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Cyclopentadienyl-ruthenium and -osmium chemistry

XXXIX *. Syntheses of novel alkynyl-ruthenium complexes. X-Ray structures of two forms of {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) and of Ru{C≡CC(O)Me}(PPh$_3$)$_2$(η-C$_5$H$_5$)

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Abstract

Reactions between [Ru(thf)(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$ and lithium acetylides have given further examples of substituted ethynyl–ruthenium complexes that are useful precursors of allenylidene and cumulenylidene derivatives. From Li$_2$C$_4$, mono- and bi-nuclear ruthenium complexes were obtained: single-crystal X-ray studies have characterised two rotamers of {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$), which differ in the relative *cis* and *trans* orientations of the RuL$_n$ groups. Protonation of Ru(C≡CC≡CH)(PPh$_3$)$_2$(η-C$_5$H$_5$) afforded the butatrienylidene cation [Ru(C=C=C=CH$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$, which reacted readily with atmospheric moisture to give the acetylethynyl complex Ru{C≡CC(O)Me}(PPh$_3$)$_2$(η-C$_5$H$_5$), also fully characterised by an X-ray structural study.

1. Introduction

There has been much interest in the synthesis and reactions of σ-alkynyl–ruthenium complexes of the type Ru(C≡CR)(PR′$_3$)$_2$(η-C$_5$H$_5$), both intrinsically and as sources of novel vinylidene and derived carbene complexes [1]. In the majority of cases, the σ-alkynyl compounds have been prepared from reactions between RuCl(PR′$_3$)$_2$(η-C$_5$H$_5$) and either alkynyl anions or the alkyne directly [2]. In the latter case, the intermediate vinylidene derivative is deprotonated readily by treatment with base. These reactions generally proceed in high yield. However, some systems are less tractable, notably the parent ethynyl complexes [3], and others which might be suitable sources of more highly unsaturated cumulene derivatives. This paper reports the

synthesis and characterisation of several complexes of this type, together with single-crystal X-ray studies of two isomers of the binuclear C$_4$ derivative, [Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$), and of the acetylethynyl complex Ru{C≡CC(O)Me}(PPh$_3$)$_2$(η-C$_5$H$_5$).

2. Results and discussion

2.1. Synthesis of alkynyl complexes

The parent ethynyl complex Ru(C$_2$H)(PPh$_3$)$_2$(η-C$_5$H$_5$) (1) has recently been reported from reactions between the corresponding chloro complex and ethynyltrimethylsilane [3]. If the reaction is carried out in the presence of NH$_4$PF$_6$, desilylation occurs and the vinylidene complexes [Ru(CCH$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)]-[PF$_6$] (PR$_3$ = PPh$_3$, PMe$_3$, 1/2dppe) are obtained in virtually quantitative yield. Subsequent deprotonation occurs with difficulty, however, and the air-sensitive ethynyls are best obtained using KO^{t}Bu in THF, in
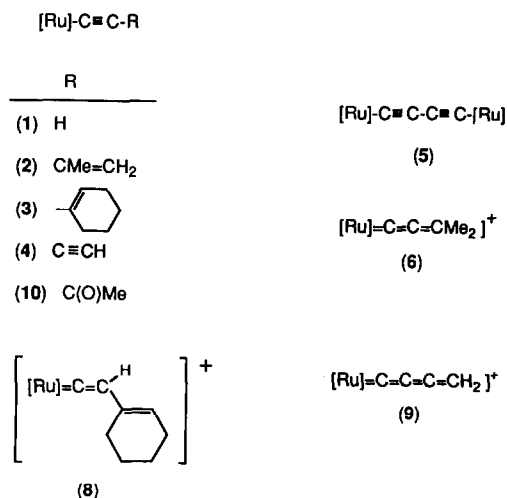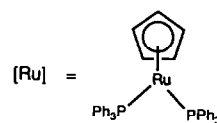

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* For part XXXVIII, see ref. 22.

75% yield. It is of interest that the corresponding iron complex [Fe(CCH$_2$)(dppe)(η-C$_5$H$_5$)]$^+$ was obtained either from ethyne or from HC$_2$SiMe$_3$ in MeOH [4]; under these conditions, the ruthenium complex gave the carbene complex [Ru{C(OMe)Me}(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$, formed by rapid addition of MeOH to the intermediate vinylidene [4,5]. Again in contrast, an η^2-ethyne complex was obtained from RuCl(PMe$_3$)$_2$(η-C$_5$H$_5$) [6]. The ethynyl-iron complex has also been obtained from Li(C$_2$H)(tmed) and [Fe(THF)(dppe)(η-C$_5$H$_5$)][BF$_4$]; protonation afforded the vinylidene cation [7].

In the present work, addition of the alkynyllithium reagents, obtained directly from the alkyne and LiBu in THF, to solutions of [Ru(THF)(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$, prepared in situ from RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$) and AgPF$_6$ in THF, gave the alkynylruthenium complexes directly after chromatography on Florisil. The ethynyl complex 1, was obtained in 47% yield as yellow crystals. The spectroscopic properties agreed with those described previously [3]. In similar fashion, the lithium reagent obtained from 3-methylbut-2-en-1-yne afforded a 61% yield of Ru(C$_2$CMe=CH$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$) (2) as a yellow powder of the mono-THF solvate, which is very air-sensitive. Characteristic spectroscopic properties include ν(C≡C) at 2048 cm^{-1}, Me, CH$_2$ and C$_5$H$_5$ proton resonances at δ 1.76, 1.84 and 3.73, and 4.27 ppm, respectively, the alkynyl carbons at δ 115.9 and 130.0 ppm, and M$^+$ in the FAB mass spectrum at m/z 755. The cyclohexenylethynyl complex 3 was prepared analogously in 73% yield, again with the expected spectroscopic features, including ν(C≡C) at 2064 cm^{-1}, the single olefinic proton at δ 5.58 ppm, the alkynyl carbons at δ 116.0 and 125.8 ppm, and M$^+$ at m/z 795.

Extension of the synthetic procedure to 1,3-butadiyne, using an equivalent amount of LiBu, afforded yellow Ru(C≡CC≡CH)(PPh$_3$)$_2$(η-C$_5$H$_5$) (4) in 56% yield, also as a mono-THF solvate. The IR spectrum contained ν(≡CH) at 3299 and two ν(C≡C) bands at 2109 and 1971 cm^{-1}; a weak M$^+$ ion cluster was found at m/z 739 in the FAB mass spectrum. The ^{1}H NMR spectrum contained the ≡CH resonance at δ 1.42 ppm, while three of the four acetylenic carbons were found at δ 73.9, 94.4 and 116.4 ppm. Most of these data are similar to those reported for the complex Fe(C≡CC≡CH)(CO)(PPh$_3$)(η-C$_5$H$_5$), which had ν(≡CH) at 3300 cm^{-1}, only one ν(C≡C) band at 2170 cm^{-1}, δ(≡CH) at 1.27 and the carbons of the C$_4$ chain at δ 54.3, 72.1, 99.1 and 109.4 [8].

When Li$_2$C$_4$ was used, the corresponding binuclear complex {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) (5) was obtained in 41% yield as yellow crystals. This complex was characterised spectroscopically and by a single-

crystal X-ray structure determination. The FAB mass spectrum contains M$^+$ at m/z 1429, while a single ν(C≡C) band was found at 1970 cm^{-1}. The acetylenic carbons were not observed in the ^{13}C NMR spectrum, while the ^{1}H NMR spectrum contained only resonances assigned to the Ph and THF protons in addition to the C$_5$H$_5$ signal at δ 4.20.

2.2. Molecular structures of two forms of {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) (5a and 5b)

Two forms of the C$_4$ complex were obtained from different reactions and were studied by single-crystal X-ray diffraction. The two forms differ in the relative arrangement of the two ML$_n$ fragments, these being trans in the better refined structure of a THF solvate 5a and cis in the second, unsolvated form 5b. Plots of the two molecules are shown in Figs. 1 and 2, while significant bond parameters are listed in Table 1. In 5a, the molecule is centrosymmetric, while in 5b it lies on a crystallographic two-fold axis. Coordination about the ruthenium atoms is nearly octahedral, as found in many other examples of complexes containing the Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) moiety. The bond parameters are also similar, with Ru–C(Cp) distances between 2.220–2.241(3) Å in 5a and 2.16–2.31(3) Å in 5b, mean values being 2.228 and 2.23 Å, respectively. The Ru–P distances are experimentally equivalent at 2.287(1) and 2.285(1) Å in 5a and equal to 2.29(1) Å in 5b, again entirely consistent with previously observed structures.
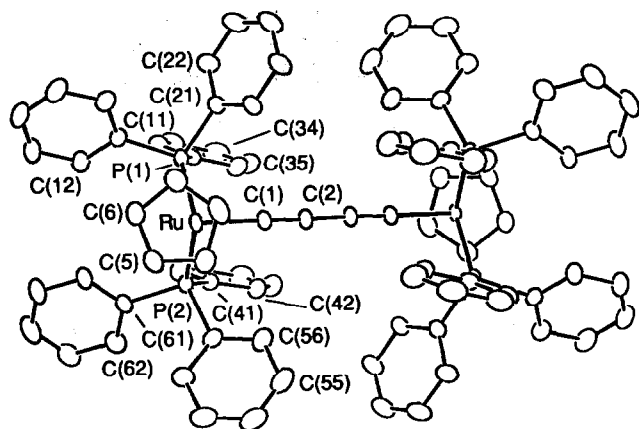
[Ru] =

[Ru]-C≡C-R

R
_____
(1) H

(2) CMe=CH$_2$

(3) —〈 〉

(4) C≡CH

(10) C(O)Me

[Ru]=C=C〈 H / 〉
(8)

[Ru]-C≡C-C≡C-[Ru]
(5)

[Ru]=C=C=CMe$_2$]$^+$
(6)

[Ru]=C=C=C=CH$_2$]$^+$
(9)

Fig. 1. Molecular structure and crystallographic numbering scheme for {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) (5a).

TABLE 1. Selected bond lengths (Å) and angles (°) for 5a and 5b

	5a (trans)	5b (cis)
Ru–C(Cp)	2.220–2.241(3)	2.16–2.31(3)
(av.)	2.228	2.23
Ru–P(1)	2.287(1)	2.29(1)
Ru–P(2)	2.285(1)	2.29(1)
Ru–C(1)	2.001(3)	2.01(3)
C(1)–C(2)	1.217(4)	1.24(4)
C(2)–C(2')	1.370(6)	1.31(4)
P(1)–Ru–P(2)	102.8(1)	102.8(4)
P(1)–Ru–C(1)	87.2(1)	90.1(8)
P(2)–Ru–C(1)	85.7(1)	86.4(8)
Ru–C(1)–C(2)	178.9(2)	174(2)
C(1)–C(2)–C(2')	177.2(3)	176(3)

The most interesting parts of the structures relate to the coordination of the C$_4$ fragments. The bond distances suggest that these ligands are somewhat delocalised, with Ru–C distances of 2.001(3) Å in 5a and 2.01(3) Å in 5b. Other values for Ru–C(sp) bonds have been found between 2.009–2.017 Å [9]. The angle subtended at the metal atoms by the two PPh$_3$ ligands is 102.8(1)° for 5a and 102.8(4) for 5b, while the P–RuC(1) angles are 85.7(1) and 87.2(1)° (5a) and 90.1(8) and 86.4(8)° (5b) showing that steric interactions between the bulky PPh$_3$ ligands cause them to bend towards the relatively much smaller acetylenic carbons. In comparison, the corresponding angles in Ru(C$_2$Ph)-(PPh$_3$)$_2$(η-C$_5$H$_5$) [9,10] are 100.9(1) (PRu–P), 88.6(1) and 89.2(1)° (P–Ru–C), movement of the PPh$_3$ ligands to the acetylide group being limited by the presence of the phenyl substituent on C(2). When a chelating bis-tertiary phosphine is present, all angles are less than 90° as a result of the restricted bite of the bidentate ligand, e.g. for Ru(C$_2$Ph)(dppe)(η-C$_5$H$_5$), P–Ru–P is 83.3(1) and P–Ru–C are 82.7(1) and 86.5(1)° [9].

Within the C$_4$ chains, the C–C distances are 1.217(4) and 1.370(6) Å for 5a, and 1.24(4) and 1.31(4) Å for 5b. The C≡C bond lengths are comparable to values of 1.204(5) Å found in Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) [9,10] and 1.214(7) Å in Ru(C$_2$Ph)(dppe)(η-C$_5$H$_5$) [9]. The C–C single bonds are shortened from the normal values of ca. 1.48 Å; in free 1,3-butadiyne in the gas phase, the C≡C and C–C bonds are 1.217 and 1.383 Å, respectively [11]. The C$_4$ chain is not strictly linear, angles of 178.9(3) and 177.2(3)° (in 5a) and 174(2) and 176(3)° (in 5b) being found at C(1) and C(2), respec-

(5b)
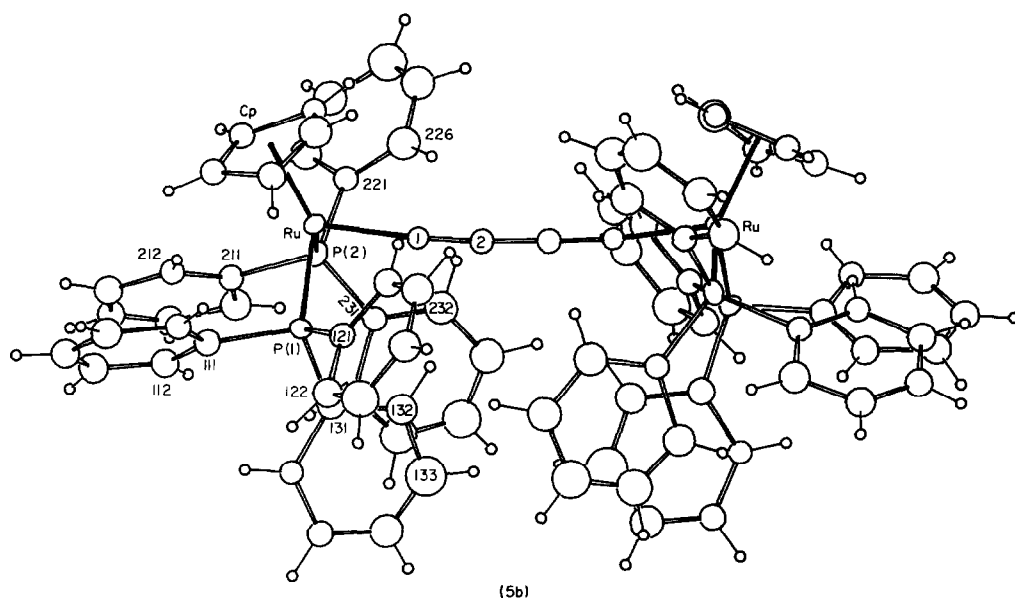
Fig. 2. Molecular structure and crystallographic numbering scheme for {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) (5b).

tively. Such minor distortions are again presumably the result of steric interactions between the two Ru-$(PPh_3)_2(\eta\text{-}C_5H_5)$ groups, closest approaches in the two forms being between atoms $H(133) \cdots H(133)$, calculated at 1.8 Å, but presumably at or close to van der Waals distances in the *trans* form.
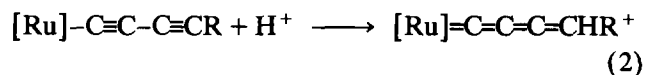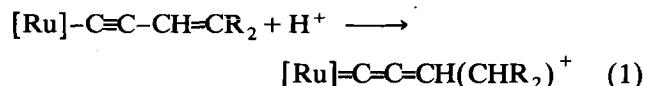
These are the first structural determinations of complexes containing mononuclear ML_n moieties at the ends of a C_4 chain. Such complexes have been known for many years [12] and are currently of interest in connection with the synthesis of unusual polymeric materials with metals incorporated in a polymeric rod structure. In recently reported studies [8], an exciting development has been the demonstration that the unsaturated C_4 chain can transfer electronic information between metal centres.

The present structures are also of interest in demonstrating for the first time the novel possibility of obtaining the *cis* and *trans* forms of C_4 complexes, whereas free rotation about the central C–C bond is anticipated. Factors responsible for the relative stabilities of the two forms may include solid state packing effects and the partial double bond character of the central $C(2)$–$C(2')$ bond. As demonstrated above, the steric interaction between the two metal groups is probably responsible for the separation of these two isomers. In solution, there is no evidence for two isomers, only single resonances being observed for the C_5H_5 groups, for example, in the ^1H and ^{13}C NMR spectra. Further studies on these and related species are being carried out. In the other previously characterised example, $\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4)$, no evidence for the formation of isomers was reported [8].

2.3. Protonation studies

Protonation of σ-alkynyl–ruthenium complexes is a well-known route to the corresponding cationic vinylidene complexes [1]. If the alkynyl substituent also contains unsaturated groups, there is the possibility of forming higher vinylogues of the vinylidenes, *i.e.* al-

lenylidene or cumulenylidene complexes. This idea has been explored by several workers, notably Selegue [13] and Dixneuf [14]. Two possible reactions are:

$$[Ru]\text{-}C\equiv C\text{-}CH\text{=}CR_2 + H^+ \longrightarrow$$
$$[Ru]\text{=}C\text{=}C\text{=}CH(CHR_2)^+ \quad (1)$$

$$[Ru]\text{-}C\equiv C\text{-}C\equiv CR + H^+ \longrightarrow [Ru]\text{=}C\text{=}C\text{=}C\text{=}CHR^+ \quad (2)$$

As mentioned above, part of the motivation for this work was the possibility of using the new acetylides as precursors of complexes containing such highly unsaturated systems. We have therefore examined the protonation of some of the complexes reported above. Thus, we find that addition of HPF_6 to the $C_2CMe\text{=}CH_2$ complex (2) affords initially the deep blue dimethylallenylidene derivative $[Ru(C\text{=}C\text{=}CMe_2)(PPh_3)_2(\eta\text{-}C_5\text{-}H_5)][PF_6]$ (6), which reacts rapidly with a second molecule of 2 to give the binuclear cyclic allenylidene cation (7). Similar reactions have been reported several years ago by Selegue [13] and the mechanism which he proposed for the attack of the first-formed vinylidene cation (6) on a second molecule of (2) is undoubtedly related to that followed here (Scheme 1).

As expected, addition of HBF_4 to 3 afforded the corresponding vinylvinylidene cation 8, characterised by $\nu(C\text{=}C)$ bands in its IR spectrum at 1637 and 1622 cm^{-1} and the vinylidene proton resonance at δ 4.96; no ^{13}C NMR spectrum could be obtained because of rapid decomposition in solution.

Finally, protonation of the buta-1,3-diynyl complex gave the butatrienylidene cation $[Ru(C\text{=}C\text{=}C\text{=}CH_2)\text{-}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (9), which readily decomposed by reaction with even traces of water in the air to give the known acetylethynyl derivative 10 [15], which has now been fully characterised by a single-crystal X-ray study. This reaction proceeds by nucleophilic attack of the water on the cationic centre, followed by loss of a proton from the hydroxyvinylidene cation so formed (Scheme 2).
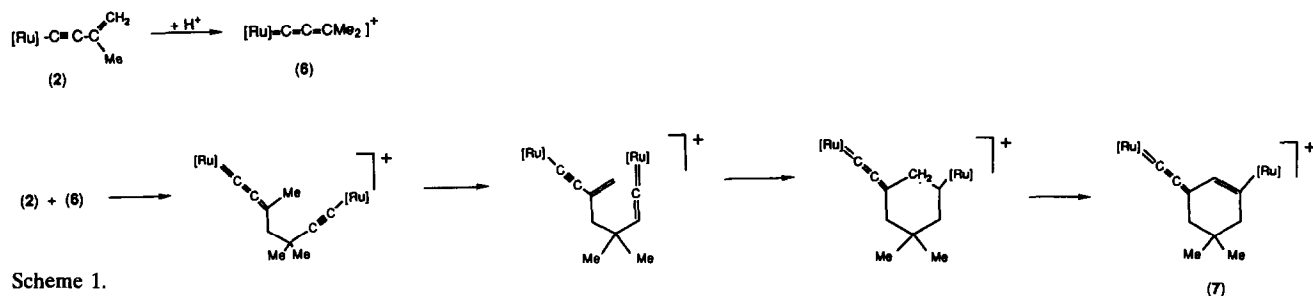
Scheme 1.
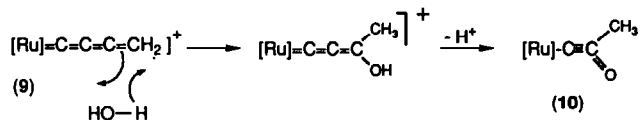
Scheme 2.
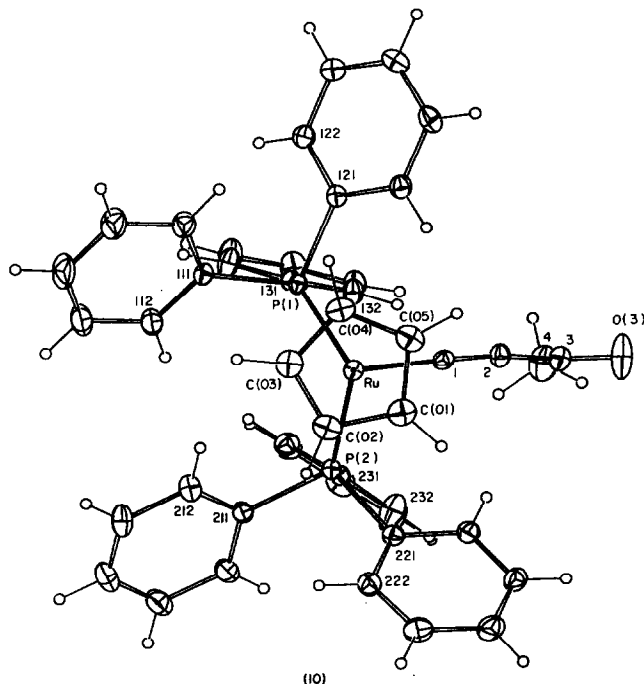
Fig. 3. Molecular structure and crystallographic numbering scheme for [Ru{C≡CC(O)Me}(PPh₃)₂(η-C₅H₅)] (10).

2.4. Molecular structure of Ru{C≡CC(O)Me}(PPh₃)₂-(η-C₅H₅) (10)

A plot of a molecule of 10 is shown in Fig. 3 and selected bond parameters are listed in Table 2. The structure contains the usual nearly octahedral ruthenium atom coordinated to the C_5H_5 group [Ru–C(cp) 2.222–2.250(4), av. 2.233 Å], two PPh_3 ligands [Ru–P both 2.297(1) Å] and the alkynyl group [Ru–C(1) 1.996(3) Å]. The angles at Ru are: C(1)–Ru–P(1) 90.6 (21), C(1)–Ru–P(2) 86.3(2), P(1)–Ru–P(2) 104.20(5)°,

TABLE 2. Selected bond lengths (Å) and angles (°) for 10

Ru–C(Cp)	2.222–2.250(3)	P(1)–Ru–P(2)	104.20(5)
(av.)	2.233	P(1)–Ru–C(1)	90.6(1)
Ru–P(1)	2.297(1)	P(2)–Ru–C(1)	86.3(1)
Ru–P(2)	2.297(1)	Ru–C(1)–C(2)	176.1(3)
Ru–C(1)	1.996(3)	C(1)–C(2)–C(3)	169.8(3)
C(1)–C(2)	1.212(5)	C(2)–C(3)–C(4)	116.4(3)
C(2)–C(3)	1.427(5)	C(2)–C(3)–O	124.7(4)
C(3)–C(4)	1.486(6)	C(4)–C(3)–O	119.0(4)
C(3)–O	1.202(5)		

again resulting from the bending of the PPh_3 ligands towards the alkynyl group. The latter contains an almost linear RuC_3 fragment (angles at C(1) and C(2) are 176.1(3) and 169.8(3)°, respectively), while the acyl carbon has almost perfect sp^2 geometry [angles 116.94, 124.7 and 119.0(4)°, sum 360.0°]. The C–C distances show localised C≡C triple [1.212(5) Å] and C–C single bonds [1.427(5) Å].

3. Conclusions

This study has produced further examples of σ-alkynyl–ruthenium complexes by displacement of weakly coordinated THF from the cation [Ru(THF)(PPh₃)₂(η-C₅H₅)]⁺ by the respective alkynyl anions, a previously neglected approach to these species. In the present instances, several complexes which are otherwise accessible only with difficulty have been prepared in moderate to good yields. Included is the first example of a complex containing a C_4 ligand bridging two ruthenium moieties, which has been found to exist as two rotamers in the solid state, as shown by single-crystal X-ray studies of the two forms.

As expected, protonation of the ethynyl complexes gave vinylidene or allenylidene complexes which are very reactive; some account of their reactivity will be given in a following paper. However, facile reaction of the butatrienylidene derivative with water has given the acetylethynyl derivative 10, for which a structural study is also reported.

4. Experimental details

All reactions were carried out under nitrogen by standard Schlenk techniques. No special precautions were taken during isolation procedures. Solvents were dried by standard methods and distilled under nitrogen before use. Alkynes were used as commercially obtained or made by literature methods [16]. RuCl-(PPh₃)₂(η-C₅H₅) was prepared from RuCl₃·nH₂O [17]. Infrared spectra were recorded on a Perkin-Elmer 1720X FT spectrometer, FAB mass spectra on a VG ZAB 2HF spectrometer, argon or xenon being used as FAB gases; ¹H- and ¹³C-NMR on a Bruker CXP-300 spectrometer at 300.133 and 75.456 MHz, respectively. Microanalyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7.

4.1. General procedure for Ru(alkynyl)(PPh₃)₂(η-C₅H₅) complexes

A solution of AgPF₆ (54 mg, 0.213 mmol) in THF (2 ml) was added to a stirred solution of RuCl(PPh₃)₂(η-C₅H₅) (150 mg, 0.207 mmol) in THF (5 ml). The precipitated AgCl was filtered off and the orange fil-

trate was added to a mixture of alkyne (0.234 mmol) and n-butyllithium (1.6 M n-butyllithium in hexane, 0.234 mmol) in THF (7 ml). After 15 min the solvent was evaporated on the vacuum line. The residue was dissolved in CH_2Cl_2 (3 ml) and rapidly chromatographed on a Florisil column (1 × 15 cm); Et_2O eluted the alkynyl complexes which were isolated by evaporation of the solvent.

4.1.1. Ru(C≡CH)(PPh₃)₂(η-C₅H₅) (1)

In a variation of the general procedure THF (7 ml) was saturated with acetylene (purified by bubbling through concentrated H_2SO_4) at −20°C. After addition of n-butyllithium (0.234 mmol) and evaporation of excess acetylene at −20°C the filtrate containing [Ru-(THF)(PPh₃)₂(η-C₅H₅)]⁺ was added. After 15 min, isolation of 1 (70 mg, 0.098 mmol, 47%), m.p. 192°C (dec.) was achieved by chromatography as described in the general procedure. Yellow crystals were obtained from THF/pentane. Found: C, 71.83; H, 5.16; M⁺, 715. C₄₃H₃₆P₂Ru calc.: C, 72.16; H, 5.07%; M, 715. IR (Nujol): 3280w [ν(≡CH)], 1932s [ν(C≡C)], 1590m, 1573w, 1482s, 1436s, 1309m, 1193s, 1120s, 1091s, 1070s, 998s, 833w, 803w, 752s, 695s cm⁻¹. ¹H NMR: δ (CDCl₃) 7.7–7.1 (30H, m, 2PPh₃), 4.27 (5H, s, C₅H₅), 2.01 [1H, t, ⁴J(PH) = 2.01 Hz, ≡CH]. ¹³C NMR: δ (CDCl₃) 139.1 (m, ipso-C, 2PPh₃); 133.7, 128.5, 127.1 (t, s, t, C2 to C6, 2PPh₃), 108.6 [t, ²J(PC) = 23.2 Hz, Cl], 98.1 (C2), 85.1 (C₅H₅). MS (FAB): m/z (%) 715 (5) M⁺, 690 (90) [M − C₂H]⁺, 428 (100) [Ru(PPh₃)(C₅H₅)]⁺.

4.1.2. Ru(C≡CCMe=CH₂)(PPh₃)₂(η-C₅H₅) (2)

The lithium reagent from 3-methyl-but-3-en-1-yne (15.4 mg, 0.234 mmol) and n-butyllithium (0.234 mmol) reacted with the ruthenium cation as described in the general procedure. After 15 min, chromatography and evaporation of the solvent gave yellow microcrystalline 2 (95 mg, 0.126 mmol, 61%), m.p. 131°C (dec.). This compound crystallises as a mono-THF solvate and is very sensitive to traces of acid. Found: C, 71.84; H, 5.39; M⁺, 755. C₄₆H₄₀P₂Ru · THF calc.: C, 72.53; H, 5.84%; M, 755. IR (Nujol): 2048s [ν(C≡C)], 1591m, 1573w, 1480s, 1436s, 1264w, 1090m, 1068m, 907w, 846w, 832w, 800w, 744m, 697s cm⁻¹. ¹H NMR: δ (CDCl₃) 7.54–7.05 (12:6:12, 30H, m, 2PPh₃), 4.77 (1H, d, ²J = 3.1 Hz, CH₂), 4.67 (1H, d, ²J = 3.0 Hz, CH₂), 4.27 (5H, s, C₅H₅), 3.73 (2H, m, THF), 1.84 (2H, m, THF), 1.76 (3H, s, CH₃). ¹³C NMR: δ (CDCl₃) 138.7 (m, ipso-C, 2PPh₃), 133.8, 127.4, 128.6 (all m, C2 to C6, 2PPh₃), 130.0 and 115.9 (C2 and C3), 113.9 [t, ²J(PC) = 25.5 Hz, Cl], 111.3 (CH₂), 85.1 (C₅H₅), 67.9 and 25.6 (both CH₂, both THF), 25.2 (CH₃). MS (FAB): m/z (%) 755 (25) M⁺, 690 (100) [Ru(PPh₃)₂(C₅H₅)]⁺, 493 (25) [M − PPh₃]⁺, 428 (100) [Ru(PPh₃)(C₅H₅)]⁺.

4.1.3. Ru{C≡CC=CH(CH₂)₄}(PPh₃)₂(η-C₅H₅) (3)

1-Ethynyl-cyclohex-1-ene (24.8 mg, 0.234 mmol) was treated with n-butyllithium (0.234 mmol) and the ruthenium cation as described in the general procedure to give yellow microcrystalline 3 (120 mg, 0.151 mmol, 73%), m.p. 162°C (dec.) after evaporation of the solvent. Found: C, 70.99; H, 5.04; M⁺, 739. C₄₁-H₄₄P₂Ru calc.: C, 73.95; H, 5.57%; M, 739. IR (Nujol): 2064s [ν(C≡C)], 1617m [ν(C=C)], 1588w, 1571w, 1481s, 1436s, 1090s, 1069s, 914m, 833m, 801m, 745s, 696s cm⁻¹. ¹H NMR: δ (CDCl₃) 7.7–7.0 (30H, m, 2PPh₃), 5.58 (1H, t (br), CH), 4.29 (5H, s, C₅H₅); 2.08, 1.94, 1.72, 1.25 (all 2H, all br, all ring CH₂). ¹³C NMR: δ (CDCl₃) 138.7 [m, ipso-C, 2PPh₃], 133.7, 127.1, 128.6 (all m, C2 to C6, 2PPh₃], 125.8 and 116.0 (C2 and C3), 124.4 (CH), 107.8 [t, ²J(PC) = 25.4 Hz, C(1)], 85.0 (C₅H₅), 30.9, 25.7, 23.2, 22.4 (all ring CH₂). MS (FAB): m/z (%) 795 (10) M⁺, 690 (100) [Ru(PPh₃)₂(C₅H₅)]⁺, 533 [M − PPh₃]⁺.

4.1.4. Ru(C≡CC≡CH)(PPh₃)₂(η-C₅H₅) (4)

An excess of 1,3-butadiyne (21 mg, 0.42 mmol) reacted at −20°C with n-butyllithium (0.234 mmol) and the ruthenium cation as described in the general procedure to give yellow microcrystalline 4 (85 mg, 0.115 mmol, 56%), m.p. 115°C (dec.), as a mono-THF solvate after chromatography and evaporation of the solvent. Found: C, 70.99; H, 5.04; M⁺, 739. C₄₅H₃₆P₂Ru · THF calc.: C, 72.49; H, 5.46%; M, 739. IR (Nujol): 3299w [ν(≡CH)], 2109s, [ν(C≡CH)], 1971m [ν(C≡C)], 1588w, 1573w, 1481s, 1436s, 1088m, 832m, 808m, 756w, 742m, 696s cm⁻¹. ¹H NMR: δ(CDCl₃) 7.42–7.14 (12:6:12, 30H, m, 2PPh₃), 4.33 (5H, s, C₅H₅), 3.73 and 1.84 (each 2H, both m, THF), 1.42 (1H, t, ⁶J(PH) = 0.9 Hz, ≡CH). ¹³C NMR δ(CDCl₃): 138.3 (m, ipso-C, 2PPh₃), 133.8, 127.3, 128.6 (each m, C2 to C6, 2PPh₃), 128.4 (CH), 116.4 (t, ²J(PC) = 24.6 Hz, C1), 94.4 and 73.9 (C2 and C3), 85.6 (C₅H₅), 67.9 and 25.6 (both CH₂, both THF). MS (FAB): m/z (%) 739 (2) M⁺, 690 (10) [Ru(PPh₃)₂(C₅H₅)]⁺, 428 (100) [Ru(PPh₃)(C₅H₅)]⁺.

4.1.5. {Ru(PPh₃)₂(η-C₅H₅)}₂(μ-C₄) (5)

In a variation of the general procedure 1,3-butadiyne (5.2 mg as a 0.1 M solution in diethyl ether, 0.104 mmol) reacted with n-butyllithium (0.208 mmol) at −20°C. A solution of the ruthenium cation was added and after 15 min product isolation was achieved by chromatography as described in the general procedure, giving yellow microcrystalline 5 (60 mg, 0.042 mmol, 41%), m.p. 141°C (dec.). A di-THF solvate was obtained from THF/pentane mixtures. Found: C, 65.98; H, 4.87; M⁺, 1429. C₈₆H₇₀P₄Ru₂ · 2THF calc.: C, 71.74; H, 5.51%; M, 1429. IR (Nujol): 1970s [ν(C≡C)], 1585w, 1572w, 1478s, 1432s, 1091m, 1085m, 830m, 802m, 746m,

737m, 694m cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 7.60, 7.00, 7.12 (12:6:12H, 'd', 't', 'd', 4PPh$_3$), 4.20 (10H, s, 2C$_5$H$_5$), 3.73 and 1.84 (each 4H, both m, both THF). ^{13}C NMR: δ (CDCl$_3$) 139.4 (m, *ipso*-C, 4PPh$_3$), 134.2, 127.04, 128.03 (each m, C-2 to 6, 4PPh$_3$), 85.4 (2C$_5$H$_5$), 67.9 and 25.6 (both CH$_2$, both THF). MS (FAB): *m/z* (%) 1429 (30) M$^+$, 1167 (25) [M − PPh$_3$]$^+$, 905 (55) [M − 2PPh$_3$]$^+$, 839 (28) [M − 2PPh$_3$ − C$_5$H$_5$]$^+$, 827 (30), 690 (70), 642 (100) [M − 3PPh$_3$]$^+$.

4.2. Protonation reactions of some alkynyl complexes

4.2.1. Preparation of [Ru{C=C=CCH$_2$CMe$_2$CH$_2$-C[Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)]=CH}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (7)

HPF$_6$ (0.07 mmol, 0.1 M solution of HPF$_6$ in THF) was slowly added to 2 (100 mg, 0.132 mmol) dissolved in THF (5 ml). The mixture immediately turned deep blue. The product was isolated by column chromatography (CH$_2$Cl$_2$/Et$_2$O = 1:2) on basic alumina (15 × 1 cm) to give 7 (84 mg, 0.051 mmol, 77%), as crystals, m.p. 173°C, from CH$_2$Cl$_2$/pentane. Found: C, 65.48; H, 5.06; M$^+$, 1512. C$_{92}$H$_{81}$F$_6$P$_5$Ru$_2$ calc.: C, 66.66; H, 4.93%; M (cation), 1512. IR (Nujol): 1975s, [ν(C=C=C)], 1627w [ν(C=C)], 1575w, 1480s, 1436s, 1339m, 1090m,

1000m, 980w, 840s [ν(PF$_6$)], 745s, 690s cm^{-1}. ^{1}H NMR: δ(CDCl$_3$): 7.70–7.07 (61H, m, 4PPh$_3$ and C=CH), 4.58 and 4.45 (each 5H, both s, both C$_5$H$_5$), 3.01 (2H, s, CH$_2$), 1.26 (6H, s, 2Me), 1.22 (2H, s, CH$_2$). ^{13}C NMR: δ(CDCl$_3$) 277.1 (Ru=C=C=C), 198.1 (t, Ru=C), 151.4 (Ru=C=C=C), 142.4 (Ru=C=C=C), 137.6 (m, *ipso*-C, 4PPh$_3$), 133.8, 133.3, 129.9, 129.3, 128.0, 127.7 (d, d, s, s, s, d, C2 to C4 of 4PPh$_3$ and C=CH), 90.8 and 87.7 (both C$_5$H$_5$), 68.2 (C), 49.0 and 32.8 (2CH$_2$), 28.0 and 29.7 (2Me). MS (FAB): *m/z* (%) 1512 (5) M$^+$, 1250 (10) [M − PPh$_3$]$^+$, 988 (10), 822 (40), 726 (22), 690 (20), 560 (28), 428 (100) [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$.

4.2.2. Preparation of [Ru{C=CH[C=CH(CH$_2$)$_4$]}-(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (8)

HBF$_4$ (0.13 mmol, 0.1 M solution of HBF$_4$ in THF) was slowly added to a solution of 3 (100 mg, 0.126 mmol) in THF (5 ml). The mixture was evaporated and the residue was washed with diethyl ether. The white powder remaining was 8 (90 mg, 0.094 mmol, 75%), m.p. 86°C (dec). This product contains one equivalent of THF and decomposes slowly at room temperature so that no ^{13}C NMR spectrum could be obtained. Found: C, 62.24; H, 5.02; M$^+$, 796. C$_{49}$H$_{45}$BF$_4$P$_2$Ru · THF calc.: C, 66.60; H, 5.59%; M (cation), 796. IR

TABLE 3. Crystal data and refinement details for 5a, 5b and 10

	5a	5b	10
Formula	C$_{86}$H$_{70}$P$_4$Ru$_2$ · 2C$_4$H$_8$O	C$_{86}$H$_{70}$P$_4$Ru$_2$	C$_{45}$H$_{38}$OP$_2$Ru
MW	1573.8	1430.0	757.8
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P$\bar{1}$ (No. 2)	Pbaa (No. 54)	P$\bar{1}$ (No. 2)
a, Å	12.688(1)	29.404(5)	14.234(5)
b, Å	15.151(4)	21.48(2)	11.393(4)
c, Å	11.264(2)	11.483(3)	11.051(8)
α, deg.	101.64(2)	–	94.32(4)
β, deg.	103.88(1)	–	93.27(4)
γ, deg.	98.41(1)	–	90.68(3)
U, Å^3	2015.3	7254	1784
Z	1	4	2
ρ_c, g cm^{-3}	1.297	1.31	1.41
F(000)	814	2936	780
Crystal size, mm	0.28 × 0.48 × 0.17	0.09 × 0.30 × 0.22	0.22 × 0.42 × 0.49
A* (min, max)	n/a	1.04, 1.14 (gaussian)	1.11, 1.27 (gaussian)
μ, cm^{-1}	4.60	4.8	5.6
2θ_{max}, deg	45	50	50
N	6119	6373	6270
N$_0$(I > nσ(I))	3962 (n = 2.5)	1789 (n = 3)	5229 (n = 4)
R	0.026	0.11	0.032
R$_w$	0.028	0.12	0.035

Abnormal features / variations in procedure

5b: A poor quality result was obtained from inferior material, presenting itself in the form of poorly diffracting, micaceously-twinned plates. Anisotropic thermal parameters were refined for Ru, P(1, 2) only, the other atoms taking the isotropic form.

(Nujol): 1637 and 1622m [ν(C=C)], 1587w, 1573w, 1481s, 1437s, 1091s, 1056s [ν(BF$_4$)], 748s, 697m cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) 7.7–6.9 (30H, m, 3PPh$_3$), 5.47 (1H, br, ring C=CH), 4.96 (1H, s, Ru=C=CH), 5.20 (5H, s, C$_5$H$_5$), 3.75 and 1.85 (each 2H, THF); 2.20, 1.90, 1.52, 1.23 (each 2H, br, 4 × ring CH$_2$). MS (FAB): m/z (%) 796 (50) M$^+$, 690 (50), [Ru(PPh$_3$)$_2$(C$_5$H$_5$)]$^+$, 534 (100) [M − PPh$_3$]$^+$.

4.2.3. Preparation of [Ru{C≡CC(O)Me}(PPh$_3$)$_2$(η-C$_5$H$_5$) (10)

Complex 5 (50 mg, 0.068 mmol) was dissolved in THF (5 ml) that contained H$_2$O and a trace of HBF$_4$ was added. After 24 h the solvent was removed and the residue was recrystallised from CH$_2$Cl$_2$/pentane to give 10 (45 mg, 0.059 mmol, 87%), m.p. 233°C (lit. [15] 213–216°C), further identified by comparison of its IR and NMR spectra with the literature values [15] and by the single-crystal X-ray study reported below.

4.3. Crystallography

Intensity data for 5a were measured at 295 K on an Enraf-Nonius CAD-4F diffractometer fitted with graphite monochromatized Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å. The $\omega:2\theta$ scan technique was employed to measure 6119 data up to a maximum Bragg angle of 22.5°. The data set was corrected for Lorentz and polarization effects and an analytical absorption correction was applied such that the maximum and minimum transmission factors were 0.924 and 0.849, respectively. Relevant crystal data are given in Table 3. The structure was solved from the interpretation of the Patterson function and refined by a block-matrix least-squares procedure based on F [18]. The crystallographic asymmetric unit comprises one half molecule, located about a crystallographic centre of inversion, and one THF molecule of crystallization. All non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model in their calculated positions. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F) + |g|F^2]$, the refinement was continued until convergence ($k = 1.05$ and $g = 0.0005$); final refinement details are listed in Table 3. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied and the maximum residual in the final difference map was 0.35 e Å^{-3}. Fractional atomic coordinates are listed in Table 4 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [19] at 25% probability ellipsoids. Scattering factors for neutral Ru (corrected for f' and f'') were from ref. 20 and those for the remaining atoms were as incorporated in the SHELX76 program

TABLE 4. Fractional atomic coordinates and B_{eq} values for {Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)}$_2$(μ-C$_4$) (5a)

Atom	x	y	z	B_{eq}
Ru	0.47521(2)	0.25483(2)	0.00884(2)	2.58
P(1)	0.3098(1)	0.2201(1)	0.0538(1)	2.82
P(2)	0.6012(1)	0.2912(1)	0.2031(1)	2.84
C(1)	0.4887(3)	0.1244(2)	0.0050(3)	2.95
C(2)	0.4969(3)	0.0448(2)	0.0005(3)	3.24
C(3)	0.4757(4)	0.2392(3)	−0.1913(3)	4.84
C(4)	0.5807(4)	0.2904(3)	−0.1135(4)	5.11
C(5)	0.5619(3)	0.3730(2)	−0.0443(3)	4.16
C(6)	0.4494(3)	0.3728(2)	−0.0794(3)	4.19
C(7)	0.3948(3)	0.2892(3)	−0.1704(3)	4.42
C(11)	0.2425(3)	0.3198(2)	0.0621(3)	3.61
C(12)	0.2783(3)	0.3935(2)	0.1679(4)	4.19
C(13)	0.2384(4)	0.4745(3)	0.1673(5)	5.34
C(14)	0.1651(4)	0.4832(3)	0.0620(5)	6.53
C(15)	0.1293(4)	0.4119(3)	−0.0434(5)	6.29
C(16)	0.1668(3)	0.3307(3)	−0.0446(4)	4.66
C(21)	0.2041(3)	0.1299(2)	−0.0714(3)	3.47
C(22)	0.0968(3)	0.1068(3)	−0.0604(4)	4.90
C(23)	0.0189(3)	0.0394(3)	−0.1533(5)	5.87
C(24)	0.0453(4)	−0.0061(3)	−0.2559(5)	6.03
C(25)	0.1511(4)	0.0151(3)	−0.2673(5)	5.76
C(26)	0.2302(3)	0.0832(3)	−0.1750(4)	4.29
C(31)	0.2908(3)	0.1739(2)	0.1882(3)	3.34
C(32)	0.2385(3)	0.2105(3)	0.2748(3)	4.16
C(33)	0.2231(3)	0.1671(3)	0.3690(4)	5.32
C(34)	0.2582(4)	0.0865(4)	0.3740(4)	6.13
C(35)	0.3086(3)	0.0487(3)	0.2887(5)	6.16
C(36)	0.3261(3)	0.0915(3)	0.1954(4)	5.11
C(41)	0.5920(3)	0.2226(2)	0.3193(3)	3.26
C(42)	0.6238(3)	0.1388(3)	0.3112(4)	4.58
C(43)	0.6125(4)	0.0900(3)	0.4022(5)	6.08
C(44)	0.5716(4)	0.1240(3)	0.4985(5)	6.42
C(45)	0.5376(4)	0.2062(3)	0.5054(4)	6.13
C(46)	0.5473(3)	0.2550(3)	0.4168(4)	4.79
C(51)	0.7405(3)	0.2901(2)	0.1799(3)	3.87
C(52)	0.8209(3)	0.3705(3)	0.2093(4)	5.21
C(53)	0.9214(4)	0.3695(4)	0.1828(6)	7.19
C(54)	0.9451(4)	0.2882(4)	0.1279(6)	7.92
C(55)	0.8661(4)	0.2076(4)	0.0965(6)	8.08
C(56)	0.7633(3)	0.2085(3)	0.1196(4)	5.74
C(61)	0.6222(3)	0.4080(2)	0.3046(3)	3.21
C(62)	0.7030(3)	0.4382(3)	0.4199(3)	4.61
C(63)	0.7141(4)	0.5266(3)	0.4946(4)	5.21
C(64)	0.6448(4)	0.5826(3)	0.4571(4)	5.66
C(65)	0.5636(4)	0.5532(2)	0.3447(4)	4.90
C(66)	0.5533(3)	0.4666(2)	0.2675(3)	3.71
O(7)	0.0695(9)	0.6334(6)	0.3522(10)	17.37
C(71)	0.1197(12)	0.7221(10)	0.3551(17)	20.79
C(72)	0.0789(17)	0.7969(9)	0.3792(21)	36.74
C(73)	0.0095(19)	0.7416(13)	0.4501(20)	22.50
C(74)	0.0056(13)	0.6643(16)	0.4436(15)	30.16

[18]; the refinement was performed on a SUN 4/280 computer.

Unique diffractometer data sets for 5b and 10 were measured at ca. 295 K within the specified $2\theta_{max}$ limits ($2\theta/\theta$ scan mode; monochromatic Mo $K\alpha$ radiation

$(\lambda = 0.7107_3$ Å)) yielding N independent reflections, N_0 being considered 'observed' and used in the full matrix least squares refinements after absorption correction [21]. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values (Tables 5 and 6). For 5b and 10 statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used; the XTAL2.6 program system [21] was employed. Conventional residuals

TABLE 5. Fractional atomic coordinates and U_{eq} values for $\{Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4)$ (5b)

Atom	x	y	z	U_{eq} (Å^2)
Ru	0.37203(8)	0.5692(1)	0.8883(2)	0.0547(9)
C(01)	0.375(1)	0.558(1)	1.081(2)	0.053(9)
C(02)	0.424(1)	0.567(2)	1.031(3)	0.060(9)
C(03)	0.425(1)	0.629(2)	0.987(3)	0.06(1)
C(04)	0.375(1)	0.652(1)	0.995(3)	0.07(1)
C(05)	0.358(1)	0.608(2)	1.062(3)	0.10(2)
P(1)	0.3614(3)	0.6329(5)	0.7306(7)	0.055(4)
C(111)	0.412(1)	0.684(2)	0.713(3)	0.06(1)
C(112)	0.452(1)	0.657(2)	0.662(3)	0.07(1)
C(113)	0.490(1)	0.696(2)	0.659(3)	0.08(1)
C(114)	0.492(1)	0.754(2)	0.701(3)	0.08(1)
C(115)	0.454(1)	0.778(2)	0.750(3)	0.09(1)
C(116)	0.414(1)	0.743(2)	0.758(3)	0.06(1)
C(121)	0.313(1)	0.690(2)	0.744(3)	0.06(1)
C(122)	0.309(1)	0.735(2)	0.661(3)	0.08(1)
C(123)	0.272(2)	0.776(2)	0.669(4)	0.13(2)
C(124)	0.243(1)	0.767(2)	0.762(4)	0.09(1)
C(125)	0.248(1)	0.726(2)	0.846(3)	0.09(1)
C(126)	0.282(1)	0.683(2)	0.839(3)	0.07(1)
C(131)	0.350(1)	0.601(1)	0.590(3)	0.07(1)
C(132)	0.310(1)	0.569(2)	0.582(3)	0.09(1)
C(133)	0.297(2)	0.555(2)	0.463(5)	0.15(2)
C(134)	0.321(1)	0.569(2)	0.369(4)	0.10(1)
C(135)	0.355(1)	0.610(2)	0.371(3)	0.06(1)
C(136)	0.369(1)	0.630(1)	0.480(3)	0.050(9)
P(2)	0.3990(3)	0.4797(5)	0.8057(8)	0.066(4)
C(211)	0.461(1)	0.479(2)	0.754(3)	0.06(1)
C(212)	0.486(1)	0.534(1)	0.776(3)	0.06(1)
C(213)	0.532(1)	0.533(2)	0.737(3)	0.07(1)
C(214)	0.547(1)	0.483(2)	0.677(3)	0.07(1)
C(215)	0.521(1)	0.432(2)	0.654(3)	0.08(1)
C(216)	0.475(1)	0.428(2)	0.690(3)	0.09(1)
C(221)	0.398(1)	0.419(2)	0.916(2)	0.056(9)
C(222)	0.438(1)	0.384(2)	0.941(3)	0.09(1)
C(223)	0.437(1)	0.335(2)	1.023(4)	0.10(1)
C(224)	0.397(2)	0.328(2)	1.091(4)	0.13(2)
C(225)	0.364(1)	0.364(2)	1.071(4)	0.10(1)
C(226)	0.361(1)	0.407(2)	0.980(4)	0.10(1)
C(231)	0.372(1)	0.438(2)	0.686(2)	0.054(8)
C(232)	0.335(1)	0.404(2)	0.702(4)	0.10(1)
C(233)	0.312(1)	0.371(2)	0.613(4)	0.11(1)
C(234)	0.330(2)	0.375(2)	0.503(5)	0.14(2)
C(235)	0.362(2)	0.418(2)	0.481(4)	0.12(2)
C(236)	0.382(1)	0.454(2)	0.556(3)	0.09(1)
C(1)	0.3097(9)	0.533(1)	0.865(2)	0.042(8)
C(2)	0.2703(8)	0.513(1)	0.861(2)	0.05(1)

TABLE 6. Fractional atomic coordinates and U_{eq} values for $[Ru\{C\equiv CC(O)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (10)

Atom	x	y	z	U_{eq} (Å^2)
Ru	0.24210(2)	0.12465(2)	0.08426(2)	0.03227(8)
C(01)	0.2513(3)	−0.0638(3)	0.1233(3)	0.053(1)
C(02)	0.3429(3)	−0.0229(3)	0.1048(3)	0.053(1)
C(03)	0.3446(3)	0.0100(3)	−0.0155(3)	0.054(1)
C(04)	0.2531(3)	−0.0104(3)	−0.0706(3)	0.051(1)
C(05)	0.1956(3)	−0.0556(3)	0.0129(3)	0.053(1)
C(1)	0.1171(2)	0.1633(2)	0.1489(3)	0.036(1)
C(2)	0.0411(2)	0.1801(3)	0.1906(3)	0.044(1)
C(3)	−0.0397(3)	0.2149(3)	0.2542(3)	0.051(1)
O(3)	−0.1023(2)	0.1495(3)	0.2758(3)	0.110(2)
C(4)	−0.0457(3)	0.3422(4)	0.2934(4)	0.084(2)
P(1)	0.22598(5)	0.27027(6)	−0.04795(7)	0.0324(2)
C(111)	0.3326(2)	0.2823(3)	−0.1322(3)	0.039(1)
C(112)	0.4120(2)	0.3371(3)	−0.0743(3)	0.053(1)
C(113)	0.4966(3)	0.3375(4)	−0.1308(4)	0.078(2)
C(114)	0.5026(3)	0.2808(5)	−0.2442(4)	0.093(2)
C(115)	0.4255(3)	0.2255(4)	−0.3013(4)	0.083(2)
C(116)	0.3402(3)	0.2253(3)	−0.2466(3)	0.057(1)
C(121)	0.1319(2)	0.2409(3)	−0.1692(3)	0.037(1)
C(122)	0.1206(2)	0.3155(3)	−0.2632(3)	0.048(1)
C(123)	0.0495(3)	0.2954(3)	−0.3531(3)	0.053(1)
C(124)	−0.0109(2)	0.2010(3)	−0.3512(3)	0.054(i)
C(125)	−0.0017(2)	0.1273(3)	−0.2586(3)	0.052(1)
C(126)	0.0690(2)	0.1476(3)	−0.1674(3)	0.043(1)
C(131)	0.1967(2)	0.4238(2)	−0.0056(3)	0.036(1)
C(132)	0.1217(2)	0.4424(3)	0.0666(3)	0.043(1)
C(133)	0.0895(2)	0.5545(3)	0.0952(3)	0.051(1)
C(134)	0.1334(3)	0.6496(3)	0.0526(4)	0.059(1)
C(135)	0.2080(3)	0.6332(3)	−0.0189(4)	0.066(2)
C(136)	0.2400(3)	0.5209(3)	−0.0486(3)	0.053(1)
P(2)	0.30660(5)	0.22000(7)	0.26070(7)	0.0338(3)
C(211)	0.4342(2)	0.2534(3)	0.2752(3)	0.040(1)
C(212)	0.4917(2)	0.2194(3)	0.1840(3)	0.051(1)
C(213)	0.5876(3)	0.2478(4)	0.1955(4)	0.065(2)
C(214)	0.6247(3)	0.3104(4)	0.2968(4)	0.067(2)
C(215)	0.5683(3)	0.3453(4)	0.3891(4)	0.064(2)
C(216)	0.4730(2)	0.3163(3)	0.3792(3)	0.054(1)
C(221)	0.2936(2)	0.1171(3)	0.3799(3)	0.039(1)
C(222)	0.3675(2)	0.0469(3)	0.4164(3)	0.052(1)
C(223)	0.3544(3)	−0.0391(3)	0.4963(4)	0.066(2)
C(224)	0.2678(3)	−0.0547(3)	0.5432(3)	0.061(1)
C(225)	0.1936(3)	0.0136(3)	0.5076(3)	0.051(1)
C(226)	0.2050(2)	0.0963(3)	0.4244(3)	0.044(1)
C(231)	0.2665(2)	0.3626(3)	0.3263(3)	0.038(1)
C(232)	0.2193(3)	0.3794(3)	0.4306(4)	0.067(2)
C(233)	0.1951(3)	0.4915(4)	0.4743(4)	0.086(2)
C(234)	0.2175(3)	0.5879(3)	0.4163(4)	0.063(1)
C(235)	0.2659(3)	0.5733(3)	0.3135(4)	0.058(1)
C(236)	0.2912(2)	0.4613(3)	0.2693(3)	0.049(1)

(R, R_w) on $|F|$ at convergence are quoted, neutral atom complex scattering factors being employed. Material deposited with the Cambridge Crystallographic Data Centre comprises structure factor amplitudes, thermal and hydrogen atom parameters, and full molecular non-hydrogen geometries.

Acknowledgments

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