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Synthesis of Trinuclear Tin(II), Germanium(II), and Aluminum(III) Cyclophane Complexes

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Supporting Information

ABSTRACT: The synthesis and characterization of trinuclear Ge^{II} and Sn^{II} chlorides and a trialuminum complex supported by a trinucleating tris(β -diketiminate) cyclophane ligand (L^{3-}) are reported. The in situ deprotonation of H₃L with benzylpotassium and subsequent reaction with $GeCl_2$ ·dioxane or $SnCl_2$ afforded $(GeCl)_3L$ (1) and $(SnCl)_3L$ (2) in 42 and 60% yields, respectively. Each Ge^{II} and Sn^{II} atom is three-coordinate and exhibit pseudotrigonal pyramidal geometry as anticipated for three-coordinate divalent group 14 cations. UV/visible spectra collected on THF solutions of 1 and 2 display a bathochromic shift in the absorption from 1 to 2 (from 361 to 375 nm). Addition of AlMe₃ to toluene solutions of H₃L resulted in the formation of (AlMe₃) AlMe HL (3) which possesses two NCCCN chelter



 $(AIMe_2)_2AIMe_3HL$ (3), which possesses two NCCCN chelated $AIMe_2$ moieties. The third β -diketimine arm remains protonated and adopts an atypical *trans* conformation with an $AIMe_3$ coordinated to the solvent exposed imine N atom.

INTRODUCTION

There has recently been significant interest in the chemistry of group 14 compounds, particularly from the perspective of accessing transition-metal-like reactivity in *p*-block complexes. Sequential oxidative addition (oa) and reductive elimination (re) are hallmarks of transition metal catalysis and rely on being able to cycle between two or more oxidation states during turnover. By contrast, main group compounds are typically capable of either re or oa and therefore rely on more activated reagents (e.g., silanes vs dihydrogen) for catalytic or stepwise turnover. Whereas oxidative addition formally across the metal-metal bonds in main-group dimetallic compounds is well-precedented and proceeds either by dissociation into reactive carbenoid fragments or by utilizing the frontier orbitals of the dimetallic fragment to activate substrate bonds,¹ only one example is known for which both oa and re occur to afford welldefined products: the addition and elimination of alkynes to the distannyl complexes, RSnSnR (R = C_6H_3 -2,6(C_6H_3 -2,6-iPr₂)₂ or $C_6H-2,6(C_6H_3-2,4,6-iPr_2)2-3,5-iPr_2)$, reported by Power and co-workers.²

An alternative approach to the multinuclear one mentioned above has been to design carbenoid complexes in which the low-lying triplet state is thermally accessible. Indeed, carbene, silylene, germylene, and stannylene complexes can oxidatively add small-molecule substrates, including the reduction and insertion of $\text{CO}_{2^{,3}}$ H₂ activation,⁴ OH- and NH-bond activation,^{4d,5} and alkyne and nitrile insertion.⁶ However, these systems similarly suffer from an either-or reactivity manifold, that is, *oa* or *re* are possible, but both are not observed in a given system. One exception is the recent report of a bis(borylide)tin(II) complex which adds into X–H bonds (X = B, N, Si, and H) with uncontrolled elimination of products with N–H and N–B bonds.⁷ Relatedly, frustrated Lewis pairs (FLPs) of group 13 acids and group 15 bases have garnered substantial interest; these systems can heterolytically cleave substrate bonds (Scheme 1).⁸ As a hybrid between the



carbenoid and FLP approach, dehydrohalogenation of group 14 β -diketiminate complexes yields ylide-like species in which the metal center and the terminal unsaturated ligand C atom function as the acid and base, respectively (Scheme 1).⁹

Within this context, the targeted synthesis and reactivity studies of designed trinuclear group 13 and 14 complexes remains largely underexplored beyond their use as polymerization catalysts.¹⁰ Two classes of these compounds have been

Received: April 29, 2016

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reported: metal-metal bonded complexes and those in which metal-metal interactions are minimal. For the former, the triangular M₃ compounds exhibit comparable reactivity to the dimetallic metal-metal bonded complexes.²⁶ These compounds are not designed a priori but synthesized from selfassembly reactions, and their nuclearity and metal-metal separation are controlled by the steric demands of the supporting ligands. The latter class comprises multitopic tetrylenes (e.g., N-heterocyclic carbenoids), of which many are used as ligands for transition or other p-block metals.²⁷ We note that trinuclear species have been isolated as reaction products of di- or monometallic complexes with substrates such as CO₂ and CS₂, demonstrating the potential for cooperative activation of substrates.²⁸ Ligand design approaches that template, target, and control cooperative reactivity between main group centers remain rare.²⁹

Given our prior success in utilizing a macrobicyclic ligand to control the spatial disposition and electronic environment of transition metals within a trinuclear cluster,¹¹ we posited that L^{3-} would serve as a suitable platform for assembling trinuclear group 13 and 14 compounds and potentially allow access to systems with the combined reactivity of the metal-metal bonded and the ylide-like species. Specifically, we sought to combine the ability to perform *re* and *oa* as observed in Power's distannyl complex with the rich reactivity of group 14 carbenoid β -diketiminates by enforcing specific metal-metal distances in a multimetallic architecture. Herein, we report the first examples of trimetallic complexes of Ge^{II}, Sn^{II}, and Al^{III} that are proximally positioned by design and the preliminary reactivity of the germanium and tin complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization of 1 and 2. The addition of a THF solution of the potassium salt of L^{3-} to either GeCl₂·dioxane or SnCl₂ yielded the trinuclear complexes $(M-Cl)_3L$, where $M = Ge^{II}$ (1) or Sn^{II} (2) as yellow solids in reasonable yields (Scheme 2). Combustion analysis data on solid 1 and 2 agrees with the proposed formulations. NMR experiments on C_6D_6 solutions of 1 and 2 support both as C_{3h} -symmetric, displaying diastereotopic splitting patterns of the N-CH₂ and Ar-CH₂ groups (Figures S1 and S2).

Solid-state structural analysis of 1 and 2 shows that each metal center resides in a pseudotrigonal pyramidal geometry,

Scheme 2



supported by the *N*,*N*-chelate of L^{3-} and is bound to a single chloride, with one vertex occupied by the lone pair of electrons (Figure 1). The aryl rings in 1 and 2 are nearly parallel, with



Figure 1. Solid-state structures of 1 (top) and 2 (bottom) with atoms represented as 80% (1) or 65% (2) thermal ellipsoids. C, N, Ge, Sn, and Cl atoms are illustrated as gray, blue, purple, tan, and green ellipsoids, respectively. Hydrogen atoms and solvents of crystallization omitted for clarity.

dihedral angles of 1.32 and 1.02°, respectively. The larger M… M distances in 1 compared to those in 2 are consistent with the larger Sn^{II} atomic radius (1.12 Å) compared to that in Ge^{II} (0.93 Å).¹² These distances are much larger than reported N-chelated Ge^{II}–Ge^{II} (2.550–2.709 Å)¹³ and Sn^{II}–Sn^{II} (3.014–3.068 Å),¹⁴ complexes and M…M interactions are not predicted in either 1 or 2. Overall, the deviations in structural parameters between 1 and 2, such as N_L–M–N_L bond angles, displacement of M from the NCCCN plane, and M–Cl bond lengths, are consistent with the larger atomic radius of Sn^{II} as compared to Ge^{II} and are in agreement with the trends found in other group 14 β -diketiminates (Table S1).^{12,15,16}

There are three structural features of 1 and 2 that are counter to trends previously observed in Ge and Sn nacnac complexes. The M^{II}-Cl bond distance in di(aryl)nacnac complexes typically decreases as the steric bulk of the substituents on the aryl ring increases following the order Ph > Mes > 2,6-i $pr_2C_6H_3$ where M^{II} = Ge and Sn (Table S1).^{12,15} In contrast, 1 and 2 have long M-Cl bond lengths compared to other those of germylene and stannylene β -diketiminates; the Ge–Cl bond lengths in 1 (2.3865(8) - 2.3956(7) Å) are longer than all other reported Ge-Cl bond lengths in nitrogen-based threecoordinate complexes (2.174(2)-2.3776(8) Å; Table S1).^{13a,b,17} There are two reported N-ligated three-coordinate Sn-Cl complexes with bond lengths longer than those in 2, with this value for all other reported compounds ranging from 2.4359(10) to 2.502(3) Å.^{13c,16c,18,21} One is a H nacnac(Sn^{II}-Cl) complex,¹⁹ which is expected to have a long bond length from the trend observed for ^{Ar}nacnac(M^{II}–Cl) complexes. The other is a diisopropyl-substituted aminotroponiminate complex, which displays weak intramolecular Sn-Cl interactions that elongate the Sn-Cl bond.²⁰ The reason for the longer M-Cl

bonds in 1 and 2 as compared to those in other compounds may be the steric conflicts between the chloride and the ethyl groups on the benzene caps. The N_L-M-N_L bond angles and the M-N_L bond distances are comparable with those of the monometallic analogs, suggesting that the observed differences are unlikely due to electronic effects. As expected because of the relative position of the Sn^{II} versus Ge^{II} in the NCCCN plane (i.e., the Sn^{II} is further out of the plane), the ethyl-chloride contacts are larger in 2 compared to those in 1. Compounds 1 and 2 exhibit surprisingly acute N_L-M-Cl bond angles as compared to those in the monometallic congeners, yet the metal centers in 1 and 2 simultaneously lie closer to the NCCCN plane of the respective diketiminate arm as compared to those in mononuclear complexes. Contrastingly, a more acute N_I-M-Cl angle is observed as the metal center lies further out-of-plane of the diketiminate backbone in mononuclear complexes.²² It is evident then that the cyclophanate employed enforces atypical steric constraints on the metal center. We cannot exclude, however, the role that repulsive effects between the occupied molecular orbitals of significant Ge or Sn s-character, which are directed slightly off-center of the centroid of the internal cavity.

UV/visible spectroscopy performed on THF solutions of **1** and **2** reveal absorptions at 361 and 375 nm, respectively (Figure 2). These transitions are assigned as metal lone pair to



Figure 2. Ultraviolet-visible spectra of 1 (black) and 2 (red) recorded in THF.

p-orbital transitions $(n \rightarrow p)$ by analogy to similar absorptions reported in monometallic complexes. The observed redshift of the absorption maximum from Ge^{II} to Sn^{II} was previously reported for the divalent group 14 amides and correlates with a decreasing HOMO–LUMO gap following the trend Ge > Sn > Pb.²³ The monomer [Ar[#]N](Ge–Cl) reported by Power and co-workers has a absorption energy similar to that of 1 (λ_{max} = 320 nm), where Ar[#] = [C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂].^{23b}

Synthesis and Characterization of 3. In contrast to 1 and 2 which required deprotonation of the ligand prior to metalation, direct metalation of H_3L could be carried out by addition of $AlMe_3$ (2.0 M in hexanes) to a suspension of the free-base ligand in toluene to yield the trialuminum complex, 3, as a pale yellow solid (Scheme 2). NMR spectra demonstrate that the complex lacks the higher symmetry of 1 or 2, for example, the $-CH_2CH_3$ protons on each ethyl group on the benzene caps are in a unique magnetic environment (Figure S3). The Al-CH₃ resonances appear upfield of the internal TMS standard ($\delta = -0.08$ to -1.45 ppm), and the number of observed peaks is also suggestive of distinct methyl ligands and

consequent low molecular symmetry. These chemical shifts are within the range of reported mono- and dinuclear AlMe₂ β -diketiminates ($\delta = -0.02$ to -1.48 ppm).²⁴ We observe an absorption in infrared spectra of 3 at 3410 cm⁻¹, which is of the expected energy for a N–H bond stretching mode.

The crystal structure of **3** agrees with the asymmetry observed in NMR spectra and with the retention of one protonated ligand arm in IR measurements. In the structure, two Al-centers are held in a pseudotetrahedral coordination environment (Al1 and Al2, $\tau_4 = 0.88-0.98$), with each metal ligated by the N,N-chelate of a β -diketiminate arm and the remaining two vertices occupied by methyl donors (Figure 3).



Figure 3. Side-on (left) and top-down (right) views of the solid-state structure of 3 with atoms represented as 80% thermal ellipsoids. C, N, Al, and H atoms are illustrated as gray, blue, lavender, and black ellipsoids or spheres, respectively. Hydrogen atoms (except for the N–H proton) and solvents of crystallizations omitted for clarity.

Of the four Me ligands in the two (nacnac)AlMe₂ units, one is accommodated within the internal cavity of the ligand, and the remaining three are located outside of the internal pocket. Surprisingly, the third nacnac arm remains protonated and adopts a *trans* rather than the typical *cis* orientation. The protonated N atom is proximal to a methyl group on Al2 and nominally oriented toward the internal cavity. Al3 coordinates to the imine N atom of this *trans* nacnac arm, and together with three methyl ligands, affords a pseudotetrahedral ($\tau_4 = 1.02$) environment around this metal center.

Two aspects of the structure of 3 are worth noting: the trans orientation of one nacnac arm and the retention of one acidic N–H proton. Other examples in which β -diketiminates adopt an open conformation have been reported. The preference for this conformer has been attributed to the electron count of the metal (e.g., d^{10} in the case of Ag^I, Au^I, and Cs⁺),²⁵ which predisposes a linear coordination mode, or as a result of significant steric congestion, as in $bis(\beta$ -diketiminato)metal complexes.¹² Roesky and co-workers reported the thermally sensitive [Mes(Me)NacNacH](AlMe2Cl), which adopted a neutral monodentate mode of the diketimine; however, the ligand is in an elongated cis-conformation rather than the trans arrangement seen in 3.^{24f} We posit that the constraints of our cyclophane ligand enforce the monodentate binding of one diketimine as three AlMe2 units cannot be simultaneously accommodated within the ligand cavity. The resulting steric conflicts between the methyl ligands on Al1 and Al2 and the ethyl substituents on the benzene rings likely also contribute to forcing the third nacnac arm into a trans orientation.

The larger dihedral angle of $18.42(9)^{\circ}$ between the two aromatic rings in 3 is expected given the significant opening of one side of the cyclophane to accommodate the *trans* β diketimine. We have previously shown that L^{3-} can accommodate different mono- and diatomic donors within the internal void (e.g., Br⁻, S²⁻, N₂, and N³⁻)¹¹, which highlight the surprising flexibility of this ligand; however, this is the largest structural change observed for this ligand to date. All other bond metrics are comparable to reported monometallic species (Table S2).²⁴

Metalation of H₃L with AlMe₃ likely occurs in a stepwise fashion, in which the first and second equivalents of AlMe₃ react to afford (AlMe₂)H₂L and (AlMe₂)₂HL, respectively, with release of 2 equiv of CH₄. We have unsuccessfully attempted to use fewer equivalents to trap the mono- and dimetallic compounds. As a consequence of the steric conflicts created by the four methyl donors, the third β -diketimine adopts a *trans* orientation and coordinates an AlMe3 on the exterior of the complex. Here, we envision two possiblilities: formation of a third β -diketiminate arm or retention of one β -diketimine. Deprotonation would generate in an anionic N-donor coordinated to the exterior AlMe₃. Independent of which methyl ligand (e.g., on Al1 or Al2) facilitates this deprotonation, a three-coordinate Al center would necessarily be generated, counter to the crystallographic data. Alternatively, deprotonation could be adventitious (e.g., sacrificial AlMe₃). However, this would yield an anionic complex, and we do not observe a countercation. Given these constraints and that an IR absorption consistent with an N-H vibration is observed, we surmise that the third arm remains protonated, which is surprising in the presence of reactive methyl ligands on the Al^{III} centers. The reaction is also performed in a noncoordinating solvent, precluding solvent stabilization of coordinatively unsaturated Al^{III} centers.

Reactivity Studies of 1 and 2. Armed with 1 and 2, we then sought to dehydrohalogenate these complexes to generate the corresponding tri(ylide-like) complexes. Stirring a mixture of 1 or 2 and $\text{LiN}(\text{SiMe}_3)_2$ in ethereal solvents led to the formation of intractable bright red precipitates 1a and 2a, respectively (Scheme 3). We observe new vibrational modes in



the IR spectra of the products that are consistent with vibrational modes of C= \hat{C} (1625 and 1620 cm⁻¹) and C=C-H (695, 758, 766, 805, 865, 900, and 932 cm⁻¹) functionalities. Preliminarily, this observation agrees with the formation of an unsaturated β -diketiminate backbone (Figure S7). These solids are insoluble in all organic solvents tested (including HMPA, THF, DMF, and aromatic solvents), which hampered complete characterization. The poor solubility is surprising, however, given the previous reports on the monometallic germylene and stannylene complexes. The poor solubility here could arise from incorporating LiCl through interactions with the terminal C atom, affording "ate" complexes held together in an amorphous extended network. Alternatively, aggregation could be occurring, analogous to the C–C bond linked dimeric products reported previously, or incomplete dehydrohalogenation could also occur.

To probe the role of the base, we employed benzylpotassium, butyllithium, and methyllithium; however, we obtained intractable and intensely colored solids in all cases. This class of mononuclear germylenes and stannylenes have been previously shown to react with polar X-H groups resulting in M-X bond formation with concomitant protonation of the terminal unsaturated C atom.^{6c,9a-c} We reacted the isolated red solids 1a or 2a with 3 equiv of HCl in THF, which resulted in the formation of starting complex 1 or 2 as confirmed by ¹H NMR spectroscopy (Figure S8). In the case of the reaction of 2a with HCl, we observe $H_{2}L$ as a byproduct in a 2:1 ratio with 2 based on the integrals in the ¹H NMR spectrum, which is not surprising given that 2 readily demetallates in the presence of HCl. Similar reaction of 1a or 2a with 3 equiv of methanol resulted in dissolution and decolorization of the mixtures. ¹H NMR spectra of the germanium product from these reactions were complex and not readily interpretable. Contrastingly, ¹H NMR spectra recorded on C₆D₆ solutions of the yellow solid isolated from reaction of 2a and methanol additions support formation of the methoxide analog of 2; a new singlet at 4.01 ppm occurs at a resonance nearly coincident with the methoxide resonance in the monometallic complexes with retention of the expected diastereotopic resonances of the ethyl groups (Figure S11).^{15b,16a} We were unable to characterize the putative methoxide products as single crystals suitable for diffraction, and combustion analyses were unsuccessful. Importantly, 2 is unstable to methanol and demetalates to afford free ligand. This observation suggests that 2a is distinct from 2, and that this reaction is not a simple metathesis of HCl for MeOH. Attempts to improve the solubility of the deprotonated products (1a and 2a) and detailed reactivity studies of these target species are ongoing.

CONCLUSIONS

We have reported the synthesis and characterization of two trinuclear Ge^{II} and Sn^{II} chlorides and a trinuclear aluminum complex supported by a tris(β -diketimine) cyclophane, H₃L. Compounds 1 and 2 represent the first examples of trinuclear group 14 complexes that can be accessed in a templated fashion through ligand design. The trinuclear aluminum complex displays a rare monodentate coordination mode of the β -diketimine backbone and demonstrates how flexible L³⁻ may be to accommodate different metal ions and guest small molecule ligands.

EXPERIMENTAL METHODS

General Considerations. All reactions were performed under a dinitrogen atmosphere in an Innovative Technologies (IT) glovebox. Solvents were purchased from Sigma-Aldrich, then dried using an IT solvent purification system, and stored over activated 3 Å molecular sieves. AlMe₃ (2.0 M in hexanes) and SnCl₂ were purchased from Sigma-Aldrich or Acros Organics and used as received unless stated otherwise. GeCl2 · dioxane was purchased from Sigma-Aldrich and recrystallized from dioxane prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, purified according to reported procedures, and then stored over activated 3 Å molecular sieves.³⁰ IR spectra were collected in a nitrogen-filled glovebox using a Bruker Alpha with an ATR diamond crystal stage using the Opus 7.0 software package. NMR spectra were collected on a Varian Inova operating at 500 MHz or a Mercury operating at 300 MHz equipped with a three-channel 5 mm indirect detection probe with z-axis gradients. All chemical shifts are reported in parts per million (ppm) and referenced to tetramethylsilane (TMS) for ¹H and ¹³C. Complete Analysis Laboratories, Inc. (Parsippany, NJ) conducted elemental analyses on samples shipped under vacuum. H_3L and benzylpotassium (BnK) were synthesized as described previously.^{11a,31}

(GeCl)₃L (1). BnK (180 mg, 1.37 mmol) and H₃L (300 mg, 0.430 mmol) were dissolved in THF (10 mL) and stirred for 10 min to produce a dark purple solution which was then added dropwise to a suspension of $GeCl_2$ ·dioxane (310 mg, 1.37 mmol) in THF (5 mL). The reaction was stirred at room temperature for 12 h, after which the reaction mixture was filtered through a fine-porosity fritted funnel. The solvent was removed from the filrate under reduced pressure. The product was extracted from the dried filtrate with hot benzene (15 mL), filtered through a fine-porosity fritted funnel packed with a Celite plug. The solvent was then removed from the filtrate in vacuo to yield crude 1 as a yellow solid. Slow evaporation of a saturated benzene solution at room temperature yielded yellow crystals (186 mg, 42%). ¹H NMR (300 MHz, d_6 -benzene, δ , ppm) 1.05 (-CH₂CH₃, t, ³J = 7.6 Hz, 18H), 1.81 (NCCH₃, s, 18H), 2.48 (Ar-CH-CH₃, dq, ²J = 15.1 Hz, ${}^{3}J = 7.5$ Hz, 6 H), 3.66 (Ar-CH-CH₃, dq, ${}^{2}J = 14.7$ Hz, ${}^{3}J = 7.6$ Hz, 6H), 4.53 (Ar–CH–N, d, ${}^{2}J$ = 14.2 Hz, 6 H), 4.77 (Ar–CH–N, d, ^{2}J = 14.2 Hz, 6 H), 4.98 (HC(CN)₂, s, 3H). ^{13}C {¹H} NMR (75 MHz, d_6 -benzene, δ , ppm) 16.71, 23.14, 24.62, 47.31, 102.07, 132.83, 146.80, 163.57. Combustion Analysis on $1_{1}[C_{45}H_{63}Cl_{3}Ge_{3}N_{6}] \cdot (C_{6}H_{6})_{0.8}$ (calculated): C, 55.57 (55.66); H, 6.46 (6.36); N, 7.64 (7.82). IR (cm⁻¹) 472, 774, 897, 1329, 1530.

(SnCl)₃L (2). BnK (122 mg, 0.934 mmol) and H_3L (208 mg, 0.301 mmol) were dissolved in THF (10 mL) and stirred for 15 min to produce a dark purple solution. SnCl₂ (187 mg, 0.995 mmol) was added to the solution to form a dark yellow suspension which was stirred at 35 °C for 48 h. The reaction was then filtered through a fineporosity fritted funnel, and the solvent was removed from the filtrate under reduced pressure. The product was extracted for 12 h from the dried filtrate into toluene (10 mL) at 50 °C with stirring, at which point the mixture was filtered through a fine-porosity fritted funnel and the solvent removed from the filtrate in vacuo to yield crude 2 as a yellow solid. Diffusion of pentane into a THF solution of 2 yielded yellow crystals (220 mg, 61%). ¹H NMR (300 MHz, d_6 -benzene, δ , ppm) 1.01 (CH₂-CH₃, t, ${}^{3}J$ = 7.5 Hz, 18H), 1.83 (NCCH₃, s, 18H), 2.56 (Ar-CH-CH₃, dq, ${}^{2}J$ = 15.0 Hz, ${}^{3}J$ = 7.3 Hz, 6H), 3.54 (Ar- $CH-CH_3$, dq, ²J = 15.0 Hz, ³J = 7.3 Hz, 6H), 4.61 (Ar-CH-N, d, ²J = 14.3 Hz, 6H), 4.70 (Ar–CH–N, d, ${}^{2}J$ = 14.3 Hz, 6H), 4.90 $(HC(CN)_2, s, 3H)$. ¹³C {H} NMR (75 MHz, d_6 -benzene, δ , ppm) 16.49, 23.79, 24.67, 47.53, 101.99, 133.80, 146.41, 165.02. Combustion Analysis on 2, C₄₅H₆₃Cl₃Sn₃N₆ (calculated): C, 46.79 (46.98); H, 5.67 (5.52); N, 7.33 (7.30). IR (cm⁻¹) 462, 682, 737, 887, 1525.

 $(AIMe_2)_2(AIMe_3)HL$ (3). AIMe₃ (456 μ L, 0.912 mmol) was added dropwise to a slurry of H_3L (0.200 g, 0.289 mmol) in toluene (15 mL). The pale-yellow reaction mixture was stirred at 50 °C for 2 d, after which, the solvent was removed from the reaction in vacuo. The resulting yellow oil was washed twice with hexanes (5 mL) to afford a white powder. This powder was extracted with benzene (10 mL) and that mixture filtered. Drying the filtrate under vacuum yielded the crude product as a free-flowing off-white powder. Recrystallization of the crude material by slow evaporation of a saturated toluene solution gave the desired product as colorless crystals (115 mg, 46%). Despite numerous attempts to obtain exclusively a crystalline sample of 3, the crystals could only be isolated with a minor contamination of a yellow oil. ¹H NMR (500 MHz, d_6 -benzene, δ , ppm) -1.10 (s, 6H), -0.34 (s, 12H), -0.14 (s, 3H), 0.97 (m, 18H, minor peak corresponds to residual hexanes), 1.97 (s, 18H), 2.67 (m), 2.90 (m, 4H), 3.09 (m, 8H), 4.44 (d, 4H), 4.62 (s+d, 8H), 4.79 (s, 1H). ¹³C {H} NMR (125 MHz, d₆-benzene, δ, ppm) 16.63, 16.67, 20.42, 22.51, 23.37, 24.62, 45.97, 46.34, 95.44, 98.04, 131.52, 133.18, 143.41, 143.91, 158.92, 167.58, 226.04, 226.92. Despite several attempts, combustion analysis on 3 failed to meet theoretical predictions as expected given the contamination. IR (cm⁻¹) 584, 667, 1022, 1168, 1516, 1586, 3410.

Synthesis of 1a. A portion of **1** (50 mg, 0.049 mmol) and LiHMDS (26 mg, 0.16 mmol) were placed in a 20 mL vial and diluted with dimethoxyethane (10 mL) with stirring. Within seconds the reaction mixture became dark red. After several minutes, the reaction was evidently a suspension of a dark orange/red precipitate and an almost colorless solution. The reaction was nonetheless allowed to stir

overnight and then filtered through a fine porosity glass-fritted funnel. The resulting orange precipitate was washed with DME (5 mL), THF (5 mL), and hexanes (5 mL) and dried under reduced pressure to yield a red solid (34 mg, 75%). IR (cm⁻¹) 462, 498, 671, 766, 805, 900, 932, 1046, 1625.

Synthesis of 2a. Compound 2a was synthesized in a similar manner to 1a using $(SnCl)_3L$ instead of $(GeCl)_3L$ to yield a dark red powder (21.9 mg, 80.5%). IR (cm⁻¹) 458, 656, 695, 758, 865, 1027, 1532. 1620.

Reaction of 1a with HCl. To a portion of 1a (5.3 mg, 0.0059 mmol) suspended in THF (5 mL), HCl in dioxane (4.3 μ L, 0.018 mmol) was added at ambient temperature with vigorous stirring. The reaction immediately presented as a light yellow solution and was stirred for 10 min. The solvent was removed under reduced pressure to yield a light-yellow solid. ¹H NMR of the yellow-solid in C₆D₆ is consistent with that of 1 (Figure S8).

Reaction of 2a with HCl. This reaction was performed in a similar manner to that of **1a** and HCl. ¹H NMR in C_6D_6 is consistent with starting complex **2** and H_3L (Figure S8).

Reaction of 2a with MeOH. A solution of MeOH (1.7 μ L, 0.16 mmol) and toluene (8 mL) was added dropwise to a slurry of **2a** (15 mg, 0.014 mmol) in toluene (8 mL). The solution immediately turned bright yellow. The reaction was stirred for 2 days and the solvent was removed under reduced pressure to yield a yellow solid. ¹H NMR (500 MHz, *d*₆-benzene, δ , ppm) 1.13 (t, ³J = 7.44 Hz, 18H), 1.89 (s, 18H), 2.63 (dq, ²J = 14.64 Hz, ³J = 7.21 Hz, 6H), 3.32 (dq, ²J = 15.53 Hz, ³J = 7.09 Hz), 4.01 (s, 6H), 4.67 (d, ²J = 18.42, 12H), 4.67 (s, 3H) (Figure S12).

Single-Crystal X-ray Diffraction Experiments. X-ray intensity data were collected at 100 K on a Bruker DUO diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms.³² The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

(GeCl)₃L (1). X-ray intensity data were collected at 100 K on a Bruker **DUO** diffractometer using Mo K α radiation (α = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations.³² The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL2013, using full-matrix least-squares refinement.³³ The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the Ge₃Cl₃ complex and three and a half benzene solvent molecules, one of which lies on a 2-fold rotational axis. Two benzene molecules are disordered and were refined in two parts each with the minor parts constrained to maintain ideal geometry using command "AFIX 66" in the refinement. In the final cycle of refinement, 14 650 reflections (of which 12 268 are observed with $I > 2\sigma(I)$) were used to refine 682 parameters, and the resulting R₁, wR₂, and S (goodness of fit) were 3.04%, 8.14%, and 1.041, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value, but its function is not minimized.

 $(SnCl)_{3L}$ (2). The structure was solved and refined in SHELXTL2013, using full-matrix least-squares refinement.³³ The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of two chemically equivalent but crystallographically independent Sn₃ complexes and eight THF solvent molecules. The THF molecules were disordered and could not be modeled properly; thus, the program SQUEEZE, a part of the PLATON package of crystallographically

graphic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.³² In the final cycle of refinement, 29 170 reflections (of which 17 287 are observed with $I > 2\sigma(I)$) were used to refine 1051 parameters and the resulting R_1 , wR_2 , and S (goodness of fit) were 4.77%, 10.65%, and 0.877, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value, but its function is not minimized.

(AIMe₂)₂(AIMe₃)HL (3). X-ray intensity data were collected at 100 K on a Bruker **DUO** diffractometer using Cu K α radiation ($\alpha = 1.54178$ Å), from an ImuS power source and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms.³² The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL2014, using full-matrix least-squares refinement.³³ The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of the Al complex and two toluene solvent molecules. The solvent molecules are disordered along the a-axis and close to inversion centers. The complex to solvent ratio is 1:2. The toluene molecules were disordered and could not be modeled properly; thus, program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.³² There is also one major disorder in the complex where the chain of N3 to N6 and all atoms in between including Al3 and its methyl groups are refined in two positions with their site occupation factors refined to 0.54(1) and consequently 0.46(1) for the major and minor parts, respectively. In the final cycle of refinement, 11 275 reflections (of which 9436 are observed with I > $2\sigma(I)$ were used to refine 553 parameters, and the resulting R_1 , wR_2 , and S (goodness of fit) were 7.45%, 18.89%, and 1.076, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00354.

Experimental details, characterization data (PDF) X-ray crystallographic data for 1, 2, and 3 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

L.J.M.: University of Florida and ACS Petroleum Research Fund (ACS-PRF 52704-DNI3), a departmental instrumentation award from the NSF (CHE-1048604), and Dr. Brian J. Cook and Ricardo Ferreira for assistance with NMR data collection. K.A.A.: NSF (CHE-0821346) and University of Florida for funding X-ray equipment purchase. D.M.E.: University of Florida, College of Liberal Arts and Sciences Graduate Research Fellowship. J.B.G.: University of Florida, University Scholars Program.

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