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Heavy Silylchalcogenido Lanthanates $\text{Ph}_4\text{P}[\text{Cp}_3\text{La-ESiMe}_3]$ (E = S, Se, Te) via Fluoride-Induced Demethylation of Dimethylcarbonate to $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ Key Intermediate

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We report a new high-yield synthesis of so far not accessible tetraphenylphosphonium methylcarbonate $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ via solvothermal fluoride-induced demethylation and MeF elimination at Me_2CO_3 (DMC) by $\text{Ph}_4\text{P-F}$, XRD structurally characterized as λ^5 -fluorophosphoran. The synthetic value of $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ key compound for preparing nearly all kind of other $\text{Ph}_4\text{P}[\text{anion}]$ salts with perfectly crystallizing (not symmetry frustrated) cation is demonstrated by examples beyond ionic liquid research: A complete set of silylchalcogenide salts $\text{Ph}_4\text{P}[\text{ESiMe}_3]$ (E = S, Se, Te) including a first example of a structurally characterized non-coordinating, naked $[\text{Te-SiMe}_3]^-$ anion is presented. With this set of soft Lewis bases and metal organic Lewis acid $[\text{Cp}_3\text{La}]$ at hand, a comprehensive series of crystalline 1:1 lanthanate complexes $\text{Ph}_4\text{P}[\text{Cp}_3\text{La-ESiMe}_3]$ has been prepared. Their structural features and trends such as complexation induced Si-E bond elongation and a pronounced trend in La-E-Si bond angle contraction with E = S < Se < Te are discussed. Heteronuclear ^1H , ^{13}C , ^{29}Si , ^{139}La NMR studies provide a set of ^{139}La NMR shifts for homologues of heavy chalcogen-lanthanum complexes.

Introduction

Organic salts and ionic liquids containing a methylcarbonate anion are well established as versatile precursors for an atom efficient green synthesis of other ionic liquids (ILs) and organic cation salts. They inevitably contain an asymmetric methylonium cation, e.g. methyltrialkylammonium, methyltrialkylphosphonium, 1,3-methylethylimidazolium, methylpyridinium, or methylpentaalkylguanidinium, because they are prepared from dimethylcarbonate as mild methylating reagent and corresponding N- or P-nucleophiles under solvothermal conditions in MeOH¹ or even without any added solvent.^{2,3} The quantitative conversion of the methylcarbonate anion into other valuable functional anions usually follows simple deprotonation^{3,4} or desilylation⁵ protocols with only volatile by-products CO_2 and MeOH/MeOSiMe₃. As this implies the absence of any traces of water, metal- or halide impurities from ion exchange, the obtained ionic liquids are suitable for applications with respect to electrochemical, spectroscopic applications, as solvent or in materials research demanding a high degree of purity.^{3,5}

This green synthesis of the methylcarbonate ionic liquids and onium salts intrinsically leads to methyl-onium cations (Scheme 1, a).^{6,7} This strategy is of advantage, if low-melting ionic liquids with non-symmetric, symmetry-frustrated onium cations are required, but of disadvantage if perfectly crystallizing solids with large and symmetric onium cations are targeted. Numerous metallate salts with a large anion volume

require highly symmetrically and bulky substituted cations like e. g. Ph_4P^+ (TPP⁺) or $[\text{Ph}_3\text{P-N=PPh}_3]^+$ (PPN⁺) to yield single-crystals suitable for purification, anion stabilization and XRD analysis. Yet, there was no synthetic access to TPP and PPN methylcarbonates. As these salts have the potential of drastically simplifying the access to single-crystalline, highly pure intermediates and products, they are highly valuable synthetic targets.

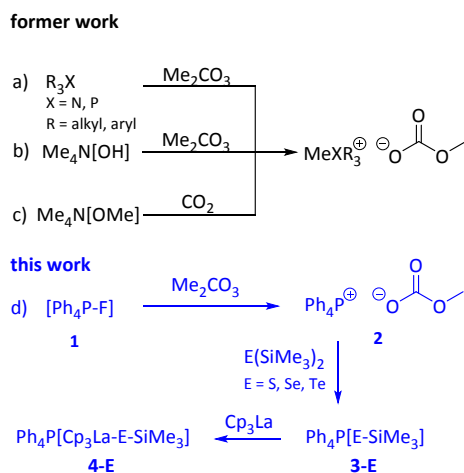
Inspired by the demethylation of Me_2CO_3 by neutral nucleophiles ER_3 and with $\text{R}_4\text{N}[\text{OH}]$ in MeOH⁸ (Scheme 1) we developed a new strategy of using the bench-stable TPP fluoride, predicted on the basis of IR and NMR data to be a λ^5 -fluorophosphane $\text{Ph}_4\text{P-F}$ (**1**).⁹ With this paper we intend to add XRD proof for its trigonal bipyramidal molecular structure and to use **1** as donor for a highly basic and nucleophilic fluoride anion attacking DMC at the methyl, not carbonyl group in order to form methyl fluoride and unsolvated, water-free $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ (**2**) (Scheme 1, d). The tendency of phosphonium cations to decompose in the presence of alternative highly basic and nucleophilic, non-solvated anions $[\text{OH}]^-$ or $[\text{OR}]^-$ prevented so far a simple strategy transfer applying TPP $[\text{OH}]$ or TPP $[\text{OR}]$ as alternative to $\text{R}_4\text{N}[\text{OMe}]_{\text{solv}}$ (Scheme 1, c)¹⁰ in the synthesis of **2**.

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Electronic Supplementary Information (ESI) available: Synthetic procedures, experimental detail, NMR spectra and XRD data, TGA measurements. The CIF files of the presented structures. CCDC 2087069-2087077. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Synthetic strategies of generating organic methycarbonate salts.^{6–8,10,11}

Furthermore, we intend to demonstrate the use of $Ph_4P[OCO_2Me]$ in the synthesis of trimethylsilylchalcogenide new salts $Ph_4P[ESiMe_3]$ (**3-E**, $E = S, Se, Te$) via desilylation of $E(SiMe_3)_2$. Similar onium salts have gained considerable interest as chalcogen source in the synthesis of thermoelectric materials M_2E_3 ($M = Sb, Bi$; $E = Se, Te$),¹² precursors such as $Cat[M(ESiMe_3)_4]$ ($M = Ga, In$; $E = S, Se$) or $Cat[M(ESiMe_3)_3]$ ($Cat = \text{organic cation}$; $M = Zn, Sn$; $E = S, Se$) for CIGS and CZTS photovoltaic materials¹³, finally for the investigation of doubly ionic H-bonding interactions in $MMIm[ESiMe_3]$ ($E = S, Se$, $MMIm^+ = 1,3\text{-dimethylimidazolium}$).¹¹

Furthermore, we intend to demonstrate the favourable use of $Ph_4P[ESiMe_3]$ ($E = S, Se, Te$) in the synthesis of a complete set of complexes with highly water sensitive organometallic Lewis acid $[Cp_3La]$ and to investigate yet unreported lanthanates $Ph_4P[Cp_3La-ESiMe_3]$ ($E = S, Se, Te$) via XRD and ¹³⁹La-NMR spectroscopy. Systematic investigations of heavy chalcogen bond interactions involving lanthanum or 4f block metals such as in Cp_2LnSPh ($Ln = La, Lu$)¹⁴ are rare. Structural data for a La-E-Si bond sequences have not been reported at all. Fluoride induced desilylation of our target compounds $[Cp_3La-ESiMe_3]^-$ might provide access to high-charge stabilized pseudo tetrahedral lanthanates $Cat_2[Cp_3La=E]$ interesting for their La-E bonding or as building block for heteronuclear clusters and materials.¹⁵ They could serve as models for unknown paramagnetic lanthanido metallates $Cat[Cp_3Ln-ESiMe_3]$ potentially of interest as precursors in the design and synthesis of single molecular magnets¹⁶ or as catalysts for functional group transfer processes.¹⁷ Beyond the aspect of having reactive anions and sources of heavy chalcogens $X = E-SiMe_3$ attached to lanthanum, rare earth metal complexes of the type $[Cp_3M-X]^-$ ($M = La$ or Ln) with more common inert anions X have been reported¹⁸, even those containing an organic onium cation.¹⁹

Results and discussion

Fluoride-induced demethylation of Me_2CO_3

Ph_4P-F (**1**) was prepared following the anion exchange between $Ph_4P[BF_4]$ and dry KF in absolute methanol. **1** was isolated after precipitation of $K[BF_4]$, filtration and removal of all volatiles *in vacuo*.^{20,21} Single-crystals for an X-ray analysis were obtained by storing a saturated solution of **1** in toluene at 0 °C. **1** crystallizes in monoclinic space group $P2_1/n$ with four formula units per unit cell (Figure 1). As suggested by previous studies^{9,22} – and similarly to corresponding PPN-F²⁰ – **1** is rather a neutral fluoridophosphorane than a pair of separated ions. The fluoride ion is covalently attached to the valence-sphere of a five-coordinate, distorted trigonal bipyramidal coordination sphere of the central P atom. Fluorine, the smaller substituent compared to phenyl, occupies the axial position. The terminal P-F bond of 1.758 Å is much longer than P-F bonds of PF_5 in the gas phase (P-F_{ax}: 1.580 Å, P-F_{eq} 1.522 Å)²³ but much shorter than the two P-F bonds (2.646 Å and 1.820 Å) in the PPN-F displaying an intramolecular P-F-P bridge.²⁰ This covalent P-F interaction persists in toluene-d₈ solution proven by the observed coupling constants in ³¹P-NMR ($^1J_{PF} = 557.2$ Hz) and ¹⁹F-NMR ($^1J_{FP} = 557.4$ Hz) spectra.

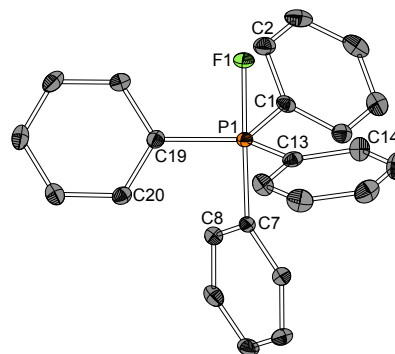
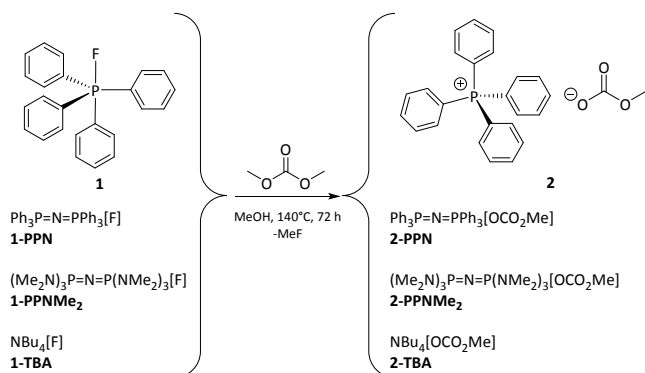


Figure 1. Crystallographically determined molecular structure of Ph_4P-F (**1**). Hydrogen atoms are omitted for clarity. Ellipsoids are shown at 50% level. Selected bond lengths in Å and angles in °: P1-F1 1.7582(8), P1-C1 1.842(1), P1-C7 1.902(1), P1-C13 1.826(1), P1-C19 1.836(1), C2-C1 1.398(2), C7-C8 1.403(2), C13-C14 1.391(2), C19-C20 1.400(2), F1-P1-C1 85.77(5), F1-P1-C7 178.24(5), F1-P1-C13 85.05(5), F1-P2-C19 87.25(5) C1-P1-C7 92.49(6), C1-P1-C13 118.82(6), C1-P1-C19 122.23(6), C7-P1-C13 95.57(6), C7-P1-C19 93.91(6).

Although fluoride is covalently attached to a highly distorted latent tetraphenylphosphonium moiety, the P-F bond can easily be cleaved by suitable, even weak electrophiles. This high nucleophilicity of the fluorine atom can be utilized in the demethylation of Me_2CO_3 under solvothermal conditions at 140 °C for 72 h in the presence of methanol to form $Ph_4P[OCO_2Me]$ (**2**) which is nearly quantitatively obtained after removing all volatiles *in vacuo* (Scheme 2). The driving force for this reaction is on the one hand the formation of the stable C-F bond in the gaseous by-product H_3C-F compared to the rather instable P-F bond in **1**, and on the other hand the release of strain during the formation of the Ph_4P^+ cation.



Scheme 2. Preparation of Ph₄P[OCO₂Me] (**2**) by fluoride induced demethylation of Me₂CO₃ with Ph₄P-F (**1**) and similar fluoride donors under solvothermal conditions.

The purity of **2** is verified by elemental analysis and ¹H/¹³C NMR spectra. In contrast to **1**, TPP methylcarbonate **2** is an ionic compound, which is proven by the ¹H-, ¹³C- and ³¹P-NMR spectra in DMSO-d₆ showing exactly the identical shifts of the methylcarbonate anion²⁴ and TPP cation as observed for literature known examples with a non-coordinating anion like BF₄.²⁵ Besides that, product **2** is free of solvent such as H-bonded methanol or acetonitrile as observed for PPN[OCO₂Me] (**2-PPN-0.5 MeCN**). The latter is synthesized from PPNF in an analogue synthesis. Its full characterization is described in the SI. **2** forms rather large orthorhombic crystals – surprisingly too large for successful diffraction experiments. Several trials failed at the refinement stage due to drastic disordering of the [OCO₂Me]⁻ anion in the matrix of tetrahedral Ph₄P⁺ cations. The applicability of this synthesis protocol has been expanded to a set of quarternary phosphonium and ammonium cations, namely *n*-Bu₄N[OCO₂Me] (**2-TBA**), PPN[OCO₂Me] (**2-PPN**), and (Me₂N)₃P=N=P(NMe₂)₃[OCO₂Me] (**2-PPNMe₂**) prepared from (Me₂N)₃P=N=P(NMe₂)₃[F].²¹ The XRD molecular structures of ionic methylcarbonate **2-PPN** is presented in the SI (Figure S36). Figure 2 presents an ionic methylcarbonate with PPN related, weakly coordinating cation [(Me₂N)₃P=N=P(NMe₂)₃]⁺ (**2-PPNMe₂**) prone for forming perfect single crystals via secondary weak C-H...O anion cation interactions.

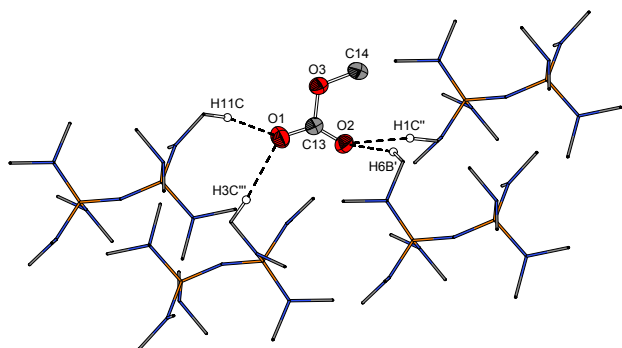


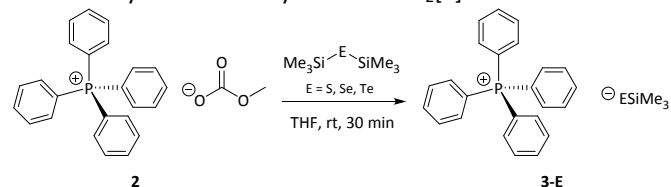
Figure 2. Molecular structure of PPNMe₂[OCO₂Me] (**2-PPNMe₂**), as cut-out of the lattice. Ellipsoids of the anions are shown at 50% level. Only protons involved in H-bonds shown for clarity. Selected bond lengths (in Å) and angles (in °): O3-C14 1.424(3), C13-

O3 1.421(3), C13-O1 1.223(3), C13-O2 1.226(3), O2-H1C'' 2.487(2), O2-H6B' 2.481(2), O1-H11C 2.472(2), O1-H3C''' 2.497(2), O1-C13-O2 131.3(2), O2-C13-O1 116.6(2), O1-C13-O3 112.1(2), Symmetry operations: I: x, -1+y, z; II: 1+x, -1+y, z, III: 1-x, 1-y, 1-z.

Although fluoride induced demethylation of Me₂CO₃ is a reliable process, we were not able to demethylate other acid methylesters such as dimethyl oxalate or dimethyl acetylenedicarboxylate under similar solvothermal conditions. It seems, that better charge delocalization within a trigonal planar [O-CO₂] moiety as leaving group, not available in [C-CO₂], is needed for this S_N2-type reactivity pattern of a masked fluoride ion.

Synthesis and structures of Ph₄P[ESiMe₃] (E = S, Se, Te)

The applicability of **2** is demonstrated by the preparation of a representative set of homologue trimethylsilylchalcogenide salts Ph₄P[ESiMe₃] (E = S (**3-S**), Se (**3-Se**), Te (**3-Te**)). These were obtained as colourless crystalline solids in quantitative yields and high purity by reacting **2** with E(SiMe₃)₂ (E = S, Se, Te) in thf at room temperature and removing all volatiles *in vacuo* (Scheme 3). In accord with our previous studies we did not observe any twofold desilylation to TPP₂[E].²⁴



Scheme 3. Preparation of Ph₄P[ESiMe₃] (**3-E**, E = S, Se, Te) by desilylation of E(SiMe₃)₂ with Ph₄P[OCO₂Me] (**2**).

X-ray diffractive crystals of all representatives were grown by slow diffusion of *n*-pentane into a solution of the trimethylsilylchalcogenide salts in thf at -30°C (Figure 3, refer to SI for more detailed structural data and Figure S38-Figure S40). **3-S** crystallizes in the space group *Pbca* with eight formula units per unit cell, **3-Se** in the space group *P2₁/c* with four formula units per unit cell, while **3-Te** crystallizes in the space group *P2₁* with two formula units per unit cell. Interestingly, hydrogen bond pattern present in the crystalline state of **3-S**, **3-Se**, and **3-Te** differ significantly. The more basic sulfur and selenium anions are stabilized by two C_{Ph}-H...E interactions.

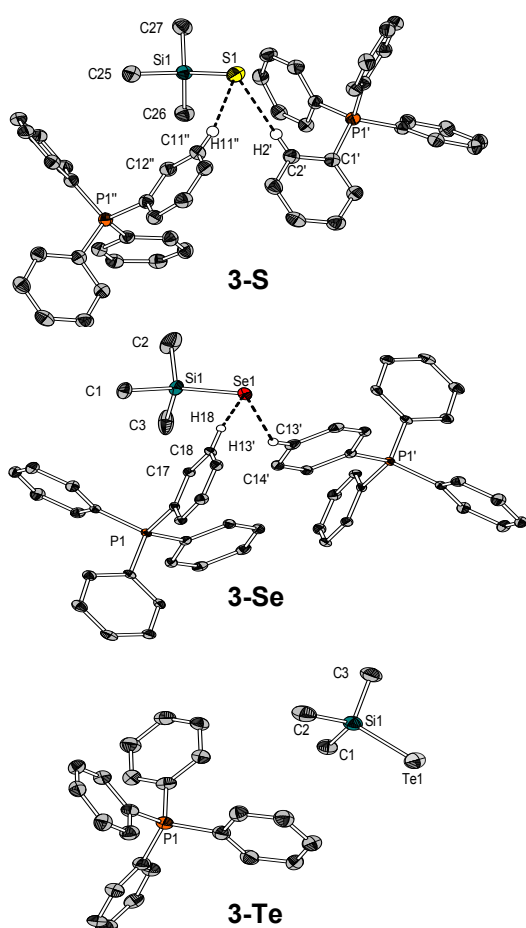


Figure 3: Molecular structures of $\text{Ph}_4\text{P}[\text{ESiMe}_3]$ **3-S** (top), **3-Se** (middle) and **3-Te** (bottom). Only H-atoms involved in H-bonds shown. Thermal ellipsoids are displayed at 50% level. E-Si Bond-lengths: S-Si 2.0647(8) Å, Se-Si 2.2102(9) Å, Te-Si 2.447(2) Å.

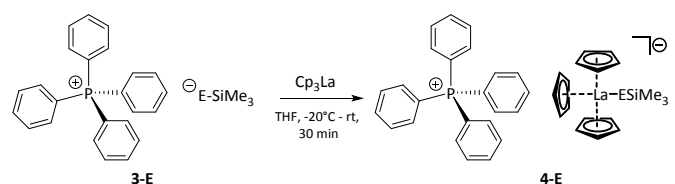
While smaller and harder S atom in **3-S** shows H-bonds to *ortho* and *para* $\text{C}_{\text{Ph}}\text{-H}$ -positions of two neighbouring lattice TPP cations, larger Se atom in **3-Se** displays only interactions to the sterically less shielded *meta* and *para* $\text{C}_{\text{Ph}}\text{-H}$ -positions, and the least basic Te-atom in **3-Te** does not form any of such secondary anion cation interactions at all. It displays a naked anion $[\text{Te-SiMe}_3]^-$ with only weak purely ionic interaction with the TPP cation matrix. The structural characterization of this naked tellurium anion is unprecedented. Studies correlating the number of anion cation hydrogen bonds with the strength of $\text{C-H}\cdots\text{E}$ anion cation interactions were limited to $[\text{S-SiMe}_3]^-$ and $[\text{Se-SiMe}_3]^-$ anions in a lattice of 1,3-dimethylimidazolium cations.^{11,24} Structural key parameters of the H-bonds present in **3-S** and **3-Se** are listed in Table 1. The atomic radius of the chalcogen atom not only determines the $\text{E}\cdots\text{H}$ connectivity but also results in an increase of the corresponding H-bond lengths. Surprisingly, all $\text{C-H}\cdots\text{E}$ angles are smaller for **3-Se** than in **3-S**. This smaller angle suggests a more pronounced interaction between the chalcogen atom and the aromatic systems of the cations' phenyl groups as visualized elsewhere.¹¹ Contrastingly, the $\text{H}\cdots\text{E}\cdots\text{H}$ bond angle is way smaller for **3-S** than for **3-Se**.

Table 1: Crystallographically determined bond parameters for the H-bonds in **3-S** and **3-Se** (bond lengths in Å, bond angles in °).

	$\text{E}\cdots\text{H}_{\text{ortho/para}}$	$\text{CH}_{\text{ortho/para}}\cdots\text{E}$	$\text{E}\cdots\text{H}_{\text{meta}}$	$\text{CH}_{\text{meta}}\cdots\text{E}$	$\text{H}\cdots\text{E}\cdots\text{H}$
3-S	2.8202(5)	143.2(1)	2.8465(5)	130.2(1)	109.0(1)
3-Se	2.926(1)	132.4(1)	2.9226(6)	132.4(1)	114.88(2)

Synthesis, structures and NMR-spectra of $\text{Ph}_4\text{P}[\text{Cp}_3\text{LaESiMe}_3]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$)

Reactive onium trimethylsilylchalcogenide salts are established in the synthesis of metallate complexes $\text{Cat}[\text{M}(\text{ESiMe}_3)_{n+1}]$ having considerable potential to serve as precursors in the synthesis of a variety of chalcogenide based materials and clusters.^{13,26,27} Up to date, the synthesis of corresponding rare earth metallate complexes cannot be realized with similar protocols described for main group (Ga, In and Sn^{II}) and late transition metals (Cu, Ag, Au, Zn). In order to investigate a complementing strategy to incorporate the $[\text{ESiMe}_3]^-$ ligand into such rare earth metallates, equimolar conversions of organometallic Lewis acid $[\text{Cp}_3\text{La}]$ with $\text{Ph}_4\text{P}[\text{ESiMe}_3]$ were studied. A comprehensive series of complexes $\text{Ph}_4\text{P}[\text{Cp}_3\text{La-ESiMe}_3]$ (**4-E**, $\text{E} = \text{S}, \text{Se}, \text{Te}$) was synthesized and – thanks to the nicely crystallizing TPP^+ cation – also XRD structurally characterized (Scheme 3).



Scheme 3. $\text{Ph}_4\text{P}[\text{Cp}_3\text{La-ESiMe}_3]$ (**4-E**, $\text{E} = \text{S}, \text{Se}, \text{Te}$) prepared by reaction of $[\text{Cp}_3\text{La}]$ with **3-S**, **3-Se** and **3-Te**.

Single crystals of all compounds **4-E** were grown by slow diffusion of *n*-pentane into a thf solution. **4-S** crystallizes with four ion pairs per unit cell in space group $P2_1/c$, **4-Se** with $Z = 4$ in space group $P2_1/n$, and **4-Te** with $Z = 2$ in space group $P2_1$. The molecular structures of the lanthanate anions are shown in Figure 4. A comparison of crystallographically obtained bond parameters of anions **3-E** and corresponding anionic lanthanocenes **4-E** are listed in Table 2 (for more crystallographic detail refer to SI, Figure S41 and Table S4).

Table 2: Comparison of important bond parameters obtained from XRD analyses of **3-S, 3-Se, 3-Te** and **4-S, 4-Se, 4-Te** (bond lengths Å and angles °)

	E-Si	La-E	La-E-Si	$\Sigma 3 \times (\text{Cp-La-Cp})^a$
3-S	2.0647(8)	-	-	-
4-S	2.097(1)	2.9211(1)	128.40(4)	347.64(6)
3-Se	2.2102(9)	-	-	-
4-Se	2.235(2)	2.9977(6)	117.34(3)	348.04(3)
3-Te	2.447(2)	-	-	-
4-Te	2.4756(1)	3.2833(8)	106.27(3)	348.49(3)

^a $\text{Cp}_{\text{centr.1-La-Cp}_{\text{centr.2}} + \text{Cp}_{\text{centr.2-La-Cp}_{\text{centr.3}} + \text{Cp}_{\text{centr.3-La-Cp}_{\text{centr.1}}$

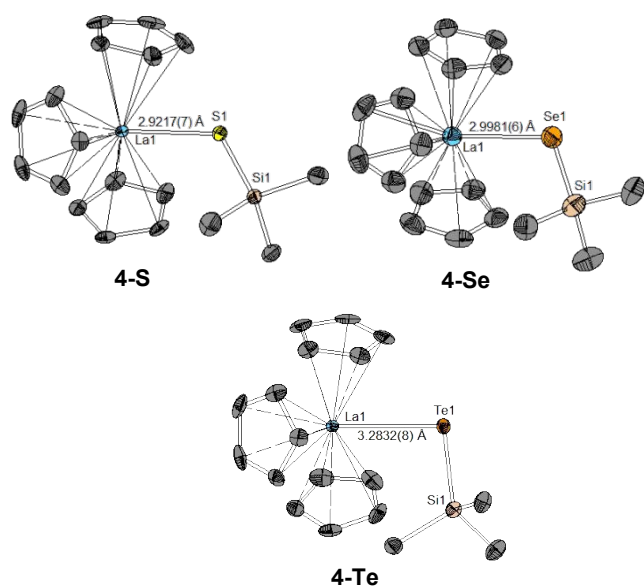


Figure 4: Molecular structures of lanthanate anions $[\text{Cp}_3\text{La-ESiMe}_3]^-$ in **4-E** ($E = \text{S} -$ top left, $\text{Se} -$ top right, $\text{Te} -$ bottom). TPP cations and H-atoms are omitted for clarity. Thermal ellipsoids are displayed at 50% level.

As expected La-E bonds increase with increase of the atomic radii $\text{S} < \text{Se} < \text{Te}$. At the same time, La-E-Si bond angles decrease in the order $\text{S} > \text{Se} > \text{Te}$, a trend explained by the more pronounced p-orbital character of the molecular orbitals for increasingly heavy main group elements.²⁸ The same trend was observed in the XRD structural analyses of other heteroleptic E-SiMe₃ ($E = \text{S}, \text{Se}, \text{Te}$) complexes.²⁹ In all structures, a significant E-Si bond elongation is observed upon coordinating the weakly proton (H-bridge) stabilized $[\text{E-SiMe}_3]^-$ anion of **3-E** to Lewis acid $[\text{Cp}_3\text{La}]$. Next to this weak H-bond interaction the anions should in part stabilize their high electron density at E via negative hyperconjugation: The antibonding $\sigma^*-\text{Si-C}$ or $\pi^*-\text{SiMe}_3$ orbitals are expected to withdraw more electron density from a chalcogenide anion of non-coordinated $[\text{E-SiMe}_3]^-$ than from a Lewis acid stabilized chalcogenide atom in $[\text{Cp}_3\text{La-E-SiMe}_3]^-$. Electron density of the chalcogenide anion is also delocalized into π -dative bonds to La^{3+} (Figure 5). However, this extra stabilization in the La-E bond is expected to be relatively small due to so called π -bond saturation by four competing $\sigma, 2\pi$ donors at the pseudo-tetrahedrally coordinated d^0 -La center, a situation discussed in similar cyclopentadienyl silylimido complexes of d^0 group 5 metals.³⁰ There are only a few examples of La-E-complex series.^{31–33} In this case, the homologous series of $[\text{La}\{\text{N}(\text{EPiPr}_2)_2\}_3]$ should be highlighted, which show a comparable trend of bond lengths (La-S: 2.892 Å, La-Se: 3.019 Å, La-Te: 3.224 Å).³¹

Comparing our homologue series **4-E** with the most structurally related dinuclear La-E complex $[(\text{C}_5\text{Me}_5)_2\text{La}(\text{EPH})]_2$ ^{33,34} the La-S bond length (3.009 Å) and La-Se bond length (3.123 Å) are shorter, as the μ -bridged Se atoms in the mentioned dinuclear complex form weaker bonds resulting in elongated La-Se bond length. To the best of our knowledge there are only four crystallographically determined La-Te species known, which are divided into two cluster structures and two mononuclear

complexes. The La-Te bonds average 3.160 Å and 3.224 Å in the two known mononuclear complexes $(\text{dmpe})_2\text{La}(\text{TeSiMe}_3)_4$ ³⁵ and $\text{La}\{[\text{N}(\text{TEPiPr}_2)_2]_3\}$,³² respectively. So, herein, we describe the longest La-Te bond (3.283 Å) until now.

Upon complexation of the chalcogenide anions, the three La-Cp_{centroid} bonds typically found in $[\text{Cp}_3\text{La}]$ are distorted from a trigonal planar into a pseudo tetrahedral configuration. However, despite drastic differences and trends in E-Si and La-E-bond lengths and La-E-Si angles, the angle-sum of three Cp_{centroid}-La-Cp_{centroid} angles is only little increasing from 347.6° for $E = \text{S}$ via 348.0° for $E = \text{Se}$ to 348.5° for $E = \text{Te}$. The Cp ligands at La-E are oriented in a preferred conformation displaying one La-Cp_{centroid} vector in *anti* fashion with respect to the E-SiMe₃ vector. For all homologues, the Cp ring *anti* to the SiMe₃ group is displaying Cp_{centroid}-La-E bond angles around 95°, while the remaining two Cp rings show Cp_{centroid}-La-E bond angles around 105°.

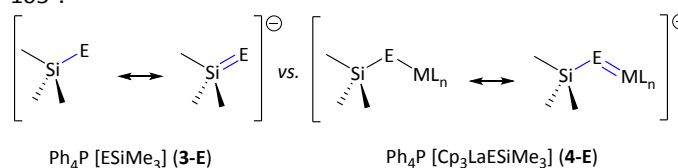


Figure 5: Resonance forms with partial extra bond stabilization of uncoordinated $[\text{E-SiMe}_3]^-$ anions **3-E** and their complexes $[\text{Cp}_3\text{LaESiMe}_3]^-$ (**4-E**).

NMR spectra of **4-E** were recorded in thf-*d*₈ as these molecules decompose rapidly when using other polar solvents like DMSO-*d*₆ or CDCl₃. Figure 6 displays trends in ¹H-, ²⁹Si- and ¹³⁹La-NMR spectra of $\text{Ph}_4\text{P}[\text{Cp}_3\text{La-ESiMe}_3]$ ($E = \text{S}, \text{Se}, \text{Te}$) compared to parent $[\text{Cp}_3\text{La}]$. While ¹H- and ¹³C{¹H}-NMR signals of $[\text{Cp}_3\text{La}]$ are only little shifted upon addition of $[\text{ESiMe}_3]^-$, ²⁹Si-NMR signals of $[\text{ESiMe}_3]^-$ are systematically 4-5 ppm deshielded upon coordination of the anions. The ²⁹Si signals appear within a range of 29 ppm, and silyltelluride **4-Te** displays the most shielded ²⁹Si resonance at -24 ppm vs external standard (LaCl₃ aq.). ¹³⁹La-NMR signals are shifted with increasingly heavy chalcogen atom by 123 ppm (S), 146 ppm (Se), and 162 ppm (Te) to higher field (Figure 6).

This is one of the few examples for a full set of ¹³⁹La-NMR spectra of homologues organolanthanum compounds. Comparable ensembles of related compounds of similar, however more narrow range of ¹³⁹La-NMR resonances are Cp₃La-nitrile adducts (-575 ppm for Cp₃La-NcTbu to -614 ppm for Cp₃La-NC-Cyclohexyl in CD₂Cl₂)³⁶ or Cp₃La-O-donor adducts (-564 ppm for Cp₃La-OS(CH₃)₂ to -584 ppm for Cp₃La-O(CH₃)₂).³⁷ For **4-Se** and **4-Te** we were not able to detect ⁷⁷Se- and ¹²⁵Te-NMR signals. This is plausibly due to the quadrupole momentum of the lanthanum nucleus directly attached. Same was observed in homo- and heteroleptic E-SiMe₃ complexes with quadrupole nucleus, previously.^{13,26} Even our trial to use a heteronuclear HMQC method published recently³⁸ failed in obtaining ⁷⁷Se- and ¹²⁵Te-NMR signals for **4-Se** and **4-Te**.

Table 3: ¹H-, ¹³C-, ²⁹Si- and ¹³⁹La-NMR shifts of relevant singlets for **4-E** recorded in thf-*d*₈ (*shifts for **3-E** in DMSO-*d*₆). Refer to SI for further details.

	¹ H-NMR ^a	¹³ C-NMR ^a	²⁹ Si-NMR
Cp ₃ La	5.96	113.0	-

4-S	5.75	111.1	5.2 (3-S* -1.0)
4-Se	5.76	111.1	0.1 (4-Se* -5.3)
4-Te	5.77	110.9	-24.0 (4-Te* -28.0)

^a Signals for the Cp ligands

Conclusions

We described a new, highly useful solvothermal method of fluoride induced demethylation of dimethylcarbonate. It is proceeding with naked fluoride ions, salts but also with masked fluoride donors such as fluoridophosphorane Ph₄P-F (**1**), which

was XRD structurally characterized. The products, are ionic methylcarbonate salts **2**, **2-TBA**, **2-PPN** and **2-PPNMe₂**, the latter two were characterized via XRD analyses. The synthetic value of such salts with symmetric large cations was demonstrated for **2**, which was used in desilylation of silanes (Me₃Si)₂E (E = S, Se, Te), isolation and structural characterization of their activated silylchalcogenide salts Ph₄P[ESiMe₃] **3-E** (E = S, Se, Te). Their potential to act as ligands was demonstrated in the synthesis and full structural characterization of heavy chalcogenido lanthanates Ph₄P[Cp₃La-ESiMe₃] (**4-E**, E = S, Se, Te). The trend of a pronounced La-E-Si bond angle contraction from 128.4° (E = S) via 117.3° (E = Se) down to 106.3° (E = Te) was discussed. ¹³⁹La-NMR spectra of **4-E** were recorded and show an increasing low-field shift from -438.7 ppm (E = S) via -415.6 ppm (E = Se) up to 399.9 ppm (E = Te).

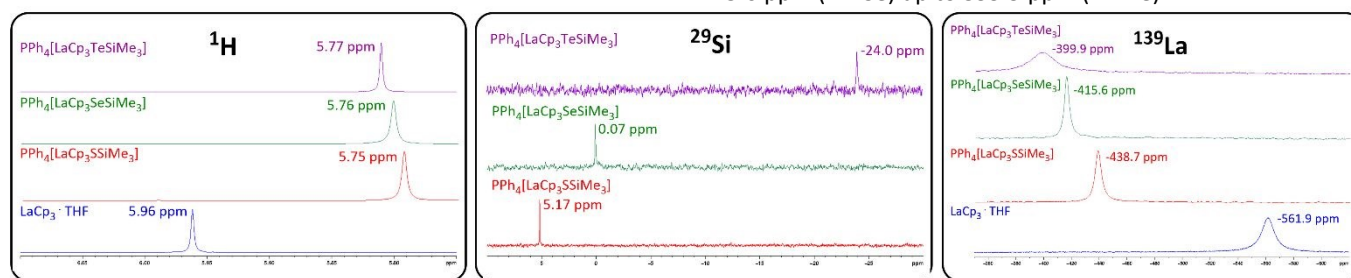


Figure 6: Comparison of ¹H-NMR (298 K, 300.1 MHz, left), ²⁹Si-NMR (298 K, 99.37 MHz, center) and ¹³⁹La-NMR spectra (298K, 42.41 MHz, right) of Ph₄P[Cp₃La-ESiMe₃] (**4-E**, E = S, Se, Te) and LaCp₃ in thf-d₆.

Experimental Section

General considerations

All preparative operations were conducted by using standard Schlenk techniques and freshly dried solvents. All solvents were dried according to common procedures³⁹ and passed through columns of aluminium oxide, R3-11G-catalyst (BASF) or stored over molecular sieves (3 Å or 4 Å). Other reagents were used as received, unless stated otherwise. Tellurium based compounds tend to decompose under exposure to light. Reactions involving tellurium reagents were prepared with aluminum foil wrapped around all relevant flasks. For the lighter homologues this is not necessary. Literature known procedures were used as reported or slightly modified to synthesize E(SiMe₃)₂ (E = S, Se, Te).⁴⁰ Elemental analyses (C, H, N, S) were carried out by the service department for routine analysis with a vario MICRO cube (Elementar). Samples for the elemental analysis were weighted into tin capsules inside a nitrogen filled glovebox. ¹H and proton decoupled ¹³C NMR spectra were recorded in automation with a Bruker Avance II 300 spectrometer, ²⁹Si-, ⁷⁷Se, ¹²⁵Te and ¹³⁹La NMR spectra were recorded by the service department for NMR analyses with a Bruker Avance II HD 300, DRX 400 or Avance III 500 spectrometer. All spectra were recorded at ambient temperature. ¹H- and ¹³C-NMR spectra were calibrated using residual proton signals of the solvent (dms₂-d₆: δ_H 2.50 ppm, δ_C 39.52 ppm, thf-d₆: δ_H 3.58 & 1.72 ppm, δ_C 67.21 & 25.31 ppm, Toluene-d₈: 2.08, 6.97, 7.01 & 7.09 ppm). ²⁹Si-NMR spectra were referenced externally (SiMe₄: δ_{Si} 0.00 ppm) just as

the ⁷⁷Se NMR spectra (Me₂Se δ_{Se} 0.00 ppm) and the ¹²⁵Te-NMR spectra (Me₂Te, δ_{Te} 0.00 ppm) and the ¹³⁹La-NMR spectra (LaCl₃ δ_{La}, 0.00 ppm). TGA measurements were conducted with a DSC-TGA 3 (Mettler Toledo) in a glovebox. Decomposition temperatures were determined using data of the DSC-TGA. PXRD measurements were conducted by giving a small amount of the sample between two layers of Scotch tape. The diffractograms were recorded on a Stoe Stadi MP using Cu or Mo-Kα1 radiation that passed a bent focusing monochromator and a high sensitivity Mythen-detector. The transmission diffractograms were recorded from 2θ = 5° - 105° (5°min⁻¹). TBAF · 3 H₂O was used as obtained by commercial supplier. PPN[F] and PPNMe₂[F] were prepared according to literature.^{20,21} Ph₄P-F was prepared analogously starting from Ph₄P[Cl] instead of PPN[Cl].

Synthesis of Ph₄P-F (1): The preparation of **1** is similar to the literature-known method that was used to prepare PPN[F].²⁰ Instead of PPN[Cl] the corresponding salt Ph₄P[Cl] was used as starting point. Anhydrous methanol (3 mL) was added to a mixture of [PPh₄][BF₄] (5.00 g, 11.7 mmol) and freshly dried KF (865 mg, 14.9 mmol). The reaction mixture was stirred for 1 h at room temperature and filtrated through celite[®]. The filtrate cake was washed with methanol. The solvent was removed, the desired product was extracted with hot toluene and finally filtered by syringe filter. After removal of the solvent or by overlaying a saturated solution of product with *n*-pentane, PPh₄[F] (**1**) is obtained as a colorless powder or crystals, respectively (3.74 g, 10.4 mmol, 89%). ¹H-NMR (300.19 MHz, toluene-d₈): δ = 7.64 (br s, 20H) ppm. ¹³C-NMR (75.48 MHz,

toluene- d_8): δ = 133.7 (d, $^3J_{PC}$ = 9.4 Hz, 1C), 127.7 (d, $^2J_{PC}$ = 13.5 Hz, 1C) ppm. (Note: Due to solvent signal overlaps, the carbon signals cannot be identified properly). **$^{31}\text{P-NMR}$** (122.5 MHz, toluene- d_8): δ = -62.04 (d, $^1J_{PF}$ = 557.2 Hz). **$^{19}\text{F-NMR}$** (282.4 MHz, toluene- d_8): δ = 44.25 (d, $^1J_{FP}$ = 557.4 Hz). **Elemental analysis** found (calcd.) (%) for $\text{C}_{24}\text{H}_{20}\text{PF}$ (358.4 g mol $^{-1}$): 80.4 (80.4), 5.5 (5.6).

Synthesis of $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ (2): In an autoclave vessel $\text{Ph}_4\text{P}[\text{F}]$ (1) (7.60 g, 0.021 mol, 1.00 eq.) was diluted with a mixture of Me_2CO_3 (20 mL, 0.24 mol, 11.4 eq.) and MeOH (5 mL). The reaction mixture was stirred for 3 days at 140 °C. All volatiles were removed in fine vacuum until a colorless residue is obtained. MeCN is added to this residue until a clear solution is obtained. To this solution diethyl ether is added slowly until the precipitation of product begins. The solution is stored at -30 °C for crystallization. The huge colorless blocks can be isolated by filtration, and the mother liquor can be collected for further crystallization steps. **2** is obtained in a yield of 5.62 g (0.014 mol, 65%). **$^1\text{H-NMR}$** (300.13 MHz, $\text{dms}\text{-}d_6$): δ = 7.99-7.71 (m, 20H, $[\text{PPh}_4]^+$), 3.15 (s, 3H, $[\text{OCO}_2\text{CH}_3]^-$) ppm. **$^{13}\text{C-NMR}$** (75.48 MHz, $\text{dms}\text{-}d_6$): δ = 155.4 (s, $[\text{OCO}_2\text{CH}_3]^-$), 135.3 (d, $^4J_{PC}$ = 3.2 Hz) & 134.5 (d, $^3J_{PC}$ = 10.3 Hz) & 130.4 (d, $^2J_{PC}$ = 13.0 Hz) & 117.7 (d, $^1J_{CP}$ = 88.7 Hz) (signals for the Ph_4P^+ cation), 50.7 (s, $[\text{OCO}_2\text{CH}_3]^-$) ppm. **Elemental analysis** found (calcd.) (%) for $\text{C}_{26}\text{H}_{23}\text{O}_3\text{P}$ (414.4 g mol $^{-1}$): C 74.9 (75.3), H 5.8 (5.6).

Synthesis of $\text{Ph}_4\text{P}[\text{SSiMe}_3]$ (3-S): $\text{S}(\text{SiMe}_3)_2$ (0.52 g, 2.92 mmol, 1.3 eq) was added dropwise to a solution of $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ (2) (0.93 g, 2.25 mmol, 1.0 eq.) in thf (10 mL) at 0 °C and stirred for five minutes at 0 °C. The solution was warmed to room temperature and stirred for further 30 min. After removing all volatiles in fine vacuum an yellowish solid is obtained. The residue is diluted in 10 mL thf and *n*-pentane is added until saturation of this solution, and this mixture is stored at -30 °C for some days. After filtration colorless crystals of $\text{Ph}_4\text{P}[\text{SSiMe}_3]$ (3-S) were obtained with a yield of 0.83 g (1.87 mmol, 83%). **$^1\text{H-NMR}$** (300.19 MHz, $\text{dms}\text{-}d_6$): δ = 8.00-7.71 (m, 20H, $[\text{PPh}_4]^+$), -0.07 (s, 9H, $[\text{SSiMe}_3]^-$) ppm. **$^{13}\text{C-NMR}$** (75.48 MHz, $\text{dms}\text{-}d_6$): δ = 135.3 (d, $^4J_{PC}$ = 3.0 Hz), 134.5 (d, $^3J_{PC}$ = 10.4 Hz), 130.4 (d, $^2J_{PC}$ = 12.8 Hz), 117.6 (d, $^2J_{PC}$ = 88.7 Hz), 8.9 (s) ppm. **$^{29}\text{Si-NMR}$** (59.65 MHz, $\text{dms}\text{-}d_6$): δ = -0.76 (s, $[\text{SSiMe}_3]^-$) ppm. **Elemental analysis** found (calcd.) (%) for $\text{C}_{27}\text{H}_{29}\text{PSSi}$ (444.65 g mol $^{-1}$): C 72.9 (72.9), H 6.3 (6.6).

Synthesis of $\text{Ph}_4\text{P}[\text{SeSiMe}_3]$ (3-Se): The synthesis was performed analogously to the preparation of 3-S, using **2** (0.17 g, 0.41 mmol, 1.0 eq.) and $\text{Se}(\text{SiMe}_3)_2$ (0.14 g, 0.44 mol, 1.1 eq.). **3-Se** was obtained with a yield of 0.15 g (0.31 mmol, 75%). **$^1\text{H-NMR}$** (300.25 MHz, $\text{dms}\text{-}d_6$): δ = 8.00-7.71 (m, 20H, $[\text{Ph}_4\text{P}]^+$), 0.08 (s, 9H, $[\text{SeSiMe}_3]^-$) ppm. **$^{13}\text{C-NMR}$** (75.50 MHz, $\text{dms}\text{-}d_6$): δ = 135.3 (d, $^4J_{PC}$ = 2.8 Hz), 134.5 (d, $^3J_{PC}$ = 10.5 Hz), 130.4 (d, $^2J_{PC}$ = 12.3 Hz), 117.8 (d, $^2J_{PC}$ = 8.9), 9.2 (s, $[\text{SeSiMe}_3]^-$) ppm. **$^{29}\text{Si-NMR}$** (59.65 MHz, $\text{dms}\text{-}d_6$): δ = -5.33 (superimposed s and d with $^1J_{Sise}$ = 181.6 Hz, $[\text{SeSiMe}_3]^-$) ppm. **$^{77}\text{Se-NMR}$** (57.26 MHz, $\text{dms}\text{-}d_6$): δ = -423.7 (s*, $[\text{SeSiMe}_3]^-$) ppm. *the expected multiplicity by coupling with the silicon-

nuclei is not resolved. **Elemental analysis** found (calcd.) (%) for $\text{C}_{27}\text{H}_{29}\text{PSeSi}$ (491.55 g mol $^{-1}$): C 66.0 (66.0), H 6.0 (6.0).

Synthesis of $\text{Ph}_4\text{P}[\text{TeSiMe}_3]$ (3-Te): $\text{Te}(\text{SiMe}_3)_2$ (0.084 g, 0.31 mmol, 1.1 eq) was added dropwise to a degassed solution of $\text{Ph}_4\text{P}[\text{OCO}_2\text{Me}]$ (2) (0.115 g, 0.28 mmol, 1.0 eq.) in thf (10 mL) at 0 °C and stirred for five minutes at 0 °C. The solution was warmed to room temperature and stirred for further 30 min. After removing all volatiles in fine vacuum an orange solid is obtained. The residue is diluted in 10 mL thf. *n*-pentane is added until saturation of this solution, and this mixture is stored at -30 °C for some days. After filtration orange crystals of $\text{Ph}_4\text{P}[\text{TeSiMe}_3]$ (3-Te) were obtained with a yield of 0.094 g (0.17 mmol, 63%). **$^1\text{H-NMR}$** (300.25 MHz, $\text{dms}\text{-}d_6$): δ = 8.00-7.71 (m, 20H, $[\text{Ph}_4\text{P}]^+$), 0.32~ (s, < 9H, $[\text{TeSiMe}_3]^-$) ppm. **$^{13}\text{C-NMR}$** (75.50 MHz, $\text{dms}\text{-}d_6$): δ = 135.3 (d, $^4J_{PC}$ = 2.8 Hz), 134.5 (d, $^3J_{PC}$ = 10.5 Hz), 130.4 (d, $^2J_{PC}$ = 12.3 Hz), 117.6 (d, $^2J_{PC}$ = 89.2 Hz), 10.2~ (s, $[\text{TeSiMe}_3]^-$) ppm. **$^{29}\text{Si-NMR}$** (59.65 MHz, $\text{dms}\text{-}d_6$): δ = -28.0~ (s, $[\text{TeSiMe}_3]^-$) ppm. **$^{125}\text{Te-NMR}$** (94.73 MHz, $\text{dms}\text{-}d_6$): δ = -1138.7 (s, $[\text{TeSiMe}_3]^-$) ppm. **Elemental analysis** found (calcd.) (%) for $\text{C}_{27}\text{H}_{29}\text{PTeSi}$ (540.19 g mol $^{-1}$): C 59.6 (60.0), H 5.0 (5.4). ~Note that the anion signal is always accompanied with a signal for $\text{O}(\text{SiMe}_3)_2$, the hydrolysis product at 0.06 ppm ($^1\text{H-NMR}$), 2.0 ppm ($^{13}\text{C-NMR}$), and 7.6 ppm ($^{29}\text{Si-NMR}$) which arises due to diffusion of H_2O into the NMR-sample and the extreme sensitivity of the compound. The sum over the signal for the anion and $\text{O}(\text{SiMe}_3)_2$ yields the correct amount of anion related protons.

Synthesis of $\text{Ph}_4\text{P}[\text{Cp}_3\text{LaSSiMe}_3]$ (4-S): A mixture of $\text{Ph}_4\text{P}[\text{SSiMe}_3]$ (3-S) (100 mg, 0.225 mmol, 1.0 eq.) and $[\text{Cp}_3\text{La}]$ (75 mg, 0.225 mmol, 1.0 eq.) was dissolved in thf (10 mL) at -20 °C and heated up to room temperature over 18 h. The reaction mixture was overlaid with *n*-pentane (10 mL) and stored at -30 °C for a few days obtaining the target compound as colourless crystals by filtration. **$^1\text{H-NMR}$** (300.13 MHz, thf- d_8): δ = 7.96-7.91 (m, 4H), 7.81-7.70 (m, 16H), 5.75 (s, 15H, LaCp_3), 0.18 (s, 9H, $[\text{SSiMe}_3]^-$). **$^{13}\text{C-NMR}$** (75.48 MHz, thf- d_8): δ = 136.1 (d, $^4J_{PC}$ = 3.0 Hz), 135.6 (d, $^3J_{PC}$ = 10.4 Hz), 131.3 (d, $^2J_{PC}$ = 12.8 Hz), 118.9 (d, $^1J_{CP}$ = 89.4 Hz), 111.1 (s), 7.7 (s, $[\text{SSiMe}_3]^-$). **$^{29}\text{Si-NMR}$** (99.37 MHz, thf- d_8): δ = 5.17 (s, $[\text{SSiMe}_3]^-$) ppm. **$^{139}\text{La-NMR}$** (42.41 MHz, thf- d_8): δ = -438.7 (s) ppm. **Elemental analysis** found (calcd.) (%) for $\text{C}_{42}\text{H}_{44}\text{LaPSSi}$ (778.8 g mol $^{-1}$): 64.7 (64.8), 5.6 (5.7).

Synthesis of $\text{Ph}_4\text{P}[\text{Cp}_3\text{LaSeSiMe}_3]$ (4-Se): A mixture of $\text{Ph}_4\text{P}[\text{SeSiMe}_3]$ (3-Se) (100 mg, 0.203 mmol, 1.0 eq.) and $[\text{Cp}_3\text{La}]$ (68 mg, 0.203 mmol, 1.0 eq.) was dissolved in thf (10 mL) at -20 °C and heated up to room temperature over 18 h. The reaction mixture was overlaid with *n*-pentane (10 mL) and stored at -30 °C for a few days obtaining the target compound as colourless crystals by filtration. **$^1\text{H-NMR}$** (300.13 MHz, thf- d_8): δ = 7.97-7.90 (m, 4H), 7.81-7.69 (m, 16H), 5.77 (s, 15H, LaCp_3), 0.34 (s, 9H, $[\text{SeSiMe}_3]^-$). **$^{13}\text{C-NMR}$** (75.48 MHz, thf- d_8): δ = 136.2 (d, $^4J_{PC}$ = 2.9 Hz, 4C), 135.5 (d, $^3J_{PC}$ = 10.4 Hz, 4C), 131.2 (d, $^2J_{PC}$ = 13.0 Hz, 4C), 118.9 (d, $^1J_{CP}$ = 89.3 Hz, 4C), 111.1 (s, 15C), 8.0 (s, 3C, $[\text{SeSiMe}_3]^-$). **$^{29}\text{Si-NMR}$** (99.37 MHz, thf- d_8): δ = -0.07 (s, $[\text{SeSiMe}_3]^-$) ppm. **$^{139}\text{La-NMR}$** (42.41 MHz, thf- d_8): δ = -415.6

(s) ppm. **Elemental analysis** found (calcd.) (%) for $C_{42}H_{44}LaPSeSi$ (825.8 g mol^{-1}): 60.8 (61.0), 5.4 (5.4).

Synthesis of $Ph_4P[Cp_3LaTeSiMe_3]$ (4-Te): A mixture of $Ph_4P[TeSiMe_3]$ (3-Te) (100 mg, 0.185 mmol, 1.0 eq.) and $[Cp_3La]$ (62 mg, 0.185 mmol, 1.0 eq.) was dissolved in thf (10 mL) at -20°C and heated up to room temperature over 18 h. The reaction mixture was layered with *n*-pentane (10 mL) and stored at -30°C for a few days obtaining the target compound as colourless crystals by filtration. Note: Reaction and isolation was performed under exclusion of light. **$^1\text{H-NMR}$** (300.13 MHz, thf- d_8): $\delta = 7.96\text{--}7.92$ (m, 4H), $7.80\text{--}7.72$ (m, 16H), 5.77 (s, 15H, $LaCp_3$), 0.49 (s, 9H, $[TeSiMe_3]^-$). **$^{13}\text{C-NMR}$** (75.48 MHz, thf- d_8): $\delta = 136.1$ (d, $^4J_{PC} = 3.1 \text{ Hz}$, 4C), 135.6 (d, $^3J_{PC} = 10.5 \text{ Hz}$, 4C), 131.3 (d, $^2J_{PC} = 12.9 \text{ Hz}$, 4C), 118.9 (d, $^1J_{CP} = 89.4 \text{ Hz}$, 4C), 110.9 (s, 15C), 9.5 (s, 3C, $[TeSiMe_3]^-$). **$^{29}\text{Si-NMR}$** (99.37 MHz, thf- d_8): $\delta = -24.0$ (s, $[TeSiMe_3]^-$) ppm. **$^{139}\text{La-NMR}$** (42.41 MHz, thf- d_8): $\delta = -399.9$ (broad s) ppm. **Elemental analysis** found (calcd.) (%) for $C_{42}H_{44}LaPSSi$ (874.4 g mol^{-1}): 57.6 (57.7), 5.0 (5.1).

Conflicts of interest

There are no conflicts to declare.

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