One- and two-step [2 + 2] cycloaddition reactions of group 4 imides with the phosphaalkyne Bu^{t}CP. Crystal and molecular structures of [Zr(η^5-C_5H_5)$_2$(PCBu^{t}N$C_6H_3Me_2$-2,6)] and [TiCl_2(P_2C_2Bu$^t_2$NBu^t)(py)] (py) = pyridine)

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The structures of novel complexes resulting from one- and two-step [2 + 2] cycloaddition reactions of four group 4 imides with the phosphaalkyne Bu^{t}CP are described.

Regitz and coworkers[1] have recently reported novel reactions of the phosphaalkyne Bu^{t}CP with vanadium(v) imido complexes to afford either 3-aza-1,2,4,6-tetraphosphaquadricyclanes **B** or 1,3,5-triphosphabenzenes **A**, the products critically depending on reaction conditions (Scheme 1). They proposed a mechanism for the formation of **A** and **B** which involves an initial [2 + 2] cycloaddition step of the vanadium imide with the phosphaalkyne, but no metal containing complexes have been characterised.

In order to better understand this interesting type of reaction, we now describe the first fully structurally characterised complexes of Zr(IV) and Ti(IV) resulting from one- and two-step [2 + 2] cycloaddition reactions of Bu^{t}CP with '[Zr(η^5-C_5H_5)$_2$(N$C_6H_3Me_2$-2,6)]' **1**[2] and [TiCl_2(NBu^t)(py)$_3$] **2**[3,4] respectively. In addition we report the NMR spectroscopically characterised [2 + 2] phosphaalkyne adducts of '[Zr(η^5-C_5H_5)$_2$(NBu^t)]' **3**[2], and [Ti{(SiMe_3)N[CH_2CH_2N(SiMe_3)]$_2$}(NBu^t)(py)][5] **4**.

Treatment of the transient imide complex **1** (prepared from the thermolysis of [Zr(η^5-C_5H_5)$_2$(NH$C_6H_3Me_2$-2,6)$_2$])[2] with an excess of Bu^{t}CP in toluene at 100 °C for 48 h yielded the orange crystalline complex [Zr(η^5-C_5H_5)$_2$(PCBu^{t}N$C_6H_3Me_2$-2,6)] **5** in 45% yield.† A single crystal X-ray diffraction study on **5**‡ established that its molecular structure (Fig. 1) contains the four membered planar metallacycle ($\Sigma_{\text{internal angles}}$ = 360 °C) resulting from the [2 + 2] phosphaalkyne–imide cycloaddition, in which the phosphorus is bonded to the nitrogen of the imide function, consistent with the bond polarity of the unsaturated reactive sites. This geometry is similar to that observed for the addition of internal alkynes to **1**.[2] The Zr–N–C(6) bond angle in **5** (147.8°) is typical of double bond character of the metal–nitrogen linkage. A similar adduct [Zr(C_5H_5)$_2$(PCBu^{t}NBu^t)] **6** can also be prepared from '[Zr(η^5-C_5H_5)$_2$(NBu^t)]' (generated *in situ* by thermolysis of [Zr(η^5-C_5H_5)$_2$(NHBu^t)$_2$])[2], as determined by NMR spectroscopy.§

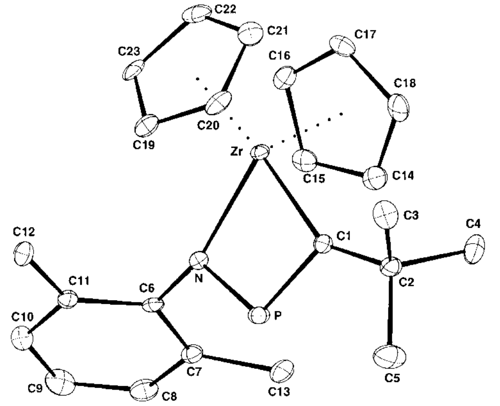
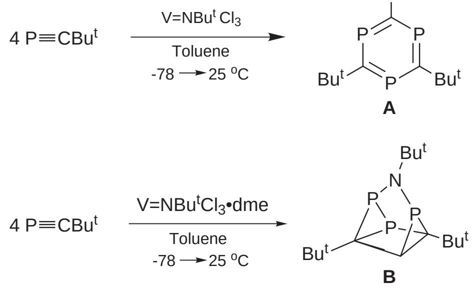


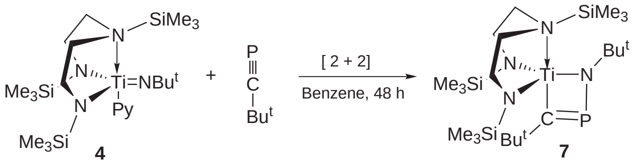
Fig. 1 Molecular structure of [(C_5H_5)$_2$Zr(PCBu^{t}N$C_6H_3Me_2$-2.6)] **5**. Selected distances (Å) and angles (°): Zr–N 2.101(4), P–N 1.729(4), P–C(1) 1.692(5), Zr–C(1) 2.188(5); Zr–N–P 91.0(2), C(1)–P–N 102.8(2), P–C(1)–Zr 89.1(2), N(1)–Zr–C(1) 77.1(2)°. Displacement ellipsoids are shown at 50% probability level.

The investigation of this type of addition was subsequently extended to the sterically encumbered titanium imide **4**. Treatment of **4** with an excess of Bu^{t}CP at room temperature in toluene, yielded an orange oil after work up. NMR spectroscopic data were found to be very similar to that of **5** indicative of formation of the [2 + 2] cycloadduct [Ti{N(SiMe_3)[CH_2CH_2N(SiMe_3)]$_2$}(PCBu^{t}NBu^t)] **7**¶ (Scheme 2).

Since the reactivity presumably results from release of steric strain, complex **2** was reacted with an excess of Bu^{t}CP in toluene at 55 °C for 72 h to yield the dark-red crystalline complex [TiCl_2(P_2C_2Bu$^t_2$NBu^t)(py)] **8** (61% yield).‖** The corresponding pyridine free complex [TiCl_2(P_2C_2Bu$^t_2$NBu^t)] **8a** can be obtained (25%) by subliming **8** *in vacuo* at 110 °C. A single crystal X-ray diffraction study was carried out on **8**‡ and its molecular structure, (Fig. 2), reveals a TiC_2P_2N core in which the Ti(IV) centre is in an unsymmetrical environment resulting from being capped by a puckered 1,3-diphosphacyclobutadiene unit, whose P(1) atom is σ-bonded to the nitrogen of the imide function [interplanar angle between C(1)P(2)C(2) and C(1)P(1)P(2), 23.3°]. One representation of the bonding to the Ti centre involves an η^3-interaction with the 2-phosphaallyl fragment of the C_2P_2 ring which is augmented by interaction



Scheme 1



Scheme 2

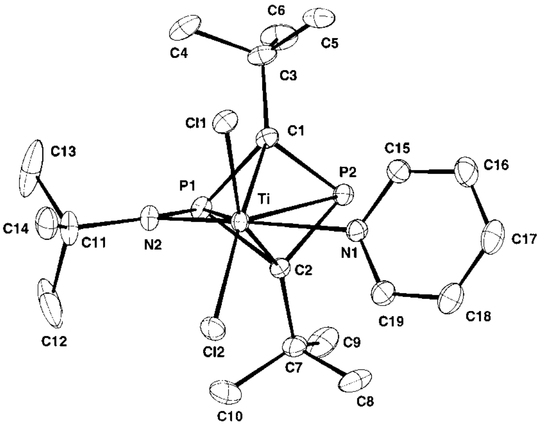
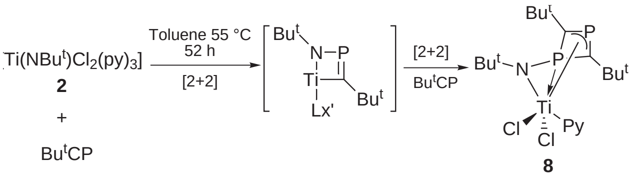


Fig. 2 Molecular structure of [Ti{NBu^{t}PCBu^{t}PCBu^t}Cl$_2$(py)]**8**. Selected distances (Å) and angles (°): P(1)–N(2) 1.727(2), Ti–N(2) 1.880(2), P1–C(1) 1.825(2), P(2)–C(1) 1.735(2), P(2)–C(2) 1.768(2), C(2)–P(1) 1.847(2), Ti–N(1) 2.394(2), Ti–P(2) 2.784(2), Ti–C(2) 2.221(2), Ti–P(1) 2.442(1), Ti–C(1) 2.439(2); Ti–N(2)–C(11) 148.31(14), Cl(2)–Ti–Cl(1) 109.57(2), C(2)–P(1)–C(1) 80.86(8), C(1)–P(2)–C(2) 85.65(8). Displacement ellipsoids are shown at 50% probability level.

with the N, two Cl ions, P lone pair and the pyridine. As expected the Ti–N(2) bond length [1.880(2) Å] in **8** is considerably elongated when compared with the starting imide complex **2** [1.705(3) Å] and the Ti–N(pyridine) bond length [2.394(2) Å] is very long. The Ti–N–C(α) bond angle in **8** (148.3°) is typical for a metal–nitrogen double bond.

Although no reaction intermediates have been spectroscopically characterised, the formation of the TiC$_2$P$_2$N core in **8** is presumed to proceed by sequential [2 + 2] cycloaddition of Bu^{t}CP with (i) the titanium–nitrogen double bond and (ii) the resulting P=C double bond (Scheme 3).



Scheme 3

Interestingly, the course of the reactions involving complexes of type **2** is also affected by the nature of the imido N-substituent. Thus treatment of [Ti(NR)Cl$_2$(py)$_3$] (R = Ph, *p*-MeC$_6$H$_4$, *p*-NO$_2$C$_6$H$_4$ or Pr^i) with Bu^{t}CP gave the previously unknown 1,2,4-azadiphospholes P$_2$C$_2$Bu$^t_2$NR. The molecular structure of P$_2$C$_2$Bu$^t_2$NPh has been determined and this new class of heteroaromatic ring systems will be the subject of a separate publication.[6] The range of products obtained with different metal and N-substituents indicates the possibility for a rich and diverse derivative chemistry.

Philip Mountford is the Royal Society of Chemistry Sir Edward Frankland Fellow for 1998–9.

Notes and references

† **5**: NMR (d$_6$-benzene, 295 K), ^{1}H δ 7.16, 7.09 (m, 3H, C$_6$H$_3$), 5.69 [(s, 10H, C$_5$H$_5$)], 2.28 [s , 6H, C$_6$H$_3$(C*H*$_3$)$_2$], 1.52 [s, 9H, PCC(CH$_3$)$_3$] ^{31}P{^{1}H} δ 81.7. EI-MS *m/z* (%): 439 (20) [M]$^+$, 339 (100) [M − PCCMe$_3$]$^+$. Elemental analysis: Calc. for C$_{23}$H$_{28}$NPZr; C, 62.69; H, 6.40, N, 3.18. Found: C, 62.41; H, 6.37, N, 3.12%.

‡ *Crystal data*: **5**: C$_{23}$H$_{28}$NPZr, M = 440.6, monoclinic space group $P2_1/c$, a = 11.622(3), b = 21.830(8), c = 8.389(4) Å, β = 107.01(3), U = 2035.3(13) Å^3, Z = 4, D_c = 1.44 Mg m^{-3}, crystal dimensions 0.40 × 0.30 × 0.02 mm, T = 173(2) K, Mo-Kα, radiation λ = 0.71073 Å. Data were collected on an Enraf-Nonius CAD4 diffractometer and of the total 3811 reflections measured, 3563 unique (R_{int} = 0.042). Refinement on F^2, $wR2$ = 0.138 (all data), $R1$ = 0.048 [for 2651 reflections with $I > 2\sigma(I)$].

7: C$_{19}$H$_{32}$Cl$_2$N$_2$P$_2$Ti, M = 469.2, monoclinic, space group $P2_1/n$, a = 12.728 (2), b = 12.170(1), c = 15.596(1) Å, β = 97.5(1)°, U = 2395.1(5) Å^3, Z = 4, D$_c$ = 1.3 Mg m^{-3}, T = 173(2) K, Mo-Kα, radiation λ = 0.71073 Å. Data were collected on an Enraf-Nonius CAD4 diffractometer and of the total 7242 reflections measured, 6969 unique (R_{int} = 0.017). Refinement on F^2, $wR2$ = 0.095 (all data), $R1$ = 0.040 [for 5271 reflections with $I > 2\sigma(I)$]. CCDC 182/1184. See http:/www rsc.org/suppdata/cc/1999/661/ for crystallographic files in .cif format.

§ **6**: NMR (d$_6$-benzene, 295 K), ^{1}H δ 5.68 (s, 10H, C$_5$H$_5$), 1.31 [s , 9H, NC(CH$_3$)], 1.52 [s, 9H, PCC(CH$_3$)$_3$]. ^{31}P{^{1}H} δ 64.1. EI-MS *m/z* (%): 391 (30) [M]$^+$, 376 (20) [M − Me]$^+$, 276 (55) [M − Me − PCCMe$_3$]$^+$.

¶ **7**: NMR (d$_6$-benzene, 295 K), ^{1}H δ 4.12, 3.8, 2.81 (3 × m, 8H, CH$_2$CH$_2$), 1.5 [s, 9H, NC(CH$_3$)], 1.48 [s, 9H, PC(CH$_3$)], 0.2 (s, 9H, NSiMe$_3$), 0.09 (s, 18H, NSiMe$_3$). ^{13}C{^{1}H δ 53.7, 51.6 (CH$_2$CH$_2$), 35.2 [d, NC(*C*H$_3$), $^3J_{\text{PC}}$ 12.2 Hz], 34.4 [d, PCC(*C*H$_3$)$_3$, $^3J_{\text{PC}}$ 8 Hz] 2.5 [SiC(*C*H$_3$)], 0.2 [SiC(*C*H$_3$)]. ^{31}P{^{1}H} δ 209.4. EI-MS *m/z* (%): 536 (20) [M]$^+$, 436 (45) [M − (PCBu^t)]$^+$. The oily nature of this compound precluded satisfactory microanalysis.

‖ **8**: NMR (d$_6$-benzene, 295 K), ^{1}H δ 9.5, 6.78, 6.53 (m, 5H, NC$_5$H$_5$), 1.46 [s, 9H, NC(CH$_3$)$_3$], 1.32, 1.30 [s × 2, 18H, PC(CH$_3$)$_3$]. ^{13}C{^{1}H} (d$_8$-toluene, 295 K): 198.3 (dd, PCP, $^1J_{\text{PC}}$ 61.95, $^2J_{\text{PC}}$ 29.9 Hz), 151.1, 123.2 (m, NC$_5$H$_5$), 68.89 [d, N*C*(CH$_3$)$_3$, $^2J_{\text{PC}}$ 8.10 Hz], 41.33 [pseudo-t, {PC*C*(CH$_3$)$_3$}$_2$, $^2J_{\text{PC}}$ 6.50 Hz], 33.96 [pseudo-t, {PCC(*C*H$_3$)$_3$}$_2$, $^3J_{\text{PC}}$ 4.97 Hz], 32.37 [d, NC(*C*H$_3$)$_3$, $^3J_{\text{PC}}$ 6.03 Hz]. ^{31}P{^{1}H} (d$_6$-benzene, 295 K) δ 296.5, −139.5 (d × 2, $^2J_{\text{PP}}$ 40.5 Hz). EI-MS *m/z* (%): 465 (85) [M]$^+$, 389 (10) [M − py]$^+$, 333 (12) [M − Py −Bu^t)]$^+$.

** Similarly [Ti(η^8-C$_8$H$_8$)(NBu^t)] readily reacted with Bu^{t}CP in toluene at room temp. to afford, after recrystallisation from pentane, dark brown crystals of [Ti(η^8-C$_8$H$_8$)(P$_2$C$_2$Bu$^t_2$NBu^t)] **9** in 71% yield. Although not shown here, the molecular structure of **9** has also recently been obtained and reveals a common TiC$_2$P$_2$N core comfirming its structural significance for this type of reaction.

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