

Hydroruthenation of Prop-2-ynyltriphenylphosphonium Bromide: Synthesis, Crystal Structure and Reactions of $[\text{RuBr}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$

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The reaction of the complex $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ with prop-2-ynyltriphenylphosphonium bromide ($[\text{Ph}_3\text{PCH}_2\text{C}\equiv\text{CH}]\text{Br}$) followed by NH_4PF_6 provides the crystallographically characterised salt $[\text{RuBr}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ which by virtue of the coordinative unsaturation at the ruthenium centre undergoes addition of the ligands $\text{CNC}_6\text{H}_3\text{Me}_2$ -2,6, and CO to Ru and insertion of SO_2 into the Ru–C σ -bond.

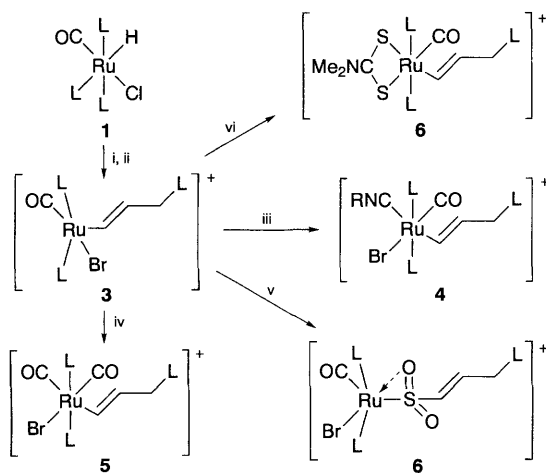
The phosphonium salt obtained from the reaction of triphenylphosphine with prop-2-ynyl bromide, $[\text{Ph}_3\text{PCH}_2\text{C}\equiv\text{CH}]\text{Br}$, represents an example of a class of cationic alkynes which should display unusual coordination chemistry. We report herein the reaction of this activated alkyne with the hydridoruthenium complex $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$, the structural characterisation of the product, and preliminary reactivity studies.

The reaction of $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ **1** with $[\text{Ph}_3\text{PCH}_2\text{C}\equiv\text{CH}]\text{Br}$ **2** in dichloromethane followed by treatment with an ethanolic solution of NH_4PF_6 provides the orange salt $[\text{RuBr}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ (**3**· PF_6)[†] which features a σ -*E*-vinyl ligand resulting from the *cis* addition of the ruthenium hydride bond to the activated alkyne. Under mild conditions partial substitution of the chloride ligand in the precursor complex for the bromide counter ion of the phosphonium salt occurs; however if the reaction is carried out in refluxing ethanol, metathesis is complete (Scheme 1). The characterisation of **3**· PF_6 included an X-ray diffraction analysis[‡] (Fig. 1) that confirmed the coordination sphere of ruthenium and the geometry of the unusual *hetero*-vinyl ligand. The vinylic Ru–C separation of 2.012 Å is unremarkable for vinyl ligands coordinated to divalent ruthenium¹ despite the presence of the phosphonium group. The ruthenium coordination is square pyramidal [Ru(1) displaced by *ca.* 0.2 Å from the basal plane] and coordinatively unsaturated despite the possibility of σ - π vinyl coordination. A similar preference for coordinative unsaturation has been observed for the related σ -vinyl complex $[\text{RuCl}(\text{CPh}=\text{CHPh})(\text{CO})(\text{PPh}_3)_2]$ prepared from **1** and diphenyl acetylene.² The orientation of the vinyl plane perpendicular to the P(1)–P(2) vector is consistent with both a π -acceptor role and the steric requirements of the bulky phosphonium substituent.

The coordinative unsaturation at ruthenium in **3** is reflected in subsequent reactions with potential ligands. Treatment of **3** with 2,6-dimethylphenylisonitrile ($\text{CNC}_6\text{H}_3\text{Me}_2$ -2,6) provides the yellow salt $[\text{RuBr}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ **4**.[†] A similar colourless *cis*-dicarbonyl derivative of formulation $[\text{RuBr}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{CO})_2(\text{PPh}_3)_2]\text{PF}_6$ **5**[†] may be isolated from solutions of **3** treated with carbon monoxide. No evidence for migratory insertion processes was obtained for either of the above reactions suggesting an enhanced Ru–C bond strength due to the β -phosphonomethyl vinyl substituent.

The reaction of **3** with sulfur dioxide was compared with that previously reported for the simple σ -tolyl complex $[\text{RuCl}(\text{C}_6\text{H}_4\text{Me}-4)(\text{CO})(\text{PPh}_3)_2]$:³ an immediate decolourisation occurs upon passing a stream of SO_2 through solutions of **3** and the insertion compound $[\text{RuBr}(\text{SO}_2\text{CHCH}_2\text{PPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ **6**[†] is obtained. As in the case of $[\text{RuCl}(\text{SO}_2\text{C}_6\text{H}_4\text{Me}-4)(\text{CO})(\text{PPh}_3)_2]$,³ a weakly bidentate *S,O*-sulfinato complex appears to be formed with IR activity assignable to $\nu(\text{SO}_2)$ being observed at 1045, 975 and 942 cm^{-1} .

Reaction of **3** with dimethyldithiocarbamate anion provides the expected 18-electron cationic complex $[\text{Ru}(\text{CH}=\text{CHCH}_2\text{PPh}_3)(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]\text{PF}_6$ **7**; however treating **3** with potentially basic ligands leads to an as yet obscure reaction involving loss of the σ -vinyl ligand and replacement with hydride. Thus, *e.g.* dimethylpyrazole and $\text{NMe}_4[\text{B}_3\text{H}_8]$ provide $[\text{RuBrH}(\text{CO})(\text{PPh}_3)_2(\text{HpzMe}_2)]$ (pz = pyrazol-1-yl) and $[\text{RuH}(\text{B}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$,⁴ respectively and ethanolic KOH in the presence of PPh_3 provides $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$. The most plausible mechanism involves β -Ru–H elimination to generate the original propargylphosphonium salt, however, we note that this reaction also proceeds very readily with the coordinatively saturated derivative **7** to provide $[\text{RuH}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]$.



Scheme 1 Reagents and conditions: i, $[\text{Ph}_3\text{PCH}_2\text{C}\equiv\text{CH}]\text{Br}$; ii, NH_4PF_6 , $-\text{NH}_4\text{Cl}$; iii, $\text{CNC}_6\text{H}_3\text{Me}_2$ -2,6; iv, CO; v, SO_2 ; vi, $\text{NaS}_2\text{CNMe}_2$ $-\text{NaBr}$. L = PPh_3 ; R = $\text{C}_6\text{H}_3\text{Me}_2$ -2,6.

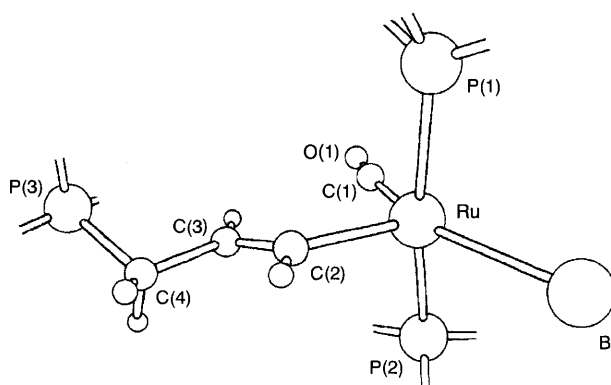


Fig. 1 The molecular geometry of the cation of **3**. Phenyl rings omitted for clarity. Hydrogen atoms in calculated positions. Bond distances (Å) are: Ru–P(1) 2.371(4), Ru–P(2) 2.357(4), Ru–Br 2.541(2), Ru–C(1) 1.898(16), Ru–C(2) 2.012(10), C(2)–C(3) 1.320(14), C(3)–C(4) 1.468(16), C(4)–P(3) 1.793(11) Å. Ru(1) is displaced from the plane defined by Br, C(1), P(1), and P(2) by 0.2 Å.

When **3** is treated with a non-nucleophilic base (DBU) in dichloromethane the acidic allylic/ α -phosphonio proton is removed and we are currently investigating the pseudo-Wittig chemistry of this species as a precursor to further and otherwise unaccessible γ -functionalised σ -vinyl ligands.

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Footnotes

† Spectroscopic data for **3**·PF₆: Yield 54%. IR (CH₂Cl₂): 1932 [ν (CO)]; (Nujol) 1946, 1911 cm⁻¹ [ν (CO)]. A band which occurs at ca. 1113 cm⁻¹ for **3** and its derivatives **4**·PF₆–**6**·PF₆ is apparently associated with and characteristic of the CHCHCH₂PPh₃ moiety. ¹H NMR data (CDCl₃) for **3** and its derivatives were not readily amenable to detailed analysis due to the extreme insolubility of the compounds and the complex splittings produced by the P₂RuCHCHCH₂P spin systems: δ 3.4–3.6 [q(br), CH₂ PPh₃], 4.0–4.15 [m(br), 1 H, RuCHCHCH₂], 7.98 [d(br), 1 H, P₂RuCHCH]. ³¹P {¹H} NMR (CDCl₃) δ 35.4 (s, Ru–P), 16.00 (s, CH₂–P), FABMS *m/z* 756 [M–CH₂PPh₃]⁺.

For **4**·PF₆: Yield 70%. IR (CH₂Cl₂): 2149 [ν (C \equiv N)], 1967 [ν (CO)]; (Nujol): 2124 [ν (C \equiv N)], 1958 [ν (CO)], 1113 cm⁻¹. ¹H NMR (CDCl₃) δ 2.00 (s, 6 H, C₆H₃Me₂), 3.4, 4.6, (2xm, 3 H, CH CH₂), 6.85–7.8 (m, 48 H, C₆H₅ and C₆H₃), 8.08 [d, 1 H, RuCH, *J*(HH) 14.7 Hz]. ³¹P{¹H} NMR

(CDCl₃) δ 26.88, 25.67 (2xs, Ru–P), 16.87 (s, CH₂–P), FABMS: *m/z* 1167 [M]⁺, 904 [M–PPh₃]⁺.

For **5**·PF₆: Yield 85%. IR (CH₂Cl₂) 2042, 1980 [ν (CO)]; (Nujol): 2040, 1977 [ν (CO)], 1114 cm⁻¹ [CH=CHCH₂PPh₃]. ¹H NMR (CDCl₃) δ 3.4, 4.6 (2xm, 3 H, CHCH₂P), RuCH obscured by PC₆H₅. ³¹P{¹H} NMR (CDCl₃) δ 24.00, 23.41 (2xs, Ru–P), 18.23 (s, CH₂–P).

For **6**·PF₆: Yield 58%. IR (Nujol): 1968 [ν (CO)], 1045, 975, 942 cm⁻¹ [ν (SO₂)]. ¹H NMR (CDCl₃) δ 4.68 [s(vbr) 3 H, RuCHCHCH₂].

‡ Crystal data for C₅₂H₄₉BrF₆OP₄Ru, *M_r* = 1108.817, monoclinic, P2₁/*n*, *a* = 14.232(9), *b* = 17.317(10), *c* = 21.873(12) Å, β = 101.86(5)°, *U* = 5276(5) Å³, *Z* = 4, *D_c* = 1.40 g cm⁻³, orange prisms, *F*(000) = 2248, λ (Mo-K α) = 0.710 69 Å, μ (Mo-K α) = 12.2 cm⁻¹, θ_{\max} 50°, 4967 observed reflections [*I* > 2 σ (*I*)] were collected on a Syntex P2₁ four-circle diffractometer, and corrected for Lorentz polarisation and absorption effects. The structure was solved by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement converged with *R* = 0.078 (*R_w* = 0.10). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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