A Fulvene Route to Group 4 Metallocene Complexes Bearing 4,7-Bis(dimethylamino)-Substituted Indenyl Ligands

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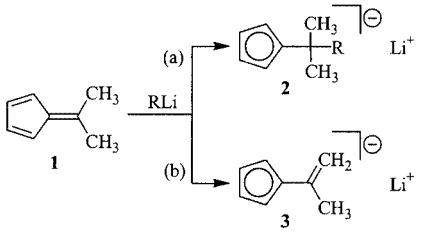
N,*N*,*N*′,*N*′-Tetramethylsuccinamide (**15**) was selectively converted into the functionalized aminofulvene **16**. Subsequent treatment with reagent **17**, $[ZrCl_2(NMe_2)_2(L)_2]$ (L = THF or 0.5 DME), resulted in the formation of the cyclization product 4,7-bis(dimethylamino)indene (**21**). Deprotonation with *n*-butyllithium, followed by the reaction of the resulting substituted indenyllithium reagent **22** with $ZrCl_4$, gave the metallocene [4,7-bis(dimethylamino)indenyl]$_2ZrCl_2$ (**23**). The reaction of **22** with $ZrCl_3Cp$ furnished the complex [4,7-bis(dimethylamino)indenyl]$CpZrCl_2$ (**24**). Fulvene **16**, as well as the metallocene dichlorides **23** and **24**, were characterized by X-ray diffraction.

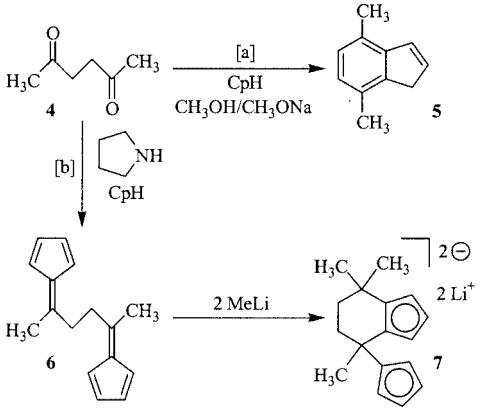
Introduction

Fulvenes are often used as precursors for the preparation of cyclopentadienyl ligands and related systems. Most of these syntheses make use of the electrophilicity of the fulvene C6 carbon center, which allows the formation of substituted cyclopentadienides by means of nucleophilic addition (a) or deprotonation (b) (see Scheme 1).[1−3]



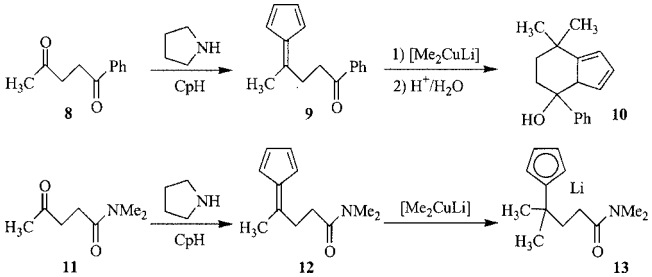
Scheme 1

We have already synthesized substituted indenyl ligands by a series of related reactions. The reaction of 2,5-hexanedione (**4**) with cyclopentadienide under "Thiele conditions"[4] (pathway [a] in Scheme 2) gave the ring-closed 4,7-dimethylindene product **5**,[5] whereas the related reaction under "Stone/Little conditions" ([b] in Scheme 2)[6] furnished the respective bis(fulvene) **6**, which was subsequently used as a starting material for the preparation of the ligand system **7** and of *ansa*-metallocenes derived thereof.[7]



Scheme 2

The unsymmetrical 1,4-diketone **8** allowed the selective preparation of the mono(fulvene) **9** (see Scheme 3). Its treatment with a cuprate nucleophile yielded the substituted tetrahydroindenyl ligand precursor **10**.[8] Similarly, the mono(fulvene) **12** was derived from **11**. In this case the subsequent nucleophilic attack did not result in a related ring-



Scheme 3

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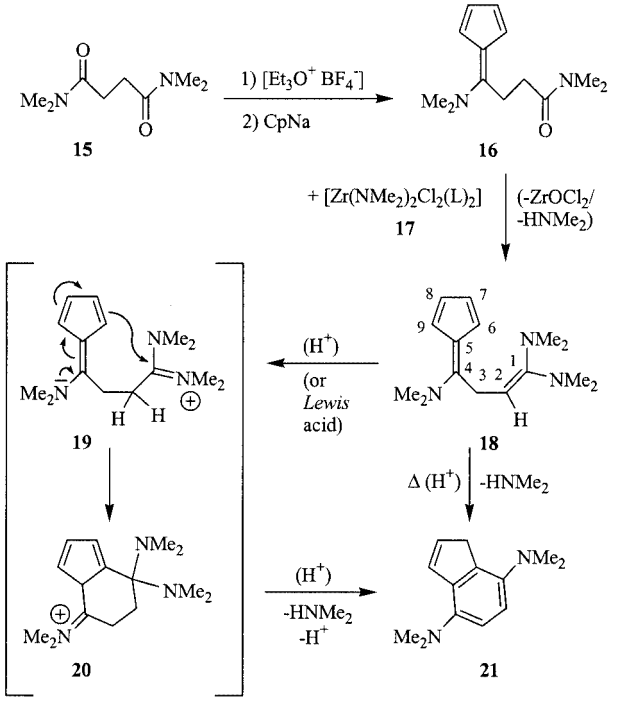
closure reaction but led to the clean formation of the functionalized Cp derivative **13** instead, which was used in the metallocene synthesis.[9]

We now used succinamide **15** as the starting material for a series of related reactions, based on the initial formation of a substituted 6-(dimethylamino)fulvene. In this case we observed a clean ring-closure reaction to yield the corresponding 4,7-bis(dimethylamino)indene product **21** upon treatment with a mild Lewis acid (see Scheme 4). Details of this reaction series, which complements the family of fulvene-to-indene conversions summarized above, are described in this account.



Scheme 4

Results and Discussion

Our synthetic scheme started from succinyl dichloride (**14**), which was treated with dimethylamine to yield the corresponding diamide **15**. The bifunctional carboxylic acid derivative **15** was then selectively converted into its mono(fulvene) derivative **16**. For this purpose, we applied a method that was developed by Hafner et al. for the synthesis of amino-substituted pentafulvenes.[10] The succinamide **15** was mono-*O*-alkylated by treatment with Meerwein's reagent, $[Et_3O^+][BF_4^-]$, and the resulting, stabilized carbenium ion reacted with sodium cyclopentadienide to selectively yield the aminopentafulvene **16**, which bears a residual $-CONMe_2$ functional group (92 % isolated). The fulvene system **16** was characterized by X-ray diffraction (see Figure 1). It shows the typical features of an aminopentafulvene moiety with alternating double and single bonds (see Figure 1) and a trigonal-planar carbon center, C6. The C6−N1 bond length amounts to 1.337(2) Å, which is slightly shorter than the C9−N2 distance [1.349(2) Å] of the delocalized pendent $-CONMe_2$ functional group [C9−O 1.222(2) Å]. In the crystal, compound **16** attains a conformation that is characterized by the antiperiplanar central section of the substituent chain [dihedral angle θ(C6−C7−C8−C9) = −173.1(2)°] with a gauche arrangement at the junction with the fulvene nucleus [θ(C1−C6−C7−C8) = 89.8(2)°].

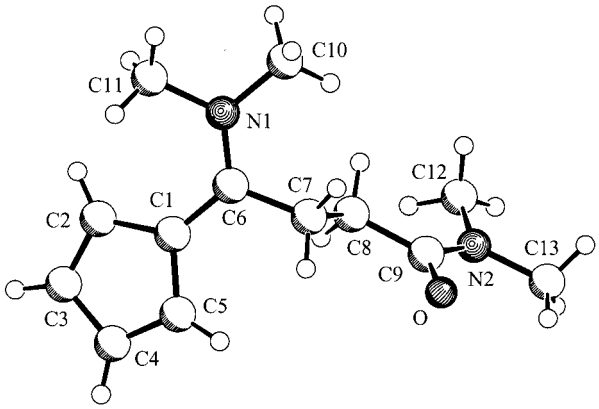


Figure 1. View of the carboxamide-functionalized aminopentafulvene system **16**; selected bond lengths [Å] and angles [°]: C1−C2 1.450(2), C2−C3 1.355(3), C3−C4 1.421(3), C4−C5 1.357(3), C5−C1 1.438(3), C1−C6 1.399(2), C6−N1 1.337(2), C6−C7 1.511(2), C7−C8 1.527(2), C8−C9 1.515(2), C9−O 1.222(2), C9−N2 1.349(2); C2−C1−C5 105.1(2), C2−C1−C6 130.1(2), C5−C1−C6 124.7(2), C1−C6−N1 124.9(2), C1−C6−N7 118.3(2), N1−C6−C7 116.8(2), C6−C7−C8 112.1(1), C7−C8−C9 111.5(1), C8−C9−O 120.9(1), C8−C9−N2 117.0(2), O−C9−N2 122.1(2)

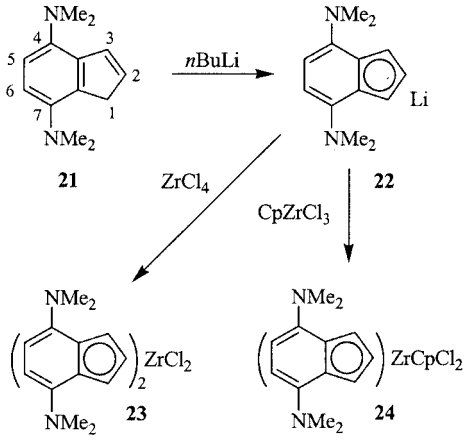
Fulvene **16** was treated with 1 mol-equiv. of $[ZrCl_2(NMe_2)_2{\cdot}DME]$[11] (**17a**) in toluene at reflux temperatures for 3 h. Workup and extraction with pentane furnished the metal-free organic product 4,7-bis(dimethylamino)indene (**21**) as a pale yellow liquid in close to 90 % yield. The product is characterized by a pair of ^1H NMR $(NCH_3)_2$ singlets (δ = 2.60 and 2.65 ppm), each representing six hydrogen atoms. We monitored a set of four indene methine-proton resonances (δ = 6.31, 6.77, 6.83, and 7.21 ppm) and the indene CH_2 ^1H NMR signal at δ = 3.31 (2 H) ppm.

Weingarten et al. have shown that ketene aminals are formed upon treatment of suitably substituted carboxamide starting materials with, for example, $Zr(NMe_2)_4$.[12] It seems that the here observed reaction sequence of the transformation **16** → **21** is initiated by a similar conversion of the *N*,*N*-dimethylcarboxamide functional group. We observed that treatment of **16** with a stoichiometric quantity of the reagent $[ZrCl_2(NMe_2)_2{\cdot}2THF]$[11b] (**17b**) in toluene at room temperature gives the corresponding ketene aminal system **18**. The intermediate **18** was not isolated in a pure form, but was obtained, after washing with pentane, as a solid that was probably still admixed with the zirconium-containing reaction product (perhaps $ZrOCl_2$ or a derivative thereof). Subsequent heating of this mixture in toluene eventually gave rise to the formation of **21**.

The intermediate **18** was characterized spectroscopically. Its ^{1}H NMR spectrum shows four clearly separated fulvene methine-hydrogen resonances at δ = 7.09, 6.97, 6.86 and 6.79 ppm (in [D_6]benzene) in addition to the typical ketene aminal ^{1}H NMR resonance at δ = 3.62 (t, ^3J = 6 Hz, 1 H) ppm. The adjacent CH_2 group gives rise to a ^{1}H NMR doublet (^3J = 6 Hz) at δ = 3.38 ppm. Compound **18** gives rise of three different NMe_2 ^{1}H NMR singlets at δ = 2.68 (6 H, "fulvene"-NMe_2) and δ = 2.48/2.12 [each 6 H, (*Z*)- and (*E*)-ketene aminal-NMe_2] ppm. The fulvene carbon center (C4−NMe_2) gives rise to a ^{13}C NMR feature at δ = 161.2 ppm, whereas the carbon atoms of the −CH=$C(NMe_2)_2$ ketene aminal show ^{13}C NMR resonances at δ = 156.2 (C1) and 88.4 (C2, $^1J_{C,H}$ = 157 Hz) ppm; the C3 resonance was found at δ = 32.6 ppm with $^1J_{C,H}$ = 133 Hz.

We assume that the observed ring-closure reaction that eventually yields the indene derivative **21** is initiated by activation of the ketene aminal intermediate **18** by protonation or addition of a zirconium-based Lewis-acid catalyst at the C2 carbon atom (see Scheme 4). Intramolecular nucleophilic addition of the Me_2N-activated cyclopentadienide ring at the strongly electrophilic incipient amidinium moiety would then give the product framework. Removal of the H^+ (or $ZrOCl_2$ Lewis acid) catalyst with concomitant dimethylamine elimination and tautomerization would directly lead to the observed product **21**.

Treatment of **21** with *n*-butyllithium results in deprotonation and formation of the substituted indenyllithium reagent **22**, which exhibits the expected ^{1}H NMR features of a C_{2v}-symmetry averaged structure in [D_6]benzene/[D_8]THF (10:1) solution at ambient temperature [δ = 6.80 (t, 1 H, 2-H), 6.42 (d, 2 H, 1-H and 3-H), 6.32 (s, 2 H, 5-H and 6-H), 2.94 (s, 12 H, NMe_2) ppm; see Scheme 5].



Scheme 5

Reagent **22** was used for the preparation of two zirconocene complexes. Treatment of $ZrCl_4$ with **22** in a toluene suspension gave bis[4,7-bis(dimethylamino)indenyl]$ZrCl_2$ (**23**). Similarly, the reaction of reagent **22** with $CpZrCl_3$[13] gave the mixed indenyl/Cp-zirconium complex **24** (isolated in ca. 70 % yield).

Both **23** and **24** were characterized by X-ray crystal structure analyses. Complex **23** is C_2-symmetric in the crystal. The symmetry-equivalent indenyl ligands are η^5-bound to the zirconium atom through their five-membered rings, although in a rather unsymmetrical way: the bonds between the zirconium atom and the "external" CH centers are short [Zr−C1 2.467(3), Zr−C2 2.484(3), Zr−C3 2.540(3) Å], whereas the Zr−C linkages to the internal indenyl carbon atoms are markedly longer [see Figure 2; Zr−C4 2.639(3), Zr−C9 2.579(3) Å]. The Zr−Cl bond length in complex **23** amounts to 2.417(1) Å.

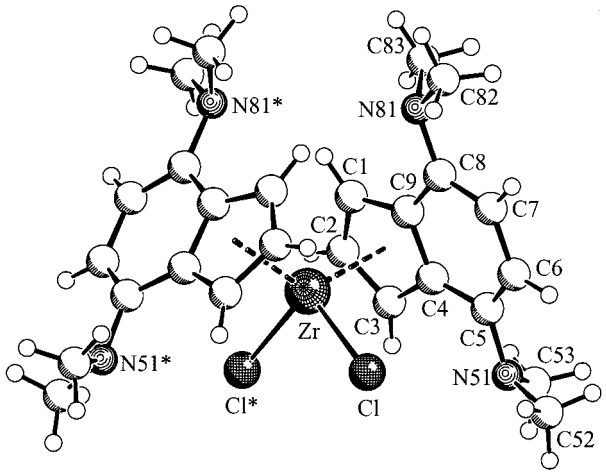


Figure 2. View of the molecular structure of complex **23** (with unsystematic atom-numbering scheme); selected bond lengths [Å] and angles [°]: Zr−Cl 2.417(1), Zr−C1 2.467(3), Zr−C2 2.484(3), Zr−C3 2.540(3), Zr−C4 2.639(3), Zr−C9 2.579(3), C1−C2 1.393(5), C1−C9 1.439(4), C2−C3 1.398(5), C3−C4 1.427(5), C4−C9 1.444(4), C8−C9 1.436(4), C4−C5 1.422(4), C8−N81 1.422(4), C5−N51 1.417(4); Cl−Zr−Cl* 98.80(5), C1−C2−C3 109.9(3), C2−C1−C9 107.6(3), C2−C3−C4 108.3(3), C1−C9−C8 132.9(3), C3−C4−C5 132.0(3), C9−C8−N81 119.0(3), C4−C5−N51 118.0(3)

In the crystal, complex **23** features a chiral metallocene conformation, in which the indenyl six-membered rings point to different lateral sides of the bent metallocene wedge. This leads to a spatial differentiation of the $-NMe_2$ substituents at each of the indenyl ligands: the Me_2N51 group points toward the open-front side and the Me_2N81 substituent is oriented toward the narrow back side of the bent metallocene wedge (see Figure 2). In solution this differentiation is not observed: here rapid rotation about the zirconium−Cp(centroid) vector leads to symmetry-averaged NMR spectra (for details see the Exp. Sect.).

Complex **24** shows an η^5-Cp ligand that is rather uniformly coordinated to the zirconium atom [with Zr−C(Cp) bond lengths ranging from 2.483(2) to 2.537(2) Å]. The bonding features of the substituted indenyl ligand are very similar to those found in the related complex **23** (see above and Figure 3). The single η^5-bis(4,7-dimethylamino)indenyl ligand in complex **24** has a similar conformational orientation to that of the ligands in **23**. In **24** the indenyl ligand has its substituted phenylene moiety oriented towards the lateral side of the bent metallocene wedge.

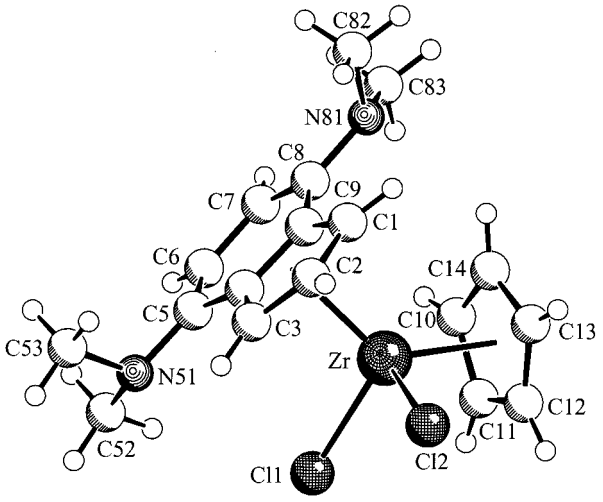


Figure 3. Molecular structure of complex **24**; selected bond lengths [Å] and angles [°]: Zr−Cl1 2.440(1), Zr−Cl2 2.441(1), Zr−C1 2.477(2), Zr−C2 2.508(2), Zr−C3 2.527(2), Zr−C4 2.601(2), Zr−C9 2.577(2), Zr−C10 2.494(2), Zr−C11 2.537(2), Zr−C12 2.514(2), Zr−C13 2.483(2), Zr−C14 2.492(2), C1−C2 1.404(3), C1−C9 1.440(3), C2−C3 1.403(3), C3−C4 1.439(3), C4−C9 1.438(3), C8−C9 1.433(3), C4−C5 1.427(3), C8−N81 1.411(3), C5−N51 1.421(3); Cl1−Zr−Cl2 96.98(2), C1−C2−C3 109.9(2), C2−C1−C9 107.5(2), C2−C3−C4 107.6(2), C1−C9−C8 132.4(2), C3−C4−C5 131.5(2), C9−C8−N81 118.7(2), C4−C5−N51 118.1(2)

Conclusion

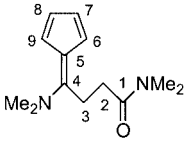
We conclude that treatment of the functionalized fulvene system **16** with the zirconium reagent **17** provides a very convenient and selective synthetic pathway to 4,7-bis(dialkylamino)indene systems. We have also shown that these can be easily attached at electrophilic transition-metal centers to yield the respective metallocene systems. The specific influence of the nucleophilic $-NR_2$ substituents on the properties of such organometallic compounds will be investigated in the future.

Experimental Section

General Remarks: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. For additional general conditions, including a list of instruments used for physical characterization of the compounds, see reference.[9]

Preparation of $C_2H_4(CONMe_2)$ (15): Succinyl dichloride (14.7 g, 94 mmol) was added dropwise to a solution of NMe_2H (24 g, 520 mmol) in diethyl ether at −78 °C. The mixture was allowed to warm to room temperature, stirred for 15 min, and filtered to separate the ammonium salt. The residue was extracted with THF (2 × 200 mL) and the solvent was removed under vacuum. The resulted solid was recrystallized from diethyl ether (5 mL) and cooled to −35 °C to give **15** as a light white crystalline solid. Suitable crystals for X-ray crystal-structure analysis[14] were obtained from a concentrated solution in diethyl ether (14.8 g, 91 %). ^{1}H NMR ($CDCl_3$): δ = 3.03 (s, 6 H, NMe), 2.92 (s, 6 H, NMe), 2.64 (s, 4 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.1 (CO), 36.9 (NMe), 35.3 (NMe), 28.1 (CH_2). $C_8H_{16}N_2O_2$ (172.22): calcd. C 55.79, H 9.36, N 16.27; found C 55.65, H 9.38, N 15.84.

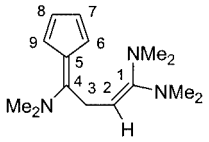
Preparation of Fulvene 16: A CH_2Cl_2 solution of $[Et_3O^+][BF_4^-]$ (14.71 g, 77.4 mmol) was added to a CH_2Cl_2 solution of **15** (13.31 g, 77.4 mmol) at −30 °C. The orange solution was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under vacuum, leading to an oily product. The brown oil was frozen with liquid nitrogen, a solution of NaCp (6.81 g, 77.4 mmol) in THF, cooled to −40 °C, was immediately added and the solution was stirred overnight. The THF was evaporated to dryness and the residue extracted and recrystallized with diethyl ether to yield **16**, as a crystalline solid. Suitable crystals for X-ray crystal-structure analysis were obtained from a concentrated solution in diethyl ether (15.7 g, 92 %). ^{1}H NMR ($CDCl_3$): δ = 6.60, 6.56, 6.43, 6.31 (each broad, each 1 H, fulvene), 3.35 (s, 6 H, 4-NMe), 3.18 (m, 2 H, CH_2), 2.96, 2.95 (each s, each 3 H, 1-NMe), 2.63 (m, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 170.8 (C1), 161.3 (C4), 122.3, 119.9, 119.7, 117.0 (fulvene), 117.1 (C5), 43.7 (4-NMe), 37.0, 35.5 (1-NMe), 33.8 (C2), 28.6 (C3) ppm. $C_{13}H_{20}N_2O$ (220.31): calcd. C 70.87, H 9.15, N 12.72; found C 70.56, H 9.27, N 12.49.



X-ray Crystal-Structure Analysis of 16: Empirical formula $C_{13}H_{20}N_2O$, M = 220.31, yellow-orange crystal 0.20 × 0.15 × 0.10 mm, a = 10.390(1), b = 13.607(1), c = 8.946(1) Å, β = 90.54(1)°, V = 1264.7(2) Å^3, $D_{calcd.}$ = 1.157 g cm^{-3}, μ = 5.79 cm^{-1}, no absorption correction ($0.893 \le T \le 0.944$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 2731 reflections collected ($\pm h$, $-k$, $-l$), [(sinθ)/λ] = 0.62 Å^{-1}, 2562 independent ($R_{int.}$ = 0.035) and 1763 observed reflections [$I \ge 2\sigma(I)$], 150 refined parameters, R = 0.047, wR^2 = 0.133, max. residual electron density 0.18 (−0.16) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Formation of the Ketene Aminal Intermediate 18: Toluene (100 mL) was added to a Schlenk flask containing **16** (0.28 g, 1.3 mmol) and $[Zr(NMe_2)_2Cl_2{\cdot}THF_2]$ (**17b**) (0.51 g, 1.3 mmol). The resulting solution was stirred at room temperature for 1 h, concentrated to dryness and washed with pentane to give **18** as a light brown solid (0.59 g). ^{1}H NMR (C_6D_6): δ = 7.09 (m, 1 H, 6-H), 6.97 (m, 1 H, 8-H), 6.86 (m, 1 H, 7-H), 6.79 (m, 1 H, 9-H), 3.62 (t, $J_{H,H}$ = 6.3 Hz, 1 H, 2-H), 3.39 (d, $J_{H,H}$ = 6.3 Hz, 2 H, 3-H), 2.68 (s, 6 H, 4-NMe), 2.48 [s, 3 H, 1-$NMe_{(Z)}$], 2.12 [s, 6 H, 1-$NMe_{(E)}$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 161.2 (C4), 156.2 (C1), 123.3 (C8), 121.4 (C6), 120.3 (C7), 119.0 (C5), 118.1 (C9), 88.4 (C2, $^1J_{C,H}$ = 157 Hz), 42.8 (NMe-4), 40.6 [$NMe_{(Z)}$], 40.6 [$NMe_{(E)}$], 32.6 (C3) ppm. ^{1}H-^{13}C GHSQC (C_6D_6): δ(^{13}C)/δ(^{1}H) = 123.3/6.97 (8-CH), 121.4/7.09 (6-CH), 120.3/6.86 (7-CH), 118.1/6.79 (9-CH), 88.4/3.62 (2-CH), 42.8/2.68 (4-NMe), 40.6/2.48 [1-$NMe_{(Z)}$], 40.6/2.12 [1-$NMe_{(E)}$], 32.6/3.39 (3-CH_2). ^{1}H-^{13}C GHMBC (C_6D_6): δ(^{13}C)/δ(^{1}H) = 161.2/3.39, 2.68 (C4/3-H, 4-NMe), 156.2/3.39, 2.48, 2.12 [C1/3-H, 1-$NMe_{(Z)}$, 1-$NMe_{(E)}$], 119.0/3.39 (C5/3-H). ^{1}D TOCSY (C_6D_6): δ($^1H_{irr}$)/δ($^1H_{res}$) = 7.09/6.97, 6.86, 6.79 (6-H/8-H, 7-H, 9-H), 3.62/3.39 (2-

H/3-H). NOE (C_6D_6): δ($^1H_{irr}$)/δ($^1H_{res}$) = 2.12/2.48, 3.62 [1-NMe$_{(E)}$/1-NMe$_{(Z)}$, 2-H]; 2.48/2.12, 3.39 [1-NMe$_{(Z)}$/1-NMe$_{(E)}$, 3-H]; 2.68/3.39, 3.62, 6.79 (4-NMe/3-H, 2-H, 9-H); 3.39/2.48, 2.68, 3.62, 7.09 [3-H/1-NMe$_{(Z)}$, 4-NMe, 2-H, 6-H]; 3.62/2.12, 3.39 [2-H/1-NMe$_{(E)}$, 3-H].



Preparation of the Substituted Indene 21: Toluene (100 mL) was added to a Schlenk flask containing **16** (1.06 g, 4.6 mmol) and [Zr(NMe$_2$)$_2$Cl$_2$·DME] (**17a**) (2.10 g, 4.6 mmol) and the mixture vigorously stirred at room temperature for 3 h. The resulting red solution was filtered, the solvent removed under vacuum and the residue extracted with pentane to yield **19** as a yellow liquid (0.82 g, 88 %). ^1H NMR (C_6D_6): δ = 7.21, 6.31 (each dt, $J_{H,H}$ = 5.6, 1.9 Hz,·each 1 H, 2,3-H), 6.83, 6.77 (AB $J_{H,H}$ = 8.7 Hz,·each 1 H, 5,6-H), 3.31 (t, $J_{H,H}$ = 1.9 Hz, 2 H, CH$_2$), 2.65, 2.60 (each s, each 6 H, NMe) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 145.1, 143.1 (C4,7), 139.5, 137.1 (C3a,7a), 132.3, 130.9 (C2,3), 116.0, 114.9 (C5,6), 44.6, 43.6 (NMe$_2$), 39.3 (CH$_2$) ppm. $C_{13}H_{18}N_2$ (202.29): calcd. C 77.18, H 8.97, N 13.85; found C 76.73, H 9.20, N 13.86.

Preparation of the Indenyllithium Reagent 22: BuLi (1.6 M) was added to a solution of **19** (0.56 g, 2.77 mmol) in pentane (150 mL), cooled to −78 °C. The white suspension formed was warmed slowly to room temperature and stirred for 12 h. Filtration and removal of the solvent at reduced pressure gave **22** as a white solid (0.55 g, 95 %). ^1H NMR (C_6D_6, TDF): δ = 6.80 (t, $J_{H,H}$ = 3.4 Hz, 1 H, 2-H), 6.42 (d, $J_{H,H}$ = 3.4 Hz, 2 H, 1,3-H), 6.32 (s, 2 H, 5,6-H), 2.94 (s, 12 H, NMe) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, TDF): δ = 142.1 (C4,7), 122.9 (C3a,7a), 112.7 (C2), 101.8 (C5,6), 92.2 (C1,3), 44.0 (NMe) ppm.

Preparation of the Zirconium Complex 23: $ZrCl_4$ (0.156 g, 0.67 mmol) was added to a suspension of **22** (0.28 g, 1.34 mmol) in toluene (100 mL) at −40 °C. The cooling bath was removed and the reaction mixture stirred at room temperature for 12 h. After filtration, the solvent was removed under vacuum and the residue washed with pentane (2 × 50 mL) to give **23** as a red crystalline solid (0.21 g, 57 %). ^1H NMR (CD_2Cl_2): δ = 6.77 (d, $J_{H,H}$ = 3.0 Hz, 2 H, 1,3-H), 6.50 (s, 2 H, 5,6-H), 6.08 (t, $J_{H,H}$ = 3.0 Hz, 1 H, 2-H), 2.90 (s,·12 H, NMe) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 143.2 (C4,7), 123.4 (C3a,7a), 118.8 (C2), 111.9 (C5,6), 104.3 (C1,3), 43.3 (NMe) ppm. $C_{26}H_{34}Cl_2N_4Zr$ (564.70): calcd. C 55.30, H 6.07, N 9.92; found C 55.15, H 6.14, N 9.72.

X-ray Crystal-Structure Analysis of 23: Empirical formula $C_{26}H_{34}Cl_2N_4Zr$, M = 564.69, red crystal 0.15 × 0.05 × 0.03 mm, a = 41.733(1), b = 7.036(1), c = 17.528(1) Å, V = 5146.8(8) Å^3, $D_{calcd.}$ = 1.458 g cm^{-3}, μ = 6.57 cm^{-1}, empirical absorption correction with SORTAV (0.908 ≤ T ≤ 0.981), Z = 8, orthorhombic, space group $Fdd2$ (No. 43), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9228 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3023 independent (R_{int} = 0.053) and 2492 observed reflections [$I \geq 2\sigma(I)$], 154 refined parameters, R = 0.038, wR^2 = 0.068, max. residual electron density 0.36 (−0.59) e·Å^{-3}, Flack −0.04(5), hydrogen atoms calculated and refined as riding atoms.

Preparation of the Zirconium Complex 24: $CpZrCl_3$ was added to a suspension of **22** in toluene (100 mL) at −40 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 12 h. After filtration, the solvent was removed under vacuum and the residue was washed with pentane (2 × 50 mL) to give **24** as a red crystalline solid (0.61 g, 71 %). ^1H NMR (CD_2Cl_2): δ = 6.73 (t, $J_{H,H}$ = 3.2 Hz, 1 H, 2-H), 6.71 (d, $J_{H,H}$ = 3.2 Hz, 2 H, 1,3-H), 6.52 (s, 2 H, 5,6-H), 6.24 (s, 5 H, Cp), 2.92 (s, 6 H, NMe) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 145.0 (C4,7), 123.9 (C3a,7a), 123.5 (C2), 118.7 (Cp), 113.3 (C5,6), 105.2 (C1,3), 44.8 (NMe) ppm. $C_{18}H_{22}Cl_2N_2Zr$ (428.50): calcd. C 50.45, H 5.17, N 6.54; found C 50.67, H 5.37, N 6.48.

X-ray Crystal-Structure Analysis of 24: Formula $C_{18}H_{22}Cl_2N_2Zr$, M = 428.50, red crystal 0.15 × 0.15 × 0.05 mm, a = 7.919(1), b = 13.135(1), c = 17.552(1) Å, V = 1825.7(3) Å^3, $D_{calcd.}$ = 1.559 g cm^{-3}, μ = 8.95 cm^{-1}, empirical absorption correction with SORTAV (0.877 ≤ T ≤ 0.957), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 198 K, ω and φ scans, 12933 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.65 Å^{-1}, 4158 independent (R_{int} = 0.034) and 3879 observed reflections [$I \geq 2\sigma(I)$], 213 refined parameters, R = 0.024, wR^2 = 0.052, max. residual electron density 0.24 (−0.57) e·Å^{-3}, refined as a racemic twin with a ratio of 0.67(3):0.33, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystallographic Study: Data sets were collected with Enraf−Nonius CAD4 and Nonius KappaCCD diffractometers; the latter was equipped with a rotating anode generator, Nonius FR591. Programs used: data collection EXPRESS (Nonius B. V., **1994**) and COLLECT (Nonius B. V., **1998**), data reduction MolEN (K. Fair, Enraf−Nonius B. V., **1990**) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**). CCDC-220797, -220798 and -220799 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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