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A homoleptic rare-earth-metal tetramethylindate†

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The homoleptic complex $La(InMe_4)_3$ is obtained from the respective aluminium congener $La(AlMe_4)_3$ *via* a donor-assisted tetramethylaluminate/tetramethylindate exchange protocol. Compound $La(InMe_4)_3$ exhibits interesting thermal lability as well as distinct cluster formation like $La_4In_7(C)(CH)_2(CH_2)_2(CH_3)_{19}$ and $La_5In_9(CH)_6(CH_3)_{24}$ upon addition of an excess of donor or thermal treatment. The neutral potentially tridentate ligand Me_3TACN (1,4,7-trimethyl-1,4,7-triazacyclononane) is used to investigate donor-triggered intermediates. Compound $La(InMe_4)_3$ is the first crystallographically characterized homoleptic rare-earth-metal tetramethylindate and may readily be used as a precursor for follow-up chemistry distinct from $La(AlMe_4)_3$ and $La(GaMe_4)_3$.

Rare-earth-metal tetraalkylaluminates $Ln(AlR_4)_3$ (R = alkyl) are proven precatalysts/intermediates in commercial Ziegler-type polymerization reactions.[1] To that end, the synthesis and reactivity of homoleptic rare-earth-metal tetramethylaluminates as well as tetramethylgallates have been intensively researched.[2,3] It was revealed early that organogallium derivatives are prone to $GaMe_3$ separation[3b,3c] and that their synthesis is particularly challenging for large rare-earth-metals like lanthanum since the putative methyl precursors $[LnMe_3]_n$ are still elusive.[4] However, an alternative synthesis protocol involving a donor-assisted tetramethylaluminate/tetramethylgallate exchange, utilising a mixture of $La(AlMe_4)_3$ (**1**) and $GaMe_3(OEt_2)$, led to the formation of the gallium congener $La(GaMe_4)_3$ (**2**) in good yield and purity.[5] It is striking that apart from alkali-metal tetramethylindates $M[InMe_4]$ (M = K, Rb, Cs),[6] so far only two structurally characterised f-block tetramethylindates are known, the heterobimetallic complex $Cp^*{}_2U[(\mu\text{-Me})(InMe_3)]_2$ (ref. 7) and ion-separated $[\{(Me_3TACN)YMe_2\}_2\{\mu\text{-Me}\}][InMe_4]$.[8] In this work, we report on $La(InMe_4)_3$ (**3**) as the first homoleptic rare-earth-metal tetramethylindate including some of its properties.

Compound $La(InMe_4)_3$ (**3**) can be obtained by treatment of $La(AlMe_4)_3$ (**1**) with $InMe_3$(thf) (Scheme 1, route a).[9] Crystallisation from a toluene solution at −40 °C afforded **3** as colourless crystals, which were analysed by ^1H NMR and FTIR spectroscopy, as well as ICP-OES and X-ray diffraction. Compared to the synthesis of the gallium congener $La(GaMe_4)_3$ (**2**), significant adjustments of the transmetalation protocol were necessary to allow for the isolation of **3**. Most importantly, compound **3** is temperature sensitive and readily decomposes at ambient temperature, as indicated by methane elimination in ^1H NMR studies. Therefore, all investigations had to be performed at 0 °C. Initial attempts using Et_2O instead of THF as a donor showed the feasibility of the **1** → **3** transformation, but neither was the procedure reliable nor did the exchange occur to a satisfactory extent as indicated by ICP-OES analysis (ratio In : Al $<$ 3 : 1). This was mainly due to side-product formation, noticeable through the precipitation of $\{La_xIn_y\}$ cluster species **4a** and **4b** (In : Al = 5.7 : 1) (*vide infra*), which also occurred in the presence of THF. Cluster precipitation was impeded by using an excess of $InMe_3$ as well as by slow addition of THF to the reaction mixture. Furthermore, it was observed that during the crystallisation process it is necessary to add toluene to the clear solution and remove residual THF *in vacuo* to counteract cluster formation. The ^1H NMR spectroscopic investigations confirmed the formation of **3** by a single signal at −0.07 ppm (0 °C) which is shifted downfield compared to its aluminium congener **1** and upfield compared to its gallium congener **2** even at ambient temperature (−0.20 (**1**); −0.14 (**3**); and −0.02 ppm (**2**)). A single proton signal for the terminal and bridging methyl groups of **3** is consistent with observations made for **1** and **2** and is due to the well-investigated methyl-group mobility.[2,3] Variable temperature ^1H NMR studies of compound **3** revealed the absence of any signal broadening/decoalescence even at −80 °C (see Fig. S3, ESI†) which is in accordance with previous studies performed on **1** and **2** as well.[2c,5] Some residual aluminium is detected in the ^1H NMR spectrum (see Fig. S1, ESI†) and was quantitatively determined *via* ICP-OES analysis (In : Al = 7.3 : 1). Complex **3** (space group $P2_1/n$) is isostructural

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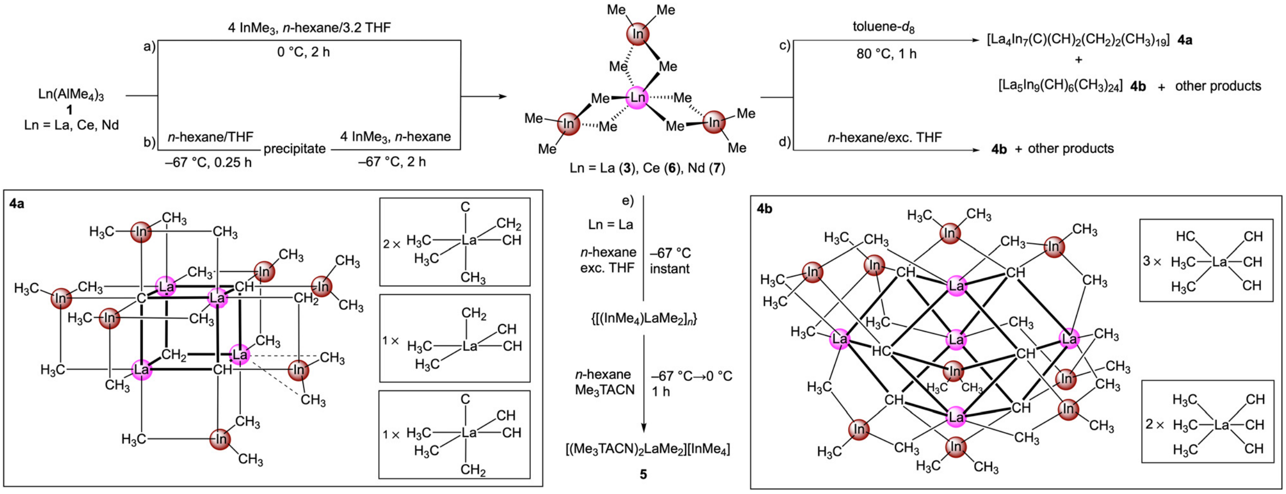


Scheme 1 Synthesis of homoleptic rare-earth-metal tetramethylindates *via* (a) donor-assisted tetramethylaluminate/tetramethylindate exchange and (b) precipitation of a reactive lanthanum methyl species with subsequent $InMe_3$ addition. Reactivity investigations at (c) elevated temperatures and (d) with an excess of THF as well as (e) the isolation of a dimethyllanthanum species are also depicted. The crystal structure of clusters **4a** and **4b** do not reveal any In/Al disorder.

to the gallium congener **2** (space group $P2_1/c$), with three η^2-coordinated anionic ligands involving planar LaC_2In moieties (Fig. 1).

For comparison, homoleptic $La(AlMe_4)_3$ (**1**) revealed three differently coordinated tetramethylaluminato ligands in the solid state (in plane η^2, bent η^2 and η^3).[2c,5] The similar electronic properties of $GaMe_3$ and $InMe_3$ compared to $AlMe_3$ certainly propel this structural behaviour in the solid state. A noticeable structural difference of heterobimetallic complex **3** is the significantly more obtuse C–La–C angle which averages 85.7°, compared to 81.7° in **2**[5] and 78.1° in **1**.[2c] Moreover, the La–C(indate) bond lengths in **3** (avg. 2.677 Å) match the respective La–C(gallate) bond lengths in **2** (avg. 2.667 Å) but are shorter than the La–C(aluminate) bond lengths detected for **1** (avg. 2.699 Å). At the same time the lanthanum-group 13 metal(E) distances average 3.352 Å in **3**, 3.194 Å in **2**[5] and 3.097 Å in **1**,[2c] reflecting the increasing ionic radii of the respective group 13 metal (Al < Ga < In) (Table 1).

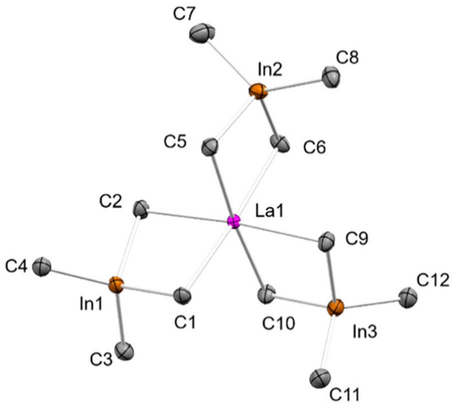


Fig. 1 Crystal structure of **3**, with atomic displacement parameters set at 50%. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): La1–C1 2.686(2), La1–C2 2.677(2), La1–C5 2.667(2), La1–C6 2.663(2), La1–C9 2.684(3), La1–C10 2.685(3), In1–C1 2.289(3), In1–C2 2.303(3), In1–C3 2.158(3), In1–C4 2.143(3), La1–In1 3.3524(2), La1–In2 3.3489(2), La1–In3 3.3569(2), C1–La1–C2 85.17(8), C1–La1–C5 91.20(8), C1–La1–C6 176.49(9), C1–La1–C9 91.76(8), C5–La1–C6 86.56(8), C1–In1–C2 104.42(9), C1–In1–C4 110.24(10), C3–In1–C4 121.90(11).

Since it is generally proposed that transient $[Ln–CH_3]$ moieties are formed during donor-induced cleavage reactions facilitating methyl group degradation,[3,10] the identification of such moieties was pursued at low temperatures. Accordingly, **1** was cooled to −67 °C and THF (3 equiv.) was added to the solution. Instant formation of a colourless sticky solid indicated the envisaged conversion of **1** into putative highly reactive $[LaMe_3]_n$, being substantiated by discolouring of the precipitate at slightly increased temperatures. Moreover, it was shown that this intermediate reacts with a slight excess of $InMe_3$ during reheating to 0 °C, forming complex **3**, which in turn was confirmed *via* ^1H NMR spectroscopy (−0.07 ppm) as well as ICP-OES analysis. This reaction while showing the existence of multiple transient $[Ln–CH_3]$ moieties at low temperatures offers a viable alternative synthesis pathway for **3** (Scheme 1, route b). To further investigate any intermediate species forming during the exchange reaction, a so far elusive lanthanum dimethyl species could be crystallised. The unique lability of **3** was used

Table 1 Selected interatomic distances [Å] and angles [°] in compounds **1**, **2** and **3** (E = group 13 metal)

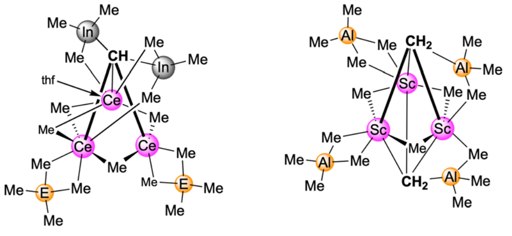
	$La(AlMe_4)_3$ (**1**)[2c]	$La(GaMe_4)_3$ (**2**)[5]	$La(InMe_4)_3$ (**3**)
La–C1	2.696(3)	2.658(9)	2.686(2)
La–C2	2.701(3)	2.678(11)	2.677(2)
La–E1[a]	3.264(1)	3.1859(12)	3.3524(2)
C2–E1–C1	78.8(1)	81.8(3)	85.17(8)
C3–E1–C4	114.3(2)	121.0(5)	121.90(11)
E1–La–E2	110.18(3)	126.30(3)	129.01(1)

[a] η^2-bonded EMe_4 moieties.

to form a colourless intermediate *via* adding an excess of THF at −67 °C, which we propose to be $[(InMe_4)LaMe_2]_n$. Subsequent reaction with 1,4,7-trimethyl-triazacyclononane (Me_3TACN) and slow reheating to 0 °C (Scheme 1, route e) afforded the less temperature sensitive ion-separated $[(Me_3TACN)_2LaMe_2]$ $[InMe_4]$ (**5**). The isolation of **5** clearly underpins the existence of transient $[Ln–CH_3]$ moieties at low temperatures even for the largest rare-earth metal. A similar ion pair has been reported for the smaller yttrium, $[(TCyTAC)YMe_2][AlMe_4]$ (TCyTAC = 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane) featuring unsurprisingly shorter Ln–CH_3 distances (2.412(2)/2.415(2) Å *versus* 2.544(3)/2.572(3) Å).[11]

Use of the slightly smaller rare-earth metals cerium and neodymium resulted in increasingly less efficient Al/In exchange for $Ce(InMe_4)_3$ (**6**) (In : Al = 6.7 : 1) and $Nd(InMe_4)_3$ (**7**) (In : Al = 3.3 : 1). It is also worth mentioning that the neodymium derivative **7** seems to be more temperature sensitive, as indicated by a colour change from blue to green and precipitation of a colourless powder when storing for two hours at 0 °C. Moreover, the cerous alkylindate **6** co-crystallized with one molecule of $InMe_3$. It was earlier shown that homoleptic $Ln(AlMe_4)_3$ (Y, Yb)[2a,d] and $Lu(GaMe_4)_3$ (ref. 3c) tend to co-crystallize with Al_2Me_6 and $GaMe_3$, respectively. Unlike in $Lu(GaMe_4)_3{\cdot}GaMe_3$,[3c] the co-crystallized planar group 13 metal alkyl in $Ce(InMe_4)_3{\cdot}InMe_3$ (**6**) does not engage in intermolecular In–CH_3 interactions. Since the two polymorphs detected for $InMe_3$ in the solid-state form In–CH_3 interconnected network topologies,[12] the "truly" isolated $InMe_3$ in **6** features a snapshot of the gaseous monomeric state.[13] Applying smaller rare-earth metals like yttrium did not result in any homoleptic tetramethylindate formation since treatment of $Y(AlMe_4)_3$ with even substoichiometric amounts of THF led to immediate formation of $[YMe_3]_n$ which does not react with $InMe_3$ under these conditions. These findings highlight the crucial impact of the rare-earth-metal size on tetramethylindato coordination as corroborated by lower residual aluminium contents and higher stability for larger rare-earth metals. Applying an excess of THF when reacting $Ce(AlMe_4)_3$ with $InMe_3$ resulted in cluster formation as well, as evidenced for the mixed methylidyne/methyl complex $Ce_3(In/Al)_4(CH)(CH_3)_{18}(thf)$ (**8**) (Fig. S24, ESI†). The solid-state structure of heptametallic cluster **8** is different from previously identified clusters from donor-induced cleavage reactions,[4] since two tetramethylaluminato/indato moieties are still intact and coordinated at two distinct cerium atoms (Fig. 2). Cluster **8** can be compared to the heptametallic mixed methylidene/methyl cluster $Sc_3Al_4(CH_2)_2(CH_3)_{17}$ (**A**) which was isolated previously as the decomposition product of $Sc(AlMe_4)_3$ at ambient temperature.[2h] Moreover, the clusters emerging from $La(InMe_4)$ (**3**) *via* treatment with THF donor (Scheme 1, route d) or by simply heating to 80 °C (Scheme 1, route c) are surprisingly similar to the clusters that resulted from $La(AlMe_4)_3$ (**1**) *via* treatment with the soft donor PMe_3.[4]

Clusters $\{La_4In_7\}$ (**4a**, colourless) and $\{La_5In_9\}$ (**4b**, yellow) formed *via* multiple C–H-bond activations, featuring methylene, methylidyne and carbide moieties,[14] and are thermally less sensitive than **3**. The unselective formation of the cluster species **4a** and **4b** is corroborated by ^1H NMR studies showing methane formation as well as the degradation of **3** into a plethora of decomposition products (Fig. S10, ESI†). The undecametallic cluster $[La_4In_7(C)(CH)_2(CH_2)_2(CH_3)_{19}]$ (**4a**, monoclinic space group $P2_1/m$) exhibits a cube-like core of lanthanum, carbide, methylidyne as well as methylidene carbon atoms occupying the corner sites. This contrasts with a similar dodecametallic cluster previously reported as $[La_4Al_8(CH)_4(CH_2)_2(CH_3)_{20}(PMe_3)]$ (**B**), the cubic core of which is composed of lanthanum and methylidyne carbon atoms exclusively.[4] Steric shielding of the core of **4a** occurs mainly through $InMe_3$ moieties. Cluster **4a** (Fig. S22, ESI†) is also reminiscent of the dodecametallic cluster $La_4Al_8(C)(CH)_2(CH_2)_2(CH_3)_{22}(toluene)$ (**C**).[4] While **C** also consists of one carbide, two methylidyne and two methylene groups, one of the metal core positions is occupied by aluminium. Furthermore, two of the lanthanum atoms in **4a** are structurally equivalent to each other and show an octahedral environment of carbon atoms (La2, La2′: 3 × CH_3, 1 × CH_2, 1 × CH, 1 × C). One lanthanum atom adopts a square pyramidal geometry (La1: 2 × CH_3, 1 × CH_2, 2 × CH) and two additional longer secondary interactions with neighbouring methyl groups (3.445(3) Å), while the fourth shows again an octahedral carbon environment (La3: 2 × CH_3, 1 × CH_2, 2 × CH, C). The five peripheral $InMe_3$ moieties interact with methylidyne and carbide carbon atoms of the cubic core, forming two $CH(InMe_3)_2$ and one $[C(InMe_3)_3]$ sites. The methylidene carbon core atom is coordinated by three lanthanum atoms showing a well-known structural motif, which was observed previously for rare-earth-metal clusters that formed upon donor-induced cleavage of mixed-ligand complexes $[(C_5Me_4R)Ln(AlMe_4)_x(Cl)_y]_z$ (Ln = Y, La; X = Cl, Br, I; R = Me, $SiMe_3$).[15,16] The La–C(methyl) bond lengths in **4a** range from 2.787(5) to 2.837(6) Å. The La–C(methylidyne) and La–C(methylene) distances are as short as 2.513(5) and 2.516(5) Å, respectively, especially the La–C(methylene) bond in **4a** is shorter than the La–C(methylene) bond in **B** (2.588(4) Å).[4] The La–C(carbide) contacts range from 2.587(5) to 2.654(7) Å. Other discrete rare-earth-metal carbide and methylidyne complexes include $(TMTAC)Ln_3Al_5(C)(CH_2)_2(CH_3)_{16}$ (Ln = Y; Sm; TMTAC = 1,3,5-trimethyl-1,3,5-triazacyclohexane),[17] $(C_5Me_5)_4Y_4Al_4(CH)_2(CH_3)_{12}$, $(TCyTAC)SmAl_3(CH)(CH_3)_9$ (ref. 18) and $(C_5Me_5)_3Sc_3(CH)(X)_3$ (X = Br, Me, OMe).[19]



$Ce_3(In/Al)_4(CH)(CH_3)_{18}(thf)]$
8 (E = Al or In)

$Sc_3Al_4(CH_2)_2(CH_3)_{17}$
A

Fig. 2 Heptametallic clusters obtained from $Ln(EMe_4)_3$ decomposition (E = Al or In). **A** (ref. 2h).

The second cluster, which could be isolated both *via* thermal treatment and THF exposure (Scheme 1, route d), is the tetradecametallic $[La_5In_9(CH)_6(CH_3)_{24}]$ (**4b**). Cluster **4b** crystallised in the monoclinic space group $C2/c$ (Fig. S23, ESI†), being isostructural with the aluminium equivalent $[La_5Al_9(CH)_6(CH_3)_{24}]$ (**D**).[4] The lanthanum atoms in these clusters are arranged in a trigonal bipyramidal fashion and show two distinct six-coordinate environments: La1, La1′, La2 (4 × CH, 2 × CH_3) and La3, La3′ (3 × CH, 3 × CH_3). The overall threefold negative charge of the core unit $\{La_5(CH)_6\}^{3-}$ in **4b** is balanced by three $\{InMe_2\}^+$ units. Considering that both $AlMe_3$ and $InMe_3$ are available in **3** for interacting with the donor THF, a minimum aluminium content of **4b** can be rationalized on the basis of the preferred formation of adduct $AlMe_3$(thf) as a better hard-acid–base match. It should also be noted that both newly obtained clusters **4a** and **4b** are substantially more soluble in aliphatic solvents than their respective aluminium counterparts.

In summary, elusive $[LaMe_3]_n$ is isolable as a trimethylindium addition compound. Homoleptic $La(InMe_4)_3$ can be obtained *via* low-temperature treatment of $La(AlMe_4)_3$ with $InMe_3$ in the presence of THF. The smaller cerium and neodymium display similar reactivity but the tetramethylindates $Ce(InMe_4)_3$ and $Nd(InMe_4)_3$ incorporate higher amounts of residual aluminium. At ambient and elevated temperatures, degradation *via* multiple C–H-bond activation prevails leading to isolable (partly In/Al exchanged) clusters $[La_4In_7(C)(CH)_2(CH_2)_2(CH_3)_{19}]$, $[La_5In_9(CH)_6(CH_3)_{24}]$ and $Ce_3(In/Al)_4(CH)(CH_3)_{18}$(thf) with recurring structural motifs. Transient terminal $[Ln–CH_3]$ species, which are proposed intermediate species of such degradation reactions, could be isolated as azacrown adduct $[(Me_3TACN)_2LaMe_2][InMe_4]$. Given the previously detected distinct reactivity of $Ln(AlMe_4)_3$ *versus* the more reactive $Ln(GaMe_4)_3$,[20] future investigations will focus on the implications of the even more labile $Ln(InMe_4)_3$ complexes for subsequent derivatization reactions.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for the compounds have been deposited in the Cambridge Crystallographic Data Centre (deposition numbers 2403533–2403539).

Conflicts of interest

There are no conflicts to declare.

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