Reactivity of $(C_5Me_5)_2Sm$ with Aryl-Substituted Alkenes: Synthesis and Structure of a Bimetallic Styrene Complex That Contains an η^2-Arene Lanthanide Interaction

William J. Evans,* Tamara A. Ulibarri, and Joseph W. Ziller

Contribution from the Department of Chemistry, University of California, Irvine, Irvine, California 92717. *Received May 1, 1989*

Abstract: $(C_5Me_5)_2Sm$ (**1**) and $(C_5Me_5)_2Sm(THF)_2$ (**2**) isomerize *cis*-stilbene to *trans*-stilbene. The stoichiometric reaction of **1** with stilbene forms $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-PhCHCHPh})$ (**3**). **1** reacts with styrene to form $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (**4**). In both **3** and **4**, the two $(C_5Me_5)_2Sm$ units coordinate on opposite sides of the alkene bond such that the Sm–Sm vector bisects the bond at right angles. In each complex, phenyl carbon atoms are oriented to interact with one of the samarium centers. In **4**, the Sm–C(C_5Me_5) distances range from 2.678 (18) to 2.847 (18) Å, the Sm–C(alkene) distances range from 2.537 (15) to 2.732 (15) Å, and two carbon atoms of the phenyl ring are positioned 2.772 (17) and 2.850 (16) Å from one samarium atom. **3** crystallizes from hexane in space group $P2_12_12$ with $a = 12.156$ (6) Å, $b = 14.405$ (9) Å, $c = 15.628$ (2) Å, and $V = 2737$ (2) Å^3 with $Z = 2$ for $D_{\text{calcd}} = 1.24$ g cm^{-3}. **4** crystallizes from hexane in space group *Pbca* with $a = 21.169$ (4) Å, $b = 17.663$ (3) Å, $c = 23.713$ (5) Å, and $V = 8866$ (3) Å^3 with $Z = 8$ for $D_{\text{calcd}} = 1.417$ g cm^{-3}. Least-squares refinement of the model based on 3134 observed reflections converged to a final $R_F = 6.2\%$.

The coordination chemistry of the lanthanides with unsaturated substrates has developed rapidly in recent years and has shown that earlier assessments of the bonding capacity of these metals were inaccurate. In the past, it was thought that neutral hydrocarbons and other nonpolar substrates would not interact extensively with these metals due to the limited radial extension of their 4f valence orbitals and the concomitant highly ionic character of the bonding. However, crystallographically characterized lanthanide complexes are now known which contain (a) η^6-arene ligands, e.g., $Sm(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}AlCl_4)_3$[1] and $Gd(\eta^6\text{-}C_6H_3Bu^t{}_3)_2$,[2] (b) η^2-alkyne ligands, e.g., $(C_5Me_5)_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$[3] and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Ph_2C_4)$,[4] (c) metal-coordinated alkene and cyclopentadienide ligands, e.g., $(C_5Me_5)_2Yb(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$[5] and $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$,[6] and even (d) an η^2-dinitrogen ligand, e.g., $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$.[7] Interestingly, although lanthanide complexes of simple alkenes have been considered in many contexts,[8-24] including lanthanide-based hydrogenations[9-15] and polymerizations,[5,10,16-24] coordination of a free alkene to a lanthanide center has not been demonstrated.

As part of our investigation of the chemistry of the strongly reducing bent metallocene $(C_5Me_5)_2Sm$ (**1**)[6,25] with unsaturated hydrocarbons, we have found that η^2-alkene complexes of lanthanides can be isolated by using aryl-substituted alkenes. We report here on the isolation and crystal structure of such a complex as well as the first example of η^2-arene coordination involving a 4f-element.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted 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.[26] *trans*-Stilbene (Aldrich) was sublimed prior to use, and *cis*-stilbene (Aldrich) was dried over 4 Å molecular sieves and degassed by freeze–pump–thaw cycles on the high vacuum line. Styrene (Aldrich) was dried with 4 Å molecular sieves, degassed by freeze–pump–thaw cycles, and vacuum transferred into the reactions. The styrene was stored over 4 Å molecular sieves and refrigerated when not in use. $(C_5Me_5)_2Sm$[25] and $(C_5Me_5)_2Sm(THF)_2$[27] were made according to the literature. $(C_5Me_5)_2Sm$ must be handled in an ether-free glovebox. Physical measurements were obtained as previously described.[24,26]

Isomerization of *cis*-Stilbene (a) by $(C_5Me_5)_2Sm(THF)_2$ (2). In the glovebox, $(C_5Me_5)_2Sm(THF)_2$ (0.0047 g, 0.0083 mmol) was placed in an NMR tube with 0.5 mL of benzene-d_6 to give a dark maroon-purple solution. *cis*-Stilbene (50 μL, 0.28 mmol) was syringed into the NMR tube, and the tube was capped with a septum. No color change was observed. The NMR tube was immediately taken out of the glovebox and shaken. The ^1H NMR spectrum contained peaks that could be assigned to $(C_5Me_5)_2Sm(THF)_2$ and free *cis*- and *trans*-stilbene, i.e., no

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complex was observed. The sample was monitored by ^{1}H NMR, and the isomerization was complete within 2 h. **(b) By $(C_5Me_5)_2Sm$ (1).** At room temperature, the ^{1}H NMR spectrum of $(C_5Me_5)_2Sm$ and stilbene contained only broad peaks which could not be readily assigned. Therefore, it was necessary to destroy the $(C_5Me_5)_2Sm$/stilbene complex by the addition of THF in order to determine the ratio of *cis*-stilbene to *trans*-stilbene. A lower limit on the rate of isomerization was determined in the following way. In an ether-free glovebox, $(C_5Me_5)_2Sm$ (0.0032 g, 0.0076 mmol) was weighed into a vial, and the vial was capped. *cis*-Stilbene (100 μL, 0.56 mmol) and 0.4 mL of benzene-d_6 were placed in a separate vial which was also capped. The two vials were placed in a Schlenk tube and transferred to a glovebox containing THF. The *cis*-stilbene/benzene-d_6 solution was quickly pipetted into the vial containing the $(C_5Me_5)_2Sm$, and the resulting dark red-brown solution was transferred to an NMR tube. The solution was capped and allowed to react for 5 min at which point THF was added to the reaction mixture to produce a dark maroon-purple solution. The NMR tube was sealed and removed from the glovebox, and a ^{1}H NMR spectrum was immediately taken. The isomerization was complete by ^{1}H NMR spectroscopy.

$[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$ (3). In the glovebox, $(C_5Me_5)_2Sm$ (0.050 g, 0.119 mmol) and *trans*-stilbene (0.011 g, 0.061 mmol) were dissolved in 8 mL of hexane. The solution immediately turned dark red-brown. After the reaction was stirred for 2 h, the solution was filtered to yield a dark red-brown solution. The solvent was removed by rotary evaporation leaving a slightly tacky dark red-brown solid which was re-extracted with hexane and filtered. Removal of hexane by rotary evaporation left a slightly tacky dark red-brown solid (0.056 g, 93%). Crystals suitable for a preliminary X-ray crystallographic study were obtained by slow concentration of a hexane solution. ^{1}H NMR (toluene-d_8, −10 °C) δ 0.17 (s, C_5Me_5), (toluene-d_8, −80 °C), 1.70 (s, C_5Me_5), −1.09 (s, C_5Me_5). Peaks associated with the stilbene molecule could not be assigned. ^{13}C NMR (toluene-d_8, −10 °C) δ 113.2 (s, C_5Me$_5$), 25.3 (q, J_{CH} = 125 Hz, C$_5$*Me*$_5$), (toluene-d_8, −80 °C), 114.5 (s, C_5Me$_5$), 112.9 (s, C_5Me$_5$), 33.2 (q, J_{CH} = 124 Hz, C$_5$*Me*$_5$), 17.7 (q, J_{CH} = 124 Hz, C$_5$*Me*$_5$). Peaks associated with the stilbene molecule could not be assigned. Magnetic susceptibility $\chi_M^{296K} = 3478 \times 10^{-6}$ (cgs), $\mu_{eff}^{296K} = 2.88\ \mu_B$; IR (KBr) 2940–2860 s, 1585 m, 1540 w, 1480 m, 1445 m, 1380 w, 1275 m, 1175 m, 1020 w, 980 w, 860 w, 760 w, 740 m, 700 m cm^{-1}. Anal. Calcd for $Sm_2C_{54}H_{72}$: Sm, 29.43. Found: Sm, 29.0.

$[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (4). In an ether-free glovebox, $(C_5Me_5)_2Sm$ (0.083 g, 0.197 mmol) was dissolved in 10 mL of toluene and placed with a Teflon stir bar in a 100-mL flask equipped with a high-vacuum greaseless stopcock. The flask was attached to a high vacuum line (2×10^{-5} Torr), cooled with a liquid nitrogen bath, and evacuated. Excess styrene (ca. 1 mL) was vacuum transferred onto the frozen solution of **1**. The reaction was closed off from the vacuum line and allowed to warm to room temperature. The previously dark green solution immediately turned an extremely dark maroon-red upon warming. The flask was returned to the glovebox. The solvent and excess styrene were removed by rotary evaporation, and the dark maroon solid was extracted with hexane. The resulting dark maroon solution was filtered, and the solvent was removed by rotary evaporation leaving a dark maroon solid (0.092 g, 99%). Crystals suitable for an X-ray crystallographic study were obtained by slow concentration of a hexane solution. ^{1}H NMR (C_6D_6) δ 26.0 (br s, C$_2$*H*$_3$Ph, 1 H), 23.0 (br s, C$_2$*H*$_3$Ph, 1 H), 5.6 (br m, C$_2$H$_3$*Ph*, 2 H), 5.2 (br m, C$_2$H$_3$*Ph*, 2 H), 5.0 (br m, C$_2$H$_3$*Ph*, 1 H), 0.15 (br s, C_5Me_5, 60 H); ^{13}C NMR (C_6D_6) δ 116.2 (C_5Me$_5$), 17.0 (C$_5$*Me*$_5$). Assignments were made with a DEPT NMR experiment.[28] Magnetic susceptibility $\chi_M^{295K} = 1558 \times 10^{-6}$ (cgs), $\mu_{eff}^{295K} = 1.93\ \mu_B$; IR (KBr) 2940–2860 s, 1590 m, 1530 w, 1480 m, 1440 m, 1380 m, 1220 w, 1020 w, 970 w, 865 w, 830 w, 750 w, 730 m, 700 m cm^{-1}. Anal. Calcd for $Sm_2C_{48}H_{68}$: Sm, 31.79. Found: Sm, 31.5.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (4). A dark red plate measuring approximately 0.10 × 0.20 × 0.33 mm was mounted in a thin-walled glass capillary under nitrogen and accurately aligned on the Nicolet P3 automated four-circle diffractometer. Laue symmetry determination, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[29] Room temperature (296 K) intensity data were collected by using a θ–2θ scan technique with Mo Kα radiation under the conditions given in Table I. All 5837 data were corrected for the effects of absorption (empirical) and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. The systematic extinctions observed were $0kl$ for $l = 2n + 1$, $h0l$ for $h = 2n + 1$, and $hk0$ for $k = 2n + 1$; the diffraction symmetry was *mmm*. The centrosymmetric orthorhombic space group *Pcab*, a nonstandard setting of *Pbca* [D_{2h}^{15}; No. 61], is thus defined. The data were later transformed to the standard setting.

Table I. Crystallographic Data on $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (4)

formula	$C_{48}H_{68}Sm_2$
fw	945.7
crystal system	orthorhombic
space group	*Pbca*
a	21.169 (4) Å
b	17.663 (3) Å
c	23.713 (5) Å
V	8866 (3) Å^3
Z	8
D_{calcd}, Mg/m^3	1.417
diffractometer	Nicolet P3
radiation	Mo Kα (λ = 0.710730 Å)
monochromator	highly oriented graphite
data collected	$+h,+k,+l$
scan type	coupled θ(crystal)–2θ(counter)
scan range	symmetrical $[(K\alpha_1) - 1.2°] \rightarrow [(K\alpha_2) + 1.2°]$
scan speed	2.0 deg min^{-1} (in ω)
$2\theta_{max}$, deg	45.0
μ(Mo Kα), mm^{-1}	2.661
absorption correction	semiempirical (ψ-scan method)
reflections collected	5837
reflections with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$	3134
no. of variables	212
r_F	6.2%
r_{wF}	6.8%
goodness of fit	1.24

All crystallographic calculations were carried out by using either our locally modified version of the UCLA Crystallographic Computing Package[30] or the SHELXTL PLUS program set.[31] The analytical scattering factors for neutral atoms were used throughout the analysis;[32a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[32b] were included. The quantity minimized during least-squares analysis was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ where $w^{-1} = \sigma^2(\lvert F_o\rvert) + 0.0013(\lvert F_o\rvert)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Refinement of positional and thermal parameters (anisotropic for the samarium atoms only) led to convergence with $R_F = 6.2\%$, $R_{wF} = 6.8\%$, and GOF = 1.24 for 212 variables refined against those 3134 data with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$. Hydrogen atom contributions were included by using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. A final difference-Fourier map was clean, ρ(max) = 0.90 e Å^{-3}. Final fractional coordinates are given in the Supplementary Material.

X-ray Data Collection for $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$ (3). A dark red-brown plate measuring approximately 0.10 × 0.20 × 0.30 mm was treated as described above for **4**. Axial photographs indicated that the crystal had a satellite crystal plate adhered to it. A full structural determination was carried out. Due to the poor crystal quality, the structural determination was not of sufficient quality to obtain reliable distance and angle data. However, the connectivity of the structure was definitely determined. Unit cell and space group data are given in the Supplementary Material.

Results and Discussion

Reactions of Stilbene. The first observation of an interaction between arylalkenes and a divalent organolanthanide complex involved the isomerization of *cis*-stilbene to the trans isomer by $(C_5Me_5)_2Sm(THF)_2$ (**2**).[33,34] Reductive isomerization of stilbene is well-known,[35] although it had not been previously observed with f-elements. Complex **2** is capable of isomerizing 30 equiv of

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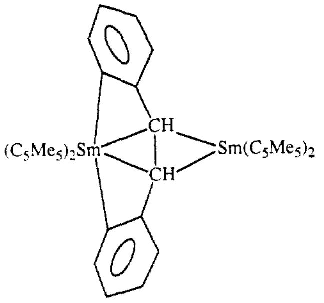

Figure 1. Structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$, **3**.

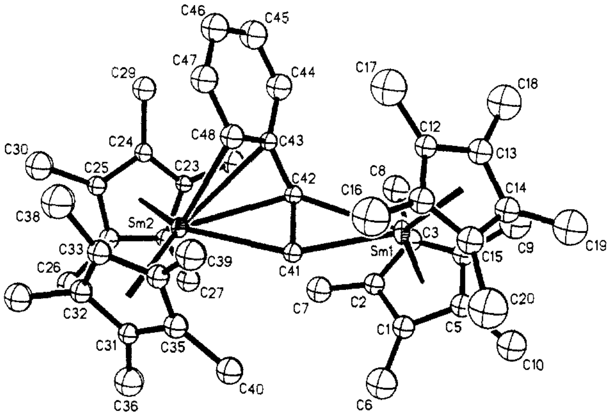

Figure 2. ORTEP diagram of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$, **4**.

cis-stilbene per samarium within 2 h. No stilbene complex was observed, however, by ^{1}H NMR spectroscopy down to −80 °C in toluene-d_8.

Given this result with **2**, it was expected that the sterically unsaturated $(C_5Me_5)_2Sm$ (**1**) would also interact with arylalkenes. Complex **1** also isomerizes *cis*-stilbene, and as anticipated on the basis of steric arguments,[34] **1** carries out the isomerization process much faster. **1** converts at least 70 equiv of *cis*-stilbene per samarium atom to *trans*-stilbene within 5 min. In this case, broad ^{1}H NMR signals were observable, but the isomerization could not be readily monitored by ^{1}H NMR spectroscopy due to the fluxionality in the system and the paramagnetism of samarium.[36]

The stoichiometric reaction of **1** with stilbene in hexane instantly forms a red-brown complex, **3**, in quantitative yield (eq 1). The

$$\underset{\mathbf{1}}{2(C_5Me_5)_2Sm} + PhCH{=}CHPh \rightarrow \underset{\mathbf{3}}{[(C_5Me_5)_2Sm]_2(PhCHCHPh)} \tag{1}$$

composition of **3** as $[(C_5Me_5)_2Sm]_2(PhCHCHPh)$ was verified by complexometric metal analysis, by the reaction of **3** with THF, which forms **2** and *trans*-stilbene in quantitative yield (eq 2), and by a single-crystal X-ray study. Unfortunately, it proved difficult

$$\underset{\mathbf{3}}{[(C_5Me_5)_2Sm]_2(PhCHCHPh)} + 4THF \rightarrow \underset{\mathbf{2}}{2(C_5Me_5)_2Sm(THF)_2} + trans\text{-}PhCH{=}CHPh \tag{2}$$

to obtain crystals of sufficient size and quality to provide reliable bond distance and angle data. However, the crystallographic data did unambiguously provide the connectivity of the atoms and revealed the unusual structural arrangement shown in Figure 1.

The Reaction with Styrene. Complex **1** also reacts instantly with styrene to form red-maroon $[(C_5Me_5)_2Sm]_2(CH_2CHPh)$ (**4**) in quantitative yield (eq 3).

$$\underset{\mathbf{1}}{2(C_5Me_5)_2Sm} + PhCH{=}CH_2 \rightarrow \underset{\mathbf{4}}{[(C_5Me_5)_2Sm]_2(CH_2CHPh)} \tag{3}$$

As in the stilbene case, the composition of **4** was established by complexometric analysis, by the reaction of **4** with THF, which quantitatively forms **2** and free styrene (eq 4), and by a single-crystal X-ray study. The X-ray

$$\underset{\mathbf{4}}{[(C_5Me_5)_2Sm]_2(CH_2CHPh)} + 4THF \rightarrow \underset{\mathbf{2}}{2(C_5Me_5)_2Sm(THF)_2} + PhCH{=}CH_2 \tag{4}$$

crystal structure of **4**, shown in Figure 2, revealed a structural arrangement similar to that in **3**, but in this case accurate bond distance and angle data were obtainable (Tables II and III).

Table II. Selected Bond Distances (Å) in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (**4**)[a]

Sm(1)–C(1)	2.764 (18)	Sm(1)–C(2)	2.738 (18)
Sm(1)–C(3)	2.678 (18)	Sm(1)–C(4)	2.690 (19)
Sm(1)–C(5)	2.733 (19)	Sm(1)–C(11)	2.722 (19)
Sm(1)–C(12)	2.712 (18)	Sm(1)–C(13)	2.717 (19)
Sm(1)–C(14)	2.723 (20)	Sm(1)–C(15)	2.694 (21)
Sm(1)–C(41)	2.537 (15)	Sm(1)–C(42)	2.647 (15)
Sm(2)–C(21)	2.799 (18)	Sm(2)–C(22)	2.822 (16)
Sm(2)–C(23)	2.805 (16)	Sm(2)–C(24)	2.772 (16)
Sm(2)–C(25)	2.763 (17)	Sm(2)–C(31)	2.720 (16)
Sm(2)–C(32)	2.802 (18)	Sm(2)–C(33)	2.802 (18)
Sm(2)–C(34)	2.847 (18)	Sm(2)–C(35)	2.785 (19)
Sm(2)–C(41)	2.674 (15)	Sm(2)–C(42)	2.732 (15)
Sm(2)–C(43)	2.850 (16)	Sm(2)–C(48)	2.772 (17)
C(41)–C(42)	1.468 (22)	C(42)–C(43)	1.449 (21)
C(43)–C(44)	1.458 (25)	C(43)–C(48)	1.401 (24)
C(44)–C(45)	1.379 (30)	C(45)–C(46)	1.350 (32)
C(46)–C(47)	1.378 (30)	C(47)–C(48)	1.411 (27)

Table III. Selected Bond Angles (deg) in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH_2CHPh)$ (**4**)

C(41)–Sm(1)–C(42)	32.8 (5)	C(42)–C(43)–C(48)	124.7 (15)
C(41)–Sm(2)–C(42)	31.5 (5)	C(44)–C(43)–C(48)	116.6 (15)
C(41)–Sm(2)–C(43)	55.2 (5)	Sm(1)–C(41)–Sm(2)	154.1 (7)
Cent(1)–Sm(1)–C(41)	105.4	Sm(1)–C(41)–C(42)	77.7 (9)
Cent(1)–Sm(1)–C(42)	106.5	Sm(2)–C(41)–C(42)	76.4 (9)
Cent(2)–Sm(1)–C(41)	116.3	Sm(1)–C(42)–Sm(2)	141.5 (6)
Cent(2)–Sm(1)–C(42)	116.1	Sm(1)–C(42)–C(41)	69.5 (8)
Cent(1)–Sm(1)–Cent(2)	135.9	Sm(2)–C(42)–C(41)	72.1 (8)
Cent(3)–Sm(2)–C(41)	127.1	Sm(1)–C(42)–C(43)	124.0 (10)
Cent(3)–Sm(2)–C(42)	104.8	Sm(2)–C(42)–C(43)	79.5 (9)
Cent(4)–Sm(2)–C(41)	98.3	Sm(2)–C(43)–C(42)	70.5 (8)
Cent(4)–Sm(2)–C(42)	126.7	Sm(2)–C(43)–C(44)	132.4 (12)
Cent(3)–Sm(2)–Cent(4)	127.4	Sm(2)–C(43)–C(48)	72.5 (9)
C(41)–C(42)–C(43)	122.9 (14)	Sm(2)–C(48)–C(43)	78.7 (10)
C(42)–C(43)–C(44)	118.7 (15)	Sm(2)–C(48)–C(47)	126.2 (13)

[a] Cent(1) is the centroid of the C(1)–C(5) ring. Cent(2) is the centroid of C(11)–C(15) ring. Cent(3) is the centroid of the C(21)–C(25) ring. Cent(4) is the centroid of the C(31)–C(35) ring.

The overall geometry in **4** is reminiscent of that found in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[7] (**5**); i.e., the unsaturated bond of the substrate, in this case the C=C double bond, is η^2-coordinated on both sides by a $(C_5Me_5)_2Sm$ unit. Sm(1), Sm(2), and the two double bond carbons, C(41) and C(42), are coplanar to within 0.03 Å. This is not a common arrangement for M_2(alkene) complexes, and it has only been observed with two other metal systems: the zirconium complexes $Zr_2X_6(PEt_3)_4(CH_2CH_2)$ (X = Cl, Br)[37] and $[(C_5H_5)_2(ClAlEt_3)Zr]_2(CH_2CH_2)$[38] and the lithium complexes [(chelate)Li]$_2$(alkene) (alkene = stilbene and *bis*-fluorenylidene; chelate = TMEDA and PMDTA).[39,40] It is noteworthy that in each of these cases, as in **4**, the metal functions as a one-electron reducing agent.

Analysis of the bond distances in **4** (Table II) shows that throughout the structure, Sm(2) bond distances are longer than those of Sm(1). This is due to the higher formal coordination number of Sm(2), which is described later. For example, the Sm–C(C_5Me_5) distances average 2.718 (25) Å for Sm(1) and 2.792 (36) Å for Sm(2). These averages can be compared with

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the 2.68–2.77 Å range previously observed for trivalent samarium complexes containing the $(C_5Me_5)_2Sm$ unit.[6] The Sm(2) average is on the long side of this range because Sm(2) has a higher formal coordination number than any trivalent $(C_5Me_5)_2Sm$-containing complex previously studied by X-ray crystallography.

The Sm(1)–C(alkene) bond distances, Sm(1)–C(41) and Sm(1)–C(42), are 2.537 (15) and 2.647 (15) Å, whereas their Sm(2) counterparts are 2.674 (15) and 2.732 (15) Å. The Sm(1)–C(41) bond distance is near the 2.484 (14)–2.511 (8) Å range of Sm–C single bond distances found for eight-coordinate $(C_5Me_5)_2SmR$(THF) complexes with terminal hydrocarbyl groups (R = Me,[24] Ph[39]). This is quite remarkable considering that the Sm–C bond in **4** involves a bridging ligand rather than a terminal ligand. Bridging Ln–C distances are generally 0.1 Å longer than analogous terminal Ln–C distances. For example, eight-coordinate $[(C_5H_5)_2Yb(\mu\text{-}Me)]_2$[40] has 2.486 (17) and 2.536 (17) Å Yb–C(Me) distances compared to the 2.36 (1) Å Yb–C(Me) terminal distance in eight-coordinate $(C_5H_5)_2Yb(Me)(THF)$.[41] Hence, the Sm(1)–C(41) interaction is close in length to a normal Sm–C single bond.

The other Sm–C(alkene) distances are longer than the Sm(1)–C(41) distance, but for each metal they are substantially shorter than the metal–$C(C_5Me_5)$ averages. This appears to be a good criterion for some significant bonding interaction. For example, in the $(C_5Me_5)_2Ln$(unsaturated ligand) complexes $(C_5Me_5)_2Yb(\mu\text{-}MeC{\equiv}CMe)$ (**6**),[3] $(C_5Me_5)_2Yb(\mu\text{-}H_2C{=}CH_2)Pt(PPh_3)_2$ (**7**),[5] and $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$ (**8**)[6], the metal–C(unsaturated ligand) distances are substantially longer (over 0.1 Å) than the metal–$C(C_5Me_5)$ average distances: **6**, 2.85 (1) Å for Yb–C(unsaturated ligand) bond vs 2.659 (9) Å for the Yb–C(ring) bond; similarly, **7**, 2.781 (6) Å vs 2.67 (2) Å; **8**, 2.986 (8) and 3.180 (9) Å vs 2.812 (4) Å. In each case, **6**–**8**, the unsaturated hydrocarbon parts of each molecule, i.e., the 2-butyne, $(H_2C{=}CH_2)Pt(PPh_3)_2$, and $(C_5H_5)Sm(C_5Me_5)_2$ moieties, have essentially the same structure as when they are not in the lanthanide complex. For example, the MeC≡CMe part of **6** has a C—C≡C angle of 177.4 (7)° and a C≡C distance of 1.154 (6) Å, which can be compared to the 180° angle and the 1.211 Å C≡C distance in free 2-butyne at −50 °C.[42] A small perturbation of the unsaturated ligand is consistent with little interaction and the long metal–C(unsaturated ligand) distances.

In contrast, the C(41)–C(42) distance in **4** is 1.468 (22) Å compared to C═C distances of 1.28–1.368 (6) Å in crystallographically characterized substituted styrenes.[43] The lengthened C(41)–C(42) distance and the short Sm–C(alkene) distances suggest that the metals have transferred considerable electron density to the double bond of styrene. This is consistent with the NMR and magnetic data which indicate that Sm(1) and Sm(2) are trivalent.[44]

The C(41)–C(42) distance in **4** is intermediate when compared to the carbon–carbon distances found in the six other $M_2(\mu\text{-}\eta^2{:}\eta^2\text{-alkene})$ complexes characterized by X-ray crystallography. It is longer than the 1.42 (5) Å C–C distance in the [(chelate)Li]$_2$(stilbene) complexes,[39] but it is shorter than the C–C distances in $Zr_2Cl_6(PEt_3)_4(CH_2CH_2)$,[37] 1.69(3) Å, $Zr_2Br_6(PEt_3)_4(CH_2CH_2)$,[37] 1.56(4) Å, and $[(C_5H_5)_2(ClAlEt_3)Zr]_2(CH_2CH_2)$,[38] 1.55 Å.

In addition to the rare M_2(alkene) geometry, **4** contains metal interactions with the arene ring to give an overall coordination mode not previously observed in 4f-element complexes or in styrene complexes. Both bond distances and bond angles in the complex indicate that Sm(2) interacts with C(43) and C(48). This is shown most clearly by using the criterion discussed above, namely, by examining these Sm–C distances in comparison to the Sm–C(ring) distances in **4** and related molecules. The Sm(2)–C(48) bond distance, 2.772 (17) Å, is comparable to the 2.792 (36) Å Sm(2)–$C(C_5Me_5)$ average and falls within the 2.720 (16)–2.847 (18) Å range found for Sm(2)–$C(C_5Me_5)$ bonds and the 2.724(10)–2.845(8) Å range found for the Sm(III)–$C(C_5H_5)$ bonds in $(C_5Me_5)_2Sm(C_5H_5)$.[6] The 2.850 (16) Å Sm(2)–C(43) bond is statistically equivalent to the larger values of these ranges.

In comparison, the average Sm(III)–C bond distance in trivalent $Sm(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}AlCl_4)_3$[1] is 2.89 (5) Å. Comparisons with the Yb(II)–C distances of 2.850 (10) and 2.781 (6) Å in $(C_5Me_5)_2Yb(\eta^2\text{-}MeCCMe)$[3] and $(C_5Me_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$,[5] respectively, are less direct due to the differences in metal oxidation state and coordination number. Extrapolation of Shannon's data[45] suggests that 10-coordinate Sm(III) is 0.028 Å larger than eight-coordinate Yb(II). If the Ln–$C(C_5Me_5)$ average distances are used to estimate radial size,[46] the 10-coordinate Sm(III) center in **4** could be as much as 0.13 Å larger than eight-coordinate Yb(II). Since the Sm–C(arene) interactions in **4** are in the range of Sm–$C(C_5Me_5)$ distances and the Yb–C(unsaturated hydrocarbon) contacts in the ytterbium complexes are over 0.1 Å larger than the Yb–$C(C_5Me_5)$ average distances, a more significant interaction appears to be occurring in the samarium complex.

Because of the extra η^2-arene coordination of Sm(2), the four C_5Me_5 rings in **4** do not have the symmetrical tetrahedral geometry of the C_5Me_5 rings in **5**.[7] The increased coordination of Sm(2) also causes the Cent–Sm(2)–Cent angle (Cent = C_5Me_5 ring centroid) to compress to 127.4°. This small value can be compared to the 135.9° angle for Sm(1), which is normal for a trivalent $(C_5Me_5)_2Sm(X)(Y)$ complex.[6,24]

Some alternative, more traditional bonding explanations for the η^2-arene interaction in **4** can also be considered. It is possible that this interaction is like the "secondary interactions" between thorium and the arene rings of the benzyl ligands in $(C_5Me_5)Th(CH_2Ph)_3$ (**8**).[47,48] However, in contrast to **4**, the Th–C(ortho) average distance of 3.36 (2) Å in **8** is larger than the Th–C(ipso) average of 2.92 (2) Å, and both of these distances are substantially longer than the Th–$C(C_5Me_5)$ average distance, 2.79 (2) Å, and the Th–$C(CH_2)$ average of 2.58 (2) Å. Hence, the η^2-arene interaction in **4** is different in orientation and magnitude. It is also possible to view the η^2-arene interaction coupled with the η^2-alkene interaction as a substituted butadienyl type of coordination, i.e., $\overline{\mathrm{M{-}CH_2{-}CH{=}CR{-}CR_2}}$. Although the Sm(2)–C(41) distance is short, as expected for the latter type of structure, the Sm(2)–C(48) distance is the longest, and the C(43)–C(48) bond (1.401 (24) Å) is shorter than the C(42)–C(43) bond (1.449 (21) Å). Yet another view of **4** is as a bimetallic allyl derivative. Although the Sm(2)–C(41), –C(42), and –C(43) distances do not match very well the analogous distances of crystallographically characterized $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ complexes (R = H, Me, Ph),[49] there are some similarities in these structures. However, metal–carbon interactions like the Sm(2)–C(48) connection in **4** are not observed in the substituted allyl systems in which this could occur. Hence, the η^2-arene interaction in **4** appears to be a new 4f-element coordination mode.

Conclusion

The results of this study clearly indicate that significant η^2-coordination of alkenes and arenes to lanthanide metal centers

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can occur. The early expectations that the lanthanides would have little chemistry with unsaturated hydrocarbons were based on too limited a set of complexes. The prediction[9] that the lanthanides would have a much broader coordination chemistry if the metals were placed in the proper oxidation state and coordination environment is continually being substantiated. The $(C_5Me_5)_2Sm$ moiety appears to be one unit which has the necessary characteristics to achieve significant interactions with a broad range of substrates. The μ-η^2:η^2-bimetallic coordination mode of $(C_5Me_5)_2Sm$ to stilbene, styrene, and dinitrogen[7] may be general for unsaturated ligands, although in many cases any initially formed $[(C_5Me_5)_2Sm]_2$(unsaturated ligand) complex may be too reactive to isolate. The chemical consequences of the μ-η^2:η^2-alkene and η^2-arene lanthanide coordination modes are under study.

Acknowledgment. We thank the National Science Foundation for support for this research. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: Tables of crystal data, final fractional coordinates, calculated hydrogen positions, bond distances and angles, and thermal parameters and a ball and stick drawing of 3 (13 pages); table of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Tetranuclear Organooxotin Cage Compounds Formed with Phosphate and Phosphonate Ligands.[1] A New Class of Organotin Clusters

K. C. Kumara Swamy, Charles G. Schmid,[2] Roberta O. Day, and Robert R. Holmes*

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.
Received May 24, 1989

Abstract: The hydrolysis of methyltin tris(diphenyl phosphate) in ether–methyl cyanide solution yielded a new tetranuclear methyltin cluster, $[Me_2Sn_2(OH)(O_2P(OPh)_2)_3(O_3POPh)]_2$ (**1**). Related derivatives resulted from the condensation reaction of phosphonic acids with *n*-butylstannonic acid in an acetone solution at room temperature, $[R'_2Sn_2O(O_2P(OH)R)_4]_2$: R' = *n*-Bu, R = *t*-Bu (**2**); R' = *n*-Bu, R = Et (**3**). Also **4** was synthesized (R' = Me, R = *t*-Bu). X-ray analysis reveals related cage structures for **1** and **2**. Both contain Sn(IV) in a hexacoordinated environment in which the tin atoms are bridged by oxygen or hydroxyl species in addition to bridges by phosphate or phosphonate groups. ^{1}H, ^{31}P, and ^{119}Sn NMR data indicate retention of the solid-state structures in solution. The structural relation between possible cage formulations for **1** and **2** and related tetranuclear crown clusters is described. The crown formulations may be considered hydrolysis products of the cage derivatives. Hydrogen bonding aids in the formation of the cage skeletal arrangement, yielding a pocket potentially useful in clathration. **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.100$ (4) Å, $b = 14.372$ (4) Å, $c = 14.958$ (5) Å, $\alpha = 65.27$ (2)°, $\beta = 74.17$ (3)°, $\gamma = 87.99$ (2)°, and $Z = 1$. **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.037$ (4) Å, $b = 12.712$ (2) Å, $c = 14.771$ (3) Å, $\alpha = 98.90$ (2)°, $\beta = 104.89$ (2)°, $\gamma = 107.41$ (2)°, and $Z = 1$. The final conventional unweighted residuals are 0.024 (**1**) and 0.050 (**2**).

We have uncovered a rich cluster chemistry describing a variety of new structural forms for monoorganooxotin compounds containing ligands that result from the use of phosphorus-based acids.[1b,3] Thio derivatives also have been prepared that show interesting and logical structural variations.[3-5] Thus far, the tin nuclearities in these derivatives range from 2 to 7. Included among the geometrical frameworks are prismanes or drums,[6] cubes,[7,8] oxygen-capped clusters[6,8,9] and related sulfur-capped derivatives,[3-5] butterfly formations,[8] crowns,[1b] double cubes,[4] and extended clusters.[1b]

A principal reaction leading to their formation has been the condensation of an organostannoic acid with either a phosphinic, phosphonic, or phosphoric acid. Other reactions start with a previously formed cluster unit, which is then treated with a phosphorus-based acid. Both of these preparative methods are employed here and lead to the novel tetranuclear clusters, $[Me_2Sn_2(OH)(O_2P(OPh)_2)_3(O_3POPh)]_2$ (**1**) and $[(n\text{-}Bu)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ (**2**), which represent yet a new structural class that may be described as "cage" formulations. Compared to previously reported cluster units, they are most closely related to the "crown" types.[1b] However, they present a unique feature in that each cage contains a flexible cavity potentially useful in clathration reactions. Reported in this paper are their syntheses, their X-ray structures, and a study of their ^{1}H, ^{119}Sn, and ^{31}P NMR solution-state spectra.

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, and Alfa and used without further purification. Methylstannonic acid was prepared according to the procedure given by Lambourne.[10] *n*-Butylstannonic acid was a gift from the Koriyama Kasei Co., Ltd., and was purified by using excess KOH in $CHCl_3$ to remove a small amount of $n\text{-}BuSn(OH)Cl_2$ and/or $n\text{-}BuSn(OH)_2Cl$ suspected[11] as a contaminant. Solvents used were of HPLC grade (Fisher). Further purification was done according to standard procedures.[12]

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