Formation of carbene and cyclopentadienyl ligands from phenylacetylene *via* oligomerisation and C≡C bond scission at a mixed-metal W–Co centre

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The 1,2,4-triphenylcyclopentadienyl ligand and the CHR carbene ligand, bound respectively to the Co and W atoms in [(η5-C5H5)W{μ-CButCC(CO2Me)=C(CO2Me)CH}(μ-PPh2)Co(η5-C5Ph3H2)], are derived from the oligomerisation and cleavage of three molecules of phenylacetylene in the reaction of [(OC)(η5-C5H5)W{μ-C(CO2Me)CC(C≡C-But)(OMe)O}(μ-PPh2)Co(CO)2] with this acetylene.

The catalytic cyclo-oligomerisation of alkynes mediated by mononuclear, binuclear and polynuclear transition metal complexes to give organic compounds such as benzenes, fulvenes and cyclooctatetraenes has been well documented.[1–4] Sometimes stable organometallic complexes can be isolated in which the metal atom is ligated by the cyclised oligomer or is incorporated in a metallocyclic ring with the oligomeric moiety as in [(η4-Ph4C4)RhCl]2 (from the dimerisation of diphenylacetylene),[5] [(η6-C6Me6)Co(η5-C5H5)] (from the trimerisation of dimethylacetylene)[6] or [Co2(CO)4{μ-C(But)-CHCHCHCHC(But)}] (from the co-trimerisation of *tert*-butylacetylene and acetylene).[7] Reports of the oligomerisation and cleavage of an acetylene to give a C5R5-ring and CR unit (R = H, alkyl or aryl) are considerably more scarce. The few examples that have been reported all feature reactions of trinuclear or higher nuclearity homometallic cluster complexes and furnish organometallic products only in low[8] to very low yields.[9]

Recently, we have been interested in C–C coupling reactions of alkynes or acetylides on mixed-metal dinuclear transition metal centres. For example, the reaction of the alkyne-bridged complex [(OC)2(η5-C5H5)W{μ-C(CO2Me)C(CO2Me)}Co-(CO)3] with PPh2C≡CBut leads to [(OC)(η5-C5H5)W{μ-C-(CO2Me)CC(C≡CBut)(OMe)O}(μ-PPh2)Co(CO)2] **1** in which an acetylide fragment, generated from P–C bond cleavage within the PPh2C≡CBut ligand, has coupled with the bridging alkyne.[10] Here, we report that phenylacetylene undergoes C≡C bond scission and oligomerisation on reaction with **1** to form a tungsten–cobalt complex containing an η5-bound triphenyl-cyclopentadienyl ligand and a terminal CHR carbene ligand (Scheme 1) both derived from phenylacetylene.

Treatment of **1** with excess phenylacetylene in toluene at 383 K for 6 h affords air stable [(η5-C5H5)W{μ-CButCC(CO2-Me)=C(CO2Me)CH}(μ-PPh2)Co(η5-C5Ph3H2)] **2** as the sole product in 46% yield.† The product was isolated by TLC on silica [hexane–ethylacetate (3:1) as eluent] as a brown crystalline solid and characterised on the basis of 1H, 13C and 31P NMR spectroscopy,‡ FAB-MS and X-ray diffraction.§

The molecular structure of compound **2** is depicted in Fig. 1. The molecule comprises a tungsten–cobalt core [W–Co 2.704(1) Å] with both metal atoms being bound terminally by mutually *cis* η5-cyclopentadienyl ligands [C5H5 on W and 1,2,4-C5Ph3H2 on Co] and bridged by a PPh2 group and a six-electron donor CButCC(CO2Me)=C(CO2Me)CH ligand. The organic bridging ligand can be considered as a η2:η2'-bridging alkyne [*via* C(45) and C(46)] with one of the alkyne substituents being a But group and the other a C(CO2Me)=C(CO2Me)CH group. This latter group further coordinates to W *via* the CH carbene carbon atom [W=C(53) 2.000(7) Å]. The metallocyclopentadienyl ring so formed, [W(1)–C(46)–C(47)=C(50)–C(53)=], is almost planar [maximum deviation from plane 0.039 Å, C(46)] with the other end of the bridging alkyne [C(45)], sitting out of this plane. Both cyclopentadienyl groups are essentially planar with the phenyl rings in the 1,2,4-triphenylcyclopentadienyl ligand being located slightly out of the plane of the C5 ring [C(11) elevation 0.243 Å, C(17) elevation 0.335 Å, C(23) elevation 0.297 Å] and tilted with torsion angles of 28.9° [C(24)–C(23)–C(9)–C(10)], 34.9° [C(12)–C(11)–C(6)–C(10)] and 49.9° [(C(18)–C(17)–C(7)–C(8)] with respect to the plane of the ring.

The key features of the structure of **2** are the presence of the 1,2,4-C5Ph3H2 ligand and the W(1)=C(53) double bond. The formation of the carbene and the substituted cyclopentadienyl ring requires the cleavage of the C≡C triple bond in phenylacetylene to give PhC and CH fragments. The C5 ring is formed by the linking of two unbroken phenylacetylene ligands with the C–Ph fragment, whereas the CH fragment inserts into the W–C bond of the bridging ligand in **1**, with resultant displacement of the coordinated vinyl and ester groups, to form a μ-CButCC-(CO2Me)=C(CO2Me)CH ligand. Examples of crystallographically characterised homo- and hetero-bimetallic tungsten complexes containing a terminally bound carbene ligands are rare[11] with the W(1)=C(53) bond distance [2.000(7) Å] in **2** falling in the mid-range. It is noteworthy that the organic transformation mediated by **1** has resulted in the loss in **2** of all the terminal carbonyl groups in **1**.

The spectroscopic data for **2** is consistent with the solid state structure being maintained in solution. In the IR spectrum two weak bands at 1727 and 1698 cm−1 can be attributed to the ketonic carbonyls of the MeO2CC=CCO2Me unit. The 1H NMR spectrum of **2** displays, in addition to phenyl and alkyl resonances, a downfield singlet at δ 11.8 which is assigned to the carbene CH proton. Similarly, a downfield shift is observed for the carbene carbon atom in the 13C NMR spectrum at δ 234.3
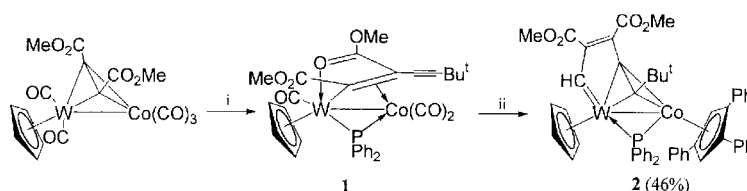
Scheme 1 *Reagents and conditions*: i, Ph2PC≡CBut, heat; ii, PhC≡CH, heat, 6 h.
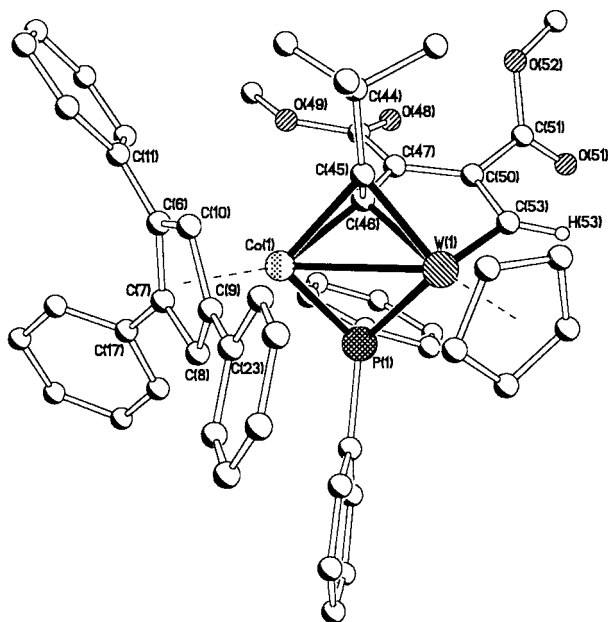
Fig. 1 The molecular structure of [(η⁵-C₅H₅)W{μ-CBuᵗCC(CO₂Me)=C-(CO₂Me)CH}(μ-PPh₂)Co(η⁵-C₅Ph₃H₂)] **2** with all hydrogen atoms except for H(53) omitted for clarity. Selected bond lengths (Å) and angles (°): W(1)–Co(1) 2.704(1), W(1)–C(53) 2.000(7), W(1)–C(46) 2.157(6), W(1)–C(45) 2.045(6), W(1)–P(1) 2.354(2), W(1)–(C₅H₅)$_{centroid}$ 2.053(6), Co(1)–C(46) 2.007(6), Co(1)–(C₅Ph₃H₂)$_{centroid}$ 1.739(6), Co(1)–C(45) 2.096(6), Co(1)–P(1) 2.187(2), C(45)–C(46) 1.443(8), C(46)–C(47) 1.429(8), C(47)–C(50) 1.383(8), C(50)–C(53) 1.431(9); Co(1)–P(1)–W(1) 72.98(5), C(53)–W(1)–Co(1) 120.1(2), C(45)–W(1)–Co(1) 50.1(2), C(46)–Co(1)–W(1) 52.0(2).

while the carbon atoms of the 1,2,4-substituted cyclopentadienyl ring are seen as upfield singlets at δ 106.7 (C–Ph) and 87.0 (C–H).

The mechanism by which the transformation of **1** to **2** occurs is uncertain but it is remarkable that only one product is formed in significant yield from such a complex reaction. A notable feature is that the acetylenic-based bridging ligand in **1** does not participate in the formation of the substituted cyclopentadienyl ligand.[12] Although the yield for the reaction of **1** to give **2** has not been fully optimised it still represents a considerable enhancement of the low yields previously obtained in the cluster-mediated formation of cyclopentadienyl and carbene ligands from acetylenes.[8,9,13] Further work is underway to assess the scope of the transformation and this will be the subject of a future publication.

Notes and references

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