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Journal of Organometallic Chemistry 483 (1994) 21–25

Journal of Organometallic Chemistry

Synthesis and structure of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2)$

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Received 18 November 1993; in revised form 7 March 1994

Abstract

$(C_5Me_5)_2Sm(THF)_2$ reacts with acetylene in THF to form $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C_2)$ (1). Compound 1 crystallized from benzene in the monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with unit cell parameters at 168 K of $a = 10.889$ (2) Å, $b = 15.048(2)$ Å, $c = 31.904(3)$ Å, $\beta = 96.38(1)°$, $V = 5196(1)$ Å^3 and $D_{calcd} = 1.391$ g cm^{-3} for $Z = 4$. Least squares refinement of the model based on 8058 reflections ($|F_o| > 2.0\sigma(|F_o|)$) converged to a final $R_F = 5.5\%$. The two $(C_5Me_5)_2Sm$ units in 1 are connected by a nearly linear Sm–C≡C–Sm bridge with SmCC angles of 175.3(6) and 176.3(6)°. Each samarium in 1 has a typical $(C_5Me_5)_2SmL_2$ geometry in which the two C_5Me_5 ring centroids, the THF oxygen atom, and the carbon of the acetylide ligand describe a distorted tetrahedron. The Sm–C distances are 2.438(7) and 2.448(8) Å and the CC bond length is 1.21(1) Å. The average Sm–C(C_5Me_5) distance is 2.742(4) Å.

Keywords: Samarium; Lanthanide; Acetylide; Alkynide; Rare earth metals; Metallocenes

1. Introduction

The divalent organosamarium complexes $(C_5Me_5)_2Sm(THF)_x$ ($x = 0$ [1], 1 [2] and 2 [3]) have a propensity to react in a 2:1 stoichiometry with unsaturated substrates to make compounds of general formula $[(C_5Me_5)_2Sm]_2$ (substrate), in which the substrate formally undergoes a two electron reduction [4–11]. In reactions involving N_2 [9], PhCH=CH$_2$ [8] and PhCH=CHPh [8], the products have planar Sm_2E_2 units (E = C, N) in which the original N=N or C=C bond in the substrate is coordinated in an η^2 fashion on either side by the two samarium centers. Related η^2-complexes are also known involving Bi_2 [12] and N_2H_2 [13] moieties. The reaction of $(C_5Me_5)_2Sm(THF)_2$ with PhC≡CPh also forms a 2:1 product, $[(C_5Me_5)_2Sm]_2$(PhCCPh), but its high solubility has precluded complete characterization by X-ray crystallography [11].

To learn more about $(C_5Me_5)_2Sm(THF)_x$/alkyne interactions, we were interested in how HC≡CH would interact with $(C_5Me_5)_2Sm$ units. This small substrate could conceivably form a 2:1 complex as in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ [9] and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2H_2)$ [13], but it could also be metallated to form the alkynide $(C_5Me_5)_2Sm$(C≡CH)(THF) (cf. $(C_5H_5)_3U$(C≡CH) [14]) which could react further to form the carbide $[(C_5Me_5)_2Sm]_2$(C≡C). This complex could have a $\mu\text{-}\eta^2:\eta^2$-structure or a $\mu\text{-}\eta^1:\eta^1$-structure as was found in $[(C_5Me_5)_2Sc]_2(\mu\text{-}\eta^1:\eta^1$-C≡C) [15]. Organolanthanide alkynides are independently interesting since they have recently been shown to undergo coupling to form trienediyl complexes [16–19] and can initiate alkyne dimerization and oligomerization reactions [17,20]. We report here on the reactions of HC≡CH with organosamarium complexes and the isolation and crystal structure of $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1$-C≡C).

2. Experimental section

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk double manifold, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Solvents were purified and measurements were obtained as previously described [21]. $(C_5Me_5)_2Sm$ [1], $(C_5Me_5)_2Sm(THF)$ [2], $(C_5Me_5)_2Sm(THF)_2$ [3,22] and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ [14] were prepared as previ-

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SSDI 0022-328X(94)24669-A

ously described. Purified acetylene was obtained from Matheson.

2.1. $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (1)

Excess acetylene was condensed at −196°C onto a frozen solution of $(C_5Me_5)_2Sm(THF)_2$ (100 mg, 0.18 mmol) in 5 ml of THF. The reaction mixture was allowed to warm up to −78°C and stirred for 30 min at this temperature. Subsequently, the reaction mixture was allowed to warm up to room temperature upon which it became yellow. As soon as the color changed, the reaction was again cooled to −196°C. The flask was opened to vacuum, the cold bath was removed, and excess acetylene and the solvent were removed as the system warmed. The crude product, a yellow oil, was dissolved in hexanes and centrifuged. Removal of solvent gave a yellow oil. The ^{1}H NMR spectrum (C_6D_6, 300 MHz, 25°C) contained at least six resonances in the δ 1–2 region typical for C_5Me_5 groups. Signals at 1.32 and 1.42 ppm were most prominent and accounted for approximately 60% of the intensity in this region. From this mixture, complex **1** crystallized from benzene at room temperature.

2.2. X-ray data collection, structure determination, and refinement for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}C{\equiv}C)$ (1)

Under nitrogen, a yellow crystal of approximate dimensions 0.30 × 0.33 × 0.40 mm was immersed in Paratone-D oil. The oil-coated crystal was then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex $P2_1$ automated four-circle diffractometer equipped with a modified LT-1 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill [23]. Intensity data were collected at 168 K using an omega scan technique with Mo-Kα radiation under the conditions given in Table 1.

All 10,109 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package [24] or the SHELXTL PLUS program set [25]. The analytical scattering factors for neutral atoms were used throughout the analysis [26]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$.

Table 1
Experimental X-ray data for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1\cdot\eta^1\text{-}C{\equiv}C)$ (1)

Formula	$C_{50}H_{76}O_2Sm2\cdot C_6H_6$
FW	1087.9
Temperature (K)	168
Crystal system	Monoclinic
Space group	$P2_1/c$ [C_{2h}^5; No. 14]
a (Å)	10.889(2)
b (Å)	15.048(2)
c (Å)	31.904(3)
β (°)	96.38(1)
V (Å^3)	5196(1)
Z	4
D_{calc} (mg m^{-3})	1.391
Diffractometer	Siemens P3 (R3m/v System)
Radiation	M-Kα (λ = 0.710730 Å)
Monochromator	Highly oriented graphite
Data collected	$+h, +k, \pm l$
Scan type	θ–2θ
Scan width	1.20° plus Kα separation
Scan speed (in ω)	3.0 deg min^{-1}
2θ range (°)	4.0–50.0
μ (Mo-Kα) (mm^{-1})	2.283
Absorption correction	Semi-empirical (Ψ-scan method)
Reflections collected	10109
Unique reflections with ($\lvert F_o\rvert > 0$)	8610
Reflections with ($\lvert F_o\rvert > 2\sigma(\lvert F_o\rvert)$)	8058
No. of variables	541
R_F (%)	5.5
R_{wF} (%)	6.3
Goodness of fit	1.33

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. There is a molecule of benzene solvent present in the asymmetric unit. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. A final difference-Fourier map yielded ρ(max) = 1.06 e Å^{-3}. The final values of the atomic coordinates are given in Table 2.

3. Results

Acetylene is highly reactive with both divalent and trivalent organosamarium reagents and a variety of products appears to form in these reactions. Acetylene reacts with a frozen solution of $(C_5Me_5)_2Sm$ in toluene as soon as it melts to generate a variety of products. To identify a more controlled reaction system, acetylene was reacted with the solvated complexes, $(C_5Me_5)_2Sm(THF)_x$ (x = 1,2). Reactions which were stopped as soon as the toluene solvent melted also gave a complex reaction mixture. To further reduce the reactivity of this Sm^{II} system, the reaction was conducted in THF at

Table 2
Final atomic coordinates ($\times 10^5$) for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (1)

	x	y	z
Sm(1)	112835(3)	26056(2)	14029(1)
Sm(2)	131121(3)	−11940(2)	12666(1)
O(1)	94948(42)	24119(33)	8725(15)
O(2)	114740(45)	−18297(36)	16569(15)
C(1)	133570(61)	27392(48)	9805(22)
C(2)	123882(63)	30847(47)	7022(21)
C(3)	119883(62)	38828(45)	8669(22)
C(4)	127013(68)	40479(50)	12564(24)
C(5)	135518(63)	33290(52)	13353(23)
C(6)	141841(66)	19663(52)	9110(25)
C(7)	119312(76)	26804(54)	2859(23)
C(8)	110366(73)	45206(52)	6508(28)
C(9)	127292(85)	49234(52)	14954(27)
C(10)	145357(75)	32472(66)	16924(29)
C(11)	112396(68)	22456(59)	22380(21)
C(12)	100775(67)	19826(54)	20494(22)
C(13)	94071(59)	27504(50)	19152(20)
C(14)	101637(70)	34942(51)	20137(21)
C(15)	113035(69)	31855(62)	22169(22)
C(16)	122462(85)	16407(80)	24396(27)
C(17)	95539(89)	10457(56)	20246(29)
C(18)	80638(63)	27866(66)	17398(24)
C(19)	97474(97)	44559(59)	19512(28)
C(20)	123122(85)	37773(78)	24429(25)
C(21)	143321(72)	−10843(58)	20563(23)
C(22)	149351(62)	−4514(48)	18227(22)
C(23)	155845(64)	−8812(50)	15244(24)
C(24)	153897(66)	−18174(51)	15795(28)
C(25)	146177(72)	−19321(54)	19043(28)
C(26)	135315(87)	−8729(80)	23994(26)
C(27)	150078(77)	5321(56)	19211(26)
C(28)	164276(76)	−4346(66)	12593(28)
C(29)	160433(85)	−25490(66)	13787(35)
C(30)	143052(94)	−28131(64)	20917(34)
C(31)	118172(62)	−21681(46)	6276(20)
C(32)	115447(66)	−12743(47)	5311(20)
C(33)	126340(73)	−8593(48)	4231(20)
C(34)	135831(63)	−15108(52)	4545(21)
C(35)	130839(65)	−23160(45)	5821(20)
C(36)	108820(68)	−28879(52)	6966(24)
C(37)	102827(72)	−8408(58)	5197(24)
C(38)	127031(85)	980(52)	2705(25)
C(39)	148451(80)	−13852(66)	3110(28)
C(40)	136820(79)	−32259(53)	5949(29)
C(41)	85852(63)	30071(51)	6617(27)
C(42)	73927(75)	24910(56)	5783(27)
C(43)	77623(75)	15303(56)	6787(25)
C(44)	91223(77)	15365(58)	7120(28)
C(45)	112142(84)	−26905(62)	18262(26)
C(46)	98554(90)	−28316(78)	17460(30)
C(47)	93394(81)	−19242(78)	16328(31)
C(48)	104030(84)	−13040(67)	17350(32)
C(49)	118623(62)	10467(46)	13561(21)
C(50)	122311(63)	2917(53)	13242(21)
C(51)	77148(104)	55732(78)	6798(53)
C(52)	74215(115)	54997(71)	10794(42)
C(53)	63927(113)	49964(69)	11572(33)
C(54)	57170(84)	45889(69)	8358(34)
C(55)	60213(97)	46804(65)	4430(33)
C(56)	70027(118)	51901(73)	3569(39)

low temperature, and in this solvent, the cleanest reaction observed so far was obtained. Under these conditions, the purple color of $(C_5Me_5)_2Sm(THF)_2$ changes upon warming above −78°C to the yellow color characteristic of trivalent samarium and removal of solvent gives a hexane soluble material. Unfortunately, the ^1H NMR spectrum of this material still contains several resonances in the C_5Me_5 region indicating the formation of a mixture. However, the carbide complex $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (**1**) could be isolated from this mixture by crystallization and hence the system minimally involves the reaction shown in Eq. (1).

$$2(C_5Me_5)_2Sm(THF)_2 + HC{\equiv}CH \longrightarrow \underset{(1)}{[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)} + H_2 \quad (1)$$

Attempts to isolate a monometallated intermediate such as $[(C_5Me_5)_2Sm(C{\equiv}CH)(THF)]_n$ were unsuccessful although changes in the ^1H NMR spectra of mixtures of initially-isolated products suggested that such intermediates were present. Acetylene reacts with $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ [11] in hexanes at −78°C, but complicated reaction mixtures were also obtained which exhibited NMR evidence for olefinic products perhaps derived from oligomerization of the acetylene [20].

3.1. Structure

The structure of **1** is shown in Fig. 1. The geometry around the samarium centers is typical of $(C_5Me_5)_2SmL_2$ complexes [27]. The two C_5Me_5 ring centroids, O(1), and C(49) [O(2) and C(50) for Sm(2)] describe a distorted tetrahedron with typical angles (Table 3).

Structurally characterized molecular complexes containing the $\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C$ unit are relatively rare, but comparison can be made with $[(C_5Me_5)_2Sc]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (**2**) [15] $[(C_5H_5)Ru(CO)_2]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (**3**) [28] and $[(PMe_3)_2IPt]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (**4**) [29]. The near linear 175.3(6) and 176.3(6)° Sm–C–C angles in **1** are similar to those in the other acetylide complexes; in

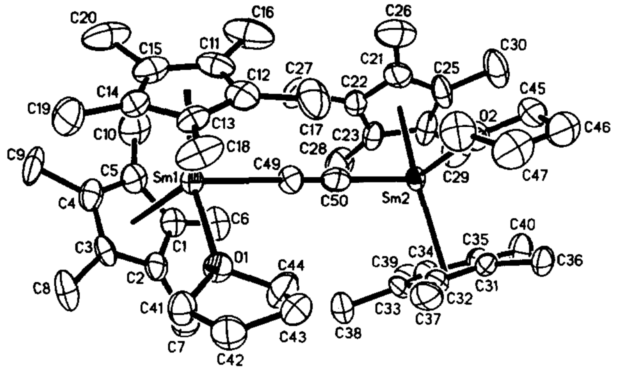

Fig. 1.

Table 3
Selected bond distances (Å) and angles (°) for $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ (**1**)

Sm(1)–O(1)	2.451(4)	Sm(1)–C(1)	2.762(7)
Sm(1)–C(2)	2.750(7)	Sm(1)–C(3)	2.738(7)
Sm(1)–C(4)	2.734(8)	Sm(1)–C(5)	2.730(7)
Sm(1)–C(11)	2.725(7)	Sm(1)–C(12)	2.731(8)
Sm(1)–C(13)	2.763(7)	Sm(1)–C(14)	2.757(7)
Sm(1)–C(15)	2.738(7)	Sm(1)–C(49)	2.438(7)
Sm(1)–Cnt(1)	2.464	Sm(1)–Cnt(2)	2.467
Sm(2)–O(2)	2.478(5)	Sm(2)–C(21)	2.720(7)
Sm(2)–C(22)	2.749(7)	Sm(2)–C(23)	2.767(7)
Sm(2)–C(24)	2.735(7)	Sm(2)–C(25)	2.705(8)
Sm(2)–C(31)	2.767(6)	Sm(2)–C(32)	2.747(6)
Sm(2)–C(33)	2.731(6)	Sm(2)–C(34)	2.739(7)
Sm(2)–C(35)	2.758(7)	Sm(2)–C(50)	2.448(8)
Sm(2)–Cnt(3)	2.455	Sm(2)–Cnt(4)	2.471
C(49)–C(50)	1.213(10)		
O(1)–Sm(1)–C(49)	92.0(2)	O(2)–Sm(2)–C(50)	90.3(2)
Cnt(1)–Sm(1)–C(49)	104.8	Cnt(1)–Sm(1)–O(1)	104.3
Cnt(2)–Sm(1)–C(49)	104.6	Cnt(2)–Sm(1)–O(1)	105.9
Cnt(1)–Sm(1)–Cnt(2)	136.6	Cnt(3)–Sm(2)–C(50)	105.9
Cnt(3)–Sm(2)–O(2)	104.1	Cnt(4)–Sm(2)–C(50)	104.6
Cnt(4)–Sm(2)–O(2)	105.0	Cnt(3)–Sm(2)–Cnt(4)	137.3
Sm(1)–C(49)–C(50)	173.3(6)	Sm(1)–C(50)–C(49)	176.3(6)

2–4, the M–C–C angles are all greater than 175°. The structure of **1** differs from **2–4** in that the larger samarium atoms are each attached to an extra THF of solvation. The end view of the complex (Fig. 2) shows that the two $(C_5Me_5)_2Sm$ units are not staggered to form a tetrahedral array of C_5Me_5 groups as is typical of many $[(C_5Me_5)_2Sm]_2$(substrate) complexes [9,14,30, 31]. This geometry, which is usually required for steric reasons when the bridging substrate is small, is not necessary with the $\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C$ bridge. In this regard, **1** also differs from **2–4** which have a staggered arrangement of the two metallic ends of each complex. The dihedral angle between the two (C_5Me_5 ring centroid)–Sm–(C_5Me_5 ring centroid) planes is 117.8° versus 90° for a perfectly staggered structure.

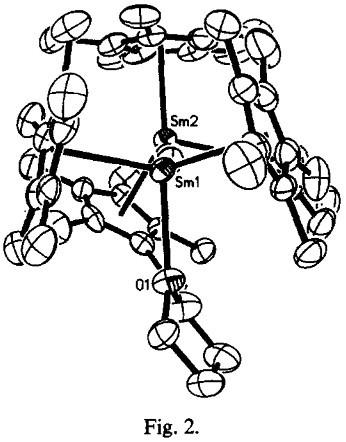

Fig. 2.

The 1.213(10) Å C(49)–C(50) bond distance in **1** is equivalent within the error limits to the distances in **2–4** (1.224(9), 1.19(1) and 1.179(48) Å, respectively) and to the 1.205 Å CC distance in free acetylene [32]. In contrast to the similarity of these distances, solid state lanthanide carbides exhibit CC distances ranging from 1.236 to 1.303 Å [33].

The 2.438(7) and 2.448(8) Å Sm–C(CC) distances in **1** are within the error limits of the 2.484(14) Å Sm–C(Me) distance in $(C_5Me_5)_2Sm(CH_3)(THF)$ [5], but they are on the short side as expected for an alkynide versus an alkyl ligand. The Sm–C distances in **1** are similarly related to the 2.50(2) Å Sm–C distance in $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (**6**), which is an unusual alkynide in that upon THF loss, it undergoes coupling to form the trienediyl $[(C_5Me_5)_2Sm]_2(PhC{=}C{=}C{=}CPh)$ [16,17]. The Sm–C bonds in **1** are closer to the 2.419(6) Å Sm–alkynide bond in unsolvated $[(C_5Me_5)_2Sm(C{\equiv}CCMe_3)]_2$ (**7**) which does not couple [17]. The C≡C bond distances in **6** and **7** are 1.11(2) and 1.208(8) Å, respectively. The 2.451(4) and 2.478(5) Å Sm–O(THF) distances in **1** are equivalent to the 2.473(9) Å and 2.49(1) Å distances in **5** and **6**, respectively.

4. Discussion

As expected, acetylene reacts readily with organosamarium complexes. The reactivity can be controlled to some extent by using the most highly solvated form of $(C_5Me_5)_2Sm$, namely $(C_5Me_5)_2Sm(THF)_2$ in THF. The reaction of the $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ [11] with acetylene follows the reactivity pattern previously observed [17] with this hydride and terminal alkynes in that a variety of products are formed. Since the primary goal of this study was to investigate the interaction of the C≡C bond with the $(C_5Me_5)_2Sm$ unit, major attempts were not made to isolate the monometallated complex $(C_5Me_5)_2Sm(C{\equiv}CH)(THF)$ which presumably is an intermediate in the formation of **1**. The analogous monometallated scandium complex proved to be difficult to isolate in the $(C_5Me_5)_2ScMe/HC{\equiv}CH$ system [15]. However, recently Teuben *et al.* have reported the structure of a bridged C≡CH complex, $\{[C_6H_5C(NSiMe_3)_2]_2Y(\mu\text{-}C{\equiv}CH\}_2$, using *N*,*N*′-bis(trimethylsilyl)benzamidinate ligands [34].

Acetylene does not form a detectable π-complex with $(C_5Me_5)_2Sm$ units. Metallation is facile enough to lead to a dimetallated acetylide dianion as the primary isolable product. Although the $C{\equiv}C^{2-}$ ligand could have conceivably been bound in a $\mu\text{–}\eta^2\text{–}\eta^2$ fashion, it crystallizes in an end-on $\mu\text{–}\eta^1\text{–}\eta^1$ form. This mode of binding is much like that found in the scandium complex, $[(C_5Me_5)_2Sc]_2(\mu\text{–}\eta^1\text{–}\eta^1\text{–}C{\equiv}C)$ (**2**) [15]. The main difference between these two complexes is that the larger size of samarium allows a THF of solvation to be included in the coordination sphere of the metal. This alters the staggered arrangement of the bent metallocenes found in **2**. The presence of THF may also inhibit polymerization of acetylene in this system and would be expected to interfere with coupling reactivity of the type found for unsolvated $(C_5Me_5)_2Sm(C{\equiv}CR)$ complexes [16–20].

5. Conclusion

The acidity of the protons on HC≡CH appears to dominate its chemistry with $(C_5Me_5)_2Sm$-containing complexes and the end-bonded carbide complex $[(C_5Me_5)_2Sm(THF)]_2(\mu\text{-}\eta^1:\eta^1\text{-}C{\equiv}C)$ can be isolated from this reaction.

Acknowledgment

We thank the National Science Foundation for support for this research and the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie, Germany for the award of a Liebig-fellowship (to G.W.R.).

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