DOI: 10.1002/ejic.201000432

Zirconocene Functional Group Chemistry: Photochemical [4+4] Cycloaddition of Isoprenyl Sidechains to the Bent Metallocene Framework

Ingo Greger,[a] Gerald Kehr,[a] and Gerhard Erker*[a]

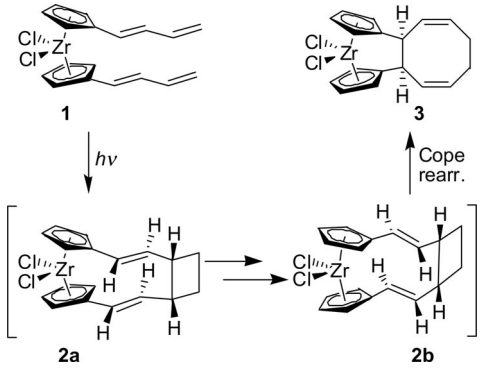
Keywords: Metallocenes / Sandwich complexes / Zirconium / Hafnium / Photochemistry / Cycloaddition

The 4-isoprenyl- and 1-isoprenylcyclopentadienides **6a** and **6b** were prepared by means of a fulvene route involving a subsequent deprotonation reaction using potassium hexamethyldisilylamide. Transmetallation to zirconium or hafnium gave the respective bis(4-isoprenyl-Cp)MCl_2 and bis(1-isoprenyl-Cp)MCl_2 complexes **7a**,**b** and **8a**,**b**, respectively. Upon photolysis, the (4-isoprenyl-Cp)$_2ZrCl_2$ and -$HfCl_2$ complexes **7a**, **8a** underwent rapid intramolecular [4+4] cycloaddition reactions to yield the cyclooctadienylene-bridged *ansa*-metallocenes **9a**, **10a** in high yields.

Introduction

Carrying out organic functional group chemistry at the group 4 bent metallocenes is difficult since many of the typical reaction conditions of conventional organic functional group interconversion are often incompatible with the sensitivity of many bent metallocene complexes.[1] This makes zirconocene chemistry markedly different from ferrocene chemistry, for instance.[2] Recently we have developed protocols for carrying out a small series of carbon–carbon coupling reactions between selected organic functional groups at the zirconocene and hafnocene frameworks, among them Mannich-type condensations[3,4] and olefin metathesis reactions.[5,6] Another group of notable examples involved photochemical cycloaddition reactions. We introduced a series of examples of photochemically induced intramolecular [2+2] cycloadditions of bis(alkenyl-Cp)MCl_2 or bis(alkenylindenyl)MCl_2 systems (M = Zr) to yield the corresponding cyclobutylene-bridged *ansa*-metallocenes which were then employed as components for the generation of active homogeneous Ziegler–Natta olefin polymerization catalysis. This reaction type proved to be somewhat substituent-sensitive but use of a proper substitution pattern at the alkenyl groups allowed very efficient *ansa*-metallocene formation by the photochemical [2+2] cycloaddition route.[7–12]

Photolysis of bis(butadienyl-Cp)$ZrCl_2$ systems takes a similar route. At ambient temperature this reaction rapidly and selectively leads to the formation of the isomeric cyclooctadienylene-bridged *ansa*-metallocenes by formal [4+4] cycloaddition. A detailed mechanistic study[13,14] had revealed that this reaction proceeds stepwise; the initial step is a [2+2] cycloaddition leading to the intermediate **2a**. Subsequent conformational equilibration – monitored by dynamic NMR spectroscopy – eventually provides a suitable situation for the final thermal Cope rearrangement of the *cis*-1,2-divinylcyclobutane substructure[15], which yields the final product (see Scheme 1).



Scheme 1.

This mechanism requires the hydrogen atoms at the C=C double bonds at the stage of the intermediates **2** to move through the inside of the metallacyclic structure during the conformational rearrangement process. Expectedly, this prerequisite might have consequences on the choice of the substitution pattern at the starting materials **1** to allow on the overall outcome of the [4+4] cycloadditon. This was investigated in this study by using a pair of isoprenyl-substituted zirconocene dichlorides. The introduction of methyl substituents at the internal positions of the dienyl sidechains had a remarkable influence on the [4+4] cycloaddition reaction at the bent metallocene core.

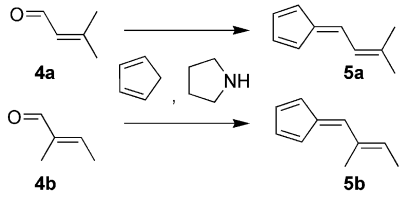
Results and Discussion

We prepared both the isomeric Cp-isoprenyl ligand systems used in this study by variations of a fulvene route. The

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany
Fax: +49-251-8336503
E-mail: erker@uni-muenster.de

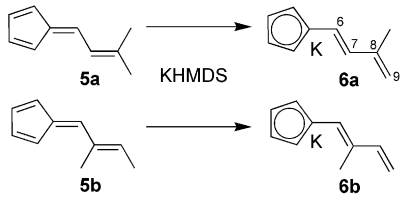
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000432.

fulvenes **5a** and **5b** were prepared by the general method devised by Stone and Little[16] using a variant toward the formation of the specific alkenyl fulvenes as it was described by Griesbeck et al. (see Scheme 2).[17] For the preparation of **5a** we treated the starting material 3-methylcrotonic aldehyde (**4a**) with pyrrolidine and cyclopentadiene. The secondary amine probably serves two purposes in this reaction, namely to activate the aldehyde by in situ forming the respective iminium salt and to deprotonate the cyclopentadiene component of the reaction to provide the nucleophile. The fulvene **5a** was obtained as a red oil in 60% yield from this reaction. The fulvene **5b** was obtained analogously by treating *trans*-2-methylcrotonic aldehyde with CpH and pyrrolidine (58% yield).



Scheme 2.

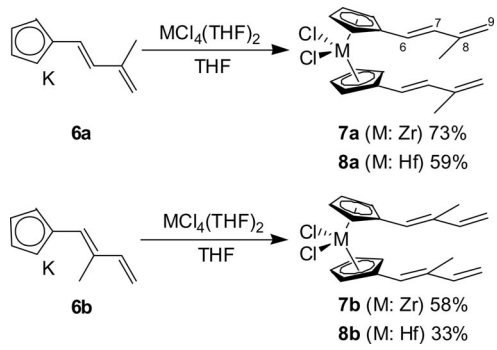
Deprotonation of the fulvene **5a** was effected by treatment with potassium hexamethyldisilylamide (KHMDS) in diethyl ether. This gave the 4-isoprenyl-substituted cyclopentadienide as an off-white solid in 92% yield. The ^{1}H NMR spectrum of **6a** indicated the presence of a *trans*-CH=CH double bond [6-H: δ = 6.48, 7-H: δ = 6.17, ^3J(6-H,7-H) = 15.7 Hz; see Scheme 3 for atom numbering]. Consequently, we observed the 9-H ^{1}H NMR signals at δ = 4.55 and 4.42, respectively.



Scheme 3.

Deprotonation of the fulvene **5b** with KHMDS yielded a single 1-isoprenyl cyclopentadienide (**6b**) that was isolated in 88% yield. It features the typical ^{1}H NMR signals of a terminal vinyl group of the doubly unsaturated side chain and a ^{1}H NMR singlet of the 6-H proton at δ = 6.39 ppm.

Transmetallation of the isoprenyl cyclopentadienides **6a**,**b** was carried out by treatment with both $ZrCl_4(THF)_2$ and $HfCl_4(THF)_2$, respectively. The anionic ligands were treated with the metal halides in THF at low temperature and then obtained as white solids after workup including extraction with dichloromethane. The NMR spectra of the Zr and Hf complexes **7a** and **8a** are very similar. The example of the bis(4-isoprenyl-Cp)hafnium dichloride complex **8a** features the typical ^{1}H NMR resonances of a *trans*-CH=CH double bond [7-H: δ = 6.46, 6-H: δ = 6.23, ^3J(6-H, 7-H) = 16.1 Hz; see Scheme 4 for atom numbering]. The 9-H ^{1}H NMR signals of complex **8a** occur at δ = 4.98 and 4.90, respectively.



Scheme 4.

Transmetallation of the 1-isoprenylcyclopentadienide reagent **6b** with $ZrCl_4(THF)_2$ or $HfCl_4(THF)_2$ in THF gave the corresponding metallocenes **7b** and **8b**, respectively (see Scheme 4). Both were obtained isomerically pure. Both show the typical ^{1}H NMR features of the terminal vinyl groups of their Cp-connected 1-isoprenyl side chains and the typical resonance of the "isolated" 6-H proton (see Figure 1).

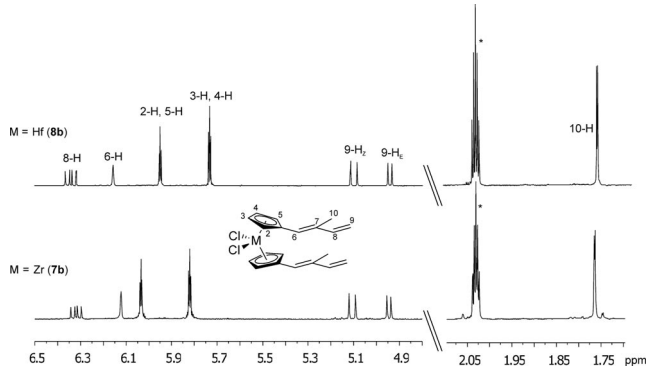
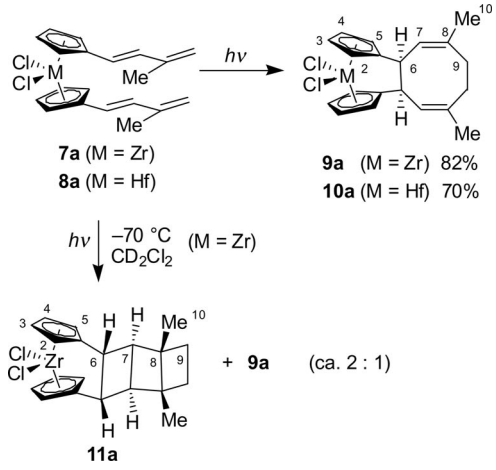


Figure 1. Comparison of the ^{1}H NMR spectra of the complexes **7b** (Zr, bottom) and **8b** (Hf, top).

Photolysis of the bis(4-isoprenyl-Cp)$ZrCl_2$ complex **7a** was carried out in dichloromethane solution using Pyrex-filtered UV light (HPK 125). This rapidly resulted in a practically complete formation of the [4+4] cycloaddition product **9a**. The cyclooctadienylene-bridged *ansa*-zirconocene was isolated in >80% yield. A single isomer was formed. We assign to it a C_S-symmetric structure with a 1,2-*cis*-attachment of the pair of Cp-rings at the *ansa*-bridge carbon atoms C6/C6′, analogous to the structure found for the unsubstituted analogue **3** (see Scheme 1) whose structure had been secured by an X-ray crystal structure analysis. Complex **9a** (see Scheme 5) exhibits a single methyl ^{1}H NMR resonance and a single olefinic CH ^{1}H NMR signal (see Table 1). Photolysis of the corresponding Hf complex **8a** proceeded analogously to give the *ansa*-metallocene complex **10a** (70% isolated).



Scheme 5.

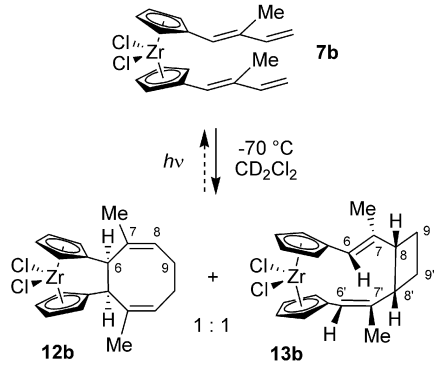
Table 1. Selected ^{1}H and ^{13}C NMR spectroscopic data[a] of the [4+4] cycloaddition products **9a** (Zr) and **10a** (Hf).

9a	**2-H/C2**	**3-H/C3**	**4-H/C4**	**5-H/C5**
	5.77/110.1	6.33/121.8	6.47/124.4	5.44/109.4
	6-H/C6	**7-H/C7**	**9-H/C9**	**10-H/C10**
	4.02/46.2	5.13/125.0	2.24,1.58/31.9	1.51/25.6
10a	**2-H/C2**	**3-H/C3**	**4-H/C4**	**5-H/C5**
	5.65/108.1	6.26/120.4	6.39/123.0	5.33/107.6
	6-H/C6	**7-H/C7**	**9-H/C9**	**10-H/C10**
	4.10/45.9	5.16/125.2	2.26,1.59/31.9	1.51/25.6

[a] Chemical shifts in ppm; [D_8]toluene solvent.

We also photolyzed the (4-isoprenyl-Cp)$_2$ZrCl_2 complex **7a** at low temperature. Irradiation of **7a** for 2.5 h in CD_2Cl_2 at ca. –70 °C resulted in a complete conversion of the starting material to give a mixture that contained the ladderane derivative **11a** as the major product along with the eight-membered ring product **9a** (**11a**/**9a** ca. 2:1) plus some unidentified decomposition products. The structure of **11a** was tentatively assigned to the ladderane structure in comparison with the previously described analogous product obtained by low-temperature photolysis of the parent compound **1**[13] Complex **11a** features a typical ^{1}H NMR ABCD pattern of the Cp-ligands and ^{1}H/^{13}C NMR signals of the newly formed tricyclic *ansa*-bridge at δ = 4.06 (6-H), 3.09 (7-H), 2.14/2.12 (9-H) and 1.08 (8-CH_3) [^{13}C: δ = 46.9 (C7), 45.0 (C8), 44.5 (C6), 32.1 (C9), 16.5 (8-CH_3)].

We then photolyzed the (1-isoprenyl-Cp)$_2$MCl_2 complexes **7b** and **8b**. Photolysis at room temperature in both cases gave very complicated mixtures of products, the structures of which could not absolutely be assigned, probably due to rapid decomposition under these conditions. Irradiation of the zirconium complex **7b** at –70 °C in CD_2Cl_2 gave a mixture that contained two major components in a ca. 1:1 ratio along with ca. 20–30% unidentified decomposition products (Scheme 6). The two products were tentatively assigned as the structures of the formal [4+4] cycloadduct **12b** and the cyclobutane derivative **13b** by detailed NMR analysis. The former shows typical ^{1}H NMR signals of the pair of symmetry-equivalent Cp-rings at δ = 6.68, 6.67, 6.36 and 6.24, the 6-H resonance at δ = 5.08, the olefinic 8-H signal at δ = 5.54 and a sharp methyl resonance at δ = 1.83 (6 H intensity). The ^{1}H NMR spectrum of **13b** features two ABCD sets of Cp signals of equal intensity, a 1:1 pair of CH_3 singlets (δ = 2.27, 2.00) and two olefinic =CH– resonances (δ^1H/δ^{13}C 6.22/122.7, 6.15/117.2).



Scheme 6.

Our study shows that methyl substituents at the butadienyl side chains of the Group 4 bent metallocenes exert a profound influence on the photochemical behaviour of these compounds. The 4-isoprenyl derivatives behave very similar to the parent (Cp-butadienyl)$_2$MCl_2 systems, both at ambient as well as low temperature. Their rapid and clean intramolecular photochemical [4+4] cycloaddition reaction provides a useful method for *ansa*-metallocene formation. Surprisingly, the photochemical behaviour of the isomeric (1-isoprenyl-Cp)$_2$MCl_2 system is much less straightforward and thus synthetically not useful. These formally related but in detail rather different cases may serve to determine scope and limitations of this photochemical method of *ansa*-zirconocene and -hafnocene production.

Experimental Section

General Procedures: Reactions with air- and water-sensitive compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried under vacuum. Solvents were dried and distilled under argon prior to use. The fulvenes **5a**, **5b** were prepared as described in the literature.[17] The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss–Heraeus CHNO-Rapid. NMR: Varian UNITY plus NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz). Assignments of the resonances were supported by 2D NMR experiments.

6a: KHMDS (1.54 g, 7.7 mmol) was dissolved in diethyl ether (30 mL) and the mixture was cooled to 0 °C. A solution of 6-(2-methyl-1-propenyl)fulvene (**5a**) (1.02 g, 7.7 mmol) in diethyl ether (20 mL) was added slowly and the reaction mixture was stirred for another 2 h at room temperature. The solvent was removed in vacuo and the remaining solid was suspended in pentane (50 mL). The yellow product (1.21 g, 7.1 mmol, 92%) was collected by filtration, washed several times with pentane and dried under vacuum. ^{1}H NMR (600 MHz, [D_8]THF, 298 K): δ = 6.48 [d, ^3J(H,H) = 15.7 Hz, 1 H, 6-H], 6.17 (d, $^3J_{H,H}$ = 15.7 Hz, 1 H, 7-H), 5.80 (m,

2 H, 2-H, 5-H), 5.63 (m, 2 H, 3-H, 4-H), 4.55 (m, 1 H, 9-H_Z), 4.42 (m, 1 H, 9-H_E), 1.86 (m, 3 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]THF, 298 K): δ = 145.0 (C8), 130.5 (C6), 120.0 (C1), 117.3 (C7) 108.2 (C3, C4), 106.3 (C2, C5), 106.1 (C9), 19.5 (C10) ppm.

6b: KHMDS (0.68 g, 3.4 mmol) was dissolved in diethyl ether (30 mL) and cooled to 0 °C. A solution of 6-[(*E*)-1-methyl-1-propenyl]fulvene (**5b**) (0.45 g, 3.4 mmol) in diethyl ether (5 mL) was added and the reaction mixture was warmed to room temperature within 2 h. The solvent was removed in vacuo and the remaining solid was suspended in pentane (50 mL). The yellow product (0.51 g, 3.0 mmol, 88%) was collected by filtration, washed several times with pentane and dried under vacuum. ^1H NMR (600 MHz, [D_8]THF, 298 K): δ = 6.41 (dd, $^3J_{H,H}$ = 17.0, 10.5 Hz, 1 H, 8-H), 6.39 (s, 1 H, 6-H), 5.88 (m, 2 H, 2-H, 5-H), 5.73 (m, 2 H, 3-H, 4-H), 4.63 (dd, $^3J_{H,H}$ = 17.0, $^4J_{H,H}$ = 1.5 Hz, 1 H, 9-H_Z), 4.42 (dd, $^3J_{H,H}$ = 10.5, $^4J_{H,H}$ = 1.5 Hz, 1 H, 9-H_E), 1.94 (m, 3 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]THF, 298 K): δ = 145.7 (C8), 135.0 (C6), 120.3 (C1), 118.9 (C7), 110.0 (C2, C5), 108.5 (C3, C4), 100.9 (C9), 13.6 (C10) ppm.

Metallocene Complexes: Throughout the procedure the compounds have to be kept in the dark to avoid a photochemical reaction. The potassium salt of the ligand and $MCl_4(THF)_2$ (M: Zr, Hf) were put together in a Schlenk flask in a 2:1 ratio and cooled to –78 °C. Precooled THF was added slowly and the stirred mixture was warmed to room temperature overnight. The THF was removed in vacuo and the same amount of dichloromethane was added. The resulting suspension was filtered through Celite to remove the potassium chloride. The solid was washed with several portions of dichloromethane until the portion remained colourless. The filtrate was evaporated to dryness and the resulting crude product was suspended in pentane, filtered and dried under vacuum.

7a: From the reaction of potassium 4-isoprenylcyclopentadienide (**6a**) (400 mg, 2.35 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (443 mg, 1.17 mmol) in THF (40 mL) and workup a yellowish solid (362 mg, 0.85 mmol, 73%) was obtained. ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.52 (d, $^3J_{H,H}$ = 16.2 Hz, 2 H, 7-H), 6.24 (d, $^3J_{H,H}$ = 16.2 Hz, 2 H, 6-H), 6.09 (m, 4 H, 2-H, 5-H), 5.90 (m, 4 H, 3-H, 4-H), 4.98 (m, 2 H, 9-H_Z), 4.89 (m, 2 H, 9-H_E), 1.72 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]-toluene, 298 K): δ = 141.9 (C8), 133.9 (C7), 127.8 (C1), 122.1 (C6), 118.0 (C9), 114.93 (C3, C4), 114.87 (C2, C5), 18.3 (C10) ppm. $C_{20}H_{22}Cl_2Zr$ (424.5 g/mol): calcd. C 56.59, H 5.22; found C 55.93, H 4.39.

8a: The reaction of potassium 4-isoprenylcyclopentadienide (**6a**) (1.0 g, 5.87 mmol) with bis(tetrahydrofuran)hafnium tetrachloride (1.37 mg, 2.94 mmol) in THF (60 mL) and workup using dichloromethane gave a white solid (0.89 g, 1.74 mmol, 59%). ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.46 (d, $^3J_{H,H}$ = 16.1 Hz, 2 H, 7-H), 6.23 (d, $^3J_{H,H}$ = 16.1 Hz, 2 H, 6-H), 5.89 (m, 4 H, 2-H, 5-H), 5.71 (m, 4 H, 3-H, 4-H), 4.98 (m, 2 H, 9-H_Z), 4.90 (m, 2 H, 9-H_E), 1.72 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]-toluene, 298 K): δ = 141.9 (C8), 134.0 (C7), 125.9 (C1), 122.0 (C6), 118.0 (C9), 113.6 (C2, C5), 113.4 (C3, C4), 18.5 (C10) ppm. $C_{20}H_{22}Cl_2Hf$ (511.8 g/mol): calcd. C 46.94, H 4.33; found C 46.20, H 4.68.

7b: From the reaction of potassium 1-isoprenylcyclopentadienide (**6b**) (200 mg, 1.17 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (222 mg, 0.59 mmol) in THF (25 mL) and workup using dichloromethane a yellow solid (146 mg, 0.34 mmol, 58%) resulted. ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.32 (ddm, $^3J_{H,H}$ = 17.4, 10.7 Hz, 2 H, 8-H), 6.12 (s, 2 H, 6-H), 6.04 (m, 4 H, 2-H, 5-H), 5.82 (m, 4 H, 3-H, 4-H), 5.10 (d, $^3J_{H,H}$ = 17.4 Hz, 2 H, 9-H_Z), 4.95 (d, $^3J_{H,H}$ = 10.7 Hz, 2 H, 9-H_E), 1.76 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]toluene, 298 K): δ = 141.7 (C8), 137.3 (C7), 126.8 (C1), 125.0 (C6), 117.4 (C2, C5), 114.6 (C3, C4), 113.6 (C9), 13.5 (C10) ppm. $C_{20}H_{22}Cl_2Zr$ (424.5): calcd. C 56.59, H 5.22; found C 55.83, H 4.87.

8b: From the reaction of potassium 1-isoprenylcyclopentadienide (**6b**) (300 mg, 1.76 mmol) and bis(tetrahydrofuran)hafnium tetrachloride (410 mg, 0.88 mmol) in THF (35 mL) and workup using dichloromethane a white solid (150 mg, 0.29 mmol, 33%) resulted. ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.34 (ddm, $^3J_{H,H}$ = 17.3, $^3J_{H,H}$ = 10.7 Hz, 2 H, 8-H), 6.15 (s, 2 H, 6-H), 5.95 (m, 4 H, 2-H, 5-H), 5.73 (m, 4 H, 3-H, 4-H), 5.10 (dm, $^3J_{H,H}$ = 17.3 Hz, 2 H, 9-H_Z), 4.94 (dm, $^3J_{H,H}$ = 10.7 Hz, 2 H, 9-H_E), 1.77 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]toluene, 298 K): δ = 141.7 (C8), 137.2 (C7), 125.02 (C1), 124.99 (C6), 116.2 (C2, C5), 113.5 (C9), 113.1 (C3, C4), 13.4 (C10) ppm. $C_{20}H_{22}Cl_2Hf$ (511.8 g/mol): calcd. C 46.94, H 4.33; found C 46.01, H 4.60.

9a: Complex **7a** (1.0 g, 2.36 mmol) was dissolved in dichloromethane (150 mL) and irradiated for 2.5 h (HPK 125, Pyrex filter). The solvent was removed in vacuo and the remaining solid was suspended in pentane (40 mL). Filtration and drying of the obtained solid in vacuo gave a light yellow solid (0.82 g, 1.93 mmol, 82%). ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.47 (m, 2 H, 4-H), 6.33 (m, 2 H, 3-H), 5.77 (m, 2 H, 2-H), 5.44 (m, 2 H, 5-H), 5.13 (br., 2 H, 7-H), 4.02 (br., 2 H, 6-H), 2.24 (m, 2 H, 9-Ha), 1.58 (m, 2 H, 9-Hb), 1.51 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]toluene, 298 K): δ = 137.6 (C1), 136.6 (C8), 125.0 (C7) 124.4 (C4), 121.8 (C3), 110.1 (C2), 109.4 (C5), 46.2 (C6), 31.9 (C9), 25.6 (C10) ppm. $C_{20}H_{22}Cl_2Zr$ (424.5 g/mol): calcd. C 56.59, H 5.22; found C 56.92, H 5.27.

10a: Complex **8a** (0.4 g, 0.78 mmol) was suspended in dichloromethane (60 mL) and irradiated for 2 h (HPK 125, Pyrex filter). The solvent was removed in vacuo and the remaining solid was suspended in pentane (40 mL). Filtration and drying of the obtained solid in vacuo gave a white solid (0.28 g, 0.54 mmol, 70%). ^1H NMR (600 MHz, [D_8]toluene, 298 K): δ = 6.39 (m, 2 H, 4-H), 6.26 (m, 2 H, 3-H), 5.65 (m, 2 H, 2-H), 5.33 (m, 2 H, 5-H), 5.16 (br., 2 H, 7-H), 4.10 (br., 2 H, 6-H), 2.26 (m, 2 H, 9-Ha), 1.59 (m, 2 H, 9-Hb), 1.51 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, [D_8]toluene, 298 K): δ = 136.6 (C8), 135.7 (C1), 125.2 (C7) 123.0 (C4), 120.4 (C3), 108.1 (C2), 107.6 (C5), 45.9 (C6), 31.9 (C9), 25.6 (C10) ppm. $C_{20}H_{22}Cl_2Hf$ (511.8 g/mol): calcd. C 46.94, H 4.33; found C 45.97, H 4.33.

Photolyses of 7a and 7b at Low Temperature: Complex **7a** (10 mg, 0.024 mmol) was dissolved in CD_2Cl_2 (0.6 mL) in a NMR tube and irradiated for 2.5 h (HPK 125, Pyrex filter) at-70 °C. Immediately after irradiation the reaction mixture was controlled by ^1H NMR experiments at –70 °C. The NMR sprectroscopic characterization of the obtained mixture with the main components **11a** and **9a** (ca. 2:1) was performed at 25 °C.

9a: ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.72, 6.59, 6.14 (2×, each m, each 2 H, Cp), 5.41 (br., 2 H, 7-H), 4.73 (m, 2 H, 6-H), 2.76, 2.05 (each m, each 2 H, 9-H), 1.79 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = n. o. (C1), 137.9 (C8), 125.1, 122.2, 110.8, 110.1 (Cp), 124.5 (C7), 46.7 (C6), 32.2 (C9), 25.8 (C10) ppm.

11a: ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.69, 6.64, 6.43 (5-H), 6.25 (2-H, each m, each 2 H, Cp-H), 4.06 (br., 2 H, 6-H), 3.09 (m, 2 H, 7-H), 2.14 (m, 2 H, 9-Hb), 2.12 (m, 2 H, 9-Ha), 1.08 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ =

140.6 (C1), 124.5, 122.4, 110.8, 109.7 (Cp), 46.9 (C7), 45.0 (C8), 44.5 (C6), 32.1 (C9), 16.5 (C10) ppm.

Irradiation of **7b** (10 mg, 0.024 mmol) in CD_2Cl_2 (0.6 mL) gave a reaction mixture with the main components **12b** and **13b** (ca. 1:1).

12b: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.68 (Cp^β-H), 6.67 (Cp^β-H), 6.36 (Cp^α-H), 6.24 (Cp^α-H, each m, each 2 H, Cp-H), 5.54 (m, 2 H, 8-H), 5.08 (br., 2 H, 6-H), 2.49 (m, 2 H, 9-Ha), 2.06 (m, 2 H, 9-Hb), 1.83 (m, 6 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = 136.2 (C1), 135.5 (C7), 123.3 (β), 122.8 (β), 113.8 (α), 112.0 (α, Cp), 127.3 (C8), 51.1 (C6), 26.7 (C9), 23.4 (C10) ppm. **13b**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.73, 6.71, 6.69 (α), 6.39, 6.33, 6.28 (α′), 6.26, 6.23 (each m, each 1 H, Cp, Cp′), 6.22 (m, 2 H, 6′-H), 6.15 (m, 2 H, 6-H), 3.59 (m, 2 H, 8′-H), 3.18 (m, 2 H, 8-H), 2.27 (m, 3 H, 10-H), 2.11, 1.82 (each m, each 1 H, 9′-H), 2.16, 1.91 (each m, each 1 H, 9-H), 2.00 (m, 3 H, 10′-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = n. o. (C1, C1′), 143.4 (C7), 141.8 (C7′), 127.6, 126.3, 120.4, 118.5, 115.3, 110.5 (Cp'^α), 110.1 (Cp^α), 108.3 (Cp, Cp′), 122.7 (C6′), 117.2 (C6), 49.4 (C8), 47.7 (C8′), 22.6 (C10′), 22.5 (C9′), 21.8 (C9), 17.5 (C10) ppm.

Supporting Information (see also the footnote on the first page of this article): More experimental and spectroscopic details.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank the BASF for a gift of chemicals.

[1] a) G. Erker, *Polyhedron* **2005**, *24*, 1289–1297; b) G. Erker, G. Kehr, R. Fröhlich, *Coord. Chem. Rev.* **2006**, *250*, 36–46; c) G. Erker, G. Kehr, R. Fröhlich, *J. Organomet. Chem.* **2004**, *689*, 1402–1412.

[2] a) *Ferrocenes: homogeneous catalysis, organic synthesis, materials science* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, Germany, **1995**; b) *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Štěpnička), John Wiley & Sons, Chichester, UK, **2008**.

[3] a) S. Knüppel, G. Erker, R. Fröhlich, *Angew. Chem.* **1999**, *111*, 2048–2051; *Angew. Chem. Int. Ed.* **1999**, *38*, 1923–1926; b) S. Knüppel, C. Wang, G. Kehr, R. Fröhlich, G. Erker, *J. Organomet. Chem.* **2005**, *690*, 14–32.

[4] S.-D. Bai, X.-W. Wei, J.-P. Guo, D.-S. Liu, Z.-Y. Zhou, *Angew. Chem*. **1999**, *111*, 2051–2054; *Angew. Chem. Int. Ed.* **1999**, *38*, 1926–1928.

[5] a) D. Hüerländer, N. Kleigrewe, G. Kehr, G. Erker, R. Fröhlich, *Eur. J. Inorg. Chem.* **2002**, 2633–2642; b) J. Cano Sierra, D. Hüerländer, M. Hill, G. Kehr, G. Erker, R. Fröhlich, *Chem. Eur. J.* **2003**, *9*, 3618–3622; c) M. Ogasawara, T. Nagano, T. Hayashi, *J. Am. Chem. Soc.* **2002**, *124*, 9068–9069; d) J. Kuwabara, D. Takeuchi, K. Osakada, *Organometallics* **2005**, *24*, 2705–2712.

[6] T. A. Tumay, G. Kehr, R. Fröhlich, G. Erker, *Dalton Trans.* **2009**, 8923–8928.

[7] G. Erker, S. Wilker, C. Krüger, M. Nolte, *Organometallics* **1993**, *12*, 2140–2151; G. Erker, M. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, *J. Am. Chem. Soc.* **1991**, *113*, 7594–7602.

[8] J. Paradies, G. Kehr, R. Fröhlich, G. Erker, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15333–15337.

[9] I. Greger, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **2010**, *29*, 860–866.

[10] T. A. Tumay, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **2009**, *28*, 4513–4518.

[11] a) J. Paradies, R. Fröhlich, G. Kehr, G. Erker, *Organometallics* **2006**, *25*, 3920–3925; b) N. Iwama, T. Kato, T. Sugano, *Organometallics* **2004**, *23*, 5813–5817.

[12] See also: a) J. Paradies, G. Erker, R. Fröhlich, K. Bergander, *Angew. Chem.* **2006**, *19*, 3150–3153; *Angew. Chem. Int. Ed.* **2006**, *45*, 3079–3082; b) P. J. Sinnema, P. J. Shapiro, B. Höhn, T. E. Bitterwolf, B. Twamley, *Organometallics* **2001**, *20*, 2883–2888.

[13] J. Paradies, I. Greger, G. Kehr, G. Erker, K. Bergander, R. Fröhlich, *Angew. Chem.* **2006**, *118*, 7792–7795; *Angew. Chem. Int. Ed.* **2006**, *45*, 7630–7633.

[14] I. Greger, G. Kehr, R. Fröhlich, G. Erker, *Organometallics* **2010**, *29*, 3210–3221.

[15] E. Vogel, *Justus Liebigs Ann. Chem.* **1958**, *615*, 1–14.

[16] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849–1853.

[17] A. Griesbeck, *J. Org. Chem.* **1989**, *54*, 4981–4982.

Received: April 20, 2010
Published Online: August 27, 2010

