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Ruthenium complexes containing butatrienylidene and related ligands: synthesis, characterisation and chemistry

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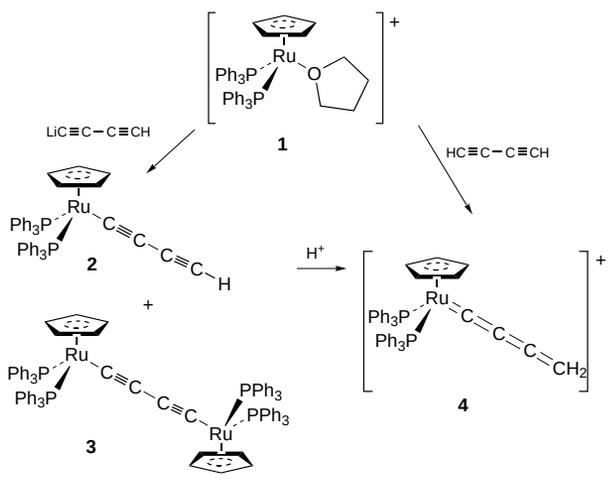
The reaction of buta-1,3-diyne with $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (thf = tetrahydrofuran) to give $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ has been studied. This complex adds nucleophiles at C_γ, as expected from theory and consideration of the protection afforded to C_α by the bulky PPh_3 ligands. The products were alkenylethynyl complexes (from aprotic nucleophiles) or methylallenylidene complexes (from protic nucleophiles, with H migration to C_δ). With water, the complex $[Ru\{C{\equiv}CC(O)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ is formed. The single-crystal structures of $[Ru\{C{=}C{=}CMe(X)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (X = NPh_2 or C_4H_3NMe-2) and $[Ru(C{\equiv}CCH{=}CHCl\text{-}trans)(PPh_3)_2(\eta\text{-}C_5H_5)]$ have been determined.

The chemistry of transition-metal complexes containing unsaturated carbene ligands continues to attract attention. Most is known about the simplest of these ligands, vinylidene,[1] and complexes containing these species are likely intermediates in coupling of alkynes to give enynes[2] or butatrienes,[3] and in the synthesis of unsaturated ketones from alkynes and allylic alcohols.[4] The next higher member, allenylidene, is receiving increased attention, and much novel chemistry has been reported recently.[1,5] Complexes containing five-carbon chains have recently been isolated for the first time, albeit protected with aryl groups,[6,7] while a complex with a seven-carbon chain is considered to be an intermediate in the formation of an alkenylpentatrienylidenetungsten derivative.[8] However, complexes containing even-numbered carbon chains appear to be restricted to the ruthenium–butatrienylidene complex trapped by addition of trifluoroacetate to C_γ described by Lomprey and Selegue.[9]

Theoretical calculations on the reactivity of unsaturated carbon chains attached to metals suggest[10] that the carbon atoms are alternatively electron-poor and electron-rich, as one moves along the chain from the metal centre: $M{=}C_\alpha^{\delta+}{=}C_\beta^{\delta-}{=}C_\gamma^{\delta+}{=}C_\delta^{\delta-}{=}\ldots$ This behaviour is also found in the case of alkynyl ligands, in which C_β is a strong nucleophile, being readily attacked by electrophiles such as H^+, R^+, $R'N_2^+$ (R′ = aryl), Me_3S^+ or $C_7H_7^+$, for example.[1] The protonation of vinylidenes to carbynes reflects the ease of addition of electrophiles to C_β.[11] Similarly, allenylidene complexes are well known for their tendency to add nucleophiles at C_γ.[5,12] Extensive studies of the series of complexes containing $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ or $Ru(PR_3)_2(ind)$ (ind = $\eta^5\text{-}C_9H_7$) have been reported recently.[13–15]

We have begun an investigation into the chemistry of both mono-[16] and poly-nuclear complexes[17] derived from 1,3-diynes. In particular, we were interested to determine whether addition of 1-substituted 1,3-diynes to metal centres where the 1,2-H shift is well established for alk-1-ynes would proceed analogously to give alkynylvinylidenes or would lead to the sought-after butatrienylidenes. As far as we are aware, the only report describing a derivative of this ligand is that of Lomprey and Selegue,[9] mentioned above, who treated $[Ru\{C{\equiv}CC(O)Pr^i\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ with $(CF_3CO)_2O$ to give $[Ru\{C{\equiv}CC(OCOCF_3)CMe_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ which was considered to resemble the corresponding cation $[Ru(C{=}C{=}C{=}CMe_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ trapped by addition of a trifluoroacetate anion to C_γ. We have recently communicated the synthesis of a cationic intermediate, obtained from reactions between



Scheme 1

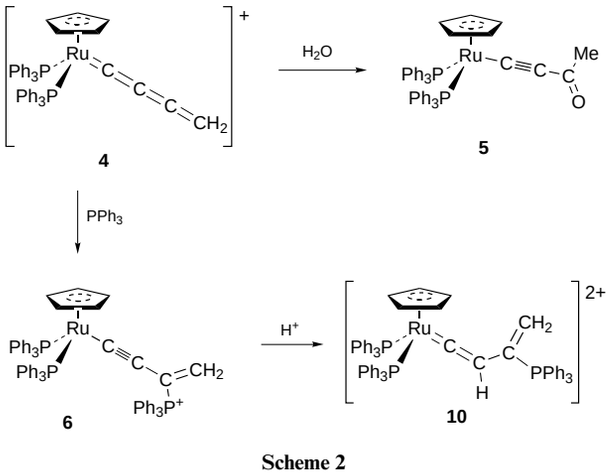
$[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (thf = tetrahydrofuran) and buta-1,3-diyne, which appears from its reactions to be a complex containing the parent ligand, **:**C=C=C=CH_2.[18] This paper reports these studies in detail, including X-ray structural studies of derived alkynyl complexes. In a separate investigation, we have also found that combination of a cluster-bound C_2 ligand with vinylidene, produced *in situ* from $HC{\equiv}CSiMe_3$, followed by desilylation, produces the same ligand, which is stabilised by an Ru_5 cluster.[19]

Results

Synthesis of $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ 4

The synthesis of $[Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **2** (Scheme 1) was readily achieved by reaction of $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **1** {obtained in solution from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $AgPF_6$ in tetrahydrofuran, followed by removal of the precipitated AgCl} with LiC≡CC≡CH (from LiBu and buta-1,3-diyne). This chemistry has been described elsewhere[20] and the product is accompanied by the μ-C_4 complex $[\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4)]$ **3**, which is also the source of much interesting chemistry.[21]

Protonation of complex **1** occurred directly at C_δ to give the cationic butatrienylidene complex $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **4**, the first complex containing the parent ligand to be characterised. The synthesis of **4** was more conveniently



Scheme 2

performed by the direct reaction of buta-1,3-diyne with $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$.[20] The compound is exceedingly reactive and we have not been able to isolate it in a pure state. Instead, it has been characterised by examining the products obtained from reactions with a variety of substrates.

We have not been able to determine whether formation of complex **4** proceeds *via* an initial 1,2-H shift to give the ethynylvinylidene complex, which then further rearranges to **4**, or whether a direct 1,4-H shift is involved. The vinylidene would be expected to be a relatively strong acid [*cf.* the pK_a for the C=CHMe complex of 7.78 (in thf–water, 2 : 1)],[22] so that migration of the proton from C_β to C_δ would be expected to be a facile process.

The structure of complex **4** can be expressed as a series of mesomeric formulae **4a**–**4c**, from which the electron-poor nature of C_α and C_γ can be appreciated, in agreement with the more sophisticated molecular orbital (MO) studies discussed below. Consequently, addition of nucleophiles at either of these

$$[Ru]^+{=}C{=}C{=}C{=}CH_2 \Longleftrightarrow [Ru]{-}C^+{=}C{=}C{=}CH_2 \Longleftrightarrow [Ru]{-}C{\equiv}C{-}C^+{=}CH_2$$

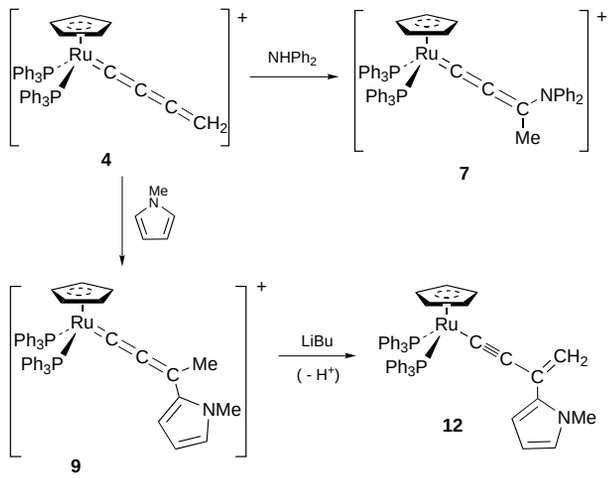
4a **4b** **4c**

carbon atoms would be expected. However, the steric protection afforded to C_α by the large PPh_3 ligands suggests that addition to C_γ would be preferred.

Reactions of $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ 4 (Schemes 2 and 3)

(*a*) **PPh_3.** The reaction of complex **4** with PPh_3 gave the cationic alkenynyl complex $[Ru\{C{\equiv}CC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **6** as a yellow powder. The IR spectrum contains ν(C≡C) at 2032 cm^{-1}, while the ^1H NMR spectrum contains the C_5H_5 resonance at δ 4.03. In the ^{13}C NMR spectrum the Ru–C resonance is found at δ 110.4 and the C_5H_5 resonance at δ 85.7. These data are consistent with the substituted ethynyl formulation illustrated, in which the positive charge is localised on the phosphonium P atom, rather than a vinylidene-like tautomer.

(*b*) **$NHPh_2$.** In complex **4**, protonic nucleophiles are expected to react with the metal, or with C_α or C_γ. An intramolecular migration of the proton to C_β or C_δ can also occur. The reaction with $NHPh_2$ proceeds *via* nucleophilic addition to C_γ to give the allenylidene complex $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **7**. In the IR spectrum of **7** a band at 1998 cm^{-1} can be assigned to the Ru=C=C=C system, while in the ^{13}C NMR spectrum the metal-bonded carbon is found at δ 219.2. Atoms C_β and C_γ resonate at δ 153.0 and 145.4 (although they cannot be specifically assigned). The C_5H_5 group gives rise to the resonances at δ 4.29 (^1H) and 88.7 (^{13}C). No evidence for the formation of the isomeric vinylidene cation $[Ru\{C{=}CHC(NPh_2){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ was obtained.



Scheme 3

Table 1 Significant bond lengths (Å) and angles (°) for complexes **7**, **9** and **11**

	7 (molecules 1, 2)	**9**	**11**
Ru–P(1)	2.306(4), 2.306(4)	2.312(3)	2.289(2)
Ru–P(2)	2.306(4), 2.310(5)	2.313(4)	2.286(2)
Ru–C (C_5H_5)	2.21–2.27(2)	2.21–2.26(1)	2.210–2.242(8)
(average)	2.24	2.24	2.229
Ru–C(1)	1.94(1), 1.97(1)	1.92(1)	2.002(6)
C(1)–C(2)	1.22(2), 1.18(2)	1.24(2)	1.206(9)
C(2)–C(3)	1.36(2), 1.41(2)	1.37(2)	1.41(1)
C(3)–C(4)			1.26(1)
C(3)–C(30)		1.49(1)	
C(3)–C(31)	1.50(2), 1.50(2)	1.40(2)	
C(4)–Cl(4)			1.71(1)
C(3)–N	1.33(2), 1.34(2)		
P(1)–Ru–P(2)	100.0(1), 102.0(1)	99.6(1)	102.08(7)
P(1)–Ru–C(1)	92.1(4), 92.7(4)	87.9(3)	90.1(2)
P(2)–Ru–C(1)	89.7(1), 88.0(4)	92.2(3)	85.0(1)
Ru–C(1)–C(2)	174(1), 171(1)	173.5(8)	176.5(5)
C(1)–C(2)–C(3)	173(2), 178(2)	172(1)	175.3(6)
C(2)–C(3)–C(4)			126.9(7)
C(2)–C(3)–C(30)		118(1)	
C(2)–C(3)–C(31)	121(1), 120(1)	125.7(9)	
C(2)–C(3)–N	122(1), 120(1)		
C(3)–C(4)–Cl(4)			125.4(7)

The crystal structure of complex **7** was reported in our preliminary communication,[18] but the salient features (Fig. 1, Table 1) are worthy of discussion here. A conventional $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ group is attached to the heterosubstituted vinylidene *via* C(1) [Ru–C(1) 1.94(1) Å], with the C(1)–C(2) and C(2)–C(3) separations being 1.22(2) and 1.36(2) Å, respectively (values for molecule 1 given: those for molecule 2 did not differ significantly). Two tautomeric forms **7a** and **7b** may be written and the relative shortness of the C(1)–C(2) separation implies a major contribution from the alkynyl tautomer $[Ru(C{\equiv}CCMe{=}N^+Ph_2)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **7b**, which contributes to the stability of this complex. The three-carbon chain is approximately linear [angles at C(1) and C(2) are 174(1) and 173(2)°, respectively].

$$[Ru]^+{=}C{=}C{=}CMe(NPh_2) \Longleftrightarrow [Ru]{-}C{\equiv}C{-}CMe{=}N^+Ph_2$$

7a **7b**

(*c*) **Water.** With water the acetylethynyl complex $[Ru\{C{\equiv}CC(O)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ **5**, was obtained. This complex has been fully characterised by an X-ray structural study[20] so the only comment we make here is that it is probably formed by

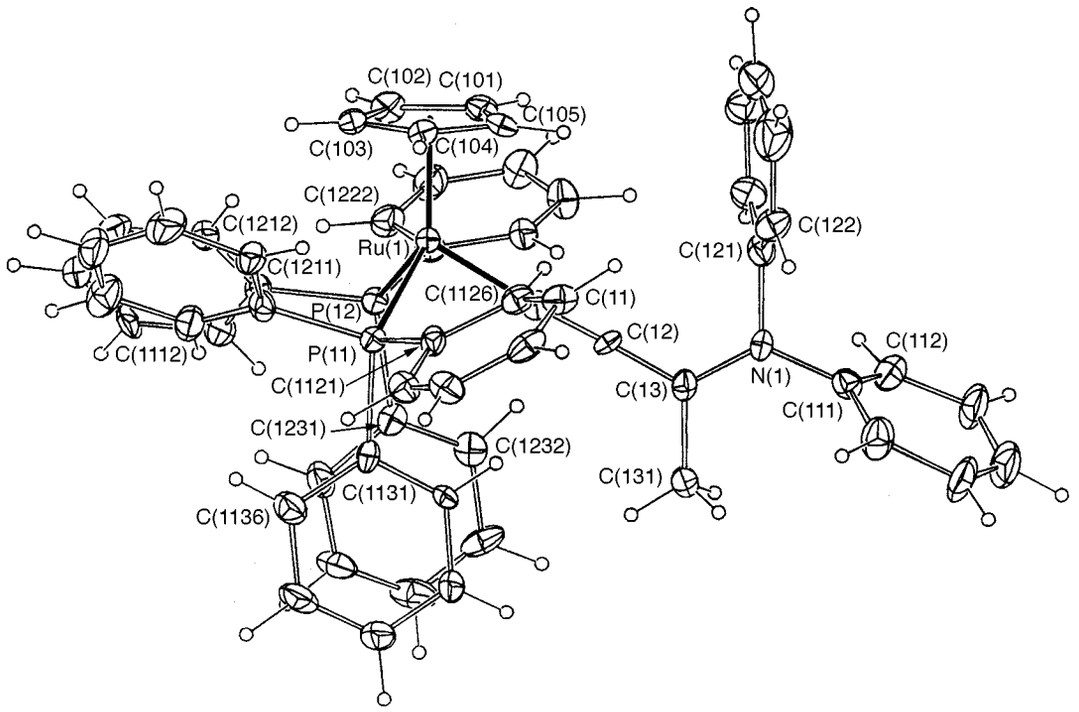
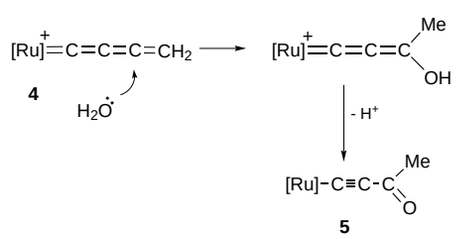


Fig. 1 Plot of cation 1 in $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **7**, showing the atom numbering scheme (cation 2 is similar). In all figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å



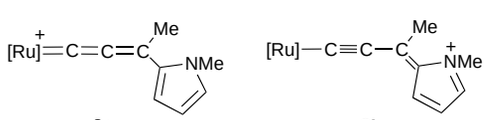
Scheme 4

addition of water to C_α, followed by elimination of one proton and migration of the second proton to the CH_2 group (Scheme 4). These reactions also afforded small amounts of the oxidation product, namely $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **8**. Formation of both **5** and **8** occurs rapidly in air and is the major cause of the instability of **4**.

***(d) N*-Methylpyrrole.** The electron-rich aromatic heterocycle *N*-methylpyrrole reacts by attack at C_γ and proton migration to give the allenylidene complex $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **9**. The strong electron-donor effect of the pyrrolic nucleus is shown by the large low-field shift found for the C_5H_5 protons (δ 4.78). In the ^{13}C NMR spectrum C_α is found at δ 256.7, while C_β and C_γ are at δ 167.4 and 146.0 (again these cannot be distinguished). Isomerisation to the vinylidene $[Ru\{C{=}CHC(C_4H_3NMe){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ was not found.

Molecular structure of complex 9

Fig. 2 shows a plot of the cation in complex **9** and selected bond parameters are collected in Table 1. The familiar pseudo-octahedral geometry about ruthenium is found, with P–Ru–P or P–Ru–C angles of between 87.9 and 99.6(1)°. Of interest is the allenylidene ligand, which is attached to Ru by C(1) [1.92(1) Å], which value can be compared with that in the previously described $[Ru(C{=}C{=}CPh_2)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ cation [1.884(5) Å].[9] Within the three-carbon chain, which is almost linear [angles at C(1) and C(2) are 173.5(8) and 172(1)°, respectively], the C(1)–C(2) and C(2)–C(3) separations are 1.24(2) and 1.37(2) Å. As for **7** above, two mesomeric forms **9a** and **9b** can be written and the short C(1)–C(2) separation again suggests that the alkyne mesomer **9b** is a significant contributor to the observed structure. Angles at C(3) sum to 360.$_0$°, although individual ones differ significantly from the expected value of 120° because of the relative sizes of the pyrrolyl and Me groups.

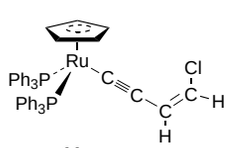


9a **9b**

Some reactions of complexes 6, 7 and 9

Further protonation of complex **6** was achieved by addition of HPF_6 with formation of the dicationic vinylidene complex $[Ru\{C{=}CHC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ **10**. This complex was characterised spectroscopically, the three protons of the vinylidene ligand being found at δ 4.14 (on C_β) and 5.92 and 6.42 (*cis* and *trans* to P on C_δ).

A slow reaction of complex **7** with CH_2Cl_2 afforded the chlorovinylalkynyl complex $[Ru(C{\equiv}CCH{=}CHCl\text{-}trans)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **11**, which was identified from an X-ray structural determination. The IR spectrum contains ν(C≡C) and ν(C=C) bands at 2056 and 1616 cm^{-1}, respectively, while M^+ is found at *m/z* 776 in the FAB mass spectrum. These data are in accord with the solid-state structure.



11

Molecular structure of complex 11

Fig. 3 contains a plot of a molecule of complex **11** and significant bond parameters are collected in Table 1. Again, the pseudo-octahedral geometry about Ru is shown by the P–Ru–P and P–Ru–C angles of between 85.0 and 102.08(7)°; in this case the distortions from octahedral geometry about Ru are more

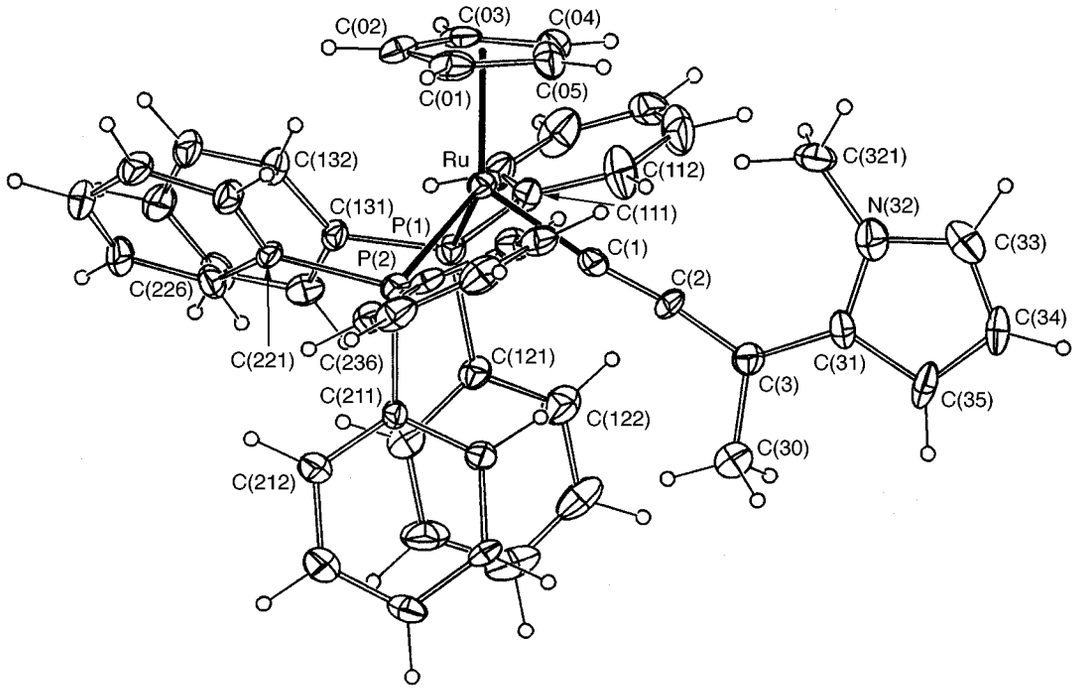


Fig. 2 Plot of the cation in $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **9**, showing the atom numbering scheme

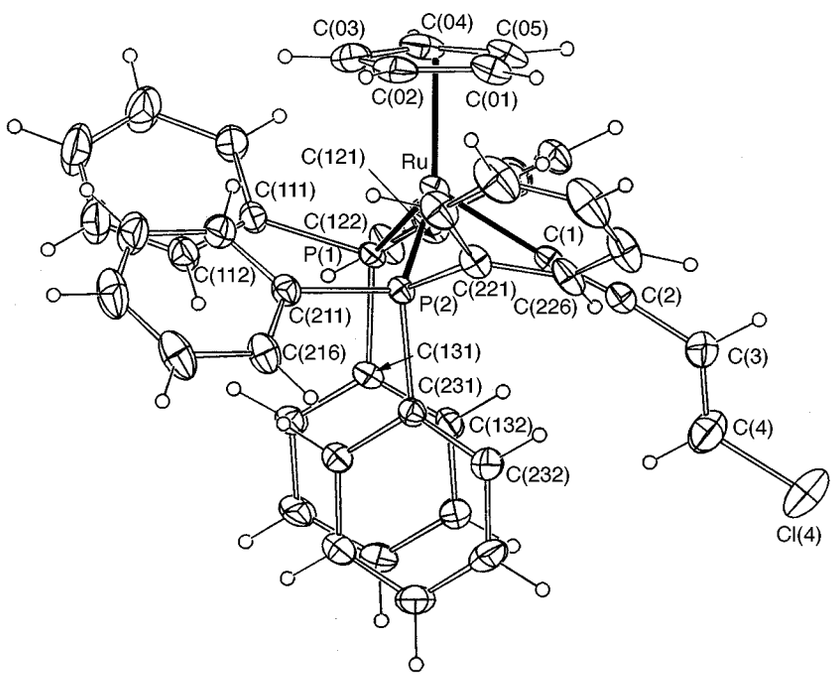


Fig. 3 Plot of a molecule of $[Ru(C{\equiv}CCH{=}CHCl)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **11**, showing the atom numbering scheme

marked than found in **9**. Complex **11** contains the first structurally characterised example of a vinylacetylide ligand attached to the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety. Within the four-carbon chain C(1)–C(4) the C–C separations are 1.206(9), 1.41(1) and 1.26(1) Å, respectively, consistent with a sequence of triple, single and double bonds, the latter seemingly affected by libration. Angles at C(1)–C(4) are 176.5(5), 175.3(6), 126.9(7) and 125.4(7)°, respectively and support the vinylacetylide formulation even though the H atoms attached to C(3) and C(4) were not located. Importantly, the structural determination revealed the presence of the Cl atom on C(4) [C(4)–Cl 1.71(1) Å], thus solving the problem of identity.

Deprotonation of complex **9** was achieved with LiBu to give the related vinylalkynyl complex $[Ru\{C{\equiv}CC(C_4H_3NMe){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ **12**. The reaction is easily reversible, protonation of **12** being observed even with water. The IR spectrum of **12** contains ν(C≡C) at 2060 cm^{-1}, while the ^{13}C NMR spectrum has resonances at δ 104.0 (Ru–C) and 106.5 and 107.8 (for C_γ and C_δ).

Discussion

The experiments described above have shown that the complex formed from $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and buta-1,3-diyne is likely to contain the parent butatrienylidene ligand, $:C{=}C{=}C{=}CH_2$.[18] This is deduced not only from its method of preparation from the diyne, but also from the products of its reactions with selected nucleophiles, which attack C_γ of the four-carbon chain, as predicted by theory. If the intermediate was the ethynylvinylidene, nucleophilic attack is expected to occur (with difficulty) at C_α.

Our studies are the first to have been reported on the chem-

istry of this unsaturated carbene. Addition of nucleophiles to C_γ results in the formation of new C–E (E = P, N or O) bonds. If the nucleophile contains a hydrogen atom, accompanying proton migration to C_δ gives a methyl-substituted allenylidene complex, while if an aprotic reagent is used then simple addition to give a cationic vinylalkynyl complex occurs.

Further reactions of several of these products have been studied. Thus, protonation of the cationic PPh_3 adduct **6**, in which the positive charge is presumably centred on the P atom, results in addition to C_β to give a dicationic vinylvinylidene derivative. Conversely, deprotonation of the *N*-methylpyrrolyl adduct **9** results in further stabilisation of the acetylenic centre found in the cation by loss of one of the methyl protons. This reaction is readily reversible, addition of water being sufficient to reform the cationic complex **9**.

It is presently unclear how the unusual replacement of the NPh_2 group in complex **7** proceeds. One possibility is attack of CH_2Cl_2 by the Ru–C≡C–C(N^+HPh_2)=CH_2 mesomer, with subsequent elimination of HCl and formation of $[NH_2Ph_2]Cl$. Alternatively, traces of HCl may cause deamination of **7**, regenerating **1**, which could react with chloride at C_δ to give **11**.

In summary, we have shown that the butatrienylidene ligand in complex **4** undergoes at least three characteristic reactions with nucleophiles, namely: (i) addition of aprotic nucleophiles (such as PPh_3) to C_γ gives alkenylethynyl complexes in which the positive charge is centred on the heteroatom; (ii) addition of protic nucleophiles (such as $NHPh_2$) to C_γ is accompanied by proton migration to C_δ to give methylallenylidene derivatives; (iii) addition of oxygen nucleophiles (such as water) is followed by loss of proton to give the acylalkynyl complex **5**.

These complexes can be readily distinguished by their IR ν(CC) spectra, with the alk-1-ynyl ligand having an absorption between 2030 and 2060 cm^{-1}, the allenylidene ligand with an absorption between 1950 and 2000 cm^{-1} and the vinylidene ligand having an absorption at *ca*. 1615 cm^{-1}.

Experimental

Instrumentation

IR: Perkin-Elmer 1700X Fourier-transform spectrometer. NMR: Bruker CXP300 or ACP300 spectrometer (^1H at 300.13 MHz, ^{13}C at 75.47 MHz). FAB mass spectrum: VG ZAB 2HF instrument (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen; solvents were distilled under nitrogen before use. The complex $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ was obtained from $RuCl_3{\cdot}nH_2O$, PPh_3 and cyclopentadiene as described previously.[23] Buta-1,3-diyne was prepared from 1,4-dichlorobut-2-yne.[24] **CAUTION:** care must be taken not to isolate neat buta-1,3-diyne. The work described herein was carried out using a solution of the diyne, obtained by condensing the diyne directly into diethyl ether or tetrahydrofuran at −78 °C.

Preparations

$[Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)]$ 2. An excess of buta-1,3-diyne (21 mg, 0.42 mmol, as a 0.1 M solution in EtO) was treated with LiBu (0.234 mmol) at −20 °C. A filtered solution of $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ {from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (150 mg, 0.207 mmol) and $AgPF_6$ (54 mg, 0.213 mmol) in thf (2 cm^3)} was added. After 10 min the solution was evaporated and the residue extracted with CH_2Cl_2 (3 cm^3). Chromatography (alumina, 15 × 1 cm column) afforded $[Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (85 mg, 0.115 mmol, 56%) as a yellow powder, m.p. 115 °C (decomp.), as a mono-thf solvate.

$[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ 4 and its reactions with nucleophiles. *General procedure.* A solution of $AgPF_6$ (954 mg, 0.213 mmol) in thf (2 cm^3) was treated with $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (150 mg, 0.207 mmol) in thf (7 cm^3). The mixture was filtered into a solution of buta-1,3-diyne (0.234 mmol, 2 M solution in Et_2O) containing the nucleophile (0.234 mmol in 7 cm^3 thf). After 15 min the reaction mixture was evaporated to dryness and the residue extracted with CH_2Cl_2 (3 cm^3). The product was isolated by column chromatography on alumina, eluting with Et_2O–CH_2Cl_2 (2:1).

(*a*) $[Ru\{C{\equiv}CC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **6**. As above, from PPh_3 (61 mg, 0.233 mmol), as a yellow powder, containing 1 equivalent of thf (150 mg, 0.131 mmol, 63%), m.p. 102 °C (decomp.) (Found: C, 66.73; H, 5.01. Calc. for $C_{63}H_{52}F_6P_4Ru{\cdot}C_4H_8O$: C, 65.95; H, 4.96%). IR (Nujol): 2032s [ν(C≡C)], 1586w, 1573w, 1548w, 1438s, 1186w, 1159w, 1110m, 1090m, 1070w, 840s [ν(PF)], 742m and 696s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.8–7.1 (45 H, m, PPh_3), 6.08 [1 H, d, $^3J(PH) = 47.7$, *trans* CH_2], 5.38 [1 H, d, $^3J(PH) = 19.8$ Hz, *cis* CH_2], 4.03 (5 H, s, C_5H_5), 3.75 and 1.85 (both 2 H, thf). ^{13}C NMR ($CDCl_3$): δ 149.8, 137.9 (m, *ipso*-C, Ru–PPh_3), 134.4–127.5 (m, PPh_3), 119.4 and 118.2 [2 × s, C(2) and C(4)], 116.6 [d, $^1J(PC) = 79.8$, C(3)], 110.4 [t, $^2J(PC) = 9.6$ Hz, C(1)], 85.7 (C_5H_5), 67.9 and 25.6 (2 × s, both CH_2, thf). Mass spectrum (FAB): *m*/*z* (%) 1003 (80, M^+), 741 (100, $[M - PPh_3]^+$) and 479 (70, $[M - 2PPh_3]^+$).

(*b*) $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **7**$[PF_6]$ *and* $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ **7**$[BF_4]$. As above, from $NHPh_2$ (40 mg, 0.237 mmol). Column chromatography of the reaction mixture with dichloromethane gave a brown fraction which after removal of the solvent gave $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **7**$[PF_6]$ (150 mg, 0.131 mmol, 64%), m.p. 146 °C. The product contains 1 equivalent of thf. Crystals of the $0.5CH_2Cl_2$ solvate were obtained from CH_2Cl_2–pentane (Found: C, 64.38; H, 4.82; N, 1.24. Calc. for $C_{57}H_{48}F_6NP_3Ru{\cdot}C_4H_8O$: C, 65.00; H, 5.01; N, 1.24%). IR (Nujol): 1998s [ν(C=C=C)], 1591w, 1492s, 1436s, 1091m, 1070w, 842s [ν(PF)], 747m and 697s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.7–6.9 (40 H, m, PPh_3 + NPh_2), 4.29 (5 H, s, C_5H_5), 3.75 and 1.85 (both 2 H, thf) and 2.11 (3 H, s, CH_3). ^{13}C NMR: δ($CDCl_3$) 219.2 [t, $^2J(PC) = 21$, Ru=C], 153.0 (Ru=C=*C*), 145.4 (Ru=C=C=*C*), 143.0 and 136.6 (both *ipso*-C, NPh_2), 135.0 (m, *ipso*-C, PPh_3), 133.2 and 129.7 [t, $^3J(PC) = 5$, $^4J(PC) = 4$ Hz, C(2) or C(6) and C(3) or C(5), PPh_3], 130.3–117.6 (m, NPh_2), 129.7 [C(4), PPh_3], 88.7 (C_5H_5), 67.9 and 25.6 (both CH_2, thf), 26.4 (CH_3). Mass spectrum (FAB): *m*/*z* (%) 910 (100, M^+) and 648 (95, $[M - PPh_3]^+$).

The salt **7**$[BF_4]$ (145 mg, 0.136 mmol, 66%), m.p. 214 °C (decomp.), was obtained similarly, using $AgBF_4$ in place of $AgPF_6$. It contains 1 equivalent of Et_2O as shown in its NMR spectrum. Crystals of the analytical sample were obtained as the $0.5CH_2Cl_2$ solvate from CH_2Cl_2–pentane (Found: C, 66.33; H, 4.78; N, 1.31. Calc. for $C_{57}H_{48}BF_4NP_2Ru{\cdot}0.5CH_2Cl_2$: C, 66.45; H, 4.75; N, 1.35%). IR (Nujol): 1997s [ν(C=C=C)], 1591w, 1573w, 1436m, 1313w, 1184m, 1119m, 1090s, 1057s [ν(BF)], 1001m, 834w, 814w, 746m and 696s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.6–7.01 (40 H, m, PPh_3 + NPh_2), 4.23 (5 H, s, C_5H_5), 3.40 (2 H, q, CH_2 of Et_2O), 2.06 (3 H, s, CH_3) and 1.13 (3 H, t, CH_3 of Et_2O). ^{13}C NMR: δ($CDCl_3$) 218.9 [t, $^2J(PC) = 21$, Ru=C], 153.0 (Ru=C=*C*), 145.4 (Ru=C=C=*C*), 141.5 and 136.5 (both *ipso*-C, NPh_2), 136.2 (m, *ipso*-C, PPh_3), 133.1 and 129.4 [both t, $^3J(PC) = 5$, $^4J(PC) = 4$ Hz, C(2) or C(6) and C(3) or C(5), PPh_3], 132.0–126.1 (m, NPh_2), 129.4 [C(4), PPh_3], 88.7 (C_5H_5), 65.7 (CH_2 of Et_2P), 26.4 (CH_3) and 15.16 (CH_3 of Et_2O). Mass spectrum (FAB): *m*/*z* (%) 910 (100, M^+) and 648 (95, $[M - PPh_3]^+$).

(*c*) $[Ru\{C{\equiv}CC(O)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ **5** *and* $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **8**. The solution of cation **4**, prepared as described above, was treated with water, MeOH or EtOH (1 cm^3). Column chromatography of the mixture with Et_2O gave a yellow fraction which after evaporation of the solvent gave **5** (60 mg, 0.079 mmol, 38%) m.p. 233 °C (decomp.) (lit.,[20] m.p.

233 °C). Yellow crystals were obtained from dichloromethane–pentane. Further elution with CH_2Cl_2 gave yellow **8** (80 mg, 45%) m.p. 128 °C (decomp.).

Complex **5** (Found: C, 70.60; H, 5.02. Calc. for $C_{45}H_{38}OP_2Ru$: C, 71.32; H, 5.05%): IR (Nujol) 2040 and 2000s [ν(C≡C)], 1615s [ν(CO)], 1479m, 1435s, 1343w, 1216m, 1094m, 1086m, 862w, 833m, 810m, 755m, 741s and 693s cm^{-1}; ^1H NMR δ($CDCl_3$) 7.6–6.86 (12:6:12, 30 H, m, PPh_3), 4.39 (5 H, s, C_5H_5) and 1.99 (3 H, s, CH_3); ^{13}C NMR δ($CDCl_3$) 181.5 (CO), 147.0 [t, ^2J(PC) = 23, RuC], 138.1 (m, *ipso*-C, PPh_3), 133.5 and 127.4 [both d, ^3J(PC) = 5, ^4J(PC) = 4 Hz, C(2) or C(6) and C(3) or C(5), PPh_3], 128.8 [C(4), PPh_3], 122.4 [C(2)], 86.4 (C_5H_5) and 32.3 (CH_3); mass spectrum (FAB) *m*/*z* (%) 758 (100, M^+), 691 {10, $[Ru(PPh_3)_2(C_5H_5)]^+$}, 496 (50, $[M - PPh_3]^+$) and 429 {100, $[Ru(PPh_3)(C_5H_5)]^+$}.

Complex **8** (characterised by comparison with an authentic sample): IR (Nujol) 1975s [ν(CO)], 1560w, 1437s, 1288m, 1285m, 1090m, 845s [ν(PF)], 744m and 696s cm^{-1}; ^1H NMR δ($CDCl_3$) 7.4–7.09 (6:12:12, 30 H, m, PPh_3) and 4.98 (5 H, s, C_5H_5); ^{13}C NMR δ($CDCl_3$) 202.8 [t, ^2J(PC) = 17 Hz, CO], 132.8 (m, *ipso*-C, PPh_3), 133.5 and 128.3 [both d, C(2) or C(6) and C(3) or C(5), PPh_3], 130.7 [C(4), PPh_3] and 90.72 (C_5H_5); mass spectrum (FAB) *m*/*z* (%) 719 (100, M^+), 691 {40, $[Ru(PPh_3)_2(C_5H_5)]^+$} and 429 {90, $[Ru(PPh_3)(C_5H_5)]^+$}.

Alternatively, a solution of $[Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (50 mg, 0.068 mmol) in thf (5 cm^3) was treated with HBF_4 for 24 h. Evaporation and recrystallisation (CH_2Cl_2–pentane) gave complex **5** (45 mg, 0.059 mmol, 87%), identified as above.

(*d*) $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **9**$[PF_6]$ *and* $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ **9**$[BF_4]$. As above, from *N*-methylpyrrole (19 mg, 0.235 mmol). The mixture immediately turned deep blue and column chromatography gave a blue fraction which after evaporation of solvent gave $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **9**$[PF_6]$ (150 mg, 0.155 mmol, 75%), m.p. 139 °C (Found: C, 61.29; H, 4.60; N, 1.33. Calc. for $C_{50}H_{44}F_6NP_3Ru$: C, 62.11; H, 4.59; N, 1.45%). IR (Nujol): 1948s [ν(C=C=C)], 1532m, 1464m, 1436s, 1343m, 1090m, 1057m, 840s [ν(PF)], 744m and 696s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.6–7.17 (33 H, m, $PPh_3 + C_4H_3N$), 4.78 (5 H, s, C_5H_5), 4.39 (3 H, s, NCH_3) and 2.06 (3 H, s, CH_3). ^{13}C NMR ($^{13}C-^1H$ coupled): δ($CDCl_3$) 256.7 [t, ^2J(PC) = 20, Ru=C], 167.4 (s, Ru=C=*C*), 146.0 (s, Ru=C=C=*C*), 140.5 [s, C(2), C_4H_3N], 140.5 [d, ^1J(CH) = 189, C(3), C_4H_3N], 135.6 (m, *ipso*-C, PPh_3), 133.1 and 128.5 [both d, both ^1J(CH) = 162, C(2) or C(6) and C(3) or C(5), PPh_3], 129.1 [d, ^1J(CH) = 161, C(4), PPh_3], 125.1 and 112.6 [both d, ^1J(CH) = 183 and 177, C(4) and C(5), C_4H_5N], 90.3 [d, ^1J(CH) = 179, C_5H_5], 38.5 [q, ^1J(CH) = 141, NCH_3] and 27.8 [q, ^1J(CH) = 129 Hz, CH_3]. Mass spectrum (FAB): *m*/*z* (%) 822 (100, M^+), 560 (90, $[M - PPh_3]^+$), 494 (25, $[M - PPh_3 - C_4H_4N]^+$) and 429 {30, $[Ru(PPh_3)(C_5H_5)]^+$}.

The BF_4 salt was obtained by using $AgBF_4$ instead of $AgPF_6$. Column chromatography gave a deep blue fraction containing $[Ru\{C{=}C{=}CMe(C_4H_3NMe)\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ **9**$[BF_4]$ (155 mg, 0.189 mmol, 91%), m.p. 143 °C (Found: C, 66.33; H, 4.78; N, 1.31. Calc. for $C_{50}H_{44}BF_4NP_2Ru$: C, 66.09; H, 4.88; N, 1.54%). IR (Nujol): 1951s [ν(C=C=C)], 1586w, 1575w, 1535m, 1481s, 1403m, 1199w, 1160w, 1090m, 1056s [ν(BF)], 746m and 697s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.7–7.0 (33 H, m, $PPh_3 + C_4H_3N$), 4.79 (5 H, s, C_5H_5), 4.43 (3 H, s, NCH_3) and 2.06 (3 H, s, CH_3). ^{13}C NMR: δ($CDCl_3$) 256.0 [t, ^2J(PC) = 20 Hz, RuC], 166.7 (s, Ru=C=*C*), 141.0 (s, Ru=C=C=*C*), 140.5 [s, C(2) and C(3), C_4H_3N], 133.1 [m, *ipso*-C, PPh_3 and C(2) or C(6), PPh_3], 130.1 [C(4), PPh_3], 128.2 [C(3) or C(5), PPh_3], 125.2 and 112.8 [C(4) and C(5), C_4H_3N], 90.3 (C_5H_5), 38.6 (NCH_3) and 28.8 (CH_3). Mass spectrum (FAB): *m*/*z* (%) 822 (100, M^+), 560 (90, $[M - PPh_3]^+$), 494 (30, $[M - PPh_3 - C_4H_4N]^+$) and 429 {25, $[Ru(PPh_3)_2(C_5H_5)]^+$}.

$[Ru\{C{=}CHC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ 10. Hexafluorophosphoric acid (0.1 mmol in 3 cm^3 dichloromethane) was added to $[Ru\{C{\equiv}CC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **6** (100 mg, 0.082 mmol) in CH_2Cl_2 (4 cm^3). The mixture was evaporated and the residue was washed with Et_2O (3 × 2 cm^3) to give $[Ru\{C{=}CHC(PPh_3){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ **10** as a white powder (90 mg, 0.070 mmol, 85%), m.p. 137 °C (decomp.). The compound decomposes slowly and a ^{13}C NMR spectrum could not be obtained (Found: C, 58.03; H, 4.10. Calc. for $C_{63}H_{53}F_{12}P_5Ru$: C, 58.48; H, 4.13%). IR (Nujol): 1615m [ν(C=C)], 1586w, 1481s, 1438s, 1110m, 1091m, 999w, 840s [ν(PF)], 746m and 697s cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.9–6.8 (45 H, m, PPh_3), 6.42 [1 H, d, ^3J(PH) = 47, *trans* H–C(4)], 5.92 [1 H, d, ^3J(PH) = 17, *cis* H–C(4)], 5.33 (5 H, s, C_5H_5) and 4.14 [1 H, d, ^3J(PH) = 62 Hz, H–C(2)]. Mass spectrum (FAB): *m*/*z* (%) 1004 (50, M^+), 742 (40, $[M - PPh_3]^+$), 691 {80, $[Ru(PPh_3)_2(C_5H_5)]^+$}, 480 (90, $[M - 2PPh_3]^+$) and 429 {100, $[Ru(PPh_3)(C_5H_5)]^+$}.

$[Ru(C{\equiv}CCH{=}CHCl)(PPh_3)_2(\eta\text{-}C_5H_5)]$ 11. Complex **11** was obtained serendipitously by reaction of $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ **7**$[PF_6]$ (40 mg, 0.035 mmol) with CH_2Cl_2 at 4 °C over 3 d. Filtration through basic Al_2O_3 gave $[Ru(C{\equiv}CCH{=}CHCl)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **11** (20 mg, 0.026 mmol, 74%) as yellow crystals, m.p. 130 °C, from CH_2Cl_2–pentane (Found: C, 68.81; H, 4.78. Calc. for $C_{45}H_{37}ClP_2Ru$: C, 69.63; H, 4.80%). IR (Nujol): 2056s [ν(C≡C)], 1616w [ν(C=C)], 1586w, 1572w, 1479s, 1434s, 1311w, 1282w, 1219m, 1093s, 1088s, 1070m, 1027w, 1005w, 1000w, 909m, 831m, 821m, 805m, 751m and 698s cm^{-1}. Mass spectrum (FAB): *m*/*z* (%) 776 (80, M^+), 691 {100, $[Ru(PPh_3)_2(C_5H_5)]^+$}, 514 (10, $[M - PPh_3]^+$) and 429 {95, $[Ru(PPh_3)(C_5H_5)]^+$}.

$[Ru\{C{\equiv}CC(C_4H_3NMe){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ 12. Butyllithium (0.65 cm^3 of a 1.6 M solution in hexane; 0.104 mmol) was added at 0 °C to $[Ru\{C{=}C{=}CMe(NPh_2)\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **7** (100 mg, 0.103 mmol) in thf (10 cm^3). The solution immediately became yellow. Evaporation of the filtered solution gave $[Ru\{C{\equiv}CC(C_4H_3NMe){=}CH_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ **12** as a yellow powder (65 mg, 0.079 mmol, 77%), m.p. 68 °C. It is sensitive to moisture and traces of acid. Contamination of **12** with solvent precluded reproducible microanalyses (Found: C, 75.29; H, 7.77; N, 1.03. Calc. for $C_{50}H_{43}NP_2Ru$: C, 73.16; H, 5.28; N, 1.71%). IR (Nujol): 2060s [ν(C≡C)], 1585w, 1435s, 1090m, 739w and 697m cm^{-1}. ^1H NMR: δ($CDCl_3$) 7.7–7.0 (33 H, m, $PPh_3 + C_4H_3N$), 4.29 (5 H, s, C_5H_5), 4.22 and 4.21 (both 1 H, d, both ^2J = 5.9 Hz, C=CH_2), 3.62 (3 H, s, NCH_3). The other resonances for the C_4H_3N group could not be unambiguously identified among the aromatic multiplets. ^{13}C NMR: δ($CDCl_3$) 138.8 (*ipso*-C, PPh_3), 133.8 and 127.4 [C(2) or C(6) and C(3) or C(5), PPh_3], 128.7 [C(4), PPh_3], 122.5 [C(2)], 121.2 and 120.2 [C(3) and C(4), C_4H_3N], 107.8 and 106.5 [C(3) and C(4)], 104 [C(1)], 85.1 (C_5H_5) and 38.9 (NCH_3). Mass spectrum (FAB): *m*/*z* (%) 821 (30, M^+), 691 {20, $[Ru(PPh_3)_2(C_5H_5)]^+$}, 559 (50, $[M - PPh_3]^+$) and 429 {100, $[Ru(PPh_3)_2(C_5H_5)]^+$}.

Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{max}$ limits using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); *N* independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals *R*, *R′* on |*F*| are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system[25] implemented by S. R. Hall; neutral atom complex scattering factors were employed.

Table 2 Crystal data and refinement details for complexes **7**, **9** and **11**

	7	**9**	**11**
Formula	$C_{57}H_{48}F_6NP_3Ru\cdot0.5CH_2Cl_2$	$C_{50}H_{44}F_6NP_3Ru$	$C_{45}H_{37}ClP_2Ru$
M	1097.5	966.9	776.3
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	Pc (no. 7)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	11.666(10)	15.673(4)	15.013(9)
b/Å	14.156(13)	14.748(3)	11.337(8)
c/Å	31.392(8)	21.824(4)	11.027(5)
α/°			92.76(4)
β/°	98.01(8)	119.88(2)	95.85(4)
γ/°			93.03(5)
U/Å^3	5134	4374	1862
Z	4	4	2
D_c/g cm^{-3}	1.42	1.47	1.38
F(000)	2244	1976	796
Crystal size/mm	0.40 × 0.35 × 0.42	0.60 × 0.10 × 0.12	0.25 × 0.37 × 0.55
$A^*_{min,\ max}$	1.15, 1.20	1.04, 1.05	1.12, 1.24
μ/cm^{-1}	4.45	5.3	5.4
$2\theta_{max}$/°	46	50	50
N	7143	5858	6525
N_o	5290	2605	5643
R	0.055[a]	0.056	0.056
R'	0.055[a]	0.051	0.074

[a] Preferred hand.

Abnormal features. Components with high thermal motion (encompassing disorder?) were found in all three structures [PF_6/solvent (**7**, **9**), Cl (**11**)], resulting in somewhat high residuals and, in the case of complex **11**, where it lies within a significant feature of the molecule, libration effects on the geometry.

CCDC reference number 186/803.

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References

1 M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; H. Werner, *Nachr. Chem. Tech. Lab.*, 1992, **40**, 435; *J. Organomet. Chem.*, 1994, **475**, 45.
2 C. Bianchini, M. Peruzzini and P. Frediani, *J. Am. Chem. Soc.*, 1991, **113**, 5453.
3 Y. Wakatsuki, H. Yamazaki, N. Kumegawa and P. S. Johar, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 987; Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J. Y. Satoh, *J. Am. Chem. Soc.*, 1991, **113**, 9604.
4 B. M. Trost and R. J. Kulawiec, *J. Am. Chem. Soc.*, 1992, **114**, 5579; B. M. Trost, G. Dyker and R. J. Kulawiec, *J. Am. Chem. Soc.*, 1990, **112**, 7809.
5 H. Werner, *Chem. Commun.*, 1997, 903; H. Le Bozec and P. H. Dixneuf, *Izv. Akad. Nauk*, *Ser. Khim.*, 1995, **5**, 827; *Russ. Chem. Bull.*, 1995, **44**, 801; *Chem. Abstr.*, 1996, **124**, 29802c; R. Aumann, B. Jasper and R. Frohlich, *Organometallics*, 1994, **13**, 3173 and refs. therein.
6 D. Touchard, P. Haquette, A. Daridor, L. Toupet and P. H. Dixneuf, *J. Am. Chem. Soc.*, 1994, **116**, 11 157.
7 R. W. Lass, P. Steinert, J. Wolf and H. Werner, *Chem. Eur. J.*, 1996, **2**, 19.
8 G. Roth and H. Fischer, *Organometallics*, 1996, **15**, 5766.
9 J. R. Lomprey and J. P. Selegue, *Organometallics*, 1993, **12**, 616.
10 N. M. Kostic and R. F. Fenske, *Organometallics*, 1982, **1**, 974; B. E. R. Schilling, R. Hoffmann and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
11 C. Kelley, N. Lugan, M. R. Terry, G. L. Geoffroy, B. S. Haggerty and A. L. Rheingold, *J. Am. Chem. Soc.*, 1992, **114**, 6735.
12 D. Touchard, N. Pirio and P. H. Dixneuf, *Organometallics*, 1995, **14**, 4920.
13 T. Braun, P. Meuer and H. Werner, *Organometallics*, 1996, **15**, 4075; T. Braun, P. Steinert and H. Werner, *J. Organomet. Chem.*, 1995, **488**, 169.
14 V. Cadierno, M. P. Gamasa, J. Gimeno, M. González-Cueva, E. Lastra, J. Borge, S. García-Granda and E. Pérez-Carreño, *Organometallics*, 1996, **15**, 2137; V. Cadierno, M. P. Gamasa, J. Gimeno, E. Lastra, J. Borge and S. García-Granda, *Organometallics*, 1994, **13**, 745; V. Cadierno, M. P. Gamasa, J. Gimeno and E. Lastra, *J. Organomet. Chem.*, 1994, **474**, C27.
15 G. Jia, H. P. Xia, W. F. Wu and W. S. Ng, *Organometallics*, 1996, **15**, 3634.
16 M. I. Bruce, M. Ke and P. J. Low, *Chem. Commun.*, 1996, 2405; M. I. Bruce, P. J. Low, A. Werth, B. W. Skelton and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1551; M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3151.
17 M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White, *J. Cluster Sci.*, 1996, **7**, 109; *Polyhedron*, 1995, **14**, 2647; *Inorg. Chim. Acta*, 1996, **250**, 129; M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *Aust. J. Chem.*, 1996, **49**, 155.
18 M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1009; M. I. Bruce, P. Hinterding, M. Ke, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1997, 715.
19 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2661.
20 M. I. Bruce, P. Hinterding, E. R. T. Tiekink, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **450**, 209.
21 M. I. Bruce, L. I. Denisovich, P. J. Low, S. M. Peregudova and N. A. Ustynyuk, *Mendeleev Commun.*, 1996, 200.
22 A. Davison and J. P. Selegue, *J. Am. Chem. Soc.*, 1978, **100**, 7763.
23 M. I. Bruce, C. Hameister, A. G. Swincer and R. C. Wallis, *Inorg. Synth.*, 1982, **21**, 78; 1990, **28**, 270.
24 L. Brandsma, *Preparative Acetylene Chemistry*, Elsevier, Amsterdam, 2nd edn., 1988, p. 203.
25 S. R. Hall and J. M. Stewart (Editors), *XTAL Users' Manual*, *Version 3.0*, Universities of Western Australia and Maryland, 1990.

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