Organoimido Complexes of Tungsten(ιv) containing σ- and π-Bound Acetylenes. The X-Ray Crystal Structure of Diphenylacetylenebis(phenylacetylide)phenylimidobis(trimethylphosphine)tungsten(ιv), [W(σ-C≡CPh)₂(NPh)(η²-PhC≡CPh)(PMe₃)₂]
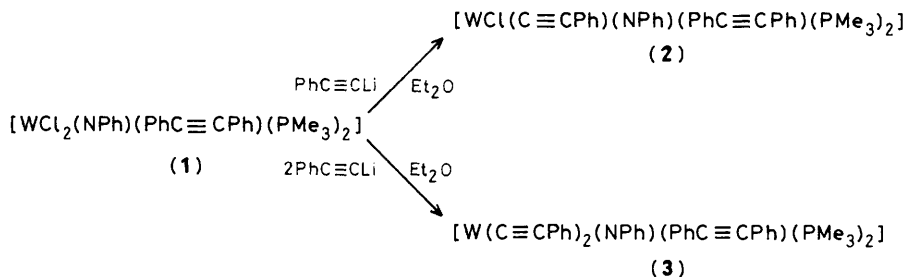
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Reaction of [WCl₂(NPh)(PhC≡CPh)(PMe₃)₂] with PhC≡CLi yields [WCl(C≡CPh)(NPh)(PhC≡CPh)(PMe₃)₂] and [W(C≡CPh)₂(NPh)(PhC≡CPh)(PMe₃)₂]; the structure of the latter complex, established by X-ray crystallography, confirms the simultaneous σ- and π-bonding of the acetylenes in the presence of the phenylimido ligand.

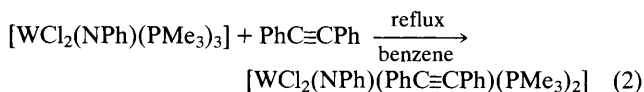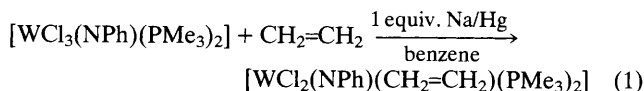We recently reported that complexes of tungsten(ιv) containing an organoimido ligand (≡NR) and a π-bound alkene or alkyne can be prepared either by reduction or by phosphine replacement reactions[1] [equations (1) and (2)]. Crystal structure determinations of the complexes established that the organoimido and unsaturated ligands occupied *cis* positions. As a consequence of this geometry the complexes show increased air stability and more sharply defined non-decomposition melting points when compared with most other tungsten(ιv) complexes. The stabilising influence arises as the

two d electrons are able to lie paired in an orbital perpendicular to the metal–nitrogen multiple bond, where they π-bond to the unsaturated ligand. Similar bonding is involved in d² oxo-π-alkene and oxo-π-alkyne complexes.[2] Without π-backbonding the electrons would be unconstrained, with possible unfavourable consequences for bonding in the equatorial plane.

By utilising the enhanced stability, we have successfully prepared complexes containing terminal σ-bound acetylide ligands in the presence of phenylimido and diphenylacetylene

$$[WCl(C\equiv CPh)(NPh)(PhC\equiv CPh)(PMe_3)_2]$$
$$(2)$$

$$[WCl_2(NPh)(PhC\equiv CPh)(PMe_3)_2]$$
$$(1)$$

PhC≡CLi / Et$_2$O

2PhC≡CLi \ Et$_2$O

$$[W(C\equiv CPh)_2(NPh)(PhC\equiv CPh)(PMe_3)_2]$$
$$(3)$$

Scheme 1

$$[WCl_3(NPh)(PMe_3)_2] + CH_2=CH_2 \xrightarrow[\text{benzene}]{1\,\text{equiv. Na/Hg}}$$
$$[WCl_2(NPh)(CH_2=CH_2)(PMe_3)_2] \quad (1)$$

$$[WCl_2(NPh)(PMe_3)_3] + PhC\equiv CPh \xrightarrow[\text{benzene}]{\text{reflux}}$$
$$[WCl_2(NPh)(PhC\equiv CPh)(PMe_3)_2] \quad (2)$$

ligands (Scheme 1) without coupling of the unsaturated moieties taking place.† In the i.r. spectrum complex (2) exhibits a weak W–Cl stretch at 310 cm^{-1} and a strong C≡C stretch at 1750 cm^{-1}. The PMe$_3$ methyl group protons and carbons appear as virtually coupled triplets in the ^{1}H and ^{13}C{^{1}H} n.m.r. spectra, suggesting *trans* orientated phosphines. The phenylimido ligand *ipso* carbon and diphenylacetylene acetylenic carbons appear in the ^{13}C{^{1}H} n.m.r. spectrum at δ 156 and 120 respectively, indicating that the ligands act as 4- and 2-electron donors, respectively.[3,4] A structure incorporating *trans* phosphines and a single σ-bound phenylacetylide situated *trans* to the π-bound diphenylacetylene is proposed for the complex.

In the ^{1}H and ^{13}C{^{1}H} n.m.r. spectra of (3), two PMe$_3$ doublets suggest that the phosphine ligands are mutually *cis*. One phosphine doublet in the ^{1}H n.m.r. spectrum lies well upfield of the other (δ 0.91 *vs.* δ 1.84), showing different environments for the two PMe$_3$ ligands. The phenylimido ligand *ipso* carbon and diphenylacetylene acetylenic carbons in the ^{13}C{^{1}H} n.m.r. spectrum both resonate in the vicinity of δ 156 but still represent 4- and 2-electron donor ligands, respectively.

The overall geometry of (3) was obtained unequivocally from an X-ray crystal structure determination (Figure 1).‡

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† By contrast, reaction of PhC≡CLi with [WCl$_2$(NPh)(PMe$_3$)$_3$] under the same conditions gives ill-defined, apparently polymerised, products.

‡ *Crystal data* for [W(C≡CPh)$_2$(NPh)(PhC≡CPh)(PMe$_3$)$_2$]: C$_{42}$H$_{43}$NP$_2$W, M = 807.62, monoclinic, space group $P2_1/n$, a = 15.455(5), b = 31.360(16), c = 8.951(3) Å, β = 104.51(3)°, U = 4199.7 Å^3, $F(000)$ = 1344, D_c = 1.277 g cm^{-3}, Z = 4, μ(Mo-K_α) = 30.1 cm^{-1}. Intensity data were recorded on a Nonius CAD4 diffractometer with Mo-K_α radiation and corrected for Lorentz, polarisation, and absorption effects. The structure was solved from Patterson and heavy-atom electron density syntheses and refined by full-matrix least-squares, omitting hydrogens, with tungsten and phosphorus atoms anisotropic, to an R value of 0.069 for 4836 independent reflections for which I > 3σ(I). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
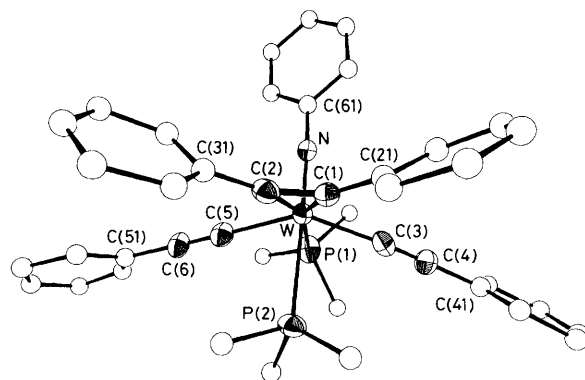

Figure 1. Molecular structure of [W(C≡CPh)$_2$(NPh)(PhC≡CPh)(PMe$_3$)$_2$] (3). Important bond lengths (Å) and bond angles (°): W–P(1) 2.624(4), W–P(2) 2.727(4), W–C(1) 2.124(12), W–C(2) 2.125(13), W–C(3) 2.148(15), W–C(5) 2.152(13), W–N 1.781(10), C(1)–C(2) 1.306(16), C(3)–C(4) 1.165(19), C(5)–C(6) 1.165(17); N–W–P(1) 87.7(4), N–W–P(2) 176.2(4), N–W–C(1) 101.9(5), N–W–C(2) 101.2(5), N–W–C(3) 102.9(5), N–W–C(5) 102.3(5), C(61)–N–W 175.3(9), C(3)–W–C(5) 144.1(5), C(1)–C(2)–C(31) 145.9(12), C(2)–C(1)–C(21) 141.0(12).

The metal co-ordination is that of a severely distorted octahedron in which the phenylimido and π-bound diphenylacetylene ligands lie mutually *cis*, the σ-bound acetylides lie mutually *trans*, and the PMe$_3$ ligands are mutually *cis*. The two formally *trans* acetylide ligands are bent away from both the π-bound acetylene and the phenylimido ligand to such an extent that the C(3)–W–C(5) angle is reduced to 144.1(5)°. Bond lengths and angles associated with the phenylimido and π-acetylene ligands are similar to those found in complex (1) and confirm the n.m.r. determinations as 4- and 2-electron donors, respectively. However, in (3) there is no twist observed about the W–acetylene axis [N–W–C$_{\text{acetylenic}}$ bond angles 101.9(5) and 101.2(5)° compared with 94.9(7) and 104.6(7)° in complex (1)[1]]. The geometry of the co-ordinated acetylene and acetylides is normal.

The X-ray analysis finds that the *cis* orientated PMe$_3$ ligands in (3) now occupy the positions filled by the chloro ligands in complex (1),[1] revealing that during the reaction isomerisation has occurred to place the acetylenic ligands *trans* to each other. The *cis* phosphines therefore lie *trans* to the π-donating phenylimido and diphenylacetylene ligands, resulting in long W–P bond lengths. The arrangement in which a phosphine ligand co-ordinates *trans* to an imido function has not been observed before in an organoimido complex.[5] The W–P(2) bond length at 2.727(4) Å is extremely long and must represent a distance close to the limit of W–P bonding.

Isolation of complexes (2) and (3) shows that both σ- and

π-bound acetylene ligands can simultaneously co-ordinate to a tungsten(IV) centre in the presence of an organoimido ligand. That no further interaction of the unsaturated ligands takes place is apparently attributable to enhanced stability arising from the combined electronic properties of the organoimido and π-acetylene ligands. This particular combination of ligands represents a new stabilising function for higher oxidation states of the earlier transition metals and further exploitation should lead to a wider range of complexes exhibiting unusual co-ordination modes.

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