Synthesis of (t-C₄H₉C₅H₄)₂Sm(DME) and its reactivity with phenylacetylene: synthesis and structure of ((t-C₄H₉C₅H₄)₂SmC≡CPh)₂

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Abstract

The reaction of $(t\text{-}C_4H_9C_5H_4)_2SmCl(DME)$ with Na in THF at 65°C gives $(t\text{-}C_4H_9C_5H_4)_2Sm(DME)$. The complex $(t\text{-}C_4H_9C_5H_4)_2Sm(DME)$ reacts with PhC≡CH in toluene to form $((t\text{-}C_4H_9C_5H_4)_2SmC≡CPh)_2$. $((t\text{-}C_4H_9C_5H_4)_2\text{-}SmC≡CPh)_2$ crystallizes from toluene in the monoclinic space group $C2/n$ with unit-cell dimensions a 13.064(2), b 17.279(2), c 20.019(5) Å, β 99.62(2)°, V 4455.4 Å³ and D_{calcd} 1.47 gcm⁻³ for $Z = 4$. Least-squares refinement of 2201 unique observed reflections converged to a final R of 0.0498. The two $(t\text{-}C_4H_9C_5H_4)_2Sm$ units are connected by asymmetrical alkynide bridges with independent Sm–C (alkynide) bond lengths of 2.56(1) and 2.62(1) Å, Sm–C≡C angles of 158.8(1) and 100.6(9)°. The average Sm–C(ring) bond length is 2.722(13) Å.

Introduction

Pentamethylcyclopentadienyl samarium(II) has been studied extensively as a reducing agent in oxidation-addition with a variety of substances [1–4]. Less attention has been given to the effect of ring-substituents on the reactivity of biscyclopentadienyl samarium(II) in these reactions. We used t-butylcyclopentadiene as a ligand to synthesize a divalent complex $(t\text{-}C_4H_9C_5H_4)_2Sm(DME)$ and examined its reactivity with a terminal alkyne. Here we describe the synthesis of $(t\text{-}C_4H_9C_5H_4)_2Sm(DME)$ and its reaction with phenylacetylene to form a trivalent alkynyl-bridged complex $((t\text{-}C_4H_9C_5H_4)_2SmC≡CPh)_2$.

Experimental

Since the complexes described below were extremely air- and moisture-sensitive, all experiments were conducted under pure argon by Schlenk techniques. THF,

DME (dimethoxyethane) and pentane were predried with $CaCl_2$ and distilled from sodium benzophenoneketyl. Anhydrous $SmCl_3$ was prepared by Taylor's method [5]. t-$C_4H_9C_5H_5$ was prepared by a procedure published previously [6]. PhC≡CH (Fluka AG) was dried over molecular sieves and distilled before use.

Metal analysis was carried out by complexometric titration and the direct burning technique was used for the carbon and hydrogen analysis. Melting points were determined in sealed argon-filled capillaries. Infrared spectra were recorded on an Digilab FTS-20E spectrometer as KBr pellets.

(t-$C_4H_9C_5H_4$)$_2$Sm(DME) (I)

To a suspension of $SmCl_3$ (1.38 g, 5.38 mmol) in 10 ml of THF was added a solution of Na(t-$C_4H_9C_5H_4$) (1.54 g, 10.7 mmol) in THF (50 ml) and the suspension was stirred at 60°C for 2 days. After centrifugation to remove NaCl, metallic sodium (115 mg, 5 mmol) was added to the resulting clear yellow solution. Another 2-day reaction at 65°C with stirring gave a red-brown suspension. After centrifugation, the red-brown solution was dried in vacuum, then 10 ml of DME was added and the mixture was cooled at −30°C. Red-brown crystals of I, 342 mg (13%), were obtained. Anal. Found: C, 53.97; H, 8.00; Sm, 31.9. $C_{22}H_{36}O_2Sm$ calcd.: C, 54.73; H, 7.52; Sm, 31.2%. IR(KBr): 3060w, 2960s, 2860w, 1670w, 1600m, 1460s, 1365s, 1280m, 1250m, 1200m, 1140m, 1080m, 1020m, 980m, 850m, 750s, 670s.

((t-$C_4H_9C_5H_4$)$_2$Sm(C≡CPh))$_2$ (II)

PhC≡CH (91.8 mg, 0.9 mmol) and (t-$C_4H_9C_5H_4$)$_2$Sm(DME) (227 mg, 0.47 mmol) were placed in a Schlenk flask, and toluene (10 ml) was added. The mixture was stirred at 60°C until the red-brown suspension turned to a clear yellow solution. The solution was concentrated and crystallized at room temperature to give the bright yellow crystals of II, 149.5 mg (yield 66.0%). mp: 194–196°C. Anal. Found: Sm, 31.1. $Sm_2C_{52}H_{62}$ calcd.: Sm, 30.5%. IR((KBr): 3070m, 3955s, 2860s, 2036s, 1660s, 1595s, 1490m, 1460s, 1360s, 1280m, 1157s, 1050m, 1025m, 920m, 855w, 825m, 760s, 690m, 620w.

X-Ray structure determination of II

A crystal of dimensions 0.36 × 0.32 × 0.44 mm sealed in a thin-walled glass capillary under argon was placed in a Nicolet R3m/E automatic diffractometer. Cell parameters obtained by a least-squares refinement of 25 reflections with $1.5 < \theta < 13°$ are given in Table 1.

Data were collected by the ω scan technique. During data collection, the intensities of the standard reflections monitored every 70 reflections decreased by 0.4% and so decay was not corrected for. The intensities were corrected for Lorentz, polarization, and absorption effects ($\mu = 26.9$ cm^{-1}). The range for h was 0 to 18, for k 0 to 23, and for l −27 to 27.

Calculations were carried out with the SHELXTL system of computer programs. Systematic absences showed the space group to be $C2/n$. The position of the samarium atom was determined from a three dimensional Patterson map followed by the use of Fourier technique. The positions of all the non-hydrogen atoms could be fixed on difference Fourier maps. They were refined by least squares and, at the final stage, refined anisotropically. The final agreement factors are $R = 0.0498$ and $R_w = 0.0616$. The final values of the positional parameters are given in Table 2.

Table 1

Crystal data

Compound	$((t\text{-}C_4H_9C_5H_4)_2SmC\equiv CPh)_2$
Molecular weight	987.2
Crystal size, mm	$0.36 \times 0.32 \times 0.44$
Cell constants	
a, Å	13.064(2)
b, Å	17,279(2)
c, Å	20.019(5)
β, deg	99.62(2)
V, Å^3	4455.4
Scan range 2θ, deg	3–56
Reflections	5319
Reflections for $I > 3\sigma(I)$	2201
Space group	$C2/n$
Z	4
D, g/cm^3	1.47
R	0.0498
R_w	0.0616
$F(000)$	1967

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (e.s.d.'s refer to last significant digit)

	x	y	z	U
Sm	2795(1)	−50(1)	8508(1)	28(1)
C(1)	3746(10)	66(8)	7461(6)	37(4)
C(2)	4625(11)	164(7)	7740(6)	38(4)
C(3)	5726(11)	243(7)	8048(7)	42(4)
C(4)	6147(12)	977(9)	8134(9)	59(6)
C(5)	7204(14)	1082(11)	8403(9)	79(8)
C(6)	7804(12)	429(12)	8595(9)	70(7)
C(7)	7364(14)	−302(12)	8503(11)	85(9)
C(8)	6352(14)	−386(10)	8237(9)	65(7)
C(11)	2357(10)	1396(7)	9013(6)	33(4)
C(12)	2492(12)	882(7)	9564(7)	41(5)
C(13)	3532(13)	645(7)	9710(7)	48(5)
C(14)	4090(12)	1002(7)	9207(8)	49(5)
C(15)	3313(11)	1454(7)	8778(6)	36(4)
C(16)	1376(11)	1917(7)	8772(7)	38(4)
C(17)	1390(12)	2217(8)	8039(7)	51(5)
C(18)	1464(13)	2624(8)	9251(7)	53(5)
C(19)	357(11)	1445(9)	8795(8)	53(6)
C(21)	1999(12)	−1400(6)	8964(7)	34(5)
C(22)	2394(11)	−1598(7)	8369(6)	34(4)
C(23)	3526(13)	−1497(8)	8489(7)	49(5)
C(24)	3781(10)	−1223(7)	9197(7)	38(4)
C(25)	2853(12)	−1174(7)	9461(6)	40(5)
C(26)	868(10)	−1504(7)	9085(7)	39(5)
C(27)	503(12)	−752(9)	9360(9)	56(6)
C(28)	859(14)	−2168(9)	9579(8)	64(7)
C(29)	185(12)	−1690(9)	8398(8)	59(6)

Supplementary material available. Tables of bond lengths and angles, temperature factors and least-squares planes (8 pages) a listing of calculated and observed structure factors (13 pages) are available from the authors.

Results and discussion

Syntheses

The yellow THF solution of $(t\text{-}C_4H_9C_5H_4)_2SmCl(DME)$ reacts with one equiv. of metallic sodium to give a red-brown solution. When the solution is evaporated to dryness, extracted with DME and cooled, the red-brown product is obtained. The product was characterized by complete elemental analysis and infrared spectroscopy. Owing to the strong reducing potential of Sm^{II} the divalent organosamarium complex is a good single-electron transfer reagent. In order to study the one-electron oxidation addition of compound I with a terminal alkyne we have examined the reactivity of compound I with phenylacetylene. Compound I reacts with $C_6H_5C{\equiv}CH$ to form the phenylalkynide compound II (eq. 1):

$$(t\text{-}C_4H_9C_5H_4)_2Sm(DME) + PhC{\equiv}CH \rightarrow ((t\text{-}C_4H_9C_5H_4)_2SmC{\equiv}CPh)_2 \qquad (1)$$
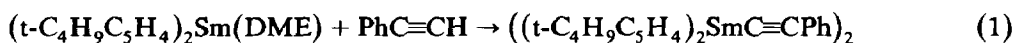
During the reaction period, the red-brown color of the divalent starting material gradually changes into the yellow color characteristic of Sm^{III}; yellow crystals of compound II were obtained after suitable workup. The infrared spectrum of compound II shows a strong sharp absorption at 2036 cm^{-1} assignable to $\nu(C{\equiv}C)$ ($Yb_3(C_5Me_5)_4(C{\equiv}CPh)_4$, 2040 cm^{-1}; $Eu_2(C_5Me_5)_2(C{\equiv}CPh)_2(THF)_4$, 2025 cm^{-1} [7]).

It has been reported that the reaction of divalent metallocene $(C_5Me_5)_2Yb(OEt_2)$ or $(C_5Me_5)_2Eu(OEt_2)$ with $PhC{\equiv}CH$ yields a mixed-valence complex $(C_5Me_5)_4Yb_3$ $(\mu\text{-}C{\equiv}CPh)_4$ or a divalent complex $((THF)_2(C_5Me_5)Eu(\mu\text{-}C{\equiv}CPh))_2$ [7]. We isolated only the trivalent complex II. These results are consistent with the order of reducing power, viz.: $Sm^{2+} > Yb^{2+} > Eu^{2+}$.

Molecular structure of II

As shown in Fig. 1, complex II has an alkynyl-bridged dimer structure which is similar to that of $((CH_3C_5H_4)_2SmC{\equiv}CC(CH_3)_3)_2$ (III) [8]. The t-butyl groups on the two cyclopentadienyl rings bonded to a single metal centre are approximately eclipsed with respect to each other. The t-butyl groups on adjacent rings on two different metals point away from each other in a 'trans' disposition. The phenyl group in the $C{\equiv}CPh$ ligand points away from the eclipsed t-butyl groups on one samarium and toward the un-butylated part of the rings on the other metal. Bond distances and angles are given in Tables 3 and 4.

The average Sm–C (ring) distances are 2.733(13) and 2.722(12) Å compared with 2.72(4) and 2.71(4) Å for III. The metal-to-ring centroid distances 2.450(1) and 2.420(1) Å are similar to those (2.43 and 2.44 Å) found in III. The Sm–C(1) and Sm–C(1′) bond distances are 2.617(13) and 2.560(11) Å, respectively, which indicates that the carbon atom of the electron-deficient alkynyl bridge is positioned asymmetrically between the samarium atoms. The difference (0.06 Å) is similar to the 0.05 Å difference reported for $((C_5H_5)_2ErC{\equiv}CC(CH_3)_3)_2$ (IV) [9]. The asymmetry of the alkynide bridges in II is also be reflected in the disparity in Sm–C≡C and Sm′–C≡C angles, which are 158.8(11) and 100.6(9)°, respectively. The 58.2° dif-
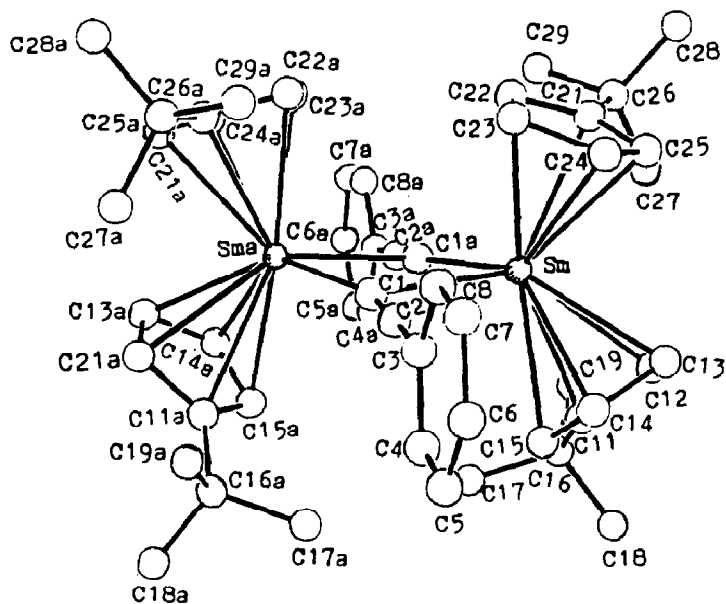
Fig. 1. Molecular structure of ((t-C$_4$H$_9$C$_5$H$_4$)$_2$SmC≡CPh)$_2$.

ference is large compared with that expected for bridging alkynides which have no π component in their bonding and much greater than the difference of 34° found in IV and 39° in III. The Sm–C(2) distance (3.074 Å) is shorter than that (3.2 Å) in III

Table 3

Bond lengths (Å) (e.s.d.'s refer to last significant digit)

Sm–Sm′	3.982(1)	Sm–C(2)	3.074
Sm–C(11)	2.789(12)	Sm–C(12)	2.736(13)
Sm–C(13)	2.717(14)	Sm–C(14)	2.708(14)
Sm–C(15)	2.717(12)	Sm–C(21)	2.770(13)
Sm–C(22)	2.731(11)	Sm–C(23)	2.680(14)
Sm–C(24)	2.661(12)	Sm–C(25)	2.715(12)
Sm–C(1)	2.617(13)	Sm–C(1′)	2.560(11)
C(1)–C(2)	1.202(17)	C(2)–C(3)	1.473(19)
C(3)–C(4)	1.383(20)	C(4)–C(5)	1.407(23)
C(5)–C(6)	1.391(27)	C(6)–C(7)	1.387(29)
C(7)–C(8)	1.348(24)	C(3)–C(8)	1.374(21)
C(11)–C(12)	1.404(17)	C(12)–C(13)	1.402(22)
C(13)–C(14)	1.474(23)	C(14)–C(15)	1.444(19)
C(11)–C(15)	1.409(20)	C(11)–C(16)	1.575(18)
C(16)–C(17)	1.560(20)	C(16)–C(18)	1.544(18)
C(16)–C(19)	1.569(21)	C(21)–C(22)	1.416(20)
C(22)–C(23)	1.469(22)	C(23)–C(24)	1.479(19)
C(24)–C(25)	1.404(21)	C(21)–C(25)	1.421(19)
C(21)–C(26)	1.546(21)	C(26)–C(27)	1.518(21)
C(26)–C(28)	1.519(21)	C(26)–C(29)	1.542(19)
Sm–cent(1)	2.450(1)	Sm–cent(2)	2.420(1)
Av. Sm–C(ring1)	2.733(13)	Av. Sm–C(ring2)	2.714
Av. Sm–C(ring)	2.722(12)		

Table 4

Bond angles ($^\circ$) (e.s.d.'s refer to last significant digit)

C(11)–Sm–C(12)	29.4(4)	C(12)–SM–C(13)	29.8(5)
C(13)–Sm–C(14)	31.5(5)	C(14)–Sm–C(15)	30.9(4)
C(11)–Sm–C(15)	29.6(4)	C(21)–Sm–C(22)	29.8(4)
C(22)–Sm–C(23)	31.5(5)	C(23)–Sm–C(24)	32.1(4)
C(24)–Sm–C(25)	30.2(4)	C(21)–SM–C(25)	30.0(4)
C(1)–Sm–C(1')	78.8(4)	Sm–C(1)–Sm'	100.5(4)
Sm–C(1)–C(2)	100.6(9)	Sm'–C(1)–C(2)	158.8(11)
Cent(1)–Sm–Cent(2)	124.3(1)	Cent(1)–Sm–C(1)	110.4(4)
Cent(1)–Sm–C(1')	116.4(5)	Cent(2)–Sm–C(1)	108.4(4)
Cent(2)–Sm–C(1')	108.4(5)	C(1)–C(2)–C(3)	175.9(13)
C(2)–C(3)–C(4)	118.5(12)	C(2)–C(3)–C(8)	122.5(12)
C(4)–C(3)–C(8)	119.0(14)	C(3)–C(4)–C(5)	120.6(25)
C(4)–C(5)–C(6)	118.3(17)	C(5)–C(6)–C(7)	120.6(15)
C(6)–C(7)–C(8)	120.5(17)	C(3)–C(8)–C(7)	121.6(16)
C(12)–C(11)–C(15)	107.8(11)	C(11)–C(12)–C(13)	109.8(13)
C(12)–C(13)–C(14)	107.9(12)	C(13)–C(14)–C(15)	104.7(13)
C(15)–C(11)–C(16)	125.4(11)	C(11)–C(16)–C(17)	109.9(12)
C(11)–C(16)–C(18)	106.9(10)	C(11)–C(16)–C(19)	110.2(10)
C(17)–C(16)–C(18)	108.0(10)	C(17)–C(16)–C(19)	110.1(11)
C(18)–C(16)–C(19)	111.6(13)	C(22)–C(21)–C(25)	107.6(13)
C(21)–C(22)–C(23)	109.4(11)	C(22)–C(23)–C(24)	104.7(13)
C(23)–C(24)–C(25)	108.1(11)	C(21)–C(25)–C(24)	110.3(11)
C(22)–C(21)–C(26)	126.5(12)	C(25)–C(21)–C(26)	125.5(12)
C(21)–C(26)–C(27)	108.9(11)	C(21)–C(26)–C(28)	108.0(11)
C(21)–C(26)–C(29)	108.1(12)	C(27)–C(26)–C(28)	111.7(13)
C(27)–C(26)–C(29)	109.3(11)	C(28)–C(26)–C(29)	110.7(12)

and IV. The shorter Sm–C(2) distance clearly indicates that there is a little η^2 interaction of the triple-bond π orbitals with the samarium center. The observed angles of 158.8(11) and 100.6(9)$^\circ$ in II are similar to 158 and 110° found in $((CH_3)_2AlC\equiv CCH_3)_2$ (V) [10]. The bonding in V is described as being covalent, with one normal Al–C single bond and one bridging C–Al dative bond involving the electron pair in the C≡C bond.

Acknowledgment

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