

**Table I.** MLCT Bands, Rate Constants for Peroxydisulfate Oxidation, and Reduction Potentials of Complexes of Ru(NH<sub>3</sub>)<sub>5</sub> and Fe(CN)<sub>5</sub> with BPA<sup>a</sup>

complex	λ, nm	10 <sup>-3</sup> ε, M <sup>-1</sup> cm <sup>-1</sup>	k, M <sup>-1</sup> s <sup>-1</sup>	E°, V vs NHE
Fe <sup>II</sup> (CN) <sub>5</sub> BPA <sup>3-</sup>	365 <sup>b</sup>	4.7	0.10	0.440
Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> BPA <sup>2+</sup> c	410	7.2	1.0 × 10 <sup>5</sup>	0.293
(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>III</sup> (BPA)Fe <sup>II</sup> (CN) <sub>5</sub>	368	4.3	4.3 × 10 <sup>2</sup>	
(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>II</sup> (BPA)Fe <sup>II</sup> (CN) <sub>5</sub> <sup>-</sup>	408, 368 <sup>d</sup>	8.7, 5.7	5.0 × 10 <sup>4</sup> e	
(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>III</sup> (BPA)Fe <sup>III</sup> (CN) <sub>5</sub> <sup>+</sup>	415, 365	1.4, 1.3		0.447,f 0.290 <sup>g</sup>
(NH <sub>3</sub> ) <sub>5</sub> Rh <sup>III</sup> (BPA)Fe <sup>II</sup> (CN) <sub>5</sub>	367	3.3	0.50	0.440
(NH <sub>3</sub> ) <sub>5</sub> Co <sup>III</sup> (BPA)Fe <sup>II</sup> (CN) <sub>5</sub>	365 <sup>b</sup>	4.5		
(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>II</sup> (BPA)Co <sup>III</sup> (CN) <sub>5</sub> <sup>h</sup>	403			

<sup>a</sup> At 25 °C, I = 0.10 M (NaCl), pH = 5.5 (H<sub>2</sub>EDTA<sup>2-</sup>/CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>). <sup>b</sup> Reference 6. <sup>c</sup> In 0.10 M HCl. <sup>d</sup> Shoulder. <sup>e</sup> Oxidation of Ru<sup>II</sup>. <sup>f</sup> Reduction of 2 to 1. <sup>g</sup> Reduction of 1 to 3. <sup>h</sup> In KBr pellet; solution studies precluded by insolubility of complex.

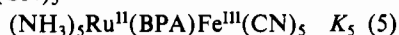
× 10<sup>-5</sup> M were obtained by reduction of **1** with ascorbic acid<sup>10</sup> or via eq 4 by mixing equimolar solutions of Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>2+</sup>



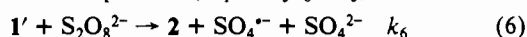
(prepared by reduction of Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>3+</sup> with ascorbic acid or with zinc amalgam) and Fe<sup>II</sup>(CN)<sub>5</sub>OH<sub>2</sub><sup>3-</sup>. Solutions of **3** display the MLCT bands of both Ru(II) and Fe(II) centers (Table I). Values of k<sub>4</sub> = (2.1 ± 0.1) × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> were measured by a competitive method (490 nm) with [4-acetylpyridine] = 2.3 × 10<sup>-3</sup> M and [Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>2+</sup>] = (1.5–10) × 10<sup>-3</sup> M.<sup>11</sup> Values of k<sub>-4</sub> = (1.9 ± 0.1) × 10<sup>-3</sup> s<sup>-1</sup> were measured by the same procedure as for k<sub>-3</sub>. When solutions of **3** are mixed with excess S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, biphasic kinetics are observed at 410 nm. The first, rapid change corresponds to oxidation of **3** to **1** with a rate constant of (5.0 ± 0.2) × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>. The second, slower changes corresponds to oxidation of **1** to **2**<sup>12</sup> with k<sub>1</sub> = (4.6 ± 0.3) × 10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup>, in acceptable<sup>13</sup> agreement with the value reported above.

Rate constants for the peroxydisulfate oxidations of Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>2+</sup>, Fe<sup>II</sup>(CN)<sub>5</sub>BPA<sup>3-</sup>, and (NH<sub>3</sub>)<sub>5</sub>Rh<sup>III</sup>(BPA)Fe<sup>II</sup>(CN)<sub>5</sub><sup>14</sup> and relevant reduction potentials (cyclic voltammetry) are presented in Table I.

Peroxydisulfate discriminates by a factor of 10<sup>6</sup> in its reactions with Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>2+</sup> and Fe<sup>II</sup>(CN)<sub>5</sub>BPA<sup>3-</sup> (Table I). Therefore, the oxidation of **3** to **1**, which proceeds at a rate comparable with that of Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>2+</sup>, undoubtedly involves electron loss from Ru(II).<sup>12</sup> On the basis of present and earlier<sup>12</sup> reactivity patterns, it is apparent that the oxidation of **1** proceeds at an anomalously high rate for removal of an electron from a Fe(II) center. The ca. 10<sup>3</sup> difference between **1** and (NH<sub>3</sub>)<sub>5</sub>Rh<sup>III</sup>(BPA)Fe<sup>II</sup>(CN)<sub>5</sub> is particularly noteworthy since the two complexes have equal charges, geometry, and E° values. We propose that the oxidation of **1** proceeds *via* rapid and reversible isomerization to **1'** (eq 5) and is followed by reaction of **1'** with S<sub>2</sub>O<sub>8</sub><sup>2-</sup>



(eq 6). In this interpretation, k<sub>1</sub> = K<sub>5</sub>k<sub>6</sub>. K<sub>5</sub>, estimated from



E° values of 0.44 and 0.29 V for reduction of Fe(III) and Ru(III) centers, respectively, is 2.9 × 10<sup>-3</sup>. Therefore, k<sub>6</sub> = 1.5 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, a perfectly reasonable value for oxidation of a Ru(II) center. The key finding herein, namely, that the electron to be lost from a given site is first transferred (in a rapid preequilibrium) to a

site which is oxidized more readily, could have important implications in biological electron-transport chains.

**Acknowledgment.** J.A.O. acknowledges financial support from the Asociacion Química Argentina and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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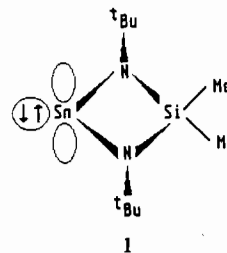
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Received June 19, 1989

### Facile Substitution of Triphenylphosphine in Wilkinson's Catalyst by Sn(N<sup>t</sup>Bu)<sub>2</sub>SiMe<sub>2</sub>. Syntheses and Molecular Structures of Square-Planar and Homoleptic Trigonal-Bipyramidal Stannylene Complexes of Rhodium(I)

It has been known for some time that certain tin(II) compounds, such as SnCl<sub>3</sub><sup>-</sup>,<sup>1</sup> Sn(acac)<sub>2</sub>,<sup>2</sup> and Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>3</sup> are excellent ligands for late transition elements—particularly those of the platinum-metal group. The monomeric, divalent tin species bear some resemblance, both in structure and reactivity, to carbenes and thus the name stannylene has been proposed for these compounds.<sup>4</sup>

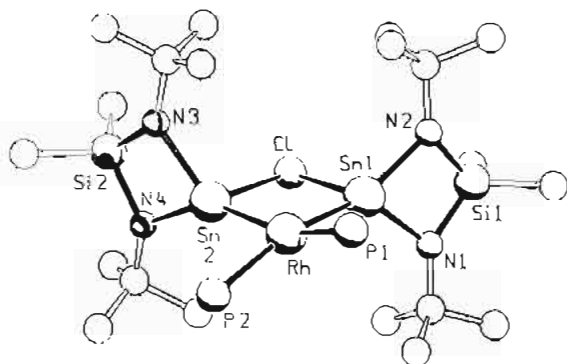
A considerable portion of the research in our group has been concerned with synthesis and chemical characterization of the cyclic bis(amino)stannylene **1** and its lighter and heavier homo-



logues.<sup>5</sup> The presence of both a filled σ-donor orbital and an

- (10) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608.  
 (11) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679.  
 (12) Freshly prepared solutions of **2** could be reduced to **3** with ascorbic acid. But after several minutes, less than quantitative formation of **3** was observed. Evidently, solutions of **2** undergo decomposition upon aging, a phenomenon previously observed for the corresponding pyrazine complex: Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *106*, 369.  
 (13) Solutions of **1** and **3** contain small and variable amounts of Ru(NH<sub>3</sub>)<sub>5</sub>BPA<sup>3+/2+</sup>, which are extremely efficient catalysts for the peroxydisulfate oxidation of Fe(II) complexes.  
 (14) Prepared by reaction of Fe<sup>II</sup>(CN)<sub>5</sub>OH<sub>2</sub><sup>3+</sup> with Rh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>BPA<sup>3+</sup> which in turn was prepared by reaction of Rh(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>3+</sup> with BPA following the procedure for making [Rh(NH<sub>3</sub>)<sub>5</sub>py](ClO<sub>4</sub>)<sub>3</sub>: Petersen, J. D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3188. Rate constants for formation and dissociation of (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup>(BPA)Fe<sup>II</sup>(CN)<sub>5</sub> are (3.0 ± 0.3) × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> and (3.2 ± 0.2) × 10<sup>-3</sup> s<sup>-1</sup>, respectively.

- (1) (a) Cramer, R. D.; Lindsey, R. V., Jr.; Prewitt, C. T.; Stolberg, U. G. *J. Am. Chem. Soc.* **1965**, *87*, 658. (b) Cramer, R. D.; Jenner, E. L.; Lindsey, R. V., Jr.; Stolberg, U. G. *Ibid.* **1963**, *85*, 1961. (c) Davies, A. G.; Wilkinson, G.; Young, J. F. *Ibid.* **1963**, *85*, 1692. (d) Young, J. F. *Adv. Inorg. Chem. Radiochem.* **1968**, *11*, 91.  
 (2) Bushnell, G. W.; Eadie, D. T.; Pidcock, A.; Sam, A. R.; Holmes-Smith, R. D.; Stobart, S. R.; Brennan, E. T.; Cameron, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 5837.  
 (3) (a) Al-Allaf, T. A. K.; Eaborn, C.; Hitchcock, P. B.; Lappert, M. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1985**, 548. (b) Hitchcock, P. B.; Lappert, M. F.; Misra, M. C. *Ibid.* **1985**, 863.  
 (4) Cotton, J. D.; Davidson, P. J.; Goldberg, D. E.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1974**, 893.

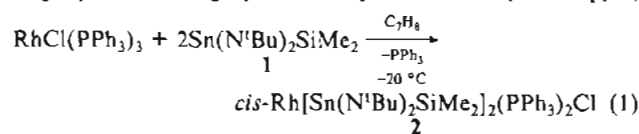


**Figure 1.** Perspective drawing of **2**. Phenyl rings of PPh<sub>3</sub> and hydrogens have been omitted for clarity. Selected dimensions (not mentioned in text): Sn(1)–Rh–P(2) = 160.1 (1)°; Sn(2)–Rh–P(1) = 161.8 (1)°; Sn(1)–Rh–Sn(2) = 83.3 (1)°; P(1)–Rh–P(2) = 97.3 (1)°; average N–Sn–N = 75.6 (4)°; average Sn–N = 2.06 (1) Å; average Si–N = 1.73 (1) Å.

empty low-lying  $\pi$ -acceptor orbital on the tin atom of monomeric **1** suggests electronic similarities to PR<sub>3</sub> (R = Alkyl, phenyl) and to a certain extent to the isolobal CO.<sup>6</sup>

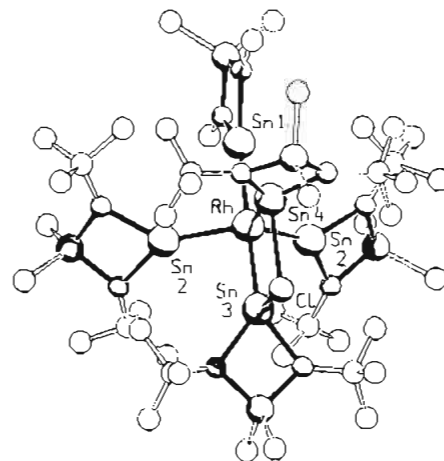
Here we report on our initial results of the controlled reactions between the classical platinum-metal complex RhCl(PPh<sub>3</sub>)<sub>3</sub><sup>7</sup> and **1**. Our findings suggest that **1** is as good a ligand as any of the previously reported tin(II) compounds and that it may rival tertiary phosphines as ligand for soft acids.

The addition of exactly 2 equiv of **1** to a RhCl(PPh<sub>3</sub>)<sub>3</sub> suspension in toluene at –20 °C leads to the rapid formation of a single product in high yield. Only one doublet (–109.9 ppm,



$J(\text{Rh-P}) = 164 \text{ Hz}$ ) is observed in the <sup>31</sup>P NMR spectrum of the reaction mixture from (1),<sup>8</sup> while the <sup>1</sup>H NMR spectrum shows the product to contain two moieties of **1** and PPh<sub>3</sub> each. Absence of observable Sn–P couplings did not allow a firm assignment for the configuration of **2** and necessitated a single-crystal X-ray study of the toluene solvate (**2**·2-toluene).<sup>9</sup>

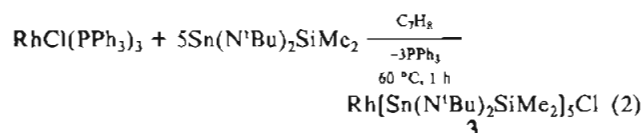
As can be seen in Figure 1, **2** crystallizes in a highly distorted square-planar cis geometry. Thus the plane defined by Rh–P(1)–P(2) is twisted by 15.8° relative to the plane defined by the three metal atoms. Complex **2** may be considered to be derived from RhCl(PPh<sub>3</sub>)<sub>3</sub> through the formal insertion of one stannylene unit into the Rh–Cl bond of the coordinatively unsaturated RhCl(PPh<sub>3</sub>)<sub>2</sub><sup>10</sup>—known to be present in solution—followed by the subsequent coordination of a second moiety of **1**. The most peculiar structural feature of **2** is the presence of a chlorine-bridged, chelating bis(stannylene) ligand. This fragment is somewhat reminiscent of the Sn<sub>2</sub>Cl<sub>5</sub><sup>–</sup> complex anion. It is pre-



**Figure 2.** Molecular structure of **3**. For clarity only the quaternary carbons on N(11) and N(12) have been drawn. Selected dimensions: Rh–Sn(1) = 2.526 (1) Å; Rh–Sn(2) = 2.549 (1) Å; Rh–Sn(3) = 2.568 (1) Å; Rh–Sn(4) = 2.574 (1) Å; Sn(1)–Rh–Sn(2) = 87.3 (1)°; Sn(1)–Rh–Sn(3) = 178.1 (1)°; Sn(1)–Rh–Sn(4) = 95.7 (1)°; Sn(2)–Rh–Sn(3) = 93.7 (1)°; Sn(2)–Rh–Sn(4) = 122.3 (1)°.

sumably the presence of this Sn–Cl–Sn bridge that has led to the formation of only the cis isomer, despite the greater steric strain brought on by this configuration. The perspective view in Figure 1 demonstrates the symmetrical coordination of the chlorine atom through the empty p orbitals of the tin atoms. Both metal–metal bond distances in **2** are equal within experimental error: Rh–Sn(1) = 2.571 (2) Å, and Rh–Sn(2) = 2.577 (2) Å. Despite apparent chemical equivalence the rhodium–phosphorus bond lengths are decidedly different (Rh–P(1) = 2.273 (4) Å and Rh–P(2) = 2.328 (4) Å), a feature we ascribe to the distortion of the plane.

When reaction 1 is allowed to continue at room temperature, the formation of a second product, at the expense of **2**, is observed by NMR techniques. This new compound, **3**, is also produced, in nearly quantitative yield, according to eq 2. NMR spectral



evidence (<sup>1</sup>H, <sup>31</sup>P) shows **3** to be free of PPh<sub>3</sub> and to contain the cyclic bis(amino)stannylene **1** as its only ligand. The comparatively mild conditions employed in reaction 2 have thus led to the complete substitution of triphenylphosphine by **1**. An air-sensitive dark red crystal of the toluene solvent (**3**·toluene) was subjected to a single-crystal X-ray analysis,<sup>11</sup> the results of which can be seen in Figure 2.

In the solid state pentakis[bis(aminostannylene)]rhodium(I) chloride is present in an almost ideal trigonal-bipyramidal geometry, the pseudo-3-fold axis passing through Sn(3), Rh, and Sn(1). The molecule is situated on a crystallographic mirror plane, which contains, among others, the Rh, Sn(1), Sn(3) and Cl atoms. We find, again, the interesting structural element of two stannylene moieties bridged by the chlorine atom. In contrast to the square-planar complex **2**, however, the tin–chloride bond distances here are distinctly nonsymmetrical, being Sn(3)–Cl = 2.585 (3) Å and Sn(4)–Cl = 2.768 (3) Å. This is presumably due to the electronic nonequivalence of axial and equatorial ligands.<sup>12</sup> The

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(6) (a) A detailed account on the coordination of stannylenes to transition metals has been given.<sup>5b</sup> (b) Lapper, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* 1985, 51.

(7) Young, J. F.; Osborne, J. A.; Jardine, F. H.; Wilkinson, G. J. *J. Chem. Soc., Chem. Commun.* 1965, 131.

(8) Chemical shift relative to external P(OMe)<sub>3</sub>, with shifts to high field assigned a negative value.

(9) Crystal data for **2**: C<sub>56</sub>H<sub>78</sub>N<sub>4</sub>ClP<sub>2</sub>RhSi<sub>2</sub>Sn<sub>2</sub>·2C<sub>7</sub>H<sub>8</sub>; monoclinic; space group P2<sub>1</sub>/n; a = 13.459 (7) Å, b = 33.100 (17) Å, c = 16.314 (8) Å, β = 98.81 (4)°, V = 7182 Å<sup>3</sup>, Z = 4; D(calcd) = 1.374 g cm<sup>–3</sup>; μ(Mo Kα) = 10.70 cm<sup>–1</sup>; empirical absorption correction. Of 4054 unique data collected, 3° ≤ 2θ ≤ 35° (Siemens AED2 diffractometer, 20 °C) 3486 were considered observed (I > 3σ(I)). Final agreement indices: R = 0.064; R<sub>w</sub> = 0.068.

(10) Parshall, G. W. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Interscience: New York, 1980; p 12.<sup>10b</sup> (b) We have no evidence for this dissociative mechanism; an associative rate determining step would also be plausible for the 16-electron RhCl(PPh<sub>3</sub>)<sub>3</sub>.

(11) Crystal data for **3**: C<sub>50</sub>H<sub>120</sub>N<sub>10</sub>ClRhSi<sub>2</sub>Sn<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>; orthorhombic; space group Cmc2<sub>1</sub>, centrosymmetrical group failed in refinement; a = 16.55 (2) Å, b = 22.33 (2) Å, c = 22.63 (2) Å; V = 8363 Å<sup>3</sup>, Z = 4; D(calcd) = 1.448 g cm<sup>–3</sup>; μ(Mo Kα) = 18.10 cm<sup>–1</sup>; empirical absorption correction. Data were collected out to 45° in 2θ, leading to 2737 unique observed (I > 3σ(I)) reflections. Agreement indices: R = 0.034; R<sub>w</sub> = 0.036.

(12) (a) In trigonal-bipyramidal d<sup>8</sup> systems the equatorial ligands apparently are better π-acceptors than the axial ligands;<sup>12b</sup> in **3** this should lead to an enhanced Lewis acidity of axial vs equatorial tin atoms. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* 1975, 14, 365.

presence of this chelating bis(stannylene) unit dominates the relative orientation of the remaining ligands. There are two distinct trends in the Rh-Sn bond distances. First, one can observe the expected longer metal-metal bonds of four-coordinate vs three-coordinate tin. Second, the rhodium-tin bond distances of the equatorial ligands are shorter than those of the axial stannylenes. This latter feature is in line with the general trends observed in a number of related trigonal-bipyramidal  $d^8$  systems.<sup>13</sup> Compounds containing rhodium-tin bonds have been known for only 25 years;<sup>16</sup> few of these have been X-ray structurally characterized. To our knowledge, no homoleptic trigonal-bipyramidal Rh/Sn complexes have been reported, although accounts of studies on the structurally similar  $[\text{Rh}(\text{SnCl}_3)_4\text{SnCl}_4]^{5-}$  and  $\text{Pt}(\text{SnCl}_3)_5^{3-}$  have appeared in the literature.<sup>14,15</sup>

In summary, the cyclic stannylene **1** seems to be a highly useful ligand in its ability to stabilize low-valent metal complexes. The facile replacement of  $\text{PPh}_3$  by **1** is particularly noteworthy, since  $\text{SnCl}_2$  apparently does not react with  $\text{RhCl}(\text{PPh}_3)_3$  at all.<sup>16</sup> Platinum-metal/tin(II) chloride mixtures are known to be useful catalysts for a number of industrial processes,<sup>17</sup> and our efforts toward understanding the bonding in these interesting complexes and their chemical behavior are continuing.

**Acknowledgment.** L.S. thanks the Deutsche Forschungsgemeinschaft (DFG) for a stipend.

**Supplementary Material Available:** An Experimental Section, ORTEP drawings and complete atomic numbering schemes for **2**-toluene and **3**-toluene, and tables of crystallographic parameters, final positional and anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters, bond lengths, and bond angles for the two structures (16 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

(13) See references cited in ref 12b and 15.

(14) Kimura, T.; Sakurai, T. *J. Solid State Chem.* **1980**, *34*, 369.

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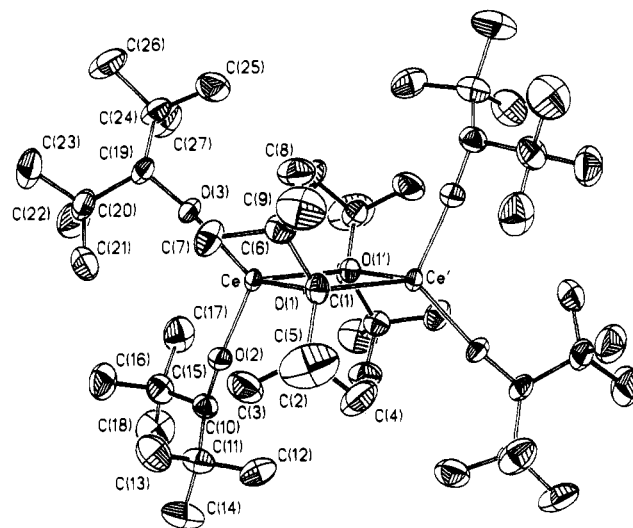
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Received March 15, 1989

### Synthesis, Structure, and Reactivity of Cerium(III) Alkoxides. 2. Thermal Decomposition of $\text{Ce}(\text{OC}^t\text{Bu}_3)_3$ and the Structure of $[\text{Ce}(\text{OCH}^i\text{Bu}_2)_3]_2$

Well-characterized homoleptic metal alkoxides are of considerable interest as precursors to metal oxides. Both thermolytic and hydrolytic methods have been employed to convert alkoxides to the corresponding oxides.<sup>1</sup> Little, however, is known concerning the mechanistic steps involved in the thermal decomposition of metal alkoxides, especially those that lack accessible  $\beta$ -hydrogen atoms.<sup>2</sup> This contrasts with extensive mechanistic information available for the decomposition of the corresponding metal alkyl

- (1) Recent reviews: (a) Brinker, C. J.; Clark, D. E.; Ulrich, D. R. *Better Ceramics Through Chemistry II. Mater. Res. Soc. Symp. Proc.* **1986**, *73*. (b) *Science of Ceramic Chemical Processing*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1986. (c) *Ultrastructure Processing of Ceramics, Glasses and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984. (d) Mazdiyasi, K. S. *Chem. Int.* **1982**, *8*, 42.
- (2) (a) Reference 1d. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (c) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978. (d) Zook, H. D.; March, J.; Smith, D. F. *J. Am. Chem. Soc.* **1959**, *81*, 1617.



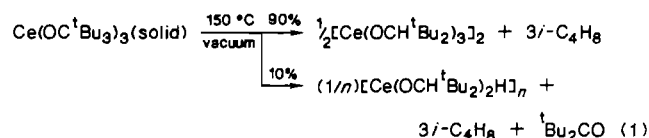
**Figure 1.** The molecular structure of **3** drawn with 40% probability thermal ellipsoids. Distances: Ce-O(1), 2.363 (3) Å; Ce-O(2), 2.142 (2) Å; Ce-O(3), 2.152 (3) Å. Angles: O(1)-Ce-O(1'), 74.3 (1)°; O(1)-Ce-O(2), 115.4 (1)°; O(1)-Ce-O(3), 114.0 (1)°; O(2)-Ce-O(3), 113.3 (1)°; O(2)-Ce-O(1'), 107.8 (1)°; O(3)-Ce-O(1'), 126.7 (1)°; Ce-O(1)-Ce', 105.7 (1)°.

species.<sup>3</sup> Herein, we report the preliminary results of our study of the thermal decomposition of  $\text{Ce}(\text{OC}^t\text{Bu}_3)_3$  (**1**) and the related  $[\text{LiOC}^t\text{Bu}_3]_n$  (**2**) to the corresponding  $\text{M}(\text{OCH}^i\text{Bu}_2)_n$  derivatives ( $\text{M} = \text{Ce}, \text{Li}$ ).<sup>4</sup> Our study provides a glimpse of the nucleation process that occurs during the formation of a metal oxide from the corresponding alkoxide through the loss of hydrocarbon fragments.

$\text{Ce}(\text{OC}^t\text{Bu}_3)_3$  (**1**) was synthesized by the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$  with  $\text{HO}C^t\text{Bu}_3$  in pentane, and was isolated as an  $\text{O}_2$ - and  $\text{H}_2\text{O}$ -sensitive yellow solid. **1** is monomeric in solution, and although its crystal structure has not been determined, it is safe to assume that it is also monomeric in the solid state. We have previously shown that the compound  $\text{Ce}(2,6\text{-}^i\text{Bu}_2\text{-C}_6\text{H}_3\text{O})_3$  is monomeric in the solid state,<sup>5</sup> and models indicate that  $\text{OC}^t\text{Bu}_3$  is significantly more bulky than  $2,6\text{-}^i\text{Bu}_2\text{-C}_6\text{H}_3\text{O}$ .

The lithium analogue, **2**, was obtained from  $^t\text{Bu}_3\text{COH}$  and  $^n\text{BuLi}$  in alkane solvent. It was assumed to be oligomeric based on the fact that the THF complex  $[(^t\text{Bu}_3\text{CO})\text{Li}(\mu\text{-THF})]_2$ , was shown to be a dimer in the solid state.<sup>4b</sup>

Thermolysis of solid **1** at 150 °C under vacuum resulted in its decomposition to  $[\text{Ce}(\text{OCH}^i\text{Bu}_2)_3]_2$  (**3**)<sup>6</sup> and isobutylene. In addition, a small quantity of  $^i\text{Bu}_2\text{CO}$  was detected, indicating the formation of a cerium(III) hydride. These results are summarized in eq 1. Hydrolysis of a  $\text{C}_6\text{D}_6$  solution of the solid residue left



(3) Recent reviews: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; p 39. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 94.

(4) While a similar reaction was reported for a bimetallic system, the mechanism of decomposition was not examined; see: (a) Hvostef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1438. (b) Murray, B. D.; Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 169.

(5) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1987**, *27*, 1130.

(6)  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) (25 °C) (ppm): 31.5 (br, terminal  $\text{OCH}^t\text{Bu}_2$ ); 7.0 (br, terminal  $\text{OCH}^i\text{Bu}_2$ ); -18.0 (br, bridging  $\text{OCH}^i\text{Bu}_2$ ). The resonance due to bridging  $\text{OCH}^i\text{Bu}_2$  could not be located. The broadness of the spectrum was due to the paramagnetic Ce(III) ion. This compound was also independently synthesized by the reaction of  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$  with 3 equiv of  $\text{HOCH}^i\text{Bu}_2$  in pentane.