# X-Ray Crystal Structure of Bis-[1,2-bis(dimethylphosphino)ethane]dicarbonyltrifluorophosphinetitanium, a Phosphine-substituted Derivative of $\mathbf{T i}(\mathbf{C O})_{7}$ 

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Summary Carbonylation of $\mathrm{Ti}\left(\eta-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{dmpe})$ [dmpe $=$ 1,2-bis(dimethylphosphino)ethane] or reduction of $\mathrm{TiCl}_{4} \cdot 2 \mathrm{THF}$ in the presence of dmpe and CO affords $\left[\mathrm{Ti}(\mathrm{CO})_{3}(\mathrm{dmpe})_{3 / 2}\right]_{n}$ which reacts with $\mathrm{PF}_{3}$ and dmpe to form $\mathrm{Ti}(\mathrm{CO})_{2}\left(\mathrm{PF}_{3}\right)(\mathrm{dmpe})_{2}$, [a derivative of the nonexistent $\left.\mathrm{Ti}(\mathrm{CO})_{7}\right]$, 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 $\mathrm{Sc}, \mathrm{Ti}$, and Cu . Indeed, $\left(\eta-\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2} \mathrm{Ti},{ }^{1}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\eta-\mathrm{C}_{7} \mathrm{H}_{7}\right) \mathrm{Ti},{ }^{2} \mathrm{Ti}\left(\eta-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}-$ (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 $\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{TiII}$ and analogous species. ${ }^{4}$ Recently developed preparative methods for $\mathrm{Ti}\left(\eta-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}$ (bidentate phosphine) $)^{\mathbf{3}, 5}$ make this labile $\mathrm{Ti}^{0}$ complex readily available and provide a precursor to simple, phosphine-substituted carbonyl complexes.

Treatment of a tetrahydrofuran (THF) solution of $\mathrm{Ti}\left(\eta-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}$ (dmpe) and dmpe with $1000 \mathrm{lb} \mathrm{in}^{-2}$ of CO for 12 h at $0^{\circ} \mathrm{C}$ results in the formation of a red solution from which red needles of a complex formulated as $\left[\mathrm{Ti}(\mathrm{CO})_{3}-\right.$ (dmpe) $\left.)_{3 / 2}\right]_{n}$ (1) $\left[\mathrm{v}_{\mathrm{co}}\right.$ (Nujol) 1810 and $\left.1720 \mathrm{~cm}^{-1}\right]$ can be isolated ( $55 \%$ ). The complex may also be prepared in lower yield by direct reduction of $\mathrm{TiCl}_{4} \cdot 2 \mathrm{THF}$ in THF with $\mathrm{Na}-\mathrm{Hg}$ in the presence of dmpe and $1000 \mathrm{lb} \mathrm{in}^{-2}$ of CO at $0{ }^{\circ} \mathrm{C}(28 \%)$. The analogous $\left[\mathrm{Ti}(\mathrm{CO})_{3}(\mathrm{depe})_{3 / 2}\right]_{n}$ (2) $\left[\nu_{\mathrm{co}}\right.$ (Nujol) 1820 and $1780 \mathrm{~cm}^{-1}$ ] [depe $=1,2$-bis(diethylphos-


Figure 1. Molecular structure of (3).
phino)ethane] has been prepared similarly ( $\mathbf{2 5 \%} \%$ ). Solids (1) and (2) are indefinitely stable under nitrogen but decompose in solution unless cooled ( $0^{\circ} \mathrm{C}$ ) or kept under a CO atmosphere. Although no structural information is available, ( $\mathbf{1}$ ) is at least a tetramer ( $n \geqslant 4$ ), as four equally populated ${ }^{31} \mathrm{P}$ 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 $\mathrm{PF}_{3}$ ( 1 equiv.) and an excess of dmpe, with periodical removal of evolved CO , affords the red $\mathrm{Ti}(\mathrm{CO})_{2}-$ $\left(\mathrm{PF}_{3}\right)(\mathrm{dmpe})_{2}(\mathbf{3})$.

Crystal data: $\mathrm{C}_{14} \mathrm{H}_{32} \mathrm{~F}_{3} \mathrm{O}_{2} \mathrm{P}_{5} \mathrm{Ti}, \quad M=492 \cdot 2$, monoclinic, space group $P 2_{1} / c, \quad a=15 \cdot 663(5), \quad b=9.570(3), \quad c=$ $15 \cdot 776(7) \AA, \quad \beta=95 \cdot 51(2)^{\circ}, \quad U=2354 \AA^{3}, \quad Z=4, \quad D_{\mathrm{c}}=$ $1.389 \mathrm{~g} \mathrm{~cm}^{-3}, \mu\left(\mathrm{Cu}-K_{\alpha}\right)=47.8 \mathrm{~cm}^{-1}$. Of 3760 independent reflections, 2773 with $I>2 \sigma(I)$ were considered significant. After solution of the structure (MULTAN), refinement with hydrogen atoms ( $B=5 \AA^{2}$ ) and atom $\mathrm{C}(\mathrm{A} 21)$ 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 $\mathrm{C}(\mathrm{A} 11)-\mathrm{C}(\mathrm{A} 21)$ refined to an improbably short


Figure 2. Inner co-ordination sphere of (3). Selected bond angles: $\mathrm{P}(\mathrm{F})-\mathrm{Ti}-\mathrm{C}(\mathrm{O} 2) 69 \cdot 1(3), \mathrm{P}(\mathrm{B} 2)-\mathrm{Ti}-\mathrm{P}(\mathrm{Bl}) 77 \cdot 14(7), \mathrm{P}(\mathrm{B} 2)-$ Ti-P(Al) 90.66(7), and $\mathrm{P}(\mathrm{B} 2)-\mathrm{Ti}-\mathrm{C}(\mathrm{Ol}) 81 \cdot 6(2)^{\circ}$. Bond lengths are in $\AA$.
$1.33 \AA$. Accordingly, C(A21) was fixed in a position calculated by the use of the other dmpe ligand as a geometric model. $\dagger$ 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, $\mathrm{P}(\mathrm{A} 1), \mathrm{P}(\mathrm{A} 2), \mathrm{P}(\mathrm{Bl})$, and $\mathrm{C}(\mathrm{O} 1)$, which define the capped quadrilateral face, are approximately coplanar (deviations $0.11,-0.11,0.13$, and $-0.13 \AA$, respectively). The capping ligand (dmpe) phosphorus atom, $\mathrm{P}(\mathrm{B} 2)$, and the unique-
edge-ligands, carbonyl carbons $\mathrm{C}(\mathrm{O} 2)$ and trifluorophosphine phosphorus atoms $\mathrm{P}(\mathrm{F})$, define a plane normal $\left(89 \cdot 9^{\circ}\right)$ to the quadrilateral face.
The complex ( 3 ) is a simple derivative of the non-existent, apparently unstable, $\mathrm{Ti}(\mathrm{CO})_{7} \cdot \ddagger$ Evidently, $\mathrm{Ti}^{0}$ carbonyl complexes are stable when substituted with electrondonating 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 1 EW . Any request should be accompanied by the full literature citation for this communication.
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