X-Ray Crystal Structure of Bis-[1,2-bis(dimethylphosphino)ethane]-dicarbonyltrifluorophosphinetitanium, a Phosphine-substituted Derivative of $Ti(CO)_7$

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Summary Carbonylation of $Ti(\eta\text{-}C_4H_6)_2(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane] or reduction of $TiCl_4{\cdot}2THF$ in the presence of dmpe and CO affords $[Ti(CO)_3(dmpe)_{3/2}]_n$ which reacts with PF_3 and dmpe to form $Ti(CO)_2(PF_3)(dmpe)_2$, [a derivative of the non-existent $Ti(CO)_7$], the *X*-ray crystal structure of which is reported.

Stable, binary metal carbonyl complexes are known for all elements of the first transition series except Sc, Ti, and Cu. Indeed, $(\eta\text{-}C_6H_6)_2Ti$,[1] $(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)Ti$,[2] $Ti(\eta\text{-}C_4H_6)_2(dmpe)$[3] and related derivatives appear to be the only formal zerovalent Ti complexes known. The only stable Ti carbonyl complexes reported are derivatives of $(\eta\text{-}C_5H_5)_2Ti^{II}$ and analogous species.[4] Recently developed preparative methods for $Ti(\eta\text{-}C_4H_6)_2$(bidentate phosphine)[3,5] make this labile Ti^0 complex readily available and provide a precursor to simple, phosphine-substituted carbonyl complexes.

Treatment of a tetrahydrofuran (THF) solution of $Ti(\eta\text{-}C_4H_6)_2(dmpe)$ and dmpe with 1000 lb in^{-2} of CO for 12 h at 0 °C results in the formation of a red solution from which red needles of a complex formulated as $[Ti(CO)_3(dmpe)_{3/2}]_n$ (**1**) [ν_{CO} (Nujol) 1810 and 1720 cm^{-1}] can be isolated (55%). The complex may also be prepared in lower yield by direct reduction of $TiCl_4{\cdot}2THF$ in THF with Na–Hg in the presence of dmpe and 1000 lb in^{-2} of CO at 0 °C (28%). The analogous $[Ti(CO)_3(depe)_{3/2}]_n$ (**2**) [ν_{CO} (Nujol) 1820 and 1780 cm^{-1}] [depe = 1,2-bis(diethylphosphino)ethane] has been prepared similarly (25%). Solids (**1**) and (**2**) are indefinitely stable under nitrogen but decompose in solution unless cooled (0 °C) or kept under a CO atmosphere. Although no structural information is available, (**1**) is at least a tetramer ($n \geqslant 4$), as four equally populated ^{31}P n.m.r. resonances are observed at low temperatures.

Crystals of (**1**) or (**2**) of adequate quality for *X*-ray studies have not yet been obtained; however, a related, monomeric complex has been isolated and structurally characterized. Stirring (**1**) with PF_3 (1 equiv.) and an excess of dmpe, with periodical removal of evolved CO, affords the red $Ti(CO)_2(PF_3)(dmpe)_2$ (**3**).

Crystal data: $C_{14}H_{32}F_3O_2P_5Ti$, $M = 492{\cdot}2$, monoclinic, space group $P2_1/c$, $a = 15{\cdot}663(5)$, $b = 9{\cdot}570(3)$, $c = 15{\cdot}776(7)$ Å, $\beta = 95{\cdot}51(2)°$, $U = 2354$ Å^3, $Z = 4$, $D_c = 1{\cdot}389$ g cm^{-3}, $\mu(Cu\text{-}K_\alpha) = 47{\cdot}8$ cm^{-1}. Of 3760 independent reflections, 2773 with $I > 2\sigma(I)$ were considered significant. After solution of the structure (MULTAN), refinement with hydrogen atoms ($B = 5$ Å^2) and atom C(A21) in fixed positions gave a conventional *R* factor of 0·077. One dmpe ligand is, apparently, disordered, as C(A11), C(A21), C(A22), and C(A23) all have large thermal ellipsoids (Figure 1) and the bond C(A11)–C(A21) refined to an improbably short

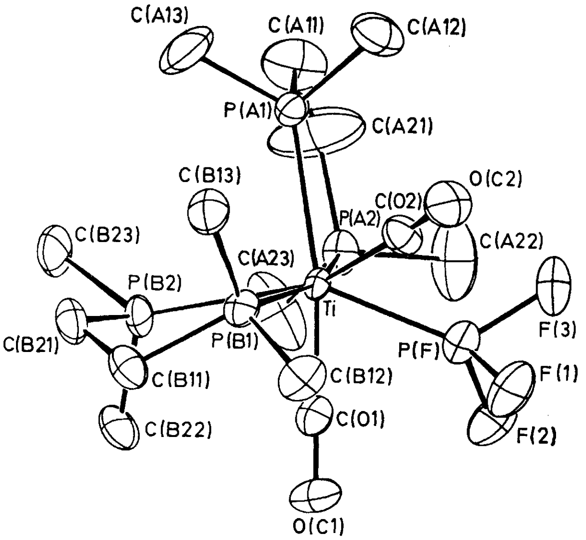

Figure 1. Molecular structure of (**3**).

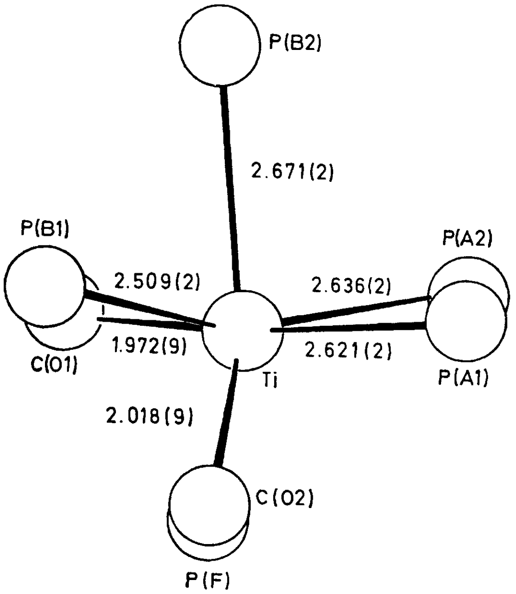

Figure 2. Inner co-ordination sphere of (**3**). Selected bond angles: P(F)–Ti–C(O2) 69·1(3), P(B2)–Ti–P(B1) 77·14(7), P(B2)–Ti–P(A1) 90·66(7), and P(B2)–Ti–C(O1) 81·6(2) °. Bond lengths are in Å.

1·33 Å. Accordingly, C(A21) was fixed in a position calculated by the use of the other dmpe ligand as a geometric model.† Backbone disorder is common for dmpe complexes.[6] Although the geometry of the ligand containing C(A21) is poorly determined, the co-ordination geometry of (**3**) is accurate.

The co-ordination geometry about Ti (Figure 2) can be described as an approximate capped trigonal prism. Thus, P(A1), P(A2), P(B1), and C(O1), which define the capped quadrilateral face, are approximately coplanar (deviations 0·11, − 0·11, 0·13, and − 0·13 Å, respectively). The capping ligand (dmpe) phosphorus atom, P(B2), and the unique-edge-ligands, carbonyl carbons C(O2) and trifluorophosphine phosphorus atoms P(F), define a plane normal (89·9°) to the quadrilateral face.

The complex (**3**) is a simple derivative of the non-existent, apparently unstable, $Ti(CO)_7$.‡ Evidently, Ti^0 carbonyl complexes are stable when substituted with electron-donating ligands.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ $Ti(CO)_6$ has been observed at low temperatures in matrix deposition experiments, but decomposes on warming: R. Busby, W. Klotzbücher, and G. A. Ozin, *Inorg. Chem.*, 1977, **16**, 822.

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