

Preliminary communication

New classes of zerovalent zirconium carbonyls and related species.  
Structural characterizations of  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$  and  
 $[\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]^-$ ,  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ <sup>1</sup>

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Received 24 August 1995

Abstract

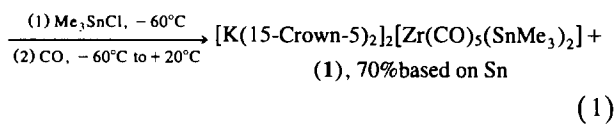
The first examples of a pentacarbonylzirconium complex,  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$  and an arylphosphine substituted zirconium(0) species,  $[\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]^-$  were obtained by the reaction of  $[\text{Zr}(\eta^4\text{-naphthalene})_3]^{2-}$  with  $\text{Me}_3\text{SnCl}$  followed by carbonylation in the absence or presence of dppe, respectively. Both compounds were structurally characterized and represent the initial organotin derivatives of Zr(0). Solutions of  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$  decompose within hours in  $\text{CH}_3\text{CN}$  at 20°C to provide an especially robust formally divalent zirconium complex,  $[\text{Zr}(\text{CO})_4(\text{SnMe}_3)_4]^{2-}$  containing eight coordinate zirconium. The latter has been unambiguously characterized by IR, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra.

Keywords: Zirconium; Carbonyl complex; Tin; Phosphorus

Although numerous zerovalent titanium carbonyls are now known [1], the situation for corresponding carbonyls of zirconium is far less satisfactory [2]. Since the first report on a formally Zr(0) carbonyl,  $\text{Zr}(\text{butadiene})_2(\text{dmpe})\text{CO}$ ,  $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ , [3] only three other classes of zerovalent zirconium carbonyls have been described, including  $\text{Zr}(\eta^6\text{-1,3,5-tri-}t\text{-butylbenzene})_2\text{CO}$ , [4]  $[\text{Zr}(\text{CO})_4(\eta^5\text{-C}_5\text{R}_5)]^-$ , for  $\text{R} = \text{H}$ ,  $\text{Me}$ , [5] and  $\text{M}(\text{CO})_4(\eta^3\text{-L})$ , for  $\text{L} = 1,1,1\text{-tris}(\text{dimethylphosphinomethyl})\text{ethane}$  or  $\text{trmpe}$  [6] and 1,4,7-triazacyclononanes [7]. Among these compounds only  $\text{Zr}(\text{CO})_4(\text{trmpe})$  has been structurally characterized [8]. For these reasons we are prompted to report on the syntheses of two new types of Zr(0) carbonyls including the first pentacarbonylzirconium species,  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$ , and an arylphosphine substituted Zr(0) complex,  $[\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]^-$ , where  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ . Both of these complexes have been structurally characterized and also represent the first examples of organotin stabilized zerovalent zirconium carbonyls. Also,  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$  may be consid-

ered to be the first derivative of the presently unknown  $[\text{Zr}(\text{CO})_5]^{4-}$  [8a].

Treatment of the recently reported  $\text{tris}(\eta^4\text{-naphthalene})\text{zirconate}(2-)$ , [8b] at  $-60^\circ\text{C}$  in THF (tetrahydrofuran) with one equivalent of  $\text{Me}_3\text{SnCl}$ , followed by carbonylation at atmospheric pressure from  $-60$  to  $20^\circ\text{C}$  over a period of 16 h (Eq. (1)), provided a 70% yield (based on Sn) of deep red, microcrystalline and satisfactorily pure  $[\text{K}(\text{15-Crown-5})_2]_2[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]$ , (1), following filtration, removal of most THF and crystallization by addition of ethyl ether. Spectral data for (1), IR( $\nu(\text{CO})$  in THF): 1934 (m), 1839 (s), 1801 (s)  $\text{cm}^{-1}$ ; <sup>13</sup>C NMR ( $\delta$  <sup>13</sup>CO in THF-*d*<sub>8</sub>): 277.6 s, ppm. <sup>119</sup>Sn NMR ( $\delta$  <sup>119</sup>SnMe<sub>3</sub> in THF-*d*<sub>8</sub> for 99% <sup>13</sup>CO enriched product, 20°C): 16.4 (sextet, <sup>2</sup>*J*(<sup>119</sup>Sn–<sup>13</sup>C) = 49 Hz). When  $[\text{Zr}(\text{C}_{10}\text{H}_8)_3]^{2-}$  was allowed to react with  $\text{Me}_3\text{SnCl}$  and then carbonylated under the same conditions in the presence of one equivalent of dppe, a difficult to separate mixture of (1) and the new substance  $[\text{K}(\text{15-Crown-5})_2][\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]$ , (2),  $[\text{K}(\text{15-Crown-5})_2]_2[\text{Zr}(\text{C}_{10}\text{H}_8)_3]$



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<sup>1</sup> J.E. Ellis, K.J. Fjare and G.F. Warnock, Highly Reduced Organometallics 39; Part 38, *Inorg. Chim. Acta*, in press.



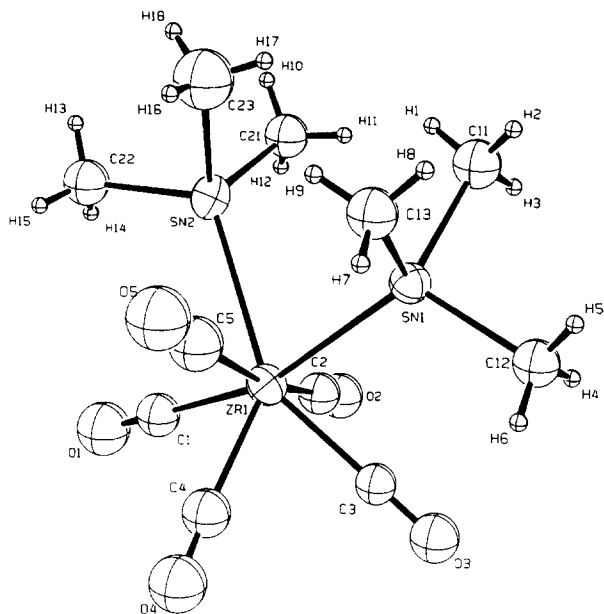


Fig. 1. Molecular structure of  $[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]^{2-}$ , 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (°): Zr–Sn(1) 3.011(3), Zr–Sn(2) 3.013(3), Zr–C(1) 2.21(2), Zr–C(2) 2.17(2), Zr–C(3) 2.18(2), Zr–C(4) 2.15(2), Zr–C(5) 2.20(3), C(1)–O(1) 1.16(2), C(2)–O(2) 1.20(2), C(3)–O(3) 1.17(2), C(4)–O(4) 1.18(2), C(5)–O(5) 1.15(3), Sn(1)–Zr–Sn(2) 80.73(7), Zr–C(1)–O(1) 179(2), Zr–C(2)–O(2) 175(2), Zr–C(3)–O(3) 178(1), Zr–C(4)–O(4) 171(2), Zr–C(5)–O(5) 178(2).

are generally not sensitive functions of the ligand environment or oxidation state of zirconium [13]. The cations in (1) and (2) are well separated from the anions and have sandwich type structures containing formally ten coordinate potassium ions and are very similar to that previously reported for  $[\text{Rb}(15\text{-Crown-5})_2]^+$  [14]. The mean K–O distances for the cations in (1) are 2.98(12) and 2.94(10) Å, while that in (2) is 2.88(9) Å, which is

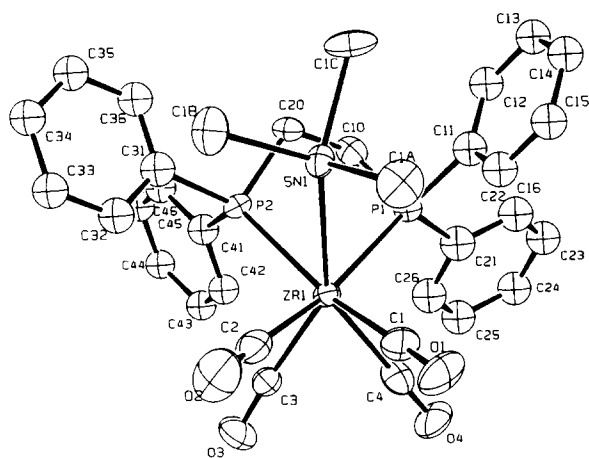


Fig. 2. Molecular structure of  $[\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]^-$ , 50% probability thermal ellipsoids. Selected bond distances (Å): Zr–Sn 3.061(2), Zr–P(1) 2.782(4), Zr–P(2) 2.779(4), Zr–C(1) 2.21(2), Zr–C(2) 2.20(2), Zr–C(3) 2.13(2), Zr–C(4) 2.18(2), C(1)–O(1) 1.15(2), C(2)–O(2) 1.14(3), C(3)–O(3) 1.20(2), C(4)–O(4) 1.13(2).

slightly shorter than the mean Rb–O distance of 3.02(4) reported for the rubidium sandwich [14]. In our chemistry [9,15] and especially that of Tinkham and Dye, [16]  $[\text{K}(15\text{-Crown-5})_2]^+$  has often been found to be a relatively inexpensive but effective substitute for  $[\text{K}(\text{cryptand } 2.2.2)]^+$  in the isolation and stabilization of highly reactive anions.

Further investigations of the properties and reactivity patterns of these compounds and extensions of this research to hafnium are in progress.

## Acknowledgments

We thank the US National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society for support of this research and are grateful to Suzanne Exstrom for assistance in the preparation of the manuscript. J.E.E. thanks the Alexander von Humboldt Foundation for a Senior US Scientist Award which enabled him to complete the manuscript while in residence at the Institut für Anorganische Chemie der Universität München, which is under the direction of Prof. Dr. Wolfgang Beck.

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- [12] (a) Crystal data for (1),  $[\text{K}(15\text{-Crown-5})_2]_2[\text{Zr}(\text{CO})_5(\text{SnMe}_3)_2]$ : single crystals grown from THF/Et<sub>2</sub>O at  $-20^\circ\text{C}$  in 7 days, C<sub>51</sub>H<sub>98</sub>O<sub>25</sub>K<sub>2</sub>Sn<sub>2</sub>Zr; orthorhombic, P<sub>bca</sub> (no. 61),  $a = 18.09$  (1),  $b = 26.210$ (8),  $c = 29.249$ (6) Å,  $V = 13870$ (16) Å<sup>3</sup>,  $Z = 8$ ,  $\rho$  calcd. = 1.454 gcm<sup>-3</sup>,  $\mu$  (MoK $\alpha$ ) = 10.50 cm<sup>-1</sup>, crystal dimensions: 0.40 × 0.25 × 0.10 mm<sup>3</sup>. The intensities of 10253 reflections were measured at  $-101^\circ\text{C}$  ( $0 < \theta < 26^\circ$ ) on an Enraf-Nonius CAD 4 diffractometer using Mok $\alpha$  radiation. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically (full matrix least squares).

For 2912 unique observed reflections [ $I \geq 2.0\sigma(I)$ ],  $R = 0.070$  and  $R_w = 0.072$ ,  $GOF = 1.518$ . (b) (2),  $[\text{K}(15\text{-Crown-5})_2][\text{Zr}(\text{CO})_4(\text{dppe})\text{SnMe}_3]$ : single crystals grown from THF/Et<sub>2</sub>O at 0°C for one week. C<sub>53</sub>H<sub>73</sub>O<sub>14</sub>P<sub>2</sub>SnZr; orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19),  $a = 17.351(7)$ ,  $b = 16.790(5)$ ,  $c = 19.900(8)$  Å,  $V = 5797(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho$  calcd. = 1.426 gcm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 7.92$  cm<sup>-1</sup>, crystal dimensions: 0.40 × 0.40 × 0.20 mm<sup>3</sup>. The intensities of 12520 reflections were measured at -101°C ( $0 < \theta < 26$ ) on an Enraf-Nonius CAD 4 diffractometer using MoK $\alpha$  radiation. The structure was solved by direct methods and all non hydrogen atoms were refined anisotropically (full matrix least squares). For 3751 unique observed reflections [ $I \geq 2.0\sigma(I)$ ],  $R = 0.064$  and  $R_w = 0.062$ ,  $GOF = 1.137$ . A complete set of Friedel pairs of data was collected. With both Zr and Sn atoms this should have allowed a clear-cut choice between the two enantiomeric possibilities for the crystal structure. Refinement of both enantiomers led to

exactly the same values of  $R$ ,  $R_w$  and  $GOF$ . This suggests that the crystals were twinned with equal amounts of the two enantiomeric crystals present. In view of this, the data were averaged and the final refinement carried out on the averaged values. Further details of the crystal structure determinations are available on request from the Cambridge Crystallographic Data Centre on quoting the full journal citation.

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