Complete metal-mediated reduction of the triple bond of a phosphaalkyne: X-ray structure of $[Ru(PHFCH_2Bu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]BF_4\cdot CH_2Cl_2$

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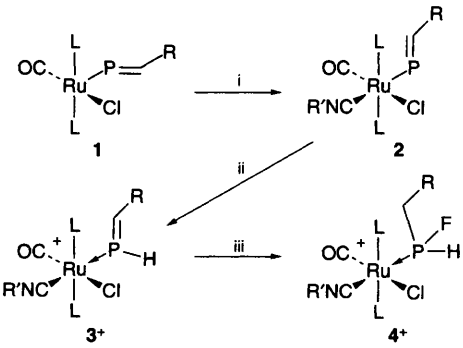
The reaction of $[Ru(P{=}CHBu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ with HBF_4 provides, rapidly and reversibly, the phosphaalkene complex $[Ru(HP{=}CHBu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]^+$ which is converted by $K[HF_2]$ or $[NBu^n_4]F$ to the structurally characterised fluorophosphine complex $[Ru(PHFCH_2Bu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]^+$.

Phosphines bearing both a proton and a nucleofugic group PHXR (X = F, Cl, Br, OMe) are independently unstable with respect to HX elimination and formation of oligomeric compounds of the form $(PR)_n$. Complexes of such phosphines, have, however, been prepared by elaboration of the phosphine within the protective environment of metal coordination spheres.[1] In this report we discuss the synthesis and structural characterisation of a complex of the unstable phosphine $PHFCH_2Bu^t$, demonstrating for the first time the complete reduction of the triple bond of a phosphaalkyne, $P{\equiv}CBu^t$, within the coordination sphere of divalent ruthenium.

Hydroruthenation of $P{\equiv}CBu^t$ by $[RuHCl(CO)(PPh_3)_3]$ provides the remarkably stable, though highly reactive, phosphaalkenyl complex $[Ru(P{=}CHBu^t)Cl(CO)(PPh_3)_2]$ **1**.[2] The *apparent* coordinative unsaturation of **1** allows the introduction of two-electron ligands *e.g.* $CNC_6H_3Me_2$-2,6 to provide $[Ru(P{=}CHBu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ **2**.† The effective atomic number requirements of the ruthenium centre in this complex dictate that the phosphaalkenyl ligand has a non-linear and therefore potentially nucleophilic (at P) Ru–P–C linkage. Treating a dichloromethane solution of **2** with $HBF_4\cdot OEt_2$ followed immediately by precipitation with diethyl ether provides the phosphaalkene salt $[Ru(HP{=}CHBu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]BF_4$ **3**BF_4 (Scheme 1). The gross molecular formulation follows from FABMS data,† and the site of protonation is unambiguously determined from NMR spectroscopy. In particular, the proton-coupled ^{31}P NMR spectrum is informative. This reveals a peak at δ 164.3 showing coupling to two chemically equivalent phosphine phosphorus nuclei [^2J(PP) 47.5 Hz] and one proton [^1J(PH) 376.4 Hz], this latter coupling disappearing upon proton decoupling of the spectrum. The protonation is reversible upon treatment with a non-nucleophilic base (dbu); however if the crude complex is left to stand in solution (1–2 d) a second product forms which on the basis of spectroscopic† and crystallographic data‡ has been characterised as the fluorophosphine salt $[Ru(PHFCH_2Bu^t)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]BF_4$ **4**BF_4. The ^{31}P NMR resonance arising from the phosphorus of the fluorophosphine appears at δ 161.8 showing coupling to the phosphorus centres of the two PPh_3 ligands [^2J(PP) 30.5 Hz], one proton [^1J(PH) 418 Hz, identified by proton coupling] and the fluoride substituent [^1J(PF) 844 Hz].



Scheme 1 *Reagents and conditions*: i, CNR′; ii, $HBF_4\cdot OEt_2$; iii, $K[HF_2]$ or $[NBU^n_4]F$. L = PPh_3, R = CMe_3, R′ = $C_6H_3Me_2$-2,6.

The molecular geometry of the cation **4**$^+$ is shown in Fig. 1 and reveals an essentially octahedral geometry at ruthenium [*cis* inter-ligand angles of 83.7(2)–93.7(2)°]. The stereochemistry at ruthenium, involving $PHFCH_2Bu^t$ *trans* to $CNC_6H_3Me_2$, confirms those proposed (Scheme 1) for complexes **2** and **3**$^+$. Interest focuses on those parameters associated with the fluorophosphine ligand. The fluorine and hydrogen substituents are disordered (1 : 1) within the crystal, however the chiral tetrahedral coordination at phosphorus is clearly defined, with a ruthenium–phosphorus separation of 2.352(2) Å suggesting an enhanced π-acid rôle for this phosphine relative to that of PPh_3 [Ru(1)–P(2) 2.431(2), Ru(1)–P(3) 2.443(2) Å], despite coordination *trans* to a π-acid ligand. This is also perhaps marginally reflected in the P(1)–F(5) [1.563(7) Å] and P(1)–F(6) [1.562(7) Å] distances which are somewhat long when compared to free fluorophosphines but more typical of those for coordinated PF_3. The P(1)–C(11) bond at 1.794(6) Å is particularly short for a P–C single bond and this is also reflected in the Ru–P(1)–C(11) angle of 120.1(2)°.

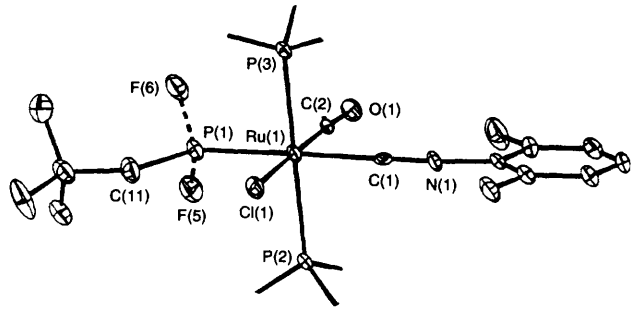
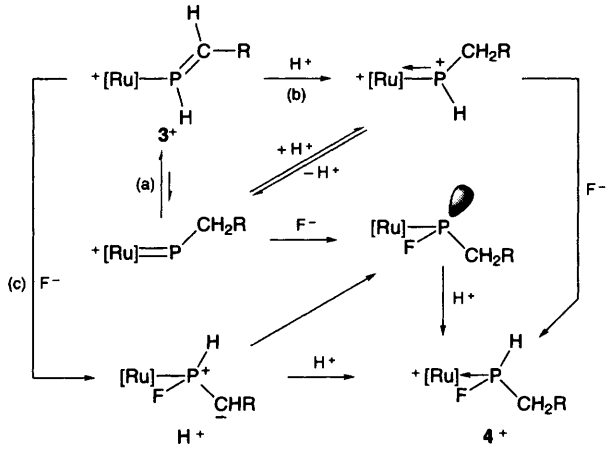


Fig. 1 Molecular geometry of **4**$^+$. Hydrogen atoms and phenyl groups omitted. F(5) and F(6) represent sites refined with 50% occupancy. Thermal ellipsoids represent 30% probability levels. Selected structural features: Ru–P(1) 2.352(2), Ru–P(2) 2.430(2), Ru–P(3) 2.443(3), Ru–Cl(1) 2.445(2), Ru–C(1) 2.052(7), Ru–C(2) 1.868(6), P(1)–F(5) 1.563(7), P(1)–F(6) 1.562(7) P(1)–C(11) 1.794(6) Å; Ru–P(1)–F(5) 114.1(3), Ru–P(1)–F(6) 111.0(3), Ru–P(1)–C(11) 120.1(2)°.

Recently a fluorophosphaalkene salt $[FeH(PF{=}CHBu^t)(dppe)_2][FeCl_2F_2]$ has been obtained from the decomposition of an iron hydrido–phosphaalkyne complex $[FeH(P{\equiv}CBu^t)(dppe)_2]BF_4$.[3] Such a ligand might initially appear a mechanistic candidate for the ultimate formation of $\mathbf{4}BF_4$ from **2**; however, we are inclined rather to favour one of the processes outlined in Scheme 2. Two mechanistic proposals which would feature fluorophilic phosphorus centres are considered. The first (route a) involves a 1,2 proton shift to provide an electrophilic phosphinidene which abstracts fluoride to generate a neutral (and therefore pyramidal and nucleophilic) fluorophosphido complex which may be subsequently protonated. The second (route b) proceeds *via* a second protonation of the phosphaalkene β to the metal to generate a dicationic (and therefore trigonal and electrophilic) phosphenium complex which abstracts fluoride from BF_4. We favour the former mechanism for the following reasons. (*i*) Recrystallised samples of $\mathbf{3}BF_4$ are indefinitely stable in dichloromethane solution. (*ii*) Treating purified $\mathbf{3}BF_4$ with a small excess (2–3 equiv.) of commercial $HBF_4{\cdot}OEt_2$ leads to initial formation of a small amount of $\mathbf{4}BF_4$ however the reaction stops after approximately 10% conversion suggesting that protons are not the limiting reagent but rather an impurity present in the acid. We believe this to be fluoride anion (HF). (*iii*) Treating $\mathbf{3}BF_4$ with $K[HF_2]$ in tetrahydrofuran causes complete conversion, although $\mathbf{4}BF_4$ is eventually decomposed by excess of this reagent to provide a plethora of uncharacterised compounds. (*iv*) Treating purified $\mathbf{3}BF_4$ with $[NBu^n_4]F$ leads to formation of $\mathbf{4}BF_4$. Thus the limiting reagent appears to be fluoride. Direct attack by fluoride at the trigonal phosphorus of $\mathbf{3}^+$ seems less likely in that it would provide the metallated ylide (route c). This possibility can however not be excluded since such a ligand could be expected to undergo rapid 1,2-hydrogen shift to provide the fluoroneopentylphosphido ligand. It should also be noted that the hypothetical phosphinidene and phosphenium intermediates represent an acid–base conjugate pair which are in principle interconvertible.



Scheme 2 Mechanisms for the hydrofluorination of coordinated phosphaalkene. (a) Phosphinidene route; (b) phosphenium route; (c) ylide route. [Ru] = $RuCl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2$.

The proposed phosphaalkene/phosphinidene tautomerism offers considerable promise for synthetic applications. We are therefore currently investigating the possibility of generating such species in the presence of nucleophiles other than fluoride as a route to further functionalised but independently unstable phosphines.

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Footnotes

† *Data*: for **2**: Yield 69% (0.2 mmol scale). IR (Nujol) 2121vs, 2111(sh) ν(NC), 1962vs ν(CO), 1250m, 863w cm^{-1}; (CH_2Cl_2) 2109vs ν(NC), 1960vs ν(CO) cm^{-1}. NMR (CD_2Cl_2, 25 °C) ^1H: δ 0.86 (s, 9 H, CMe_3), 2.10 (s, 6 H, $C_6H_3\mathit{Me}_2$), 6.98, 7.06 (2 × m, 3 H, C_6H_3), 7.29, 7.81 (2 × m, 30 H, Ph), 8.10 [dt, 1 H, P=CH, ^2J(PH) 19.2 Hz, $^3J(P_2H)$ not resolved at 400 MHz], $^{31}P\{^1H\}$: δ 391.0 [t, P=CH, ^2J(PP) 11.1 Hz], 24.5 [d, PPh, ^2J(PP) 11.1 Hz]. FABMS: *m/z* 922 (45%) $[HM]^+$.

For $\mathbf{3}BF_4$: Yield 68% (0.25 mmol scale). IR (Nujol) 2161vs ν(NC), 2005 ν(CO) cm^{-1}; (CH_2Cl_2) 2163 ν(NC), 2008 ν(CO) cm^{-1}. NMR (CD_2Cl_2, 25 °C) ^1H: δ 0.81 (s, 9 H, CMe_3), 2.07 (s, 6 H, $C_6H_3\mathit{Me}_2$), 5.72 [dd, 1 H, HP=C, ^3J(HH) 20.5, ^1J(PH) 374.5 Hz], 7.08, 7.22 [2 × m, 3 H, C_6H_3], 7.45, 7.72 [2 × m, 31 H, Ph and P=CH]. $^{31}P\{^1H\}$: δ 164.1 [t, P=CH, ^2J(PP) 47.5 Hz], 18.2 [d, PPh, ^2J(PP) 47.5 Hz]. ^{31}P–proton coupled: δ 164.3 [t, P=CH, ^2J(PP) 47.5, ^1J(PH) 376.4 Hz], 18.1 [d, PPh, ^2J(PP) 47.5 Hz]. FABMS: *m/z* 922 (82%) $[M]^+$.

For $\mathbf{4}BF_4$: IR (CH_2Cl_2) 2197vs ν(NC), 2003vs ν(CO) cm^{-1}. NMR (CD_2Cl_2, 25 °C) $^{31}P\{^1H\}$: 161.8 [dt, PFH, ^2J(PP) 30.5 ^1J(PF) 844 Hz], 24.4 [dd, PPh, ^2J(PP) 30.1, ^3J(FP) 10.1 Hz]. ^{31}P–proton coupled: δ 161.7 [ddt, PFH, ^2J(PP) 33, ^1J(PF) 851, ^1J(PH) 418 Hz]. FABMS: *m/z* 942 (51%) $[M]^+$.

‡ *Crystal data for* $\mathbf{4}BF_4{\cdot}CH_2Cl_2$. $C_{52}H_{53}BCl_2F_5NOP_3Ru$, M = 1114.09, triclinic, space group $P\bar{1}$ (no. 2), a = 12.129(4), b = 13.815(3), c = 17.279(4) Å, α = 72.18(2), β = 87.00(2), γ = 69.62(3)°, Z = 2, U = 2579.1(12) $Å^3$, D_c = 1.435 g cm^{-3}, $F(000)$ = 1140, μ(Mo-Kα) = 6.09 cm^{-1}; 2θ < 50.1° (Mo-Kα), λ = 0.71069 Å. Fast area detector diffractometer, 150(2) K. The structure was solved by direct methods and refined on F^2 with all non-hydrogen atoms anisotropic and hydrogen atoms other than that bound to P(1) included in calculated positions to give R_1 = 0.053 and wR_2 = 0.131 for 7066 independent observed reflections with $|F_o| > 4\sigma(|F_o|)$ and 636 parameters. Further details of the crystal structure investigation are available from the authors (D. E. H., M. B. H. and K. M. A. M.). 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 182/105.

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