Organometallics **1998,** *17,* 3070−3076

Synthesis, Structure, and Reactivity of *β*-Diketiminato Aluminum Complexes

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Received October 14, 1997

The preparation and reaction chemistry of *β*-diketiminato aluminum complexes are described. (TTP)$AlCl_2$ (**1**) (TTPH = 2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentene) is formed by the treatment of $AlCl_3$ with LiTTP. Sequential alkylation of **1** with CH_3Li results in the formation of the mono- and dimethyl aluminum complexes (TTP)AlMeCl (**2**) and (TTP)-$AlMe_2$ (**3**), respectively. Only monoalkyl complexes are produced when more hindered alkyllithium reagents are used. Compounds **2** and **3** are more conveniently prepared by treating $Al(CH_3)_3$ with TTPH·HCl and TTPH, respectively. The more sterically hindered *β*-diketimine ligand 2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene (DDPH) also reacts smoothly with $Al(CH_3)_3$ to yield (DDP)$Al(CH_3)_2$ (**4**). Compound **3** undergoes methyl abstraction reactions upon addition of $B(C_6F_5)_3$ or AgOTf. Cationic species formed from **3** and $B(C_6F_5)_3$ are unstable and decompose to (TTP)$Al(CH_3)(C_6F_5)$ and MeB-$(C_6F_5)_2$. In contrast, (TTP)$Al(CH_3)$(OTf) (**6**) is thermally stable, but the triflate group is surprisingly inert toward displacement by Lewis bases. Compounds **1**, **3**, **4**, and **6** were crystallographically characterized. The structures all indicate that the *β*-diketiminato backbone is essentially planar. The pseudotetrahedral aluminum center is displaced from the plane formed by the ligand backbone in **4** by 0.72 Å.

Introduction

Reactivity of transition-metal and main-group alkyl complexes holds considerable scientific and economic importance. In polymerization catalysis, main-group compounds play important roles as activators in the generation of cationic transition-metal alkyl species that polymerize α-olefins. Aluminum alkyl complexes have long been known to catalyze olefin oligomerizations;[1] however, the rates have been generally inferior to those attainable using transition-metal catalysts for preparing high molecular weight polymers. From the extensive body of work in group 4 metallocene polymerization catalysis, cationic alkyl species of the formula Cp_2MR^+ are catalytically active while the neutral Cp_2MR_2 complexes are not.[2,3] The importance of cationic species has emerged as a common theme demonstrated by recent reports on group 4[4−7] and late-metal systems.[8] This was recently shown to be the case in main-group systems as Coles and Jordan's recent report of ethylene polymerization by cationic aluminum species demonstrates.[9] As is the case in transition-metal chemistry, the stability of group 13 alkyl cations will depend on the ancillary ligand set and the choice of counteranion.[10−12]

We have begun to explore reaction chemistry of main-group and transition-metal alkyl complexes supported by mono- and diketiminato ligands. Synthesis of this class of compounds by condensation reactions between primary amines and 2,4-pentanedione has been known for many years.[13] The chemistry of mono- and diketiminato ligand complexes has been explored;[14−17] however, complexes with these ligands have received less attention than those with tetraazamacrocylic ligands derived from 2,4-pentanedione and diamines.[18,19] Ketiminato ligands share some similarities with their acetylacetonato counterparts but offer potential advantages of modulating steric and electronic properties by varying the amine used in the ligand synthesis. In

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(17) The chemistry of diketiminato Ti, V, and Cr compounds was recently presented: Kim, W.-K.; MacAdams, L.; Fevola, M.; Liable-Sands, L.; Rheingold, A. L. Theopold, K. H. *Abstracts of Papers*, 215th National Meeting of the American Chemical Society, Dallas, TX, March 29−April 2, 1998; American Chemical Society: Washington, DC, 1998; No. INOR 279.

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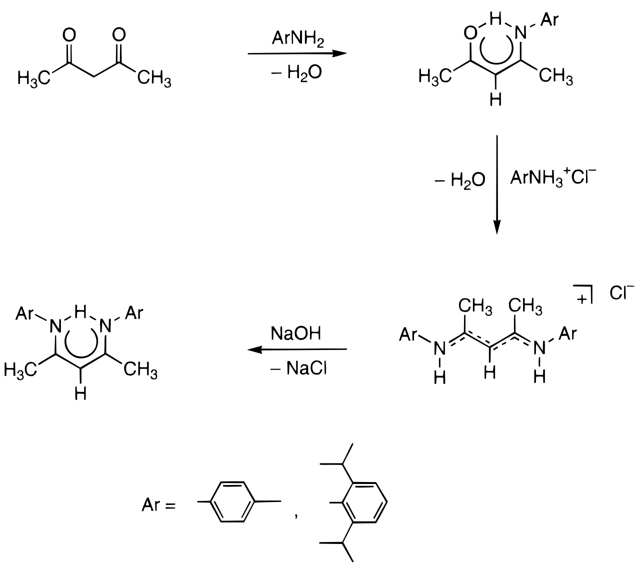
S0276-7333(97)00886-8 CCC: $15.00

Scheme 1



addition, ketimines can be prepared in good yields and on large scale from inexpensive starting materials (Scheme 1). In this paper, we describe initial efforts in preparing aluminum alkyl complexes supported by β-diketiminato ligands derived from 2,4-pentanedione and arylamines (Scheme 2).

Results and Discussion

The reaction of ^{n}BuLi with 2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentene (TTPH) gives the yellow LiTTP in good yield. This toluene-soluble lithium compound is a useful reagent for effecting metathesis reactions with various main-group and transition-metal halides. For example, the reaction of LiTTP with $AlCl_3$ affords the dichloride (TTP)$AlCl_2$ (**1**) in reasonable yield (71%) (Scheme 2). Compound **1** is sparingly soluble in aliphatic hydrocarbon solvents and is conveniently crystallized as pale yellow crystals from toluene. Compound **1** is moisture sensitive and gives TTPH as the primary organic hydrolysis product. Attempts to prepare $(TTP)_2AlCl$ by halide metathesis of compound **1** with LiTTP were not successful.

Compound **1** reacts with alkyllithium reagents to produce mono- and dialkyl aluminum complexes. Reaction of **1** with 1 equiv of CH_3Li gives (TTP)Al(CH_3)Cl (**2**); however, the isolation of a pure compound is hampered by contamination by significant quantities of **1** and the dimethyl complex (TTP)Al$(CH_3)_2$ (**3**, eq 1).

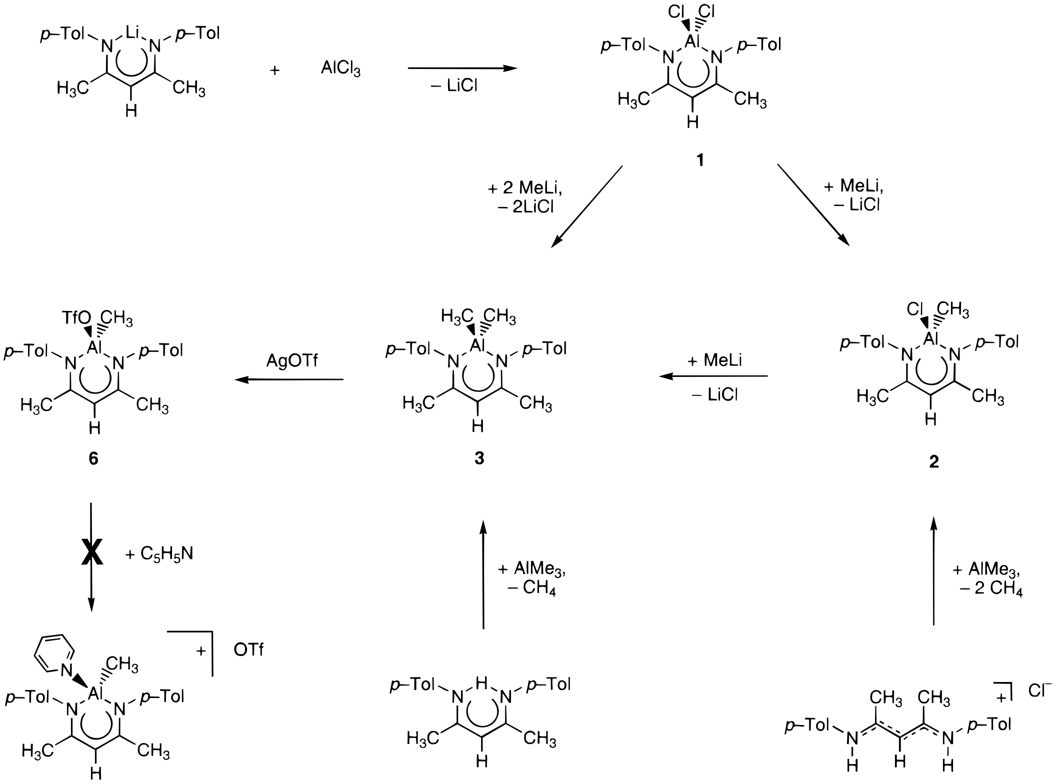
$$\mathbf{1} + \text{MeLi} \rightarrow \mathbf{1} + \underset{\mathbf{2}}{(\text{TPP})\text{AlMeCl}} + \underset{\mathbf{3}}{(\text{TPP})\text{AlMe}_2} \tag{1}$$

With more hindered lithium reagents, only monoalkylation is observed as demonstrated by the reaction of compound **1** with Li[CH(TMS)$_2$], which cleanly affords (TTP)Al[CH(TMS)$_2$]Cl (**5**) in 43% yield (eq 2). Reaction

$$(\text{TPP})\text{AlCl}_2 + \text{Li}[\text{CH}(\text{TMS})_2] \rightarrow \underset{\mathbf{5}}{(\text{TTP})\text{Al}[\text{CH}(\text{TMS})_2]\text{Cl}} \tag{2}$$

of **1** with 2 equiv of CH_3Li gives compound **3**, which can be isolated in 64% yield upon crystallization from pentane. Compound **3** can be handled in air without decomposition. The kinetic stability of **3** toward hydrolysis is considerable and markedly contrasts that of (TP)Al$(CH_3)_2$, the compound derived from 4-toluidinopent-3-en-2-one or $CH_3C(O)CH{=}C(NH\text{-}p\text{-}Tol)(Me)$ (TPH)

Scheme 2



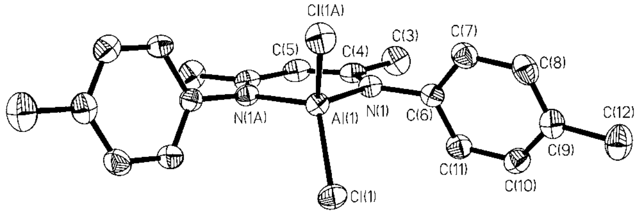


Figure 1. ORTEP diagram of **1** (ellipsoids drawn at 50% probability level).

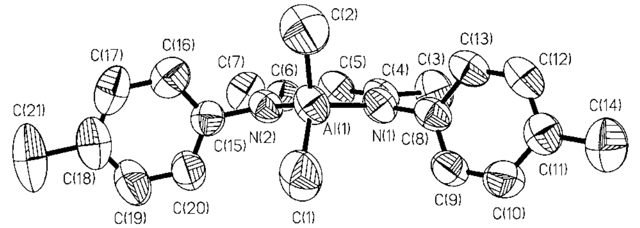


Figure 2. ORTEP diagram of **3** (ellipsoids drawn at 50% probability level).

and $Al(CH_3)_3$.[20] Under forcing conditions, compound **3** hydrolyzes slowly to give TTPH and uncharacterized aluminum species. Compound **3** does not react with additional TTPH to give $(TTP)_2AlCH_3$. Compounds **2** and **3** are more conveniently prepared by reacting trimethylaluminum with TTPH·HCl and TTPH, respectively. In the reaction between $Al(CH_3)_3$ and TTPH·HCl, compounds **2** and **3** are present in the crude reaction mixture, with **2** being the major product (**2**:**3** = 15:1). Recrystallization from hot heptane gives pure **2** in 84% yield. The reaction between $Al(CH_3)_3$ and TTPH gives compound **3** in high yield (90% isolated) on a large scale (10 g). ^{1}H NMR (tol-d_8, −50 to +85 °C) data indicate that mirror symmetry of the TTP ligand is maintained in these compounds, and characteristic high-field resonances for the aluminum methyl groups are observed for compounds **2** (δ −0.98, s) and **3** (δ −1.05, s). Although ^{27}Al resonances can be detected for compounds **1**−**3**, with the exception of those for 1, the peaks are broad ($\nu_{1/2} \cong 4000$ Hz); thus application of ^{27}Al NMR for characterization is limited.

To test the accessibility of compounds with more sterically demanding ligands, 2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene (DDPH) was synthesized in a similar fashion from 2,6-diisopropylaniline and 2,4-pentanedione.[16] Despite the increased steric bulk of the ligand, DDPH and $Al(CH_3)_3$ react smoothly to afford $(DDP)Al(CH_3)_2$ (**4**) in 75% yield. Compound **4** is considerably more soluble than compound **3** and can be crystallized from concentrated pentane solutions at low temperature. ^{1}H NMR spectra exhibit the expected set of ligand proton signals and a high-field singlet for the Al methyl groups (δ −1.00, s).

To glean more detailed information with respect to the coordination environment about aluminum, the molecular structures of compounds **1**, **3**, and **4** were determined. ORTEP diagrams of the compounds are shown in Figures 1−3, data collection parameters and refinement statistics are listed in Table 1, and selected bond distances and angles are given in Table 2. Although we were able to obtain what appeared to be single crystals of compound **2**, we were not able to satisfactorily refine its structure due to disorder of C and Cl that were linked to aluminum.

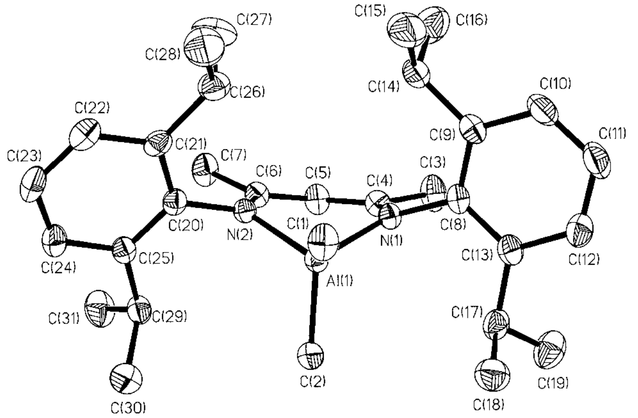
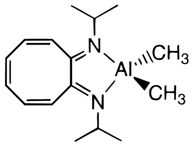


Figure 3. ORTEP diagram of **4** (ellipsoids drawn at 50% probability level).

Compounds **3** and **4** are related to N-isopropyl-2-(isopropylamino)troponimine ([(*i*-Pr)$_2$ATI]) and amidinate dimethylaluminum complexes. The Al−CH_3 distances in **3** (1.955(4) and 1.961(3) Å) and **4** (1.958(3) and 1.970(3) Å) are comparable to the Al−CH_3 distance in [(*i*-Pr)$_2$ATI]Al(CH_3)$_2$ (**A**) (1.969(1) Å).[21] The Al−N distances in **3** and **4** are also similar to those in **A** for Al^{III}−N bonds, while the slightly shorter Al−N distances in **1** are likely due to the difference in inductive effects for Cl and CH_3 ligands. The N−Al−N angles in compounds **1**, **3**, and **4** are more obtuse than the corresponding angle in **A**.



A

The ArN=C(CH_3)−C(H)=C(CH_3)−NAr backbone of the β-diketiminato ligand in compounds **1**, **3**, and **4** is essentially planar. While compound **1** has rigorous C_2 symmetry as C(3) and Al(1) lie on a crystallographic 2-fold axis, the Al center in compounds **3** and **4** is displaced from the β-diketiminato plane. This puckering is most pronounced in compound **4** where Al(1) lies 0.72 Å above the least-squares plane defined by N(1), N(2), C(4), C(5), and C(6). Displacement of the Al center in compound **3** is significant (0.33 Å from the ligand plane) but less severe than that observed in **4**. In the solid state, the methyl group environments are distinct, with C(1) lying in the least-squares plan of the ligand while C(2) is displaced 2.32 Å from the ligand plane. A single methyl environment is observed in low-temperature ^{1}H NMR spectra for compounds **3** and **4**. Hence, if the solid-state structures are maintained in solution, methyl site exchange is rapid on the NMR time scale.

We have examined methyl abstraction by $B(C_6F_5)_3$ for compound **3**. The complex ^{1}H NMR spectra that result when **3** and $B(C_6F_5)_3$ dissolved at low temperature (CD_2Cl_2) are not readily interpreted in terms of a simple cationic species or rotamers of [{(TTP)AlMe}$_2$(μ-Me)]-

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Table 1. Data Collection Parameters for Compounds 1, 3, 4, and 6

	1	3	4	6
empirical formula	$C_{19}H_{21}AlCl_2N_2$	$C_{21}H_{27}AlN_2$	$C_{31}H_{47}AlN_2$	$C_{21}H_{24}AlF_3N_2O_3S$
fw	375.26	334.43	474.69	468.46
temp (K)	142(2)	142(2)	142(2)	173(1)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	15.014(3)	8.737(2)	12.6955(7)	7.562(2)
b (Å)	7.782(2)	14.114(3)	19.4992(11)	12.049(2)
c (Å)	17.037(3)	17.021(3)	13.4623(8)	25.411(5)
β (deg)	102.97(3)	93.82(3)	116.8980(10)	90
V (Å^3)	1940.0(7)	2094.4(7)	2972.1(3)	2315.4(8)
Z	4	4	4	4
d(calc) (Mg/m^3)	1.285	1.061	1.061	1.344
abs coeff (mm^{-1})	0.383	0.101	0.088	0.226
F(000)	784	720	1040	976
cryst size (mm)	0.15 × 0.12 × 0.12	0.18 × 0.16 × 0.15	0.18 × 0.15 × 0.14	0.25 × 0.12 × 0.05
2θ range (deg)	4.90−56.58	3.76−46.50	3.66−56.58	3.2−56.36
index ranges	$-15 \le h \le 20$ $-9 \le k \le 10$ $-21 \le l \le 22$	$-9 \le h \le 9$ $-10 \le k \le 15$ $-18 \le l \le 17$	$-16 \le h \le 14$ $-25 \le k \le 25$ $-17 \le l \le 16$	$-10 \le h \le 10$ $-15 \le k \le 15$ $-32 \le l \le 32$
no. of reflns collected	5875	8078	17 525	25 453
no. of indep reflns	2291 [R(int) = 0.0354]	2965 [R(int) = 0.0995]	6926 [R(int) = 0.0703]	5471 [R(int) = 0.1255]
data/restraints/params	2291/0/110	2965/0/218	6926/0/307	5471/0/280
GOF/F^2	1.249	0.946	1.017	1.102
R indices [$I > 2\sigma(I)$]	$R1 = 0.0385$, $wR2 = 0.0912$	$R1 = 0.0460$, $wR2 = 0.0894$	$R1 = 0.0723$, $wR2 = 0.1670$	$R1 = 0.1022$, $wR2 = 0.1868$
R indices (all data)	$R1 = 0.0556$, $wR2 = 0.0970$	$R1 = 0.1184$, $wR2 = 0.1057$	$R1 = 0.1432$, $wR2 = 0.1950$	$R1 = 0.1770$, $wR2 = 0.2183$
largest diff peak (e Å^{-3})	+0.492 to −0.511	+0.137 to −0.148	+0.410 to −0.385	+0.301 to −0.307

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1, 3, 4, and 6

	1	3	4	6
Al−N1	1.850(2)	1.905(3)	1.922(2)	1.875(4)
Al−N2		1.907(3)	1.935(2)	1.873(4)
Al−C1		1.955(4)	1.958(3)	1.928(6)
Al−C2		1.961(3)	1.970(3)	
N(1)−Al(1)−N(1)#1	99.41(12)			
N(1)−Al(1)−Cl(1)#1	113.56(6)			
N(1)#1−Al(1)−Cl(1)#1	110.04(6)			
N(1)−Al(1)−Cl(1)	110.04(6)			
N(1)#1−Al(1)−Cl(1)	113.56(6)			
Cl(1)#1−Al(1)−Cl(1)	109.95(6)			
N(2)−Al(1)−N(1)		94.72(14)	96.18(9)	99.1(2)
N(2)−Al(1)−C(2)		111.2(2)	107.15(11)	
N(1)−Al(1)−C(2)		109.6(2)	108.67(11)	
N(2)−Al(1)−C(1)		111.4(2)	114.49(11)	117.9(2)
N(1)−Al(1)−C(1)		112.7(2)	110.79(11)	117.5(2)
C(2)−Al(1)−C(1)		115.4(2)	117.40(13)	

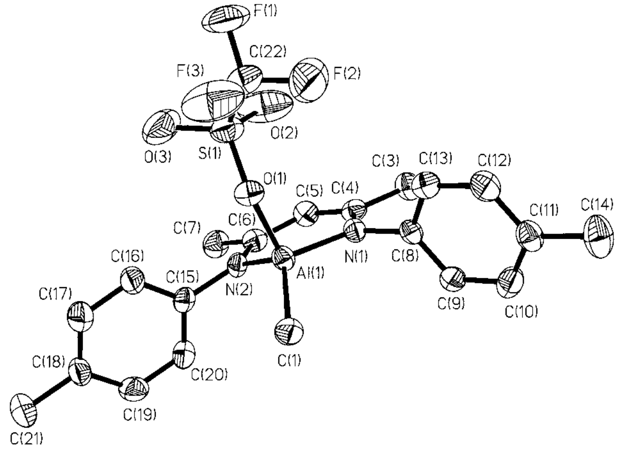

Figure 4. ORTEP diagram of **6** (ellipsoids drawn at 50% probability level).

[$MeB(C_6F_5)_3$]; however, a single resonance in ^{11}B NMR (δ −14) is consistent with the formation of $MeB(C_6F_5)_3^-$.[9] Attempts to isolate putative cationic species were not successful because degradation occurred (as judged by ^{19}F and ^{11}B data). We propose that the degradation products are (TTP)Al(CH_3)(C_6F_5) and $MeB(C_6F_5)_2$.

Formation of (TTP)Al(CH_3)(C_6F_5) is supported by (i) a high-field triplet (δ −0.18, $|^5J_{H-F}| = 1.6$ Hz) in the ^1H NMR spectrum and (ii) the fact that reaction of (TTP)-Al(CH_3)(OTf) and LiC_6F_5 affords an oil that is spectroscopically identical to (TTP)Al(CH_3)(C_6F_5) generated from **3** and $B(C_6F_5)_3$. We have not been able to obtain an analytically pure compound because all attempts to crystallize (TTP)Al(CH_3)(C_6F_5) have been unsuccessful.

For $MeB(C_6F_5)_2$ the following evidence is offered: (i) a quintet at 1.33 ppm ($|^5J_{H-F}| = 1.8$ Hz) is assigned to $CH_3B(C_6F_5)_2$ where the H−F coupling arises from four chemically equivalent ortho fluorines and (ii) a resonance in the ^{11}B spectrum (δ 72) that is intermediate between those of BMe_3 (δ 86.0) and BPh_3 (δ 60.0). These data have not been confirmed by independent synthesis.[22]

The reaction between compound **3** and AgOTf (OTf = OSO_2CF_3) deposits silver metal and affords modest yields of (TTP)Al(CH_3)(OTf) (**6**). This reaction is similar to reaction between Ag salts and d^0 Zr alkyl compounds.[23] The X-ray structure indicates η^1 coordination for the triflate ligand (Figure 4). Compound **6** is surprisingly inert for a triflate complex. For example, the triflate ion does not undergo metathesis with Na[$B(3,5(CF_3)_2-C_6H_3)_4$],[24,25] nor is it displaced by pyri-

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[22] A comprehensive literature search for $Me(C_6F_5)_2$ retrieved one citatation: Biagini, P.; Lugli, G.; Garbassi, F. Andreussi, P. Eur. Pat. Appl. EP 667,357, 1995; *Chem. Abstr.* **1995**, *123*, 341326t.

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dine. Compounds **2** and **6** will undergo metathesis reactions with alkyllithium reagents. Thus, **3** can be generated upon reaction of **2** or **6** with CH_3Li, and mixed-alkyl complexes of the formula $(TTP)Al(CH_3)(R)$ from **2** and RLi ($R \neq CH_3$).

Summary

Our initial results suggest that β-diketiminato ligands are well-suited for preparing various alkyl aluminum products. In particular, it should be possible to modulate reactivity at the aluminum center by designing ligands with different steric and electronic properties. Significantly, we have seen no evidence for ligand methylation reactions that have been observed for related reactions between $Al(CH_3)_3$ and 1,4-diazabutadiene systems.[26,27] The ability to prepare mixed-alkyl complexes $(TTP)Al(CH_3)(R)$, $R \neq CH_3$, in addition to the flexible ligand syntheses, may prove to be useful in the preparation of unassociated, three-coordinate aluminum cations with the proper match of ligand, alkyl group, and counterion. Efforts along these lines and extension syntheses to other group 13 complexes will be the subject of future reports.[28]

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques. Solvents were freshly distilled over sodium/benzophenone ketyl and were saturated with N_2 before use. Elemental analyses (C, H, N) were performed by Desert Analytics, Tucson, AZ, and Atlantic Microlabs, Inc. A Nicolet IR/42 spectrometer was used to record IR spectra. Varian Gemini-300 andVXR-300 NMR spectrometers were used to record ^1H (300 MHz), ^{11}B (96 MHz), ^{13}C (75 MHz), ^{19}F (282 MHz), and ^{27}Al (78 MHz) NMR spectra. ^1H and ^{13}C chemical shifts were referenced to the residual solvent peaks. ^{11}B chemical shifts were referenced to a neat $BF_3{\cdot}OEt_2$ (0 ppm) external standard. ^{27}Al NMR spectra were referenced to an $[Al(H_2O)_6]^{3+}$ (0 ppm) external standard. ^{19}F NMR spectra were referenced to a neat $CFCl_3$ (0 ppm) external standard. $CDCl_3$ was dried over activated 4 Å molecule sieves and vacuum-transferred to an air-free flask. C_6D_6 was dried over activated 4 Å molecule sieves and vacuum-transferred to a sodium-mirrored air-free flask. Uncorrected melting points of crystalline samples in sealed capillaries (under an argon atmosphere) were reported as ranges. Low-resolution mass spectra were obtained on a portable Trio-1 VG Masslab Ltd. mass spectrometer and were reported in the form (M, %I), where M is the highest mass observed for a molecular ion or fragment peak and %I is the intensity of the peak relative to the most intense peak in the spectrum. High-resolution mass spectra were obtained at the MSU Mass Spectrum Facility.

^{n}BuLi, $AlMe_3$, and AgOTf were purchased from Aldrich and used as received. $AlCl_3$ was purchased from Aldrich and sublimed prior to use. 2-(*p*-Tolylamino)-4-(*p*-tolylimino)-2-pentene (TTPH) and 2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene (DDPH) were prepared by straightforward modification of the literature methods.[13,16] $B(C_6F_5)_3$ was prepared from BCl_3 and C_6F_5Li.[29] MeLi was prepared from lithium metal and $ClCH_3$ and stored as a 1.4 M solution in ether. $LiCH(SiMe_3)_2$ was prepared from lithiation of $ClCH(SiMe_3)_2$.[30]

LiTTP. ^{n}BuLi (45 mL, 1.6 M in hexanes, 72 mmol) was added dropwise via syringe over 10 min to a stirred solution of TTPH (20 g, 72 mmol) in 350 mL of pentane at −78 °C. The mixture was stirred at −78 °C for an additional 10 min and allowed to warm to room temperature, and reduced in volume to approximately 150 mL after 2 h at room temperature. Yellow solid LiTTP was isolated by filtration, washed with 3 × 20 mL of pentane, and dried in vacuo (18 g, 88% yield): mp 185−187 °C dec; ^1H NMR (C_6D_6) δ 1.79 (s, 6 H), 2.15 (s, 6 H), 4.67 (s, 1 H), 6.61 (d, $^3J_{H-H} = 8.1$ Hz, 4 H), 6.91 (d, $^3J_{H-H} = 8.1$ Hz, 4 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 20.87, 23.08, 95.49, 124.3, 129.6, 131.2, 151.4, 165.6. Anal. Calcd for $C_{19}H_{21}LiN_2$: C, 80.26; H, 7.44; N, 9.85. Found: C, 80.18; H, 7.15; N, 9.50.

$(TTP)AlCl_2$ (1). Freshly sublimed $AlCl_3$ (1.07 g, 8.0 mmol) in 10 mL of ether was added to an orange solution of LiTTP (2.3 g, 8.0 mmol) in 20 mL of toluene at 0 °C. The cloudy solution was allowed to warm to room temperature and stirred for 12 h. The mixture was filtered, and the filtrate was reduced in volume to approximately 5 mL. Yellow **1** deposited overnight at −78 °C. The solid was isolated by filtration, washed with copious amounts of pentane, and dried in vacuo (2.1 g, 71% yield): mp 199−201 °C dec; ^1H NMR ($CDCl_3$) δ 1.88 (s, 6 H), 2.33 (s, 6 H), 5.16 (s, 1 H), 7.05 (d, $^3J_{H-H} = 8.4$ Hz, 4 H), 7.18 (d, $^3J_{H-H} = 8.4$ Hz, 4 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.02, 23.26, 98.29, 126.5, 130.0, 136.8, 139.7, 171.0; ^{27}Al NMR ($CDCl_3$) δ 98.6 ($\nu_{1/2} = 189$ Hz). LRMS 374 (M^+, 1); HRMS calcd for $C_{19}H_{21}AlCl_2N_2$ 376.0868, found 376.0862. Anal. Calcd for $C_{19}H_{21}AlCl_2N_2$: C, 60.81; H, 5.64; N, 7.46. Found: C, 60.87; H, 5.47; N, 7.35.

(TTP)AlClMe (2). Method a. MeLi (2 mL, 1.4 M in ether, 2.8 mmol) was added to a stirred suspension of $(TTP)AlCl_2$ (1.07 g, 2.8 mmol) in 15 mL of ether at 0 °C. The mixture was allowed to warm to room temperature, stirred for 14 h, and was filtered, and the filtrate was reduced in volume to approximately 3 mL. **2** can be obtained by repeated crystallization from toluene at −78 °C (0.15 g, 15% yield).

Method b. $AlMe_3$ (7.2 mL, 2 M, 14.4 mmol) was added over a 5 min period to a stirred suspension of throughly dried TTPH·HCl (4.55 g, 14.5 mmol) in 100 mL of toluene at 0 °C. Following the addition, the mixture was stirred at room temperature for 4 h, during which a clear yellow solution was formed. The solution was reduced in volume to approximately 20 mL and layered with 30 mL of pentane. Cooling at −78 °C overnight deposited **2** as a pale yellow solid which was isolated by filtration, washed with pentane, and dried in vacuo (4.3 g, 84%): mp 129−133 °C dec; ^1H NMR ($CDCl_3$) δ −0.98 (s, 3 H), 1.86 (s, 5 H), 2.33 (s, 6 H), 5.07 (s, 1 H), 7.01 (d, $^3J_{H-H} = 8.4$ Hz, 4 H), 7.15 (d, $^3J_{H-H} = 8.4$ Hz, 4 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −10.9 (br, $\nu_{1/2} = 30$ Hz), 20.98, 23.13, 97.81, 126.2, 129.8, 136.0, 141.3, 169.1; ^{27}Al NMR ($CDCl_3$) δ 126 ($\nu_{1/2} = 3920$ Hz); LRMS 354 (M^+, 5), 339 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{20}H_{24}AlClN_2$: C, 67.70; H, 6.82; N, 7.89. Found: C, 67.82; H, 6.84; N, 7.91.

$(TTP)AlMe_2$ (3). Method a. $AlMe_3$ (3.6 mL, 2 M in hexanes, 7.2 mmol) was added to a solution of TTPH (2.0 g, 7.2 mmol) in 20 mL of pentane at 0 °C with stirring. The mixture was stirred at 0 °C for 5 min, allowed to warm to room temperature, stirred for an additional hour, and filtered, and the filtrate was reduced in volume to approximately 3 mL. Pale yellow **3** deposited overnight at −78 °C. The solid was collected by filtration, washed with cold pentane, and dried in vacuo (2.2 g, 90% yield).

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Method b. MeLi (2 mL, 1.4 M in ether, 2.8 mmol) was added to a stirred suspension of **1** (0.50 g, 1.3 mmol) in 15 mL of ether at 0 °C. The mixture was allowed to warm to room temperature and stirred for 14 h. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane extracts were reduced in volume, and **3** deposited at −78 °C (0.28 g, 64% yield).

Method c. MeLi (1 mL, 1.4 M in ether, 1.4 mmol) was added to **2** (0.38 g, 1.1 mmol) suspended in 20 mL of ether at 0 °C. The mixture was allowed to warm to room temperature and stirred for 5 h. The solvent was removed in vacuo, and the residue was extracted with pentane. The pentane extracts were reduced in volume, and **3** deposited at −78 °C (0.30 g, 84%): mp 110−113 °C dec; ^{1}H NMR (CDCl$_3$) δ -1.05 (s, 6 H), 1.78 (s, 5 H), 2.32 (s, 6 H), 4.83 (s, 1 H), 6.88 (d, $^{3}J_{\mathrm{H-H}} = 8.1$ Hz, 4 H), 7.12 (d, $^{3}J_{\mathrm{H-H}} = 8.1$ Hz, 4 H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ -9.67 (br, $\nu_{1/2} = 16$ Hz), 20.96, 22.90, 96.02, 126.0, 129.6, 135.1, 142.8, 167.9; ^{27}Al NMR (CDCl$_3$) δ 143 ($\nu_{1/2} = 3900$ Hz); LRMS 319 (M^{+} − CH$_3$, 100). Anal. Calcd for $C_{21}H_{27}AlN_2$: C, 75.42; H, 8.14; N, 8.37. Found: C, 75.07; H, 7.97; N, 8.18.

(DDP)AlMe$_2$ (4). This was prepared by the same procedure described for **3** (method a) using AlMe$_3$ and DDPH in 75% yield: mp 163−164 °C dec; ^{1}H NMR (CDCl$_3$) δ -1.00 (s, 6 H), 1.14 (d, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 12 H), 1.23 (d, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 12 H), 3.22 (sept, d, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 4 H), 5.12 (s, 1 H), 7.14−7.25 (m, 6 H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ -10.78 (br, $\nu_{1/2} = 17$ Hz), 23.58, 24.61, 25.15, 28.02, 97.02, 124.0, 126.5, 140.7, 144.22, 169.56; ^{27}Al NMR (CDCl$_3$) δ 160 ($\nu_{1/2} = 4060$ Hz); LRMS 459 (M^{+} − CH$_3$, 100). Anal. Calcd for $C_{31}H_{47}AlN_2$: C, 78.44; H, 9.98; N, 5.90. Found: C, 77.73; H, 10.00; N, 5.79.

(TTP)Al[CH(TMS)$_2$]Cl (5). LiCH(TMS)$_2$ (0.42 g, 2.5 mmol) in 10 mL of ether was added to **1** (0.94 g, 2.5 mmol) in 15 mL of toluene at 0 °C. The mixture was allowed to warm to room temperature, stirred for 10 min, and then filtered. The ether was removed in vacuo, and the residue was extracted with 3 × 10 mL of pentane. The combined pentane extracts were reduced in volume to approximately 5 mL. Pale yellow **5** deposited overnight at −78 °C and was collected by filtration (0.54 g, 43%): mp 159−162 °C. ^{1}H NMR (CDCl$_3$) δ -1.65 (s, 1 H), -0.23(s, 1 H), 1.84 (s, 6 H), 2.34 (s, 6 H), 5.08 (s, 1 H), 7.06−7.18 (m, 8 H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ -1.88 (br), 3.26, 21.00, 23.69, 98.05, 126.7, 129.7, 136.2, 141.5, 169.3; ^{27}Al NMR (CDCl$_3$) δ 135 ($\nu_{1/2} = 4600$ Hz); LRMS 483 (M^{+} − CH$_3$, 6); HRMS calcd for $C_{26}H_{40}AlClN_2Si_2$ 498.2234, found 498.2241. Anal. Calcd for $C_{26}H_{40}AlClN_2Si_2$: C, 62.55; H, 8.08; N, 5.36. Found: C, 61.90; H, 7.81; N, 5.67.

(TTP)AlMe(OTf) (6). A 20 mL portion of toluene was added to a Schlenk flask containing **3** (0.75 g, 2.24 mmol) and AgOTf (1.15 g, 4.47 mmol) at −78 °C. The reaction mixture immediately turned black and was slowly warmed to room temperature. After 12 h, during which a silver mirror developed inside the Schlenk flask, the mixture was filtered. The filtrate was concentrated, the concentrate was layered with pentane, and the mixture was cooled to −78 °C. Yellow **6** deposited overnight and was collected by filtration, washed with pentane, and dried in vacuo (0.34 g, 32% yield). Using of 1 equiv of AgOTf led to the same compound **6**, but in lower yield. We were not able to observe ^{27}Al NMR signals for **6**. Analytical data: mp 140 °C (dec); IR (Nujol) 1537, 1383, 1302, 1244, 1203, 1109, 1031, 1020, 943; ^{1}H NMR (C$_6$D$_6$) δ -0.62 (s, 3 H), 1.54 (s, 6 H), 1.99 (s, 6 H), 4.85 (s, 1 H), 6.87 (d, $^{3}J_{\mathrm{H-H}} = 8.1$ Hz, 4 H), 7.00 (m, $^{3}J_{\mathrm{H-H}} = 8.1$ Hz, 4 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ -14.1 (br, s, $\nu_{1/2} = 75$ Hz), 20.78, 22.88, 99.28, 120.0 (q, $^{1}J_{\mathrm{C-F}} = 316$ Hz), 126.1, 130.46, 136.8, 141.0, 171.0; ^{19}F NMR (C$_6$D$_6$) δ -77.9 (s, $\nu_{1/2} = 8.9$ Hz); LRMS 453 (M^{+} − CH$_3$, 5). Anal. Calcd for $C_{21}H_{24}AlF_3N_2O_3S$: C, 53.84; H, 5.16; N, 5.98. Found: C, 53.44; H, 4.98; N, 5.92.

(TTP)AlMe$_2$ + B(C$_6$F$_5$)$_3$. A solution of B(C$_6$F$_5$)$_3$ (0.60 g, 1.2 mmol) in 20 mL of pentane was added to a stirred suspension of **3** (0.39 g, 1.2 mmol) in 5 mL of pentane at −78 °C. The mixture was allowed to warm to room temperature, stirred for 24 h, and filtered, and the filtrate was placed under vacuum. The resulting yellow oil (0.90 g) contained both (TTP)AlMe(C$_6$F$_5$) and MeB(C$_6$F$_5$)$_2$. The oil was placed under high vacuum at 45 °C overnight to remove the relatively volatile MeB(C$_6$F$_5$)$_2$. The gel residue was redissolved in pentane, the solution was concentrated, and the concentrate was cooled to −78 °C. A colorless oil deposited overnight and was isolated by decantation and dried in vacuo (0.37 g, 65% yield). Attempts to crystallize this oil have been unsuccessful. The identity of (TTP)AlMe(C$_6$F$_5$) was confirmed by an independent synthesis. Compound **6** (1.31 g, 2.8 mmol) was suspended in 20 mL of ether, and the solution was treated with an ether solution of C$_6$F$_5$Li, which was generated by treating freshly distilled C$_6$F$_5$Br (0.69 g, 2.8 mmol) with ^{n}BuLi (2.5 M, 1.1 mL, 2.8 mmol) at −78 °C. The mixture was warmed to room temperature and was stirred at room temperature for 2 h. After filtration and solvent removal, an oil remained. All attempts to crystallize the product were unsuccessful, and chromatography on silica gel gave decomposition. Nonetheless, chemical shifts of the major component in ^{1}H NMR spectra of the crude reaction mixture corresponded to those assigned to (TTP)AlMe(C$_6$F$_5$) generated in the reaction between (TTP)AlMe$_2$ and B(C$_6$F$_5$)$_3$. In (TTP)AlMe(C$_6$F$_5$), the two carbon atoms directly attached to aluminum were not observed in ^{13}C NMR spectra. Spectroscopic data for (TTP)AlMe(C$_6$F$_5$): ^{1}H NMR (C$_6$D$_6$) δ -0.18 (t, $^{5}J_{\mathrm{HF}} = 1.6$ Hz, 3 H), 1.60 (s, 6 H), 1.93 (s, 6 H), 4.88 (s, 1 H), 6.80 (m, 8 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 20.74, 22.86, 98.25, 125.9, 130.3, 136.1, 137.4 (d, $|J_{\mathrm{CF}}| = 260$ Hz), 142.1, 147.5 (d, $|J_{\mathrm{CF}}| = 240$ Hz), 151.1 (d, $|J_{\mathrm{CF}}| = 238$ Hz), 169.6; ^{19}F NMR (C$_6$D$_6$) δ -162.4 (m), -154.9 (t, $J = 19.2$ Hz), -121.7 (dd, $J = 12.8, 27.8$ Hz); LRMS 486 (M^{+}, 1), 471 (M^{+} − CH$_3$, 12); HRMS calcd for $C_{26}H_{24}AlF_5N_2$, 486.1675, found 486.1701. MeB(C$_6$F$_5$)$_2$ has only been spectrosopically identified in the reaction mixture. Since pure material was not obtained, collection of ^{13}C data was not possible for MeB(C$_6$F$_5$)$_2$, but we were able to assign the ^{1}H and ^{19}F NMR data by comparing the spectrum of the reaction mixture with that of **7**. Spectroscopic data for MeB(C$_6$F$_5$)$_2$: ^{1}H NMR (C$_6$D$_6$) δ 1.33 (quintet, $^{5}J_{\mathrm{H-F}} = 2.0$ Hz); ^{11}B NMR (C$_6$D$_6$) δ 72 (br, $\nu_{1/2}$ ∼252 Hz); ^{19}F NMR (C$_6$D$_6$) δ -161.3 (m), -147.0 (m), -130.0 (m); LRMS 360 (M^{+}, 15).

Crystal Structure Determination and Refinement. Crystals of **1**, **3**, **4,** and **6** were coated with Paratone-N oil, and a suitable single crystal was selected and mounted on a glass fiber. The crystals were then transferred to the goniometer of a Siemens CCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data were collected as 30 s frames at 142 or 173 K. An initial cell was calculated by Smart from three sets of 15 frames. All data sets were collected over a hemisphere of reciprocal space. SAINT was used to integrate 1025 frames and to generate the raw file. Final unit cell parameters were obtained by least-squares refinement of strong reflections obtained. Absorption and time decay were applied to the data by SADABS. In all structures, the non-hydrogen atoms were found using SHELXS-86. Atomic coordinates and thermal parameters were refined using the full-matrix least-squares program SHELXL-97, and calculations were based on F^2 data. All non-hydrogen atoms were refined using anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions using HFIX. All crystallographic computations were performed on Silicon Graphics Indigo computers.

Crystals of **1** (fw 375.26) were grown via pentane diffusion into a concentrated toluene solution at room temperature. Compound **1** crystallized in a monoclinic crystal system. The space group *C*2/*c* was chosen over *Cc* on the basis of intensity statistics and the successful refinement of the structure. Al and C(5) were located on a 2-fold rotation axis; therefore $Z = 4$. Relevant details and data statistics are summarized in Table 1.

Crystals of **3** (fw 334.43) were grown from a concentrated pentane solution cooled to −78 °C. Compound **3** crystallized in a monoclinic crystal system with systematic absences indicating the space group $P2_1/c$. Relevant details and data statistics are summarized in Table 1.

Crystals of **4** (fw 474.69) were grown from a concentrated pentane solution cooled to −78 °C. Compound **4** crystallized in a monoclinic crystal system with systematic absences indicating the space group $P2_1/n$. Relevant details and data statistics are summarized in Table 1.

Crystals of **6** (fw 468.46) were grown by diffusing pentane into a toluene solution of **6** at −30 °C. Compound **6** crystallized in an orthorhombic crystal system with systematic absences indicating the space group $P2_12_12_1$. Relevant details and data statistics are summarized in Table 1.

Acknowledgment. We are grateful for support from the Center for the Fundamental Material Research at MSU. We also thank Mr. Sung W. Baek, who aided in ligand synthesis. The single-crystal X-ray equipment at MSU was supported by the National Science Foundation (Grant CHE-8403823), and the NMR equipment was provided by the National Science Foundation (Grant CHE-8800770) and the National Institutes of Health (Grant 1-S10-RR04750-01).

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1**, **3**, **4**, and **6** (19 pages). Ordering information is given on any current masthead page.

OM970886O