Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 690 (2005) 6217–6226
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New metal aminocarbene-substituted cyclopentadienyliron half sandwich complexes

Markus Schwarz [a], Rudolf Wartchow [b], Holger Butenschön [a,*]

[a] Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, D-30167 Hannover, Germany
[b] Institut für Anorganische Chemie, Callinstraße 9, D-30167 Hannover, Germany

Received 24 May 2005; accepted 12 September 2005
Available online 2 November 2005

Abstract

Some new half sandwich cyclopentadienyl aminocarbene complexes were prepared by treatment of the corresponding alkoxycarbene complexes with primary and secondary amines, including enantiopure chiral aminoalcohols and amines with acetyl, phosphine, alkene, and alkyne functionalities, all of which proved to be compatible with the substrates. In two cases the complexes were crystallographically characterized indicating that the metal–carbon double bond is – in contrast to some alkoxycarbene analogues – not in conjugation with the cyclopentadienyl π-system in the solid state. Some of the complexes were characterized by cyclic voltammetry showing similar behavior as the corresponding alkoxycarbene complexes. The complexes are the first examples of half sandwich complexes with a cyclopentadienyl-aminocarbene ligand system.

Keywords: Carbene complexes; Bimetallic complexes; Aminocarbene complexes; Iron complexes; Chromium complexes

1. Introduction

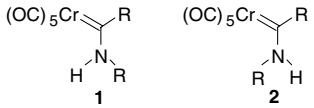
Carbene complexes are among the few classes of organometallic complexes, which have had a tremendous bearing on organic chemistry under a wide variety of aspects [1–17]. The unique feature of carbene complexes is their metal–carbon double bond. Conjugated carbene complexes such as vinyl or phenyl carbene complexes have been intensely investigated and are now standard substrates for many reactions [1,3]. Among the aromatic systems used for these complexes, phenyl-substituted complexes are the most widely investigated ones, other aromatic systems have hardly been used. Among the organometallic aromatic systems few reports about ferrocenylcarbene complexes have been published [18,19]. Prior to our work only one half sandwich cyclopentadienylcarbene complex [20] and a related thiophene complex had been reported [21]. Some bimetallic half sandwich iron cyclopentadienyl alkoxycarbene complexes were reported by our group [22,23], and these complexes showed interesting structural and electrochemical behavior. Half sandwich cyclopentadienyl aminocarbene complexes have so far not been reported. Bimetallic cyclopentadienylcarbene complexes deserve interest as the carbene bearing metal atom may be part of the ligand π-system and by this way electronically interact with the metal coordinating the cyclopentadienyl system.

Here, we report the syntheses of the first half sandwich cyclopentadienyl-aminocarbene complexes and some related compounds. In contrast to alkyoxycarbene complexes aminocarbene complexes are known to show a more interesting stereochemical behavior, because, similar to carboxylic acid amides, the rotation around the

* Corresponding author. Tel.: +49 511 762 4661; fax: +49 511 762 4616.
E-mail address: holger.butenschoen@mbox.oci.uni-hannover.de (H. Butenschön).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.09.039

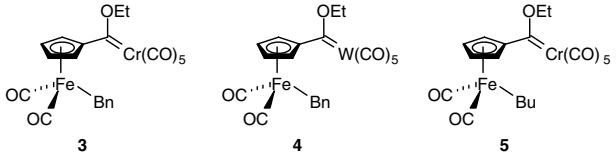
carbene carbon–nitrogen bond is more restricted often resulting in the formation of isolable *E* and *Z* isomers **1** and **2** [24].



1 **2**

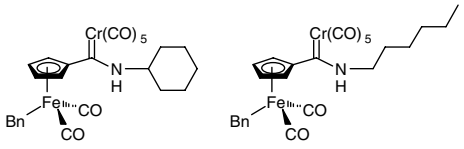
2. Results and discussion

Aminocarbene complexes can be obtained from alkoxycarbene complexes by aminolysis in an addition–elimination mechanism [24,25]. Here, ethoxycarbene complexes **3**–**5** served as starting materials [22,23].

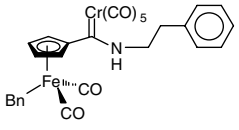


3 **4** **5**

Generally, the solutions of the ethoxycarbene complex and of the amine in THF were mixed at −78 °C and stirred for 1.5 h. After warming to 25 °C over 1 h the product was isolated chromatographically at silica gel. First, simple primary amines were tried. By this way aminocarbene complexes **6**–**8** were obtained in 10–28% yield from the respective unfunctionalized amines. While **6** and **8** were obtained as single isomers, **7** was isolated as a 7:1 mixture of isomers according to ^{1}H NMR. Due to the steric bulk of the cyclopentadienyliron moiety we regard the *Z* isomers as the obtained only or dominating component, which is also in accord with a crystal structure analysis (vide infra). Presumably because of the conformational flexibility of the alkyl chain in **7** a small amount of the *E* isomer exists.

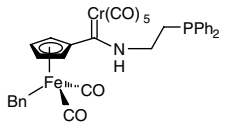


6 (23 %) **7** (28 %)

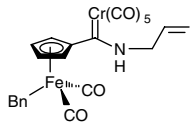


8 (10 %)

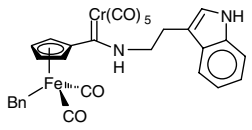
Next, some functionalized amines were tried. The functionalities applied include a tertiary phosphane, an allyl moiety, and the 2-indol-3-yl substituent as well as acetylenic derivatives. In all cases the additional functionality proved compatible with the formation of the respective carbene complexes, no reactions at the iron atom were observed. Remarkably, in some cases the yields achieved with functionalized amines were higher than those with non-functionalized amines. Thus, aminocarbene complexes **9**–**14** were obtained in 30–64% yield. While most of the products were isolated as a single isomer, **11** was obtained as a 3:1 mixture (^{1}H NMR) of stereoisomers with presumably the *Z* isomer dominating. In **9** the phosphane unit might serve as a ligand thus allowing the formation of either a chelate at the iron atom or at chromium. However, attempts to achieve this by photolytic decarbonylation (Pyrex, Phillps HPK 125 immersion lamp, 25 °C, 20 min, THF) failed and resulted in decomposition of **9**. The formation of alkyne derivatives **12**–**14**, which were obtained as single isomers in good yields, demonstrates the compatibility of the alkyne functional group with the organometallic moieties under the reaction conditions.



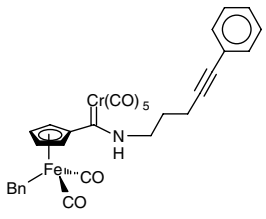
9 (41 %)



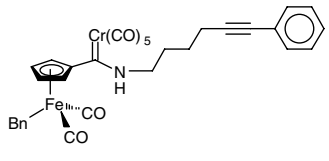
10 (30 %)



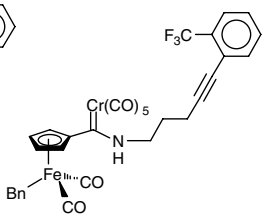
11 (32 %)



12 (64 %)

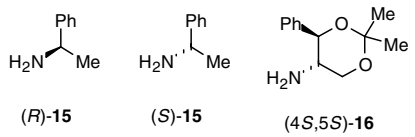


13 (41 %)

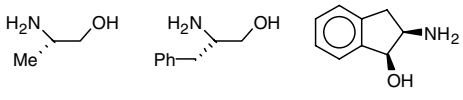


14 (31 %)

The products were characterized spectroscopically by the diagnostic ^{13}C NMR signal at $\delta \approx 260$ ppm being assigned to the aminocarbene carbon atom. In general, the aminocarbene complexes prepared are more air sensitive than corresponding alkoxycarbene complexes.

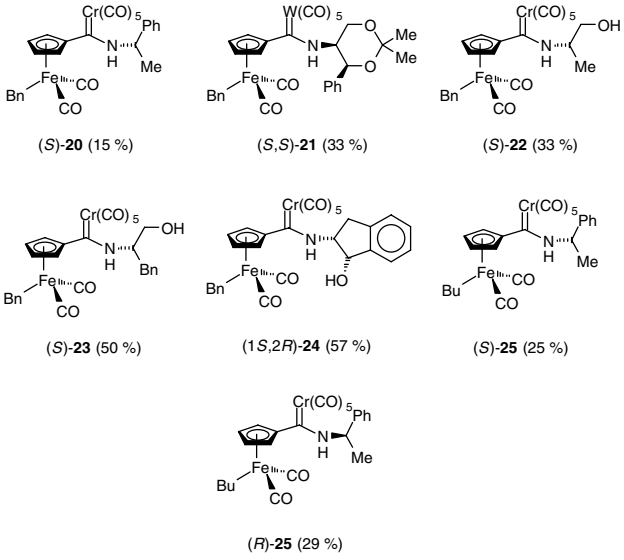


(*R*)-**15** (*S*)-**15** (4*S*,5*S*)-**16**



(*S*)-**17** (*S*)-**18** (1*S*,2*R*)-**19**

The availability of chiral amines, aminoacetal, and amino alcohols **15**–**19** in enantiomerically pure form allowed the introduction of chirality into the heterobimetallic carbene complexes starting from the respective complexes **3**–**5**. Chiral bimetallic aminocarbene complexes **20**–**25** were obtained in 15–57% yield. The chirality of most of these complexes is reflected in their ^{1}H NMR spectra by a clear differentiation of all four cyclopentadienyl protons. The diastereotopic methylene protons of the benzyl ligands give rise to two very close signals. Remarkably, the highest yields were obtained for those complexes, which bear an additional hydroxy group.



Whereas complexes (*S*)-**20**, (*S*)-**25**, and (*R*)-**25** were obtained as single stereoisomers, (2*S*,3*S*)-**21**(ca. 1:1), (*S*)-**22** (3:1), (*S*)-**23** (3:1), and (1*S*,2*R*)-**24** (2:1) were isolated as mixtures of isomers according to ^{1}H NMR. While most of the aminocarbene complexes were obtained as oils, we obtained crystals of (*S*,*S*)-**21**, which were suitable for an X-ray crystal structure analysis (Fig. 1).

The structure clearly shows that the carbene tungsten double bond is not coplanar with the cyclopentadienyl ligand system with a dihedral angle W1–C1–C2–C6 [108.5(14)°], so that no conjugation can be expected in the solid state. This contrasts the structure of **3**, in which the cyclopentadienyl system and the carbene complex moiety are more or less coplanar [23]. In addition, the configuration of the carbene carbon–nitrogen bond is *Z* as revealed from the dihedral angle C7–N1–C1–W1 [−8(2)°]. The steric interaction between the pentacarbonylchromium moiety and the substituent at N1 is minimized by adoption of a slightly bisected conformation as indicated by the torsional angle C28–W1–C1–N1 [−18.1(2)°]. In addition, the axial position of the amino substituent and the equatorial position of the phenyl group at the six-membered heterocyclic chair allow the heterocyclic system to be positioned further away from the pentacarbonyltungsten group than in the alternative chair conformation of the heterocycle. This would result in a closer interaction between the pentacarbonyltungsten group and the then axial phenyl group. Similar to the structure of **3** the four equatorial carbonyl ligands at tungsten are not fully coplanar, presumably for steric reasons. Just like in **3** the benzyl group and the carbene complex substituent at the cyclopentadienyl ligand adopt a quasi antiperiplanar conformation.

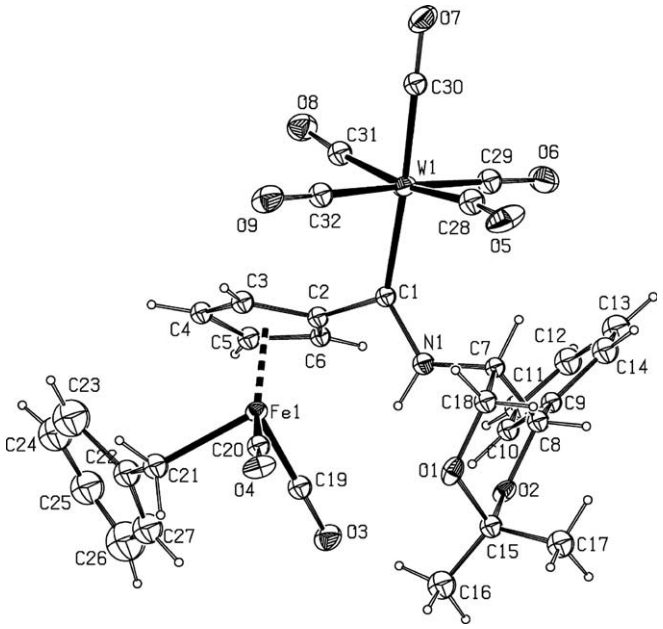
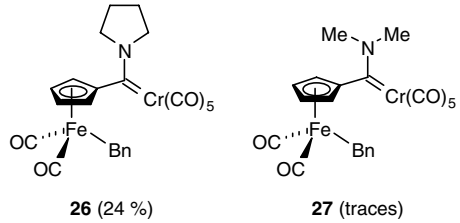


Fig. 1. Structure of (*S*,*S*)-**21** in the crystal (numbering scheme arbitrary). Selected bond lengths (pm), bond angles (°), and dihedral angles (°): C1–C2 154(2), C1–N1 142(2), C1–W1 214(2), C2–C3 144(2), C2–C6 144(2), C2–Fe1 207.6(14), C3–C4 141(2), C3–Fe1 210(2), C4–C5 139(2), C4–Fe1 214(2), C5–C6 139(2), C5–Fe1 206(2), C7–N1 145(2), C21–Fe1 211(2), C28–W1 191(2), C30–W1 195(2); C2–C1–W1 121.1(10), C2–C1–N1 104.6(12), C1–W1–C30 176.6(7), C28–W1–C31 170.9(9), C29–W1–C32 177.6(9); W1–C1–C2–C6 108.5(14), C7–N1–C1–C2 173.3(11), C7–N1–C1–W1 −8(2), C28–W1–C1–N1 −18.1(2).

Treatment of ethoxycarbene complex **3** with secondary amines afforded the corresponding aminocarbene complexes in moderate yields. Reaction of **3** with pyrrolidine gave complex **26** in 24% yield, while the corresponding dimethylamino derivative **27** was obtained only in trace amounts. The complexes were characterized spectroscopically, **26** gave crystals allowing a crystal structure analysis (Fig. 2).



26 (24 %) **27** (traces)

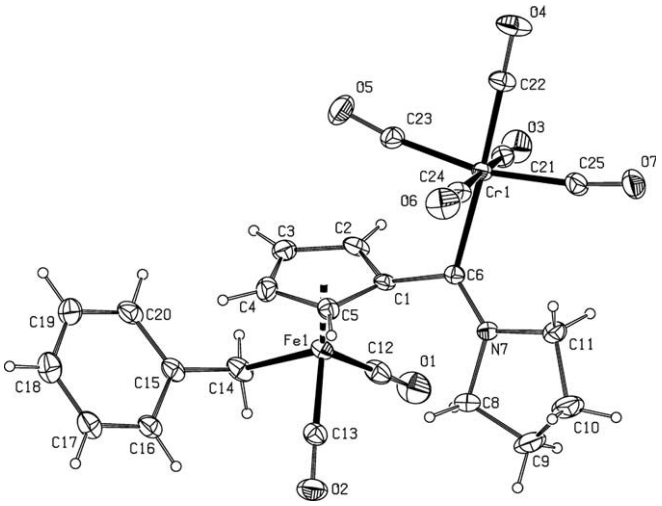


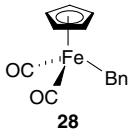
Fig. 2. Structure of **26** in the crystal. Selected bond lengths (pm), bond angles (°), and dihedral angles (°): C1–C2 143.0(3), C1–C5 141.6(3), C1–C6 149.1(3), C2–C3 141.1(4), C3–C4 139.9(4), C4–C5 141.8(4), C6–Cr1 214.5(2), Cr6–N7 131.1(3); C1–C6–Cr1 113.87(14), C1–C6–N7 117.1(2), Cr–C6–N7 128.5(2), C21–Cr1–C24 175.90(11), C23–Cr1–C25 166.95(11); C2–C1–C6–Cr1 52.9(3), C5–C1–C6–Cr1 −106.4(2), C2–C1–C6–N7 −134.2(2), C1–C6–N7–C11 −174.0(2), C5–C1–C6–C7 66.3(3).

The structure of **26** is rather similar to that of (*S*,*S*)-**21** in that the pentacarbonylmetal moiety is not part of the plane defined by the cyclopentadienyl π-system with dihedral angles C2–C1–C6–Cr1 [52.9(3)°] and C5–C1–C6–Cr1 [−106.4(2)°]. The carbene carbon–nitrogen bond also deviates significantly from coplanarity with the cyclopentadienyl π system [C5–C1–C6–C7 66.3(3)°]. The equatorial carbonyl ligands at chromium are bent away a little bit from the carbene carbon atom. As in (*S*,*S*)-**21** the compound adopts an antiperiplanar conformation with respect to the substituents at the cyclopentadienyl ring and the benzyl ligand at iron.

Overall the yields for the formation of the cyclopentadienyl aminocarbene complexes are only moderate in most cases and product formation is accompanied by formation of some decomposed material. The yields are, however, comparable to and in some cases higher than those obtained in the syntheses of other cyclopentadienyl carbene half sandwich and sandwich complexes [18,20,22,23].

As representative examples aminocarbene complexes **6**, **7**, and (*S*)-**20** were subjected to cyclic voltammetry measurements. Over all the plots obtained are rather similar to that of **3** [22] and of other bimetallic alkoxycarbene complexes [23]. Fig. 3 shows the representative CV plot of complex **6**.

The CV results are summarized in Table 1. For comparison the data of the unsubstituted cyclopentadienyl complex **28** is included [22].



28

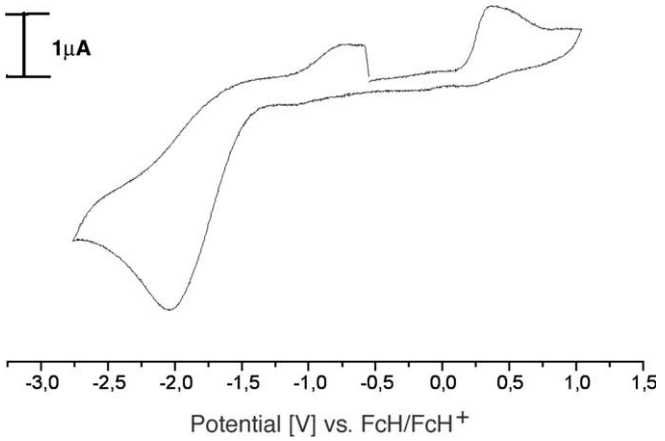


Fig. 3. CV plot of complex **6** (2 V/s, $T = 25$ °C, $c = 0.1$ mmol/L, $c_{TBAHFP} = 0.1$ mol/L, solvent acetonitril).

Table 1
Cyclic voltammetry of cyclopentadienyl aminocarbene complexes

Complex	v (V/s)	E_A (V)	E_K (V)
6	2	0.504	−2.029
7	2	0.361	−2.03
(*S*)-**20**	1	0.697	−1.872
	2	0.745	−1.922
28	0.1	0.688[a] [22]	

$T = 25$ °C, $c = 0.1$ mmol/L, $c_{TBAHFP} = 0.1$ mol/L (TBAHFP = tetrabutylammonium hexafluorophosphate), solvent acetonitrile. Potentials vs. FcH/FcH^+.

[a] In CH_2Cl_2.

For (*S*)-**20**, in addition a multi-sweep cyclovoltammogram was obtained, which is given in Fig. 4.

The cyclovoltammograms of aminocarbene complexes **6** and **7** are not well structured. As in the case of cyclopentadienyl alkoxycarbene complexes only one oxidation wave is observed in spite of the presence of two metals prone to oxidation. This might indicate a common HOMO of both metal atoms due to conjugation or two oxidation waves, which are not sufficiently resolved. In contrast to **6** and **7**, the multi-sweep CV of (*S*)-**20** shows two oxidation waves at 0.502 and at 0.739 V, the first one showing a corresponding reduction wave at 0.407 V indicating reversibility of this process. Thus it appears that two oxidations take place in this case, one of them presumably due to the oxidation of Fe(II) to Fe(III) and the other due to the oxidation of Cr(0). The oxidation potential of **28** (0.688 V), which is in between those observed for (*S*)-**20**, makes it difficult to decide, which of the observed oxidations is the Fe(II)/Fe(III) oxidation. The slight variation visible in the plot of the two circles might be due to some electrode surface passivation during the preceding circle. The oxidation potentials E_A of the aminocarbene complexes are somewhat lower than those of comparable alkoxycarbene complexes. This effect possibly reflects the increased electron donation of the amino substituent as compared to an alkoxy one. The observed reduction potentials E_K between −1.87 and −2.03 V

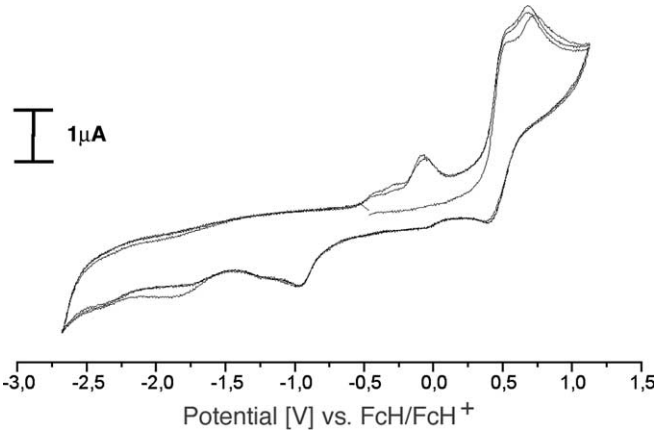


Fig. 4. Multisweep CV of (*S*)-**20** ($T = 25$ °C, $c = 0.1$ mmol/L, $v = 1$ V/s, $c_{TBAHFP} = 0.1$ mol/L, number of scans = 2, solvent acetonitril).

are most likely due to an electron transfer to the carbene ligand system with formation of the respective radical anion. Comparable values were observed by Casey for $(OC)_5Cr{=}(OEt)Ph$ (−1.34 V vs. SCE) [26].

In conclusion, a number of cyclopentadienyl aminocarbene half sandwich complexes have been prepared including functionalized as well as enantiomerically pure chiral amino substituents. Crystal structure analyses of two representatives do not show coplanarity of the cyclopentadienyl and the carbene complex π systems.

3. Experimental part

3.1. General

Unless otherwise indicated all operations were carried out under argon using standard Schlenk techniques. Petroleum ether (PE), *tert*-butyl methyl ether (TBME), tetrahydrofuran (THF) were distilled from sodium–potassium alloy with a small amount of benzophenone. Dichloromethane was dried over P_4O_{10} and distilled under argon. ^{1}H NMR: Bruker AVS 400 (400.1 MHz), AVS 200 (200.1 MHz); ^{13}C NMR: Bruker AM 400 (100.6 MHz), AVS 200 (50.3 MHz), signal multiplicities were determined with the APT [27] technique where indicated. IR: Bruker ISS 25, Perkin–Elmer FTIR spectrometers 580 and 1710. MS: Finnigan MAT 112, MAT 312; elemental analyses: Hareaeus CHN Rapid, Analysensysteme GmbH Elementar Vario EL. CV: Potentiostat Heka PG 285, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire, 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) (Fluka, electrochemical grade), dichloromethane, potential normalized to ferrocene/ferrocenium ion ($E_0 = 0.35$ V vs. Ag/AgCl).

3.2. General procedure for the synthesis of bimetallic aminocarbene complexes (GP)

The primary or secondary amine is added to the bimetallic alkyoxy(cyclopentadienyl)carbene complex in THF at −78 °C. After stirring at this temperature for 1.5 h the solution is warmed to 25 °C over 1 h. The solvent is removed at reduced pressure, and the yellow brown residue is purified by column chromatography at silica gel. The yellow product fraction is collected as the second fraction after the starting material. The product is obtained after solvent removal at reduced pressure and drying at 0.001 bar.

3.3. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](cyclohexylamino)carbene}pentacarbonylchromium (**6**)

GP: 350 mg (0.7 mmol) of **3**, 130 Ml of THF, 200 mg (2.0 mmol) of cyclohexylamine, column chromatography (30 × 5 cm PE/TBME 5:1 → 3:1). 90 mg (0.2 mmol, 23%) of **6**, yellow oil, 1 isomer.

IR (ATR): $\tilde{\nu} = 3303$ cm^{-1} (w, NH), 3021 (w, CH), 2934 (w, CH), 2858 (w, CH), 2051 (m, CrCO), 1999 (m, FeCO), 1970 (m), 1898 (s, br, CrCO, FeCO), 1536 (m), 1450 (m), 1220 (w), 1065 (m), 760 (m), 660 (s), 640 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.04$ (m, 2H, CH_2), 1.15 (m, 2H, CH_2), 1.32 (d br, 2H, CH_2), 1.47 (d br, 2H, CH_2), 1.78 (d br, 2H, CH_2), 2.60 (s, 2H, $FeCH_2$), 3.35 (m, 1H, CH), 3.78 (s br, 2H, Cp), 4.09 (s br, 2H, Cp), 6.09–7.11 (m, 5H, arom H), 8.54 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, APT, BB, C_6D_6): $\delta = 6.7$ (+, $FeCH_2$), 24.3 (+, $2CH_2$), 24.7 (+, $2CH_2$), 32.5 (+, $2CH_2$), 62.5 (−, CH), 84.4 (−, Cp), 86.2 (−, Cp), 117.8 (+, *ipso* Cp), 124.3–129.8 (−, arom. C), 152.4 (+, *ipso* Bn), 216.4 (+, FeCO), 217.5 (+, $CrCO_{cis}$), 223.3 (+, $CrCO_{trans}$), 262.7 (+, Cr=C) ppm. MS (70 eV, 140 °C): *m*/*z* (%) = 569 (9) [M^+], 541 (9) [$M^+ - CO$], 513 (3) [$M^+ - 2CO$], 484 (8) [$M^+ - 3CO$], 455 (4) [$M^+ - 4CO$], 427 (22) [$M^+ - 5CO$], 399 (31) [$M^+ - 6CO$], 371 (86) [$M^+ - 7CO$], 336 (35), 238 (32), 212 (16), 148, 121 (16) [$FeCp^+$], 91 (100) [$C_7H_7^+$], 65 (23) [Cp], 56 (10) [Fe^+], 51 (22). HRMS ($C_{26}H_{22}CrFeNO_7$): calc. 567.9708, found 568.0151. CV ($T = 25$ °C, $c = 0.1$ mmol/L, $c_{TBAHFP} = 0.3$ mol/L, number of scans, $v = 2$ V/s) $E_A = 0.361$ V.

3.4. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](hexylamino)carbene}pentacarbonylchromium (**7**)

GP: 350 mg (0.7 mmol) of **3**, 100 mL of THF, 150 mg (1.5 mmol) of hexylamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 110 mg (0.2 mmol, 28%) of **7**, yellow oil, 2 isomers (7:1), which were not separated. NMR signal assignments on the basis of C,H-correlated spectra.

IR ($CHCl_3$): $\tilde{\nu} = 3223$ cm^{-1} (w), 3060 (w, CH), 2930 (m, CH), 2873 (w, CH), 2054 (s, CrCO), 2004 (s, FeCO), 1929 (s br, CrCO, FeCO), 1545 (m), 1452 (m), 1262 (m), 1084 (m), 758 (m), 672 (m), 633 (m). ^{1}H NMR (400 MHz, C_6D_6, 2 isomers): $\delta = 0.63$ (m, 3H, CH_3), 0.88 (t, 3H, CH_3), 1.14–1.31 (m, 4H, CH_2), 1.65 (m, 4H, CH_2), 2.06 (m, 4H, CH_2), 2.51 (s, 2H, NCH_2, $FeCH_2$), 2.68 (s, 2H, NCH_2, $FeCH_2$), 3.35 (m, 8H, CH_2), 3.82 (s, 2H, Cp), 3.91 (s, 4H, Cp), 4.07 (s,

2H, Cp), 6.87–7.23 (m, arom. H), 8.21 (s, 1H, NH) ppm. One NH resonance could not be detected. ^{13}C NMR (100.6 MHz, APT, BB, C_6D_6): $\delta = 5.4$ (+, C-6, $FeCH_2$), 6.0 (+, C-6, $FeCH_2$), 12.0 (−, CH_3), 24.3 (−, CH_3), 22.7 (+, CH_2), 25.8 (+, CH_2), 26.4 (+, CH_2), 29.3 (+, CH_2), 31.5 (+, CH_2), 48.9 (+, $2CH_2$), 53.6 (+, $2CH_2$), 59.9 (+, CH_2), 85.630 (−, Cp), 85.635 (−, Cp), 85.638 (−, Cp), 85.9 (−, Cp), 118.5 (+, *ipso* Cp), 123.5–134.9 (−, arom. C), 153.2 (+, *ipso* Bn), 153.6 (+, *ipso* Bn), 216.5 (+, FeCO), 217.5 (+, $CrCO_{cis}$), 223.3 (+, $CrCO_{trans}$), 265.6 (+, Cr=C) ppm. One (*ipso* Cp) and one (+, Cr=C) resonance could not be detected. MS (70 eV, 70 °C): m/z (%) = 571 (1) [M^+], 431 (1) [$M^+ - 5CO$], 375 (1) [$M^+ - 7CO$], 360 (4), 212 (59) [$CpFeBn^+$], 148 (12) [$FeBn^+$], 121 (49) [$CpFe^+$], 91 (100) [$C_7H_7^+$], 65 (30) [Cp]. HRMS ($C_{26}H_{25}CrFeNO_7$): calc. 571.0015, found 571.0386. CV ($T = 25$ °C, $c =$ 0.1 mmol/L, $c_{TBAHFP} = 0.3$ mol/L, number of scans = 1: $E_A = 0.504$ V, $v = 2$ V/s).

3.5. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](2-phenylethylamino)carbene}pentacarbonylchromium (**8**)

GP: 350 mg (0.7 mmol) of **3**, 100 mL of THF, 250 mg (2.0 mmol) of 2-phenylethylamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 40 mg (0.7 mmol, 10%) of **8**, yellow oil, 1 isomer.

IR (CH_3Cl): $\tilde{\nu} = 3220$ cm^{-1} (w, NH), 3027 (w, CH), 2929 (w, CH), 2054 (m, CrCO), 2005 (m, FeCO), 1895 (s, br, CrCO, FeCO), 1712 (w), 1538 (m), 1488 (w), 1453 (w), 1396 (w), 1088 (w), 1029 (w), 698 (m), 657 (s), 639 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.45$ (s, 2H, $FeCH_2$), 2.51 (t, $^3J = 7.2$ Hz, 2H, NCH_2CH_2), 3.76 (s, 2H, Cp-H), 3.77 (t, $^3J = 6.4$ Hz, 2H, NCH_2), 4.03 (s, 2H, Cp-H), 6.87–7.16 (m, 10H, arom. H), 8.20 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, APT, BB, C_6D_6): $\delta = 6.2$ (+, $FeCH_2$), 35.0 (+, NCH_2CH_2), 54.2 (+, NCH_2), 84.88 (−, Cp-C), 84.93 (−, Cp-C), 117.3 (+, *ipso* Cp), 124.3–139.4 (−, arom. C), 136.6 (+, *ipso* arom. C), 152.9 (+, *ipso* Bn), 216.2 (+, FeCO), 217.4 (+, $CrCO_{cis}$), 223.2 (+, $CrCO_{trans}$), 267.3 (+, Cr=C) ppm. MS (70 eV, 140 °C): m/z (%) = 591 (12) [$M^+ - CO$], 563 (11) [$M^+ - 2CO$], 535 (4) [$M^+ - 3CO$], 507 (15) [$M^+ - 4CO$], 478 (17) [$M^+ - 5CO$], 449 (24) [$M^+ - 6CO$], 421 (11) [$M^+ - 7CO$], 393 (87), 302 (59), 275 (87), 251 (71), 212 (41), 148 (22) [$FeBn^+$], 121 (29) [$FeCp^+$], 91 (100) [$C_7H_7^+$], 65 (29) [Cp], 56 (14) [Fe^+], 52 (38) [Cr^+]. $C_{28}H_{21}CrFeNO_7$ (590.9693): calc. C 56.85, H 3.55, N 2.37; found C 56.32, H 3.89, N 0.97. HRMS ($C_{28}H_{21}CrFeNO_7$): calc. 590.9693, found 591.0073.

3.6. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](2-diphenylphosphanylethylamino)carbene}pentacarbonylchromium (**9**)

GP: 370 mg (0.7 mmol) of **3**, 30 mL of THF, 340 mg (1.5 mmol) of 2-diphenylphosphanylethylamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 200 mg (0.2 mmol, 41%) of **9**, yellow solid (m.p. 90 °C), 1 isomer.

IR (ATR): $\tilde{\nu} = 2927$ cm^{-1}, 2052 (s, CrCO), 2007 (s, FeCO), 1899 (s, br, CrCO, FeCO), 1553 (m), 1437 (m), 1260 (m), 1171 (w), 1026 (m), 800 (w), 719 (w), 695 (w), 672 (w). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.95$ (s, 2H, PCH_2) 2.85 (s, H, $FeCH_2$), 3.98 (s, 2H, Cp-H), 4.10 (m, 2H, 7-H, NCH_2), 5.37 (s, 2H, Cp-H), 6.98–7.54 (m, 15H, arom. H), 11.05 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, BB, C_6D_6): $\delta = 7.3$ ($FeCH_2$), 28.2 (PCH_2), 48.8 (C-7, NCH_2), 85.9 (Cp-C), 89.4 (Cp-C), 107.9 (*ipso* Cp-C), 123.9–132.4 (arom. C), 152.4 (*ipso* Bn-C), 216.2 (FeCO), 218.2 ($CrCO_{cis}$), 223.1 ($CrCO_{trans}$), 262.3 (Cr=C) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): $\delta = 28.9$ (s) ppm. HRMS ($C_{34}H_{26}CrFeNO_7P$): calc. 698.9620, found 699.0201.

3.7. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](allylamino)carbene}pentacarbonylchromium (**10**)

GP: 370 mg (0.7 mmol) of **3**, 100 mL of THF, 0.3 mL (0.7 mmol) of allylamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 120 mg (0.2 mmol, 30%) of **10**, yellow solid (m.p. 85 °C (dec.)), 1 isomer. NMR signal assignments were made on the basis of C,H-correlated spectra.

IR (ATR): $\tilde{\nu} = 2963$ (w) cm^{-1}, 2054 (s, CrCO), 2004 (s, FeCO), 1885 (s, br, CrCO, FeCO), 1594 (m), 1450 (m), 1259 (m), 1094 (m), 1011 (s), 865 (w), 797 (s), 700 (m), 670 (s) 656 (s), 626 (m), 537 (w). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.60$ (s, 2H, $FeCH_2$), 3.55 (s br, 2H, NCH_2), 3.89 (s, 2H, Cp-H), 4.76 (d, 1H, $^3J = 10.3$ Hz, CH=CH_{cis}H), 4.85 (d, 1H, $^3J = 17.2$ Hz, CH=CHH_{trans}), 5.09 (m, 1H, CH=CH_2), 6.96–7.36 (m, 5H, arom. H), 8.41 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, BB, C_6D_6): $\delta = 6.4$ ($FeCH_2$), 51.5 (CH_2), 84.6 (Cp-H), 90.6 (Cp-H), 101.2 (*ipso* Cp), 118.1 (=CH_2) 123.7–130.7 (arom., olef. C), 150.9 (*ipso* Bn), 215.1 (FeCO), 217.1 ($CrCO_{cis}$), 221.7 ($CrCO_{trans}$), 272.5 (Cr=C) ppm. MS (70 eV, 140 °C): m/z (%) = 527 (12) [M^+], 499 (16) [$M^+ - CO$], 471 (3) [$M^+ - 2CO$], 445 (3) [$M^+ - 3CO$], 415 (18) [$M^+ - 4CO$], 387 (34) [$M^+ - 5CO$], 359 (20) [$M^+ - 6CO$], 331 (47) [$M^+ - 7CO$], 263 (34), 239 (74), 212 (16), 149 (21), 119 (32), 91 (100) [$C_7H_7^+$], 57 (26) [Fe^+] 52 (22), [Cr^+]. HRMS ($C_{23}H_{17}NO_7CrFe$): calc. 526.9761, found 526.9760.

3.8. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][2-(3-indenyl)ethylamino]carbene}pentacarbonylchromium (**11**)

GP: 240 mg (0.5 mmol) of **3**, 100 mL of THF, 220 mg (1.4 mmol) of tryptamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 92 mg (0.2 mmol, 32%) of **11**,

yellow-green oil, 2 isomers I and II (3:1, ^{1}H NMR). NMR signal assignments were made by means of correlated spectra.

IR (ATR): $\tilde{\nu} = 3222$ cm^{-1} (w), 3022 (w), 2930 (w), 2054 (m, CrCO), 2004 (m, FeCO), 1899 (s, br, FeCO, CrCO), 1773 (m), 1715 (m), 1594 (m, arom. C=C), 1542 (m, arom. C=C), 1489 (m, arom. C=C), 1450 (m), 1398 (m), 1068 (w), 1028 (w), 756 (m), 659 (m), 641 (m) 585 (m). ^{1}H NMR (400 MHz, C_6D_6) Isomer I: $\delta = 2.38$ (s, 2H, 6-H, $FeCH_2$), 2.80 (t, $^3J = 6.5$ Hz, 2H, 9-H), 3.72 (s, 2H, Cp), 3.99 (s, 2H, Cp), 4.03 (dt, 2H, 8-H), 6.79 (s br, 1H, NH or 10-H), 6.96–7.20 (m, 9H, arom. H), 7.49 (d, 1H, NH or 10-H), 8.45 (s, 1H, NH) ppm. ^{1}H NMR (400 MHz, C_6D_6) Isomer II: $\delta = 2.56$ (t br, 2H, 9-H), 2.63 (s, 2H, 6-H, $FeCH_2$), 2.62 (dt, 2H, H-8), 3.89 (s, 2H, Cp), 4.34 (s, 2H, Cp), 6.96- 7.20 (m, arom. H), 6.97 (d, $^3J =$ 7.9 Hz, 1H, NH or 10-H), 6.96–7.20 (m, 9H, arom. H), 7.42 (d, 1H, NH or 10-H), 8.71 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, APT, C_6D_6) Isomer I: $\delta = 4.4$ (C-6), 23.0 (CH_2), 51.0 (C-8), 82.3 (Cp), 84.0 (Cp), 108.3 (*ipso* Cp), 109.8 (CH), 116.7 (CH or arom. H), 118.2 (CH or arom. C), 120.8 (CH or arom. C), 120.9–135.0 (arom. C), 150.5 (*ipso* Bn), 214.2 (FeCO), 215.6 ($CrCO_{cis}$), 221.3 ($CrCO_{trans}$), 264.3 (Cr=C) ppm. ^{13}C NMR (400 MHz, C_6D_6) Isomer II: $\delta = 5.0$ (C-6), 23.0 (CH_2), 51.0 (C-8), 83.8 (Cp), 89.3 (Cp), 107.4 (*ipso* Cp), 109.8 (CH), 116.7 (CH or arom. H), 118.2 (CH or arom. C), 120.9 (CH or arom. C), 120.9–135.0 (arom. C), 150.1 (*ipso* Bn), 214.2 (FeCO), 215.6 ($CrCO_{cis}$), 221.3 ($CrCO_{trans}$), 266.9 (Cr=C) ppm. HRMS ($C_{30}H_{22}CrFeN_2O_7$): calc. 629.9748, found 630.0182.

3.9. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](5-phenylpent-4-ynylamino)carbene} pentacarbonylchromium (**12**)

GP: 360 mg (0.7 mmol) of **3**, 100 mL of THF, 110 mg (0.7 mmol) of 5-phenylpent-4-ynylamine [28], column chromatography (30×5 cm, PE/TBME 5:1 → 3:1). 280 mg (0.5 mmol, 64%) of **12**, yellow oil, one isomer. ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated spectra.

IR (ATR): $\tilde{\nu} = 3224$ cm^{-1} (w), 2930 (w, CH_2), 2055 (m, CO), 2003 (m, CO), 1899 (s, br, CO), 1597 (m), 1455 (m), 1260 (m), 1170 (m) 1095 (m), 1032 (s), 769 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.08$ (m br, 2H, CH_2), 2.03 (m br, 2H, CH_2), 2.48 (s, 2H, $FeCH_2$), 3.13 (br, 2H, CH_2), 3.91 (s, 2H, Cp), 4.49 (s, 2H, Cp), 7.01–7.47 (m, 10H, arom. H), 8.52 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, APT, C_6D_6): $\delta = 6.4$ ($FeCH_2$), 16.0 (CH_2), 27.4 (CH_2), 49.4 (C-6, NCH_2), 82.4 (≡C), 84.8 (Cp), 86.8 (≡C), 90.9 (Cp), 101.2 (*ipso* Cp), 123.0 (arom. C), 123.6–128.0 (arom. C), 131.3 (*ipso* arom. C), 151.0 (*ipso* Bn), 215.3 (FeCO), 217.2 ($CrCO_{cis}$), 221.8 ($CrCO_{trans}$), 270.8 (Cr=C) ppm. HRMS ($C_{31}H_{23}CrFeNO_7$): calc. 628.9634, found 629.0229.

3.10. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](6-phenylhex-5-ynylamino)carbene} pentacarbonylchromium (**13**)

GP: 240 mg (0.5 mmol) of **3**, 100 mL of THF, 220 mg (1.4 mmol) of 6-phenylhex-5-ynylamine [28], column chromatography (30×5 cm, PE/TBME 5:1 → 3:1). 120 mg (0.2 mmol, 41%) of **13**, yellow solid (m.p. 97 °C) 1 isomer. ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated spectra.

IR (ATR): $\tilde{\nu} = 3468$ cm^{-1} (w, NH), 3413 (w, NH), 3021 (w, CH_2), 2927 (w, CH_2), 2054 (m, CO), 2003 (m, CO), 1889 (s, br, CO), 1593 (m, C=C), 1530 (m, C=C), 1488 (m, C=C), 1454 (m), 1260 (m), 1227 (m) 1086 (m), 1028 (m), 740 (s), 656 (s), 640 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.34$ (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 2.17 (t, 2H, $^3J = 6.6$ Hz, CH_2), 2.48 (s, 2H, $FeCH_2$), 3.43 (m, 2H, 6-H, CH_2), 3.83 (s, 2H, Cp), 4.05 (s, 2H, Cp), 7.00–7.54 (m, 10H, arom. H), 8.12 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 6.0$ ($FeCH_2$), 19.9 (CH_2), 26.5 (CH_2), 29.3 (CH_2), 53.8 (CH_2), 83.0 (Cp), 84.2 (≡C), 86.5 (Cp), 89.2 (≡C), 118.2 (*ipso* Cp), 124.3 (arom. C), 127.9 (arom. C), 129.1–131.9 (arom. C), 153.3 (*ipso* Bn), 216.5 (FeCO), 217.4 ($CrCO_{cis}$), 223.3 ($CrCO_{trans}$), 266.2 (Cr=C) ppm. MS (70 eV, 130 °C): *m*/*z* (%) = 451 (2) [$M^+ - 7CO + 4H$], 423 (6), 395 (14), 360 (4), 331 (10), 304 (36), 220 (84), 212 (33), 108 (73), 91 (100) [$C_7H_7^+$], 52 (80) [Cr^+]. HRMS ($C_{32}H_{25}CrFeNO_7$): calc. 642.9598, found 643.0386.

3.11. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](5-ortho-trifluoromethylphenylpent-4-ynylamino)carbene} pentacarbonylchromium (**14**)

GP: 360 mg (0.7 mmol) of **3**, 100 mL of THF, 160 mg (0.7 mmol) of (5-*ortho*-trifluoromethyl)phenylpent-4-ynylamine [28], column chromatography (30×5 cm, PE/TBME 5:1 → 3:1). 150 mg (0.2 mmol, 31%) of **14**, yellow oil, 1 isomer.

IR (ATR): $\tilde{\nu} = 3222$ cm^{-1} (w, NH), 2962 (w), 2929 (w, CH_2), 2056 (m, CO), 2006 (m, CO), 1902 (s, br, CO), 1593 (m), 1541 (m), 1489 (m), 1450 (m), 1259 (m), 1168 (m) 1095 (s), 1032 (s), 764 (s), 660 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.53$ (qui, 2H, 7-H, CH_2), 2.17 (t, 2H, 8-H, CH_2), 2.49 (s, 2H, 9-H, $FeCH_2$), 3.65 (q, 2H, 6-H, NCH_2), 3.82 (s, 2H, Cp), 4.05 (s, 2H, Cp), 7.42–6.69 (m, 9H, arom. H), 8.18 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 5.3$ ($FeCH_2$), 16.1 (CH_2), 27.2 (CH_2), 51.7 (NCH_2), 78.1 (≡C), 83.1 (Cp), 85.0 (Cp), 93.3 (≡C), 117.3 (*ipso* Cp), 123.6 (arom. C), 125.3–130.8 (arom. C), 133.4 (*ipso* arom. C), 152.5 (*ipso* Bn), 215.7 (FeCO), 216.6 ($CrCO_{cis}$), 222.6 ($CrCO_{trans}$), 267.0 (Cr=C) ppm. MS (70 eV, 160 °C): *m*/*z* (%) = 614 (22) [$M^+ + 1 - 3CO$], 502 (100) [$M^+ + 1 - 7CO$], 450 (34), 392 (91), 353 (34), 328 (18), 251 (48), 191 (32), 149 (39), 121 (16), 91 (29) [$C_7H_7^+$], 67 (18), 56 (23) [Fe^+]. HRMS ($C_{31}H_{22}CrFeF_3NO_6$): calc. 668.9691, found 669.0154.

3.12. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][(S)-phenylethylamino]carbene}pentacarbonylchromium [(S)-20]

GP: 200 mg (0.4 mmol) of **3**, 100 mL of THF, 142 mg (1.2 mmol) of (*S*)-1-phenylethylamine, column chromatography (30×5 cm, PE/TBME 10:1 → 2:1). 35 mg (0.06 mmol, 15%) of (*S*)-**20**, yellow oil, 1 isomer. ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated spectra.

IR (ATR): $\tilde{\nu} = 2963$ cm^{-1} (w, CH), 2115 (w), 2055 (s, CO), 2005 (m), 1982 (m, CO), 1900 (s, br, CO), 1773 (m), 1488 (m), 1449 (m), 1260 (m) 1200 (m), 1183 (m), 841 (m), 799 (m) 663 (s). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.42$ (d, $^3J = 6.8$ Hz, 3H, CH_3), 2.55 + 2.56 (2s, 2H, $FeCH_2$), 3.61 (s, 1H, Cp), 3.72 (s, 1H, Cp), 3.79 (s, 1H, Cp), 4.28 (s, 1H, Cp), 5.56 (dq, $^3J = 9.4$, 6.8 Hz, 1H, NCH), 7.00 (m, 10H, arom. H), 9.12 (br s, 1H, NH) ppm . ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 6.9$ ($FeCH_2$), 21.8 (CH_3), 62.8 (CH), 83.9 (Cp), 84.1 (Cp), 85.2 (Cp), 88.5 (Cp), 117.8 (*ipso* Cp), 124.2–129.6 (arom. C), 139.3 (*ipso* arom. C), 152.0 (*ipso* Bn), 216.1 (FeCO), 216.3 (FeCO), 217.3 ($CrCO_{cis}$), 223.1 ($CrCO_{trans}$), 264.5 (Cr=C) ppm. MS (70 eV, 120 °C): *m*/*z* (%) = 591 (5) [M^+], 563 (3) [$M^+ - CO$], 507 (8) [$M^+ - 3CO$], 451 (5) [$M^+ - 5CO$], 423 (3) [$M^+ - 6CO$], 395 (12) [$M^+ - 7CO$], 360 (12), 332 (5), 238 (20), 212 (24), 177 (10), 147 (18) [$FeBn^+$], 119 (51) [$C_8H_7O^+$], 91 (100) [$C_7H_7^+$], 52 (10) [Cr^+]. HRMS ($C_{28}H_{21}CrFeNO_7$): calc. 590.9656, found 591.0072. $C_{28}H_{21}CrFeNO_7$ (590.9656): calc. C 56.85, H 3.55, N 2.37; found C 57.14, H 3.95, N 2.01. CV ($T = 25$ °C, $c =$ 0.1 mmol/L, $c_{TBAHFP} = 0.1$ mol/L, number of scans = 1): $E_A = 0.697$ V ($v = 1$ V/s), 0.745 V ($v = 2$ V/s); multisweep CV ($T = 25$ °C, $c = 0.1$ mmol/L, $c_{TBAHFP} = 0.1$ mol/L, 2 scans, $v = 1$ V/s): $E_A = 0.502$, 0.739 V, $E_K = 0.407$ V.

3.13. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][(S,S)-2,2-dimethyl-4-phenyl-[1,3]dioxan-5-ylamino]carbene}pentacarbonyltungsten(0) [(S,S)-21]

GP: 1300 mg (2.0 mmol) of **4**, 100 mL of THF, 830 mg (4.0 mmol) of (4*S*,5*S*)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxane [(4*S*,5*S*)-**16**], column chromatography (30×5 cm, PE/TBME 5:1). 520 mg (0.6 mmol, 33%) of (*S*,*S*)-**21**, yellow oil, 2 isomers (ca. 1:1, separated by column chromatography). Crystallization from THF/hexane afforded orange prismatic crystals suitable for a crystal structure analysis. ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated spectra.

IR (ATR): $\tilde{\nu} = 2927$ (w) cm^{-1}, 2062 (s, CO), 2003 (s, CO), 1889 (s, br, CO), 1594 (m), 1451 (m), 1261 (m), 1095 (m), 1029 (m), 845 (m), 757 (m), 737 (m), 689 (s), 628 (s), 578 (s). Isomer I: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.09$ (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.56 (d, 2H, $FeCH_2$), 3.23 (s br, 1H, Cp), 3.63 (d, 1H, CH_2), 3.70 (s br, 1H, Cp), 3.76 (d, 1H, CH_2), 3.89 (s br, 1H, Cp), 4.45 (d, 1H, NC*H*), 4.48 (s br, 1H, Cp), 4.78 (s, 1H, CH), 6.97–7.33 (m, 10H, arom. H), 10.03 (d br, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, BB, APT, C_6D_6): $\delta = 7.3$ (+, $FeCH_2$), 18.1 (−, CH_3), 29.5 (−, CH_3), 58.2 (−, CH_3), 64.9 (+, CH_2), 73.4 (−, CH), 83.79 (−, Cp), 84.8 (−, Cp), 85.0 (−, Cp), 97.1 (−, Cp), 101.0 (+, *ipso* C), 104.8 (+, *ipso* Cp), 124.4–129.2 (−, Ph), 137.5 (+, *ipso* arom. C), 151.6 (+, *ipso* Bn), 199.0 (+, WCO_{cis}), 204.4 (+, WCO_{trans}), 216.4 (+, FeCO), 216.6 (+, FeCO), 246.9 (W=C). Isomer II: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.13$ (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 2.68 (s , 2H, $FeCH_2$), 3.42 (d br, $^3J = 1.5$ Hz, 1H, Cp), 3.74 (s br, 1H, Cp), 3.88 (m, 2H, CH_2), 3.92 (s br, 1H, Cp), 4.01 (dt br, 1H, Cp), 4.47 (m, 1H, NCH), 4.76 (s br, 1H, Cp), 6.96–7.38 (m, 10H, arom. H), 9.42 (d br, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, BB, APT, C_6D_6): $\delta = 5.4$ (+, $FeCH_2$), 18.4 (−, CH_3), 29.4 (−, CH_3), 62.2 (−, CH_3), 65.0 (+, CH_2), 71.0 (−, CH), 81.7 (−, Cp), 83.3 (−, Cp), 86.1 (−, Cp), 94.0 (−, Cp), 100.3 (+, *ipso* C), 117.4 (+, *ipso* Cp), 123.5–128.8 (−, arom. C), 137.4 (+, *ipso* arom. C), 152.0 (+, *ipso* Bn), 198.0 (+, WCO_{cis}), 215.6 (+, WCO_{trans}), 217.5 (+, FeCO), 246.9 (W=C). C_{32} $H_{27}FeNO_9W$ (809): calc. C 47.46, H 3.33 N 1.73; found C 47.90, H 3.53 N 1.99. HRMS ($C_{32}H_{27}FeNO_9W$): calc. 809.2123, found 809.2330.

3.14. Crystal structure analysis of (S,S)-21 [29]

C_{32} $H_{27}FeNO_9W$, molecular weight 809.25, crystal system monoclinic, space group $P2_1$, $a = 9.896(3)$ Å, $\alpha = 90°$, $b = 25.842(5)$ Å, $\beta = 91.00(3)°$, $c = 12.700(3)$ Å, $\gamma = 90°$, $V = 3247.3(14)$ Å^3, $Z = 4$, $d_{calc.} = 1.655$ g/cm^3, $F(000) =$ 1592e, $\mu = 4.039$ mm^{-1}, crystal color red, crystal size $0.15 \times 0.07 \times 0.04$ mm, Stoe IPDS area detector diffractometer, $T = 300(2)$ K, Mo K$\alpha = 0.71073$ Å, $\theta_{min} = 2.06$, $\theta_{max} = 26.05°$, $-12 \leqslant h \leqslant 12$, $-31 \leqslant k \leqslant 31$, $-15 \leqslant l \leqslant 15$, absorption correction semiempiric, no extinction correction, 47011 collected, 12124 unique reflections, [R(int) = 0.1856], refinement program: SHELXL-93, refinement by least squares method (F^2), $F^2 = 0.463$, R-Indices: [$I > 2$ $\sigma(I)$] $R_1 = 0.0351$, $wR_2 = 0.0550$, R-Indices (all data): $R_1 =$ 0.1795 , $wR_2 = 0.0885$, residual electron density: 0.413, −0.734 Å^{-3}, completeness of data 94.3%.

3.15. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][(S)-2-hydroxy-1-methylethylamino]carbene}pentacarbonylchromium [(S)-22]

GP: 300 mg (0.6 mmol) of **3**, 100 mL of THF, 90 mg (1.2 mmol) of (*S*)-2-aminopropan-1-ol, column chromatography (30×5 cm, PE/TBME 5:1). 105 mg (0.2 mmol, 33%) of (*S*)-**22**, yellow oil, 2 isomers (ca. 3:1). ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated as well as by 1D-TOCSY spectra.

IR (ATR): $\tilde{\nu} = 2965$ (w) cm^{-1}, 2054 (s, CrCO), 2001 (s, FeCO), 1889 (s, br, CrCO, FeCO), 1450 (m), 1260 (m), 1048 (m), 1009 (s), 700 (m), 677 (m). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.08$ (d, 3H, $^3J = 6.6$ Hz, CH_3), 2.62 (s, 1H, $FeCH_{2'}$), 2.65 + 2.66 (2s, 2H, $FeCH_2$), 2.90 (d, 1H, CH_2),

3.04 (s, 1H, OH), 3.23 (d, 1H, CH_2), 3.73 (s, 1H, Cp), 3.82 (s, 1H, Cp), 3.90 (s, 1H, Cp), 3.95 (s, 1H, Cp), 4.18 (s, 1H, Cp), 4.22 (s, 1H, Cp), 4.32 (m, 1H, CH), 4.47 (s, 1H, Cp), 4.52 (m, 1H, CH), 4.81 (s, 1H, Cp), 6.94–7.26 (m, 10H, arom. H), 8.96 (s, 1H, NH), 9.23 (s, 1H, NH) ppm. ^{1}H NMR (500 MHz, TOCSY, C_6D_6, Cp signals): $\delta = 3.82$ (s, 1H, Cp), 3.90 (s, 1H, Cp), 4.22 (s, 1H, Cp), 4.47 (s, 1H, Cp) ppm. ^{1}H NMR (500 MHz, TOCSY, C_6D_6, Cp signals of minor isomer): $\delta = 3.73$ (s, 1H, Cp), 3.95 (s, 1H, Cp), 4.18 (s, 1H, Cp), 4.81 (s, 1H, Cp) ppm. ^{13}C NMR (100.6 MHz, BB, C_6D_6, major isomer): $\delta = 7.5$ ($FeCH_2$), 17.7 (CH_3), 60.2 (CH_3CH), 65.2 (CH_2), 84.5 (Cp), 85.5 (Cp), 86.2 (Cp), 88.4 (Cp), 116.7 (*ipso* Cp), 124.1–130.3 (arom. C), 152.9 (*ipso* Bn), 212.2 (FeCO), 216.9 (FeCO), 218.3 ($CrCO_{cis}$), 223.9 ($CrCO_{trans}$), 264.6 (Cr=C). HRMS ($C_{23}H_{19}CrFeNO_8$): calc. 544.9725, found 544.9865.

3.16. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][(*S*)-2-hydroxy-1-benzylethylamino]carbene}pentacarbonylchromium [(*S*)-**23**]

GP: 103 mg (0.2 mmol) of **3**, 15 mL of THF, 70 mg (0.4 mmol) of (*S*)-2-amino-3-phenylpropanol, column chromatography (30 × 5 cm, PE/TBME 5:1). 70 mg (0.1 mmol, 50%) of (*S*)-**23**, yellow oil, 2 isomers (ca. 3:1), which could not be separated by column chromatography.

IR (ATR): $\tilde{\nu} = 3338$ (w) cm^{-1}, 3024 (w), 2929 (w), 2054 (s, CO), 2002 (s, CO), 1896 (s, br, CO), 1594 (m), 1450 (m), 1260 (m), 1180 (w), 1028 (m), 800 (m), 741 (w), 699 (w), 666 (w), 646 (m), 583 (m), 540 (w). ^{1}H NMR (400 MHz C_6D_6, major isomer): $\delta = 2.52$ (m, 2H, CH_2), 2.59 (s, 1H, OH), 2.69 (s, 2H, $FeCH_2$), 3.22 (m, 2H, CH_2), 3.77 (s, 1H, Cp), 3.81 (s, 1H, Cp), 4.13 (s, 1H, Cp), 4.31 (s, 1H, Cp), 4.57 (m, 1H, CH), 6.96–7.21 (m, 10H, arom. H), 9.33 (s br, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, BB, C_6D_6, major isomer): $\delta = 7.5$ ($FeCH_2$), 17.7 (CH_3), 60.2 (CH_3CH), 65.2 (CH_2), 84.5 (Cp), 85.5 (Cp), 86.2 (Cp), 88.4 (Cp), 116.7 (*ipso* Cp), 124.1–130.3 (arom. C), 152.9 (*ipso* Bn), 212.2 (FeCO), 216.9 (FeCO), 218.3 ($CrCO_{cis}$), 223.9 ($CrCO_{trans}$), 264.6 (Cr=C). HRMS ($C_{29}H_{23}CrFeNO_8$): calc. 620.9694, found 621.0178.

3.17. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl][(1*S*,2*R*)-1-hydroxyindan-2-ylamino]carbene}pentacarbonylchromium [(1*S*,2*R*)-**24**]

GP: 1000 mg (2.0 mmol) of **3**, 100 mL of THF, 600 mg (4.0 mmol) of (1*S*,2*R*)-2-amino-1-indanol, column chromatography (30 × 5 cm, PE/TBME). 710 mg (0.1 mmol, 57%) of (1*S*,2*R*)-**24**, yellow oil, 2 isomers (ca. 2:1). ^{1}H and ^{13}C NMR signal assignments were made on the basis of correlated spectra.

IR (CH_3Cl): $\tilde{\nu} = 2928$ (w) cm^{-1}, 2054 (s, CO), 2005 (s, CO), 1894 (s, br, CO), 1594 (m), 1449 (m), 1267 (m), 1199 (w), 1021 (m), 943 (w), 846 (w), 802 (w), 771 (w), 741 (w), 699 (w). ^{1}H NMR (400 MHz, C_6D_6, major isomer): $\delta = 2.35$ (d br, 2H, CH_2), 2.60 (d br, 2H, CH_2), 2.64 (s, 2H, $FeCH_2$), 3.76 (s br, 2H, Cp), 3.93 (s br, 1H, Cp), 4.44 (s br, 1H, Cp), 4.51 (s br, 1H, Cp), 5.11 (s, 1H, *CH*OH), 5.84 (dd, 1H, NCH), 5.90 (dd, 1H, NCH), 6.90–7.38 (m, 18H, arom. H), 9.54 (s br, 1H, NH). ^{13}C NMR (100.6 MHz C_6D_6, APT, major isomer): $\delta = 7.4$ (+, $FeCH_2$), 41.3 (+, CH_2), 71.0 (−, NH*C*H), 75.1 (−, *C*HOH), 84.24 (−, Cp), 84.26 (−, Cp), 87.4 (−, Cp), 89.8 (−, Cp), 114.1 (+, *ipso* Cp), 124.0–129.4 (−, arom. C), 138.7 (+, *ipso* arom. C), 141.2 (+, *ipso* arom. C), 152.8 (+, *ipso* Bn), 216.6 (+, br, FeCO), 218.3 (+, $CrCO_{cis}$), 222.9 (+, $CrCO_{trans}$), 223.9 (+, $CrCO_{trans}$), 266.4 (Cr=C). MS (70 eV, 170 °C): *m*/*z* (%) = 535 (12) [$M^+ - 4CO$], 436 (14), 369 (20), 331 (14), 277 (17), 249 (12), 220 (21), 191 (19), 162 (17), 91 (100) [$C_7H_7^+$], 73 (42), 65 (23). HRMS ($C_{29}H_{21}CrFeNO_8$): calc. 618.9700, found 619.0022.

3.18. {[Butyldicarbonyliron(II)-η^5-cyclopentadienyl][(*S*)-1-phenylethyl-1-amino]carbene}pentacarbonylchromium [(*S*)-**25**]

GP: 400 mg (0.8 mmol) of **5**, 50 mL of THF, 200 mg (1.6 mmol) of (*S*)-1-phenylethylamine, column chromatography (30 × 5 cm, PE/TBME 5:1). 35 mg (0.2 mmol, 25%) of (*S*)-**25**, yellow oil, 1 isomer.

IR (ATR): $\tilde{\nu} = 2963$ cm^{-1} (w, CH), 2053 (s, CO), 2005 (m), 1987 (m, CO), 1902 (s, br, CO), 1776 (m), 1450 (m), 1263 (m) 1198 (m). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.9$ (m, CH_3), 1.2–1.45 (m, 6H, CH_2), 1.49 (d, 3H, $^3J = 6.8$ Hz, CH_3), 3.77 (s, 2H, Cp), 3.93 (s, 1H, Cp), 4.36 (s, 1H, Cp), 5.59 (dq, 1H, CH), 7.05–7.24 (m, 5H, arom. H), 7.69 (s, 1H, NH). ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 5.6$ ($FeCH_2$), 14.6 (CH_3), 22.8 (CH_3 or CH), 28.7 (CH_2), 41.4 (CH_2), 63.4 (CH_3 or CH), 82.9 (Cp), 84.0 (Cp), 86.1 (Cp), 87.4 (Cp), 119.7 (*ipso* Cp), 127.1 (arom. C), 128.9–129.6 (arom. C), 140.1 (*ipso* arom. C), 217.5 (FeCO), 217.7 ($CrCO_{cis}$), 223.9 ($CrCO_{trans}$), 264.8 (Cr=C). HRMS ($C_{25}H_{23}CrFeNO_7$): calc. 556.9818, found 557.0011.

3.19. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](*N*-pyrrolidinyl)carbene}pentacarbonylchromium (0) (**26**)

GP: 280 mg (0.5 mmol) of **3**, 110 mL of THF, 0.14 mL (1.6 mmol) of pyrrolidine, column chromatography (30 × 5 cm, PE/TBME 5:1 → 3:1). 70 mg (0.13 mmol, 24%) of **26**, yellow solid (m.p. 86 °C). Yellow, prismatic crystals were obtained by crystallization from THF/hexane.

IR (CH_3Cl): $\tilde{\nu} = 3747$ cm^{-1} (w), 3688 (w, NH), 3612 (w, NH), 3041 (w), 2052 (m, CO), 2005 (m, CO), 1926 (s, br, CO), 1602 (w), 1489 (w), 1446 (w), 1260 (w), 1091 (w), 931 (w), 810 (w), 631 (w), 590 (w). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.09$ (m, 4H, CH_2), 2.59 (s, 2H, $FeCH_2$), 3.25 (t, 2H, CH_2), 3.70 (t, 2H, CH_2), 3.96 (s, 2H, Cp), 4.25 (s, 2H, Cp), 6.97–7.15 (m, 5H, arom. H). ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 7.2$ ($FeCH_2$), 24.1 (CH_2), 25.5

(CH_2), 55.1 (CH_2), 63.0 (CH_2), 83.6 (Cp), 89.0 (Cp), 110.3 (*ipso* Cp), 124.2–128.6 (arom. C), 152.1 (*ipso* Bn), 216.9 (FeCO), 218.0 ($CrCO_{cis}$), 223.5 ($CrCO_{trans}$), 260.4 (Cr=C). MS (70 eV, 240 °C): m/z (%) = 483 (18) [$M^+ - 2CO$], 459 (10) [$M^+ - 3CO$], 429 [$M^+ - 4CO$], 400 (10) [$M^+ - 5CO$], 373 (16) [$M^+ - 6CO$], 345 (12) [$M^+ - 7CO$], 292 (100), 259 (12), 223 (30), 202 (18), 167 (22), 118 (26), 91 (31) [$C_7H_7^+$], 70 (22) [$C_4H_8N^+$], 52 (20) [Cr^+]. HRMS ($C_{17}H_{19}NFeCr$): calc. 344.9921, found 345.0272.

3.20. Crystal structure analysis of **26** [29]

$C_{24}H_{19}CrFeNO_7$, molecular weight 541.25 crystal system monoclinic, space group $P2_1/c$, $a = 8.753(2)$ Å, $\alpha = 90°$, $b = 10.782(2)$ Å, $\beta = 94.16(3)°$, $c = 25.378(5)$ Å, $\gamma = 90°$, $V = 2388.7(8)$ Å^3, $Z = 4$, $d_{calc.} = 1.505$ g/cm^3, $F(000) =$ 1104e, $\mu = 1.106$ mm^{-1}, crystal color yellow, crystal size $0.63 \times 0.56 \times 0.04$ mm, Stoe IPDS (Area Detector) diffractometer, $T = 300(2)$ K, λ(Mo Kα) = 0.71073 Å, $\theta_{min} = 2.05$, $\theta_{max} = 25.96°$, $-10 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-31 \leqslant l \leqslant 31$, no absorption correction, no extinction correction, 32303 collected, 4626 unique reflections, [R(int) = 0.0622], refinement program: SHELXL-93, refinement by least squares method (F^2), $S = 1.223$, R-Indices: [$I > 2\sigma(I)$] $R_1 = 0.0322$, $wR_2 = 0.0638$, R-Indices (all data): $R_1 = 0.0549$, $wR_2 =$ 0.0658, min., max. residual electron density: −0.235, 0.348 Å^{-3}, completeness of data 99.2%.

3.21. {[Benzyldicarbonyliron(II)-η^5-cyclopentadienyl](*N*,*N*-dimethylamino)carbene}pentacarbonylchromium (**27**)

GP: 91.5 mg (0.18 mmol) of **3**, 12.5 mL of THF, 0.01 mL (0.2 mmol) of dimethylamine in 2 mL of toluene, column chromatography (30×5 cm, PE/TBME 5:1). Traces of **27** along with a small amount of benzyldicarbonyl(*N*,*N*-dimethylaminocarbonylcyclopentadienyl)iron(II). Due to the sensitivity of the compounds attempts to separate the products were without success.

IR (ATR): $\tilde{\nu} = 2962$ (w) cm^{-1}, 2052 (s, CO), 2001 (s, CO), 1895 (s, br, CO), 1593 (m), 1450 (m), 1258 (m), 1179 (w), 1027 (m), 843 (w), 738 (w), 699 (w), 671 (w). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.56$ (s br, CH_2 or CH_3), 2.68 (s br, CH_2 or CH_3), 2.96 (s br, CH_2 or CH_3), 3.80 (s, 2H, Cp), 3.94 (s, 2H, Cp), 4.09 (s, 2H, Cp), 4.53 (s, 2H, Cp), 6.96–7.20 (m, 10H, arom. H). ^{13}C NMR (100.6 MHz C_6D_6, BB): $\delta = 7.3$ (CH_2), 7.4 (CH_2), 43.9 ($2CH_3$), 48.6 (CH_3), 53.4 (CH_3), 83.0 (Cp), 87.1 (Cp), 88.7 (Cp), 90.4 (Cp), 110.6 (*ipso* Cp), 124.2–128.7 (arom. 12C), 152.0 (*ipso* Bn), 152.3 (*ipso* Bn), 186.9 (CO), 215.2 (CO), 216.7 (CO), 217.4 (CO), 223.4 (CO), 265.2 (Cr=C). HRMS ($C_{22}H_{17}CrFeNO_7$): calc. 514.9696, found 514.9760.

Acknowledgements

We thank Boehringer Mannheim GmbH for a donation of (2*S*,3*S*)-**16**. We thank Boehringer Ingelheim Pharma GmbH & Co. KG and Degusssa AG for donations of amino alcohols.

References

[1] K.H. Dötz, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983.
[2] D.J. Cardin, B. Cetinkaya, M.F. Lappert, Chem. Rev. 72 (1972) 545.
[3] F.Z. Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999.
[4] K.H. Dötz, Pure Appl. Chem. 55 (1983) 1689.
[5] K.H. Dötz, Angew. Chem. 96 (1984) 573;
K.H. Dötz, Angew. Chem. Int. Ed. Engl. 23 (1984) 587–608.
[6] W.D. Wulff, Adv. Met. Org. Chem. 1 (1989) 209.
[7] L.S. Hegedus, Tetrahedron 53 (1997) 4105.
[8] J. Barluenga, F.J. Fananás, Tetrahedron 56 (2000) 4597.
[9] R.H. Grubbs, S.J. Miller, G.C. Fu, Acc. Chem. Res. 28 (1995) 446.
[10] R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413.
[11] A. Fürstner, Angew. Chem. 112 (2000) 3140;
A. Fürstner, Angew. Chem. Int. Ed. 39 (2000) 3012–3043.
[12] A.H. Hoveyda, R.R. Schrock, Chem. Eur. J. 7 (2001) 945.
[13] T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 43 (2001) 18.
[14] C.S. Poulsen, R. Madsen, Synthesis (2003) 1.
[15] R.R. Schrock, A.H. Hoveyda, Angew. Chem. 115 (2003) 4740;
R.R. Schrock, A.H. Hoveyda, Angew. Chem. Int. Ed. 42 (2003) 4592–4633.
[16] O.R. Thiel, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 1, Wiley-VCH, Weinheim, 2004, p. 321.
[17] R.H. Grubbs, T.M. Trnka, in: S.-I. Murahashi (Ed.), Ruthenium in Organic Synthesis, Wiley-VCH, Weinheim, 2004, p. 153.
[18] M.A. Sierra, Chem. Rev. 100 (2000) 3591.
[19] L. Meca, D. Dvorak, J. Ludvik, I. Cisarova, P. Stepnicka, Organometallics 23 (2004) 2541.
[20] E.O. Fischer, V.N. Postnov, F.R. Kreissl, J. Organomet. Chem. 127 (1977) C19.
[21] T.A. Waldbach, R. van Eldik, P.H. van Rooyen, S. Lotz, Organometallics 16 (1997) 4056.
[22] U. Behrendt, R.-M. Pfeifer, R. Wartchow, H. Butenschön, New J. Chem. 23 (1999) 891.
[23] M. Schwarz, M. Vollmann, R. Wartchow, H. Butenschoön, J. Organomet. Chem. 690 (2005) 2300.
[24] D.B. Grotjahn, K.H. Dötz, Synlett (1991) 381.
[25] U. Klabunde, E.O. Fischer, J. Am. Chem. Soc. 89 (1967) 7141.
[26] C.P. Casey, L.D. Albin, M.C. Saeman, D.H. Evans, J. Organomet. Chem. 155 (1978) C37.
[27] H. Friebolin, Ein- und zweidimensionale NMR-Spektroskopie, VCH, Weinheim, 1992.
[28] M. Schwarz, Dissertation, Universität Hannover, 2003.
[29] The crystallographic data (without structure factors) of the structures described in this publication were deposited as "supplementary publications no. CCDC 271717 (**26**) and CCDC 271718 [(*S*,*S*)-**21**]" at the Cambridge Crystallography Data Centre. Copies of the data can be obtained with no charge from the following address in Great Britain: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax Int.: +1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).