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Communication

Synthesis and structural characterization of a homoleptic cerium (III) propiolamidinate

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Dedicated to Professor Henri Brunner on the occasion of his 75th birthday

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ABSTRACT

The first potassium salt of a propiolamidinate ligand, K[PhC≡C(N^{i}Pr)$_2$] (**1**), was prepared in 51% yield by addition of potassium phenylacetylide to *N,N′*-diisopropylcarbodiimide. Subsequent reaction of **1** with anhydrous cerium(III) trichloride in a molar ratio of 3:1 in THF afforded the first homoleptic lanthanide tris(propiolamidinate) derivative, [PhC≡C(N^{i}Pr)$_2$]$_3$Ce (**2**), in the form of bright yellow crystals in 71% yield.

1. Introduction

Propiolamidines of the general type R–C≡C–C(=NR′)NHRR′ [1] are highly valuable precursors for the synthesis of various nitrogen- and sulfur-containing heterocycles [2]. Certain propiolamidines have also been found to be useful antitussives [3]. More recently, propiolamidines have gained considerable attention due to their diverse applications in biological and pharmacological systems [4]. General synthetic routes to such amidine derivatives involve the reaction of chloroformamidine derivatives with lithium acetylides or alkynyl Grignard reagents or, more convenient, the catalytic addition of terminal alkynes to carbodiimides (Scheme 1) [1,5].

Recent work by Hou et al. [6,7] and others [8] has revealed that the latter reaction is affectively catalyzed by organolanthanide complexes. Lanthanide propiolamidinate complexes have been shown to be key intermediates in the catalytic cycles [6–8]. These findings motivated us to develop a straightforward synthetic route to hitherto unknown lanthanide tris(propiolamidinate) complexes. Lanthanide tris(amidinates) have recently been demonstrated to be highly effective catalysts for the polymerization of polar monomers as well as promising precursors for the production of Ln_2O_3 thin films [9]. We report here the preparation of the first potassium propiolamidinate reagent as well as the synthesis and structural characterization of a homoleptic cerium(III) tris(propiolamidinate) complex.

2. Results and discussion

Scheme 2 illustrates the synthetic route leading to the title compound. The new potassium propiolamidinate derivative K[PhC≡C(N^{i}Pr)$_2$] (**1**) was prepared in a straightforward manner by nucleophilic addition of potassium phenylacetylide to *N,N′*-diisopropylcarbodiimide. The starting material Ph–C≡C–K was obtained according to a modified literature procedure [10] by deprotonation of phenylacetylene using potassium hydride in THF. The subsequent reaction with *N,N′*-diisopropylcarbodiimide was carried out in DME solution at room temperature (Scheme 2).

Crystallization of the product directly from the filtered and concentrated reaction mixture afforded bright yellow, block-like crystals of the DME solvate of **1**. These crystals were found to lose the DME solvent very easily upon drying. Thus thorough drying *in vacuo* afforded the unsolvated potassium salt K[PhC≡C(N^{i}Pr)$_2$] (**1**) as a pale green, very air- and moisture-sensitive solid in 51% isolated yield. All spectroscopic data were in agreement with the formation of the desired propiolamidinate salt. Unfortunately,

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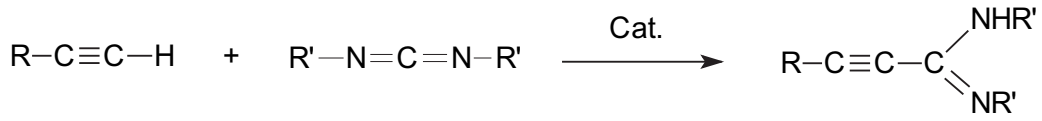


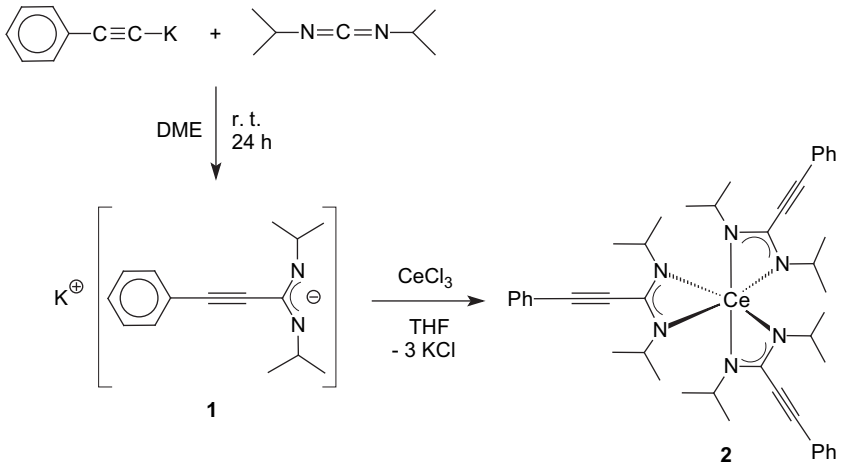
Scheme 1. Catalytic formation of propiolamidines from terminal alkynes and carbodiimides.

attempted recrystallization from various solvents or solvent mixtures such as toluene, pentane, cyclopentane, diethyl ether, THF, DME/toluene or DME/pentane did not provide single-crystals suitable for X-ray diffraction. Only on one occasion one of the well-formed block-like crystals obtained directly from the concentrated reaction mixture could be successfully subjected to X-ray diffraction, but the crystal quality was too poor to allow full refinement of the crystal structure of **1**. However, the main structural features could clearly be derived showing a dimeric solid state structure for the DME adduct of **1** in which two potassium ions are symmetrically bridged by the propiolamidinate ligands. Each potassium becomes hexacoordinated through addition of a DME ligand (Scheme 3).

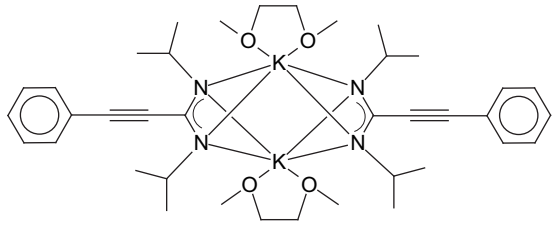
The preparation of a homoleptic cerium(III) tris(propiolamidinate) complex was carried out in THF solution according to Scheme 2 by treatment of anhydrous $CeCl_3$ with three equivalents of **1**. The reaction proceeded smoothly under formation of a golden-yellow solution and precipitaion of finely divided KCl. Extraction of the crude product with pentane followed by crystallization at 5 °C afforded well-formed, bright yellow, block-like single-crystals of $[PhC{\equiv}C(N^iPr)_2]_3Ce$ (**2**) in high yield (71%). Like many other cerium (III) amides and organocerium(III) complexes [11], crystals of **2** are very sensitive to traces of air and moisture. Spectroscopic characterization of **2** was straightforward. In the IR spectrum, a medium strong band at 2207 cm^{-1} could be assigned to the C≡C stretching vibration. The mass spectrum showed the molecular ion with 20% relative intensity. Despite the paramagnetic nature of the Ce^{3+} ion, meaningful ^1H and ^{13}C NMR spectra could also be obtained for **2**. Both were in agreement with the formation of an unsolvated, homoleptic cerium(III) propiolamidinate. This was further verified by a single-crystal X-ray diffraction study of **2**. Large block-like single-crystals were obtained by slow cooling of a saturated solution in pentane to 5 °C. Crystal data and structure refinement details are listed in Table 1, and selected bond lengths and angles for **2** are summarized in Table 2. Fig. 1 depicts the molecular structure of **2**.

In the solid state, $[PhC{\equiv}C(N^iPr)_2]_3Ce$ (**2**) crystallizes in the hexagonal space group P3c1 with two molecules in the asymmetric unit. The X-ray study clearly established the presence of the first homoleptic, unsolvated lanthanide(III) tris(propiolamidinate) complex. The central cerium(3+) ion is coordinated by three chelating propiolamidinate ligands in a heavily distorted octahedral fashion. The effective shielding of the cerium by six isopropyl groups obviously prevents the coordination of additional solvent molecules. The Ce–N distances are in the narrow range of 2.487 (5)–2.502(5) Å and are in good agreement with those found *e.g.* in the homoleptic acetamidinates $[MeC(N^tBu)_2]_3La$ (La–N: 2.530–2.553 Å) and $[MeC(N^tBu)_2]_3Eu$ (Eu–N: 2.432–2.469 Å) [12]. Thus the overall bond lengths and angles follow the trends which are expected taking into account the ionic radius of six-coordinated Ce(III) of 1.15 Å. Amidinate ligands generally have small N–M–N bite angles typically in the range of 63–65°. In lanthanide amidinates these bite angles are even smaller by ca. 10° due to the large ionic radii of the lanthanide ions. With values of 54.16(15)° and 54.31(17)° the N–Ce–N angles in **2** are virtually identical with those reported for $[MeC(N^tBu)_2]_3Eu$ (N–Eu–N: 54.1(3)° and 54.7 (3)°) [12]. Quite remarkable are the dihedral angles between the phenyl ring planes and the N–C–N units of the chelating amidinate ligands. With 55.9° and 60.6°, respectively, the dihedral angles are surprisingly large despite the presence of the –C≡C– spacer groups between the two planes. They are also large enough to minimize potential conjugation between the two π-systems.

In summarizing the results reported here, the first potassium propiolamidinate derivative, $K[PhC{\equiv}C(N^iPr)_2]$ (**1**), was readily prepared through nucleophilic addition of potassium phenylacetylide to *N,N′*-diisopropylcarbodiimide. A preliminary X-ray diffraction study revealed a dimeric solid state structure for the DME adduct of **1**. Compound **1** can be expected to be a valuable precursor for the synthesis of lanthanide propiolamidinates as exemplified by the reaction with anhydrous cerium trichloride which produced the homoleptic cerium(III) tris(propiolamidinate) $[PhC{\equiv}C(N^iPr)_2]_3Ce$ (**2**) in high yield. Future work in this



Scheme 2. Synthetic route to $K[PhC{\equiv}C(N^iPr)_2]$ (**1**) and $[PhC{\equiv}C(N^iPr)_2]_3Ce$ (**2**).



Scheme 3. Schematic representation of the dimeric structure of the DME adduct of K [PhC≡C(N^{i}Pr)$_2$] (**1**) in the solid state.

area should be direct towards the synthesis of other lanthanide propiolamidinates which could exhibit interesting catalytic activities.

3. Experimental section

3.1. General procedures

The reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. All solvents were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under vacuum prior to use. The starting materials potassium phenylacetylide [10] and anhydrous $CeCl_3$ [13] were prepared according to the literature procedures. NMR spectra were recorded in THF-d_8 or C_6D_6 solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Microanalyses were performed using a Leco CHNS 923 apparatus. The intensity data of **2** were collected on a Stoe IPDS 2T diffractometer with MoK_α radiation. The data were collected with the Stoe XAREA [14] program using ω-scans. The space group was determined with XRED32 [14] program. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [15].

Table 1
Crystal data and structure refinement for [PhC≡C(N^{i}Pr)$_2$]$_3$Ce (**2**).

Identification code	ip83
Empirical formula	$C_{45}H_{57}CeN_6$
Formula weight	822.09
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	P3c1
Unit cell dimensions	a = 16.074(2) Å α = 90° b = 16.074(2) Å β = 90° c = 19.577(4) Å γ = 120°
Volume	4380.3(12) Å^3
Z	4
Density (calculated)	1.247 Mg/m^3
Absorption coefficient	1.075 mm^{-1}
F(000)	1708
Crystal size	0.60 × 0.17 × 0.15 mm^3
Theta range for data collection	2.53–28.28°
Index ranges	$-19 \le h \le 16$, $-21 \le k \le 21$, $-20 \le l \le 26$
Reflections collected	11715
Independent reflections	6246 [R(int) = 0.0623]
Completeness to theta = 28.28°	99.8%
Absorption correction	None
Max. and min. transmission	0.8554 and 0.5648
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6246/1/321
Goodness-of-fit on F^2	1.029
Final R indices [I > 2sigma(I)]	$R1$ = 0.0463, wR2 = 0.0941
R indices (all data)	$R1$ = 0.0763, wR2 = 0.1047
Absolute structure parameter	0.03(3)
Largest diff. peak and hole	0.724 and −1.032 e.Å^{-3}

Table 2
Selected bond lengths [Å] and angles [°] for [PhC≡C(N^{i}Pr)$_2$]$_3$Ce (**2**).

Ce(1)–N(1)	2.499(6)	Ce(1)–N(2)	2.502(5)
Ce(2)–N(3)	2.487(5)	Ce(2)–N(4)	2.500(5)
N(1)–C(1)	1.332(8)	N(2)–C(1)	1.341(8)
N(3)–C(21)	1.343(8)	N(4)–C(21)	1.317(7)
N(1)–Ce(1)–N(2)	54.16(15)		
N(3)–Ce(2)–N(4)	54.31(17)		
N(1)–C(1)–N(2)	116.8(5)		
N(4)–C(21)–N(3)	117.6(5)		

3.2. Synthesis of potassium propiolamidinate, K[PhC≡C(N^{i}Pr)$_2$] (**1**)

A 250 ml Schlenk flask was charged with 2.71 g (19.3 mmol) potassium phenylacetylide and 120 ml of DME. To the resulting suspension were added with stirring 2.43 g (21.2 mmol, slight excess) of *N,N′*-diisopropylcarbodiimide, causing a yellow-green color to develop. Stirring was continued for 24 h at room temperature, and insoluble material was removed by filtration. The clear, yellow-brown filtrate was concentrated *in vacuo* to a total volume of 30 ml. Cooling to 5 °C for another 24 h afforded bright yellow, block-like crystals of the DME solvate of **1**. These crystals easily lose DME upon drying. Thus, in order to obtain a well-defined material, the product was thoroughly dried under vacuum to give unsolvated **1** as a pale green powder in 51% yield (2.61 g). M.p. 175 °C (dec.). Analysis ($C_{15}H_{19}KN_2$, Mw = 266.42 g/mol): C 67.55 (calcd. 67.62), H 7.44 (7.19), N 9.49 (10.51) %. IR (KBr): ν_{max} 3055 (w), 3032 (w), 2965 (vs), 2857 (s), 2605 (w), 2197 (w, ν C≡C), 1596 (s, ν C=N), 1501 (vs), 1441 (s), 1373 (vs), 1354 (vs), 1328 (vs), 1243 (w), 1226 (w), 1164 (s), 1119 (s), 1069 (w), 1028 (s), 998 (w), 929 (w), 847 (w), 756 (vs), 720 (m), 690 (st), 540 (w), 529 (w), 445 (w) cm^{-1}. ^{1}H NMR (THF-d_8, 400.1 MHz): δ = 7.40 (d, ^3J = 6.5 Hz, 2H, $C_6\boldsymbol{H}_5$), 7.31–7.22 (m, 3H, $C_6\boldsymbol{H}_5$), 3.93 (sept, ^3J = 6.2Hz,

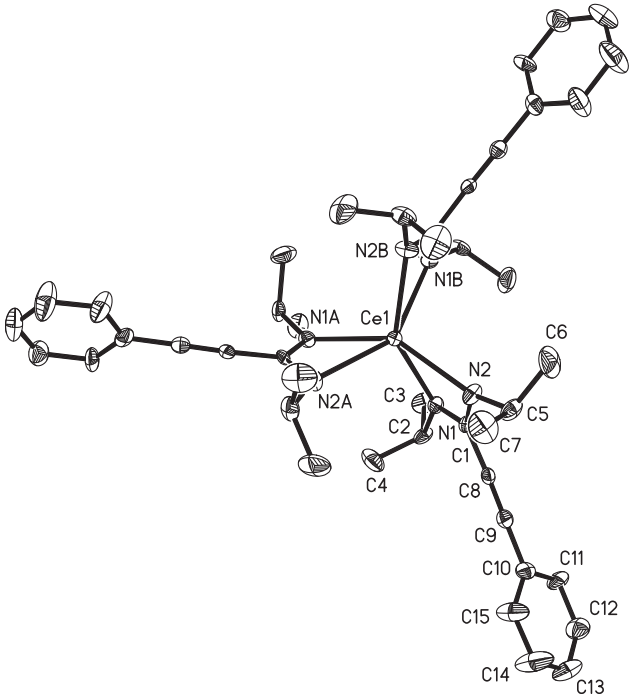


Fig. 1. ORTEP view of the molecular structure of [PhC≡C(N^{i}Pr)$_2$]$_3$Ce (**2**) with thermal ellipsoids at the 50% probability level (H atoms are not shown for clarity).

2H, {$(CH_3)_2CHN$}$_2$CC≡CPh), 1.09 (s, 6H, {$(CH_3)_2$CHN}$_2$CC≡CPh), 1.08 (s, 6H, {$(CH_3)_2$CHN}$_2$CC≡CPh) ppm. ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C): δ = 153.62 ((^{i}PrN)$_2$CC≡CPh), 132.27 (C_6H_5), 128.91 (C_6H_5), 128.19 (C_6H_5), 125.48 (C_6H_5), 91.48 ((^{i}PrN)$_2$CC≡CPh), 84.27 ((^{i}PrN)$_2$CC≡CPh), 50.51 ([$(CH_3)_2$CHN]$_2$CC≡CPh), 27.66 ([$(CH_3)_2$CHN]$_2$CC≡CPh). MS (EI, ^{140}Ce): *m/z* (%) 227.1 (12) [(^{i}PrN)$_2$CC≡CPh]$^+$; 171.1 (15) [(^{i}PrN)$_2$CC≡CPh−NCH$(CH_3)_2$ + H]$^+$; 151.1 (10) [(^{i}PrN)$_2$CC≡C•]$^+$, 128.0 (100) [(^{i}PrN)$_2$CC≡CPh−NCH$(CH_3)_2$−CH$(CH_3)_2$]$^+$, 58.0 (18) [N^{i}Pr + H]$^+$.

3.3. Synthesis of tris(N,N′-diisopropyl-propiolamidinato)cerium(III), [PhC≡C(N^{i}Pr)$_2$]$_3$Ce (**2**)

0.34 g (1.4 mmol) anhydrous cerium(III) trichloride were added as a solid to a stirred solution of **1** (1.13 g, 4.1 mmol) in 120 ml of THF. A rapid color change from yellow to bright orange was observed. The reaction flask was submerged in a water bath preheated to 80 °C, and stirring was continued for 3 h. Evaporation to dryness followed by extraction with pentane (3 × 20 ml) and filtration produced a clear, golden-yellow solution. The filtrate was concentrate *in vacuo* to a total volume of *ca.* 20 ml. Crystallization at 5 °C (24 h) afforded **2** in the form of bright yellow, block-like crystals in 71% yield (0.80 g). M.p. 85 °C (beginning dec.). Analysis ($C_{45}H_{57}CeN_6$, *Mw* = 822.09 g/mol): C 67.01 (calcd. 65.74), H 7.71 (6.99), N 10.62 (10.22) %. IR (KBr): ν_{max} 3081 (w), 3057 (w), 3035 (w), 3021 (w), 2966 (vs), 2929 (vs), 2866 (s), 2610 (w), 2207 (m, ν C≡C), 1611 (s), 1598 (s, ν C=N), 1492 (vs), 1476 (vs), 1390 (vs), 1376 (vs), 1358 (vs), 1335 (vs), 1244 (m), 1189 (vs), 1136 (s), 1124 (s), 1070 (m), 1043 (st), 999 (m), 939 (w), 917 (m), 855 (m), 832 (w), 755 (vs), 704 (m), 689 (vs), 542 (m), 528 (s) cm^{-1}. ^{1}H NMR (C_6D_6, 400.1 MHz): δ = 12.07 (s br, 6H, ($(CH_3)_2$CHN)$_2$CC≡CPh), 9.52 (s br, 6H, Ar−***H***), 7.94 (s, 6H, Ar−***H***), 7.78 (s, 3H, Ar−***H***), −2.74 (s br, 36H, (($CH_3)_2$CHN)$_2$CPh) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ = 171.30 ((^{i}PrN)$_2$CC≡CPh), 134.37 (C_6H_5), 130.26 (C_6H_5), 129.84 (C_6H_5), 125.31 (C_6H_5), 105.22 ((^{i}PrN)$_2$CC≡CPh), 91.93 ((^{i}PrN)$_2$CC≡CPh), 56.11 ([$(CH_3)_2$CHN]$_2$CC≡CPh), 23.25 ([$(CH_3)_2$CHN]$_2$CC≡CPh). MS (EI, ^{140}Ce): *m/z* (%) 820.6 (20) [M]$^+$; 806.9 (10) [M−CH_3 + H]$^+$; 778.8 (10) [M-^{i}Pr + H]$^+$, 595.7 (35) [M−(^{i}PrN)$_2$CC≡CPh + 2H]$^+$, 593.8 (100) [M−(^{i}PrN)$_2$CC≡CPh]$^+$.

4. Supplementary Material

Crystallographic data for the crystal structure reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition code CCDC 770170 (**2**).

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