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Synthesis and Structure of Neutral and Cationic Aluminum Complexes Incorporating Bis(oxazolinato) Ligands

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Treatment of the bis(oxazolines) 1,1-bis[4,4-dimethyl-1,3-oxazolin-2-yl]ethane (**1a**, {BOX-Me_2}H) and 1,1-bis[(4*S*)-4-isopropyl-1,3-oxazolin-2-yl]ethane (**1b**, {BOX-(*S*)-^{i}Pr}H) with ^{n}-BuLi, followed by the addition of 1 equiv of $ClAlMe_2$, affords the corresponding dimethyl Al complexes {BOX-Me_2}$AlMe_2$ (**2a**) and {BOX-(*S*)-^{i}Pr}$AlMe_2$ (**2b**) in reasonable yields. The dichloro Al complex {BOX-Me_2}$AlCl_2$ (**3a**) was synthesized in a similar way using 1 equiv of $AlCl_3$. Compounds **2a**,**b** and **3a** are monomeric four-coordinate mono[bis(oxazolinato)-aluminum] complexes, on the basis of X-ray analyses for **2b** and **3a** and NMR data for **2a**,**b** and **3a**. The dimethylaluminum complexes {BOX-Me_2}$AlMe_2$ (**2a**) and {BOX-(*S*)-^{i}Pr}$AlMe_2$ (**2b**) react in C_6D_5Br with $B(C_6F_5)_3$ to yield the quantitative formation of cations {BOX-Me_2}$AlMe^+$ (**4a**$^+$) and {BOX-(S)-^{i}Pr}$AlMe^+$ (**4b**$^+$), respectively, as fully dissociated $MeB(C_6F_5)_3^-$ salts. Cations **4a**,**b**$^+$, which are most likely either base-free three-coordinate cationic species or four-coordinate cationic Al−C_6D_5Br adducts, are unstable at room temperature in C_6D_5Br and decompose to unidentified species. When these ionization reactions are performed in the presence of a Lewis base L (L = THF, NMe_2Ph), corresponding four-coordinate Al−L Lewis base adducts are cleanly generated, {BOX-Me_2}Al(Me)(L)$^+$ (**5a**$^+$, L = THF; **6a**$^+$, L = NMe_2Ph) and {BOX-(S)-^{i}Pr}Al(Me)(L)$^+$ (**5b**$^+$, L = THF; **6b**$^+$, L = NMe_2Ph), as determined by solution studies and, in the case of **6a**$^+$, by X-ray analysis. In contrast, the reaction of {BOX-Me_2}$AlMe_2$ (**2a**) with $[Ph_3C][B(C_6F_5)_4]$ yields the bis(imine) Al cation **7a**$^+$, as determined by NMR and X-ray analysis. The formation of **7a**$^+$ most likely proceeds via a hydride abstraction by Ph_3C^+ at the Me group located at the back of the bis(oxazolinato) ligand in **2a**.

Introduction

Cationic aluminum complexes are of interest because the enhanced Lewis acidity of the Al center versus that of their neutral analogues is attractive for potential applications in catalysis.[1] Some of these cationic complexes have already found applications in ethylene,[2] alkene oxide,[3] and D,L-lactide[4] polymerization catalysis. In this regard, low-coordinate Al cations are particularly attractive, since they combined a cationic charge and a low coordination number and are thus expected to be highly electrophilic species. Recent studies in this area showed that chelate cationic Al alkyls such as three- and four-coordinate Al alkyl cations {L−X}AlR^+ and {L−X}Al(R)(L)$^+$ (L−X$^-$ is a monoanionic bidentate ligand; L is a labile ligand), readily obtained by reaction of {L−X}AlR_2 with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$, are powerful Lewis acids.[5] As such, these cationic species may mediate unusual transformations in Lewis acid based catalysis.

To extend the scope of applications of low-coordinate Al cations, we are interested in the synthesis of chiral Al alkyl complexes {L−X*}Al(R)(L)$^+$, where L−X*$^-$ is a monoanionic chiral bidentate chelating ligand and L is labile, because such species may be useful for ap-

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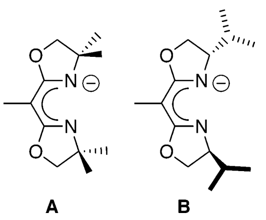
Chart 1

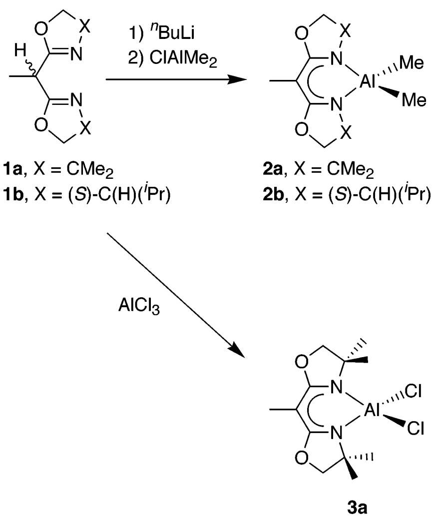


plications in asymmetric catalysis. For this purpose, our interest was driven toward the use of C_2-symmetric chiral bis(oxazolinato) ligands (BOX$^-$) of type **B** (Chart 1) for coordination to aluminum. Whereas neutral bis(oxazolines) have been extensively used in numerous catalytic asymmetric reactions,[6] anionic versions of such ligands remain less studied. Efficient catalysts that bear the anionic ligand family were reported with titanium,[7] rhodium,[8] copper,[6a] zinc,[9] magnesium,[10]and more recently lanthanides.[11] Moreover, the catalysts are usually prepared in situ and not isolated. Only few examples have been completely characterized.[8,11−15]

As for the aluminum metal center, although there have been no reports of group 13 metal complexes containing the bis(oxazolinato) ligand, this chelate ligand, i.e., a monoanionic bidentate dinitrogen donor with a six-electron π-delocalized system, should yield a rather stable and rigid six-membered metallacycle ring when coordinated to an Al center.

Here we report our initial efforts in the synthesis and structural characterization of neutral and cationic, achiral and chiral mono[bis(oxazolinato)aluminum] complexes. The coordination chemistry of the achiral ligand **A** (Chart 1) with Al was first investigated, because the dimethyl substitution of a carbon α to the nitrogen of the oxazolinyl ring in **A** should provide a significant steric shielding of the metal center and thus yield stable and monomeric Al complexes. We then extended our studies, when appropriate, to the chiral version **B** (Chart 1).

Scheme 1



Results and Discussion

The mono[bis(oxazolinato)aluminum] dimethyl complexes **2a**,**b** and the dichloro Al derivative **3a** were synthesized via a salt metathesis pathway by reaction of the desired bis(oxazolinato) lithium salt, generated in situ, and the corresponding Al chloride reagent ($AlClMe_2$ or $AlCl_3$) (Scheme 1). For example, the reaction of the bis(oxazoline) ligand {BOX-Me$_2$}H (**1a**) with ^{n}BuLi at −78 °C in pentane followed by the addition, at −40 °C, of $AlClMe_2$ or $AlCl_3$ affords the corresponding Al complex {BOX-Me$_2$}AlMe$_2$ (**2a**) or {BOX-Me$_2$}AlCl$_2$ (**3a**), respectively, in reasonable yields (**2a**, 57% yield; **3a**, 62% yield). The chiral C_2-symmetric dimethyl Al complex {BOX-(*S*)-^{i}Pr}AlMe$_2$ (**2b**) was obtained in moderate yield (48%) by a similar procedure using {BOX-(*S*)-^{i}Pr}H and $AlClMe_2$. Alternatively, it is noteworthy that the NMR-scale reaction of {BOX-Me$_2$}H with $AlMe_3$ in C_6D_6 at room temperature yields, along with methane generation, the quantitative formation of **2a**, thus showing that the alkane elimination method is also a viable pathway to access bis(oxazolinato)-aluminum dialkyl derivatives. Compounds **2a**,**b** and **3a** were isolated as colorless crystalline solids that are quite soluble in hydrocarbon solvents and stable for months under N_2 either in hydrocarbon solution or in the solid state.

The molecular structures of the chiral Al complex **2b** and the dichloro Al compound **3a** were determined by X-ray crystallographic analysis, establishing their monomeric nature as well as the bidentate chelation of one bis(oxazolinato) ligand (Figures 1 and 2 and Tables 1 and 2).

The Al metal center in both complexes adopts a distorted-tetrahedral structure with N−Al−N bite angles (**2b**, 93.13(7)°; **3a**, 97.35(8)°) similar to those in the related β-diketiminato Al complexes (TTP)AlX$_2$ (Chart 2; **C**, 94.72(14)°; **D**, 99.41(12)°), which contain a similar six-membered C_3N_2Al metallacycle.[16] The Al−N bond distances in **3a** (1.857(2) and 1.843(2) Å) are comparable to those in **D** (1.850(2) Å) but are slightly shorter than those in **2b** (1.906(2) and 1.899(2) Å), due to the more electrophilic Al center in **3a**. The Al−C bond distances

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Table 1. Crystallographic Data for 2b, 3a, [6a][MeB(C_6F_5)$_3$], and [7a][B(C_6F_5)$_4$]

	2b	**3a**	[**6a**][MeB(C_6F_5)$_3$]	[**7a**][B(C_6F_5)$_4$]
formula	$C_{16}H_{29}AlN_2O_2$	$C_{12}H_{19}AlCl_2N_2O_2$	$C_{40}H_{36}AlBF_{15}N_3O_2$	$C_{37}H_{18}AlBF_{21}N_2O_2$
fw	308.39	321.17	913.51	959.38
cryst size (mm)	0.09 × 0.08 × 0.07	0.13 × 0.10 × 0.08	0.13 × 0.10 × 0.08	0.09 × 0.08 × 0.07
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	12.462(5)	8.528(1)	13.349(5)	12.842(1)
b (Å)	16.896(5)	10.190(1)	16.348(5)	19.392(2)
c (Å)	17.501(5)	18.087(1)	18.623(5)	15.786(1)
α (deg)	90.00	90.00	89.25(5)	90.00
β (deg)	90.00	90.00	89.68(5)	98.21(5)
γ (deg)	90.00	90.00	89.30(5)	90.00
V (Å^3)	3685(2)	1571.8(3)	4063(2)	3890.9(6)
Z	8	4	4	4
D_{calcd} (g cm^{-3})	1.112	1.357	1.493	1.638
no. of indep rflns	10 777	4554	23 476	9290
no. of params	379	168	1117	589
R1[a]	0.0488	0.0521	0.1043	0.0555
wR2 (all data)	0.1306	0.1370	0.2449	0.1761
goodness of fit	0.971	1.090	1.109	1.025

[a] R1 ($I > 2\sigma(I)$).

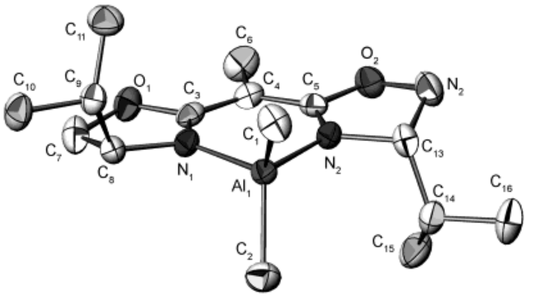


Figure 1. Molecular structure of complex **2b**. The H atoms are omitted for clarity. Selected torsion angles (deg): N(2)−Al(1)−N(1)−C(3) = 6.09(17), Al(1)−N(2)−C(5)−C(4) = −1.5(3), N(2)−C(5)−C(4)−C(3) = 4.1(3).

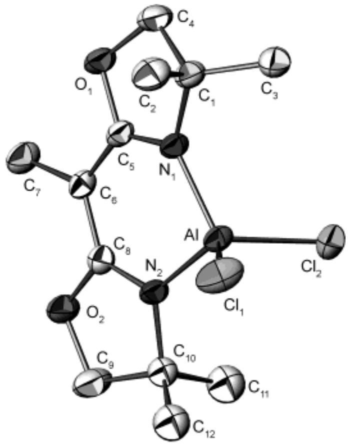


Figure 2. Molecular structure of complex **3a**. The H atoms are omitted for clarity. Selected torsion angles (deg): Al−N(1)−C(5)−C(6) = 4.9(3), N(1)−Al−N(2)−C(8) = 6.5(2), C(5)−C(6)−C(8)−N(2) = −2.5(4).

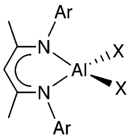
in **2b** and the Al−Cl bond distances in **3a** are also similar to those in **C** and **D**, respectively.

In both **2b** and **3a** complexes, the six-membered ring {BOX}Al moiety forms a nearly planar metallacycle (|C−C−Al−N| < 7° in **2b** and (|C−C−Al−N| < 6° in **3a**), with the carbon and nitrogen atoms exhibiting a trigonal-planar coordination (sum of angles ca. 360°). The bonding in the $Me_2CN{=}C(O)C(CH_3)C(O){=}NC(Me_2)$ backbone of the bis(oxazolinato) ligand in both **2b** and **3a** is delocalized, as shown by the C−C bond distances (1.39(1) Å average), which are close to the C−C bond distances in aromatic systems (1.395 Å), and the C−N bond distances (1.33(1) Å average), which are intermediate between C═N double-bond distances in imines (1.28 Å) and C(sp^2)−N single-bond distances (1.47 Å). As a result of the nearly planar Al metallacycle combined bonding π-delocalization of the ligand backbone, complexes **2b** and **3a** approach overall C_2 and C_{2v} symmetry, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2b and 3a

2b		**3a**	
Al(1)−N(1)	1.906(2)	Al−N(1)	1.857(2)
Al(1)−N(2)	1.899(2)	Al−N(2)	1.843(2)
Al(1)−C(1)	1.967(2)	Al−Cl(1)	2.123(1)
Al(1)−C(2)	1.968(3)	Al−Cl(2)	2.136(2)
N(1)−C(3)	1.331(3)	N(1)−C(5)	1.328(3)
N(2)−C(5)	1.336(3)	N(2)−C(8)	1.341(3)
C(5)−C(4)	1.384(3)	C(5)−C(6)	1.393(3)
C(4)−C(3)	1.394(3)	(C(6)−C(8)(	1.393(3)
N(2)−Al(1)−N(1)	93.13(7)(	N(2)−Al−N(1)	97.35(8)
N(2)−Al(1)−C(1)	110.30(9)(	N(2)−Al−Cl(1)	114.27(8)
N(1)−Al(1)−C(1)	115.9(1)(	N(1)−Al−Cl(1)	113.71(7)
N(2)−Al(1)−C(2)	115.2(1)	N(2)−Al−Cl(2)	111.20(8)
N(1)−Al(1)−C(2)	109.3(1)	N(1)−Al−Cl(2)	112.06(7)
C(1)−Al(1)−C(2)	111.8(1)(	Cl(2)−Al−Cl(1)	108.06(4)

Chart 2

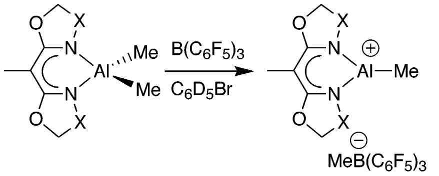


Ar = p-tolyl

C, X = Me
D, X = Cl

The ^{1}H and ^{13}C NMR data for **2b** and **3a** are consistent with their solid-state structure being retained in solution, and these data are similar to those for **2a**. For example, the ^{1}H NMR spectra of **2a** and **3a** in C_6D_6 each exhibit one O−CH_2 resonance (4H) and one CMe_2 resonance (12H), which is consistent with an effective C_{2v} symmetry for these two complexes. As for **2b**, the presence of one N−CH resonance (2H), one AlMe_2 resonance (6H), and two CH_3-^{i}Pr resonances are in

Scheme 2



2a, X = CMe$_2$
2b, X = (*S*)-C(H)(^{i}Pr)

[**4a-b**][MeB(C$_6$F$_5$)$_3$]
4a$^+$, X = CMe$_2$
4b$^+$, X = (*S*)-C(H)(^{i}Pr)

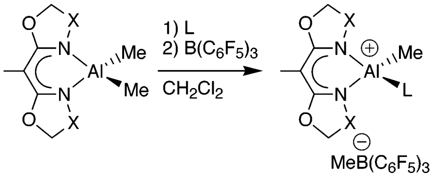
agreement with a C_2-symmetric complex under the studied conditions.

Reaction of the Mono[bis(oxazolinato)aluminum] Dimethyl Complexes (2a,b) with B(C$_6$F$_5$)$_3$. The conversion of neutral Al complexes **2a**,**b** to cationic Al alkyl species was investigated using the well-known strong Lewis acid $B(C_6F_5)_3$ for Me$^-$ abstraction at the Al metal center.

The reaction of the {BOX}AlMe$_2$ complexes **2a**,**b** with 1 equiv of $B(C_6F_5)_3$ (C_6D_5Br, room temperature, 15 min) yields the quantitative formation of cations {BOX-Me$_2$}-AlMe$^+$ (**4a$^+$**) and {BOX-(S)-^{i}Pr}AlMe$^+$ (**4b$^+$**), respectively, as $MeB(C_6F_5)_3^-$ salts (Scheme 2). Cations **4a**,**b$^+$** are highly unstable species at room temperature in C_6D_5Br and rapidly decompose to unidentified species, thus preventing the isolation of these salts in a pure form. In the present case, although the decomposition pathway is unknown, it does not appear to involve the $MeB(C_6F_5)_3^-$ anion, since the ^{1}H, ^{13}C, and ^{19}F NMR resonances of this anion remain unaffected all along the decomposition process. Degradation reactions between cationic Al alkyls incorporating various bidentate L−X$^-$ ligands and the $MeB(C_6F_5)_3^-$ anion have been previously reported and usually proceed cleanly via a $C_6F_5^-$ transfer from the anion to the cationic center.[5b,16,17]

The ^{1}H, ^{13}C, and ^{19}F NMR data for the [**4a**,**b**][MeB(C$_6$F$_5$)$_3$] salts in C_6D_5Br at −20 °C show that the $MeB(C_6F_5)_3^-$ anion is free in solution.[18] As for cations **4a**,**b$^+$**, the ^{1}H and ^{13}C NMR data are consistent with C_{2v}-symmetric and C_2-symmetric structures for **4a$^+$** and **4b$^+$**, respectively. For example, key ^{1}H NMR resonances for **4a$^+$** are (i) the Al*Me*$^+$ resonance (δ −0.21) shifted downfield as compared to that of the neutral precursor (δ −0.51), a result of the cationic charge on Al, and (ii) the presence of only three ^{1}H NMR singlet resonances for the ligand backbone (C*Me*$_2$, O−C*H*$_2$, and C*Me*). The latter observation agrees with a C_{2v}-symmetric structure for **4a$^+$**. Overall, on the basis of NMR data and under the studied conditions, cations **4a**,**b$^+$** in C_6D_5Br solution are most likely either base-free three-coordinate cationic species similar to cationic three-coordinate β-diketiminato Al complexes previously reported,[5c] or four-coordinate cationic Al solvent adducts (i.e. C_6D_5Br adducts) with a fast C_6D_5Br coordination/decoordination process on the NMR time scale under the studied conditions. Solid-state structures of four-coordinate cationic Al−ClPh adducts have been recently reported.[19]

Scheme 3



2a, X = CMe$_2$
2b, X = (*S*)-C(H)(^{i}Pr)

[**5a-b/6a-b**][MeB(C$_6$F$_5$)$_3$]
5a$^+$; X = CMe$_2$, L = THF
6a$^+$; X = CMe$_2$, L = NMe$_2$Ph
5b$^+$; X = (*S*)-C(H)(^{i}Pr)
L = THF
6b$^+$; X = (*S*)-C(H)(^{i}Pr)
L = NMe$_2$Ph

The instability of cations **4a**,**b$^+$** prompted us to study the ionization chemistry of **2a**,**b** in the presence of Lewis bases such as NMe$_2$Ph and THF, to stabilize the formed cationic Al alkyls. The NMR-scale reaction of the dimethylaluminum complexes **2a**,**b** with 1 equiv of $B(C_6F_5)_3$ (CD_2Cl_2, room temperature, 15 min) in the presence of 1 equiv of L (L = THF, NMe$_2$Ph) leads to the quantitative formation of the corresponding four-coordinate cationic Al−L adducts {BOX-Me$_2$}Al(Me)(L)$^+$ (**5a$^+$**, L = THF; **6a$^+$**, L = NMe$_2$Ph) and {BOX-(S)-^{i}Pr}-Al(Me)(L)$^+$ (**5b$^+$**, L = THF; **6b$^+$**, L = NMe$_2$Ph), respectively, as $MeB(C_6F_5)_3^-$ salts (Scheme 3). The generation of [**5a**,**b**][MeB(C$_6$F$_5$)$_3$] and [**6a**,**b**][MeB(C$_6$F$_5$)$_3$] on a preparative scale (CH_2Cl_2, room temperature, 30 min) allowed, in each case, their isolation in a pure form as colorless solids in good yields (see Experimental Section). These four salt compounds are stable for several days in CD_2Cl_2 solution and for months in the solid state under an inert atmosphere. To the best of our knowledge, complexes **5b$^+$** and **6b$^+$** are the first examples of chiral cationic Al alkyls.

Compounds [**5a**,**b**][MeB(C$_6$F$_5$)$_3$] and [**6a**,**b**][MeB(C$_6$F$_5$)$_3$] are fully dissociated in CD_2Cl_2 with no cation−anion interactions at room temperature, as observed by ^{1}H and ^{19}F NMR spectroscopy. In particular, the ^{1}H NMR spectrum in CD_2Cl_2 of each salt exhibits a *Me*B resonance (δ 0.48) characteristic of a free $MeB(C_6F_5)_3^-$ anion in solution. The ^{1}H NMR data at room temperature for the cationic THF and NMe$_2$Ph adducts **5a**,**b$^+$** and **6a**,**b$^+$** all contain Al*Me* resonances that are significantly shifted downfield as compared to those of the neutral precursors **2a**,**b**, as expected from the presence of the cationic charge on the Al center. Similarly, the coordination of the Lewis base L (L = THF, NMe$_2$Ph) to the Al cationic center is also evidenced by significant downfield shifts of the ^{1}H and ^{13}C NMR resonances of the coordinated L versus those of free L.[20] Overall, the NMR data for the THF-adduct Al cations **5a$^+$** and **5b$^+$** at room temperature are consistent with effective C_{2v}- and C_2-symmetric structures, respectively, which can be ascribed to a fast face exchange of THF on the NMR time scale under the studied conditions. In contrast, under the same conditions, the Al−NMe$_2$Ph cationic adducts **6a$^+$** and **6b$^+$** exhibit lower overall symmetries: i.e., C_s symmetry for **6a$^+$** and C_1 symmetry for chiral

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(17) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *22*, 3732.

(18) The *Me*B ^{1}H NMR resonance (δ 1.43) in [**4a**,**b**][MeB(C$_6$F$_5$)$_3$] is nearly identical with that of [NBu$_3$(CH$_2$Ph)][MeB(C$_6$F$_5$)$_3$] (δ 1.39) in C_6D_5Br at −20 °C.

(19) Korolev, A.; Delpech, F.; Dagorne, S.; Guzei, I.; Jordan, R. F. *Organometallics*, **2001**, *20*, 3367.

(20) For information, NMR data for free THF in CD_2Cl_2 are as follows. ^{1}H NMR: δ 3.67, 1.81. ^{13}C{^{1}H} NMR: δ 67.4, 25.2. NMR Data for free NMe$_2$Ph in CD_2Cl_2 are as follows. ^{1}H NMR: δ 7.23 (Ph, 2H), 6.75 (Ph, 2H), 6.70 (Ph, 1H), 2.94 (Me, 6H). ^{13}C{^{1}H} NMR: δ 150.1 (C$_{ipso}$ Ph), 128.6 (Ph), 116.0 (Ph), 112.2 (Ph), 40.0 (Me).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6a$^+$ and 7a$^+$

6a$^+$		**7a$^+$**	
Al(1)−N(1)	1.852(5)(	Al(1)−N(1)	1.936(3)
Al(1)−N(2)	1.857(4)(	Al(1)−N(2)	1.933(3)
Al(1)−C(1)(	1.942(6)(	N(1)−C(5)	1.283(4)
Al(1)−N(3)	2.018(4)(	N(2)−C(8)	1.281(4)
N(1)−C(6)	1.325(8)(	C(6)−C(8)	1.465(5)
N(2)−C(9)	1.319(7)(	C(5)−C(6)	1.476(5)
C(6)−C(7)	1.413(8)(	C(6)−C(7)	1.320(5)
C(7)−C(9)	1.395(7)		
N(1)−Al(1)−N(2)	95.8(2)	N(1)−Al(1)−N(2)	92.8(1)
N(1)−Al(1)−C(1)	119.3(2)	N(2)−Al(1)−C(13)	109.5(1)
N(2)−Al(1)−C(1)	117.0(2)	N(1)−Al(1)−C(13)	111.2(1)
N(1)−Al(1)−N(3)	105.6(2)	N(2)−Al(1)−C(14)	113.5(1)
N(2)−Al(1)−N(3)	106.1(2)	N(1)−Al(1)−C(14)	111.9(1)
C(1)−Al(1)−N(3)	111.3(2)	C(13)−Al(1)−C(14)	115.7(1)

6b$^+$. These NMR observations agree with an effective and nonlabile coordination of NMe$_2$Ph in both **6a**$^+$ and **6b**$^+$, which may reflect the more Lewis basic character of NMe$_2$Ph vs THF. In fact, cations **6a**$^+$ and **6b**$^+$ are rather robust adducts, since NMe$_2$Ph face exchange does not proceed at room temperature even in the presence of free NMe$_2$Ph, as observed by ^{1}H NMR spectroscopy.

Preliminary studies on the use of cations **5a**,**b**$^+$ as Lewis acid catalysts in a hetero-Diels−Alder (DA) reaction between a diene and a glyoxylate derivative showed the quantitative conversion of the reactants to the hetero-DA product and the ene product in a 1/1 ratio.[21] In the case of chiral Al cation **5b**$^+$, chiral GC analysis revealed that the ene product is racemic, whereas the hetero-DA product was obtained with 5% ee. Although disappointing in term of enantioselectivity, the excellent activity of **5a**,**b**$^+$ first shows that such cationic Al alkyls appear suitable for hetero-Diels−Alder catalysis.

Solid-State Structure of [6a][MeB(C$_6$F$_5$)$_3$]. The molecular structure of the salt compound [**6a**][MeB(C$_6$F$_5$)$_3$] was confirmed by X-ray crystallographic analysis (Tables 1 and 3). [**6a**][MeB(C$_6$F$_5$)$_3$] crystallizes as **6a**$^+$ and MeB(C$_6$F$_5$)$_3$$^-$ anions with no cation−anion close contacts. The **6a**$^+$ cation (Figure 3) is an aniline-stabilized four-coordinate cationic Al species. The geometry at the Al center is best described as distorted tetrahedral with a N−Al−N bite angle (95.8(2)°) similar to that in **2b** and **3a**. In contrast to the neutral derivatives {BOX}AlX$_2$ (**2b**, X = Me; **3a**, X = Cl), in which the two X ligands are symmetrically displaced from the N−Al−N plane, the Al-Me and Al−NMe$_2$Ph groups in **6a**$^+$ are displaced from the N−Al−N plane by 45.3(5) and 66.0(5)°, respectively. This difference in the coordination geometry of **6a**$^+$ vs that of **2b** and **3a** may be related to the different donor abilities of Me$^-$ vs NMe$_2$Ph. A similar structural trend has previously been observed with related In complexes when comparing {LX}InX$_2$ to {LX}In(Me)(NMe$_2$Ph)$^+$.[22] The Al−N(1) and Al−N(2) bond distances (1.852(5) and 1.857(4) Å, respectively) are a bit shorter than those in the Al dimethyl complex **2b** (1.906(2) and 1.899(2) Å), which may reflect the increased ionic character of the Al−N bond distances resulting from the cationic charge at the Al center. The Al−N(3) bond distance (2.018(4) Å) is in the normal range for Al−N dative bonds (1.957(3)−2.238(4) Å)[23] and nearly identical with that in the dinuclear Al cation (^{t}BuMe$_2$SiO)$_2$Al$_2$Me$_3$(NMe$_2$Ph)$^+$, which also contains an aniline-stabilized four-coordinate cationic Al center.

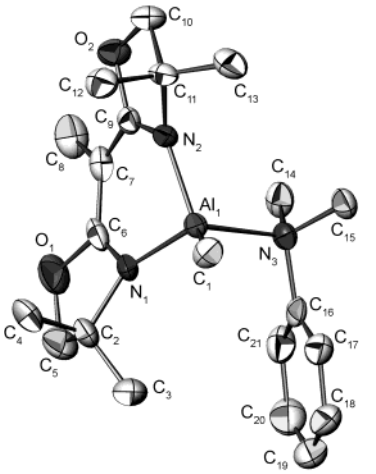

Figure 3. Molecular structure of cation **6a**$^+$. The H atoms are omitted for clarity. Selected torsion angles (deg): N(2)−C(9)−C(7)−C(6) = 15.3(1), N(1)−C(6)−C(7)−C(9) = 12.7(2), N(1)−Al(1)−N(2)−C(9) = −24.5(4), N(2)−Al(1)−N(1)−C(6) = 26.3(4).

Unlike **2b** and **3a**, the Al chelate six-membered-ring metallacycle (C$_3$N$_2$Al) is significantly distorted from planarity, with the Al center being displaced 0.46 Å out of the N(2)−C(9)−N(1)−C(6) average plane toward the coordinated NMe$_2$Ph. The bis(oxazolinato) ligand backbone (C$_3$N$_2$) is itself slightly distorted from planarity, as shown by the N(2)−C(9)−C(7)−C(6) and N(1)−C(6)−C(7)−C(9) torsion angles (15.3 and 12.7°, respectively). In fact, as shown in Figure 3, the bidentate chelating ligand appears to be pushed away from the Al−NMe$_2$Ph group, which may be to avoid significant steric interactions between the aniline and the bidentate ligand.[24]

Hydride Abstraction Reaction by Ph$_3$C$^+$ on {BOX-Me$_2$}AlMe$_2$ (2a). The NMR-scale reaction of **2a** with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (CD$_2$Cl$_2$, room temperature, 15 min) results in the quantitative formation of the diimine cationic Al complex {H$_2$C=C(OX-Me$_2$)$_2$}AlMe$_2$$^+$ (**7a**$^+$), as a B(C$_6$F$_5$)$_4$$^-$ salt, and Ph$_3$CH in a 1/1 ratio (Scheme 4). The preparative-scale generation of [**7a**][B(C$_6$F$_5$)$_4$] allowed its isolation in a pure form as a bright yellow solid. The formation of cation **7a**$^+$ proceeds via an hydride abstraction by Ph$_3$C$^+$ at the Me group

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[21] For a preliminary study, 2,3-dimethyl-1,3-butadiene was used as a diene and ethyl glyoxylate as a dienophile. The catalysis was performed using 10% mol of **5a**,**b**$^+$ at 0 °C in toluene. For more details concerning the hetero-Diels−Alder reaction between the aforementioned diene and ethyl glyoxylate, see: Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1995**, *60*, 5757.

[22] Delpech, F.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2002**, *21*, 1167.

[23] (a) Hogerheide, M. P.; Wesseling, M.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1995**, *14*, 4483. (b) Hill, J. B.; Eng, S. J.; Pennington, W. T.; Robinson, G. H. *J. Organomet. Chem.* **1993**, *445*, 11. (c) Kumar, R.; Sierra, M. L.; Oliver, J. P. *Organometallics* **1994**, *13*, 4285.

[24] A close analysis of the molecular structure of **6a**$^+$ reveals that the shortest C−H distances between the phenyl carbons in NMe$_2$Ph and the hydrogens bonded to C(3) (Figure 3) are 2.82 Å, which is slightly less than the sum of the van der Waals radii (2.97 Å). It is likely that the observed distortion of the BOX ligand is to minimize the steric interactions between the aniline and the aforementioned ligand that would otherwise result. For van der Waals radii, see: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

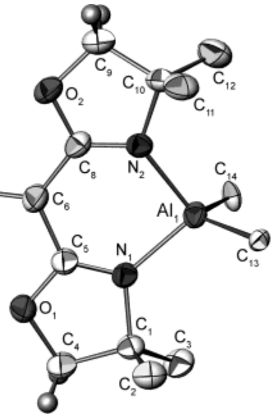
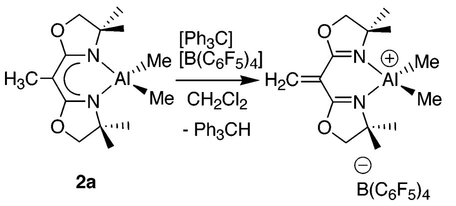


Figure 4. Molecular structure of cation $\mathbf{7a}^+$. The H atoms are omitted for clarity, except those on C(4), C(9), and C(7).

Scheme 4



2a

[7a]$[B(C_6F_5)_4]$

located at the back of the BOX ligand in complex **2a**. Typically, hydride abstraction reactions by Ph_3C^+ at hydride or alkyl metal complexes occur either at the metal center for metal hydrides to yield Ph_3CH and a $M-H^+$ cation[25] or in its vicinity for some alkylmetal complexes: at the C_β of a metal-bonded alkyl group, for instance.[26] In particular, $[Ph_3C][B(C_6F_5)_4]$ has been shown to β abstract a H^- at neutral Al complexes {LX}-Al(^{i}Bu)$_2$ to lead to the formation of Ph_3CH, isobutene, and a Al$-^i$Bu$^+$ cation.[5a] However, to our knowledge, hydride abstraction reactions of the type observed here: i.e., at the bidentate LX^- ligand chelating the metal center and rather far away from the metal center, have not been previously reported. The observed reactivity further illustrates the strong Lewis acid character of Ph_3C^+ and shows an unexpected Lewis base character for the BOX ligand incorporated in **2a**.

The molecular structure of $\mathbf{7a}^+$ was determined by X-ray crystallographic analysis of the salt [**7a**]$[B(C_6F_5)_4]$, which crystallizes as $\mathbf{7a}^+$ and $B(C_6F_5)_4^-$ ions with no cation−anion interactions. The molecular structure of $\mathbf{7a}^+$ is illustrated in Figure 4. As expected, removal of a hydride from the formally anionic BOX^- ligand results in a disruption of the π-delocalization C_3N_2 backbone and the formation of a formally neutral bidentate ligand, which is now best described as a classical neutral bis(oxazoline). The C(5)−N(1) and C(8)−N(2) bond distances of the ligand backbone (1.283(4) and 1.281(4) Å) are characteristic of C(sp^2)=N double bonds (1.30 Å), whereas the C(6)−C(7) bond distance (1.320(5) Å) is comparable with that of a C=C double bond (1.337 Å). The Al−N$_{\text{imine}}$ bond distances (Al(1)−N(1), 1.936(3) Å; Al(1)−N(2), 1.933(3) Å) are shorter than those in neutral Al imine complexes (1.97 Å average),[27] as expected from the electrophilic Al center in $\mathbf{7a}^+$, but are longer than those in **2b** (1.906(2) and 1.899(2) Å), due to the poorer donor ability of the bis(imine) ligand vs that of BOX^-. Apart from ligand backbone changes, the structural features for $\mathbf{7a}^+$ can be related to those of **2b** and **3a**.

The ^{1}H and ^{13}C NMR data for cation $\mathbf{7a}^+$ (room temperature, CD_2Cl_2) are consistent with a C_{2v}-symmetric structure and with the solid-state structure being retained in solution. For example, the ^{1}H NMR spectrum of $\mathbf{7a}^+$ in CD_2Cl_2 only contains four singlet resonances (δ 7.38, 4.59, 1.59, −0.52) assigned to the CH_2 (olefinic), O−CH_2, CMe_2, and AlMe_2 groups, respectively, which is consistent with a C_{2v}-symmetric structure for $\mathbf{7a}^+$. In addition, the combination of ^{13}C NMR and DEPT NMR data for $\mathbf{7a}^+$ allowed the assignment of two characteristic ^{13}C NMR resonances to the C=CH$_2$ olefinic moiety (see Experimental Section), thus confirming the presence of such a group in $\mathbf{7a}^+$ in solution.

Summary and Conclusions

Our initial studies show that the bidentate bis(oxazolinato) ligand is suitable for coordination to aluminum, allowing the synthesis of neutral Al dimethyl and dichloro complexes **2a**,**b** and **3a** via salt metathesis routes. The alkane elimination method appears to be also effective for the preparation of **2a**. The solution and solid-state data for the chiral compound **2b** are consistent with a C_2-symmetric structure. Complexes **2a**,**b** react in C_6D_5Br with $B(C_6F_5)_3$ to afford the highly unstable cations $\mathbf{4a},\mathbf{b}^+$, which are either three-coordinate base-free Al cations or four-coordinate Al−C_6D_5-Br cationic adducts, on the basis of NMR data. When these ionization reactions are performed in the presence of Lewis bases such THF and NMe_2Ph, the corresponding four-coordinate Al−Lewis base adducts are cleanly generated, $\mathbf{5a},\mathbf{b}^+$ and $\mathbf{6a},\mathbf{b}^+$, as determined by solution studies and, in the case of $\mathbf{6a}^+$, by X-ray crystallographic analysis. These cationic adducts are quite stable in solution and in the solid state, illustrating the suitability of the bis(oxazolinato) ligand for the generation of cationic chiral Al alkyls such as $\mathbf{5b}^+$ and $\mathbf{6b}^+$. Initial studies showed that cations $\mathbf{5a},\mathbf{b}^+$ effectively catalyze a hetero-Diels−Alder reaction between a simple diene and a glyoxylate derivative. Unlike $B(C_6F_5)_3$, $[Ph_3C]$-$[B(C_6F_5)_4]$ does not abstract a Me^- at the Al center when reacted with **2a** but, instead, abstracts a H^- at the back of the bis(oxazolinato) ligand to afford the unexpected bis(imine) Al cation $\mathbf{7a}^+$, as determined by X-ray crystallographic analysis.

Experimental Section

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a MBraun Unilab glovebox. Toluene, pentane, and THF were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. CH_2Cl_2 and CD_2Cl_2 were

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[25] (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (b) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325.

[26] For two recent examples, see: (a) Reference 5a. (b) Mehrkhodavanti, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746.

[27] For representative examples of neutral chelate Al complexes of the type {LX}AlMe$_2$ containing an Al−N$_{\text{imine}}$ bond, see: (a) Kanters, J. A.; Van Mier, G. P. M.; Nijs, R. L. L. M.; van der Steen, F.; van Koten, G. *Acta Crystallogr., Sect. C* **1988**, *44*, 1391. (b) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Dalton* **2001**, 1472.

distilled from CaH_2 and stored over activated molecular sieves (4 Å) in a glovebox prior to use. C_6D_6 was degassed under an N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. (*S*)-Valinol was synthesized by reduction of the commercially available (*S*)-valine according a a literature procedure.[28] $B(C_6F_5)_3$ was purchased from Strem Chemicals and was extracted with dry pentane prior to use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Asahi Glass Europe and used as received. CD_2Cl_2, C_6D_6, and C_6D_5Br were purchased from Eurisotope. All other chemicals were purchased from Aldrich and were used as received. All NMR spectra were recorded at room temperature (unless otherwise indicated) on a Bruker AC 200 or 400 MHz spectrometer, except those for **1a**,**b**, which were recorded on a Bruker Avance 300 MHz spectrometer. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{11}B and ^{19}F chemical shifts are reported respectively versus $BF_3{\cdot}Et_2O$ in CD_2Cl_2 and versus neat $CFCl_3$. Elemental analyses were all performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany, except those for **1a**,**b** performed by the microanalysis laboratory of the Université Louis Pasteur, Strasbourg, France. EI mass spectra of **1a**,**b** were recorded by the mass spectroscopy laboratory of the Université Louis Pasteur, Strasbourg, France. The cationic Al complexes **5a**,**b**$^+$ and **6a**,**b**$^+$ were all obtained as fully dissociated $MeB(C_6F_5)_3^-$ salts in CD_2Cl_2 solutions. The corresponding NMR data for the $MeB(C_6F_5)_3^-$ anion are listed below for all compounds.

Data for $MeB(C_6F_5)_3^-$. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.48 (B*Me*). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ −11.9 (br s, *B*Me). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 148.6 (d, $^1J_{CF} = 233$ Hz, *o*-C_6F_5), 137.9 (d, $^1J_{CF} = 238$, *p*-C_6F_5), 136.7 (d, $^1J_{CF} = 233$ Hz, *m*-C_6F_5), 10.3 (*Me*B). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −133.5 (d, $^3J_{FF} = 19$ Hz, 2F, *o*-C_6F_5), −165.7 (t, $^3J_{FF} = 20$ Hz, 1F, *p*-C_6F_5), −168.2 (m, $^3J_{FF} = 19$ Hz, 2F, *p*-C_6F_5).

1,1-Bis[(4*S*)-4-isopropyl-1,3-oxazolin-2-yl]ethane (1b, {BOX-(*S*)-^{i}Pr}H). Diethyl methylmalonate (2.06 g, 11.8 mmol) and (*S*)-valinol (2.44 g, 23.6 mmol) were added in a Schlenk flask. NaH (10 mg, 0.25 mmol; 60% dispersion in mineral oil) was then added under nitrogen to the flask, which was sealed and placed at 130−140 °C (sand bath). After 3−4 h, the ethanol was removed under vacuum to leave a white solid pure enough to be used for the next step without further purification (3.35 g, 98% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.26−7.13 (s, 2H, N*H*), 3.85−3.38 (m, 6H, $-C(C_3H_7)HCH_2-$), 3.32 (q, *J* = 7.3 Hz, 1H, C*H*CH$_3$), 1.80 (m, 2H, $-CH(CH_3)_2$), 1.49 (d, *J* = 7.3 Hz, 3H, CHC*H*$_3$), 0.96−0.87 (m, 12H, CH(C*H*$_3$)$_2$).

To an ice-cooled solution of the dihydroxy diamide (3.35 g, 11.6 mmol) and triethylamine (5.9 g, 58 mmol) in CH_2Cl_2 (75 mL) was added MsCl (3.3 g, 29 mmol). The mixture was warmed to room temperature, stirred for 1 h, and washed with a solution of NH_4Cl. The organic phase was dried with Na_2SO_4 and concentrated in vacuo to give a yellow oil, which was used in the next step without purification. The bis-mesylated compound was treated with NaOH (2.0 g, 50 mmol) in 80 mL of a 1:1 $MeOH/H_2O$ mixture. The solution was refluxed for 2 h and then concentrated to remove methanol and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried with Na_2SO_4 and concentrated in vacuo. Distillation under vacuum afforded 1.2 g (41% from diethyl methylmalonate) of **1b** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 4.23 (m, 4H, C*H*$_2$), 3.98 (m, 2H, C*H*(C$_3$H$_7$)), 3.53 (q, 1H, C*H*CH$_3$(apical)), 1.77 (m, 2H, C*H*(CH$_3$)$_2$), 1.47 (d, *J* = 7.1 Hz, 3H, C*H*$_3$(apical)), 0.95−0.84 (m, 12H, CH(C*H*$_3$)$_2$)). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.5 (*C*=N), 71.8 (*C*HC$_3$H$_7$), 70.2 (*C*H$_2$), 34.0 (*C*HCH$_3$), 32.4 (*C*H(CH$_3$)$_2$), 18.7 (CH(*C*H$_3$)$_2$), 17.7 (CH(*C*H$_3$)$_2$), 15.3 (*C*H$_3$-(apical)). MS (EI; *m*/*z* (%)): 252.3 $[M]^+$ (2), 209.3 $[M - (CH(CH_3)_2)]^+$ (94), 123.3 (100). Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.6; H, 9.6; N, 11.1, Found: C, 66.8; H, 9.5; N, 10.8.

1,1-Bis[4,4-dimethyl-1,3-oxazolin-2-yl]ethane (1a, {BOX-Me$_2$}H). The bis(oxazoline) **1a** was prepared from diethyl methylmalonate and 2-amino-2-methylpropanol in 42% overall yield, following the same procedure as that for **1b**. ^1H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 4H, C*H*$_2$), 3.45 (q, *J* = 7.3 Hz, 1H, C*H*CH$_3$), 1.47 (d, *J* = 7.3 Hz, CHC*H*$_3$), 1.27 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 164.2 (*C*=N), 79.4 (*C*H$_2$), 67.0 (*C*(CH$_3$)), 34.0 (*C*HCH$_3$), 28.1 (C(*C*H$_3$)$_2$), 15.2 (*C*H$_3$-(apical)). MS (EI; *m*/*z* (%)): 224.4 $[M]^+$ (50), 209.3 $[M - CH_3]^+$ (100).

{BOX-Me$_2$}AlMe$_2$ (2a). In a glovebox, ^{n}BuLi (2.38 mL of a 1.6 M hexanes solution, 3.80 mmol) was added dropwise via a pipet to a pentane solution (15 mL) of {BOX-Me$_2$}H (852 mg, 3.81 mmol) which had been precooled to −40 °C in a freezer. Upon addition of ^{n}BuLi, immediate precipitation of a colorless solid occurs, along with gas bubbles formation (^{n}BuH). After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting thick colorless suspension was then filtered through a glass frit and the obtained colorless solid washed with cold pentane and dried under vacuum for 1 h. After this time, the solid residue was dissolved in toluene (10 mL) and the resulting pale yellow solution stored at −40 °C for 30 min. The solution was then taken out of the freezer and $ClAlMe_2$ (3.80 mL of a 1 M hexanes solution, 3.80 mmol), also precooled to −40 °C, was quickly added to the toluene solution. Immediate precipitation occurs most likely due to LiCl formation. The reaction mixture was then warmed to room temperature and vigorously stirred overnight at this temperature to yield a suspension of a colorless solid in a pale yellow solution. The mixture was evaporated to dryness under vacuum to yield an oily and sticky orange residue which was extracted with a 10/1 pentane/Et_2O mixture (11 mL). The mixture was then filtered through a frit under vacuum. The obtained yellow filtrate was concentrated to ∼4 mL and stored overnight at −40 °C, causing the precipitation of a colorless crystalline solid. Filtration through a glass frit and subsequent drying of the obtained solid in vacuo afforded pure **2a** (607 mg, 57% yield) as colorless crystals. ^1H NMR (400 MHz, C_6D_6): δ −0.26 (s, 6H, Al*Me$_2$*), 1.09 (s, 12H, C*Me$_2$*), 2.18 (s, 3H, *Me*CCN), 3.38 (s, 4H, OC*H$_2$*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ −5.4 (Al*Me$_2$*), 9.7 (*Me*CCN), 27.4 (C*Me$_2$*), 63.2 (*C*Me$_2$), 64.0 (Me*C*CN), 79.1 (O*C*H$_2$), 171.5 (N*C*O). ^1H NMR (300 MHz, C_6D_5Br, −20 °C): δ −0.51 (s, 6H, Al*Me$_2$*), 1.18 (s, 12H, C*Me$_2$*), 1.94 (s, 3H, *Me*CCN), 3.64 (s, 4H, OC*H$_2$*). Anal. Calcd for $C_{14}H_{25}AlN_2O_2$: C, 59.98; H, 8.99. Found: C, 59.71; H, 8.85.

NMR-Scale Generation of {BOX-Me$_2$}AlMe$_2$ (2a) via Methane Elimination. In a drybox, the neutral ligand {BOX-Me$_2$}H (41.0 mg, 0.183 mmol) was charged in a J. Young NMR tube and dissolved in 0.5 mL of CD_2Cl_2, resulting in a colorless solution. The NMR tube was then stored in a freezer at −35 °C for 30 min, after which $AlMe_3$ (17.5 uL, 0.183 mmol) was quickly added via a syringe. The tube was then vigorously shaken and warmed to room temperature. After 30 min at room temperature, a ^1H NMR spectrum of the reaction mixture was recorded, showing the quantitative formation of {BOX-Me$_2$}AlMe$_2$, along with methane formation (δ 0.17).

{BOX-(*S*)-^{i}Pr}AlMe$_2$ (2b). Compound **2b** was synthesized by following the same procedure as that for **2a**, using equimolar amounts of {BOX-(S)-^{i}Pr}H (138.0 mg, 0.534 mmol), ^{n}BuLi (0.34 mL of a 1.6 M hexanes solution, 0.534 mmol), and $ClAlMe_2$ (0.53 mL of a 1 M hexanes solution, 0.534 mmol). After evaporation of the reaction mixture, the solid residue was extracted twice with pentane (2 × 10 mL). The pentane filtrate was then concentrated to ∼2 mL and stored in a freezer at −40 °C for 2 days to yield pure **2b** as colorless crystals (77 mg, 48% yield). ^1H NMR (400 MHz, C_6D_6): δ −0.29 (s, 6H, Al*Me$_2$*), 0.48 (d, $^3J = 7.0$ Hz, 6H, *Me* ^{i}Pr), 0.74 (d, $^3J = 6.6$ Hz, 6H, *Me* ^{i}Pr), 2.05 (d of septet, $^3J_{doublet} = 3.5$ Hz, $^3J_{septet} = 7.0$ Hz, 2H, C*H* ^{i}Pr), 2.13 (s, 3H, *Me*CCN), 3.60 (t, *J* = 8.6 Hz, 2H, OC*H$_2$*), 3.69 (d of d, $^2J = 8.6$ Hz, $^3J = 5.9$ Hz, 2H, OC*H$_2$*), 3.82

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[28] Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1992**, *33*, 5517.

(m, 2H, C*H*N). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −8.5 (Al*Me*$_2$), 9.9 (*Me*CCN), 14.2 (*C*H$_3$ ^{i}Pr), 18.9 (*C*H$_3$ ^{i}Pr), 31.0 (*C*H ^{i}Pr), 62.9 (Me*C*CN), 65.8 (O*C*H$_2$), 67.3 (N*C*H), 172.3 (N*C*O). Anal. Calcd for $C_{16}H_{29}AlN_2O_2$: C, 62.31; H, 9.48; N, 9.08. Found: C, 62.53; H, 9.25; N, 9.21.

{BOX-Me$_2$}AlCl$_2$ (3a). The same procedure as that for **2a**,**b** was used, with equimolar amounts of {BOX-Me$_2$}H (136.0 mg, 0.605 mmol), ^{n}BuLi (0.38 mL of a 1.6 M hexanes solution, 0.605 mmol), and $AlCl_3$ (colorless solid, 80.7 mg, 0.607 mmol). After filtration of the reaction mixture through a glass frit to remove LiCl and subsequent drying under vacuum, crude **3a** was obtained as a colorless powder and was recrystallized from a 5/1 Et_2O/toluene mixture (5 mL) to afford pure **3a** as a colorless crystalline solid (121 mg, 62% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 1.23 (s, 12H, C*Me*$_2$), 1.98 (s, 3H, *Me*CCN), 3.27 (s, 4H, OC*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 9.2 (*Me*CCN), 27.1 (C*Me*$_2$), 63.9 (*C*Me$_2$), 67.1 (Me*C*CN), 79.7 (O*C*H$_2$), 172.1 (N*C*O). Anal. Calcd for $C_{12}H_{19}AlCl_2N_2O_2$: C, 44.87; H, 5.96; N, 8.72. Found: C, 44.85; H, 6.17; N, 8.59.

NMR-Scale Generation of [{BOX-Me$_2$}AlMe][MeB(C$_6$F$_5$)$_3$] ([4a][MeB(C$_6$F$_5$)$_3$]) and [{BOX-(*S*)-^{i}Pr}AlMe][MeB(C$_6$F$_5$)$_3$] ([4b][MeB(C$_6$F$_5$)$_3$]). In a drybox, equimolar amounts of the bis(oxazolinato) aluminum dimethyl complex **2a**,**b** (**2a**, 9.1 mg, 0.0324 mmol; **2b**, 10 mg, 0.0324 mmol) and $B(C_6F_5)_3$ (16.6 mg, 0.0324 mmol) were weighed into a small sample vial and were quickly dissolved in C_6D_5Br (0.5 mL). The resulting colorless solution was transferred to a J. Young NMR tube, and a ^{1}H NMR spectrum was immediately recorded at −20 °C, showing the quantitative formation of [**4a**][MeB(C$_6$F$_5$)$_3$] and [**4b**][MeB(C$_6$F$_5$)$_3$], respectively, as fully dissociated $MeB(C_6F_5)_3^-$ salt species in solution under the studied conditions. The poor stability of these salt compounds precluded their isolation in pure form.

Data for 4a$^+$. ^{1}H NMR (400 MHz, C_6D_5Br, −20 °C): δ −0.21 (s, 3H, Al*Me*), 0.96 (s, 12H, C*Me*$_2$), 1.75 (s, 3H, *Me*CCN), 3.61 (s, 4H, OC*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br, −20 °C): δ −6.3 (Al*Me*), 11.1 (*Me*CCN), 29.5 (C*Me*$_2$), 65.7 (*C*Me$_2$), 72.1 (Me*C*CN), 81.1 (O*C*H$_2$), 174.6 (N*C*O).

Data for 4b$^+$. ^{1}H NMR (400 MHz, C_6D_5Br, −20 °C): δ −0.21 (s, 3H, Al*Me*), 0.45 (d, ^3J = 6.5 Hz, 6H, *Me* ^{i}Pr), 0.57 (d, ^3J = 6.7 Hz, 6H, *Me* ^{i}Pr), 1.61 (m, 2H, C*H* ^{i}Pr), 1.78 (s, 3H, *Me*CCN), 3.81−3.90 (m, 6H, C*H*N and OC*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br, −20 °C): δ −7.3 (Al*Me*), 11.6 (*Me*CCN), 16.0 (*Me* ^{i}Pr), 20.8 (*Me* ^{i}Pr), 34.2 (C*H* ^{i}Pr), 65.7 (*C*Me$_2$), 66.7 (*C*HN), 71.1 (O*C*H$_2$), 71.2 (Me*C*CN), 175.3 (N*C*O).

Data for MeB(C$_6$F$_5$)$_3^-$. ^{1}H NMR (400 MHz, C_6D_5Br, −20 °C): δ 1.43 (*Me*B). ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br, −20 °C): δ 16.4 (*Me*B), 139.2 (d, $^1J_{CF}$ = 241 Hz, MeB(C_6F_5)$_3^-$), 140.7 (d, $^1J_{CF}$ = 247 Hz, MeB(C_6F_5)$_3^-$), 150.7 (d, $^1J_{CF}$ = 246 Hz, MeB(C_6F_5)$_3^-$). ^{19}F NMR (376 MHz, C_6D_5Br, −20 °C): δ −164.7 (t, $^3J_{FF}$ = 19.2 Hz, 2F, C_6F_5), −160.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, C_6F_5), −133.4 (d, $^3J_{FF}$ = 19.2 Hz, 2F, C_6F_5).

[{BOX-Me$_2$}Al(Me)(THF)][MeB(C$_6$F$_5$)$_3$] ([5a][MeB(C$_6$F$_5$)$_3$) and [{BOX-(*S*)-^{i}Pr}Al(Me)(THF)][MeB(C$_6$F$_5$)$_3$] ([5b][MeB(C$_6$F$_5$)$_3$). In a drybox, equimolar amounts of the appropriate bis(oxazolinato)aluminum dimethyl complex (**2a**, 50.0 mg, 0.178 mmol; **2b**, 55.5 mg, 0.180 mmol) and THF (14.5 and 14.6 μL, respectively) were dissolved in 0.75 mL of CH_2Cl_2, resulting in a colorless solution. One equivalent of $B(C_6F_5)_3$ (91.3 and 92.1 mg, respectively) was added all at once. The colorless solution was charged in a small Schlenk flask and stirred at room temperature for 30 min, after which it was evaporated under vacuum to yield a colorless foam. In both cases, trituration of the foamy residue with cold pentane (precooled at −40 °C) caused the precipitation of a colorless solid which, after filtration through a glass frit and drying under vacuum, afforded the salts [**5a**][MeB(C$_6$F$_5$)$_3$] and [**5b**][MeB(C$_6$F$_5$)$_3$] in a pure form ([**5a**][MeB(C$_6$F$_5$)$_3$], 101 mg, 66% yield; [**5b**][MeB(C$_6$F$_5$)$_3$], 125 mg, 78% yield), respectively.

Data for 5a$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −0.23 (s, 3H, Al*Me*), 1.41 (s, 12H, C*Me*$_2$), 1.76 (s, 3H, *Me*CCN), 2.17 (m, 4H, H(β) THF), 4.15 (m, 4H, H(α) THF), 4.19 (s, 4H, OC*H*$_2$ BOX). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ −12.8 (Al*Me*), 8.1 (*Me*CCN), 25.0 (C(β) THF), 27.5 (C*Me*$_2$), 63.2 (*C*Me$_2$), 68.1 (Me*C*CN), 73.5 (C(α) THF), 79.7 (O*C*H$_2$ BOX), 172.4 (N*C*O). Anal. Calcd for $C_{36}H_{33}AlBF_{15}N_2O_3$: C, 50.02; H, 3.85. Found: C, 50.47; H, 3.96.

Data for 5b$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −0.36 (s, 3H, Al*Me*), 0.84 (d, ^3J = 6.8 Hz, 6H, *Me* ^{i}Pr), 0.96 (d, ^3J = 6.9 Hz, 6H, *Me* ^{i}Pr), 1.75 (s, 3H, *Me*CCN), 1.84 (d of septet, $^3J_{doublet}$ = 3.3 Hz, $^3J_{septet}$ = 6.9 Hz, 2H, C*H* ^{i}Pr), 2.13 (m, 4H, H(β) THF), 4.05−4.17 (m, 6H, C*H*N and H(α) THF), 4.36 (d of d, ^2J = 9.2 Hz, ^3J = 5.8 Hz, 2H, OC*H*$_2$), 4.41 (t, *J* = 8.6 Hz, 2H, OC*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ −14.8 (Al*Me*$_2$), 8.1 (*Me*CCN), 13.3 (*C*H$_3$ ^{i}Pr), 18.2 (*C*H$_3$ ^{i}Pr), 24.7 (C(β) THF), 31.6 (*C*H ^{i}Pr), 64.5 (N*C*H), 67.1 (Me*C*CN), 68.2 (O*C*H$_2$), 74.1 (C(α) THF), 172.9 (N*C*O). Anal. Calcd for $C_{38}H_{37}AlBF_{15}N_2O_3$: C, 51.14; H, 4.18. Found: C, 50.85; H, 4.12.

[{BOX-Me$_2$}Al(Me)(NMe$_2$Ph)][MeB(C$_6$F$_5$)$_3$] ([6a][MeB(C$_6$F$_5$)$_3$)]) and [{BOX-(*S*)-^{i}Pr}Al(Me)(NMe$_2$Ph)][MeB(C$_6$F$_5$)$_3$] ([6b][MeB(C$_6$F$_5$)$_3$]). The salt compounds [**6a**,**b**][MeB(C$_6$F$_5$)$_3$] were obtained as analytically pure colorless solids ([**6a**][MeB(C$_6$F$_5$)$_3$], 73% yield; [**6b**][MeB(C$_6$F$_5$)$_3$], 55% yield), following the same procedure as that for the synthesis of [**5a**,**b**][MeB(C$_6$F$_5$)$_3$]- using equimolar amounts of **2a**,**b** (**2a**, 60.0 mg, 0.214 mmol; **2b**, 51.0 mg, 0.195 mmol), NMe_2Ph, and $B(C_6F_5)_3$.

Data for 6a$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −0.13 (s, 3H, Al*Me*), 1.09 (s, 6H, CH$_2$C*Me*), 1.22 (s, 6H, CH$_2$C*Me*), 1.71 (s, 3H, *Me*CCN), 3.05 (s, 6H, N*Me*$_2$Ph), 3.85 (d, ^2J = 8.7 Hz, 2H, OC*H*$_2$ BOX), 4.01 (d, ^2J = 8.7 Hz, 2H, OC*H*$_2$ BOX), 7.27 (d, ^3J = 7.4 Hz, 2H, Ph), 7.42 (t, ^3J = 7.2 Hz, 1H, Ph), 7.53 (t, ^3J = 6.9 Hz, 2H, Ph). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ −13.2 (Al*Me*), 8.1 (*Me*CCN), 22.0 (CH$_2$C*Me*$_2$), 27.9 (CH$_2$C*Me*$_2$), 46.2 (N*Me*$_2$Ph), 63.5 (*C*Me$_2$), 70.9 (Me*C*CN), 78.8 (O*C*H$_2$ BOX), 120.6 (*C*H Ph), 128.2 (*C*H Ph), 131.4 (*C*H Ph), 120.6 (Ph), 144.1 (C_{ipso} Ph), 173.2 (N*C*O). Anal. Calcd for $C_{40}H_{36}AlBF_{15}N_3O_2$: C, 52.59; H, 3.97. Found: C, 52.86; H, 3.61.

Data for 6b$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −0.17 (s, 3H, Al*Me*), 0.55 (d, ^3J = 7.0 Hz, 3H, *Me* ^{i}Pr), 0.56 (d, ^3J = 7.0 Hz, 3H, *Me* ^{i}Pr), 1.01 (d, ^3J = 6.7 Hz, 3H, *Me* ^{i}Pr), 1.03 (d, ^3J = 6.7 Hz, 3H, *Me* ^{i}Pr), 1.45 (d of septet, $^3J_{doublet}$ = 3.5 Hz, $^3J_{septet}$ = 6.6 Hz, 1H, C*H* ^{i}Pr), 1.70 (s, 3H, *Me*CCN), 1.84 (d of septet, $^3J_{doublet}$ = 3.3 Hz, $^3J_{septet}$ = 6.9 Hz, 2H, C*H* ^{i}Pr), 2.02 (d of triplet, $^3J_{doublet}$ = 8.6 Hz, $^3J_{triplet}$ = 3.5 Hz, 1H, NC*H*), 2.98 (s, 3H, N*Me*$_2$Ph), 3.09 (s, 3H, N*Me*$_2$Ph), 3.86 (t, ^3J = 9.0 Hz, 1H, OC*H*$_2$), 4.09 (d. of d., ^2J = 9.0 Hz, ^3J = 3.5 Hz, 1H, OC*H*$_2$), 4.16 (ddd, ^3J = 9.8 Hz, ^3J = 7.0 Hz, ^3J = 2.7 Hz, 1H, NC*H*), 4.36 (d of d, ^2J = 9.0 Hz, ^3J = 7.0 Hz, 1H, OC*H*$_2$), 4.42 (t, *J* = 9.4 Hz, 1H, OC*H*$_2$), 7.39 (d, ^3J = 7.8 Hz, 1H, Ph), 7.50 (t, ^3J = 7.0 Hz, 1H, Ph), 7.59 (t, ^3J = 7.6 Hz, 1H, Ph). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ −13.6 (Al*Me*), 8.7 (*Me*CCN), 13.7 (*C*H$_3$ ^{i}Pr), 15.0 (*C*H$_3$ ^{i}Pr), 18.0 (*C*H$_3$ ^{i}Pr), 20.3 (*C*H$_3$ ^{i}Pr), 31.8 (*C*H ^{i}Pr), 32.1 (*C*H ^{i}Pr), 44.3 (N*Me*$_2$Ph), 48.2 (N*Me*$_2$Ph), 64.8 (N*C*H), 66.0 (N*C*H), 68.3 (O*C*H$_2$), 68.4 (Me*C*CN), 68.9 (O*C*H$_2$), 120.7 (*C*H Ph), 129.1 (*C*H Ph), 131.0 (*C*H Ph), 144.1 (C_{ipso} Ph), 173.2 (N*C*O), 174.6 (N*C*O). Anal. Calcd for $C_{42}H_{40}AlBF_{15}N_3O_2$: C, 53.58; H, 4.28. Found: C, 54.74; H, 4.37.

[{H$_2$C=C(OX-Me$_2$)$_2$}AlMe$_2$][B(C$_6$F$_5$)$_4$] ([7a][B(C$_6$F$_5$)$_4$]). NMR Scale. Equimolar amounts of compound **2a** (8.0 mg, 0.028 mmol) and [Ph_3C][B(C_6F_5)$_4$] were added to a small sample vial and dissolved in CD_2Cl_2 (0.5 mL). The resulting bright orange solution was then transferred to a J. Young NMR tube, and a ^{1}H NMR spectrum was immediately recorded, showing the quantitative formation of [**7a**][B(C$_6$F$_5$)$_4$] and Ph_3CH in a 1/1 ratio.

Preparative Scale. In a glovebox, compound **2a** (12.0 mg, 0.043 mmol) and [Ph_3C][B(C_6F_5)$_4$] (39.5 mg, 0.043 mmol) were charged in a small Schlenk flask and dissolved in CH_2Cl_2 (1 mL). The resulting bright orange solution was stirred for 30 min at room temperature, after which the volatiles were removed under vacuum to yield an orange foam. This foamy residue was washed twice with toluene (2 × 2 mL) to remove

Ph_3CH and any excess $[Ph_3C][B(C_6F_5)_4]$, as follows: addition of toluene provoked the formation of a reddish orange oil at the bottom of the flask. The supernatant toluene solution was discarded and the oily residue dried under vacuum to afford a sticky red oil. Subsequent trituration of the residue with cold pentane (precooled at −35 °C) caused the precipitation of a yellow solid. The mixture was then filtered under reduced pressure through a glass frit and the solid residue dried under vacuum to afford pure [**7a**]$[B(C_6F_5)_4]$ as a bright yellow solid (32 mg, 78% yield). Anal. Calcd for $C_{38}H_{24}AlBF_{20}N_2O_2$: C, 47.62; H, 2.52. Found: C, 47.10; H, 2.25. ^1H NMR (400 MHz, CD_2Cl_2): δ −0.52 (s, 6H, Al*Me*$_2$), 1.59 (s, 12H, C*Me*$_2$), 4.59 (s, 4H, OC*H*$_2$), 7.38 (s, 2H, *H*$_2$C═C). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −8.4 (Al*Me*$_2$), 26.8 (C*Me*$_2$), 69.4 (*C*Me$_2$), 81.4 (O*C*H$_2$), 118.0 (H$_2$C═*C*), 136.7 (d, $^1J_{CF} = 243$ Hz, $B(C_6F_5)_4^-$), 138.6 (dt, $^1J_{CF} = 243$ Hz, $^2J_{CF} = 14$ Hz, $B(C_6F_5)_4^-$), 147.6 (H$_2$*C*═C), 148.5 (d, $^1J_{CF} = 239$ Hz, $B(C_6F_5)_4^-$), 164.3 (N═*C*O).

X-ray Structure Analysis of Complexes 2b, 3a, [6a][MeB(C_6F_5)$_3$)], and [7a][B(C_6F_5)$_4$]. Selected crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, $\lambda = 0.710\,73$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given in Table 1. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in ψ angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software. In the case of **2b** and [**6a**]$[MeB(C_6F_5)_3)]$, the absorption was corrected empirically (with Sortav). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

For complex **3a**, two positions must be considered for the C_{10} atom (C_{10} and C_{10A}). The same disorder was applied on the bonded C_{11} and C_{12} methyl groups. In the case of [**7a**]$[MeB(C_6F_5)_3)]$, rigorous interpretation of the electronic density around the aluminum atom was required to consider a partial substitution of the methyl group's carbon atoms by fluorine atoms. Best refinements are obtained for equal occupancies (50% carbon, 50% fluorine) on each position. Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 231414−231417. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files for **2b**, **3a**, [**6a**]$[MeB(C_6F_5)_3]$, and [**7a**]$[B(C_6F_5)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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