 (C – O), 880 and 825 cm^{-1} (oxazolidine ring deformation). – ^{1}H NMR (CCl_4): δ = 3.0 – 3.8 (several mult.), 1.7 (broad, NH), 1.3 (s), 1.1 (m), 0.9 (t). – ^{13}C NMR ($CDCl_3$): δ = 84.3, 68.2, 48.6, 25.1, 21.6, 9.7.

$C_{12}H_{24}N_2O_2$ (228.3) Calcd. C 63.12 H 10.59 N 12.27 Found C 61.1 H 10.3 N 12.3

Tetracarbonylmolybdenum complexes of N,N'-bis[(1-hydroxymethyl)propyl]-1,2-ethanediimine and -2,3-butanediimine (**11** and **12**): About 200 mg (ca. 1 mmol) of **9** or **10**, resp., were dissolved in 10 ml of toluene, 260 mg (1.0 mmol) of hexacarbonylmolybdenum added, and the mixture heated to reflux temperature. After a few minutes the deep violet colour, characteristic for (dad)$Mo(CO)_4$ complexes appeared (**11**: λ_{max} = 528 nm; **12**: λ_{max} = 495 nm) at λ-values similar to the *N,N'*-diisopropyl-1,2-ethanediimine or -2,3-butanediimine tetracarbonylmolybdenum complexes[4b)]. Molybdenum(0) complexes with amino compounds such as **9** or **10** or even with non-conjugated azomethines[15)] do not show intense absorption bands in the visible region. – IR (nujol): **11**: 2020, 1920, 1890, 1845 cm^{-1} (C≡O); **12**: 2020, 1930, 1895, 1850 cm^{-1} (C≡O).

(S)-1-(Trimethylsiloxy)-2-butanamine (**13**): 20 ml (212 mmol) of **3** and 27 ml (212 mmol) of chlorotrimethylsilane in 200 ml of diethyl ether reacted overnight. The resulting hydrochloride was shaken for 15 min with 8.5 g of sodium hydroxide (212 mmol) in 100 ml of water. The organic layer, dried over sodium sulfate, gave after distillation 23.7 g (65%) of colourless **13**. – IR (film): 3400 (N – H), 1600 (N – H def.), 1250 (Si – CH_3), 1100 (Si – O), 890, 850, 750 cm^{-1}. – ^1H NMR (CCl_4): δ = 2.9 – 3.2 (several mult.), 2.4 (broad), 1.1 (m), 0.9 (t), 0.1 (s).

N,N'-Bis[(S)-1-(trimethylsiloxymethyl)propyl]-1,2-ethanediimine (**14**): A solution of 1.0 ml of aq. glyoxal (40%) in 50 ml of diethyl ether was stirred for 10 min with 10 g of molecular sieve (3 Å). After this 3.0 g (17.5 mmol) of **13** were added and stirring was continued for 1 h. After 2 d reaction time at ambient temperature, filtration and removal of the solvent 2.5 g (86%) of a yellowish oil remained. – IR (film): 1632 (C = N), 1250 (Si – CH_3), 1100 (Si – O), 875, 845, 750 cm^{-1}. – ^1H NMR (CCl_4): δ = 7.77 (s), 3.2 – 3.4 (several mult.), 1.5 (m), 0.85 (t), 0.15 (s). – ^{13}C NMR ($CDCl_3$): δ = 162.1, 74.7, 65.7, 24.8, 10.5 and 0.45.

$C_{16}H_{36}N_2O_2Si_2$ (344.6) Calcd. C 55.76 H 10.53 N 8.13 Found C 55.2 H 10.5 N 8.2

N,N'-Bis[(S)-1-(trimethylsiloxymethyl)propyl]-2,3-butanediimine (**15**): To 1.9 g (8.2 mmol) of **10** in 40 ml of dichloromethane 2.3 ml (16.4 mmol) of triethylamine and 2.08 ml (16.4 mmol) of chlorotrimethylsilane were added and the solution stirred for 1 d. After evaporation of the solvent, the solid residue was treated with petroleum ether and the hydrochloride filtered off. After drying with molecular sieve (3 Å) and evaporation of the solvent 2.6 g (85%) of yellow oil remained. – IR (film): 1645 (C = N), 1250 (Si – CH_3), 1100 (Si – O), 875, 845, 750 cm^{-1}. – ^1H NMR (CCl_4): δ = 3.4 – 3.7 (several mult.), 2.15 (s), 1.5 (m), 0.9 (t), 0.15 (s).

$C_{18}H_{40}N_2O_2Si_2$ (372.7) Calcd. C 58.01 H 10.82 N 7.52 Found C 56.3 H 10.5 N 7.6

{N,N'-Bis[(R)-1-phenylethyl]-2,3-butanediimine}dichloroiron(II) (**16**): 2.19 g (7.5 mmol) of **6** in 30 ml of THF reacted with 0.95 g (7.5 mmol) of anhydrous iron dichloride for 19 h at room temperature. The pure, wine-red complex crystallized from the solution in 35% yield (1.4 g). – UV (THF): λ_{max} = 580, 538, 498 (sh) nm. – CD (THF): At 570 nm Δε = –2.8 $l \cdot mol^{-1} \cdot cm^{-1}$. – IR (nujol mull): 1650 and 1600 (C = N), 360 and 320 cm^{-1} (Fe – Cl).

$C_{20}H_{24}Cl_2FeN_2$ (419.2)	Calcd.	C 57.31	H 5.77	N 6.68	Fe 13.32
	Found	C 57.4	H 5.8	N 6.5	Fe 13.4

{N,N'-Bis[(1S,2S,3S,5R)-pinan-3-ylmethyl]-1,2-ethanediimine}dichloroiron(II) (**17**): 7.0 g (20 mmol) of **7** and 1.7 g (13.4 nmmol) of anhydrous iron dichloride were stirred for 20 h in 50 ml of THF. After the evaporation of the solvent the light blue solid material was treated with 50 ml of diethyl ether, filtrated and washed several times with ether. The rather pure material, obtained in quantitative yield, was recrystallized from dichloromethane/hexane. – UV (THF): λ_{max} = 610, 550, 500 (sh) nm. – CD (THF): At 605 nm Δε = –0.72 $l \cdot mol^{-1} \cdot cm^{-1}$. – IR (nujol mull): 1595 and 1645 (C = N), 370 and 330 cm^{-1} (Fe – Cl).

$C_{24}H_{40}Cl_2FeN_2$ (483.3)	Calcd.	C 59.64	H 8.34	N 5.79	Fe 11.55
	Found	C 57.0	H 8.4	N 5.4	Fe 11.9

Examples of catalytic reactions: About 12 ml (150 mmol) of 1,3-butadiene were condensed through a column, packed with molecular sieve (65 Å), into a cooled thick-walled glass tube, previously heated in vacuo to eliminate traces of surface water. Then 67 mg of **16** (0.16 mmol) or 110 mg of **17** (0.23 mmol), resp., were added together with 15 – 20 ml of ether, the contents shaken to dissolve the complex and then a fourfold molar quantity (rel. to iron) of ethylmagnesium iodide (ethereal solution) added. With **17** a fast colour change from a light violet to dark violet and then to brown was observed, with **16** the reaction was much slower. The tube was then cooled in liquid nitrogen, evacuated and sealed. After reaching room temperature the meniscus was marked and the contraction observed. After 2 d at 25°C (**16**) and 3 d at 5°C (**17**), resp., the ampullae were opened at −20°C under nitrogen, the contents poured into 50 ml of petroleum ether (30−50°C), the solution washed with dilute sulfuric acid and water to eliminate active organometallics, dried over sodium sulfate and distilled in vacuo to separate dimers, trimers and higher oligomers. With **16** 62% dimers, 35% trimers, and 3% higher oligomers were obtained. The dimer fraction contained 37% 4-vinyl-1-cyclohexene (**18**) with an enantiomeric excess of 9.2% **18**-*R* and 47% 1,5-cyclooctadiene. With **17** 61% dimers, 33% trimers, and 6% higher oligomers were obtained. Here the dimer fraction contained 44.5% **18** (with 16.4% e.e. of **18**-*S*) and 55% 1,5-cyclooctadiene.

With dads derived from aromatic amines the dimer specifity can be raised to 95−99%[5], with dads from 1*R*,3*R*,4*S*-*p*-menthan-3-amine e.e.-results up to 24% **18**-*S* (glyoxal derivative)[5] or 30% **18**-*S* (2-acetylpyridine derivative)[14] are obtained[13].

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