Carbon monoxide–phosphaalkyne coupling and C–H activation of an N–Me group in the 4e-η^2-phosphaalkyne complex $[\mathrm{WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)(\eta^2\text{-}P{\equiv}CBu^t)}]$. Crystal and molecular structure of $[\mathrm{WF\{CH_2N(CH_2Ph)CH_2CH_2NMe_2\}(CO)\{\eta^4\text{-}PCBu^t(CO)CBu^tP\}}]$

Maria Helena A. Benvenutti,[a] Peter B. Hitchcock,[a] Jaqueline L. Kiplinger,[b] John F. Nixon*[a] and Thomas G. Richmond*[b]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA*

An unusual series of reactions involving an intermediate 4e η^2-phosphaalkyne tungsten complex is described.

There is current interest in the coordination chemistry of phosphaalkynes, RC≡P, and transition-metal compounds containing phosphorus analogues of unsaturated ring systems such as 1,2- and 1,3-diphosphacyclobutadiene, 1,2- and 1,2,4- di- and tri-phosphacyclopentadienyl, and most recently 1,3,5-triphosphabenzene, which can all be derived from the parent phosphaalkyne.[1–3]

The number of examples of phosphaalkynes acting as η^2-(4e) ligands to transition-metal centres is very limited and to date none have been structurally characterised owing to their ready further reaction to afford 1,3-diphosphacyclobutadiene complexes.[4] In order to extend the range of such complexes we have now synthesised the $\mathrm{Bu^tC{\equiv}P}$ analogue of the recently described[5] structurally related η^2-(4e) nitrile complex $[\mathrm{WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)(\eta^2\text{-}N{\equiv}CC_6F_5)}]$. Although NMR spectroscopic evidence† (P≡C, δ_P 452.4, δ_C 315.2; $^1J_\mathrm{PC}$ 117.7, $^1J_\mathrm{PW}$ 82.0 Hz) fully confirmed[4] the expected formation of the green η^2-(4e) phosphaalkyne complex $[\mathrm{WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)(\eta^2\text{-}P{\equiv}CBu^t)}]$ **2**, when $[\mathrm{WF(C_6H_4CH_2NMeCH_2CH_2NMe_2)(CO)_3}]$ **1**,[6] was treated with $\mathrm{Bu^tC{\equiv}P}$ for 3 h in toluene at room temp. it proved impossible to isolate it in crystalline form. A facile further reaction of **2** with $\mathrm{Bu^tC{\equiv}P}$ (5 equiv. at 90 °C for 2 h in toluene in a closed system) affords the novel red complex $[\mathrm{WF\{CH_2N(CH_2Ph)CH_2CH_2NMe_2\}(CO)\{\eta^4\text{-}PCBu^t(CO)CBu^tP\}}]$ **3**, (30% yield), containing an η^4-ligated 3,4-diphosphacyclopentadieneone and a three-membered $\mathrm{NCH_2W}$ ring system. Complex **3** has been structurally characterised by spectroscopic data‡ and by a single-crystal X-ray diffraction study§ (Fig. 1). The reactivity of **2** contrasts with the behaviour of the analogous η^2-(4e) nitrile complex which does not undergo coupling reactions and whose chemistry is dominated by ready dissociation of the nitrile ligand.

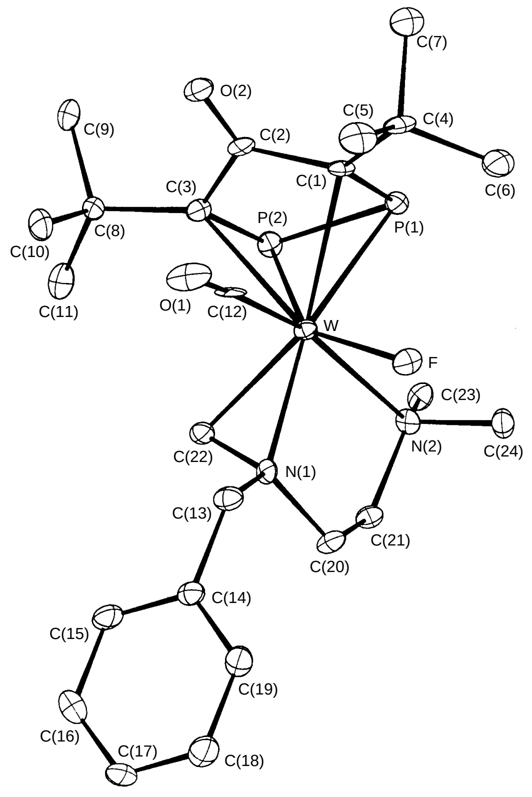
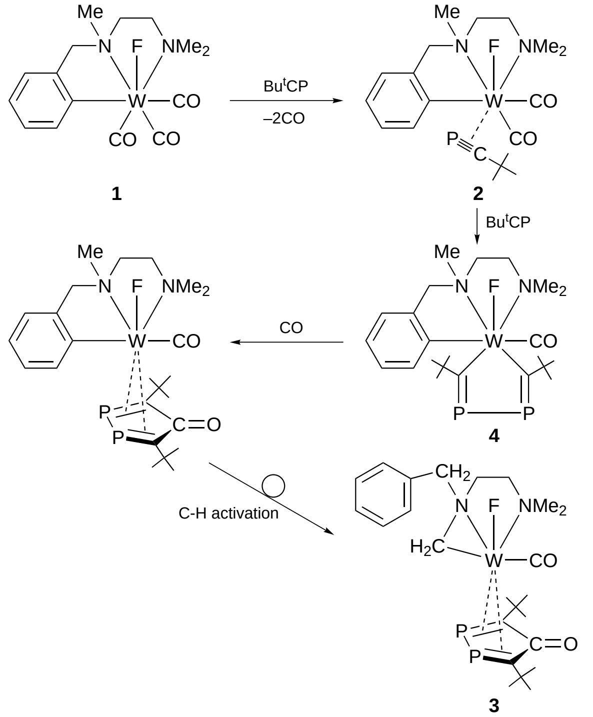


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): W–P(1) 2.504(2), W–P(2) 2.490(2), W–C(1) 2.412(7), W–C(3) 2.443(8), W–C(12) 1.992(9), W–C(22) 2.169(9), W–F 1.997(4), W–N(1) 2.175(6), W–N(2) 2.408(6), P(1)–P(2) 2.173(3), P(1)–C(1) 1.740(8), P(2)–C(3) 1.769(8), O(1)–C(12) 1.158(10), O(2)–C(2) 1.233(9), N(1)–C(22) 1.441(10), C(1)–P(1)–P(2) 94.6(3), C(3)–C(2)–C(1) 109.4(6), C(3)–P(2)–P(1) 93.8(3).



Scheme 1

We believe that **3** results either from CO insertion into an intermediate η^4-ligated 1,2-diphosphacyclobutadiene complex formed from **2** and $Bu^tC{\equiv}P$, or alternatively into the five-membered tungstadiphosphacyclopentadiene ring of complex **4**, followed by reductive elimination (Scheme 1). No such intermediates could be detected spectroscopically, however we showed previously[7] that carbonyl insertion and reductive elimination occurs in the closely related tungsten(II) alkoxide. Presumably the bulky η^4-ligated 3,4-diphosphacyclopentadieneone ring system generated from **2** causes crowding at the metal centre, and subsequent relief of steric strain results in the formation of **3** *via* (*i*) C–H activation of the uncoordinated NCH_3 group to generate the NCH_2W ring system and (*ii*) hydrogen transfer to the metallated C_6H_4 fragment.

Previously we described (*i*) CO coupling of two phosphaalkynes to give rhodium(I) complexes of the six membered ring system RhPCORCRP, (R = Bu^t, adamantyl),[8] and (*ii*) carbonylation of coordinated phosphaalkynes to give phosphinidene $[Bu^t(CO)P]$ complexes,[9,10] however the formation of the 3,4-diphosphacyclopentadienone ring in **3** is unprecedented, although Cowley and coworkers[11] have structurally characterised the isomeric diphosphatricyclo[1.2.0.0^{2,5}]pentane ring system. Likewise, reports of C–H activation of an N–Me group are also rare in organometallic systems. A recent report by van Koten *et al.*[12] described the stereoselective C–H activation of an N–Me group in the tantalum complex $[TaCl_2(CH_2Ph)_2\{C_6H_4\text{-}(Me)NMe\text{-}2\}]$, in which the key step proceeds by a σ-bond metathesis which also involves the relief of steric strain.

Footnotes and References

* E-mail: j.nixon@sussex.ac.uk

† *Spectroscopic data* for **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, Bu^t, 9 H). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 85% H_3PO_4 external ref. δ 0.00) δ 452.42 (s, $^1J_{PW}$ 82.0). $^{13}C\{^1H\}$ (75.4 MHz, $CDCl_3$) δ 315.18 (d, P≡C, $^1J_{PC}$ 117.7 Hz), 225.60 (d, CO, $^2J_{CF}$ 21.0, $^1J_{CW}$ 137.0), 124.50 (s, C_6H_5), 125.17 (s, C_6H_5), 128.98 (s, C_6H_5), 144.02 (s, C_6H_5), 143.45 (s, C_6H_5), 188.25 (d, W–C, $^2J_{CF}$ 4.0 Hz), 34.33 (d, C*C*H_3, J_{PC} 5.2 Hz), 30.40 (s, *C*CH_3), 57.20 (s, CH_2), 61.35 (s, CH_2), 66.14 (s, CH_2), 56.25 (s, CH_3), 47.41 (d, CH_3, J_{CF} 8.7 Hz), 48.51 (d, CH_3, J_{CF} 20.6 Hz).

‡ *Spectroscopic data* for **3**: IR ($CHCl_3$) ν_{CO} 1966s, 1611m cm^{-1}. MS (70 eV, EI) *m/z* (%) 650 (2) [M^+], 622 (25) [$M^+ - CO$]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (dd, CH_2, 1 H, *J* 13.6, 4.1 Hz), 2.40 (dt, CH_2, 1 H, *J* 13.7, 4.5 Hz), 2.70 (dd, CH_2, 1 H, *J* 12.5, 4.3), 2.85 (dt, CH_2 1 H, *J* 13.1, 4.5 Hz), 3.10 (d, CH_2, 1 H, *J* 4.7 Hz), 3.33 (d, CH_2, 1 H, *J* 6.2 Hz), 4.70 (d, CH_2, 2 H, *J* 32.8, 5.3 Hz), 2.27 (d, CH_3, 3 H, *J* 5.8 Hz), 2.77 (d, CH_3, 3 H, *J* 2.2 Hz), 1.21 (s, Bu^t, 9 H), 0.98 (s, Bu^t, 9 H), 7.35–7.26 (m, Ph, 5 H). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$) δ −62.02 (dd, $^1J_{PP}$ 263.0, $^2J_{PF}$ 15.0 Hz) −87.60 (dd, $^1J_{PW}$ 29.0, $^2J_{PF}$ 15.0 Hz). $^{13}C\{^1H\}$ (75.4 MHz, $CDCl_3$) δ 216.26 (d, CO, J_{CP} 8.1 Hz), 186.67 (s, CO), 134.24 (s, C_6H_5, *ipso*), 128.81 (s, C_6H_5), 128.50 (s, C_6H_5, *para*), 128.43 (s, C_6H_5), 58.39 (dd, CH_3, *J* 23.6, 12.0 Hz, J_{CF} or J_{CP}), 49.31 (dd, CH_3 *J* 21.4, 7.1 Hz, J_{CF} or J_{CP}), 30.52 (dd, C*C*H_3, J_{PC} 2.2, 8.7 Hz), 30.27 (d, C*C*H_3, J_{PC} 8.8 Hz), 38.40 (d, *C*CH_3, J_{PC} 13.6 Hz), 37.09 (d, *C*CH_3, J_{PC} 14.6 Hz), 65.02 (s, CH_2), 55.96 (s, CH_2), 48.63 (s, CH_2), 44.00 (dd, CH_2, *J* 9.4, 5.7 Hz, J_{CF} or J_{CP}), 125.55 (d, PCP, J_{PC} 85.7 Hz), 109.02 (d, PCP, J_{PC} 81.2 Hz). ^{19}F NMR (376.3 MHz, CD_2Cl_2, $CFCl_3$ external ref., δ 0.00) δ 42.05 (m, $^2J_{FP}$ 15.0 Hz).

§ *Crystal data* for **3**: $C_{24}H_{37}FN_2O_2P_2W{\cdot}CH_2Cl_2$, $M = 735.27$, monoclinic, space group $C2/c$ (no. 15), $a = 34.036(9)$, $b = 9.861(2)$, $c = 18.313(8)$ Å, $\beta = 112.05(3)°$, $U = 5697(3)$ Å^3, $Z = 8$, $D_c = 1.72$ Mg m^{-3}, $F(000) = 2928$. The data were obtained with an Enraf-Nonius CAD4, diffractometer using Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 4.39$ mm^{-1}, on a crystal 0.25 × 0.25 × 0.10 mm. 4031 reflections measured for $2 < \theta < 23°$ giving 3962 unique. Refinement on F^2 using SHELXL-93, non-H atoms anisotropic, H atoms in riding mode, except for those on C(22) which were freely refined. $R_1 = 0.035$ [for 3202 reflections with $I > 2\sigma(I)$], $wR_2 = 0.093$ (all data). CCDC 182/498.

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