

Highly Electron-Deficient Neutral and Cationic Zirconium Complexes with Bis(*s*-aryl)amine Dianionic Tridentate Ligands[†]

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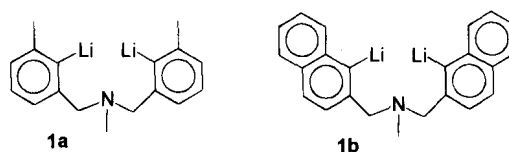
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Summary: A highly electron-deficient zirconium dibenzyl complex with a dianionic tridentate bis(*s*-aryl)amine ligand, $[(C_{10}H_6CH_2)_2NMe]Zr(CH_2Ph)_2$, was prepared and structurally characterized. The cationic benzyl derivative with the $[B(C_6F_5)_4]^-$ counterion catalytically polymerizes olefins, whereas with the $h^0-[PhCH_2B(C_6F_5)_3]^-$ counterion the system is inactive.

Chelating dianionic diamido ligands are successfully being used as ancillary ligands for group 4 metals. Both bidentate¹ and tridentate² (amido-amine/amido-ether) varieties are known, and both types of ligands give rise to complexes with interesting performance in the catalytic polymerization of olefins when activated with the appropriate activators. For example, several well-defined systems are now known to effect the living polymerization of 1-hexene.^{1e,2e} The amido ligand is a good *p*-donor when attached to an electron-deficient metal center, and this donation reduces the electron deficiency of the metal center. The effect of ligand-to-metal *p*-donation on the reactivity of the metal center is not fully clear as yet, but in some cases evidence is present that it can be deleterious to the reactivity of the cationic species active in olefin polymerization. For example, in $[(pyridyl-alkoxide)_2ZrCH_2Ph]^+$ species olefin polymerization activity was found to be enhanced by the presence of electron-withdrawing substituents on the alkoxide α -carbon, prompting the suggestion that in these systems the metal center may not be sufficiently electrophilic to obtain high activities.³

One approach to design ancillary ligand systems that lack this strong ligand-to-metal *p*-donation is to use ligands with C-based (rather than N-based) anionic moieties. The use of C-anion-based ancillary ligands requires the relative inertness of the C-M bonds of the ligand relative to those of the other hydrocarbyl groups attached to the metal where reactivity is desired. In general, M-C(sp²) bonds are less reactive than M-C(sp³) bonds, and because in M-(*s*-aryl) complexes *p*-donation from the aryl *p*-system to the metal is of relatively minor importance,⁴ we chose the *s*-aryl anion as an anionic functionality in our ligand system. The ligands of the type $[(s\text{-aryl})-o\text{-CH}_2]_2NMe$ are readily obtained by NBS bromination of the methyl group in *o*-methylbromobenzenes followed by reaction of the bromomethylene functionality with MeNH₂ and subsequent Br/Li exchange with *n*-BuLi. The ligands described here use 2-bromoxylene or 2-methyl-1-bromonaphthalene as starting material to yield the dilithium salts **1a** and **1b**. A



similar ligand type, with unsubstituted aryl groups and a more heavily substituted amine, prepared along the same route, was recently reported by Corriu *et al.* for use in the synthesis of Si compounds.⁵

Reaction of the dilithium salt of the *o*-Me-substituted ligand (**1a**) with ZrCl₄ yielded colorless crystals of the complex $[(o\text{-Me-C}_6\text{H}_3\text{CH}_2)_2NMe]_2Zr$ (**2**),⁶ with two dianionic ligands bound to one Zr atom, irrespective of the ligand-to-Zr ratio employed. Thus, it appears that a strong preference for formation of these tetraaryl com-

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(2) (a) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. (b) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, 501, 333. (c) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, 15, 2672. (d) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, 16, 1491. (e) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, 119, 3830. (f) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

(3) Tsukehara, T.; Swenson, D.; Jordan, R. F. *Organometallics* **1997**, 16, 3303.

(4) Both $[ZrMe_6]^{2-}$ and $[ZrPh_6]^{2-}$ show trigonal-prismatic rather than octahedral geometries, which is attributed to the lack of ligand-to-metal *p*-donation. See: (a) Morse, P. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4114. (b) Girolami, G. S.; Nelsen, M. J. *Abstracts of Papers*, 213th National Meeting of the American Chemical Society, San Francisco, April 1997; American Chemical Society: Washington, DC, 1997; INOR 710.

(5) Carré, F. H.; Corriu, R. J. P.; Lanneau, G. F.; Merle, P.; Soulaire, F.; Yao, J. *Organometallics* **1997**, 16, 3878.

(6) ¹H NMR (C₆D₆, 25 °C) δ 1.97 (s, Me), 2.28 (s, Me), 2.37 (s, Me), 2.64 and 5.03 (d, $J_{HH} = 14$ Hz, NCH₂), 2.90 and 3.99 (d, $J_{HH} = 14$ Hz, NCH₂), 6.78, 6.83, 6.94, 6.99 (all d, $J_{HH} = 7.3$ –7.6 Hz, Ar H), 7.10 (t, Ar H, other signal overlapped by solvent); ¹³C{¹H} NMR (C₆D₆, 25 °C) δ 26.11 and 26.30 (Ar Me), 48.04 (NMe), 61.54 and 64.90 (NCH₂), 122.38, 123.06, 126.98, 127.22 (Ar CH, other two resonances overlapped by solvent), 144.48, 144.64, 145.27, 146.14 (Ar C-C), 195.05, 195.87 (Ar C-Zr).

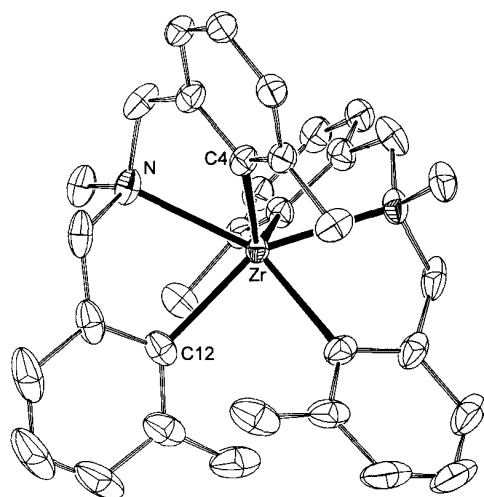


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Zr-C(3) = 2.299(2), Zr-C(12) = 2.328(1), Zr-N = 2.402(1), N-Zr-C(3) = 71.28(6), N-Zr-C(3a) = 151.18(6), N-Zr-C(12) = 71.74(5), N-Zr-C(12a) = 87.95(5), N-Zr-N(a) = 135.69(5), C(3)-Zr-C(3a) = 85.18(6), C(3)-Zr-C(12) = 114.80(6), C(3)-Zr-C(12a) = 105.20(5), C(12)-Zr-C(12a) = 124.85(5).

plexes is present when insufficient steric hindrance is introduced in the ligand. An X-ray structure determination of **2**⁷ (Figure 1) shows that the ligands adopt a pseudo-facial geometry (the angle between the two ZrNCH₂CC least-squares planes is 117°). The molecule contains a C₂ symmetry axis. The Zr-C(aryl) distances of 2.299(2) and 2.328(1) Å are quite normal for Zr-(*s*-aryl) bonds (e.g. 2.291 Å in (C₅Me₄H)₂Zr(Cl)Ph)⁸ and are substantially longer than the Zr-N(amido) distances in chelating diamido Zr complexes (around 2.05–2.10 Å).^{1,2} The Zr-N distance of 2.402(1) Å is short compared to the Zr-amine distance in the diamido-amine complex {[Me₃SiN(CH₂CH₂)₂NSiMe₃]₂Zr(BH₄)₂} (2.561(4) Å).^{2a} The coordination geometry around Zr is considerably distorted due to the geometric constraints of the ligand, but the observed bond angles around Zr suggest it is best described as a distorted trigonal prism (compare, for example, with [Li(TMEDA)]₂[ZrMe₆]^{4a}).

To obtain complexes of the type [(*s*-aryl-CH₂)₂NMe]₂ZrR₂, reactions of **1a** and **1b** with Zr(CH₂Ph)₂Cl₂(Et₂O)₂ were performed. Whereas the reaction of **1a** produced a mixture of products (including **2**), the addition of Zr(CH₂Ph)₂Cl₂(Et₂O)₂ to a solution of the dilithium salt **1b** in diethyl ether produces the dibenzyl zirconium complex [(C₁₀H₆CH₂)₂NMe]Zr(CH₂Ph)₂ (**3**),¹⁰ which was obtained as yellow crystals in 30% isolated yield after recrystallization from diethyl ether. The ¹H NMR spectrum of **3** shows one AB system for the ligand CH₂ groups and two singlets for two distinct benzyl CH₂

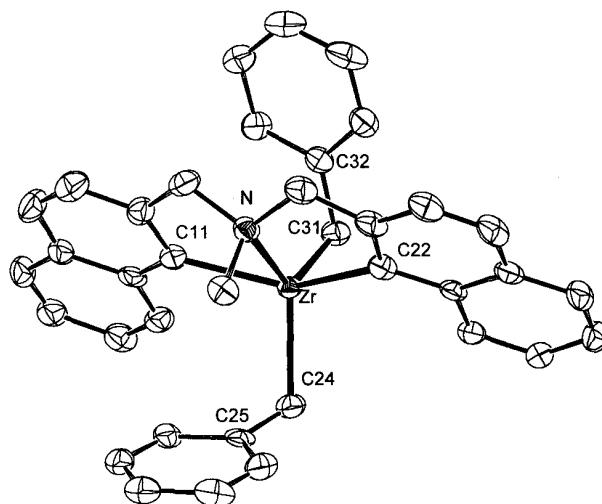


Figure 2. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Zr-N = 2.376(5), Zr-C(11) = 2.296(6), Zr-C(22) = 2.292(6), Zr-C(24) = 2.261(7), Zr-C(31) = 2.218(6), Zr...C(32) = 2.824(8), C(11)-Zr-C(22) = 141.8(2), C(24)-Zr-C(31) = 112.4(3), N-Zr-C(11) = 71.3(2), N-Zr-C(22) = 71.4(2), N-Zr-C(24) = 122.7(2), N-Zr-C(31) = 124.9(2), Zr-C(24)-C(25) = 110.1(4), Zr-C(31)-C(32) = 97.7(4).

groups. This indicates a structure in solution where a mirror plane is present containing the Zr, N, and benzyl CH₂ groups. The ¹³C NMR spectrum of **3** shows two benzyl methylene carbon resonances with two different ¹J_{CH} coupling constants (*d* 82.23 ppm, 131.9 Hz; *d* 85.46 ppm, 119.6 Hz). This suggests that in this highly electron-deficient compound (formally 10 valence electrons) one of the benzyl groups may have some *h*²-bonding character. The compound is thermally stable for days in benzene solution at ambient temperature.

An X-ray structure determination of **3** (Figure 2)¹¹ revealed that the complex has a strongly distorted trigonal bipyramidal geometry with the *s*-aryl carbons in the axial positions and the N and benzyl CH₂ carbons in the plane. The structure of **3** can best be compared with that of the recently reported complex {[(*c*-C₆H₁₁)NSiMe₂]₂O}Zr(CH₂Ph)₂ (**4**) with a diamido-ether ligand, which has a similar distorted tbp geometry.^{2f} As indicated by the ¹³C NMR spectra, one of the non-equivalent benzyl groups in **3** has *h*² character: the Zr-C(31)-C(32) angle of 97.7(4)° is significantly smaller than the Zr-C(24)-C(25) angle of 110.1(4)°. Remarkably, this deviation from the tetrahedral angle around

(10) **3**: ¹H NMR (C₆D₆, 25 °C) *d* 1.88 (s, NMe), 3.21 (s, ZrCH₂), 3.55 (s, ZrCH₂), 3.29 and 3.86 (d, ²J_{HH} = 14.3 Hz, NCH₂), 6.18 (d, ³J_{HH} = 7.0 Hz, Bz *o*-H), 6.4–6.5 (m, Bz *m*-H and *p*-H), 6.61 (d, ³J_{HH} = 6.3 Hz, Bz *o*-H), 6.98 (d, ³J_{HH} = 8.0 Hz, Ar H), 7.44 (t, ³J_{HH} = 7.5 Hz, Ar H), 7.43 (t, Ar H), 7.45 (d, Ar H), 7.85 (d, ³J_{HH} = 8.0 Hz, Ar H), 9.13 (d, ³J_{HH} = 8.1 Hz, Ar H). ¹³C NMR (C₆D₆, 25 °C) *d* 43.43 (q, J_{CH} = 147.8 Hz, NMe), 71.51 (t, J_{CH} = 136.7 Hz, NCH₂), 82.23 (t, J_{CH} = 131.9 Hz, ZrCH₂), 85.45 (t, J_{CH} = 119.6 Hz, ZrCH₂), 121.59, 122.35, 123.36, 125.14, 126.17, 127.43, 128.41, 128.47, 129.52, 129.80, 129.83, 131.06 (all d, Ar CH), 132.65, 136.59, 141.11, 143.94, 146.48 (all s, Ar C), 192.07 (s, Ar C-Zr).

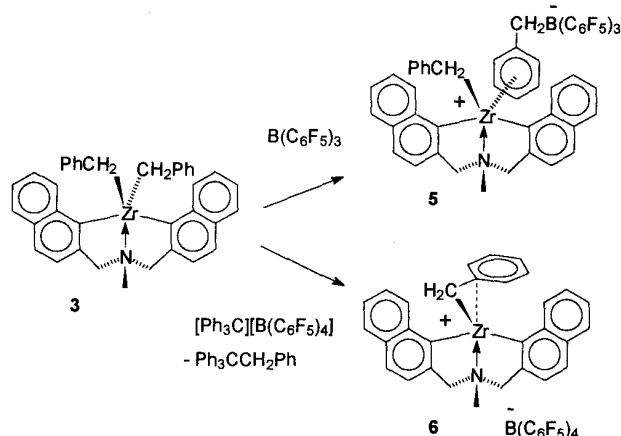
(11) Crystal data for **3**: C₃₇H₃₃NZr, *M*_r = 582.90, monoclinic, *P*2₁/c, *a* = 16.587(3) Å, *b* = 11.016(1) Å, *c* = 15.870(2) Å, *b* = 105.96(3)°, *V* = 2788.0(9) Å³, *Z* = 4, *D*_c = 1.389 g cm⁻³. Data were collected on an Enraf-Nonius CAD-4F diffractometer at 130 K with *I*(Mo Kα radiation) = 0.710 73 Å. The structure was solved by Patterson methods and extended by direct methods applied to difference structure factors. A final refinement converged at *R*_w(*F*²) = 0.1910 for 5466 reflections with *F*_o² ≥ 0 and *R*(*F*) = 0.0717 for 3615 reflections with *F*_o ≥ 4.0σ(*F*_o) and 484 parameters.

(7) Crystal data for **2**: (C₁₇H₁₉N)₂Zr, *M*_r = 565.92, monoclinic, *P*2₁/n, *a* = 8.718(1) Å, *b* = 9.278(1) Å, *c* = 17.567(3) Å, *b* = 100.12(2)°, *V* = 1398.8(3) Å³, *Z* = 2, *D*_c = 1.344 g cm⁻³. Data were collected on an Enraf-Nonius CAD-4F diffractometer at 130 K with *I*(Mo Kα radiation) = 0.7107 3 Å. The structure was solved by Patterson methods and extended by direct methods applied to difference structure factors. A final refinement converged at *R*_w(*F*²) = 0.0667 for 3375 reflections with *F*_o² ≥ 0 and *R*(*F*) = 0.0243 for 3204 reflections with *F*_o ≥ 4.0σ(*F*_o) and 244 parameters.

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Scheme 1



the h^2 -benzyl methylene group is less pronounced than in the diamido-ether dibenzyl complex **4** (where this angle is $84.9(2)^\circ$). It is presently unclear if this is because in the two complexes the benzyls have a different geometric orientation or if this is a consequence of the electronic differences between the two tridentate ligands. In **3** both benzyl phenyl groups are pointing outward (*exo,exo*), whereas in **4** the phenyl group of the h^2 -benzyl is pointing inward (*endo,exo*), thus having a different orbital overlap with the Zr center. In this respect it may be noted that in **3** the two Zr-CH₂ distances are significantly different (Zr-C(31) being relatively short) but that for **4** these are essentially the same.

The dibenzyl complex **3** reacts with the Lewis acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 or $\text{C}_6\text{D}_5\text{Br}$ solvent by abstraction of one of the benzyl groups to give the ionic species $\{[(\text{C}_{10}\text{H}_6\text{CH}_2)_2\text{NMe}]\text{Zr}(\text{CH}_2\text{Ph})\}[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$ (**5**; Scheme 1).¹² The NMR characteristics of the anion in **5** suggest that it is bound to the cationic metal center

through an h^6 interaction with the phenyl group of the anion.¹³ The Zr-benzyl group in **5** is h^1 -bound, as seen from the $^1J_{\text{CH}}$ value of 127 Hz for the methylene group. This is distinct from the ionic species $\{[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{NSiMe}_3]\text{ZrCH}_2\text{Ph}\}[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$,^{2c} with a dianionic tridentate diamido-amine ligand, where a solvent-separated ion pair is formed and the benzyl group is h^2 -bound. It shows that the cationic metal center in **5** is sterically less encumbered than in the diamido compound. The anion in **5** appears to be quite strongly bound, as in $\text{C}_6\text{D}_5\text{Br}$ solution the compound remains unreacted in the presence of ethene or propene at ambient temperature and pressure.

Reaction of **3** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{D}_5\text{Br}$ solution produces $\text{Ph}_3\text{CCH}_2\text{Ph}$ and another ionic species, $\{[(\text{C}_{10}\text{H}_6\text{CH}_2)_2\text{NMe}]\text{ZrCH}_2\text{Ph}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**6**; Scheme 1).¹⁴ The ^{13}C NMR spectrum of **6** shows that now the remaining benzyl group is h^2 -bound (benzyl CH_2 $^1J_{\text{CH}} = 141$ Hz) to Zr, as expected when a weakly coordinating anion is employed. In solution, **6** decomposes gradually at ambient temperatures over a few hours. As seen in NMR tube experiments, complex **6** now polymerizes both ethene and propene. In an autoclave experiment (bromobenzene solvent, ambient temperature, 4 bar, 30 min run time) propene was polymerized at a modest rate of $26 \text{ kg mol}^{-1} \text{ h}^{-1}$ to give atactic polypropene. GPC analysis showed that the product is not fully monomodal, however, with $M(\text{top})$ of the main distribution at 21 000 and a shoulder at higher molecular weight. Further investigations will focus on determining the properties of the primary catalyst and the possibilities for competitive insertion into the Zr-C(sp³) and Zr-C(sp²) bonds in complex **6**.

Supporting Information Available: Text giving experimental procedures and characterization data for the reported compounds and text, tables, and figures giving details of the X-ray structure determinations of **2** and **3** (33 pages). Ordering information is given on any current masthead page.

OM980358S

(12) Selected NMR data for **5**: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, 25 $^\circ\text{C}$) δ 2.11 (s, NMe), 2.88 (br, BCH_2), 3.05 (s, ZrCH_2), 3.46 and 4.05 (d, $^2J_{\text{HH}} = 14.4$ Hz, NCH_2), 6.13 (t, $J = 7.6$ Hz, 3H, BBz *m*-H), 6.43 (t, $J = 7.3$ Hz, 1H, BBz *p*-H), 6.51 (d, $J = 7.8$ Hz, BBz *o*-H), 6.85 (t, $J = 7.3$ Hz, 2H, ZrBz *m*-H), 6.96 (t, $J = 7.3$ Hz, 1H, ZrBz *p*-H), 7.03 (d, $J = 7.3$ Hz, 2H, ZrBz *o*-H); ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$, 25 $^\circ\text{C}$) δ 30 (br, BCH_2), 47.65 (q, $J_{\text{CH}} = 138.0$ Hz, NMe), 72.05 (t, $J_{\text{CH}} = 138.0$ Hz, NCH_2), 92.93 (t, $J_{\text{CH}} = 127.2$ Hz, ZrCH_2), 190.94 (s, Ar C-Zr); ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$, 25 $^\circ\text{C}$) δ -132.82 (d, $^3J_{\text{FF}} = 21$ Hz, *o*-F), -162.31 (t, $^3J_{\text{FF}} = 21$ Hz, *p*-F), -166.72 (t, $^3J_{\text{FF}} = 21$ Hz, *m*-F), $\Delta d(p-m) = 4.41$ ppm.

(13) See for example ref 2c and: Sinnema, P.-J.; Liekelema, K.; Staal, O. K. B.; Hessen, B.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1998**, 128, 143.

(14) Selected NMR data for **6**: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, 25 $^\circ\text{C}$) δ 2.66 (s, NMe), 2.98 (s, ZrCH_2), 3.99 and 4.51 (d, $^2J_{\text{HH}} = 15.8$ Hz, NCH_2); ^{13}C NMR ($\text{C}_6\text{D}_5\text{Br}$, 25 $^\circ\text{C}$) δ 50.20 (q, $J_{\text{CH}} = 141.6$ Hz, NMe), 65.34 (t, $J_{\text{CH}} = 140.4$ Hz, NCH_2), 90.65 (t, $J_{\text{CH}} = 141.6$ Hz, ZrCH_2), 198.85 (s, Ar C-Zr).