Formation of a Constrained-Geometry Ziegler Catalyst System Containing a C_1 Instead of the Usual Si_1 Connection Between the Cyclopentadienyl and Amido Ligand Components☆

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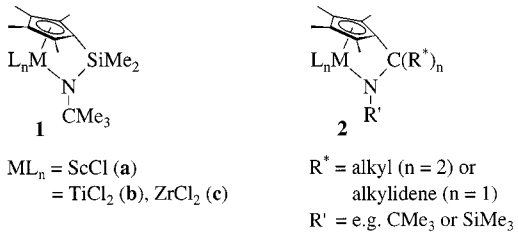
6-Amino-6-methylfulvene (**4**) is cleanly *N*-acylated by treatment with pivaloylchloride/triethylamine to give the fulvene (C_5H_4)=C(CH_3)NHCOCMe_3 (**5c**). Treatment of **4** with trimethylchlorosilane similarly yields the mono-*N*-silylated fulvene (C_5H_4)=C(CH_3)NHSiMe_3 (**7**). Both **5c** and **7** are cleanly doubly deprotonated e.g. by treatment with LDA to give ligand systems $[(C_5H_4)C(=CH_2)NR]Li_2$ [**8a** (R = COCMe_3) and **8b** (R = SiMe_3), respectively]. Their treatment with $MCl_4 \cdot 2$ THF (M = Ti, Zr) yield the *spiro*-metallocenes $[(C_5H_4)C(=CH_2)NR]_2M$ (**9**, **10**). Complex **10a** (M = Zr, R = COCMe_3) was characterized by X-ray diffraction. The reaction of **8a** with $(Et_2N)_2ZrCl_2$ in THF gives rise to the formation of $[(C_5H_4)C(=CH_2)NCOCMe_3]Zr(NEt_2)_2$ (**11**) (70 % isolated), and the reaction of **8b** with $(Et_2N)_2ZrCl_2$ yields $[(C_5H_4)C(=CH_2)NSiMe_3]Zr(NEt_2)_2$ (**12**) (76 % isolated). Treatment of complex **12** with an excess of methylalumoxane (MAO) in toluene solution results in the generation of an active homogeneous Ziegler catalyst for the polymerization of ethene. A comparison with the usually employed $[(Me_5C_4)SiMe_2NCMe_3]ZrCl_2$/MAO "constrained-geometry" Ziegler catalyst system reveals a similar catalyst activity and performance of this novel type of a C_1-bridged "constrained-geometry" catalyst as it is exemplified by the $[(C_5H_4)C(=CH_2)NSiMe_3]ZrX_2$ (**12**)/MAO combination.

Introduction

Homogeneous Ziegler catalysts on the basis of group-4 bent metallocenes have become of enormous importance in metal-catalyzed α-olefin polymerization and related processes.[1] Variation of the ligand systems and the development of novel types of catalyst precursors have been of great interest recently in order to expand the scope of the application of this general type of very active and at the same time often extremely selective catalyst systems.[2] In this context the "constrained-geometry catalysts" have recently found a special attention. They are catalyst systems that are formally derived from the dimethylsilylene-bridged ansa-metallocenes in which one of the Cp units is replaced by an amido-nitrogen atom. The most frequently employed ligand system was introduced by J. E. Bercaw et al. at a group-3 metal complex.[3] It is comprized by a tetramethylcyclopentadienyl moiety that is connected with a *tert*-butylamido building block by means of a bridging Me_2Si group. The scandium complex **1a** (ML_n = Sc−Cl) is a typical early example. The corresponding titanium and zirconium complexes (**2b**, **c**) were prepared consecutively and used as Ziegler catalyst precursors. These systems have achieved a great interest with regard to the practical application of ligand-controlled Ziegler catalysts in α-olefin polymerization processes.[4]

The use of the silylene bridge for connecting the Cp and amido subunits has appeared to be essential for these organometallic systems for quite some time. The presence of the silylene group prevents the elimination reaction to the corresponding fulvene system and additional fragmentation reactions to occur at some intermediate stages of the synthesis, reaction alternatives that are very favourable and have been observed in previous attempts to prepare the corresponding C_1-bridged constrained-geometry Ziegler systems.[5] These facile alternative reactions have probably favoured the design of hydrocarbyl-bridged $Cp(CR_2)_n-NR'$ systems with longer bridging chains ($n > 1$).[6] Practically feasible synthetic pathways to C_1-bridged constrained Ziegler catalyst systems to the best of our knowledge appear not to have been reported on so far with one potential exception.[7] We have now developed a simple synthetic entry to such organometallic complexes of the group-4 metals and shown that homogeneous Ziegler catalysts can be derived from examples of such $[Cp-C_1(R)-NR']ML_n$ systems that

Scheme 1



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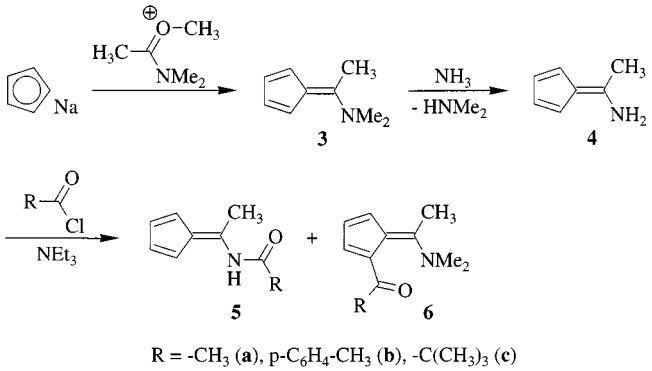
are of at least equal catalyst quality as compared to the commonly employed [Cp*−SiR_2−NR′]MCl_2 derived systems.

Results and Discussion

Starting material for our synthesis is 6-dimethylamino-6-methylfulvene (**3**), which is readily available by treatment of cyclopentadienide with *O*-methylated *N,N*-dimethylacetamide. As also described by K. Hafner et al.[8] **3** was treated with excess NH_3 to give 6-amino-6-methylfulvene (**4**). We have then acylated the aminofulvene system. Here the general problem arises that in **4** two positions are amenable to electrophilic attack, namely the amino group and the α-carbon center (C-2) at the five-membered carbocyclic ring.[9]

Scheme 2



Treatment of the aminofulvene **4** with acetyl chloride indeed furnished a mixture of the regioisomers **5a**, resulting from *N*-acylation, and **6a**, resulting from *C*-acylation at the fulvene α-carbon center C-2, respectively. The isomers **5a** (major) and **6a** (minor) were separated by column chromatography and isolated in ca. 70 and 5% yield, respectively. The spectral appearance of the two regioisomeric acetylation products is quite different. The four fulvene CH groups in the major product **5a** are just marginally differentiated [^{1}H NMR ($CDCl_3$): δ = 6.58−6.35 (m, 4 H); ^{13}C NMR: δ = 129.2, 128.3, 122.2, 116.8], whereas a clearly separated AMX system is characterized for the ^{1}H NMR fulvene section of **6a** (δ = 7.56, 7.27, 6.42; coupling constants: J_{HH} = 1.9, 3.2, 4.8 Hz). The situation is even less favourable for the aroylation of **4** with *p*-methylbenzoyl chloride. In this case a mixture of products was obtained from which the required *N*-aroylated product **5b** was isolated only in ca. 20% yield after chromatographic workup. In contrast, the acylation reaction with the bulky pivaloyl chloride reagent was very clean and selectively resulted in the formation of the *N*-pivaloylfulvene system **5c**, which was obtained in 80% yield as a yellow crystalline material after recrystallization from ether.

Single crystals were obtained from the three *N*-acylated fulvenes **5a−c** that allowed their characterization by X-ray crystal structure analyses. As a typical example, a view of the molecular structure of the *N*-acetylated fulvene **5a** is depicted in Figure 1. It can be seen from Table 1 that all three fulvenes exhibit the typical carbon−carbon bond length alternation in their frameworks and a transoidal connection of fulvene and carboxamide structural subunits with conformer **B** being favoured over **A** (see Scheme 3).

Scheme 3

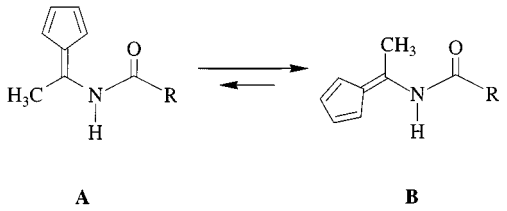


Table 1. Compilation of typical bond lengths, bond angles, and torsional angles of the *N*-acylated fulvenes **5a−c**

	5a	**5b**	**5c**[a]
C1−C2	1.447(5)	1.447(3)	1.458(2)
C2−C3	1.348(5)	1.345(3)	1.348(2)
C3−C4	1.428(6)	1.435(4)	1.442(3)
C4−C5	1.339(5)	1.352(4)	1.346(2)
C1−C5	1.462(5)	1.456(3)	1.457(2)
C1−C6	1.359(5)	1.354(3)	1.358(2)
C6−C7	1.487(5)	1.489(3)	1.491(2)
C6−N	1.395(5)	1.404(3)	1.399(2)
N−C8	1.380(5)	1.365(3)	1.370(2)
C8−O	1.207(4)	1.228(2)	1.219(1)
C8−C9	1.504(5)	1.483(3)	1.533(2)
C1−C6−N	118.6(3)	117.9(2)	118.5(1)
C6−N−C8	127.9(3)	129.0(2)	128.4(1)
N−C8−O	124.0(4)	123.4(2)	122.3(1)
N−C8−C9	113.6(3)	115.0(2)	115.2(1)
C7−C6−N−H	171(3)	152(2)	154(1)
C7−C6−N−C8	12.3(6)	28.4(3)	25.9(2)
C6−N−C8−O	6.9(7)	7.2(4)	2.0(2)
C6−N−C8−C9	−173.3(4)	−172.9(2)	177.5(1)
O−C8−N−H	−170(3)	−173(2)	179(1)

[a] Averaged absolute values of the three independent molecules in the unit cell of **5c**.

The fulvenes **5** are not monomeric in the crystal but connected by intermolecular hydrogen bonds, that link the carbonyl and NH functionalities of the amide groups,[10] to form oligomeric chain-type structures. In the resulting supra-structure the core atoms of the individual amide groups of **5a** and **5b** are oriented in a single plane, giving rise to elongated narrow sheet-like structures. The two-dimensional arrangement of the self-assembled associate of **5a** is depicted in Figure 1. It is probably due to the steric bulk of the *tert*-butyl substituent that a related but spatially different supra-structure is found for **5c**. Again a linear arrangement of fulv−NHCO−R units is found, with the individual carboxamide functionalities being connected via intermolecular N−H···O=C−NHR hydrogen bonds, only in this case are the individual −NH−CO− planes rotated substantially [angle between the planes O1−C8−N1/O2−C18−N2: 8.8(2)°; O1−C8−N1/O3−C28−N3: 54.5(2)°; O2−C18−N2/O3−C28−N3: 58.8(2)°]. A projection of the resulting three-dimensional arrangement is given in Figure 2.

Treatment of **4** with chlorotrimethylsilane in the presence of excess triethylamine results in the selective *N*-silylation

Figure 1. A view of the hydrogen-bonded associated structure of **5a** (**5b** exhibits a similar two-dimensional supramolecular core structure in the crystal)

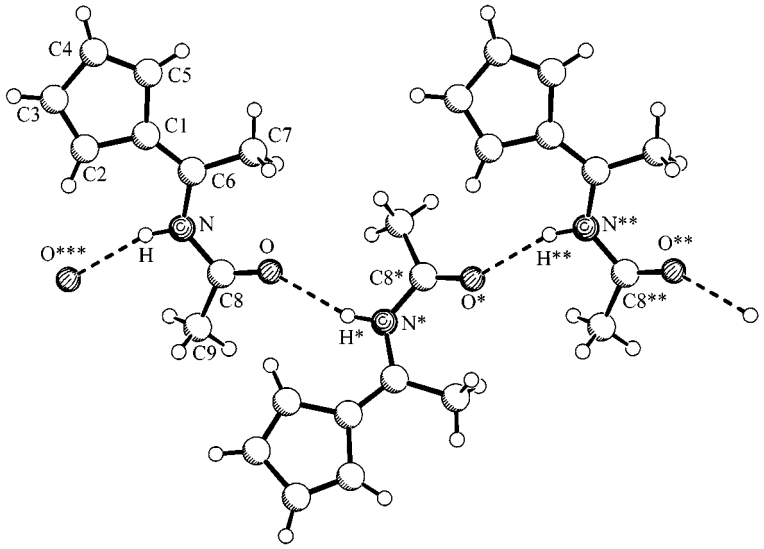
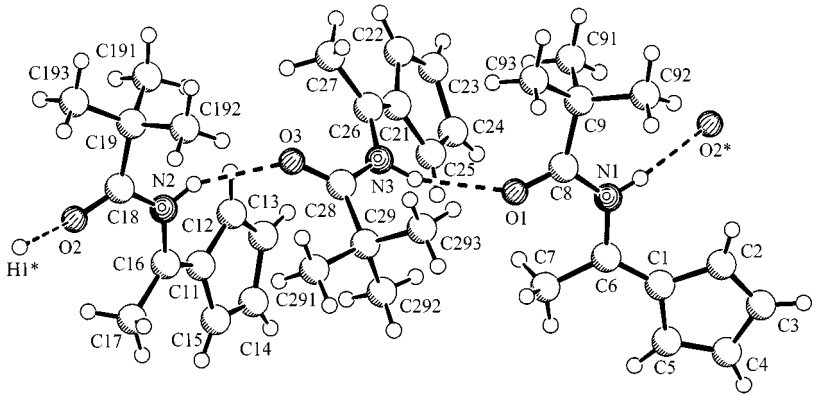
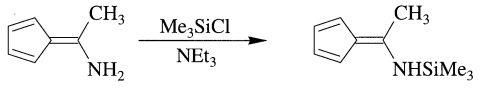


Figure 2. The three-dimensional assembled supramolecular solid-state structure of the *N*-pivaloylfulvene **5c**



of the aminofulvene. Only mono-silylation is achieved under these conditions to give the product **7** which was isolated in near-to-quantitative yield. Compound **7** shows a very characteristic ^{13}C-NMR spectrum with the electrophilic fulvene carbon center C-6 (δ = 154.7) being spectroscopically clearly differentiated from the remaining sp^2-carbon atoms of the ring system (C-1: δ = 117.9; C2−C5: δ = 124.6, 122.1, 119.7, 112.3).

Scheme 4



4 **7**

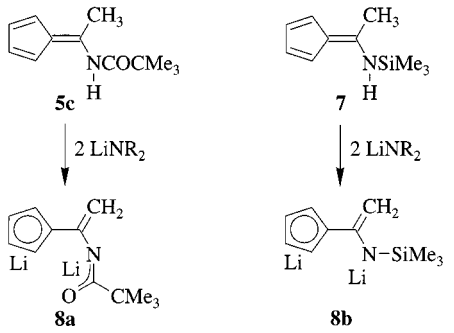
Our experiments had thus shown that 6-methyl-6-(pivaloylamino)fulvene (**5c**) and 6-methyl-6-(trimethylsilylamino)fulvene (**7**) among the investigated series of compounds were the easiest and most selective to be synthesized on a preparative scale,[11] and we consequently have decided to use these two compounds as the starting materials for the preparation of the anticipated Cp−C(R)$_n$−NR′ dianion-type ligands and the corresponding C$_1$-bridged constrained-geometry group-4 metal complex systems.

Principally, fulvene systems can be converted to cyclopentadienides by either the addition of a suitable nucleophile to the electrophilic C-6 carbon center[12] or by a deprotonation reaction at the alkyl carbon atom directly adjacent to the C-6 fulvene center.[13] For this study we have briefly tested the former procedure. We found out that a sufficiently soft nucleophile can be added to the C-6 carbon atom of the systems **5**. Thus the reaction of **5c** with two molar equivalents of lithium dimethylcuprate[14] eventually leads to the formation of the $[Cp-CMe_2-N(COCMe_3)]^{2-}$ ligand system that can be transmetallated with $Cl_2Zr(NEt_2)_2$. However, the resulting ansa-metallocene-like system was never obtained free of sizable amounts of as yet unidentified contaminants. For practical purposes it has thus turned out to be advantageous to rely on the second alternative methode and deprotonate the fulvenes at the C^6-CH_3 group (in addition to the kinetically rapid NH deprotonation) to generate the required C$_1$-bridged ligand system. This route has turned out to be very convenient and

successful. It can easily be applied to all the *N*-monosubstituted fulvene systems described above. The outcome of the reactions starting from **5c** and **7** will be described in the following as very typical examples.

Treatment of 6-methyl-6-(pivaloylamino)fulvene (**5c**) with two molar equivalents of methyllithium or even better with the less nucleophilic bases lithium hexamethyldisilazide or lithium diisopropylamide cleanly furnished the corresponding ligand system $[Cp-C(=CH_2)-N(COCMe_3)]^{2-}$ as the dilithio compound **8a** [$^1H/^{13}C$ NMR ([D_8]THF, 200.1 MHz): δ = 5.82, 5.89/118.2 (*ipso*-C), 106.3, 103.2 (C_5H_4); 4.47, 3.66 (^2J = 2.4 Hz)/155.4, 87.5 ($C=CH_2$), 1.08/179.3, 39.0, 29.5 ($COCMe_3$)]. Analogously, treatment of 6-methyl-6-(trimethylsilylamino)fulvene (**7**) with these bases gave the corresponding ligand system $[Cp-C(=CH_2)-NSiMe_3]^{2-}$ (obtained and isolated as the dilithio compound **8b**).

Scheme 5



The reaction of **8b** with zirconium tetrachloride results, under all reaction conditions tested by us, in a rapid substitution of all four halogen atoms[7b][15] to yield the organometallic *spiro*-metallocene complex **10b**. The product **10b** was isolated in close to 80% yield. It shows typical $^1H/^{13}C$-NMR spectra {in [D_6]benzene: C_5H_4 resonances at δ = 6.36, 6.00, 5.41, 5.36/118.4 (*ipso*-C), 116.3, 114.4, 112.6, 109.1; ($C=CH_2$): δ = 4.22, 4.18/144.7, 88.7; $SiMe_3$: δ = 0.24/1.75}. The analogous reaction of the dilithio ligand system **8b** with $TiCl_4$ gives the corresponding *spiro*-titanocenebisamido complex **9b** (isolated in 81% yield). Treatment of the *N*-acylated ligand system employed as the dilithiated reagent **8a** with $TiCl_4$ or $ZrCl_4$ proceeds quite analogously. In these cases the corresponding chiral *spiro*-metallocene complexes **9a** (M = Ti, 58% yield) and **10a** (M = Zr, isolated in 74% yield) were obtained (see Scheme 6).

The *spiro*-metallocene complex **10a** was characterized by an X-ray crystal structure analysis. Single crystals of **10a** suitable for X-ray diffraction were obtained by crystallization from pentane/toluene. The central zirconium atom in complex **10a** is coordinated to two cyclopentadienyl units and the acylamido groups of the pair of near-to-symmetry-equivalent $[Cp-C(=CH_2)-NC(CMe_3)O]$ ligand systems in an overall pseudotetrahedral coordination geometry [D1−Zr1−D2 = 131.0° (D1 and D2 denote the centroids of the Cp ring systems), O14−Zr1−O34 = 99.95(13)°]. Complex **10a** is chiral; in the crystal it is chemically, but not strictly crystallographically, to be regarded as C_2-symmetric (see Figure 3).

The C6=C7 double bond of **10a** [1.332(6) Å; accordingly C26−C27: 1.341(6) Å] is oriented approximately coplanar with the adjacent cyclopentadienyl ring system. The dihedral angle θ C4−C5−C6−C7 amounts to −31.9(7)°; the corresponding value of θ C21−C25−C26−C27 is −29.4(7)°. The adjacent nitrogen atom N8 is also oriented in this substituent plane [dihedral angles θ C1−C5−C6−N8 −19.2(6)°, and correspondingly C24−C25−C26−N28 −15.6(6)°]. The N8−C9 bond is short [1.278(5) Å; N28−C29 1.289(5) Å] and must be regarded as an N=C double bond. Consequently, the C9−O14 linkage is elongated [1.338(5) Å; C29−O34 1.334(5) Å]. Apparently the ambidentate *N*-acylamido functional group is present as the imino tautomer in complex **10a**. Coordination of this group to the group-4 metal takes place exclusively by means of the oxygen atom [O14−Zr1 2.026(2) Å; O34−Zr1 2.038(3) Å] and not through the nitrogen center [the N8···Zr1 separation is 3.682(4) Å; N28···Zr1 3.666(4) Å]. Consequently, the individual ligand systems in **10a** are not planar but the two sections used for coordinating to the transition-metal center are segregated by a strong rotation about the C6−N8 vector [dihedral angles θ C5−C6−N8−C9 −52.1(5)°, C25−C26−N28−C29 −52.9(5)°, C7−C6−N8−C9 130.5(5)°, C27−C26−N28−C29 129.6(4)°, C6−N8−C9−O14 −5.4(6)°, C26−N28−C29−O34 −6.6(6)°] to allow for the thermodynamically favourable coordination of the ligand system to the zirconium center through the carboxamido oxygen atom. The bond angles at these oxygen atoms are substantially enlarged at 136.5(3)° (C9−O14−Zr1) and 136.0(2)° (C29−O34−Zr1), respectively. This probably indicates a tendency to form a stabilizing Zr−O π interaction, similar as it has been observed in a variety of Zr−O linkages in metallacyclic systems of ring sizes of 6 and larger.[16] The remaining angles inside the metallacyclic framework of **10a** are in a normal and expected range [C6−N8−C9 117.9(4)°, C26−N28−C29 118.3(3)°, N8−C9−O14 125.2(4)°, N28−C29−O34 124.8(4)°].

We have then treated the dilithio compound **8a** with the dichlorobis(diethylamido)zirconium reagent, employed as its bis(tetrahydrofuran) adduct.[17] This results in a clean reaction that takes place by a selective displacement of the two chloride ligands by the $[Cp-C(=CH_2)-N(CMe_3)O]^{2-}$ ligand system. The $Zr(NEt_2)_2$ moiety is retained during this transformation.[18] The resulting zirconium complex **11** was obtained in 70% yield. The spectroscopic data of the newly introduced $[Cp-C=CH_2)-N(CMe_3)O]$ ligand in **11** are quite similar as previously observed for the *spiro* complexes **9a** and **10a** {**11**: $^1H/^{13}C$ NMR in [D_8]THF: δ = 6.60, 5.95/111.3, 110.5 (C_5H_4), 4.77, 4.72 ($^2J_{HH}$ = 1.8 Hz)/147.6, 102.4 ($C=CH_2$), 171.4 (NCO)}. Therefore, we assume that the $[Cp-C(=CH_2)N(CMe_3)O]$ ligand system in **11** is coordinated by means of the Cp ring and the carboxamido oxygen, and not the nitrogen center, just analogously as it was previously observed for the *spiro*-metal complexes **9a** and **10a** (see above).

Scheme 6

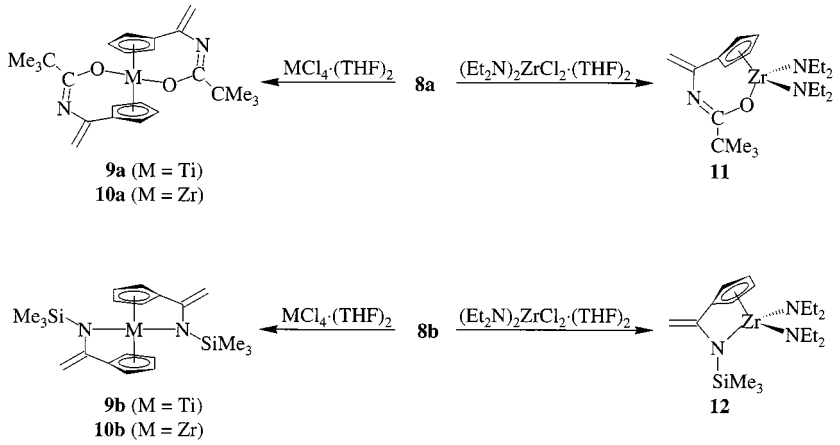
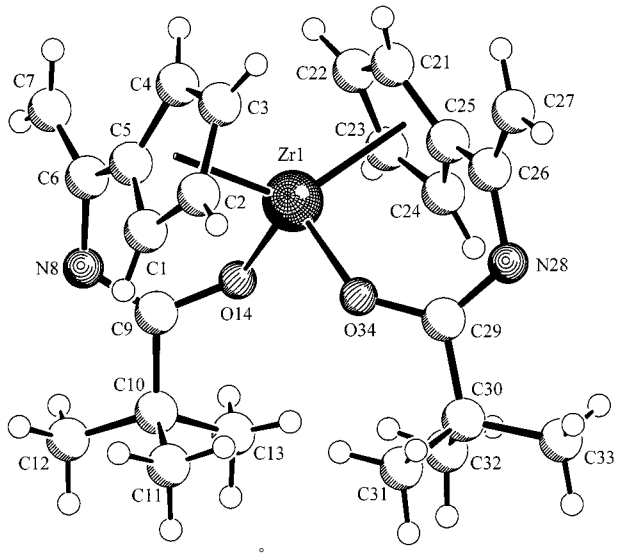


Figure 3. Molecular structure of **10a**[a]



[a] Selected bond lengths [A] and angles [°]: Zr1−O14 2.026(2), Zr1−O34 2.038(3), Zr1−N8 3.682(4), Zr1−N28 3.666(4), Zr1−C_{Cp} 2.511(5), C5−C6 1.474(6), C25−C26 1.466(6), C6−C7 1.332(6), C26−C27 1.341(6), C6−N8 1.418(5), C26−N28 1.414(5), N8−C9 1.278(5), N28−C29 1.289(5), C9−O14 1.338(5), C29−O34 1.334(5), C9−C10 1.523(6), C29−C30 1.524(6); O14−Zr1−O34 99.95(13), Zr1−O14−C9 136.5(3), Zr1−O34−C29 136.0(2), C5−C6−C7 122.2(4), C25−C26−C27 123.5(4), C5−C6−N8 116.5(4), C25−C26−N28 116.0(3), C7−C6−N8 121.3(4), C27−C26−N28 120.5(4), N8−C9−O14 125.2(4), N28−C29−O34 124.8(4), N8−C9−C10 120.8(4), N28−C29−C30 120.0(4), O14−C9−C10 113.9(4), O34−C29−C30 115.2(3); see text for additional values.

As expected, the $[Cp-C(=CH_2)-NSiMe_3]^{2-}$ ligand, employed as the respective dilithio reagent **8b**, reacts analogously with the $(Et_2N)_2ZrCl_2(THF)_2$ reagent very cleanly and in good yield to give the C_1-bridged constrained-geometry metal-complex system $[Cp-C(=CH_2)-NSiMe_3]Zr(NEt_2)_2$ (**12**). Exclusive metathetical exchange of the chloride ligands takes place, and the C_1-bridged Cp/amido-zirconium complex **12** was isolated in 76% yield. It shows very typical $^1H/^{13}C$-NMR spectra {in [D_6]benzene: δ = 6.03, 5.92/112.2 (*ipso*-C), 115.4, 111.3 (C_5H_4), 4.36, 4.34/150.9, 87.9 ($C=CH_2$), 0.39/0.8 ($SiMe_3$), 3.13, 0.90/43.2, 15.6 (NEt_2)}.

We have employed the $[Cp-C(=CH_2)-NSiMe_3]Zr(NEt_2)_2$ complex **12** as a starting material for generating a homogeneous Ziegler catalyst system and used it for carrying out a small series of preliminary ethene polymerization experiments. These few and as yet unoptimized polymerization reactions have revealed that the Ziegler catalysts, based on the C_1-bridged constrained-geometry framework, are at least comparable in activity and performance to the commonly used and studied Si_1-bridged "parent" system. This lets us hope that future variations of our here described $[Cp-C(R^*)NR']MX_2$ complexes will indeed lead to an even better catalyst performance and open ways to novel and advanced catalytic applications.

For the series of catalytic experiments carried out in the course of this study we have activated the zirconium complex **12** by treatment with a large excess of methylalumoxane (employed as a standard toluene solution).[19] In a typical experiment a solution of 19.4 mg (47.0 μmol) of **12** was activated by treatment with 10 ml of a 10% solution of methylalumoxane in toluene (Al/Zr = 340) at ambient temperature under an initial ethene pressure of 37 bar. After a short induction period a rapid temperature increase took place (up to 87°C) and the pressure dropped due to rapid consumption of the monomer. Ethene pressure was reestablished and the monomer constantly fed into the reactor for a time period of ca. 10 min. The reaction was stopped by ceasing the monomer fed. Opening of the reactor revealed that the interior of the reaction vessel was almost filled with an amorphous lump of polymer. Workup, as described in the Experimental Section, gave 16.6 g of polyethylene (mp 129°C, DSC), which corresponds to an overall catalyst activity of ca. 57 g polymer/mmol [Zr]·bar·h under these unoptimized non-isothermal conditions. A number of similar experiments, which gave comparable results, are listed in the Experimental Section.

For a direct comparison we have carried out a few ethene polymerization experiments under analogous reaction conditions using the Si_1-bridged "Bercaw/Exxon/Dow" system $[Me_4C_5-SiMe_2-NCMe_3]ZrCl_2$ (**1c**, see Scheme 1)[4] as the Ziegler catalyst precursor. In a typical experiment under very similar conditions as described above a sample of **1c**

(8.6 mg, 20.9 μmol) was activated by treatment with methylalumoxane (Al/Zr = 1530) in toluene under ethene (40 bar) in an autoclave. Rapid polymerization set in at once; the contents of the autoclave increased its temperature up to 103°C. A yield of 14.4 g of polyethylene was obtained under these conditions (mp 135°C, by DSC), corresponding to an overall catalyst activity of ca. 52 g polymer/mmol [Zr]·h·bar under these non-isothermal conditions.

We have also carried out the ethene polymerization reaction in a thermostated glass autoclave employing the **12**/methylalumoxane system in toluene (Al/Zr = 700) at 25°C and a constant pressure of 2.2 bar and obtained polyethylene (mp 137°C) with a slightly lower activity of a = 23 g polymer/mmol [Zr]·h·bar.

Conclusions

We had recently shown that the C_1-bridged fluorenyl/amido system $[Flu-CH_2-NCMe_3]^{2-}$ (generated and studied as the corresponding lithiated compound) is kinetically and thermodynamically rather stable, but, of course, difficult to handle because of its high basicity.[5] Much more problematic seems to be a prediction of the chemistry of related systems on the mono-anionic stage. For the examples $[Flu(H)-CH_2-NCMe_3]^-$/$[Flu-CH_2-NHCMe_3]^-$ (Flu = fluorenylidene) we had in a detailed study been able to characterize a number of readily available competing reaction pathways, involving e.g. fulvene formation and fragmentation pathways.[5] It appears, that similar multiple reaction pathways are getting involved when such dianions are treated with early transition-metal reagents that, due to the highly covalent character of e.g. the N−Zr or C−Zr bonds, can lead to very reactive intermediates, that then are prone to enter into the manifold of the competing pathways that are so typical for the respective $[Cp-CR_2-NR']^-$ mono-anion systems. This effect does not generally preclude the successful synthesis of such $[Cp-CR_2-NR']MX_2$-type systems,[7] but will in very many cases lead to complicated organometallic mixtures of products and will make the handling of such systems probably rather difficult. This is very likely to be the reason why reports on such C_1-bridged constrained-geometry systems are extremely sparse, in contrast to their Si_1- or their elongated C_n-bridged analogues.[3][4][6][7] The system developed by us and described with some first examples in this article seems to provide a useful and generally easily accessible alternative. Introduction of the sp^2-carbon center in the system adjacent to the Cp-ring as a bridging atom between the C_5H_4 and N−R′ moieties appears very effectively to make all the usually encountered reactive alternatives and diversions on the intermediate stages of the overall reaction sequence to the final group-4 metal complexes sufficiently unfavourable to allow for a straightforward and easily performed synthesis of the respective $[Cp-C(=CH_2)-NR]ML_n$-type systems. Our preliminary ethene polymerization experiments have shown that the first examples of the thus derived C_1-bridged constrained-geometry Ziegler catalysts are at least equally effective, very active polymerization catalysts as the commonly employed $[Cp^*-SiMe_2-NCMe_3]ZrCl_2$ system.

Our entry into the novel class of the $[Cp-C(=CH_2)-NR']ZrX_2$-type catalyst precursors should allow for the synthesis of a large number of easily accessible variations of such systems. We are confident that this will lead to a significant extension and further development of the scope of application of such interesting catalyst types in polymerization reactions and in organic synthesis.[20] The further development of the C_1-bridged "constrained-geometry catalysts" is, therefore, actively pursued in our laboratory.

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Experimental Section

General Information: All reactions with organometallic reagents or substrates were carried out under argon using Schlenk-type glassware or in a glove-box. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. − The following instruments were used for spectroscopic and physical characterization of the compounds: Bruker AC 200P (^{1}H: 200.13, ^{13}C: 50.3 MHz), Bruker ARX 300, and Varian Unity Plus (^{1}H: 599.2, ^{13}C: 150.8 MHz) NMR spectrometers (spectral assignments were usually secured by GCOSY, GHSQC and GHMBC experiments[21]); Nicolet 5 DXC FT-IR spectrometer; melting points: DSC 2910 (Thermo Analysis/DuPont); elemental analyses: Foss-Heraeus CHN-Rapid; X-ray crystal structure analyses: Enraf-Nonius CAD4 and MACH3 diffractometers (programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92). − The reagent $(Et_2N)_2ZrCl_2(THF)_2$ was prepared according to a literature procedure.[17] The aminofulvenes were synthesized by variations of the procedures previously described by K. Hafner et al.[8]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101213. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

6-Dimethylamino-6-methylfulvene (**3**): Dimethyl sulfate (49 ml, 62 g, 0.49 mol) was added dropwise with gentle heating in such a way to 49 ml (43 g, 0.49 mol) of freshly distilled *N,N*-dimethylacetamide that the temperature was maintained at 50−60°C. Then the solution was kept at 70−80°C for 2 h. The viscous oil was added with stirring to a solution of 44 g (0.50 mol) of sodium cyclopentadienide in 300 ml of tetrahydrofuran with external cooling at a rate that the reaction temperature was kept between −5 and −10°C. The precipitated sodium methyl sulfate was filtered off and the solvent removed from the filtrate in vacuo. The dark brown oil was treated with 2 g of active charcoal in 400 ml of hot cyclohexane and filtered. The product **3** crystallizes upon cooling. The mother liquor was concentrated and treated again with charcoal to give a combined yield of 59.5 g (88%) of **3**, mp 90°C. − $C_9H_{13}N$ (135.2): calcd. C 79.95, H 9.69, N 10.36; found C 79.81, H 9.90, N 10.18. − ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 6.83−6.44 (m, 4 H, C_5H_4), 3.48 (s, 6 H, NCH_3), 2.62 (s, 3 H, 6-CH_3). − ^{13}C NMR (50.3 MHz, [D$_1$]chloroform): δ = 158.5 (C-6), 121.4, 120.1, 118.5, 116.5 (Cp, C-2−5), 117.3 (C-1), 43.4 (NCH_3), 20.5 (6-CH_3).

6-Amino-6-methylfulvene (**4**): A 300-ml autoclave, containing an internal glass vessel, was charged with 59.7 g (400 mmol) of **3** and ca. 150 ml condensed NH_3 at −78°C. The closed system was left for 7 d at 40°C (at 10 bar pressure). The system was then cooled (< −33°C) and the autoclave opened. NH_3 was allowed to evaporate and the yellow product dried in vacuo to give 41.6 g (97%) of **4**, mp. 85°C. − C_7H_9N (107.1): calcd. C 78.46, H 8.47, N 13.07; found C 78.33, H 8.72, N 12.68. − ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 6.56−6.27 (m, 4 H, C_5H_4), 5.13 (br., 2 H, NH_2), 2.31 (s, 3 H, 6-CH_3). − ^{13}C NMR (50.3 MHz, [D$_1$]chloroform): δ = 154.7 (C-6), 117.9 (C-1), 124.6, 122.1, 119.7, 112.3 (Cp, C-2−5), 19.5 (6-CH_3).

6-Acetylamino-6-methylfulvene (**5a**) *and 2-Acetyl-6-amino-6-methylfulvene* (**6a**): A solution of acetyl chloride (314 mg, 4.03 mmol) in 15 ml of ether was added dropwise to a solution of 599 mg (4.00 mmol) of the fulvene **4** in 30 ml of ether containing 3 ml of triethylamine at 0°C. The mixture was stirred overnight and was then concentrated to one half of its volume in vacuo. Triethylammonium chloride was removed by filtration. The product was precipitated by cooling to −20°C. The resulting crude product was purified by column chromatography (silica gel, 60 mesh, diethyl ether/triethylamine, 50:1). Compound **6a** (30 mg, 5% yield) was recovered from the first eluate, compound **5a** (406 mg, 68%) was collected from the third fraction. **5a**: mp 119°C (DSC). − $C_9H_{11}NO$ (149.2): calcd. C 72.46, H 7.43, N 9.39; found C 70.98, H 7.38, N 8.75. − ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 7.78 (br., NH), 6.58−6.35 (m, 4 H, C_5H_4), 2.68 (s, 3H), 2.17 (s, 3 H, COCH_3). − ^{13}C NMR (50.3 MHz, [D$_8$]tetrahydrofuran): δ = 169.5 (C=O), 146.8 (C-6), 129.4 (C-1), 129.0, 128.3, 122.2, 116.8 (Cp, C-2−5), 24.3 (COCH_3), 19.2 (C-7).

X-ray Crystal Structure Analysis of **5a**: Formula $C_9H_{11}NO$, M = 149.19, 0.25 × 0.20 × 0.10 mm, a = 7.265(2), b = 11.576(3), c = 9.729(1) A, β = 104.84(2)°, V = 790.9(3) A^3, $\rho_{calcd.}$ = 1.253 g cm^{-3}, μ = 0.82 cm^{-1}, no absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 A, T = 223 K, ω/2θ scans, 1721 reflections collected (−h, +k, ±l), [(sinθ)/λ] = 0.62 A^{-1}, 1596 independent and 733 observed reflections [$I \geq 2\ \sigma(I)$], 105 refined parameters, R = 0.063, wR^2 = 0.158, max. residual electron density 0.28 (−0.33) e A^{-3}, hydrogen atom at N from difference Fourier, others calculated and all refined as riding atoms.

6a: ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 14.6 (br., 2 H, NH), 7.56 (1 H), 7.27 (1 H), and 6.42 (1 H, ABX, C_5H_3, J_{HH} = 1.9, 3.2, and 4.8 Hz), 2.87, 2.56 (s, each 3 H, CH_3).

6-Methyl-6-[(p-methylbenzoyl)amino]fulvene (**5b**): Triethylamine (7 ml) was added to a solution of 4.14 g (38.7 mmol) of the aminofulvene **4** in 150 ml of ether. *p*-Methylbenzoyl chloride (5.40 ml, 41.0 mmol) was very slowly added by syringe to the vigorously stirred solution at 0°C. After 24 h, the mixture was concentrated to half its volume in vacuo and the precipitated triethylammonium chloride removed by filtration. The remaining solvent was then removed in vacuo. The resulting crude product (5.6 g, ca. 60%) was purified by column chromatography at a deactivated (by treatment with 5% triethylamine in pentane/ether, 8:1) silica gel column (60 mesh). Elution with pentane/ether (8:1) gave the product **5b** as the third fraction, yield 1.8 g (21%). Single crystals suited for the X-ray crystal structure analysis were obtained from ether at 0°C; mp 104°C (DSC). − $C_{15}H_{15}NO$ (225.3): calcd. C 79.97, H 6.71, N 6.22; found C 78.62, H 7.05, N 6.10. − ^{1}H NMR (200.1 MHz, [D$_8$]tetrahydrofuran): δ = 9.32 (br., 1 H, NH), 7.83 (m, 2 H), 7.29 (m, 2 H, *o*,*m*-Ph), 6.66−6.54 (m, 2 H), 6.32−6.28 (m, 2 H, C_5H_4), 2.73 (s, 3 H, 6-CH_3), 2.40 (s, 3 H, Ph-CH_3). − ^{13}C NMR (150.8 MHz, [D$_1$]chloroform): δ = 165.1 (C=O), 145.9 (C-6), 143.4 (*p*-C, Ph), 131.3 (*ipso*-C, Ph), 130.2 (C-5), 129.7 (*m*-C, Ph), 128.9 (C-1), 128.7 (C-3), 127.1 (*o*-C, Ph), 121.8 (C-2), 113.9 (C-4), 21.5 (Ph-CH_3), 18.6 (6-CH_3). − IR (KBr): ν = 3335, 1662, 1622 cm^{-1}.

X-ray Crystal Structure Analysis of **5b**: Formula $C_{15}H_{15}NO$, M = 225.28, 0.50 × 0.30 × 0.10 mm, a = 7.169(1), b = 24.276(2), c = 7.289(1) A, β = 97.99(1)°, V = 1256.2(3) A^3, $\rho_{calcd.}$ = 1.191 g cm^{-3}, μ = 5.84 cm^{-1}, no absorption correction, Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 A, T = 223 K, ω/2θ scans, 2743 reflections collected (±h, −k, +l), [(sinθ)/λ] = 0.62 A^{-1}, 2547 independent and 1673 observed reflections [$I \geq 2\ \sigma(I)$], 160 refined parameters, R = 0.056, wR^2 = 0.146, max. residual electron density 0.20 (−0.20) e A^{-3}, hydrogen atom at N from difference Fourier, others calculated and all refined as riding atoms.

6-Methyl-6-(pivaloylamino)fulvene (**5c**): Pivaloyl chloride (5.60 g, 46.7 mmol) was added at 0°C to a solution of 5.00 g (46.7 mmol) of **4** and 3 ml of triethylamine in 30 ml of tetrahydrofuran. After warming and stirring overnight at room temperature, the emulsion was filtered. The solvent was removed in vacuo. The residue was taken up in ether, filtered and the product crystallized from the clear ethereal solution at −30°C. Some of the thus obtained crystals were suitable for X-ray diffraction. Yield of **5c**: 7.14 g (80%), mp 82°C (DSC). − $C_{12}H_{17}NO$ (191.3): calcd. C 75.35, H 8.96, N 7.32; found C 75.14, H 9.08, N 7.25. − ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 8.17 (br., 1 H, NH), 6.60−6.34 (m, 4 H, C_5H_4), 2.70 (s, 3 H, 6-CH_3), 1.29 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR (50.3 MHz, [D$_1$]chloroform): δ = 176.5 (C=O), 146.3 (C-6), 128.3 (C-1), 130.1, 128.5, 121.8, 113.6 (Cp, C-2−5), 40.4 [C(CH$_3$)$_3$], 27.4 [C(CH_3)$_3$], 18.6 (6-CH_3). − IR (KBr): ν = 3342, 1683, 1620 cm^{-1}. − HRMS (70eV); $C_{12}H_{17}NO$: calcd. 191.13101; found 191.13054; *m*/*z* (%): 191 [M$^+$] (38), 134 [M$^+$ − C_4H_9] (10), 107 [M$^+$ − COC_4H_8] (9), 57 [$C_4H_9^+$] (100).

X-ray Crystal Structure Analysis of **5c**: Formula $C_{12}H_{17}NO$, M = 191.27, 0.60 × 0.30 × 0.10 mm, a = 14.076(1), b = 8.474(1), c = 28.982(3) A, β = 91.16(1)°, V = 3456.3(6) A^3, $\rho_{calcd.}$ = 1.103 g cm^{-3}, μ = 5.44 cm^{-1}, empirical absorption correction with ψ scan data (0.945 ≤ C ≤ 0.999), Z = 12, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 A, T = 223 K, ω/2θ scans, 7207 reflections collected (±h, +k, −l), [(sinθ)/λ] = 0.62 A^{-1}, 7057 independent and 5847 observed reflections [$I \geq 2\ \sigma(I)$], 401 refined parameters, R = 0.040, wR^2 = 0.116, max. residual electron density 0.21 (−0.15) e A^{-3}, hydrogen atom at N from difference Fourier, others calculated and all refined as riding atoms.

6-Methyl-6-[(trimethylsilyl)amino]fulvene (**7**): To a cold solution (0°C) of 702 mg (6.55 mmol) of the aminofulvene **4** in 100 ml of ether, containing three molar equivalents of triethylamine (2.0 g) was slowly added with stirring 1.5 molar equivalents (1.25 ml, 1.07 g, 9.83 mmol) of chlorotrimethylsilane. After 8 h at ambient temperature, the mixture was filtered and the solvent removed in vacuo to give the product **7** as a viscous oil. Yield of **7**: 1.15 g (98%), mp 12°C (DSC). − $C_{10}H_{17}NSi$ (179.3): calcd. C 66.97, H 9.55, N 7.81; found C 66.83, H 9.50, N 8.03. − ^{1}H NMR (200.1 MHz, [D$_1$]chloroform): δ = 6.57−6.28 (m, 4 H, C_5H_4), 5.4 (br., 1 H, NH), 2.39 (s, 3 H, 6-CH_3), 0.35 (s, 9 H, SiCH_3). − ^{13}C NMR (50.3 MHz, [D$_1$]chloroform): δ = 158.8 (C-6), 125.0, 122.4, 119.5, 111.9 (C-2−5), 122.1 (C-1), 19.3 (6-CH_3), 0.8 [Si(CH$_3$)$_3$]. − IR (NaCl): ν = 3353, 1616 cm^{-1}. − MS (70eV); *m*/*z* (%): 179 [M$^+$] (84), 164 [M$^+$ − CH_3] (100), 73 [$SiMe_3^+$] (71).

Lithium [1-(Lithio-N-pivaloylamido)ethenyl]cyclopentadienide (**8a**): A solution of the fulvene **5c** (380 mg, 1.99 mmol) in 30 ml of ether was treated at −20°C with two molar equivalents of lithium hexamethyldisilazide (675 mg, 4.04 mmol), dissolved in 20 ml of ether. The mixture was warmed to room temperature and stirred

for 4 h. The resulting precipitate of **8a** was collected by filtration, washed with ether (10 ml), then with pentane (20 ml), and dried in vacuo to give 363 mg (81%) of **8a** (· 0.3 Et_2O). – ^1H NMR (200.1 MHz, [D_8]tetrahydrofuran): δ = 5.82 (m, 2 H), 5.69 (m, 2 H, Cp), 4.47 (1 H), and 3.66 (1 H, AB system, $^2J_{HH}$ = 2.3 Hz, C=CH_2), 1.08 [s, 9 H, C(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, [D_8]tetrahydrofuran): δ = 179.3 (C=O), 155.4 (*C*=CH_2), 118.2 (*ipso*-C, Cp), 106.3, 103.2 (Cp), 87.5 (C=*C*H_2), 39.0 [*C*(CH_3)$_3$], 29.5 [C(*C*H_3)$_3$].

Lithium [1-(Lithio-N-trimethylsilylamido)ethenyl]cyclopentadienide (**8b**): A solution of lithium diisopropylamide (LDA, 2.1 g, 20 mmol) in 5 ml of tetrahydrofuran was added to a solution of 1.81 g (10 mmol) of the fulvene **7** in 30 ml of ether at 0°C. The mixture was stirred for 20 h at ambient temperature, then the solvent was removed in vacuo. The residue was suspended in pentane and the solid product collected by filtration, washed with pentane and dried in vacuo to yield 3.10 g (89%) of **8b** (· 1.5 THF). – ^1H NMR (200.1 MHz, [D_8]tetrahydrofuran): δ = 5.81 (m, 2 H) and 5.66 (m, 2 H, Cp), 3.61 (1 H) and 3.17 (1 H, AB system, $^2J_{HH}$ = 2.6 Hz, C=CH_2), −0.01 [s, 9 H, Si-CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, [D_8]tetrahydrofuran): δ = 130.0 (*C*=CH_2), 119.1 (*ipso*-C of Cp), 104.5, 101.3 (Cp), 73.3 (C=*C*H_2), 2.4 [Si(*C*H_3)$_3$].

Reaction of **8a** *with Titanium Tetrachloride, Preparation of Bis{η⁵:κ-O-[1-(pivaloylamido)ethenyl]cyclopentadienyl}titanium* (**9a**): A suspension of the dilithium compound **8a**, generated by treatment of 191 mg (1.00 mmol) of the fulvene **5c** with 220 mg (2.06 mmol) of LDA in 50 ml of THF at −20°C (24 h), was slowly added at −20°C to a solution of 167 mg (502 μmol) $TiCl_4$ · 2 THF in 50 ml of THF. The dark red mixture was warmed to room temperature and then stirred for 3 h. The solvent was removed in vacuo and the residue extracted with 80 ml of pentane. Removal of the solvent in vacuo gave the product **9a** as a red, microcrystalline solid, yield 124 mg (58%), mp 123°C (DSC, decomp.), that was characterized spectroscopically. – ^1H NMR ([D_2]dichloromethane): δ = 6.21, 6.12, 6.07, 5.82 (m, each 2 H, Cp), 5.32, 4.89 (d, ^2J = 0.96 Hz, each 1 H, C=CH_2), 1.13 [s, 18 H, C(CH_3)$_3$]. – ^{13}C NMR (CD_2Cl_2): δ = 176.9 (N*C*O), 146.0 (*C*=CH_2), 124.5 (*ipso*-C, Cp), 126.3, 117.3, 109.9, 107.3 (Cp), 105.3 (C=*C*H_2), 39.1, 28.6 [C(CH_3)$_3$]. – IR (KBr): ν = 1619, 1566, 1557 cm^{-1}.

Preparation of Bis(η⁵:κ-N-{1-[(trimethylsilyl)amido]ethenyl}-cyclopentadienyl)titanium (**9b**): Analogously as described above, treatment of 688 mg (3.84 mmol) of the fulvene **7** with 822 mg (7.68 mmol) of LDA followed by reaction with 641 mg (1.92 mmol) of $TiCl_4$ · 2 THF gave **9b**, yield 626 mg (81%), mp 135°C (DSC, decomp.). – ^1H NMR ([D_6]benzene): δ = 6.55, 6.91, 5.28, 5.11 (m, each 2 H, Cp), 4.07, 3.95 (d, each 1 H, =CH_2), 0.27 [s, 18 H, Si(CH_3)$_3$]. – ^{13}C NMR ([D_8]tetrahydrofuran): δ = 151.3 (*C*=CH_2), 122.3 (*ipso*-C, Cp), 117.7, 116.6, 115.4, 114.0 (Cp), 84.3 (C=*C*H_2), 2.65 ($SiMe_3$). – IR (KBr): ν = 1623 cm^{-1}.

Synthesis of Bis{η⁵:κ-O-[1-(pivaloylamido)ethenyl]cyclopentadienyl}zirconium (**10a**): 546 mg (2.86 mmol) of the fulvene **5c** was doubly deprotonated by treatment with 614 mg (5.74 mmol) of LDA in 50 ml of THF, analogously as described above. A solution of $ZrCl_4$ · 2 THF (539 mg, 1.43 mmol) in 50 ml of THF was added at ambient temperature. After stirring for 20 h at room temperature, the solvent was removed in vacuo. Extraction with pentane yielded 739 mg (74%) of the product **10a**, mp 111°C (DSC, decomp.). – $C_{24}H_{30}N_2O_2Zr$ (469.8): calcd. C 61.37, H 6.44, N 5.96; found C 59.84, H 6.63, N 5.96. – ^1H NMR ([D_8]tetrahydrofuran, 600 MHz): δ = 6.40, 6.35, 6.17, 5.82 (m, each 2 H, Cp), 4.80, 4.73 (d, ^2J = 1.4 Hz, each 2 H, =CH_2), 1.12 [s, 18 H, C(CH_3)$_3$]. – ^{13}C NMR ([D_2]dichloromethane, 50 MHz): δ = 174.1 (N*C*O), 145.9 (*C*=CH_2), 125.8 (*ipso*-C, Cp), 120.9, 113.0, 108.3, 106.0 (Cp), 103.9 (C=*C*H_2), 38.7, 28.4 (CMe_3). – IR (KBr): $\tilde{\nu}$ = 1621, 1589, 1502 cm^{-1}.

X-ray Crystal Structure Analysis of **10a**: Formula $C_{24}H_{30}N_2O_2Zr$, *M* = 469.72, 0.40 × 0.40 × 0.10 mm, *a* = 13.301(1), *b* = 14.968(1), *c* = 11.099(1) A, *V* = 2209.7(3) A^3, $\rho_{calcd.}$ = 1.412 g cm^{-3}, μ = 5.19 cm^{-1}, no absorption correction, *Z* = 4, orthorhombic, space group $Pna2_1$ (No. 33), λ = 0.71073 A, *T* = 223 K, ω/2θ scans, 2364 reflections collected (−*h*, +*k*, −*l*), [(sinθ)/λ] = 0.62 A^{-1}, 2364 independent and 1960 observed reflections [$I \geq 2\sigma(I)$], 268 refined parameters, R = 0.025, wR^2 = 0.061, Flack parameter 0.00(6), max. residual electron density 0.27 (−0.34) e A^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Bis(η⁵:κ-N-{1-[(trimethylsilyl)amido]ethenyl}cyclopentadienyl)zirconium (**10b**): 362 mg (2.62 mmol) of the fulvene **7** was doubly deprotonated by treatment with 566 mg (5.28 mmol) of LDA in 50 ml of THF. This solution was then added dropwise at −20°C to a solution of 489 mg (1.30 mmol) of $ZrCl_4$ · 2 THF in 40 ml of THF. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent was then removed in vacuo and the product extracted from the residue with 100 ml of pentane to yield 446 mg (77%) of **10b**, mp 117°C (DSC, decomp.). – $C_{20}H_{30}N_2Si_2Zr$ (445.9): calcd. C 53.88, H 6.78, N 6.28, found C 53.42, H 7.35, N 6.18. – ^1H NMR ([D_2]dichloromethane): δ = 6.36 (m, 4 H), 6.20, 5.80 (m, each 2 H, Cp), 3.95, 3.90 (AB, each 2 H, =CH_2), 0.16 [s, 18 H, Si(CH_3)$_3$]. – ^{13}C NMR ([D_2]dichloromethane): δ = 150.1 (*C*=CH_2), 118.2 (*ipso*-C, Cp), 116.3, 114.7, 122.9, 109.6 (Cp), 87.6 (=*C*H_2), 1.6 ($SiMe_3$). – IR (KBr): ν = 1591 cm^{-1}.

Synthesis of Bis(diethylamido){η⁵:κ-O-[1-(pivaloylamido)ethenyl]cyclopentadienyl}zirconium (**11**): A suspension of the dilithium reagent **8a**, generated by treatment of the fulvene **5c** (339 mg, 1.78 mmol) with 381 mg (3.56 mmol) of LDA in 50 ml of THF, was combined with a suspension of 794 mg (1.77 mmol) of $(Et_2N)_2ZrCl_2$ · 2 THF in 50 ml of THF at 0°C. After stirring for 2 h at room temperature, the solvent was removed in vacuo and the product isolated from the residue by extraction with 50 ml of pentane. Yield of **11**: 528 mg (70%) as a red viscous oil. – $C_{20}H_{35}N_3OZr$ (424.7): calcd. C 56.56, H 8.31, N 9.89, found C 55.66, H 8.54, N 9.71. – ^1H NMR ([D_6]benzene): δ = 5.97, 5.90 (m, each 2 H, Cp), 5.25, 5.00 (d, ^2J = 1.6 Hz, each 1 H, C=CH_2), 3.12 (q, ^3J = 7.4 Hz, 8 H, NCH_2), 1.38 [s, 9 H, C(CH_3)$_3$], 0.88 (t, ^3J = 7.4 Hz, 12 H, NCH_2CH_3). – ^{13}C NMR ([D_8]THF): δ = 171.4 (N*C*O), 147.6 (*C*=CH_2), 125.3 (*ipso*-C, Cp), 111.3, 110.5 (Cp), 102.4 (C=*C*H_2), 44.3 (N*C*H_2), 38.8, 28.6 (CMe_3), 15.6 (NCH_2*C*H_3). – IR (NaCl): ν = 1590 cm^{-1}.

Synthesis of Bis(diethylamido)(η⁵:κ-N-{1-[(trimethylsilyl)amido]ethenyl}cyclopentadienyl)zirconium (**12**): Analogously as described above, the fulvene **7** (100 mg, 55.9 mmol) was doubly deprotonated by treatment with 120 mg (112 mmol) of LDA in 50 ml of THF. The resulting solution of **8b** was then allowed to react with a solution of 253 mg (561 μmol) of $(Et_2N)_2ZrCl_2$ · 2 THF in 50 ml of THF. After workup of the mixture as described above and extraction with pentane, complex **12** was obtained as a dark colored viscous oil, yield 176 mg (76%). – $C_{18}H_{35}N_3SiZr$ (412.8): calcd. C 52.37, H 8.55, N 10.18; found C 52.39, H 7.98, N 9.85. – ^1H NMR ([D_6]benzene): δ = 6.03, 5.92 (m, each 2 H, Cp), 4.36, 4.34 (AB, each 1 H, =CH_2), 3.13 (q, ^3J = 6.9 Hz, 8 H, NCH_2), 0.90 (t, ^3J = 6.9 Hz, 12 H, NCH_2CH_3), 0.39 [s, 9 H, Si(CH_3)$_3$]. – ^{13}C NMR ([D_6]benzene): δ = 150.9 (*C*=CH_2), 112.2 (*ipso*-C, Cp), 115.4, 111.3 (Cp), 87.9 (=*C*H_2), 43.3 (N*C*H_2), 15.6 (NCH_2*C*H_3), 0.8 [Si(CH_3)$_3$]. – IR (NaCl): ν = 1626 cm^{-1}.

Ethene Polymerization Reactions: For the high-pressure polymerization reactions [p(ethene) ≈ 40 bar] a steel autoclave was used that was equipped with a connected steel dropping funnel that could be kept under the same pressure. This 100-ml autoclave was charged through the dropping funnel under argon with 20 ml of a 10% methylalumoxane solution in toluene. The dropping funnel was rinsed with 20 ml of toluene which was added to the contents of the autoclave. Ethene pressure (ca. 40 bar) was applied to the reaction vessel, and the system was allowed to equilibrate for 0.5 h with stirring. 10 ml of a toluene solution of the organometallic catalyst precursor (**12** or **1c**, respectively) was added under pressure. The temperature of the reaction mixture raised rapidly, in a specific case (see Table 2, entry 2) to 141°C. After a typical reaction time of e.g. 20 min the monomer feed was stopped which resulted in a rapid termination of the polymerization reaction. The autoclave was vented and its contents hydrolyzed by treatment with 20 ml of a 1:1 volume mixture of methanol and 2 N aqueous hydrochloric acid. The polymer was collected by filtration, extracted with toluene and then washed 3 × consecutively with half conc. HCl, H_2O, and then with acetone. The resulting polyethylene samples were then dried for 24 h at 70°C. Details of the respective polymerization experiments carried out according to this general procedure are compiled in Table 2. In a number of experiments (Table 2, entries 4, 5, and 7) the starting materials **12** and **1c** were pretreated with trimethylaluminum in toluene before they were given into the reactor.

Table 2. Details of the ethene polymerization reactions employing the C_1-(**12**-) and Si_1-(**1c**-)bridged constrained-geometry Ziegler catalyst systems

Entry	Precursor (mg/μmol)	ml MAO[a]	Al/Zr	p[b]	t[c]	T[d]	PE[e]	mp [°C]	act[f]
1	**12** (19.4/47.0)	10	340	37	10	87	16.6	129	57.7
2	**12** (11.0/26.7)	20	1200	42	25	141	15.2	145	32.5
3	**12** (9.8/23.8)	20	1340	42	20	78	10.1	137	30.3
4	**12** (5.9/14.3)	20[g]	2590	40	25	53	3.8	132	15.9
5	**12** (5.6/13.6)	20[g]	2730	40	25	70	7.0	138	30.9
6	**1c** (8.6/20.9)	20	1530	40	20	103	14.4	135	51.7
7	**1c** (7.1/17.2)	20[g]	2150	40	20	81	11.5	137	50.1

[a] Ca. 1.6 M methylalumoxane solution in toluene. – [b] Ethene pressure [bar]. – [c] Reaction time [min]. – [d] Final temperature [°C] reached under the employed non-isothermal conditions. – [e] Polyethylene isolated [g]. – [f] Catalyst activity in g polymer/mmol [Zr]·bar·h. – [g] 5 ml of ca. 1 M $AlMe_3$ solution in toluene added for in situ methylation.

Ethene Polymerization at Low Pressure: A thermostated Büchi glass autoclave (25°C) was charged with 200 ml of toluene and 20 ml of a 10% MAO solution in toluene. Ethene was introduced at a pressure of 2.2 bar. After 0.5 h, a solution of 18.9 mg of **12** in 10 ml of toluene was added and the polymerization reaction allowed to proceed for 1.5 h. The system was then vented and its contents quenched by treatment with aqueous HCl/CH_3OH. Workup analogously as described above gave 3.6 g polyethylene [mp 137°C, DSC (after premelting)].

☆ Dedicated to Professor *Carl Krüger* on the occasion of his 65th birthday.

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