

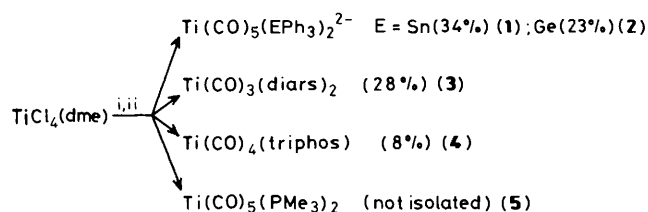
**New Classes of Zerovalent Titanium Carbonyls; First Structural Characterisation of a Seven-co-ordinate Titanium Complex containing only Unidentate Ligands:****Kai Ming Chi, Scott R. Frerichs, and John E. Ellis\****Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.*

Seven-co-ordinate zerovalent titanium carbonyls containing only unidentate ligands,  $\text{Ti}(\text{CO})_5(\text{EPh}_3)_2^{2-}$  (E = Ge, Sn, structurally characterized for Sn), and organoarsine and arylphosphine ligands,  $\text{Ti}(\text{CO})_3[\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2]_2$  and  $\text{Ti}(\text{CO})_4[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]$ , respectively, have been prepared for the first time from highly reactive and quite thermally unstable low valent titanium intermediates, one of which has been characterized as  $\text{Ti}(\text{CO})_5(\text{PMe}_3)_2$  on the basis of  $^{13}\text{C}$  and  $^{31}\text{P}$  n.m.r. spectra.

Substantial progress has been made recently in the development of zerovalent titanium carbonyl chemistry, but all materials reported to date have been stabilized by polydentate ligands such as carbocyclic anions, hydro-tris(1-pyrazolyl)-borate, or bi- and tridentate alkylphosphines.<sup>2,3</sup> We now report on the first examples of seven-co-ordinate titanium compounds containing only unidentate ligands and the initial examples of arylphosphine- and organoarsine-substituted

Ti(O) carbonyls. A single crystal X-ray structure determination of  $\text{Ti}(\text{CO})_5(\text{SnPh}_3)_2^{2-}$  was carried out to verify the seven-co-ordinate nature of titanium in this dianion and also to provide the first structural characterization of a pentacarbonyl titanium species. Of key importance in the synthesis of these new substances is the use of trimethylphosphine in the stabilization of low valent titanium intermediates.

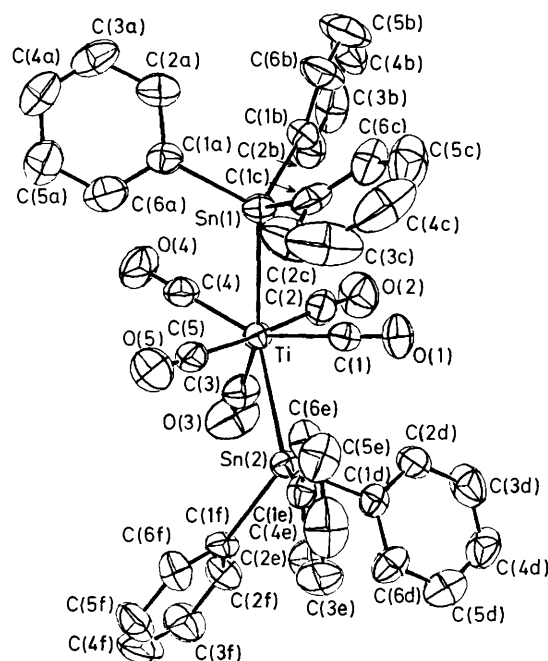
Treatment of a cold ( $-70^\circ\text{C}$ ) mixture of  $\text{TiCl}_4(\text{dme})$  (dme



**Scheme 1.** New zerovalent titanium carbonyls. *Reagents and conditions:* i, dme, 4  $\text{PMe}_3$  followed by 4  $\text{NaC}_{10}\text{H}_8$ , Ar,  $-70^\circ\text{C}$ ; ii, addition of ligand (2  $\text{Na}[\text{EPh}_3]$ , 2 diars, or triphos) followed by CO (1 atm.), slow warming to  $0^\circ\text{C}$ .

= 1,2-dimethoxyethane) and  $\text{PMe}_3$  (4.0 equiv.) in dme with a vigorously stirred solution containing sodium naphthalenide (4.0 equiv.) and naphthalene (2.0 equiv.) in dme under argon provided a red-brown solution within minutes. After replacement of the argon atmosphere by carbon monoxide at  $-70^\circ\text{C}$ , the slurry rapidly assumed a much darker appearance owing to the formation of finely divided brown-black solid and a red solution (*vide infra*). After stirring for 1 h  $\text{Na}[\text{SnPh}_3]$  (2.0 equiv.)<sup>2</sup> in cold dme ( $-70^\circ\text{C}$ ) was added. The mixture was stirred for 12 h at  $-60^\circ\text{C}$  and then allowed to warm slowly to room temperature under a CO atmosphere. After filtration and metathesis with dry  $[\text{Et}_4\text{N}]\text{Br}$ , a red solid formed. This was collected, washed thoroughly with absolute ethanol, and recrystallized from MeCN-toluene to provide  $[\text{Et}_4\text{N}]_2[\text{Ti}(\text{CO})_5(\text{SnPh}_3)_2]$  (1) of satisfactory purity in 22% yield. When  $\text{Na}[\text{SnPh}_3]$  was added *before* carbonylation, the isolated yield of (1) increased to 34%. With this important modification (adding the ligand before carbonylation), satisfactorily pure red to red-violet samples of  $[\text{Et}_4\text{N}]_2[\text{Ti}(\text{CO})_5(\text{GePh}_3)_2]$  (2),  $\text{Ti}(\text{CO})_3(\text{diars})_2$  (3) [diars =  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ ], and  $\text{Ti}(\text{CO})_4(\text{triphos})$  (4) [triphos =  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ] were isolated in 8–28% (Scheme 1).<sup>†</sup> It is noteworthy that compounds (1)–(4) could not be prepared from  $\text{Ti}(\text{CO})_5(\text{dmpe})$  (dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ )<sup>2</sup> or from reductive carbonylations of titanium halides carried out in the absence of trimethylphosphine. Except for compound (3), all are stable indefinitely as crystalline solids at room temperature under an inert atmosphere.

Attempts to isolate or observe, by i.r. spectra, titanium carbonyls from the aforementioned red solution were unsuccessful owing to the compounds' great thermal instability especially under argon or reduced pressure. However,  $^{13}\text{C}$  and  $^{31}\text{P}$  n.m.r. spectra of corresponding solutions made with 99%  $^{13}\text{C}$  enriched carbon monoxide in the presence of  $\text{PMe}_3$  (2 or 4 equiv., respectively) indicated that the major (*ca.* 80%) carbonyl titanium complex present was  $\text{Ti}(\text{CO})_5(\text{PMe}_3)_2$  (5), a derivative of  $\text{Ti}(\text{CO})_7$  containing only unidentate phosphines. Compound (5) has a very similar  $^{13}\text{C}$  resonance position to those of all other known pentacarbonyltitanium species including compounds (1) and (2) and the previously reported



**Figure 1.** ORTEP view of  $\text{Ti}(\text{CO})_5(\text{SnPh}_3)_2^{2-}$ , the anion in (1), showing the atom numbering scheme. Selected bond lengths and angles: Ti–Sn(1) 2.841(2), Ti–Sn(2) 2.811(2), Ti–C(1) 2.05(1), Ti–C(2) 2.02(1), Ti–C(3) 2.01(1), Ti–C(4) 2.04(1), Ti–C(5) 2.07(1), C(1)–O(1) 1.15(1), C(2)–O(2) 1.18(1), C(3)–O(3) 1.16(1), C(4)–O(4) 1.16(1), C(5)–O(5) 1.15(1), Sn–C(mean) 2.20(1) Å; Sn(1)–Ti–Sn(2) 141.07(6), Ti–C(1)–O(1) 174.0(9), Ti–C(2)–O(2) 175.7(9), Ti–C(3)–O(3) 174.3(9), Ti–C(4)–O(4) 178.8(9), Ti–C(5)–O(5) 178.1(9)<sup>°</sup>.

$\text{Ti}(\text{CO})_5(\text{dmpe})$  { $\delta$  260.6 [t,  $J(\text{P}-\text{C})$  8.9 Hz]}.<sup>2,‡</sup> Also present in solution at  $0^\circ\text{C}$  was *ca.* 20% of (6) which was formulated as the tetracarbonyl species  $\text{Ti}(\text{CO})_4(\text{PMe}_3)_3$ , on the basis of the similarity of its  $^{13}\text{C}$  resonance position to those of known tetracarbonyltitanium species including compound (3),  $\text{Ti}(\text{CO})_4(\text{dmpe})(\text{SnPh}_3)^-$  ( $\delta$  272.0),<sup>2</sup> and  $\text{Ti}(\text{CO})_4[\text{Bu}^t\text{-Si}(\text{CH}_2\text{PMe}_2)_3]$  ( $\delta$  276.7).<sup>3</sup> The possibility that (5) or (6) contain co-ordinated naphthalene seems unlikely but cannot be ruled out at present.

The *X*-ray structure of the anion in (1) (Figure 1)<sup>§</sup> is very similar to that found previously for  $\text{V}(\text{CO})_5(\text{SnPh}_3)_2^-$ ,<sup>4</sup> and may be described as an approximate monocapped octahedron, where one triphenyltin group is the capping ligand. Somewhat longer M–Sn and M–C bonds are present in (1) than in the vanadium complex, owing to the larger size of titanium compared to vanadium. None of the interatomic distances or angles are unusual. Also, cations are well

<sup>†</sup> Spectroscopic properties and elemental analyses were found to be in complete accord with the proposed formulations.

*Selected spectroscopic data for (1):* i.r. (Nujol)  $\nu(\text{CO})$  1913m, 1809s, 1782s, 1772s;  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r. [75 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $20^\circ\text{C}$ ]  $\delta$  259.2s, (CO). For (2): i.r. (Nujol)  $\nu(\text{CO})$  1927w, 1839s, 1789s, 1752s;  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r. [75 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $20^\circ\text{C}$ ]  $\delta$  258.1s (CO). For (3): i.r. (toluene)  $\nu(\text{CO})$  1867 s, 1779 s;  $^1\text{H}$  n.m.r. (300 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ )  $\delta$  1.06 (s, 6H, MeAs), 1.14 (s, 6H, Me'As), 7.20 (m, 4H,  $\text{C}_6\text{H}_4$ );  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r. (75 MHz,  $[\text{D}_6]\text{toluene}$ ,  $-60^\circ\text{C}$ , 99%  $^{13}\text{C}$  enriched product)  $\delta$  298.7 (t, 1CO,  $J(\text{C}-\text{C})$  20 Hz), 277.1 (d, 2CO,  $J(\text{C}-\text{C})$  20 Hz). For (4): i.r. (toluene)  $\nu(\text{CO})$  1930m, 1815s;  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. (121.5 MHz,  $[\text{D}_6]\text{thf}$ ,  $20^\circ\text{C}$ )  $\delta$  13.4 s p.p.m.  $^{13}\text{C}$ - $\{^1\text{H}\}$  n.m.r. (75 MHz,  $[\text{D}_6]\text{thf}$ ,  $60^\circ\text{C}$ ,  $^{13}\text{C}$  enriched)  $\delta$  273.9 (q,  $J(\text{P}-\text{C})$  7.4 Hz).

<sup>‡</sup> *N.m.r. spectral data for (5):* for  $^{13}\text{C}$ - $\{^1\text{H}\}$  (dme,  $0^\circ\text{C}$ , 75 MHz)  $\delta$  259.2 [t,  $J(\text{P}-\text{C})$  8.4 Hz];  $^{31}\text{P}$ - $\{^1\text{H}\}$  (121.5 MHz)  $\delta$  -11.4 (m). For (6):  $^{13}\text{C}$ - $\{^1\text{H}\}$  (75 MHz)  $\delta$  275.2 (m);  $^{31}\text{P}$ - $\{^1\text{H}\}$  (121.5 MHz)  $\delta$  -20.8 (m).

<sup>§</sup> *Crystal data for (1):*  $\text{C}_{57}\text{H}_{70}\text{O}_5\text{N}_2\text{Sn}_2\text{Ti}$ , monoclinic,  $P2_1/a$  (no. 14),  $a = 31.352(8)$ ,  $b = 16.339(3)$ ,  $c = 10.777(8)$  Å,  $\beta = 95.62(5)^\circ$ ,  $U = 5494(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.388$  g m<sup>-3</sup>,  $\mu(\text{Mo}-K_\alpha) = 10.9$  cm<sup>-1</sup>. A total of 6739 unique reflections were collected on an Enraf-Nonius CAD-4 diffractometer at  $23^\circ\text{C}$ : The data were corrected for Lorentz, polarization, and absorption effects. 4040 Reflections were considered observed unique [ $I > 1.0\sigma(I)$ ] and used to solve (Patterson synthesis) the structure with final residuals  $R = 0.047$  and  $R_w = 0.044$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

separated from anions in the crystalline lattice. Selected mean interatomic distances are Ti–C 2.04(1), Ti–Sn 2.83(2), and C–O 1.16(2) Å. The mean Ti–C distance is close to that observed in the divalent complex  $(C_5H_5)_2Ti(CO)_2$  [2.03(1) Å],<sup>5</sup> while previous structurally characterized zero-valent titanium carbonyls, including  $Ti(CO)_3(dmpe)_2$ ,<sup>6</sup>  $C_5H_5Ti(CO)_4^-$ ,<sup>7</sup> and  $Ti(CO)_4[Bu^tSi(CH_2PMe_2)_3]$ ,<sup>3</sup> have somewhat shorter mean Ti–C distances of about 1.99 Å. Since the isoelectronic anion  $V(CO)_5(SnPh_3)_2^-$  is derived from  $V(CO)_5^{3-}$ ,<sup>8</sup> compounds (1) and (2) may be considered to be derivatives of the presently unknown  $Ti(CO)_5^{4-}$ .

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## References

- 1 For the previous article in this series, see D. W. Blackburn, K. M. Chi, S. R. Frerichs, M. L. Tinkham, and J. E. Ellis, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 437.
- 2 K. M. Chi, S. R. Frerichs, B. K. Stein, D. W. Blackburn, and J. E. Ellis, *J. Am. Chem. Soc.*, 1988, **110**, 163, and references cited therein.
- 3 T. G. Gardner and G. S. Girolami, *Organometallics*, 1987, **6**, 2551.
- 4 J. E. Ellis, T. G. Hayes, and R. E. Stevens, *J. Organomet. Chem.*, 1981, **216**, 191.
- 5 J. L. Atwood, K. E. Stone, H. G. Alt, D. C. Hrncir, and M. D. Rausch, *J. Organomet. Chem.*, 1977, **132**, 367.
- 6 P. J. Domaille, R. L. Harlow, and S. S. Wreford, *Organometallics*, 1982, **1**, 935.
- 7 B. A. Kelsey and J. E. Ellis, *J. Am. Chem. Soc.*, 1986, **108**, 1344.
- 8 G. F. P. Warnock, S. B. Philson, and J. E. Ellis, *J. Chem. Soc., Chem. Commun.*, 1984, 893, and references cited therein.