

The Synthesis of Octahedral Mixed Bis-alkyne and Alkyne–Alkene Complexes of Tungsten

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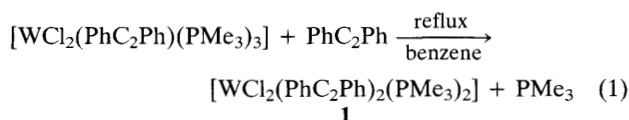
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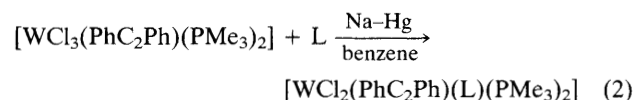
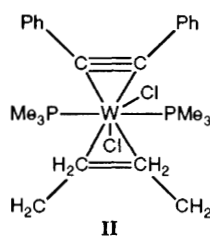
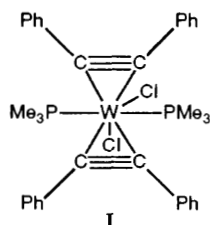
Replacement of a phosphine ligand in $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{PMe}_3)_3]$ by $\text{PhC}\equiv\text{CPh}$, $\text{PhC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CH}$, or reduction of $[\text{WCl}_3(\text{PhC}_2\text{Ph})(\text{PMe}_3)_2]$ in the presence of MeC_2Me and $\text{Me}(\text{CH}_2)_2\text{C}_2\text{Me}$ yields mixed bis-alkyne complexes; under ethylene or propene the reduction reactions afford mixed alkyne–alkene complexes, and the structure of $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ has been confirmed by X-ray crystallography.

Octahedral mono-alkyne complexes of tungsten are traditionally prepared from low-valent precursors.¹ However, complexes containing two different alkyne ligands, or an alkyne ligand and a simple alkene, have so far been inaccessible using these methods. In order to develop a synthetic path to such mixed complexes a route *via* high valent alkyne complexes has been investigated. This strategy makes use of complexes such as $[\text{WCl}_4(\text{PhC}_2\text{Ph})_2]$ and $[\text{WCl}_3(\text{PhC}_2\text{Ph})(\text{P})_2]$ ($\text{P} = \text{PMe}_3$, PMe_2Ph , PMePh_2) which exhibit properties consistent with d^0 and d^1 complexes respectively.² We report here the successful preparation of octahedral mixed bis-alkyne and mixed alkyne–alkene complexes of tungsten.

Reaction of $[\text{WCl}_3(\text{PhC}_2\text{Ph})(\text{PMe}_3)_2]$ with sodium–mercury amalgam in the presence of PMe_3 gives rise to $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{PMe}_3)_3]$ ² which reacts with diphenylacetylene according to eqn. (1). An IR spectrum of the complex indicates *cis*-chloro ligands and ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show *trans* phosphines. Collectively the spectra are consistent with structure I.



Phenylacetylene and acetylene react similarly to give the mixed acetylene complexes $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{PhC}_2\text{H})(\text{PMe}_3)_2]$ **2** and $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{HC}_2\text{H})(\text{PMe}_3)_2]$ **3** as stable, distinct species. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** show the phosphine protons and carbons as doublet of doublet sets and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows non equivalent *trans*-phosphine ligands [AB system $^2J(\text{PP})$ 103.7 Hz] arising from coordination of the asymmetric PhC_2H ligand. For the alkynes L [$\text{L} = \text{MeC}_2\text{Me}$, $\text{Me}(\text{CH}_2)_2\text{C}_2\text{Me}$] this phosphine replacement reaction is not successful but the desired bis-alkyne complexes may be prepared according to eqn. (2). IR and



NMR spectra again indicate that these complexes are distinct species with a *cis*-chloro–*trans*-phosphine structure, but alkyne exchange appears to occur slowly on standing in solution.

Reduction of $[\text{WCl}_3(\text{PhC}_2\text{Ph})(\text{PMe}_3)_2]$ with sodium–mercury amalgam in benzene under ethylene leads to the mixed alkyne–alkene complex $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ **4** for which IR and NMR spectra indicate a *cis*-chloro–*trans*-phosphine geometry (structure II). Under propene the reduction reaction yields $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CHMe})(\text{PMe}_3)_2]$ **5** as characterised by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows an AB system [$^2J(\text{PP})$ 167.0 Hz] consistent with non equivalent *trans* PMe_3 ligands. Under the conditions used alkene complexes are not formed with *cis*- and *trans*-but-2-ene or 2-methylpropene.

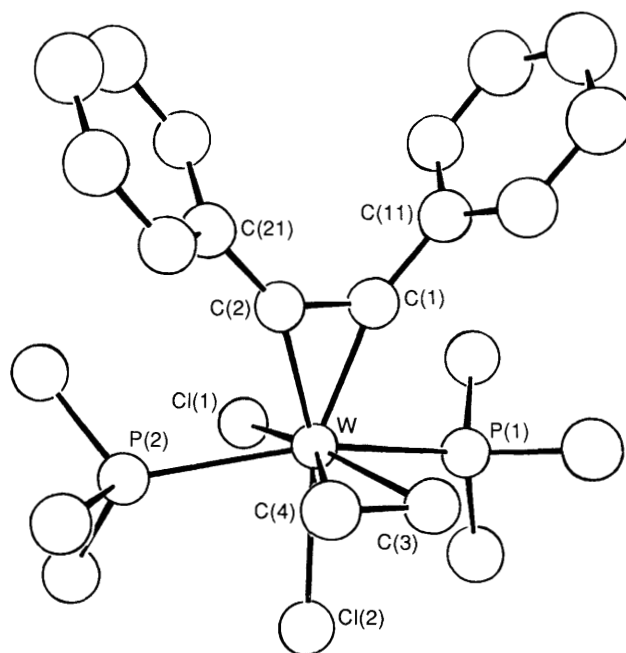


Fig. 1 Molecular structure of $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ **4**. Important bond lengths (Å) and bond angles (°): W–Cl(1) 2.443(2), W–Cl(2) 2.489(2), W–P(1) 2.548(2), W–P(2) 2.548(2), W–C(1) 2.033(5), W–C(2) 2.033(5), W–C(3) 2.248(5), W–C(4) 2.248(5), C(1)–C(2) 1.330(10), C(3)–C(4) 1.399(13); Cl(1)–W–Cl(2) 85.8(2), P(1)–W–P(2) 153.3(2), P(1)–W–Cl(1) 79.8(2), P(2)–W–Cl(1) 78.1(1), P(1)–W–Cl(2) 82.8(2), P(2)–W–Cl(2) 80.7(2), C(1)–C(2)–C(21) 135.7(5), C(2)–C(1)–C(11) 128.0(5).

An X-ray crystal structure determination of $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$ **4** was carried out.[†] The asymmetric unit contains three crystallographically distinct but structurally similar molecules. The structure of one of these (Fig. 1) shows a distorted octahedral geometry about tungsten with *cis*-chloro ligands, *trans*-phosphines and a *cis* orientation of the diphenylacetylene and ethylene ligands. The phosphine ligands are repelled from the alkyne and alkene ligands and both these ligands straddle the respective P–W–P plane without any significant twists. The W–C_{acetylene} and C–C_{acetylene} bond lengths in **4** [2.033(5), 2.033(5) and 1.330(10) Å] are similar to those found in $[\text{WCl}_2(\text{PhC}_2\text{Ph})(\text{PMe}_3)_3]$ [‡] [2.019(11), 2.006(11) and 1.330(16) Å], a complex which has properties consistent with a d² tungsten(IV) formulation.² In both molecules the acetylene ligand exerts a strong *trans* influence [W–Cl_{trans} bond lengths 2.489(2) and 2.500(3) Å, respectively]. The W–C_{alkene}

bond lengths in **4** [2.248(5) and 2.248(5) Å] are not significantly different to those found in the d² tungsten(IV) oxo-alkene complex $[\text{W}(\text{O})\text{Cl}_2(\text{CH}_2=\text{CH}_2)(\text{PMePh}_2)_2]$ [2.218(12) and 2.221(12) Å].³ In this complex as well as in **4** the *trans* chloro ligands have identical W–Cl bond lengths [2.443(2) and 2.444(3) Å, respectively].

The isolation of these complexes shows that stable octahedral complexes containing diphenylacetylene and a different alkyne ligand or ethylene or propene are easily obtainable. Our initial studies indicate that the respective unsaturated ligands do not interact further. The preparative chemistry outlined here is similar to that used to obtain d² tungsten(IV) oxo or organoimido complexes containing alkyne or alkene ligands,^{3,4} which further emphasises the high-valent character of the precursors to the present alkyne complexes.

Received, 27th April 1992; Com. 2/02170F

[†] Crystal data for $[\text{WCl}_2(\text{PhC}\equiv\text{CPh})(\text{CH}_2=\text{CH}_2)(\text{PMe}_3)_2]$: $\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{P}_2\text{W}$, $M = 613.20$, monoclinic, space group $P2_1/c$, $a = 21.143(11)$, $b = 17.911(2)$, $c = 20.415(3)$ Å, $\beta = 107.83(2)^\circ$, $U = 7359.5$ Å³, $F(000) = 3645$, $D_c = 1.660$, $D_x = 1.64$ g cm⁻³, $Z = 12$, $\mu(\text{Mo-K}\alpha) = 52.67$ cm⁻¹. Intensity data were recorded on a Nonius CAD4 diffractometer with Mo-K α radiation and corrected for Lorentz, polarization and absorption effects. The structure was solved from Patterson and heavy-atom electron-density syntheses using the program SHELX.⁵ During attempted refinement it became apparent that the crystal studied contained a stacking fault, and it was necessary to carry out a constrained restrained least-squares refinement using the program RAELS89.⁶ Full details of the stacking fault mechanism and the refinement process will be published separately elsewhere. The R value for the final cycle was 0.048 for 5958 reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] The crystal structure of this complex will be published elsewhere.

References

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