sulfones **8b** and **9b** (878 mg, 2.47 mmol) in 4 mL of THF at –78 °C was added dropwise a solution of lithium diisopropylamide [prepared from diisopropylamine (494 μL, 357 mg, 3.50 mmol) and *n*-butyllithium (1.9 mL of a 1.55 M solution, 2.96 mmol) in 4 mL of THF]. An immediate intense red color was produced. This solution was allowed to warm to room temperature during 20 min, then recooled to –78 °C. To this solution was added neat methyl iodide (2 mL, 4.28 g, 30 mmol) whereupon most of the color was discharged. After reaction and workup as for the above case, the crude product was first purified by filtration through a short silica gel plug (5% ethyl acetate/hexane) to give the products in a 77/23 ratio as judged by ^{1}H NMR [signal for the major 1*R**,5*S** isomer **26b** of δ 5.92 and signal for the minor isomer **27b** at δ 5.76]. Subsequent purification was performed by HPLC (2% ethyl acetate/hexane) to give two initial fractions containing 43 mg of the pure major 1*R**,5*S** isomer **26b** and 590 mg of subsequent fractions containing mixtures of the two isomers (total product 633 mg, 69%). An analytical sample of the major 1*R**,5*S** isomer was obtained by recrystallization from hexane to give plates of mp 104–105 °C.

IR ($CHCl_3$): 1645, 1570, 1470, 1450, 1385, 1300, 1285, 1270, 1135 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.64 (4 H, m), 5.92 (1 H, br s), 4.70 (1 H, m), 4.62 (1 H, s), 2.60 (1 H, m), 2.25–1.70 (3 H, m), 2.01 (3 H, m), 1.65 (3 H, s), 1.50 (3 H, s), 1.40 (1 H, dd, *J* = 14.8, 13.6 Hz). MS, *m/e* (%): 150 (2), 149 (39), 148 (4), 133 (5), 121 (43), 108 (6), 107 (100), 105 (9), 93 (16), 91 (6), 77 (6), 69 (12). Anal. Calcd for $C_{17}H_{21}{}^{79}BrO_2S$: MW 368.0446; C, 55.28; H, 5.73; Br, 21.64; S, 8.68. Found: MW 367.9862; C, 55.46; H, 5.83; Br, 21.81; S, 8.61.

(1*R,2*R**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (31) and (1*R**,2*S**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (30).** To a solution of sulfone **28a**^{31} (176 mg, 0.72 mmol) in 4 mL THF at –78 °C was added dropwise a solution of 1.6 M *n*-butyllithium (500 μL, 0.80 mmol). This mixture was stirred for 40 min at this temperature and then neat methyl iodide (500 μL, 1.14 g, 0.83 mmol) was added. This mixture was allowed to come to room temperature during 1 h and then partitioned between 60 mL of ether and 15 mL of 10% sodium bisulfate. The organic layer was then extracted with 200 mL of saturated sodium bicarbonate, separated, and dried, and the solvent was removed in vacuo. The crude product was judged to be a 77:32 mixture of sulfones **31** and **30** based on integration of the ^{1}H NMR [an olefinic signal at δ 6.20 for **31** and at δ 6.31 for **30**]. The identity of the two isomers has been previously established.^{15}

The sulfone **28b**^{15} (178 mg, 0.72 mmol) was dissolved in 4 mL of THF and treated in a manner similar to that described above [also using *n*-butyllithium (500 μL, 0.80 mmol) and methyl iodide (500 μL, 1.14 g, 8.03 mmol)]. The crude alkylation product was judged to be a 77:23 mixture of **31** and **30**, the same ratio as that obtained from **28a**, so these crude products were combined and purified first by preparative TLC (1/1, hexane/ethyl acetate) to give 282 mg (76%) of a mixture of **31** and **30**. These two isomers were separated by preparative TLC using a freshly activated plate (baked at 110 °C for 2 h), and performing two elutions (5/1, hexane/ethyl acetate). This gave a mixture of 50 mg (13%) of **30** and 193 mg (52%) of **31** identified by a comparison of ^{1}H NMR data with that previously reported.^{15}

(1*R,2*R**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)-bicyclo[2.2.1]heptane (33) and (1*R**,2*S**,4*S**)-2-Methyl-3-methylene-2-(phenylsulfonyl)bicyclo[2.2.1]heptane (32).** To a solution of sulfone **29** (745 mg, 3.04 mmol) in 20 mL of THF at –78 °C was added dropwise a solution of 1.6 M *n*-butyllithium (2.0 mL, 3.2 mmol). The solution at first becomes light yellow, then becomes dark red during 1 h (solution allowed to warm to –50 °C). The solution was recooled to –78 °C and neat methyl iodide was added. The solution was gradually allowed to warm. No fading of the intense red color was noted until the mixture reached a temperature of between –55 and –50 °C. The solution was pale yellow at –30 °C. After further warming to room temperature during 1 h, this mixture was partitioned between 50 mL of ether and 50 mL of brine. The organic layer was separated and dried, and the solvent was removed in vacuo to give a crude yellow solid. Purification was accomplished by chromatography on a silica gel column (ethyl acetate-/hexane gradient) to give 718 mg (90%) of a mixture of sulfones **32** and **33** in an 81:19 ratio as determined by integration of ^{1}H NMR [signal for **32** at δ 5.09 and for **33** at δ 5.14]. This mixture was a solid of undetermined melting point. The identity of the two isomers was determined by comparison with the ^{1}H NMR data reported by Veniard.^{15}

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Synthesis and X-ray Crystallographic Characterization of an Oxo-Bridged Bimetallic Organosamarium Complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$

William J. Evans,*[1a,b] Jay W. Grate,[1b] Ira Bloom,[1c] William E. Hunter,[1d] and Jerry L. Atwood*[1d]

Contribution from the Departments of Chemistry, The University of California, Irvine, Irvine, California 92717, The University of Chicago, Chicago, Illinois 60637, and The University of Alabama, University, Alabama 35486. *Received May 17, 1984*

Abstract: $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ is a common product in reactions of $(C_5Me_5)_2Sm(THF)_2$ with oxygen-containing substrates such as NO, N_2O, $CH_3CH_2\overline{CHCH_2O}$, or C_5H_5NO. The epoxide reaction, which liberates $CH_3CH_2CH{=}CH_2$ as a byproduct, gives the best yield, 55%. $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ crystallizes from toluene/hexane under pentane diffusion at –3 °C in space group $I\bar{4}2m$ with unit cell dimensions a = 11.560 (5) Å, c = 14.236 (6) Å, and Z = 2 (dimers) for D_c = 1.50 g cm^{-3}. Least-squares refinement on the basis of 962 observed reflections led to a final R value of 0.036. The two $(C_5Me_5)_2Sm$ units of the dimer are connected by a linear Sm–O–Sm bridge with Sm–O distances of 2.094 (1) Å. The centroids of the four C_5Me_5 rings define a tetrahedron which surrounds the Sm–O–Sm unit. The C_5Me_5 rings are in an eclipsed conformation on each samarium. In contrast to the above oxidation reactions, $(C_5Me_5)_2Sm(THF)_2$ reacts with $OP(C_6H_5)_3$ to form the divalent adduct $(C_5Me_5)_2Sm[OP(C_6H_5)_3](THF)$.

The organometallic chemistry of the lanthanide metals in low oxidation states is currently undergoing rapid development. Investigations of both zero-valent metal-vapor chemistry and divalent metal-complex chemistry have led to a variety of new classes of complexes and reactivity patterns.[2-10] In the divalent area, only three of the lanthanide elements, Eu, Yb, and Sm, have 2+ oxidation states accessible under normal chemical conditions. Of these, samarium is the most reactive, both because it is the strongest reducing agent[11] and because it is the largest of these metals, which means its complexes are often coordinatively less saturated and less stable.[12] As part of our general investigation of low-valent lanthanide chemistry,[2-5] we have recently synthesized and structurally characterized the first soluble organosamarium(II) complex, $(C_5Me_5)_2Sm(THF)_2$ (I).[3] As expected, this complex is highly reactive with a wide range of substrates[3] and it has also allowed the preparation of the most active f-element based catalysts for activation of hydrogen, $[(C_5Me_5)_2Sm]_2(C_6H_5)_2C_2$ (II), and $[(C_5Me_5)_2SmH]_2$ (III).[4] Given the high reactivity of Sm(II) and the great oxophilicity of the lanthanides in general, $(C_5Me_5)_2Sm(THF)_2$ is also very reactive with oxygen-containing substrates. We report here the synthesis and crystal structure of a bridged trivalent oxide complex, $(C_5Me_5)_2Sm\text{-}O\text{-}Sm(C_5Me_5)_2$ (IV), which is a product in several of these reactions.

Organometallic oxide complexes are rare in f-element chemistry and only in the actinide area have examples been briefly mentioned. $[(C_5H_5)_3U]_2O$ has been reported in a review[13] and $(C_5Me_5)\text{-}U\text{-}O$ units have been postulated as intermediates during the preparation of heterogeneous catalytic systems derived from organoactinide complexes deposited on aluminum oxide supports.[14] Since lanthanide oxygen bonds are very strong and since in the largely ionic lanthanide complexes oxide ligands may be compatible with reactive alkyl and hydride functionalities, a Ln–O–Ln unit may provide a stable framework on which to build reactive organometallic complexes. In addition to their intrinsic worth, such complexes may be of interest with respect to the oxide-supported heterogeneous organometallic catalysts and to lanthanide oxide containing catalysts. This report describes how divalent lanthanide complexes can be used to provide a direct route to a trivalent bimetallic organolanthanide oxide complex prototype.

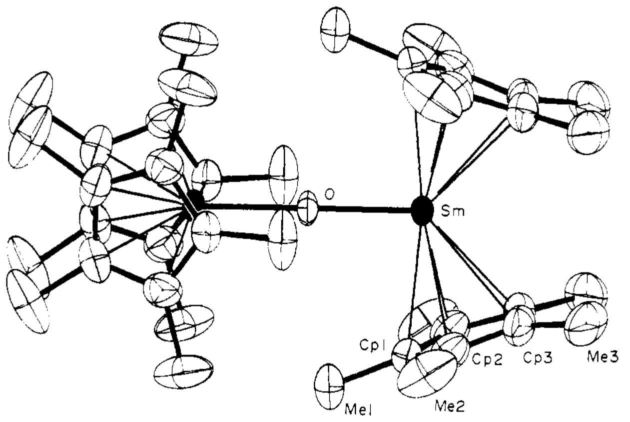

Figure 1. Molecular structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ with samarium atoms darkened.

Table I. Bond Lengths (Å) and Angles (deg) for $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$

atoms	distance	atoms	distance
Sm–Sm	4.189 (1)	Sm–O	2.094 (1)
Sm–Cp(1)	2.72 (1)	Sm–Cp(2)	2.73 (1)
Sm–Cp(3)	2.77 (1)	Sm–Cnt(1)	2.470
Cp(1)–Cp(2)	1.42 (1)	Cp(1)–Me(1)	1.54 (2)
Cp(2)–Cp(3)	1.42 (1)	Cp(2)–Me(2)	1.55 (2)
Cp(3)–Cp(3)′	1.38 (2)	Cp(3)–Me(3)	1.50 (2)
atoms	**angle**	**atoms**	**angle**
Cnt(1)–Sm–Cnt(1)	137.177	O–Sm–Cnt(1)	111.412
Sm–O–Sm	180.000	Cp(2)–Cp(1)–Cp(2)′	107.6 (9)
Cp(2)–Cp(1)–Me(1)	126.1 (6)	Cp(1)–Cp(2)–Cp(3)	107.5 (9)
Cp(1)–Cp(2)–Me(2)	128 (1)	Cp(3)–Cp(2)–Me(2)	125 (1)
Cp(2)–Cp(3)–Cp(3)′	108.6 (8)	Cp(2)–Cp(3)–Me(3)	127 (1)

Results and Discussion

Reactions of $(C_5Me_5)_2Sm(THF)_2$ Leading to $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$. $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ (IV) was first obtained while surveying the reactivity of $(C_5Me_5)_2Sm(THF)_2$ (I) with a variety of small molecules.[3] In the reaction with NO, purple solutions of I were rapidly oxidized to give orange solutions containing mixtures of trivalent products. Varying the reaction conditions and stoichiometry failed to simplify the complex distribution of products, but a toluene-soluble yellow product was consistently formed and could be isolated. Recrystallization gave single crystals which were identified as IV by X-ray crystallography.

The ^1H NMR spectrum of IV consists of a characteristic singlet at 0.06 ppm, allowing it to be conveniently identified when it is formed in other reactions. N_2O, a reagent used to prepare bridging oxo complexes of transition metals,[15,16] also yields IV on reaction with I. Desolvation of I at 75–125 °C under vacuum, a reaction which results primarily in the sublimation of $(C_5Me_5)_2Sm$ (V),[5] also forms small amounts of IV. In this case, the bridging oxygen atom would appear to be derived from THF. IV is also observed as a minor product in reactions of a variety of $(C_5Me_5)_2SmZ$ systems such as $[(C_5Me_5)_2SmH]_2$,[4] $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$,[4] and $(C_5Me_5)_2Sm(C_6H_5)(THF)$[17] if any trace amount of a reactive oxygen-containing material is available. These divalent and trivalent organosamarium compounds are so reactive that the absence of IV in reaction solutions provides a very sensitive indication that no contamination by oxygen-containing species has occurred.

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(1) (a) Alfred P. Sloan Research Fellow. (b) University of California, Irvine. (c) University of Chicago. (d) University of Alabama.

(2) (a) Evans, W. J.; Engerer, S. C.; Neville, A. C. *J. Am. Chem. Soc.* **1978**, *100*, 331–333. (b) Evans, W. J.; Wayda, A. L.; Chang, C. W.; Cwirla, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 333–334. (c) Zinnen, H. A.; Evans, W. J.; Pluth, J. J. *J Chem. Soc., Chem. Commun.* **1980**, 810–812. (d) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007–1008. (e) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. "Fundamentals of Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Publishing Corp.: New York, 1979; Vol. 3, pp 941–952. (f) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672–6677. (g) Evans, W. J.; Coleson, K. M.; Engerer, S. C. *Inorg. Chem.* **1981**, *20*, 4115–4119. (h) Evans, W. J. In "The Rare Earths in Modern Science and Technology"; McCarthy, G. J., Rhyne, J. J., Silber, H. E., Eds.; Plenum Press: New York, 1982; Vol. 3, pp 61–70. (i) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217–226. (j) Evans, W. J.; Bloom, I.; Engerer, S. C. *J. Catal.* **1982**, *104*, 2008–2014.

(3) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

(4) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

(5) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272.

(6) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652–653.

(7) (a) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003. (b) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772–1774. (c) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725–3727. (d) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432–437.

(8) Lappert, M. F.; Yarrow, P. I. W.; Atwood, J. L.; Shakir, R.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1980**, 987–988.

(9) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121–141 and references therein.

(10) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.

(11) The Sm^{3+}/Sm^{2+} reduction potential is −1.5 V vs. NHE: Morss, L. R. *Chem. Rev.* **1976**, *76*, 827–841.

(12) (a) Evans, W. J. In "The Chemistry of the Metal–Carbon Bond"; Hartley, F. R., Patai, S., Eds.; John Wiley: New York, 1982; Chapter 12, pp 489–537. (b) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21. (c) Evans, W. J. *Adv. Organomet. Chem.*, in press.

(13) Baumgärtner, F.; Fischer, E. O.; Kanellakopulos, B., unpublished results reported in: Marks, T. J., Fischer, R. D., Eds. "Organometallics of the f-Elements"; D. Reidel Publishing Co.: Dordrecht, Holland, 1979; pp 1–35.

(14) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. *Organometallics* **1983**, *2*, 566–569.

(15) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1978**, 234–235.

(16) Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 28–29. Bottomley, F.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **1981**, 271–275.

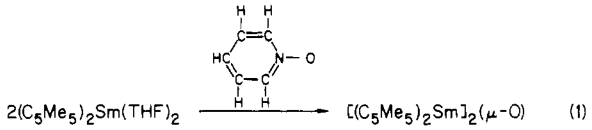
(17) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics*, in press.

Table II. Bond Distances (Å) and Angles (deg) in Oxo-Bridged Early Transition Metal and Lanthanide Complexes

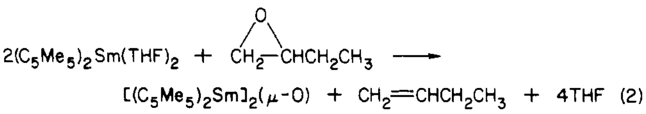
complex	angle	(1) M–O distance	(2) general M radius[a]	(3) "effective oxo radius" (1)–(2)	(4) coord no.	(5) coord no. modified radius[b]	(6) "effective oxo radius" (1)–(5)	ref
$[C_5H_5TiCl_2](\mu\text{-}O)$	180	1.777 (1)	0.68	1.10	6	0.605	1.17	23
$[TiCl(acac)_2]_2(\mu\text{-}O)(CHCl_3)$	167.5 (11)	1.79 (2)	0.68	1.11	6	0.605	1.18	24
		1.81 (2)	0.68	1.13	6	0.605	1.20	
$[(C_6H_5CH_2)_3Ti]_2(\mu\text{-}O)$	180	1.798 (0)	0.68	1.12	4	0.42	1.38	25
$[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$	180	2.094 (1)	0.964	1.13	7	1.02	1.07	this work
$K_2[TiO_2(C_7H_3O_4N)]_2(\mu\text{-}O)(H_2O)_5$	178.1 (8)	1.825 (2)	0.68	1.14	7	0.67	1.16	26
$[(C_5H_5)_2Ti(H_2O)]_2[\mu\text{-}O)(ClO_4)_2(H_2O)_2$	175.8 (5)	1.829 (2)	0.68	1.15	8	0.74	1.09	27
$[(C_5H_5)_2Ti(H_2O)]_2(\mu\text{-}O)S_2O_6$	177.0	1.834	0.68	1.15	8	0.74	1.09	28
$[(C_5H_5)_2TiCl]_2(\mu\text{-}O)$	173.8	1.837 (2)	0.68	1.16	8	0.74	1.10	29
$\{[(C_5H_5)ZrCl[\eta^1\text{-}NC_4H_4)]_2\text{-}(\mu\text{-}O)(\mu\text{-}Cl)\}\{Li(DME)_2\}$	132.5 (8)	1.910 (6)	0.74	1.17	7	0.67	1.24	30
$[(C_5H_5)_2Ti(CF_3C{=}CCF_3H)]_2(\mu\text{-}O)$	170.0 (2)	1.856 (6)	0.68	1.18	8	0.74	1.12	31
$[(C_5H_5)_2HfCH_3]_2(\mu\text{-}O)$	173.9 (3)	1.941 (3)	0.75	1.19	8	0.83	1.11	32
$[(C_5H_5)_2HfO]_3$	144 (2)	1.95 (2)	0.75	1.20	8	0.83	1.12	33
$[(C_5H_5)_2ZrCl]_2(\mu\text{-}O)$	168.9 (8)	1.94 (1)	0.74	1.20	8	0.84	1.10	34
		1.95 (1)	0.74	1.21	8	0.84	1.11	
$[(C_5H_5)_2ZrCH_3]_2(\mu\text{-}O)$	174.1 (3)	1.948 (1)	0.74	1.21	8	0.84	1.11	35
$\{[(Me_3Si)_2N]_2ZrMe\}_2(\mu\text{-}O)$	180	1.950 (1)	0.74	1.21	4	0.59	1.36	36
$[(C_5H_5)_2ZrO]_3$	142.5 (2)	1.950 (6)–	0.74	1.21–	8	0.84	1.11–	37
		1.9665 (0)	0.74	1.23	8	0.84	1.13	
$[(C_5H_5)_2NbCl]_2(\mu\text{-}O)(BF_4)_2$	169.3 (8)	1.88 (1)	0.66[c]	1.22	8	0.79	1.09	38
$[(C_5H_5)_2Nb(C_4H_9)]_2(\mu\text{-}O)$	180	1.926 (2)	0.71[c]	1.22	8	0.79	1.14	39
$[(C_5H_5)_2Zr(SPh)]_2(\mu\text{-}O)$	165.8 (2)	1.964 (3)	0.74	1.22	8	0.84	1.12	40
		1.968 (3)	0.74	1.23	8	0.84	1.13	
$[(CH_3C_5H_4)NbCl_3(OH_2)]_2(\mu\text{-}O)$	171.8 (1)	1.901 (2)	0.66[c]	1.24	8	0.79	1.11	41
		1.926 (2)	0.66[c]	1.27	8	0.79	1.14	

[a] Reference 22. [b] Reference 42. [c] ±0.02. Estimated from ref 22 and 42.

Preparative Scale Syntheses of IV. Since IV may prove to be an interesting starting material for mixed organometallic–oxide chemistry, we were interested in developing a synthesis for it that was higher in yield and cleaner in product purity and isolation procedure than the complex reactions discussed above. Among the reagents surveyed were pyridine *N*-oxide and 1,2-epoxybutane. Pyridine *N*-oxide is a convenient solid reagent, yielding IV as a microcrystalline yellow powder in 47% yield (eq 1). 1,2-Epoxybutane, a liquid, is also easy to handle and yields IV in 55% yield (eq 2). The byproduct of reaction 2, 1-butene, was identified by gas chromatography. Solutions of SmI_2 in THF are known to convert epoxides to alkenes, but the nature of the samarium-containing product was not investigated.[10]



$$2(C_5Me_5)_2Sm(THF)_2 \xrightarrow{C_5H_5NO} [(C_5Me_5)_2Sm]_2(\mu\text{-}O) \quad (1)$$



$$2(C_5Me_5)_2Sm(THF)_2 + CH_2(O)CHCH_2CH_3 \longrightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}O) + CH_2{=}CHCH_2CH_3 + 4THF \quad (2)$$

Reaction of I with $(C_6H_5)_3PO$. Addition of a solution of $(C_6H_5)_3PO$ in toluene to a purple solution of I in toluene does not yield either IV or a product with the pale yellow-orange color characteristic of Sm(III) complexes. On standing, black crystals were obtained which were identified as the divalent complex $(C_5Me_5)_2Sm[OP(C_6H_5)_3](THF)$ by ^1H NMR spectroscopy, IR spectroscopy, magnetic moment measurement, and complete elemental analysis. Although $(C_6H_5)_3PO$ has been used to advantage as a coordinating base in actinide chemistry,[18] its use with organolanthanides has been limited until recently.[19,20]

Structure of IV. Single crystals of IV were obtained by slow diffusion of pentane into a saturated toluene/hexane solution at −3 °C. As shown in the ORTEP plot in Figure 1, the complex crystallizes as an oxygen bridged dimer. The molecule has perfect S_4 symmetry with the oxygen residing at the center of the rotation axis. The relatively few independent bond distances and angles for this highly symmetric structure are shown in Table I.

The most similar previously characterized organolanthanide complex is the dimer $[(C_5Me_5)_2SmH]_2$ (III).[4] The hydride complex has near S_4 symmetry, i.e., its four C_5Me_5 ligands are arranged in a nearly tetrahedral array around the Sm_2H_2 core just as the four C_5Me_5 are arranged around the Sm_2O core. The relative tetrahedral orientation of the four C_5Me_5 groups in IV and III (and in $[(C_5Me_5)_2Th(H)(\mu\text{-}H)]_2$[21]) is of course the geometry best suited to minimize steric interaction of these bulky groups.

The range of Sm–C bond distances in IV, 2.72 (1)–2.77 (1) Å, is within the range found for III, 2.72 (2) → 2.81 (2) Å. In each structure the short distances in these ranges are found with the cyclopentadienyl carbons near the center of the molecule and the long distances are found for the cyclopentadienyl carbons furthest from the center.

The most interesting structural parameters of IV are the 180° Sm–O–Sm angle and the Sm–O distance of 2.094 (1) Å. Simple Z–O–Z units (where Z is alkyl, hydrogen, or some other univalent group) involving only single bonds are generally bent.[22] When Z is $(C_5Me_5)_2Sm$ this is obviously not the case. Since the $(C_5Me_5)_2Sm$ units are rather large, a steric argument could be used to rationalize the observed geometry: the linear geometry is sterically the best two-coordinate geometry around oxygen. A sterically crowded molecule might be expected to have Sm–O bond distances which are somewhat long. However, as described below, the Sm–O distances in IV are comparatively short.

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(18) Bagnall, K. W.; Lopez, O. V.; Xing-fu, L. *J. Chem. Soc., Dalton Trans.* **1983**, 1153–1158 and references therein.

(19) This work and: Evans, W. J.; Grate, J. W. "Industrial Associates Conference on Recent Trends in Heterogeneous and Homogeneous Catalysis"; California Institute of Technology, March 21–23, 1984.

(20) Phosphine oxides have been used for extraction of lanthanide metals from non-organometallic aqueous solutions: *Gmelin* **1983**, *System No. 39, Part D6*, 121–123.

(21) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* **1979**, *203*, 172–174.

(22) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

Several early transition metal oxide bridged dimers have been found to have linear or nearly linear M–O–M units by X-ray crystallography[23–41] and are worth comparing with IV. A summary of their bond angles and distances is given in Table II. The M–O bond distances in several of these complexes are considered to be short compared to simple M–O single bonds. In these cases, the observed shortening and the near-linear angles have been attributed to metal oxygen bond orders greater than one arising from sp hybridization of the bridging oxygen and (d-p)π interactions between the metal and oxygen.[24,30,32–35,37–40] The data in Table IV can be compared by subtracting the metals' radii from the M–O bond distances to get an "effective radius" for the oxide bridge. A smaller oxide radius is expected when a larger M–O bond order exists.

With use of general ionic radii[22] (column (2)), complex IV is found to have one of the smallest values for oxide radius in the table (column 3). With use of metallic radii corrected for coordination number[42] (column 5), complex IV has *the lowest* value for an oxide radius (column 6). Clearly, the Sm–O distances in IV are among the shortest bond lengths observed in these oxide bridged systems when the varying size of the metal is taken into account. This is consistent with the high oxophilicity of the lanthanide metals. The orbital rationale for such a short distance is less clear.

The Sm–O distance in IV can also be compared to the Nd–O bond distances for the six nonbridged NdOCH(CH$_3$)$_2$ units in Nd$_6$[OCH(CH$_3$)$_2$]$_{17}$Cl.[43] An average Nd–O distance of 2.05 ± 0.02 Å was observed for the terminal NdOCH(CH$_3$)$_2$ units which had Nd–O–C angles ranging from 158.9° to 171.2° with an average of 166.3°. Similarly short M–O bond lengths and large M–O–C angles previously have been observed in early transition metal alkoxide complexes and have been attributed to multiple bonding in the M–O linkage caused by π donation of an oxygen lone pair.[44–46] For example, the dimeric alkoxide [C$_5$H$_5$TiCl]$_2$O$_2$C$_2$Me$_4$ has a Ti–O–C angle of 166.2 (2)° and a Ti–O bond length of 1.750 (2) Å, which is shorter than that in [C$_5$H$_5$TiCl$_2$]$_2$(μ-O). Consistent with this, the alkoxide Nd–O distances in Nd$_6$[OCH(CH$_3$)$_2$]$_{17}$Cl are smaller than the μ-oxide Sm–O distances in IV when the difference in radial size is taken into account.[47]

In summary, the 180° Sm–O–Sm bond angle and the short Sm–O bond length are consistent with a bridging oxygen ligand which has perpendicular π interactions[40] with both (C$_5$Me$_5$)$_2$Sm units. However, these structural features are also consistent with the high oxophilicity of samarium and the steric requirements of the (C$_5$Me$_5$)$_2$Sm units and the four, large C$_5$Me$_5$ groups. A more precise description of the metal oxygen bonding in organolanthanides will require additional structurally characterized examples.

Conclusion

The synthesis and complete characterization of [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-O) establishes the existence of oxide bridged organometallic complexes in the lanthanide series. Similar complexes are likely to exist for all the lanthanide metals, although their stabilities and structures will vary depending on the relative size of the metal and the coligands. Since the organometallic complexes of these oxophilic metals can readily form such oxide complexes, characterization of these species is important if complete identification of components of product mixtures is desired. The synthesis of other oxide bridged organolanthanides as well as reactivity studies on this complex related to oxide supported catalysis is currently under investigation.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, all syntheses and subsequent manipulations of these compounds were conducted with the rigorous exclusion of air and water with use of Schlenk, vacuum line, and glove box (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Materials. Pentane, hexane, and heptane were washed with sulfuric acid, dried over MgSO$_4$, and distilled from potassium benzophenone ketyl solubilized with tetraglyme. Toluene and THF were distilled from potassium benzophenone ketyl. THF-d_8 and benzene-d_6 were vacuum transferred from potassium benzophenone ketyl. 1,2-Epoxybutane was purified by vacuum transfer from activated 4A molecular sieves. Pyridine *N*-oxide was stored over P$_2$O$_5$ and purified by sublimation. Nitric oxide was purified by passage through silica gel (100–400 mesh) at −78 °C. OP(C$_6$H$_5$)$_3$ (Aldrich) was used as received. (C$_5$Me$_5$)$_2$Sm(THF)$_2$ was prepared from SmI$_2$ and KC$_5$Me$_5$.[48]

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ^{1}H NMR spectra were obtained on a Bruker 250-MHz spectrometer. Chemical shifts were assigned relative to C$_6$D$_5$H, 7.15 ppm, for spectra in benzene-d_6, or relative to proteo-THF, 1.72 ppm, for spectra in THF-d_8. Magnetic moments were obtained on the Bruker 250-MHz NMR spectrometer by the Evans method.[49] Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany.

Reaction of (C$_5$Me$_5$)$_2$Sm(THF)$_2$ with NO. In the glove box, (C$_5$Me$_5$)$_2$Sm(THF)$_2$ (206.3 mg, 0.37 mmol), a Teflon-coated magnetic stir bar, and heptane (86.5 mL) were placed in a 250-mL reaction vessel fitted with a high-vacuum greaseless stopcock. The assembly was removed to a high-vacuum line and degassed thoroughly. The reaction vessel was brought to ~0 °C and NO (0.37 mmol) was added. The reaction was stirred for 4 h while it slowly warmed to room temperature. The reaction vessel was taken into the glove box and the heptane removed by rotary evaporation to give an orange oil. Addition of pentane and filtration through a medium porosity frit produced an orange filtrate (which upon solvent removal gave an oil) and a yellow precipitate. The ^{1}H NMR spectrum of the orange oil in C$_6$D$_6$ displayed at least seven absorptions in the 0–1.5 ppm range which could arise from C$_5$Me$_5$ groups attached to a Sm(III) center. Several of these signals were so closely spaced that they were barely resolved. A solution of the yellow precip-

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(23) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169–174.

(24) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1967**, *6*, 963–967.

(25) Stoeckli-Evans, H. *Helv. Chim. Acta* **1974**, *57*, 684–689.

(26) Schwarzenbach, D. *Inorg. Chem.* **1970**, *9*, 2391–2397.

(27) Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59–66.

(28) Thewalt, U.; Schleussner, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531.

(29) LePage, Y.; McCowan, J. D.; Hunter, B. K.; Heyding, R. D. *J. Organomet. Chem.* **1980**, *193*, 201–207.

(30) Atwood, J. L.; Rogers, R. D.; Bynum, R. V. *Acta Crystallogr.*, submitted.

(31) Rausch, M. D.; Sikora, D. J.; Hrncir, D. C.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 3817–3821.

(32) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284–2289.

(33) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Cryst. Spec. Res.* **1982**, *12*, 239–244.

(34) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2267–2269.

(35) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750–755.

(36) Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774–7775.

(37) Fachinetti, G.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–1775.

(38) Prout, K.; Cameron, T. S.; Forder, R. A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290–2304.

(39) Kirillova, N. I.; Lemenovskii, D. A.; Baukova, T. V.; Struchkov, Y. T. *Koord. Khim.* **1977**, *3*, 1600–1606; cited in *Chem. Abstr.* **1977**, *87*, 538: 192389Z.

(40) Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179–192.

(41) Prout, K.; Daran, J.-C. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2882–2888.

(42) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(43) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 1962–1964.

(44) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014.

(45) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782–1786.

(46) Kamenar, B.; Prout, C. K. *J. Chem. Soc. A* **1970**, 2379–2384.

(47) Nd^{3+} is 0.031[22]–0.037[42] Å larger than Sm^{3+}.

(48) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.*, in press.

(49) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. Becconsall, J. K. *Mol. Phys.* **1968**, *15*, 129–139.

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(C_5Me_5)_2Sm]_2(\mu$-O)

compound	$Sm_2OC_{40}H_{60}$
mol wt	857.68
space group	$I\bar{4}2m$
cell constants	
a, Å	11.560 (5)
c, Å	14.236 (6)
cell vol, Å^3	1902.4
molecules/unit cell	2 dimers
ρ(calcd), g cm^{-3}	1.50
μ(calcd), cm^{-1}	31.37
radiation	Mo Kα
max crystal dimensions, mm	0.40 × 0.30 × 0.20
scan width	0.8 + 0.2 tan θ
standard reflections	400, 040, 004
decay of standards	<3%
reflections measured	962
2θ range	1–50
obsd reflections	493
no. of parameters varied	55
GOF	2.55
R	0.036
R_w	0.037

itate in C_6D_6 exhibited a ^{1}H NMR spectrum which contained at least four signals attributable to C_5Me_5 entities bound to Sm(III). In light of the complexity of these spectra (as well as spectra from other reactions of $(C_5Me_5)_2Sm(THF)_2$), in subsequent reactions spectral data were obtained primarily on crystalline products. Extraction of the precipitate with toluene gave a yellow filtrate which produced yellow microcrystals upon solvent removal. The product was re-extracted with toluene, and the solvent was removed to give yellow crystals of $[(C_5Me_5)_2Sm]_2(\mu$-O) (IV) (46.4 mg, 29%): ^{1}H NMR (benzene-d_6) δ 0.06 (s, C_5Me_5). X-ray quality crystals of IV were grown by slow diffusion of pentane into a saturated toluene/hexane solution at −3 °C.

Synthesis of $[(C_5Me_5)_2Sm]_2(\mu$-O) from an Epoxide. In the glove box, 1,2-epoxybutane (22 μL, 0.255 mmol) was added via syringe to a solution of $(C_5Me_5)_2Sm(THF)_2$ (0.246 g, 0.435 mmol) in 35 mL of toluene. Within seconds, the solution color changed from purple to yellow-brown. After ca. 1 h, the solvent was removed by rotary evaporation, leaving yellow solids coated with a brown oil. This residue was suspended in 10 mL of hexane, and the solid yellow product was recovered by centrifugation (the brown supernatant was discarded). The solid was rinsed with another 10 mL of hexane and then dissolved in 30 mL of toluene. Centrifugation of this solution removed a small amount of green solid. The solvent was removed by rotary evaporation, leaving a yellow microcrystalline powder (0.103 g, 55%), identified as IV by ^{1}H NMR spectroscopy. Recrystallization by layering hexane over a saturated solution in toluene and allowing diffusion to occur at −25 °C yields X-ray quality crystals (0.071 g, 38%): IR (KBr, cm^{-1}) 2969 (s), 2906 (s), 2862 (s), 1438 (m), 1384 (m), 1085 (w), 937 (w), 796 (w). Anal. Calcd for $Sm_2C_{40}H_{60}O$: Sm, 35.07; C, 56.01; H, 7.05; O, 1.87. Found: Sm, 35.30; C, 55.86; H, 6.96; O, 1.88 (by difference). Magnetic susceptibility: χ_M^{298K} = 1280 × 10^{-6} (cgs); μ_{eff} = 1.8 μ_B.

Synthesis of $[(C_5Me_5)_2Sm]_2(\mu$-O) from Pyridine *N*-Oxide. In the glove box, solid C_5H_5NO (0.017 g, 0.18 mmol) was added to a solution of $(C_5Me_5)_2Sm(THF)_2$ (0.200 g, 0.354 mmol) in 30 mL of toluene. The purple solution became amber as the solid dissolved. After ca. 2 h, the solvent was removed by rotary evaporation and the residue was examined by ^{1}H NMR spectroscopy in C_6D_6. Numerous signals attributable to C_5Me_5 complexes were obtained. The sample was worked up as above to yield $[(C_5Me_5)_2Sm]_2(\mu$-O) as a microcrystalline powder (0.072 g, 47%) identified by ^{1}H NMR spectroscopy.

Synthesis of $(C_5Me_5)_2Sm[OP(C_6H_5)_3](THF)$. Addition of triphenylphosphine oxide to purple solutions of $(C_5Me_5)_2Sm(THF)_2$ in toluene yields brown black solutions which deposit black solids on standing. If sufficient THF is added to prevent precipitate formation, the solution retains its dark color for days. It is possible that the material insoluble at room temperature is a bis(Ph_3PO) complex which is converted to a more soluble (THF)(Ph_3PO) adduct upon THF addition. To isolate the product, triphenylphosphine oxide (67 mg, 0.24 mmol) dissolved in 5 mL of toluene was added to a solution of $(C_5Me_5)_2Sm(THF)_2$ (123 mg, 0.219 mmol) in 5 mL of toluene. This solution was cooled to −25 °C, and black crystals were collected after 1 day. The crystals were rinsed three times with 1 mL of toluene and dried under vacuum. Yield: 136 mg, 81%. IR (KBr, cm^{-1}): 3058 (m), 2852 (s), 2719 (w), 1594 (w), 1487 (w), 1439 (s), 1168 (s), 1117 (s), 1090 (m), 1040 (m), 996 (w), 888 (w), 741 (m), 719 (s), 689 (m). ^{1}H NMR (THF-d_8): δ 10.40 (s br, $OP(C_6H_5)_3$, ortho), 8.27 (s br, $OP(C_6H_5)_3$, meta), 7.82 (t, $OP(C_6H_5)_3$, para), 2.22 (s, C_5Me_5), 3.58 (m, THF), 1.72 (m, THF). Anal. Calcd for $SmC_{42}H_{53}PO_2$: Sm, 19.52; C, 65.42; H, 6.87; P, 4.02; O, 4.15. Found: Sm, 19.75; C, 65.34; H, 6.75; P, 3.84; O (by difference), 4.32. Magnetic susceptibility: χ_M^{295K} = 5600 × 10^{-6} (cgs); μ_{eff} = 3.7 μ_B. Although the crystals appeared to be good enough for X-ray diffraction studies, this was not pursued since a structure analogous to that of $(C_5Me_5)_2Sm(THF)_2$[3] is likely.

Table IV. Final Fractional Coordinates for $[(C_5Me_5)_2Sm]_2(\mu$-O)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eqv), Å
O	0.0000	0.0000	0.0000	0.042
Sm	0.0000	0.0000	0.14712 (4)	0.034
Cp(1)	−0.1658 (8)	−0.1658 (8)	0.1308 (8)	0.058
Cp(2)	−0.2179 (8)	−0.0778 (9)	0.1859 (8)	0.066
Cp(3)	−0.1632 (9)	−0.0785 (9)	0.2749 (6)	0.069
Me(1)	−0.203 (1)	−0.203 (1)	0.0318 (8)	0.098
Me(2)	−0.3183 (8)	0.005 (2)	0.1576 (9)	0.107
Me(3)	−0.202 (1)	−0.015 (2)	0.3611 (7)	0.116

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm]_2(\mu$-O). Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table III.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique as previously described.[50] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[51]

Calculations were carried out with the SHELX system of computer programs.[52] Neutral atom scattering factors for Sm, O, and C were taken from Cromer and Waber,[53] and the scattering for samarium was corrected for the real and imaginary components of anomalous dispersion with use of the table of Cromer and Liberman.[54] Scattering factors for hydrogen were from ref 55.

The space group was shown to be $I\bar{4}2m$ by the successful solution and refinement of the structure. The position of the samarium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atom revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.073$.

All non-hydrogen atoms were refined with anisotropic thermal parameters. The final agreement factors are $R = 0.036$ and $R_w = 0.037$. A final difference Fourier showed no feature greater than 0.4 e$^-$/A.^{3} The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

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Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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(50) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc.*, Dalton *Trans.* **1979**, 45–53.

(51) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962.

(52) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(53) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109.

(54) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(55) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.