

Lanthanide Complexes

 η^3 -Coordination and Functionalization of the 2-Phosphaethynthiolate Anion at Lanthanum(III)**

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In memory of Gerd Becker

Abstract: We present the η^3 -coordination of the 2-phosphaethynthiolate anion in the complex $(PN)_2La(SCP)$ (**2**) [$PN = N$ -(2-(diisopropylphosphanyl)-4-methylphenyl)-2,4,6-trimethylanilide)]. Structural comparison with dinuclear thiocyanate-bridged $(PN)_2La(\mu-1,3-SCN)_2La(PN)_2$ (**3**) and azide-bridged $(PN)_2La(\mu-1,3-N_3)_2La(PN)_2$ (**4**) complexes indicates that the $[SCP]^-$ coordination mode is mainly governed by electronic, rather than steric factors. Quantum mechanical investigations reveal large contributions of the antibonding π^* -orbital of the $[SCP]^-$ ligand to the LUMO of complex **2**, rendering it the ideal precursor for the first functionalization of the $[SCP]^-$ anion. Complex **2** was therefore reacted with CAACs which induced a selective rearrangement of the $[SCP]^-$ ligand to form the first CAAC stabilized group 15–group 16 fulminate-type complexes $(PN)_2La\{SPC^R(CAAC)\}$ (**5 a, b**, $R = Ad, Me$). A detailed reaction mechanism for the SCP-to-SPC isomerization is proposed based on DFT calculations.

Introduction

The (coordination) chemistry of the 2-phosphaethynolate ($[OCP]^-$) anion continues to be a vibrant, highly topical research field in the chemical sciences^[1] and has already led to the isolation of a plethora of novel or rare phosphorus-containing heterocycles,^[2] the first stable singlet phosphinidene,^[3] as well as many (functional) coordination compounds covering the whole periodic table^[1,4]—from main group elements^[5,6] and transition metals^[7] to the lanthanides^[8] and actinides.^[9] In contrast, the chemistry of the heavier ana-

logues, for example, the 2-phosphaethynthiolate ($[SCP]^-$) anion, has been much less developed so far, although both the $[OCP]^-$ ^[10] and the $[SCP]^-$ anion^[11] were first reported in the 1990s by Becker and co-workers as their lithium salts. This can partly be attributed to the notorious instability of $Li(DME)_3SCP$ (similar to $Li(DME)_2OCP$).^[11] However, even after establishing high-yielding routes to long-term stable (room temperature and moderately air tolerant) sodium or potassium salts of both $[SCP]^-$ and $[OCP]^-$,^[12,13] the chemistry of the former remains largely dormant. To date, apart from electrochemical and spectroscopic investigations,^[14] only one $[SCP]^-$ coordination compound in the form of $[K(18\text{-crown-}6)][W(CO)_5(SCP)]$ has been reported.^[12] This first example demonstrated the potential difficulties to be encountered in $[SCP]^-$ coordination chemistry: Due to the unusually high negative charge density on the central carbon atom of the $[SCP]^-$ anion (natural bond orbital (NBO) atomic charges correspond to -0.28 for S, -0.74 for C and 0.03 for P),^[13] only a mixture of S- and P-bound isomers could be obtained, which decomposed at room temperature within four days.

We have recently begun to investigate the chemistry of anilidophosphine-supported lanthanum(III) complexes of the general formula $(PN)_2LaX$ with $X = Cl$ (**1-Cl**) and **I** (**1-I**),^[15] and have shown them to be versatile precursors for the synthesis of pentacoordinate lanthanum(III) primary phosphido and sulfido complexes $(PN)_2La(EMes)$ ($E = PH, S$). Due to the insertion reactivity of the La–P phosphide bond, the former allowed us to construct phosphareate and phosphathioureate ligands, which can be used to build

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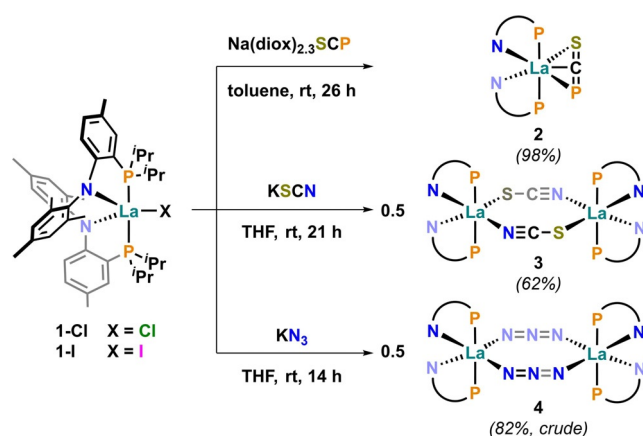
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heterobimetallic systems.^[16] Furthermore, the same phosphido complex led us to study a transient (terminal) phosphinidene complex.^[17] Acknowledging that the use of a neutral metal atom such as tungsten(0) did not favor a defined coordination of the [SCP][−] anion and considering the high utility of our anilidophosphine-supported lanthanum(III) framework to obtain relatively stable, yet still potentially reactive La–P and La–S bonds, we envisioned that the use of a Lewis-acidic metal ion such as lanthanum(III) might alter the charge distribution of the [SCP][−] anion sufficiently to give access to a defined S- or P-bound version and to study its chemistry in more detail.

Results and Discussion

Starting from either **1-Cl** or **1-I**, salt metathesis with an excess of Na(diox)_{2,3}SCP (1.4 equiv) in toluene was found to take place at room temperature and to result in the formation of a single new product **2** overnight (Scheme 1). This was



Scheme 1. Syntheses of complexes **2–4**, starting from **1-X**.

evident by the darkening of the initially pale yellow suspension and the ³¹P{¹H} NMR spectrum, showing a new singlet at $\delta = -44.9$ ppm which was assigned to the [SCP][−] phosphorus atom. After filtration, removal of toluene in vacuo and trituration with *n*-pentane, **2** was obtained as an amber solid in 98% isolated yield. In the ¹³C{¹H} NMR spectrum (C₆D₆) of the isolated material a doublet at $\delta = 191.8$ ppm (¹J_{CP} = 20.6 Hz), corresponding to the [SCP][−] carbon atom,^[13] suggested a defined coordination. Additionally, sharp signals indicated little to no rearrangement on the NMR timescale. Notably, **2** is well soluble and stable for weeks in aromatic (benzene, toluene) and for days in etheric (diethyl ether, tetrahydrofuran) solvents at room temperature, in stark contrast to the previously reported [K(18-crown-6)][W(CO)₅(SCP)].^[12] It is also slightly soluble and very stable in aliphatic solvents (*n*-pentane, *n*-hexane), and decomposes only very slowly (over days of refluxing at 45 °C) in dichloromethane to reform the halide complex **1-Cl** (Figure S10) and intractable, insoluble precipitates. Having uncovered a clean reaction for the [SCP][−] anion, we sought to assess the influence of the charge distribution of the (hetero-)cumulene anion on its

binding mode at lanthanum(III). Due to the different distribution of negative charge density in the thiocyanate anion ([SCN][−]; NBO atomic charges correspond to −0.47 for S, 0.06 for C and −0.59 for N),^[13] complex **3** was selected as a reference compound. To also study a trinuclear anion with a more evenly distributed charge density, we synthesized the azide complex **4**. Complexes **3** and **4** were both obtained by salt metathesis from **1-I** and KSCN (1.2 equiv) or KN₃ (1.5 equiv) in THF at room temperature overnight and isolated in 62% yield (for **3**) and 82% crude yield (for **4**).^[18] Besides a minor shift of the PN ligand singlet resonance in the ³¹P{¹H} NMR spectrum (C₆D₆) from $\delta = 9.9$ ppm for **1-I** to $\delta = 10.1$ ppm for **3** and a new broad singlet resonance at $\delta = 142.6$ ppm in the ¹³C{¹H} NMR spectrum, a dominant absorption band in the IR spectrum at $\nu = 2008$ cm^{−1} indicated the coordination of thiocyanate.^[19] Similarly, the coordination of the azide anion in complex **4** was inferred from a shift of the PN ligand resonance in the ³¹P{¹H} NMR spectrum (C₆D₆) to $\delta = 5.1$ ppm and a strong IR absorption band at $\nu = 2113$ cm^{−1}.^[20]

X-ray quality crystals of complex **2** could be grown by slow evaporation of a concentrated toluene solution at room temperature (Figure 1). To our great surprise, we found that the [SCP][−] anion is neither solely S- nor P-coordinated, but instead is bound in a side-on η^3 -fashion. Although this was unexpected, considering the fact that most of the negative charge density is located on the central carbon atom of a linear [S–C≡P][−] unit,^[13] the participation of all three atoms in the coordination to a strongly Lewis-acidic metal ion such as lanthanum(III) can be reasonably rationalized. In fact, significant coordination of the central carbon atom to lanthanum(III) is evident by comparing the La1–S1, La1–C1, and La1–P5 distances which lie at 3.036(2), 2.837(7), and 3.343(2) Å, respectively. These values also show that the [SCP][−] anion is slightly tilted with respect to the lanthanum(III) ion in the solid state. The bond lengths within the [SCP][−] anion are 1.607(7) and 1.568(7) Å for S1–C1 and C1–P5, respectively, resembling the values which are reported for the

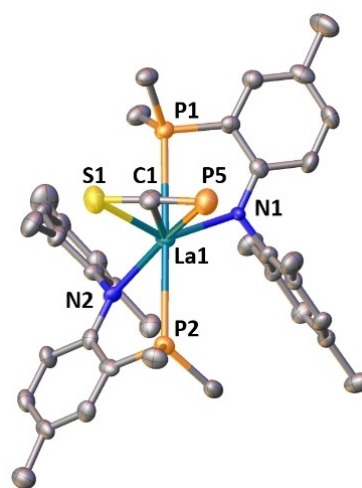


Figure 1. Thermal ellipsoid plot of complex **2**. Thermal ellipsoids are shown at a probability level of 50%. Hydrogen atoms have been omitted and ⁱPr groups truncated for clarity.^[35]

free $[\text{SCP}]^-$ anion (S–C 1.613(4) Å and C–P 1.579(4) Å).^[12,13] The S1–C1–P5 angle of 175.4(5)° in complex **2** is slightly more acute compared to 179.3(3)° in the free anion. X-ray quality crystals of reference compounds **3** and **4** were obtained either by gas diffusion of *n*-hexane into a C_6D_6 solution of **3** at room temperature overnight or by storing a concentrated toluene extract of **4** at room temperature for 24 h. In contrast to the $[\text{SCP}]^-$ anion, in both reference complexes, the thiocyanate and the azide anions do not engage in side-on coordination, but instead show a 1,3-bridging coordination mode in the solid state (see Figure S49). In this context, the dinuclear structures of **3** and **4** strongly suggest that the unique binding mode of the $[\text{SCP}]^-$ anion in **2** is not enforced by potentially unfavorable steric interactions, but rather results from the distinctive electronic structure of 2-phosphaethynthiolate.^[13]

To gain further insights into the reasons for the stability of the unexpected side-on η^3 -coordination mode of the $[\text{SCP}]^-$ ligand, we investigated complex **2** by means of density functional theory^[21] with functionals PBE^[22] and PBE0^[23] together with def2-SV(P) bases,^[24] for details concerning the calculations see the Supporting Information (Section 5). The total interaction energy between $[\text{SCP}]^-$ and the cationic moiety amounts to 523 kJ mol^{-1} , calculated as energy difference without structure relaxation for the fragments. The interaction is mainly ionic, as is evident from the indicators for covalent bonds being very small. For the sum of the contacts S–La, C–La and P–La, the Mulliken overlap population^[25] is 0.01, and the shared electron number^[26] is 0.12. An increase of the La–E–C angles (E = P or S) from the optimum structure results in a rise of energy (by approx. 20 kJ mol^{-1} for 15–20°) to a maximum at 65 kJ mol^{-1} and 75 kJ mol^{-1} for a linearly S-bound and P-bound isomer of complex **2**, respectively (Figure 2, Tables S3 and S4). The overall distance of the $[\text{SCP}]^-$ anion to the cation is larger for these configurations, and thus the favorable ionic interaction is smaller. For clarity we note that for none of the structures shown in Figure 2 significant covalent interactions between

$[\text{SCP}]^-$ anion and the cation are observed. More strikingly however, for the η^3 -coordination mode of $[\text{SCP}]^-$ ligand the LUMO of **2** corresponds to the antibonding $[\text{SCP}]^- \pi^*$ -orbital (Figure 3, top) with a significant admixture of the matching

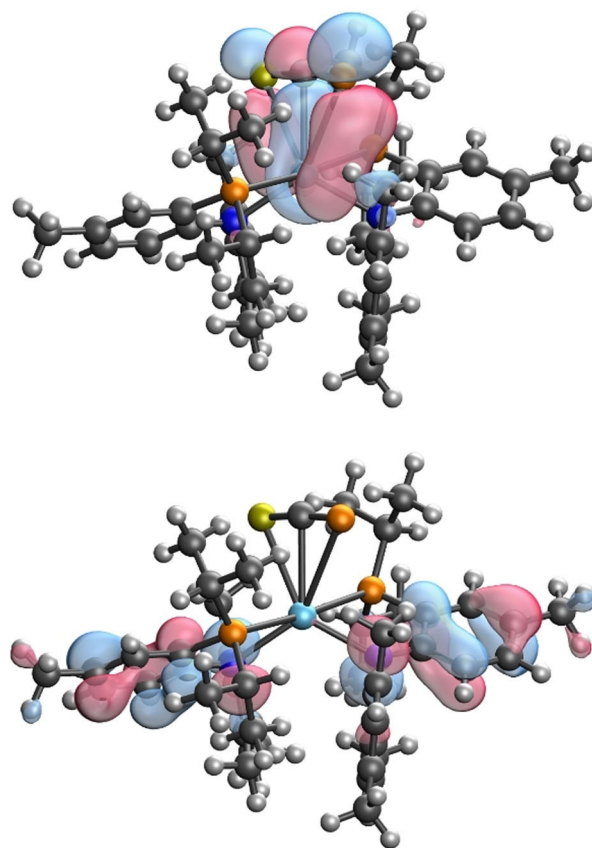


Figure 3. Frontier orbitals (HOMO, bottom; and LUMO, top) of complex **2**. Note that the LUMO of complex **2** reflects the bonding interaction of a π^* -orbital of the $[\text{SCP}]^-$ ligand with the matching d-orbital of the lanthanum(III) center.

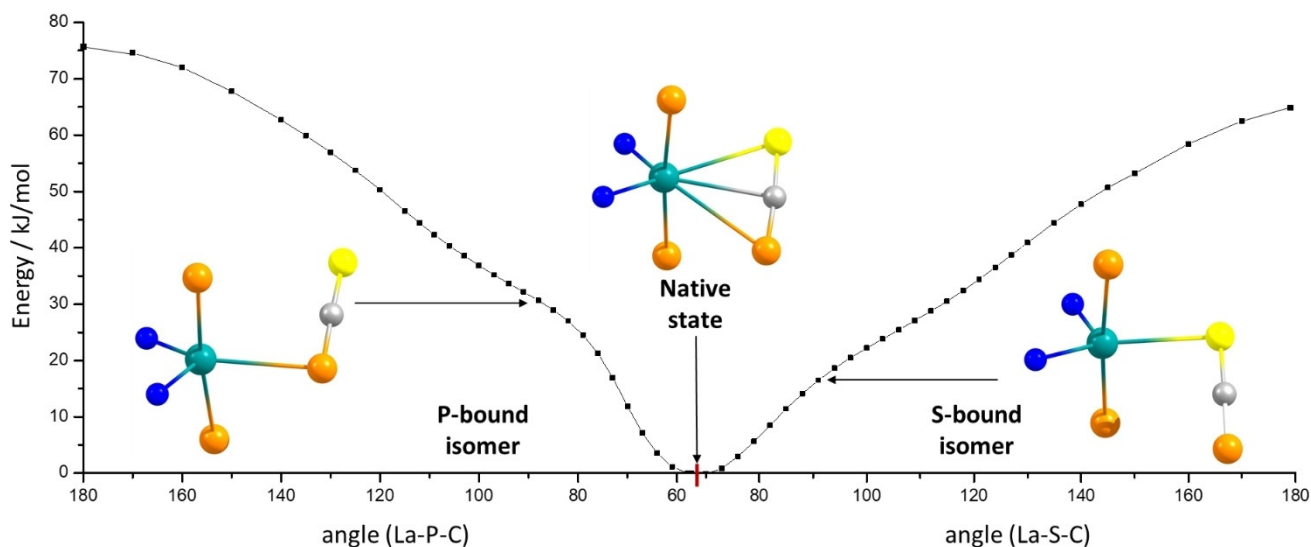
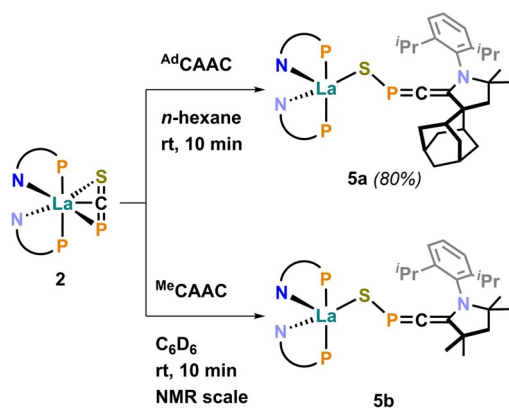


Figure 2. Relative energies of differently bound $[\text{SCP}]^-$ coordination isomers (P- vs. S-bound) compared to the side-on η^3 -coordinated $[\text{SCP}]^-$ anion, depending on the La–E–C (E = P or S) bond angles. The PN supporting ligands have been truncated for clarity.

La(d) orbital (Mulliken contribution ca. 35%). This should render complex **2** an ideal candidate to study the reactivity of the [SCP][−] anion towards nucleophiles.

Since cyclic alkyl amino carbenes (CAACs) are generally known for their ability to stabilize highly reactive, exotic structural motifs of main group elements,^[27] we decided to focus our efforts on this class of carbenes to achieve a potential functionalization of the [SCP][−] ligand. Indeed, when the sterically encumbering 1-(2,6-diisopropylphenyl)-3-adamantyl-5,5-dimethyl-pyrrolidin-2-ylidene (^{Ad}CAAC) was employed, a highly selective reaction with **2** in aromatic (benzene, toluene) and aliphatic (*n*-pentane, *n*-hexane) solvents was observed at room temperature (Scheme 2).



Scheme 2. Reactivity of complex **2** towards CAACs, yielding the “fulminate-type” complexes **5a** and **5b**.

Independent of the chosen solvent, the initially yellow reaction mixture immediately turned dark red upon addition of the CAAC (1 equiv), but returned to pale yellow within seconds. The ³¹P{¹H} NMR spectrum showed that the singlet of the former [SCP][−] ligand shifted from $\delta = -44.9$ ppm for **2** to $\delta = 139.4$ ppm for **5a**, indicating a major change of the electronic situation around the phosphorus atom. Product **5a** could be isolated in 80% yield by crystallization (see below). Its ¹³C{¹H} NMR spectrum (C₆D₆) showed a resonance at $\delta = 237.3$ ppm (vs. $\delta = 191.8$ ppm for **2**). A doublet splitting of this resonance with a larger coupling constant ($^1J_{CP} = 34.9$ Hz for **5a** vs. $^1J_{CP} = 20.6$ Hz for **2**) suggested that the phosphorus atom of the newly formed ligand in **5a** remained bound to the carbon atom, apparently with a stronger electronic interaction than in **2**. Importantly, no typical *C*_{carbene} resonance above $\delta = 200$ ppm could be detected for **5a**. Instead, ¹H–¹³C HMBC NMR spectroscopic studies of the new compound revealed the former *C*_{carbene} of the CAAC moiety to resonate at $\delta = 152.2$ ppm ($^2J_{CP} = 6.1$ Hz), indicating a nucleophilic attack of the CAAC at the central carbon atom of the [SCP][−] ligand. This reactivity does not seem to depend on the steric profile of the CAAC, since the less sterically encumbering CAAC 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene (^{Me}CAAC, Scheme 2, complex **5b**) gave comparable results (for details see Figures S34–S44 in the Supporting Information).

Due to the high solubility of **5b** even in non-polar solvents such as hexamethyldisiloxane (HMDSO), this product could

not be crystallized under any conditions tested (see experimental section in the Supporting Information). On the contrary, X-ray quality crystals of **5a** could be grown from a concentrated *n*-hexane solution (see above) over three days at room temperature (Figure 4). Strikingly, the connectivity as

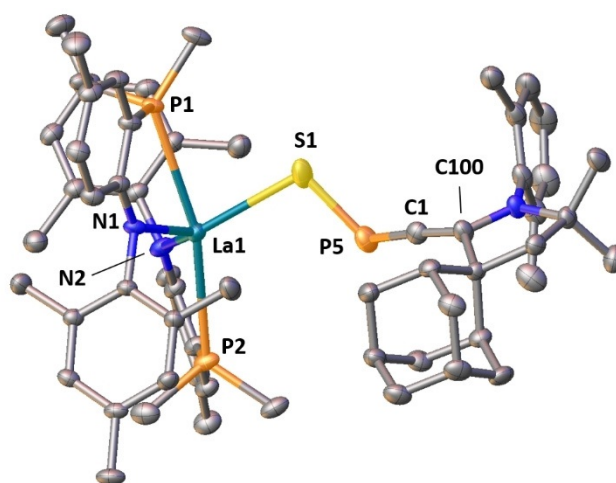


Figure 4. Thermal ellipsoid plot of complex **5a**. Thermal ellipsoids are shown at a probability level of 50%. Hydrogen atoms have been omitted and ⁱPr groups truncated for clarity.^[35]

found in the former [SCP][−] ligand has changed to a formally CAAC-stabilized “fulminate-like” [CPS][−] anion, with the sulfur atom binding κ^1 to lanthanum(III). A closer examination of the bond metrics within the [^{Ad}CAAC–CPS][−] ligand of **5a** suggests a *C*_{CAAC}=C=P–S[−] heteroallene structure (C100–C1 1.36(2) Å; C1–P5 1.63(2) Å). While the *C*_{CAAC}=C=P unit is almost linear (C100–C1–P5 173.8(1)°), the angle around the phosphorus atom is strongly bent (C1–P5–S1 111.1(5)°). The La1–S1 distance was found to be 2.950(2) Å and is slightly longer compared to the reported lanthanum–sulfur single bond in (PN)₂La(SMes) (2.718(1) Å),^[15] indicating a reduced negative charge on the sulfur atom and a potential partial conjugation of the *C*_{CAAC}=C=P unit with the P–S bond. This would be in line with the P5–S1 bond length of 2.081(3) Å, which lies in between the values for a S=P double (ca. 1.95 Å)^[28] and S–P single bond (ca. 2.12 Å).^[29] A phosphoalkene thioether has recently been reported by Jones and Kollmann,^[30] showing a S–P bond length (2.095(1) Å) comparable to the one determined in **5a**. Additionally, the solid state structure of **5a** reveals a close contact between the CPS phosphorus atom and one of the Dipp–CH₃ substituents of the formal ^{Ad}CAAC unit (P⋯C distance of approx. 3.682 Å). The retention of this close contact in solution can be inferred from a strong cross correlation peak between the corresponding Dipp–CH₃ protons and the CPS phosphorus atom at $\delta = 1.36/139.3$ ppm in the ¹H–³¹P HMBC NMR spectrum of **5a** (Figure S33). Furthermore, in the ¹³C{¹H} NMR spectrum a doublet splitting of the corresponding methyl resonance at $\delta = 27.0$ ppm ($^1J_{CP} = 9.8$ Hz) gives further evidence for a through-space interaction. Similar interactions have been previously shown to be harbingers of intriguing reactivity.^[31] Finally, in contrast to the IR spectrum of **2**, complex **5a** shows

a distinct strong absorption band at $\nu = 1674 \text{ cm}^{-1}$, which serves as another useful indicator for the $\text{C}=\text{C}=\text{P}-\text{S}^-$ structural motif.

For a better understanding of the SCP to CPS rearrangement, the reaction pathway from **2** and $^{\text{Ad}}\text{CAAC}$ to **5a** was calculated and optimized as specified in detail in the Supporting Information. The results are shown in Figure 5,

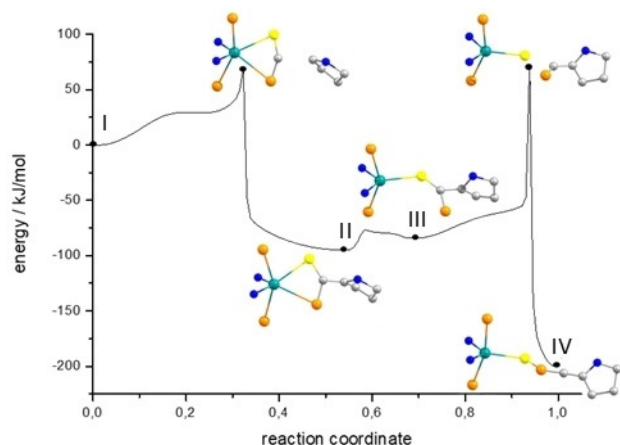


Figure 5. Optimized reaction pathway for the formation of **5a** out of **2** and $^{\text{Ad}}\text{CAAC}$. Stationary points (black circles) are fully optimized; imaginary frequencies: TS1: $166i \text{ cm}^{-1}$, TS2: $244i \text{ cm}^{-1}$. The pathways between the stationary points are optimized by a nudged-elastic-band-type procedure. The PN ligands and the $^{\text{Ad}}\text{CAAC}$ fragment have been truncated for clarity.

with the stationary points (black circles) being fully optimized. Structures II–IV are local minima (no imaginary frequencies); for the two transition structures, which are ca. 50 kJ mol^{-1} higher in energy than the initial structure I, the imaginary frequencies amount to $166i \text{ cm}^{-1}$ and $244i \text{ cm}^{-1}$. Finally, the pathways between the stationary points were optimized by a nudged-elastic-band-type procedure proposed by Plessow.^[32] The initial step is the nucleophilic attack of the CAAC at the central carbon atom of the $[\text{SCP}]^-$ unit, leading to structure II, a thio-carboxphosphide (a heavy analogue of a carboxamide). A barrier of ca. 70 kJ mol^{-1} needs to be overcome to reach this intermediate structure, which is lower in energy by ca. 100 kJ mol^{-1} compared to structure I. Proceeding along the reaction coordinate, the next step is the dissociation of the phosphorus atom from the lanthanum(III) center, leading to structure III, which is higher in energy by ca. 20 kJ mol^{-1} than structure II and can be reached without a significant barrier. For the ultimate “flip” of the CP unit to the CPS arrangement in the fulminate anion (structure IV) another transition state must be passed, which is as high in energy as the first one. We note in passing that for this transition structure the covalent interactions between S and P or C are very weak, with shared electron numbers^[26] of ca. 0.1 between S and the other two atoms; the two units are held together rather by ionic interactions between the negatively charged S and the positively charged P atom, as worked out in detail in the Supporting Information (Figure S52). The formation of a thermodynamically favored P–S bond might be one of the driving forces of this unusual rearrangement

reaction with an overall energy gain of ca. 200 kJ mol^{-1} . The experimental observation that upon addition of the CAAC the reaction mixture initially turns dark red, before brightening up to a yellow color within the first 30 seconds of the reaction, is in line with the calculated electronic excitation spectra (Figure S51). The lowest-energy excitations for the product (structure IV) are at 2.8 eV, for the starting material (structure I) at 2.6 eV, but at only 2.2 eV for the “thio-carboxphosphide-type” intermediate structure II. Moreover, the character of the excitation for structure II is of a very different form compared to that of the other structures, see Figure S51. Similar carbene-induced rearrangements of the $[\text{OCP}]^-$ anion to “fulminate-like” structural motifs have been described by Grützmaier^[33,34] and Goicoechea^[6] and co-workers for systems based on phosphorus,^[33] silicon,^[34] and boron.^[6] With the synthesis of complexes **5a** and **5b** we could extend this type of isomerization chemistry to a f-block metal-based system, yielding the first heavier group 15–group 16 analogue of a substituted “fulminate-like” anion.

Conclusion

We have presented the first stable coordination of the $[\text{SCP}]^-$ anion to a lanthanum(III) ion. Strikingly, the $[\text{SCP}]^-$ anion in complex **2** neither adopts a S- nor a P-bound end-on coordination mode as is typically encountered for other (hetero)-cumulene ligands such as, for example, thiocyanate or azide (complexes **3** and **4**). Instead, η^3 -coordination was found, which had been an unknown coordination behavior for such (heavy) $[\text{ChCPn}]^-$ ($\text{Ch} = \text{Chalcogen}$, $\text{Pn} = \text{Pnictogen}$) anions up to this point and which is likely governed by the electronic structure of the $[\text{SCP}]^-$ anion. Despite the interactions between the lanthanum(III) complex fragment and the $[\text{SCP}]^-$ ligand being mostly ionic, theoretical studies revealed the LUMO of complex **2** to correspond mainly to a linear combination of the antibonding π^* -orbital of the $[\text{SCP}]^-$ ligand and the geometrically compatible lanthanum(III) d-orbital. Complex **2** therefore showed a high reactivity towards strongly nucleophilic CAACs, which resulted in the rearrangement and concomitant functionalization of the $[\text{SCP}]^-$ unit to give formally CAAC-stabilized heavy fulminate-type anions in the products **5a,b**. Future work will be dedicated to expanding our studies towards other heavy $[\text{ChCPn}]^-$ anions, to investigating different modes of reactivity of the side-on coordinate $[\text{SCP}]^-$ anion and to exploring the synthetic utility of the new fulminate-type anions (in, for example, cycloadditions) for disclosing new avenues of f- and heavy main group element chemistry.

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Keywords: cyanates · f-elements · lanthanides · main-group chemistry · phosphines

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