

Compositional variations in monomeric trimethylsilylated allyl lanthanide complexes

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Abstract

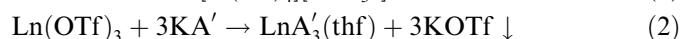
Treatment of three equivalents of the potassium salt of the bis(1,3-trimethylsilyl)allyl anion with various late lanthanide triflates ($M = \text{Dy, Ho, Er, Tm, Lu}$) produces the unsolvated triallyllanthanide complexes LnA'_3 ($A' = 1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3$). The use of lanthanide halides (Cl, I) with the potassium allyl also generates neutral complexes, but when lanthanide iodides and the corresponding lithium allyl are combined, the lanthanate species $\text{Li}(\text{thf})_4[\text{LnA}'_3\text{I}]$ are formed. Trends in the bonding of lanthanide allyl complexes with the trimethylsilylated-allyl ligand are explored and compared with those of cyclopentadienyl lanthanide complexes.
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1. Introduction

Lanthanide complexes containing the bulky (1,3-trimethylsilyl)allyl ligand have recently been investigated as pre-catalysts for the polymerization of methyl methacrylate, ϵ -caprolactone, and 1,3-butadiene [1–4]. Among these complexes are neutral $\text{Ln}^{\text{II}}\text{A}'_2(\text{thf})$ and $\text{Ln}^{\text{III}}\text{A}'_n\text{X}_{3-n}(\text{thf})_m$ species ($n = 1\text{--}3$; $m = 0, 1$; $A'_2 = [1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]$; $X = \text{halide}$) and anionic lanthanates $[\text{Ln}^{\text{III}}\text{A}'_3\text{I}]^-$. The formation of these compounds is not completely straightforward, as the stoichiometric ratios of the reactants are not always reliable guides to the composition of the product. ‘Spectator’ ions and solvents appear to have a strong influence on the outcome of the reactions. For example, it has been reported that when 3 equiv. of KA' are treated with anhydrous LnI_3 ($\text{Ln} = \text{Ce, Pr, Nd, Gd, Tb, Dy, Er}$) in THF, lanthanate complexes of the type $[\text{K}(\text{thf})_4][\text{LnA}'_3\text{I}]$ are isolated (Eq. (1)) [1]. Replacement of the lanthanide iodide starting material with the analogous triflate

($\text{Ln} = \text{Ce, Nd, Tb}$) generates neutral triallyl species with a coordinated THF molecule (Eq. (2)) [1,4].



The number of moles of allyl anion used in the reaction do not always match those found in the product(s), however. For example, when 2 equiv. of KA' are treated with the solvated halide $\text{NdI}_3(\text{thf})_{3.5}$, a mixture of two neutral species, $\text{NdA}'_2\text{I}(\text{thf})_{1.25}$ and $\text{NdA}'_2\text{I}(\text{thf})_2$, is isolated [2,3]. Furthermore, when either 2 or 3 equiv. of KA' are treated with YCl_3 in THF, only the unsolvated triallylyttrium product YA'_3 is isolated [5]. Surprisingly, however, $\text{LaA}'_2\text{Cl}(\text{thf})$ is isolated when LaCl_3 is treated with either 2 or 3 equiv. of the potassium allyl starting material, a counterintuitive outcome based on the metal radius size, as lanthanum should easily be able to accommodate three allyl ligands in its coordination sphere (cf. $\text{La}(\text{III}) = 1.03 \text{ \AA}$ for CN = 6; $\text{Y}(\text{III}) = 0.90 \text{ \AA}$ for CN = 6) [6].

We have explored some of the complex interactions between steric effects and the relative basicities of ligands involved in these reactions with the use of a variety of lanthanide salts and different alkali metal allyl starting

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materials. The latter are found to have an unanticipated influence on the composition of the lanthanide complexes. In the course of this work, we have also analyzed the metal–ligand distances in bis(1,3-trimethylsilyl)allyl lanthanide complexes, and found trends similar to those in cyclopentadienyl lanthanide complexes [7].

2. Experimental

2.1. General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or dry box techniques. ^1H NMR spectra were collected on a Bruker NMR spectrometer at 300 MHz. Solution magnetic susceptibility data were obtained in toluene- d_8 on a Bruker DRX300 spectrometer using the Evans' NMR method [8–11]. Complexometric methods were used for elemental analysis of lanthanide metals [12].

2.2. Materials

Nominally anhydrous lanthanide triflates (Aldrich) were dried under vacuum (10^{-2} Torr) for 12 h at 100–120 °C prior to use. Anhydrous HoCl_3 , DyI_3 , ErCl_3 (Strem), and HoI_3 (Aldrich) were used as received. LiA' and KA' ($\text{A}' = [1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$) were prepared according to the literature procedure [4,13]. Hexanes was distilled under nitrogen from potassium benzophenone ketyl [14]. Anhydrous tetrahydrofuran (THF) was purchased from Aldrich and used as received. Toluene- d_8 was vacuum distilled from Na/K (22/78) alloy and stored over type 4A molecular sieves.

2.3. Synthesis of LuA'_3

A 125 mL Schlenk flask was charged with $\text{Lu}(\text{OTf})_3$ (0.221 g, 0.355 mmol), THF (50 mL), and a stirring bar. An addition funnel was prepared with KA' (0.239 g, 1.065 mmol) in THF (40 mL). After assembly in the glovebox, the apparatus was placed on a Schlenk line, and the $\text{Lu}(\text{OTf})_3$ solution was cooled to -78 °C. The KA' solution

was then added dropwise with stirring over 30 min. After warming to room temperature overnight, the orange reaction mixture was evaporated to dryness, and then extracted with hexanes. The extract was filtered through a medium porosity frit, and the removal of hexanes under vacuum yielded an orange oil with small crystals along the side of the flask. Dissolution of the product in a small amount of toluene and cooling to -30 °C allowed the growth of orange crystals (0.20 g, 77%). Anal. Calc. for $\text{C}_{27}\text{H}_{63}\text{LuSi}_6$: Lu, 23.93. Found: Lu, 23.84%. ^1H NMR (25 °C, 300 MHz, toluene- d_8): δ 0.20 (s, 72H, SiMe_3), 3.73 (d, $J = 16.2$ Hz, 6H, CHCHCH), 7.49 (t, $J = 16.2$ Hz, 3H, CHCHCH).

2.4. Synthesis of LnA'_3 ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$)

The procedure follows that of the synthesis of LuA'_3 . All reactions yielded orange products that crystallized upon cooling to -30 °C. The yield, metal analysis, and solution magnetic moments for each complex are listed in Table 1.

2.5. Synthesis of $[\text{Li}(\text{thf})_4][\text{HoA}'_3\text{I}]$

A 125 mL Schlenk flask was charged with HoI_3 (0.221 g, 0.355 mmol), THF (50 mL), and a stirring bar. An addition funnel was prepared with LiA' (0.239 g, 1.065 mmol) in THF (40 mL). After assembly in the glovebox, the apparatus was placed on a Schlenk line. After cooling the HoI_3 solution to -78 °C, the LiA' solution was added dropwise with stirring over 30 min. After warming to room temperature overnight, the orange reaction mixture was evaporated to dryness, and then extracted with hexanes. The extract was filtered through a medium porosity frit, and removal of hexanes under vacuum yielded an orange oil with small crystals along the side of the flask. Dissolution of the product in a small amount of toluene and cooling to -30 °C allowed the growth of small orange crystals (0.52 g, 89%). Attempts to obtain single crystal X-ray data were unsuccessful, evidently due to facile loss of solvent from the crystals. Anal. Calc. for $\text{C}_{43}\text{H}_{95}\text{HoILiO}_4\text{Si}_6$: Ho, 14.42. Found: Ho, 14.36%. Solution magnetic moment (μ_{eff}); calculated: 10.60 BM. Experimental: 10.37 BM.

Table 1
Experimental data for LnA'_3 ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$)

Complex	Precursor	Yield (%)	Analysis for Ln (%)		μ_{eff} (BM)	
			Calculated	Experimental	Calculated	Experimental
DyA'_3	$\text{Dy}(\text{OTf})_3$	76	22.61	22.85	10.65	10.64
DyA'_3	DyI_3	74	22.61	22.03	10.65	10.52
HoA'_3	$\text{Ho}(\text{OTf})_3$	86	22.87	22.60	10.60	10.00
HoA'_3	HoI_3	91	22.87	22.50	10.60	10.25
HoA'_3	HoCl_3	80	22.87	22.18	10.60	9.95
ErA'_3	$\text{Er}(\text{OTf})_3$	88	23.12	22.89	9.58	8.94
ErA'_3	ErCl_3	77	23.12	23.24	9.58	9.23
TmA'_3	$\text{Tm}(\text{OTf})_3$	77	23.29	23.48	7.56	7.13
LuA'_3	$\text{Lu}(\text{OTf})_3$	77	23.93	23.84	–	–

2.6. X-ray crystallography

Data collection and structure solution for TmA'_3 were conducted at the X-ray Crystallographic Laboratory at the University of Minnesota. All calculations were performed using the current SHELXTL [15] suite of programs. A suitable crystal was located and attached to the tip of a glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K [16]. The intensity data were corrected for absorption with SADABS [17], and final cell constants were calculated from strong reflections from the actual data collection after integration (SAINT) [18]. Relevant crystal and collection data parameters for TmA'_3 are found in Table 2.

The structure was solved using SHELXS-97 and refined using SHELXL-97 [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The twin law [010100001], corresponding to a mirror

Table 2
Crystal data and summary of X-ray data collection of $\text{Tm}[\text{1,3}-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_3$

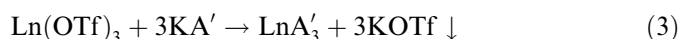
Empirical formula	$\text{C}_{27}\text{H}_{63}\text{Si}_6\text{Tm}$
Formula weight	725.24
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$R\bar{3}$
Unit cell dimensions	
<i>a</i> (Å)	10.8486(5)
<i>b</i> (Å)	10.8486(5)
<i>c</i> (Å)	30.357(3)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å ³)	3094.1(4)
<i>Z</i>	3
D_{calc} (Mg/m ³)	1.168
Absorption coefficient (mm ⁻¹)	2.338
<i>F</i> (000)	1134
Crystal color, morphology	Orange, block
Crystal size (mm)	0.25 × 0.20 × 0.15
θ Range for data collection (°)	2.01–25.04
Index ranges	–12 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 12, –36 ≤ <i>l</i> ≤ 30
Reflections collected	5724
Independent reflections (R_{int})	1220 0.0197
Observed reflections	1219
Completeness to $\theta = 25.04^\circ$ (%)	99.8
Absorption correction	Multi-scan
Maximum and minimum transmission	0.5926 and 0.7206
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1220/366/139
Goodness-of-fit on F^2	1.044
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0888$
<i>R</i> indices (all data)	$R_1 = 0.0335$, $wR_2 = 0.0889$
Largest difference in peak and hole (e Å ⁻³)	0.529 and –0.301

perpendicular to the [1–10] axis, was applied and refined to 85:15.

3. Results

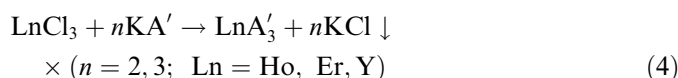
3.1. Synthesis of triallyllanthanide complexes

Unsolvated triallyllanthanide complexes were prepared by treating anhydrous $\text{Ln}(\text{OTf})_3$ ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Lu}$) with 3 equiv. of KA' in THF at -78°C (Eq. (3)). After the reactions were stirred overnight, THF was removed under reduced pressure from the orange reaction mixtures, the residues were extracted with hexanes, and the solutions were filtered to remove KOTf.



Removal of hexanes under reduced pressure, dissolution in toluene, and cooling to -30°C overnight allowed for the growth of orange crystals of each product in good yield (75–81%). Each product is indefinitely stable at room temperature under an inert atmosphere and tolerates brief (<5 min) exposure to air without visible decomposition.

In four separate experiments, HoCl_3 and ErCl_3 were treated with two or three equiv. of KA' under the reaction conditions previously described. All reactions produced orange oils from which X-ray quality crystals could be grown. The unit cells of the crystallized products were isomorphous with the disordered complex TmA'_3 (see below). These results are analogous to the reaction of KA' with YCl_3 ; i.e., YA'_3 is isolated if either 2 or 3 equiv. of KA' are used (Eq. (4)) [5].



Under the same reaction conditions, 3 equiv. of KA' were treated with HoI_3 (Eq. (5)), and a concentrated toluene solution crystallized overnight, yielding X-ray quality crystals. The crystal structure was afflicted with the same disorder seen in all of these complexes, but enough information was available to indicate that the product was the unsolvated complex HoA'_3 . When HoI_3 was treated with 2 equiv. of KA' , HoA'_3 was again isolated, despite the mismatch in stoichiometry.



The isolation of the triallylholmium complex from the iodide starting material was unexpected, since it has been reported that the use of iodide salts of the neighboring metals (dysprosium and erbium) in the same reaction scheme produced lanthanate products $[\text{LnA}'_3\text{I}]^-$ (Eq. (1)) [1]. The crystal structure of the erbium complex was reported, but the dysprosium complex was not fully characterized. The reaction with dysprosium was repeated under the previously described conditions, and the product was found instead to be the unsolvated DyA'_3 (see Table 1) [20]. Single

crystal X-ray diffraction indicates that the unit cell is isomorphous with the previously described unsolvated neutral complexes.

3.2. Synthesis of triallyllanthanate complexes

Even with the reformulation of “[DyA₃I][−]” as DyA₃, its formation and that of HoA₃ from LnI₃ starting materials is puzzling, as crystallographically confirmed lanthanate products are formed with neighboring metals (Tb and Er, Eq. (1)) [1]. Although there is no doubt about the lanthanide anions, the cations suffer from considerable disorder in the crystal structure. Despite the ostensible use of the potassium salt of the [A[−]] anion, it is likely that the alkali metal in all three of the crystal structures of “[K(thf)₄][LnA₃I]” (Ln = Ce, Tb, Er) is mostly lithium. This is consistent both with typical coordination numbers for Li⁺ and K⁺ with THF (4 and 6, [21,22], respectively), and also with the M–O bond lengths (ca. 1.9–2.0 Å [23,24] and 2.6–2.8 Å [21,22,25] in [Li(thf)₄]⁺ and [K(thf)₆]⁺, complexes, respectively). There are no other examples of an isolated “[K(thf)₄]⁺” cation in the Cambridge Crystallographic Database (November, 2006) [26]. Incomplete transmetalation of LiA[−] with potassium *t*-butoxide in the synthesis of KA[−] would leave Li⁺ in the reaction mixture. Furthermore, unlike KI, LiI is slightly soluble in THF, which could cause incomplete metathesis and allow the capture of the iodide in lanthanate products [Li(thf)₄][LnA₃I].

To test whether the change in the counterion of the allyl starting materials accounts for the variation in products when lanthanide iodide salts are used, HoI₃ was treated with 3 equiv. of LiA[−] under the previously described reaction conditions. Solution magnetic susceptibility data, elemental analysis, and a halide test with AgNO₃ indicate that [Li(thf)₄][HoA₃I] is the product. Thus whereas HoA₃ is formed upon treatment of HoI₃ with KA[−], the same reaction with LiA[−] leads to the isolation of [Li(thf)₄][HoA₃I].

3.3. Solid state structure of TmA₃

Although the thulium complex TmA₃ was the only structure that could be solved, crystallographic informa-

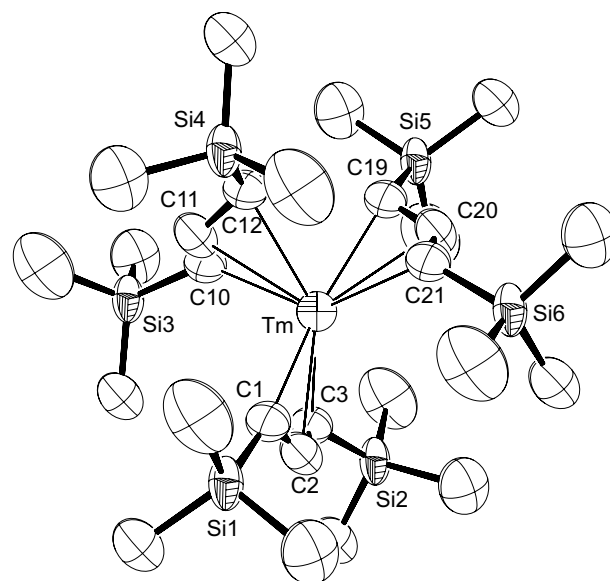


Fig. 1. ORTEP of TmA₃, with thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

tion for the other complexes indicates that analogous unsolvated triallyllanthanide products were isolated. As was found for YA₃ [5], multiple conformations of the allyl ligands are present around the metal center in TmA₃, a difficulty compounded by twinning. Although a reasonable solution could be found (as measured by, for example, the final residual of $R_1 = 0.0335$ for all data), a substantial number of restraints were required to model the disorder. Consequently, some fine details of the structure will be obscured.

The molecule is disordered over a position of $\bar{3}$ (S_6) point symmetry, generating six orientations. Three allyl ligands are η^3 -bound to the metal center, with the ligands arranged around the metal center such that one allyl ligand is oriented roughly anti-parallel to the other two (Fig. 1). The trimethylsilyl groups are in a *syn, syn* configuration, as is found with other trimethylsilyl-substituted allyl lanthanide complexes [1–4]. There are no interligand Me \cdots Me' contacts closer than 4.05 Å, a distance that is outside the sum of their van der Waals radii [27].

Table 3
Bond distances for monomeric trivalent lanthanide allyl complexes

Complex	Radius	M–C	M–C (average)	R_{M-C}^a
CeA ₃ (thf) [4]	1.07 (CN 7)	2.658(8)–2.805(6)	2.75(2)	1.68
[CeA ₃ I] [1]	1.07 (CN 7)	2.677(9)–2.859(10)	2.77(3)	1.70
NdA ₃ (thf) [1]	1.03 (CN 7)	2.634(8)–2.786(7)	2.73(2)	1.70
NdA ₂ I(thf) ₂ [3]	1.03 (CN 7)	2.671(6)–2.781(6) ^b	2.73(1)	1.70
		2.678(6)–2.757(5)	2.72(1)	1.69
TbA ₃ (thf) [4]	0.98 (CN 7)	2.556(9)–2.765(9)	2.66(2)	1.68
[TbA ₃ I] [1]	0.98 (CN 7)	2.56(2)–2.835(19)	2.68(3)	1.70
[ErA ₃ I] [1]	0.945 (CN 7)	2.462(19)–2.88(2)	2.62(2)	1.675
TmA ₃	0.88 (CN 6)	2.326(2)–2.606(2)	2.53(1)	1.65

All distances and radii are in Å. A[−] = [1,3-(SiMe₃)₂C₃H₃].

^a R_{M-C} is the allyl anion ‘radius’, defined from metal-carbon distances.

^b The unit cell of NdA₂I(thf)₂ contains two molecules; bond distances for both are listed.

The Tm–C bond distances range from 2.326(2) to 2.606(2) Å, with an average of 2.53(1) Å. As the data in Table 3 suggests, the spread in distances (0.28 Å) is not unusual for bulky allyl complexes of trivalent metals, although the average length (see below) appears to be somewhat short. The disorder in the structure may be responsible for some of this shortening, and until other complexes like it are structurally characterized, it should not be ascribed too much significance.

Unlike the previously isolated solvated complexes $\text{LnA}'_3(\text{thf})$ (Ln = Ce, Nd, Tb) [1,4], those described here (Ln = Dy–Lu) are isolated without associated THF. This is an understandable consequence of the smaller radii of the late lanthanide metals (Dy(III)–Lu(III) = 0.912–0.861 Å for CN 6; cf. Ce(III)–Tb(III) = 1.01–0.923 Å) [6], which could sterically inhibit the binding of THF molecules. The unsolvated triallyl yttrium complex YA'_3 [5] follows this trend as well, as its radius is in the range of that of the late lanthanides (Y(III) = 0.90 Å for CN 6) [6].

4. Analysis of metal–ligand distances in bulky allyl complexes

The reason that certain metal–ligand ratios are favored in the lanthanide allyl complexes, in apparent defiance of reactant stoichiometry, is unclear. Although it seems unlikely that covalent bonding would play a substantial role in the compounds, we thought it would be useful to determine whether the coordinated allyl ligands display the additive metal–ligand distances that are characteristic of ionic bonding (i.e., $D_{\text{M-L}} = r_+ + r_-$). With non-spherical ligands, the ligand ‘radius’ is difficult to define; in cases such as cyclopentadienyl rings, the difference between the metal–carbon distance of the ligand and the metal radius has been taken as the Cp ‘radius’ [7,28,29]. The determination of whether the addition of metal and Cp radii reproduce observed metal–Cp distances is equivalent to determining whether the Cp radius has a constant value, and hence whether the metal–ligand bonding can be considered to be ionic.

Unfortunately, it was shown some time ago that even in compounds of the alkaline-earth and f-elements, where the bonding should be largely ionic, a unique value for the cyclopentadienyl radius does not exist [7]. Metal–Cp distances are found to be a function not only of the radius of the metal center, but also of the amount of ligand–ligand contact on the coordination sphere of the metal. The latter

can be correlated with the oxidation state and, to a lesser extent, the coordination number of the metal center. Consequently, in our examination of bond distances for structurally authenticated monomeric bis(1,3-trimethylsilyl)allyllanthanide complexes, those with trivalent and divalent metals were analyzed separately (Tables 3 and 4, respectively).

The hundreds of crystal structures that have been used in analyzing M–Cp' distances do not exist for the allyl complexes, yet analysis of the available data are still instructive. With the exception of TmA'_3 , the range in allyl radii for the trivalent compound is very narrow (1.675–1.70 Å), consistent with ionic bonding in these complexes. This is similar to the trend observed with cyclopentadienyl lanthanide complexes, where complexes with the same metal oxidation state display a small range of bond lengths [7]. Although the ligand radius in TmA'_3 is slightly smaller (1.65 Å), this difference is possibly an artifact of the disorder in the crystal structure. As evidenced by the cerium and terbium compounds, the net charge on the complex seems to have little influence on the radius of the allyl ligand. The allyl radius in each anionic complex is not significantly different from that of the corresponding neutral complex ($\Delta = 0.02$ Å).

In general, the allyl radii for divalent lanthanide bis(1,3-trimethylsilyl)allyl complexes (Table 4) are smaller than those of the trivalent compounds; similar charge dependence is observed in cyclopentadienyl lanthanide complexes [7]. The diallyllanthanide complexes $\text{LnA}'_2(\text{thf})_2$ (Ln = Eu, Sm, Yb) are isostructural with calcium [30] and strontium [31] allyl complexes, the bond distances of which are also listed in Table 4. Curiously, the allyl radii for the europium, samarium, and strontium complexes are almost identical (1.60–1.621 Å), but the analogous value for the calcium complex (1.654 Å) is slightly higher, and that of $\text{YbA}'_2(\text{thf})_2$ is larger still (1.72 Å). These two compounds contradict the typical structural similarities observed in divalent lanthanide and alkaline earth complexes [7].

As previously noted [4], the dissimilarity in the calcium and ytterbium complexes' M–C bond distances is unexpected. Because the ionic radii of calcium and ytterbium differ only slightly (Ca(II), 1.00 Å; Yb(II), 1.02 Å for CN 6) [6], bond distances and angles of the ligands in their respective complexes are usually similar [32]. An argument has been made that the longer Yb–C bonds reflect bond weakening arising from the filled f^{14} shell of the Yb(II) ion [4].

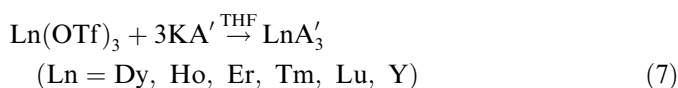
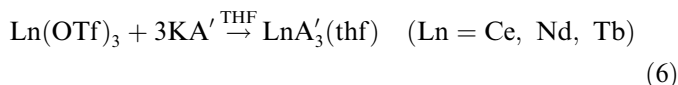
Table 4
Bond distances for monomeric divalent lanthanide and alkaline-earth allyl complexes

Metal	Radius	M–C	M–C (average)	$R_{\text{M-C}}$
$\text{SrA}'_2(\text{thf})_2$ [30]	1.18 (CN 6)	2.797(3)–2.805(3)	2.801(5)	1.621
$\text{EuA}'_2(\text{thf})_2$ [4]	1.17 (CN 6)	2.762(14)–2.789(14)	2.77(2)	1.60
$\text{SmA}'_2(\text{thf})_2$ [4]	1.17 (CN 6)	2.765(6)–2.796(6)	2.78(1)	1.61
$[\text{SmA}'_3]$ [2]	1.17 (CN 6)	2.743(5)–2.895(5)	2.84(1)	1.67
$\text{YbA}'_2(\text{thf})_2$ [4]	1.02 (CN 6)	2.729(9)–2.754(9)	2.74(1)	1.72
$\text{CaA}'_2(\text{thf})_2$ [29]	1.00 (CN 6)	2.648(3)–2.662(3)	2.654(5)	1.654

All bond distances and radii are in Å. $\text{A}' = [1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_5]$.

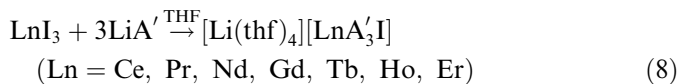
5. Conclusions

The allyl/metal ratios in lanthanide complexes with bis(1,3-trimethylsilyl)allyl ligands do not always match the stoichiometric ratios of the reacting allyl anions and metal cations, and variations in the metal cation of the allyl starting material can affect the product isolated. After correcting the characterizations of several previously reported complexes, some generalizations about the products of the reactions are now possible. Specifically, there are two consistent sets of reactions observed with lanthanide triflates (Eqs. (6) and (7)):

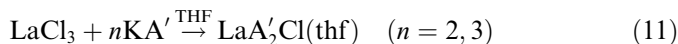
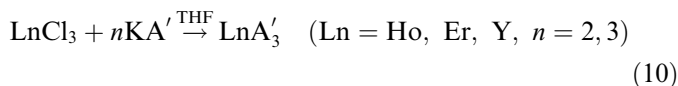
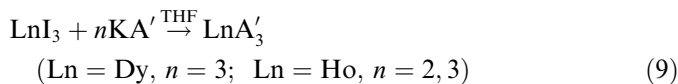


Although it would be desirable to have more data with the earlier lanthanides, it appears that there is a sharp break in composition between Tb and Dy; with the smaller lanthanides, the coordination sphere must be too sterically crowded to accommodate a tetrahydrofuran ligand.

With lanthanide iodides and lithium allyl starting materials, lanthanates are produced regardless of the lanthanide (Eq. (8)); it is evidently possible to accommodate an iodide even around the smaller lanthanides:



If the potassium derivative of the lanthanide allyl is used as a starting material, neutral species are again formed, although the stoichiometry of the reagents is not always reflected in the composition of the products (Eqs. (9)–(11)). This differs from observations in cyclopentadienyl lanthanide chemistry, where varying the metal of the cyclopentadienyl starting material does not usually influence the outcome of the reaction so starkly [33].



More explorations with the earlier lanthanides are needed, but a comparison of Eqs. (9) and (10) with (11) suggests that there are strongly favored combinations of ligands that might be radii dependent. These may form regardless of the stoichiometric ratios of the starting materials.

Despite the geometrically irregular shape of the substituted allyl anion, metal–ligand distances in monomeric lanthanide and alkaline-earth allyl complexes appear to be reasonably predictable based on metal radius and oxidation state. This is an expected consequence of a high degree

of ionic character in the bonding. Additional structural data will be necessary before it can be determined whether these trends hold in polymetallic species.

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Appendix A. Supplementary material

CCDC 639252 contains the supplementary crystallographic data (excluding structure factors) for TmA'_3 . These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.04.016](https://doi.org/10.1016/j.jorganchem.2007.04.016).

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