Formation of a Doubly C,N-Bridged Six-Membered Metallacyclic Bis[(2-imidazolyl)zirconocene] Dication

Dominik Vagedes, Gerhard Erker, Gerald Kehr, Roland Fröhlich *, Stefan Grimme **, and Christian Mück-Lichtenfeld **

Organisch-Chemisches Institut der Universität, Corrensstraße 40, D-48149 Münster, Germany

Reprint requests to Prof. Dr. G. Erker. Fax: (+49) 251 83 36503. E-mail: erker@uni-muenster.de

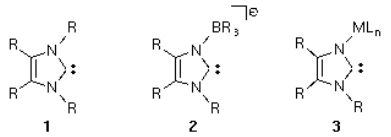
Z. Naturforsch. **58b,** 305 – 310 (2003); received October 23, 2002

Treatment of 1-methylimidazol-2-yl lithium with $Cp_2Zr(Cl)CH_3$ (**6**) gave the corresponding methyl(1-methyl-2-imidazolyl)zirconocene complex **7**. Treatment of **7** with $B(C_6F_5)_3$ (**8**) led to selective methyl abstraction. The resulting (imidazolyl)zirconocene cation **9** dimerized under the reaction conditions to yield the dinuclear imidazolyl bridged bis(zirconocene) dication complex **10** that was structurally characterized by X-ray diffraction and by DFT calculations.

Key words: Zirconocene Cation, Methyl Abstraction, Arduengo Carbene, Imidazole, DFT Calculation

Introduction

1,3-Dialkyl (or -aryl) imidazole-2-ylidenes [1, 2] have become important ligands in organometallic chemistry and catalysis [3, 4]. Charged analogues of these strong σ-donor ligands could in principle be obtained by a formal replacement of one of the hydrocarbyl substituents at a nitrogen center of the imidazole ring by a neutral Lewis acid or metal complex fragment. Such anion equivalents (**2**) of the neutral "Arduengo carbenes" (**1**) were prepared using BR_3 fragments, and the chemistry of the systems **2** was explored [5,6]. We here describe a rare example of an early transition metal variant of such species. The system was obtained by spontaneous dimerization of a (2-imidazolyl)zirconocene cation complex under the conditions of its generation from a neutral precursor [7].



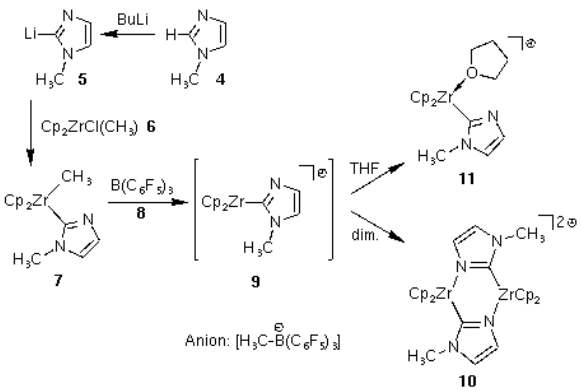
Scheme 1.

N-Methylimidazole (**4**) was deprotonated at C-2 by treatment with n-butyl lithium to yield 2-lithium-1-methylimidazolide (**5**). We have then reacted the carbanion equivalent **5** with $Cp_2Zr(Cl)CH_3$ (**6**) in toluene solution. The resulting precipitate of lithium chloride was removed by filtration and the neutral (2-imidazolyl)zirconium complex **7** was isolated in $> 90\%$ yield from the solution (Scheme 2). The product is characterized by a ^{1}H NMR singlet at $\delta = 0.06$ originating from the Zr-CH_3 σ-ligand, a Cp ^{1}H NMR singlet at $\delta = 5.62$ (in d_6-benzene) and a set of imidazolyl proton NMR resonances at $\delta = 6.79$ (4-H), 6.41 (5-H) and 3.07 (N-CH_3). All the ^{1}H NMR signals of the Zr-bound heterocycle occur markedly shifted to smaller δ values as compared to the imidazolide starting material [**5**: $\delta = 7.23$ (4-H), 6.89 (5-H), 3.64 (N-CH_3)]. A similar effect is observed in the ^{13}C NMR spectrum, the C-2 resonance of **5** ($\delta = 201.7$) is shifted considerably to low field as compared to the Zr complex **7** ($\delta = 191.0$). This trend probably reflects the electrostatic nature of the Li^+[imidazolide]$^-$ interaction in **5** as opposed to the pronounced covalent Zr-C σ-bond in **7**.

We then converted complex **7** into a cationic zirconocene complex. We chose to employ tris(pentafluorophenyl)borane (**8**) [8] as the reagent to abstract a carbanion equivalent from zirconium. The abstraction reaction starting from **7** poses a selectivity problem as principally either the imidazolide or a methyl anion could be transferred from the transition metal to zirconium. There was evidence from the literature that both cases might be feasible [9,10]. However, the reaction between **7** and $B(C_6F_5)_3$ turned out to be very selective.

* X-ray crystal structure analysis; ** computational chemistry.

0932–0776 / 03 / 0400–0305 $ 06.00 © 2003 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com



Scheme 2.

Treatment of $Cp_2Zr(CH_3)$(imidazolyl) (**7**) with the strong Lewis acid **8** resulted only in removal of the methyl group from zirconium to give the $[CH_3B(C_6F_5)_3]^-$ anion [^{1}H/^{13}C NMR: δ = 0.50/10.2 (B-CH_3), ^{11}B NMR: $\delta = -15.2$]. The cation section of the product **10** showed a Cp singlet (^{1}H/^{13}C NMR at δ = 6.23/112.9) and the imidazolide resonances [^{1}H NMR: δ = 6.79 (4-H), 7.01 (5-H), and 3.83 (N-CH_3)]. The C-2 ^{13}C NMR resonance of **10** is observed at δ = 192.7, which is a similar value as found in the neutral starting material **7** (see above).

The X-ray crystal structure analysis of **10** (single crystals were obtained from dichloromethane) revealed a dimeric dication structure in the solid state. We assume an analogous structure of **10** in solution.

In the crystal of **10** separated, non-interacting cations and anions were found. The $[CH_3B(C_6F_5)_3]^-$ anion shows the typical structural features [9]. The cationic counterpart in **10** is a dimetallic dication, probably formed by dimerization of the alleged intermediate **9** (see Scheme 2). In the dication we find two symmetry-equivalent mono-nuclear $Cp_2Zr(\text{imidazolyl})^+$ halves, which are related by an intramolecular C_2 operation. The (η^5-Cp)-Zr distances are in the usual range. The organometallic core of the molecule is almost planar. The bonding angle at zirconium amounts to 98.8(3)° (C2*-Zr-N3). The endocyclic bonding angle at C2 is in the typical C(sp^2) range at 124.4(9)° (Zr*-C2-N3) and the angle at the adjacent nitrogen is rather large at 135.9(9)° (C2-N3-Zr). This increase may be due to geometric reasons to allow for the formation of a planar central core: the sum of the six endocyclic bonding angles is 718.2°, which indicates only a marginal deviation of the central $Zr_2N_2C_2$ framework from planarity.

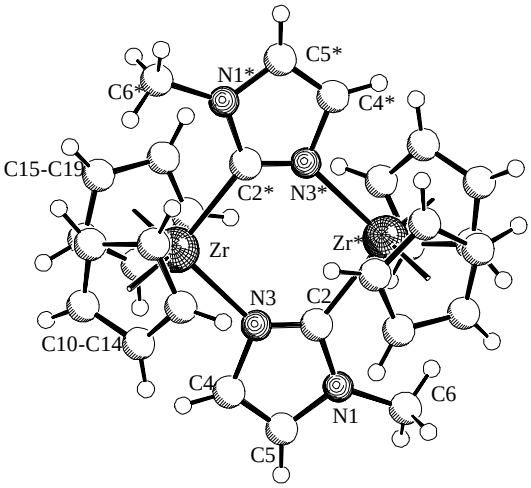


Fig. 1. Molecular structure of **10** (dication section only).

The Zr-C2 bond length (2.295(12) Å) is in the typical zirconocene-carbon σ-bond range [11]. Corresponding alkenyl-C(sp^2)-Zr linkages were described to typically be around this value [12], and iminoacyl-C(sp^2)-Zr bond distances were found in the same range [13]. The Zr-N3 bond length in the dication **10** amounts to 2.266(7) Å which is slightly longer than found in other N-coordinated zirconocene complexes [11, 14].

The crystal structure analysis yielded a pronounced probably arbitrary bond localization inside the imidazolide nuclei. The bonding features of these moieties will, therefore, not be discussed. A DFT calculation [15, 16] revealed the likely CN bond lengths of the typical delocalized structure of the imidazolide ring systems inside the dication (see Fig. 2). The X-ray crystal structure analysis of the organic molecule 1-methyl-4,5-diphenylimidazole (**12**), whose molecular geometry is depicted in Fig. 3, may serve as a suitable reference for comparison. It shows the typical tendency of aromatic bond delocalization with a sequence of typical C $\cdots$ C and C $\cdots$ N bond distances of 1.349(2) Å (N1-C2), 1.312(2) Å (C2-N3), 1.384(2) Å (N3-C4), 1.378(2) Å (C4-C5), and 1.386(2) Å (C5-N1), with only the geminal pair of N(1/3)-C(2) bonds being slightly shorter as compared to the remaining bonds inside the five-membered heterocycle.

Eventually, we have carried out the cation-forming reaction starting from **7** in the presence of THF as a donor ligand and obtained the corresponding adduct **11** (see Scheme 2), which was characterized by NMR. It shows a ^{13}C NMR resonance at δ = 194.4 for

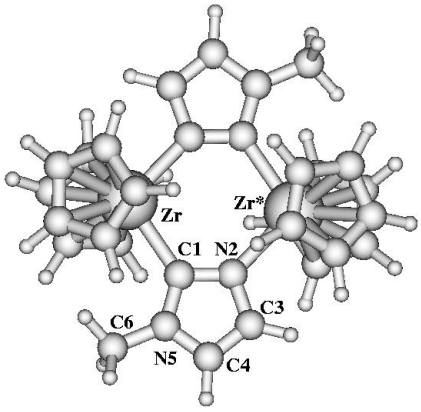


Fig. 2. DFT-calculated structure of the dication **10** (RI-BP86/TZVP [17], calcd. for C_1 symmetry, optimized structure is C_i). Selected calculated bond lengths (Å) and angles (°): Zr-C1 2.358; Zr*-N2 2.286; C1- N5 1.376; C1-N2 1.370; N5-C4 1.383; C4-C3 1.362; C3-N2 1.396; N5-C6 1.465; C1- Zr-N2* 101.2.

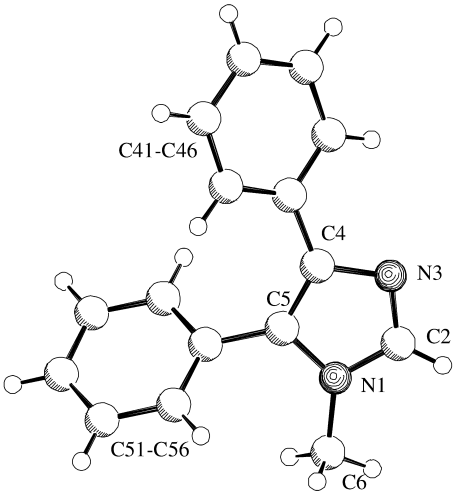


Fig. 3. A view of the structure of **12**. Selected bond lengths and angles for **12**: N1-C2 1.349(2), C2-N3 1.312(2), N3-C4 1.384(2), C4-C5 1.378(2), C5-N1 1.386(2), N1-C6 1.459(2), C4-C41 1.468(2), C5-C51 1.473(2); C5-N1-C2 106.8(1), C5-N1-C6 128.5(1), C6-N1-C2 124.7(1), N1-C2-N3 113.1(1), C2-N3-C4 104.8(1), N3-C4-C5 110.2(1), N3-C4-C41 119.2(1), C41-C4-C5 130.6(1), C4-C5-N1 105.2(1), C4-C5-C51 131.6(1), C51-C5-N1 122.9(1).

C-2(imidazole), which is intermediate between the neutral precursor **7** and the dinuclear dication complex **10**, respectively, and the anionic starting material **5**.

Conclusions

The reaction of the $Cp_2Zr(CH_3)$(2-imidazolyl) complex **10** with $B(C_6F_5)_3$ is remarkable in several aspects. First, the abstraction reaction poses a selectivity problem with the electrophilic borane having to choose between abstraction of a methyl anion equivalent or the imidazolide from the Group 4 metal center. Although $[Cp_2ZrCH_3]^+$ would have been a very favorable product, the selective transfer of CH_3^- is observed. This is probably due to several reasons, including steric effects in the actual abstraction step. However, the 2-imidazolide ligand is probably a stronger σ-donor which exceeds the methyl anion in its ability to stabilize a neighboring zirconocene cation. A mononuclear $[Cp_2Zr(2\text{-imidazolyl})]^+$ cation was indeed trapped from the reaction mixture by added THF. The imidazole nitrogen serves as a very effective σ-donor ligand toward $[Cp_2Zr]^+$. This leads to a very favorable dimer formation, as we have observed in this study.

Experimental Section

All reactions with organometallic compounds were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The starting materials 2-lithium-1-methylimidazolide (**5**) [18], $Cp_2Zr(Cl)CH_3$ (**6**) [19], $B(C_6F_5)_3$ (**8**) [8], and 1-methyl-4,5-diphenylimidazole (**12**) [20] were prepared according to published methods, or were used as commercial products [methylimidazole (**4**) and BuLi (1.6 M)] without further purification. The following instruments were used for physical characterization of the compounds: NMR: Bruker AC 200 P-FT and Varian UNITY plus 600 spectrometers were used (δ^1H = 7.15 (C_6D_5H), 5.32 ($CDHCl_2$); δ^{13}C = 128.0 (d_6-benzene), 53.8 (CD_2Cl_2); δ^{11}B = 0 for ext. BF_3-OEt_2 with Ξ (^{11}B) = 32.083971 MHz; δ^{19}F = 0 for ext. CCl_3F with Ξ (^{19}F) = 94.094033 MHz). The connectivity was confirmed by 1D and 2D NMR experiments. IR spectra were recorded with a Nicolet 5DXC FT-IR-spectrometer, melting points were measured with a Differential Scanning Calorimeter 2010 CE (TA Instruments). For elemental analysis a Foss Heraeus CHN-O-Rapid and a Vario El III Mikro CHN-O-Rapid instrument, for mass spectra a Finnigan MAT 312 and a micromass-quatro LC-Z-electrospray mass spectrometers were used.

Crystal structure analysis: Data sets were collected with Enraf-Nonius CAD4 and Nonius KappaCCD diffractometers, the latter one equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B. V., 1994) and COLLECT (Nonius B. V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B. V., 1990) and Denzo-SMN [Z. Otwinowski, W. Minor, Methods in Enzymology **276**, 307 (1997)], absorption correction for CCD

data SORTAV [R. H. Blessing, Acta Crystallogr. **A51**, 33 (1995); R. H. Blessing, J. Appl. Crystallogr. **30**, 421 (1997)], structure solution SHELXS-97 [G. M. Sheldrick, Acta Crystallogr. **A46**, 467 (1990)], structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-195057 and 195058. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Technical details of the quantum chemical calculations: The calculations were performed with the TURBOMOLE suite of programs [15]. The structure of the dication (**10**) was fully optimized without any symmetry restrictions at the density functional (DFT) level employing the BP86 functional [16], a Gaussian AO basis of valence-triple-zeta quality including polarization functions (TZVP) [17] and the resolution-of-the-identity (RI) approximation to represent the Coulomb operator [21]. For zirconium a [5s3p3d] basis set and an effective core potential with 28 core electrons [22] was used.

*2-Lithium-1-methylimidazolide (**5**)*

At −78 °C butyl lithium (9.00 ml, 14.4 mmol) in pentane was added to a suspension of 1-methylimidazole (1.18 g, 14.4 mmol) in toluene (20 ml). The reaction mixture was allowed to warm to room temperature and was stirred for another 3 days. The precipitate was collected by filtration and washed with pentane to obtain a slight green solid. Yield: 1.24 g (99%). – ^{1}H NMR (599.9 MHz, d_6-benzene / d_8-THF = 10:1): $\delta = 7.23$ (s, ^{1}H, 4-H), 6.89 (s, ^{1}H, 5-H), 3.64 (s, 3H, NCH_3). – $^{13}C\{^1H\}$ NMR (150.8 MHz, d_6-benzene / d_8-THF = 10:1): $\delta = 201.7$ (C-2), 128.4 (C-4), 117.8 (C-5), 35.7 (NCH_3).

*Bis(η^5-cyclopentadienyl)(1-methylimidazol-2-yl)methylzirconium (**7**)*

At 0 °C 2-lithium-1-methylimidazolide (**5**, 97.1 mg, 1.10 mmol) was added to a solution of chlorobis(η^5-cyclopentadienyl)methylzirconium (**6**, 300 mg, 1.10 mmol) in toluene (15 ml). The reaction mixture was allowed to warm to room temperature and was stirred for further 2 hours. The suspension was filtered and the filtrate was dried in vacuo to yield a brown solid. Yield: 320 mg (91%). – M.p.: 108 °C. – IR (KBr): $\tilde{\nu} = 1646$ (s), 1627 (m), 1519 (vs), 1465 (vs), 1378 (m), 1282 (s), 1166 (m), 1095 (vs), 981 (vs), 800 (s), 764 (m), 702 (m) cm^{-1}. – ^{1}H NMR (599.8 MHz, d_6-benzene): $\delta = 6.79$ (d, $^3J = 1.0$ Hz, 1H, 4-H), 6.41 (d, $^3J = 1.0$ Hz, 1H, 5-H), 5.62 (s, 10H, Cp), 3.07 (s, 3H, NCH_3), 0.06 (s, 3H, $ZrCH_3$); δ (CD_2Cl_2) = 6.96 (d, $^3J = 1.0$ Hz, 1H, 5-H), 6.71 (d, $^3J = 1.0$ Hz, 1H, 4-H), 5.71 (s, 10H, Cp), 3.78 (s, 3H, NCH_3), 0.02 (s, 3H, $ZrCH_3$). – $^{13}C\{^1H\}$ NMR (150.8 MHz, d_6-benzene): $\delta = 191.0$ (C-1), 126.9 (C-5), 123.7 (C-4), 107.7 (Cp), 35.1 (NCH_3), 17.0 ($ZrCH_3$); (CD_2Cl_2): $\delta = 190.9$ (C-1), 127.4 (C-5), 123.2 (C-4), 107.8 (Cp), 36.0 (NCH_3), 15.8 ($ZrCH_3$). – $C_{15}H_{18}N_2Zr$ (317.5): calcd. C 56.74, H 5.71, N 8.82; found C 55.32, H 5.36, N 7.56.

*Bis{[bis(η^5-cyclopentadienyl)(1-methylimidazol-2-yl)zirconium]}bis[methyl-tris(pentafluorophenyl)borate] (**10**)*

At 0 °C dichloromethane (10 ml) was added to a mixture of **7** (150 mg, 472 μmol) and tris(pentafluorophenyl)borane (**8**, 242 mg, 472 μmol). After 30 minutes at 0 °C the formed yellow suspension was stored for 12 hours at −30 °C. Subsequently the resulting precipitate was collected by filtration, washed with a small amount of pentane and dried in vacuo. This fractional precipitation was repeated twice. Single crystals for the X-ray structure analysis were obtained by recrystallization of **10** from dichloromethane. Yield: 270 mg (69%). – M.p.: 122 °C (dec.). – IR (KBr): $\tilde{\nu} = 1644$ (w), 1512 (vs), 1457 (vs), 1380 (w), 1267 (m), 1087 (vs), 1018 (w), 993 (m), 950 (s), 826 (s), 745 (m) cm^{-1}. – ^{1}H NMR (599.8 MHz, CD_2Cl_2): $\delta = 7.01$ (d, $^3J = 1.0$ Hz, 1H, 5-H), 6.79 (d, $^3J = 1.0$ Hz, 1H, 4-H), 6.23 (s, 10H, Cp), 3.83 (s, 3H, NCH_3), 0.50 (broad, 3H, BCH_3). – $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2): $\delta = 192.7$ (C-1), 146.6 (dm, $^1J_{CF} = 236$ Hz, Ph^F_{ortho}), 137.9 (dm, $^1J_{CF} = 243$ Hz, Ph^F_{para}), 136.8 (dm, $^1J_{CF} = 245$ Hz, Ph^F_{meta}), 131.1 (C-5), 129.0 (broad, Ph^F_{ipso}), 124.1 (C-4), 112.9 (Cp), 36.4 (NCH_3), 10.2 (broad, BCH_3). – $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2): $\delta = -15.2 (\nu_{1/2} = 50 \pm 20$ Hz). – ^{19}F NMR (563.6 MHz, CD_2Cl_2): $\delta = -133.1$ (m, 6F, Ph^F_{ortho}), −164.7 (m, 3F, Ph^F_{para}), −167.5 (m, 6F, Ph^F_{meta}).

*[Bis(η^5-cyclopentadienyl)(1-methylimidazol-2-yl)(tetrahydrofuran)zirconium][methyltris(pentafluorophenyl) borate] (**11**)*

At room temperature tetrahydrofuran (8.0 μl) was added to a solution of **7** (30.0 mg, 94.4 μmol), tris(pentafluorophenyl)borane (**8**, 48.3 mg, 94.4 μmol), and d_2-dichloromethane (0.7 ml) to give **11**, which was directly characterized by NMR spectroscopy. – ^{1}H NMR (599.8 MHz, CD_2Cl_2): $\delta = 7.01$ (d, $^3J = 1.2$ Hz, 1H, 5-H), 6.74 (d, $^3J = 1.2$ Hz, 1H, 4-H), 6.10 (s, 10H, Cp), 3.84 (s, 3H, NCH_3), 3.81 (broad, 4H, THF), 1.91 (broad, 4H, THF), 0.51 (s, 3H, BCH_3). – $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2): $\delta = 194.4$ (C-1), 148.7 (dm, $^1J_{CF} = 236$ Hz, Ph^F_{ortho}), 137.8 (dm, $^1J_{CF} = 245$ Hz,

Ph^F_{para}), 136.8 (dm, $^1J_{CF} = 248$ Hz, Ph^F_{meta}), 130.2 (C-5), 128.7 (broad, Ph^F_{ipso}), 123.9 (C-4), 111.6 (Cp), 70.1 (THF), 36.1 (NCH_3), 25.9 (THF), 10.3 (broad, BCH_3). – $^{11}B\{^1H\}$ NMR (64.2 MHz, CD_2Cl_2): $\delta = -15.3 (\nu_{1/2} = 45 \pm 20$ Hz). – ^{19}F NMR (563.6 MHz, CD_2Cl_2): $\delta = -133.0$ (m, 6F, Ph^F_{ortho}), −165.0 (m, 3F, Ph^F_{para}), −167.7 (m, 6F, Ph^F_{meta}).

*4,5-Diphenyl-1-methylimidazole (**12**) [20]*

1,1-dimethylhydrazine (3.00 g, 3.79 ml, 23.8 mmol) was added to benzil (5.00 g, 23.8 mmol) in ethanol (10 ml). The reaction flask was sealed and heated to 110 – 120 °C for 5 hours. The generated precipitate was collected by filtration and recrystallized in ethanol (5 ml) (white solid). Yield: 4.52 g (81%). – ^1H NMR (200.1 MHz, $CDCl_3$): $\delta =$ 7.55 (s, 1H, CH), 7.50 – 7.13 (m, 10H, Ph), 3.46 (s, 3H, CH_3). – $^{13}C\{^1H\}$ NMR (50.3 MHz): $\delta = 138.3$ (CH), 137.4, 134.6 (each Ph), 130.6 (C_{ipso}), 128.9, 128.5, 128.1, 126.6, 126.3 (Ph), 32.1 (CH_3).

X-ray crystal structure analysis of **10**

Formula $C_{28}H_{30}N_4Zr_2 \cdot 2CH_3B(C_6F_5)_3$, $M = 1659.05$, light yellow crystal $0.20 \times 0.10 \times 0.03$ mm. Crystal data: $a =$ 11.751(1), $b = 13.080(1)$, $c = 20.057(1)$ Å, $\beta = 98.85(1)°$, $V = 3046.1(4)$ Å^3, $\rho_{calc} = 1.809$ g cm^{-3}, $\mu = 4.83$ cm^{-1}, $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14). Data collection and structure refinement: Mo-K$_\alpha$ ($\lambda = 0.71073$ Å), $T = 198$ K, ω and φ scans, empirical absorption correction *via* SORTAV (0.910 $\leq$ transmission factor $\leq$ 0.986), 10398 reflections collected ($\pm h, \pm k, \pm l$), $[(sin\,\theta)/\lambda] = 0.59$ Å^{-1}, 5351 independent ($R_{int} = 0.087$) and 3365 observed reflections [$I \geq 2\sigma(I)$], 471 refined parameters, $R = 0.089$, $wR^2 =$ 0.252, max. residual electron density 0.64 (−0.61) e Å^{-3}. Hydrogen atom positions were calculated and hydrogen atoms refined as riding atoms. The results of the analysis are less accurate due to the small crystals of poor quality.

X-ray crystal structure analysis of **12**

Formula $C_{16}H_{14}N_2$, $M = 234.29$, colourless crystal $0.50 \times 0.30 \times 0.05$ mm. Crystal data: $a = 11.563(1)$, $b = 8.935(1)$, $c = 12.135(1)$ Å, $\beta = 94.37(1)$, $V = 1250.1(2)$ Å^3, $\rho_{calc} = 1.245$ g cm^{-3}, $\mu = 5.74$ cm^{-1}, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14). Data collection and structure refinement: Cu-K$_\alpha$ ($\lambda = 1.54178$ Å), $T = 223$ K, $\omega/2\theta$ scans, empirical absorption correction *via* ψ scan data (0.762 $\leq$ transmission factor $\leq$ 0.972), 5071 reflections collected ($\pm h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2540 independent ($R_{int} = 0.028$) and 2094 observed reflections [$I \geq 2\sigma(I)$], 162 refined parameters, $R = 0.038$, $wR^2 = 0.106$, max. residual electron density 0.21 (−0.25) e Å^{-3}. Hydrogen atom positions were calculated and hydrogen atoms refined as riding atoms.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] a) K. Öfele, J. Organomet. Chem. **12**, P42 (1968); b) H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. **80**, 154 (1968); Angew. Chem. Int. Ed. **7**, 141 (1968); c) A. J. Arduengo III, R. L. Harlow and M. Kline, J. Am. Chem. Soc. **113**, 361 (1991); d) A. J. Arduengo II, H. V. R. Dias, R. L. Harlow and M. Kline, J. Am. Chem. Soc. **114**, 5530 (1992).

[2] Reviews: A. J. Arduengo III, Acc. Chem. Res. **32**, 913 (1999); b) W. A. Herrmann, C. Köcher, Angew. Chem. **109**, 2256 (1997); Angew. Chem. Int. Ed. **36**, 2162 (1997); c) T. Weskamp, P. W. Böhm, W. A. Herrmann, J. Organomet. Chem. **600**, 39 (2000); d) D. Bourissou, O. Guerret, F. P. Gabaï, G. Bertrand, Chem. Rev. **100**, 39 (2000).

[3] a) T. M. Trnka, R. H. Grubbs, Acc. Chem. Res. **34**, 18 (2001); b) W. A. Herrmann, Angew. Chem. **114**, 1342 (2002); Angew. Chem. Int. Ed. **41**, 1290 (2002).

[4] a) M. Niehues, G. Erker, G. Kehr, P. Schwab, R. Fröhlich, O. Blacque, H. Berke, Organometallics **21**, 2905 (2002); b) see also: W. A. Herrmann, K. Öfele, M. Elison, F. E. Kühn, P. W. Roesky, J. Organomet. Chem. **480**, C7 (1994); c) N. Kuhn, T. Kratz, D. Bläser, R. Boese, Inorg. Chim. Acta **238**, 179 (1995); d) M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, J. Organomet. Chem., in press.

[5] A. Wacker, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. 843 (1998).

[6] D. Vagedes, G. Kehr, D. König, K. Wedeking, R. Fröhlich, G. Erker, C. Mück-Lichtenfeld, S. Grimme, Eur. J. Inorg. Chem. 2015 (2002).

[7] D. Röttger, G. Erker, R. Fröhlich, S. Kotila, J. Organomet. Chem. **518**, 17 (1996).

[8] a) A. G. Massey, A. J. Park, F. G. A. Stone, Proc. Chem. Soc. London, 212 (1963); b) A. G. Massey, A. J. Park, J. Organomet. Chem. **2**, 245 (1964); c) A. G. Massey, A. J. Park, in R. B. King and J. J. Eisch (eds): Organometallic Syntheses, Vol. 3, p. 461, Elsevier, New York (1986); d) J. L. W. Pohlmann, F. E. Brinckmann, Z. Naturforsch. **20b**, 5 (1965); e) J. Lambert, S. Zhang, S. M. Ciro, Organometallics **13**, 2430 (1994).

[9] a) X. Yang, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. **116**, 10015 (1994); b) Review: E. Y.-X. Chen, T. J. Marks, Chem. Rev. **100**, 1391 (2000).

[10] D. Röttger, G. Erker, M. Grehl, R. Fröhlich, Organometallics **13**, 3897 (1994).
[11] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans S1 (1989).
[12] a) G. Erker, R. Zwettler, C. Krüger, R. Schlund, I. Hyla-Kryspin, R. Gleiter, J. Organomet. Chem. **346**, C15 (1988); b) I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwettler, G. Erker, Organometallics **9**, 517 (1990); c) G. Erker, R. Zwettler, C. Krüger, I. Hyla-Kryspin, R. Gleiter, Organometallics **9**, 524 (1990); d) P. J. Walsh, F. J. Hollander, R. G. Bergmann, J. Am. Chem. Soc. **112**, 894 (1990).
[13] G. Erker, R. Zwettler, C. Krüger, Chem. Ber. **122**, 1377 (1989).
[14] a) I. I. Padilla-Martinez, M. de Jesus Rosalez-Hoz, R. Contreras, S. Kerschl, B. Wrackmeyer, Chem. Ber. **127**, 343 (1994) ; b) F. Bonati, L. A. Oro, M. T. Pinillos, C. Tejel, J. Organomet. Chem. **465**, 267 (1994); c) A. Wacker, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. 789 (1999).
[15] TURBOMOLE (Vers. 5.3): R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss. Universität Karlsruhe (2000).
[16] a) A. D. Becke, J. Chem. Phys. **84**, 4524 (1986); b) J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[17] (TZVP-Basissatz): A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. **100**, 5829 (1994).
[18] A. Hassner, P. Munger, B. A. Belinka, Tetrahedron Lett. **23**, 699 (1982).
[19] J. R. Surtress, J. Chem. Soc., Chem. Commun. 567 (1965).
[20] W. L. Collibee, J.-P. Anselme, Tetrahedron Lett. **26**, 1595 (1985).
[21] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Letters **240**, 283 (1995).
[22] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta **77**, 123 (1990).