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Synthesis and X-ray Structure of the Novel Aluminum Complex $[\{\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}_2\text{Al}][\text{AlCl}_4]$. Catalysis of CO_2/Propylene Oxide to Propylene Carbonate by the $AlCl_4^-$ Anion

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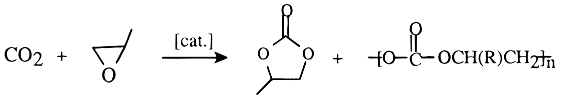
The coupling reaction of carbon dioxide and epoxides in the presence of various catalysts leads to either cyclic carbonates and/or polycarbonates (eq 1).[1] While zinc dicarboxylates have been shown to be the most active catalysts for polycarbonate production,[2] a metalloporhyrinate system containing aluminum, although not very active, has proven to be quite interesting.[3] This latter catalyst is a living system and hence effective in block polyether−polycarbonate synthesis. Furthermore, the addition of 1-methylimidazole rendered the catalyst active for cyclic carbonate production under mild reaction conditions. Kisch and co-workers have also reported $AlCl_3/PPh_3$ to be an active catalyst system for cyclic carbonate synthesis at ambient temperature and atmospheric pressure.[4] Hence, these reports suggest that Al(III) complexes may have a rich chemistry with epoxides and carbon dioxides.



(1)

Recently, the coordination chemistries of aluminum, gallium, and indium have been explored with the tridentate derivatives of pyrazolyl hydroborates.[5] A variety of interesting complexes have been characterized, and the chemistry associated with these derivatives is still in its infancy. As an ongoing part of our efforts in carbon dioxide activation we have initiated studies concerning the reactivity of groups 12 and 13 complexes with epoxides and carbon dioxide.[6] Of particular interest is a comparison of the reactivities of a range of Al(III) complexes with various structural motifs. In this regard an investigation of the reaction of $AlCl_3$ with one equivalent of potassium tris(3-phenylpyrazolyl)hydroborate has been carried out, and herein, we report the X-ray characterization of $[\{\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}_2\text{Al}][\text{AlCl}_4]$ (**1**), an interesting and unanticipated product.

Table 1. Crystallographic Data for **1**

formula	$C_{62}H_{62}Al_2B_2Cl_4N_{12}O_2$	density (calcd), g/cm^3	0.278
fw	1224.65	abs coeff, mm^{-1}	0.278
space group	orthorhombic $P2_12_12_1$	λ, Å	0.710 73
a, Å	16.924(2)	T, K	163
b, Å	17.483(6)	$R(F)$,[a] %	7.28
c, Å	20.572(3)	wR(F^2),[b] %	17.18
V, Å^3	6087(2)	GOF	1.016
Z	4		

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

The reactivity of **1** with epoxide and carbon dioxide is also briefly explored.

Experimental Section

All manipulations were performed on a double-manifold Schlenk line under a nitrogen atmosphere or in an argon-filled glovebox. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere before use. Potassium hydrotris(3-phenylpyrazol-1-yl)borate was prepared according to the published procedure.[7] ^{1}H and ^{27}Al NMR spectra were recorded on a Varian XL-200E and XL-200 equipped with a broadband probe, respectively. Aluminum(III)chloride was purchased from Baker Chemicals and used as received.

Synthesis of $[\{\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}_2\text{Al}][\text{AlCl}_4]$. To 0.56 g of $AlCl_3$ in 30 mL of THF was cannulated an equimolar quantity of $KHB(3\text{-Phpz})_3$ in 20 mL of THF. The reaction mixture was stirred overnight at ambient temperature during which time KCl precipitated from solution, and was recovered by filtration. The solvent was removed by vacuum from the filtrate to provide a white solid product in slightly less than 50% yield, which analyzed for $[C_{54}H_{44}B_2N_{12}Al][AlCl_4]\cdot 2THF/AlCl_3\cdot THF$. Anal. Calcd for $C_{66}H_{68}B_2N_{12}Al_3Cl_7O_3$: C, 55.51; H, 4.80. Found: C, 56.03; H, 5.05. The ^{1}H and ^{13}C NMR spectra of **1** exhibited an array of peaks in the region 6−8 ppm and 120−130 ppm, respectively. Although these are consistent with other related derivatives, in this instance we were unable to unequivocally assign the resonances. The complex was more definitely identified by ^{27}Al NMR spectroscopy in $CDCl_3$. The $AlCl_4^-$ species showed up as a sharp singlet at $\delta = 100$ ppm with the cation, $[\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}]_2\text{Al}^+$, displaying a broad resonance centered at 4 ppm. Crystals of the title complex were grown from a concentrated CH_2Cl_2/THF solution of the complex by a slow diffusion of diethylether. The complex cocrystallized with one molecule of THF and one molecule of diethyl ether.

Synthesis of [PPN][$AlCl_4$]. A 70 mL of aliquot of tetrahydrofuran was added to a Schlenk flask containing 0.50g of bis(triphenylphosphoranylidene)ammonium chloride ([PPN][Cl]) and an equimolar quantity of aluminum trichloride, and the reaction mixture was stirred at ambient temperature for 4 h. The solvent was removed in vacuo leaving behind a white, solid product which was isolated in near quantitative yield. Anal. Calcd for $C_{36}H_{30}P_2NAlCl_4$: C, 61.12; H, 4.27. Found: C, 60.87; H, 4.39. An ^{27}Al NMR spectrum of the product exhibited one sharp resonance for the $AlCl_4^-$ anion at $\delta = 100$ ppm.

Production of Propylene Carbonate from Propylene Oxide and CO_2. In a typical run, 0.10 g (0.099 mmol) of $[\{\eta^3\text{-HB(3-Phpz)}_2\text{(5-Phpz)}\}_2\text{Al}][\text{AlCl}_4]$ was placed in a Parr stainless steel reactor along with approximately 15 mL (0.209 mol) of propylene oxide. The reactor was charged with 750−1200 psi of carbon dioxide and heated at 60 °C with stirring for 24 h. ^{1}H NMR spectroscopy was used to determine the conversion of propylene oxide to propylene carbonate. The percent conversion using complex **1** as catalyst was 38% or 802 turnovers for a 24-h time period. On the other hand, [PPN][$AlCl_4$] employed as catalyst resulted in 56.8% conversion of PO/CO_2 to propylene carbonate during the same time period.

X-ray Crystallography of Complex 1. Crystal data and details of data collection are given in Table 1. A colorless block for **1** was mounted on a glass fiber with epoxy cement, at room temperature and

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(2) (a) Soga, K.; Imai, E.; Hattori, I. *Polym. J.* **1981**, *13*, 407. (b) U.S. Patent 4,943,677, 1990, to A. Rokicki, Air Products and Chemicals, Inc., and Arco Chemical Co. (c) U.S. Patent 5,026,676, 1991, to S. Motika, Air Products and Chemicals, Inc., Arco Chemical Co., and Mitsui Petrochemical Industries Ltd.

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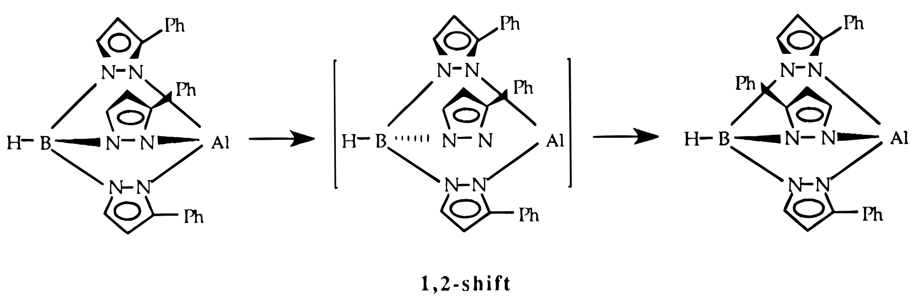
Scheme 1



cooled to 163 K in a N_2 cold stream. Preliminary examination and data collection were performed on a Rigaku AFC5 diffractometer (Mo Kα $\lambda = 0.710\,73$ Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. The ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \leq 2\theta \leq 50.0°$. Three control reflections, collected every 150 reflections, showed no significant trends. Background measurement by stationary crystal and stationary counter technique at the beginning and end of each scan for 0.50 of the total scan time. Lorentz and polarization corrections were applied to 5923 reflections for **1**. An empirical absorption correction was applied ($T_{max} = 0.9999$, $T_{min} = 0.8458$). A total of 5923 unique reflections for **1**, with $|I| \geq 2.0\sigma I$, were used in further calculations. The structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1988)]. Full-matrix least-squares anisotropic refinement on F^2, for all non-hydrogen atoms yielded $R(F) = 0.0728$, $wR(F^2) = 0.1718$, and $S = 1.016$ at convergence for **1** [Shelxl-93, Shedrick (1993)]. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral atom scattering factors and anomalous scattering correction terms were taken from ref 11.

Results and Discussion

In an attempt to synthesize [η^3-HB(3-Phpz)$_3$]AlCl$_2$ from AlCl$_3$ and 1 equiv of K[HB(3-Phpz)$_3$] in THF, we have prepared the product which results from a redistribution process. This was immediately evident from an ^{27}Al NMR spectrum of the product, where the strong, sharp signal for AlCl$_4^-$ was observed at 100 ppm. The analogous reaction carried out using the sterically less-demanding K[HB(3,5-Me$_2$pz)] reagent had previously been demonstrated by Cowley and coworkers to afford the salt resulting from a redistribution reaction (eq 2).[8] Nevertheless, it was anticipated that the bulky nature of the HB(3-Phpz)$_3^-$ anion would, combined with the small ionic radius of the aluminum cation, prevent such a reaction from occurring. Indeed, an X-ray crystallographic study of the reaction product revealed one phenyl pyrazolyl group belonging to each of the HB(3-Phpz)$_3$ ligands had isomerized to the 5-position in order to relieve steric strain (*vide supra*).

$$\mathrm{K[HB(3{,}5\text{-}Me_2pz)_3] + AlCl_3 \rightarrow [\{\eta^3\text{-}HB(3{,}5\text{-}Me_2pz)_3\}_2Al][AlCl_4]} \quad (2)$$

X-ray quality single crystals of [{η^3-HB(3-Phpz)$_2$(5-Phpz)}$_2$Al][AlCl$_4$], (**1**), were grown from a concentrated dichloromethane/tetrahydrofuran solution of the complex by slow diffusion of diethylether over a period of several hours. The structure consists of discrete [{η^3-HB(3-Phpz)$_2$(5-Phpz)}$_2$Al]$^+$ and [AlCl$_4$]$^-$ ions with no short interionic contacts. One molecule each of THF and diethylether were also found in the crystal lattice. Figure 1 illustrates a drawing of the cation, and selected bond lengths and angles for the cation are listed in Table 2. The geometry about the aluminum center in the cation is that of a slightly distorted octahedron; i.e., it exhibits a tetragonal distortion where the AlN$_6$ octahedron is compressed along the N(1)−Al(1)−N(7) axis relative to the other two. The Al(1)−N(1) and Al(1)−N(7) bond distances are 1.949(8) and 1.951(9) Å respectively, whereas the other four Al(1)−N bond distances have an average value of 2.047[9] Å. This most probably results from an electronic effect, as a consequence of the electron-withdrawing phenyl substituents migrating to the 5-position. The average deviation from planarity of the three AlN$_4$ planes is 0.008Å. The AlCl$_4^-$ unit is tetrahedral as expected with an average Al−Cl bond distance of 2.118[6]Å.

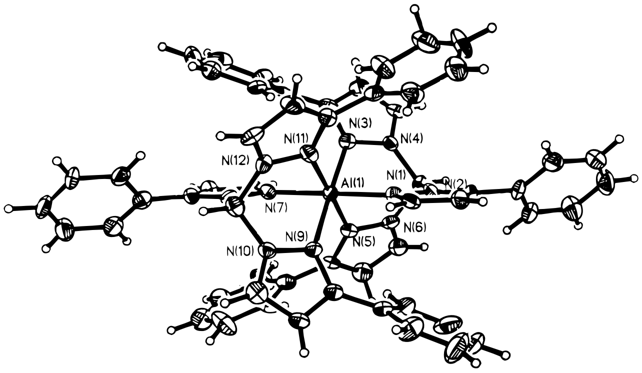


Figure 1. Thermal ellipsoid drawing of the cation of complex **1** in 50% probability with the atomic numbering scheme.

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for the Cation in **1**

Cl(1)−Al(2)	2.128(6)	Cl(2)−Al(2)	2.115(6)
Cl(3)−Al(2)	2.118(6)	Cl(4)−Al(2)	2.112(6)
Al(1)−N(7)	1.949(8)	Al(1)−N(1)	1.951(9)
Al(1)−N(11)	2.037(9)	Al(1)−N(5)	2.039(8)
Al(1)−N(3)	2.045(9)	Al(1)−N(9)	2.066(8)
N(7)−Al(1)−N(1)	179.3(4)	N(7)−Al(1)−N(11)	90.3(3)
N(1)−Al(1)−N(11)	89.4(3)	N(7)−Al(1)−N(5)	89.3(3)
N(1)−Al(1)−N(5)	90.9(3)	N(11)−Al(1)−N(5)	179.4(4)
N(7)−Al(1)−N(3)	89.6(3)	N(1)−Al(1)−N(3)	91.0(3)
N(11)−Al(1)−N(3)	95.7(3)	N(5)−Al(1)−N(3)	84.8(3)
N(7)−Al(1)−N(9)	91.7(3)	N(1)−Al(1)−N(9)	87.7(3)
N(11)−Al(1)−N(9)	85.0(3)	N(5)−Al(1)−N(9)	94.5(3)
N(3)−Al(1)−N(9)	178.5(4)	Cl(4)−Al(2)−Cl(2)	108.8(3)
Cl(4)−Al(2)−Cl(3)	112.0(3)	Cl(2)−Al(2)−Cl(3)	110.2(2)
Cl(4)−Al(2)−Cl(1)	109.3(3)	Cl(2)−Al(2)−Cl(1)	109.2(3)
Cl(3)−Al(2)−Cl(1)	107.4(2)	C(1)−N(1)−Al(1)	129.9(7)
N(2)−N(1)−Al(1)	123.3(6)	N(4)−N(3)−Al(1)	113.9(6)
C(12)−N(3)−Al(1)	40.5(7)	N(6)−N(5)−Al(1)	115.2(6)
C(21)−N(5)−Al(1)	139.0(7)	C(28)−N(7)−Al(1)	132.5(6)
N(8)−N(7)−Al(1)	121.4(6)	C(39)−N(9)−Al(1)	138.8(7)
N(10)−N(9)−Al(1)	114.1(6)	N(12)−N(11)−Al(1)	116.6(6)
C(48)−N(11)−Al(1)	138.5(7)		

[a] Estimated standard deviations are given in parentheses.

Rearrangement of the 3-phenyl substituent is schematically represented in Scheme 1. A similar isomerization has previously been observed by Looney and Parkin, where a unimolecular

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(8) Cowley, A. H.; Jones, R. A.; Geerts, R. L.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277.

rearrangement of the bis(3-*tert*-butylpyrazoyl)hydroborate ligand in (η^2-H_2B(3-*t*-butylpz)$_2$)Al(CH_3)$_2$ to provide the more stable isomer {η^2-H_2B(3-*t*-butylpz)(5-*t*-butylpz)}Al(CH_3)$_2$ was noted.[9] On the basis of kinetic measurements obtained *via* ^{1}H NMR spectroscopy, a free energy of activation of 32.7 kcal/mol was determined, which is consistent with the proposal that the reaction occurs by a 1,2-shift of the *tert*-butylpyrazole group. In the instance reported upon herein the barrier for rearrangement is somewhat lower, since the process occurs readily at ambient temperature.

Complex **1** was found to be an effective catalyst or catalyst precursor for the production of propylene carbonate (PC) from CO_2 and propylene oxide (PO) under rather mild reaction conditions. That is, at 60 °C under CO_2 pressures less than 1200 psi, complex **1** catalyzed the conversion of propylene oxide and carbon dioxide to the corresponding cyclic carbonate with a turnover rate of 800 mol of PC/mol of **1**/24 h. *No* copolymerization of propylene oxide and CO_2 to afford polycarbonates was observed.[10] However, a control experiment employing $AlCl_4^-$ with the innocent PPN^+ counterion as a catalyst for the PO/CO_2 cycloaddition revealed it to be even more effective, providing a turnover rate of 1200 mol of PC/mol of [PPN][$AlCl_4$]/24 h. Hence, the presence of the cation in complex **1** does not significantly affect the catalytic process.

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Supporting Information Available: Tables of atomic coordinates and isotropic displacement parameters, anisotropic thermal parameters and complete bond lengths and angles for complex **1** and ball-and-stick drawings of complex **1** including solvent molecules and complete atomic numbering scheme (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Preliminary results from our laboratory indicates the neutral aluminum(III) complex, {η^3-HB(3,5-Me_2pz)$_3$}AlMe_2,[9] affords, in addition to cyclic carbonates, some polycarbonates.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.