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Communications

Novel Synthetic Route to Hydrocarbyl-Bridged Dinuclear Zirconium/Aluminum Complexes Exhibiting a Planar Tetracoordinate Carbon Center

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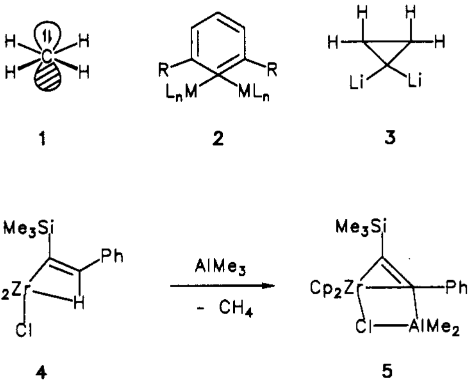
Summary: Several examples are described where dimethylzirconocene is reacted with 1 molar equiv of dimeric alkynyldimethylaluminum reagents to give the doubly hydrocarbyl-bridged $Cp_2Zr(\mu\text{-}C{\equiv}CR)(\mu\text{-}CR{=}CMe)\text{-}AlMe_2$ complexes **8** exhibiting a planar tetracoordinate carbon atom within the central metallacyclic ring system. The molecular structure of an example (**8a**, R = Ph) was determined by X-ray diffraction methods. Complex **8a** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 9.760$ (1) Å, $b = 16.453$ (2) Å, $c = 17.076$ (2) Å, $\alpha = 67.53$ (1)°, $\beta = 84.40$ (1)°, $\gamma = 81.22$ (1)°, $Z = 4$, $R = 0.035$, and $R_W = 0.042$. The planar tetracoordinate carbon center (C3) exhibits four strong bonding interactions to neighboring atoms, namely two metal centers (Zr, Al) and two carbon atoms, all located in the same plane [bond distances (Å), C3–C1 = 1.324 (4), C3–C4 = 1.508 (5), C3–Al = 2.103 (3), C3–Zr = 2.47(1); bond angles (deg), C1,C3,C4 = 118.9 (2), C4,C3,Al = 96.8 (3), Al,C3,Zr = 83.2 (3), C1,C3,Zr = 61.0 (6) (all values averaged over the two observed independent molecules)].

Scheme I



van't Hoff's and Le Bel's perception of the tetrahedral coordination geometry of "saturated" carbon in organic compounds, independently developed and made public almost simultaneously in 1874, marked the onset of organic stereochemistry.[1] Since then it has remained a great challenge to know about the limits of this all-important structural concept. State of the art computational chemistry has revealed that such an unnatural compound as square-planar methane (1) (Scheme I) [i.e. the hypothetical D_{4h}-symmetric isomer of the ordinary CH_4 molecule, exhibiting a central planar tetracoordinate carbon atom instead of the ubiquitous tetrahedral (sp^3)C] is not likely to become an observable species because of its extremely high energy content (ca. 150 kcal/mol above the "natural" methane molecule, which is some 45 kcal/mol above the borderline of molecular existence posed by the magnitude

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[1] van't Hoff, J. H. *Arch. Neerl. Sci. Exactes Nat.* **1874**, 445. Le Bel, J. A. *Bull. Soc. Chim. Fr.* **1874**, *22*, 337.

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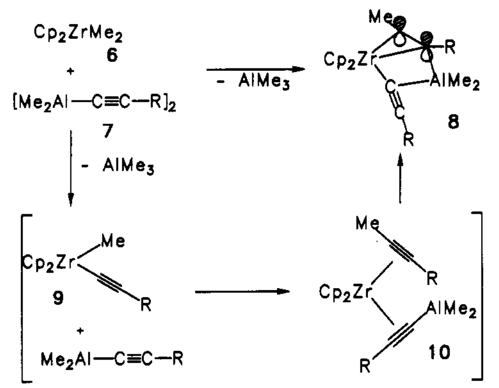
Scheme II



R = phenyl (a); cyclohexyl (b); trimethylsilyl (c)

of the C–H bond dissociation energy).[2]

The principal electronic features of planar tetracoordinate carbon, and hence the possible ways to thermodynamically stabilize this unusual carbon coordination geometry by a choice of substituents, have been known from Hoffmann's theoretical work since 1970.[3] Planar tetracoordinate carbon is supposed to have a strongly electron-deficient σ system (counting six electrons in four σ bonds) and a doubly occupied p orbital normal to the σ plane (1). Thus, a good combination of σ-donor/π-acceptor substituents would stabilize the uncommon planar D_{4h} geometry of CR_4-type compounds. This effect has been substantiated by computational chemistry[2] on e.g. 1,1-dilithiocyclopropane (**3**), but to our knowledge only four very special examples of stable, isolable molecules have been reported so far where carbon is surrounded by four substituents in a single plane. These compounds all have two σ-donating metal substituents (**2a**, Li; **2b** V; **2c**, Zr; **5**, Zr and Al) and an aromatic or olefinic system that is providing the necessary delocalizing π-acceptor properties.[4] The dimetallic complex **5** is by far the simplest system in this series. We have shown that it is formed by reacting the "β-agostic" alkenylmetallocene complex **4** with trimethylaluminum.[4d] We have now found a novel and more general way of synthesizing such relatively simple dimetallic compounds featuring a central planar tetracoordinate carbon. This synthetic entry may eventually allow for developing the organic chemistry of this "unnatural" form of tetravalent carbon.

Dimethylzirconocene (**6**) reacts cleanly with 1 molar equiv of (phenylethynyl)dimethylaluminum dimer (**7a**) at ambient temperature in toluene solution to give the dimetallic product **8a** and trimethylaluminum. The $AlMe_3$ dimer is removed by extraction with pentane to give analytically pure **8a** in 93% yield, mp 153 °C dec. Recrystallization of **8a** from toluene at −50 °C furnished orange-red crystals of the Zr,Al complex.

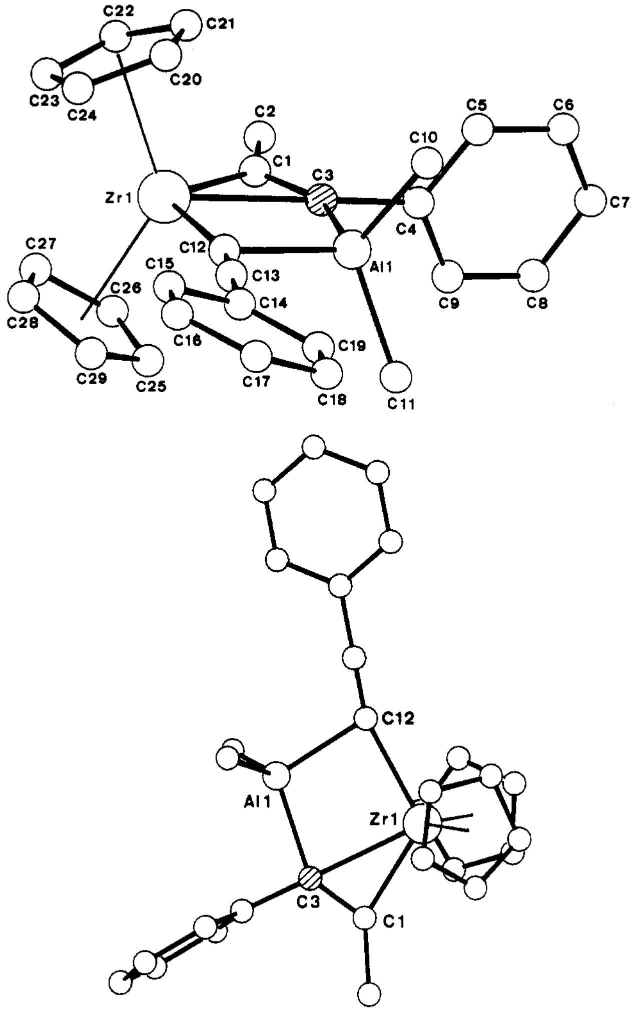


Figure 1. Two projections of the molecular structure of **8a** in the crystal (only one of the independent molecular entities shown) exhibiting the planar tetracoordinate carbon atom C3.

As outlined in Scheme II the reaction between Cp_2ZrMe_2 and $[RC{\equiv}CAlMe_2]_2$ (**7**) is probably initiated by a σ-ligand exchange yielding $AlMe_3$ and $Cp_2Zr(Me)C{\equiv}CR$ (**9**). The latter then adds another 1 equiv of $RC{\equiv}CAlMe_2$ and forms the alkyne ligand at zirconium by reductive elimination. The resulting metal acetylene π complex (**10**) is apparently not stable under the reaction conditions but undergoes a rapid intramolecular cyclization to yield the final metallacyclic product (**8**). This reaction sequence was carried out with three differently substituted aluminum acetylides (**7a–c**, R = phenyl, cyclohexyl, trimethylsilyl). The high-yield formation of the respective dimetallic products (**8a–c**) proceeded equally facile.

The molecular structure of **8a** was determined by X-ray diffraction methods. In the crystal **8a** contains two independent pairs of molecules per unit cell. These differ mainly in the orientation of the plane of the aromatic alkynyl substituent (C14–C19) relative to the mean central metallacyclic plane (Zr,C1,C3,Al,C12) [e.g. dihedral angles C19,C14,C12,Al = −16.1 and 83.9°, respectively]. Beyond this conformational difference and a slightly different orientation of the Cp_2Zr units both structures may be regarded as chemically equivalent. Therefore, averaged bond lengths and angles will be given and discussed below.

A view of the molecular geometry of **8a** is given in Figure 1. The dimetallic complex contains a zirconium atom that is bonded to two η-cyclopentadienyl ligands. The bonding features at the Cp_2Zr unit (e.g. angle D1,Zr,D2 = 129.3°)

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[2] Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, A. *J. Am. Chem. Soc.* **1976**, *98*, 5419 and references cited therein. For an additional discussion about the stabilization of unusual tetracoordinate carbon geometries, see, e.g.: Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. Keese, R. *Nachr. Chem. Techn. Lab.* **1982**, *30*, 844. Krohn, K. *Ibid.* **1987**, *35*, 264. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921. Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1981**, 260.

[3] Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181.

[4] Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802. (b) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886. (c) Buchwald, S. L.; Lucas, E. A.; Davies, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397. (d) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. *J. Am. Chem. Soc.* **1990**, *112*, 9620.

are as typically found for many other bent metallocene complexes.[5] It is doubly bridged to an ordinary $Al(CH_3)_2$ group [bond distances Al-C10 = 1.953 (8) Å, Al-C11 = 1.958 (4) Å; bond angle C10,Al,C11 = 117.4 (4)°]. The very nature of the two bridging ligands in **8a** is quite remarkable. To our knowledge, the Al,Zr(μ-C≡CPh) unit in **8a** represents one of the very few examples exhibiting a μ-alkynyl linkage between a transition and main-group metal.[6] Its bonding situation is structurally and stereoelectronically related to what is found in M(CO)M complexes exhibiting a semibridging carbon monoxide ligand.[7] In **8a** the Zr-C12 separation is 2.340 (3) Å whereas the Al-C12 bond distance is 2.103 (5) Å. The bonding parameters of the C≡CR unit are 1.209 (4) Å (C12-C13), 1.438 (4) Å (C13-C14), and 179 (2)° (C12,C13,C14). The C12,C13,C14 vector is oriented coplanar with the central metallacyclic framework. The C≡C triple bond is slightly leaning over toward the aluminum atom [bond angles around C12 = 110 (1) (C13,C12,Al), 162.8 (4) (C13,C12,Zr), 86.4 (4)° (Al,C12,Zr)].

The extraordinary geometric arrangement of the other bridging ligand between Al and Zr represents the truly outstanding structural feature of **8a**. The MeCCPh moiety is bonded to zirconium by means of carbon atom C1 [bond distances C1-Zr = 2.163 (3) Å, C1-C2 = 1.497 (6) Å, C1-C3 = 1.324 (4) Å; angles C2,C1,C3 = 129.2 (4)°, Zr,C1,C3 = 86.6 (6)°] and to zirconium *and* aluminum by means of C3. This additional strong carbon to zirconium interaction (the Zr-C3 linkage is only about 0.3 Å longer than the very short Zr-C1 σ bond) results in a very unusual coordination environment for carbon atom C3, featuring four strong bonding interactions to neighboring atoms in one plane [namely C3-C1 (1.324 (4) Å), C3-C4 (1.508 (5) Å), C3-Al (2.103 (3) Å), and C3-Zr (2.47 (1) Å)]. The bond angles around the planar tetracoordinate carbon atom C3 are 118.9 (2) (C1,C3,C4) 96.8 (3) (C4,C3,Al), 83.2 (3) (Al,C3,Zr), and 61.0 (6)° (C1,C3,Zr). In the central metallacyclic plane the Al···C4 and Al···C13 separations are 2.73 and 2.77 Å, respectively.

Complex **8a** exhibits an IR ν(C≡C) band at 2065 cm^{-1}. The ^{13}C NMR spectrum of **8a** features quarternary carbon resonances at δ 208.6 ($^2J_{CH}$ = 4 Hz, C1), 144.1, 142.8, 122.9, 114.8, and 110.9. One of the latter is to be attributed to the planar tetracoordinate carbon center. Complexes **8b,c** exhibit similar spectroscopic features.[8]

We have begun to use variations of this synthetic approach for preparing analogous compounds with other metal substituent and $M^1(\mu\text{-}X)M^2$ bridging ligand combinations and to actively investigate the chemistry of stable, isolable compounds containing planar tetracoordinate carbon.

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Registry No. 6, 12636-72-5; 7a, 17439-66-6; 7b, 136408-15-6; 7c, 136408-16-7; 8a, 136408-17-8; 8b, 136408-18-9; 8c, 136408-19-0.

Supplementary Material Available: For **8a**, full listings of bond distances, bond angles, anisotropic thermal parameters, and atomic coordinates and isotropic thermal parameters (10 pages); a table of structure factors (36 pages). Ordering information is given on any current masthead page.

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(5) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(6) Kukina, G. A.; Porai-Koshits, M. A.; Sadikov, G. G.; Shevchenko, Y. N.; Esaulenko, A. N. *Koord. Khim.* **1986**, 1279.

(7) Kumar, P. N. V. P.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125.

(8) **8b**: 0.8 g isolated (52%), mp = 121 °C dec; ^{13}C NMR (benzene-d_6) δ 197.7, 152.0, 106.9, 100.5 (quart C), 107.2 (Cp), 43.3, 32.6 (CH), 32.1, 31.4, 27.9, 26.8, 25.9, 25.2 (CH_2), 23.9 (CH_3), -6.4 ($AlMe_2$); IR (KBr) ν 2065 (C≡C), 1612 (C=C) cm^{-1}. **8c**: 1.2 g isolated (83%), mp = 105 °C dec; ^{13}C NMR (benzene-d_6) δ 224.0, 162.6, 141.6, 100.4 (quart C), 106.7 (Cp), 26.7 (CH_3), 3.3, -0.42 (2 × $SiMe_3$), -1.4 ($AlMe_2$); IR (KBr) ν 2003 (C≡C), 1563 (C=C) cm^{-1}.

Conformational Analysis of Phenylpentamethyldisilane and Related Compounds As Studied by Free-Jet Laser Spectroscopy[1]

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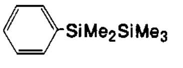
Summary: Conformational studies of phenylpentamethyldisilane (**1**) and related cyclic aryldisilanes by using free-jet laser spectroscopy and force-field calculations revealed that, in the preferred ground-state conformation of **1**, the Si-Si bond was perpendicular to the benzene ring plane, compatible with remarkable stereoelectronic effects on the absorption and fluorescence spectra of aryldisilanes.

Intriguing electronic properties of aryldisilanes have been demonstrated by means of UV, CT, and photoelectron spectroscopy.[2] For instance, phenylpentamethyldisilane (**1**) and 1-(trimethylsilyl)-1-methyl-2,3-benzo-1-silacyclopentane (**2**) showed intense absorption (^1L_a) maxima at around 230 nm, which are significantly longer than the usual maxima for substituted benzenes, while no



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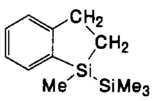

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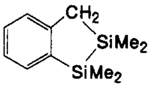

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