

Mechanochemical Synthesis of $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_3(\text{Al}, \text{Sc})$, a Base-Free Tris(allyl)aluminum Complex and Its Scandium Analogue

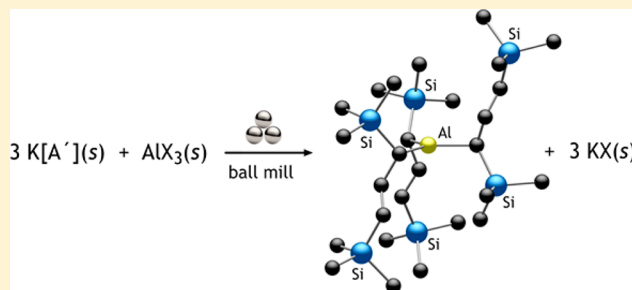
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S Supporting Information

ABSTRACT: Unsolvated tris(allyl)aluminum, $(\text{C}_3\text{H}_5)_3\text{Al}$, has never been isolated, although adducts with THF, OPPh_3 , and pyridine are known. Attempts to make a base-free derivative with the bulky 1,3-bis(trimethylsilyl)allyl anion (A') from the reaction of aluminum halides and $\text{K}[\text{A}']$ in ethers or by deprotonation of HA' with R_3Al ($\text{R} = \text{Me}, \text{Et}$) were not successful. However, grinding AlX_3 and $\text{K}[\text{A}']$ in the solid state, followed by extraction of the mixture with hexanes, produces $\text{A}'_3\text{Al}$ in high yield. A single-crystal X-ray structure demonstrated that the monomeric molecule contains σ -bonded allyl ligands (average $\text{Al}-\text{C}$ 1.964(3) Å) and, like the known gallium analogue, is fluxional in solution. A DFT study of the parent $(\text{C}_3\text{H}_5)_3\text{Al}$ indicates that the ligands would be of mixed hapticity, i.e., $(\eta^1\text{-C}_3\text{H}_5)_2(\eta^3\text{-C}_3\text{H}_5)\text{Al}$, although the trimethylsilylated ligands evidently prevent that conformation in $\text{A}'_3\text{Al}$. $\text{A}'_3\text{Al}$ reacts immediately with benzophenone in hexanes to produce $\text{Al}(\text{OCPh}_2)_3$ but negligibly with the bulky alcohol HOCPh_3 . Grinding $\text{A}'_3\text{Al}$ with ScCl_3 yields no observable product, although the same reaction with $\text{K}[\text{A}']$ produces the hexane-soluble $\text{A}'_3\text{Sc}$, whose X-ray crystal structure reveals three π -bound A' ligands.



Solvent-free organometallic reactions, although far less common than solvent-mediated versions, can encompass a variety of transformations, including isomerization, ligand rearrangement and replacement, and oxidative addition/reductive elimination.¹ Solid-state reactions provide the opportunity to investigate compounds not attainable when a solvent is present, either because usable solvents interfere with the interaction of the reagents or because solvent molecules bind strongly to the product and change its structure and reactivity. They can also expand the range of suitable reagents for a reaction, as solubility is not a requirement for reactivity. We report here a mechanochemical synthesis of an aluminum allyl that is not available via conventional solvent-based routes and that displays reactivity different from a related solvated version.

Among organoaluminum compounds, the tris(allyl) complex $(\text{C}_3\text{H}_5)_3\text{Al}$ is a surprisingly elusive species; it has never been isolated in pure form, although attempts to generate it date from the time of Grignard.² Compounds known or believed to be allyl chloro “ate” or $(\text{C}_3\text{H}_5)_3\text{Al}_2\text{Br}_3$ species have been prepared in situ and used in organic synthesis.³ More recently, Okuda and co-workers have synthesized the THF adduct of tris(allyl)aluminum, $(\text{C}_3\text{H}_5)_3\text{Al}(\text{THF})$, as a yellow oil from the halide metathesis reaction of AlBr_3 and $\text{K}[\text{C}_3\text{H}_5]$.⁴ THF can be replaced with the stronger base OPPh_3 to form the solid $(\eta^1\text{-C}_3\text{H}_5)_3\text{Al}(\text{OPPh}_3)$ or with pyridine to form the yellow oil $(\text{C}_3\text{H}_5)_3\text{Al}(\text{py})$.⁵ The THF adduct has been transformed into the bis(allyl)aluminum cations $[(\eta^1\text{-C}_3\text{H}_5)_2\text{Al}-$

$(\text{THF})_{3-n}]^+[\text{BPh}_4]^{-(n+1)}\text{THF}$ ($n = 0, 1$), and the tetrakis(allyl)aluminate $\text{K}^+[(\eta^1\text{-C}_3\text{H}_5)_4\text{Al}]^-$.⁴ Reactions of the allyl complexes with benzophenone, allyl halides, halogens, and pyridines have also been explored.^{4,5}

Our interest in metal complexes of trimethylsilylated allyl ligands stems from the considerable kinetic stability and high hydrocarbon solubility they exhibit, particularly in comparison to unsubstituted versions, which may be unknown or substantially less stable.⁶ The 1,3- $(\text{SiMe}_3)_2\text{C}_3\text{H}_3$ (A') ligand has previously been used to generate the group 13 complex $\text{A}'_3\text{Ga}$ with halide metathesis,⁷ and we believed preparation of the aluminum analogue would be straightforward.

This proved not to be the case; for example, treatment of AlX_3 ($\text{X} = \text{Cl}, \text{I}$) with $\text{K}[\text{A}']$ in either THF or diethyl ether, followed by removal of the solvent, yields thick orange oils containing unidentifiable mixtures of products. Variation in the temperature (room temperature, -78°C) does not change the outcome. A typical oil from the reaction of AlI_3 with $\text{K}[\text{A}']$ in THF displays at least eight resonances in its ^1H NMR spectrum in the SiMe_3 region (δ 0.0–0.4), plus another eight multiplets in the olefinic region (δ 5–7), indicative of a complex mixture. As part of a different synthetic approach, attempts were made to deprotonate HA' with Et_3Al or Me_3Al in hexanes. These were not successful; evidently HA' is not a sufficiently acidic substrate for such proton transfer reactions.

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A procedure used for the production of magnesium borohydrides⁸ was adopted for the solid-state synthesis of the aluminum allyl. AlX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{K}[\text{A}']$ were combined in a 50 mL round-bottom flask containing stainless steel ball bearings (6 mm) and turned on a rotary evaporator for 1–2 h, producing an off-white to yellow powder. Extraction with hexanes gives the solid product $\text{A}'_3\text{Al}$ (**1**) in approximately 30% yield. No reaction occurred if the reagents were simply magnetically stirred in hexanes without grinding, confirming that mechanochemical activation was responsible for the production of **1** and did not occur during the extraction procedure.

Although the flask reactor is inexpensive and sufficient for test reactions, significantly shorter reaction times (15 min) and higher yields (up to 85%) were obtained with the use of a tube disperser,⁹ which provides more energetic impact of the ball bearings. Even shorter reaction times (5 min, 600 rpm) and equivalent yields (up to 88%) on a multigram scale were obtained with the use of a planetary ball mill. Compound **1** is a low-melting solid (40–44 °C), is soluble in both aromatic and aliphatic hydrocarbons, and is stable indefinitely under an inert atmosphere at room temperature. It can survive only 30–60 s exposure to air before decomposition occurs with the production of white smoke. In THF, **1** readily dissolves to form a pale yellow solution. Removal of the THF leaves a yellow oil that does not solidify over a period of days; ^1H NMR spectra contain multiple broad resonances that suggest a mixture of products is present.

The ^1H NMR spectrum of **1** at room temperature gives the appearance of a structure with symmetrically bound (“ π -type”) allyl ligands; e.g., in benzene- d_6 , the resonance for all six SiMe_3 groups appears as a sharp singlet (δ 0.19) and the central hydrogen atom on the allyl ligands appears as a triplet (δ 6.38); the terminal hydrogens are represented by a doublet (δ 3.66). At room temperature in toluene- d_8 , the terminal hydrogens appear as a broad resonance ($w_{1/2} \approx 125$ Hz) that sharpens at –20 °C into a doublet ($J = 15$ Hz). Further cooling to –70 °C produces no additional major changes in the spectrum. In particular, the SiMe_3 resonance broadens slightly but remains unsplit. This behavior is reminiscent of the fluxional $\text{A}'_3\text{Ga}$ complex, which also displays “ π -type” allyl ligands in solution and whose resonance for SiMe_3 remains unresolved at –75 °C.

A single-crystal X-ray diffraction study of **1** reveals that it crystallizes from hexanes as a monomer with the aluminum atom σ -bound to the bis(trimethylsilyl)allyl ligands in a trigonal-planar manner (Figure 1). All three ligands are roughly perpendicular to the AlC_3 plane, with one antiparallel to the other two. The complex is isostructural with the gallium analogue.⁷

The average $\text{Al}-\text{C}$ distance of 1.964(3) Å is typical for aluminum–carbon single bonds: cf. those of the mononuclear trimesitylaluminum (1.951(1) Å),¹⁰ (*t*-Bu)₃Al (2.006(7) Å),¹¹ and (PhCH_2)₃Al (1.99(1) Å).¹² The nearly perfect planarity of the central AlC_3 unit in **1** is indicated by the sum of the $\text{C}-\text{Al}-\text{C}'$ angles of 359.8°; the Al atom lies only 0.046 Å from the C_3 plane. The planarity reflects the isolation of the metal center from neighboring molecules; in contrast, close intermolecular $\text{Al}\cdots\text{C}$ contacts in the solid-state structures of (*t*-Bu)₃Al and (PhCH_2)₃Al lead to puckering of the AlC_3 units, with the metal center lifted 0.25 Å¹¹ and 0.475 Å,¹² respectively, from the C_3 planes. The fully localized carbon–carbon bonding in the allyl ligands in **1** is indicated by the average $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bond distances of 1.334(5) and 1.503(5) Å, respectively.

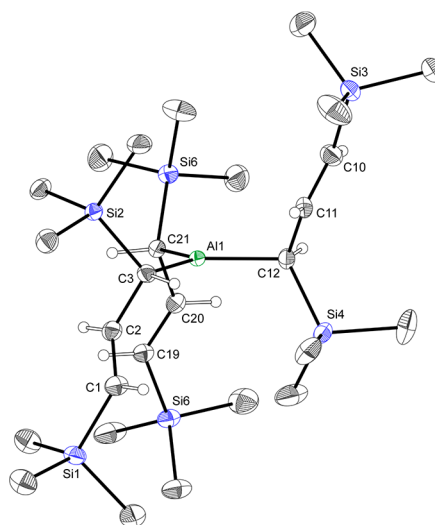


Figure 1. Thermal ellipsoid plot of **1**. Ellipsoids are drawn at the 50% level, and hydrogen atoms on the trimethylsilyl groups have been omitted for clarity. Selected bond distances (Å): $\text{Al}-\text{C}_3$ 1.964(2), C_1-C_2 1.330(3), C_2-C_3 1.512(3), $\text{Al}-\text{C}_{12}$ 1.965(2), $\text{C}_{10}-\text{C}_{11}$ 1.337(3), $\text{C}_{11}-\text{C}_{12}$ 1.495(3), $\text{Al}-\text{C}_{21}$ 1.962(2), $\text{C}_{19}-\text{C}_{20}$ 1.335(3), $\text{C}_{20}-\text{C}_{21}$ 1.501(3).

The bulkiness of the A' ligands not only shields the Al center in **1** from adjacent molecules in the solid state but also apparently affects the internal coordination of the allyl ligands. Computational modeling of the parent (C_3H_5)₃Al indicates that the binding mode of the ligands is a sensitive function of the level of theory employed. At the Hartree–Fock level with the def2-TZVP basis set (Figure 2a), the ligands are clearly σ

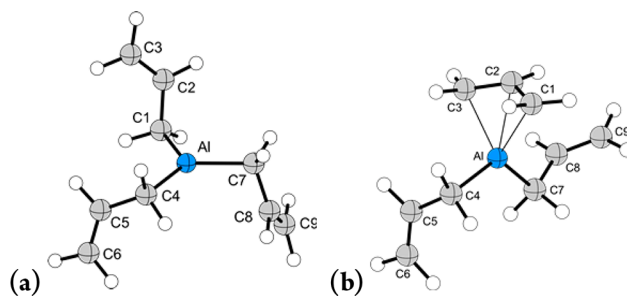


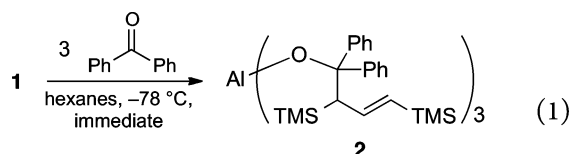
Figure 2. Optimized geometries of (C_3H_5)₃Al. Selected bond distances (Å): (a) with HF/def2TZVP, $\text{Al}-\text{C}_1$ 1.981, $\text{Al}-\text{C}_4$ 1.984, $\text{Al}-\text{C}_7$ 1.984; (b) with M06-L/def2TZVP, $\text{Al}-\text{C}_4$ 1.976, $\text{Al}-\text{C}_7$ 1.971, $\text{Al}-\text{C}_1$ 2.127, $\text{Al}-\text{C}_2$ 2.136, $\text{Al}-\text{C}_3$ 2.159.

bonded with localized bonding (e.g., all $\text{Al}-\text{C}_\alpha-\text{C}_\beta$ angles are $>105^\circ$), and there is an average 0.18 Å difference between the carbon–carbon single- and double-bond lengths. The $\text{Al}-\text{C}$ bond lengths (1.983 Å, average) are close to those in **1**.

In contrast, a DFT calculation using a functional that provides some accounting for dispersion effects (M06-L) leads to a conformation with ligands of clearly mixed hapticity: i.e., ($\eta^1\text{-C}_3\text{H}_5$)₂($\eta^3\text{-C}_3\text{H}_5$)Al (Figure 2b). The $\text{Al}-\text{C}$ bonds to the two η^1 -bonded allyls average 1.974 Å, with a $\text{C}_4-\text{Al}-\text{C}_7$ angle of 122.4°. The π electrons are also strongly localized, with average $\text{C}-\text{C}$ and $\text{C}=\text{C}$ distances of 1.477 and 1.331 Å, respectively. The third allyl ligand has moved into a π -bonded arrangement; the $\text{Al}-\text{C}$ distances vary only from 2.13 to 2.16 Å, and the carbon–carbon distances in the ligand are almost identical, at 1.400 and 1.408 Å. Complexes with allyl ligands of

mixed hapticity are known in both main-group¹³ and d- and f-block chemistry,^{14,15} but $(C_3H_5)_3Al$ is one of the few neutral homoleptic complexes that is predicted to adopt such a conformation.¹⁶ The calculated appearance of π bonding in an allyl ligand is not observed in the solid-state structure of **1**.¹⁷

As the first example of a base-free tris(allyl)aluminum compound, several survey reactions were conducted with **1** to determine how the bulky allyl ligands might affect its reactivity. No reaction is observed when **1** is treated with 1 equiv of $HOCPh_3$. Even with 3 equiv, there is negligible evidence of interaction, and no new product can be isolated. The inhibited reactivity may stem from the combined bulk of the alcohol and allyl ligands. The reaction of **1** with benzophenone was conducted to test the ability of the bulky A' ligand to add to a ketone.¹⁸ In contrast to the behavior with $HOCPh_3$, the formation of $(A'Ph_2CO)_3Al$ (**2**) in hexanes, even at $-78^\circ C$, is immediate (as demonstrated by the appearance of a light orange color) and quantitative (no evidence in NMR spectra for residual **1** (eq 1). Notable is the faster reaction of **1** in



comparison to that of $(C_3H_5)_3Al(THF)$ (up to 10 min at room temperature), despite the bulk of the A' ligand, which may be facilitated by the base-free Al center.

In a test of the interaction of a rare-earth halide with **1**,¹⁹ it was ball-milled with $ScCl_3$ and the ground mixture extracted with hexanes. Only the starting **1** was evident in the 1H NMR spectrum. In contrast, repeating the procedure with $K[A']$ and $ScCl_3$ yielded the allyl complex A'_3Sc (**3**). The 1H NMR spectrum of **3** at room temperature displays the resonances expected for a typically π bound A' ligand;²⁰ this is also true of the unsolvated parent complex $(C_3H_5)_3Sc$, although the THF-solvated versions exhibit various combinations of η^1 - and η^3 -bonded ligands.¹⁵ The single-crystal X-ray structure of **3** (Figure 3), like that of the A'_3Y homologue,²¹ suffers from

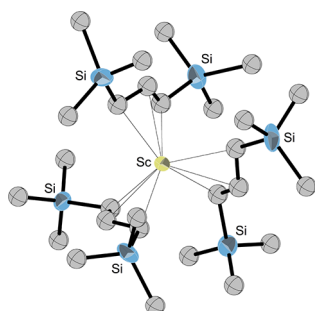


Figure 3. Plot of the non-hydrogen atoms of **3**. Only one conformation of the disordered allyl ligands is shown. Thermal ellipsoids for Sc and Si are drawn at the 50% level, and carbons have been assigned an arbitrary radius.

considerable disorder in the allyl ligands, rendering it essentially of connectivity-only quality. Nevertheless, the ligands are clearly π bound, and the average $Sc-C$ distance of $2.38(3)$ Å is shorter than the equivalent distance in A'_3Tm ($2.53(1)$ Å) by roughly the difference in ionic radii (0.14 Å).²²

In summary, the first unsolvated tris(allyl) complex of aluminum and its monomeric scandium analogue have been isolated through a mechanochemical route. This sidesteps the formation of either solvated complexes or ill-defined ate species. Preliminary results indicate that the aluminum compound displays the reactivity expected of an allyl complex, although the combination of an unsolvated metal center and bulky ligands may moderate it in unanticipated ways. These results suggest that mechanochemical approaches could be more widely explored to expand the palette of other base-free/low-coordinate organometallic complexes.

■ ASSOCIATED CONTENT

Supporting Information

Text giving details of the experimental procedures, CIF files giving crystallographic data for **1** and **3**, and xyz files giving coordinates of the geometry-optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Coville, N. J.; Cheng, L. J. *Organomet. Chem.* **1998**, 571, 149–169. (b) Bala, M. D.; Coville, N. J. *J. Organomet. Chem.* **2007**, 692, 709–730. (c) Murugavel, R.; Gogoi, N. J. *Organomet. Chem.* **2008**, 693, 3111–3116. (d) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. *Chem. Soc. Rev.* **2012**, 41, 413–447. (e) Egbert, J. D.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2013**, 32, 2271–2274. (f) Hernandez, J. G.; Butler, I. S.; Friščić, T. *Chem. Sci.* **2014**, 5, 3576–3582.
- (2) Grignard, V.; Jenkins, R. L. *Bull. Soc. Chim. Fr.* **1925**, 37, 1376–1385.
- (3) (a) Rainier, J. D.; Cox, J. M. *Org. Lett.* **2000**, 2, 2707–2709. (b) Majumder, U.; Cox, J. M.; Johnson, H. W. B.; Rainier, J. D. *Chem. Eur. J.* **2006**, 12, 1736–1746. (c) Picotin, G.; Miginiac, P. *J. Org. Chem.* **1985**, 50, 1299–1301. (d) Shen, K.-H.; Yao, C.-F. *J. Org. Chem.* **2006**, 71, 3980–3983. (e) Shen, K. H.; Liu, J. T.; Wu, Y. R.; Yao, C. F. *Synth. Commun.* **2007**, 37, 3677–3687. (f) Shen, K.-H.; Kuo, C.-W.; Yao, C.-F. *Tetrahedron Lett.* **2007**, 48, 6348–6351. (g) Kulkarni, N. A.; Yao, C.-F.; Chen, K. *Tetrahedron* **2007**, 63, 7816–7822.
- (4) Lichtenberg, C.; Robert, D.; Spaniol, T. P.; Okuda, J. *Organometallics* **2010**, 29, 5714–5721.
- (5) Lichtenberg, C.; Spaniol, T. P.; Okuda, J. *Organometallics* **2011**, 30, 4409–4417.
- (6) (a) Solomon, S. A.; Layfield, R. A. *Dalton Trans.* **2010**, 39, 2469–2483. (b) Chmely, S. C.; Hanusa, T. P. *Eur. J. Inorg. Chem.* **2010**, 1321–1337.
- (7) Gren, C. K.; Hanusa, T. P.; Brennessel, W. W. *Polyhedron* **2006**, 25, 286–292.
- (8) Kim, D. Y.; Yang, Y.; Abelson, J. R.; Girolami, G. S. *Inorg. Chem.* **2007**, 46, 9060–9066.

- (9) IKA Ultra-Turrax Tube Drive, which provides a range of 300–4000 oscillations per minute.
- (10) Tang, J. A.; Masuda, J. D.; Boyle, T. J.; Schurko, R. W. *ChemPhysChem* **2006**, *7*, 117–130.
- (11) Cowley, A. R.; Downs, A. J.; Marchant, S.; Macrae, V. A.; Taylor, R. A.; Parsons, S. *Organometallics* **2005**, *24*, 5702–5709.
- (12) Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *Organometallics* **1982**, *1*, 881–883.
- (13) Jochmann, P.; Spaniol, T. P.; Chmely, S. C.; Hanusa, T. P.; Okuda, J. *Organometallics* **2011**, *30*, 5291–5296.
- (14) (a) Alberti, D.; Goddard, R.; Ruffńska, A.; Pörschke, K.-R. *Organometallics* **2003**, *22*, 4025–4029. (b) Layfield, R. A.; Buehl, M.; Rawson, J. M. *Organometallics* **2006**, *25*, 3570–3575. (c) Erker, G.; Berg, K.; Angermund, K.; Krueger, C. *Organometallics* **1987**, *6*, 2620–2621. (d) John, K. D.; Salazar, K. V.; Scott, B. L.; Baker, R. T.; Sattelberger, A. P. *Organometallics* **2001**, *20*, 296–304. (e) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500–2502. (f) Yue, N.; Hollink, E.; Guérin, F.; Stephan, D. W. *Organometallics* **2001**, *20*, 4424–4433. (g) Wielstra, Y.; Duchateau, R.; Gambarotta, S.; Bensimon, C.; Gabe, E. *J. Organomet. Chem.* **1991**, *418*, 183–190. (h) John, K. D.; Salazar, K. V.; Scott, B. L.; Baker, R. T.; Sattelberger, A. P. *Chem. Commun.* **2000**, 581–582. (i) Webster, C. L.; Ziller, J. W.; Evans, W. J. *Organometallics* **2012**, *31*, 7191–7197. (j) Langeslay, R. R.; Walensky, J. R.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **2014**, *53*, 8455–8463.
- (15) Standfuss, S.; Abinet, E.; Spaniol, T. P.; Okuda, J. *Chem. Commun.* **2011**, *47*, 11441–11443.
- (16) Pu, M. P.; Li, Q.-s.; Xie, Y.; King, R. B.; Schaefer, H. F. J. *Phys. Chem. A* **2011**, *115*, 4491–4504.
- (17) Calculation of the complete A'_3Al molecule at the M06-L/def2TZVP level leaves the allyl ligands σ bonded (Al–C bond lengths average 1.958 Å).
- (18) Amemiya, F.; Fuse, K.; Fuchigami, T.; Atobe, M. *Chem. Commun.* **2010**, *46*, 2730–2732.
- (19) Fischbach, A.; Anwender, R. Rare-Earth Metals and Aluminum Getting Close in Ziegler-Type Organometallics. In *Neodymium Based Ziegler Catalysts-Fundamental Chemistry*; Nuyken, O., Ed.; Springer: Berlin, Heidelberg, 2006; Vol. 204, pp 155–281. Although not an f element, scandium is traditionally included among the rare-earth metals.
- (20) The 1H NMR spectrum displays a singlet for the $SiMe_3$ groups (δ 0.23 in C_6D_6), a triplet for the central hydrogen atom on the allyl ligands (δ 7.60, J = 16 Hz), and a doublet for the terminal hydrogens (δ 3.83, J = 16 Hz).
- (21) White, R. E.; Hanusa, T. P. *Organometallics* **2006**, *25*, 5621–5630.
- (22) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.