Zirconium alkyl and borohydride complexes stabilized by a sterically demanding anionic organic amide. The crystal structures of $ZrMeL_3$ (2) and $Zr(BH_4)L_3$ (3) (L = $(3,5\text{-}Me_2Ph)N(Ad)$; Ad = adamantyl)

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Abstract: The lithium amide $[3,5\text{-}Me_2PhN(Ad)]Li\cdot Et_2O$ (**L**) reacts with $ZrCl_4(THF)_2$ to give $ZrClL_3$. Reactions of $ZrClL_3$ with MeLi and $NaBH_4$ produce the corresponding $ZrMeL_3$ (**2**) and $Zr(BH_4)L_3$ (**3**), respectively. The molecular structures of **2** and **3** were determined by X-ray crystallography. Crystal data are as follows. **2**: $C_{55}H_{75}N_3Zr$, FW 869.45, orthorhombic, *Pcab*; a = 19.2436(3) Å, b = 45.9342(4) Å, c = 21.2935(3) Å, V = 18822.2(4) Å^3, Z = 8; **3**: $C_{54}H_{76}BN_3Zr$, FW 869.25, orthorhombic; *Pbc*21, a = 11.5399(3) Å, b = 19.4091(4) Å, c = 20.4471(5) Å, V = 4579.72(19) Å^3, Z = 4.

Key words: zirconium, amide, alkyl, borohydride, structure.

Résumé : L'amide lithié $[3,5\text{-}Me_2PhN(Ad)]Li\cdot Et_2O$ (**L**) réagit avec le $ZrCl_4(THF)_2$ pour donner du $ZrClL_3$. Les réactions du $ZrClL_3$ avec le MeLi et le $NaBH_4$ conduisent respectivement au $ZrMeL_3$ (**2**) et $Zr(BH_4)L_3$ (**3**). On a déterminé les structures moléculaires des composés **2** et **3** par diffraction des rayons X. Les données crystallographiques sont les suivantes : **2** : $C_{55}H_{75}N_3Zr$; PF : 869,45; orthorhombique; *Pcab*; a = 19,2436(3), b = 45,9342(4) et c = 21,2935(3) Å, V = 18822,2(4) Å^3; Z = 8; **3** : $C_{54}H_{76}BN_3Zr$; PF : 869,25; orthorhombique; *Pbc*21; a = 11,5399(3), b = 19,4091(4) et c = 20,4471(5) Å; V = 4579,72(19) Å^3; Z = 4.

Mots clés : zirconium, amide, alkyle, borohydrure, structure.

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Introduction

Among early transition metals, zirconium is certainly the element that has received very special attention as demonstrated by the massive organometallic chemistry that has been developed for this metal. The extensive literature available describes an impressive variety of transformations (1), from metal-promoted organic synthesis (2), to Ziegler–Natta catalysis (3), olefin isomerization (4), insertion reactions (5), C—N bond activation (6), C_1 chemistry (7), etc. Another unique characteristic of zirconium, which is also common to the other group IV metals, is that the majority part of its chemistry was developed with the help of cyclopentadienyl and related ligand systems. Therefore, attempts to explore the reactivity of these metals with alternative ligands is the next and most obvious development in this field. This is certainly the key to understanding the strong revival of interest, which can be observed in the recent literature, for chemistry with non-Cp ligands of these metals and of zirconium in particular. The employment of sterically demanding alkoxides and aryloxides has already proved to be a useful strategy for a number of transformations (8). What remains relatively unexplored for zirconium is the chemistry of the lower oxidation states. The extreme reactivity of low-valent zirconium and the limited resistance of the traditional ligand systems to strong reducing agents (9) is probably the cause of this lacuna in the literature.

Nitrogen donor based ligands (formamidinate, amides, porphyrinogens, etc.) have been shown to be rather versatile in the chemistry of low-valent early transition metals (10), allowing the stabilization of the low oxidation states (11) and displaying a reduced possibility of being involved in the reactivity of the metal center. In addition, what makes these ligands particularly interesting is the possibility of easily adjusting the electronic features and steric hindrance around the transition metal via a virtually unlimited choice of organic substituents attached to the nitrogen donor atom. In the chemistry of zirconium, Fryzuk et al. have demonstrated that the employment of bulky chelating amide–phosphine ligand systems enables the stabilization of rare Zr(III) derivatives (12) and the coordination of highly reduced dinitrogen (13). More recently, anionic organic amides with a particularly large steric hindrance have been employed for a number of

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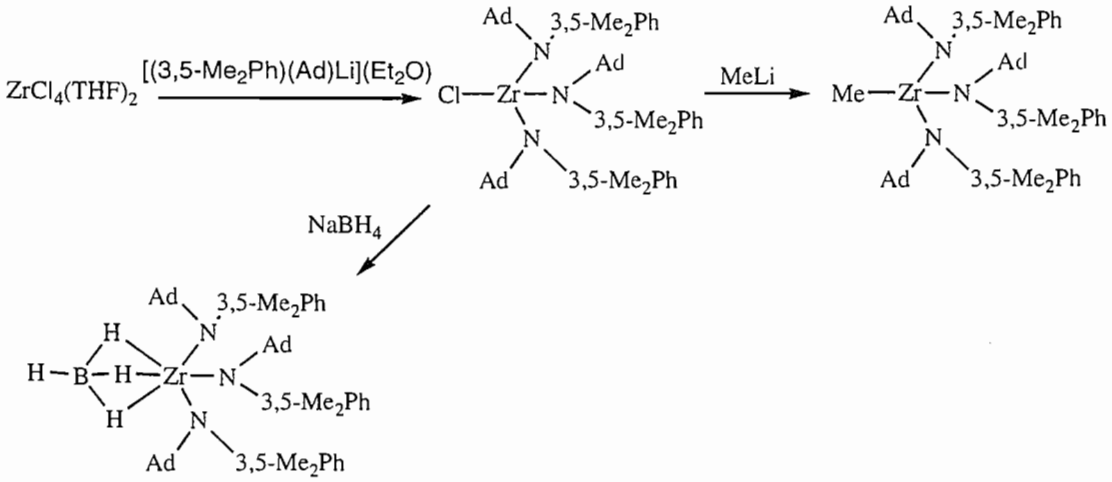
Scheme 1.



remarkable reactions that include dinitrogen cleavage (14), formation of stable and reactive nitrides (15), and assemblage of heterodimetallic structures (16).

The remarkable robustness of these ligands has prompted us to attempt its employment for preparing zirconium complexes that may work as substrates for further reduction towards lower oxidation states or for the trapping of reactive functions (hydride, alkyl, etc.). The large-scale preparation in our lab of the sterically demanding [3,5-Me_2PhN(Ad)] anion (17) has enabled the preparation and characterization of a number of transition metal complexes in the medium oxidation state and the trapping of rare functions. Herein we describe the result of our attempts to use this ligand in zirconium chemistry.

Results and discussion

The reaction between [3,5-Me_2PhN(Ad)]Li·Et_2O and [$ZrCl_4(THF)_2$] in diethyl ether at room temperature resulted in the formation of a pale yellow solution from which [ZrCl{3,5-Me_2PhN(Ad)}$_3$] (**1**) was isolated in moderate yield as a white crystalline solid (Scheme 1).

The product of the reaction was remarkably insensitive to the stoichiometric ratio between the two reagents since similar reactions with different ratios invariably yielded the same compound. The formula of compound **1** was based on chlorine and combustion analyses. The ^{1}H and ^{13}C NMR spectra indicate the presence of a rather symmetric ligand environment in the compound. Two different methylene resonances are observed in equal ratio for the adamantyl group, while a single resonance is observed for the two methyl groups attached to the aryl rings. Two lines present in the aromatic region in a 2:1 ratio are assigned to the *ortho* and *meta* protons of the aryl rings.

Reaction of **1** with methyllithium in ether resulted in the precipitation of lithium chloride and formation of the corresponding zirconium methyl derivative, [ZrMe{3,5-Me_2PhN(Ad)}$_3$] (**2**) (Scheme 1). Compound **2** was isolated in moderate yield from hexane as colorless and very air-sensitive crystals. The infrared spectra of compounds **1** and **2** were nearly identical, thus suggesting that the two complexes may be isostructural. The ^{1}H NMR spectrum of **2** displays amide ligand resonances similar to those observed for **1** with slightly different chemical shifts. The Me group resonance was clearly visible as a sharp new singlet at −0.01 ppm. Similar considerations apply to the ^{13}C NMR spectrum, which shows only one set of ligand resonances, slightly shifted with respect to those of complex **1**, and one additional resonance at 37.4 ppm. DEPT experiments assigned this resonance to the methyl group. The assignment was further supported by HQMC experiments, which showed correlation of the ^{1}H resonance at −0.01 ppm with the ^{13}C NMR resonance of 37.4 ppm. Complex **2** is thermally stable and chemically inert. It does not react with molecular H_2 and carbon monoxide at room temperature and atmospheric pressure, and it is stable for 24 h in refluxing benzene.

The structure of compound **2** (Fig. 1) was elucidated by a single-crystal X-ray diffraction analysis. The coordination geometry around zirconium is distorted tetrahedral and is defined by three nitrogen atoms of the three amide ligands and one methyl group. The bond distances (Zr1—N1 = 2.083(3) Å, Zr1—N2 = 2.072(4) Å, Zr1—N3 = 2.089(4) Å) and angles (N1-Zr1-N2 = 111.52(14)°, N1-Zr1-N3 = 109.57(13)°, N2-Zr1-N3 = 114.82(14)°), as well as the Zr—C bond distance (Zr1—C1 = 2.258 (5) Å) are in the expected range. The amide nitrogen atoms possess the characteristic trigonal planar geometry (sums of the angles around the nitrogen atoms are close to 360°), which indicates the presence of a Zr—N multiple bond character. Relevant bond distances and angles are given in Table 1.

The surprising and unexpected chemical inertness of complex **1** suggested that this particular ligand system may be versatile for the preparation of stable and terminal Zr-H functions. However, since the hydrogenolysis of **2** was not a viable method, we have explored other possible synthetic pathways such as chlorine replacement of **1** with hydridic reagents. Unfortunately, reactions of **1** with NaH, $NaHBEt_3$, Bu_3SnH, and $LiAlH_4$ proved to be unsuccessful since they led only to highly soluble and intractable materials or no reaction. In addition, the ^{1}H NMR spectra were rather complicated and possibly indicative of the presence of a mixture of products. Conversely, the reaction of **1** with an excess of $NaBH_4$ in THF resulted in the precipitation of NaCl and formation of the corresponding tetrahydroborate compound, [Zr(BH_4){3,5-Me_2PhN(Ad)}$_3$] (**3**), in good yield. The infrared spectrum

Fig. 1. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.

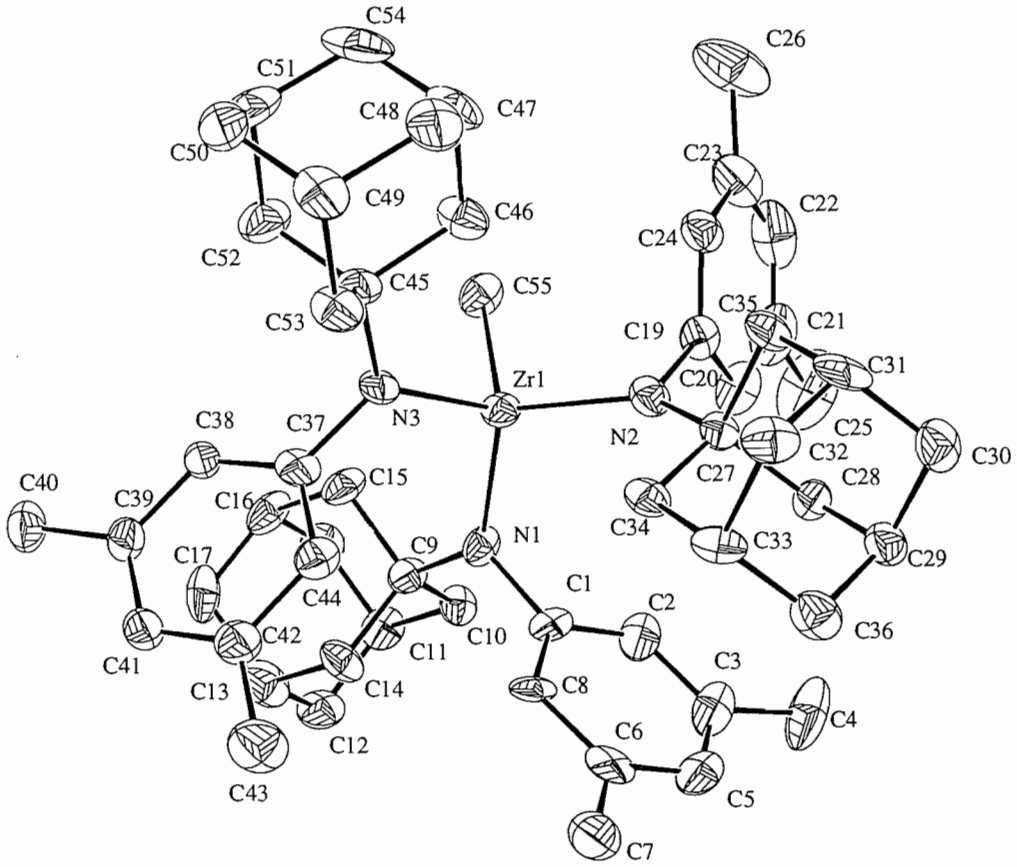


Table 1. Selected bond distances (Å) and angles (deg).

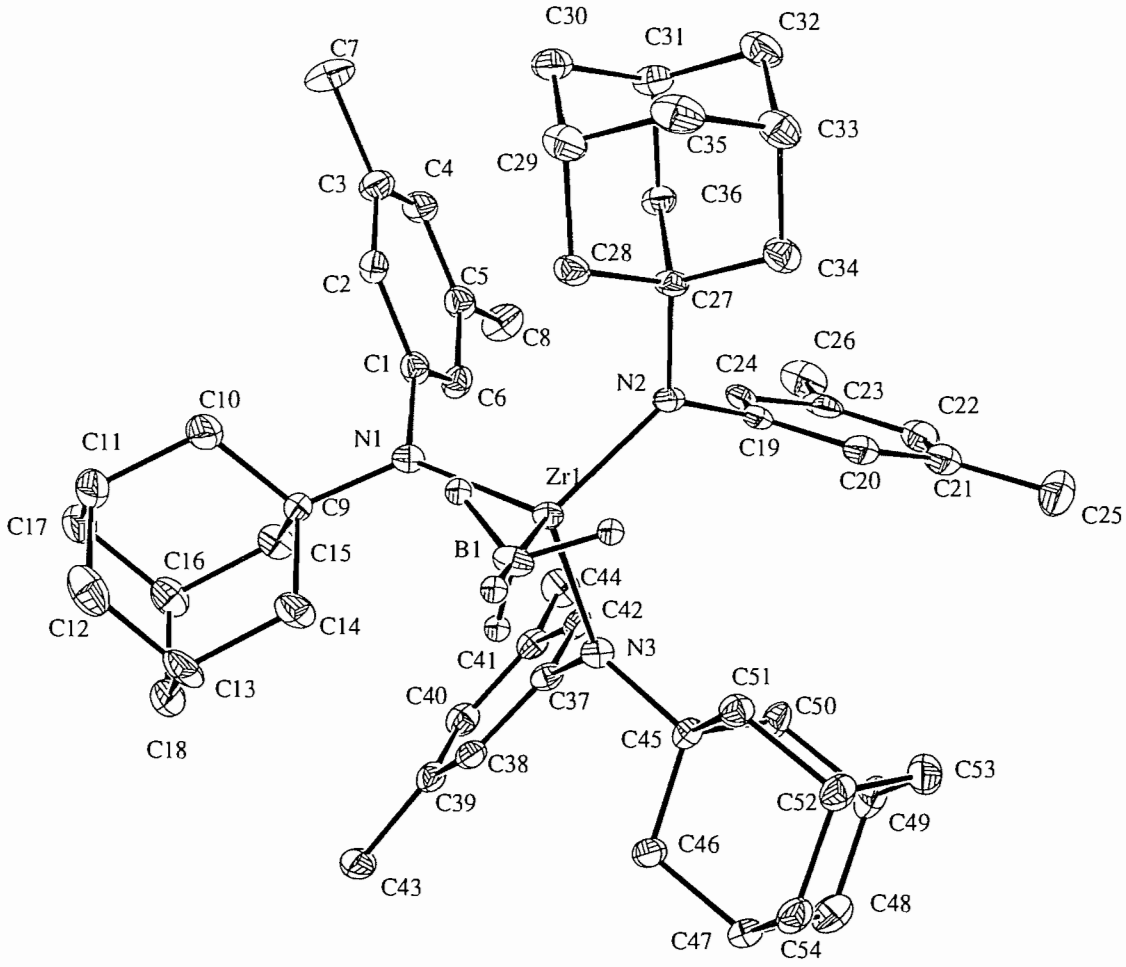
2	3
Zr1—N1 = 2.083(3)	Zr1—N1 = 2.071(3)
Zr1—N2 = 2.072(4)	Zr1—N2 = 2.066(3)
Zr1—N3 = 2.089(4)	Zr1—N3 = 2.072(3)
Zr1—C55 = 2.258(5)	Zr1—B1 = 2.400(4)
N1—C1 = 1.442(6)	Zr1—H = 2.16(4)
N1—C9 = 1.497(6)	Zr1—H = 2.21(4)
N1-Zr1-C55 = 105.26(15)	Zr1—H = 2.23(4)
N2-Zr1-C55 = 108.24(16)	N1-Zr1-N2 = 107.33(11)
N2-Zr1-N3 = 114.82(14)	N1-Zr1-B1 = 110.71(13)
N3-Zr1-N1 = 109.57(13)	B1-Zr1-N3 = 109.88(13)
C1-N1-C9 = 114.9(3)	N3-Zr1-N2 = 106.97(11)
Zr1-N1-C9 = 131.2(3)	C1-N1-C9 = 112.0(3)
Zr1-N1-C1 = 113.2(3)	C9-N1-Zr1 = 128.02(23)
N3-Zr1-C55 = 106.87(16)	N1-Zr1-N3 = 108.05(11)
N1-Zr1-N2 = 111.52(14)	Zr1-N1-C1 = 119.87(23)
	N2-Zr1-N3 = 106.97(11)

showed the characteristic absorptions of $[BH_4]^-$ as an intense sharp line at 2500 cm^{-1} (terminal B-H stretching) and broad doublet at 2172 cm^{-1} (B-H stretching). This pattern usually diagnoses a tridentate bonding mode for the $[BH_4]$ group. The ^1H NMR showed the resonance corresponding to tetrahydroborate as a broad singlet at 1.91 ppm, which nicely correlates with the ^{11}B resonance at −15.6 ppm in HQMC experiments. Attempts to transform complex **3** into terminal hydride by abstracting the BH_3 group with Me_3P or TMEDA were unsuccessful.

The structure of compound **3** was confirmed by an X-ray crystal structure (Fig. 2). The zirconium metal is coordinated to three amide ligands and one borohydride group. Similar to the case of complex **2**, the geometry around the metal center is distorted tetrahedral and is defined by the three nitrogen atoms (N1-Zr1-N2 = 107.3(1)°, N1-Zr1-N3 = 108.0(1)°, N2-Zr1-N3 = 107.0(1)°) of the three amide groups and one boron atom (N1-Zr1-B1 = 110.7(1)°, N2-Zr1-B1 = 113.7(1)°, N3-Zr1-B1 = 109.9(1)°). The Zr···B nonbonding distance (Zr1-B1 = 2.400(4) Å) is rather short, possibly indicating the presence of an η^3-bonding mode of the BH_4 group. The positions of the tetrahydroborate hydrogen atoms were yielded by difference Fourier maps, thus confirming the tridentate mode (Zr1—H55 = 2.16(4) Å, Zr1—H57 = 2.21(4) Å, Zr1—H58 = 2.23(4) Å). The relatively short Zr—N bond distances (Zr1—N1 = 2.071(3) Å, Zr1—N2 = 2.066(3) Å, Zr1—N3 = 2.072(3) Å) compare well with those of **2** and of other Zr–amide complexes present in the literature, and are consistent with the existence of a Zr—N multiple bond character.

In conclusion, with this work it was possible to prepare and characterize new zirconium alkyl and borohydride complexes supported by bulky amide ligands. These species were found to be remarkably stable and unreactive. At this stage, it is

Fig. 2. ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level.



tempting to attribute the surprising stability of these functions to either: (*i*) steric protection, which makes the reactive function inaccessible by incapsulating the metal; or (*ii*) the π-donating ability of the amide ligands that increases the covalency of the M—C and M—H bonds.

Experimental section

All the operations were performed under an inert atmosphere of a nitrogen-filled dry box or by using standard Schlenk techniques. $[ZrCl_4(THF)_2]$ (18) and $[3,5\text{-}Me_2PhN(Ad)]Li\cdot Et_2O$ (Ad = adamantyl) (17) were prepared according to reported procedures. Methyllithium and sodium borohydride (Aldrich) were used as received. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $[ZrCl\{3,5\text{-}Me_2PhN(Ad)\}_3]$ (1)

A suspension of $[ZrCl_4(THF)_2]$ (3.35 g, 8.88 mmol) in diethyl ether (150 mL) was stirred with $[3,5\text{-}Me_2PhN(Ad)]Li\cdot Et_2O$ (8.94 g, 26.65 mmol) at room temperature. After stirring for 24 h, the mixture was filtered to eliminate LiCl. After concentrating the filtrate to about 50 mL, colorless crystals of **1** were obtained upon allowing the solution to stand at –30°C for 8 h (5.20 g, 5.84 mmol, 66%). IR (Nujol mull, NaCl, cm^{-1}) *v*: 1599 s, 1585 s, 1356 m, 1343 w, 1303 s, 1290 s, 1188 w, 1151 s, 1106 w, 1088 w, 1067 s, 1029 s, 990 m, 977 w, 950 m, 924 s, 891 w, 851 m, 817 w, 787 w, 763 w, 710 s, 694 s, 682 m, 617 m. ^1H NMR (C_6D_6, 20°C, 500 MHz) δ: 6.82 (s, 2H, Ar), 6.80 (s, 1H, Ar), 2.30 (s, 6H, Me, Ar), 2.03 (bs, 6H, CH_2, Ad), 2.03 (bs, 3H, CH, Ad), 1.56 (q, 6H, CH_2, Ad). ^{13}C NMR (C_6D_6, 20°C, 125.7 MHz) δ: 144.5 (quaternary aryl), 137.4 (quaternary aryl), 130.7 (C-H aryl), 60.1 (quaternary Ad), 43.1 (CH_2, Ad), 36.8 (CH_2, Ad), 30.5 (CH, Ad), 21.7 (CH_3, aryl). Anal. calcd. for $C_{54}H_{72}ClN_3Zr$: C 72.89, H 8.16, N 4.72; found: C 73.52, H 8.00, N 4.85.

Preparation of $[ZrMe\{3,5\text{-}Me_2PhN(Ad)\}_3]$ (2)

A solution of methyllithium (0.80 mL, 1.4 M) in ether was added to a solution of **1** (1.0 g, 1.12 mmol) in the same solvent (80 mL). After stirring the mixture for 8 h at room temperature, the solvent was removed in vacuo. The residue was extracted with hexane (100 mL) and filtered to eliminate LiCl. Upon concentration to about 20 mL and cooling to −30°C for 24 h, colorless crystals of **2** were obtained (0.40 g, 0.46 mmol, 41%). IR (Nujol mull, NaCl, cm^{-1}) *v*: 1592 s, 1304 m, 1290 m, 1261 s, 1152 s, 1074 s, 1027 s, 950 m, 924 s, 848 w, 803 s, 710

Table 2. Crystal data and structure analysis results.[a]

	2	3
Empirical formula	$C_{55}H_{75}N_3Zr$	$C_{54}H_{76}BN_3Zr$
Formula weight	869.45	869.25
Space group	*Pcab*	*Pbc*21
a (Å)	19.2436(3)	11.5399(3)
b (Å)	45.9342(4)	19.4091(4)
c (Å)	21.2935(3)	20.4471(5)
V (Å^3)	18822.2(4)	4579.72(19)
Z	8	4
Radiation (Å)	0.70930	0.70930
T (°C)	−153	−153
D_{calcd} (g cm^{-3})	1.226	0.819
μ_{calcd} (mm^{-1})	0.27	0.25
R_w	0.077, 0.072	0.038, 0.040

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2}$.

m, 692 s. ^{1}H NMR (C_6D_6, 20°C, 500 MHz) δ: 7.01 (s, 6H, 2,6-CH, Ar), 6.82 (s, 3H, 4-CH, Ar), 2.34 (s, 18H, CH_3, Ar), 2.06 (s, 9H, CH, Ad), 2.00 (s, 18H, CH_2, Ad), 1.60 (s, 18H, CH_2, Ad), −0.01 (s, 3H, Zr-CH_3). ^{13}C NMR (C_6D_6, 20°C, 125.7 MHz) δ: 142.8 (quaternary aryl), 137.5 (quaternary aryl), 132.0 (C-H aryl), 59.1 (quaternary Ad), 43.9 (CH_2, Ad), 37.4 (Zr-CH_3), 37.1 (CH_2, Ad), 30.5 (CH, Ad), 21.6 (CH_3, Ar).

Preparation of [Zr(BH$_4$){3,5-Me$_2$PhN(Ad)}$_3$] (3)

A solution of **1** (1.62 g, 1.82 mmol) in THF (100 mL) was treated with $NaBH_4$ (0.138 g, 3.64 mmol). After stirring at room temperature for 3 days, the solvent was removed in vacuo and the residue was extracted with diethyl ether (100 mL). After filtration to eliminate NaCl and unreacted $NaBH_4$, the solution was concentrated to 40 mL and allowed to stand at room temperature for 24 h, upon which colorless crystalline **3** was obtained (1.20 g, 1.38 mmol, 76%). IR (Nujol, mull, NaCl, cm^{-1}) *ν*: 2500 s, 2234 bw, 2180 bm, 2154 bw, 1598 s, 1583 s, 1356 s, 1344 w, 1304 s, 1286 s, 1261 m, 1185 m, 1148 s, 1103 m, 1061 s, 1026 s, 975 m, 951 s, 924 s, 888 m, 855 m, 817 m, 801 m, 709 s, 691 s. ^{1}H NMR (C_6D_6, 20°C, 200 MHz) δ: 6.80 (s, 3H, 4-Ar), 6.55 (s, 6H, 2,6-Ar), 2.30 (s, 18H, Me, Ar), 2.05 (s, 9H, CH, Ad), 1.90 (s, 18H, CH_2, Ad), 1.52 (q, 18H, CH_2, Ad). ^{13}C NMR (C_6D_6, 20°C, 125.7 MHz) δ: 146.4 (quaternary aryl), 136.7 (quaternary aryl), 131.1 (C-H aryl), 127.3 (C-H aryl), 60.4 (quaternary Ad), 43.2 (CH_2, Ad), 36.8 (CH_2, Ad), 30.5 (CH, Ad), 21.8 (CH_3, Ar). ^{11}B{^{1}H} NMR (C_6D_6, 20°C, 160.5 MHz) δ: −15.6. Anal. calcd. for $C_{54}H_{76}BN_3Zr$: C 74.62, H 8.81, N 4.83; found: C 75.24, H 9.05, N 4.88.

X-ray crystallography

Data were collected at −158°C using the ω–2θ scan technique to the maximum 2θ value of 50.0° for suitable air-sensitive crystals mounted on glass fibers of the goniometer of a CCD Siemens X-ray diffractometer. Cell constants and orientation matrices were obtained from the least-squares refinement of carefully centered high-angle reflections. Redundant reflections were averaged. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods. The positions of most of the non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were introduced at their idealized positions. The final cycles of full-matrix least-squares refinement were based on the number of observed reflections with $I > 2.5\sigma(I)$. Neutral atomic scattering factors were taken from Cromer and Waber (19)[2]. Anomalous dispersion effects were included in F_c. All calculations were performed using an NRCVAX package on a silicone Graphics station. Complex **2** contains two crystallographically independent and chemically equivalent molecules in the lattice. Details on crystal data and structure solution have been given in Table 2. Selected bond distances and bond angles are given in Table 1. Listings of atomic coordinates and thermal parameters have been given as supplementary information.[3]

Acknowledgments

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[2] The discrepancy indices were calculated from the expressions $R(F_o) = \Sigma|F_o - F_c|/\Sigma F_o$ and $R_w(F_o) = \Sigma(w_i)^{1/2}|F_o - F_c|/\Sigma(w_i)^{1/2}F_o$; the standard deviation of an observation of unit weight σ_1 is equal to $[(\Sigma w_i|F_o - F_c|^2)/(n - p)]^{1/2}$, where *n* is the number of observations and *p* is the number of parameters varied during the last refinement cycle.

[3] Supplementary material available includes tables of atomic coordinates, crystal data, bond distances and angles, torsion angles, and temperature factors for both **2** and **3**. Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of atomic coordinates and of bond lengths and angles have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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