

Synthesis, structure and reactivity of the hexaphospha-titanocene, bis-(η^5 -3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl)titanium(II)

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The novel, fully structurally characterised, 14e-titanocene $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t)_2]$ made by (i) cocondensation of titanium vapour with the phosphalkyne Bu^tCP (ii) reaction of Bu^tCP with $[\text{Ti}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]$ at -78°C or (iii) by heating TiCl_n with $n(\text{KP}_3\text{C}_2\text{Bu}^t_2)$ ($n = 2, 3$) in toluene at 110°C , undergoes an unusual [2+2] cycloaddition reaction with Bu^tCP to give $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\eta^3\text{-}\eta^2\text{-P}_4\text{C}_3\text{Bu}^t_3)]$.

Despite several attempts by different workers using a variety of routes, isolation and structural characterisation of a monomeric, (non C–H activated), titanocene has failed owing to the high reactivity of the carbene-equivalent $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$ unit. The addition of neutral ligands such as CO, N₂, PF₃, PMe₃, C₂H₄ and bulky ethynes facilitated isolation of derivatives of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$ and $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$,^{1–7} however, the use of bulky substituents on the cyclopentadienyl rings proved less successful until the very recent report of $[\text{Ti}(\eta^5\text{-Cp}^s)_2]$ [Cp^s = C₅Me₄(SiMe₂Bu^t)] by Lawless and coworkers⁸

Previously^{9,10} we showed that cocondensation of the phosphalkyne Bu^tCP with transition metal vapours affords a wide variety of organometallic compounds of which those containing the di- and tri-phosphorus substituted cyclopentadienyl rings are by far the most common. We now report that cocondensation of titanium atoms with Bu^tCP yields the first example of a phosphorus substituted titanocene which has been fully characterised and its molecular structure established by a single crystal X-ray diffraction study.

Cocondensation of electron beam generated¹¹ titanium atoms with an excess of Bu^tCP at 77 K (i) affords the hexaphospha-titanocene complex $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$ **1** (ca. 2.5% after work up, based on titanium) (Scheme 1). **1**, which was obtained as dark-red air and moisture-sensitive crystals by sublimation (180°C , 1×10^{-5} mbar) followed by recrystallisation from pentane (-20°C)† can also be prepared, in slightly better yield (ii) by adding an excess of Bu^tCP to a pentane solution of $[\text{Ti}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]$ at -78°C or in moderate (ca. 30%) yield (iii) by heating TiCl_n with $n(\text{KP}_3\text{C}_2\text{Bu}^t_2)$ ¹² ($n = 2, 3$) in toluene at 110°C .

A single crystal X-ray diffraction study‡ (Fig. 1) confirms the formulation of **1** and shows it to be a slightly bent, monomeric sandwich compound (angle between the planes of the two P₃C₂Bu^t₂ rings = 16.05° ; centroid–Ti–centroid angle = 173.9°). The rings are approximately planar, with the *tert*-butyl groups staggered so as to minimize inter-ring interactions and the phosphorus atoms lying slightly above the plane containing the carbons. Although several phosphorus-containing sandwich

compounds are known, the only other reported hexaphospha-metalloocene structures are for Cr, Fe and Ru^{13–15} although there also exists an unpublished Mn structure.¹⁶ As expected, the metal to ring-centroid distances steadily decrease in the series $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$ (M = Ti, Cr, Mn, Fe), as the size of the metal decreases (Ti 1.942, Cr 1.815, Mn 1.710, Fe 1.687 Å). A similar trend in metal–ring distances has been observed and rationalised in the analogous metallocenes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2]$ (M = V, Cr, Fe).^{17–20} The $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$ complexes all have slightly bent sandwich structures with centroid–metal–centroid angles of 173.5° (Cr), 173.2° (Fe), 171.0° (Mn). Since the 18e Fe and Ru compounds and the 16e Cr compound would be expected to have parallel rings, the slight distortion has been attributed to the steric effect of the *tert*-butyl groups being unable to fully intermesh. As expected, the pentaphosphametallocenes, $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\eta^5\text{-P}_2\text{C}_3\text{Bu}^t_3)]$ (M = V, Fe)^{10,14} have essentially parallel rings as here the *tert*-butyl groups can fully intermesh.

Only limited structural comparisons can be made between **1** and other titanocenes because the parent titanocene is not monomeric but exists instead as various dimers.¹ Likewise, although decamethyltitanocene $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$ is monomeric, (in equilibrium with a C–H activated species), no structural data are available.¹ The X-ray structure of the very recently synthesised $[\text{Ti}(\eta^5\text{-Cp}^s)_2]$ shows that the two rings are planar, staggered and exactly parallel, with the SiMe₂Bu^t substituents rotated by 180° with respect to each other.⁸ The metal–centroid distance [$2.014(8)$ Å] is larger than that determined for **1** [$1.942(2)$ Å], presumably either because of the more sterically demanding Cp^s ligand and/or the stronger bonding of the phosphorus substituted cyclopentadienyl rings.⁹ The exactly parallel nature of the two Cp^s rings is also presumably due to steric factors. Although **1** has a 3d² electronic configuration, it is found to be diamagnetic. At room temperature the ¹H,

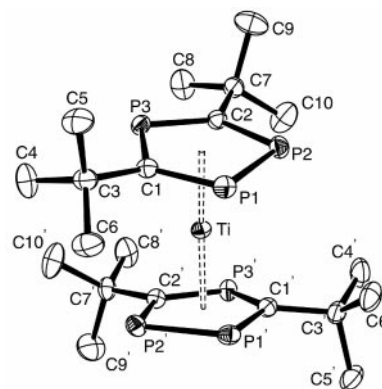
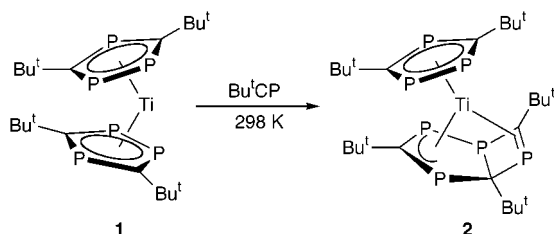


Fig. 1 Molecular structure of $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$, **1**. Selected distances (Å) and angles ($^\circ$): Ti–M(1) 1.942(2), Ti–C(1) 2.354(2), Ti–C(2) 2.470(2), Ti–P(1) 2.477(1), Ti–P(2) 2.535(1), Ti–P(3) 2.637(1), P(1)–C(1) 1.790(2), P(1)–P(2) 2.167(1), P(2)–C(2) 1.784(2), P(3)–C(2) 1.739(2), P(3)–C(1) 1.764(2), C(1)–P(1)–P(2) $97.84(7)$, C(2)–P(2)–P(1) $98.72(7)$, C(2)–P(3)–C(1) $99.92(10)$, P(3)–C(1)–P(1) $121.47(12)$, P(3)–C(2)–P(2) $121.74(12)$, M(1)–Ti–M(1') $173.9(1)$, angle between the least-squares planes of the two rings $16.05(0.07)$. M(1) and M(1') refer to the centroids of the two rings.



Scheme 1

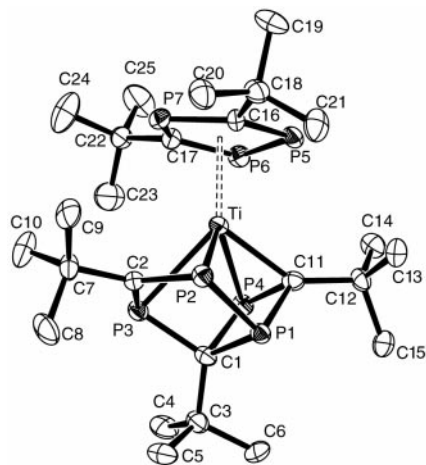


Fig. 2 Molecular structure of $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)(\eta^3\text{-}\eta^2\text{-P}_4\text{C}_3\text{Bu}_3)]$ **2**. Selected distances (Å): Ti–M(1) 2.120(6), Ti–C(2) 2.503(6), Ti–C(11) 2.210(6), Ti–C(16) 2.465(5), Ti–C(17) 2.663(6), Ti–P(2) 2.472(2), Ti–P(3) 2.662(2), Ti–P(4) 2.577(2), Ti–P(5) 2.609(2), Ti–P(6) 2.673(3), Ti–P(7) 2.709(2), C(1)–P(1) 1.876(5), P(1)–P(2) 2.216(2), P(2)–C(2) 1.790(5), C(2)–P(3) 1.752(5), P(3)–C(1) 1.831(6), P(1)–C(11) 1.858(5), C(11)–P(4) 1.828(5), P(4)–C(1) 1.909(5). M(1) refers to the centroid of the ring P(5)C(16)P(7)C(17)P(6).

$^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra \S are all sharp (and temperature invariant over the range 185–385 K) and indicate that in solution the two $\text{P}_3\text{C}_2\text{Bu}_2$ rings are equivalent and that there is no inter-ring coupling. This is in contrast to the iron and ruthenium analogues which exhibit fluxional behaviour and inter-ring coupling constants of 53 Hz (Fe) and 37.4 Hz (Ru). 13,14

Decamethyltitanocene forms dinitrogen complexes (some reversibly), and although **1** does not react with dinitrogen, it readily undergoes addition reactions with CO or tBuNC to give the 16e and 18e complexes $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)_2\text{L}]$ (L = CO) and $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)_2\text{L}_2]$ (L = CO, tBuNC) respectively, which will be reported in detail elsewhere. 21 However, with an excess of Bu^tCP the novel red-brown 14e-complex $[\text{Ti}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)(\eta^3\text{-}\eta^2\text{-P}_4\text{C}_3\text{Bu}_3)]$ **2** is formed as a result of an unusual [2+2] cycloaddition with a P=C bond of one of the $\eta^5\text{-P}_3\text{C}_2\text{Bu}_2$ rings of **1** (Scheme 1). No reaction is observed in an analogous experiment with Bu^tCN . The molecular structure of **2**, determined by a single crystal X-ray diffraction study, \ddagger is shown in Fig. 2. The titanium is attached in an η^5 -fashion to the one remaining $\text{P}_3\text{C}_2\text{Bu}_2$ ring and $\eta^3\text{-}\eta^2$ -ligated to the new $\text{P}_4\text{C}_3\text{Bu}_3$ moiety. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** exhibits the expected seven different resonances and the ^1H NMR spectrum contains the expected five singlets. \S

The mechanism of formation of **2** from **1** might involve the intermediacy of an η^1 - (or less likely η^2 -ligated) Bu^tCP complex and the subsequent η^5 - to η^3 -ring slippage of one of the $\text{P}_3\text{C}_2\text{Bu}_2$ facilitating a [2+2] cycloaddition with the resulting uncoordinated P=C bond leading to the product **2**. Interestingly, although **2** can be sublimed (170 °C, 1×10^{-5} mbar) with only slight decomposition to **1**, it was not isolated from the original cocondensation experiment.

To our knowledge, the only related metallocene ring addition reactions previously reported concern nickelocene and fluoroalkenes or an activated norbornadiene however no structural data are available for comparison. 22,23

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Notes and references

\ddagger $\text{C}_{20}\text{H}_{36}\text{P}_6\text{Ti}$: MS (EI, 70 eV), m/z 510 (100%) (M^+), 57 (8%) (Bu^t+) with the expected isotope pattern. Elemental analysis: C, 47.08 (46.57), H, 7.11 (7.15%).

\ddagger Crystal data: for **1**: $\text{C}_{20}\text{H}_{36}\text{P}_6\text{Ti}$, $M = 510.2$, orthorhombic, space group $C22_2$ (no. 20), $a = 11.632(6)$, $b = 16.114(5)$, $c = 13.920(4)$ Å, $U = 2609(2)$ Å 3 ; $Z = 4$, $D_c = 1.30$ Mg m $^{-3}$, $T = 173(2)$ K. Data were obtained with an Enraf-Nonius CAD4 diffractometer using Mo-K α radiation, $\lambda = 0.71073$ Å, ($\mu = 0.70$ mm $^{-1}$), on a crystal of dimensions $0.4 \times 0.4 \times 0.2$ mm; 2112 unique reflections were measured for $2 < 2\theta < 30^\circ$ and 2035 reflections with $I > 2\sigma(I)$ were used in the refinement. The final residuals were $R = 0.025$, $wR2 = 0.062$ for $I > 2\sigma(I)$. Hydrogen atoms were refined isotropically. The molecule lies on a crystallographic two fold rotation axis.

For **2**: $\text{C}_{25}\text{H}_{45}\text{P}_7\text{Ti}$, $M = 610.3$, triclinic, space group $P\bar{1}$ (no.2), $a = 10.299(5)$, $b = 11.910(6)$, $c = 14.230(10)$ Å, $\alpha = 86.48(5)$, $\beta = 71.00(5)$, $\gamma = 68.75(4)^\circ$, $U = 1535(2)$ Å 3 ; $Z = 2$, $D_c = 1.32$ Mg m $^{-3}$, $T = 173(2)$ K. Data were obtained with an Enraf-Nonius CAD4 diffractometer using Mo-K α radiation, $\lambda = 0.71073$ Å, ($\mu = 0.66$ mm $^{-1}$), on a crystal of dimensions $0.4 \times 0.3 \times 0.05$ mm; 5362 unique reflections were measured for $2 < 2\theta < 25^\circ$ and 4021 reflections with $I > 2\sigma(I)$ were used in the refinement. The final residuals were $R = 0.077$, $wR2 = 0.196$ for $I > 2\sigma(I)$.

CCDC 182/1348. See <http://www.rsc.org/suppdata/cc/1999/1731/> for crystallographic files in .cif format.

\S NMR for **1** (d_8 -toluene, 298 K). ^1H (300.13 MHz): δ 0.18 (s, 36 H, $\text{Ti}\{\text{P}_3\text{C}_2[\text{C}(\text{CH}_3)_3]_2\}_2$). $^{13}\text{C}\{^1\text{H}\}$ (75.47 MHz): δ 35.2 (d, $^2J_{\text{CP}} 7$ Hz, $\text{Ti}\{\text{P}_3\text{C}_2[\text{C}(\text{CH}_3)_3]_2\}_2$), 42.6 (d, $^2J_{\text{CP}} 18$ Hz, $\text{Ti}\{\text{P}_3\text{C}_2[\text{C}(\text{CH}_3)_3]_2\}_2$). $^{31}\text{P}\{^1\text{H}\}$ (121.49 MHz): d 342.5 (t, 1P, $^2J_{\text{PP}} 44.2$ Hz, PPCPC), 386.0 (d, 2P, $^2J_{\text{PP}} = 46.7$ Hz, PPCPC).

NMR for **2** (d_6 -benzene, 298 K). ^1H (300.13 MHz): δ 1.05 (s, 9 H) 1.29 (s, 9 H), 1.38, 1.40 [2s (overlapping) 18 H], 1.67 (s, 9 H). $^{31}\text{P}\{^1\text{H}\}$ (121.49 MHz): $\delta_{\text{P}(1)}$ -60.3 (ddd, $^1J_{\text{P}(1)\text{P}(2)}$ 290, $^2J_{\text{P}(1)\text{P}(3)}$ 12, $^2J_{\text{P}(1)\text{P}(4)}$ 12 Hz), $\delta_{\text{P}(2)}$ 309 (dd, $^1J_{\text{P}(1)\text{P}(2)}$ 290, $^2J_{\text{P}(2)\text{P}(3)}$ 40 Hz), $\delta_{\text{P}(3)}$ 98.7 (dddd, $^2J_{\text{P}(2)\text{P}(3)}$ 40, $^2J_{\text{P}(3)\text{P}(4)}$ 32, $^2J_{\text{P}(3)\text{P}(1)}$ 12, $^2J_{\text{P}(3)\text{P}(5)}$ = 5 Hz), $\delta_{\text{P}(4)}$ 283.9 (dddd of m, $^2J_{\text{P}(4)\text{P}(6)}$ 70, $^2J_{\text{P}(4)\text{P}(3)}$ 32, $^2J_{\text{P}(4)\text{P}(5)}$ or $\text{P}(1)$ 14, $^2J_{\text{P}(4)\text{P}(1)}$ or $\text{P}(5)$ = 12, plus other ca. 5 Hz inter-ring couplings), $\delta_{\text{P}(5)}$ 260.8 [dd, $^1J_{\text{P}(5)\text{P}(6)}$ 430, $^2J_{\text{P}(5)\text{P}(7)}$ 50, $^2J_{\text{P}(5)\text{P}(4)}$ 12 Hz (inter-ring)], $\delta_{\text{P}(6)}$ 301.3 [dd, $^1J_{\text{P}(6)\text{P}(5)}$ 430, $^2J_{\text{P}(6)\text{P}(7)}$ 52, $^2J_{\text{P}(6)\text{P}(4)}$ 70 Hz (inter-ring)], $\delta_{\text{P}(7)}$ 225.2 (dd, $^2J_{\text{P}(7)\text{P}(6)}$ = 50, $^2J_{\text{P}(7)\text{P}(5)}$ 50 Hz).

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