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Article

Bis(allyl)aluminum Cation, Tris(allyl)aluminum, and Tetrakis(allyl)aluminate: Synthesis, Characterization, and Reactivity[†]

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Cationic, neutral, and anionic aluminum allyl compounds were synthesized, and their reactivity toward electrophiles was studied. The THF adduct of the previously elusive tris(allyl)aluminum, $[\mathrm{Al}(\eta^1\text{-}\mathrm{C_3H_5})_3(\mathrm{THF})]$ (**1**), was isolated as an oil. Protonolysis of one allyl ligand in **1** using $[\mathrm{NEt_3H}][\mathrm{BPh_4}]$ gave the cationic bis(allyl)aluminum, a fragment of the crystalline $[\mathrm{Al}(\eta^1\text{-}\mathrm{C_3H_5})_2(\mathrm{THF})_{3-n}]^+[\mathrm{BPh_4}]^-\cdot(n+1)\mathrm{THF}$ ($n = 0, 1$) (**2**). Single-crystal X-ray diffraction of $[\mathrm{Al}(\eta^1\text{-}\mathrm{C_3H_5})_2(\mathrm{THF})_2]^+[\mathrm{BPh_4}]^-$ (**2a**) revealed a tetrahedral aluminum center, while $[\mathrm{Al}(\eta^1\text{-}\mathrm{C_3H_5})_2(\mathrm{THF})_3]^+[\mathrm{BPh_4}]^-$ (**2b**) contains a trigonal-bipyramidal aluminum center with both allyl ligands in the equatorial plane. The tetrakis(allyl)aluminate $\mathrm{K}^+[\mathrm{Al}(\eta^1\text{-}\mathrm{C_3H_5})_4]^-$ (**3**) was also synthesized from the reaction of **1** with $\mathrm{K(C_3H_5)}$. Reactions of the allyl compounds **1**−**3** with (i) benzophenone, (ii) allyl halides $\mathrm{C_3H_5X}$ (X = Cl, Br, I), and (iii) halogen $\mathrm{X_2}$ (X = Br, I) showed considerable difference with respect to the ionic charge of the aluminum allyl.

Introduction

The allyl group represents an important building block in organic synthesis.[1] Tris(allyl)aluminum could be a valuable allyl transfer agent, since aluminum organyls exhibit a chemoselectivity different from that of organolithium, -magnesium, -copper, and -tin reagents.[2b] Peculiarly, tris(allyl)aluminum has eluded isolation and characterization to date, although a number of attempts to synthesize this simple compound have been reported.[3] Allyl aluminum reagents generated in situ have been applied in organic synthesis as substitutes for the pure compounds.[2] They were generated either by salt metathesis of aluminum trichloride with Grignard reagents or by oxidative addition of allyl bromide to activated aluminum metal. The former ones are suspected to be mixed allyl chloro ate complexes,[2b−d] and the latter ones are in fact mixed species of the general formula $[\mathrm{Al_2Br_3(C_3H_5)_3}]$.[2a,e−j]

Cationic aluminum species have been studied intensively in the last two decades.[4] This interest mainly stems from possible applications of such compounds in polymerization catalysis and in organic chemistry due to their high Lewis acidity and electrophilicity. Cationic aluminum complexes have been reported to catalyze the polymerization of ethylene,[5] isobutene,[6] higher olefins,[7] methyl methacrylate,[8] propylene oxide,[9] and

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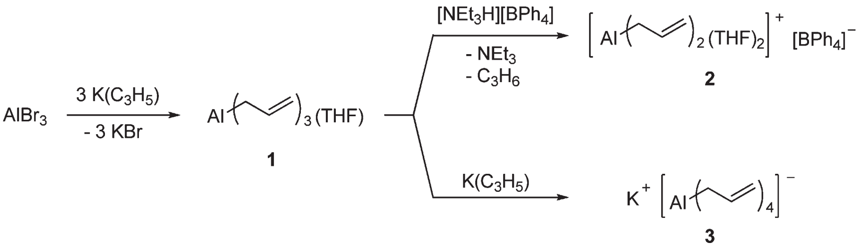
Scheme 1. Synthesis of Tris(allyl)aluminum (1), the Bis(allyl)aluminum Cation 2, and the Tetrakis(allyl) Aluminate 3



ε-caprolactone,[10] as well as Diels–Alder reactions,[11] dealkylation reactions,[12] and alkyne dimerizations.[13] Reactivity studies of cationic aluminum complexes toward substrates such as alcohols, nitriles, and ketones have also been performed.[11,13] Here we present the synthesis and characterization of tris(allyl)aluminum as well as cationic and anionic allyl derivatives of aluminum along with their reactivity toward electrophilic substrates.

Results and Discussion

Synthesis and Characterization. Former synthetic approaches to tris(allyl)aluminum generated in situ faced the problem of separating the magnesium salts[2b–d] or led to allyl aluminum sesquibromide [$Al_2Br_3(C_3H_5)_3$].[2a,e–i] Treating aluminum tribromide with allyl potassium allowed isolation of tris(allyl)aluminum as a THF adduct, [Al(η^1-$C_3H_5)_3$(THF)] (**1**), in 83% yield as a slightly yellow oil (Scheme 1). The formation of ate complexes was ruled out by a negative $AgNO_3$ test.

A cationic aluminum allyl species was obtained by protonolysis of one allyl group in tris(allyl)aluminum. Addition of the weak Brønsted acid [NEt_3H][BPh_4] to a solution of **1** in THF gave the bis(allyl)aluminum cation **2** (Scheme 1). This compound was isolated with two molecules of THF bound to the metal center, as indicated by ^{1}H NMR spectroscopic measurements and elemental analysis.

Two batches of single crystals suitable for single-crystal X-ray diffraction were obtained from two solutions of **2** in pentane/THF, one at 4 °C and one at −40 °C. In both cases, the unit cell parameters showed triclinic lattice symmetry with similar unit cell volumes of 2080.5(8) and 2069.9(14) Å^3. The structure solution of the former crystal revealed a compound of composition [$Al(C_3H_5)_2(THF)_2]^+[BPh_4]^-$ (**2a**). In addition, the asymmetric unit includes two THF molecules in the lattice. The latter crystal contains the compound [$Al(C_3H_5)_2(THF)_3]^+[BPh_4]^-$ (**2b**). Here, the asymmetric unit contains only one molecule of THF in the lattice. In both cases, the composition within the unit cell is identical, leading to a chemical formula of $C_{46}H_{62}AlBO_4$ for the asymmetric unit. This is a rare case of solvate isomerism accompanied by a change in the coordination number from four (compound **2a**) to five (compound **2b**).[14]

In **2a**, the aluminum atom adopts a tetrahedral coordination geometry with C/O–Al–C/O angles between 100.23(20)° and 126.54(28)°, as frequently observed for cationic aluminum compounds.[4b] The Al–C and Al–O bond lengths are comparable to those found in cationic aluminum compounds containing alkyl and ether ligands, the Al–allyl bonds being slightly lengthened.[15] This was ascribed to the stabilization of negative charge in the allyl ligands. Both allyl ligands are bound in an η^1-fashion to the metal center, leading to one long (C1–C2 and C4–C5) as well as one short C–C bond (C2–C3 and C5–C6). These distances correspond to a single and a double bond.[16]

In **2b**, the aluminum atom is coordinated by two allyl ligands and three THF molecules, leading to a trigonal-bipyramidal coordination geometry around the metal center. Both axial positions are occupied by THF ligands with an O2–Al–O3 angle of 170.16(9)°. The Al–O2/3 distances are slightly longer than the distance from Al to the oxygen atom O1 within the equatorial plane due to the *trans* influence and steric interactions. Being strong σ-donors, the allyl ligands occupy equatorial positions, avoiding interaction with one and the same orbital of the aluminum atom. The metal center deviates by only 0.014(1) Å from the equatorial plane given by C1, C4, and O1, and the bond angles within the equatorial plane add to 360°. All Al–O and Al–C bond lengths are similar to values reported for other five-coordinate aluminum cations;[17a,b,f] they are slightly increased compared to the corresponding bond lengths in **2a**, which is ascribed to the increase of the coordination number. As in **2a**, both allyl ligands are coordinated to the metal center in an η^1-fashion. Due to pronounced libration of the terminal carbon atom C6, the C5–C6 bond appears short. The molecular structure of **2b** is a rare example of a structurally characterized five-coordinate Al(III) cation.[17] To the best of our knowledge this is the first example of a

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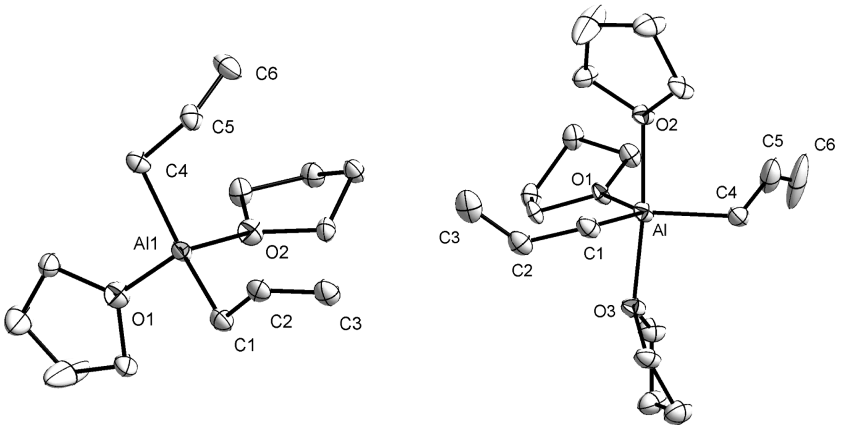


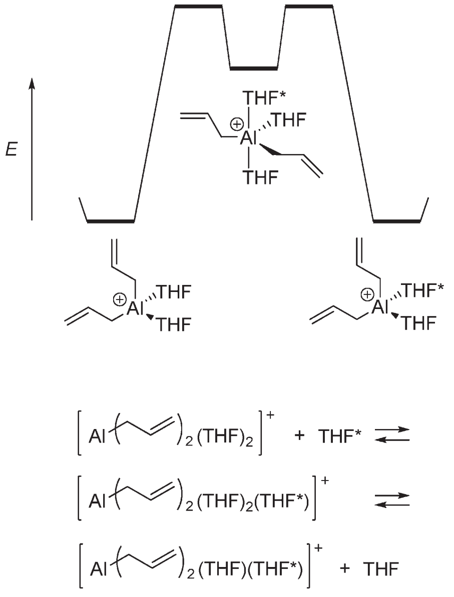
Figure 1. ORTEP drawing of the molecular structures of the cationic part in $[Al(\eta^1\text{-}(C_3H_5)_2(THF)_2]^+[BPh_4]^-$ (**2a**) (left) and $[Al(\eta^1\text{-}(C_3H_5)_2(THF)_3]^+[BPh_4]^-$ (**2b**) (right). Thermal ellipsoids are drawn at the 30% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (deg), and angle sums (deg): **2a** (left): Al1−C1, 1.960(6); Al1−C4, 1.960(6); Al1−O1, 1.847(5); Al1−O2, 1.849(4); C1−C2, 1.502(10); C2−C3, 1.328(11); C4−C5, 1.492(11); C5−C6, 1.312(10); C1−Al1−C4, 126.54(28); C1−Al1−O1, 108.92(25); C4−Al1−O1, 105.08(25); C1−Al1−O2, 105.89(25); C4−Al1−O2, 107.16(24); O1−Al1−O2, 100.23(20). **2b** (right): Al−C1, 1.983(3); Al−C4, 1.978(4); Al−O1, 1.862(2); Al−O2, 2.031(3); Al−O3, 2.066(3); C1−C2, 1.478(5); C2−C3, 1.332(5); C4−C5, 1.452(5); C5−C6, 1.184(7); C1−Al−C4, 128.01(14); C1−Al−O1, 116.85(14); C4−Al−O1, 115.13(12); O2−Al−O3, 170.15(10); sum(C1/4/O1−Al−C1/4/O1), 359.99(40).

five-coordinate aluminum cation that is not stabilized by a chelating ligand.

The η^1-coordination mode of the allyl ligands was found not only in the solid state (in **2a** and **2b**) but also in THF-d_8 solution within a temperature range of −80 to +50 °C, as determined by ^{1}H NMR spectroscopy. The parent compound tris(allyl)aluminum (**1**) can be transformed into the potassium aluminate **3** (Scheme 1). This ate compound was also obtained directly from aluminum bromide with four equivalents of allyl potassium in moderate yield.

Substitution of THF in 1 and 2. The time scale on which the THF ligands in compounds **1** and **2** are substituted by THF-d_8 was investigated. These reactions proceed with half-lives $t_{1/2} \leq 10$ min at 25 °C, as determined by ^{1}H NMR spectroscopy. These reactions could occur via a dissociative or an associative mechanism. The crystal structures of **2a** and **2b** show that three THF molecules can coordinate to the metal center, reaching a coordination number of five without the aid of chelating ligands in the solid state. This supports an associative mechanism for the ligand exchange reactions of cationic aluminum compounds (Scheme 2).

Scheme 2. Schematic Energy Diagram and Chemical Equation for a Ligand Exchange Reaction of 2 via an Associative Mechanism



Not surprisingly, the THF ligands in **1** and **2** are readily substituted by addition of the stronger donor pyridine. One or two equivalents of this ligand react within reaction times of ≤10 min. After coordination of pyridine, an allyl ligand is slowly transferred to the *ortho* position of the pyridine ring in both cases. This type of reaction is being further investigated.

Reactions of 1−3 with Benzophenone. The nucleophilic addition of allyl moieties to ketones is an important type of organic transformation.[18,19] In order to test the allyl ligand transfer ability in this type of reaction, compounds **1**−**3** were each reacted with benzophenone as a representative electrophile. The stoichiometry of one equivalent of ketone per allyl substituent was adjusted in all of these reactions (Scheme 3). Quantitative conversions of the starting materials to the aluminum alcoholates **4**−**6** were observed with >99% (**4**, **6**) and 90% (**5**) selectivity. Tris(allyl)aluminum (**1**) and the

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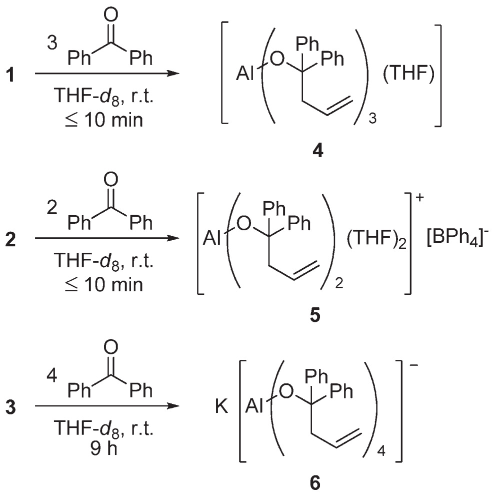
(19) Boron compounds $B(C_3H_5)R_2$ (R = alkyl, alkoxide) are well-established allylating agents for carbonyl compounds. For representative selection from the literature including stereoselective reactions, see: (a) Mikhailov, B. M.; Bubnov, Y. N. *Izvest. Akad. Nauk SSSR, Ser. Khim.* **1964**, *10*, 1874. (b) Ter-Sarkisyan, G. S.; Nikolaeva, N. A.; Mikhailov, B. M. *Izvest. Akad. Nauk SSSR, Ser. Khim.* **1970**, *4*, 876. (c) Dallacker, F.; Leidig, H. *Chem. Ber.* **1979**, *112*, 2672. (d) Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. (e) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092. (f) Reetz, M. T. *Pure Appl. Chem.* **1988**, *60*, 1607. (g) Hoffmann, R. W. *Pure Appl. Chem.* **1988**, *60*, 123. (h) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495. (i) Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewicz, M.; Racherla, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389. (j) Mears, R. J.; De Silva, H.; Whiting, A. *Tetrahedron* **1997**, *53*, 17395. (k) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892. (l) Wu, T. R.; Shen, L.; Chong, J. M. *Org. Lett.* **2004**, *6*, 2701.

Scheme 3. Reactions of the Aluminum Allyl Compounds 1−3 with Benzophenone to Give Aluminum Alcoholate Complexes 4−6

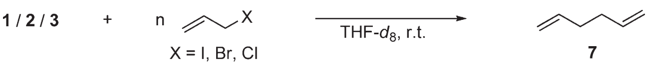


cation **2** underwent insertion within reaction times of ≤10 min. The reaction with the aluminate **3** reached completion only after a comparatively long reaction time of 9 h. This hints at the importance of an activation of the carbonyl compound by a Lewis acidic aluminum center.[20] All allyl ligands of compounds **1**−**3** were transferred to the carbonyl substrate. In an earlier report on tris(allyl)aluminum generated in situ as an allylating agent toward ketones, a maximum of 48% of the allyl ligands was transferred to the substrates and the use of an excess of the aluminum organyl was required.[2e] This demonstrates the advantage of the isolated and defined tris(allyl)aluminum **1** and the cation **2** compared with aluminum allyl species generated in situ.

Reactions of 1−3 with Allyl Halides. It is known that the first substituent of tetra(organyl) aluminates readily displaces a halogen atom of an alkyl halide in a nucleophilic substitution.[21] Tris(alkyl)aluminum reagents were reported to react slowly under harsh conditions in an analogous manner.[22] Detailed studies on reactions of cationic aluminum species with alkyl halides have not been reported to date.[23] Since the ligand transfer of compound **1** and **2** was too fast to be distinguishable in reactions with benzophenone, their reactions with alkyl halides were expected to show a difference in reactivity.

The aluminum compounds **1**, **2**, and **3** were reacted with one equivalent of allyl halide C_3H_5X ($X = I, Br, Cl$) per allyl substituent to give 1,5-hexadiene (**7**) (Table 1; for X = Br, Figure 2). The results obtained in reactions of **2** and **3** with the previously mentioned substrates correspond to earlier reports.[21,22] The first allyl substituent of the aluminate **3** was transferred fast when allyl iodide or allyl bromide was used and slower when allyl chloride was used. In all three cases, the reactivity appears to be determined by the nature of the leaving group (I > Br≫Cl).[24] After the transfer of the first allyl substituent further reaction slowed dramatically. Tris(allyl)aluminum (**1**) reacted slowly with each of the allyl halides. It is noteworthy that the reaction with allyl bromide proceeded most readily.[25] This is ascribed to two effects that operate in opposite directions. On the one hand, there is the before-mentioned quality of the leaving group (I > Br > Cl).[24] On the other hand, the hard/soft acid/base (HSAB) pair fit between the aluminum center and the halides has to be considered (Cl > Br > I).[26] Allyl bromide thus is the most

Table 1. Reactions of Aluminum Compounds 1−3 with One Equivalent of Allyl Halide per Allyl Substituent (1: $n = 3$; 2: $n = 2$; 3: $n = 4$)



	X = I		X = Br		X = Cl	
compound	t/d	%- conv of C_3H_5X	t/d	% conv of C_3H_5X	t/d	% conv of C_3H_5X
1	0.2	traces	0.2	traces	2.0	traces
1	1.9	< 1	0.8	1	5.1	traces
1	4.8	1	1.5	2	14	1
2	0.2	11	0.2	2	2.0	5
2	1.9	23	0.8	68	5.1	11
2	4.8	51	1.5	≥99	14	32
3	0.2	27	0.2	24	2.0	10
3	1.9	33	0.8	29	5.1	20
3	4.8	43	1.5	34	14	25

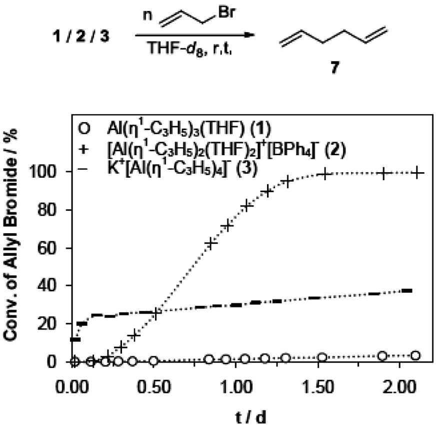


Figure 2. Time conversion plot for the reactions of allyl bromide with compounds **1**, **2**, and **3** to give 1,5-hexadiene (**7**), as determined by ^{1}H NMR spectroscopy. The course of the reactions of allyl chloride and allyl iodide with these aluminum compounds is qualitatively similar (for details see the Supporting Information).

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[20] As pointed out by one reviewer, we cannot exclude the existence of an equilibrium between K[Al(η^1-C_3H_5)$_4$] (**3**) and the starting materials K(η^3-C_3H_5) and Al(η^1-C_3H_5)$_3$, although we have no direct evidence.

[21] Pearson, N. R.; Hahn, G.; Zweifel, G. *J. Org. Chem.* **1982**, *47*, 3364. (b) Hahn, G.; Zweifel, G. *Synthesis* **1983**, 885.

[22] (a) Miller, D. B. *J. Org. Chem.* **1966**, *31*, 908. (b) Mole, T; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972; pp 349−358.

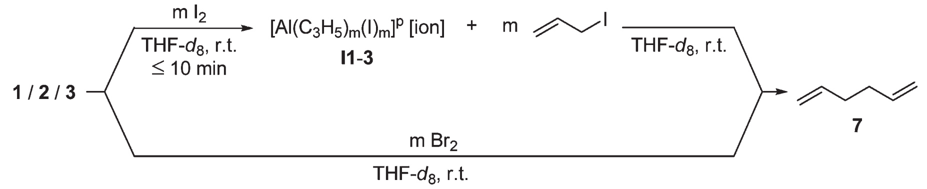
[23] Some information about the reactivity of aluminum cations toward alkyl halides can be found in the literature: see refs 6b and 11. The decomposition of the [AlCp$_2$]$^+$ cation in CH_2Cl_2 was reported in ref 6a.

[24] For information on the quality of halides as leaving groups see: (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanism*, 5th ed.; Springer: New York, 2007; p 413. (b) Ayers, P. W.; Anderson, J. S. M.; Rodriguez, J. I.; Jawed, Z. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1918.

[25] Allyl bromide reacted most readily in the hydrolysis of allyl halides under neutral conditions. In these systems the acid strengths of HX and the nucleophilicity of X$^-$ also have to be considered: Robertson, R. E.; Scott, J. M. W. *J. Chem. Soc.* **1961**, 1596.

[26] For qualitative and quantitative evaluations of aluminum compounds and halides in terms of the HSAB principle, see: (a) Pearson, R. G. *Phys. Inorg. Chem.* **1963**, *85*, 3533. (b) Pearson, R. G. *Science* **1966**, *151*, 172.

Table 2. Reactions of the Aluminum Compounds 1−3 with 0.5 Equivalent of X_2 (X = I, Br) per Allyl Substituent (1: m = 1.5, p = 0, [ion]: not present; 2: m = 1, p = +1, [ion] = $[BPh_4]^-$; 3: m = 2, p = −1, [ion] = K^+)



	I_2			Br_2		
compound	t/d	% conv of allyl iodide	selectivity toward **7**	t/h	% conv of Br_2	selectivity toward **7**
1	>6	≪1		1	≥99	39
2	18	≥95	80	1	≥99	71
3	18	39	67	1	≥99	64

reactive substrate in this reaction, as it bears a halogen atom showing both an acceptable leaving group quality and an adequate HSAB pair fit. Whereas this effect is only slightly pronounced in the case of the neutral aluminum organyl **1** (see Table 1), it becomes dominating in reactions of the cationic species **2**. The ease of the reactions of this cationic aluminum complex with allyl halides increases in the order Cl ≪ I < Br. The reaction of **2** with allyl bromide was complete after 1.5 days at ambient temperature. Under the chosen reaction conditions the cationic aluminum species **2** was the only one to transfer all allyl ligands to the substrate. This study of the reactivity of the aluminum allyl complexes **1**−**3** toward allyl halides provides a striking example of enhancement of reactivity by enhancement of Lewis acidity (shown for X = Br in Figure 2).

Reactions of 1−3 with Halogens. Reactions of neutral alkyl aluminum compounds and aluminates with halogens to form the corresponding alkyl halides and aluminum halides are well established.[27] We became interested in the oxidatively induced coupling of the allyl ligands at a non-redox-active metal center, as reported for bis(allyl)calcium, $Ca(\eta^3\text{-}C_3H_5)_2$, giving the coupling product 1,5-hexadiene (**7**) selectively.[28,29] This type of reaction has not been reported to date for aluminum allyl compounds and has rarely been mentioned for alkyl aluminum compounds in general.[30] Such coupling of allyl ligands is known to proceed for transition metal complexes of Ni^{2+}, Fe^{2+}, and Mo^{3+}.[31]

When iodine was reacted with the aluminum compounds **1**−**3**, the first step of the reaction readily proceeded in all three cases. After reaction times of ≤10 min a quantitative conversion of iodine had taken place to give the appropriate amount of allyl iodide and the intermediates **I1**−**3** (Table 2). Each of the intermediates **I1**−**3** exists as a mixture of aluminum complexes due to ligand scrambling, to which aluminum complexes are easily susceptible.[32] The fate of the allyl iodide generated in the reaction mixture depends on the nature of the organometallic intermediate (Table 2). Allyl aluminum sesqui(iodide), **I1**, is not reactive enough to produce detectable amounts of the C−C coupling product 1,5-hexadiene (**7**), even after a reaction time of >6 days. The bis(allyl)iodide $[Al(C_3H_5)_2I]$ (along with precipitation of one equivalent of KI), **I3**, can be expected to show a higher nucleophilicity. Indeed, it slowly reacted with allyl iodide to give low yields of **7**. Out of the three intermediates, the cationic aluminum species **I2** proved to undergo the coupling reaction most readily in a slow quantitative reaction with 80% selectivitiy. Thus the cation $[Al(\eta^1\text{-}C_3H_5)_2]^+$ in **2** exhibits a reactivity pattern similar to that of the isoelectronic $[Ca(\eta^3\text{-}C_3H_5)_2]$.[28] The difference observed in the reactions of **1**−**3** with iodine may be due to the Lewis acidity of these compounds.

Compounds **1**−**3** were reacted also with bromine to give **7** with 39% to 71% selectivity (Table 2). In analogy with the results obtained with iodine, allyl bromide should be produced as an intermediate in these reactions. It should react faster with the aluminum complexes formed in situ to give the coupling product **7** due to the better HSAB pair fit.[26] However, the double-bond bromination proved to be a competing reaction pathway in all three cases.[33]

Conclusion

The THF adduct of tris(allyl)aluminum, $[Al(\eta^1\text{-}C_3H_5)_3(THF)]$ (**1**), can be converted into the cationic aluminum allyl compound $[Al(\eta^1\text{-}C_3H_5)_2(THF)_{3-n}]^+[BPh_4]^-\cdot(n+1)THF$ (n = 0, 1) (**2**) by protonolysis of one allyl ligand. Two different molecular structures, **2a** (n = 1) and **2b** (n = 0), have been established in the solid state. They exhibit similar unit cell volumes and identical formula sums, but show different coordination numbers (**2a**: CN = 4; **2b**: CN = 5) and a different number of THF molecules in the lattice. **2b** is the first example of an aluminum cation adopting a coordination number of five

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(27) For example: (a) Gavrilenko, V. V.; Zakharkin, L. I.; Smagin, V. M.; Golubev, V. K. *Zh. Obshch. Khim.* **1978**, *48*, 2073. (b) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739. (c) Al-Hassan, M. I. *Synth. Commun.* **1987**, *17*, 583. (d) Dostál, L.; Jambor, R.; Ruzička, A.; Císařová, I.; Holeček, J. *J. Appl. Organomet. Chem.* **2005**, *19*, 797. (e) Ohashi, M.; Kishizaki, O.; Ikeda, H.; Ogoshi, S. *J. Am. Chem. Soc.* **2009**, *131*, 9160.

(28) Jochmann, P.; Dols, T. S.; Spaniol, T. P.; Perrin, L.; Maron, L.; Okuda, J. *Angew. Chem.* **2009**, *121*, 5825; *Angew. Chem., Int. Ed.* **2009**, *48*, 5715.

(29) Recently, the oxidatively induced coupling of 1,3-bis(trimethylsilyl)allyl ligands has been observed for Ca and Sr compounds as well as heterobimetallic species containing K and Ba: Quisenberry, K. T.; White, R. E.; Hanusa, T. P.; Brennessel, W. W. *New J. Chem.* **2010**, *34*, 1579–1584.

(30) The coupling of phenyl ligands in $AlPh_3$ by addition of I_2 in the presence of *p*-benzoquinone was reported: Alberola, A.; Gonzalez Nogal, A. M.; Martinez de Ilarduya, J. A.; Pulido, F. J. *An. Quim. C* **1982**, *78*, 166.

(31) (a) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47. (b) Poli, R.; Wang, L.-S. *Polyhedron* **1998**, *17*, 3689.

(32) Fisher, J. D.; Wie, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324, and references therein.

(33) 1,2,3-Tribromopropane was observed as a side product in all cases, resulting from the bromination of allyl bromide. Allyl bromide was detected as an intermediate by ^1H NMR spectroscopy, when the reactions were carried out at low temperatures.

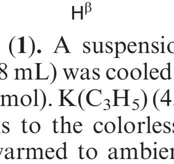
in the absence of chelating ligands. The THF ligands in compounds **1** and **2** are highly labile. The corresponding aluminate, $K^+[Al(\eta^1\text{-}C_3H_5)_4]^-$ (**3**), was also synthesized.

Compounds **1**−**3** have been studied with respect to their reactivity toward electrophiles, (i) benzophenone, (ii) allyl halides, and (iii) halides. The Lewis acidic complexes **1** and **2** reacted faster with benzophenone than the anion **3**. Compared with aluminum allyl reagents generated in situ,[2b] **1** and **2** proved to be superior. The hard/soft acid/base (HSAB) pair fit in combination with the quality of leaving groups influences the reactivity of **1**−**3** with allyl halides. These two effects operate in opposite directions and make allyl bromide the most suitable substrate. The strong Lewis acid **2** was the only aluminum organyl to react quantitatively with allyl bromide. Upon reaction of the cationic complex **2** with X_2 (X = I, Br), the allyl ligands underwent coupling to give 1,5-hexadiene. The reaction with bromine was faster, but less selective.

Experimental Section

General Remarks. All operations were carried out under argon using standard Schlenk-line and glovebox techniques. Starting materials were purchased from ABCR Chemicals or Sigma Aldrich and purified following standard laboratory procedures. Starting materials that were not commercially available were synthesized according to the literature. Nondeuterated solvents were purified using an MB SPS-800 solvent purification system. Benzene-d_6 and THF-d_8 were distilled from sodium benzophenone ketyl. NMR spectra were recorded at ambient temperature using a Varian Mercury-200 or a Bruker Avance II 400 MHz spectrometer. The variable-temperature NMR spectrum was carried out using the latter one. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and are reported relative to the chemical shift of tetramethylsilane. The resonances in ^{1}H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HMQC, HMBC). The ^{11}B and ^{27}Al NMR resonances are reported relative to external standards, an ethereal solution of $BF_3 \cdot Et_2O$ and an aqueous solution of $Al(NO_3)_3$. Elemental analyses were performed by the microanalytical laboratory of the Institute of Organic Chemistry at the RWTH Aachen University.

In all analytical data given except for single-crystal X-ray studies, the labeling of allyl ligands that are bound in an η^1-fashion and of allyl substituents corresponds to the labeling scheme below.



[Al(η¹-C₃H₅)₃(THF)] (1). A suspension of $AlBr_3$ (503 mg, 1.89 mmol) in pentane (8 mL) was cooled to −78 °C and treated with THF (2.0 mL, 25 mmol). $K(C_3H_5)$ (457 mg, 5.70 mmol) was added in small portions to the colorless suspension, and the reaction mixture was warmed to ambient temperature over a period of 16 h, after which all volatiles were removed under reduced pressure. The residue was taken up in pentane (10 mL) and filtered. After washing the solid with pentane (3 × 5 mL) all volatiles were removed from the filtrate under reduced pressure. The residue was dried in vacuo to give a slightly yellow oil of low viscosity (350 mg, 1.57 mmol, 83%). ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.99−1.03 (m, 4H, β-THF), 1.37 (br d, $^3J_{HH}$ = 8.7 Hz, 6H, H^α), 3.41−3.45 (m, 4H, α-THF), 4.80 (ddt, $^2J_{HH}$ = 2.7 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 0.9 Hz, 3H, H^γ), 4.90 (ddt, $^2J_{HH}$ = 2.7 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.4 Hz, 3H, H^δ), 6.30 (ddt, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, H^β) ppm. ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.08 (br d, $^3J_{HH}$ = 8.7 Hz, 6H, H^α) 1.75−1.79 (m, 4H, β-THF), 3.60−3.63 (m, 4H, α-THF), 4.38 (dm, $^3J_{HH}$ = 10.0 Hz, 3H, H^γ), 4.45 (dm, $^3J_{HH}$ = 16.8 Hz, 3H, H^δ), 5.99 (ddt, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, H^β) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ 19.34 (br s, C^1), 24.87 (s, β-THF), 72.00 (s, α-THF), 105.91 (s, C^3), 141.70 (s, C^2) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 19.35 (br s, C^1), 26.30 (s, β-THF), 68.21 (s, α-THF), 105.43 (s, C^3), 141.96 (s, C^2) ppm. ^{27}Al NMR (104.3 MHz, C_6D_6): δ 163.52 (br s) ppm. ^{27}Al NMR (104.3 MHz, THF-d_8): δ 159.67 (br s) ppm. Anal. Calcd for $C_{13}H_{23}AlO$ (220.30 g/mol): C, 70.24; H, 10.43. Found: C, 71.28; H, 10.34. A test for bromide was negative.

[Al(η¹-C₃H₅)₂(THF)₂]⁺[BPh₄]⁻ (2). Tris(allyl)aluminum (**1**) (216 mg, 972 μmol) was dissolved in THF (4 mL) at ambient temperature and treated with a solution of $[NEt_3H]^+[BPh_4]^-$ (337 mg, 800 μmol) in THF (11 mL) over a period of 5 min. The colorless mixture was stirred for 5 min. All volatiles were removed under reduced pressure to give a colorless solid, which was washed with THF/pentane (1:2) (4 × 9 mL) and dried in vacuo. Colorless solid (335 mg, 585 μmol, 73%). ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.24 (br d, $^3J_{HH}$ = 8.5 Hz, 4H, H^α), 1.76−1.79 (m, 8H, β-THF), 3.60−3.63 (m, 8H, α-THF), 4.68 (dm, $^3J_{HH}$ = 10.1 Hz, 2H, H^γ), 4.79 (dm, $^3J_{HH}$ = 16.9 Hz, 2H, H^δ), 5.93 (ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 16.9 Hz, 2H, H^β), 6.76 (br t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 6.89 (br t, $^3J_{HH}$ = 7.4 Hz, 8H, *o*-Ph), 7.28−7.32 (m, 8H, *m*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 16.62 (br s, C^1), 26.36 (s, β-THF), 62.27 (s, α-THF), 110.46 (s, C^3), 122.06 (s, *p*-Ph), 125.91 (s, *o*-Ph), 137.08 (s, *m*-Ph), 137.86 (s, C^2) 165.08 (q, $^1J_{BC}$ = 49.4 Hz, *ipso*-Ph) ppm. ^{11}B NMR (128.4 MHz, THF-d_8): δ −6.58 (s) ppm. ^{27}Al NMR (104.3 MHz, THF-d_8): δ 68.80 (br s) ppm. Anal. Calcd for $C_{38}H_{46}AlBO_2$ (572.56 g/mol): C, 79.71; H, 8.10. Found: C, 78.99; H, 8.08.

K⁺[Al(η¹-C₃H₅)₄]⁻ (3). A suspension of $AlBr_3$ (1.456 g, 5.46 mmol) in pentane (10 mL) was cooled to −78 °C, and THF (10 mL) was slowly added, followed by $K(C_3H_5)$ (1.751 g, 21.84 mmol) in small portions. The reaction mixture was allowed to warm to ambient temperature over a period of 20 h and filtered. The colorless solid was washed with THF/pentane (1:1) (1 × 10 mL). Solvents were removed from the colorless filtrate under reduced pressure to give a colorless solid, which was dried in vacuo to give a colorless solid (695 mg, 3.02 mmol, 55%). ^{1}H NMR (400.1 MHz, THF-d_8): δ 0.87 (br s, 4H, $H^{\alpha(1)}$), 0.94 (br s, 4H, $H^{\alpha(2)}$), 4.01 (br d, $^3J_{HH}$ = 9.1 Hz, 4H, H^γ), 4.23 (br d, $^3J_{HH}$ = 16.8 Hz, 4H, H^δ), 6.06 (br ddt, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 16.8 Hz, 4H, H^β) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 22.70 (br sext, $^1J_{AlC}$ = 61.3 Hz, C^1), 99.03 (s, $C^{3(1)}$), 99.15 (s, $C^{3(2)}$), 147.43 (s, $C^{2(1)}$), 147.54 (s, $C^{2(2)}$) ppm. ^{27}Al NMR (104.3 MHz, THF-d_8): δ 144.65 (s) ppm. Elemental analyses of **3** gave no satisfactory results. The metal content was determined by titration.[34] Anal. Calcd for $C_{12}H_{20}AlK$ (230.37 g/mol): Al, 17.71. Found: Al, 17.55. A test for bromide was negative.

Substitution of THF Ligands in 1 and 2. The aluminum compound (**1**: 28 mg, 126 μmol; **2**: 36 mg, 63 μmol) was dissolved in THF-d_8 (600 μL). Pyridine (in the case of **1**: 10 mg, 126 μmol; in the case of **2**: 10 mg, 126 μmol) was added to the colorless solutions, whereupon they turned yellow (in the case of **1**) and slightly yellow (in the case of **2**).

$[Al(\eta^1\text{-}C_3H_5)_3(C_5H_5N)]$: ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.20 (br d, $^3J_{HH}$ = 8.7 Hz, 6H, H^α), 4.33 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 1.0 Hz, 3H, H^γ), 4.45 (ddt, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 16.8 Hz, $^4J_{HH}$ = 1.4 Hz, 3H, H^δ), 5.98 (ddt, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.8 Hz, 3H, H^β), 7.61−7.64 (m, 2H, *m*-py), 8.03−8.08 (m, 1H, *p*-py), 8.58−8.69 (m, 2H, *o*-py) ppm. THF was also detected.

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[34] (a) Malissa, H.; Kotzian, H. *Anal. Chim. Acta* **1962**, *28*, 128. (b) Wänninen, E.; Ringbon, A. *Anal. Chim. Acta* **1955**, *12*, 308.

[Al(η^1-C$_3$H$_5$)$_2$(C$_5$H$_5$N)$_2$]$^+$[BPh$_4$]$^-$: ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.58 (br d, $^3J_{HH}$ = 8.5 Hz, 4H, H$^{\alpha}$), 4.59 (br d, $^3J_{HH}$ = 10.0 Hz, 2H, H$^{\gamma}$), 4.67 (br d, $^3J_{HH}$ = 16.9 Hz, 2H, H$^{\delta}$), 5.93 (br ddt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 16.9 Hz, 2H, H$^{\beta}$), 6.72 (br t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 6.85 (br t, $^3J_{HH}$ = 7.4 Hz, 8H, *o*-Ph), 7.28−7.31 (m, 8H, *m*-Ph), 7.32−7.34 (m, 4H, *m*-py), 7.75−7.79 (m, 2H, *p*-py), 8.37−8.39 (m, 4H, *o*-py) ppm. THF was also detected.

Reactions of 1, 2, and 3 with Benzophenone. The aluminum compound (**1**: 27 mg, 121 μmol, **2**: 19 mg, 33 μmol, **3**: 13 mg, 56 μmol) was dissolved in THF-d_8 (300 μL). A solution of benzophenone (in the case of **1**: 66 mg, 362 μmol; in the case of **2**: 12 mg, 66 μmol; in the case of **3**: 41 mg, 226 μmol) in THF-d_8 (300 μL) was slowly added. In all three cases colorless solutions were obtained.

1: After a reaction time of $\leq$10 min a quantitative conversion to the insertion product **4** was observed. ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.74−1.78 (m, 4H, β-THF), 3.06 (br d, $^3J_{HH}$ = 6.7 Hz, 6H, H$^{\alpha}$), 3.60−3.63 (m, 4H, α-THF), 4.78 (br dd $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 10.3 Hz, 3H, H$^{\gamma}$), 4.85 (br dd $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 17.3 Hz, 3H, H$^{\delta}$), 5.75 (br ddt, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 17.3 Hz, 3H, H$^{\beta}$), 7.09 (br t, $^3J_{HH}$ = 7.2 Hz, 6H, *p*-Ph), 7.17 (br t, $^3J_{HH}$ = 7.4 Hz, 12H, *m*/*o*-Ph), 7.37 (br d, $^3J_{HH}$ = 7.4 Hz, 12H, *m*/*o*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 26.38 (s, β-THF), 48.69 (s, C^1), 68.33 (s, α-THF), 79.71 (s, *C*(O[Al])(C$_3$H$_5$)Ph$_2$), 116.24 (s, C^3), 126.49 (s, p-Ph), 128.10 (s, *m*/*o*-Ph), 128.24 (s, *m*/*o*-Ph), 137.53 (s, C^2), 151.28 (s, *ipso*-Ph) ppm.

2: After a reaction time of $\leq$10 min a quantitative conversion of the reactants into 90% of the insertion product **5** was observed. ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.75−1.78 (m, 8H, β-THF), 2.96 (br d, $^3J_{HH}$ = 6.7 Hz, 4H, H$^{\alpha}$), 3.60−3.63 (m, 8H, α-THF), 4.91 (dm $^3J_{HH}$ = 10.3 Hz, 2H, H$^{\gamma}$), 4.95 (dm $^3J_{HH}$ = 17.2 Hz, 2H, H$^{\delta}$), 5.49 (ddt, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 17.2 Hz, 2H, H$^{\beta}$), 6.76 (br t, $^3J_{HH}$ = 7.2 Hz, 4H, B(*p*-Ph)), 6.89 (br t, $^3J_{HH}$ = 7.4 Hz, 8H, B(*o*-Ph)), 7.18−7.20 (m, 8H, C(*m-Ph*)), 7.21−7.24 (m, 4H, C(*m-Ph*)), 7.25−7.30 (m, 8H, C(*o-Ph*)) 7.30−7.33 (m, 8H, B(*m*-Ph)) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 26.29 (s, β-THF), 48.14 (s, C^1), 68.20 (s, α-THF), 80.34 (s, *C*(O[Al])(C$_3$H$_5$)Ph$_2$), 118.08 (s, C^3), 121.98 (s, B(*p*-Ph)), 125.84 (s, B(*o*-Ph)), 127.35 (C(*m*/*o-Ph*)), 127.78 (s, C(*p-Ph*)), 128.95 (s, C(*m*/*o-Ph*)), 135.63 (s, C^2), 137.03(s, B(*m*-Ph)), 149.08 (s, C(*ipso-Ph*)) 165.03 (s, B(*ipso*-Ph)) ppm.

3: After a reaction time of 10 min a conversion of only 3% was observed. After 9 h a conversion of 99% to the insertion product **6** was observed. ^{1}H NMR (400.1 MHz, THF-d_8): δ 3.07 (d, $^3J_{HH}$ = 6.8 Hz, 8H, H$^{\alpha}$), 4.51 (dm $^3J_{HH}$ = 10.3 Hz, 4H, H$^{\gamma}$), 4.62 (dm $^3J_{HH}$ = 17.2 Hz, 4H, H$^{\delta}$), 6.85 (ddt, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 17.2 Hz, 4H, H$^{\beta}$), 6.91−6.95 (m, 8H, *p*-Ph), 6.97−7.00 (m, 16H, *m*/*o*-Ph), 7.40−7.42 (m, 16H, *m*/*o*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 49.47 (s, C^1), 79.70 (s, *C*(O[Al])(C$_3$H$_5$)Ph$_2$), 114.02 (s, C^3), 125.19 (s, *p*-Ph), 127.36 (s, *m*/*o*-Ph), 129.18 (s, *m*/*o*-Ph), 140.17 (s, C^2), 153.09 (s, *ipso*-Ph) ppm.

Reactions of 1, 2, and 3 with C$_3$H$_5$X (X = I, Br, Cl). 1: **1** (22 mg, 100 μmol) was dissolved in THF-d_8 (600 μL), and CH$_2$CHCH$_2$X (X = I: 51 mg, 304 μmol, X = Br: 37 mg, 305 μmol, X = Cl: 23 mg, 301 μmol) was added. A colorless solution was obtained.

2: **2** (51 mg, 89 μmol) was dissolved in THF-d_8 (600 μL), and CH$_2$CHCH$_2$X (X = I: 30 mg, 179 μmol, X = Br: 21 mg, 174 μmol, X = Cl: 14 mg, 183 μmol) was added. A colorless solution was obtained.

3: **3** (19 mg, 82 μmol) was dissolved in THF-d_8 (600 μL), and CH$_2$CHCH$_2$X (X = I: 55 mg, 327 μmol, X = Br: 40 mg, 331 μmol, X = Cl: 25 mg, 327 μmol) was added. Upon addition of the allyl halide, a colorless solid began to precipitate (X = I: immediately; X = Br: after 30 s; X = Cl: 30 min) from the colorless solution.

In all nine cases, the course of the reaction was monitored by ^{1}H and ^{13}C NMR spectroscopic measurements, and the formation of the desired product, 1,5-hexadiene, was observed.[35]

Competition Experiment of 3 with an Equimolar Mixture of Allyl Iodide and Allyl Bromide. Allyl iodide (39 mg, 232 μmol) and allyl bromide (28 mg, 231 μmol) were dissolved in THF-d_8 (600 μL). The resulting colorless solution was analyzed by means of ^{1}H NMR spectroscopy. Upon addition of **3** (27 mg, 117 μmol), a colorless solid precipitated immediately. After 30 min ^{1}H NMR spectroscopic measurements confirmed the formation of 1,5-hexadiene (117 μmol).[35] These analyses also showed the consumption of allyl iodide to be 3.2 times higher than the consumption of allyl bromide.

Reactions of 1, 2, and 3 with X$_2$ (X = I, Br). X = I, one equivalent of I$_2$ per allyl substituent: The aluminum compound (**1**: 28 mg, 125 μmol; **2**: 20 mg, 35 μmol; **3**: 8 mg, 35 μmol) was dissolved in THF-d_8 (600 μL). Iodine (in the case of **1**: 97 mg, 382 μmol; in the case of **2**: 18 mg, 71 μmol; in the case of **3**: 35 mg, 138 μmol) was added to the colorless solution. After 2 min a colorless solution (in the case of **1** and **2**) or a suspension of a colorless solid in a colorless solution (in the case of **3**) was obtained. Quantitative amounts of allyl iodide were formed in each case according to NMR spectroscopic analyses.[36]

X = I, 0.50 equivalent of I$_2$ per allyl substituent: The aluminum compound (**1**: 28 mg, 125 μmol; **2**: 20 mg, 35 μmol; **3**: 8 mg, 35 μmol) was dissolved in THF-d_8 (600 μL). I$_2$ (in the case of **1**: 97 mg, 382 μmol; in the case of **2**: 18 mg, 71 μmol; in the case of **3**: 35 mg, 138 μmol) was added to the colorless solution. After 2 min a colorless solution (in the case of **1** and **2**) or a suspension of a colorless solid in a colorless solution (in the case of **3**) was obtained. The reaction mixtures were analyzed by means of ^{1}H and ^{13}C NMR spectroscopy. In all three cases the iodine was quantitatively converted and the appropriate amount of allyl iodide was detected after a reaction time of $\leq$20 min.[36] The in situ generated aluminum allyl iodides and the allyl iodide were allowed to further react, and the course of these reactions was monitored by means of ^{1}H and ^{13}C NMR spectroscopy.

1: no 1,5-hexadiene was detected over a period of more than 6 days. **2**: After 18 days a conversion of >95% of the in situ generated allyl iodide was observed with a selectivity of 80% toward 1,5-hexadiene.[35] **3**: After 18 days a conversion of 39% of the in situ generated allyl iodide was observed with a selectivity of 67% toward 1,5-hexadiene.[35]

X = Br, 0.50 equivalent of Br$_2$ per allyl substituent: The aluminum compound (**1**: 33 mg, 148 μmol; **2**: 36 mg, 63 μmol; **3**: 25 mg, 109 μmol) was dissolved in THF-d_8 (600 μL). Bromine (in the case of **1**: 36 mg, 225 μmol; in the case of **2**: 10 mg, 63 μmol; in the case of **3**: 35 mg, 219 μmol) was added to the colorless solution. After 2 min a colorless solution (in the case of **1** and **2**) or a suspension of a colorless solid in a colorless solution (in the case of **3**) was obtained. In all three reactions full conversion of the starting materials was observed within less than 1 h and the reaction mixtures were analyzed by means of ^{1}H and ^{13}C NMR spectroscopy. **1**: 1,5-Hexadiene was formed as the main product with 39% selectivity;[35] 1,2,3-tribromopropane was also detected next to unidentified side products.[37] **2**: 1,5-Hexadiene was

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[35] Analytical data for 1,5-hexadiene: ^{1}H NMR (400.1 MHz, THF-d_8): δ 2.12 (br d, $^3J_{HH}$ = 2.9 Hz, 2H, H^{aliph}), 2.13 (br d, $^3J_{HH}$ = 2.9 Hz, 2H, H^{aliph}), 4.92 (dm, $^3J_{HH}$ = 10.2 Hz, 2H, H$^{\gamma}$), 4.99 (dm, $^3J_{HH}$ = 17.0 Hz, 2H, H$^{\delta}$), 5.75−5.85 (m, 2H, H$^{\beta}$) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 34.09 (s, C^1), 115.00 (s, C^3), 138.93 (s, C^2) ppm.

[36] Analytical data for allyliodide: ^{1}H NMR (400.1 MHz, THF-d_8): δ 3.90 (dm, $^3J_{HH}$ = 7.8 Hz, 1H, H$^{\alpha}$), 4.91 (dm, $^3J_{HH}$ = 9.8 Hz, 1H, H$^{\gamma}$), 5.22 (dm, $^3J_{HH}$ = 16.7 Hz, 1H, H$^{\delta}$), 6.06 (br ddt, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 16.7 Hz, 1H, H$^{\beta}$) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 5.60 (s, C^1), 117.71 (s, C^3), 137.24 (s, C^2) ppm.

[37] Analytical data for 1,2,3-tribromopropane: ^{1}H NMR (400.1 MHz, THF-d_8): δ 3.88 (br dd, $^3J_{HH}$ = 6.7 Hz, $^{2/4}J_{HH}$ = 11.1 Hz, 2H, C(H^1)$_2$Br), 3.99 (br dd, $^3J_{HH}$ = 4.5 Hz, $^{2/4}J_{HH}$ = 11.1 Hz, 2H, C(H^2)$_2$Br), 4.56 (br tt, $^3J_{HH}$ = 4.5 Hz, $^{2/4}J_{HH}$ = 6.7 Hz, 1H, CBrH) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ 36.07 (s, CH$_2$Br), 50.07 (s, CHBr) ppm.

formed as the main product with 71% selectivity;[35] 1,2,3-tribromopropane was also detected next to unidentified side products.[37] **3**: 1,5-Hexadiene was formed as the main product with 64% selectivity;[35] 1,2,3-tribromopropane was also detected next to unidentified side products.[37]

X-ray Crystal Structure Determination. X-ray diffraction data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å) using φ and ω scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT; absorption corrections were applied with SADABS.[38] The structures were solved by direct methods and refined against F^2 using all reflections with the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions.[39]

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Supporting Information Available: CIF files giving crystallographic data for compounds **2a** and **2b**; time−conversion plots for reactions of allyl chloride and allyl iodide with compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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