Pergamon

0277-5387(95)00485-8

Polyhedron Vol. 15, No. 13, pp. 2165–2169, 1996

0277-5387/96 $15.00+0.00

THE REACTIVITY OF LANTHANIDE ALKYL COMPOUNDS WITH PHENYLACETYLENE: SYNTHESIS AND STRUCTURE OF $[(Bu^tCp)_2LnC\equiv CPh]_2$ (Ln = Nd, Gd)

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(*Received* 2 *June* 1995; *accepted* 11 *October* 1995)

Abstract—$[(Bu^tCp)_2LnCH_3]_2$ (Ln = Nd, Gd) react with $PhC\equiv CH$ to form the dimeric alkynide-bridged complexes $[(Bu^tCp)_2LnC\equiv CPh]_2$ [Ln = Nd (**I**), Gd (**II**)]. Both compounds crystallized from toluene in the monoclinic space group *C*2/*c*. The two complexes are homologous, composed of asymmetric metal–alkynide bridges with Nd—C, Gd—C (alkynide) bond lengths of 2.602(4), 2.641(5) (**I**) and 2.532(6), 2.601(7) Å (**II**), respectively. The average Nd—C (ring) and Gd—C (ring) distances are 2.746(13) and 2.703(19) Å.

Recently, the chemistry of organolanthanide acetylides has made great progress. A variety of organolanthanide acetylides has been synthesized by different methods such as the transmetallation between lanthanide halides and alkali metal acetylides,[1–3] metathesis between lanthanide alkyls or hydrides or amides and terminal alkyne,[4–8] and the reaction of divalent lanthanocene with terminal alkyne.[9–12] X-ray structure determination shows that most of the complexes have a dimeric structure with acetylide bridges, and some with bulk auxiliary ligands have the unexpected structure containing a bridged RC_4R moiety,[13] the latter structure being formed by the coupling reaction of two phenylethynyl ligands.

We have reported that the reaction of $(Bu^tCp)_2Sm\cdot DME$ with $PhC\equiv CH$ at 60°C for 24 h gives the dimer $[(Bu^tCp)_2SmC\equiv CPh]_2$ and no coupling reaction was obtained. However, the same reaction with $(C_5Me_5)_2Sm$ gives the coupling product $[(C_5Me_5)_2Sm]$ $(\mu\text{-}\eta^2\text{: }\eta^2\text{-}PhC_4Ph)$.[13] To determine whether the metal or the size of auxiliary ligands is the main reason causing the coupling reaction, we chose $[(Bu^tCp)_2LnCH_3]_2$ (Ln = Nd, Gd) as precursor. Only dimeric complexes $[(Bu^tCp)_2LnC\equiv CPh]_2$ (Ln = Nd, Gd) were synthesized from the reaction of $(Bu^tCp)_2LnCH_3$ with $PhC\equiv CH$. We report here the synthesis and molecular structure of $[(Bu^tCp)_2LnC\equiv CPh]_2$ (Ln = Nd, Gd).

EXPERIMENTAL

All manipulations were performed under argon using the Schlenk technique. The solvents were dried over anhydrous $CaCl_2$ and then refluxed over sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous $NdCl_3$ and $GdCl_3$ were prepared by Taylor's method.[14] $PhC\equiv CH$ (Fluka AG) was dried over molecular sieve and distilled before use. $[(Bu^tCp)_2NdCH_3]_2$ and $[(Bu^tCp)_2GdCH_3]_2$ were prepared according to the method reported in the literature.[15]

Metal analyses were performed by complexometric titration using EDTA. IR spectra were re-

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corded as KBr pellets on an Alpha Centauri Fourier Spectrometer. ^{13}C and ^{1}H NMR were obtained on a Unity-400 Spectrometer in benzene-d_6. Mass spectra were obtained on a VG-Quattro spectrometer recorded under electron impact conditions (70 eV, source temperature 200°C).

$[(Bu^tCp)_2NdC{\equiv}CPh]_2$

PhC≡CH (0.12 cm^3, 18 mmol) was added to a solution of $[(Bu^tCp)_2NdCH_3]_2$ (0.7 g, 17 mmol) in toluene (20 cm^3). After stirring for 24 h at 40°C, the solution was concentrated and crystallized at room temperature to give violet crystals of **I** (0.36 mg, 50.0%). Found: Nd, 29.0. Calc. for $Nd_2C_{52}H_{62}$: Nd, 29.6%. IR (KBr), cm^{-1}: 3074m, 2959s, 2860m, 2030m, 1660w, 1593s, 1461m, 1391m, 1361s, 1276s, 1200m, 1154s, 1040s, 917m, 895m, 820s, 761s, 684s, 626w. ^{1}H NMR (benzene-d_6): δ 16.68 (t, C_5H_4), 17.62 (t, C_5H_4), 7.07 (t, Ph), 7.13 (t, Ph), 7.49 (t, Ph), −11.02 (s, t-C_4H_9). ^{13}C NMR: δ 259.62 (C_5H_4), 270.16 (C_5H_4), 111.34 (Ph), 125.21 (Ph), 132.75 (Ph), 29.03 (t-C_4H_9), 3.78 (t-C_4H_9). MS, *m*/*z*: 384 ($[Cp'_2Nd]^+$, 30.9), 368 ($[Cp'_2Nd-CH_4]^+$, 5.5), 122 ($[Cp'+H]^+$, 23.1), 102 ($[CH{\equiv}CPh]^+$, 77.9).

$[(Bu^tCp)_2GdC{\equiv}CPh]_2$

The reaction was carried out in a similar way to the preparation of **I**, starting with 0.3 g (0.73 mmol) of $[(Bu^tCp)_2GdCH_3]_2$ and 0.05 cm^3 (0.76 mmol) of PhC≡CH in 20 cm^3 of toluene. The reaction mixture was stirred for 24 h at 40°C to give yellow crystals (0.20 g, 64.1%). Found: Gd, 31.6. Calc. for $Gd_2C_{52}H_{62}$: Gd 31.4%. IR, cm^{-1}: 3065m, 2960s, 2866m, 2045s, 1657m, 1594s, 1460s, 1393m, 1361s, 1277s, 1201m, 1155s, 1043s, 918m, 895s, 827s, 759s, 630w, 688s. MS, *m*/*z*: 400 ($[Cp'_2Gd]^+$, 40.8), 384 ($[Cp'_2Gd-CH_4]^+$, 6.4), 122 ($[Cp'+H]^+$, 19.3), 102 ($[CH{\equiv}CPh]^+$, 100.0).

X-ray structure determination of **I** *and* **II**

Crystals of dimension 0.3 × 0.4 × 0.3 mm^3 for **I** and 0.4 × 0.5 × 0.5 mm^3 for **II** were mounted in a thin-walled glass capillary on a Nicolet R_3M/E four-circle X-ray diffractometer. Cell dimensions were determined by measurement of 25 accurately centred reflections in the range $7.86 < 2\theta < 23.63°$ for **I** and $6.91 < 2\theta < 24.09°$ for **II**. Data were collected at 25°C using graphite monochromated Mo-K_α radiation with the ω scan mode. The intensities Lorentz and polarization were corrected for factors and absorption.

Calculations were carried out with the SHELXTL system of computer program. The position of the heavy atom was found from Patterson maps and the positions of other non-hydrogen atoms could be fixed on difference Fourier maps.

The solution of the structure of **II** was similar to that of **I**. Further details for **I** and **II** are given in Table 1. Selected bond lengths and angles are given in Tables 2 and 3, respectively.

RESULTS AND DISCUSSION

There are three main methods for the synthesis of lanthanide acetylides in the literature. The σ-bond metathesis between lanthanide alkyls or hydrides or amides is one of broad application. The alkyl complex used here is $Cp^*_2Ln{-}CH(SiMe_3)_2$.[8,16] The use of the bulky alkyl ligand gives the alkyl complex free of alkali metal adduct. We have reported that the dimeric methyl complex free from alkali metal adduct can be conveniently isolated from the reaction of $(Bu^tCp)_2LnCl$ with LiMe.[15] We now report the use of the methyl complex as a precursor, having studied its reaction with PhC≡CH. Work-up of the reaction afforded the corresponding acetylide complex: $[(Bu^tCp)_2LnCH_3]_2 + HC{\equiv}CPh \rightarrow [(Bu^tCp)_2LnC{\equiv}CPh]_2$ (Ln = Nd, Gd).

The IR spectra of **I** and **II** show strong absorptions at 2030 and 2045 cm^{-1}, respectively, which can be compared to reported μ-C≡CPh values of 2036 cm^{-1} for $[(Bu^tCp)_2SmC{\equiv}CPh]_2$,[11] 2040 cm^{-1} for $Yb_3(C_5Me_5)_4(C{\equiv}CPh)_4$[9] and 2050 cm^{-1} for $[(C_5Me_5)_2Nd(C{\equiv}CPh)_2K]_n$.[7] These values can be compared to reported values for the other alkynide complexes of lanthanides: 2050 cm^{-1} for $[(CH_3Cp)_2YbC{\equiv}CBu^t]_2$,[4] 2020 cm^{-1} for $[(C_5Me_5)_2LaC{\equiv}CBu^t]_2$,[16] 2050 cm^{-1} for $[Cp_2ErC{\equiv}CBu^t]_2$.[4] In comparison with the three $[(Bu^tCp)_2LnC{\equiv}CPh]_2$, the terminal ν(C≡CPh) stretches occur at somewhat higher energies in the order Nd, Sm, Gd. This is reasonable because the terminal C≡CR stretches for metals of the same mass generally occur at slightly higher energies, for example 2060 cm^{-1} for $(C_5Me_5)_2LaC{\equiv}CBu^t(THF)$[16] and 2072 cm^{-1} for $(C_5Me_5)_2Sm(THF)C{\equiv}CBu^t$.[7]

The mass spectra of the complexes did not show a parent molecular ion and gave only some fragments, such as $[Cp'_2Ln]^+$, $[Cp'_2Ln-CH_4]^+$, $[Cp'+H]^+$ and $[CH{\equiv}CPh]^+$. The data indicate that the Ln—C≡CPh bond is first cleaved, giving very high relative intensity peaks of $[Cp'_2Ln]^+$ and $[CH{\equiv}CPh]^+$.

The ^{1}H NMR spectrum of the neodymium complex shows that protons of the benzene ring appear at δ 7.07, 7.13 and 7.49, cyclopentadienyl protons at δ 16.68 and 17.62, and Bu^t protons at δ −11.02.

Table 1. Crystal data and collection parameters for complexes **I** and **II**

	$[(\mathrm{Bu^tCp})_2\mathrm{NdC{\equiv}CPh}]_2$	$[(\mathrm{Bu^tCp})_2\mathrm{GdC{\equiv}CPh}]_2$
Molecular weight	975.54	1001.56
Space group	$C2/c$	$C2/c$
a (Å)	20.102(3)	19.902(3)
b (Å)	17.312(2)	17.193(4)
c (Å)	13.026(2)	13.054(2)
β (°)	99.50(1)	99.66(1)
V (Å^3)	4470.95(1.20)	4403.48(1.37)
Z	4	4
D_c (g cm^{-3})	1.45	1.51
$F(000)$	1976	2008
μ (cm^{-1})	23.33	31.09
Measured temperature	25	25
Radiation (λ, Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
Data set, h, k, l	0–15, 0–20, −23 to 23	0–15, 0–20, −23 to 23
Scan range, 2θ (°)	2–47	2–47
Reflections collected	3718	3652
Reflections with $I > 3\sigma(I_0)$	2430	2807
R	0.0269	0.0344
R_w	0.0267	0.0343

Table 2. Selected bond lengths (Å) for complexes **I** and **II**

	Complex **I**	Complex **II**
Ln—Ln(a)	4.025(1)	3.934(1)
Ln—C(1)	2.641(5)	2.601(7)
Ln—C(1a)	2.602(4)	2.532(6)
Ln—C(11)	2.814(4)	2.768(6)
Ln—C(12)	2.753(4)	2.698(7)
Ln—C(13)	2.720(4)	2.670(7)
Ln—C(14)	2.714(4)	2.675(7)
Ln—C(15)	2.768(4)	2.721(7)
Ln—C(21)	2.785(4)	2.745(6)
Ln—C(22)	2.767(4)	2.732(6)
Ln—C(23)	2.730(4)	2.680(7)
Ln—C(24)	2.686(4)	2.641(7)
Ln—C(25)	2.727(4)	2.696(7)
C(1)—C(2)	1.204(6)	1.204(9)
C(2)—C(3)	1.442(6)	1.454(9)
C(3)—C(4)	1.386(7)	1.360(10)
C(4)—C(5)	1.378(8)	1.402(11)
C(5)—C(6)	1.316(9)	1.350(14)
C(6)—C(7)	1.399(10)	1.339(15)
C(7)—C(8)	1.348(8)	1.357(12)
C(3)—C(8)	1.384(7)	1.405(11)
Ln—Cent(1)	2.483(1)	2.546(1)
Ln—Cent(2)	2.462(1)	2.415(1)
Av. Ln—C (ring 1)	2.756(16)	2.706(16)
Av. Ln—C (ring 2)	2.739(15)	2.699(17)
Av. Ln—C (ring)	2.748(15)	2.703(19)

The ^{13}C NMR spectrum shows benzene ring resonances at δ 111.34, 125.1, 132.75 and C≡C resonance at δ 140.89 and 234.48, respectively. The cyclopentadienyl resonances appear at δ 259.62 and 270.16, and those of Bu^t at δ 29.03 and 3.78.

Table 3. Selected bond angles (°) for complexes **I** and **II**

	Complex **I**	Complex **II**
Ln—C(1)—Ln(a)	100.3(2)	100.0(2)
C(1)—Ln—C(1a)	78.9(2)	79.1(2)
Ln—C(1)—C(2)	101.6(3)	100.7(5)
Ln(a)—C(1)—C(2)	158.1(4)	159.2(6)
Cent(1)—Ln—Cent(2)	124.7(1)	121.2(1)
Cent(1)—Ln—C(1)	110.4(1)	114.1(1)
Cent(1)—Ln—C(1a)	116.6(1)	117.0(2)
Cent(2)—Ln—C(1)	108.2(1)	109.1(1)
Cent(2)—Ln—C(1a)	108.4(1)	108.5(2)
C(11)—Ln—C(12)	29.6(1)	30.0(2)
C(12)—Ln—C(13)	29.6(1)	30.3(2)
C(13)—Ln—C(14)	29.6(1)	30.6(2)
C(14)—Ln—C(15)	29.7(1)	29.9(2)
C(11)—Ln—C(15)	29.0(1)	30.0(2)
C(1)—C(2)—C(3)	177.0(5)	177.7(7)
C(2)—C(3)—C(4)	121.5(4)	120.8(6)
C(3)—C(4)—C(5)	120.7(5)	120.2(7)
C(4)—C(5)—C(6)	121.0(6)	119.8(9)
C(5)—C(6)—C(7)	119.7(6)	120.4(8)
C(6)—C(7)—C(8)	120.3(6)	121.4(9)
C(3)—C(8)—C(7)	120.9(5)	120.0(8)

The results of IR, X-ray diffraction (see below) and ^{13}C NMR (for the neodymium complex only) analyses show that both the complexes have the normal dimeric structure with bridged $C{\equiv}CPh$ group. In our case no coupling reaction was observed. It seems that whether the coupling reaction occurs or not depends mainly on the steric arrangement of the ligands around the metal.

Molecular structures of I *and* II

As shown in Figs 1 and 2, complexes **I** and **II** are isostructural, both having asymmetric alkynide bridges. They have an overall structure typical of other species, e.g. $[Cp_2ErC{\equiv}CC(CH_3)_3]_2$,[4] $[(CH_3CP)_2SmC{\equiv}CC(CH_3)_3]_2$[10] and $[(Bu^tCp)_2SmC{\equiv}CPh]_2$.[11]

Nd(Gd)—C (Cp ring) distances range from 2.686(4) [2.641(7) Å] to 2.814(4) Å [2.768(6) Å], with the longest distances being those involving carbon atoms bonded to Bu^t groups. The average Nd(Gd)—C (Cp ring) distance of 2.746(13) Å [2.703(19) Å] is also comparable to 2.722(12) Å in $[(Bu^tCp)_2Sm{\equiv}CPh]_2$ and 2.72(4) Å in $[(CH_3Cp)_2SmC{\equiv}CC(CH_3)_3]_2$.

The average Nd—C (alkynyl) distances of 2.641(5) and 2.602(4) Å are comparable with the analogous values of 2.617(13) and 2.560(11) Å in $[(Bu^tCp)_2SmC{\equiv}CPh]_2$ and 2.601(7) and 2.532(6) Å in complex **II**, within 0.016 Å, after corrections of 0.031 and 0.057 Å for the difference in ionic radii of Sm^{3+} and Gd^{3+}.[17] However, the distances are somewhat longer than the distances in $[Cp_2ErC{\equiv}CC(CH_3)_3]_2$, 2.47(2) and 2.42(2) Å, even though the difference in the ionic radius of Er^{3+} was taken into account.

The $C{\equiv}C$ bond lengths of the alkynide ligand in **I** [1.204(6) Å] and **II** [1.204(9) Å] are comparable to 1.202(17) Å in $[(Bu^tCp)_2SmC{\equiv}CPh]_2$ and 1.20(2) Å in $[(CH_3Cp)_2SmC{\equiv}CC(CH_3)_3]_2$.

The neodymium (gadolinium) atom is surrounded in a distorted tetrahedral fashion (Cp_2NdC_2), with Cp (centroid of ring)—Nd(Gd)—C angles ranging from 108.2(1) to 116.6(1)° [108.5(2)–117.0(2)°], and C(1)—Nd(Gd)–C(1a) and Cp(1)—Nd(Gd)–Cp(2) angles

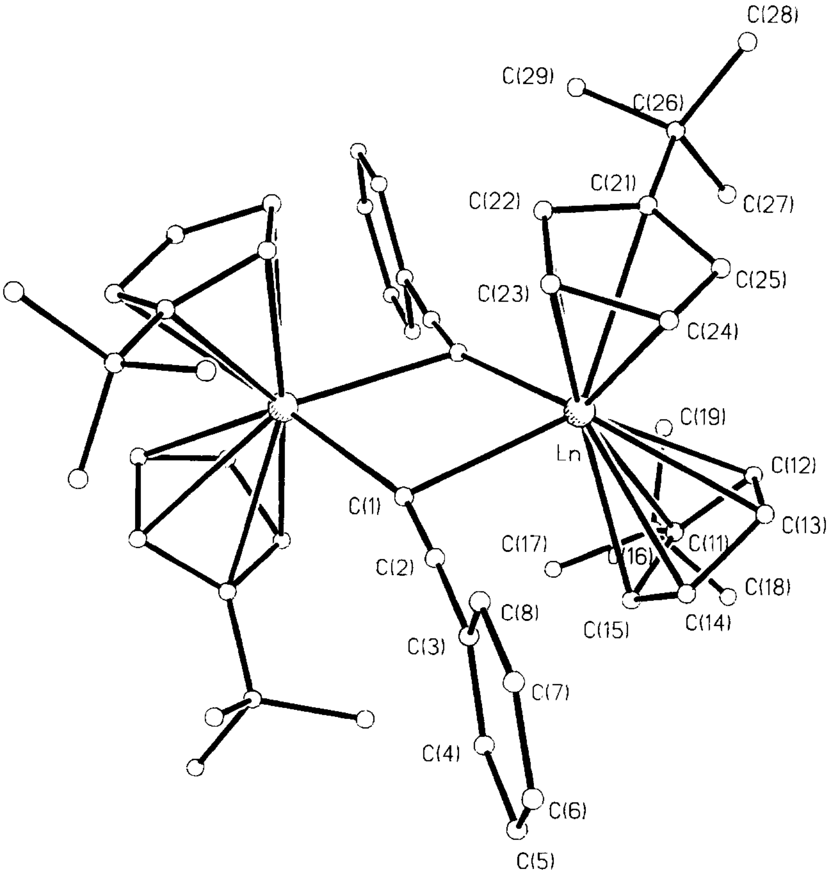

Fig. 1. Molecular structure of $[(Bu^tCp)_2LnC{\equiv}CPh]$.

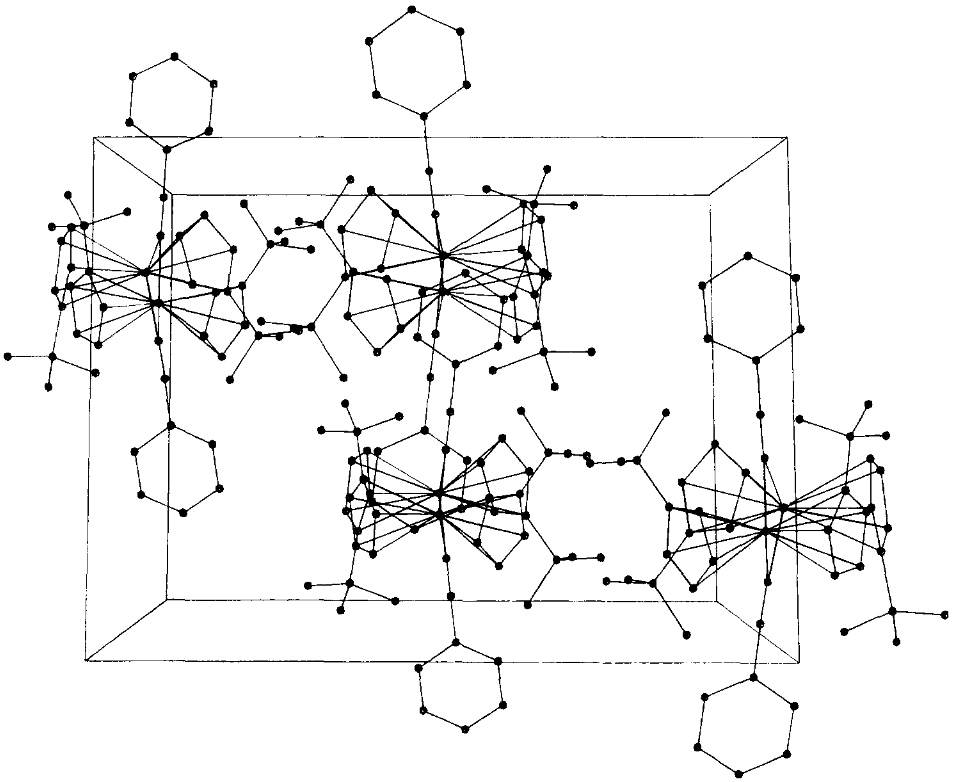

Fig. 2. The molecular packing of [$(Bu^tCp)_2LnC{\equiv}CPh$] in the unit cell.

of 78.9(2)° [79.1(2)°] and 124.7(1)° [121.2(1)°], respectively.

Acknowledgements—We thank the National Science Foundation of China and the State Key Program of Basic Research for financial support of this research.

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