Reactions of the μ-Alkyne Dimer $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$: Synthesis and Bonding Analysis of a μ-Alkyne–μ-Imido Bridged Ditungsten Complex†

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The new compounds $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PR_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ (PR_3 = PMe_3 **2a**, PMe_2Ph **2b**, PH_2Ph **2c** or PPh_2H **2d**), $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)]$ **3**, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(PMe_3)_2(\mu\text{-}C_2Et_2)]$ **4**, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(PMe_3)(\mu\text{-}C_2Et_2)]$ **5**, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(OEt)(\mu\text{-}C_2Et_2)]$ **6**, $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(SMe)(\mu\text{-}C_2Et_2)]$ **7** and $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ (R = H **8a**, Me **8b** or Ph **8c**) have been prepared. The crystal structures of compounds **2a** and **8c** have been determined. The compounds **8a**–**8c** contain a three-centre, two-electron W–N–W 'banana' π bond.

The W≡W triply bonded complexes $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ (R = alkyl, X = Cl or Br) have a rich chemistry[1] including reactions with alkynes giving the μ-alkyne species $[W_2(\eta\text{-}C_5H_4R)_2X_4(\mu\text{-}C_2R'_2)]$.[2] The μ-hexyne derivative $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ **1** in particular is accessible in multigram quantities and is a relatively uncommon example of a μ-alkyne complex bearing halide ligands.[3] Therefore, we decided to explore the chemistry of this molecule and have investigated Lewis base and substitution reactions, as described below. We have previously communicated related studies.[4]

Results and Discussion

Treatment of complex **1** with the Lewis base PMe_3 gives the adduct $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ **2a**.[4] When the same compound is treated with PMe_2Ph or PH_2Ph, the corresponding adducts $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PR_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ (PR_3 = PMe_2Ph **2b** or PH_2Ph **2c**) are formed. Further increasing the steric bulk of the PR_3 group by using diphenylphosphine gives $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PPh_2H)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ **2d** and in this compound the phosphine ligand is labile; therefore it was not possible to obtain a satisfactory elemental analysis. There was no evidence for adduct formation in the reaction between **1** and triphenylphosphine and it seems likely that this is due to the large size of the PPh_3 ligand. The analytical and spectroscopic data characterising compounds **2a**–**2d**, and all the other new compounds described in this paper, are given in Table 1 and the proposed structures are shown in Scheme 1.

The crystal structure of complex **2a** has been determined and the molecular structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 2 and the atomic coordinates for the non-hydrogen atoms in Table 3. The structure shows that the trimethylphosphine ligand co-ordinates to a tungsten atom [W(1)] and, in consequence, a chloride atom forms a bridge across the W–W bond. The bond angle Cp_{cent}–W(1)–W(2) 111.3° is much less than Cp'_{cent}–W(2)–W(1) 154.3°, and this may be attributed to the steric bulk of the phosphine ligand. Similarly the value of Cp_{cent}–W(1)–Cl(4) 112.3°, is greater than for Cp'_{cent}–W(2)–Cl(1) 100.9°, although this difference is not as significant. To satisfy electron-counting procedures we propose that complex **2a** contains a W–W single bond, consistent with the observed bond length.

The binuclear W≡W triply bonded complex $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ is prepared by Na/Hg amalgam reduction of the monomeric tetrachloride species $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$.[5] However, addition of 2 equivalents of Na/Hg amalgam to a tetrahydrofuran (thf) solution of $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$, followed by the immediate addition of PMe_3 leads to the isolation of claret red crystals of the W≡W triply bonded dimer $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)]$ **3** (see Scheme 2). In contrast, treatment of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ with 1 equivalent of PMe_3 produces an uncharacterizable material. Clearly the PMe_3 traps some intermediate during the reduction process. Circumstantial evidence for the existence of such an intermediate is provided by the isolation of thf adducts of tungsten multiply bound dimers, *e.g.* $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Me_2)(thf)_2]$[3a] and $Na[W_2Cl_7(thf)_5]$.[3f] The NMR spectra of complex **3** suggest that the molecule adopts the conformation shown in Scheme 2. This conformation is analogous to that of the crystallographically characterised isoelectronic dimolybdenum complex $[Mo_2(\eta\text{-}C_5H_5)_2Cl_4(\mu\text{-}Cl)]^-$ for which Fenske–Hall molecular orbital calculations suggest a Mo≡Mo triple bond.[6]

Reduction of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ **1** in thf with 2 equivalents of Na/Hg amalgam in the presence of an excess of PMe_3 gives the sky blue compound $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(PMe_3)_2(\mu\text{-}C_2Et_2)]$ **4** in *ca.* 55% yield. The NMR data for complex **4** are consistent with the C_2 structure shown in Scheme 1, and electron-counting procedures suggest the presence of a W=W double bond. The molecular orbital levelling found for the model complex $[W_2(\eta\text{-}C_5H_5)_2Br_4(\mu\text{-}C_2H_2)]$ also suggests that a formal metal–metal double bond (of configuration $\sigma^2\,\pi^2$) is present in **4**.[2b,4] Complexes such as **4** which have a perpendicular bridging alkyne and a metal–metal double bond are uncommon: other examples include $[Ta_2Cl_4(thf)_2(\mu\text{-}Cl)_2(\mu\text{-}C_2Bu^t_2)]$[3b] and $[Fe_2(CO)_6(\mu\text{-}C_2Bu^t_2)]$.[7]

Reduction of complex **2a** with 2 equivalents of Na/Hg amalgam in thf gives $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ **5** in 65% yield. The structure of **5** is assigned on the basis of NMR data, and a W=W double bond is proposed for electron-counting purposes in order to conform to the 18-electron rule. The formation of complexes **4** and **5** shows that the reductive substitution of **1** gives new μ-alkyne complexes with increasing metal–metal bond orders.

We have also explored metathesis reactions of the chloride ligands of **1** with anionic ligands. Treatment of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ **1** with 1 equivalent of NaOEt or LiSMe in thf gave the new monosubstituted ethoxide complex $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(OEt)(\mu\text{-}C_2Et_2)]$ **6** or the methylsulfanyl complex $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(SMe)(\mu\text{-}C_2Et_2)]$ **7**, respectively,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

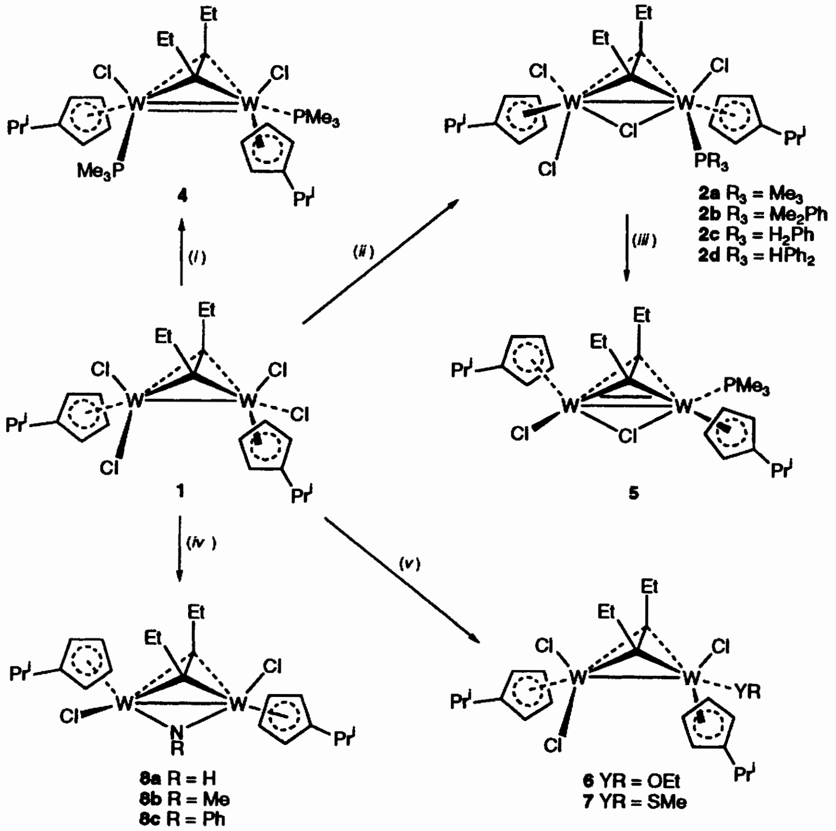
Table 1 Analytical^a and spectroscopic data

Compound	NMR data^b
2a^c Red C 34.3 (34.3) H 4.8 (4.8) Cl 15.8 (16.2)	^{1}H:^{d} 6.99 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.79 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.74 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.67 (2 × overlapping virtual q, 2 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.59 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.53 [d of virtual q, 1 H, $^3J(^1\text{H-}^{31}\text{P})$ 7.5, $\eta\text{-C}_5H_4\text{Pr}^i$], 4.46 (d of q, 1 H, ^2J 16.1, ^3J 7.3, $\text{C}H_\text{A}\text{H}_\text{B}\text{Me}$), 4.36 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 4.07 (d of q, 1 H, ^2J 15.1, ^3J 7.3, $\text{C}H_\text{A}\text{H}_\text{B}\text{Me}$), 3.84 (d of q, 1 H, ^2J 15.1, ^3J 7.3, $\text{CH}_\text{A}H_\text{B}\text{Me}$), 3.39 (d of q, 1 H, ^2J 16.1, ^3J 7.3, $\text{CH}_\text{A}H_\text{B}\text{Me}$), 2.95 (sept, 1 H, J 7.3, $\text{C}H\text{Me}_2$), 2.35 (sept, 1 H, J 7.3, $\text{C}H\text{Me}_2$), 1.68 [d, 9 H, $^2J(^1\text{H-}^{31}\text{P})$ 8.8, PMe_3], 1.27 (d, 3 H, J 7.3, $\text{CH}Me_2$), 1.21 (overlapping 2 × d and t, 9 H, $\text{CH}Me_2$ and CH_2Me), 1.10 (t, 3 H, J 7.3, CH_2Me), 1.00 (d, 3 H, J 7.3, $\text{CH}Me_2$) ^{13}C-{^{1}H}:^{d} 141.4 [d, $^2J(^{13}\text{C-}^{31}\text{P})$ 7, $\mu\text{-}C_2\text{Et}_2$], 138.4 (s, $C\text{Pr}^i$), 132.6 (s, $C\text{Pr}^i$), 121.3 [d, $^2J(^{13}\text{C-}^{31}\text{P})$ 7, $\mu\text{-}C_2\text{Et}_2$], 106.3 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 103.3 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 102.2 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 98.3 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 95.6 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 91.5 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 89.9 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 89.6 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 31.4 [d, $^3J(^{13}\text{C-}^{31}\text{P})$ 7, $C\text{H}_2\text{Me}$], 29.9 (s, $C\text{H}_2\text{Me}$), 28.7 (s, $C\text{HMe}_2$), 28.3 (s, $C\text{HMe}_2$), 23.1 (s, $\text{CH}Me_2$), 22.9 (s, $\text{CH}Me_2$), 22.4 (s, $\text{CH}Me_2$), 21.6 (s, $\text{CH}Me_2$), 18.8 (s, CH_2Me), 17.7 (s, CH_2Me), 15.7 [s, $^1J(^{31}\text{P-}^{13}\text{C})$ 28, PMe_3] ^{31}P-{^{1}H}:^{d} 45.1 [s, $^1J(^{31}\text{P-}^{183}\text{W})$ 222.4, PMe_3]
2b Brick red C 37.9 (38.2) H 4.6 (4.6) Cl 15.1 (15.0)	^{1}H:^{d} 7.63–7.44 (m, 5 H, C_6H_5), 7.00 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.73–5.53 (4 × overlapping virtual q, 6 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 4.28 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 4.00–3.80 (2 × overlapping d of q, 2 H, $\text{C}H_2\text{Me}$), 3.75 (d of q, 1 H, ^3J 7.3, $\text{C}H_2\text{Me}$), 2.98 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 2.83 (d of q, 1 H, ^2J 15.5, ^3J 7.4, $\text{C}H_\text{A}\text{H}_\text{B}\text{Me}$), 2.34 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 1.93 [overlapping d of d, 6 H, $^1J(^1\text{H-}^{31}\text{P})$ 9.4, $\text{PPh}Me_2$], 1.26–1.00 (4 × overlapping d and t, 15 H, J 6.9, $\text{CH}Me_2$ and CH_2Me), 0.84 [t, 3 H, J 7.4, CH_2Me] ^{13}C-{^{1}H}:^{d} 140.8 [d, $^2J(^{13}\text{C-}^{31}\text{P})$ 5, $\mu\text{-}C_2\text{Et}$], 138.4 (s, $C\text{Pr}^i$, other quaternary obscured by phenyl region), 136.4 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 37, *ipso*-C_6H_5], 131.7 [d, $^3J(^{13}\text{C-}^{31}\text{P})$ 6, *m*-C_6H_5], 129.8 (s, *p*-C_6H_5), 128.2 [d, $^2J(^{13}\text{C-}^{31}\text{P})$ 8, *o*-C_6H_5], 121.7 [d, $^2J(^{13}\text{C-}^{31}\text{P})$ 5, $\mu\text{-}C_2\text{Et}_2$], 107.2, 104.5, 101.4, 98.1, 96.4, 91.0, 89.9, 89.5 (8 × CH of $C_5\text{H}_4\text{Pr}^i$), 30.1 (s, $C\text{H}_2\text{Me}$), 28.9 [d, $^3J(^{13}\text{C-}^{31}\text{P})$ 6, $C\text{H}_2\text{Me}$], 28.7 (s, $C\text{HMe}_2$), 28.2 (s, $C\text{HMe}_2$), 23.1 (s, $\text{CH}Me_2$), 23.0 (s, $\text{CH}Me_2$), 22.0 (s, $\text{CH}Me_2$), 21.8 (s, $\text{CH}Me_2$), 18.4 (s, CH_2Me), 17.9 (s, CH_2Me), 15.2 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 27, $\text{PPh}Me_2$], 14.4 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 29, $\text{PPh}Me_2$] ^{31}P-{^{1}H}:^{a} −42.5 [$^1J(^{31}\text{P-}^{183}\text{W})$ 211.7 *ca.* 15% by area, PPhMe_2]
2c Red C 36.5 (36.7) H 4.3 (4.3) Cl 15.8 (15.5)	^{13}C-{^{1}H}:^{d} 135.2–129.2 (4 × s, 1 × d, quaternaries of CPr^i, $\mu\text{-C}_2\text{Et}_2$ and phenyl carbons), 109.8, 106.9, 100.0, 99.4, 97.2, 94.5, 91.3, 82.2 (8 × CH of $C_5\text{H}_4\text{Pr}^i$), 32.7 (s, $C\text{H}_2\text{Me}$), 28.8 (s, $C\text{H}_2\text{Me}$), 27.8 (s, $C\text{HMe}_2$), 26.9 (s, $C\text{HMe}_2$), 22.8 (s, $\text{CH}Me_2$), 22.5 (s, $\text{CH}Me_2$), 22.0 (s, $\text{CH}Me_2$), 21.5 (s, $\text{CH}Me_2$), 18.0 (s, CH_2Me), 14.6 (s, CH_2Me) ^{31}P-{^{1}H}:^{d} −65.9 [$^1J(^{31}\text{P-}^{183}\text{W})$ 256.2 *ca.* 15% by area, PH_2Ph_2]
2d Red	^{1}H:^{e} 7.20 (m, Ph region), 6.76 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 6.38 (d, 1 H, $\text{P}H\text{Ph}_2$, other peak obscured by Ph or cyclopentadienyl region), 5.50 (m, 6 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 4.79 (virtual q, 1 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 4.00–3.80 (m, 4 H, $\text{C}H_2\text{Me}$), 2.90 (sept, 1 H, J 7.0, $\text{C}H\text{Me}_2$), 2.08 (sept, 1 H, J 7.0, $\text{C}H\text{Me}_2$), 1.24 (d, 3 H, J 7.0, $\text{CH}Me_2$), 1.10 (m, 12 H, $\text{CH}Me_2$ and CH_2Me), 0.68 (d, 3 H, J 7.0, $\text{CH}Me_2$) ^{31}P-{^{1}H}:^{e} −19.9 [s, $^1J(^{31}\text{P-}^{183}\text{W})$ 155.8, PPh_2H]
3 Claret C 28.8 (28.5) H 4.3 (4.0) Cl 16.6 (17.7)	^{1}H:^{e} 7.50, 6.93, 6.53, 6.31 (4 × virtual q, 4 H, 4 × $\eta\text{-C}_5H_4\text{Pr}^i$), 5.58 [d of virtual q, 1 H, $^3J(^1\text{H-}^{31}\text{P})$ 7, $\eta\text{-C}_5H_4\text{Pr}^i$), 5.30, 5.21, 4.90 (3 × virtual q, 3 H, $\eta\text{-C}_5H_4\text{Pr}^i$), 2.29 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 2.19 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 1.65 [d, 9 H, $^2J(^1\text{H-}^{31}\text{P})$ 9.0, PMe_3], 0.99 (4 × d, 12 H, J 6.9, $\text{CH}Me_2$) ^{13}C-{^{1}H}:^{e} 136.9 (s, $C\text{Pr}^i$), 130.8 (s, $C\text{Pr}^i$), 106.2 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 103.7 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 102.3 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 98.5 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 98.3 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 96.9 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 96.4 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 94.6 (s, CH, $\eta\text{-}C_5\text{H}_4\text{Pr}^i$), 27.4 (s, $C\text{HMe}_2$), 27.2 (s, $C\text{HMe}_2$), 23.1 (s, $\text{CH}Me_2$), 22.2 (s, $\text{CH}Me_2$), 21.9 (s, $\text{CH}Me_2$), 21.1 (s, $\text{CH}Me_2$), 17.5 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 19, PMe_3] ^{31}P-{^{1}H}:^{e} −24.7 [$^1J(^{31}\text{P-}^{183}\text{W})$ 290.6 *ca.* 15% by area, PMe_3]
4 Sky blue C 38.4 (38.0) H 5.7 (5.7) Cl 7.8 (8.0)	^{1}H:^{d} 6.33, 5.15 (2 × virtual q, 2 × 2 H, J 2.4, 2 × C_5H_4Pr^i), 4.70 (d, of q, 2 H, ^2J 16.1, ^3J 7.4, $\text{C}H_2\text{Me}$), 2.83 (d of q, 2 H, ^2J 16.1, ^3J 7.4, $\text{C}H_2\text{Me}$), 3.79, 3.49 (2 × virtual q, 2 × 2 H, J 2.4, 2 × C_5H_4Pr^i), 2.98 (sept, 2 H, J 7.0, $\text{C}H\text{Me}_2$), 1.35 (overlapping d and t, 12 H, $\text{CH}Me_2$ and CH_2Me), 1.23 (d, 6 H, J 7.0, $\text{CH}Me_2$), 1.14 [d, 18 H, $^2J(^1\text{H-}^{31}\text{P})$ 8.0, PMe_3] ^{13}C-{^{1}H}:^{b} 145.7 ($\mu\text{-}C_2\text{Et}_2$), 133.0 ($C\text{Pr}^i$), 89.0, 86.4, 75.5, 69.4 (4 × CH of $C_5\text{H}_4\text{Pr}^i$), 40.6 ($\text{C}H_2\text{Me}$), 27.9 ($C\text{HMe}_2$), 24.0, 21.5 (2 × $\text{CH}Me_2$), 19.0 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 19, PMe_3], 16.6 (CH_2Me) ^{31}P-{^{1}H}:^{b} −53.05 [$^1J(^{31}\text{P-}^{183}\text{W})$ 274.7 *ca.* 15% by area, PMe_3]
5 Orange-brown C 36 4 (37.0) H 5.1 (5.1) Cl 8.7 (8.2)	^{1}H:^{d} 6.16, 5.82, 5.79, 5.70, 5.45, 5.42, 5.26, 5.14 (8 × virtual q, 8 × 1 H, J 2.4, 8 × C_5H_4Pr^i), 5.05 (d of q, 1 H, ^2J 14.0, ^3J 7.3, $\text{C}H_2\text{Me}$), 4.75 (d of q, 1 H, ^2J 15.6, ^3J 7.5, $\text{C}H_2\text{Me}$), 3.87 (d of q, 1 H, ^2J 15.6, ^3J 7.6, $\text{C}H_2\text{Me}$), 2.83 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 2.38 (d of q, 1 H, ^2J 14.0, ^3J 7.3, $\text{C}H_2\text{Me}$), 1.76 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 1.60 (t, 3 H, J 7.3, CH_2Me), 1.56 (overlapping d and t, 5 H, $\text{CH}Me_2$ and CH_2Me), 1.12, 1.03, 0.98 (3 × d, 3 × 3 H, J 6.9, 3 × $\text{CH}Me_2$), 0.93 [d, 9 H, $^2J(^1\text{H-}^{31}\text{P})$ 9.0, PMe_3] ^{13}C-{^{1}H} DEPT:^{b} 111.8, 104.9, 101.8, 100.5, 99.9, 98.8, 95.0, 92.3 (8 × CH of $C_5\text{H}_4\text{Pr}^i$), 31.0, 30.2 (2 × $C\text{H}_2\text{Me}$), 27.9, 27.0 (2 × $C\text{HMe}_2$), 25.8 (overlapping 2 × $\text{CH}Me_2$), 24.0, 22.1 (2 × $\text{CH}Me_2$), 21.0, 19.0 (2 × CH_2Me), 15.5 [d, $^1J(^{13}\text{C-}^{31}\text{P})$ 26, PMe_3]
6 Purple C 34.0 (33.9) H 4.3 (4.6) Cl 12.55 (12.9)	^{1}H:^{e} 5.71, 5.64, 5.37, 5.27, 5.17, 5.00 (6 × virtual q, 6 × 1 H, J 2.4, 6 × C_5H_4Pr^i), 4.75 (d of q, 1 H, ^2J 14.0, ^3J 7.7, $\text{C}H_2\text{Me}$), 4.59 (virtual q, 1 H, J 2.4, C_5H_4Pr^i), 4.50–4.30 (overlapping q and virtual q, 3 H, OCH_2 and C_5H_4Pr^i), 3.87 (d of q, 1 H, ^2J 14.0, ^3J 7.3, $\text{C}H_2\text{Me}$), 3.69 (d of q, 1 H, ^2J 14.0, ^3J 7.7, $\text{C}H_2\text{Me}$), 3.41 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 3.20 (d of q, 1 H, ^2J 14.0, ^3J 7.3, $\text{C}H_2\text{Me}$), 2.92 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 1.56 (overlapping d and 2 × t, 9 H, $\text{CH}Me_2$ and 2 × CH_2Me), 1.43, 1.39, 1.21 (3 × d × 3 H, J 6.9, 3 × $\text{CH}Me_2$), 1.17 (t, 3 H, J 7.7, CH_2Me)
7 Pale blue C 33.6 (33.8) H 4.4 (4.3) Cl 12.8 (13.0)	^{1}H:^{d} 5.76, 5.15, 5.07 (3 × virtual q, 3 × 1 H, J 2.4, C_5H_4Pr^i), 4.91 (d of q, 1 H, ^2J 14.6, ^3J 7.3, $\text{C}H_2\text{Me}$), 4.57, 4.48 (2 × virtual q, 2 × 1 H, J 2.4, C_5H_4Pr^i), 4.21 (overlapping d of q and sept, 2 H, $\text{C}H_2\text{Me}$ and $\text{C}H\text{Me}_2$), 3.98 (virtual q, 1 H, J 2.4, C_5H_4Pr^i), 3.80 (overlapping d of q and virtual q, 2 H, $\text{C}H_2\text{Me}$ and C_5H_4Pr^i), 3.32 (virtual q, 1 H, J 2.4, C_5H_4Pr^i), 2.75 (sept, 1 H, J 6.9, $\text{C}H\text{Me}_2$), 2.42 (s, 3 H, SCH_3), 2.32 (d, of q, 1 H, ^2J, 14.6, ^3J 7.3, $\text{C}H_2\text{Me}$), 1.54 (t, 3 H, J 7.3, CH_2Me), 1.28, 1.22, 1.17 (3 × d, 3 × 3 H, J 6.9, 3 × $\text{CH}Me_2$), 1.10 (t, 3 H, J 7.3, CH_2Me), 1.05 (d, 3 H, J 6.9, $\text{CH}Me_2$)
8a^f Royal blue	^{1}H:^{d} 5.92, 5.31, 4.91, 4.76 (4 × virtual q, 4 × 2 H, J 2.4, 4 × C_5H_4Pr^i), 3.58, 3.07 (2 × d of q, 2 × 2 H, ^2J 12.6, ^3J 7.2, 2 × $\text{C}H_2\text{Me}$), 2.75 (sept, 2 H, J 6.9, $\text{C}H\text{Me}_2$), 1.55 (t, 6 H, J 7.2, CH_2Me), 1.21, 1.10 (2 × d, 2 × 6 H, J 6.9, 2 × $\text{CH}Me_2$), (NH not observed)
8b Royal blue C 35.9 (36.2) H 4.6 (4.6) Cl 9.6 (9.3) N 1.8 (1.8)	^{1}H:^{d} 5.88, 5.49, 4.86, 4.16 (4 × virtual q, 4 × 2 H, J 2.4, 4 × C_5H_4Pr^i), 4.56 (s, 3 H, $\text{N}Me$), 3.57 (d of q, 2 H, ^2J 12.6, ^3J 7.2, $\text{C}H_2\text{Me}$), 3.13 [overlapping d of q and sept, 4 H, $\text{C}H_2\text{Me}$ and $\text{C}H\text{Me}_2$], 1.49 (t, 6 H, J 7.2, CH_2Me), 1.22, 1.19 (2 × d, 6 H, J 6.9, 2 × $\text{CH}Me_2$) ^{13}C-{^{1}H}:^{b} 140.3 ($\mu\text{-}C_2\text{Et}_2$), 122.6 ($C\text{Pr}^i$), 97.6, 97.0, 95.9, 91.8 (4 × CH of $C_5\text{H}_4\text{Pr}^i$), 71.7 ($\text{N}Me$), 29.1 ($\text{C}H_2\text{Me}$), 28.2 ($C\text{HMe}_2$), 23.0, 22.6 (2 × $\text{CH}Me_2$), 17.3 (CH_2Me)

Table 1 (*contd.*)

Compound	NMR data[b]
8c[g] Royal blue	^{1}H:[d] 8.03 (d, 2 H, J 7.3, o-C_6H_5), 7.29 (overlapping d and t, 3 H, m- and p-C_6H_5), 5.68 (2 × overlapping virtual q, 4 H, 2 × $C_5H_4Pr^i$), 4.68, 4.51 (2 × virtual q, 2 × 2 H, 2 × $C_5H_4Pr^i$), 3.57, 3.13 (2 × d of q, 2 × 2 H, ^2J 13.1, ^3J 7.3, 2 × CH_2Me), 2.98 (sept, 2 H, J 6.9, $CHMe_2$), 1.35 (t, 6 H, J 7.3, CH_2Me), 1.23 [overlapping 2 × d, 12 H, 2 × $CHMe_2$] ^{13}C-{^{1}H}:[d] 172.6 (s, *ipso*-C_6H_5), 140.2 (s, μ-C_2Et_2), 129.7 (s, o- or m-C_6H_5), 124.9 (s, CPr^i), 124.6 (s, p-C_6H_5), 122.6 (s, o- or m-C_6H_5), 100.4 (s, CH, η-$C_5H_4Pr^i$), 99.2 (s, CH, η-$C_5H_4Pr^i$), 95.1 (s, CH, η-$C_5H_4Pr^i$), 90.7 (s, CH, η-$C_5H_4Pr^i$), 29.2 (s, CH_2Me), 27.9 (s, $CHMe_2$), 22.6 (s, $CHMe_2$), 22.4 (s, $CHMe_2$), 17.2 (s, CH_2Me)

[a] Calculated values (%) given in parentheses. [b] Spectra recorded at ambient probe temperature at 300 MHz (^{1}H), 121.6 MHz (^{31}P) or at 75 MHz (^{13}C) and given as δ relative to $SiMe_4$ (for ^{1}H and ^{13}C) or externally to trimethyl phosphate in D_2O (^{31}P), multiplicity, relative intensity, coupling constant in Hz, and assignment. J refers to the ^{1}H–^{1}H coupling constant unless stated otherwise (J for virtually coupled multiplets refers to the apparent coupling constant). [c] NMR data are given in ref. 4. [d] In [$^2H_6$]benzene. [e] In [$^2H_2$]dichloromethane. [f] IR (mull, cm^{-1}): 3423m (br) ν(N–H). Characterisation by spectroscopic data only. [g] Characterisation by NMR and X-ray diffraction data only.



Scheme 1 (*i*) PMe_3 (excess), thf, Na/Hg (2 equiv.), 55%; (*ii*) PR_3 (1 equiv.), thf, 58%; (*iii*) Na/Hg (2 equiv.), thf, 65%; (*iv*) **8a** (R = H) and **8b** (R = Me), $RN(SiMe_3)_2$, thf, *ca.* 70%; **8c** (R = Ph), $PhNH_2$ (3 equiv.), thf, 73%; (*v*) **6** (YR = OEt), NaOEt (1 equiv.), thf, 60%; **7** (YR = SMe), LiSMe (1 equiv.), thf, 65%

in *ca.* 60–65% yields. Interestingly, treatment of complex **1** with 2 or more equivalents of either NaOEt or LiSMe still only afforded the monosubstituted products **6** or **7**. For both of these monosubstituted complexes, the observed diamagnetism and electron-counting suggests that compounds **6** and **7** have W–W single bonds.

Treatment of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ **1** with 1 equivalent of hexa- or hepta-methyldisilazane, or with 3 equivalents of aniline, gave the μ-alkyne–μ-imido complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ (R = H **8a**, Me **8b** or Ph **8c**, respectively), in *ca.* 60–73% yields. Compounds **8a**–**8c** were characterized by elemental analysis and by NMR spectroscopy, and the crystal structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)]$ **8c** has been determined. The molecular structure of **8c** is shown in Fig. 2, selected bond lengths and angles are given in Table 4 and fractional atomic coordinates in Table 5. The asymmetric unit of **8c** contains one and a half crystallographically independent molecules; discussion hereafter is restricted to only one of these molecules since the metric data for the other do not differ significantly.

The structure of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)]$ **8c** contains two $W(\eta\text{-}C_5H_4Pr^i)Cl$ fragments linked by a metal–metal bond [W(1)–W(2) 2.5923(5) Å] which is, in turn, bridged in a perpendicular manner by a μ-hexyne ligand and also by a planar μ-phenylimido moiety. Although the metal–metal separation in **8c** is certainly consistent with the formation of a bond between the two atoms, the formal bond order in such complexes cannot be inferred from the bond length alone. The carbon–carbon bond length for the metal-bound atoms of the μ-C_2Et_2 ligand [C(1)–C(2) 1.36(1) Å] is normal for a bridging

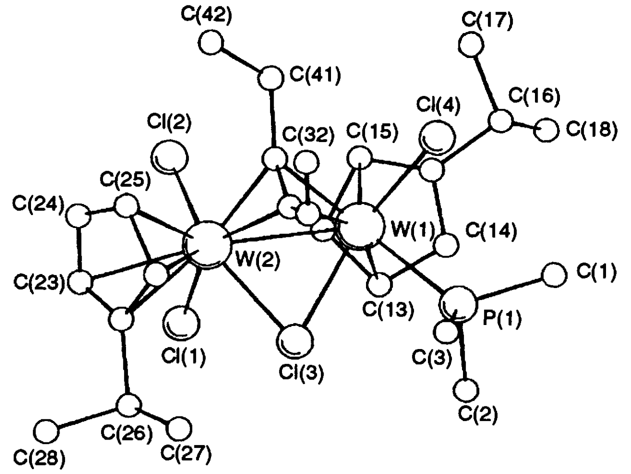
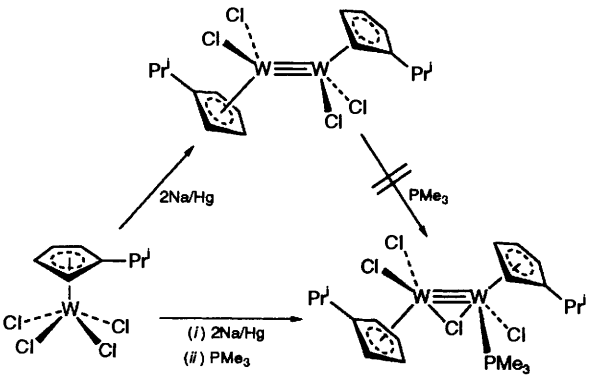


Fig. 1 The molecular structure of $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)}]$ **2a**. Hydrogen atoms omitted for clarity



Scheme 2

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)}]$ **2a**; $\mathrm{Cp_{cent}}$ and $\mathrm{Cp'_{cent}}$ refer to computed η-$\mathrm{C_5H_4Pr^i}$ ring centroids for W(1) and W(2) respectively

W(1)–W(2)	2.814(2)	W(1)–Cl(3)	2.508(7)
W(1)–Cl(4)	2.458(7)	W(1)–P(1)	2.565(7)
W(2)–Cl(1)	2.534(6)	W(2)–Cl(2)	2.460(7)
W(2)–Cl(3)	2.424(6)	C(30)–C(40)	1.35(3)
W(1)–C(30)	2.20(2)	W(1)–C(40)	2.17(3)
W(2)–C(30)	2.20(2)	W(2)–C(40)	2.10(3)
W(1)–$\mathrm{Cp_{cent}}$	2.031	W(2)–$\mathrm{Cp'_{cent}}$	2.049
Cl(3)–W(1)–W(2)	53.8(1)	Cl(4)–W(1)–W(2)	126.7(2)
Cl(3)–W(2)–W(1)	56.6(2)	Cl(1)–W(2)–W(1)	99.6(2)
$\mathrm{Cp_{cent}}$–W(1)–W(2)	111.3	$\mathrm{Cp'_{cent}}$–W(2)–W(1)	154.3
$\mathrm{Cp_{cent}}$–W(1)–Cl(4)	112.3	$\mathrm{Cp'_{cent}}$–W(2)–Cl(1)	100.9

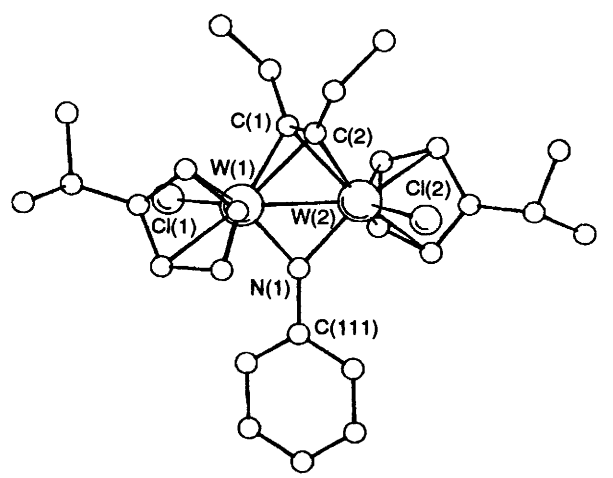


Fig. 2 The molecular structure of $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)}]$ **8c**. Hydrogen atoms omitted for clarity. Only one of the one and a half crystallographically independent molecules contained in the asymmetric unit is shown

Table 3 Fractional atomic coordinates for the non-hydrogen atoms of $[\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)}]$ **2a** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
W(1)	0.974 10(7)	0.215 47(8)	0.730 84(5)
W(2)	0.985 25(8)	0.421 73(9)	0.692 88(6)
Cl(1)	0.795 1(5)	0.473 3(5)	0.667 5(4)
Cl(2)	0.905 4(6)	0.403 1(7)	0.545 5(4)
Cl(3)	0.949 7(5)	0.364 2(5)	0.811 4(3)
Cl(4)	1.104 5(5)	0.082 8(6)	0.735 7(4)
P(1)	1.016 7(7)	0.144 8(6)	0.874 0(4)
C(1)	1.026(3)	0.007(2)	0.888(2)
C(2)	0.910(2)	0.172(2)	0.914(2)
C(3)	1.128(3)	0.194(4)	0.954(2)
C(11)	0.867(2)	0.073(2)	0.647(1)
C(12)	0.812(2)	0.239(2)	0.637(1)
C(13)	0.799(2)	0.199(2)	0.710(1)
C(14)	0.829(2)	0.095(2)	0.713(1)
C(15)	0.866(2)	0.157(2)	0.604(1)
C(16)	0.900(3)	−0.040(3)	0.640(3)
C(17)	0.930(4)	−0.044(4)	0.565(3)
C(18)	0.808(4)	−0.106(3)	0.623(2)
C(21)	1.119(2)	0.525(3)	0.770(2)
C(22)	1.019(2)	0.580(2)	0.752(2)
C(23)	0.978(3)	0.603(2)	0.675(2)
C(24)	1.042(3)	0.575(3)	0.639(2)
C(25)	1.125(3)	0.521(2)	0.690(3)
C(26)	0.983(3)	0.619(3)	0.828(2)
C(27)	1.059(3)	0.583(3)	0.912(2)
C(28)	0.983(3)	0.739(2)	0.822(2)
C(30)	1.113(1)	0.313(1)	0.752(1)
C(31)	1.218(2)	0.311(4)	0.819(2)
C(32)	1.309(2)	0.295(4)	0.811(3)
C(40)	1.068(2)	0.296(3)	0.672(1)
C(41)	1.106(2)	0.256(3)	0.605(2)
C(42)	1.183(3)	0.323(4)	0.582(2)

alkyne ligand and indicative of substantial back-donation of electron density from the dimetal centre to the alkyne π^* orbitals.[8] The angles around the N atom of the imido ligand sum to 359.9° and the coplanarity of the W(1), W(2), N(1) and C(111) atoms shows the nitrogen atom is sp^2 hybridised.

Complex **8c** is a rare example of a binuclear system with both bridging imido *and* bridging alkyne ligands. There are several examples of mononuclear complexes in which an imido and alkyne ligand coexist in the metal co-ordination sphere,[9] but we are aware of only one other example of a complex containing a $\{\mathrm{M(\mu\text{-}C_2R_2)(\mu\text{-}NR')M}\}$ unit, namely $[\mathrm{Mo_2(\eta\text{-}C_5H_5)_2(Ph)(\mu\text{-}NC_6H_4Me\text{-}}p)\{\mu\text{-}\sigma,\eta^2\text{-}\mathrm{PhC{\equiv}CC_6H_3(Me)NCH{=}CPh_2}\}]$.[10]

Complexes $(\mathrm{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)}]$ **8a**–**8c** present an interesting problem in electron counting. Electron-counting procedures are often useful for the prediction and rationalisation of certain structures. Electron-counting procedures for **8a**–**8c** are not straightforward. Thus, each W atom (six valence electrons) receives two electrons from the μ-hexyne ligand, five from a η-$\mathrm{C_5H_4Pr^i}$ ligand and one from a chlorine ligand. Further, the bridging sp^2-hybridised nitrogen ligand may formally donate one electron to each tungsten atom through σ-bond interactions. At this point each W centre has an electron count of 15. There remains the 2 electrons in the out-of-plane p_π orbital on the sp^2 hybridised nitrogen atom. If it is supposed that these do not significantly contribute to the W–N bonding then a W≡W triple bond is required to give an 18 electron count. However, if it is supposed that the p_π electrons contribute one electron to each W atom then a W=W double bond is required to achieve the 18-electron count. Finally if the two p_π electrons *formally* contribute two electrons to *both* tungsten atoms then a W–W single bond is required to account for the observed diamagnetism and achieve 18 electrons.

This latter method of counting is most appropriate since we propose that each W atom in **8a**–**8c** has a formal d^1 configuration and to be in a +5 oxidation state. This arises since molecular orbital calculations for models of **8a**–**8c** (see later) and for related μ-alkyne complexes[2b,3a,8b] suggest that the alkyne ligand in **8a**–**8c** is best formally treated as a 4^- ligand. If the W atoms are d^1 then compounds **8a**–**8c** can contain only a W–W single bond and this is consistent with the observed W–W bond length for **8a**. To find a satisfactory description of the bonding in **8a**–**8c** we carried out a series of extended-Hückel molecular orbital (EHMO) calculations for the model complex $[W_2(\eta\text{-}C_5H_5)_2Cl_2(\mu\text{-}NH)(\mu\text{-}C_2H_2)]$.[11] The model was based on the structure of **8c** but was idealised to have C_2 symmetry.

We shall focus on the interactions in the W(μ-NR)W bridge. These show, as expected, that the sp^2-hybridised nitrogen atom forms a single σ bond to each W atom (two two-centre, two-electron bonds in terms of the valence bond theory, each bond requiring one electron from the N atom). It is the interaction of this p_π lone pair of the nitrogen atom with the W_2 centre which holds the key to understanding the electron counting for **8a**–**8c**. Fig. 3 shows an analysis (based on the EHMO calculations) of the W(μ-NR)W π bonding in which we consider the interaction between possible π-acceptor functions of a $\{W_2(\eta\text{-}C_5H_5)_2Cl_2\}$ fragment and the μ-NR p_π donor orbital.* There are two linear combinations of W d basis set orbitals, labelled ψ_1 and ψ_2 (these are the in-phase combinations of d_{xy} and d_{yz} atomic orbitals respectively), which have non-zero overlap with the nitrogen p_y orbital (labelled ψ_3 in Fig. 3). In the model complex, $[W_2(\eta\text{-}C_5H_5)_2Cl_2(\mu\text{-}NH)(\mu\text{-}C_2H_2)]$, these orbitals combine to give two new linear combinations ($\psi_1 + \psi_2$ and $\psi_1 - \psi_2$) which are much better oriented for π interactions with the bridging ligands.

Table 4 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for one of the crystallographically independent molecules of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)]$ **8c**; Cp_{cent} and Cp'_{cent} refer to computed $\eta\text{-}C_5H_4Pr^i$ ring centroids for W(1) and W(2) respectively

W(1)–W(2)	2.5923(5)	W(1)–Cl(1)	2.385(2)
W(1)–N(1)	1.930(7)	W(1)–C(1)	2.182(9)
W(2)–C(1)	2.117(9)	C(1)–C(2)	1.36(1)
W(1)–Cp_{cent}	2.060	W(2)–Cl(2)	2.283(2)
W(2)–N(1)	1.925(7)	W(1)–C(2)	2.111(8)
W(2)–C(2)	2.182(8)	W(2)–$Cp_{cent'}$	2.040
N(1)–C(111)	1.41(1)		
Cl(1)–W(1)–W(2)	104.97(7)	Cp_{cent}–W(1)–W(2)	146.33
Cl(2)–W(2)–W(1)	109.67(7)	$Cp_{cent'}$–W(2)–W(1)	140.53
W(2)–N(1)–W(1)	84.5(3)	W(1)–N(1)–C(111)	137.0(6)
W(2)–N(1)–C(111)	138.4(6)		

We recognise now that the W(μ-NR)W π system is in fact a classical three-orbital interaction, in this case involving the fragment orbitals ($\psi_1 + \psi_2$), ($\psi_1 - \psi_2$) and ψ_3. For a three-orbital interaction one anticipates a resultant bonding, non-bonding and anti-bonding combination. In our case these combinations are ($\psi_1 + \psi_2 + \psi_3$), ($\psi_1 - \psi_2$) and ($\psi_1 + \psi_2 - \psi_3$) respectively.† The ($\psi_1 - \psi_2$) combination is essentially metal–nitrogen non-bonding because it is incorrectly oriented for significant overlap with ψ_3 (but it is superbly set up for back-bonding with one of the μ-alkyne π* orbitals). Therefore the key to understanding the electron counting for **8a**–**8c** lies in viewing the interaction of the nitrogen p_π lone pair with the W_2 centre as a three-centre, two-electron π bond. In fact, this π bond formed from the combination ($\psi_1 + \psi_2 + \psi_3$) is topologically exactly equivalent to the three-centre, two-electron 'banana' σ

Table 5 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)]$ **8c** with e.s.d.s in parentheses. The asymmetric unit contains one and a half crystallographically independent molecules

Atom	*X/a*	*Y/b*	*Z/c*
W(1)	0.790 58(1)	0.260 98(3)	0.212 23(2)
W(2)	0.870 89(1)	0.298 68(3)	0.297 46(2)
Cl(1)	0.757 29(8)	0.395 7(2)	0.242 2(2)
Cl(2)	0.909 12(8)	0.182 9(2)	0.264 9(2)
C(1)	0.839 5(3)	0.162 3(7)	0.301 0(5)
C(2)	0.827 8(3)	0.240 6(7)	0.330 5(5)
C(3)	0.822 7(3)	0.253 9(9)	0.396 2(5)
C(4)	0.790 0(4)	0.177(1)	0.392 5(7)
C(5)	0.848 4(3)	0.045 9(8)	0.315 0(6)
C(6)	0.884 9(4)	0.025(1)	0.396 0(7)
C(11)	0.735 2(4)	0.250(1)	0.080 7(5)
C(12)	0.766 9(4)	0.177(1)	0.099 4(8)
C(13)	0.767 7(4)	0.104(1)	0.150 2(7)
C(14)	0.735 3(3)	0.132 2(8)	0.161 5(6)
C(15)	0.714 3(3)	0.220 5(8)	0.116 5(5)
C(16)	0.676 0(4)	0.275(1)	0.107 8(8)
C(17)	0.664 6(6)	0.231(1)	0.161(1)
C(18)	0.638 2(4)	0.259(2)	0.033(1)
C(21)	0.917 9(3)	0.354 4(9)	0.425 6(5)
C(22)	0.943 6(3)	0.355 5(8)	0.395 2(5)
C(23)	0.926 2(3)	0.428 4(8)	0.334 7(6)
C(24)	0.890 7(3)	0.475 3(8)	0.329 8(6)
C(25)	0.884 7(3)	0.428 0(8)	0.383 3(6)
C(26)	0.985 3(3)	0.300(1)	0.425 6(7)
C(27)	1.020 7(4)	0.374(1)	0.474 8(9)
C(28)	0.989 1(4)	0.201(1)	0.469 1(8)
C(111)	0.825 5(3)	0.416 3(8)	0.142 6(5)
C(112)	0.855 4(4)	0.414 5(9)	0.123 5(6)
C(113)	0.850 5(5)	0.481(1)	0.066 1(7)
C(114)	0.816 9(6)	0.547(1)	0.029 8(7)
C(115)	0.787 5(5)	0.551(1)	0.051 0(8)
C(116)	0.791 6(4)	0.485 6(9)	0.106 5(6)
N(1)	0.828 5(2)	0.347 7(6)	0.198 4(4)
W(3)	0.959 90(1)	0.199 60(3)	0.724 71(2)
Cl(3)	0.923 21(8)	0.210 0(2)	0.590 4(1)
C(31)	0.943 4(3)	0.178 4(9)	0.815 2(5)
C(32)	0.936 6(3)	0.283 7(9)	0.795 8(6)
C(33)	0.902 7(3)	0.290 5(8)	0.722 5(6)
C(34)	0.886 0(3)	0.188 6(8)	0.695 9(6)
C(35)	0.912 3(3)	0.118 6(8)	0.753 5(5)
C(36)	0.846 0(3)	0.163 5(9)	0.623 4(6)
C(37)	0.810 0(3)	0.189(1)	0.633 2(8)
C(38)	0.843 3(3)	0.050 8(9)	0.597 9(7)
C(41)	0.994 1(3)	0.075 0(7)	0.713 2(5)
C(42)	0.987 6(3)	−0.004 2(8)	0.655 3(6)
C(43)	0.054 2(3)	−0.084 4(9)	0.640 3(7)
C(211)	1.0000	0.422(1)	0.7500
C(212)	1.031 1(4)	0.477 3(9)	0.808 8(8)
C(213)	1.030 4(5)	0.587(1)	0.808(1)
C(214)	1.0000	0.641(2)	0.7500
N(2)	1.0000	0.312 2(8)	0.7500

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* Atomic orbital basis sets taken from refs. 12 (C, H, N), 13 (Cl) and 14 (W). Model based on the structure of **8c** but idealised to have C_2 symmetry.

† The in-phase combination of W $6p_y$ orbitals can, in principle, interact with the N p_y atomic orbital. However, in the $\{W_2(\eta\text{-}C_5H_5)_2Cl_2\}$ fragment, this W $6p_y + 6p_y$ combination lies at high energy due to interactions with the Cl and $\eta\text{-}C_5H_5$ ligands and interacts only weakly with the nitrogen p_y orbital.

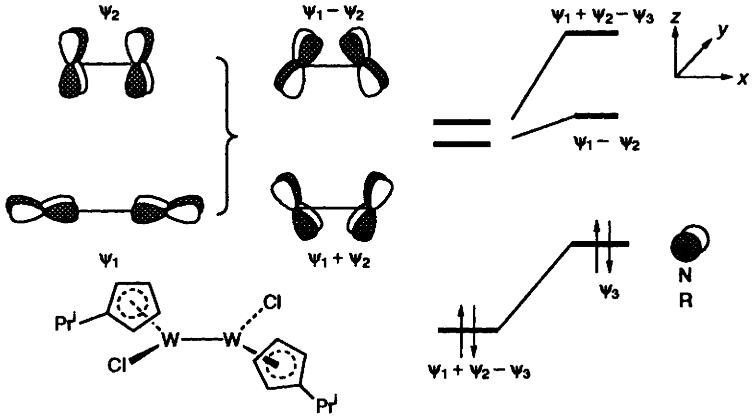

Fig. 3 Molecular orbital description of the μ-imido p_π lone pair interaction in the W(μ-NR)W bridge of the complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$. At the left are the two available π-acceptor orbitals of the $\{W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2\}$ fragment before (ψ_1, ψ_2) and after [($\psi_1 + \psi_2$), ($\psi_1 - \psi_2$)] mixing. At the right is the filled nitrogen p_π donor orbital of a μ-NR fragment

Table 6 Crystal data collection and processing parameters for $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ **2a** and $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NPh)(\mu\text{-}C_2Et_2)]$ **8c**

	2a	**8c**
Formula	$C_{25}H_{41}Cl_4PW_2$	$C_{28}H_{37}Cl_2NW_2$
M	881.76	826.21
Crystal size/mm	0.25 × 0.4 × 0.7	0.5 × 0.4 × 0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a/Å	13.446(8)	37.23(2)
b/Å	13.17(1)	12.736(3)
c/Å	17.66(2)	20.835(3)
β/°	110.29(5)	121.85(2)
U/Å^3	2937.4	8391.9
Z	4	12
D_c/g cm^{-3}	1.99	1.962
μ/cm^{-1}	84.32	86.07
F(000)	1688	4728
2θ limits/°	3–50	C–48
ω scan width [+0.35 tan θ]/°	1.0	1.0
Zone	−1 15, −1 15, −20 20	−1 42, −1 14, −23 23
Scan mode	ω–2θ	ω
Total data collected	4613	7976
No. of observations [$I > 3\sigma(I)$]	2433	6576
R(merge)	0.061	0.037
Structure solution method	Direct	Direct
No. of variables	290	452
Obs./variables	8.4	14.5
Weighting scheme	Unit weights	Unit weights
Max., min. peaks in final difference map/e Å^{-3}	1.7, −0.10	1.04, −0.02
R^a	0.051	0.026
R'^b	0.057	0.028

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$.

bond proposed for B–H–B linkages (such as those in diborane) to explain their apparent electron deficiency.[15] Therefore, the occupied out of plane p_π orbital of the μ-NR group in the complexes $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ must, *for the purpose of formal electron counting*, be considered as donating *two* electrons to *each* tungsten centre in the same way as the bridging H atom in diborane formally contributes, *for the purpose of formal electron counting*, a total of *three* electrons (one to one boron atom and two to the other) to achieve a valence electron count of eight (a Lewis octet) for each B atom.

In conclusion, we have demonstrated that the μ-alkyne dimer $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ is a versatile synthon for the preparation of new μ-alkyne ditungsten complexes. The novel μ-alkyne–μ-imido derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ pose an intriguing problem in electron counting which has prompted us to propose the formal description of the bonding in terms of a three-centre, two-electron 'banana' π bond.

Experimental

All manipulations of air- and moisture-sensitive materials were performed using standard Schlenk-line techniques under an atmosphere of dinitrogen, which had been purified by passage over MnO (or a BASF catalyst) and 4 Å molecular sieves or in a dry-box containing dinitrogen.

Solvents were pre-dried by standing over 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentaoxide or calcium hydride (dichloromethane), potassium (thf), sodium (toluene) or sodium/potassium alloy (1:3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents (Aldrich) for NMR studies were transferred into Youngs ampoules under an atmosphere of dinitrogen in a dry-box and stored over molecular sieves ([$^2H_6$]benzene) or distilled from phosphorus pentaoxide ([$^2H_2$]dichloromethane).

The NMR spectra were recorded using a Brüker AM300 (^1H 300 MHz, ^{13}C 75.5 MHz, ^{31}P 121.6 MHz) instrument. Spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances relative to $SiMe_4$ (δ 0), or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are in ppm and coupling constants are in Hz. Elemental analyses were performed by the Microanalytical Department of this laboratory. The compounds $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ and $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$ were prepared as described previously.[2a,5]

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PR_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ ($PR_3 = PMe_3$ **2a**, PMe_2Ph **2b** *or* PH_2Ph **2c**).—A typical preparation for **2a** is as follows. A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (270 mg, 0.34 mmol) in CH_2Cl_2 (20 cm^3) was treated with 1 equivalent of PMe_3 (26 mg) to give an immediate colour change from green to claret red. The solvent was removed under reduced pressure and the resultant residue extracted in toluene (10 cm^3). Filtering this extract, followed by cooling to −25 °C gave a red crystalline material. Yield, 236 mg, 77%. The same procedure was used for **2b** and **2c** using the appropriate tertiary phosphine.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PPh_2H)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ **2d**.—A stirred solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (300 mg, 0.37 mmol) in CH_2Cl_2 (25 cm^3) was treated with 1 equivalent of diphenylphosphine (46 mg, 0.066 cm^3) causing a colour change from moss green to dark red. Whilst removing the solvent under reduced pressure (10^{-1} mbar, 10 Pa), it was noticed that the solid began to acquire the original silver-grey colour of the starting material. Further addition of phosphine ensured the re-formation of the adduct; the solvent was then removed under reduced pressure. Recrystallisation from toluene (15 cm^3) gave a scarlet powder. Yield, 210 mg, 58%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)]$ **3**.—A solution of $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$ (0.67 g, 155 mmol) in thf (50 cm^3) was reduced with 2 equivalents of Na/Hg (0.69 g, 310 mmol) to give an olive-green solution. An excess of PMe_3 (1.5 cm^3) was added over a period of 5 min giving a burgundy red solution. The volatiles were removed under reduced pressure and the resultant residue was dried *in vacuo* for 30 min. The residue was dissolved in the minimum amount of diethyl ether (30 cm^3). On cooling the extract to −25 °C, a burgundy red microcrystalline material was obtained. Yield, 450 mg, 36%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(PMe_3)_2(\mu\text{-}C_2Et_2)]$ **4**.—Two equivalents of Na/Hg amalgam (17 mg, 0.50 mmol, ≈0.5% w/w) were added to a stirred solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (200 mg, 0.25 mmol) in thf (10 cm^3), resulting in a colour change from green to light brown. After 5 min, an excess of PMe_3 (0.2 cm^3) was added leading to an immediate colour change to azure blue. The volatiles were removed under reduced pressure and the residue was dissolved in light petroleum (20 cm^3). Following filtration and cooling the filtrate to −25 °C a sky-blue microcrystalline material was obtained. Yield, 120 mg, 55%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(PMe_3)(\mu\text{-}C_2Et_2)]$ **5**.—A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(PMe_3)(\mu\text{-}Cl)(\mu\text{-}C_2Et_2)]$ (200 mg, 0.23 mmol) was treated with 2 equivalents of Na/Hg amalgam (10 mg, 0.46 mmol) in thf (25 cm^3). There was a gradual colour change from burgundy to light brown over a period of 30 min. After stirring for 2 h to ensure complete reaction, the volatiles were removed under reduced pressure. Extraction of the residue with diethyl ether (10 cm^3) produced a dark orange solution. Filtration followed by cooling the filtrate to −25 °C yielded brown microcrystals. Yield, 120 mg, 65%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(OEt)(\mu\text{-}C_2Et_2)]$ **6**.—*Method A*. The compound NaOEt (18 mg, 0.25 mmol) in thf (10 cm^3) was added to a stirred solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (200 mg, 0.25 mmol) in thf (20 cm^3) and over a period of 3 h the solution became purple. The solution was stirred overnight. The solution was filtered and solvent was removed from the filtrate under reduced pressure, giving a dark purple residue. This was dissolved in the minimum of toluene (15 cm^3) and the solution was cooled to −80 °C. A purple polycrystalline material was isolated. Yield >60%.

Method B. The addition of an excess of EtOH (5 cm^3) to a stirred solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (200 mg, 0.25 mmol) in thf (20 cm^3) provided no colour change. An excess of NEt_3 was added to the stirred solution giving a brown-red solution and a white precipitate. After filtration and removal of the volatiles under reduced pressure the residue was extracted into pentane giving a purple solution. This was cooled to −80 °C giving **6** as a purple crystalline material. Yield ≈30%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_3(SMe)(\mu\text{-}C_2Et_2)]$ **7**.—A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (200 mg, 0.25 mmol) in CH_2Cl_2 (20 cm^3) was treated with 1 equivalent of LiSMe in thf (13 mg, 0.25 mmol). The solution was stirred for 12 h and changed from green to light blue whilst depositing a white precipitate. The volatiles were removed under reduced pressure, and the residue was extracted using toluene (15 cm^3). After filtration the volume of the toluene filtrate was reduced (to 10 cm^3) and subsequently cooled to −25 °C to give blue microcrystals. Yield, 130 mg, 65%.

Preparation of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NR)(\mu\text{-}C_2Et_2)]$ (R = H **8a**, Me **8b** *or* Ph **8c**).—*Method A: for* **8a**. A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)]$ (200 mg, 0.25 mmol) in thf (15 cm^3) was treated with hexamethyldisilazane (130 mg, 0.75 mmol) resulting in a royal blue solution and a white crystalline material. This was stirred for 3 h to ensure complete reaction. After the volatiles were removed under reduced pressure, the residue was extracted into pentane (10 cm^3), filtered, and the extracts were cooled to −25 °C. Purple-blue microcrystalline $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NH)(\mu\text{-}C_2Et_2)]$ was isolated. Yield, 130 mg, 69%. This rapidly turns yellow when exposed to air. The same procedure was used for **8b** except using heptamethyldisilazane giving $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}NMe)(\mu\text{-}C_2Et_2)]$. Yield >65%.

Method B: for **8c**. The same procedure was carried out as above except that aniline (70 mg, 0.75 mmol) was used instead of heptamethyldisilazane. The royal blue single crystals of the product were isolated and dried *in vacuo*. Yield, 150 mg, 73%.

Crystal-structure Determinations of **2a** *and* **8c** (*see Table* 6).—Crystals of **2a** or **8c** were sealed in a Lindemann glass capillary under N_2 and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[16] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The tungsten atom positions were determined by direct methods. Subsequent Fourier difference syntheses revealed the positions of all other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.3 × the equivalent isotropic thermal parameter of the carbon atom to which they were bonded) and refined riding their supporting carbon atoms. No weighting scheme was necessary and unit weights were used for all cycles of refinement. The data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[17]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[18] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral-atom scattering factors were taken from the usual sources.[19] For **8c** the asymmetric unit contained one and a half crystallographically independent molecules.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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