

Article

New Lanthanide Alkynylamidates and Diiminophosphinates

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Abstract: This contribution reports the synthesis and structural characterization of several new lithium and lanthanide alkynylamidate complexes. Treatment of $\text{PhC}\equiv\text{CLi}$ with N,N' -diorganocarbodiimides, $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ ($\text{R} = i\text{Pr}, \text{Cy}$ (cyclohexyl)), in THF or diethyl ether solution afforded the lithium-propiolamidates $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2] \text{S}$ (**1**: $\text{R} = i\text{Pr}$, $\text{S} = \text{THF}$; **2**: $\text{R} = \text{Cy}$, $\text{S} = \text{THF}$; **3**: $\text{R} = \text{Cy}$, $\text{S} = \text{Et}_2\text{O}$). Single-crystal X-ray diffraction studies of **1** and **2** showed the presence of typical ladder-type dimeric structures in the solid state. Reactions of anhydrous LnCl_3 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}$ or Ho) with **2** in a 1:3 molar ratio in THF afforded a series of new homoleptic lanthanide tris(propiolamidate) complexes, $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2]_3\text{Ln}$ (**4**: $\text{Ln} = \text{Ce}$; **5**: $\text{Ln} = \text{Nd}$; **6**: $\text{Ln} = \text{Sm}$; **7**: $\text{Ln} = \text{Ho}$). The products were isolated in moderate to high yields (61%–89%) as brightly colored, crystalline solids. The chloro-functional neodymium(III) bis(cyclopropylethynylamidate) complex $[\{i\text{-C}_3\text{H}_5-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2\}_2\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$ (**8**) was prepared from NdCl_3 and two equiv. of $\text{Li}[i\text{-C}_3\text{H}_5-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]$ in THF and structurally characterized. A new monomeric Ce(III)-diiminophosphinate complex, $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**), has also been synthesized in a similar manner from CeCl_3 and two equiv. of $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]$. Structurally, this complex resembles the well-known “ate” complexes $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$. Attempts to oxidize compound **9** using trityl chloride or phenyliodine(III) dichloride did not lead to an isolable cerium(IV) species.

Keywords: amidinate; alkynylamidinate; diiminophosphinate; lithium; lanthanide complexes; crystal structure

1. Introduction

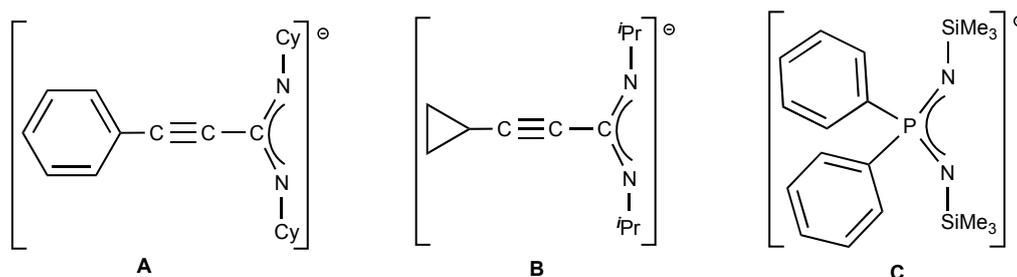
Monoanionic *N,N'*-chelating ligands like amidinates, $[\text{RC}(\text{NR}')_2]^-$, guanidates, $[\text{R}_2\text{NC}(\text{NR}')_2]^-$, and diiminophosphinates, $[\text{R}_2\text{P}(\text{NR}')_2]^-$, are commonly regarded as steric equivalents of the omnipresent cyclopentadienyl ligands [1–7]. In the case of rare-earth metals, mono-, di- and trisubstituted lanthanide amidinate and guanidate complexes are all accessible, just like the mono-, di- and tricyclopentadienyl complexes. Over the past *ca.* 25 years, lanthanide amidinates have undergone an impressive transformation from laboratory curiosities to highly efficient homogeneous catalysts as well as versatile precursors in materials science. Lanthanide amidinates have been demonstrated to be efficient homogeneous catalysts e.g., for ring-opening polymerization reactions of lactones, the guanylation of amines, the addition of terminal alkynes to carbodiimides, as well as hydroamination and hydroamination/cyclization reactions [8,9]. Moreover, homoleptic alkyl-substituted lanthanide tris(amidinate) complexes often exhibit high volatility and can be employed as promising precursors for ALD (atomic layer deposition) and MOCVD (metal-organic chemical vapor deposition) processes, e.g., for the deposition of lanthanide oxide (Ln_2O_3) or lanthanide nitride (LnN) thin layers [10–19].

What makes the amidinate and guanidate ligands extremely versatile is the possibility of varying the substituents at all three atoms of the N–C–N unit. Attachment of an alkynyl substituent to the central carbon atom of amidines leads to alkynylamidines, $\text{R}-\text{C}\equiv\text{C}-\text{C}(=\text{NR}')(\text{NHR}')$. Alkynylamidines are of significant interest due to their diverse applications in organic synthesis [20–23] as well as in biological and pharmacological systems [24–27]. Alkynylamidinate complexes of various transition metals and lanthanides have been shown to be efficient and versatile catalysts e.g., for C–C and C–N bond formation, the addition of C–H, N–H and P–H bonds to carbodiimides as well as ϵ -caprolactone polymerization [28–33]. Previously used alkynylamidinate ligands include e.g., the propiolamide derivatives $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NR}')_2]^-$ ($\text{R} = \textit{i}\text{Pr}, \textit{t}\text{Bu}$) [16,28,34] and the trimethylsilylacetylene-derived anions $[\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}(\text{NR}')_2]^-$ ($\text{R} = \text{cyclohexyl (Cy)}, \textit{i}\text{Pr}$) [35]. In 2008, the compound $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}\textit{i}\text{Pr})_2]$ has been reported to be suitable precursor for the preparation of *d*-transition metal complexes containing bridging alkynylamidinate ligand [36]. Moreover, the same ligand has been used in the synthesis of the unsolvated homoleptic Ce(III) complex $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}\textit{i}\text{Pr})_2]_3\text{Ce}$ [16].

In the course of our ongoing investigation of lanthanide amidinates we recently started a project to study lanthanide alkynylamidinates derived from phenylacetylene and cyclopropylacetylene. The cyclopropyl group was chosen because of the well-known electron-donating ability of this substituent to an adjacent electron-deficient center [37–43]. This would provide a rare chance to electronically influence the amidinate ligand system rather than altering only its steric demand. In the course of this study, we first reported the synthesis and full characterization of a series of lithium-cyclopropylethynylamidinates [44]. These precursors are readily available on a large scale using commercially available starting materials (cyclopropylacetylene, *N,N'*-diorganocarbodiimides). In subsequent contributions, we described the first trivalent rare-earth metal complexes comprising

the new cyclopropylethynylamidinate ligands and their use as guanylation, hydroamination, and hydroacetylenation catalysts [45–47].

We now report the synthesis and structural characterization of two lithium-propiolamidinates and their use as precursors for new homoleptic lanthanide(III)-tris(propiolamidinate) complexes. Moreover, the synthesis and crystal structures of a dimeric neodymium(III) bis(cyclopropylethynylamidinate) complex and a monomeric Ce(III)-diiminophosphinate complex are reported. Scheme 1 shows the anionic N,N' -chelating ligands employed in this study.

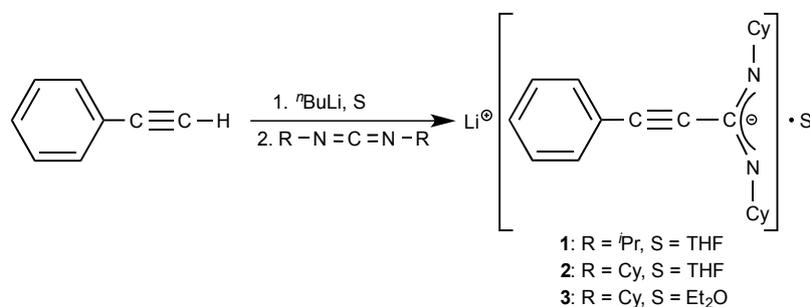


Scheme 1. Anionic N,N' -chelating ligands employed in this study: N,N' -Dicyclohexylpropiolamidinate (**A**); N,N' -diisopropyl-cyclopropylethynylamidinate (**B**); and N,N' -bis(trimethylsilyl)- P,P -diphenyldiiminophosphinate (**C**).

2. Results and Discussion

2.1. Lithium-Propiolamidinate Precursors

While the N,N' -isopropyl-substituted lithium-propiolamidinate salt $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]$ THF (**1**) was already known from previous studies [16,28,34], we prepared the cyclohexyl derivatives **2** and **3** in a straightforward manner according to Scheme 2 by *in situ* deprotonation of phenylacetylene with $n\text{BuLi}$ at $-20\text{ }^\circ\text{C}$ in THF or Et_2O followed by addition of N,N' -dicyclohexylcarbodiimide. After 10 min, the reaction mixtures were warmed to room temperature and stirred for two hours. The solvent was removed under vacuum, affording white solids of $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2]\cdot\text{S}$ (**2**: $\text{S} = \text{THF}$, **3**: $\text{S} = \text{Et}_2\text{O}$) in good yields (**2**: 88%, **3**: 76%).



Scheme 2. Synthesis of the lithium-propiolamidinates **1–3**.

Both alkynylamidinates **2** and **3** have been fully characterized by spectroscopic methods and elemental analysis. The IR spectrum of **2** shows a medium band at 2217 cm^{-1} , which could be assigned to the $\text{C}\equiv\text{C}$ triple bond, while in the spectrum of **3** it appears as a weak band at 2211 cm^{-1} . The $\text{C}=\text{N}$

stretching vibrations of the NCN unit of amidinate moieties is observed at 1610 cm^{-1} as a very strong band in the spectrum of **2** and at 1592 cm^{-1} as strong band in that of **3** [16]. The NMR spectra were recorded in toluene- d_8 and C_6D_6 for **2** and **3**, respectively. The ^1H and ^{13}C NMR analyses were in good agreement with the formation of $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2]$. Resonances of all protons and carbons were observed except for the carbon atom of the NCN unit and one C atom of the two acetylenic carbon atoms in **3**.

Single-crystal X-ray diffraction studies were carried out on the lithium-propiolamidinates **1** and **2**. In both cases, X-ray quality, block-like single-crystals were obtained by cooling saturated solutions in THF to $5\text{ }^\circ\text{C}$ for a few days. Figures 1 and 2 depict the molecular structures of **1** and **2** along with selected bond lengths and angles, while crystallographic details are listed in Table 1. Full crystallographic data can be found in the Supplementary Information. The crystal structure determinations of $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]$ THF (**1**) and $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2]$ THF (**2**) in both cases revealed the presence of a ladder-type dimeric structure, which is the most characteristic structural motif of most previously characterized lithium amidinates and guanidates [48–58]. The dimers are centrosymmetric with the central Li_2N_2 ring being strictly planar. In the solid state, both lithium propiolamidinates crystallize in the triclinic space group P-1 with one dimeric molecule in the unit cell. The bond lengths and bond angles are in good agreement with similar structures of amidinate ligands [48–58]. The N–C distances in the amidinate N–C–N unit are $1.321(2)$ and $1.330(2)$ Å in **1** and $1.3201(13)$ and $1.3407(12)$ Å in **2**. These values clearly indicate uniform π -delocalization within the N–C–N moieties. The distances Li–N distances $1.990(3)$ and $2.261(3)$ Å in **1** and $2.031(2)$ and $2.188(2)$ Å in **2**, while the $\text{C}\equiv\text{C}$ bond lengths are virtually identical with $1.189(2)$ Å (**1**) and $1.2018(18)$ Å (**2**). The bond angles N–C–N and N–Li–N are $119.13(13)^\circ$ and $64.67(10)^\circ$ in the isopropyl derivative **1** and $118.89(8)^\circ$ and $65.67(6)^\circ$, respectively, in the cyclohexyl-substituted derivative **2**.

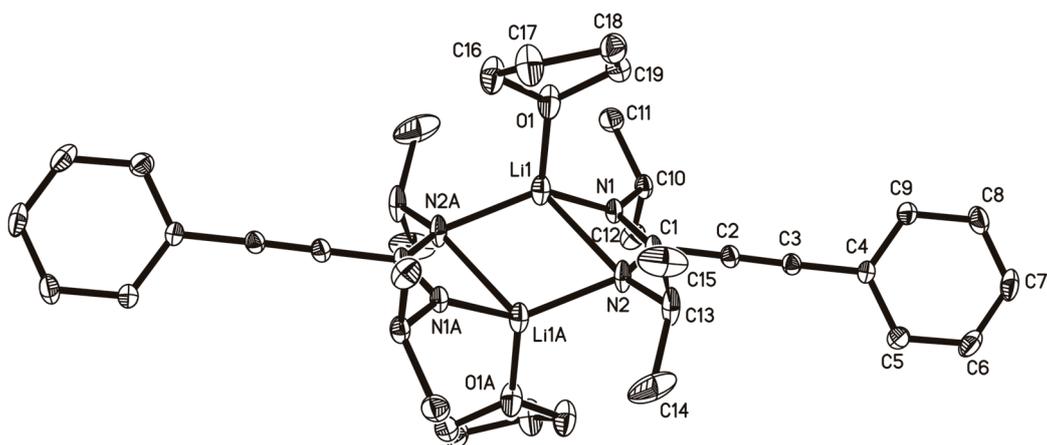


Figure 1. Molecular structure of **1** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): O(1)–Li(1) $1.908(3)$, Li(1)–N(1) $1.990(3)$, Li(1)–N(2) $2.261(3)$, N(1)–C(1) $1.321(2)$, N(2)–C(1) $1.330(2)$, C(1)–C(2) $1.470(2)$, C(2)–C(3) $1.189(2)$, C(3)–C(4) $1.439(2)$, O(1)–Li(1)–N(1) $118.80(16)$, O(1)–Li(1)–N(2) $113.49(14)$, N(1)–Li(1)–N(2) $64.67(10)$, N(1)–C(1)–N(2) $119.13(13)$, N(1)–C(1)–C(2) $120.72(14)$, N(2)–C(1)–C(2) $120.15(14)$, C(3)–C(2)–C(1) $179.05(18)$, C(2)–C(3)–C(4) $178.56(17)$.

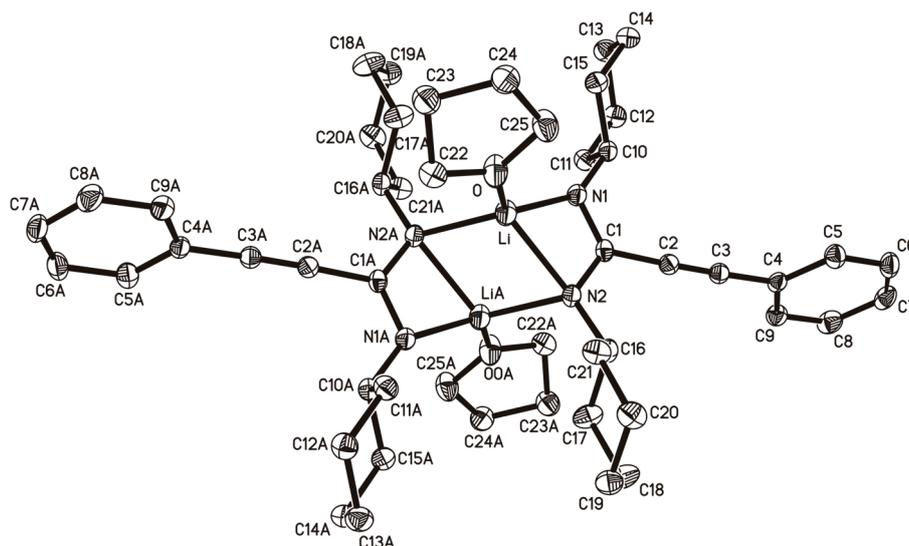
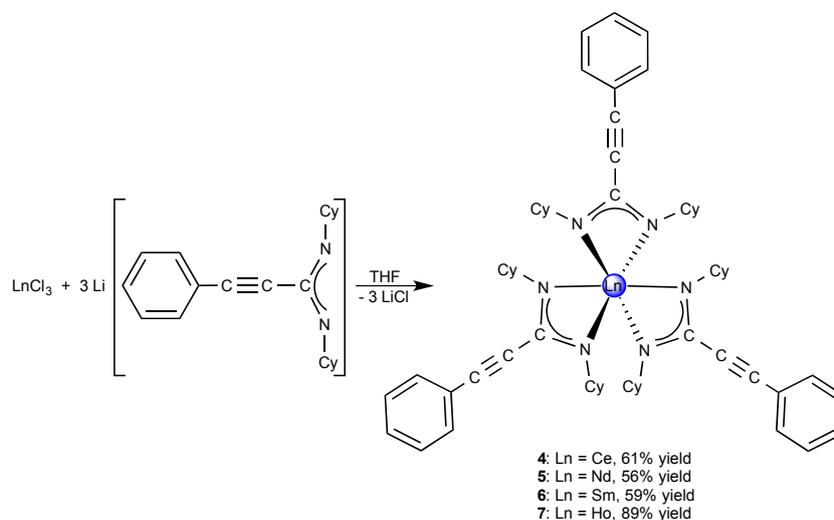


Figure 2. Molecular structure of **2** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): O–Li 1.9518(19), N(1)–C(1) 1.3201(13), N(1)–Li 2.031(2), N(2)–Li 2.188(2), N(2)–C(1) 1.3407(12), C(1)–C(2) 1.4681(13), C(2)–C(3) 1.2018(14), C(3)–C(4) 1.4366(13), O–Li–N(1) 126.92(10), O–Li–N(2) 122.23(9), N(1)–Li–N(2) 65.67(6), N(1)–C(1)–N(2) 118.89(8), N(1)–C(1)–C(2) 120.49(9), N(2)–C(1)–C(2) 120.58(9), C(3)–C(2)–C(1) 175.39(10), C(2)–C(3)–C(4) 178.27(11).

2.2. Homoleptic Lanthanide(III)-tris(Propiolamidinate) Complexes

A series of homoleptic lanthanide(III)-tris(propiolamidinates) were prepared in a straightforward manner according to Scheme 3. The reaction of anhydrous LnCl_3 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}$ or Ho) with **2** in a 1:3 molar ratio using THF as solvent afforded a series of new homoleptic lanthanide tris(propiolamidinate) complexes, $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2]_3\text{Ln}$ ($\text{Ln} = \text{Ce}$ (**4**), Nd (**5**), Sm (**6**), Ho (**7**)). The products were isolated in moderate to high yields (**4**: 61%, **5**: 56%, **6**: 59%, **7**: 89%) yields as unsolvated complexes in the form of brightly colored crystals (**4**: orange, **5**: pale green, **6**: yellow, **7**: bright yellow).



Scheme 3. Synthesis of the unsolvated, homoleptic lanthanide-tris(propiolamidinates) **4–7**.

The new unsolvated lanthanide-tris(propiolamidinate) complexes, $[\text{Ph-C}\equiv\text{C-C}(\text{NCy})_2]_3\text{Ln}$ (**4–7**), have been fully characterized by spectroscopic methods and elemental analysis. Unfortunately, attempted recrystallization of complexes **4–7** from various solvents such as toluene, pentane, THF or diethyl ether did not provide single-crystals suitable for X-ray diffraction. Only on one occasion, well-formed crystals of **7** obtained from *n*-pentane could be successfully subjected to X-ray diffraction, but the crystal quality was too poor to allow full refinement of the crystal structure. The NMR spectra were in good agreement with those of similar unsolvated homoleptic lanthanide amidinate complexes, $[\text{Ph-C}\equiv\text{C-C}(\text{N}^i\text{Pr})_2]_3\text{Ce}$ [16], $[\text{Ph-C}\equiv\text{C-C}(\text{N}^i\text{Pr})_2]_3\text{Y}$ and $[\text{Ph-C}(\text{NCy})_2]_3\text{Ln}$ (Ln = Pr, Nd or Sm) [59]. Due to the strongly paramagnetic nature of Ho^{3+} ion, it was impossible to obtain NMR spectra for **7**. According to the ^1H – ^{13}C correlation (HSQC) technique, the protons of CH in the cyclohexyl group observed at three different positions, $\delta = 9.49, 3.76$ and 3.56 ppm in **4** (Figure 3) and at $\delta = 18.33, 3.77$ and 3.57 ppm in **5** (Figure S1) are in agreement with the CH-protons in the complex $[\text{Ph-C}(\text{NCy})_2]_3\text{Ln}$ (Ln = Pr or Nd), whereas the CH-protons of *c*- C_6H_{11} in **6** (Figure S2) appear at $\delta 3.71$ and 3.30 ppm [34]. The significantly different chemical shifts of the CH proton resonances originate from the different paramagnetism of the Ce^{3+} , Nd^{3+} , and Sm^{3+} ions, respectively. The protons of the phenyl group appear in the range of $\delta = 7.40$ – 9.41 ppm [16,34].

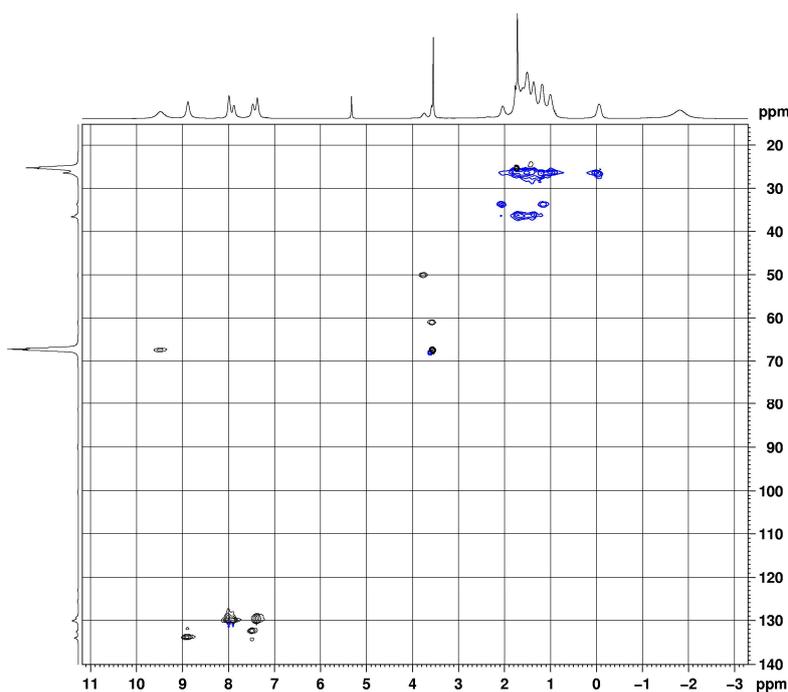


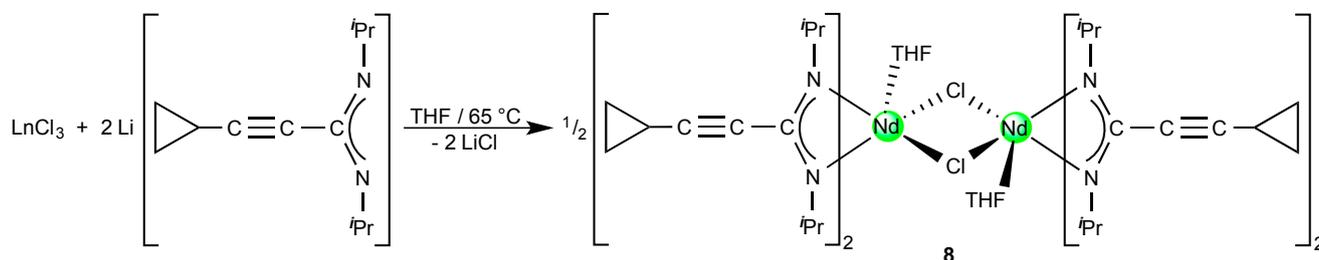
Figure 3. HSQC spectrum (400 MHz, $\text{THF-}d_8$, 25°C) of $[\text{Ph-C}\equiv\text{C-C}(\text{NCy})_2]_3\text{Ce}$ (**4**).

The ^1H NMR spectra reflected the stronger paramagnetic properties for the complexes of cerium **4** and neodymium **5** as compared to the less paramagnetic samarium complex **6**. On the other hand, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showed that the signals of the phenyl carbon atoms are observed in the range of $\delta = 125$ – 140 ppm in all three cases. The carbon atoms of the CH of the cyclohexyl groups are observed at $\delta = 67.1, 61.1$ and 56.3 ppm in **4**, and at $\delta = 78.5, 61.1$ and 50.0 ppm in **5**, whereas in **6** they appear at $\delta = 59.5$ and 57.4 ppm. The carbon atoms of the CH_2 in the cyclohexyl group appear in the same range at $\delta = 25.7$ – 36.5 ppm for all of three complexes. All data clearly showed that the new complexes

4–7 are unsolvated, homoleptic lanthanide(III)-tris(propiolamidinates) like the previously reported $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]_3\text{Ce}$ [16] and $[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]_3\text{Y}$ [34].

2.3. A Neodymium(III)-bis(Cyclopropylethynylamidinate)

We recently reported that reactions between anhydrous lanthanide trichlorides LnCl_3 ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}$) with two equiv. of the lithium-cyclopropylethynylamidinates $\text{Li}[c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C}-\text{C}(\text{NR})_2]$ ($\text{R} = ^i\text{Pr}, \text{Cy}$) in THF solution afford the chloro-functional lanthanide(III) bis(cyclopropylethynylamidinate) complexes $[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C}-\text{C}(\text{NR})_2\}_2\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$ ($\text{Ln} = \text{Ce}, \text{Nd}; \text{R} = ^i\text{Pr}, \text{Cy}$). In the course of this study, we carried out an X-ray diffraction study of the neodymium derivative $[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2\}_2\text{Nd}(\mu\text{-Cl})(\text{THF})_2]$ (**8**). This complex was prepared according to Scheme 4 by treatment of anhydrous NdCl_3 with two equiv. of $\text{Li}[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2]$ [44] following our synthetic protocol [45].



Scheme 4. Preparation of **8**.

Dark green, needle-like single crystals of **8** suitable for X-ray diffraction were obtained by slow cooling of saturated solutions in *n*-pentane to $-30\text{ }^\circ\text{C}$. The single-crystal X-ray diffraction study clearly established the presence of a chloro-bridged dimer of the composition $[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C}-\text{C}(\text{NR})_2\}_2\text{Nd}(\mu\text{-Cl})(\text{THF})_2]$. The molecular structure of **8** is depicted in Figure 4; the crystal and structural refinement data are summarized in Table 1. Complete structural data of **8** can be found in the Supplementary Information. The molecule is a centrosymmetric dimer of the type $[\text{L}_2\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$ comprising a planar four-membered Nd_2Cl_2 ring. With angles of $106.85(5)^\circ$ ($\text{Nd}-\text{Cl}-\text{Nd}$) and $73.15(5)^\circ$ ($\text{Cl}-\text{Nd}-\text{Cl}$), the central Nd_2Cl_2 moiety is rhomb-shaped. The cyclopropyl-ethynylamidinate ligands are coordinated in the “classical” N,N' -chelating coordination mode, and the chloro ligands act as bridging ligands. The coordination sphere around the large Nd^{3+} ion still leaves room for an additional THF ligand, resulting in a formal coordination number of seven around neodymium. It has been pointed out earlier [45], that in this respect the cyclopropylethynylamidinates differ from the related dimeric yttrium, ytterbium, and lutetium bis(guanidinato) complexes such as $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2\}_2\text{Y}(\mu\text{-Cl})_2]$ [60] and $[\{(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2\}_2\text{Ln}(\mu\text{-H})_2]$ [61]. In these compounds, the higher steric demand of the supporting guanidinate ligands prevents the formation of THF adducts, resulting in six-coordinate lanthanide ions. This shows that the steric demand of the cyclopropylethynylamidinate anions is significantly lower than that of the N,N -bis(trimethylsilyl)-substituted guanidinate anion $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NCy})_2]^-$. Within the $\text{N}-\text{C}-\text{N}$ groups the $\text{C}-\text{N}$ distances are equal (average $\text{C}-\text{N} = 1.335\text{ \AA}$), indicating full π -electron delocalization within the chelating amidinate units. The bond lengths of the triple bonds in the cyclopropylethynyl units are $\text{C}(2)-\text{C}(3) 1.186(9)\text{ \AA}$ and $\text{C}(22)-\text{C}(23) 1.188(9)\text{ \AA}$.

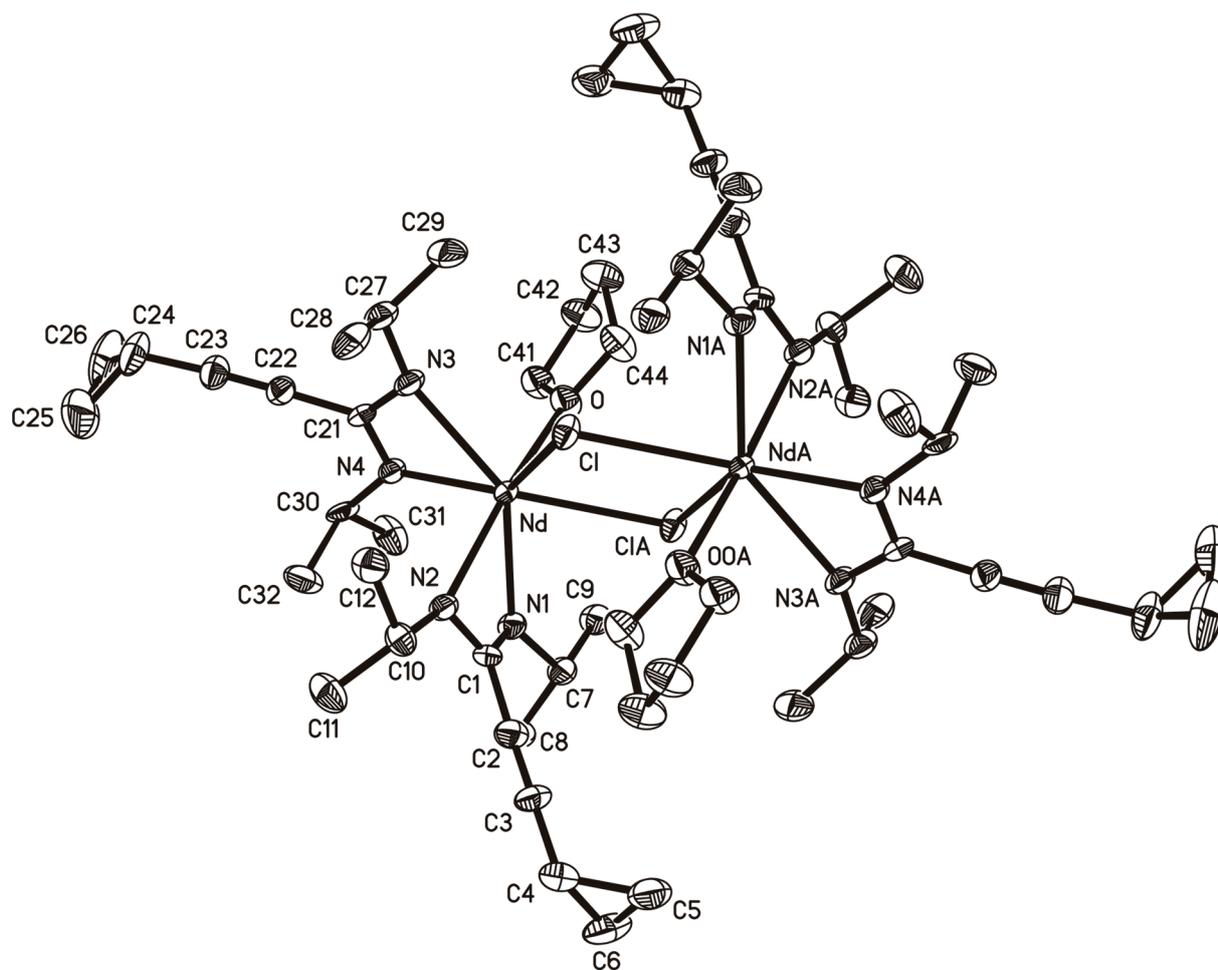
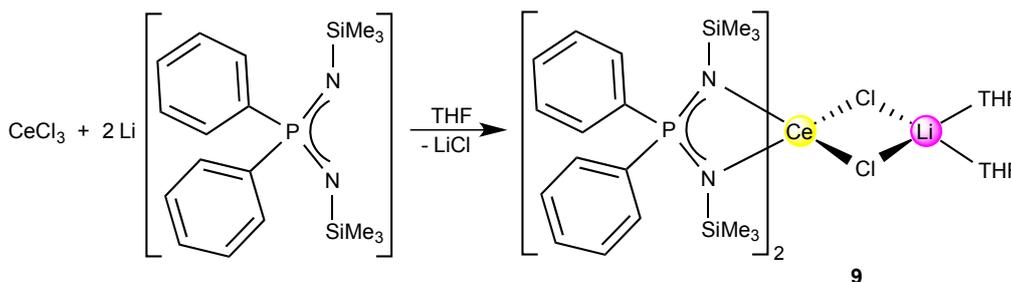


Figure 4. Molecular structure of **8** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cl–Nd 2.7961(16), Nd–N(1) 2.478(5), Nd–N(2) 2.423(5), Nd–N(4) 2.464(5), Nd–N(3) 2.484(5), Nd–O 2.504(5), N(1)–C(1) 1.338(8), N(2)–C(1) 1.332(7), N(3)–C(21) 1.321(8), N(4)–C(21) 1.345(7), N(4)–C(30) 1.456(8), C(1)–C(2) 1.444(8), C(2)–C(3) 1.186(9), C(3)–C(4) 1.425(10), C(21)–C(22) 1.458(8), C(22)–C(23) 1.188(9), C(23)–C(24) 1.439(9), Nd–Cl–NdA 106.85(5), Cl–Nd–ClA 73.15(5), N(2)–Nd–N(4) 91.56(17), N(2)–Nd–N(1) 54.95(17), N(4)–Nd–N(3) 54.74(16), N(2)–C(1)–N(1) 115.9(5), N(3)–C(21)–N(4) 117.1(5).

2.4. A Cerium(III)-bis(Diiminophosphinate) Complex

Rare-earth metal complexes comprising related N–P–N chelating diiminophosphinate ligands $[R_2P(NR')_2]^-$ were first reported in the literature in 1989 [62], although the number of well-characterized examples remains small [63,64]. However, there is renewed interest in this class of compounds. A recent report by Cui *et al.* demonstrated that new diiminophosphinato-supported lanthanide dialkyl complexes are valuable catalysts for the 3,4-polymerization of isoprene. The NPN-bidentate diiminophosphinate-ligated rare-earth metal complexes provided both high *syndio*- and *iso*-3,4-selectivities (3,4 > 99%, *rr* = 66%, *mmmm* = 96%), depending on the frameworks, steric environment and geometry of the ligands. The regio- and stereoselective mechanisms proceeding in these systems

were explicated by DFT simulation [65]. A new monomeric Ce(III)-diiminophosphinate complex, $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**), has been synthesized in the course of this work. The starting material $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]$ was prepared according to the literature method [66,67]. According to Scheme 5, a suspension of anhydrous CeCl_3 in THF was added to a solution of $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]$ in THF. The reaction mixture was stirred over night at room temperature. The product **9** was extracted as a golden-yellow solution in *n*-pentane. Complex **9** was isolated as an exceedingly air- and moisture-sensitive bright yellow, block-like crystals at 5 °C in 78% yield.



Scheme 5. Preparation of **9**.

The new compound $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**) has been fully characterized by spectroscopic methods, elemental analysis and single-crystal X-ray diffraction. The molecular structure of **9** is in good agreement with related structures such as $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Sm}(\mu\text{-I})_2\text{Li}(\text{THF})_2$ [63]. The IR spectrum showed medium bands at 1180 and 1116 cm^{-1} , which can be assigned to the PNSi unit. The strong bands that appear at 1246, 933 and 840 cm^{-1} can be attributed to the SiMe_3 groups. The ^1H NMR spectrum of **9** shows sets of signals assignable to the phenyl groups and the coordinated THF molecules. Due to the paramagnetic nature of the Ce^{3+} ion, the protons of the $\text{Si}(\text{CH}_3)_3$ groups appear as singlets at high magnetic field at $\delta = -6.50$ ppm. The X-ray study revealed the presence of the “ate” complex $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**). The cerium(III) ion is coordinated with four nitrogen atoms of the diiminophosphinate ligands and two bridging chloride ions, giving a formal coordination number of six, as shown in Figure 5. The phenomenon of “ate” complex formation via retention of alkali metal halides in the products is quite common in organolanthanide chemistry [68]. It can be traced back to the strong tendency of the large Ln^{3+} ions to adopt high coordination numbers.

Compound **9** crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ with four molecules of the complex in the unit cell. The average Ce–N bond distance (2.551 Å) is almost identical compared to the Ce–N distances in cerium(III) amidinate complexes such as $[\text{Ph-C}\equiv\text{C-C}(\text{N}^i\text{Pr})_2]_3\text{Ce}$ [16] and $[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C-C}(\text{NR})_2\}]_2\text{Ce}(\mu\text{-Cl})(\text{THF})_2$ ($\text{R} = ^i\text{Pr}, \text{Cy}$) [45]. Likewise, the Ce–Cl distance (average 2.810 Å) is very similar. The bond lengths P1–N1 (1.593(2) Å), P1–N2 (1.594(2) Å), P2–N3 (1.597(2) Å) and P2–N3 (1.593(2) Å) are almost equal, confirming the delocalization of the negative charge in the N1–P1–N2 and N3–P2–N4 units, respectively. The bond angles N1–Ce–N2 (60.96(7)°) and N3–Ce–N4 (60.80(7)°) in **9** are somewhat larger than those observed in $[\{c\text{-C}_3\text{H}_5\text{-C}\equiv\text{C-C}(\text{NR})_2\}]_2\text{Ce}(\mu\text{-Cl})(\text{THF})_2$ ($\text{R} = ^i\text{Pr}, \text{Cy}$) [45]. The bond angles Ce–Cl1–Li, Cl1–Li–Cl2, and Cl1–Ce–Cl2 are 39.80(10)°, 97.7(2)° and 79.01(3)°, respectively, to form the rhomb-shaped Ce–Cl1–Li–Cl2 unit. Two THF ligands complete the distorted tetrahedral coordination sphere around lithium.

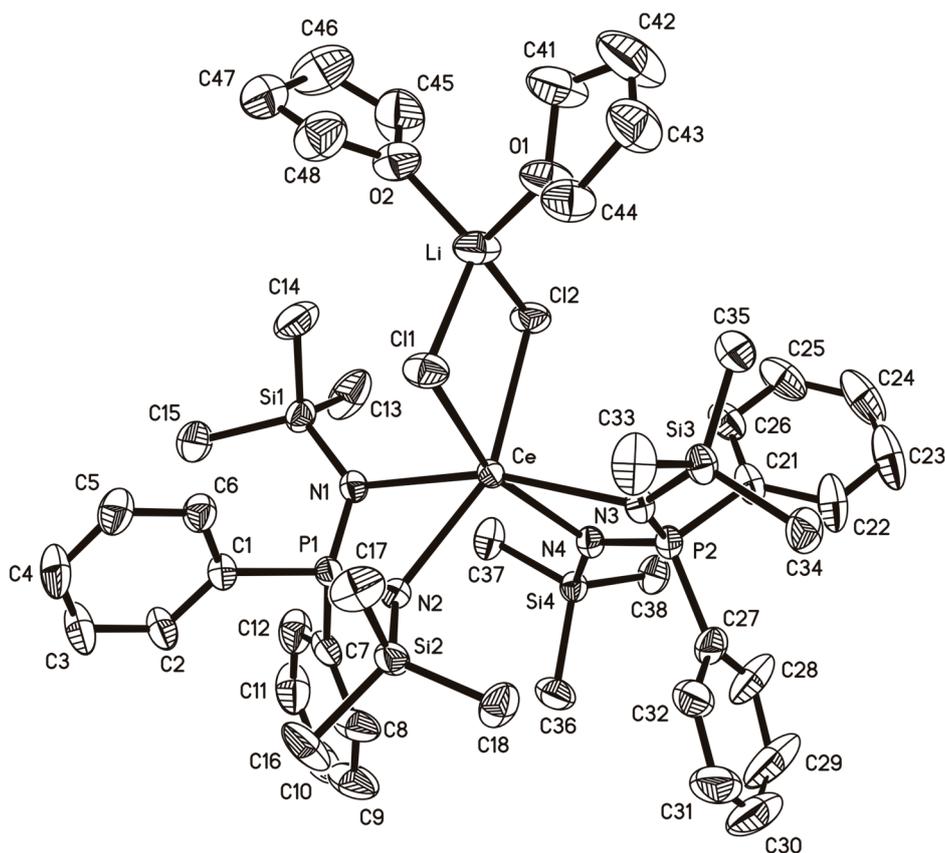


Figure 5. Molecular structure of **9** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Li–O(1) 1.938(6), Li–O(2) 1.948(6), Li–Cl(1) 2.359(6), Li–Cl(2) 2.385(6), Ce–N(1) 2.555(2), Ce–N(2) 2.499(2), Ce–N(3) 2.557(2), Ce–N(4) 2.483(2), Ce–Cl(1) 2.8095(8), Ce–Cl(2) 2.8069(8), P(1)–N(1) 1.593(2), P(1)–N(2) 1.594(2), P(2)–N(4) 1.593(2), P(2)–N(3) 1.598(2), O(1)–Li–O(2) 99.1(3), Cl(1)–Li–Cl(2) 97.7(2), N(2)–Ce–N(1) 60.96(7), N(4)–Ce–N(3) 60.80(7), Cl(2)–Ce–Cl(1) 79.00(3), N(1)–P(1)–N(2) 107.10(11), N(4)–P(2)–N(3) 106.18(12).

2.5. Attempted Oxidation of **9** to A Cerium(IV) Complex

The preparation and characterization of well-defined molecular cerium(IV) complexes remains a considerable synthetic challenge. However, significant progress has been made in the field of cerium(IV) amides and related species. Various Ce(IV) amide complexes such as heteroleptic $\text{Ce}[\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_2\text{tBu})\}_3]\text{I}$ [69], $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3\text{X}$ (X = Cl, Br) [70] and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ce}(\text{OC}_6\text{H}_4\text{O})\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ [71] as well as homoleptic $\text{Ce}(\text{N}^i\text{Pr}_2)_4$ [72] $\text{Ce}(\text{NCy}_2)_4$ [73] and $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_4$ [74] have been successfully synthesized by oxidation of cerium(III) precursors. Suitable oxidizing agents are e.g., TeCl_4 , trityl chloride (Ph_3CCl), hexachloroethane (C_2Cl_6) or phenyliodine(III) dichloride (PhICl_2). The first cerium(IV) amidinate complex, $[p\text{-MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_3\text{CeCl}$, was obtained in 61% yield upon oxidation of the cerium(III) precursor $[p\text{-MeOC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_3\text{Ce}(\text{N}\equiv\text{CC}_6\text{H}_4\text{OMe-}p)$ with PhICl_2 in *n*-pentane [75]. Thus it seemed reasonable to attempt a similar oxidation reaction of $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**). Compound **9** was treated with calculated amounts of either trityl chloride or PhICl_2 in different

solvents (*n*-pentane, toluene, THF). In all cases, intensely colored (dark green or green-brown) solutions were obtained, but we were unable to isolate the tentative cerium(IV) complex $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{CeCl}_2$ under any circumstances.

Table 1. Crystallographic Data for **1**, **2**, **8** and **9**.

Parameter	1	2	8	9
Empirical formula	$\text{C}_{38}\text{H}_{54}\text{Li}_2\text{N}_4\text{O}_2$	$\text{C}_{50}\text{H}_{70}\text{Li}_2\text{N}_4\text{O}_2$	$\text{C}_{56}\text{H}_{92}\text{Cl}_2\text{N}_8\text{Nd}_2\text{O}_2$	$\text{C}_{44}\text{H}_{72}\text{CeCl}_2\text{LiN}_4\text{O}_2\text{P}_2\text{Si}_4$
<i>a</i> (Å)	9.6687(19)	9.8768(3)	10.049(2)	11.117(2)
<i>b</i> (Å)	9.948(2)	10.2082(3)	11.337(2)	36.425(7)
<i>c</i> (Å)	19.611(4)	11.6883(4)	14.471(3)	13.538(3)
α (°)	93.77(3)	104.144(3)	82.53(3)	90
β (°)	91.33(3)	90.248(3)	83.02(3)	96.70(3)
γ (°)	90.96(3)	104.209(2)	73.74(3)	90
<i>V</i> (Å ³)	1881.3(6)	1105.18(6)	1562.9(5)	5444.3(19)
<i>Z</i>	2	1	1	4
formula weight	612.73	772.98	1268.76	1081.32
space group	P-1	P-1	P-1	P2 ₁ /n
<i>T</i> (°C)	−120	−173	−120	−120
λ (Å)	0.71073	1.54184	0.71073	0.71073
<i>D</i> _{calcd} (g cm ^{−3})	1.082	1.161	1.348	1.319
μ (mm ^{−1})	0.066	0.530	1.771	1.118
<i>F</i> (000)	664	420	654	2244
data/restraints/parameters	7395/0/469	4628/0/262	8340/0/324	12,841/0/569
goodness-of-fit on <i>F</i> ²	1.013	1.027	1.219	0.977
<i>R</i> (Fo or Fo ²)	0.0520	0.0392	0.0547	0.0363
<i>R</i> _w (Fo or Fo ²)	0.1347	0.0974	0.1663	0.0859

3. Experimental Section

3.1. General Procedures

All experiments were carried out under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques (<1 ppm O₂, <1 ppm H₂O). *n*-Pentane and THF were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 120 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials, anhydrous LnCl₃ (Ln = Ce, Nd) [76] and Li[Ph₂P(NSiMe₃)₂] [66,67], and compound **8** [45] were prepared according to the literature methods. ⁿBuLi, phenylacetylene, and *N,N'*-dicyclohexylcarbodiimide were purchased from Aldrich and used as received. ¹H-NMR (400 MHz) and ¹³C-NMR (100.6 MHz) were recorded in C₆D₆ or CDCl₃ solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Assignment of signals was made from ¹H–¹³C HSQC 2D NMR experiments. IR spectra were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer system 2000 (Perkin Elmer, Rodgau, Germany) between 4000 and 400 cm^{−1}. Microanalyses of the compounds were performed using a LECO CHNS 932 apparatus (LECO Corp., St. Joseph, MI, USA).

3.2. Syntheses

Li[Ph-C≡C-C(NCy)₂]-THF (**2**). A solution of phenylacetylene (3.30 mL, 30 mmol) in THF (80 mL) was cooled to -20 °C and treated slowly with *n*-butyllithium (18.85 mL, 1.6 M solution in *n*-hexane). The solution was stirred for 15 min, before *N,N'*-dicyclohexylcarbodiimide (6.20 g, 30 mmol) was added. The reaction mixture was stirred for 10 min at -20 °C, and then warmed to room temperature and stirred for another 2 h. The solution was reduced to a small volume under vacuum (25 mL) and stored at -25 °C in a freezer to obtain single-crystals of **2**. Yield: 10.20 g, 88%. Elemental analysis for C₂₅H₃₅LiN₂O (386.51 g·mol⁻¹): C, 77.69%; H, 9.13%; N, 7.25%; found C, 77.15%; H, 9.33%; N, 7.08%. ¹H NMR (400 MHz, toluene-*d*₈, 25 °C): δ (ppm) 7.52 (d, *J* = 6.6 Hz, 2H, C₆H₅), 6.99 (m, 3H, C₆H₅), 3.96 (m, 2H, CH, Cy), 3.65 (m, 4H, THF), 1.44 (m, 4H, THF), 1.31–2.12 (m, 20H, CH₂, Cy); ¹³C{¹H} NMR (100.6 MHz, toluene-*d*₈, 25 °C): δ (ppm) 159.3 (NCN), 158.5 (C≡C-C), 132.2 (C₆H₅), 123.8 (C₆H₅), 94.4 (C₆H₅), 82.4 (C₆H₅-C≡C), 68.2 (THF), 59.8 (CH, Cy), 37.6 (CH₂, Cy), 26.8 (CH₂, Cy), 25.6 (THF), 23.0 (CH₂, Cy).

Li[Ph-C≡C-C(NCy)₂]-Et₂O (**3**). The compound was prepared by following the procedure for **2** using diethyl ether as solvent. The solvent was removed under vacuum affording **2** as white solid. Yield: 8.85 g, 76%. Elemental analysis for C₂₅H₃₇LiN₂O (388.52 g·mol⁻¹): C, 77.29%; H, 9.60%; N, 7.21%; found C, 76.06%; H, 9.52%; N, 7.60%. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 7.56 (d, *J* = 6.8 Hz, 2H, Ph), 6.95 (m, 3H, Ph), 4.01 (s, br, 2H, CH, Cy), 3.25 (q, 4H, CH₂, Et₂O), 2.40 (m, 4H, CH₂, Cy), 1.93 (m, 6H, CH₂, Cy), 1.24–1.80 (m, 10H, CH₂, Cy), 1.15 (t, 6H, CH₃, Et₂O); ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 25 °C): δ (ppm) 132.3 (Ph), 123.8 (Ph), 94.3 (Ph), 83.1 (Ph-C≡C), 65.9 (Et₂O), 59.9 (CH, Cy), 37.7 (CH₂, Cy), 26.9 (CH₂, Cy), 26.5 (CH₂, Cy), 15.3 (Et₂O).

[Ph-C≡C-C(NCy)₂]₃Ce (**4**). A solution of anhydrous CeCl₃ (1.0 g, 4 mmol) in 20 mL of THF was added to a solution of **2** (4.6 g, 12 mmol) in 60 mL of THF. The reaction mixture was stirred over night at the room temperature. The solvent was removed under vacuum to dryness followed by extraction with *n*-pentane (3 × 10 mL) to give a clear, orange solution. The filtrate was evaporated under vacuum to afford **4** as yellow solid. Yield: 3.4 g, 81%. Elemental analysis for C₆₃H₈₁CeN₆ (1062.50 g·mol⁻¹): C, 71.22%; H, 7.68%; N, 7.91%; found C, 71.36%; H, 7.64%; N, 7.90%. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 9.49 (s, br, 2H, CH, Cy), 8.81 (s, 3H, Ph), 7.8–8.05 (m, 6H, Ph), 7.29–7.56 (m, 6H, Ph), 3.76 (s, br, 2H, CH, Cy), 3.56 (m, 2H, CH, Cy), 0.93–2.12 (m, 50H, CH₂, Cy), -0.05 (s, br, 4H, CH₂, Cy), -1.82 (s, br, 6H, CH₂, Cy); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25 °C): δ (ppm) 160.7 (NCN), 140.5 (Ph), 134 (Ph), 132.6 (Ph), 130.2 (Ph), 129.4 (Ph), 100.5 (C≡C-C), 90.1 (Ph-C≡C), 67.1 (CH, Cy), 61.1 (CH, Cy), 56.3 (CH, Cy), 36.4 (CH₂, Cy), 34.1 (CH₂, Cy), 26.2 (CH₂, Cy).

[Ph-C≡C-C(NCy)₂]₃Nd (**5**). A solution of anhydrous NdCl₃ (0.5 g, 2 mmol) in 20 mL of THF was added to a solution of **2** (2.3 g, 6 mmol) dissolved in 60 mL of THF. Following the procedure described for **4**, compound **5** was isolated as a pale green solid. Yield: 1.5 g, 73%. Elemental analysis for C₆₃H₈₁N₆Nd (1066.63 g·mol⁻¹): C, 70.94%; H, 7.65%; N, 7.88%; found C, 68.88%; H, 7.41%, N, 7.79%. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 18.33 (s, 2H, CH, Cy), 9.40 (m, 3H, Ph), 8.25 (m, 4H, Ph), 8.05 (m, 2H, Ph), 7.48 (m, 2H, Ph), 7.38 (m, 4H, Ph), 3.77 (s, 2H, CH, Cy), 3.57 (s, 2H, CH, Cy), 0.56–2.10 (m, br, 50H, CH₂, Cy), -0.66 (s, 4H, CH₂, Cy), -3.55 (s, 6H, CH₂, Cy); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25 °C): δ (ppm) 140.5 (Ph), 135.5 (Ph), 132.6 (Ph), 131.0 (Ph), 130.4

(Ph), 129.8 (Ph), 125.3 (Ph), 102.0 (C≡C–C), 90.0 (Ph–C≡C), 78.5 (CH, Cy), 61.1 (CH, Cy), 50.0 (CH, Cy), 36.0 (CH₂, Cy), 33.7 (CH₂, Cy), 27.2 (CH₂, Cy), 25.7 (CH₂, Cy).

[Ph–C≡C–C(NCy)₂]₃Sm (**6**). Reaction of anhydrous SmCl₃ (0.5 g, 2 mmol) with **2** (2.3 g, 6 mmol) following the procedure described for **4** afforded **6** as pale yellow solid. Yield: 1.3 g, 64%. Elemental analysis for C₆₃H₈₁N₆Sm (1072.74 g·mol⁻¹): C, 70.54%; H, 7.61%; N, 7.83%; found C, 69.62%; H, 7.70%; N, 7.60%. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 8.23 (d, 3H, Ph), 8.04 (s, br, 3H, Ph), 7.30–7.64 (m, 9H, Ph), 3.71 (s, br, 3H, CH, Cy), 3.30 (m, 3H, CH, Cy), 0.00–0.16 (m, 4H, CH₂, Cy), 0.30–2.06 (m, br, 50H, CH₂, Cy), –1.70 (s, br, 6H, CH₂, Cy); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25 °C): δ (ppm) 183.3 (NCN), 133.1 (Ph), 130.1 (Ph), 129.6 (Ph), 124.4 (Ph), 97.7 (C≡C–C), 84.1 (Ph–C≡C), 59.5 (CH, Cy), 57.4 (CH, Cy), 36.6 (CH₂, Cy), 33.7 (CH₂, Cy), 26.9 (CH₂, Cy).

[Ph–C≡C–C(NCy)₂]₃Ho (**7**). Reaction of anhydrous HoCl₃ (1.0 g, 3.7 mmol) with **2** (4.3 g, 11.1 mmol). Following the procedure described for **4**, the reaction afforded **7** as pale yellow solid. Yield: 3.6 g, 91%. Elemental analysis for C₆₃H₈₁HoN₆ (1087.31 g·mol⁻¹): C, 69.59%; H, 7.51%; N, 7.73%; found C, 69.45%; H, 7.41%; N, 7.73%.

[Ph₂P(NSiMe₃)₂]₂Ce(μ-Cl)₂Li(THF)₂ (**9**). A solution of anhydrous CeCl₃ (1.0 g, 4.1 mmol) in 30 mL of THF was added to a solution of Li[Ph₂P(NSiMe₃)₂] (3.0 g, 8.2 mmol) in 60 mL of THF. The reaction mixture was stirred over night at room temperature. The solution color changed to golden yellow. The solvent was removed under vacuum followed by extraction with *n*-pentane (30 mL) to give a clear, bright yellow solution. The filtrate was concentrated under vacuum to *ca.* 10 mL. Crystallization at 5 °C afforded **9** in the form of bright yellow, block-like crystals. Yield: 3.4 g, 78%. Elemental analysis for C₄₄H₇₂CeCl₂LiN₄O₂P₂Si₄ (1081.32 g·mol⁻¹): C, 48.82%; H, 6.65%; N, 5.17%; found C, 42.10%; H, 6.70%; N, 5.30%. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 10.22 (m, 8H, C₆H₅), 9.50 (s, br, 4H, C₆H₅), 7.70 (m, 8H, C₆H₅), 1.44 (m, 8H, THF), –4.80 (s, br, 3H, Si(CH₃)₃), –5.83 (s, br, 33H, Si(CH₃)₃); ¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 25 °C): δ (ppm) 144.0 (C₆H₅), 133.2 (C₆H₅), 132.5 (C₆H₅), 131.2 (C₆H₅), 64.7 (THF), 24.1 (THF), –1.3 (Si(CH₃)₃); ²⁹Si NMR (80 MHz, THF-*d*₈, 25 °C): δ (ppm) –13.90 (Si(CH₃)₃), –21.24 (Si(CH₃)₃); ³¹P NMR (162 MHz, THF-*d*₈, 25 °C): δ (ppm) –4.94.

3.3. X-ray Crystallography

The intensity data of **1**, **2**, **8**, and **9** were collected on a Stoe IPDS 2T diffractometer with MoK_α radiation. The data were collected with the Stoe XAREA [77] program using ω-scans. The space groups were determined with the XRED32 [78] program. Absorption corrections were applied using the multi-scan method. The structures were solved by direct methods (SHELXS-97) [79] and refined by full matrix least-squares methods on *F*² using SHELXL-97 [80]. Data collection parameters are given in Table 1. CCDC 1419935 (**1**), 1419937 (**2**), 1400418 (**8**), and 1419934 (**9**) contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

In summarizing the results reported here, we extended the series of homoleptic lanthanide tris(propiolamidinate) complexes by preparing four new representatives, [Ph–C≡C–C(NCy)₂]₃Ln

(4: Ln = Ce; 5: Ln = Nd; 6: Ln = Sm; 7: Ln = Ho). Two lithium propiolamidinate precursors, $\text{Li}[\text{Ph}-\text{C}\equiv\text{C}-\text{C}(\text{NCy})_2] \text{ S}$ (**1**: R = *i*-Pr, S = THF; **2**: R = Cy, S = THF), have been structurally characterized by X-ray diffraction. Moreover, crystal structure determinations of $[\{\epsilon\text{-C}_3\text{H}_5-\text{C}\equiv\text{C}-\text{C}(\text{N}^i\text{Pr})_2\}_2\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$ (**8**) and the new monomeric Ce(III)-diiminophosphinate complex, $[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]_2\text{Ce}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**9**), have been carried out. Attempts to oxidize compound **9** using trityl chloride or phenyliodine(III) dichloride did not lead to an isolable cerium(IV) species.

Supplementary

Supplementary materials can be found at <http://www.mdpi.com/2304-6740/3/4/0429/s1>.

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Author Contributions

Farid M. Sroor carried out the experimental work. Cristian G. Hrib did the crystal structure determinations. Frank T. Edelmann conceived and supervised the experiments and wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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