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[5] a) X-ray crystal structure analysis of **7a**: $C_{16}H_{17}NCl_2Zr$, $M_r = 385.43$, yellow crystal, $0.50 \times 0.40 \times 0.15$ mm, $a = 10.774(1)$, $b = 10.501(1)$, $c = 13.930(1)$ Å, $\beta = 101.52(1)°$, $V = 1544.3(2)$ Å^3, $\rho_{calcd} = 1.658$ g cm^{-3}, $F(000) = 776$ e, $\mu = 10.47$ cm^{-1}, empirical absorption correction with φ scan data ($0.945 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans; of 3261 reflections collected ($\pm h, -k, -l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 3132 were independent and 2744 observed $[I \geq 2\sigma(I)]$; 183 refined parameters, $R = 0.045$, $wR^2 = 0.165$, max./min. residual electron density $0.76/-0.97$ e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[5c] b) X-ray crystal structure analysis of **9a**: $C_{16}H_{17}NCl_2Hf$, $M_r = 472.70$, yellow crystal, $0.25 \times 0.20 \times 0.20$ mm, $a = 10.756(2)$, $b = 10.458(2)$, $c = 13.909(3)$ Å, $\beta = 101.71(2)°$, $V = 1532.0(5)$ Å^3, $\rho_{calcd} = 2.049$ g cm^{-3}, $F(000) = 904$ e, $\mu = 71.46$ cm^{-1}, empirical absorption correction with φ scan data ($0.737 \leq C \leq 0.998$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans; of 3244 reflections collected ($\pm h, -k, -l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 3116 were independent and 2903 observed $[I \geq 2\sigma(I)]$; 184 refined parameters, $R = 0.028$, $wR^2 = 0.087$, max./min. residual electron density $1.58/-1.95$ e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[5c] c) Data sets were collected with Enraf Nonius CAD4 or MACH3 diffractometers, equipped with sealed tube or rotating anode generators. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-112078 (**7a**) and -112077 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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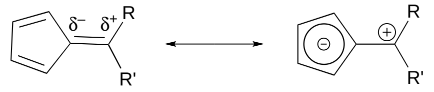
Intramolecular NMe$_2$H Elimination and Fulvene Coupling Leading to Novel Allyl-Bridged Zirconocene and Hafnocene Complexes[**]

Sheng-Di Bai, Xue-Hong Wei, Jian-Ping Guo, Dian-Sheng Liu,[*] and Zhong-Yuan Zhou

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$_2$H 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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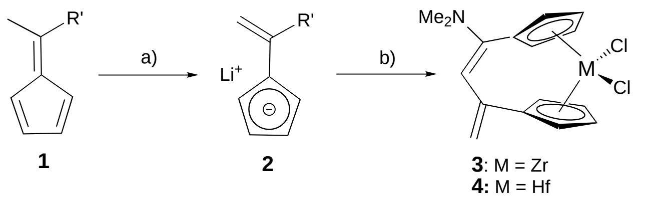
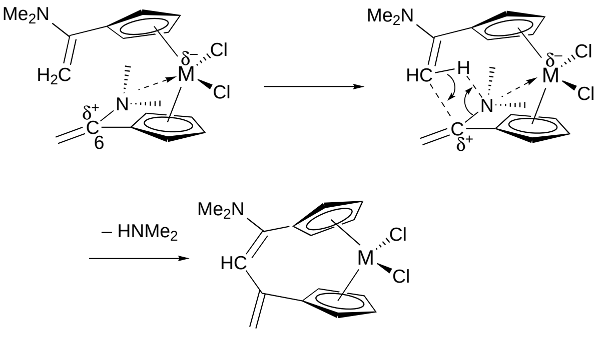


Scheme 2. Synthesis of **2**–**4**. a) $LiCH(SiMe_3)_2$, THF, 2 h, 0–25 °C; b) MCl_4 (M = Zr or Hf), THF or Et_2O, 12 h, −78 °C → room temperature. R' = NMe_2.

organolithium compound, but rather the weak nucleophilic behavior of, for example, $LiN\textit{i}Pr_2$ (LDA),[10] $LiNMe_2$, or, in our case, $LiCH(SiMe_3)_2$. Alkyl- and aryllithium compounds normally cause an addition or reductive coupling reaction. Lithium naphthalenide, a reductive reagent, reacted with aminofulvene **1**, leading to bridged and cyclic bridged bifulvenes.[11] However, $LiCH(SiMe_3)_2$ did not prove to be a strong nucleophilic reagent like alkyllithium, possibly due to its steric effect. It may be used as a relatively stronger bulky base than lithium amides.

Subsequent treatment of **2** with MCl_4 (M = Zr or Hf) in THF or Et_2O at −78 °C proceeded, unexpectedly, by an intramolecular NMe_2H elimination that resulted in the coupling of fulvenyl groups to give complexes **3** and **4** (Scheme 2). When the reaction of **2** with $ZrCl_4$ was carried in a sealed NMR tube, two ^1H resonances were observed at $\delta = 2.26$ and 1.50, consistent with the presence of free NMe_2H. The ^1H NMR data of **3** and **4** are in accord with their X-ray structures (see below).

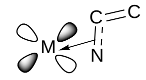
The reaction discussed is a useful synthetic pathway to allyl-bridged ansa-metallocenes, especially those with a conjugated 14π electron system (three sp^2 carbon bridging atoms). We propose the following mechanism for the reaction (Scheme 3): 1) primary formation of a metallocene with a N → M donor bond from the dimethylamino group (which is more or less similar to the formation of a tertiary amine in the Mannich reaction), 2) nucleophilic attack on C6 of one of the fulvenyl ligands to form a transition state, and 3) loss of one molecule of dimethylamine, maybe by a concerted reaction, to give complex **3** or **4**.



Scheme 3. Proposed mechanism for the formation of **3** and **4**.

The N → Zr donor bond was observed for a zirconocene cation derived from aminofulvene **1**.[7] However, the question of importance for the mechanism is whether this donor bond would occur for the 16-electron configuration of the zirconium or hafnium atom. Our experiments have shown that there was no intramolecular NMe_2H elimination and fulvene coupling during the deprotonation of **1** (see the ^1H NMR data of **2**). We believe that in polar solvents, such as THF or Et_2O, formation of an ionized zirconium atom enhances the N → Zr interaction and induces the positive charge on C6, which is probably crucial for the subsequent nucleophilic attack. This thermodynamically favorable coupling reaction may also result from formation of a conjugated 14π electron system including two Cp fragments and the bridging allyl group (for carbon).

According to this mechanism the positive charge on the N atom will influence the intramolecular NMe_2H elimination, which should be related to Lewis acidic and, in our view, d-electron backbonding effects of the central metal. Since the C=C–N moiety in the enamino group could form a three-centered 4π electron system, the C–N bond would preferably act as a p donor to the central metal and cause a backbonding effect (Scheme 4). Thus the early transition metal might easily steer the intramolecular NMe_2H elimination to give the allyl-bridged metallocene.



Scheme 4. Schematic representation of the p donor bonding in **3** and **4**.

The X-ray structure of **3** is shown in Figure 1. The average Cp(centroid)–Zr bond distances are 2.205 and 2.192 Å, and the corresponding Cp(centroid)-Zr-Cp'(centroid) angle is 128.0°, which is smaller than that of the propyl-bridged zirconocene $[\{(\eta^5\text{-Cp})_2C_3H_6\}ZrCl_2]$ (129.5°).[12] The single and double bonds of the bridging allyl group are 1.471(2) and 1.345(2) Å long, respectively, and the N1–C11 bond length of 1.390(2) Å means that the N atom engages in the conjugate system with the allyl and cyclopentadienyl fragments.

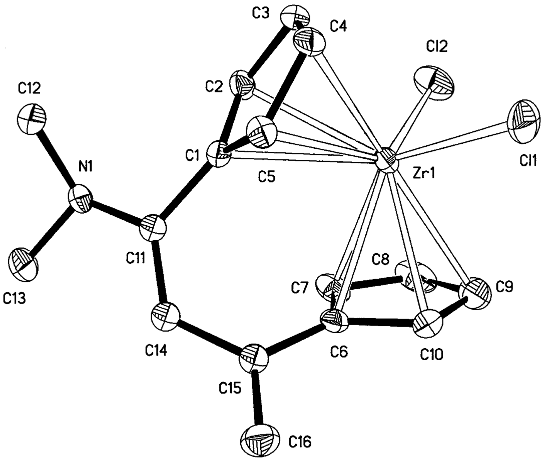


Figure 1. The molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.5266(11), Zr1–C2 2.5020(12), Zr1–C3 2.5068(11), Zr1–C4 2.5135(11), Zr1–C5 2.4903(12), C1–C11 1.495(2), C11–C14 1.345(2), C14–C15 1.471(2), C6–C15 1.470(2), C15–C16 1.336(2), N1–C11 1.390(2), N1–C13 1.460(2); Cl2-Zr1-Cl1 97.33(2), C1-Zr1-C6 73.96(3), C14-C11-C1 122.99(10), C11-C14-C15 125.37(11), C6-C15-C14 118.10(10), C16-C15-C6 119.83(11).

The X-ray structure of **4** (Figure 2) is quite similar to that of **3**. The average Cp(centroid)–Zr bond distances are 2.189

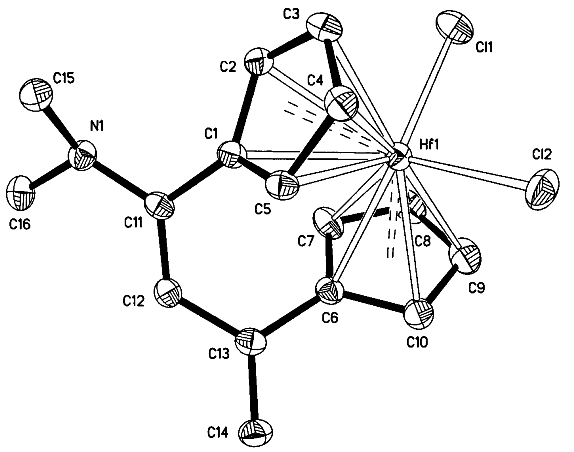


Figure 2. The molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Hf1–C1 2.509(4), Hf1–C2 2.486(4), Hf1–C3 2.495(5), Hf1–C4 2.513(4), Hf1–C5 2.479(4), C1–C11 1.476(6), C11–C12 1.363(6), C12–C13 1.459(6), C6–C13 1.492(6), C13–C14 1.354(6), N1–C11 1.389(6), N1–C16 1.414(7); Cl2-Hf1-Cl1 96.31(5), C1-Hf1-C6 73.77(14), C12-C11-C1 123.0(4), C11-C12-C13 124.6(4), C6-C13-C12 117.9(4), C14-C13-C6 119.4(4).

and 2.163 Å, and the corresponding Cp(centroid)-Zr-Cp′(centroid) angle is 128.4°. The single and double bonds of the bridging allyl group are 1.476(6) and 1.363(6) Å long, respectively, and the N1–C11 bond length is 1.389(6) Å.

Experimental Section

2: In an typical run a solution of $LiCH(SiMe_3)_2$ (7.4 mmol, 1.23 g) in THF (ca. 10 mL) was added dropwise to a solution of **1** (1 g, 7.4 mmol) in THF (ca. 20 mL) at 0 °C with stirring. The mixture was allowed to warm to room temperature for 2 h. The solvent was removed in vacuo to give **2** as a light brown powder (1.02 g, 98 %). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 6.76$, 6.54 (d, 4H; Cp), 4.48, 4.05 (d, 2H; CH$_2$), 2.94 (*s*, 6H; NMe$_2$).

3: $ZrCl_4$ (0.85 g, 3.6 mmol) was added in several portions with stirring to a solution of **2** (1.02 g, 7.2 mmol) in THF (ca. 20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo. The residue was extracted with dichloromethane, and the extract filtered. The solvent was slowly removed from the filtrate in vacuo to give yellow crystalline **3** (1.30 g, 91 %). Elemental analysis calcd for $C_{16}H_{17}Cl_2NZr$ (385.43): C 49.81, H 4.41, N 3.63; found: C 48.71, H 4.28, N 3.41; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.74$, 6.14, 6.08 (m, 8H; Cp), 5.62 (s, 1H; CH), 5.03, 4.93 (d, 2H; CH$_2$), 2.62 (s, 6H; NMe$_2$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 148.7$, 140.2, 138.0, 126.9 (*ipso*-C), 125.0, 124.5, 114.9, 112.0 (CH of Cp), 111.6 (CH$_2$), 105.8 (CH), 42.7 (NMe$_2$).

4: The procedure is similar to that of **3**, except that Et$_2$O was used as the solvent instead of THF. The reaction of $HfCl_4$ (1.20 g, 3.74 mmol) and **2** (1.05 g, 7.44 mmol) resulted in yellow crystalline **4** (1.10 g, 77 %). Elemental analysis calcd for $C_{16}H_{17}Cl_2NHf$ (472.70): C 40.65, H 3.62, N 2.96; found: C 40.64, H 3.39, N 3.00; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.65$, 6.07, 5.99 (m, 8H; Cp), 5.62 (s, 1H; CH), 4.99, 4.95 (d, 2H; CH$_2$), 2.64 (s, 6H; NMe$_2$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 147.3$, 138.8, 134.5, 124.6 (*ipso*-C), 122.1, 121.7, 111.9, 108.9 (CH of Cp), 110.7 (CH$_2$), 104.3 (CH), 41.4 (NMe$_2$).

Crystal data for **3**: $C_{16}H_{17}Cl_2NZr$, $M_r = 385.43$, monoclinic, space group $P2_1/n$, $a = 10.8208(9)$, $b = 10.5382(12)$, $c = 13.9891(10)$ Å, $\beta = 101.380(5)°$, $V = 1563.8(2)$ Å^3, $F(000) = 776$; $Z = 4$, $\rho_{calcd} = 1.637$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 10.33$ cm^{-1}, $T = 294(2)$ K, crystal size $0.38 \times 0.36 \times 0.08$ mm, 3504 unique reflections for $2.18 < \theta < 25.00°$, 2722 reflections with $I > 2\sigma(I)$; $R = 0.0269$, $R' = 0.0380$, $S = 0.917$.

Crystal data for **4**: $C_{16}H_{17}Cl_2NHf$, $M_r = 472.70$, monoclinic, space group $P2_1/n$, $a = 10.830(2)$, $b = 10.516(2)$, $c = 13.965(3)$ Å, $\beta = 101.51(3)°$, $V = 1558.5(2)$ Å^3, $F(000) = 904$; $Z = 4$, $\rho_{calcd} = 2.015$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 10.33$ cm^{-1}, $T = 294(2)$ K, crystal size $0.40 \times 0.38 \times 0.20$ mm, 2827 unique reflections for $2.18 < \theta < 25.55°$, 2813 reflections with $I > 2\sigma(I)$; $R = 0.0446$, $R' = 0.0482$, $S = 0.933$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-114199 (**3**) and CCDC 114200 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Convenient and Versatile Route to Hydroquinolines by Inter- and Intramolecular Aza-Diels–Alder Pathways[**]

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Described herein is a practical method for the generation of *o*-azaxylylenes and their application to the synthesis of a variety of hydroquinoline derivatives. The formation of *o*-azaxylylenes has previously been reported by photochemical fragmentation,[1, 2] fluoride induced elimination of *o*-trime-

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