of the enzyme to the electrode surface gained by a covalent link. Combination of covalent bonding of the enzyme via the biotin/avidin/biotin link described previously[3] with our smaller electrodes[8] might provide response times approaching or less than the 100-ms mark.

Acknowledgment. This work was supported, in part, by the Office of Naval Research. A.G.E. is a recipient of a Presidential Young Investigator Award from the National Science Foundation (CHE-8657193), an Alfred P. Sloan Fellow, and a Camille and Henry Dreyfus Teacher-Scholar.

---

(8) The total tip diameters of these electrodes range from 2 to 10 μm; however, the thickness of the electroactive ring has been estimated by scanning electron microscopy to be in the range from 50 to 150 nm (Saraceno, R. A.; Ewing, A. G. *J. Electroanal. Chem.* **1988**, *257*, 83-93).

Synthesis and X-ray Crystal Structure of the First Tris(pentamethylcyclopentadienyl)-Metal Complex: (η^5-$C_5Me_5)_3Sm$

William J. Evans,* Shirley L. Gonzales, and
Joseph W. Ziller

Department of Chemistry
University of California, Irvine
Irvine, California 92717

Received May 23, 1991

The pentamethylcyclopentadienyl ligand is one of the most broadly utilized ligands in organometallic chemistry.[1-3] This moiety has been complexed to nearly all of the metals in the periodic table, as well as to some non-metals, and the resulting compounds have been investigated extensively. All of these studies have involved molecules containing one or two pentamethylcyclopentadienyl ligands per metal. In no case has a tris(pentamethylcyclopentadienyl) complex been observed, nor was it expected. Due to the large size of the C_5Me_5 ligand, it has been assumed that only two C_5Me_5 groups can coordinate to a single metal atom even for metals as large as the actinides.[4] We report here the synthesis and structure of the first example of a (η^5-$C_5Me_5)_3M$ complex.

As part of our studies of the reactivity of the bent Sm(II) metallocene, $(C_5Me_5)_2Sm$ (**1**), with unsaturated hydrocarbon substrates,[5-8] we examined the reaction of **1** with cyclooctatetraene. On the basis of the strong reduction potential of **1**,[8,9] formation of a complex containing the $C_8H_8^{2-}$ dianion was expected. However, the reaction generated *two* organosamarium products, a red and an orange complex which were separable by sublimation.[10] The less soluble and less volatile red product was identified by X-ray crystallography[11] as the tris(pentamethylcyclopentadienyl) complex, (η^5-$C_5Me_5)_3Sm$ (**2**)[12] (Figure 1). Elemental, chemical, and spectroscopic analysis[13] of the more volatile orange product was consistent with the expected $(C_5Me_5)Sm(C_8H_8)$ (**3**). The THF adduct of **3**, $(C_5Me_5)Sm(C_8H_8)(THF)$, had been previously reported, but since it could not be desolvated,[14] this is the first synthesis of **3**. The stoichiometry of the overall reaction, which occurs immediately upon mixing the reagents in toluene, is shown in eq 1.

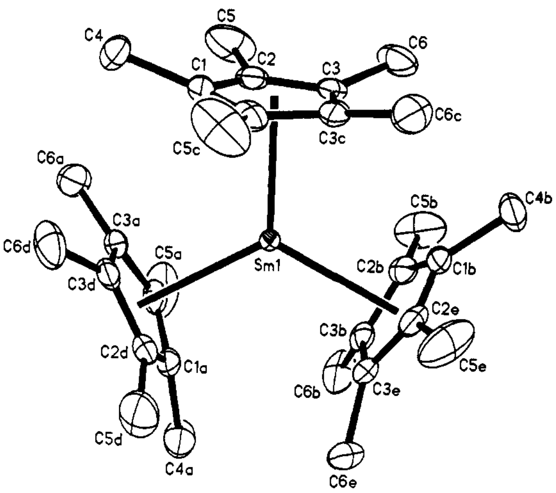

Figure 1. Molecular structure of $(C_5Me_5)_3Sm$ (**2**) with probability ellipsoids drawn at the 50% level.

$$\underset{\mathbf{1}}{2(C_5Me_5)_2Sm} + 1,3,5,7\text{-}C_8H_8 \rightarrow \underset{\mathbf{2}}{(C_5Me_5)_3Sm} + \underset{\mathbf{3}}{(C_5Me_5)Sm(C_8H_8)} \quad (1)$$

Complex **2** crystallizes in space group $P6_3/m$ with crystallographic $\bar{6}$ symmetry at the samarium center. The trigonal coordination geometry around samarium, which is obviously optimal for the three large ligands, is similar to that found in $(C_9H_7)_3Sm$,[16] $[(Me_3Si)_2C_5H_3]_3Sm$,[17] and $Y(OC_6H_3{}^tBu_2\text{-}2,6)_3$,[18] but contrasts with the pyramidal structures found for the complexes $Ln[N(SiMe_3)_2]_3$,[19] $La[CH(SiMe_3)_2]_3$,[20] and $Ce(OC_6H_3{}^tBu_2\text{-}2,6)_3$.[21]

The steric crowding in **2** leads to structural parameters that are beyond the limits previously observed in other pentamethylcyclopentadienyl lanthanide complexes. The average Sm-C(C_5Me_5) bond distance, 2.82 (5) Å, is the longest observed for a trivalent samarium complex,[7] and the individual 2.910 (3) Å Sm-C(1) distance is particularly large. The 120° (ring cen-

---

(1) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287-297. (b) King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155-169.

(2) (a) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *167*, 136-148. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121-127. (c) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301-307.

(3) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, **1982**.

(4) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267-3270.

(5) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219-223.

(6) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314-2324.

(7) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292-4297.

(8) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. In preparation.

(9) Evans, W. J. *Polyhedron* **1987**, *6*, 803-835.

(10) Addition of 1,3,5,7-C_8H_8 (5.7 μL, 0.050 mmol) to a green solution of $(C_5Me_5)_2Sm$ (0.0421 g, 0.100 mmol) in toluene (2 mL) caused immediate formation of a red-brown solution. After the mixture was stirred for 5 min, the solvent was removed by rotary evaporation. Extraction of the red-brown solid with hexane gave a mixture containing a small amount of $(C_5Me_5)_3Sm$ (**2**) and primarily $(C_5Me_5)Sm(C_8H_8)$ (**3**). Extraction of the remaining solid with toluene gave a mixture of primarily **2** with some **3** present. Direct sublimation of the reaction mixture (70 °C, 10^{-4} Torr) yielded **3** as an orange sublimate (18 mg, 93%) and **2** (26 mg, 93%) as a red residue. Both were pure by NMR spectroscopy.

(11) **2** crystallizes from benzene in space group $P6_3/m$ with $a = 9.990$ (1) Å, $c = 15.532$ (2) Å, $V = 1342.5$ Å^3, and $D_{calcd} = 1.375$ g cm^{-3} for $Z = 2$. Least-squares refinement of the model based on 1068 reflections ($|F_o| > 0.0$) converged to a final $R_F = 2.0\%$.

(12) **2**: ^1H NMR (C_6D_6) δ -1.24 (br s, C_5Me_5). ^{13}C NMR (C_6D_6) δ 113.16 (C_5Me_5), 28.31 (C_5Me_5). IR (KBr) 2958 s, 2910 s, 2861 s, 1438 m, 1378 w, 1263 m, 1099 m, 1021 m, 803 m cm^{-1}. Anal. Calcd for $SmC_{30}H_{45}$: Sm, 27.05; C, 64.80; H, 8.16. Found: Sm, 27.30; C, 64.52; H, 8.03.

(13) **3**: ^1H NMR (C_6D_6) δ 8.88 (br s, C_8H_8), 0.65 (C_5Me_5). ^{13}C NMR (C_6D_6) δ 114.32 (C_5Me_5), 85.15 (C_8H_8), 16.88 (C_5Me_5). IR (KBr) 2958 m, 2910 m, 2855 m, 1438 w, 1378 w, 1263 m, 1099 m, 1021 m, 893 m, 803 m, 718 s cm^{-1}. Anal. Calcd for $SmC_{18}H_{23}$: Sm, 38.59. Found: Sm, 38.3. Treatment of **3** with THF quantitatively formed $(C_5Me_5)Sm(C_8H_8)(THF)$.[14]

(14) Schumann, H.; Kohn, R. D.; Reier, F.-W.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388-1392.

(15) $[(C_5Me_5)La(C_8H_8)]_n$ has been reported: Bruin, P.; Booij, M.; Teuben, J. H.; Oskam, A. *J. Organomet. Chem.* **1988**, *350*, 17-23.

(16) Atwood, J. L.; Burns, J. H.; Lauberau, P. G. *J. Am. Chem. Soc.* **1973**, *95*, 1830-1833.

(17) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *J. Organomet. Chem.* **1990**, *394*, 87-97.

(18) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *Inorg. Chim. Acta* **1987**, *139*, 183-184.

(19) (a) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317-2319. (b) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669-670. (c) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1-95.

(20) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1007-1009.

(21) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 1132-1133.

0002-7863/91/1513-7423$02.50/0

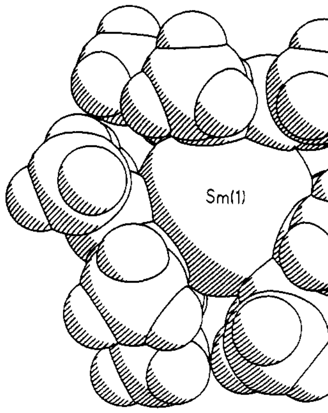

Figure 2. Space-filling model of $(C_5Me_5)_3Sm$ (**2**).

troid)–Sm–(ring centroid) angle is the smallest observed to date between two pentamethylcyclopentadienyl ligands in lanthanide complexes. Previously, the smallest observed angle, 127.0°, was found in $(C_5Me_5)_2Sm(C_5H_5)$ and the usual range is 130–138°.[7]

The rings are oriented to minimize the steric interactions as much as possible. The progression Sm–C(1) > Sm–C(2) > Sm–C(3) shows that each ring is tipped away from samarium such that the Sm–(ring centroid)–C(1) angle, 94.7°, is larger than the idealized 90° angle as well as the Sm–(ring centroid)–C(3) angle, 87.8°. The rings are oriented with respect to each other such that the C_5Me_5 carbon atom most distant from samarium in each ring (C(1)) is closest to the ring carbon atoms least distant from samarium in the next ring (the C(3)'s). The methyl groups are bent away from the center of the molecule such that the methyl carbon atoms lie out of the plane of the ring carbons by 0.17 (C(5)) to 0.52 Å (C(4)). These values can be compared to methyl group displacements of 0.09 to 0.31 Å in other $(C_5Me_5)_2Ln$ complexes.[22,23] This methyl group displacement causes the (ring centroid)–C(ring)–C(methyl) angles to deviate from 180° and again the angle involving C(4) is distorted most: Cn–C(1)–C(4), 162.3°; Cn–C(2)–C(5), 171.1°; Cn–C(3)–C(6), 166.5°.[23] These data demonstrate further the remarkable flexibility of the $(C_5Me_5)_2Sm$ unit to accommodate different ligand sets.[24]

The isolation of **2** has several implications for pentamethylcyclopentadienyl chemistry. First, the existence of **2** implies that a family of $(C_5Me_5)_3M$ complexes involving metals larger than Sm^{3+} should be sterically allowed. On the basis of Shannon radii,[25] $(C_5Me_5)_3M$ complexes may exist for M = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Th^{3+}, and U^{3+}. Since it is unknown if Sm^{3+} provides the limit in steric congestion in $(C_5Me_5)_3M$ complexes, it is possible that tris(pentamethylcyclopentadienyl) complexes may exist for smaller metals later in the lanthanide series, i.e., Eu^{3+} etc., as well as for other metals such as Th^{4+}, e.g., in a complex of the type $[(C_5Me_5)_3Th]^+$. Obviously, synthetic pathways to these compounds remain to be found.

The second implication involves the special reactivity of the pentamethylcyclopentadienyl–Sm^{2+} complexes.[9] In the past, the chemistry of $(C_5Me_5)_2Sm(THF)_{0-2}$ complexes was differentiated from that of other soluble Sm(II) complexes such as $SmI_2(THF)_2$,[26] $[(Me_3Si)_2N]_2Sm(THF)_2$,[27] and $[(Me_3Si)_2C_5H_3]_2Sm(THF)$[17] in that the latter complexes readily formed the tris(ligand) species (e.g., in reactions with CO), whereas $(C_5Me_5)_3Sm$ was not believed to exist.[4] Although formation of tris(ligand) complexes may be more facile for ligands smaller than C_5Me_5, eq 1 demonstrates that $(C_5Me_5)_3Sm$ can form under mild reaction conditions. Hence, the absence of ligand redistribution reactions leading to $(C_5Me_5)_3Sm$ cannot be a basis for the unusual chemistry observed.

Finally, despite the steric congestion in **2**, which may imply limited reactivity, $(C_5Me_5)_3M$ complexes may prove to have interesting chemistry. As shown in the space-filling model (Figure 2), access to the metal center is available via a channel down the $\bar{6}$ axis which may allow reactions with cylindrically symmetrical reagents of appropriate size. $(C_5Me_5)_3M$ complexes may also provide an opportunity to study reactions involving C_5Me_5 ring slippage. Studies in this direction are in progress.

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, positional parameters, bond distances and angles, and thermal parameters (5 pages); listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

---

[22] Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285–1291.

[23] Cf. the average methyl carbon atom displacement and centroid–(ring carbon)–(methyl carbon) angle in $(C_5Me_5)_2Sm(C_5H_5)$[7] are 0.23 Å and 171°, respectively.

[24] Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693–1703.

[25] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

[26] Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.* **1981**, *5*, 479–484.

[27] Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575–579.

Highly Stereo- and Regiocontrolled Cyclopentannulation via Allylphosphonate Conjugate Addition and Hydroboration–Oxidation–Elimination. Synthesis of Pentalenic Acid with Virtually Complete Stereo- and Regiocontrol

Gilbert Agnel and Ei-ichi Negishi*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received May 22, 1991

Construction of complex carbon structures with a high degree of stereo- and regiocontrol, such as those in which the degree of stereoselectivity and/or regioselectivity in each pertinent step is ≥98–99%, continues to be a synthetic challenge. In putting together the carbon structures of triquinanes **1**,[1] **2**,[1b,2] **3**,[3] and **4**,[4] one frequently employed strategy involving annulation of the C ring onto the A–B bicyclic intermediates has been plagued by either the difficulty in controlling the stereochemistry of the C-ring

---

[1] Isolation: Seto, H.; Sasaki, T.; Uzawa, J.; Takeuchi, S.; Yonehara, H. *Tetrahedron Lett.* **1978**, 4411. Synthesis: (a) Sakai, K.; Ohtsuka, T.; Misumi, S.; Shirahama, H.; Matsumoto, T. *Chem. Lett.* **1981**, 355. (b) Crimmins, M. T.; Deloach, J. A. *J. Org. Chem.* **1984**, *49*, 2976; *J. Am. Chem. Soc.* **1986**, *108*, 800. (c) Ihara, M.; Katogi, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 721. (d) Hudlicky, T.; Sinai-Zingde, G.; Natchus, M. G.; Ranu, B. D.; Papadopolous, P. *Tetrahedron* **1987**, *23*, 5685.

[2] (a) For earlier references, see: Paquette, L. A.; Annis, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 7358 and references therein. (b) Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* **1984**, 959. (c) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3825. (d) Hudlicky, T.; Natchus, M. G.; Sinai-Zingde, G. *J. Org. Chem.* **1987**, *52*, 4644. (e) Pattenden, G.; Teague, S. J. *Tetrahedron* **1987**, *43*, 5637.

[3] (a) Paquette, L. A.; Han, Y. K. *J. Org. Chem.* **1979**, *44*, 4014; *J. Am. Chem. Soc.* **1981**, *103*, 1835. (b) Oppolzer, W.; Bättig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493. (c) Pirrung, M. *J. Am. Chem. Soc.* **1979**, *101*, 7130; **1981**, *103*, 82. (d) Wender, P. A. *Tetrahedron* **1981**, *37*, 4445. (e) Wenkert, E.; Arrhenius, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 2030. (f) Ranu, B. C.; Kavka, M.; Higgs, L. A.; Hudlicky, T. *Tetrahedron Lett.* **1984**, *25*, 2447. (g) Tobe, Y.; Yamashita, T.; Kakiuchi, K.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 898. (h) Manzardo, G. G. G.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1986**, *69*, 659.

[4] (a) Leone-Bay, A.; Paquette, L. A. *J. Org. Chem.* **1982**, *47*, 4174. Paquette, L. A.; Leone-Bay, A. *J. Am. Chem. Soc.* **1983**, *105*, 7352. (b) Tsunoda, T.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1983**, *24*, 83. (c) Wender, P. A.; Temansky, R. J. *Tetrahedron Lett.* **1985**, *26*, 2625. (d) Sternbach, D. D.; Hughes, J. W.; Burdi, D. F.; Banks, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 2149. (e) Crimmins, M. T.; Mascarella, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 3435.

0002-7863/91/1513-7424$02.50/0