Base Effects on the Formation of Four- and Five-Coordinate Cationic Aluminum Complexes

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This work was conducted as part of our continuing effort to determine the factors that affect cation formation for organometallic aluminum complexes. In this study, the interactions of R_2AlX (where R = Me, ^iBu, ^tBu; X = Cl, Br, I) with the monodentate bases thf, pyridine, NEt_3, HN^iPr_2, H_2N^iBu, H_2N^tBu, and $O{=}PPh_3$ are examined to determine the role of the base in cation formation. These reactions resulted in the neutral adducts of the general form $R_2AlX{\cdot}base$ (**1**−**6**, **8**, **10**, and **12**) as well as the cationic complexes $[R_2Al(base)_2]X$ (**7**, **9**, and **11**). The reactions of Me_2AlX (where X = Cl, Br) with PMDETA (*N,N′,N″,N‴*-pentamethyldiethylenetriamine) and the catalytic activity of the resulting cationic complexes (**13** and **14**) are also discussed. All of the compounds were characterized by mp, IR, ^1H-NMR, and elemental analyses, and in one an X-ray crystallographic study was carried out. X-ray data for **13**: triclinic, $P\bar{1}$, $a = 6.9542(6)$ Å, $b = 12.2058(10)$ Å, $c = 13.2417(11)$ Å, $\alpha = 106.236(2)°$, $\beta = 98.885(2)°$, $\gamma = 93.807(2)°$, $V = 1059.06(15)$ Å^3, and $Z = 2$ for 181 parameters refined on 4358 reflections having $F > 6.0\sigma(F)$, $R = 0.0697$, and $R_w = 0.0697$.

Introduction

Some of the transformations that are possible through the use of alkylaluminum reagents include the reduction of ketones[1] and the living polymerization of oxiranes.[2] Cationic organoaluminum complexes may be expected to find as much relevance in organic transformations and catalysis as neutral derivatives.[1] They may possess enhanced Lewis acidity due to the positive charge on the aluminum center. They may also be made to be coordinatively unsaturated through the use of labile ligands. Preliminary work would seem to support this conclusion. Evans[3a] and Castellino[3b] have postulated that four-coordinate aluminum cations promote certain Diels−Alder reactions. We have previously reported the use of six-coordinate aluminum cations of the form $[SalenAl(MeOH)_2]^+$ as propylene oxide oligomerization catalysts.[4ab] Additionally, Corey has recently reported the use of a cationic boron complex for enantioselective Diels−Alder reactions.[5]

Our interest in cationic aluminum chemistry has led us to investigate the factors affecting the formation of alkylaluminum cations. We recently reported the results of a study into the type of halide which may be displaced from R_2AlX (X = halide) by *tert*-butylamine to form the cations $[R_2Al(H_2N^tBu)_2]X$.[6] Previous work in this area has shown that a variety of bases such as crown ethers,[7] TMEDA,[8] $2\text{-}C(SiMe_3)_2C_5H_4N$,[9] and azamacrocycles[10] lead to the formation of alkylaluminum cations. Additionally, the use of other ligands such as pyridine,[11] thf,[12] acac,[13] $(Me_3SiNHCH_2CH_2)_2NSiMe_3$,[14] (3-phenylpyrazolyl)hydroborate,[15] and $HN{=}CMeN(CH_2)_5$[16] has led to the formation of cations from $AlCl_3$. Lastly, PMDETA (*N,N′,N″,N‴*-pentamethyldiethylenetriamine) has been used to synthesize a novel cationic aluminum dihydride.[17] Surprisingly, however, there has been no systematic study into the role of the base in the formation of aluminum cations.

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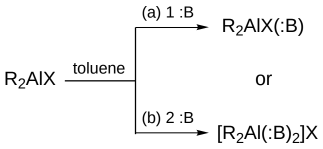
Scheme 1. General Synthesis of **1**−**12**



As a continuation of our study of the factors affecting the formation of alkylaluminum cations, we have undertaken an investigation into the role of the base. The interactions of R_2AlX (where R = Me, ^{i}Bu, ^{t}Bu; X = Cl, Br, I) with the monodentate bases thf, pyridine, NEt_3, $HN^{i}Pr_2$, $H_2N^{i}Bu$, $H_2N^{t}Bu$, and $O{=}PPh_3$ will be discussed. The reactions of Me_2AlX (where X = Cl, Br) with PMDETA and the catalytic activity of the resulting complexes will also be addressed.

Results and Discussion

Four-Coordinate Cations. Previous work exploring the interactions of $AlCl_3$ with pyridine and thf yielding the cationic complexes $[AlCl_2(py)_4][AlCl_4]$[11] and $[AlCl_2(thf)_4][AlCl_4]$[12] as well as the proposed asymmetric cleavage of diborane by thf to yield $[BH_2(thf)_2][BH_4]$[18] in thf solution prompted us to investigate whether these bases would produce the ion pair $[Me_2Al(base)_2]Br$. The general synthesis of compounds **1**−**12** can be seen in Scheme 1. The use of excess base can lead to either the 1:1 adduct or the cationic 2:1 complex. Reaction of Me_2AlBr with excess thf or pyridine in toluene at ambient temperatures leads only to the adducts $Me_2AlBr{\cdot}thf$ **(1)** and $Me_2AlBr{\cdot}py$ (**2**) (Scheme 1a). In the case of **2**, conducting the reaction in refluxing toluene for 3 h does not affect the product outcome. These bases do not displace the halide from R_2AlBr, nor do they lead to a cationic product such as $[Me_2Al(base)_2]^+[Me_2AlBr_2]^-$ as evidenced by the presence of only one AlMe resonance in the ^{1}H-NMR (Table 1).

Due to our success in synthesizing alkylaluminum cations using *tert*-butylamine,[6] we turned our attention to other alkylamines. The reaction of Me_2AlBr with NEt_3 and $HN^{i}Pr_2$ under the same conditions again leads only to the isolation of the adducts $Me_2AlBr{\cdot}NEt_3$ **(3)** and $Me_2AlBr{\cdot}HN^{i}Pr_2$ **(4)**. The identity of **3** was confirmed by a single-crystal X-ray study.[19] Brown had shown that a similar reaction between Me_2AlBr and NMe_3 also leads to a product of 1:1 stoichiometry.[20]

We had previously shown that the demarcation between adduct and cation formation from the combination of excess *tert*-butylamine and Me_2AlX is X = Br.[6] In an attempt to induce cation formation, Me_2AlI was reacted with excess $HN^{i}Pr_2$ in toluene. Surprisingly, this also leads to the formation of an adduct, $Me_2AlI{\cdot}HN^{i}Pr_2$ (**5**). Thus it appears that secondary and tertiary amines are not strong enough bases to displace the halide from Me_2AlX, while primary amines are. To test this hypothesis Me_2AlX (X = Cl, Br) was reacted with $H_2N^{i}Bu$ in toluene. As expected, when X = Cl, the adduct $Me_2AlCl{\cdot}H_2N^{i}Bu$ (**6**) is isolated (Scheme 1a), but when X = Br, the result is the cationic complex $[Me_2Al(H_2N^{i}Bu)_2]Br$ (**7**) (Scheme 1b).

The relative order of base strength for amines toward Lewis acids has been attributed to F-strain, or the steric repulsion between the base and the reference acid. While the relative order for H^+ is $R_3N < RNH_2 < R_2NH$, the order for Lewis acids such as BMe_3 and $B^{t}Bu_3$ is $R_3N < R_2NH < RNH_2$.[21] Thus the basicity of NEt_3 and $HN^{i}Pr_2$ toward Me_2AlBr is reduced and a second equivalent of base does not displace the bromide.

Table 1. Selected Spectroscopic Data for Compounds **1**−**14**[a]

	^{1}H NMR: δ (ppm)		IR: ν (cm^{-1})
compd	Al−R	N−H	N−H
$Me_2AlBr{\cdot}thf$ (**1**)	−0.27 (s)		
$Me_2AlBr{\cdot}py$ (**2**)	−0.09 (s)		
$Me_2AlBr{\cdot}NEt_3$ (**3**)	−0.23 (s)		
$Me_2AlBr{\cdot}HN^{i}Pr_2$ (**4**)	−0.14 (s)	1.94	3173
$Me_2AlI{\cdot}HN^{i}Pr_2$ (**5**)	−0.03 (s)	2.12	3169
$Me_2AlCl{\cdot}H_2N^{i}Bu$ (**6**)	−0.35 (s)	2.04	3261, 3215
$[Me_2Al(H_2N^{i}Bu)_2]Br$ (**7**)	−0.74 (s)[b]	5.32	3140 (br)
$^{i}Bu_2AlCl{\cdot}H_2N^{t}Bu$ (**8**)	0.26 (d), 1.25 (d), 2.22 (m)	2.39	3240, 3203
$[^{i}Bu_2Al(H_2N^{t}Bu)_2]Br$ (**9**)	0.32 (d), 1.26 (d), 2.26 (m)	1.72	3121 (br)
$^{t}Bu_2AlBr{\cdot}H_2N^{t}Bu$ (**10**)	0.77 (s)	2.24	3217, 3232
$[Me_2Al(O{=}PPh_3)_2]Br$ (**11**)	−0.01 (s)		
$Me_2AlCl{\cdot}O{=}PPh_3$ (**12**)	−0.10 (s)		
$[(PMDETA)AlMe_2]$-$[Me_2AlCl_2]$ (**13**)	−0.95 (s), −0.91 (s) −0.81 (s)[b] −0.77 (s), −0.81 (s)[c]		
$[(PMDETA)AlMe_2]Br$ (**14**)	−0.83 (s)[c]		

[a] All NMR data were obtained for C_6D_6 solutions except where noted otherwise. [b] d_8-thf. [c] $CDCl_3$.

In order to see how steric considerations affect the formation of alkylaluminum cations, it is necessary to use larger alkyl groups on R_2AlBr. We have previously shown that a cationic complex is produced from Et_2AlBr and $H_2N^{t}Bu$.[6] The reaction of $^{i}Bu_2AlX$ (X = Cl, Br) with $H_2N^{t}Bu$ leads to the expected adduct $^{i}Bu_2AlCl{\cdot}H_2N^{t}Bu$ (**8**) when X = Cl and the cationic $[^{i}Bu_2Al(H_2N^{t}Bu)_2]Br$ (**9**) when X = Br. However, the reaction between $^{t}Bu_2AlBr$ and $H_2N^{t}Bu$ under the same conditions leads only to the adduct $^{t}Bu_2AlBr{\cdot}H_2N^{t}Bu$ (**10**). While this may be attributed to increased F-strain, it is also consistent with an S_N2 mechanism and increased steric congestion around a potential five-coordinate transition state. An S_N2 mechanism has been proposed in the formation of related boronium cations.[22]

It was noticed that the only bases which thus far had lead to the formation of alkylaluminum cations were all protic. This may lead to the conclusion that there is hydrogen bonding with the halide in the transition state, which helps in the displacement of the halide. A strong, nonprotic base is needed to determine if the use of a protic base is a prerequisite for cation formation. Reaction of Me_2AlBr with 2 molar equiv of $O{=}PPh_3$ in refluxing toluene leads to the formation of the cationic product $[Me_2Al(O{=}PPh_3)_2]Br$ (**11**). Thus it appears that the use of a protic base is not necessary. We were also curious to see whether $O{=}PPh_3$ is strong enough to displace chloride in this reaction. Reaction of Me_2AlCl and 1 or 2 molar equiv of $O{=}PPh_3$ in refluxing toluene leads only to the formation of the adduct $Me_2AlCl{\cdot}O{=}PPh_3$ (**12**). A summary of the interactions of various bases with Me_2AlBr can be seen in Scheme 2.

Adducts **1**−**6**, **8**, **10**, and **12** are all soluble in toluene and can be recrystallized from hexane or toluene/hexane (see Experimental Section). Compound **7**, like the previously reported dimethylaluminum cations, is soluble only in polar solvents such as thf. The use of larger alkyl groups on aluminum such as Et and ^{i}Bu as well as the use of bases such

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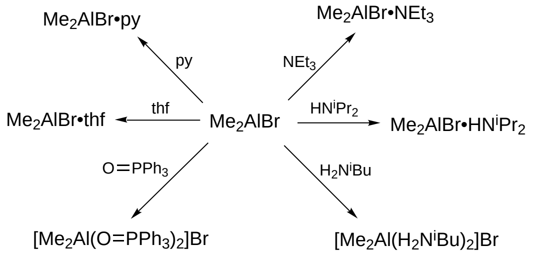
Scheme 2. Interaction of Me_2AlBr with Lewis Bases

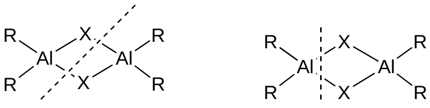


as $O{=}PPh_3$ imparts toluene solubility to compounds **9** and **11**. Selected spectroscopic data is given in Table 1. Identification of the products as adducts or cationic complexes can be determined by integration of the base resonances versus the AlR resonances in the ^1H-NMR as well as by the N−H stretching frequency in the IR (where applicable). The presence of only one AlR resonance in the ^1H-HMR for **1**−**6**, **8**, **10**, and **12** confirms the formation of adducts rather than a $[R_2Al(base)_2][R_2AlBr_2]$ formulation. The presence of a cationic, rather than neutral, aluminum center has little effect on the chemical shift of the protons on the carbon bonded to the aluminum. The downfield shift is 0.06 ppm for cation **9** versus adduct **8** and 0.09 ppm for cation **11** versus adduct **12**.

In the cases where primary or secondary amines were used, the N−H IR stretches are indicative of cation formation. In **4** and **5**, the secondary N-H stretches are present in the form of strong sharp peaks. In **6** and **8** both the symmetric and asymmetric stretching modes of the primary amine are apparent. In cations **7** and **9**, however, these groups are manifested as broad peaks shifted to lower frequency (3261 and 3215 cm^{-1} vs 3140 cm^{-1} for **7** and **6**, respectively). These changes can be explained by the presence of hydrogen bonding between the NH_2 groups on the aluminum cation and the bromide counterion in the solid state. These secondary interactions have also been noticed previously.[6]

Five-Coordinate Cations. During the course of our investigation it became apparent that the reaction between R_2AlX and monodentate Lewis bases leads exclusively to the dissociation of the Al−X bond when cationic products are formed. This is in contrast to the formation of complex ions, usually in the form $[R_2Al(base)][R_2AlX_2]$, when neutral, polydentate Lewis bases such as crown ethers,[7] TMEDA,[8] and tridentate amines[17] are used. This can be viewed in terms of the symmetric versus asymmetric cleavage of the $[R_2AlX]_2$ dimer (Scheme 3). However, when charged polydentate ligands, where one or more of the donor atoms are covalently bonded to the aluminum center, such as Schiff bases[4] and $Me_3SiNHCH_2CH_2)_2NSiMe_3$,[14] are used, the halide is usually displaced.

Scheme 3. Symmetric and Asymmetric Cleavage of $[R_2AlX]_2$



The reaction of Me_2AlX (X = Cl, Br) with PMDETA (*N,N′,N″,N‴*-pentamethyldiethylenetriamine) serves two purposes. It allows for the investigation of the effect of a polydentate amine base on the formation of alkylaluminum cations. It was also postulated that this would lead to a five-coordinate cation. We have previously reported on the catalytic activity of four- and six-coordinate cations in the oligomerization of propylene oxide and are interested in the activity of a five-coordinate species.

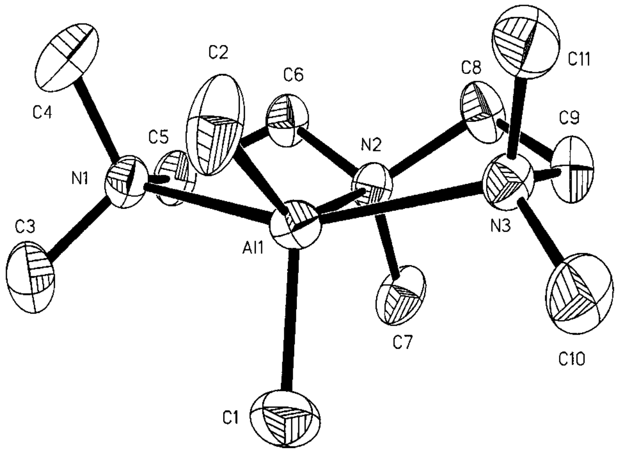


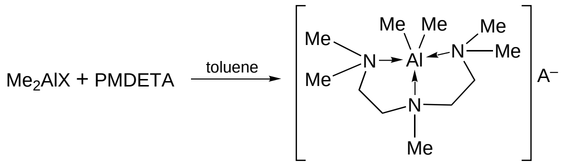
Figure 1. Molecular structure and atom-numbering scheme for $[(PMDETA)AlMe_2]^+$ (**13**).

Table 2. Crystal Data for $[(PMDETA)AlMe_2][Me_2AlCl_2]$ (**13**)

formula	$C_{13}H_{35}Al_2Cl_2N_3$	temp, K	298
formula wt	358.3	2θ range, deg	0.0−55
cryst syst	triclinic	scan type	$2\theta-\theta$
space group	$P\bar{1}$	scan range, deg	110
a, Å	6.9542(6)	reflns collected	6098
b, Å	12.2058(10)	indep reflns	6098
c, Å	13.2417(11)	obsd reflns	4358
α, deg	106.236(2)	$F > X\sigma(F)$	4.0
β, deg	98.885(2)	no. of params	214
γ, deg	93.807(2)	*R*	0.0697
V (Å^3)	1059.06(15)	R_w	0.0697
Z	2	GOF	1.17
D_{calcd}, g/cm^3	1.124	max diff peak, e/Å^3	0.63
cryst size, mm	0.8 × 0.3 × 0.3		

Reaction of Me_2AlCl with PMDETA in a 1:1 molar ratio leads to the expected product $[(PMDETA)AlMe_2][Me_2AlCl_2]$ **(13)** (Scheme 4). Repeating the reaction in a 2:1 molar ratio also leads to **13**. This complex is extremely soluble in polar solvents such as thf and $CHCl_3$. The identity of **13** can be determined from its ^1H-NMR spectrum, which has two sets of AlMe resonances in both d_8-thf and $CDCl_3$ (Table 1). The ^{27}Al-NMR also has two aluminum environments at 132 and 154 ppm which are assigned to the aluminum cation and anion, respectively.

Scheme 4. Syntheses of Compounds **13** and **14**[a]



[a] X = Cl, A = $[Me_2AlCl_2]$; X = A = Br.

This formulation is confirmed by X-ray crystallography. The molecular structure of the cation can be seen in Figure 1. Important bond distances and angles are listed in Table 3. The cation consists of a central five-coordinate aluminum atom in a distorted trigonal bipyramidal geometry where the aluminum methyls (C(1) and C(2)) and one of the nitrogens of the triamine (N(2)) occupy the equatorial positions. N(1) and N(3) of the triamine occupy the axial positions. Deviations from this geometry can be seen in the N(1)−Al(1)−N(3) angle of 151.9(2)° and the C(2)−Al(1)−N(2) angle of 139.9(2)°. The Al−N bond lengths range from 2.067(3) Å for the equatorial N(2) to 2.286(4) Å for the axial N(1). These are consistent with, though slightly longer than, a structurally characterized

Table 3. Bond Lengths and Angles for $[(PMDETA)AlMe_2][Me_2AlCl_2]$ (**13**)

Bond Lengths (Å)			
Al(1)−N(1)	2.286(4)	N(2)−C(8)	1.499(6)
Al(1)−N(2)	2.067(3)	N(3)−C(9)	1.476(5)
Al(1)−N(3)	2.238(4)	N(3)−C(10)	1.469(7)
Al(1)−C(1)	1.952(5)	N(3)−C(11)	1.492(6)
Al(1)−C(2)	1.969(4)	C(5)−C(6)	1.505(7)
N(1)−C(3)	1.466(7)	C(8)−C(9)	1.503(7)
N(1)−C(4)	1.489(7)	Al(2)−Cl(1)	2.216(2)
N(1)−C(5)	1.482(5)	Al(2)−Cl(2)	2.201(2)
N(2)−C(6)	1.502(6)	Al(2)−C(12)	1.953(5)
N(2)−C(7)	1.492(5)	Al(2)−C(13)	1.962(5)
Bond Angles (deg)			
N(1)−Al(1)−N(2)	79.3(1)	Al(1)−N(2)−C(8)	109.6(2)
N(1)−Al(1)−N(3)	151.9(2)	C(6)−N(2)−C(8)	108.3(3)
N(2)−Al(1)−N(3)	80.1(1)	C(7)−N(2)−C(8)	108.5(3)
N(1)−Al(1)−C(1)	101.5(2)	Al(1)−N(3)−C(9)	107.9(2)
N(2)−Al(1)−C(1)	107.1(2)	Al(1)−N(3)−C(10)	112.9(3)
N(3)−Al(1)−C(1)	102.7(2)	C(9)−N(3)−C(10)	109.3(4)
N(1)−Al(1)−C(2)	91.1(2)	Al(1)−N(3)−C(11)	110.9(3)
N(2)−Al(1)−C(2)	139.9(2)	C(9)−N(3)−C(11)	107.7(4)
N(3)−Al(1)−C(2)	92.5(2)	C(1)−N(3)−C(11)	108.1(4)
C(1)−Al(1)−C(2)	113.0(3)	N(1)−C(5)−C(6)	107.8(3)
Al(1)−N(1)−C(3)	112.2(3)	N(2)−C(6)−C(5)	108.2(4)
Al(1)−N(1)−C(4)	111.6(3)	N(2)−C(8)−C(9)	108.1(4)
C(3)−N(1)−C(4)	108.0(4)	N(3)−C(9)−C(8)	108.6(4)
Al(1)−N(1)−C(5)	107.0(3)	Cl(1)−Al(2)−Cl(2)	103.5(1)
C(3)−N(1)−C(5)	109.2(3)	Cl(1)−Al(2)−C(12)	108.7(2)
C(4)−N(1)−C(5)	108.7(4)	Cl(2)−Al(2)−C(12)	110.3(1)
Al(1)−N(2)−C(6)	111.0(2)	Cl(1)−Al(2)−C(13)	109.2(2)
Al(1)−N(2)−C(7)	110.8(3)	Cl(2)−Al(2)−C(13)	108.4(1)
C(6)−N(2)−C(7)	108.6(3)	C(12)−Al(2)−C(13)	116.0(2)

five-coordinate dihydridoaluminum cation which utilizes this ligand (2.02(1) and 2.158(7) Å).[17] They are also longer than the previously characterized four-coordinate cations (1.99−2.00 Å).[6] In the solid state, the aluminum methyl groups appear to be inequivalent due to their proximity to one of the amine methyl groups (C(7)). This is confirmed in the solution state (d_8-thf), where the methyl groups of the cation appear as two broad singlets, thus implying a rigid solution state geometry. The molecule appears to be less configurationally rigid in $CDCl_3$, however, as these peaks collapse into a singlet. The geometry around the aluminum center in the anion is distorted T_d.

Reaction of Me_2AlBr with PMDETA under the same conditions leads to a different product, which is extremely insoluble in thf but soluble in chloroform (Scheme 4). The ^{1}H-NMR spectrum ($CDCl_3$) shows only one resonance for the AlMe groups, which corresponds to the AlMe resonance of **13**. This is confirmed by the ^{27}Al-NMR (134 ppm), which is consistent with a five-coordinate aluminum center and also corresponds to the ^{27}Al-NMR shift of **13**. It was concluded that the complex was $[(PMDETA)AlMe_2]Br$ (**14**). Thus **13** is produced from the asymmetric cleavage and **14** by the symmetric cleavage of $[Me_2AlX]_2$. This difference in mechanism may be attributed to the relative stabilities of the anions.

We were interested to see if the five-coordinate complexes were catalytically active in the living polymerization of an oxirane. Dissolution and stirring of **13** in propylene oxide at ambient temperature and pressure for 24 h followed by evaporation of the volatiles leads to the isolation of a glassy solid. This solid is presumably the oligomer attached to the catalytically active site. One of the important features of living polymerization is the absence of chain termination steps in the polymerization. The ^{1}H-NMR of this solid in $CDCl_3$ confirms the presence of an oligoether, which is manifested as broad multiplets centered at 1.20 and 3.45 ppm, as well as the presence of AlMe resonances. The ^{27}Al-NMR in $CDCl_3$ of this solid exhibits an upfield shift to 107 ppm for the cationic aluminum center while the peak assigned to the aluminate counterion remains unchanged. This data is consistent with the cation being the active site. After workup using a previously reported procedure,[6] the molecular weight of the oligomer is approximately 530 by GPC. A similar procedure using **14** shows only very small oligomers in the preworkup ^{1}H-NMR. From these results it appears that the anion, as well as the cation, plays a role in the catalytic activity of these complexes.

Conclusion

This work was conducted as part of a broad-based effort to understand the factors affecting the formation of alkylaluminum cations. The use of strong monodentate bases such as primary amines or a phosphine oxide is necessary to induce cation formation. The resulting cationic complexes are all derived from the dissociation of the Al−X bond. The reaction of a tridentate base with R_2AlX is halide dependent, producing cationic complexes resulting from both the asymmetric (X = Cl) and symmetric (X = Br) cleavage of $[R_2AlX]_2$. These complexes are also shown to be catalytically active in the living polymerization of propylene oxide.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glovebox. All solvents were rigorously dried before use. Pyridine, triethylamine, diisopropylamine, isobutylamine, *tert*-butylamine, and propylene oxide were dried over and distilled from CaH_2 prior to use. *N,N′,N″,N‴*-Pentamethyldiethylenetriamine was dried with *tert*-butyllithium and distilled before use. Dimethylaluminum iodide was synthesized according to the literature.[23] NMR data were obtained on JEOL-GSX-270 and -400 instruments at 270.17 (^{1}H) and 104.17 (^{27}Al) MHz. Chemical shifts are reported relative to $SiMe_3$ (^{1}H) and $Al(H_2O)_6^{3+}$ (^{27}Al) and are in parts per million. Infrared data were recorded as KBr pellets on a Matheson 2020 Galaxy Series spectrometer and are reported in cm^{-1}. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer.

$Me_2AlBr\cdot thf$ (1). Dimethylaluminum bromide (11.25 mmol) was prepared *in situ* by the addition of aluminum bromide (3.750 mmol, 1.000 g) to a stirred solution of trimethylaluminum (7.500 mmol, 0.541 g) in toluene (40 mL). The resulting solution was stirred at 25 °C for 20 min before thf (123 mmol, 10.0 mL) was added. The solution became warm upon addition of the thf and was allowed to cool to 25 °C and stirred for 3 h. The volatiles were removed under reduced pressure, resulting in a colorless oil. To this was added hexane (5 mL), and the two-phase mixture was cooled to −30 °C for several days, yielding **1** as colorless needles, which were isolated by filtration (2.134 g, 91%). Mp: 32−4 °C. ^{1}H-NMR (C_6D_6): δ −0.27 (s, 6H, AlCH_3), 0.95 (m, 4H, thf), 3.38 (m, 4H, thf). IR: ν 2984 w, 2941 w, 1458 w, 1196 s, 1003 s, 918 m, 862 s, 787 m, 690 s (br). Anal. Calcd: C, 34.47; H, 6.75. Found: C, 34.22; H, 6.29.

$Me_2AlBr\cdot py$ (2). Dimethylaluminum bromide (22.50 mmol) was prepared as described for **1** using trimethylaluminum (15.00 mmol, 1.082 g), aluminum bromide (7.500 mmol, 2.000 g), and toluene (50 mL). To this solution was added pyridine (60.00 mmol, 4.85 mL), and the solution was stirred at 25 °C overnight. The volatiles were removed under reduced pressure until crystalline solid appeared (approximately 15 mL). Hexane (25 mL) was carefully layered on top of this solution, and colorless needles formed as the hexane diffused into solution. The mixture was cooled to −30 °C and kept at that temperature for 4 days yielding **2** as a mass of colorless needles, which were isolated by filtration and washed with 25 mL of cold hexane (4.304 g, 89%). Refluxing a similar reaction mixture for 3 h did not lead to the formation of a cationic product. Mp: 69−70 °C. ^{1}H-NMR (C_6D_6): δ −0.09 (s, 6H, AlCH_3), 6.37 (t, 2H, pyr), 6.77 (t, 1H, pyr), 8.19 (d, 2H, pyr). IR: ν 3067 w, 2928 m, 2891 m, 2825 m, 1614 s,

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(23) Grosse, A. V.; Mavity, J. M. *J. Org. Chem.* **1940**, *5*, 106.

1489 m, 1448 s, 1400 m, 1190 s, 1060 s, 1018 m, 682 s (br), 574 m. Anal. Calcd: C, 38.91; H, 5.13; N, 6.48. Found: C, 38.43; H, 4.97; N, 6.34.

$\mathrm{Me_2AlBr\cdot NEt_3}$ (3). Dimethylaluminum bromide (22.5 mmol) was prepared as described for **1** using trimethylaluminum (15.00 mmol, 1.082 g), aluminum bromide (7.500 mmol, 2.000 g), and toluene (50 mL). To this solution was added triethylamine (90.0 mmol, 12.6 mL). The resulting colorless solution was stirred overnight, and then the volatiles were removed under reduced pressure, resulting in an off-white solid. This was redissolved in toluene (15 mL), the solution was filtered, and hexane (40 mL) was added to the solution. The solution was stored at −30 °C for several days, yielding **3** as colorless crystals (4.423 g, 83%). Crystals suitable for single-crystal X-ray analysis were grown from a concentrated solution in toluene stored at −10 °C for several days. Mp: 117−20 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.23$ (s, 6H, $\mathrm{AlC}H_3$), 0.67 (t, 9H, $\mathrm{NCH_2C}H_3$), 2.25 (q, 6H, $\mathrm{NC}H_2\mathrm{CH_3}$). IR: ν 2990 m, 2943 s, 1475 m, 1400 s, 1195 m, 1163 m, 1099 s, 806 s, 686 s (br). Anal. Calcd: C, 40.35; H, 8.89; N, 5.88. Found: C, 39.88; H, 8.43; N, 5.86.

$\mathrm{Me_2AlBr\cdot HN^iPr_2}$ (4). Dimethylaluminum bromide (22.5 mmol) was prepared as described for **1** using trimethylaluminum (15.00 mmol, 1.082 g), aluminum bromide (7.500 mmol, 2.000 g), and toluene (60 mL). To this solution was added diisopropylamine (90.0 mmol, 12.6 mL). The resulting solution was stirred overnight, and the volatiles were removed under reduced pressure, resulting in a white solid. This was redissolved in toluene (20 mL), and the solution was filtered and concentrated by $^1/_2$. To this was added hexane (40 mL) and the solution was cooled to −30 °C for several days, yielding **4** as colorless plates (4.344 g, 81%). Mp: 64−5 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.14$ (s, 6H, $\mathrm{AlC}H_3$), 0.68 (dd, 12 H, $\mathrm{NCH(C}H_3)_2$), 1.94 (s (br), 1H, $\mathrm{N}H$), 3.05 (m, 2H, $\mathrm{C}H\mathrm{(CH_3)_2}$). IR: ν 3173 s, 2980 m, 2837 m, 1467 m, 1396 s, 1188 s, 1138 s, 1082 m, 777 w, 686 s (br). Anal. Calcd: C, 40.35; H, 8.89; N, 5.88. Found: C, 40.26; H, 8.35; N, 5.86.

$\mathrm{Me_2AlI\cdot HN^iPr_2}$ (5). To a solution of dimethylaluminum iodide (5.436 mmol, 1.000 g) in toluene (35 mL) was added diisopropylamine (21.74 mmol, 3.10 mL). The solution was stirred at 25 °C overnight, and then the volatiles were removed under reduced pressure, resulting in a colorless solid. This was dissolved in hexane (35 mL), and the solution was filtered to remove a small amount of insoluble material, concentrated to incipient crystallization, cooled to −30 °C, and kept at that temperature for several days, yielding **5** as colorless plates (1.169 g, 75%). Mp: 61−3 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.03$ (s, 6H, $\mathrm{AlC}H_3$), 0.70 (dd, 12 H, $\mathrm{NCH(C}H_3)_2$), 2.12 (s (br), 1H, $\mathrm{N}H$), 3.15 (m, 2H, $\mathrm{NC}H\mathrm{(CH_3)_2}$). IR: ν 3169 s, 2976 m, 2945 m, 2983 w, 2833 w, 1465 m, 1396 s, 1190 s, 1134 m, 1091 m, 960 w, 825 m, 775 m, 688 s (br). Anal. Calcd: C, 33.70; H, 7.42; N, 4.91. Found: C, 33.28; H, 7.06; N, 4.73.

$\mathrm{Me_2AlCl\cdot H_2N^iBu}$ (6). To a stirred solution of dimethylaluminum chloride (10.81 mmol, 1.000 g) was added isobutylamine (43.2 mmol, 4.30 mL). The colorless solution was stirred overnight. The volatiles were removed under reduced pressure, resulting in a white solid. This was dissolved in warm hexane (75 mL), and the solution was concentrated to incipient crystallization and then cooled to −30 °C, yielding **6** as a mass of fine, colorless needles (1.759 g, 98%). Mp 55−7 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.35$ (s, 6H, $\mathrm{AlC}H_3$), 0.47 (d, 6H, $\mathrm{NCH_2CH(C}H_3)_2$), 1.09 (m, 1H, $\mathrm{NCH_2C}H\mathrm{(CH_3)_2}$), 2.04 (s (br), 2H, $\mathrm{N}H_2$), 2.14, (d, 2H, $\mathrm{NC}H_2\mathrm{CH(CH_3)_2}$). IR: ν 3261 s, 3215 s, 2964 m, 1608 m, 1581 m, 1512 m, 1471 s, 1398 s, 199 s, 1143 w, 1016 m, 788 m, 713 s (br). Anal. Calcd: C, 43.51; H, 10.35; N, 8.46. Found: C, 43.19; H, 9.95; N, 8.18.

$\mathrm{[Me_2Al(H_2N^iBu)_2]Br}$ (7). Dimethylaluminum bromide (22.50 mmol) was prepared as described for **1** using trimethylaluminum (15.00 mmol, 1.082 g), aluminum bromide (7.500 mmol, 2.000 g), and toluene (60 mL). To this solution was added isobutylamine (90.0 mmol, 8.95 mL). The reaction was very exothermic, and after 5 min a colorless crystalline precipitate formed. The mixture was stirred at 25 °C for 3 h. The volatiles were removed under reduced pressure, resulting in a white solid. This was dissolved in thf (65 mL), and the solution was filtered to remove a small amount of insoluble material. The solution was cooled to −30 °C for 2 days, yielding **7** as a mass of colorless plates (5.542 g, 87%). Crystals suitable for single-crystal X-ray analysis were grown from a dilute solution in thf stored at −10 °C for 3 weeks. Mp: 112−6 °C dec. ^{1}H-NMR (d_8-thf): $\delta\ -0.74$ (s, 6H, $\mathrm{AlC}H_3$), 0.98, (d, 12H, $\mathrm{NCH_2CH(C}H_3)_2$), 1.83 (m, 2H, $\mathrm{NCH_2C}H\mathrm{(CH_3)_2}$), 2.58 (d, 4H, $\mathrm{NC}H_2\mathrm{CH(CH_3)_2}$), 5.32 (s (br), 4H, $\mathrm{N}H_2$). IR: ν 3140 s (br), 3065 s (br), 2960 m, 1577 m, 1469 m, 1396 m, 1213 s, 1198 s, 1118 m, 1018 s, 790 w, 746 s, 721 s. Anal. Calcd: C, 42.41; H, 9.96; N, 9.89. Found: C, 42.30; H, 9.52; N, 9.95.

$\mathrm{^iBu_2AlCl\cdot H_2N^tBu}$ (8). To a solution of diisobutylaluminum chloride (11.32 mmol, 2.000 g) in toluene (40 mL) was added *tert*-butylamine (45.3 mmol, 4.80 mL). The colorless solution was stirred for 3 h, and the volatiles were removed under reduced pressure, yielding **8** as a colorless crystalline solid (2.619 g, 93%), which was recrystallized from hexane. Mp: 80−3 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): δ 0.26 (d, 4H, $\mathrm{AlC}H_2\mathrm{CH(CH_3)_2}$), 0.69 (s, 18H, $\mathrm{NC(C}H_3))$), 1.25 (d, 12H, $\mathrm{AlCH_2CH(C}H_3)_2$), 2.22 (m, 2H, $\mathrm{AlCH_2C}H\mathrm{(CH_3)_2}$), 2.39 (s (br), 4H, $\mathrm{N}H_2$). IR: ν 3240 m, 3203 m, 2958 s, 2896 m, 1577 m, 1464 m, 1402 s, 1377 s, 1218 w, 1176 m, 1070 m, 1024 m, 702 s. Anal. Calcd: C, 57.70; H, 11.70; N, 5.61. Found: C, 57.32; H, 11.46; N, 5.43.

$\mathrm{[^iBu_2Al(H_2N^tBu)_2]Br}$ (9). Diisobutylaluminum bromide (11.25 mmol) was prepared *in situ* by the addition of aluminum bromide (3.750 mmol, 1.000 g) to a stirred solution of triisobutylaluminum (7.500 mmol, 1.487 g) in toluene (30 mL). The solution was stirred at 25 °C for 30 min, and then *tert*-butylamine (45.0 mmol, 4.73 mL) was added. The reaction was extremely exothermic. The solution was stirred at 25 °C overnight. The solution was concentrated to approximately 10 mL, and hexane (25 mL) was added. The solution was stored at −30 °C for 1 week, yielding **9** as a large mass of colorless crystals (2.966 g, 75%). Mp: 78−82 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): δ 0.32 (d, 4H, $\mathrm{AlC}H_2\mathrm{CH(CH_3)_2}$), 0.82 (s (br), 18H, $\mathrm{NC(C}H_3))$), 1.26 (d, 12H, $\mathrm{AlCH_2CH(C}H_3)_2$), 1.72 (s (br), 4H, $\mathrm{N}H_2$), 2.26 (m, 2H, $\mathrm{AlCH_2C}H\mathrm{(CH_3)_2}$). IR: ν 3121 m (br), 2966 m, 1525 w, 1402 s, 1377 m, 1261 m, 1070 m, 1030 m, 810 s (br). Anal. Calcd: C, 52.31; H, 10.97, N, 7.63. Found: C, 51.99; H, 10.49; N, 7.34.

$\mathrm{^tBu_2AlBr\cdot H_2N^tBu}$ (10). To a stirred solution of di-*tert*-butylaluminum bromide (4.522 mmol, 1.000 g) in toluene (20 mL) was added *tert*-butylamine (18.9 mmol, 1.90 mL). The colorless solution was stirred overnight. The volatiles were removed under reduced pressure, yielding an oily, colorless solid. This was dissolved in warm hexane (40 mL) and then stored at −30 °C for 2 days, yielding **10** as a large mass of very fine, colorless needles. Concentration of the filtrate resulted in formation of additional needles (0.994 g, 75%). Mp: 70−2 °C dec. ^{1}H-NMR ($\mathrm{C_6D_6}$): δ 0.77 (s, 9H, $\mathrm{NC(C}H_3)_3$), 1.18 (s, 18H, $\mathrm{AlC(C}H_3)_3$), 2.24 (s (br), 2H, $\mathrm{N}H_2$). IR: ν 3271 m, 3232 m, 2974 m, 2833 m, 1562 m, 1465 s, 1404 m, 1379 s, 1292 m, 1209 w, 1159 m, 1003 w, 814 s, 651 s. Anal. Calcd: C, 48.98; H, 9.93; N, 4.76. Found: C, 48.56; H, 9.38; N, 4.71.

$\mathrm{[Me_2Al(O{=}PPh_3)_2]Br}$ (11). To a stirred solution of triphenylphosphine oxide (22.50 mmol, 6.260 g) in toluene (100 mL) was added a solution of dimethylaluminum bromide (11.25 mmol) prepared as described for **1**. The solution turned yellow upon initial addition of the aluminum solution and then turned colorless. After 15 min a crystalline precipitate began to form. The mixture was refluxed for 2 h, and the solid slowly dissolved. The resulting solution was then cooled to −10 °C overnight, yielding **11** as colorless needles (7.703 g). These were shown by ^{1}H-NMR to be a toluene solvate. The crystals began to lose solvent, so they were dried under vacuum for 15 h, resulting in a nearly quantitative loss of 1 molar equiv of toluene. **11** was isolated as a white powder (6.711 g, 87%). Mp: 147−50 °C. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.01$ (s, 6H, $\mathrm{AlC}H_3$), 6.94−7.00, 7.64−68 (m, 30H, $\mathrm{Ph}H$). IR: ν 3059 w, 2996 w, 2887 w, 1589 m, 1437 s, 1400 s, 1192 m, 1163 m, 1122 m, 725 s, 692 s. Anal. Calcd: C, 65.81; H, 5.23. Found: C, 65.34; H, 5.08.

$\mathrm{Me_2AlCl\cdot O{=}PPh_3}$ (12). Method A. To a stirred solution of triphenylphosphine oxide (5.405 mmol, 1.504 g) in toluene (20 mL) was added a solution of dimethylaluminum chloride (5.405 mmol, 0.500 g) in toluene (20 mL). The solution was refluxed for 3 h and then concentrated to approximately 15 mL. To this was added hexane (20 mL), and the solution was stored at −30 °C for several days, yielding **12** as a mass of colorless crystals (1.702 g, 85%). Mp: 128−32 °C dec. ^{1}H-NMR ($\mathrm{C_6D_6}$): $\delta\ -0.10$ (s, 6H, $\mathrm{AlC}H_3$), 6.85−7.08, 7.47−52 (m, 15H, $\mathrm{Ph}H$). IR: ν 3053 w, 2928 m, 2887 w, 1438 s, 1398 m, 1176 s (br), 1122 s, 727 s, 690 s, 540 m. Anal. Calcd: C, 64,79; H, 5.71. Found: C, 63.88; H, 5.55.

Method B. To a stirred solution of 2 molar equiv of triphenylphosphine oxide (10.81 mmol, 3.008 g) in toluene (20 mL) was added a solution of dimethylaluminum chloride (5.405 mmol, 0.500 g). The solution was refluxed for 3 h, and the volatiles were removed under reduced pressure, resulting in a white solid residue. ^{1}H-NMR (C_6D_6) displayed a peak at −0.10 ppm (AlCH_3), which is indicative of adduct **12** rather than cation **11**.

[(PMDETA)AlMe$_2$][Me$_2$AlCl$_2$] (13). Method A. To a stirred solution of 2 molar equiv of dimethylaluminum chloride (10.81 mmol, 1.000 g) in toluene (50 mL) was added pentamethyldiethylenetriamine (5.41 mmol, 1.13 mL). The resulting pale yellow solution was stirred at 25 °C overnight. During this time the solution grew hazy and a crystalline solid appeared. The volatiles were removed under reduced pressure, resulting in a colorless solid. This was dissolved in thf (10 mL), and the solution was cooled to −30 °C and kept at that temperature for 2 days, yielding **13** as colorless blocks (0.985 g). Concentration of the filtrate and subsequent storage at −30 °C produced more crystals (total 1.449 g, 75%). Mp: 108−10 °C. ^{1}H-NMR (d_8-thf): δ −0.95 (s (br), 3H, Al$^+$CH_3), −0.91 (s (br), 3H, Al$^+$CH_3), −0.81 (s, 6H, Al$^-$CH_3), 2.37 (s, 3H, NCH_3), 2.50 (s, 12H, N(CH_3)$_2$), 2.63 (m, 4H, CH_2), 2.73 (m, 4H, CH_2). ^{1}H-NMR (CDCl$_3$): δ −0.81 (s (br), 6H, Al$^+$CH_3), −0.77 (s, 6H, Al$^-$CH_3), 2.42 (s, 12H, N(CH_3)$_2$), 2.50 (s, 3H, NCH_3), 2.63 (m (br), 4H, CH_2), 2.73 (m (br), 4H, CH_2). ^{27}Al-NMR (d_8-thf): δ 99, 134, 156. ^{27}Al-NMR (CDCl$_3$): δ 132, 154. IR: ν 2951 m, 2820 m, 1477 s, 1400 s, 1305 w, 1186 s, 1062 m, 702 s (br), 572 m. Anal. Calcd: C, 43.58; H, 9.85; N, 11.73. Found: C, 43.43; H, 9.68; N, 11.56.

Method B. To a stirred solution of dimethylaluminum chloride (10.81 mmol, 1.000g) in toluene (50 mL) was added 1 molar equiv of pentamethyldiethylenetriamine (10.8 mmol, 2.26 mL). The resulting pale yellow solution was stirred at 25 °C overnight. During this time the solution grew hazy and a crystalline solid appeared. The volatiles were removed under reduced pressure, resulting in a colorless solid. This was dissolved in thf (10 mL), and the solution was cooled to −30 °C and kept at that temperature for 2 days, yielding **13** as colorless blocks (1.025 g, 53% based upon Al). The identity of **13** was confirmed by mp and ^{1}H-NMR.

[(PMDETA)AlMe$_2$]Br (14). Dimethylaluminum bromide (11.25 mmol) was prepared *in situ* by the addition of aluminum bromide (3.750 mmol, 1.000 g) to a stirred solution of trimethylaluminum (7.500 mmol, 0.541 g) in toluene (40 mL). The resulting solution was stirred at 25 °C for 20 min. To this solution was added dropwise pentamethyldiethylenetriamine (11.25 mmol, 2.35 mL). During the addition, a highly crystalline precipitate formed and the solution became pale orange. The mixture was stirred for 3 h. **14** was isolated as a crystalline solid after filtration and washing with 15 mL of toluene (3.092 g, 89%). Mp: 113−5 °C dec. ^{1}H-NMR (CDCl$_3$): δ −0.83 (s, 6H, Al, CH_3), 2.43 (s, 12H, N(CH_3)$_2$), 2.50 (s, 3H, NCH_3), 2.84 (m (br), 4H, CH_2), 3.54 (m (br), 4H, CH_2). ^{27}Al-NMR (CDCl$_3$): δ 134. IR: ν 2920 s (br), 1469 s, 1288 m, 1199 m, 1101 m, 1047 s, 1010 s, 958 m, 938 m, 810 m, 692 s (br). Anal. Calcd: C, 42.58; H 9.42; N, 13.54. Found: C, 41.95; H, 9.06; N, 13.47.

Oligomerization of Propylene Oxide with 13. To **13** (1.395 mmol, 0.500g) was added freshly distilled propylene oxide (360 mmol, 25 mL) at −78 °C. The solid went into solution within 30 s. The solution was warmed to 25 °C and stirred for 24 h. The volatiles were removed under reduced pressure, resulting in a glassy solid. ^{1}H-NMR (CDCl$_3$) confirmed the presence of an oligomer with large broad multiplets centered at 1.20 and 3.45 ppm. ^{27}Al-NMR (CDCl$_3$) showed that the Al cation peak had shifted to 102 ppm. This solid was dissolved in CH_2Cl_2 (70 mL). To this solution was added dilute HCl (20 mL), and a gas was vigorously evolved while the mixture was stirred for 10 min. The layers were separated, and the CH_2Cl_2 layer was washed with H_2O and then dried with $MgSO_4$. The solvent was removed, yielding a viscous tan oil, which was shown by ^{1}H-NMR to be the oligoether.

Oligomerization of Propylene Oxide with 14. To **14** (1.395 mmol, 0.433 g) was added propylene oxide (360 mmol, 25 mL) at −30 °C. The solid went into solution within 30 s. The solution was warmed to 25 °C and stirred for 24 h. The volatiles were removed under reduced pressure, resulting in a glassy solid. ^{1}H-NMR (CDCl$_3$) confirmed the presence of a small oligomer with broad multiplets centered at 1.20 and 3.45 ppm. This solid was dissolved in CH_2Cl_2 (70 mL). To this solution was added dilute HCl (20 mL), and a gas was vigorously evolved while the mixture was stirred for 10 min. The layers were separated, and the CH_2Cl_2 layer was washed with H_2O and then dried with $MgSO_4$. ^{1}H-NMR showed that no oligoether was present in this layer.

X-ray Experimental Details. A summary of crystallographic data for **13** is listed in Table 2. Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα (0.710 79 Å) radiation. All calculations were performed on a personal computer using the Siemens software package SHELXTL-Plus. The structures were solved by direct methods and successive interpretations of difference Fourier maps, followed by least squares refinements. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined in calculated positions using fixed isotropic parameters.

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Supporting Information Available: Tables of X-ray experimental details, heavy atom coordinates, bond lengths and angles, anisotropic parameters, and hydrogen atom coordinates for **13** and a unit cell view for **13** (9 pages). Ordering information is given on any current masthead page.

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