Transition-metal mediated Functionalisation of a Phosphaalkyne: Crystal Structure of [Re{=C(Bu^t)P(H)OBF$_3$}Br(PPh$_3$)(η-C$_5$H$_5$)]

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Treatment of the η^2(3e)-vinyl complex [Re{=C(Ph)CH(Ph)}Br(PPh$_3$)(η-C$_5$H$_5$)] with HBF$_4$·Et$_2$O and the phosphaalkyne Bu^{t}C≡P affords the crystallographically characterised complex [Re{=C(Bu^t)P(H)OBF$_3$}Br(PPh$_3$)(η-C$_5$H$_5$)] **1** formed *via* a novel reaction involving transfer of oxygen from a metal centre to a coordinated phosphaalkyne.

The rapid development of the organotransition metal chemistry of phosphaalkynes in recent years has led to the characterisation of many novel structural types.[1–3] We have recently reported the synthesis and characterisation (by NMR spectroscopy) of the first mononuclear transition metal complex containing an η^2(4e)-bonded phosphaalkyne, [Mo(η^2-Bu^{t}C≡P){η^2-(MeO)$_2$-POBF$_2$OP(OMe)$_2$}(η-C$_5$H$_5$)], which was obtained by displacement of *trans*-stilbene from [Mo{η^2-*trans*-PhC(H)C(H)Ph}-{η^2-(MeO)$_2$POBF$_2$OP(OMe)$_2$}(η-C$_5$H$_5$)] (generated *in situ*)[4],† Also, during the course of our studies into the reactivity of η^2(3e)-vinyl complexes of the type [Re{=C(Ph)C(H)Ph}-Br(PPh$_3$)(η-C$_5$H$_5$)] **A** (Scheme 1) we have discovered that protonation (HBF$_4$·Et$_2$O) in the presence of diphenylacetylene affords *trans*-stilbene, the cationic η^2(4e)-alkyne complex [Re(η^2-PhC$_2$Ph)Br(PPh$_3$)(η-C$_5$H$_5$)][BF$_4$] **B** and a trace amount of the X-ray crystallographically identified dicationic, oxygen-bridged species [Re$_2$Br$_2$(PPh$_3$)$_2$(μ-O)(η-C$_5$H$_5$)$_2$][(BF$_4$)$_2$] **C**.[6] Interestingly, in the absence of added alkyne the binuclear oxygen-bridged species is the only rhenium-containing species isolated (68% yield) from this reaction. In these latter two reactions we assume that protonation initially generates co-ordinated *trans*-stilbene to give a thermally unstable 16 e cationic complex, from which the alkene is readily displaced by either diphenylacetylene (to afford the mononuclear reaction product **B**) or a source of O^{2-} (to afford the dinuclear reaction product **C**). These observations suggested to us that *trans*-stilbene might also be displaced from the presumed intermediate by Bu^{t}C≡P, thereby affording a cationic complex containing an η^2(4e)-bonded phosphaalkyne.

Protonation (HBF$_4$·Et$_2$O, CH$_2$Cl$_2$, −78 °C) of [Re{=C(Ph)C(H)Ph}Br(PPh$_3$)(η-C$_5$H$_5$)] **A** followed by addition of Bu^{t}C≡P and subsequent warming to ambient temperature gave, after work-up of the reaction mixture, a neutral, green crystalline solid of formulation [ReBr{P(H)CBu^t}-(BF$_3$O)(PPh$_3$)(η-C$_5$H$_5$)] **1**, in 54% yield (Scheme 2). NMR spectroscopic measurements‡ clearly showed that the η^2(3e)-

vinyl group present in **A** had been lost, presumably as *trans*-stilbene, but also indicated that the hoped-for η^2(4e)-bonded phosphaalkyne complex had not been formed. In particular, the high-field resonance at δ −62.4 due to the phosphorus nucleus originally present in the phosphaalkyne is indicative of a one-electron donor phosphorus centre. Furthermore, this signal showed couplings to one hydrogen and three fluorine nuclei, suggesting that an unusual reaction had occurred. In order to elucidate the molecular structure of **1** it was necessary to carry out a single-crystal X-ray diffraction study. Suitable crystals were grown by the slow diffusion of hexane into a dichloro-methane solution of the complex.§
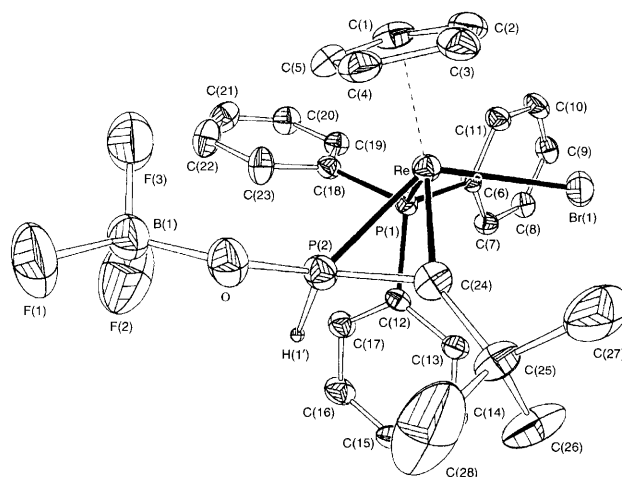
The solid-state structure of **1** is shown in Fig. 1, along with pertinent bond lengths and angles. As expected the rhenium

A

1a   **1b**
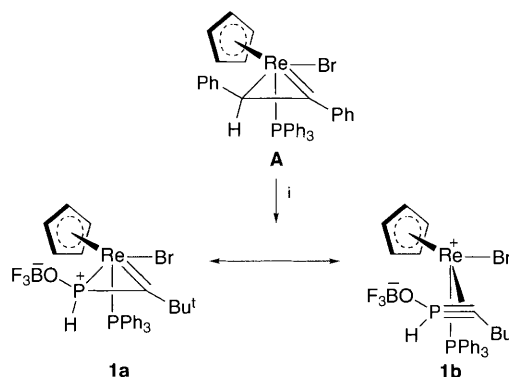
Scheme 2 *Reagents and conditions*: i, HBF$_4$·Et$_2$O, Bu^{t}C≡P, CH$_2$Cl$_2$, −78 to 25 °C, −*trans*-stilbene

Fig. 1 Molecular structure of **1**, thermal ellipsoids are shown at 30% probability. Pertinent bond lengths (Å) and angles (°): Re–P(1) 2.448(2), Re–P(2) 2.305(2), Re–Br(1) 2.570(1), Re–C(24) 1.958(7), P(2)–C(24) 1.699(7), P(2)–O 1.567(5), O–B(1) 1.465(11), P(1)–Re–Br(1) 85.48(4), P(1)–Re–C(24) 109.2(2), P(1)–Re–P(2) 90.51(6), Re–C(24)–C(25) 148.7(5), Re–C(24)–P(2) 77.8(3), Re–P(2)–C(24) 56.1(2), Re–P(2)–O 124.4(2), C(24)–P(2)–O 120.4(3).

A

B

C

[BF$_4$]$_2$

[BF$_4$] + **C** (< 10%)

Scheme 1 *Reagents and conditions*: i, HBF$_4$·Et$_2$O, PhC$_2$Ph, CH$_2$Cl$_2$, −78 to 25 °C, −*trans*-stilbene; ii, K[BHBu^s$_3$], CH$_2$Cl$_2$, −78 to 25 °C; iii, HBF$_4$·Et$_2$O, −78 to 25 °C, −*trans*-stilbene

carries a triphenylphosphine ligand, a bromide ligand and an η^5-bound cyclopentadienyl group. The remaining coordination sites are occupied by a $(F_3B^-)OP^+(H)C(Bu^t)$ fragment bound to the metal centre *via* the phosphorus and CBu^t atoms as a phospha-η^2(3e)-vinyl group. The Re–C(24) distance [1.958(7) Å] is in the accepted range for a Re=C double bond. However, the P(2)–C(24) length of 1.699(7) Å is significantly shorter than might be expected for a single bond [the average of the P–C bond lengths in the PPh_3 ligand is 1.838(3) Å], and is suggestive of a degree of multiple bond character resulting from a major contribution from the canonical form **1b**, formally containing the η^2(4e)-bonded λ^5-phosphaalkyne $(F_3B^-)OP(H)\equiv CBu^t$.

The bonding in **1** is different from that found in the previously reported compound $[ReCl_2\{\eta^4\text{-}N(COPh)PC(Bu^t)PC(Bu^t)\}\text{-}(PPh_3)]^9$ in that the phosphorus in the metallacycle $Re\{=C(Bu^t)P\}$ present in this molecule is in the oxidation state P^{III} with a long P–C distance [1.797(8) Å], whereas, in **1** a P^V centre is involved in multiple bonding to the adjacent carbon. The bonding in **1** is in fact more closely related to that found for the compounds $[Ta\{=C(H)PMe_2\}(H)_2(PMe_3)(\eta\text{-}C_5Me_5)]$ [Ta=C 2.005(10), Ta–P 2.480(2), P–C 1.714(9) Å]^{10} and $[Ta\{=C(H)PMe_2\}(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ [Ta=C 2.015(4), Ta–P 2.516(1), P–C 1.716(5) Å],^{11} for which it was also suggested that the canonical form formally having a coordinated λ^5-phosphaalkyne, $HC\equiv PMe_2$, makes a significant contribution to the bonding. Although structurally similar to **1**, these tantalum compounds were obtained by a very different method to the one described here, it being presumed that the 'TaCP' metallacycles in these compounds arise by a double intra-molecular C–H activation of a coordinated trimethylphosphine ligand.

The solution NMR data for **1**‡ are in accord with the structure determined in the solid state persisting in solution. Thus, the unsaturated carbon atom C(24) gives rise to a characteristic low-field resonance at δ 286.2 [*J*(CP) 30 Hz] in the $^{13}C\{^1H\}$ spectrum and a signal at δ 5.05 [*J*(HP) 587 and 7 Hz] in the proton spectrum is attributable to the PH hydrogen atom. The NMR spectra also show signals due to an isomeric species (*ca.* 6%) which we assign to the complex having the $(F_3B^-)OP^+(H)C(Bu^t)$ fragment rotated through 180° relative to the orientation shown in Fig. 1.

The incorporation of a 'BF$_3$O' moiety as well as an H atom into **1**, both of which become attached to the phosphorus atom of what was the phosphaalkyne, is most unusual and was totally unexpected, but can be rationalised in the light of our previous observations on the reactivity of the species formed upon protonation of complex **A**. Thus, it would appear that in the absence of added substrates capable of coordination the assumed primary product of protonation, *i.e.* $[Re\{\eta^2\text{-}trans\text{-}PhC(H)C(H)PPh\}Br(PPh_3)(\eta\text{-}C_5H_5)]^+$, is rapidly oxidised to an unsaturated rhenium–oxo compound which can be captured by the stilbene complex to give **C** (Scheme 1) or react with the added $Bu^tC\equiv P$ with subsequent transfer of oxygen from the metal to the phosphorus centre.¶ The exact source of the oxygen is at present unknown. However, the most likely origin could be the diethyl ether present in the acid or traces of water from the glassware or reagents. It is interesting to note that H_2O has been previously found to apparently add across the phosphorus-to-carbon triple bond of the η^1-phospha- alkyne which is present in the complex $[Re(\eta^1\text{-}PCBu^t)Cl(dppe)_2]$, to give an η^1-bonded phosphinidene oxide, $Bu^tCH_2P=O.^{12}$ The origin of the hydrogen atom, and consequently the BF_3, can almost certainly be traced to the Et_2O present in the acid. As shown in eqn. (1) abstraction of an hydride ion would give the cationic

$$EtOCH_2Me \xrightarrow{-H^-} [EtO^+=CHMe][BF_4^-]$$
$$\rightarrow EtOCH(F)CH_3 + BF_3 \qquad (1)$$
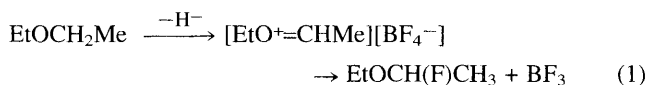
species $[MeCH_2O^+=CHCH_3]$, which might be expected to abstract fluoride from the BF_4^- counter anion, thereby generating BF_3.

Thus, in summary we have the first evidence of the apparent functionalisation, *i.e.* oxygenation, of the phosphorus centre present in an η^2-coordinated phosphaalkyne with interesting implications for reactivity studies, and the formation of unusual phosphorus substituted ligands.

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Footnotes

† It has been reported that treatment of $[Ti(\eta^2\text{-}Bu^tCP)(PMe_3)(\eta\text{-}C_5H_5)_2]$ with BEt_3 gives an equilibrium mixture of the η^2(4e)-phosphaalkyne complex $[Ti(\eta^2\text{-}Bu^tCP)(\eta\text{-}C_5H_5)_2]$ and the corresponding phosphorus bridging dimer. However, only the latter was isolated.^{5}

‡ *Selected NMR spectroscopic data* for **1** (CD_2Cl_2, 20 °C): ^1H δ 5.37 [d, 5 H, C_5H_5, *J*(HP) 1.1 Hz], 5.05 [dd, 1 H, PH, ^1J(HP) 587, ^3J(HP) 6.6 Hz], 1.51 (s, 9 H, Me); $^{13}C\{^1H\}$ δ 286.2 [d, Re=C, *J*(CP) 30 Hz], 91.0 (C_5H_5), 30.9 [d, CMe_3, *J*(CP) 8 Hz], 30.3 [d, CMe_3, *J*(CP) 5 Hz]; $^{31}P\{^1H\}$ δ 12.0 [d, PPh_3, *J*(PP) 27 Hz], −62.4 [ddq, $PCMe_3$, *J*(PH) 587, *J*(PP) 27, *J*(PF) 10 Hz]; $^{11}B\{^1H\}$ δ −0.7 (br).

§ *Crystal data* for **1**: $C_{28}H_{30}BBrF_3OP_2Re\cdot0.8CH_2Cl_2$, M = 846.32, triclinic, space group $P\bar{1}$ (no. 2), a = 9.484(2), b = 13.050(2), c = 14.184(3) Å, α = 86.58(2), β = 70.65(2), γ = 75.15(2)°, U = 1600.4(5) Å^3, Z = 2, D_c = 1.756 g cm^{-3}, μ(Mo-Kα) = 53.2 cm^{-1}, F(000) = 823.2. Data were collected at 293 K on a CAD4 automated four-circle diffractometer in the range $2.18 \le \theta \le 23.92°$. 4222 independent reflections with $F_o > 4\sigma(F_o)$ were collected and corrected for Lorentz, polarisation, and X-ray absorption effects.^{7} The structure was solved by Patterson methods and refined using the SHELX suite of programs,^{8} to yield a final $R1$ = 0.0318, $wR2$ = 0.0746 for a weighting scheme of w = $[\sigma^2(F_o^2)$ + $(0.0412P)^2 + 4.9869P]^{-1}$, where P = $(F_o^2 + 2F_c^2)/3$. The atom $H(1')$ was located in a difference-Fourier synthesis and allowed to refine isotropically at a distance of 1.45 Å from the parent phosphorus atom during the final stages of refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallo-graphic Data Centre. See Information for Authors, Issue No. 1.

¶ To avoid protonation of the phosphaalkyne the latter reagent was added to the reaction mixture only after the acid had time to react completely.

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