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α,β-Unsaturated diimines as substrates in catalytic C–H activation reactions and as ligands in iron carbonyl complexes

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Abstract

The reaction of 3-[4-(3-oxo-propenyl)-phenyl]-propenal with two equivalents cyclohexylamine as well as the treatment of cyclohexane-1,4-diamine or bis-(4-aminocyclohexyl)-methane with two equivalents of cinnamaldehyde leads to the formation of the corresponding diimines. Mono- or dinuclear iron carbonyl complexes are produced if the diimines are reacted with iron carbonyls. Two of these complexes have been characterized by X-ray crystallography showing that one or two of the α,β-unsaturated imine side chains are coordinated by an iron tricarbonyl moiety in a η^4-fashion. The packing is realized by intermolecular C–H···O contacts. The same diimines are used as the substrates in ruthenium catalyzed C–H activation reactions together with carbon monoxide and ethylene to produce bis-dihydropyrrolone derivatives in almost quantitative yields.

Keywords: Iron carbonyls; Catatlysis; C–H activation; Pyrrolones; Structure determination

1. Introduction

The reaction of acyclic α,β-unsaturated imines with $Fe_2(CO)_9$ yields mononuclear iron tricarbonyl complexes [1–7]. On the other hand, the same imine substrates are converted into γ-lactams in the reaction with carbon monoxide and α-olefins catalyzed by $Ru_3(CO)_{12}$ [8–13]. As a side product of this catalytic three component reactions 2,3-disubstituted pyrrole derivatives are observed [11]. Interestingly, one of the very few procedures to synthesize 2,3-disubstituted pyrroles starts from (η^4-azadiene)$Fe(CO)_3$ complexes and EtLi with subsequent quenching of the reaction mixture with BuBr [14,15]. During our investigations on the reactivity of bis-imines we synthesized the diimines **1**, **4** and **6** (Scheme 1) as model compounds to study the interaction of a group 8 metal carbonyl fragment with the corresponding substrates. In addition, we wanted to investigate, whether the catalytic formation of heterocyclic compounds proceeds via the same reaction pathway as it was observed for monofunctional imines. Another interesting question was, whether the catalytic formation of heterocyclic substructures was possible on both sides of the bifunctional substrates.

2. Results and discussion

The diimines **1**, **4** and **6** are easily produced from the condensation of 3-[4-(3-oxo-propenyl)-phenyl]-propenal with two equivalents cyclohexylamine (to produce **1**) as well as of cyclohexane-1,4-diamine or bis-(4-aminocyclohexyl)-methane with two equivalents of cinnamaldehyde to yield **4** and **6**, respectively. Scheme 1 shows the synthesis of the iron carbonyl compounds **2**, **3**, **5** and **7** from the corresponding diimine ligands. After chromatographic workup and recrystallization from

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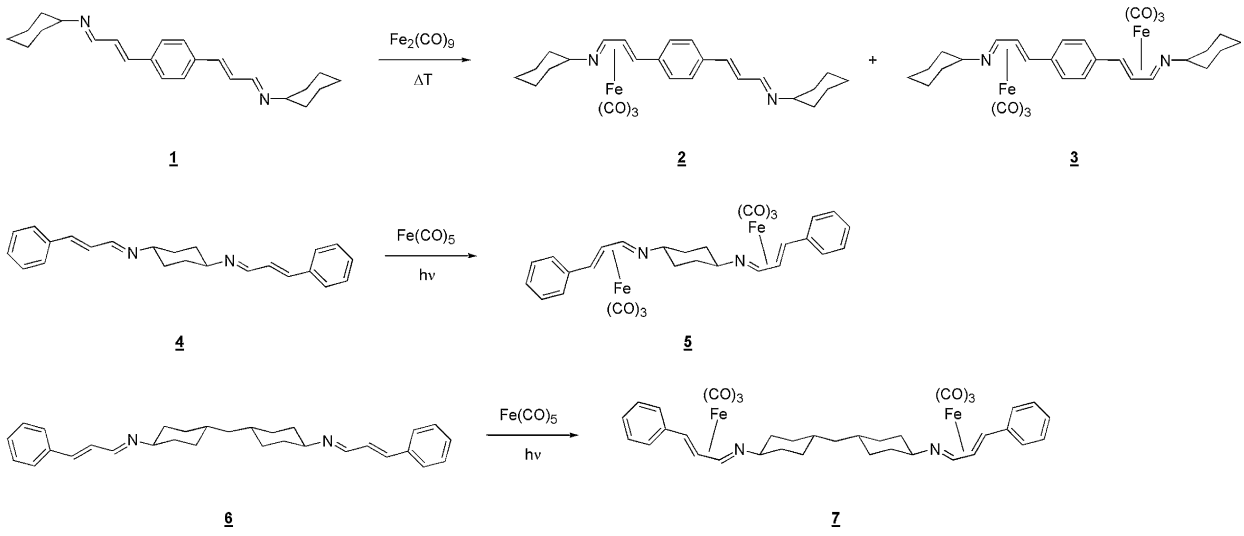


Scheme 1.

mixtures of light petroleum and dichloromethane at −20 °C **2** and **3** were obtained as crystalline compounds suitable for X-ray structure determination.

The most important bond lengths and angles of **2** and **3** are depicted in Table 1. The molecular structure of one of the three molecules per asymmetric unit observed for **2** is presented in Fig. 1. In **2** only one of the imine functions is coordinated by an iron tricarbonyl fragment. Corresponding to other (1-azadiene)$Fe(CO)_3$ complexes the ligand shows a s-*cis* conformation whereas the non-coordinated imine subunit exhibits the expected s-*trans* conformation. The iron carbon bond lengths in **2** are not identical. As it has been pointed out before [6,7], the bond of Fe1 with C3 is about 7–10 pm longer than Fe1–C2, which again is about 2–3 pm shorter compared to Fe1–C1. There are three molecules in the asymmetric unit of the unit cell, which are linked by C–H···O interactions (Fig. 2, Table 2). These trimers again are

Table 1
Selected bond lengths [Å] and angles [°] of **2** and **3**

2, Molecule 1					
Fe1–N1	2.084(4)	Fe1–C1	2.082(5)	Fe1–C2	2.051(6)
Fe1–C3	2.119(5)	N1–C13	1.480(6)	C3–C4	1.486(7)
C10–C11	1.319(8)	C11–C12	1.441(8)	C12–N2	1.280(7)
C13–N1–C1	115.9(4)	N1–C1–C2	115.8(5)	C1–C2–C3	117.1(6)
C2–C3–C4	122.5(5)	C7–C10–C11	128.6(6)	C10–C11–C12	125.7(6)
C11–C12–N2	123.1(6)	C12–N2–C19	118.4(5)		
2, Molecule 2					
Fe2–N3	2.072(4)	Fe2–C28	2.077(6)	Fe2–C29	2.052(6)
Fe2–C30	2.151(6)	N3–C40	1.475(6)	C30–C31	1.456(7)
C37–C38	1.303(8)	C38–C39	1.462(8)	C39–N4	1.262(8)
C40–N3–C28	114.5(4)	N3–C28–C29	116.2(5)	C28–C29–C30	118.5(6)
C29–C30–C31	123.4(6)	C34–C37–C38	128.1(6)	C37–C38–C39	124.4(7)
C38–C39–N4	123.0(7)	C39–N4–C46	119.0(6)		
2, Molecule 3					
Fe3–N5	2.081(4)	Fe3–C55	2.075(6)	Fe3–C56	2.045(6)
Fe3–C57	2.112(5)	N5–C67	1.468(6)	C57–C58	1.473(7)
C64–C65	1.314(8)	C65–C66	1.456(8)	C66–N6	1.264(7)
C67–N5–C55	115.0(5)	N5–C55–C56	116.4(6)	C55–C56–C57	117.0(6)
C56–C57–C58	124.6(5)	C61–C64–C65	129.4(6)	C64–C65–C66	121.7(7)
C65–C66–N6	123.3(7)	C66–N6–C73	116.1(6)		
3					
Fe1–N1	2.076(4)	Fe1–C1	2.068(5)	Fe1–C2	2.059(5)
Fe1–C3	2.141(5)	N1–C7	1.466(6)	C3–C4	1.481(7)
C7–N1–C1	115.7(4)	N1–C1–C2	115.6(5)	C1–C2–C3	116.5(5)
C2–C3–C4	124.4(5)				

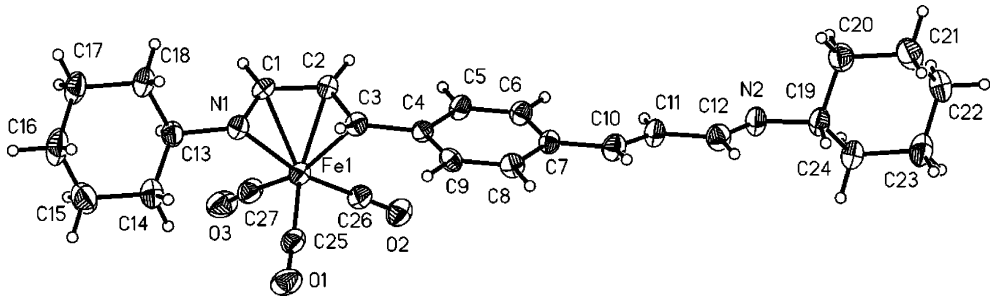


Fig. 1. Molecular structure of **2**. Displacement ellipsoids drawn at the 50% probability level.

connected by another intermolecular C–H···O contact to produce infinite chains of trimers (Fig. 2).

The molecular structure of **3** is shown in Fig. 3. The center of the aromatic ring system is a crystallographic center of inversion. So the imine substituents show a *trans*-configuration with respect to the central phenyl ring and the iron tricarbonyl moieties are situated above and below the plane of the ligand. Both imine functionalities are coordinated by $Fe(CO)_3$ fragments and thus show a s-*cis* conformation. Again Fe–C3 is about 7–8 pm longer compared to the other iron carbon bond lengths. The molecules are connected to infinite chains by intermolecular C–H···O contacts (Fig. 4, Table 2) between one of the terminal carbon monoxide ligands and the hydrogen atom at C2.

The coordination of an iron tricarbonyl fragment to the 1-azadiene units can be considered to model the first interaction of a ruthenium carbonyl moiety in a catalytic reaction. The next step in the catalytic cycle would then be the C–H activation reaction in terms of an cyclometalation (Scheme 2). There is one reaction reported in the literature, in which an imine derived from *p*-anisidine and cinnamaldehyde reacts with $Fe_2(CO)_9$ to yield a dinuclear iron carbonyl compound, in which the C–H bond in β-position relative to the C–N double bond is activated and the corresponding hydrogen atom is *trans* ferred to the former imine carbon atom [16,17]. The same reaction sequence on the other hand is typical for aromatic imines [18–24], although in one case a mononuclear iron tricarbonyl compound has been isolated from the reaction of $Fe_2(CO)_9$ with naphthalen-2-ylmethylene-phenyl-amine [21].

Table 2
Shortest intermolecular contacts [Å] and angles [°] in the crystal structures of **2** and **3**

	Interaction	C–X	C–H···X	Angle
2	C49–H49B–O1	3.593	2.619	167.7
	C51–H51B–O7	3.443	2.531	153.1
	C74–H74A–O5	3.488	2.577	153.0
3	C2–H2A–O1	3.414	2.554	150.6

Scheme 3 shows the three component reactions of **1**, **4** and **6** with carbon monoxide and ethylene in the presence of catalytic amounts of $Ru_3(CO)_{12}$. It has been

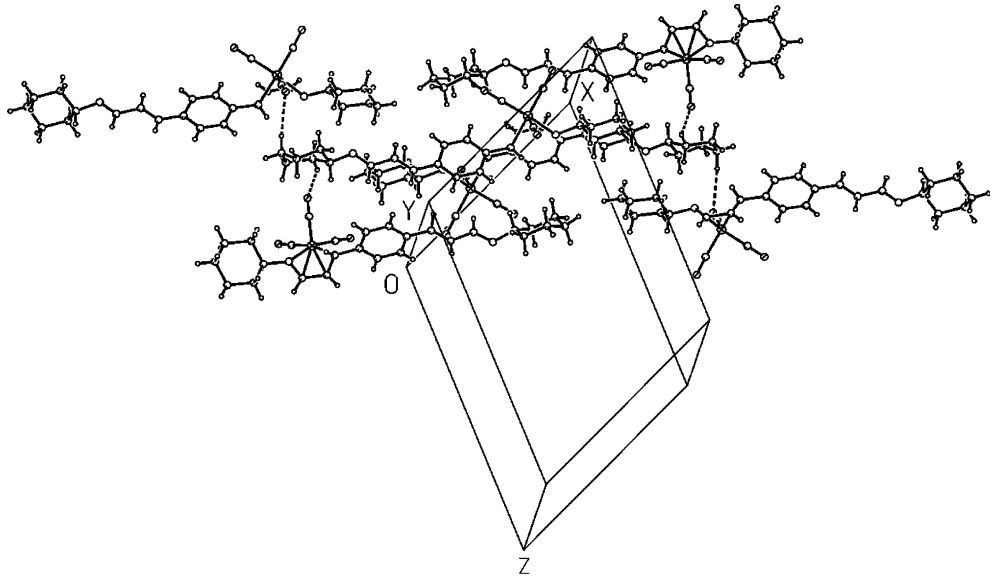


Fig. 2. Packing diagram of **2**.

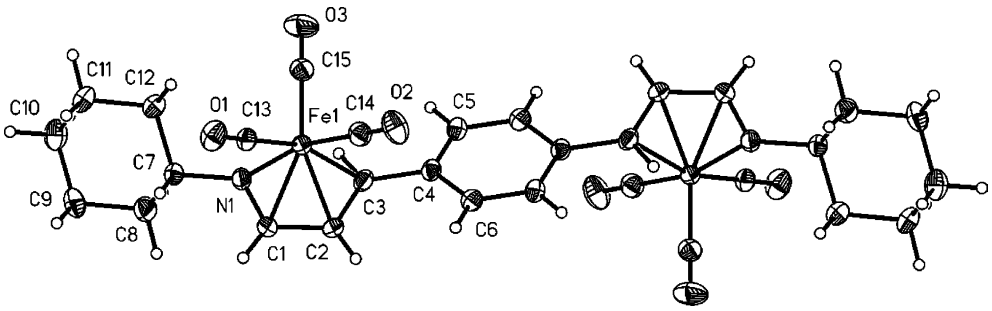


Fig. 3. Molecular structure of **3**. Displacement ellipsoids drawn at the 30% probability level.

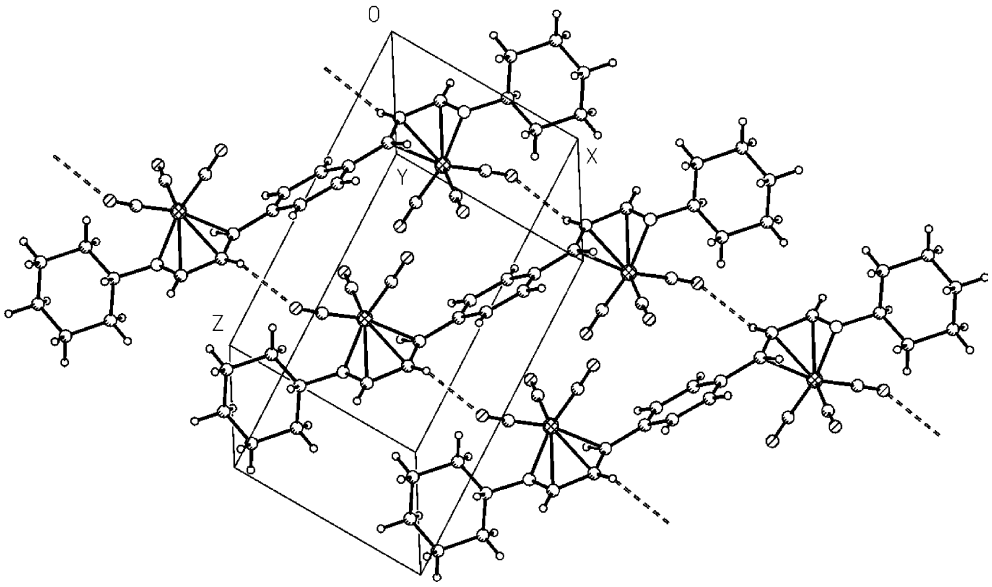
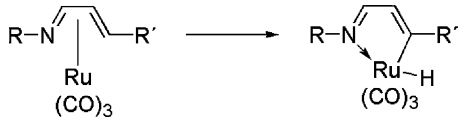


Fig. 4. Packing diagram of **3**.



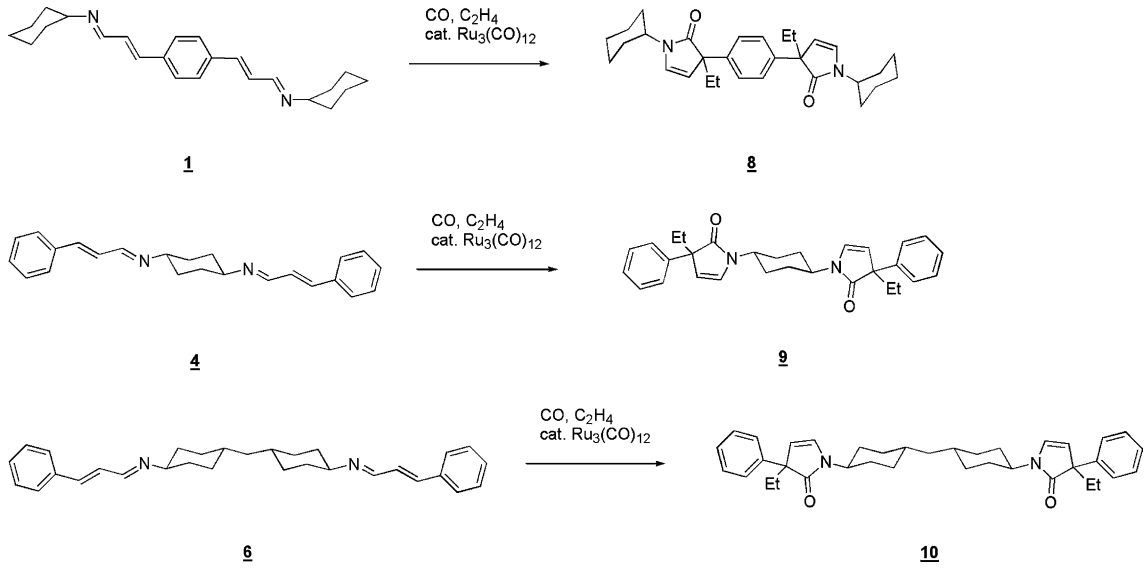
Scheme 2.

pointed out before, that the formation of pyrrolone derivatives works best if the substituents at the imine nitrogen atoms are aliphatic moieties [11]. Corresponding to this observation, the bis-dihydropyrrolone derivatives **8**–**10** are produced in yields of 90% (**9**) or >98% (**8**, **10**). Only in the reaction of **4** to produce **9** traces of a product in which the formation of the heterocycle took place only with one of the imine subunits are observed in the GC-MS investigations of the product mixture. **8**–**10** are easily identified by some NMR shifts being characteristic for this class of compounds. First of all, the C–H functions at C_4 and C_5 of the heterocycles lead to dubletts at app. $\delta = 5.5$ and 6.6 in the ^{1}H NMR spectrum. The corresponding resonances in the ^{13}C NMR spectrum are observed at app. $\delta = 113$ and 127. In addition, the methylene protons of the ethyl substituents are diastereotopic because of the new stereogenic center at C_3 of the heterocycle and thus give rise to multipletts in the hydrogen NMR spectra.

3. Experimental

General. All procedures were carried out in anhydrous, freshly distilled solvents. The syntheses of the iron carbonyl complexes **2**, **3**, **5** and **7** were performed under an argon atmosphere.

Infrared spectra were recorded on a Perkin–Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz, ^{13}C: 50.32 MHz, $CDCl_3$ as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High resolution mass spectra (HRMS) were carried out using a Finnigan MAT 95 XL spectrometer using FAB techniques. Elemental



Scheme 3.

analyses were carried out at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-University, Jena.

X-ray Crystallographic Studies. The structure determination of **2** was carried out on a Enraf–Nonius Kappa CCD diffractometer, the crystal being mounted in a stream of cold nitrogen, crystal detector distance 29 mm. The structure determination of **3** was done using a Enraf–Nonius CAD4 diffractometer, the crystal was fixed in a glass capillary. In both cases graphite monochromated Mo Kα radiation was used. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS86 and SHELXL97 [25,26]. All hydrogen atoms of **3** were constrained in idealized positions during the refinement. The isotropic replacement parameters of all hydrogen atoms were fixed. Treatment of hydrogen atoms of **2** was identical except hydrogen atoms at C1, C2 and C3, which were identified from difference Fourier map and refined without any constraints. The molecular illustrations were drawn using the program XP [27]. The crystal and intensity data are given in Table 3. Additional material on the structure analyses is available from the Cambridge Crystallographic Data Centre by mentioning the deposition number CCDC-247572 (**2**) or CCDC-247573 (**3**).

3.1. Synthesis of *1*, *4* and *6*

1 was prepared by the reaction of 1 g (5.38 mmol) 3-[4-(3-oxo-propenyl)-phenyl]-propenal with 1.06 g (10.75 mmol) cyclohexylamine in 50 ml anhydrous ethanol. After stirring the solution at room temperature for 10 h, 841 mg **1** (44.9%) precipitated as a pale yellow solid.

Table 3
Crystal and intensity data for **2** and **3**

	2	**3**
Formula	$C_{27}H_{32}N_2O_3Fe$	$C_{30}H_{32}N_2O_6Fe_2$
Molecular weight (g mol^{-1})	488.40	628.28
Radiation	Mo Kα	Mo Kα
Monochromator	Graphite	Graphite
Temperature (K)	183	183
Crystal color	Orange	Orange
Crystal size	$0.3 \times 0.1 \times 0.03$	$0.3 \times 0.2 \times 0.02$
a (Å)	14.456(1)	6.900(1)
b (Å)	17.051(2)	8.740(1)
c (Å)	17.451(2)	12.153(2)
α (°)	102.497(4)	87.48(1)
β (°)	109.566(6)	87.69(1)
γ (°)	101.748(7)	75.61(1)
Volume (Å^3)	3774.5(7)	709.0(2)
Z	6	1
$F(000)$	1548	326
ρ_{calc} (g cm^{-3})	1.289	1.472
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Absorption coefficient (mm^{-1})	0.629	1.072
θ Limit (°)	$3.11 < \theta < 23.29$	$2.41 < \theta < 29.98$
Scan mode	ω-Scan	ω-2θ-Scan
Reflections measured	10159	4169
Independent reflections	10159	3870
R_{int}	0.0000	0.1265
Reflections observed ($F_o^2 > 2\sigma(F_o^2)$)	5940	2918
No. of parameters	975	186
Goodness-of-fit	0.842	1.182
R_1	0.0626	0.0747
wR_2	0.1634	0.2088
Final diffraction map electron density peak (e Å^{-3})	0.619	1.238

MS and spectroscopical data of **1**: MS (EI) [*m*/*z* (fragment, rel. intensity in %)]: 348 (M^+, 100), 265 ($C_{18}H_{21}N_2^+$, 61), 240 ($C_{16}H_{20}N_2^+$, 6), 225 ($C_{15}H_7N_2^+$, 30),

183 ($C_{12}H_{10}N_2^+$, 12), 143 ($C_{10}H_9N^+$, 8), 115 ($C_9H_7^+$, 4), 83 ($C_6H_{11}^+$, 6), 55 ($C_4H_9^+$, 19), 41 ($C_3H_5^+$, 12); IR (nujol, 298 K) [cm^{-1}]: 1630 (m), 1610 (m) (CH=N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.10–1.80 (m, 20H, CH_2), 2.91–3.09 (m, 2H, CH), 6.73–6.93 (m, 4H, =CH), 7.35 (s, 4H, CH_{ar}), 7.96 (d, 2H, $^3J_{HH}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 24.6 (CH_2), 25.4 (CH_2), 34.3 (CH_2), 69.5 (CH), 127.4 ($C_{ar}H$), 129.0 (=CH), 136.4 (=CH), 140.0 (=CH), 159.9 (N=CH); m.p. 179 °C. Elemental analysis: Calcd.: C,82.71%; H, 9.25%; N, 8.04%; found: C, 82.07%; H, 7.32%; N 8.12%.

4 was prepared by the reaction of 2.855 g (0.025 mol) *trans*-1,4-diaminocyclohexane which were dissolved in 10 ml anhydrous ethanol and treated with 6.608 g (0.05 mol) cinnamaldehyde. After stirring at room temperature for 20 h the colorless precipitate is collected and washed three times with cold anhydrous ethanol and three times with cold diethylether to yield 6.399 g (74.7%) **4**.

MS and spectroscopical data of **4**: MS (CI, H_2O) [*m*/*z* (fragment, rel. intensity in %)]: 343 (MH^+, 100), 211 ($C_{15}H_{17}N^+$, 7), 170 ($C_{12}H_{12}N^+$, 7), 156 ($C_{11}H_{10}N^+$, 5), 132 ($C_9H_{10}N^+/C_9H_8O^+$, 4), 115 ($C_9H_7^+/C_6H_{15}N_2^+$, 4); IR (nujol, 298 K) [cm^{-1}]: 1634 (m) (CH=N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.42–2.01 (m, 8H, CH_2), 2.93–3.29 (m, 2H, CH), 6.90 (d, $^{3/4}J_{HH}$ = 1.7 Hz, 2H, CH), 6.92 (s, 2H, CH), 7.19–7.57 (m, 10H, CH_{ar}), 8.08 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 4.2 Hz, 2H, CH=N); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 32.6 (CH_2), 68.7 (CH), 127.1 (CH_{ar}), 128.3 (CH_{ar}), 128.7 (CH_{ar}), 129.0 (CH), 135.7 (C_{ar}), 141.4 (CH), 161.0 (CH=N); m.p. 177 °C. Elemental analysis: Calcd.: C, 84.17%; H, 7.65%; N, 8.18%. Found: C, 84.19%; H, 7.69%; N, 8.11%.

6 is synthesized from 5.259 g (0.025 mol) 4,4′-diamino-dicyclohexylmethane dissolved in 100 ml anhydrous ethanol and treated with 6.608 g (0.05 mol) cinnamaldehyde. After stirring at room temperature for 20 h the colorless precipitate is collected and washed three times with cold anhydrous ethanol and three times with cold diethylether to yield 3.450 g (31.5%) **6**. MS and spectroscopical data of **6**:

MS (CI, H_2O) [*m*/*z* (fragment, rel. intensity in %)]: 439 (MH^+, 100), 325 ($C_{22}H_{33}N_2^+$, 2), 307 ($C_{22}H_{29}N^+$, 4), 226 ($C_{16}H_{20}N^+$, 4), 132 ($C_9H_{10}N^+/C_9H_8O^+$, 3); IR (Nujol, 298 K) [cm^{-1}]: 1635 (s) (CH=N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.57–2.17 (m, 20H, CH, CH_2), 2.79–3.15 (m, 2H, CH), 6.88 (s, 2H, CH), 6.90 (s, 2H, CH), 7.17–7.57 (m, 10H, CH_{ar}), 8.04 (dd, $^3J_{HH}$ = 4.3 Hz, $^4J_{HH}$ = 4.3 Hz, 2H, CH=N); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 31.8 (CH_2), 33.6 (CH), 34.2 (CH_2), 44.8 (CH_2), 70.0 (CH), 127.1 (CH_{ar}), 128.5 (CH_{ar}), 128.7 (CH_{ar}), 128.9 (CH), 135.8 (C_{ar}), 141.1 (CH), 160.5 (CH=N); m.p. 151 °C. Elemental analysis: Calcd.: C, 84.88%; H, 8.73%; N, 6.39%. Found: C, 84.31%; H, 8.73%; N 6.37%.

3.2. Synthesis of **2** and **3**

348 mg **1** (1 mmol) are stirred together with 364 mg $Fe_2(CO)_9$ in 20 ml *n*-heptane at 50 °C for 2 h, the solution turns orange as the ligand and $Fe_2(CO)_9$ dissolve. After evaporation of all volatile material the crude product is chromatographed on silica gel. Use of light petroleum (b.p. 40–60 °C) as the eluent yields **3** as a orange solution (175 mg, 28%). If a mixture of light petroleum (b.p. 40–60 °C) and CH_2Cl_2 (5:1) is used as the eluent, 176 mg **2** (36%) are obtained. Crystals of **2** and **3** are produced from a concentrated solution in light petroleum (b.p. 40–60 °C) at −20 °C.

MS and spectroscopical data of **2**: MS (EI) [*m*/*z* (fragment, rel. intensity in %)]: 488 (M^+, 7), 460 (M^+–CO, 13), 432 (M^+–2CO, 4), 404 (M^+–3CO, 44), 348 (M^+–3CO–Fe, 5), 196 ($C_{13}H_{26}N^+$, 24), 168 ($C_{11}H_{22}N^+$, 32), 140 ($C_9H_{18}N^+$, 14), 112 ($C_7H_{14}N^+$, 26), 84 ($C_6H_{12}^+$, 100), 56 ($C_4H_8^+$, 65); IR (CH_2Cl_2, 298 K) [cm^{-1}]: 2050 (s), 1988 (very strong), 1967 (m); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.13–1.75 (m, 21H, CH_2, CH), 2.89 (d, 1H, $^3J_{HH}$ = 9.2 Hz, =CH), 3.02 (m, 1H, CH), 5.46 (dd, 1H, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 2.8 Hz, =CH), 6.56 (d, 1H, $^3J_{HH}$ = 2.8 Hz, =CH), 6.81–6.85 (m, 2H, =CH), 7.18–7.33 (m, 4H, CH_{ar}), 8.00 (dd, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 24.8 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 34.5 (CH_2), 36.3 (CH_2), 37.8 (CH_2), 60.3 (=CH), 67.2 (CH), 70.0 (CH), 71.6 (=CH), 111.4 (N=CH), 126.9 ($C_{ar}H$), 127.5 ($C_{ar}H$), 128.2 (=CH), 134.1 (=CH), 140.6 (=CH), 140.7 (C_{ar}), 160.4 (N=CH). Elemental analyis: Calcd.: C, 66.40%; H, 6.60%; N, 5.74%. Found: C, 66.55%; H, 6.91%; N, 5.63%.

MS and spectroscopical data of **3**: MS (EI) [*m*/*z* (fragment, rel. intensity in %)]: 628 (M^+, 1), 600 (M^+–CO, 4), 572 (M^+–2CO, 9), 544 (M^+–3CO, 2), 516 (M^+–4CO, 8), 488 (M^+–5CO, 44), 460 (M^+–6CO, 59), 432 (M^+–5CO–Fe, 11), 404 (M^+–6CO–Fe, 100), 196 ($C_{13}H_{26}N^+$, 9), 84 ($C_6H_{12}^+$, 14); IR (CH_2Cl_2, 298 K) [cm^{-1}]: 2050 (s), 1987 (very strong), 1965 (m); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.16–1.68 (m, 22H, CH_2, CH), 2.87 (dd, 2H, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.8 Hz, =CH), 5.41 (dd, 2H, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 2.3 Hz, =CH), 6.52 (d, 2H, $^3J_{HH}$ = 2.3 Hz, =CH), 7.09 (s, 4H, CH_{ar}); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 24.8 (CH_2), 24.9 (CH_2), 25.8 (CH_2), 36.3 (CH_2), 37.8 (CH_2), 61.0 (=CH), 61.1 (=CH), 67.2 (CH), 71.5 (=CH), 71.8 (=CH), 110.9 (N=CH), 111.1 (N=CH), 126.7 ($C_{ar}H$), 137.9 (C_{ar}). Elemental analysis: Calcd.: C, 57.35%; H, 5.13%; N, 4.46%. Found: C, 56.62%; H, 5.16%; N, 4.48%.

3.3. Synthesis of **5** and **7**

In a typical experiment a 0.74 mmol sample of the coresponding diimine (253 mg **4**, 325 mg **6**) is irradiated

together with 0.2 ml (290 mg) $Fe(CO)_5$ in 95 ml anhydrous THF at 0 °C for 3 h. The yellow suspension turns to a red solution during the reaction time. After evaporation of all volatile material the red oily residue is dissolved in 12 ml CH_2Cl_2 and 1 g silanized silica is added. Again the solvent is evaporated under reduced pressure and the product mixture is chromatographed on silica. **5** is obtained as a pale brown product using a mixture of light petroleum (b.p. 40–60 °C) and THF 2:1, yield 75 mg (16.3%). **7** is eluted using a mixture of light petroleum (b.p. 40–60 °C) and THF 2.5:1, yield 312 mg (58.7%).

MS and spectroscopical data of **5**: MS (FAB in nitrobenzylalcohol) [*m/z* (fragment)]: 623 (MH^+), 595 (MH^+–CO), 566 (M^+–2CO), 539 (MH^+–3CO), 511 (MH^+–4CO), 483 (MH^+–5CO), 455 (MH^+–6CO), 427 (MH^+–5CO–Fe), 343 ($C_24H_27N_2^+$); HRMS (FAB in nitrobenzylalcohol): 623.05580, $C_{30}H_{27}N_2O_6Fe_2$ (MH^+), Δ = 0.98 mmu; IR (nujol, 298 K) [cm^{-1}]: 2053 (m) (C=O), 2026 (w) (C=O), 2012 (m) (C=O), 1991 (s) (C=O), 1974 (m, br) (C=O); ^1H NMR (THF-d_8, 298 K) [ppm]: 1.25–2.09 (m, 10H, CH, CH_2), 2,95 (d, $^3J_{HH}$ = 9.4 Hz, 2H, CH), 5.75 (dd, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 9.3 Hz, 2H, CH), 6.72 (d, $^3J_{HH}$ = 2.4 Hz, 2H, CH=N), 7.03–7.43 (m, 10H, CH_{ar}); ^{13}C NMR (THF-d_8, 298 K) [ppm]: 31.3 (CH_2), 62.7 (CH), 68.0 (CH), 72.8 (CH), 112.4 (CH=N), 127.1 (CH_{ar}), 127.3 (CH_{ar}), 129.2 (CH_{ar}), 140.3 (C_{ar}), 214.4 (CO).

MS and spectroscopical data of **7**: MS (FAB in nitrobenzylalcohol) [*m/z* (fragment)]: 719 (MH^+), 691 (MH^+–CO), 663 (MH^+–2CO), 635 (MH^+–3CO), 607 (MH^+–4CO), 579 (MH^+–5CO), 551 (MH^+–6CO), 495 (MH^+–6CO–Fe), 439 ($C_{31}H_{39}N_2^+$); HRMS (FAB in nitrobenzylalcohol): 719.15150, $C_{37}H_{39}N_2O_6Fe_2$ (MH^+), Δ = −0.81 mmu; IR (nujol, 298 K) [cm^{-1}]: 2044 (very strong) (C=O), 1987 (very strong) (C=O), 1973 (versus) (C=O), 1962 (versus, br) (C=O); ^1H NMR (THF-d_8, 298 K) [ppm]: 0.62–1.91 (m, 22H, CH, CH_2), 2.97 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH), 5.71 (dd, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$= 9.2 Hz, 2H, CH), 6.72 (d, $^3J_{HH}$ = 2.4 Hz, 2H, CH=N), 6.95–7.43 (m, 10H, CH_{ar}); ^{13}C NMR (THF-d_8, 298 K) [ppm]: 32.9 (CH_2), 33.0 (CH_2), 34.8 (CH), 34.9 (CH), 37.2 (CH_2), 38.4 (CH_2), 45.1 (CH_2), 62.5 (CH), 68.4 (CH), 72.6 (CH), 112.4 (CH=N), 127.1 (CH_{ar}), 127.3 (CH_{ar}), 129.2 (CH_{ar}), 140.4 (C_{ar}), 214.5 (CO).

3.4. Synthesis of *8–10*

1 mmol of the corresponding diimine (348 mg **1**, 342 mg **4**, 438 mg **6**) and 50 mg (0.08 mmol) $Ru_3(CO)_{12}$ and 3 ml toluene are transferred into a 100 ml stainless steel autoclave. The autoclave is then pressurized with 8 bar C_2H_4 and 12 bar CO and heated to 140 °C for 16 h. After cooling the autoclave to room temperature the product mixture is transferred to a Schlenk tube and all volatile material is evaporated under reduced pressure. The remaining oily residue is used to determine the yield of **8–10** by ^1H NMR spectroscopy and GC-MS analysis (yields: >98% **8**, 90% **9**, >98% **10**).

MS and spectroscopical data of **8**: MS (EI) [*m/z* (fragment, rel intensity in %)]: 460 (M^+, 100), 431 (M^+–Et, 56), 402 (M^+–2Et, 2), 83 ($C_6H_{11}^+$, 3), 55 ($C_4H_7^+$, 6); HRMS (ESI in $CHCl_3$/methanol): 483.3002, $C_{30}H_{40}N_2O_2Na$ (MNa^+), Δ = −1.45 mmu; IR (nujol, 298 K) [cm^{-1}]: 1690 (versus) (C=O), 1603 (m), (C–N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.76 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.08–1.90 (m, 20H, CH_2), 1.91–2.05 (m, 4H, CH_2), 3.87 (m, 2H, CH), 5.52 (d, 2H, $^3J_{HH}$ = 5.0 Hz, =CH), 6.59 (d, 2H, $^3J_{HH}$ = 5.0 Hz, =CH–N), 7.36 (s, 4H, CH_{ar}); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 9.1 (CH_3), 25.3 (CH_2), 25.5 (CH_2), 31.0 (CH_2), 31.8 (CH_2), 32.1 (CH_2), 50.3 (CH), 58.5 (C), 113.3 (=CH), 127.0 ($C_{ar}H$), 128.4 (=CH–N), 138.7 (C_{ar}), 179.1 (C=O).

MS and spectroscopical data for **9**. MS (CI, H_2O) [*m/z* (fragment, rel. intensity in %)]: 455 (MH^+, 71), 427($C_2 9H_3 5N_2O^+/C_{28}H_{31}N_2O_2^+$, 10), 399 ($C_{27}H_{31}N_2O^+$, 38), 343 ($C_{24}H_{27}N_2^+$, 5), 285 ($C_{18}H_{25}N_2O^+$, 32), 268 ($C_{18}H_{22}NO^+$, 24), 161 ($C_{11}H_{13}O^+$, 36), 133 ($C_9H_{11}N^+/C_9H_9O^+$, 100), 93 ($C_6H_7N^+$, 15), 84 ($C_5H_{10}N^+$, 17); HRMS (ESI in $CHCl_3$/methanol): 477.25241, $C_{30}H_{34}N_2O_2Na$ (MNa^+), Δ = −0.61 mmu; IR (Nujol, 298 K) [cm^{-1}]: 1681 (s, br) (C=O), 1602 (m, br) (C–N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.79 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 0.79 (t, 3H $^3J_{HH}$ = 7.3 Hz, CH_3), 1.42–1.94 (m, 8H, CH_2), 2.01 (m, 4H, CH_2), 3.80–4.16 (m, 2H, CH), 5.61 (d, 2H, $^3J_{HH}$ = 5.1 Hz, =CH), 6.60 (d, 2H, $^3J_{HH}$ = 5.1 Hz, =CH–N), 7.11–7.59 (m, 10H, CH_{ar}); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 9.0 (CH_3), 30.1 (CH_2), 30.1 (CH_2), 30.4 (CH_2), 30.4 (CH_2), 31.0 (CH_2), 31.0 (CH_2), 48.9 (CH), 58.6 (C), 113.7 (=CH), 126.5 ($C_{ar}H$), 126.9 (=CH–N), 127.8 ($C_{ar}H$), 128.3 ($C_{ar}H$), 139.8 (C_{ar}), 179.1 (CO).

MS and spectroscopical data for **10**. MS (CI, H_2O) [*m/z* (fragment, rel. intensity in %)]: 551 (MH^+, 100), 521 ($C_36H_45N_2O^+/C_{35}H_{41}N_2O_2^+$, 18), 495 ($C_{34}H_{43}N_2O^+$, 3), 381 ($C_{25}H_{37}N_2O^+$, 6), 364 ($C_{25}H_{34}NO^+$, 7), 334 ($C_{23}H_{28}NO^+$, 3), 282 ($C_{19}H_{24}NO^+$, 8), 188 ($C_{12}H_{14}NO^+$, 4), 158 ($C_{11}H_{12}N^+/C_{10}H_8NO^+$, 6); HRMS (ESI in $CHCl_3$/methanol): 573.34530, $C_{37}H_{46}N_2O_2Na$ (MNa^+), Δ = 0.39 mmu; IR (Nujol, 298 K) [cm^{-1}]: 1714–1668 (very strong, several strong bonds) (C=O), 1606 (very strong, br), (C–N); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.83 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3), 1.00–1.93 (m, 20H, CH, CH_2), 1.95–2.15 (m, 4H, CH_2), 3.82–4.04 (m, 2H, CH), 5.60 (d, 2H, $^3J_{HH}$ = 5,0 Hz, =CH), 6.63 (d, 2H, $^3J_{HH}$ = 5.1 Hz, =CH–N), 7.14–7.37 (m, 6H, CH_{ar}), 7.43–7.54 (m, 4H, CH_{ar}); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 8.9 (CH_3), 31.0 (CH_2), 31.1 (CH_2), 31.4 (CH_2), 31.9 (CH_2), 33.4 (CH), 43.7 (CH_2), 50.2 (CH),

58.5 (C), 113.1 (=CH), 126.4 ($C_{ar}H$), 126.6 (=CH–N), 128.2 ($C_{ar}H$), 128.2 ($C_{ar}H$), 140.0 (C_{ar}), 178.9 (CO).

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