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{H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2}AlEt$_2$ and {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$. Structure, Dynamic Solution Behavior, and the 1,2-Borotropic Shift

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HB(3-^{t}Bupz)$_3$Tl and AlEt$_3$ in benzene yield {H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2}AlEt$_2$, **1**, as a hydrocarbon-soluble crystalline solid. Compound **1** is also obtained in a related reaction involving ClAlEt$_2$ via a preferential metathesis of the Al−Cl bond. Crystal data for **1** at −101 °C: $a = 11.770(3)$ Å, $b = 11.054(3)$ Å, $c = 21.973(6)$ Å, $\beta = 95.57(1)°$, $Z = 4$, space group $P2_1/a$. In **1** the Al center is four-coordinate with Al−C = 1.97(1) Å and Al−N = 1.99(1) Å and with C−Al−C = 127° and N−Al−N = 101° being the largest and smallest angles, respectively. The average N−B−N angle is 109(1)°. In toluene-d_8 and tetrahydrofuran-d_8, **1** shows two types of 3-^{t}Bupz groups in the integral ratio 2:1 and two distinct ethyl ligands. At low temperature there is a broadening of the 3-^{t}*Bu*pz singlet that is assigned to the η^2-^{t}Bupz ligands. Up to +60 °C, compound **1** is nonfluxional on the NMR time scale but does isomerize to {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$, **2**. Crystal data for **2** at −172 °C: $a = 29.235(5)$ Å, $b = 11.298(1)$ Å, $c = 22.033(3)$ Å, $\beta = 129.66(1)°$, $Z = 8$, space group = $C2/c$. In **2** there is a pseudotetrahedral Al center with Al−C = 1.97(1) Å (average) and Al−N = 1.95(1) Å (average) and with C−Al−C = 119° and N−Al−N = 98° as the largest and smallest angles, respectively. The average N−B−N angle is 108(1)°. In **2** the η^2-tris(alkylpyrazolyl)borate ligand isomerizes by a 1,2-borotropic shift to give one 5-^{t}Bupz fragment that is part of the η^2-*N,N′* aluminum-bonded ligand. Variable-temperature ^{1}H NMR spectra of **2** in toluene-d_8 and THF-d_8 reveal temperature-dependent exchange involving the 3-^{t}Bupz moieties, with more rapid site exchange in toluene-d_8 than in THF-d_8. At low temperature there are two ethyl signals, one of which indicates diastereotopic methylene protons, as well as three ^{t}Bu signals in the ratio 1:1:1. The dynamic behavior of **2** is consistent with an $\eta^2 \rightleftharpoons \eta^3$ exchange process as opposed to an $\eta^2 \rightleftharpoons \eta^1$ exchange wherein the Al center is transiently three-coordinate. The isomerization of **1** to **2** has been studied in benzene-d_6 ($\Delta H^\ddagger = 21.0(2)$ kcal/mol, $\Delta S^\ddagger = -15(1)$ eu) and THF-d_8 ($\Delta H^\ddagger = 18.3(4)$ kcal/mol, $\Delta S^\ddagger = -15(1)$ eu) and compared to a related isomerization involving {H$_2$B(3-^{t}Bupz)$_2$-η^2}AlMe$_2$ reported by Parkin and Looney [*Polyhedron* **1990**, *9*, 265] in benzene-d_6 ($\Delta H^\ddagger = 34.5(8)$ kcal/mol, $\Delta S^\ddagger = 6(2)$ eu). It is proposed that the rate-determining 1,2-borotropic shift in the **1** → **2** reaction occurs in a noncoordinating ^{t}Bupz group and that this is followed by a rapid associative interchange of pz groups wherein the sterically less demanding 5-^{t}Bupz moiety remains bound to the metal.

Introduction

In our attempts to prepare single-site catalysts for ring-opening polymerization of cyclic ethers and esters,[1] we wished to prepare a HB(Rpz)$_3$Al(R′)(OR″) compound, wherein the Al−C bond would be inert but the Al−OR bond active. Plausible starting materials for such compounds would be of the type HB(Rpz)$_3$AlR′$_2$, which are known for R = 3,5-Me$_2$ and 3-^{t}Bu and R′ = Me.[2] We describe here our synthesis and characterization of the related compound HB(3-^{t}Bupz)$_3$AlEt$_2$, **1**, which did not prove a suitable precursor to HB(3-^{t}Bupz)$_3$AlEt(OR) complexes via alcoholysis reactions but did show an interesting isomerization by way of a 1,2-borotropic shift to give HB(3-^{t}Bupz)$_2$(5-^{t}Bupz)AlEt$_2$, **2**. The preparations, structures, and dynamic solution behaviors of **1** and **2** are reported herein, together with studies of the conversion of **1** to **2**. These studies complement the earlier work of Looney and Parkin, who observed a related isomerization involving H$_2$B(3-^{t}Bupz)$_2$AlMe$_2$.[2]

Results and Discussion

Synthesis. The reaction between HB(3-^{t}Bupz)$_3$Tl and AlEt$_3$ in benzene yields HB(3-^{t}Bupz)$_3$AlEt$_2$, **1**, as a hydrocarbon-soluble crystalline solid, along with Tl(m). The reaction is complete within 15 min at room temperature.

In a related reaction involving HB(3-^{t}Bupz)$_3$Tl and ClAlEt$_2$ in benzene, compound **1** is also formed by the selective metathetic reaction involving the Al−Cl bond with formation of TlCl. When this reaction is carried out in THF (tetrahydrofuran), the isomerized product HB(3-^{t}Bupz)$_2$(5-^{t}Bupz)AlEt$_2$, **2**, is obtained as the major product.

Compound **1** isomerizes to **2** upon heating in benzene at a rate that is chemically significant at +60 °C. [Quantitative data are presented later.] The isomerization of **1** to **2** is observed to be significantly faster in THF.

Solid-State and Molecular Structures. HB(3-^{t}Bupz)$_3$AlEt$_2$, 1, crystallized in the space group $P2_1/a$ with 4 identical molecules in the unit cell. A view of the molecular structure of **1** is given in Figure 1, and selected bond distances and angles are listed in Table 1. Atomic coordinates are given in Table 2, and a summary of crystal data is presented in Table 3.

The Al atom is in a pseudotetrahedral environment with Al−C = 1.97(1) Å and Al−N = 1.99(1) Å and with C−Al−C = 128(1)° and N−Al−N = 101(1)° as the largest and smallest angles, respectively. The structure is related to that proposed for HB(3-^{t}Bupz)$_3$AlMe$_2$ based on its NMR spectrum, which shows two

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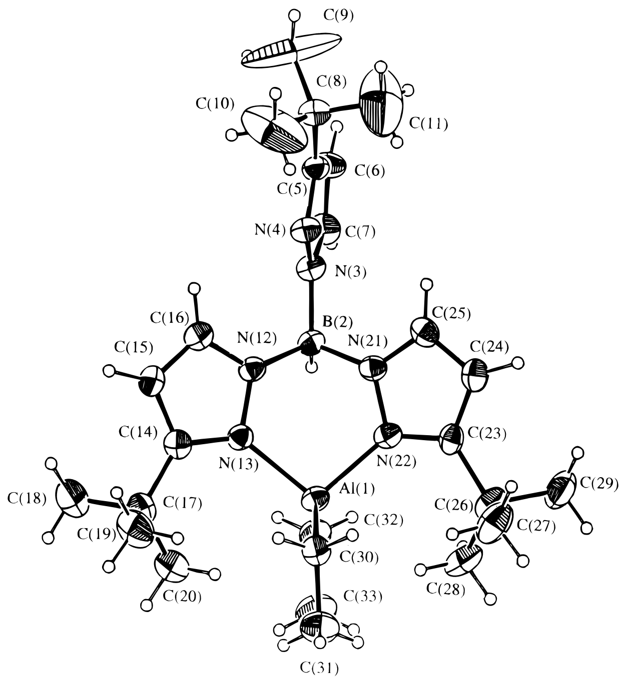

Figure 1. Molecular structure of {H(3-^{t}Bupz)B(3-^{t}Bupz)$_{2}$-η^{2}}AlEt$_{2}$, **1**, with thermal ellipsoids shown at the 50% probability level.

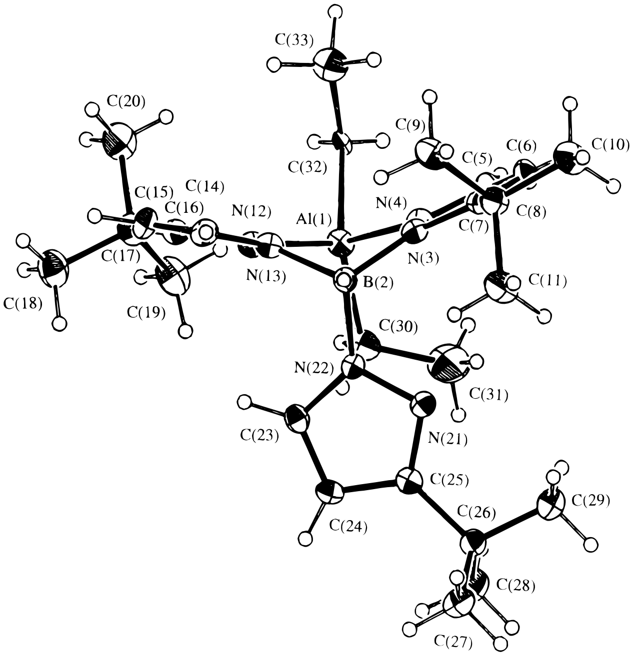

Figure 2. Molecular structure of {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^{2}}-AlEt$_{2}$, **2**, with thermal ellipsoids shown at the 50% probability level.

types of 3-^{t}Bupz groups in a 2:1 integral ratio.[2] In the present structure of **1**, the ^{t}Bu methyl carbons of the nonligated pz moiety show large thermal parameters and none of the H atoms were located.

HB(3-^{t}Bupz)$_{2}$(5-^{t}Bupz)AlEt$_{2}$, 2, crystallizes from pentane in the space group *C*2/*c* with 8 molecules in the unit cell. A drawing of the molecular structure is given in Figure 2, and a summary of crystal data is presented in Table 3. Selected bond distances and angles are presented in Table 4, and atomic coordinates are given in Table 5.

As in **1**, the Al center is in a pseudotetrahedral environment with Al−C = 1.97(1) Å and Al−N = 1.95(1) Å and with C−Al−C = 119(1)° and N−Al−N′ = 98°. The most pertinent difference between **1** and **2** involves the presence of the 5-^{t}Bupz moiety, which in **2** is bonded to the Al center. Several examples of complexes containing rearranged HB(Rpz)$_{3}^{-}$ ligands have been characterized by X-ray crystallography or NMR spectroscopy.[3−7] The structurally characterized species Co{HB-(3-^{i}Prpz)$_{2}$(5-^{i}Prpz)}$_{2}$ and Co{HB(3-^{i}Pr-4-Br-pz)$_{2}$(5-^{i}Pr-4-Br-pz)}$_{2}$ are most similar to **2** in that the tris(alkypyrazolyl)-hydroborato ligands adopt an η^{2}-coordination mode.[3] However, in these cobalt complexes, the isomerized 5-^{i}Prpz and 5-^{i}Pr-4-

Table 1. Selected Bond Distances and Angles for {H(3-^{t}Bupz)B(3-^{t}Bupz)$_{2}$-η^{2}}AlEt$_{2}$, **1**

	Distances (Å)		
Al(1)−N(13)	1.990(3)	C(5)−C(6)	1.407(6)
Al(1)−N(22)	1.990(4)	C(5)−C(8)	1.507(6)
Al(1)−C(30)	1.978(4)	C(6)−C(7)	1.364(6)
N(3)−N(4)	1.370(4)	C(8)−C(11_	1.474(8)
N(3)−C(7)	1.350(5)	C(14)−C(15)	1.383(5)
N(4)−C(5)	1.327(5)	C(14)−C(17)	1.513(6)
N(12)−N(13)	1.387(4)	C(15)−C(16)	1.360(6)
N(12)−C(16)	1.337(5)	C(17)−C(18)	1.535(6)
N(12)−B(2)	1.548(6)	C(30)−C(31)	1.531(6)
N(13)−C(14)	1.362(5)	C(32)−C(33)	1.541(6)
	Angles (deg)		
N(13)−Al(1)−N(22)	100.99(14)	C(30)−Al(1)−C(32)	127.62(19)
N(13)−Al(1)−C(30)	104.63(16)	N(4)−N(3)−B(2)	121.9(3)
N(13)−Al(1)−C(32)	107.61(17)	N(13)−N(12)−B(2)	120.4(3)
N(22)−Al(1)−C(30)	104.78(16)	N(22)−N(21)−B(2)	121.6(3)
N(22)−Al(1)−C(32)	108.15(17)		

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for {H(3-^{t}Bupz)B(3-^{t}Bupz)$_{2}$-η^{2}}AlEt$_{2}$, **1**

atom	10^4x	10^4y	10^4z	$10B_{iso}$ (Å^2)
Al(1)	6034(1)	138(1)	3181(1)	24
B(2)	4079(4)	−1071(4)	2253(2)	22
N(3)	3333(3)	−1746(3)	1770(1)	25
N(4)	3769(3)	−2308(3)	1292(1)	27
C(5)	2913(3)	−2940(4)	1003(2)	26
C(6)	1918(3)	−2806(4)	1296(2)	35
C(7)	2224(3)	−2049(4)	1777(2)	30
C(8)	3089(4)	−3705(4)	454(2)	33
C(9)	2039(6)	−3762(11)	26(4)	161
C(10)	4041(7)	−3231(7)	136(3)	113
C(11)	3400(9)	−4940(7)	665(3)	123
N(12)	4813(2)	−113(3)	1964(1)	23
N(13)	5497(3)	679(3)	2333(1)	23
C(14)	5793(3)	1587(4)	1963(2)	26
C(15)	5320(4)	1347(4)	1369(2)	30
C(16)	4718(13)	299(4)	1388(2)	28
C(17)	6478(4)	2702(4)	2169(2)	32
C(18)	5916(4)	3794(5)	1823(2)	50
C(19)	7711(4)	2593(5)	2003(2)	46
C(20)	6487(4)	2968(4)	2849(2)	38
N(21)	4889(3)	−1973(3)	2630(1)	23
N(22)	5614(3)	−1606(3)	3132(1)	24
C(23)	5987(3)	−2637(4)	3434(2)	25
C(24)	5512(3)	−3626(4)	3117(2)	29
C(25)	4827(3)	−3171(4)	2621(2)	28
C(26)	6752(3)	−2683(4)	4040(2)	32
C(27)	7987(4)	−2942(5)	3930(2)	46
C(28)	6673(4)	−1539(5)	4414(2)	42
C(29)	6332(4)	−3732(5)	4416(2)	49
C(30)	7722(3)	158(4)	3225(2)	29
C(31)	8478(4)	799(5)	3741(2)	42
C(32)	5070(4)	938(4)	3737(2)	33
C(33)	5648(4)	1675(5)	4282(2)	46

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Table 3. Summary of Crystal Data for {H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2} AlEt$_2$, **1**, and {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{5}Bupz)-η^2}AlEt$_2$, **2**

	1	**2**
empirical formula	$C_{25}H_{44}BN_6Al$	$C_{25}H_{44}BN_6Al$
color of crystal	colorless	colorless
crystal dimens (mm)	0.42 × 0.34 × 0.12	0.32 × 0.32 × 0.30
space group	$P2_1/a$	$C2/c$
temp (°C)	−101	−172
a (Å)	11.770(3)	29.235(5)
b (Å)	11.054(3)	11.298(1)
c (Å)	21.973(6)	22.033(3)
β (deg)	96.57(1)	129.66(1)
Z (molecules/cell)	4	8
vol (Å^3)	2840.00	5602.21
calcd density (g/cm^3)	1.091	1.104
wavelength (Å)	0.710 69	0.710 69
mol wt	466.45	466.45
linear abs coeff (cm^{-1})	0.896	0.908
dectector-to-sample dist (cm)	22.5	22.5
sample-to-source dist (cm)	23.5	23.5
av ω-scan width at half-height	0.25	0.25
scan speed (deg/min)	8.0	8.0
scan width (deg + dispersion)	2.0	2.0
individual bkgd (s)	5	3
aperture size (mm)	3.0 × 4.0	3.0 × 4.0
2θ range (deg)	6−45	6−45
tot. no. of reflns collected	4763	4696
no. of unique intensities	3712	3659
no. with $F(\sigma = 0.0)$	3359	3426
no. with $F(\sigma = 3.0(F))$	2442	2845
$R(F)$	0.0537	0.0418
$R_w(F)$	0.0506	0.0421
goodness of fit for last cycle	1.452	1.553
max Δ/σ for last cycle	0.02	0.05

Table 4. Selected Bond Distances and Angles for {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$, **2**

Distances (Å)

Al(1)−N(4)	1.9417(23)	N(13)−B(2)	1.553(4)
Al(1)−N(12)	1.9630(23)	C(5)−C(6)	1.372(4)
Al(1)−C(30)	1.962(3)	C(6)−C(7)	1.382(4)
Al(1)−C(32)	1.9829(27)	C(7)−C(8)	1.515(4)
N(3)−N(4)	1.373(3)	C(8)−C(11)	1.536(4)
N(3)−C(7)	1.359(3)	C(14)−C(15)	1.364(4)
N(3)−B(2)	1.547(4)	C(15)−C(16)	1.393(4)
N(4)−C(5)	1.337(3)	C(16)−C(17)	1.511(4)
N(12)−N(13)	1.388(3)	C(17)−C(18)	1.534(4)
N(12)−C(16)	1.355(3)	C(30)−C(31)	1.523(5)
N(13)−C(14)	1.340(3)	C(32)−C(33)	1.582(4)

Angles (deg)

N(4)−Al(1)−N(12)	97.65(9)	C(30)−Al(1)−C(32)	118.87(14)
N(4)−Al(1)−C(30)	109.38(12)	N(4)−N(3)−B(2)	116.10(21)
N(4)−Al(1)−C(32)	101.08(11)	N(12)−N(13)−B(2)	124.26(21)
N(12)−Al(1)−C(30)	115.22(12)	N(21)−N(22)−B(2)	119.71(21)
N(12)−Al(1)−C(32)	111.34(12)		

Table 5. Atomic Coordinates and Isotropic Thermal Parameters for {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$, **2**

atom	10^4x	10^4y	10^4z	$10B_{iso}$ (Å^2)
Al(1)	4404.0(4)	2435(1)	429.6(5)	17
B(2)	3337(1)	1759(3)	454(2)	16
N(3)	4286(1)	858(2)	890(1)	15
C(5)	4548(1)	96(3)	1155(2)	19
C(6)	4460(1)	−676(3)	1437(2)	19
C(7)	3957(1)	−184(2)	1267(1)	17
C(8)	3580(1)	−673(2)	1460(2)	19
C(9)	3556(1)	186(3)	1977(2)	23
C(10)	3966(1)	−1818(3)	1934(2)	25
C(11)	2952(1)	−966(3)	700(2)	25
N(12)	3934(1)	3538(2)	525(1)	16
N(13)	3586(1)	3040(2)	684(1)	15
C(14)	3377(1)	3909(2)	860(2)	17
C(15)	3579(1)	4970(3)	821(2)	19
C(16)	3924(1)	4726(2)	603(2)	17
C(17)	4226(1)	4621(3)	454(2)	21
C(18)	3826(2)	6718(3)	69(2)	28
C(19)	4317(2)	5145(3)	−108(2)	28
C(20)	4824(1)	4980(3)	1244(2)	30
N(21)	2959(1)	537(2)	−744(1)	15
N(22)	2994(1)	1638(2)	−440(1)	14
C(23)	2691(1)	2477(3)	−1008(2)	17
C(24)	2358(1)	1934(2)	−1723(2)	17
C(25)	2475(1)	714(2)	−1553(2)	15
C(26)	2218(1)	−302(2)	−2129(2)	18
C(27)	1549(1)	−348(3)	−2585(2)	24
C(28)	2333(2)	−92(3)	−2708(2)	28
C(29)	2502(2)	−1467(3)	−1701(2)	27
C(30)	4097(1)	2144(3)	−650(2)	24
C(31)	4156(2)	868(4)	−814(2)	49
C(32)	5268(1)	2705(2)	−1270(2)	11
C(33)	5463(2)	2815(3)	2123(2)	33

Br-pz groups are not bound to the metal, while in **2**, the 5-^{t}Bupz group has displaced a 3-^{t}Bupz group at the aluminum atom.

Solution ^{1}H NMR Characterization. Compound **1** has been examined in benzene-d_6, toluene-d_8, and THF-d_8. There are two different ethyl groups that both appear as a sharp quartet and triplets due to J_{HH} couplings. There are also two sets of signals associated with the 3-^{t}Bupz protons having the integral ratio of 2:1, as anticipated by the structure of **1** seen in the solid state. From this we can conclude that the HB(3-^{t}Bupz)$_3^-$ ligand remains η^2-bound to Al on the NMR time scale and that a conversion of $\eta^2 \rightleftharpoons \eta^3$ or $\eta^2 \rightleftharpoons \eta^1$ must be slow. Even at +60 °C in benzene, a temperature at which the isomerization of **1** to **2** becomes significant, the signals associated with **1** remain sharp.

The ^{1}H NMR spectra of **2** were more complex and varied with both temperature and solvent. At room temperature in benzene-d_6 and toluene-d_8, the spectrum of **2** contained ^{t}Bu signals in the integral ratio 1:2. The signal of intensity 2 was notably broader in THF-d_8 at this temperature. At low temperature in toluene-d_8 and THF-d_8, there are three distinct sets of ^{t}Bupz signals, as expected from the solid-state molecular structure (Figure 2). Upon warming, it is evident that two of the groups undergo exchange and that this does not involve the other ^{t}Bupz moiety. See Figure 3. It should be noted that Looney and Parkin[2] observed exchange of coordinated and uncoordinated pz′ groups in HB(pz′)$_3$AlMe$_2$ at 40 °C by magnetization transfer and estimated the activation barrier to be 17(2) kcal/mol.

Arbitrarily one cannot distinguish between a 3-^{t}Bupz and a 5-^{t}Bupz set of resonances. However, only one set remains sharp during this dynamic exchange. Two other observations are pertinent to an interpretation of the solution behavior: (1) The exchange process occurs more rapidly in toluene-d_8 (and benzene-d_6) than in the coordinating/donor solvent THF-d_8, and (2) throughout the dynamic exchange of the ^{t}Bupz groups, there are two types of ethyl ligands. Moreover, at low temperatures, one of the Al−CH_2CH_3 groups displays diastereotopic methylene protons (see Figure 3), as expected from the solid-state and molecular structure. In fact, both ethyl ligands in **2** should contain diastereotopic methylene protons (in contrast to those in **1**, where the two Al−C bonds lie on a virtual mirror plane

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(7) Cano, M.; Heras, J. V.; Jones, C. J.; McCleverty, J. A.; Trofimenko, S. *Polyhedron* **1990**, *9*, 619.

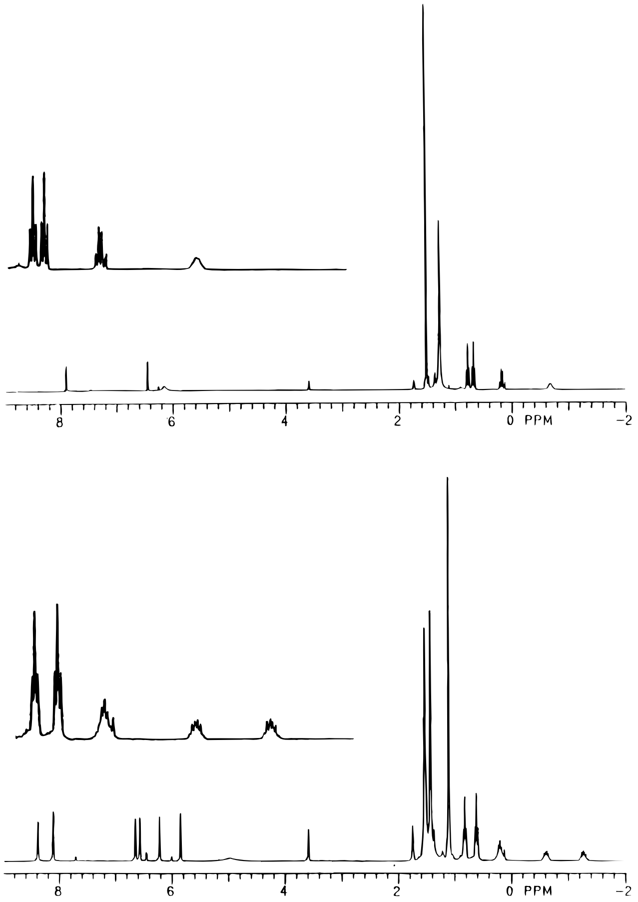

Figure 3. ^{1}H NMR spectrum of $\{H(3\text{-}^tBupz)B(3\text{-}^tBupz)(5\text{-}^tBupz)\text{-}\eta^2\}AlEt_2$, **2**, at 12 °C (upper) and −78 °C (lower) (THF-d_8 300 MHz), with insets showing expanded views of chemical shift range −2.0 to +1.0 ppm, revealing ethyl resonances.

of symmetry) and there is evidence from inspection of Figure 3 that the other CH_2 signal is not a simple first-order quartet.

Collectively these results are very informative. First, we can rule out a dissociative mechanism involving the $HB(Rpz)_3^-$ ligand because an η^1-N−$AlEt_2$ molecule (reactive intermediate) would have equivalent ethyl ligands, assuming facile rotation about the Al−N bond. Second, the intramolecular exchange process must involve the 3-^{t}Bupz groups because the isomerization to give the 5-^{t}Bupz-bound complex, **1** → **2**, is thermodynamically favored. We can thus infer that the dynamic exchange process involves an intramolecular associative displacement of one 3-^{t}Bupz group for the other, *i.e.* an $\eta^2 \rightleftharpoons \eta^3$ interconversion. In the donor solvent THF-d_8, this exchange is slower relative to that in benzene-d_6 and toluene-d_8 because the THF can compete for coordination to the four-coordinate Al center. Finally, we note that if a dissociative interchange were operative, *i.e.* $\eta^2 \rightleftharpoons \eta^1$, then we would expect that the more sterically encumbered and thermodynamically less stable isomer, compound **1**, would be more fluxional than **2**. This is not the case because **2** is fluxional on the NMR time scale while **1** is not.

Studies of the Isomerization of 1 to 2. This reaction has been studied by ^{1}H NMR spectroscopy as a function of time, temperature, and solvent (THF-d_8 versus benzene-d_6). The reaction is first order in **1** and proceeds roughly 100 times faster in THF-d_8 than in benzene-d_6. A summary of the rate data is presented in Table 6.

Table 6. Summary of Rate Data for Isomerizationof **1** to **2**

solvent	temp (K)	k (s^{-1})	solvent	temp (K)	k (s^{-1})
benzene-d_6	293	$7.70(4) \times 10^{-7}$	THF-d_8	296	$9.48(7) \times 10^{-5}$
	313	$8.12(2) \times 10^{-6}$		303	$1.68(5) \times 10^{-4}$
	334	$7.40(1) \times 10^{-5}$		314	$5.85(5) \times 10^{-4}$

From an Eyring plot we have determined reasonable estimates for the activation parameters. In benzene-d_6 we find $\Delta H^\ddagger$ = 21.0(2) kcal/mol and $\Delta S^\ddagger$ = −15(1) eu whereas in THF-d_8 $\Delta H^\ddagger$ = 18.3(4) kcal/mol and $\Delta S^\ddagger$ = −15(1) eu. Thus, in both instances, the entropy of activation is negative and medium in magnitude and the difference in reactivity as a function of solvent can be traced to the enthalpic term.

It is at this point worth noting that Looney and Parkin observed a similar 1,2-borotropic shift in the conversion of $\{H_2B(3\text{-}^tBupz)_2\text{-}\eta^2\}AlMe_2$ to $\{H_2B(3\text{-}^tBupz)(5\text{-}^tBupz)\text{-}\eta^2\}AlMe_2$.[2] From studies of the rate of the latter reaction in benzene-d_6 they determined $\Delta H^\ddagger$ = 34.5(8) kcal/mol and $\Delta S^\ddagger$ = +6(2) eu. Thus the latter reaction is much slower than that seen in the present study of the conversion of **1** to **2**. It also has a higher $\Delta H^\ddagger$ value (by *ca.* 15 kcal/mol) but a modest positive entropy of activation in contrast to the −15 eu observed for the conversion **1** → **2**.

It is worthwhile to remember that the $\Delta S^\ddagger$ values are the result of combined effects (microscopic transformations) and thus care should be used in any interpretation based solely on these terms. Nevertheless we are inclined toward the view that collectively the data provide a self-consistent picture and that the 1,2-borotropic shift involves a noncoordinated pz group. In Parkin's case, an $\eta^2 \rightleftharpoons \eta^1$ transformation would necessarily precede the ligand isomerization. In the case of **1**, the free 3-^{t}Bupz group may undergo this reaction in the rate-determining step, followed by a fast $\eta^2 \rightleftharpoons \eta^3$ site exchange whereby the 5-^{t}Bupz moiety becomes bound to the Al center.

The rate enhancement in the conversion of **1** to **2** in the polar coordinating solvent THF-d_8 (relative to benzene-d_6) may indicate that a small but chemically significant amount of an $\{H(3\text{-}^tBupz)_2B(3\text{-}^tBupz)\text{-}\eta^1\}AlEt_2$ solvate species is present in equilibrium with **1**. This then could undergo the 1,2-borotropic shift more rapidly than the η^2-bound form of the ligand (Scheme 1). Consistent with this view is the fact that the $\{HB(3\text{-}^tBupz)_3\text{-}\eta^3\}MgR$ compounds where R = Me and Et do not show such a ligand rearrangement,[8] and furthermore the preparation of **1** from $\{HB(3\text{-}^tBupz)_3\text{-}\eta^3\}Tl$ and Et_2AlCl is solvent dependent with respect to the amount of **2** that is formed (see Experimental Section). In THF up to 80% of **2** is formed relative to *ca.* 100% of **1** in benzene; and under the conditions of time and temperature, the conversion of **1** to **2** in THF would have only yielded 20% of **2**.

Reactions of 1 with Alcohols. The aluminum−alkyl bonds in $HB(3,5\text{-}Me_2pz)_3AlMe_2$ were shown to be highly reactive toward protic compounds, specifically H_2O, to form aluminum hydroxide species.[2] This result suggested that **1** should also be susceptible to reactions with alcohols to form mono- and bis(alkoxide) species. Indeed, the addition of 1 equiv of ethyl, isopropyl, or *tert*-butyl alcohol to solutions of **1** in benzene resulted in the formation of complexes whose ^{1}H NMR spectra reveal peaks consistent with the formation of mixed alkyl/alkoxide aluminum species. Each of these reactions produced a substance exhibiting a single major set of sharp pyrazole resonances, suggestive of η^3-coordination of $HB(3\text{-}^tBupz)_3^-$, η^2-coordination with rapid exchange, or ligand decomposition. These spectra also revealed the presence of several types of aliphatic resonances and, in some cases, minor pyrazole resonances. The alcohol additions to **1** produced, in addition to these soluble organometallic and organic species, a white

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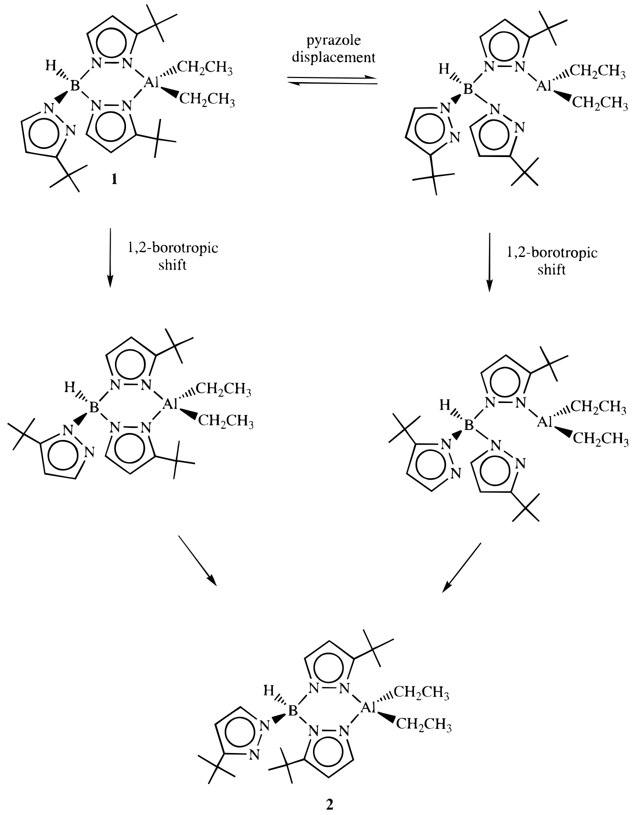
(8) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010.

Scheme 1. Potential Pathways for Isomerization of **1** in THF-d_8



precipitate that was insoluble in organic solvents. Attempts to purify these soluble species by crystallization led to loss of the alkyl resonances of the ethyl groups. These combined observations suggest that substantial decomposition of **1** to as yet uncharacterized products occurs on attempted reaction with alcohols.

Addition of 2 equiv of alcohol (ethyl, isopropyl, *tert*-butyl) to **1** results in the complete disappearance of resonances attributable to the ethyl groups of **1** as well as the formation of a white insoluble precipitate. As in reactions with 1 equiv of alcohol, each alkoxide formed a species whose ^{1}H NMR spectra revealed a single sharp set of pyrazole resonance regardless of the alcohol employed. Minor resonances attributable to O^{i}Pr groups were present in the ^{1}H NMR spectrum of the reaction product when 2 equiv of isopropyl alcohol was added to **1**; however, their intensities relative to the intensities of the pyrazole resonances were not consistent with the formation of a species of formula HB(3-^{t}Bupz)$_3$Al(O^{i}Pr)$_2$. In the case of the reaction of *tert*-butyl alcohol and **1**, several types of aliphatic and aromatic pyrazole resonances were observed, suggesting that several soluble products were formed or that significant ligand redistribution or decomposition processes had occurred. The formation of a white precipitate suggested that the decomposition of **1** had occurred to a substantial extent.

Reactions of 1 with O$_2$. The addition of 1 equiv of O$_2$ to a solution of **1** in benzene-d_6 solution did not result in any changes in the ^{1}H NMR spectrum of **1** over a period of 24 h. This lack of reactivity of the aluminum−alkyl bonds toward O$_2$ in **1** is unusual in light of the observation that O$_2$ reacts with HB(3-^{t}Bupz)$_3$MgCH$_2$CH$_3$ to form HB(3-^{t}Bupz)$_3$MgOOCH$_2$CH$_3$ quantitatively in the presence of excess oxygen[9] and in 40% yield after 10 min of exposure to 1 equiv of O$_2$.[10] The introduction of excess oxygen into a solution of **1** in benzene-d_6 over 15 min results in the immediate formation of a white, insoluble species. The benzene-soluble material exhibited a ^{1}H NMR spectrum containing only pyrazole resonances at the exact chemical shift values observed for the reaction products of **1** with alcohol. No evidence for the formation of peroxide or alkoxide aluminum species was observed.

Conclusions

The complex {H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2}AlEt$_2$, **1**, converts to {H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$, **2**, through a rate-limiting 1,2-borotropic shift involving the nonligated pyrazole group followed by an associative displacement of a 3-^{t}Bupz group bound to Al by the isomerized 5-^{t}Bupz moiety. In polar solvents such as THF, a second dissociative rearrangement pathway may also be operative. The solid-state structures of **1** and **2** reveal the η^2-coordination mode of the chelating ligand, although the room-temperature NMR spectroscopy of **2** was inconsistent with the solid state structure, indicative of fluxional behavior. Low-temperature NMR spectra of **2** in THF-d_8 and toluene-d_8 reveal three sets of pyrazole resonances, consistent with the solid-state structure. The observation that **2** is less fluxional in the coordinating solvent THF than in toluene combined with the appearance of diastereotopic ethyl methylene resonances supports a mechanism involving $\eta^2 \rightleftharpoons \eta^3$ coordination rather than $\eta^2 \rightleftharpoons \eta^1$. **1** exhibits no observable fluxional behavior in the temperature range +60 to −80 °C, although broadening of the 3-^{t}*B*upz groups at low temperature due to restricted rotation is observed. The ethyl groups in **1** are reactive toward alcohols, although the formation of mono- and bis(alkoxide) species is accompanied by decomposition reactions. O$_2$ did not insert into the Al−C bonds of **1** but resulted in the formation of insoluble inorganic species, which were not characterized. The solution-state studies of **1** and **2** provide an elegant demonstration of the binding flexibility of HB(3-^{t}Bupz)$^-$ and the facility of the ligand isomerization process in complexes of this ligand type.

Experimental Section

All manipulations were performed with rigorous exclusion of air and moisture through a combination of standard Schlenk and glovebox techniques. Solvents were dried over appropriate drying agents and deoxygenated prior to use. ^{1}H NMR spectra were recorded on a Varian XL-300 instrument while ^{13}C NMR spectra were obtained on a Bruker AM500 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091-9990, or by Desert Analytics Laboratory, P.O. Box 41838, Tucson, AZ 85775-1725. HB(3-^{t}Bupz)$_3$Tl was prepared as described in the literature,[11] while Et$_3$Al (93%) and Et$_2$AlCl (1.0 M in hexanes) were purchased from Aldrich and used as received.

{H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2}AlEt$_2$ (1). HB(3-^{t}Bupz)$_3$Tl (1.0 g, 1.70 mmol) was dissolved in benzene; then Et$_3$Al (0.23 mL, 1.70 mmol) was added dropwise by syringe at 20 °C. The resulting black slurry was allowed to stir for 15 min and then was filtered through Celite. The resulting pale yellow filtrate was dried *in vacuo* to yield a pale yellow oil which solidified upon sitting at 20 °C. Crystals of **1** were isolated in 70% yield (0.56 g) from a pentane solution cooled to −20 °C. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300 MHz): δ 7.55 (d, J = 2.4 Hz, 2H, pz), 7.15 (d, br, 1H, pz), 6.18 (d, J = 2.7 Hz, 1H, pz), 5.88 (d, J = 2.4 Hz, 2H, pz), 1.51 (s, 9H, ^{t}Bu), 1.31 (s, 18H, ^{t}Bu), 1.19 (t, J = 8.1 Hz, 3H, CH$_2$C*H*$_3$), 1.01 (t, J = 8.1 Hz, 3H, CH$_2$C*H*$_3$), 0.58 (q, J = 8.1 Hz, 2H, C*H*$_2$CH$_3$), 0.37 (q, J = 8.1 Hz, 2H, C*H*$_2$CH$_3$). ^{1}H NMR (THF-d_8, 20 °C, 300 MHz): δ 7.59 (d, J = 2.1 Hz, 2H, pz), 6.92 (d, J = 2.1 Hz, 1H, pz), 6.44 (d, J = 2.1 Hz, 2H, pz), 5.98 (d, J = 2.1 Hz, 1H, pz), 1.50 (s, 18H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 0.81 (t, J = 7.8 Hz, 3H, CH$_2$C*H*$_3$),

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0.74 (t, $J = 7.8$ Hz, 3H, $CH_2C\mathit{H}_3$), 0.28 (q, $J = 7.8$ Hz, 2H, $C\mathit{H}_2CH_2$), 0.10 (q, $J = 7.8$ Hz, 2H, $C\mathit{H}_2CH_3$). ^{13}C NMR (C_6D_6, 20 °C, 125 MHz): δ 166.7, 164.0, 139.2, 134.6, 105.2, 101.3, 32.8 (*C*Me$_3$), 31.1 (C*Me*$_3$), 30.9 (C*Me*$_3$), 30.4 (*C*Me$_3$), 9.1 ($CH_2\mathit{C}H_3$), 8.4 ($CH_2\mathit{C}H_3$), 5.0 ($\mathit{C}H_2CH_3$), 4.5 ($\mathit{C}H_2CH_3$). Anal. Calcd for $C_{25}H_{44}AlBN_6$: C, 64.37; H, 9.51; N, 18.02. Found: C, 62.88; H, 9.39; N, 17.73.

{H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$ (2). HB(3-^{t}Bupz)$_3$Tl (1.0 g, 1.70 mmol) was dissolved in THF; then Et_2AlCl (1.70 mL, 1.70 mmol, 1.0 M solution in hexanes) was added dropwise by syringe. The resulting white slurry was stirred for 15 min at 20 °C and then was filtered through Celite to yield a white crystalline solid. Large, colorless crystals of **2** (0.463 g, 58% yield) were isolated from a pentane solution cooled to −20 °C. ^{1}H NMR (C_6H_6, 20 °C, 300 MHz): δ 7.48 (d, $J = 2.4$ Hz, 1H, pz), 7.15 (d, br, 2H, pz), 6.02 (d, br, 2H, pz), 5.98 (d, $J = 2.4$ Hz, 1H, pz), 1.37 (s, 9H, ^{t}Bu), 1.32 (s, 18H, ^{t}Bu), 1.15 (t, $J = 8.1$ Hz, 3H, $CH_2C\mathit{H}_3$), 1.04 (t, $J = 8.1$ Hz, 3H, $CH_2C\mathit{H}_3$), 0.39 (q, $J = 8.1$ Hz, 2H, $C\mathit{H}_2CH_3$), −0.18 (q, br, $J = 8.1$ Hz, 2H, $C\mathit{H}_2CH_3$). ^{1}H NMR (THF-d_8, 20 °C, 300 MHz): δ 7.88 (d, $J = 2.1$ Hz, 1H, pz), 7.20 (d, br, 2H, pz), 6.44 (d, $J = 2.1$ Hz, 1H, pz), 6.14 (s, br, 2H, pz), 1.51 (s, 9H, ^{t}Bu), 1.27 (s, br, 18H, ^{t}Bu), 0.76 (t, $J = 7.8$ Hz, 3H, $CH_2C\mathit{H}_3$), 0.67 (t, $J = 7.8$ Hz, 3H, $CH_2C\mathit{H}_3$), 0.15 (q, $J = 7.8$ Hz, 2H, $C\mathit{H}_2CH_3$), −0.65 (q, $J = 7.8$ Hz, 2H, $C\mathit{H}_2CH_3$). ^{13}C NMR (C_6D_6, 20 °C, 125 MHz): δ 161.0, 139.8, 136.8, 105.0, 103.9, 102.8, 32.5 (*C*Me$_3$), 30.9 (C*Me*$_3$), 30.4 (C*Me*$_3$), 30.2 (*C*Me$_3$), 9.7 ($CH_2\mathit{C}H_3$), 8.9 ($CH_2\mathit{C}H_3$), 4.0 ($\mathit{C}H_2CH_3$), 0.1 ($\mathit{C}H_2CH_3$). Anal. Calcd for $C_{25}H_{44}AlBN_6$: C, 64.37; H, 9.51; N, 18.02. Found: C, 63.99; H, 9.66; N, 17.97.

Kinetics of Isomerization of 1 to 2. Solutions of **1** in C_6D_6 or THF-d_8 (17 mg in 0.50 mL, 73 mM) were placed in NMR tubes which were sealed and heated in constant-temperature oil baths or a pre-equilibrated NMR probe. The rate of isomerization was monitored by noting the decrease in intensity of the minor *tert*-butyl resonance (C_6D_6) or the minor pyrazole aromatic resonances (THF-d_8) of complex **1** and the growth of the corresponding resonances of complex **2**. Plots of $\ln(k/T)$ vs $1/T$ yielded the activation parameters for the rearrangement process.

Reactions of 1 with Alcohols. To a solution of **1** (0.115 g, 0.25 mmol) in benzene at 20 °C was added the appropriate alcohol in neat form (ethyl alcohol, 14.5 μL, 0.25 mmol or 29.0 μL, 0.50 mmol; isopropyl alcohol, 18.9 μL, 0.25 mmol or 37.8 μL, 0.50 mmol) or as a solution in benzene (*tert*-butyl alcohol, 63 μL, 0.25 mmol or 126 μL, 0.50 mmol; 36.6% v/v). The solutions immediately became cloudy white and were allowed to stir at 20 °C for 15 min before the solvent was removed *in vacuo*. The oily white solids were analyzed by ^{1}H NMR spectroscopy. The products of these reactions were similar regardless of the alcohol employed; however, they could not be further purified or characterized.

Reaction of 1 with O_2. (a) To a solution of **1** (0.020 g, 0.04 mmol) in C_6D_6 was added O_2 (0.96 mL, 0.04 mmol) by a gastight syringe. The reagents were thoroughly mixed, and the reaction progress was monitored by ^{1}H NMR spectroscopy. No reaction products were evident after a 24 h reaction period at 20 °C.

(b) O_2 was bubbled vigorously into a solution of **1** (0.020 g, 0.04 mmol) in C_6D_6 over 15 min. Immediately upon introduction of O_2, a fine white precipitate developed. ^{1}H NMR spectroscopic analysis of the resulting solution revealed resonances for a small quantity of unreacted **1** as well as pyrazole resonances identical to those observed for the products of reactions of **1** with alcohols. This product mixture was not characterized further.

Single-Crystal X-ray Studies. General operating procedures and a listing of programs have been previously described.[12]

{H(3-^{t}Bupz)B(3-^{t}Bupz)$_2$-η^2}AlEt$_2$, 1. A small, well-formed crystal was cleaved from a larger sample and affixed to the end of a glass fiber using silicone grease; the mounted sample was then transferred to a goniostat, where it was initially cooled to −174 °C for characterization and data collection. The initial characterization revealed a cell which appeared approximately monoclinic, but there were indications of problems in both the cell parameters and the extinctions. A data set was collected and readily solved, but the residuals failed to fall below 0.25. Careful examination of several crystals then revealed that a phase transition was present somewhere between −174 and −101 °C. A new crystal was transferred to the goniostat and cooled to the latter temperature with no difficulties.

A systematic search of a limited hemisphere of reciprocal space located for this second crystal located a set of reflections with rigorous monoclinic symmetry and systematic absences corresponding to space group $P2_1/a$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected using a standard moving-crystal, moving-detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms, and equivalent data were averaged. The structure was solved by direct methods (SHELXTL-PC) and Fourier techniques. A difference Fourier map phased on the non-hydrogen atoms clearly located all hydrogen atoms. Initial attempts to include the hydrogen atoms in the refinement were unsuccessful, primarily due to the large thermal motion present on the ^{t}Bu group C(5)−C(8,9,10,11). For this reason, all hydrogen atoms were placed in fixed idealized positions for the refinement.

A final difference Fourier map was essentially featureless, the largest peak being 0.25 e/Å^3. No attempt was made to determine the absolute structure.

{H(3-^{t}Bupz)B(3-^{t}Bupz)(5-^{t}Bupz)-η^2}AlEt$_2$, 2. A small transparent crystal was cleaved from a larger sample and affixed to the end of a glass fiber using silicone grease; the mounted sample was then transferred to the goniostat, where it was cooled to −172 °C for characterization and data collection. Standard inert-atmosphere handling techniques were used throughout the investigations.

A systematic search of a limited hemisphere of reciprocal space located a set of reflections with monoclinic symmetry and systematic absences indicating a *C*-centered space group, either $C2/c$ or Cc. Subsequent solution and refinement of the structure confirmed the proper space group to be $C2/c$.

Data was collected using a standard moving-crystal, moving-detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms, and equivalent data were averaged to yield 3659 unique data. The structure was solved by direct methods (MULTANT78) and Fourier techniques. A difference Fourier map phase on the non-hydrogen atoms clearly located all hydrogen atoms. The final cycles of least squares allowed hydrogen atoms to vary isotropically with all other atoms assigned anisotropic thermal parameters.

A final difference Fourier map was essentially featureless, the largest peak being 0.36 e/Å^3.

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Supporting Information Available: Listings of anisotropic thermal parameters and complete listings of bond distances and angles for **1** and **2** and Eyring plots for rearrangements in benzene-d_6 and THF-d_8 (10 pages). Ordering information is given on any current masthead page.

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