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# Tetrahedral *versus* square planar arrangement of cyclopentadienyl ligands in bimetallic organosamarium complexes.

## X-ray crystal structure of $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$

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### Abstract

The effects of cyclopentadienyl ring size on the geometry of bimetallic organosamarium complexes have been studied by comparing the X-ray crystal structure of  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$ , prepared from  $KC_5H_4Me$  and  $SmCl_3$  in THF, with  $C_5Me_5$  analogs. The complex crystallizes from THF at  $-30^\circ C$  in space group  $Pb\bar{c}n$  with  $a = 20.312(5)$ ,  $b = 9.626(2)$ ,  $c = 16.225(3)$  Å,  $V = 3172.5(12)$  Å<sup>3</sup> and  $D_{calc} = 1.74$  g cm<sup>-3</sup> for  $Z = 4$ . Least-squares refinement of the model based on 1759 reflections [ $|F_o| > 2.0\sigma(|F_o|)$ ] converged to a final  $R_F = 5.0\%$ . The complex adopts a geometry which has a molecular two-fold rotation axis perpendicular to the  $Sm_2Cl_2$  plane and a crystallographic inversion center. Hence, both methyl groups of each  $(C_5H_4Me)_2Sm$  unit are located on the side opposite of the THF ligands, which are *trans* to each other, and the four  $C_5H_4Me$  ring centroids define a square plane. The Sm–Cl distances are 2.759(3) and 2.819(3) Å.

### 1. Introduction

Recent studies of bimetallic organosamarium complexes containing two  $(C_5Me_5)_2Sm$  units and small bridging ligands have shown that these complexes tend to form solid state structures in which the four pentamethylcyclopentadienyl ring centroids define a tetrahedral geometry (Fig. 1(a)) rather than a square planar arrangement (Fig. 1(b)). Examples include  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-N_2)$  [1],  $[(C_5Me_5)_2Sm]_2(\mu-O)$  [2],  $[(C_5Me_5)_2Sm(\mu-H)]_2$  [3], and  $[(C_5Me_5)_2Sm]_2(\mu-HNNH)$  [4]. This contrasts with the structures of analogous bimetallic transition metal complexes. In transition metal complexes of general formula  $[(C_5R_5)_2M(\mu-Z)]_2$  [5], orbital requirements [6] favor a square planar arrangement of the ring centroids which places the Z ligands in a plane which bisects the (ring centroid)–metal–(ring centroid) angles of both  $(C_5R_5)_2M$  units (Fig. 1(b)).

The tetrahedral arrangement of ring centroids in the organolanthanide complexes can be explained on the basis of steric factors. With large  $C_5Me_5$  rings and

small bridging ligands, the rings must adopt the sterically preferred four-coordinate geometry of a tetrahedron. Indeed, bimetallic complexes containing two

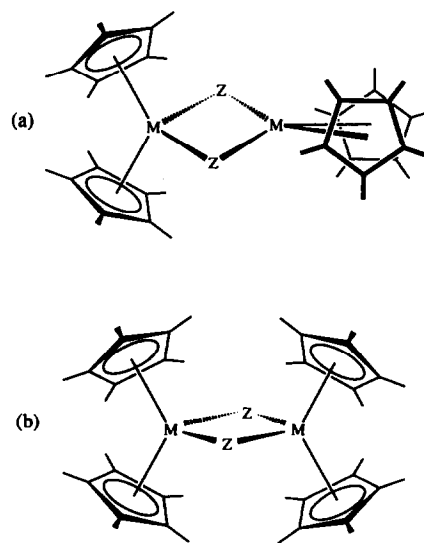


Fig. 1. Coordination geometries for the four cyclopentadienyl rings in  $[(C_5R_5)_2M(\mu-Z)]_2$  complexes. (a) Tetrahedral. (b) Square planar.

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$(C_5Me_5)_2Sm$  units which have larger bridging ligands often have a square planar arrangement of the four ring centroids. Examples include  $[(C_5Me_5)_2Sm](\mu-\eta^2-\eta^2-PhC_4Ph)$  [7],  $[(C_5Me_5)_2Sm](\mu-\eta^2-\eta^2-PhN-NPh)$  [8],  $[(C_5Me_5)_2Sm](\mu-\eta^2-\eta^2-PhNC(O)C(O)NPh)$  [9],  $[(C_5Me_5)_2Sm](\mu-\eta^2-\eta^2-pyCH=C(O)C(O)=CHpy)$  [10],  $[(C_5Me_5)_2Sm](\mu-\eta^2-\eta^2-Bi_2)$  [11] and  $[(C_5Me_5)_2Sm](\mu-Me)_2AlMe_2)_2$  [12]. This steric explanation is consistent with the observation that steric factors are generally more important relative to orbital effects in organolanthanide chemistry than in organotransition metal chemistry [13].

The above explanation is not universally accepted, however, and recently it has been suggested [14] that the X-ray crystal structure of  $[(C_5Me_5)_2Sm](\mu-H)_2$  [3], which revealed a tetrahedral arrangement of  $C_5Me_5$  ring centroids, was incorrectly determined and the structure should contain a square planar arrangement of ring centroids. We disagree with the latter suggestion and to provide further evidence on how steric effects govern the structures of these bimetallic organosamarium complexes, we report here the X-ray crystal structure of a methylcyclopentadienyl chloride complex and compare it with data on pentamethylcyclopentadienyl chloride complexes of samarium. Although the small bridging ligands favor the tetrahedral geometry, the small cyclopentadienyl rings lead to reduced steric congestion and the complex  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  (1) adopts a square planar arrangement of the ring centroids.

## 2. Experimental details

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Solvents were purified as previously described [15].  $KC_5H_4Me$  was prepared by reacting  $MeC_5H_5$  (Aldrich), freshly distilled from molecular sieves, with  $KH$  in THF.  $SmCl_3$  was prepared as previously described [16].

### 2.1. $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$ (1)

$KC_5H_4Me$  (207 mg, 1.75 mmol) was added to a stirred slurry of  $SmCl_3$  (231 mg, 0.90 mmol) in 20 mL of THF. The reaction was allowed to stir at room temperature for 16 h and became cloudy and yellow. This mixture was centrifuged to remove the insoluble salts and the resulting yellow solution was dried *in vacuo* to yield a yellow, microcrystalline material,  $[(C_5H_4Me)_2SmCl(THF)]_2$  (229 mg, 61%). Anal. Found: Sm, 36.2.  $C_{16}H_{22}SmClO$  calc.: Sm, 36.14%.  $^1H$  NMR (THF- $d_8$ ):  $\delta$  10.11 (s, 2H,  $C_5H_4$ ); 9.51 (s, 2H,  $C_5H_4$ );

TABLE 1. Crystallographic data for  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  (1)

Formula	$C_{32}H_{44}O_2Cl_2Sm_2$
Molecular weight	832.3
Temperature (K)	173
Crystal system	Orthorhombic
Space group	$Pbcn [D_{2h}^{14}; \text{No. } 60]$
$a$ (Å)	20.312(5)
$b$ (Å)	9.626(2)
$c$ (Å)	16.225(3)
$V$ (Å) <sup>3</sup>	3172.5(12)
$Z$	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.74
Diffractometer	Siemens P3 (R3m/V)
$\lambda$ (Mo $K\alpha$ ) (Å)	( $\bar{\lambda} = 0.710730$ )
Monochromator	Highly-oriented graphite
Data collected	+ $h$ , + $k$ , + $l$
Scan type	$\theta-2\theta$
Scan width (°)	1.2° plus $K\alpha$ -separation
Scan speed ( $\omega$ ) (° min <sup>-1</sup> )	3.0
$2\theta_{\text{max}}$ (°)	4.0–45.0
$\mu$ (Mo $K\alpha$ ) (mm <sup>-1</sup> )	3.88
Abs. cor. ( $\varphi$ -scan method)	Semi-empirical
No. of reflections collected	2405
No. of reflections with $ F_o  > 2.0\sigma( F_o )$	1759
No. of variables	172
$R_F$ ; $R_{wF}$ (%)	5.0; 5.1
Goodness of fit	1.47

1.23 (s, 3H, Me).  $^{13}C$  NMR (THF- $d_8$ ):  $\delta$  106.2 (s,  $C_5H_4$ ); 107.0 (d,  $J$  169 Hz,  $C_5H_4$ ); 109.0 (d,  $J$  163 Hz,  $C_5H_4$ ). IR (KBr) 3087m, 2981s, 2937s, 2887s, 2731w, 1493m, 1456s, 1375w, 1343m, 1237m, 1031s, 931m, 862s, 831s, 769s  $cm^{-1}$ . Crystals suitable for X-ray analysis were grown from THF at  $-30^\circ C$ .

### 2.2 X-Ray data collection, structure determination and refinement for $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$

A yellow crystal was coated with a heavy oil (Paratone N), mounted on a glass fiber, and transferred to the diffractometer equipped with a modified LT-2-low-temperature system. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature intensity data were carried out using standard techniques similar to those of Churchill [17]. Details appear in Table 1. Atomic positional parameters are given in Table 2.

All 2405 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. A careful examination of a preliminary data set revealed the systematic extinctions  $0kl$  for  $k = 2n + 1$ ,  $h0l$  for  $l = 2n + 1$ , and  $hk0$  for  $h + k = 2n + 1$  which uniquely defined the space group. All crystallographic calculations were carried

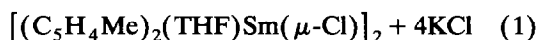
TABLE 2 Atomic coordinates ( $\times 10^4$ ) for  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  (1)

Atom	x	y	z
Sm(1)	-917(1)	1263(1)	4900(1)
Cl(1)	98(1)	604(3)	5960(1)
O(1)	-1105(3)	2785(7)	6175(4)
C(1)	-1540(5)	-1140(10)	5382(6)
C(2)	-1702(5)	-1038(11)	4541(6)
C(3)	-2103(5)	129(11)	4453(6)
C(4)	-2195(5)	767(11)	5227(6)
C(5)	-1844(5)	-26(11)	5802(6)
C(6)	-1544(6)	-2111(13)	3881(8)
C(7)	-994(6)	3958(11)	4442(7)
C(8)	-1406(5)	3263(11)	3893(6)
C(9)	-1001(5)	2427(11)	3377(6)
C(10)	-344(6)	2655(11)	3632(6)
C(11)	-357(6)	3607(11)	4291(6)
C(12)	-1228(7)	1544(12)	2673(6)
C(13)	-598(6)	3335(12)	6701(7)
C(14)	-908(6)	4504(13)	7193(7)
C(15)	-1528(7)	4778(15)	6788(10)
C(16)	-1727(6)	3439(13)	6380(7)

out using either our locally modified version of the UCLA Crystallographic Computing Package [18] or the SHELXTL-PLUS program set [19]. The analytical scattering factors for neutral atoms were used throughout the analysis [20a]; both the real ( $\Delta f'$ ) and imaginary ( $i\Delta f''$ ) components of anomalous dispersion [20b] were included. The quantity minimized during least-squares analysis was  $\sum w(|F_o| - |F_c|)^2$  where  $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_c|)^2$ . The structure was solved via an automatic Patterson method (SHELXTL-PLUS); and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with  $d(C-H) = 0.96 \text{ \AA}$  and  $U_{iso} = 0.08 \text{ \AA}^2$ . The molecule is located about an inversion center at (0, 0, 1/2). A final difference-Fourier map was devoid of significant features,  $\rho(\max) = 1.24 \text{ e \AA}^{-3}$ .

### 3. Results

Bis(methylcyclopentadienyl)samarium chloride can be prepared directly from  $SmCl_3$  by ionic metathesis (eqn. (1)). The complex crystallizes as a dimer with one  $2SmCl_3 + 4KC_5H_4Me \xrightarrow{THF}$



THF molecule solvating each samarium center (Fig. 2). In this regard, **1** differs from the unsolvated chloride dimers  $[(C_5H_5)_2Sc(\mu-Cl)]_2$  [21],  $[(C_5H_4Me)_2Yb(\mu-Cl)]_2$  [22], and  $[(C_5H_5)_2Ln(\mu-Cl)]_2$  ( $Ln = Yb$  [23],  $Er$  [24],  $Y$  [25]) which have cyclopentadienyl ligands of similar size. This difference is consistent with the fact that samarium has a larger radial size than  $Sc$ ,  $Yb$ ,  $Er$ , and

$Y$ , and, hence, there is room to coordinate a THF ligand. A THF-solvated structure is also found for the neodymium analog  $[(C_5H_5)_2(THF)Nd(\mu-Cl)]_2$  [26].

The metrical parameters in  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  are unexceptional (Table 3). The  $Sm(1)-Cl(1)$  and  $Sm(1)-Cl(1')$  distances in **1**, 2.759(3) and 2.819(3)  $\text{\AA}$ , respectively, are not equivalent, as is common in chloride-bridged organolanthanide dimers [14,21–28] (Table 4). The  $Sm-Cl$  distances are quite similar to the  $Ln-Cl$  distances in these other dimers when the differences in metallic radii are taken into account [29] (Table 4). As is typical, these bridging distances are longer than terminal distances. For example, the  $Sm-Cl$  distances in two independent molecules in the unit cell of  $(C_5Me_5)_2SmCl(THF)$  [30] are 2.709(8) and 2.765(8)  $\text{\AA}$ .

The  $Sm-O(THF)$  distance in **1**, 2.563(6)  $\text{\AA}$ , is similar to the  $Sm-O(THF)$  distances in 9-coordinate  $(C_5Me_5)_2Sm(\eta^2-PhN_2Ph)(THF)$  [31] (2.532(8) and 2.577(9)) and  $[(C_5Me_5)_2Sm(THF)]_2(\mu-\eta^2:\eta^2-N_2C_4H_4-C_4H_4N_2)$  [32] (2.555(5)  $\text{\AA}$ ). In comparison, the  $Sm-O(THF)$  distances in 8-coordinate  $(C_5Me_5)_2Sm(THF)Z$  complexes range from 2.511(4)  $\text{\AA}$  in  $(C_5Me_5)_2Sm-Ph(THF)$  [33] to 2.44(2)  $\text{\AA}$  in  $(C_5Me_5)_2SmCl(THF)$  [30,34]. The  $Sm-C(\text{ring})$  average distance of 2.72(3)  $\text{\AA}$  is identical to the 2.72(4)  $\text{\AA}$  average in  $[(C_5H_4Me)_2Sm(\mu-C\equiv CMe_3)]_2$  (**2**) [35] even though **1** is formally 9-coordinate and **2** is 8-coordinate. The  $126.4^\circ$  (ring centroid)- $Sm$ -(ring centroid) angle in **1**, compared to the  $135.3^\circ$  analog in **2**, reflects the greater size of the ligand set in **1**.

The orientation of the methyl groups on the same side of each  $(C_5H_4Me)_2Sm$  unit may occur to allow more room for the THF on the other side. Similar

TABLE 3 Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  (1)<sup>a</sup>

$Sm(1)-Cl(1)$	2.759(3)	$Sm(1)-O(1)$	2.563(6)
$Sm(1)-C(1)$	2.751(10)	$Sm(1)-C(2)$	2.791(10)
$Sm(1)-C(3)$	2.742(10)	$Sm(1)-C(4)$	2.693(10)
$Sm(1)-C(5)$	2.689(10)	$Sm(1)-C(7)$	2.703(11)
$Sm(1)-C(8)$	2.713(10)	$Sm(1)-C(9)$	2.718(9)
$Sm(1)-C(10)$	2.717(10)	$Sm(1)-C(11)$	2.713(11)
$Sm(1)-Cl(1')$	2.819(3)	$Sm(1)-Cnt(1)$	2.458
$Sm(1)-Cnt(2)$	2.437		
$Cl(1)-Sm(1)-O(1)$	74.9(2)	$Cl(1)-Sm(1)-Cl(1')$	73.8(1)
$O(1)-Sm(1)-Cl(1')$	148.4(2)	$Cl(1)-Sm(1)-Cnt(1)$	112.4
$Cl(1)-Sm(1)-Cnt(2)$	121.2	$Cl(1')-Sm(1)-Cnt(1)$	98.4
$Cl(1')-Sm(1)-Cnt(2)$	96.6	$O(1)-Sm(1)-Cnt(1)$	97.3
$O(1)-Sm(1)-Cnt(2)$	95.8	$Cnt(1)-Sm(1)-Cnt(2)$	126.4
$Sm(1)-Cl(1)-Sm(1')$	106.2(1)		

Cnt(1) is the centroid of the C(1)–C(5) ring

Cnt(2) is the centroid of the C(7)–C(11) ring

<sup>a</sup> Primed atoms are at positions corresponding to  $(-x, -y, 1-z)$ .

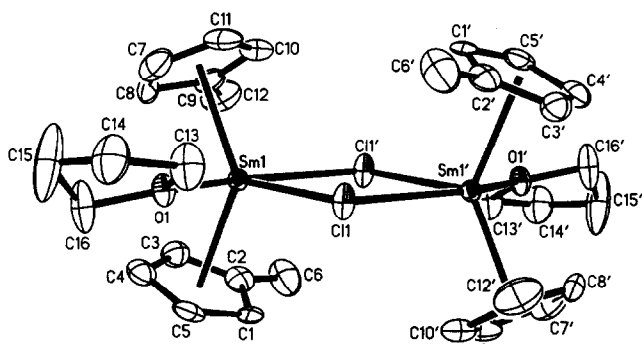


Fig. 2. ORTEP diagram of  $[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$  (**1**) with the probability ellipsoids drawn at the 50% level.

“*cis*” orientations have been observed in the THF-solvated monosubstituted-cyclopentadienyl complexes  $[(C_5H_4Me)_2Y(\mu-H)(THF)]_2$  [36] and  $[(C_5H_4Me)_2(THF)Yb]_2(\mu-O)$  [37]. For unsolvated monosubstituted-cyclopentadienyl lanthanide complexes, both “*cis*” ( $[(C_5H_4Me)_2Sm(\mu-C\equiv C^tBu)]_2$  [35],  $[(C_5H_4Me)_2Yb(\mu-NH_2)]_2$  [38],  $[(C_5H_4CMe_3)_2Sm(\mu-C\equiv CPh)]_2$  [39],  $[(C_5H_4CMe_3)_2Sm[AlH_4(THF)]]_2$  [40]), and “*trans*” ( $[(C_5H_4Me)_2Yb(\mu-Cl)]_2$  [22],  $[(C_5H_4CMe_3)_2Ce(\mu-OCHMe_2)]_2$  [41],  $[(C_5H_4CMe_3)_2Ce(\mu-SCHMe_2)]_2$  [41],  $[(C_5H_4SiMe_3)_2Y(\mu-Cl)]_2$  [42], and  $[(C_5H_4SiMe_3)_2Y(\mu-OMe)]_2$  [42]) arrangements of substituents are found in the literature.

#### 4. Discussion

Previous attempts to make a symmetric chloride-bridged dimer of samarium with  $C_5Me_5$  rings did not lead to  $[(C_5Me_5)_2Sm(\mu-Cl)]_2$ . Instead, the trimer  $[(C_5Me_5)_2Sm(\mu-Cl)]_3$  was obtained [43]. Since the trimeric structure allows the samarium centers to be further apart, the result suggests that the dimer may be too sterically crowded to form. This is also suggested by the structure of  $[(C_5Me_5)_2Sm]_5Cl_5[Me(OCH_2CH_2)_4Me]$  **3**, [43]. Compound **3** contains three variations of 8-coordinate chloride-bridged bimetallic  $C_5Me_5$  samarium moieties. Each of the three different  $[(C_5Me_5)_2SmZ]_2(\mu-Cl)$  units found in this structure [ $Z = Cl, O(\text{tetraglyme})$ ] has a tetrahedral arrangement of the four  $C_5Me_5$  rings, but none has the most symmetric bis(bridging-chloride) dimer form,  $[(C_5Me_5)_2Sm(\mu-Cl)]_2$ . Further evidence of steric crowding in  $[(C_5Me_5)_2LnCl]_2$  complexes is found in the structure of  $(C_5Me_5)_2ClY(\mu-Cl)Y(C_5Me_5)_2$  [44]. This complex again has a tetrahedral arrangement of  $C_5Me_5$  rings, but contains a seven-coordinate metal center instead of forming a sterically crowded, symmetrically bridged dimer.

The structure of **1** shows that a symmetric bis(chloride-bridged) dimer of samarium can form if the size of the cyclopentadienyl ligand is reduced from  $C_5Me_5$  to

TABLE 4. Metal–chloride distances in chloride-bridged dimers of Group 3 and lanthanide metals containing unsubstituted, monosubstituted and disubstituted cyclopentadienyl ligands

Complex	Metal–chloride distances (Å)	Avg. M–Cl distance (Å)	Ionic radius of M (Å) <sup>a</sup>	Avg. M–Cl distance normalized to $Sm^{3+}$ radius (Å) <sup>b</sup>	Ref.
$[(C_5H_5)_2Sc(\mu-Cl)]_2$	2.585(4) 2.583(4)	2.584	0.870	2.844	21
$[(C_5H_4Me)_2Yb(\mu-Cl)]_2$	2.627(2) 2.647(2)	2.637	0.985	2.785	22
$[(C_5H_5)_2Yb(\mu-Cl)]_2$	2.638(3) 2.645(3)	2.642	0.985	2.789	23
$[(C_5H_5)_2Er(\mu-Cl)]_2$	2.661(2) 2.660(1)	2.661	1.004	2.789	24
$[(C_5H_5)_2Y(\mu-Cl)]_2$	2.674(3) 2.689(3)	2.682	1.019	2.795	25
$[(C_5H_3(SiMe_3)_2)_2Pr(\mu-Cl)]_2$	2.805 2.821	2.813	1.126	2.819	27
$[(C_5H_4Me)_2(THF)Sm(\mu-Cl)]_2$	2.759(3) 2.819(3)	2.789	1.132	2.789	This paper 14
$[(C_5H_3(^tBu)_2)_2Ce(\mu-Cl)]_2$	2.868(4) 2.868(4)	2.868	1.143	2.857	
$[(C_5H_4Me)_2(THF)Nd(\mu-Cl)]_2$	2.787(4) 2.861(4)	2.824	1.163	2.793	26
$[(\eta^5-\eta^1-C_5H_4CH_2CH_2OCH_3)_2La(\mu-Cl)]_2$	2.911(7) 2.961(7)	2.936	1.27	2.799	28

<sup>a</sup> Reference 29. <sup>b</sup> (Avg. M–Cl distance) – [(M radius) – ( $Sm^{3+}$  radius)].

$C_5H_4Me$ . In this case, the four cyclopentadienyl ring centroids can adopt a square planar geometry. The fact that **1** crystallizes as a THF solvate shows that the steric effects of the substituents on the cyclopentadienyl ligands can be substantial.  $[(C_5Me_5)_2Sm(\mu-Cl)]_2$  appears to be too crowded to form whereas the analogous  $[(C_5H_4Me)_2Sm(\mu-Cl)]_2$  unit has room for a THF at each metal center. To further emphasize these steric arguments, it should be noted that both analogous reactions systems,  $SmCl_3/KC_5H_4Me$  and  $SmCl_3/KC_5Me_5$  [45], form bridged products. The  $C_5H_4Me$  reaction leads to the bimetallic samarium complex **1**, whereas the  $C_5Me_5$  reaction forms  $(C_5Me_5)_2Sm(\mu-Cl)_2K(THF)_x$  [45,46] presumably because it is less crowded than  $[(C_5Me_5)_2Sm(\mu-Cl)]_2$ .

The effect that these steric differences can have on reactivity is well illustrated by the system  $[(C_5Me_5)_2Sm]_2(CCPH)_2$  [47,48]. On the basis of its composition, spectra, and synthesis from  $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$  and  $HC=CPh$ , this complex was reported to be  $[(C_5Me_5)_2Sm(\mu-C=CPh)]_2$  [47]. However, this structure, like  $[(C_5Me_5)_2Sm(\mu-Cl)]_2$ , appeared to be too crowded to exist as a symmetrical bridged structure [48]. Indeed, subsequent X-ray crystallographic analysis showed that this compound had a different structure: during the reaction an unusual C–C coupling reaction occurred to generate a trienediyl complex  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC=C=C=CPh)$  [48]. In the latter structure, a larger bridge is present which relieves steric congestion between the two  $(C_5Me_5)_2Sm$  units which adopt a square planar arrangement of ring centroids. In contrast, the analogous  $C_5H_4CMe_3$  phenylalkynide complex,  $[(C_5H_4CMe_3)_2Sm(\mu-C\equiv CPh)]_2$  exists as a simple bridged dimer [39].

In summary, one can define three classes of bimetallic tetracyclopentadienyl organosamarium complexes: (I) large rings with small bridges such as  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-N_2)$  [1],  $[(C_5Me_5)_2Sm]_2(\mu-O)$  [2],  $[(C_5Me_5)_2Sm(\mu-H)]_2$  [3] and  $[(C_5Me_5)_2Sm]_2(\mu-HNNH)$  [4], (II) large rings with large bridges such as  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC_4Ph)$  [7],  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhNNPh)$  [8],  $[(C_5Me_5)_2Sm]_2[\mu-\eta^2:\eta^2-PhNC(O)C(O)-NPh]$  [9],  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-pyCH=C(O)C(O)=CHpy)$  [10],  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-Bi_2)$  [11] and  $[(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2]_2$  [12] and (III) small ring complexes, regardless of bridge size, as exemplified by the title complex. Class I, the sterically most crowded, prefers a tetrahedral arrangement of rings. The other classes, which possess less steric congestion, favor square planar arrangements of ring centroids.

Hence, there is no need to suggest [14] that the X-ray crystal determination of  $[(C_5Me_5)_2Sm(\mu-H)]_2$  (**4**) [3] is incorrect and that the molecule really has a square planar arrangement of  $C_5Me_5$  rings. This hy-

dride complex is a class I system using the above categories and has the tetrahedral arrangement of  $C_5Me_5$  rings for steric reasons. If a square planar arrangement had been found, that would be suspect!

As a member of class I above,  $[(C_5Me_5)_2Sm(\mu-H)]_2$  has other analogs. Two complexes are particularly pertinent to this discussion since the diffraction data allowed location of their bridging ligands:  $[(C_5Me_5)_2ThH(\mu-H)]_2$  (**5**) [49] and  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-N_2)$  (**6**) [1]. Like **4**, both of these class I species have a tetrahedral arrangement of  $C_5Me_5$  rings. In the organothorium complex, the hydride ligands were found by neutron diffraction and show that the tetrahedral arrangement of rings is compatible with two bridging hydride moieties. In a sense,  $[(C_5Me_5)_2Sm(\mu-H)]_2$  is the trivalent analog of the thorium complex: it differs by one in oxidation state and lacks one terminal hydride per metal. In  $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-N_2)$ , the locations of the bridging ligands show that there is both space and an electronic/electrostatic capacity for bridging ligands within the area spanned by the four tetrahedrally arranged  $C_5Me_5$  rings in a bimetallic samarium complex. These complexes argue strongly against the suggestion that the structure of  $[(C_5Me_5)_2Sm(\mu-H)]_2$  is wrong. It should also be noted that the published tetrahedral structure of  $[(C_5Me_5)_2Sm(\mu-H)]_2$  has been found to be consistent with a molecular orbital study of this complex [50].

## 5. Conclusion

Bimetallic tetracyclopentadienylsamarium complexes can adopt either tetrahedral or square planar geometries for the four ring centroids depending on the size of the bridging ligands and the degree of substitution on the cyclopentadienyl rings. Three classes of complexes have been differentiated crystallographically. New results which do not appear to fall into one of these three classes should be carefully studied, since they may indicate that unusual chemistry is occurring.

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