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Synthesis and Structure of $[Me_2C(C_5H_4)(Flu)Zr(\mu\text{-}H)Cl]_2$, an η^3:η^5-Bonded *ansa*-Metallocene

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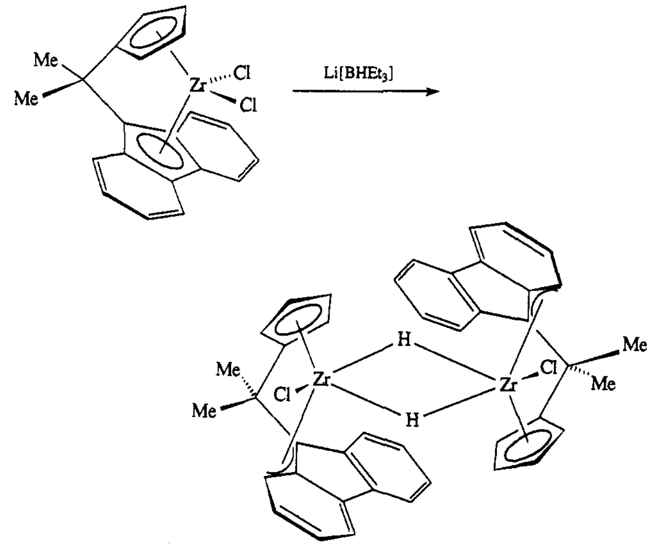
Summary: The reaction of $Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}Flu)ZrCl_2$ (Flu = fluorenyl) with $Li[BHEt_3]$ produces red crystals of $[Me_2C(C_5H_4)(Flu)Zr(\mu\text{-}H)Cl]_2$·toluene·2THF (2). In contrast to the structures of previously known ansa-zirconocenes, the fluorenyl moiety adopts an unusual η^3-allyl coordination mode involving both the five-membered and one six-membered ring. The complex is dimeric, with bridging hydrides and a short (3.0962(6) Å) Zr–Zr distance. The solid-state structure is maintained in solution.

The discovery by Brintzinger and Kaminsky[1] that "stereorigid" *ansa*-metallocenes of group 4 metals such as $C_2H_4(Ind)_2ZrCl_2$ produce highly stereospecific homogeneous propene polymerization catalysts has precipitated intense efforts to improve the stereocontrol of polymerization reactions by suitable ligand design.[2] For example, Ewen et al. developed a highly syndiospecific ligand system, $Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}Flu)MCl_2$ (Flu = fluorenyl; M = Zr (1), Hf).[3] The assumption for ligand control of the stereochemistry is, of course, that the ligands do not significantly alter their coordination mode during the course of the reaction.

We have an interest in the synthesis of base-free cationic alkyl and hydride complexes of group 4 metals as aluminum-free polymerization catalysts.[4,5] Dihydride complexes as an entry to hydrido cations are commonly accessible by reduction of the corresponding metallocene dichlorides, for example with $Li[AlH(O\text{-}t\text{-}Bu)_3]$,[6,7] $Na[AlH_2(OC_2H_4OMe)_2]$,[8] or $Na[BHEt_3]$.[5b] However, when a suspension of 1 in toluene was treated with 2 equiv of $Li[BHEt_3]$ in tetrahydrofuran (THF) at room temperature, the hydrido chloro complex $[Me_2C(C_5H_4)(Flu)Zr(\mu\text{-}H)Cl]_2$ (2) was obtained as red crystals containing toluene and THF of crystallization (Scheme I).[9]

Scheme I



The molecular structure of 2 was shown in Figure 1.[10] The complex is dimeric, with terminal chloride ligands. The hydride ligands occupy bridging positions. The Zr–Zr distance of 3.0962(6) Å is remarkably short compared

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[9] To 1.15 g (2.65 mmol) of 1, suspended in 50 mL of toluene at room temperature, was added dropwise 5.5 mL of a 1.0 M solution of $Li[BHEt_3]$ in THF. The reaction mixture darkened, with precipitation of some LiCl. After the mixture was stirred for 2 h, the supernatant was filtered off and concentrated to ca. 20 mL, and 10 mL of light petroleum was added. Cooling to −16 °C overnight yielded dark red crystals of 2 (0.8 g, 1.54 mmol, 58%), which were recrystallized from toluene. The crystals do not exhibit a clear melting point but decompose above 150 °C. According to NMR, the bulk product had the composition 2·0.66toluene·2.5THF, while the crystal chosen for X-ray analysis was of the stoichiometry 2·toluene·2THF. Anal. Calcd: C, 65.6; H, 6.2; Cl, 6.8. Found: C, 65.8; H, 5.8; Cl, 5.4.

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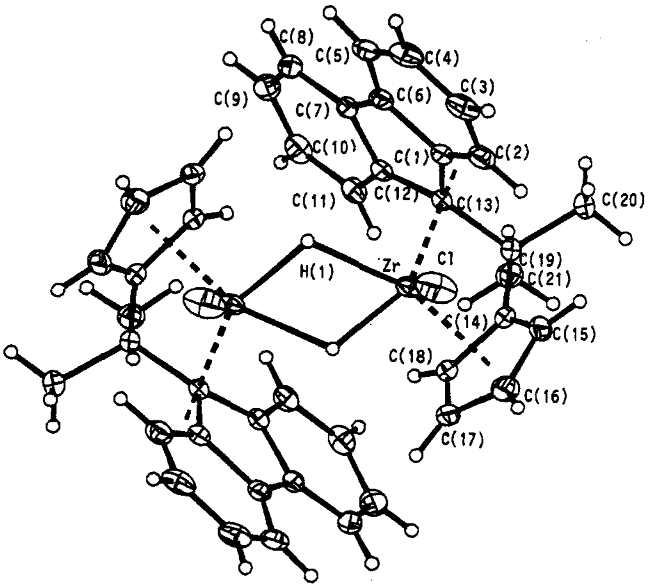

Figure 1. ORTEP drawing of [$Me_2C(C_5H_4)(Flu)ZrCl(\mu\text{-}H)]_2$ (2). Ellipsoids correspond to 30% probability. Selected bond distances (Å) and angles (deg): Zr–Zr′ = 3.0962(6), Zr–Cl = 2.5610(11), Zr–H(1) = 1.83(3), Zr–H(1′) = 2.03(3), C(1)–Zr = 2.608(3), C(2)–Zr = 2.669(3), C(13)–Zr = 2.686(3), C(14)–Zr = 2.444(3), C(15)–Zr = 2.432(3), C(16)–Zr = 2.498(3), C(17)–Zr = 2.530(3), C(18)–Zr = 2.501(3), C(1)–C(2) = 1.403(5), C(1)–C(13) = 1.443(4), C(3)–C(2) = 1.413(5), C(12)–C(13) = 1.467(4); Zr–H(1)′–Zr′ = 107(2), H(1)–Zr–H(1)′ = 62(2), Cl–Zr–H(1) = 79.6(9), C(1)–Zr–H(1) = 146.6(7), C(1)–Zr–Cl = 108.18(8), C(2)–Zr–C(13) = 58.43(10), C(14)–Zr(1)–C(13) = 55.82(9), C(2)–C(1)–C(13) = 133.4(3), C(13)–C(19)–C(14) = 103.5(2).

to those in related complexes with bridging hydride ligands such as [$(C_5H_4Me)_2Zr(H)(\mu\text{-}H)]_2$ (3.4599(2) Å),[6] [$(C_5H_4Bu^t)_2Zr(H)(\mu\text{-}H)]_2$ (3.4708(7) Å),[7] and [$SiMe_2(C_5H_4)_2$][$(C_5H_5)ZrCl(\mu\text{-}H)]_2$ (3) (3.4502(5) Å).[15] However, while these complexes are best described as 16-electron compounds, 2 has a formal electron count of 14 and may be more closely related to [$(C_5H_4Me)ZrCl(\mu\text{-}NC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)]_2$, a similarly electron-deficient complex with a Zr–Zr distance of only 3.087(2) Å.[16,17]

The bond length of the terminal Cl ligands in 2 of 2.561(1) Å is significantly longer than the Zr–Cl distance found in 1 (average 2.424 Å)[3d] but very close to the Zr–Cl distance in 3 (average 2.524 Å).[15]

The bonding of the fluorenyl ligand in 2 is unexpected. Few zirconium complexes containing fluorenyl ligands are known, structurally characterized examples being 1[3d] and $(Flu)_2ZrCl_2$ (4).[18] In 1 the metal is essentially η^5-bonded to the five-membered ring of the fluorenyl ligand, with a gradual increase in the carbon–zirconium distances on going from the bridgehead carbon toward the open side of the ligand wedge (Figure 2), although this increase is *not large enough to represent* η^3 *bonding.* In contrast, 4 has been shown to contain one η^5- and one η^3-bonded fluorenyl moiety, with two of the Zr–C distances being of the order of 2.80 Å.[18] The bonding mode in 2 differs from both these examples in that the fluorenyl ligand has slipped so that it is merely coordinated in an η^3-allyl fashion via the bridgehead carbon C(13) of the central ring and C(1) and C(2) of one six-membered ring. Such a bonding mode is, to our knowledge, without precedence for *ansa*-metallocenes. The zirconium–carbon bond lengths to C(1),

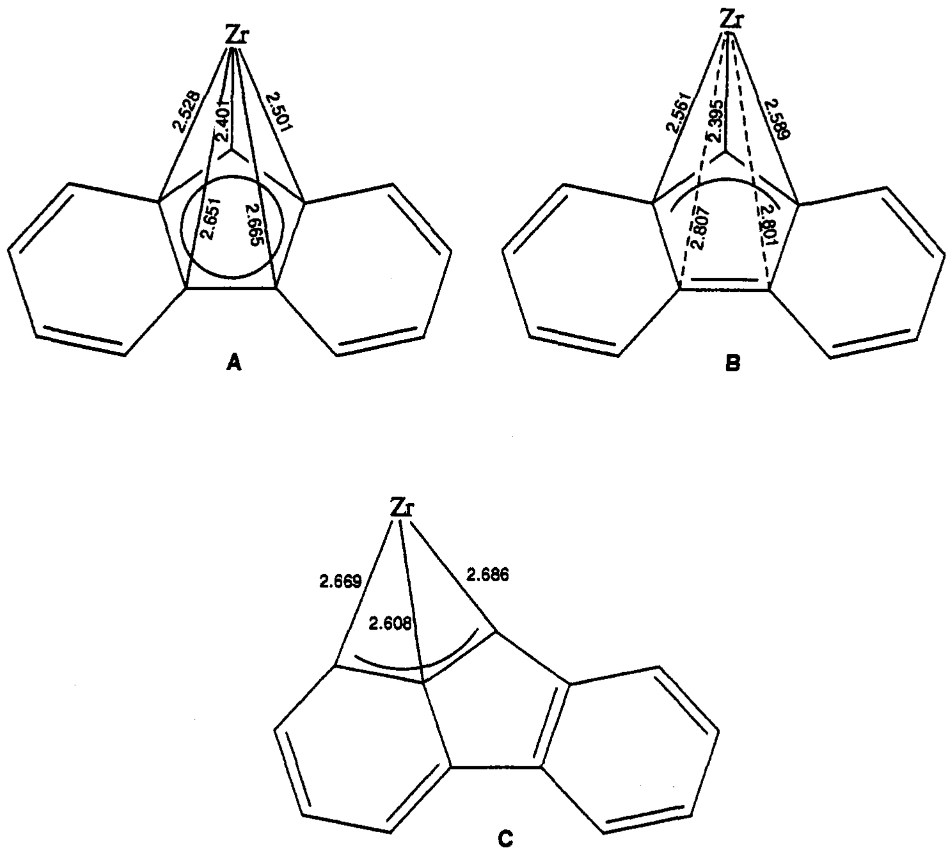

Figure 2. Comparison of the coordination modes and zirconium–carbon distances (Å) of the fluorenyl moieties in 1 (A) and in 2 (C) and of the η^3-bonded fluorenyl ligand in $(Flu)_2ZrCl_2$ (4) (B).

C(2), and C(3) are 2.608(3), 2.669(3), and 2.686(3) Å, respectively, which is rather long compared to the bonding parameters of cyclopentadienyl ligands but comparable to the longer Zr–C bond distances found for the fluorenyl ligand in 1. The ^1H NMR spectrum of 2 confirms that the solid-state structure is maintained in solution, as indicated by the observation of two resonances at δ 0.91 and 2.07 for the two inequivalent methyl groups of the CMe_2 bridge and four signals for the cyclopentadienyl protons. In agreement with this lack of mirror symmetry, the ^{13}C NMR spectrum shows distinct resonances for all 21 inequivalent carbon atoms.[19]

The structures of group 4 *ansa*-metallocenes, in particular the preservation of a chemically inert ligand framework, are crucial for the activity and stereoselectivity of these complexes in alkene polymerizations. Consideration of the source of the stereoselectivity and activity of these catalysts has typically centered on the structural parameters derived from the metallocene dichlorides.[2e,20] The observation of a facile "ring slippage" as observed for 2 implies that, at least as far as fluorenyl and analogous ligands are concerned, such a change of coordination mode must be considered as a possible source of structural irregularities in the resulting polymers, notably polypropylene. While the high syndiospecificity of propene polymerizations with catalysts based on mixtures of 1 with methylaluminoxane might argue against changes in the coordination mode of the *ansa* ligand, these catalysts have presented anomalous results before, notably the very poor polymerization activity of the methyl cation $[Me_2C(C_5H_4)(Flu)ZrMe]^+$.[3c,21]

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Supplementary Material Available: Tables giving a summary of crystal data, atomic coordinates, temperature factors, and bond lengths and angles for 2 (6 pages). Ordering information is given on any current masthead page.

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(10) X-ray structure determination for 2: data were collected using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo Kα radiation (λ(Mo Kα) = 0.710 69 Å).[11] Crystal data: orthorhombic space group *Pbcn*, $a = 15.502(1)$ Å, $b = 17.799(2)$ Å, $c = 17.774(4)$ Å, $Z = 4$, $V = 4904.2$ Å^3, $D_c = 1.398$ g cm^{-3}, $\mu = 5.75$ cm^{-1}, $F(000) = 2136$. A total of 23 016 independent reflections were recorded (slightly more than one hemisphere), of which 6269 were unique and 3394 observed ($F_o > 4\sigma(F_o)$). The structure was solved by the Patterson method using SHELX-S[12] and refined by least-squares techniques using SHELXL-93[13] and empirical absorption correction by DIFABS.[14] All hydrogen atoms were allowed to ride on their parents atoms in calculated positions. The final agreement factors were $R_1 = 0.043$ and $R(w)_2 = 0.113$.

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(19) NMR data for 2 are as follows. ^1H NMR (270 MHz, C_6D_6, 22 °C): δ 0.29 (s, 1 H, Zr–H), 0.91 (s, 3 H, CMe_2), 2.07 (s, 3 H, CMe_2); C_5H_4 3.41 (q, 1 H, $J_{HH} = 2.64$ Hz), 5.22 (q, 1 H, $J_{HH} = 2.64$ Hz), 5.69 (q, 1 H, $J_{HH} = 2.31$ Hz), 5.77 (q, 1 H, $J_{HH} = 2.31$ Hz); Flu 6.51–8.38 (m, 8 H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 23.40 (C*Me*$_2$), 30.52 (*C*Me$_2$), 36.6 (C*Me*$_2$); C_5H_4 75.03, 99.93, 107.17, 110.52, 116.45; Flu 95.40, 112.64, 118.35, 120.49, 120.85, 121.98, 122.07, 125.74, 129.28, 132.53, 134.63, 136.18, 146.11. The resonances of toluene and THF of crystallization have been omitted.

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