Reaction of [W(η^2-PhC$_2$Ph)$_3$(NCMe)] with *o*-diphenylphosphino-styrene and -allylbenzene; evidence for novel carbon–carbon double and triple bond cleavage and alkyne insertion reactions

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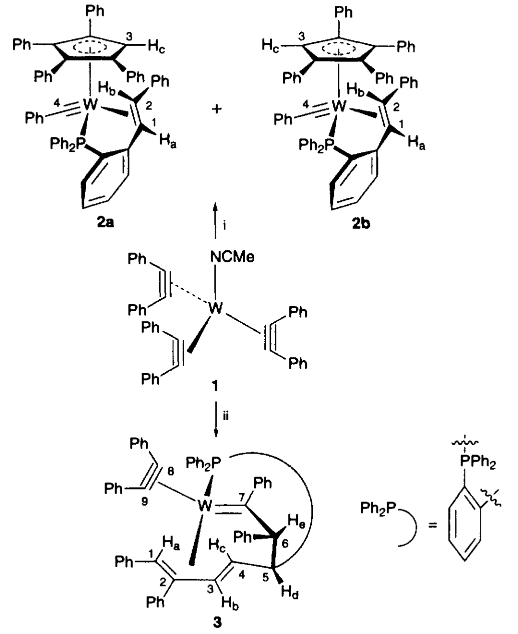
Reaction of [W(η^2-PhC$_2$Ph)$_3$(NCMe)] with *o*-diphenylphosphino-styrene or -allylbenzene leads to either novel reorganisation reactions involving cleavage of carbon–carbon double and triple bonds, or unusual insertion reactions by PhC$_2$Ph into carbon–hydrogen bonds.

We have previously used the ligating properties of *o*-diphenylphosphinostyrene (dpps) to explore carbon–carbon coupling reactions between η^2(4e)-bonded alkynes and alkenes coordinated to molybdenum[1] and rhenium[2] centres, and we were therefore interested in the recently reported synthesis of the labile complex [W(η^2-PhC$_2$Ph)$_3$(NCMe)] **1** and studies of its reactivity towards phosphines[3] and alkynes.[4] This suggested that a study of the reaction of **1** with dpps and the related *o*-diphenylphosphinoallylbenzene (dppa) could provide additional insights into these C–C bond forming reactions. However, as is described in this paper these studies have led to the discovery of new and unexpected reactions of coordinated alkynes.

When a solution of **1** and dpps in toluene was heated under reflux for 4 h the reaction mixture became deep red. Column chromatography on Al$_2$O$_3$ and elution with hexane–CH$_2$Cl$_2$ (4 : 1) afforded (63% yield) the orange–red crystalline complex **2**, Scheme 1. Elemental analysis and MS both indicated that **2** was a mononuclear complex incorporating three diphenylacetylene molecules and one dpps ligand. Examination of the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra† confirmed this stoichiometry and showed that two isomeric complexes **2a, b** had formed in the ratio 1.6 : 1. Particularly interesting was the appearance in the ^{13}C spectrum of low field resonances at δ 283.8 [d, *J*(CP) 21 Hz] and 287.1 [d, *J*(CP) 18 Hz] suggesting that both isomers contained a tungsten–carbon multiple bond. Fractional crystallisation afforded crystals of the major isomer **2a**, and a suitable crystal was subjected to a single-crystal X-ray diffraction study.‡ This showed (Fig. 1) that the complex contained a coordinated carbyne fragment [W–C(62) 1.799(5) Å], an η^5-tetraphenylcyclopentadienyl ligand, and surprisingly a modified dpps ligand, in which the alkene functionality η^2-CH=CH$_2$ had been replaced by a coordinated η^2-(*E*)-CH=CHPh moiety [W–C(55) 2.220(5), W–C(56) 2.281(5), C(55)–C(56) 1.450(7) Å]. Examination of the NMR spectra suggested that the two isomers differed only with respect to the orientation of the η^5-C$_5$Ph$_4$H ligand, variable temperature studies and NOE experiments demonstrating a high barrier to rotation.



Scheme 1 *Reagents and conditions*: i, dpps, reflux in toluene; ii, dppa, reflux in toluene

The formation of **2**, an alkenecarbyne[5] substituted metal complex, is most unusual involving apparent cleavage of both carbon–carbon triple and double bonds. In order to understand this reorganisation reaction suitable isotopic labelling experiments were carried out. Treatment of of PhC≡^{13}CPh (5% enrichment) with [W(NCMe)$_3$(CO)$_3$] gave **1** labelled only on the alkyne contact carbons, and in refluxing toluene this complex reacted with dpps to give **2a, b**, which showed (NMR) ^{13}C enrichment in the four phenyl substituted η^5-cyclopentadienyl contact carbons, position 2 (from Scheme 1) (=CHPh) and the carbyne carbon (W≡CPh) 4 (see Scheme 1). Reaction (refluxing toluene) of unlabelled **1** with dpps labelled (25% enrichment) on the methylene carbon, *i.e.* *o*-Ph$_2$PC$_6$H$_4$CH=^{13}CH$_2$, afforded **2a, b**, in which ^{13}C enrichment occurred (NMR) only on carbon 3 of the η^5-tetraphenylcyclopentadienyl ligand (Scheme 1). Finally, refluxing a

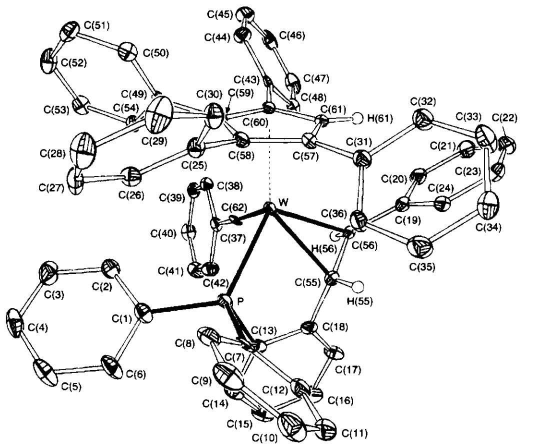


Fig. 1 ORTEX[16] plot of the molecule structure of **2a**. Pertinent bond lengths (Å) and angles (°): W–C(62) 1.799(5), W–C(57) 2.487(5), W–C(58) 2.484(5), W–C(59) 2.428(5), W–C(60) 2.369(4), W–C(61) 2.379(4), W–C(55) 2.220(5), W–C(56) 2.281(5), W–P 2.4595 (14); W–C(62)–C(37) 173.2(4), P–W–C(62) 86.82(14).

solution of [$W(\eta^2\text{-}PhC_2Ph)_3(NCCD_3)$] and dpps in toluene gave **2a**, **b** with no evidence (NMR) of deuterium incorporation.

These experiments therefore confirmed that cleavage of both carbon–carbon triple and double bonds had indeed occurred and although a detailed mechanistic discussion is deferred to a full paper it is nevertheless important to underline the existence of a possible interesting relationship between this reorganisation reaction and a recently[6–8] studied group of reactions where coordinated alkynes are formed by the coupling of carbene and carbyne ligands. Specifically, we suggest that **1** reacts with dpps to form the electron-rich species [$W(\eta^2\text{-}PhC_2Ph)_3(\eta^1\text{-}o\text{-}Ph_2PC_6H_4CH{=}CH_2)$], which is reversibly protonated by a catalytic amount of water to form the η^2(3e)-vinyl[9–12] ligand W{=C(Ph)CHPh}, and it is the cleavage of the central carbon–carbon bond of the η^2(3e)-vinyl ligand to form a carbene/carbyne intermediate, *i.e.* the reverse of the formation of an alkyne by carbene/carbyne coupling, which triggers the sequence of reactions which leads to the formation under kinetic control of **2a**, **b**.

In seeking to extend this reorganisation reaction a solution of **1** and dppa in toluene was heated under reflux for 4 h. Work-up by column chromatography on Al_2O_3 and elution with hexane–CH_2Cl_2 (4 : 1) gave (52% yield) an orange powder, which on recrystallisation afforded orange crystals of **3**, Scheme 1. Although the NMR spectra† indicated the presence of a tungsten–carbon multiple bond (δ_C 289.4) and the incorporation of three diphenylacetylene molecules and one dppa ligand, detailed examination of the spectra clearly showed that a totally different reaction from that found with dpps had occurred. A single-crystal X-ray diffraction study‡ clarified the structural identity of **3** establishing the molecular structure shown in Fig. 2.

The molecule is surprisingly a tungsten carbene complex [W–C(27) 2.000(11) Å] carrying a η^4-bonded 1,3-diene [C(34)–C(35) 1.42(2), C(35)–C(36) 1.40(2), C(36)–C(37) 1.43(2) Å], a chelating diphenylphosphino ligand [W–P 2.454(4) Å], and a diphenylacetylene ligand [W–C(50) 2.044(10), W–C(51) 2.018(13), C(50)–C(51) 1.32(2) Å] which, on the basis of the alkyne contact ^{13}C chemical shift (δ 220.0), functions as a η^2(4e)-donor. A particularly interesting structural feature is the two carbon unit C(20), C(27), which links the tungsten and the carbon atom C(19). This carbon atom, *i.e.* C(19), has its origin in the allylic CH_2 carbon of the dppa ligand and therefore a coordinated PhC_2Ph has apparently 'inserted' into an allylic CH bond in a most unusual way. This can be understood if it is again assumed that the initial product of the reaction is a phosphorus bonded species. However, because of the additional flexibility gained by the presence of an extra carbon atom the alkene part of the dppa ligand can now readily coordinate opening the way to an oxidative addition reaction and the formation of the intermediate [$HW(\eta^2\text{-}PhC_2Ph)_3(\eta^3\text{-}CH_2CHCHC_6H_4PPh_2\text{-}o)$]. This can then transform into the η^2(3e)-vinyl species [W{=C(Ph)CHPh}(η^3-$CH_2CHCHC_6H_4PPh_2$-*o*)(η^2-PhC_2Ph)$_2$] *via* a migratory insertion reaction. A reductive elimination reaction between the η^2-vinyl β-carbon and the end CH carbon of the η^3-allylic system then provides access to the C(19)C(20)C(27) unit present in the product **3**, it being reasonable to assume that the η^4-1,3-diene system is formed by an established reaction,[2] the addition of an alkene carbon–hydrogen bond to a coordinated alkyne.

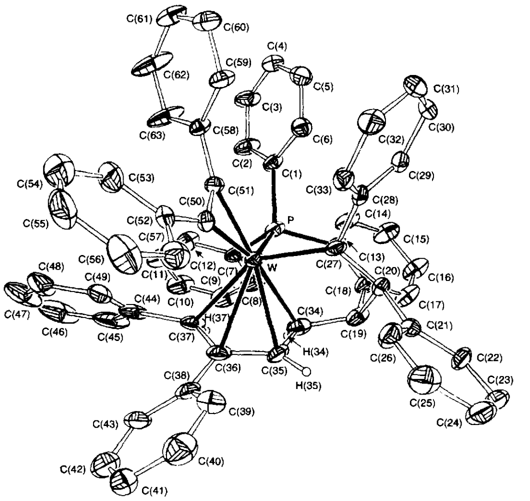


Fig. 2 ORTEX[16] plot of the molecular structure of **3**. Pertinent bond lengths (Å) and angles(°): W–C(27) 2.000(11), W–P 2.454(4), W–C(50) 2.044(10), W–C(51) 2.018(13), C(50)–C(51) 1.32(2), W–C(34) 2.302(12), W–C(35) 2.306(11), W–C(36) 2.349(12), W–C(37) 2.331(11); W–C(27)–C(28) 123.7(7), W–C(27)–C(20) 123.1(7).

In summary new and unexpected reactions of coordinated alkynes have been discovered. It is suggested that η^2(3e)-vinyl species play a pivotal role in these transformations.

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Footnotes

† *Selected NMR data* available from the authors on request.

‡ *Crystal data* for **2a**; $C_{63}H_{49}Cl_2PW$, M = 1091.74, monoclinic, space group $P2_1/n$, a = 12.785(3), b = 21.982(4), c = 17.830(4) Å, β = 99.20(2)°, U = 4946.5(18) Å^3, Z = 4, D_c = 1.466 g cm^{-3}, μ(Mo-Kα) = 2.517 mm^{-1}, F(000) = 2200. $R1$ = 0.0293 and $wR2$ = 0.0608. Goodness of fit = 1.107; max., min. residual densities 1.485, −0.678 e Å^{-3}. For **3**; $C_{63}H_{49}PW$, M = 1020.84, monoclinic, space group $P2_1/n$, a = 12.060(2), b = 18.020(3), c = 21.755(2) Å, β = 90.16(1)°, U = 4727.8 Å^3, Z = 4, D_c = 1.434 g cm^{-3}, μ(Mo-Kα) = 2.518 mm^{-1}, F(000) = 2064. The structure solution (SHELX-86)[14] and refinement (SHELX-93)[15] converged to a conventional [*i.e.* based on 3345 reflections with $F_o > 4\sigma(F_o)$] $R1$ = 0.0497 and $wR2$ = 0.0969. Goodness of fit = 1.062; max., min. residual densities 0.855 and −1.587 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/241.

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