$Cp_3Zr(acetonitrile)^+$: Structure of an Electron-Rich Organometallic d^0-Cation

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The organometallic salt $[Cp_3Zr(N{\equiv}C-CH_3)]^+$ $[CH_3B(C_6F_5)_3]^-$ (**3a**) has been prepared by treatment of Cp_3ZrCH_3 with $B(C_6F_5)_3$ followed by the addition of acetonitrile. X-ray crystal structure analysis of **3a** shows that its cation consists of three uniformly coordinated η^5-cyclopentadienyl ligands about the zirconium atom. The acetonitrile ligand is end-on coordinated. In the linear $[Zr]-N{\equiv}C-CH_3$ unit the $C{\equiv}N$ triple bond [N–C2 1.126(5) Å] is slightly shorter than in the free acetonitrile molecule [$d_{C\equiv N}$ = 1.141(2) Å], the structure of which was determined as a reference by X-ray diffraction of a crystal obtained by IR-laser-induced zone melting on the diffractometer.

Introduction

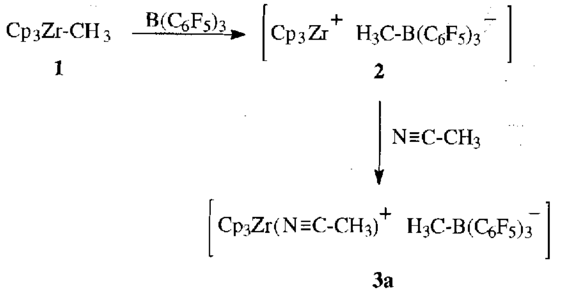
The molecular orbital scheme of tris(η^5-cyclopentadienyl) group 4 metal systems (in idealized C_{3v} symmetric arrangement) is unique inasmuch as the ligand-centered highest occupied molecular orbital (a_2) is devoid of any significant interaction with the metal center[1]. The Cp_3Zr^+ cation (in this idealized geometry) has a metal-centered LUMO, mostly of d_z2-character, available for bonding of a two-electron donor ligand, although the tris(η^5-cyclopentadienyl)zirconium cation may formally be regarded as an 18-electron complex.

We have recently generated the donor-ligand-free Cp_3Zr^+ as its $CH_3B(C_6F_5)_3^-$ salt and found it to react rapidly with a variety of typical donor ligands L to form a number of stable $[Cp_3Zr(L)]^+$ $[CH_3B(C_6F_5)_3]^-$ salts that contain individual pseudotetrahedral $Cp_3Zr(L)^+$ cations[2].

Two such examples were characterized by X-ray crystal structure analysis, namely the *tert*-butyl isocyanide complex $[Cp_3Zr(CN-CMe_3)]^+$ $[CH_3B(C_6F_5)_3]^-$ and the cationic d^0-metal carbonyl $[Cp_3Zr-C{\equiv}O]^+$ $[CH_3B(C_6F_5)_3]^-$. We have also prepared the corresponding cationic nitrile complexes $[Cp_3Zr(N{\equiv}C-R)]^+$ $[CH_3B(C_6F_5)_3]^-$ (R = CH_3: **3a**; R = Ph: **3b**)[2]. It is known from the work of Jordan on $Cp_2ZrX(L)^+$ chemistry[3] that organic nitrile ligands are very well-suited for stabilizing group 4 metal cations coordinated by cyclopentadienyl ligands. At the time when we reported the synthesis of the complexes **3** we had not succeeded in growing suitable crystals to allow characterization of these interesting novel systems by X-ray diffraction. Since then, single crystals of the complex $[Cp_3Zr(acetonitrile)]^+$ $[CH_3B(C_6F_5)_3]^-$ (**3a**) have been obtained and an X-ray crystal structure analysis has been carried out. In this article we describe the structural features of this parent $Cp_3Zr(nitrile)^+$ cation complex and compare them with the structural parameters of free acetonitrile, the structure of which was also determined in the course of this study.

Results and Discussion

The (acetonitrile)tris(η-cyclopentadienyl)zirconium cation complex **3a** was synthesized in the same manner as we described previously[2]. Thus, tris(η-cyclopentadienyl)methylzirconium (**1**) was treated with one molar equivalent of the organometallic Lewis acid tris(pentafluorophenyl)borane[4] at low temperature in dichloromethane solution, thereby generating the reactive $[Cp_3Zr]^+$ $[CH_3B(C_6F_5)_3]^-$ salt (**2**). At −78 °C, a five-fold excess of acetonitrile was added to form the $[Cp_3Zr(N{\equiv}C-CH_3)]^+$ $[CH_3B(C_6F_5)_3]^-$ product **3a**, which was isolated in ca. 70% yield after precipitation with pentane. The isolated product was found to contain one equivalent of dichloromethane, which was evident from a signal at δ = 5.32 in its ^1H NMR spectrum. The resonances of the complex were found at δ = 6.03 (s, 15H, Cp), 2.58 (s, 3H, $NC-CH_3$) and 0.35 (br. s, 3H, $CH_3[B]$) in $CD_2Cl_2/[D_8]THF$ (10:1) solution at 213 K (600 MHz).



3a

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Single crystals of $[Cp_3Zr(N{\equiv}C-CH_3)]^+$ $[CH_3B(C_6F_5)_3]^-$ (**3a**) were obtained from dichloromethane solution. X-ray crystal structure analysis of **3a** revealed the presence of independent $Cp_3Zr(N{\equiv}C-CH_3)^+$ cations and $CH_3B(C_6F_5)_3^-$ anions in the crystal. The structure found for the methyltris(pentafluorophenyl)borate anion was unremarkable, being identical to that found for this anion in X-ray diffraction studies of other ionic organometallic complexes[5].

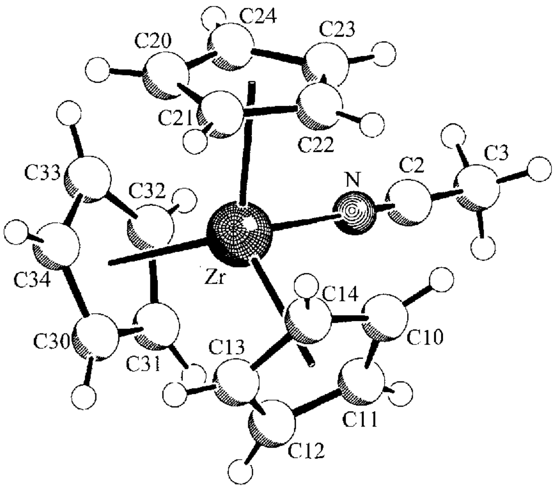
The $[Cp_3Zr(N{\equiv}C-CH_3)]^+$ cation exhibits an approximate (non-crystallographic) C_3-symmetric arrangement of the three cyclopentadienyl ligand at zirconium. The fourth position at the pseudotetrahedrally coordinated zirconium atom is occupied by the acetonitrile ligand. The three cyclopentadienyl ligands are rather uniformly η^5-bonded to the transition metal center[6]. The overall average Zr−C(Cp) bond length was found to be 2.581(5) Å.

The individual Zr−C(Cp) distances lie in a range between 2.545(4) and 2.649(4) Å. For each individual Cp-ligand three Zr−C(Cp) distances are almost identical, thus out of a total of 15 Zr−C(Cp) bond lengths 9 values fall within the very narrow range from 2.545(4) to 2.567(4) Å. The remaining six Zr−C(Cp) distances are slightly longer, i.e. between 2.594(4) and 2.649(4) Å. Each of the Cp−Zr moieties contains two of these slightly longer Zr−C(Cp) separations, although these seem to be unsystematically placed along the Cp_3Zr perimeter. We assume that these differences in bond lengths and their relative distribution are probably due to crystal packing effects.

Due to the steric bulk of three η-cyclopentadienyl ligands bonded to a single central transition metal atom, the Cp(centroid)−Zr−Cp(centroid) angles are increased from the tetrahedral angle at 118.5° (D1−Zr−D2), 118.6° (D1−Zr−D3) and 118.0° (D2−Zr−D3) (D1, D2 and D3 denote the centroids of the Cp-ring systems containing the carbon atoms C10−C14, C20−C24 and C30−C34, respectively). Consequently, the Cp(centroid)−Zr−N angles are smaller than the tetrahedral value at 97.3° (D1−Zr−N), 97.9° (D2−Zr−N) and 96.8° (D3−Zr−N).

The fourth vertex at the Zr-centered tetrahedron is occupied by the acetonitrile ligand. It is bonded to zirconium through the nitrogen of the cyano group. The Zr−N−C−C unit is essentially linear with bond angles of 177.5(3)° (Zr−N−C2) and 179.4(5)° (N−C2−C3). The C2−C3 bond length is 1.447(6) Å, which is within the expected range for a C(sp)−C(sp^3) single bond. The Zr−N bond length is 2.301(2) Å. This value is almost identical to that found previously for zirconium−nitrogen distances in cationic zirconocene(acetonitrile) complexes. The X-ray crystal structure analyses of two typical examples of such systems have been reported in the literature, namely $Cp_2Zr(benzyl)(N{\equiv}C-CH_3)^+$ (**5**)[8] and the *ansa*-metallocene system [ethylene-bis(tetrahydroindenyl)Zr](benzyl)$(N{\equiv}C-CH_3)^+$ (**6**)[9]. The respective Zr−N distances of **5** and **6** are very close to the observed value of **3a** (see Table 1).

Figure 1. View of the molecular geometry of the cation of **3a** (with non-systematical atom numbering scheme)[a]



[a] Selected bond lengths (Å) and angles (°) (cation part only): Zr−N 2.301(3), Zr−C30 2.545(5), Zr−C20 2.548(4), Zr−C11 2.550(4), Zr−C21 2.550(4), Zr−C10 2.552(4), Zr−C34 2.556(4), Zr−C33 2.560(4), Zr−C24 2.562(4), Zr−C14 2.567(4), Zr−C12 2.594(4), Zr−C22 2.609(4), Zr−C32 2.611(5), Zr−C13 2.628(4), Zr−C31 2.632(5), Zr−C23 2.649(4), N−C2 1.126(5), C2−C3 1.447(6), C10−C11 1.395(6), C10−C14 1.400(6), C11−C12 1.407(6), C12−C13 1.386(6), C13−C14 1.400(6), C20−C24 1.387(7), C20−C21 1.387(6), C21−C22 1.408(7), C22−C23 1.377(6), C23−C24 1.401(6), C30−C34 1.399(7), C30−C31 1.407(7), C31−C32 1.371(7), C32−C33 1.390(7), C33−C34 1.394(7); C11−C10−C14 107.9(4), C10−C11−C12 107.8(4), C13−C12−C11 108.2(4), C12−C13−C14 108.1(4), C13−C14−C10 108.0(4), C24−C20−C21 108.5(4), C20−C21−C22 107.4(4), C23−C22−C21 108.2(4), C22−C23−C24 108.0(4), C20−C24−C23 107.8(4), C34−C30−C31 107.6(5), C32−C31−C30 108.2(5), C31−C32−C33 108.2(5), C32−C33−C34 108.7(5), C33−C34−C30 107.1(5); for additional values see text.

Table 1. Comparison of selected bond lengths (Å) of coordinated and free nitrile moieties

Compound	CH_3–C	C≡N	N–M	[M]	ref.
4[a]	1.413(7)	1.137(8)	2.175(7)	Ti	[7]
5[a]	1.438(8)	1.122(7)	2.295(5)	Zr	[8]
6[a]	1.443(15)	1.116(11)	2.281(9)	Zr	[9]
3a[a]	1.447(6)	1.126(5)	2.301(2)	Zr	[c]
free C(sp^3)–C≡N[b]	1.470	1.136	---	--	[10]
CH_3–C≡N	1.443(2)	1.141(2)	---	--	[c]

[a] For the composition of complexes **4**−**6** see text. − [b] Average values from 140 individual structures. − [c] This work.

The N−C2 bond length of the coordinated acetonitrile ligand in the $[Cp_3Zr(N{\equiv}C-CH_3)]^+$ cation of **3a** is 1.126(5) Å. This is only slightly longer than the corresponding N−C distances in the complexes **5** and **6**, respectively. On the other hand, the N−C2 bond in **3a** is shorter than that in the related cationic (acetonitrile)titanocene complex [bis(indenyl)(−N=CMePh)Ti$(N{\equiv}C-CH_3)]^+$ (**4**)[7] (see Table 1). The average value for the N≡C bond in free organic C(sp^3)−C≡N molecules is 1.136 Å[10].

In order to allow accurate comparisons to be made, we considered it desirable to have the structural parameters of free acetonitrile, determined by X-ray diffraction in the crystal, at our disposal as a reference standard. Acetonitrile is known to form two crystalline phases, α- and β-acetonitrile, respectively. The α-phase has been reported to be stable only within a small temperature range between T_c =

211 K and T_m = 227 K[11]. Below T_c, β-phase acetonitrile is assumed to be orthorhombic by analogy with the low-temperature phase of its deuterated derivative[12]. According to Pace and Noe[13] the phase transition is a first-order process with α-N≡C−CH_3 being metastable in the stability field of the β-phase and *vice versa*. For this study, a single crystal of α-acetonitrile was grown on the diffractometer using a zone-melting technique similar to that reported by Boese et al.[14]. Under these conditions the following characteristic bonding features of the acetonitrile molecule were obtained: N≡C 1.141(2) Å, C−C 1.443(2) Å, N−C−C 179.57(14)°.

Thus, complexation of acetonitrile to the titanium cation in **4** appears not to alter the typical C−N distance of the C≡N triple bond functional group signifilantly, whereas coordination to the strongly electrophilic zirconium cations in **5**, **6** and **3a** apparently leads to a slight decrease in the C−N bond length and thus to some strengthening of the C≡N triple bond in the coordinated ligand[2,15]. We thus conclude that the Cp_3Zr^+ moiety behaves as a typical d^0-configured, very electrophilic, organometallic Lewis acid. It removes electron density from the coordinated acetonitrile ligand, thereby reducing the electron repulsion contribution of the C−N interaction; there is no indication of any significant back-donation of electron density from the Cp_3Zr-metal complex fragment to the acetonitrile π* orbitals[16]. The ligand-centered HOMO of the Cp_3Zr^+ moiety[1] (see above) does not seem to be significantly involved in forming the strong bond between zirconium and the end-on coordinated acetonitrile ligand in the $[Cp_3Zr(N{\equiv}C{-}CH_3)]^+$ cation.

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Experimental Section

$[Cp_3Zr(N{\equiv}C{-}CH_3)]^+$ $[CH_3B(C_6F_5)_3]^-$ (**3a**): Synthesis in the same manner as described previously[2]. The reaction of 100 mg (0.33 mmol) of Cp_3ZrCH_3 (**1**) with 175 mg (0.34 mmol) of $B(C_6F_5)_3$ in 15 ml of cold dichloromethane (−78 °C) followed by treatment with 68 mg (1.66 mmol) of acetonitrile gave **3a** (195 mg, 69%), m.p. 109 °C. − IR (KBr): $\tilde{\nu}$ = 2321, 2295 (coord. N≡C−CH_3)[17]. − ^1H NMR (CD_2Cl_2/[D_8]THF, 10:1, 600 MHz, 213 K): δ = 6.03 (s, 15H, Cp), 2.58 (s, 3H, CH_3), 0.35 (br. s, 3H, $CH_3B(C_6F_5)_2$) (CH_2Cl_2 from the crystal observed at δ = 5.32). − ^{13}C NMR (CD_2Cl_2/[D_8]THF, 10:1, 150 MHz, 253 K): δ = 114.6 (Cp) (acetonitrile signals not found). − $C_{36}H_{21}BF_{15}NZr \cdot CH_2Cl_2$ (939.5): calcd. C 47.30, H 2.47, N 1.49; found C 46.33, H 2.55, N 1.46.

X-ray Crystal Structure Analysis of **3a**: $C_{37}H_{23}BCl_2F_{15}NZr$, M = 939.49, single crystals were obtained from dichloromethane solution; crystal size 0.25 × 0.20 × 0.10 mm, a = 11.182(2), b = 11.884(1), c = 15.290(2) Å, α = 108.74(1), β = 104.69(1), γ = 100.80(1)°, V = 1779.3(4) Å^3, ρ_{calc} = 1.754 g cm^{-3}, μ = 5.69 cm^{-1}, empirical absorption correction via ψ-scan data ($0.930 \le C \le 0.999$), Z = 2, triclinic, space group $P1$ bar (No. 2), Enraf-Nonius MACH3 diffractometer, λ = 0.71073 Å, ω/2θ scans, 7494 reflections collected ($\pm h$, $\pm k$, $+l$), $[(\sin\theta)/\lambda]$ = 0.62 Å^{-1}, 7212 independent and 4580 observed reflections [$I \geqslant 2\sigma(I)$], 511 refined parameters, R = 0.043, wR^2 = 0.089, max. residual electron density 0.73 (−0.82) e Å^{-3}, hydrogens calculated and refined as riding model, programs used: SHELXS-86, SHELXL-93, SCHAKAL-92.

X-Ray Crystal Structure Analysis of Acetonitrile (α-Phase): A colorless single crystal of acetonitrile C_2H_3N was grown in situ on the diffractometer by a zone-melting technique. Dried acetonitrile (analytical grade), flame-sealed in a glass capillary (∅: 0.2 mm) under argon, was cooled to 30 K below its melting point (T_m = 227 K, see ref.[11]) using the low-temperature device of the Enraf-Nonius CAD4 diffractometer. The sample solidified completely as a polycrystalline white aggregate. Single crystal growth was performed at T = 208(2) K using a commercial, computer supported laser crystal growth assembly "Challenge" distributed by COMRAY ANALYTICS GmbH, Hemer, Germany. An IR laser beam (λ = 10.6 μm) emitted by a CO_2-laser unit was focused on the capillary, leading to local melting of the sample. With control of the laser power, almost the whole sample was liquefied apart from a small polycrystalline residue. Then, upon slow reduction of the laser power (time of the "laser scan": 2 h), a 0.5-mm transparent single-crystalline area grew starting from the polycrystalline residue. The quality of the crystal was proved optically using a micro video camera and by X-ray polaroid photographs. The observation of some weak reflections that could not be indexed under the monoclinic unit cell was assumed to be attributable to a small amount of the β-phase in the sample under investigation ($T_{meas} \cong T_c$). The structure of α-acetonitrile was solved for the first time by single-crystal Weissenberg film data[11]. Our reinvestigation represents the first successful attempt to determine its structure using *X-ray diffraction* data and yielded significantly improved results, especially for the lattice parameters. C_2H_3N (41.05), 0.2 × 0.2 × 0.5 mm (glass capillary ∅: 0.2 mm), a = 4.103(1), b = 8.267(2), c = 7.969(2) Å, β = 100.22(2)°, V = 266.0(1) Å^3, $\rho_{calc.}$ = 1.025 g cm^{-1}, μ = 5.3 cm^{-1}, empirical absorption correction, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), Enraf-Nonius CAD4 diffractometer, λ = 1.54178 Å, T = 208(2) K, ω/2θ scans, 425 reflections measured ($+h$, $-k$, ±l), $[\sin\theta/\lambda]_{max.}$ = 0.55 Å^{-1}, 368 independent and 346 observed reflections [$I \geqslant 2\sigma(I)$], 41 refined parameters, R = 0.055, wR^2 = 0.134, max. residual electron density 0.16 (−0.25) eÅ^{-3}, direct methods, hydrogen atoms found and refined freely. Programs used: SHELXS-86, SHELXL-93, XP. Bond lengths [Å]: C−N 1.141(2), C−C 1.443(2), C−H 0.91(3), 0.95(2), 0.92(2), bond angle N−C(1)−C(2) 179.6(1)°.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallogrpahic Data Centre as supplementary publication no. CCDC-100379. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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