metal center and the attached atoms were set based on crystallographic data, the angle and torsional terms were set to zero. Parameters for the non-bonding terms (Lennard-Jones 6–12) were set by Quanta. For further details see reference [11].

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Organic Transformations at a Group 4 Metallocene Framework: Formation of a Rigid ansa-Metallocene by Mannich-type Carbon–Carbon Coupling

Stephanie Knüppel, Gerhard Erker,* and Roland Fröhlich

Group 4 ansa-metallocenes have been prepared in great structural variety owing to their key importance in homogeneous Ziegler catalysis. In the vast majority of the cases reported the specific ansa bridge and the chosen substitution pattern was built up or incorporated into the preformed organic ligand system before final attachment to the electrophilic Group 4 metal center.[1] Examples for selective organic reactions at the Group 4 metallocene framework, especially those involving conventional organic functional group chemistry, are close to nonexistent,[2] probably because of a pronounced incompatibility of the majority of the air- and moisture-sensitive Group 4 metallocene complexes with the typical conditions involved in many classical C–C coupling procedures in organic synthesis.

We and a few others had previously investigated a number of ways for dealing with functional groups at the bent metallocene nucleus.[3] We have now, to our knowledge for the first time, found a simple way to close an ansa bridge at the preformed Group 4 metallocene complex using a variant of the Mannich reaction, a classical synthetic organic method for forming a carbon–carbon bond.

Our simple route starts with rather conventional fulvene chemistry. O-methylated *N,N*-dimethylacetamide (**1a**) was treated with sodium cyclopentadienide according to the procedure developed by Hafner et al.[4] to yield 6-(dimethylamino)-6-methylfulvene (**2a**, Scheme 1). Amine exchange by treatment with, for example, the cyclic secondary amines pyrrolidine, piperidine, or morpholine gave the corresponding 6-amino-substituted fulvenes **2b**–**d**. In some cases the direct route employing the acetamides derived from these cyclic amines proved to be advantageous.

Deprotonation of the fulvene **2a** readily takes place upon treatment with methyllithium (1 molar equiv) in diethyl ether to give **3a**, which was isolated (ca. 90% yield) and characterized spectroscopically (^{13}C NMR ([D$_6$]benzene/[D$_8$]THF 8/1): $\delta = 42.2$ (NMe$_2$), 157.6 and 81.6 (C=CH$_2$), 119.1 (*ipso*-C), 104.6 and 103.7 (CH of C$_5$H$_4$); ^{1}H NMR: $\delta = 4.33$ and 3.91 ($^2J = 1$ Hz, =CH$_2$)). The enamino-substituted cyclopentadienides **3b**–**d** were obtained accordingly by treatment of **2b**–**d** with methyllithium. The reagents **3a**–**d** were then treated with titanium, zirconium, or hafnium tetrachloride in a 2:1 molar ratio under carefully selected conditions. The reaction

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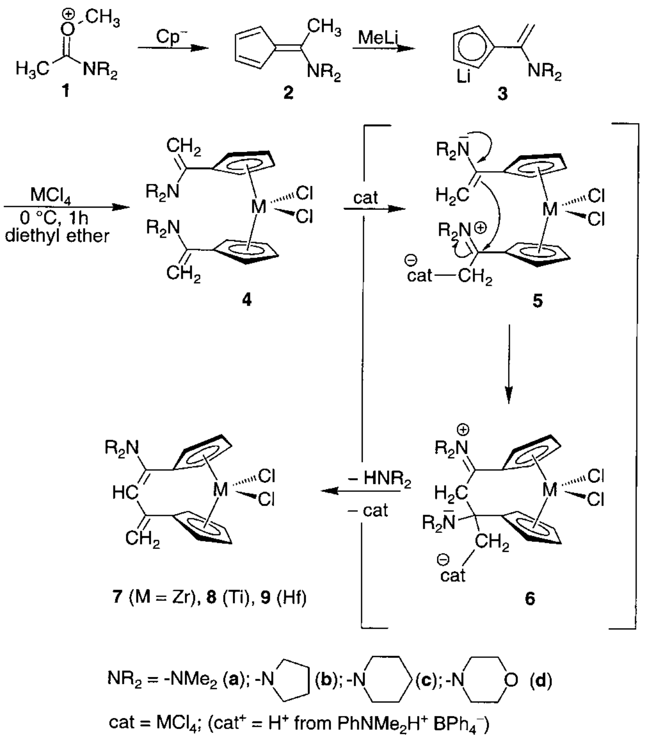

Scheme 1.

of (1-pyrrolidinoethenyl)cyclopentadienide (**3b**) with $ZrCl_4$ may serve as a representative example.

Zirconium tetrachloride (1 molar equiv) was added at 0 °C in one portion to a solution containing **3b** (2 molar equiv) in diethyl ether. After the mixture was stirred for 1 h at 0 °C, the precipitate was removed by filtration through Cellite. The bis[(1′-pyrrolidinoethenyl)cyclopentadienyl]$ZrCl_2$ metallocene (**4b**, Scheme 1) was obtained from the filtrate as a solid in greater than 50% yield. The ^1H NMR spectrum shows the characteristic signals of the monosubstituted η^5-C_5H_4 moiety at $\delta = 6.67$ and 6.18 (in $CDCl_3$) and the typical resonances of the intact enamino substituent ($\delta = 4.29$, 4.07 (=CH_2)). Treatment of **3c** and **3d** with $ZrCl_4$ under analogous conditions gave the complexes **4c** and **4d**, respectively.

We then changed the conditions for the reaction of **3** with $ZrCl_4$ slightly and obtained a different type of product. As a typical example, reagent **3b** was again treated with $ZrCl_4$ in diethyl ether, but this time the reaction mixture was allowed to remain at ambient temperature for 12 h with stirring before it was worked up. In this case the open metallocene **4b** was not found, but instead the ansa-metallocene **7b** was obtained in good yield (ca. 70% isolated). The product **7b** shows the ^1H NMR signals of two nonequivalent monosubstituted η^5-cyclopentadienyl rings ($\delta = 6.72$, 6.67, 6.17, and 6.08 in $CDCl_3$) and a typical ABX spin pattern of the condensated ansa bridge at $\delta = 5.44$ (−CH=), 4.92 and 4.84 (=CH_2) (^{13}C NMR: $\delta = 99.5$ (−CH=), 109.3 (=CH_2)) as well as a single pyrrolidyl residue.

Treatment of the enamino-substituted cyclopentadienides **3a**, **3c**, and **3d** with $ZrCl_4$ under analogous conditions (diethyl ether, room temperature, 12 h) gave the analogous C_3-bridged ansa-zirconocenes **7a**, **7c**, and **7d**, respectively, mostly in good yield. Similarly, we have also prepared the corresponding ansa-titanocene **8a** and the ansa-hafnocene dichlorides **9a** and **9b** by treatment of the respective enaminocyclopentadienides **3a** and **3b** with $TiCl_4$ or $HfCl_4$ under the standard conditions.

Single crystals suitable for crystal structure analyses were obtained for the ansa-zirconocene complex **7a** and the hafnium analogue **9a**. The two structures are very similar, aside from the expected changes resulting from the two different metals. Therefore, only the structure of the zirconium complex **7a** is briefly described here (Figure 1).[5]

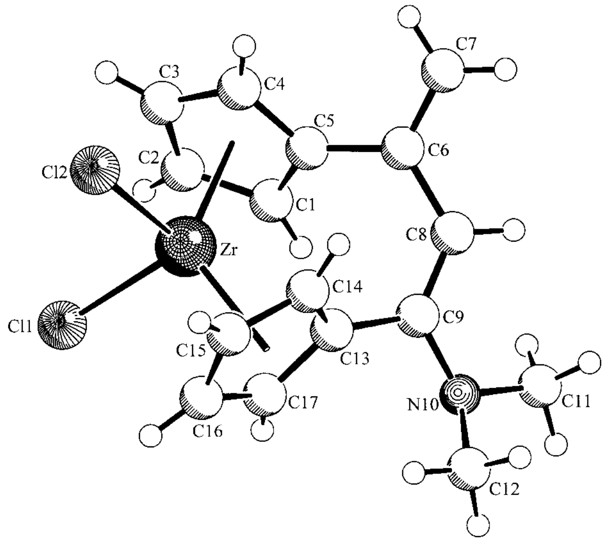

Figure 1. Molecular structure of the ansa-zirconocene complex **7a**. Selected bond lengths [Å] and angles [°]: Zr–Cl1 2.432(1), Zr–Cl2 2.441(1), Zr–C_{Cp} 2.506(5), C5–C6 1.490(5), C6–C7 1.333(6), C6–C8 1.464(6), C8–C9 1.353(6), C9–N10 1.399(5), C9–C13 1.481(5), N10–C11 1.455(5), N10–C12 1.468(6); Cl1-Zr-Cl2 97.40(5), C5-C6-C7 119.9(4), C5-C6-C8 117.5(4), C7-C6-C8 122.2(4), C6-C8-C9 125.1(3), C8-C9-N10 122.9(3), C8-C9-C13 123.1(3), N10-C9-C13 114.0(3).

The X-ray crystal structure analysis of **7a** shows that a very rigid ansa-metallocene framework has been formed. The ansa bridge consists of a conjugated *N*,*N*-dimethylaminobutadiene framework to which the Cp moieties are bonded at the positions C6 and C9 (Figure 1). The diene-amine unit shows a typical bond alternation (C7–C6 1.333(6), C6–C8 1.464(6), C8–C9 1.353(6) Å)).[6] This unit is itself planar. The nitrogen atom N10 is also oriented in the diene-amine plane; it is slightly pyramidalized but clearly in electronic conjugation with the adjacent diene π system.[6a] This orientation brings the two methyl substituents at N10 in *E* and *Z* positions at the N10-C9-C8 moiety.

The resulting C_3 ansa bridge is located at the narrow back side of the bent metallocene. There it adopts a "skew" arrangement that brings it substantially away from an expected perpendicular orientation relative to the Cp ring planes. The angle between, for example, the Cp ring (C1 - C5) and the plane of the ansa bridge (C6-C8-C9) amounts to approximately 119°. The angle between the Cp planes is 126°, which is about 3° smaller than that observed in an open Group 4 bent metallocene complex. Thus, complex **7a** (and its congeners) exhibits a very rigid ansa-metallocene framework.[7] In the crystal it is actually chiral, but inverts rapidly in solution.

In a series of experiments it was demonstrated that the ansa-metallocene complexes **7** were formed via **4** by an acid-catalyzed intramolecular condensation reaction. Treatment of, for example, the (1′-piperidinoethenyl)-substituted zirconocene dichloride **4c** with a catalytic amount of $ZrCl_4$ in diethyl ether for 12 h at room temperature resulted in clean formation of the condensation product **7c** (84% isolated). The **4d**→**7d** condensation was similarly catalyzed by the Brønsted acid dimethylanilinium tetraphenylborate (ca. 30 mol%, CD_2Cl_2, 24 h, room temperature, quantitative conversion). We conclude that the **4**→**7** condensation represents an example of an acid-catalyzed Mannich-type reaction (see Scheme 1 for a plausible mechanistic formulation). It must be assumed that residual $ZrCl_4$ has served as the Lewis acid catalyst for the condensation step in the initially described one-pot preparations of complexes **7**.

Activation of the rigid ansa-metallocenes **7**–**9** by treatment with excess methylalumoxane (MAO) in toluene[8] results in the formation of active homogeneous Ziegler catalyst systems. Table 1 contains a compilation of characteristic data from selected examples of ethene and propene polymerization reactions with these ansa-metallocene catalyst systems. The zirconium-based catalysts produce near to atactic polypropylene as expected. The **7a**/MAO and **8a**/MAO catalyst systems can also be used for ethene/norbornene and ethene/1-hexene copolymerizations. With the **7a**/MAO catalyst (Al:Zr ≈ 700) the ethene/norbornene copolymer was formed with an activity a of about 220. From the ^1H NMR analysis an ethene/norbornene ratio of approximately 57:1 was deduced (m.p. 116 °C). The norbornene incorporation was slightly less with the titanium-based catalyst system **8a**/MAO (70:1, m.p. 102 °C, $a = 92$). A random ethene/1-hexene copolymer (ratio ca. 60:1) was formed with the **7a**/MAO catalyst system at 60 °C in toluene ($a = 800$).

Table 1. Polyethylene and polypropylene formation with the catalyst systems **7**/MAO – **9**/MAO.[a]

Cat.	M	Al:M[b]	[**7**] [mmol]	PE[c] [g]	PP[d] [g]	T [°C]	a[e]	M.p. [°C]	$\bar{M}$[f] [kg mol^{-1}]
7a	Zr	750	0.044	29	–	20	320	127	
7a	Zr	670	0.049	55[g]	–	60[h]	840	125	
8a	Ti	600	0.055	8	–	60	70	130	
9a	Hf	670	0.049	41	–	60[h]	420	126	
7d	Zr	1180	0.028	10	–	20	175	132	
7d	Zr	1100	0.030	62	–	60[h]	1040	125	
7a	Zr	530	0.062	–	36[i]	20	90		185
7b	Zr	760	0.043	–	1.4[i]	0	5		230
7d	Zr	890	0.037	–	1.2[j]	– 5	8		370
7d	Zr	1030	0.032	–	2.8	20	14		–[k]
7d	Zr	1100	0.030	–	7.3	60	121		–[k]

[a] Reactions in toluene (Büchi glass autoclave) at 2 bar, reaction time 60 min, unless indicated otherwise. [b] M = Ti, Zr, Hf. [c] Yields of polyethylene. [d] Yields of polypropylene. [e] Integral catalyst activity a in g(polymer) [mmol(cat)]$^{-1}$ bar^{-1} h^{-1}. [f] Molecular weight (PP). [g] After 40 min. [h] Initial temperature, increased by 30–40 °C during the exothermic reaction. [i] After 180 min. [j] After 120 min. [k] Not determined.

These scouting polymerization experiments show that the acid-catalyzed intramolecular Mannich-type coupling reaction (**4**→**7**) has resulted in the formation of rigid ansa-metallocene systems that are suitable precursors for the generation of active homogeneous Ziegler catalysts. The catalyst systems based on **7**–**9** exhibit characteristics similar to those typically shown by the "constrained-geometry" Ziegler catalysts based on half-sandwich silyl-bridged Cp*/amido zirconium complexes.[9] Moreover, our study shows that variants of carbon–carbon bond forming reactions originating from the classical synthetic organic repertoire can be adopted and successfully used in the chemistry of even quite sensitive organometallic Group 4 metal complexes, provided that a few precautions are taken to protect these sensitive systems from undergoing undesired side reactions. We are confident that further adaptions of classical organic C–C coupling protocols will allow an extension of the scope of transformations in this area of organometallic chemistry and will help to make a variety of novel organometallic catalysts and reagents readily available.

Experimental Section

The preparation of the hafnium complex **9a** serves as a typical example: Compound **2a**[4] was cleanly deprotonated by treatment with methyllithium (1 molar equiv) in THF at – 78 °C. The lithium compound **3a** was isolated in 89% yield. ^1H NMR ([D$_6$]benzene/[D$_8$]THF 8/1, 200 MHz): $\delta = 6.26$, 6.05 (m, each 2H, C_5H_4), 4.33, 3.91 (d, $^2J = 1$ Hz, each 1H, =CH_2), 2.77 (s, 6H, CH_3); ^{13}C NMR ([D$_6$]benzene/[D$_8$]THF 8/1, 50 MHz): $\delta = 157.6$, 81.6 (C=CH_2), 119.1 (*ipso*-C), 104.6, 103.7 (CH of C_5H_4), 42.2 (CH_3). A sample of **3a** (1.50 g, 10.6 mmol) was suspended in diethyl ether (60 mL) and cooled to – 78 °C. Solid $HfCl_4$ (1.70 g, 5.3 mmol) was added in one portion with stirring. The mixture was allowed to warm to room temperature and stirred for 12 h. A precipitate was removed by filtration, and washed with a small amount of diethyl ether and dichloromethane. Solvent was removed from the combined filtrates. Recrystallization from diethyl ether gave 1.48 g (59%) of the metallocene **9a**. M.p. 174 °C (decomp., DSC); elemental analysis calcd for $C_{16}H_{17}NCl_2Hf$ (472.7): C 40.65, H 3.62, N 2.96; found: C 40.56, H 4.14, N 3.34; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 6.60$ (m, 4H), 6.03 (m, 2H), 5.94 (m, 2H, C_5H_4), 5.58 (s, 1H, –CH=), 4.96, 4.91 (br s, each 1H, =CH_2), 2.60 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta =$ 147.4 (N–C=), 138.9, 135.0, 124.5 (*ipso*-C of C_5H_4 and C=CH_2), 122.5, 121.9, 112.1, 108.9 (CH of C_5H_4), 111.1 (=CH_2), 104.6 (–CH=), 41.7 (CH_3); IR (KBr): $\tilde{\nu} = 1604$ cm^{-1}. Complex **9a** was also characterized by an X-ray crystal structure analysis.[5b]

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Intramolecular NMe$_2$H Elimination and Fulvene Coupling Leading to Novel Allyl-Bridged Zirconocene and Hafnocene Complexes**

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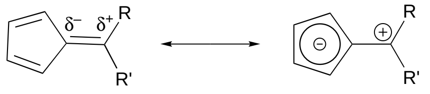
Fulvenes can be described by several resonance structures[1] that support the presence of significant dipole character (Scheme 1).[2] Therefore the exocyclic double bond is susceptible to nucleophilic addition (by, for example, alkylmetal compounds such as LiMe, $ClMgC_3H_5$, LiC_6H_5, and $KCH_2C_6H_5$),[3, 4] reduction,[5] reductive coupling,[6] or deprotonation at the 6-methyl group ($R = CH_3$) upon exposure to organometallic compounds of Group 1 or 2.



Scheme 1. Resonance structures of fulvene.

Recently there has been increased study of Group 4 aminofulvene complexes. For example, introduction of an amino group at C6 of fulvene and subsequent reaction with an organolithium compound led to chiral ligands, which upon reaction with $ZrCl_4$ provided the corresponding substituted zirconium complexes.[7] Starting from 6-(dimethylamino)-6-methylfulvene (**1**, see Scheme 1), a C_1-bridged anionic $C_5H_4CR^1_2NR^2$ ligand was obtained with which a constrained-geometry Ziegler catalyst had been synthesized.[8, 9] We report here that an unusual intramolecular NMe_2H elimination and a fulvene coupling take place when Group 4 chlorides are treated with (1-dimethylaminoethenyl)cyclopentadienyllithium (**2**), resulting in the novel allyl-bridged metallocene complexes **3** or **4** (Scheme 2).

The preparation of **2** involved the deprotonation of **1**. This type of reaction had been previously described with the use of different organolithium reagents. It was found that the deprotonation did not depend on the base strength of the

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