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Synthesis and Characterization of $[R_3SnTi(CO)_6]^-$, a New Class of Titanium Carbonyls. Molecular Structure of $(C_6H_{11})_3SnTi(CO)_6^-$ [1]

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For several years the only examples of zerovalent titanium complexes were exceedingly unstable matrix-isolated binary carbonyls, including the 16-electron species $Ti(CO)_6$.[2,3] Numerous unsuccessful attempts to stabilize $Ti(CO)_6$ with one organophosphine group, e.g., as $Me_3PTi(CO)_6$, resulted instead in the formation of more substituted carbonyl compounds, such as $(Me_3P)_2Ti(CO)_5$ or $(Me_3P)_3Ti(CO)_4$.[4] Now we report that $Ti(CO)_6$ is effectively stabilized by one $[R_3Sn]^-$ unit in the form of the complexes $[R_3SnTi(CO)_6]^-$ (R = Me (**1**), Ph (**2**), cyclohexyl (**3**)). These are the first examples of isolable hexacarbonyltitanium(0) complexes and suggest that a large family of similar seven-coordinate compounds of the general formula $[XTi(CO)_6]^-$ may be possible.

Interaction of R_3SnCl and $[Ti(CO)_6]^{2-}$ [5] led to facile formation of the monoanions $[R_3SnTi(CO)_6]^-$, which were isolated in 70–80% yields as air-sensitive bright red $[K(15\text{-crown-}5)_2]^+$ salts. For example, reaction of nearly equimolar amounts of Me_3SnCl (0.050 g, 0.25 mmol) and $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$ (0.31 g, 0.26 mmol) in 80 mL of tetrahydrofuran at 0 °C for 30 min provided an air-sensitive red solution of $[Me_3SnTi(CO)_6]^-$. After filtration, solvent removal, and thorough washing of the resulting product with a mixture of ether and pentane (2/3 v/v), 0.170 g (80% yield) of a microcrystalline orange-red product was isolated, which provided satisfactory elemental analyses for $[K(15\text{-crown-}5)_2][\mathbf{1}]$. Similar procedures gave satisfactorily pure corresponding salts containing **2** and **3**.[6] Although these products are thermally stable at room temperature as crystalline solids, solutions containing **2** were best maintained under an atmosphere of carbon monoxide. Tin-119 NMR spectra of the 99% ^{13}CO-enriched anions, prepared from $[Ti(^{13}CO)_6]^{2-}$,[5] in THF showed the expected binomial septets arising from six equivalent ^{13}CO groups coupled to Sn in these fluxional seven-coordinate complexes. Infrared and ^{13}C NMR solution spectra were also entirely consistent with the assigned formulations.[6]

Preliminary investigations indicate that $[R_3SnTi(CO)_6]^-$ are likely to be extremely useful reagents in the exploration of zerovalent titanium carbonyl chemistry. Organophosphanes and other nucleophiles were found to readily displace one or two carbonyl groups in these compounds under mild conditions. For example, $[Ph_3SnTi(CO)_6]^-$ reacted at room temperature with 1,2-bis(dimethylphosphino)ethane (dmpe) and $[Ph_3Sn]^-$ to afford 84 and 27% isolated yields of pure samples of the previously reported $[Ph_3SnTi(CO)_4(dmpe)]^-$ [7] and $[(Ph_3Sn)_2Ti(CO)_5]^{2-}$,[4] respectively. Similar substitution reactions with other donor groups provide new materials and will be reported separately.[8] In this regard, it is noteworthy that the previously known vanadium analog $Ph_3SnV(CO)_6$ [9] reacted with dmpe and $[Ph_3Sn]^-$ to provide only $[V(CO)_6]^-$ along with $Ph_3Sn(dmpe)^+$ and Ph_6Sn_2, respectively.[10] Evidently, $[Ti(CO)_6]^{2-}$ is a sufficiently poor leaving group compared to $[V(CO)_6]^-$ that CO substitution is favored over heterolysis of the M–Sn bond in $[Ph_3SnTi(CO)_6]^-$ versus $Ph_3SnV(CO)_6$. Also, it is significant that $[Ti(CO)_6]^{2-}$ does not appear to undergo analogous substitution reactions, unlike the isoelectronic species $[V(CO)_6]^-$ [11] and $Cr(CO)_6$,[12] which readily react with donor groups under thermal (M = Cr) or photolytic (M = V, Cr) conditions.

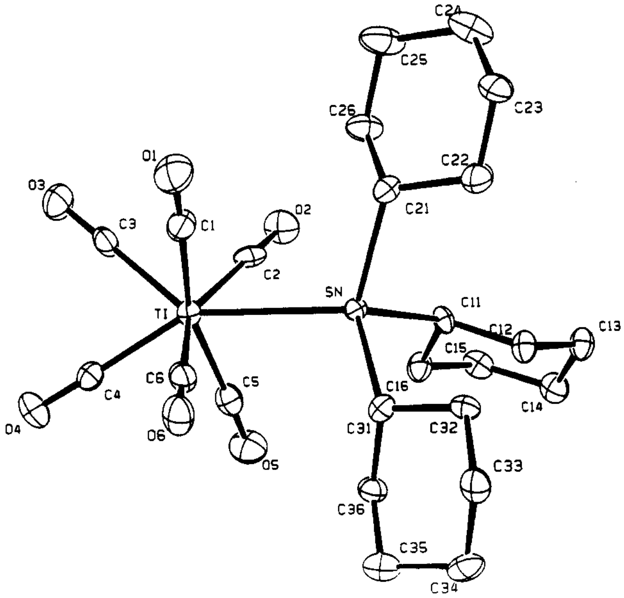

Figure 1. ORTEP diagram of **3** drawn with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Ti–Sn 2.921(1), Ti–C(1) 2.053(7), Ti–C(2) 2.066(7), Ti–C(3) 2.019(7), Ti–C(4) 2.036(7), Ti–C(5) 2.066(7), Ti–C(6) 2.050(7), C(1)–O(1) 1.151(7), C(2)–O(2) 1.156(7), C(3)–O(3) 1.164(7), C(4)–O(4) 1.161(7), C(5)–O(5) 1.154(7), C(6)–O(6) 1.168(7); Ti–C–O(1) 177.7(5), Ti–C(2)–O(2) 179.6(5), Ti–C(3)–O(3) 178.8(5), Ti–C(4)–O(4) 177.6(6), Ti–C(5)–O(5) 178.0(6), Ti–C(6)–O(6) 178.8(5).

A single-crystal X-ray study of **3** as a $[K(cryptand\ 2.2.2)]^+$ salt was carried out to corroborate our formulation and provide structural data for this new species.[13,14] As shown in Figure 1, **3** may be described as an approximate capped trigonal prism,

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[6] Elemental analyses and selected spectral data for $[K(15\text{-crown-}5)_2]^+$ salts are as follows. Anal. Calcd for salt of **1**, $C_{29}H_{49}O_{16}KSnTi$: C, 40.59; H, 5.75; Sn, 13.81. Found: C, 40.87; H, 6.23; Sn, 13.80. Calcd for salt of **2**, $C_{44}H_{55}O_{16}KSnTi$: C, 50.54; H, 5.30; Sn, 11.35. Found, C, 50.33; H, 5.52; Sn, 11.85. Calcd for salt of **3**, $C_{44}H_{73}O_{16}KSnTi$: C, 49.68; H, 6.92. Found: C, 49.15; H, 7.15. IR (THF), ν(CO): for **1**, 1994 (m), 1890 (vs), 1860 (s) cm^{-1}; for **2**, 2003 (m), 1899 (vs), 1867 (s) cm^{-1}; for **3**, 1990 (m), 1882 (vs), 1857 (s) cm^{-1}. NMR (THF-d_8, 20 °C, 99% ^{13}CO-enriched products): for **1**, $^{13}C\{^1H\}$ δ 263.2 (s with satellites, $^2J(^{117,119}Sn-^{13}C) = 92$ Hz, CO), 70.0 (s, 15-crown-5), −3.6 (s, $SnMe_3$) ppm, $^{119}Sn\{^1H\}$ $\delta = 35.1$ (septet, $^2J(^{119}Sn-^{13}C) = 94$ Hz, $SnMe_3$) ppm; for **2**, $^{13}C\{^1H\}$ $\delta = 259.5$ (s with satellites, $^2J(^{117,119}Sn-^{13}C) = 93$ Hz, CO) ppm, $^{119}Sn\{^1H\}$ $\delta = 23.6$ (septet, $^2J(^{119}Sn-^{13}C) = 97$ Hz, $SnPh_3$) ppm; for **3**, $^{13}C\{^1H\}$ $\delta = 262.3$ (s with satellites, $^2J(^{117,119}Sn-^{13}C = 80$ Hz, CO) ppm, $^{119}Sn\{^1H\}$ $\delta = 25.2$ (septet, $^2J(^{119}Sn-^{13}C) = 82$ Hz, $Sn(C_6H_{11})_3$) ppm.

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where tin is the capping atom. Mean Ti–C and C–O distances in **3** are 2.05(2) and 1.16(1) Å, respectively, which are within the range of corresponding values of 2.04(1) and 1.16(2) Å found in $[(Ph_3Sn)_2Ti(CO)_5]^{2-}$, the only other example of a structurally characterized Ti(0)–tin complex.[4] The latter contains a mean Ti–Sn distance of 2.83(2) Å, which is significantly shorter than the Ti–Sn distance of 2.921(1) Å in **3**, perhaps owing to the larger size of $(C_6H_{11})_3Sn$ compared to $(C_6H_5)_3Sn$. The counterion, $[K(cryptand\ 2.2.2)]^+$, is well separated from the anion and has interatomic parameters essentially identical with those previously reported for the iodide salt.[15] Extensions of this study to corresponding zirconium and hafnium compounds are in progress.

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Supplementary Material Available: A table of crystal data and intensity measurements, an ORTEP diagram of $[K(cryptand\ 2.2.2)]^+$, and listings of positional parameters, bond lengths and angles, and anisotropic thermal parameters for $[K(cryptand\ 2.2.2)][(C_6H_{11})_3SnTi(CO)_6]$ (25 pages). Ordering information is given on any current masthead page.

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(13) For purposes of the X-ray study, [K(cryptand 2.2.2)][**3**] was found to provide more satisfactory single crystals than the corresponding $[K(15\text{-crown-}5)_2]^+$ salt. The $[K(cryptand\ 2.2.2)]^+$ salt was obtained by exactly the same procedure except $[K(cryptand\ 2.2.2)]_2[Ti(CO)_6]$[5] was employed in the reaction. [K(cryptand 2.2.2)[**3**] had identical spectroscopic properties for the anion as the other salt and was obtained in satisfactorily pure form. Anal. Calcd for $C_{42}H_{69}O_{12}N_2KSnTi$: C, 50.46; H, 6.96, N, 2.80. Found: C, 50.23; H, 6.99; N, 2.74.

(14) Orange-red crystalline plates of [K(cryptand 2.2.2)][**3**] were obtained by diffusion of diethyl ether through a nearly saturated solution of the salt in THF at –20 °C over a 3-day period. One of these was selected and placed on a glass fiber which was mounted on a goniometer head. Crystal data for [K(cryptand 2.2.2)][**3**]: $C_{42}H_{69}N_2O_{12}KSnTi$; monoclinic, $P2_1/c$ (No. 14), $a = 10.619(2)$ Å, $b = 29.936(7)$ Å, $c = 14.934(7)$ Å, $\beta = 97.08(3)°$, $V = 4711\ (5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.409$ g cm^{-3}, μ(Mo Kα) = 8.44 cm^{-1}, crystal dimensions 0.45 × 0.40 × 0.15 mm^3. The intensities of 9947 reflections were measured at –101° ($0 < \theta < 26°$) on an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically (full-matrix least-squares). For 5778 unique observed reflections $[I \geq 2.0\sigma(I)]$, $R = 0.051$ and $R_w = 0.051$.

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