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Article

Bis(alkylamido)phenylborane Complexes of Zirconium, Hafnium, and Vanadium

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The coordination chemistry of the bis(*tert*-butylamido)phenylborane ligand, $[^t\mathrm{BuN{-}B^{Ph}{-}N^tBu}]^{2-}$, is developed. The ligand can be delivered to metals of groups 4 and 5 from its dilithio salt. The reactions of $\mathrm{PhB(^tBuNLi)_2}$, **1**, with metal halides of zirconium, hafnium, and vanadium generate complexes of the general formulas $(^t\mathrm{BuN{-}B^{Ph}{-}N^tBu})_2\mathrm{M(THF)}$ (M = Zr (**2**), Hf (**3**)), $\mathrm{Li_2[M(^tBuN{-}B^{Ph}{-}N^tBu)_3]}$ (M = Zr (**4**), Hf (**5**)), and $\mathrm{M(^tBuN{-}B^{Ph}{-}N^tBu)_2}$ (M = V (**6**)). ^{1}H and ^{11}B{^{1}H} NMR and single-crystal X-ray analysis show that these amido metal complexes are structurally analogous to amidinates.

Introduction

Simple ligand frameworks that juxtapose π-accepting groups directly adjacent to π-donating groups are unusual in transition metal chemistry. One such example that embodies this electronic construct is the bis(difluorophosphino)methylamine (dfpma) ligand, $\mathrm{CH_3N(PF_2)_2}$.[1,2] In the dfpma architecture, π-accepting fluorophosphine groups are adjacent to the lone pair of an amine bridgehead, giving rise to an acceptor−donor−acceptor ligand motif. Because the phosphine groups may π-accept electrons from the metal or from the lone pair of nitrogen, the ligand is able to concomitantly accommodate metals both in low and moderate oxidation states. We have exploited this property of dfpma and the related bis(phosphito)amine ligands to develop a rich ground and excited state multielectron chemistry of transition metal complexes.[3−10] Against this backdrop of reactivity, we became interested in exploring whether transition metal chemistry could be elaborated for ligands of the antithetical π-donor−acceptor−donor motif. One strategy to developing such an electronic structure is to catenate the π-accepting orbital of a bridgehead boron to the π-donor orbitals of amides, as observed for bis(alkylamido)phenylboranes, $\mathrm{PhB(RN)_2}^{2-}$. The ligand framework is structurally similar to the widely used monoanionic amidinate ligands with the additional caveat that an electron-accepting group is situated at the bridgehead. Like amidinates, the electronic and steric properties of the ligand can be tuned with substituents on the amide nitrogen. Additionally, the donating ability of the coordinating amides can be further modulated by R substitution at the electron-withdrawing B(R) bridgehead.

Diamines of bis(alkylamido)phenylboranes have been known since 1957,[11] and they can be prepared readily from the reaction of dichlorophenylborane with 4 equiv of a primary amine.[12] The lithiated amide derivatives of these amines were first reported in 1990;[13] a subsequent chemistry has evolved for $\mathrm{PhB(RN)_2}^{2-}$ complexed to main group elements.[14−22] The transition metal chemistry of these ligands,

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however, has been little explored, with only three such complexes reported in the literature.[13,23] Herein we expand the coordination chemistry of this novel ligand architecture with the synthesis of a series of zirconium, hafnium, and vanadium complexes.

Experimental Section

General Procedures. All synthetic manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or within the confines of a Vacuum Atmosphere HE−553−2 glovebox. Solutions were frozen in the cold well of the glovebox. Solvents for synthesis were of reagent grade or better and were dried according to standard methods.[24] Bis(*tert*-butylamino)phenylborane,[12] tetrachlorobis(tetrahydrofuran)hafnium(IV),[25] and N,N'-dilithiobis(*tert*-butylamino)phenylborane[13] were prepared by literature methods. All other materials were used as received.

(^{t}BuN−B^{Ph}−N^{t}Bu)$_2$M(THF), M = Zr (2) and M = Hf (3). $MCl_4(THF)_2$ (M = Zr, 100 mg; M = Hf, 120 mg) and PhB(^{t}BuNLi)$_2$ (129 mg for the Zr reaction and 126 mg for the Hf reaction) were each combined with 7 mL of diethyl ether to give a suspension and a solution, respectively. Both mixtures were frozen, and upon thawing, the PhB(^{t}BuNLi)$_2$ solution was added dropwise over 7 min to the partially thawed $MCl_4(THF)_2$ suspension. The resulting mixture was allowed to slowly warm to room temperature. After stirring overnight, solvent was removed by vacuum evaporation, and 10 mL of hexanes was added. The solution was filtered through Celite to remove LiCl. Concentration of the solution followed by cooling to −35 °C and finally filtration afforded 84 mg of colorless crystals (52% yield) of **2** and 124 mg of colorless crystals (67% yield) of **3**. Anal. data for **2**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 1.293 (s, 36H), 1.373 (m, 4H), 3.656 (br, 4H), 7.1−7.7 (m, 10H); ^{11}B{^{1}H} NMR (96.205 MHz, C_6D_6, 25 °C) δ 34.3. Anal. Calcd for $C_{35}H_{61}B_2N_4OZr$: C, 63.05; H, 9.22; N, 8.40. Found: C, 62.98; H, 9.08; N, 8.38. Anal. data for **3**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 1.301 (s, 36H), 1.374 (m, 4H), 3.627 (br, 4H), 7.1−7.7 (m, 10H); ^{11}B{^{1}H} NMR (96.205 MHz, C_6D_6, 25 °C) δ 33.7. Anal. Calcd for $C_{32}H_{54}B_2N_4OHf$: C, 54.06; H, 7.66; N, 7.88. Found: C, 54.14; H, 7.68; N, 7.67.

Li$_2$[M(^{t}BuN−B^{Ph}−N^{t}Bu)$_3$], M = Zr (4) and M = Hf (5). The procedure for preparing these compounds was similar, only differing in the metal tetrahalide starting material. MX_4 (100 mg) (M = Zr, X = Br; M = Hf, X = Cl) and PhB(^{t}BuNLi)$_2$ (178 mg for the Zr reaction and 228 mg for the Hf reaction) were each combined with 7 mL of diethyl ether to give a suspension and a solution, respectively. Both were frozen, and upon thawing, the PhB(^{t}BuNLi)$_2$ solution was added dropwise over 7 min to the partially thawed MX_4 suspension. The mixture was allowed to slowly warm to room temperature. After stirring overnight, solvent was removed by vacuum evaporation, and 10 mL of hexanes was added. The solution was filtered through Celite to remove LiX. Concentration of the solution followed by cooling to −35 °C and filtration afforded 108 mg of colorless crystals (56% yield) of **4** and 173 mg of colorless crystals (64% yield) of **5**. Anal. data for **4**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 1.400 (s, 54H), 7.1−7.8 (m, 15H); ^{11}B{^{1}H} NMR (96.205 MHz, C_6D_6, 25 °C) δ 36.4. Anal. Calcd for $C_{42}H_{69}B_3Li_2N_6Zr$: C, 63.41; H, 8.74; N, 10.56. Found: C, 63.35; H, 8.80; N, 10.47. Anal. data for **5**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 1.398 (s, 54H), 7.1−7.8 (m, 15H); ^{11}B{^{1}H} NMR (96.205 MHz, C_6D_6, 25 °C) δ 36.3. Anal. Calcd for $C_{42}H_{69}B_3Li_2N_6Hf$: C, 57.14; H, 7.88; N, 9.52. Found: C, 56.80; H, 7.74; N, 9.20.

V(^{t}BuN−B^{Ph}−N^{t}Bu)$_2$ (6). Diethyl ether solutions (25 mL) containing 0.136 mL of VCl_4 and 633 mg of PhB(^{t}BuNLi)$_2$ were cooled to −78 °C in a dry ice/acetone bath. The PhB(^{t}BuNLi)$_2$ solution was added dropwise via cannula to the VCl_4 solution. The mixture was allowed to stir at −78 °C for 15 min and then allowed to warm slowly to room temperature. Solvent was removed by vacuum evaporation, and 20 mL of hexanes was added. The solution was filtered through Celite to remove LiCl. Concentration of the solution followed by cooling to −35 °C and filtration afforded 382 mg of red crystals (59% yield). Anal. Calcd for $C_{28}H_{46}B_2N_4V$: C, 65.78; H, 9.07; N, 10.96. Found: C, 65.67; H, 9.15; N, 11.06. UV−vis (pentane) $\lambda_{max,abs}$/nm (ϵ/M^{-1} cm^{-1}): 482 (4893), 351 nm (2924), and 260 (sh) (13934). IR (pentane) ν(V−N) 605 cm^{-1}.

Physical Methods. ^{1}H NMR spectra were recorded on solutions at 25 °C within the magnetic fields of Varian Unity 300 or Mercury 300 spectrometers, which were located in the Department of Chemistry Instrumentation Facility (DCIF) at MIT. Chemical shifts are reported using the standard δ notation in ppm. ^{1}H spectra were referenced to the residual solvent peak. ^{11}B{^{1}H} NMR spectra were collected at the DCIF on a Varian Unity 300 spectrometer and referenced to an external $BF_3{\cdot}OEt_2$ standard at 0 ppm. Elemental analyses were performed at H. Kolbe Mikroanalytisches Laboratorium. EPR spectra were recorded on a modified Bruker EMX X-band spectrometer (9.303 GHz) with a field modulation amplitude of 2 G. Single scans of 4096 points were acquired on samples maintained at 77 K. UV−vis absorption spectra were collected on an Aviv 14DS spectrophotometer. IR spectra were collected on a Perkin-Elmer model 2000 spectrophotometer (DCIF) in pentane solutions. Only absorptions not observed in the IR spectrum of the free ligand are reported.

X-ray diffraction experiments were performed on single crystals grown from concentrated pentane or hexanes solutions at −35 °C. Crystals were removed from the supernatant liquid and transferred onto a microscope slide coated with Paratone N oil. Selected crystals were affixed to a glass fiber in wax and Paratone N oil and cooled to −90 °C. Data collection was performed by shining Mo Kα (λ = 0.71073 Å) radiation onto crystals mounted on a three-circle goniometer Siemens Platform equipped with a CCD detector. The data were processed and refined by using the program SAINT supplied by Siemens Industrial Automation, Inc. The structures were solved by direct methods (SHELXTL v6.10, Sheldrick, G. M., and Siemens Industrial Automation, Inc., 2000) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Some details regarding the refined data and cell parameters are provided in Table 1.

Results and Discussion

The dilithio salt of bis(*tert*-butylamino)phenylborane provides a convenient platform for delivery of the bis amide

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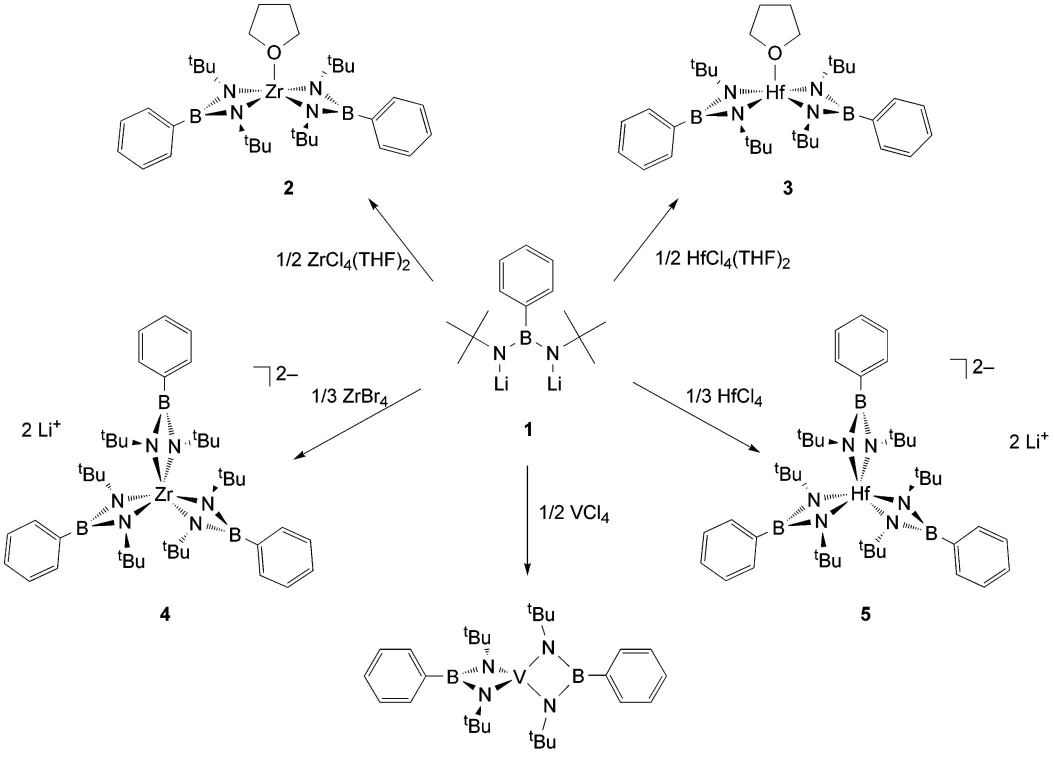
Table 1. Crystallographic Data for (^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_2$Zr(THF) (**2**), (^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_2$Hf(THF) (**3**), Li$_2$[Zr(^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_3$] (**4**), Li$_2$[Hf(^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_3$] (**5**), and V(^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_2$ (**6**)

	2·$^1/_2$*n*-hexane	**3**	**4**	**5**	**6**
empirical formula	$C_{35}H_{61}B_2N_4OZr$	$C_{32}H_{54}B_2HfN_4O$	$C_{42}H_{69}B_3Li_2N_6Zr$	$C_{42}H_{69}B_3HfLi_2N_6$	$C_{28}H_{46}B_2N_4V$
fw	666.72	710.90	795.56	882.83	511.26
T (K)	183(2)	183(2)	183(2)	183(2)	183(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$Pbcn$
a (Å)	10.8574(13)	10.6370(11)	10.1211(15)	10.1198(6)	17.297(7)
b (Å)	13.3389(16)	13.3956(13)	20.060(3)	19.8226(12)	8.976(4)
c (Å)	26.086(3)	24.502(2)	22.383(3)	22.2641(13)	20.238(9)
α (deg)	90	90	90	90	90
β (deg)	91.119(2)	94.930(2)	90	90	90
γ (deg)	90	90	90	90	90
V (Å^3)	3777.3(8)	3478.3(6)	4544.5(12)	4466.2(5)	3142(2)
Z	4	4	4	4	4
d_{calcd} (Mg/m^3)	1.172	1.358	1.163	1.313	1.081
abs coeff (mm^{-1})	0.321	3.027	0.276	2.371	0.336
$R1^a$	0.0428	0.0346	0.0430	0.0488	0.0435
$wR2^a$	0.0993	0.0915	0.0924	0.0682	0.1064

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Chart 1



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ligand [^{t}BuN$-$B$^{Ph}-$N^{t}Bu]$^{2-}$ to metal centers. The action of 2 equiv of *n*-BuLi on the parent amine affords salt **1**, PhB(^{t}BuNLi)$_2$. Single-crystal X-ray diffraction analysis of **1** reveals the heterocubane Li and N core that is familiar to other difunctional lithium amides.[26] During our studies, the crystal structure of **1** was reported by Chivers and coworkers;[27] our observations are entirely consistent with their results. The Li$-$N distances are unremarkable, ranging from 2.029 to 2.077 Å, and N$-$B distances of 1.442(5) and 1.452(5) Å as well as an N$-$B$-$N angle of 109.5(3)° are similar to the metric parameters for the ligand when it is complexed to a transition metal (vide infra).

Synthesis. Complexes of bis(*tert*-butylamido)phenylborane ligands are readily prepared via metathesis reaction between PhB(^{t}BuNLi)$_2$, **1**, and the appropriate metal halide (Chart 1) in yields ranging from 52% to 67%. The reaction of 2 equiv of **1** with the tetrahydrofuran adducts of zirconium and hafnium tetrachloride (MCl$_4$(THF)$_2$) yields colorless complexes possessing two bis(*tert*-butylamido)phenylborane ligands and a single tetrahydrofuran, (^{t}BuN$-$B$^{Ph}-$N^{t}Bu)$_2$M(THF) (M = Zr (**2**), Hf (**3**)). The addition of 3 equiv of **1** to

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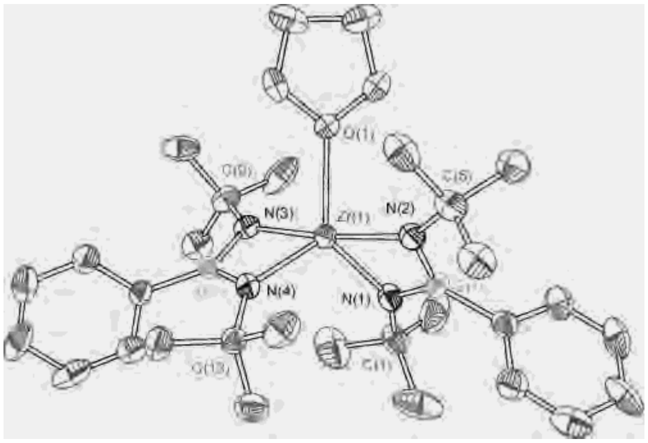

Figure 1. Solid-state structure of $(^t\mathrm{BuN{-}B^{Ph}{-}N^tBu})_2\mathrm{Zr(THF)}$ (**2**) with thermal ellipsoids shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(^t\mathrm{BuN{-}B^{Ph}{-}N^tBu})_2\mathrm{Zr(THF)}$ (**2**) and $(^t\mathrm{BuN{-}B^{Ph}{-}N^tBu})_2\mathrm{Hf(THF)}$ (**3**)

Bond Lengths

2		3	
Zr(1)−O(1)	2.299(3)	Hf(1)−O(1)	2.261(5)
Zr(1)−N(3)	2.122(4)	Hf(1)−N(3)	2.103(5)
Zr(1)−N(4)	2.044(4)	Hf(1)−N(4)	2.030(5)
N(1)−B(1)	1.467(7)	N(1)−B(1)	1.464(9)

Bond Angles

2		3	
N(1)−B(1)−N(2)	111.2(4)	N(1)−B(1)−N(2)	111.2(4)
N(1)−Zr(1)−N(3)	111.93(15)	N(1)−Hf(1)−N(3)	114.32(19)
N(2)−Zr(1)−N(3)	174.14(15)	N(2)−Hf(1)−N(3)	173.50(19)
N(1)−Zr(1)−N(2)	70.47(15)	N(1)−Hf(1)−N(2)	71.0(2)
Zr(1)−N(1)−C(1)	140.3(3)	Hf(1)−N(1)−C(1)	137.3(4)
Zr(1)−N(2)−C(5)	146.0(3)	Hf(1)−N(2)−C(5)	144.6(4)

zirconium tetrabromide or hafnium tetrachloride produces colorless dianionic complexes containing three bis(*tert*-butylamido)phenylborane ligands, $\mathrm{Li_2[M(^tBuN{-}B^{Ph}{-}N^tBu)_3]}$ (M = Zr (**4**), Hf (**5**)). Finally, the reaction of vanadium(IV) chloride with 2 equiv of **1** generates a paramagnetic blood red complex containing two bis(*tert*-butylamido)phenylborane ligands, $\mathrm{V(^tBuN{-}B^{Ph}{-}N^tBu)_2}$ (**6**). The ^{1}H NMR spectra for complexes **2**−**5** exhibit large singlets corresponding to equivalent *tert*-butyl protons, as well as multiplets in the aromatic region. Compounds **2** and **3** also show peaks corresponding to a coordinated tetrahydrofuran. The $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR spectra of these compounds demonstrate only a single resonance. All complexes gave satisfactory elemental analysis.

Structural Analysis. X-ray diffraction studies were performed on crystals of compounds **2**−**5**. Complexes **2** and **3** possess five coordinate metal centers, containing two chelating diamido ligands and a single ligating tetrahydrofuran. The solid-state structures of **2** and **3** are nearly superimposable and demonstrate pseudo-C_2 symmetry (Figure 1). The compounds are best described as trigonal bipyramidal on the basis of deviation from standard polyhedra.[28] Table 2 lists selected bond lengths and angles for compounds **2** and **3**. The observed M−N distances of **2** and **3** range from 2.044(4) to 2.122(4) Å, and from 2.019(5) to 2.105(5) Å, respectively. These distances are comparable to the M−N bond distances of Zr and Hf complexes (d(M−N) = 2.087(2)−2.109(3) Å[29−31]) of the alkyl substituted dianionic guanidinato ligand, $[\mathrm{R'NC(RN)_2}]^{2-}$ (R = ^{i}Pr, ^{t}Bu), but are significantly shorter (d(M−N) = 2.161(2)−2.329(2) Å) than the M−N bonds of coordinated monoanionic amidinato and guanidinato ligands possessing alkyl groups on the amido nitrogens.[32−40] The ligand binds to the metal to form an in plane M−N−B−N spirocycle, with a bite angle ranging from 70.47(15)° to 71.0(2)°, and a N−B−N angle ranging from 111.2(4)° to 111.9(4)°. For comparison, amidinato and guanidinato ligands form similar M−N−C−N spirocycles (bite angles of 57.15(8)−61.06(7)° and N−C−N angles of 110.5(2)−113.9(5)°).[32−40] The M−N−C angles provide a measure of the steric protection conferred by the ligand on the metal center; M−N−C angles of 137.3(4)−146.2(4)° for **2** and **3** show the alkyl groups to be pushed away from the metal center. Finally, substantial π-bonding character between the boron bridgehead and nitrogen amides is signified by d(N−B) = 1.443(9)−1.468(7) Å.[41] These distances concur with those of group 4 amido complexes containing nonbridging boryl groups.[42,43]

Complexes **4** and **5**, possessing three chelating diamido ligands, are nearly superimposable (Figure 2). These “ate” complexes exhibit pseudo-D_3 symmetry, if the two lithium counterions are ignored; their inclusion lowers the symmetry of the molecules to pseudo-C_2 symmetry. The standard polyhedron that best describes these compounds is a trigonal prism,[28] though significant deviations from ideal geometry are observed. Table 3 lists selected bond lengths and angles for compounds **4** and **5**. One coordinated bis(alkylamido)-phenylborane demonstrates metrics that are consistent with those of compounds **2** and **3**, while the other two diamido ligands are significantly elongated due to their association with the lithium cations. On the two affected ligands, one nitrogen is in close contact with a single lithium cation

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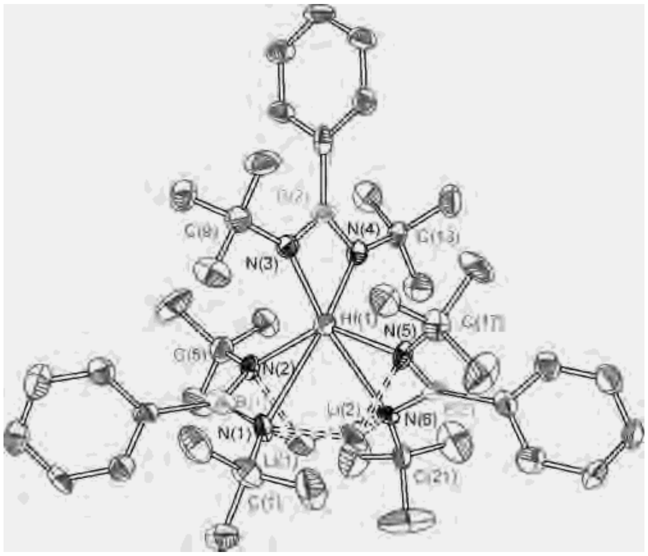

Figure 2. Solid-state structure of $Li_2[Hf(^tBuN-B^{Ph}-N^tBu)_3]$ (**5**) with thermal ellipsoids shown at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Li_2[Zr(^tBuN-B^{Ph}-N^tBu)_3]$ (**4**) and $Li_2[Hf(^tBuN-B^{Ph}-N^tBu)_3]$ (**5**)

Bond Lengths			
4		**5**	
Zr(1)−N(1)	2.802(3)	Hf(1)−N(1)	2.752(6)
Zr(1)−N(2)	2.211(3)	Hf(1)−N(2)	2.177(6)
Zr(1)−N(3)	2.068(3)	Hf(1)−N(3)	2.052(6)
N(1)−B(1)	1.446(5)	N(1)−B(1)	1.419(11)
N(2)−B(1)	1.474(5)	N(2)−B(1)	1.460(10)
N(1)−Li(1)	1.992(7)	N(1)−Li(2)	1.966(14)
N(2)−Li(2)	2.028(7)	N(1)−Li(1)	2.024(14)
Bond Angles			
4		**5**	
N(1)−B(1)−N(2)	110.4(3)	N(1)−B(1)−N(2)	110.9(8)
C(5)−N(2)−Zr(1)	128.5(2)	C(5)−N(2)−Hf(1)	129.0(5)
C(9)−N(3)−Zr(1)	145.3(2)	C(9)−N(3)−Hf(1)	145.5(5)
N(4)−Zr(1)−N(3)	71.92(11)	N(4)−Hf(1)−N(3)	71.8(2)

(d(M−N) = 2.177(6)−2.211(3) Å) while the other contacts both lithium cations (d(M−N) = 2.536(6)−2.802(3) Å). The N−B−N and N−M−N planes differ from each other by 35.6−38.9° for the ligands perturbed by lithium interactions.

The homoleptic vanadium complex of $[^tBuN-B^{Ph}-N^tBu]^{2-}$, **6**, exhibits a tetragonally compressed coordination geometry (D_{2d}) about the vanadium(IV) center (Figure 3). The distortion is almost identical to that observed by Fest and co-workers in $Ti[^tBuN-B^{Ph}-N^tBu]_2$.[13] The V−N bond distances of 1.851(3) and 1.853(3) Å are consistent with the V−N distances observed in the bis(*tert*-butylamido)silane congener, $V[Me_2Si(^tBuN)_2]_2$ (Table 4).[44] The 78.52(14)° bite angle of **6** is considerably larger than those observed for **2**−**4**. The metric parameters of **6** contrast those of alkyl amidinate vanadium complexes, which exhibit longer V−N distances (d = 1.944(2)−2.232(3) Å) and more acute bite angles (63.46(19)−64.84(1)°).[45−48]

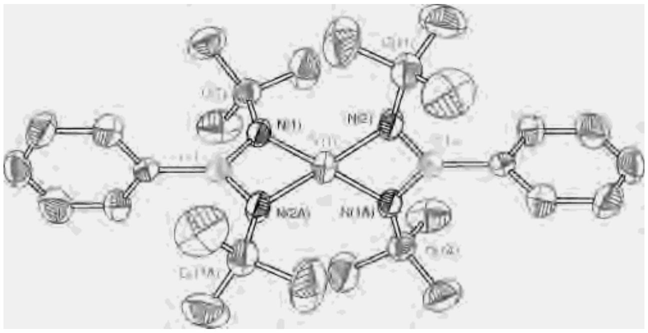

Figure 3. Solid-state structure of $V(^tBuN-B^{Ph}-N^tBu)_2$ (**6**), with thermal ellipsoids shown at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $V(^tBuN-B^{Ph}-N^tBu)_2$ (**6**)

Bond Lengths		Bond Angles	
V(1)−N(1)	1.853(3)	N(1)−B(1)−N(2A)	106.9(4)
V(1)−N(2)	1.851(3)	N(1)−V(1)−N(2A)	78.52(14)
N(1)−B(1)	1.460(5)	N(1)−V(1)−N(2)	126.57(14)
N(2)−B(1A)	1.459(6)	V(1)−N(1)−C(7)	140.8(3)
		V(1)−N(2)−C(11)	141.2(3)

Spectroscopy of 6. Room temperature EPR spectra of **6** show a strong signal with no hyperfine coupling. Conversely, a frozen pentane solution (77 K) of **6** gives a well-resolved octet in the EPR spectrum arising from the interaction of the unpaired electron with $^{51}V(I = {}^7/_2)$ (g = 1.979; $A(^{51}V)$ = 49.0 G). There is significant line broadening and an increased amplitude in the first peak and the final dip, due to superhyperfine coupling to the quadrapolar nitrogens. A simulated spectrum[49] is in accordance with the observed spectrum, yielding $A(^{14}N)$ = 4.7 G (Figure 4). The IR spectrum of **6** exhibits a strong band at 605 cm^{-1}, which is absent in the free ligand; on this basis, the absorption is assigned to the V−N stretching mode. An empty p-orbital at the B(R) bridgehead might be expected to attenuate the π-back-bonding interaction between the amido nitrogens and metal center and consequently give rise to a reduced V−N frequency. However, such simple stereoelectronic correlations may be obscured by mass and steric effects of the ligand. Accordingly, it is not unexpected that the V−N stretching frequency of **6** falls between that observed for $V(NMe_2)_4$ and $V(NEt_2)_4$.[50] Finally, the absorption spectrum of **6** is consistent with a d^1 metal center in a tetrahedrally distorted crystal field. The ^2E and $^2T_2$ terms of T_d symmetry are split in D_{2d} symmetry to a $^2B_1$ ground state and $^2A_1$, $^2B_2$, and ^2E excited states; for these three excited states, the $^2E \leftarrow {}^2B_1$ transition is Laporte allowed. An LMCT transition at 260 nm dominates the UV absorption region.

In summary, bis(*tert*-butylamido)phenylborane is a competent ligand for group 4 and 5 transition metals. The ligand demonstrates significantly shorter metal−nitrogen bonds than amidinate ligands owing to its dianionic nature, and a larger

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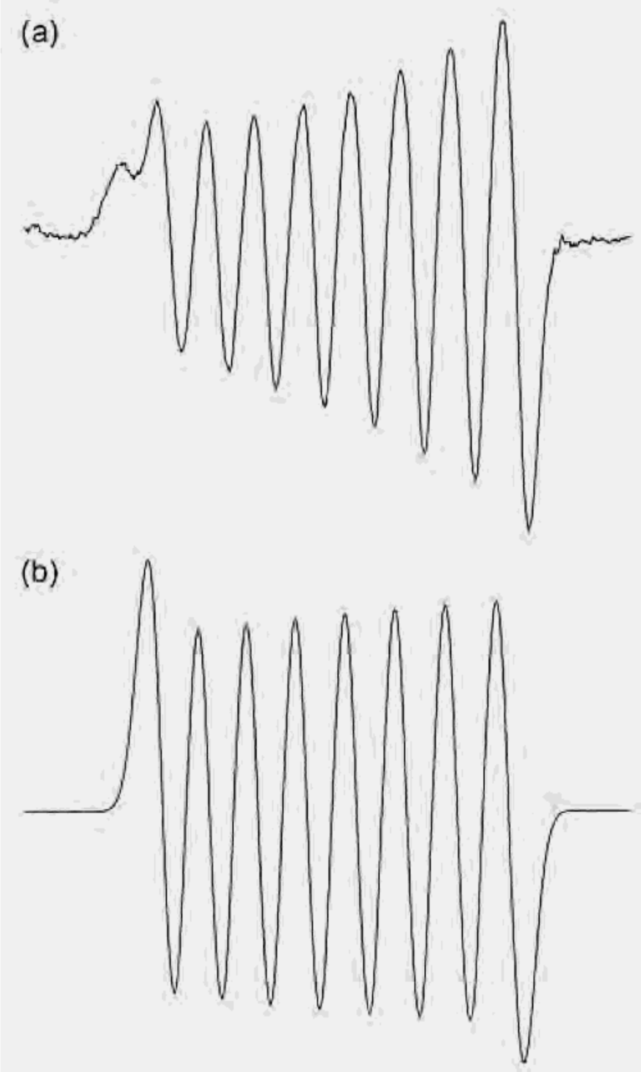
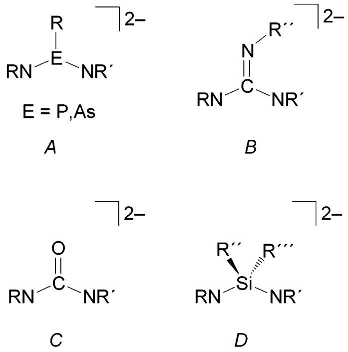


Figure 4. EPR spectrum (X-band) of V(^{t}BuN−B^{Ph}−N^{t}Bu)$_2$ (**6**) at 77 K in frozen pentane: (a) experimental; (b) simulated.

bite angle, which accompanies the shorter M−N distances. The dianionic charge of bis(*tert*-butylamido)phenylborane ligands also relaxes the need for additional ancillary *anionic* ligands on metal centers of high oxidation state. More generally, the class of diamido ligands possessing a single-atom bridgehead, [RN−X−NR]$^{2-}$, is limited. A compilation of these ligands is shown in Chart 2. From this roster of ligands, the transition metal coordination chemistry of the bis(alkylamido)phosphino[51] and bis(alkylamido)arsino[52] ligands (A) has yet to be developed. The early transition metal complexes of dianionic guanidinato[29−31,53−55] (B) and ureato[56−67] (C) ligands have been obtained, for the most part, by constructing the ligand at the metal; a general synthesis of these ligand classes has not been forthcoming. By far, the most extensively studied [RN−X−NR]$^{2-}$ system has been the bis(amido)silanes (D).[44,68−71] The bis(alkylamido)-phenylborane ligands offer a versatile counterpart to this system inasmuch as the steric electronic properties of the three-atom dianionic chelate can be tuned with substitution at nitrogen and the boron bridgehead, which is strongly coupled to the amide termini via π-bonding. Future directions include expanding the coordination chemistry of bis(alkylamido)phenylborane ligands as chelates and also as a bridging ligand of bimetallic metal centers.

Chart 2



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Supporting Information Available: Table of X-ray crystallographic data for complexes **2** through **6** including a fully labeled thermal ellipsoid plot, final atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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