A Novel η^7 Coordination Mode of a Benzyl Ligand in a Cationic Zirconium Complex[†]

Claudio Pellecchia,* Attilio Immirzi, Daniela Pappalardo, and Andrea Peluso

Dipartimento di Fisica, Università di Salerno, I-84081 Baronissi (SA), Italy

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Summary: Single-crystal X-ray analysis of the ionic complex $[(C_5Me_5)Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ *shows that no cation–anion bonding interactions exist, resulting in remarkable structural features in the highly electrophilic "naked" cation, including an unprecedented* η^7*-benzyl coordination.*

The benzyl ligand differs from simple alkyls in its potential ability to interact with electron-deficient metal centers through the π-aromatic system.[1] A more or less unsymmetrical allyl-type η^3 coordination is typically found in middle- and late-transition-metal complexes,[1,2] while a weaker π-interaction, involving mainly the *ipso* carbon and to a lesser extent the *ortho* carbons, has been recognized in d^0 and d^0f^n early-transition- or actinide-metal complexes and described as η^2 or η^4 coordination.[1,3]

In the course of studies aimed at elucidating the structure of the active species involved in the catalytic systems for the polymerization of olefins,[4] styrenes,[5] and conjugated diolefins,[6] based on Ti or Zr complexes of the type Cp_nMR_{4-n} (n = 0, 1) and a ionizing cocatalyst (methylalumoxane, $B(C_6F_5)_3$, or $[HNR_3]^+[B(C_6F_5)_4]^-$), we have recently synthesized novel "non-metallocene" base-free cationic benzyl complexes, such as $[Zr(CH_2Ph)_3]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**1**) and $[(C_5R_5)Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (R = H, **2**; R = Me, **3**).[7] X-ray analyses of **1**[7a] and **2**[7c] revealed that in both cases the highly electron-deficient Zr cations are saturated through the π-coordination of the Ph ring of the anions, while NMR studies[7] showed a dissociation equilibrium leading to solvent-separated ion pairs. Since the "naked" cationic complexes are believed to be the true catalytic species involved in the polymerization, it would be of interest to have the authentic structure of such highly unsaturated species.[8] We have now succeeded in obtaining the crystal structure of **3**, revealing remarkable bonding features in the naked $[Cp^*Zr(CH_2Ph)_2]^+$ cation ($Cp^* = C_5Me_5$), including an unprecedented η^7-benzyl coordination.

The crystal structure of **3**,[9] unlike that of the closely related zwitterionic complex **2**, consists of discrete $[Cp^*Zr(CH_2Ph)_2]^+$ and $[B(CH_2Ph)(C_6F_5)_3]^-$ ions without any cation–anion bonding interaction. Thus, the high electronic unsaturation of Zr is relieved by unusually strong π-coordination of the two benzyls, behaving as η^7 and η^3 ligands, respectively (see Figure 1). The coordination geometry around Zr, as defined by C1, C8, and the points X1 (center of gravity of the C15, ..., C19 ring) and X2 (center of gravity of the C3, C4, C6, C7 atoms; see below), is distorted tetrahedral, with an anomalous C1–Zr–X2 angle (68.4°) imposed by the small bite size of the "chelating" η^7 benzyl ligand. The geometry of the Zr–η^7-benzyl moiety is noteworthy: in previously reported η^n-benzyl Zr complexes,[1,3,7] the Zr–C_α distances range between 2.26 and 2.32 Å, while the shortest Zr–C(aromatic) separations range between 2.6 and 2.7 Å. In the case of **3**, the Zr–C(*ipso*) bond distance is the shortest one (Zr–C2 = 2.349(3) Å), while the Zr–C_α distance is the longest (Zr–C1 = 2.653(3) Å). The other Zr–C(aromatic) distances are Zr–C3 = 2.553(3), Zr–C7 = 2.537(3) (*ortho* C's), Zr–C4 = 2.624-

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[†] Dedicated to Professor Adolfo Zambelli on the occasion of his 60th birthday.

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(9) Single crystals of **3**, grown at 293 K by slow diffusion of toluene into a solution of **3**[7c] in 1,2,4-trichlorobenzene, were analyzed by three-dimensional X-ray diffraction techniques at 173 K. Crystals are orthorhombic with space group *Pbca* and lattice constants a = 16.815(4) Å, b = 31.789(7) Å, c = 15.483(8) Å, V = 8276(4) Å^3, and Z = 8. A total of 8000 unique reflections having $2\theta < 50°$ were collected on a Rigaku AFC7S diffractometer, using graphite-monochromated Mo Kα radiation and the $\omega-\theta$ scan technique. Absorption (μ_a(Mo Kα) = 3.61 cm^{-1}) was ignored. Structure analysis and least-squares refinement were based on the 4958 reflections having $F_o > 3\sigma(F)$ (weight factors set to $w_i = 1/\sigma^2(F_{o,i})$). Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were refined isotropically. Final disagreement indices are R = 0.042 and R_w = 0.036. Residues in the difference electron density map are between −0.47 and +0.35 e Å^{-3}.

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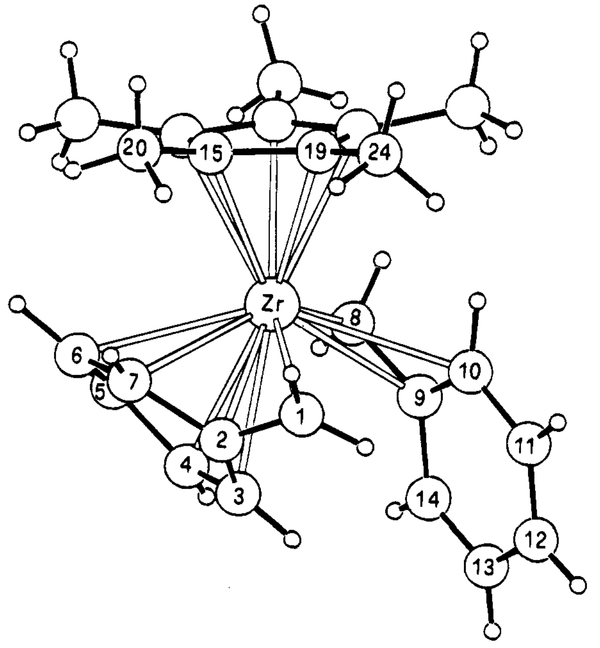

Figure 1. Crystal structure of the $[(C_5Me_5)Zr(CH_2Ph)_2]^+$ cation of **3**. Important bond distances are reported in the text. Selected bond angles (degrees) are as follows: C1—Zr—C8, 127.1(1); C1—Zr—X1, 114.2; C1—Zr—X2, 68.4; C8—Zr—X1, 104.9; C8—Zr—X2, 107.6; X1—Zr—X2, 133.8; Zr—C1—C2, 62.1(2); Zr—C8—C9, 87.6(2). X1 and X2 denote the centers of gravity of the C15, ..., C19 ring and of the C3, C4, C6, C7 atoms, respectively.

(4), Zr—C6 = 2.634(3) (*meta* C's), and Zr—C5 = 2.550(3) Å (*para* C). Consistently, a remarkable boat-type ring puckering takes place: C3, C4, C6, and C7 are coplanar within 0.005 Å, while C2 and C5 are 0.205 and 0.160 Å, respectively, out of the plane toward Zr. The angles between the quoted plane and the C2,C3,C7, and the C4,C5,C6 planes are 15.2 and 12.6°, respectively. Partial loss of the sp^2 character of the C2 atom is evident, since the C1—C2 bond is out of the C2,C3,C7 plane by 21°. Inspection of the bond lengths within the C1, ..., C7 benzyl group shows that C1—C2 (1.377(5) Å) is shorter than expected for a C(aliphatic)—C(aromatic) bond, while, among the aromatic C—C bonds, two are longer than standard (C2—C3 = 1.442(5), C2—C7 = 1.443(5) Å), two are shorter (C3—C4 = 1.380(5), C6—C7 = 1.367(5) Å), and two are comparable (C4—C5 = 1.417(5), C5—C6 = 1.403(6) Å). Very similar values of the C—C bond lengths were recently predicted from *ab initio* calculations for η^7-benzyl complexes of heavy alkali metals.[10]

The second benzyl is well described as an unsymmetrical η^3 ligand, as shown by the Zr—C8 (2.339(3) Å), Zr—C9 (2.701(3) Å), and Zr—C10 (2.751(3) Å; cf. Zr—C14 = 3.784(3) Å) distances, as well as by the Zr—C8—C9 angle (87.6(2)°). The "edge-on" mode of attachment, unusual for d^0 metal complexes, is also confirmed by the C—C bond length alternation observed in the aromatic ring, which is that expected for η^3-benzyls.[1-3]

The Cp* ligand is unexceptional (Zr—X1 = 2.218 Å), although a slight dissymmetry of the Zr—C distances is observed, as a consequnce of a slight nonorthogonality of the Zr—X1 direction to the cyclopentadienyl plane.

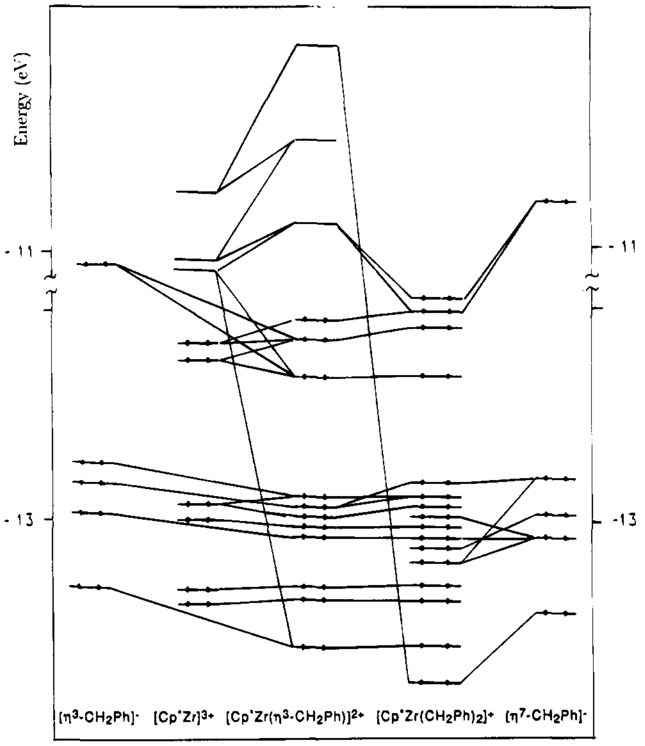

Figure 2. Energy level diagram showing the interactions of the η^3- and η^7-benzyl fragments with the $[(C_5Me_5)Zr]^{3+}$ unit.

A theoretical analysis of the MO's involved in the above unusual coordination has been performed by the extended Hückel method.[11] An energy level diagram showing the interactions of the $[Cp^*Zr]^{3+}$ fragment with the two benzyl ligands is displayed in Figure 2. The $[Cp^*Zr]^{3+}$ moiety has three low-energy unoccupied MO's which could be involved in binding the two benzyl fragments. Among those, the MO falling at the highest energy is mainly d_{yz} (64%), with smaller contributions of $d_{x^2-y^2}$ (18%) and 5s (9%) (the Cartesian frame adopted here has the z axis going through Zr and X2, with C2 and C5 lying on the x axis). The other two MO's are respectively combinations of $d_{x^2-y^2}$ (50%) and d_{yz} (25%) for the higher one and of d_{xz} (50%) and d_{xy} (50%) for the lower; their energies are slightly lower than both benzyl HOMO's, so that charge transfer from the benzyl ligands to the metal ion is to be expected.

The energy levels of the η^3- and η^7-benzyl fragments differ mainly in the HOMO, a nonbonding π-level with in-phase contributions of π-orbitals of the α and *para* carbons and out-of-phase contributions of the *ortho* carbons. For the distorted η^7-benzyl fragment, this level is shifted to higher energy (*ca.* 0.3 eV), in agreement with the fact that the ground-state geometry of the benzyl anion is planar,[10] and it is more delocalized on the whole ring (in the η^3-benzyl it is mainly localized on C_α, contributing for 64%). The interaction diagram shows that each benzyl fragment has at least two levels which can make bonding interactions with the available metal orbitals. They are the HOMO, discussed above, and a bonding π orbital, due to in-phase contributions of the α and *ipso* carbons and out-of-phase contributions

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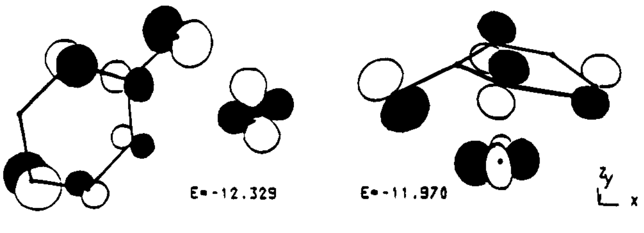
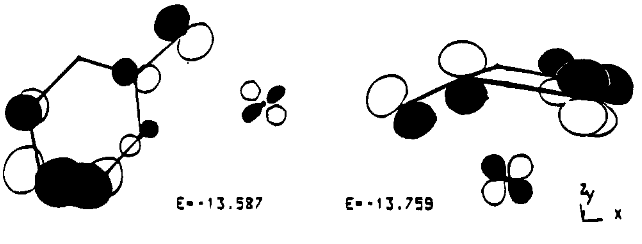
Chart 1



η^3-fragment η^7-fragment

Chart 2



η^3-fragment η^7-fragment

of the *para* and *meta* carbons, lying at *ca.* −13.3 and −13.4 eV for η^3 and η^7 fragments, respectively. Four bonding MO's result from interactions of these levels with the orbitals of the metal: two are located in the region of the frontier orbitals (see Chart 1), while the other two lie at much lower energy, around −13.7 eV (See Chart 2). It is remarkable that the η^3-benzyl ligand interacts mainly with the α and, to a lesser extent, with the *ipso* and one of the *ortho* carbons, while for the η^7-benzyl group bonding interactions are formed with all carbons. The MO calculations show clearly that the unusual η^7-benzyl coordination is due to electronic factors. In fact, the metal orbitals available for coordinating this ligand, i.e. $d_{x^2-y^2}$ and d_{xz}, have the correct phases to make bonding interactions with both the "head" and the "tail" of the benzyl fragment (see Charts 1 and 2). The driving force for the observed benzyl arrangements is likely the relieving of the electron deficiency of Zr, resulting in the formation of a formally 18-electron complex. EH computation yields a total charge of +0.234 and −0.224 au for the η^7- and the η^3-benzyl fragments, respectively, confirming a relevant charge transfer to Zr.

In solution, a fluxional process involves the two benzyl ligands, and so averaged values are observed for NMR parameters,[7c] which indicate, however, that a strong η^n coordination is maintained (e.g., the *ortho* Ph proton resonance is found at δ 4.50).[7c] The implication of **3** in catalysis and model reactions for Ziegler−Natta polymerization has been discussed elsewhere.[7c,d] It is worth mentioning that the active species involved in the syndiotactic-specific polymerization of styrene are believed to be similar cationic Ti or Zr complexes bearing a 2,1 $-CH(Ph)CH_2\cdot\cdot\cdot$ polystyryl growing chain.[5] An η^n-benzyl coordination of the last inserted monomer unit was suggested to play a role in the syndiotactic-specific steric control.[12] The molecular structure of **3** can help to suggest models accounting for the observed high stereospecificity. A theoretical investigation in this direction is in progress.

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Supplementary Material Available: Listings of X-ray data, positional and thermal parameters, and bond lengths and angles for **3** (10 pages). Ordering information is given on any current masthead page.

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