A chloroalkyne complex from the coupling of alkylidyne and carbonyl ligands

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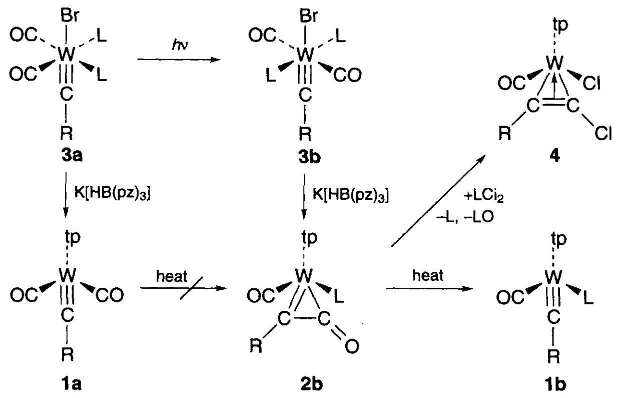
Whilst the reaction of *cis*-[W(≡CR)Br(CO)$_2$(PPh$_3$)$_2$] (R = C$_6$H$_4$Me-4) with K[HB(pz)$_3$] (pz = pyrazol-1-yl) provides [W(≡CR)(CO)$_2${HB(pz)$_3$}], photolysis of the same complex leads to the *trans* isomer, which with K[HB(pz)$_3$] provides initially [W(η^2-OCCR)(CO)(PPh$_3$){HB(pz)$_3$}] 2b; subsequent treatment with Cl$_2$PPh$_3$ leads to the chloroalkyne complex [W(η^2-ClC≡CR)Cl(CO){HB(pz)$_3$}] 4; the crystal structures of 2b and 4 are also reported.

The coupling of alkylidyne and carbonyl ligands has recently received considerable attention[1] and in a number of cases this process has been shown to be photochemically induced.[2] The complex [W(≡CR)(CO)$_2${HB(pz)$_3$}] (R = C$_6$H$_4$Me-4, pz = pyrazol-1-yl) **1a** reacts with PMe$_3$ to provide a ketenyl complex [W(η^2-OCCR)(CO)(PMe$_3$){HB(pz)$_3$}] **2a**;[3] however, we find that this reaction fails to provide [W(η^2-OCCR)(CO)(PPh$_3$){HB(pz)$_3$}] **2b** for the bulkier and less nucleophilic PPh$_3$ ligand under thermal conditions.

The complex *cis*-[W(≡CR)Br(CO)$_2$(PPh$_3$)$_2$] **3a** may be prepared conveniently in 92% yield by treating [W(CO)$_6$] in diethyl ether successively with LiR·LiBr (25 °C), (CF$_3$CO)$_2$O (−78 °C) and an excess of PPh$_3$ (−78 to 0 °C followed by warming to room temperature). The stereochemistry at tungsten follows unambiguously from a comparison of spectroscopic data with those of related complexes formed *via* multistep procedures.[4] Photolysis in dichloromethane provides the thermally unstable *trans* isomer **3b**, reflecting previous observations by Mayr *et al.*[5] for the related complex [W(≡CPh)Cl(CO)$_2$(PMe$_3$)$_2$] (Scheme 1). The reaction of **3a** with K[HB(pz)$_3$] leads to replacement of bromide and both phosphine ligands to generate the previously reported[3] complex [W(≡CR)(CO)$_2${HB(pz)$_3$}]; however, the same reaction employing **3b** initially provides the previously inaccessible ketenyl complex [W(η^2-OCCR)(CO)(PPh$_3$){HB(pz)$_3$}] **2b**‡ *via* a thermal reaction.

Complex **2b** is also thermally unstable in solution at ambient temperature, slowly extruding CO to provide the new complex [W(≡CR)(CO)(PPh$_3$){HB(pz)$_3$}] **1b**. The molecular structure of **2b** is represented in Fig. 1.§ The bonding of the ketenyl ligand is dihapto through C(1) and C(46), the C=C=O grouping lying in the equatorial coordination plane which also contains the carbonyl ligand, consistent with Templeton's criteria for the related alkyne systems.[6] Atoms W, C(1), C(46), O(47) and the two pyrazolyl nitrogen donor atoms are coplanar to within 0.28 Å (N *trans* to CO).¶ The N–W distances are unremarkable and in the range 2.185(6)–2.258(6) Å, the shortest of these being that *trans* to the phosphine, while the N–W–N angles are essentially identical [80.1(1)–81.2(2)°].



Scheme 1 L = PPh$_3$, R = C$_6$H$_4$Me-4, tp = κ^3-HB(pz)$_3$

The binding of the ketenyl group can best be described as tending towards form **A** (Scheme 2), the W–C(1) bond [1.984(8) Å] being significantly shorter than W–C(46) [2.158(8) Å]. The respective *trans*-N–W–C(1) angle [167.9(3)°] is closer to linear than the corresponding *trans*-N–W–C(46) angle [153.9(3)°]. The bonding within the ketenyl unit shows partial double-bond character for the C(1)–C(46) bond [1.360(11) Å] and a lengthening of the C(46)–O(47) distance, 1.213(10), *cf.* 1.168(10) Å for C(25)–O(26) reflecting a contribution from the 'oxyalkyne' resonance form **C** (Scheme 2).

The formulation of complexes such as **2b** as 'oxyalkyne' derivatives points to a nucleophilicity at the oxygen atom, a feature extensively exploited by Kreißl and coworkers,[7] *e.g.* in the complex [W(η^2-OCCR)(CO)(PMe$_3$)(η^2-C$_5$H$_5$)]. We have

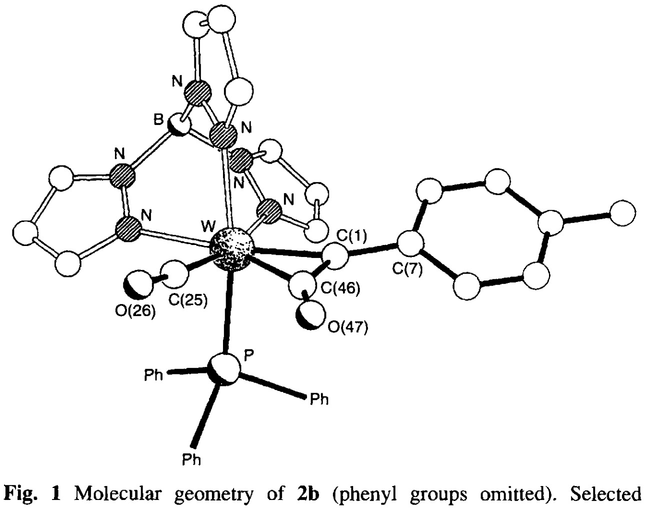
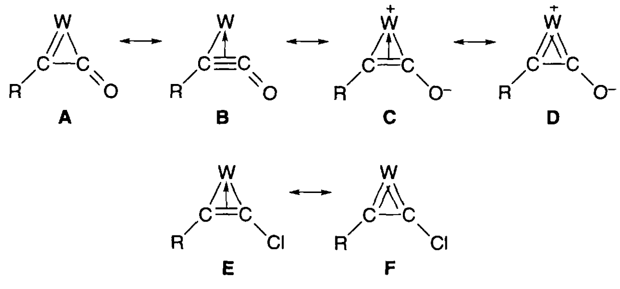


Fig. 1 Molecular geometry of **2b** (phenyl groups omitted). Selected structural features: W–C(1) 1.984(8), W–C(46) 2.158(8), W–P(27) 2.531(2), W–C(25) 1.929(9), C(1)–C(46) 1.360(11), C(46)–O(47) 1.213(10), C(1)–C(7) 1.474(11) Å; C(1)–W–C(46) 38.1(3), C(1)–C(46)–O(47) 147.2(8), C(7)–C(1)–C(46) 130.4(7), C(46)–C(1)–W 77.9(5)°.



Scheme 2 Valence bond descriptions for ketenyl and 4-electron haloalkyne ligands

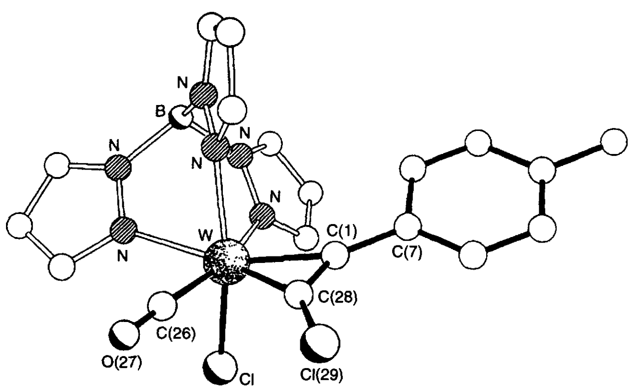


Fig 2 Molecular geometry of **4**. Selected structural features: W–C(1) 2.038(6), W–C(28) 2.026(7), W–C(26) 1.977(8), W–Cl 2.402(2), C(1)–C(28) 1.317(9), C(28)–Cl(29) 1.696(6), C(7)–C(1) 1.449(8) Å, C(1)–W–C(28) 37.8(3), C(7)–C(1)–C(28) 140.8(6), W–C(1)–C(28) 70.6(4), W–C(28)–Cl(29) 150.4(4), C(1)–C(28)–Cl(29) 138.0(6)°.

recently been concerned with the deployment of dihalophosphoranes as oxide abstracting reagents for the modification of 'C_1' ligands[8] and accordingly the reaction of **2b** with Cl_2PPh_3 in tetrahydrofuran was investigated and found to lead to a blue intermediate which on chromatographic work-up provided the green chloroalkyne complex [W(η^2-ClCCR)Cl(CO){HB(pz)$_3$}] **4** (Scheme 1). The complex can be prepared directly and in quantitative yield with Cl_2PPh_3 in refluxing dichloromethane. Similar yields are obtained from the photolysis of **1** in the presence of P(OMe)$_3$ (to provide [W(η^2-OCCR)(CO){P(OMe)$_3$}{HB(pz)$_3$}]) followed by treatment with Cl_2PPh_3. Chloroalkyne complexes are rare, in part due to the tendency of the alkynes to enter into C–Cl oxidative addition reactions with low-valent metal centres.[9] The molecular structure of **4** (Fig. 2).§ is very similar to that of the topologically related precursor **2b**. There is a slight asymmetry in the N–W–N angles which range between 77.9(2) and 85.6(2)°. The W–N bond *trans* to Cl [2.179(5) Å] is noticeably shorter that the two other two W–N distances [2.210(5) and 2.232(6) Å].

The binding of the chloroalkyne is almost directly comparable to that of the ketenyl ligand in **2b** with C(1), C(28) and Cl(29) lying in the equatorial coordination plane [the coordinating atoms, W and Cl(29), are coplanar to within 0.16 Å], but the bonding to tungsten tends more towards resonance forms **D** and **E**. The two essentially identical and clearly multiple W–C bonds [W–C(1) 2.038(6), W–C(28) 2.026(7) Å] subtend a bite angle [C(1)–W–C(28) 38°] identical to that in **2b** and with the C(1)–C(28) bond displaying marked double-bond character at 1.317(9) Å (form **E**). There is also evidence for a residual amount of multiple-bond character in the C–Cl bond at 1.696(6) Å *cf.* the longer distances (1.77 Å) observed in [PPh_4][W(ClCCCl)Cl_5][10] where C–C multiple bonding is very pronounced at 1.279 Å.

Complexes of ligands with nucleofugic halides bound α to the metal are synthetically versatile.[12] We are currently investigating this possibility and a promising indication is given by the facile reaction of **4** with NaSH in the presence of PMe_2Ph to provide the thioketenyl complex [W(η^2-SCCR)(CO)(PMe_2Ph){HB(pz)$_3$}.[13] Furthermore, initial studies employing Br_2PPh_3 indicate that the corresponding bromoalkyne complex [W(η^2-BrCCR)(CO)Br{HB(pz)$_3$}] is also readily accessible, though somewhat more reactive.

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Footnotes

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‡ Data for selected complexes (satisfactory microanalytical data obtained for all complexes). **1a** (red): IR (CH_2Cl_2) 1860; (Nujol) 1866 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H δ 2.23 (s, 3 H, CH_3), 5.71, 5.95, 6.12 [t × 3, 3 H, H^4(pz), ^3J(HH) 2 Hz], 6.76, 6.99 [(AB)$_2$, 4 H, ^3J(AB) 8 Hz, C_6H_4], 7.17–7.30 (m, 15 H, Ph), 7.52, 7.56, 7.71, 7.96 [m × 4, 6 H, H^{3,5}(pz)]. ^{13}C{^{1}H} δ 275.4 [W≡C, ^2J(PC) 12.5 Hz], 246.2 (WCO), 149.5–127.7 [Ph and C^{3,5}(pz)], 105.5, 105.1, 105.0 [C^4(pz)], 21.5 (CH_3). ^{31}P{^{1}H} δ 52.9 [^1J(WP) 359.4 Hz].

2b (purple): IR (CH_2Cl_2) 1875, 1772, 1692; (Nujol) 1883, 1702 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H δ 2.27 (s, 3 H, CH_3), 5.88, 5.92, 5.99 [t × 3, 3 H, H^4(pz), ^3J(HH) 2 Hz], 6.74, 7.16 [(AB)$_2$, 4 H, C_6H_4, ^3J(HH) 8 Hz], 7.17–7.28 (m, 15 H, Ph), 7.29, 7.30, 7.32, 7.62, 7.70, 7.80 [d × 6, 6 H, H^{3,5}(pz), ^3J(HH) 2 Hz]. ^{13}C{^{1}H} δ 227.9 [d, WCO, ^2J(WC) 5.3 Hz], 207.8 [CCO], 147.2–128.0 [Ph and C^{3,5}(pz)], 106.6, 106.0, 105.6 [C^4(pz)], 21.5 (CH_3). ^{31}P{^{1}H} δ 40.8 [^1J(WP) 332.3 Hz].

4 (emerald): IR (CH_2Cl_2) 1948 cm^{-1}. NMR ($CDCl_3$): ^{1}H (248 K, fluxional at room temp.) δ 2.27 (s, 3 H, CH_3), 6.08, 6.26, 6.78, [t × 3, 3 H, H^4(pz), ^3J(HH) 2 Hz], 6.53, 7.04 [(AB)$_2$, 4 H, ^3J(AB) 8 Hz], 6.72, 7.63, 7.66, 7.79, 7.90, 8.13 [d × 6, 6 H, H^{3,5}(pz), ^3J(HH) 2 Hz]. ^{13}C{^{1}H} (25 °C) 230.2 [WCO], 207.1, 200.0 [RCCCl], 145.9, 145.0, 143.5 [C^5(pz)], 136.8, 135.5, 135.0 [C^3(pz)], 129.0 [C^{2,3,5,6}(C_6H_4)], 107.2, 106.9, 106.5 [C^4(pz)], 21.5 [(C_6H_4*Me*)].

§ *Crystal data* for **2b**: $C_{37}H_{32}BN_6O_2PW\cdot H_2O\cdot 0.5CH_2Cl_2$, M = 878.8, triclinic, space group $P\bar{1}$, a = 10.093(1), b = 12.488(3), c = 16.725(4) Å, α = 68.96(2), β = 79.19(1), γ = 82.60(1)°, U = 1928.3(6) Å^3, Z = 2, D_c = 1.51 g cm^{-3}, μ(Cu-Kα) = 6.93 mm^{-1}, F(000) = 874. A deep red needle of dimensions 0.23 × 0.13 × 0.10 mm was used. 6170 Independent reflections were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy-atom method and all the full occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 and absorption corrected data to give R_1 = 0.048, wR_2 = 0.125 for 5437 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 125°$] and 435 parameters. For **4**: $C_{19}H_{17}$ BCl_2N_6OW, M = 611.0, monoclinic, space group $P2_1/n$, a = 10.880(1), b = 16.317(2), c = 12.394(1) Å, β = 99.05(1)°, U = 2172.9(4) Å^3, Z = 4, D_c = 1.87 g cm^{-3}, μ(Mo-Kα) = 5.59 mm^{-1}, F(000) = 1176. A dark green block of dimensions 0.53 × 0.37 × 0.20 mm was used. 2822 Independent reflections were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy-atom method and all the full-occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 and absorption corrected data to give R_1 = 0.035, wR_2 = 0.0850 for 2720 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45°$] and 272 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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