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η^2-Acetylene Sm^{II} and Sm^{III} complexes: mirage or reality?

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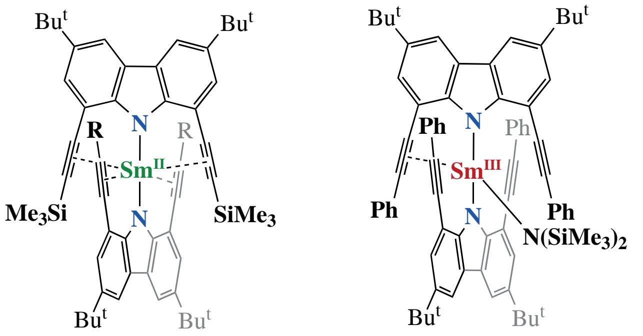
The bis(carbazolide) complex of Sm^{II}, Sm[3,6-Bu$^t_2$-1,8-(Me$_3$SiC≡C)$_2$Carb]$_2$, was synthesized by the transamination reaction of Sm[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with two molar equivalents of carbazole 3,6-Bu$^t_2$-1,8-(Me$_3$SiC≡C)$_2$CarbH. A similar reaction of the less sterically demanding carbazole 3,6-Bu$^t_2$-1,8-(PhC≡C)$_2$CarbH is accompanied by the oxidation of Sm^{II} to Sm^{III} and lead to the formation of bis(carbazolide) amido complex [3,6-Bu$^t_2$-1,8-(PhC≡C)$_2$Carb]$_2$Sm[N(SiMe$_3$)$_2$]. For both Sm complexes, η^2-interactions with C≡C bonds, which are unconventional for Ln^{II} and Ln^{III} metals, were experimentally confirmed by single-crystal X-ray diffraction, IR and Raman spectroscopy along with QTAIM analysis.



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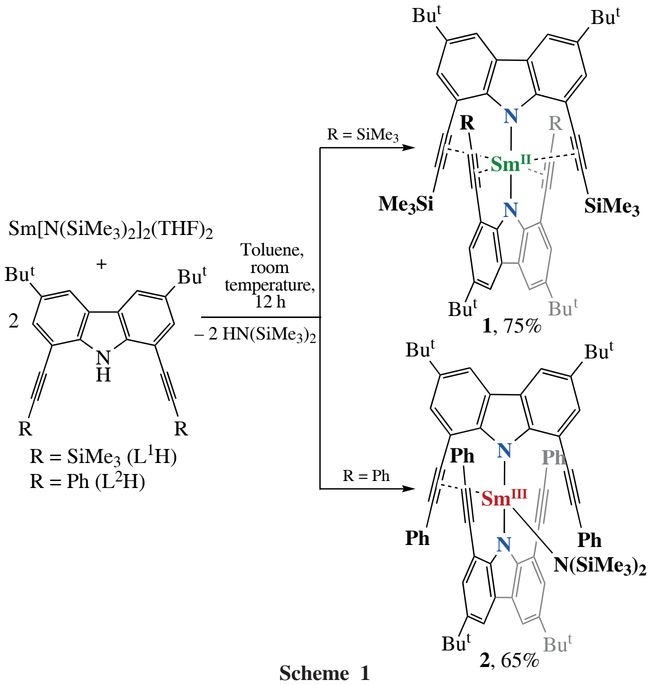
Metal–ligand bonding in organic derivatives of Ln^{II} and Ln^{III} metals has traditionally been described by a model assuming predominantly ionic interactions[1] due to their high electropositivity.[2] It has long been believed that lanthanides cannot form π-complexes with alkenes or alkynes, similar to complexes of *d*-transition metals, due to the lack of *d*-electrons and the negligible contribution of 4*f*-electrons to metal–ligand bonding.[3] Lanthanide ions cannot act as π-donors, since the filled orbitals are too low in energy,[4] however, being Lewis acids, they can accept π-electrons of acetylene orbitals with σ-symmetry.

The coordination of the C≡C triple bond with Ln^{II} and Ln^{III} ions is supposed to be the first stage in a number of practically important reactions involving acetylenes.[5–7] Despite numerous examples of successful application of organolanthanides in stoichiometric and catalytic transformations of C≡C triple bonds, such as hydrogenation, hydroelementation, dimerization and polymerization,[8–18] acetylene complexes of lanthanides still remain rare and mysterious species. The first η^2-acetylene complex of Ln^{II}, Cp$^*_2$Yb(η^2-MeC≡CMe) (Cp* = C$_5$Me$_5^-$, pentamethylcyclopentadienyl), considered as a weak Lewis acid–base adduct of the electron-deficient Yb^{II} ion with acetylene, was reported in 1987 by Andersen *et al.*[19] Attempts to synthesize similar η^2-acetylene complexes of Sm^{II} were accompanied by oxidation of the metal center to the trivalent state, caused by the lower oxidation potential of Sm^{II} compared to Yb^{II}.[2] Evans *et al.* reported that the reaction of Cp$^*_2$Sm(THF)$_2$ with diacetylene PhC≡C–C≡CPh proceeds with the oxidation of Sm^{II} to Sm^{III}, affording the bimetallic complex [Cp$^*_2$Sm]$_2$(μ-η^2,η^2-C$_4$Ph$_2$) with the dianionic ligand [PhCCCCPh]$^{2-}$. The formation of the latter was also observed in the reaction of Cp$^*_2$Sm with excess PhC≡CH, implying the reduction of two phenylacetylene molecules in two one-electron transfer steps followed by dehydrogenative C–C coupling.[20–22]

Recently, 1,8-diethynyl substituted carbazoles, in which the acetylene groups are covalently linked directly to the heterocyclic backbone, have been successfully used to prepare η^2-acetylene Yb^{II} complexes featuring the Yb(η^2-C≡C)$_4$ structural motif consisting of a metal ion encapsulated by four acetylene fragments.[23] Here, we report the synthesis and structures of samarium complexes with 1,8-diethynyl substituted carbazoles featuring lanthanide-unconventional η^2-interactions with the C≡C triple bond.

The reaction of Sm[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with two molar equivalents of 3,6-Bu$^t_2$-1,8-(Me$_3$SiC≡C)$_2$CarbH (L^{1}H) in toluene at 20 °C leads to the formation of the expected base-free bis(carbazolide) Sm^{II} complex Sm[3,6-Bu$^t_2$-1,8-(Me$_3$SiC≡C)$_2$Carb]$_2$ **1** (Scheme 1). Complex **1** was isolated as dark greenish brown crystals after recrystallization from THF–hexane in 75% yield. An analogous reaction of Sm[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with two molar equivalents of the less sterically demanding carbazole 3,6-Bu$^t_2$-1,8-(PhC≡C)$_2$CarbH (L^{2}H) proceeds with oxidation of the metal center and results in the formation of the heteroleptic bis(carbazolide) amido Sm^{III} complex [3,6-Bu$^t_2$-1,8-(PhC≡C)$_2$Carb]$_2$Sm[N(SiMe$_3$)$_2$] **2** (see Scheme 1). Complex **2** was isolated as bright orange crystals in 65% yield after recrystallization from toluene solution.

The formation of the Sm^{III} complex can be rationalized by the oxidation of the metal center with HN(SiMe$_3$)$_2$ released during the reaction. Presumably, the reduction of HN(SiMe$_3$)$_2$ was



Scheme 1

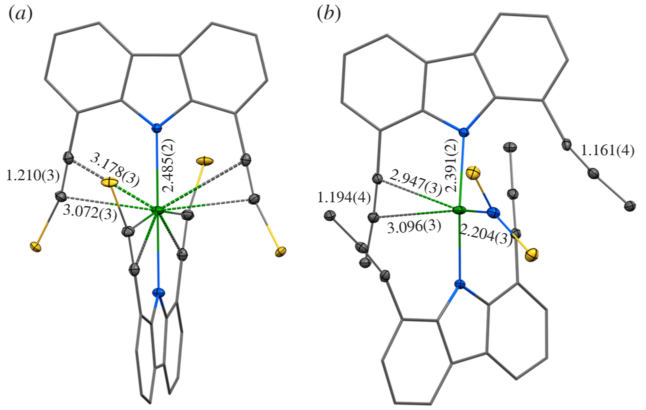


Figure 1 General appearance of the molecular structures of (*a*) complex **1** and (*b*) complex **2**. Thermal ellipsoids are given at 30% probability level. All hydrogen atoms as well as carbon atoms of Bu^t, SiMe$_3$ and Ph substituents are omitted for clarity. Color code: C, grey; N, blue; Si, yellow; Sm, green.

accompanied by the elimination of H$_2$. In the case of Yb^{II}, which is characterized by a higher oxidation potential compared to Sm^{II} (Yb^{3+}/Yb^{2+} $E_{1/2} = -1.15$ V *vs.* Sm^{3+}/Sm^{2+} $E_{1/2} = -1.55$ V),[2] oxidation of the metal center was not observed under similar conditions, and bis(carbazolides) Yb[3,6-Bu$^t_2$-1,8-(RC≡C)$_2$Carb]$_2$ were isolated in the reactions of Yb[N(SiMe$_3$)$_2$]$_2$(THF) with both carbazoles L^{1}H and L^{2}H. An attempt to synthesize complex **2** by the reaction of tris(silylamide) Sm[N(SiMe$_3$)$_2$]$_3$ with two equivalents of L^{2}H in toluene or THF solutions at 70 °C failed. The starting reagents were isolated from the reaction mixtures in the initial amounts. Moreover, according to ^{1}H NMR spectroscopy, diamagnetic yttrium tris(amide) Y[N(SiMe$_3$)$_2$]$_3$ was absolutely inert towards 1,8-diethynylcarbazoles L^{1}H or L^{2}H even under harsh conditions (C$_6$D$_6$, 90 °C, 12 h).

Complexes **1** and **2** are readily soluble in THF, moderately soluble in toluene and almost insoluble in hexane. They are extremely sensitive to air and moisture, but can be stored in vacuum or inert atmosphere in the solid state without any signs of decomposition.

According to single-crystal X-ray diffraction data,[†] complex **1** contains a formally two-coordinated Sm^{2+} ion, which is covalently bonded to two nitrogen atoms of the carbazolide ligands, forming a linear N–Sm–N fragment with a bond angle of 180°, and demonstrates a mutually orthogonal orientation of the carbazole planes forming a dihedral angle of 90° [Figure 1(*a*)]. On the one hand, the Sm–N bond length in complex **1** is 2.485(2) Å, which is significantly shorter than in six-coordinated complexes Sm(Carb)$_2$(Solv)$_4$ [Solv = THF, Sm–N 2.565(13) Å; Solv = *N*-methylimidazole, Sm–N 2.591(3) Å].[24] On the other hand, the Sm–N distances in complex **1** are very close to that in the two-coordinated bis(amide) Sm[N(SiPr$^i_3$)$_2$]$_2$, which is 2.483(6) Å.[25] As in the recently described Yb^{II} analogue, the Sm^{2+} ion in complex **1** is coordinated by four η^2-C≡C fragments with rather short pairwise nonequivalent Sm···(η^2-C≡C) distances of 3.072(3) and 3.178(2) Å, which are very close to the respective distances of 2.980(4) and 3.077(3) Å in the Yb^{II} analogue and correlate with the differences in ionic radii (R_I) of the Sm^{2+} and Yb^{2+} ions [R_I(Sm^{2+}) = 1.22 Å, R_I(Yb^{2+}) = 1.08 Å, CN = 7].[26] Analysis of the geometry of the acetylene fragments shows that the coordination of the C≡C triple bond to the Sm^{2+} ion leads to its elongation to 1.210(3) Å, compared with the value of 1.181–1.192 Å typical for the C≡C triple bond.[27] A deviation of the bond angles C$_{Carb}$–C≡C [178.8(3)°] and C≡C–Si [162.8(4)°] from the linear geometry is also observed.

Bis(carbazolide) amido complex **2** contains a Sm^{3+} ion covalently bonded to three N atoms of two carbazolide ligands and one amido group N(SiMe$_3$)$_2$, resulting in a formal coordination number (CN) of three [Figure 1(*b*)]. The presence of bulky amido group in the coordination sphere of Sm^{III} leads to significant distortion of the bis(carbazolide) fragment. In contrast to complex **1**, complex **2** exhibits a noticeable deviation from linearity, expressed in the fact that the N$_{Carb}$–Sm–N$_{Carb}$ bond angle is 140.0(2)°. The carbazoles' planes are rotated relative to each other by 51.1°. Moreover, the Sm^{III} ion deviates from the carbazoles' planes by 0.541 and 0.806 Å.

On the one hand, despite the low formal CN of three for the metal center in complex **2**, the Sm–N$_{Carb}$ distances of 2.391(2) Å are longer than the distances of 2.28(2)–2.34(2) Å in the five-coordinated tris(carbozolide) complex Sm(Carb)$_3$(Phpip)$_2$ (Phpip = 1-phenylpiperazine)[28] and the

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[†] *Crystal data for complex* **1**. C$_{60}$H$_{80}$N$_2$Si$_4$Sm, $M = 1091.97$, tetragonal, space group $I4_1/a$, at 100 K, $a = 20.7922(3)$ and $c = 13.9777(2)$ Å, $V = 6042.78(19)$ Å^3, $Z = 4$, $d_{calc} = 1.200$ g cm^{-3}, $F_{000} = 2288$. Intensities of 31669 reflections were measured with a Bruker Quest D8 CMOS diffractometer [λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 10.87 cm^{-1}, ω-scans, $2\theta < 52°$], and 2963 independent reflections ($R_{int} = 0.0518$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0247$ for 2779 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.0593$ and GOF = 1.058 for all the independent reflections.

Crystal data for complex **2**. C$_{78}$H$_{82}$N$_3$Si$_2$Sm, $M = 1267.99$, monoclinic, space group $C2/c$, at 100 K, $a = 17.3776(4)$, $b = 16.4594(3)$ and $c = 23.2416(4)$ Å, $\beta = 93.2290(10)°$, $V = 6637.1(2)$ Å^3, $Z = 4$, $d_{calc} = 1.269$ g cm^{-3}, $F_{000} = 2644$. Intensities of 37899 reflections were measured with a Bruker Quest D8 CMOS diffractometer [λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 9.66 cm^{-1}, ω-scans, $2\theta < 54°$], and 7243 independent reflections ($R_{int} = 0.0569$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0457$ for 5827 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.1018$ and GOF = 1.057 for all the independent reflections.

Using OLEX2,[32] the structures were solved with the SHELXT[33] structure solution program using Intrinsic Phasing and refined with the XL[34] refinement package using least-squares minimization. The hydrogen atom positions were calculated and refined in the isotropic approximation within the riding model.

CCDC 2391764 (**1**) and 2391765 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

distances of 2.337(5)–2.375(5) Å in the carbazolide oxo complex $[\mathrm{Sm_6O_4(Cbz)_{10}(THF)_6}]$[29] with unsubstituted carbazolide ligands. On the other hand, the Sm–$\mathrm{N_{Carb}}$ distances in complex **2** are significantly shorter compared to the bis(carbazolide) hydroxo complex of $\mathrm{Sm^{III}}$, $[\mathrm{Sm(CzT^{Pr^i})_2(\mu\text{-}OH)}]_2$, which contains the tridentate 1,8-bis(2-isopropyl-2*H*-tetrazol-5-yl)-3,6-di(*tert*-butyl)carbazolide ligand, $\mathrm{CzT^{Pr^i}}$, and in which these distances are rather large [2.512(8)–2.543(8) Å]. These differences are due to steric hindrance around the metal center in $[\mathrm{Sm(CzT^{Pr^i})_2(\mu\text{-}OH)}]_2$ and the coordination of the tetrazole ring to the $\mathrm{Sm^{3+}}$ ion, which prevents the latter from being positioned closer to the carbazole nitrogen atom.[30] The distance between the $\mathrm{Sm^{3+}}$ ion and the N atom of the silylamido group is 2.204(3) Å, which is shorter than in the three-coordinated homoleptic tris(silylamide) $\mathrm{Sm[N(SiMe_3)_2]_3}$ [2.284(3) Å].[31]

In contrast to complex **1** with four C≡C triple bonds interacting with the $\mathrm{Sm^{2+}}$ ion, in complex **2** only one of the ethynyl groups is coordinated to the $\mathrm{Sm^{3+}}$ ion. The shortest Sm···$\mathrm{C_{Carb}}$ distance of 2.947(3) Å is found between the $\mathrm{Sm^{3+}}$ ion and the C atom bound to the carbazolide fragment, while the second Sm···$\mathrm{C_{Ph}}$ distance of 3.096(3) Å is slightly longer. Both distances are shorter than in complex **1** due to the smaller ionic radius of $\mathrm{Sm^{3+}}$ compared to $\mathrm{Sm^{2+}}$. The ethynyl fragment coordinated with the $\mathrm{Sm^{2+}}$ ion has similar geometric parameters as in complex **1**: the C≡C bond is slightly elongated [1.194(4) Å], and the $\mathrm{C_{Carb}}$–C≡C and C≡C–$\mathrm{C_{Ph}}$ bond angles are 173.2(3) and 174.3(3)°, respectively. Note that there is no elongation of the C≡C triple bond, which does not interact with the $\mathrm{Sm^{3+}}$ ion, and its value of 1.161(4) Å is close to the bond length in the starting carbazole $\mathrm{L^2H}$ [1.165(6) and 1.178(6) Å].

Since the C≡C triple bonds in complex **1** and ligand $\mathrm{L^1H}$ have different substituents, $\mathrm{SiMe_3}$ and carbazolyl C, at the ethynyl C atoms, their stretching vibrations are clearly visible in the IR spectra and appear as sharp absorption lines at 2101 $\mathrm{cm^{-1}}$ in complex **1** and 2150 $\mathrm{cm^{-1}}$ in ligand $\mathrm{L^1H}$ (Figure S1, see Online Supplementary Materials). The shift of the C≡C vibrations in complex **1** by ~50 $\mathrm{cm^{-1}}$ compared to the starting $\mathrm{L^1H}$ is similar to that in the $\mathrm{Yb^{II}}$ analogue.[23] The Raman spectrum of complex **2** (Figure S2) is consistent with the X-ray diffraction data, namely, a split line is observed at 2179/2199 $\mathrm{cm^{-1}}$, the two components of which correspond to the stretching of the coordinated and free C≡C bonds, respectively. The frequency shift of ~20 $\mathrm{cm^{-1}}$ due to coordination is comparable to that for the related Ca complex.[23]

To evaluate the interactions of the Sm ion with the C≡C bonds in complexes **1** and **2**, QTAIM analysis of the electron density distribution was performed. The molecular graphs (Figure S3) of the complexes show all expected bond critical points (BCPs) and the corresponding bond paths. Complex **1** exhibits four BCPs (3;–1) and bond paths between the Sm atom and the triple bonds (see Figure S3), with the corresponding interatomic distances being equal, leading to equal estimated energy values ($E_{\mathrm{cont}} = 3.7$ kcal $\mathrm{mol^{-1}}$). The molecular graph of complex **2** demonstrates three BCPs and bond paths for the Sm···(η^2-C≡C) interactions, which differ in distances, QTAIM parameters (see Figure S3) and E_{cont} values of 1.6, 2.5 and 4.7 kcal $\mathrm{mol^{-1}}$. In particular, the longest Sm···(η^2-C≡C) contact of 3.376 Å is also retained with BCP (3;–1). The Sm–N bonds are significantly stronger in complex **2** than in complex **1** (Table S1, see Online Supplementary Materials), especially in the case of the Sm–$\mathrm{N(SiMe_3)_2}$ bond (~35 kcal $\mathrm{mol^{-1}}$). This is likely to be the reason for the difference in the strength of the Sm···(η^2-C≡C) interaction and the presence of one coordinated C≡C bond in complex **2**. The Sm···(η^2-C≡C) interactions in complexes **1** and **2** are characterized by T-shaped bond paths and interaction energies similar to those of the previously described complexes with Ca and Yb.[23]

Thus, the first examples of acetylene $\mathrm{Sm^{II}}$ and $\mathrm{Sm^{III}}$ complexes based on 1,8-diethynylcarbazolide ligands were synthesized and structurally characterized. It was shown that the introduction of ethynyl groups into the carbazole framework made it possible to implement Sm···(η^2-C≡C) interactions that are atypical for rare earth metals. In contrast to the $\mathrm{Yb^{II}}$ analog $\mathrm{Yb[3,6\text{-}Bu^t_2\text{-}1,8\text{-}(RC{\equiv}C)_2Carb]_2}$,[23] in the case of Sm the valence state of the metal center in the reaction products is determined by the steric bulk of the $\mathrm{SiMe_3}$ and Ph substituents in the ethynyl fragment of the ligand, and the formation of bis(carbazolide) complexes of $\mathrm{Sm^{II}}$ and $\mathrm{Sm^{III}}$, respectively, is observed. For both $\mathrm{Sm^{II}}$ and $\mathrm{Sm^{III}}$ complexes, the QTAIM analysis of the electron density distribution revealed the existence of BCPs (3;–1) between the Sm atom and the carbon atoms of the C≡C bonds, which are connected by a T-shaped bond pathway. These Sm···(η^2-C≡C) interactions are electrostatic in nature and are characterized by a relatively low bonding energy (2–5 kcal $\mathrm{mol^{-1}}$).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7667.

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