

Journal of Organometallic Chemistry 507 (1996) 283-286



Preliminary communication

## New classes of zerovalent zirconium carbonyls and related species. Structural characterizations of $[Zr(CO)_5(SnMe_3)_2]^{2-}$ and $[Zr(CO)_4(dppe)SnMe_3]^-$ , dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub><sup>-1</sup>

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Received 24 August 1995

## Abstract

The first examples of a pentacarbonylzirconium complex,  $[Zr(CO)_5(SnMe_3)_2]^{2-}$  and an arylphosphine substituted zirconium(0) species,  $[Zr(CO)_4(dppe)SnMe_3]^-$  were obtained by the reaction of  $[Zr(\eta^4-naphthalene)_3]^{2-}$  with Me<sub>3</sub>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  $[Zr(CO)_5(SnMe_3)_2]^{2-}$  decompose within hours in CH<sub>3</sub>CN at 20°C to provide an especially robust formally divalent zirconium complex,  $[Zr(CO)_4(SnMe_3)_4]^{2-}$  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,  $Zr(butadiene)_2(dmpe)CO, dmpe = Me_2PCH_2CH_2PMe_2,$ [3] only three other classes of zerovalent zirconium carbonyls have been described, including  $Zr(\eta^{6}-1,3,5-1)$ tri-t-butylbenzene)<sub>2</sub>CO, [4]  $[Zr(CO)_4(\eta^5-C_5R_5)]^-$ , for R = H, Me, [5] and M(CO)<sub>4</sub>( $\eta^{3}$ -L), for L = 1,1,1tris(dimethylphosphinomethyl)ethane or trmpe [6] and 1,4,7-triazacyclononanes [7]. Among these compounds only  $Zr(CO)_4$  (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, [Zr(CO)<sub>s</sub>(Sn- $Me_3)_2$ <sup>2-</sup>, and an arylphosphine substituted Zr(0) complex,  $[Zr(CO)_4(dppe)SnMe_3]^-$ , where dppe = Ph<sub>2</sub>-PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>. Both of these complexes have been structurally characterized and also represent the first examples of organotin stabilized zerovalent zirconium carbonyls. Also,  $[Zr(CO)_{5}(SnMe_{3})_{2}]^{2-}$  may be consid-

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

Treatment of the recently reported tris( $\eta^4$ -naphthalene)zirconate(2-), [8b] at  $-60^{\circ}$ C in THF (tetrahydrofuran) with one equivalent of Me<sub>3</sub>SnCl, followed by carbonylation at atmospheric pressure from - 60 to 20°C over a period of 16 h (Eq. (1)), provided a 70% yield (based on Sn) of deep red, microcrystalline and satisfactorily pure  $[K(15-Crown-5)_2]_2[Zr(CO)_5(SnMe_3)_2], (1),$ following filtration, removal of most THF and crystallization by addition of ethyl ether. Spectral data for (1), IR( $\nu$ (CO) in THF): 1934 (m), 1839 (s), 1801 (s) cm<sup>-1</sup>; <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  $[Zr(C_{10}H_8)_3]^2$  was allowed to react with Me<sub>3</sub>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  $[K(15-Crown-5)_2]$  [Zr(CO)<sub>4</sub>(dppe)SnMe<sub>3</sub>], (2),  $[K(15-Crown-5)_2]_2[Zr(C_{10}H_8)_3]$ 

$$\xrightarrow{(1) Me_3 SnCl, -60^{\circ}C}_{(2) CO, -60^{\circ}C to + 20^{\circ}C} [K(15-Crown-5)_2]_2[Zr(CO)_5(SnMe_3)_2] + (1), 70\%$$
based on Sn

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

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were formed in roughly equal amounts. The nature of the initial product(s) arising from the reaction of  $[Zr(C_{10}H_8)_3]^{2-}$  and Me<sub>3</sub>SnCl is still under investigation but may be related to recently reported trimethylstannyl derivatives of bis(naphthalene)titanium(0), e.g.,  $[Ti(C_{10}H_8)_2(SnMe_3)_2]^{2-}$  [9]. Deep red brown and satisfactorily pure (2) was subsequently obtained from the reaction of  $[K(15-Crown-5)_2]_2[Zr(CO)_6]$  [8] with Me<sub>3</sub>SnCl at  $-78^{\circ}$ C in THF, followed by the addition of one equivalent of dppe (Eq. (2)). After filtration and removal of most of the THF, the product was isolated in 18% yield following crystallization from THF-diethyl ether. Compound (2) had an infrared spectrum in the  $\nu$ (CO) region consisting of two absorptions at 1916 (m), 1793 (s)  $cm^{-1}$  in THF. The positions and relative intensities of these bands are very similar to those previously reported for  $[C_5H_5Zr(CO)_4]^-$  [5]. When the same reaction was carried

$$[K(15-Crown-5)_{2}]_{2}[Zr(CO)_{6}]$$

$$\xrightarrow{(1) Me_{3}SnCl, -78^{\circ}C}_{(2) dppe, -78^{\circ}C-+20^{\circ}C} [K(15-Crown-5)_{2}]$$

$$\times [Zr(CO)_{4}(dppe)SnMe_{3}] +$$
(2), 18%
(2)

out in the absence of dppe, only noncarbonyl decomposition products were obtained. In contrast, the analogous reaction of  $[Ti(CO)_6]^{2-}$  with Me<sub>3</sub>SnCl was recently shown to provide high yields of  $[Ti(CO)_6 SnMe_3]^-$  [10]. For this reason it seems likely that a corresponding, but very unstable zirconium complex forms initially in the reaction of  $[Zr(CO)_6]^{2-}$  with Me<sub>3</sub>SnCl, but attempts to observe this species have been so far unsuccessful. This putative  $[Zr(CO)_6SnMe_3]^-$  may also be trapped in low (5%) yield as pure (1) from THF by the sequence shown in Eq. (3).

$$[K(15-Crown-5)_2]_2[Zr(CO)_6]$$

$$\xrightarrow{(1) \text{ Me}_3 \text{SnCl}, -60^{\circ}\text{C}}_{(2) \text{ Me}_3 \text{SnK}, -60^{\circ}\text{C}} (1) + \text{decomp.}$$

$$\sim 5\%$$

$$(3)$$

When (1) was stirred in acetonitrile at 20°C for 3 h, the infrared spectrum of the solution in the  $\nu$ (CO) region changed from the three band pattern characteristic of (1), vide supra, to a strong intense single band at 1857 cm<sup>-1</sup> due to a new compound. Following filtration and crystallization from CH<sub>3</sub>CN-Et<sub>2</sub>O, satisfactorily pure dark red, microcrystalline [K(15-Crown-5)<sub>2</sub>]<sub>2</sub>[Zr(CO)<sub>4</sub>(SnMe<sub>3</sub>)<sub>4</sub>], (3), was isolated in 22% yield. Compound (3) was also obtained in 21% yield from the reaction of (1) with two equiv. of Me<sub>3</sub>SnCl as shown in Eq. (4). However, no information on possible intermediates or optimal amounts of Me<sub>3</sub>SnCl are yet available for this interesting conversion of (1) to the formally divalent zirconium complex (3). Compound (3) is  $(1) + Me_3SnCl$ 

$$\xrightarrow{\text{THF, 20^{\circ}C}} [K(15\text{-}Crown\text{-}5)_2]_2[Zr(CO)_4(SnMe_3)_4] + (4)$$
(3), 21%

closely related to the extremely robust and structurally characterized eight coordinate complex, [Zr(CO)<sub>4</sub>(Sn- $Ph_{3}_{4}^{2}$ , which has a highly symmetric dodecahedral coordination environment about zirconium [11]. The latter species has an infrared spectrum in the  $\nu(CO)$ region also consisting of one band (at  $1880 \text{ cm}^{-1}$ ), which is similar in shape and intensity to that of (3), strongly suggesting that both anions have similar molecular structures. To confirm this formulation, NMR spectra of 99% <sup>13</sup>CO enriched (3) were obtained at 20°C in THF-d<sub>8</sub>. The <sup>13</sup>CO carbonyl resonance at  $\delta = 244.9$ ppm consisted of an approximate 1:3:1 triplet,  $J({}^{13}C ^{117,119}$ Sn) = 89 Hz, which is the expected pattern for the three most intense peaks when four equivalent tin groups couple to <sup>13</sup>CO [11], while the <sup>119</sup>Sn NMR spectra consisted of a binomial pentet at  $\delta = 49.5$  ppm with  $J({}^{13}\text{C}-{}^{119}\text{Sn}) = 92$  Hz. These spectra are consistent with the presence of a fluxional eight coordinate complex in which four equivalent Me<sub>3</sub>Sn groups are coupled to four equivalent CO groups and are very similar to those previously reported for  $[Zr(CO)_4(SnPh_3)_4]^{2-}$  [11].

Single crystal X-ray studies on (1) and (2) were carried out to corroborate our formulations and provide structural data for these new compounds [12]. Fig. 1 shows the molecular structure of  $[Zr(CO)_5(SnMe_3)_2]^{2-}$ , which is approximately capped trigonal prismatic about zirconium, with Sn(2) as the capping atom. Mean Zr-Cand C-O distances in (1) are 2.18(3) and 1.17(3) Å, respectively, which are close to corresponding distances of 2.17(3) and 1.16(3) Å observed in Zr(CO)<sub>4</sub>(trmpe), the only previous structurally characterized Zr(0) carbonyl [6]. The mean Zr-Sn distance of 3.012(3) Å in (1) is significantly shorter than the corresponding value of 3.086(1) Å in the very crowded  $[Zr(CO)_4(SnPh_3)_4]^{2-1}$ [11]. Fig. 2 depicts the X-ray structure of  $[Zr(CO)_4-$ (dppe)SnMe<sub>3</sub>]<sup>-</sup>, which bears a strong resemblance to that of  $Zr(CO)_4$  (trmpe) [6]. For example, the  $Zr(CO)_4$ units in both complexes are virtually identical, with respect to mean interatomic Zr-C and C-O distances and cis-Zr(CO), and trans-Zr(CO), angles, which are 2.16(3) Å, 1.16(3) Å, 70(1)° and 108(1)°, respectively in (2) and 2.17(3) Å, 1.16(3) Å, 70.7(5)° and 109.7(5)°, respectively for the trmpe complex. The Zr-Sn distance of 3.061(2) Å in (2) is significantly longer than that in (1) but shorter than the corresponding value observed in  $[Zr(CO)_4(SnPh_3)_4]^{2-}$ , while the mean Zr-P distance of 2.781(2) Å is in the range of Zr-P distances observed previously in zirconium phosphine complexes. Fryzuk has pointed out that Zr-P distances in these complexes



Fig. 1. Molecular structure of  $[Zr(CO)_5(SnMe_3)_2]^{2-}$ , 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  $[Rb(15-Crown-5)_2]^+$  [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  $[Zr(CO)_4(dppe)SnMe_3]^-$ , 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] [K(15-Crown-5)<sub>2</sub>]<sup>+</sup> has often been found to be a relatively inexpensive but effective substitute for [K(cryptand 2.2.2)]<sup>+</sup> 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 Institüt 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),  $[K(15-Crown-5)_2]_2[Zr(CO)_5(SnMe_3)_2]$ : single crystals grown from THF/Et<sub>2</sub>O at  $-20^{\circ}$ C in 7 days,  $C_{51}H_{98}O_{25}K_2Sn_2Zr$ ; orthorhombic,  $P_{bca}$  (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>,  $\mu$  (Mo<sub>ka</sub>) = 10.50 cm<sup>-1</sup>, crystal dimensions:  $0.40 \times 0.25 \times 0.10$  mm<sup>3</sup>. The intensities of 10253 reflections were measured at  $-101^{\circ}$ 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  $[(I) \ge 2.0\sigma (I)]$ , R =0.070 and  $R_w = 0.072$ , GOF = 1.518. (b) (2), [K(15-Crown-5)<sub>2</sub>][Zr(CO)<sub>4</sub>(dppe)SnMe<sub>3</sub>]: single crystals grown from THF/Et<sub>2</sub>O at 0°C for one week.  $C_{53}H_{73}O_{14}P_2SnZr$ ; orthorhombic,  $P2_12_12_1$  (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>,  $\mu(Mo_{k\alpha}) = 7.92$  cm<sup>-1</sup>, crystal dimensions:  $0.40 \times 0.40$  $\times 0.20$  mm<sup>3</sup>. The intensities of 12520 reflections were measured at  $-101^{\circ}$ 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 [(1)  $\ge 2.0\sigma$  (1)], 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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