Formation of a [μ-(η^1-*N*:η^2-*C*,*N*)-Aryl cyanide]biszirconocene Cation by Ligand Exchange Reaction

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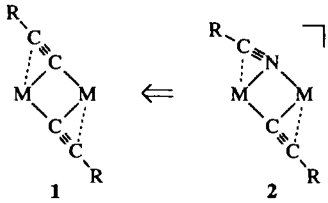
The planar-tetracoordinate carbon compound **4** exchanges the bridging μ-(η^1-*C*:η^2-*C*,*C*)-2-butyne ligand for *p*-tolunitrile in dichloromethane at 90 °C to yield the [μ-(η^1-*N*:η^2-*C*,*N*)-aryl cyanide]dizirconium cation complex **2a**. X-ray diffraction revealed an aza-allenyl-type character of the RCNZr moiety in this thermodynamically favored (μ-nitrile)zirconium cation complex.

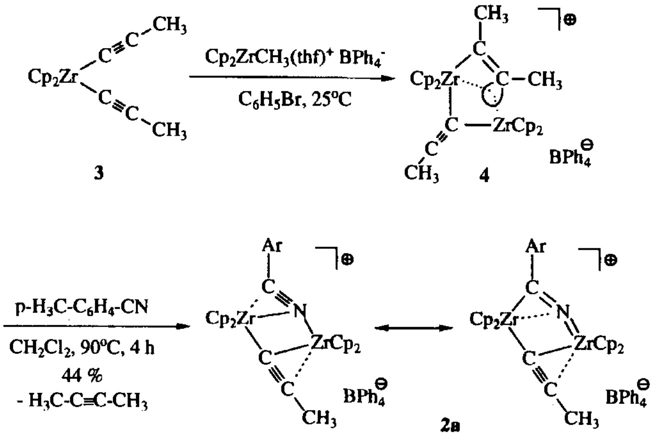
Alkyl and aryl cyanides are very frequently used as stabilizing ligands in metal complex chemistry. The R−CN moiety is mostly η^1-coordinated through nitrogen, but there are a few examples known where the organonitrile ligand is bound "side-on" in a η^2-coordination mode[1]. In a metal complex neutral R−C≡N ligands could in principle function as electronic equivalents of acetylide ligands. The latter are found to serve as two- to four-electron bridging ligands in very stable dinuclear complexes of the electrophilic d metals of the left side of the periodic table, in many dinuclear f element complexes and in main group metal chemistry[2]. Thus, it appears that the R−C≡N ligand should be able to substitute acetylide in its role as a bridging ligand in such complexes. Starting e.g. from a neutral (μ-acetylide)zirconocene dimer such as **1**, one would then formally arrive at a structurally related cationic (μ-R−C≡N)(μ-acetylide)($ZrCp_2$)$_2$ complex (**2**). Whereas a few examples of neutral dinuclear [μ-(η^1-*N*:η^2-*C*,*N*)-R−CN]metal complexes are known[3], we have now for the first time prepared a cationic μ-(aryl cyanide)biszirconocene complex (**2a**), a structural and electronic analogue of the well-known neutral bis(μ-acetylide)bismetallocene systems **1**.



1 **2**

The starting material for the ligand exchange reaction was prepared as previously described[4] by treating the methyl zirconocene cation (THF-stabilized, with tetraphenylborate anion) with one molar equivalent of dipropynylzirconocene **3**. The obtained very stable compound **4** was characterized by X-ray diffraction to contain a planar-tetracoordinate carbon center (C2). To a solution of **4** in dichloromethane was added a ca. sevenfold excess of *p*-tolunitrile, and the mixture was thermolyzed in a sealed tube at 90 °C for 4 h. Removal of the solvent, washing of the residue with toluene, and precipitation of the product with ether from a dichloromethane solution gave **2a** in 44% yield. Crystals for the X-ray structural analysis (see below) were obtained by letting ether diffuse into a dichloromethane solution of **2a** at room temperature. An analogous experiment carried out in [D_2]dichloromethane solution in a sealed 5-mm NMR tube revealed that a stoichiometric quantity of 2-butyne was liberated during this reaction.

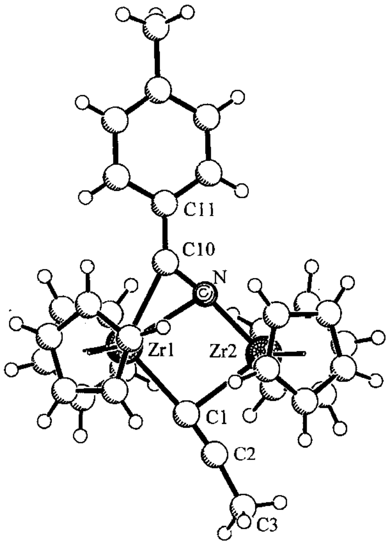
Complex **2a** contains two non-equivalent zirconocene moieties (^1H/^{13}C Cp signals at δ = 5.93, 5.64/110.5, 115.4 in [D_2]dichloromethane). In the ^{13}C-NMR spectrum the −C=N− carbon signal appears at δ = 230.8, and the H_3C−C≡C− resonances are observed at δ = 11.6, 124.8, and 129.4. In the IR spectrum (KBr) no strong bands in the typical carbon-carbon or carbon-nitrogen tripple bond range are found, but there are several rather strong bands at $\tilde{\nu}$ = 1647, 1597, and 1579 cm^{-1}.



Complex **2a** was characterized by X-ray diffraction. It exhibits clearly separated cations and BPh_4^- anions in the crystal. The dizirconium cation contains a planar-central framework composed of the two zirconium atoms and the Ar−CN and −C≡C−Me bridging ligands. The μ-acetylide appears to be three-center two-electron σ-bridging[2] [Zr1−C1 2.273(13), Zr2−C1 2.393(12) Å, angles Zr1−C1−C2 171.8(11), C1−C2−C3 175(2), and Zr2−C1−C2

93.4(9)°]. The C1–C2 bond is very short [1.20(2) Å], and the Zr2–C2 distance is 2.741 Å.

Figure 1. A view of the molecular geometry of the cation **2a** (with atom numbering scheme)



The aryl cyanide ligand is μ-(η^1-*N*:η^2-*C,N*)-coordinated to the zirconium atoms. The C10–N bond length is 1.230(14) Å and thus in the C=N double bond range. The Zr1–C10 distance [2.266(14) Å] corresponds to that of a zirconium to sp^2-carbon σ-bond, whereas the Zr1–N distance is much longer at 2.338(10) Å[5]. The bond angles at C(10) are 130.1(13)° (C11–C10–N), 152.1(10)° (C11–C10–Zr1) and 77.8(8)° (Zr1–C10–N). The aryl substituent at C10 is oriented coplanarly with the central plane of the cation **2a**. A very short Zr2–N bond [2.075(11) Å] completes the dimetallabicyclic framework of complex **2a**. This short bond length probably indicates the presence of a substantial π-bonding component of the zirconium-to-nitrogen linkage. The corresponding C10–N–Zr2 angle is close to linear [173.3(10)°]. The Zr2–N–Zr1 angle is 102.0(4)° and Zr1–N–C10 is 71.3(8)°.

These results indicate that an organonitrile ligand can assume a role similar to the connection of a μ-acetylide in dinuclear group-4 metallocene cations. The major structural difference of the μ-RCN group compared to its all-carbon analog arises from a strong in-plane participation of the C≡N π system in the bonding to *both* metal atoms in addition to the nitrogen lone pair, resulting in an aza-allenium-type geometry that probably contains a pronounced Zr=N π interaction[6]. Overall, these specific bonding features should make the μ-η^1:η^2-RCN ligand in general very suitable for stabilizing dinuclear early transition metal cations. The easy and favorable formation of complex **2a** by a simple ligand exchange reaction indicates that the development of dinuclear group-4 metallocene cation chemistry might benefit from the use of the stabilizing μ-RCN ligand effect.

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Experimental

Complex **2a**: 800 mg (0.94 mmol) of **4** was treated with 740 mg (6.32 mmol) of *p*-tolunitrile in 40 ml of CH_2Cl_2 to give 380 mg (44%) of **2a**, m.p. (DSC) 190 °C (dec.). – $C_{55}H_{50}BNZr_2$ (918.3): calcd. C 71.94, H 5.49; found C 70.58, H 5.58. – ^1H NMR (CD_2Cl_2): δ = 7.92, 7.59 (AA'BB', each 2H, *p*-tolyl), 5.93, 5.64 (s, each 10H, Cp), 2.57, 2.41 (s, each, 3H, CH_3), BPh_4^- signals at δ = 7.35 (m, 8H), 7.05 (m, 8H), 6.90 (m, 4H). – ^{13}C NMR (CD_2Cl_2): δ = 230.8 (C=N), 146.5, 145.0 (*ipso*-C, tolyl), 132.1, 131.2 (CH, tolyl), 129.4, 124.8 (C≡C), 110.5, 115.4 (Cp), 22.2 ($^1J_{CH}$ = 127 Hz, *p*-$C_6H_4CH_3$), 11.6 ($^1J_{CH}$ = 134 Hz, C≡C–CH_3), BPh_4^- signals at δ = 164.3 ($^1J_{CB}$ = 50 Hz), 136.4, 126.0, 122.1.

X-ray Structural Analysis of **2a**: Monoclinic space group $P2_1/n$, a = 11.583(2), b = 14.035(4), c = 26.762(10) Å, β = 95.25(2)°, T = –50 °C, $\rho_{calcd.}$ = 1.408 g cm^{-3}, λ = 0.71073 Å, 5804 reflections collected (±*h*, –*k*, +*l*), 5665 independent and 2460 observed reflections, 534 refined parameters, R = 0.068, R_w^2 = 0.157, programs used: SHELX-86, SHELX-93, SCHAKAL-92. Additional information about the X-ray structural analysis of **2a** can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-401926, the names of the authors, and the journal citation.

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