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CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY

XXV *. CONVERSION OF ALKOXYCARBENE COMPLEXES TO VINYL ETHER DERIVATIVES: X-RAY STRUCTURE OF $Ru\{C(OPr^i)=CHPh\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$

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Summary

Several cationic alkoxy(alkyl)carbene complexes containing the $Ru(L)(PPh_3)(\eta\text{-}C_5H_5)$ ($L = CO$ or PPh_3) moiety have been deprotonated with NaOMe to the corresponding vinyl ether derivatives. The reaction is reversed by addition of HPF_6. Many of the vinyl ether complexes were obtained as mixtures of *E* and *Z* isomers; the X-ray structure of $Ru\{C(OPr^i)=CHPh\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ shows that it is obtained only as the *E* isomer, and that the unit cell contains equal numbers of the two enantiomers. $Ru\{C(OPr^i)=CHPh\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ is monoclinic, space group $P2_1/c$, with *a* 10.337(5), *b* 15.161(4), *c* 18.714(5) Å, β 90.83(3)°, and $Z = 4$; 2240 reflections [$I > 2.5\sigma(I)$] were refined to $R = 0.0388$, $R_w = 0.0436$. Important distances: Ru–C(vinyl) 2.103(6), Ru–CO 1.832(7), Ru–P 2.298(2), C=C(vinyl) 1.335(8), C–OMe 1.381(7) Å. Addition of NaOMe to the product of the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and HC≡CC(O)Me in MeOH afforded a mixture of $Ru\{C\equiv CC(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)$ and $Ru\{C(OMe)=CHC(O)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)$. The latter loses PPh_3 on standing in solution at ambient temperatures, forming the chelate complex $Ru\{C(OMe)=CHC(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)$. The similar conversion of $Ru\{C(OMe)=CHC(O)OMe\}(PPh_3)_2(\eta\text{-}C_5H_5)$ to the corresponding chelate complex required heating at 65°C for 75 minutes.

Introduction

We have previously described the synthesis of cationic alkoxy(alkyl)carbene complexes of ruthenium and osmium from the reactions between the corresponding

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vinylidene derivatives and alcohols [1], e.g.

$$[Ru(C{=}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+ + MeOH \rightarrow [Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$$

and the formation of the cyclic carbene complexes, $[Ru\{\overline{C(CH_2)_nCH_2O}\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ ($n = 2$, 3) from ω-hydroxyalkynes [2]. These cyclic carbene complexes can be metallated, and undergo H–D exchange at the β-carbon, but unlike their nickel, palladium, and platinum analogues [3], cannot be deprotonated with NaOMe or NEt_3 to give neutral vinylic derivatives. This paper describes some related reactions of the acyclic carbene complexes, which do afford vinyl ether derivatives; the nature and course of the reaction between $HC{\equiv}CC(O)Me$ and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ is also discussed.

Results and discussion

The cationic complex $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (**1**) readily undergoes H–D exchange at the β-carbon, for example, on addition of MeOD. The acidity of these protons is further demonstrated by the reaction of NaOMe with the cation, which results in deprotonation and formation of the neutral yellow vinyl ether complex $Ru[C(OMe){=}CHPh](PPh_3)_2(\eta\text{-}C_5H_5)$ (**2**). This complex was readily identified from its IR spectrum, which contained a $\nu(C{=}C)$ band at 1566 cm^{-1}, and the ^1H NMR spectrum, in which singlet resonances at δ 3.37, 4.52 and 6.03 ppm (with relative intensities 3/5/1) can be assigned to the OMe, C_5H_5 and CH protons, respectively. In the ^{13}C NMR spectrum the α-carbon resonates at δ 193.1 ppm, rather than in the carbene region observed for **1**. The mass spectrum did not contain a molecular ion, the highest peaks centred on m/z 793 corresponding to the ion $[M - OMe]^+$.

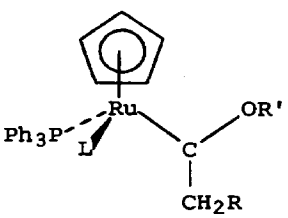
Complex **2** is relatively unstable towards oxidation, the solid decomposing in air over a few days; solutions in $CDCl_3$ or CS_2 decompose readily. Addition of $HPF_6 \cdot OEt_2$ results in immediate regeneration of the alkoxycarbene complex **1**.

Extension of the deprotonation reaction to related cations gave several analogous complexes of varying stability. Thus, $[Ru\{C(OMe)Et\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (**3**) afforded the very unstable yellow complex $Ru\{C(OMe){=}CHMe\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**4**), which could be identified only on the basis of the similarity of its IR spectrum to that of **2**. The ethoxy(benzyl)carbene complex **5** similarly afforded $Ru\{C(OEt){=}CHPh\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**6**), also yellow, whose ^1H NMR spectrum contained two C_5H_5 resonances, suggesting the formation of isomers. Attempted separation by preparative TLC was unsuccessful. In like manner, the complexes $Ru\{C(OR'){=}CHR\}(L)(L')(\eta\text{-}C_5H_5)$ (L = L' = PPh_3, R = CO_2Me, R' = Me (**7**), Et (**8**); L = CO, L' = PPh_3, R = Ph, R' = Me (**9**), Pr^i (**10**); LL' = dppm, R = Ph, R' = OMe (**11**)) were obtained from the corresponding alkoxycarbene cations, and were readily identified from analytical and spectroscopic data (see Experimental).

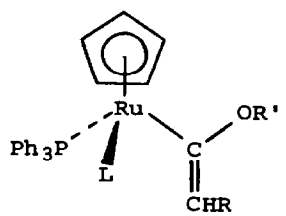
We find that the stability of these complexes in the solid state is increased by the presence of π-acidic ligands, and of electron-withdrawing substituents on the vinyl group. Thus, the mixed CO, PPh_3 complexes are more stable than the bis(triphenylphosphine) derivatives, while a marked decrease in stability ensues as the substituent on the β-carbon is changed along the series: CO_2Me > Ph > Me. These observations

are entirely consistent with the stabilisation of an electron-rich vinyl ether moiety, and run counter to the trend found with the alkoxycarbene complexes, in which electron-withdrawing substituents or good π-acceptor ligands destabilise the system by increasing the electron deficiency of the α-carbon.

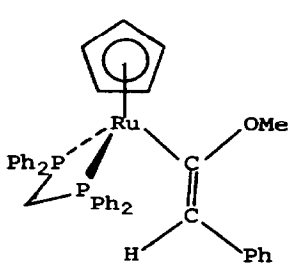
These reactions parallel those of the neutral Fischer-type carbene complexes, such as $M[C(OMe)Me](CO)_5$ (M = Cr, Mo, W), which also undergo similar H–D exchange [4] and deprotonation reactions (for M = Cr) [5]. Conversion of cationic alkoxycarbene complexes of nickel, such as $[Ni(C_6Cl_5)\{C(OMe)Me\}(PMe_2Ph)_2]^+$ [6], and platinum, such as *trans*-$[PtX\{C(OMe)Me\}L_2]^+$ (X = Cl, L = PMe_2Ph; X = CF_3, L = $AsMe_3$), to σ-vinyl ether derivatives has been described earlier [7]. An alternative synthesis of vinyl ether complexes, from chlorometal derivatives and $LiC(OMe)=CH_2$, has been reported, together with their protonation to the corresponding alkoxycarbenes [8].



	L	R	R'
(1)	PPh_3	Ph	Me
(3)	PPh_3	Me	Me
(5)	CO	Ph	Et



	L	R	R'
(2)	PPh_3	Ph	Me
(4)	PPh_3	Me	Me
(6)	CO	Ph	Et
(7)	PPh_3	CO_2Me	Me
(8)	PPh_3	CO_2Me	Et
(9)	CO	Ph	Me
(10)	CO	Ph	Pr^i



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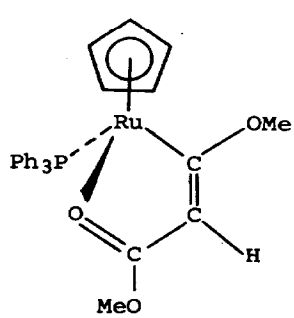


(12)

Isomerism of vinyl ether complexes

The deprotonation of $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ affords only one isomer of **2**, as indicated by its ^1H NMR spectrum, although, in principle, both the *E* and *Z* isomers could be formed. In contrast, the NMR spectra of complexes **7** and **8** showed them to consist of approximately 3/1 mixtures of isomers, as indicated by the doubling of the CH, CO_2Me and C_5H_5 resonances. Similarly, complex **11** was found to be a 4/1 mixture of isomers. This isomerism results from the formation of both *E* and *Z* isomers, probably because of the smaller size of the CO_2Me group compared with the Ph group in **2**. We cannot definitely assign the stereochemistries, although steric considerations suggest that the most abundant isomer should have the *E* configuration about the double bond.

An added source of isomerism is present in complexes **6**, **9** and **10**. The ruthenium atom is bonded to four different ligands, and is thus a chiral centre. While the NMR spectra of **6** and **9** show the presence of geometrical isomers in ca. 1/1 ratio, complex **10** is obtained as the *E* isomer (see below), but the non-equivalence of the $CHMe_2$ methyl groups results from the presence of the chiral centre. Indeed, the unit cell of this complex contains equal numbers of each enantiomer.

*X-ray structure of **10***

The molecular structure of complex **10** has been determined by means of a single-crystal X-ray study, to obtain further information concerning the configuration of the vinyl group. Crystals of **10** contain discrete molecules, with no non-hydrogen intermolecular distances less than 3.5 Å.

A plot of the molecular structure of **10** is shown in Fig. 1. The ruthenium atom is

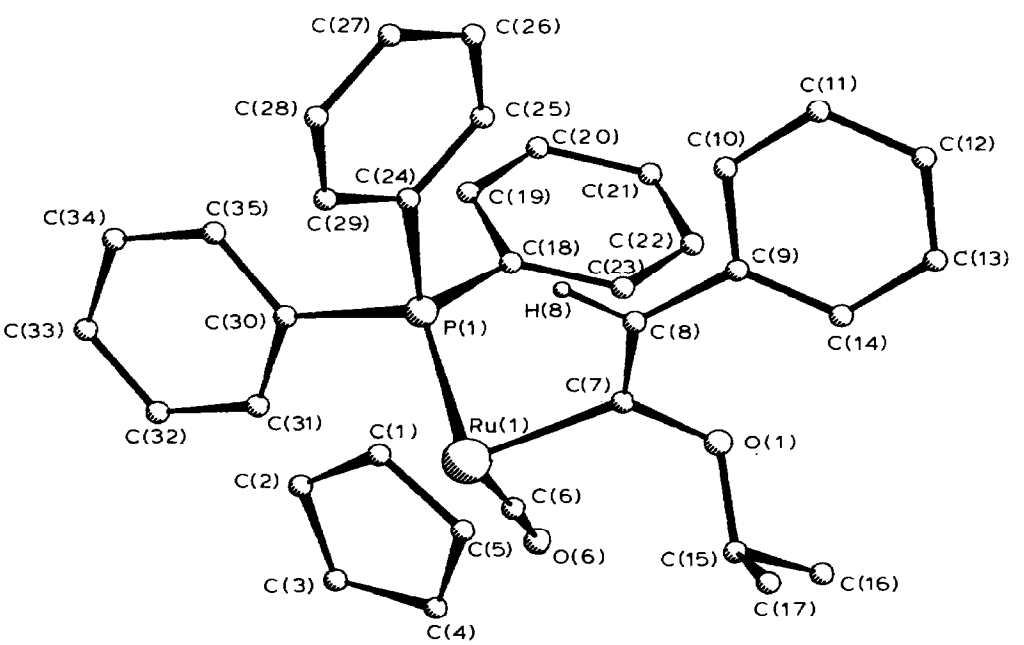


Fig. 1. Molecular structure of $Ru\{C(OPr^i)=CHPh\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**10**), showing atom numbering scheme.

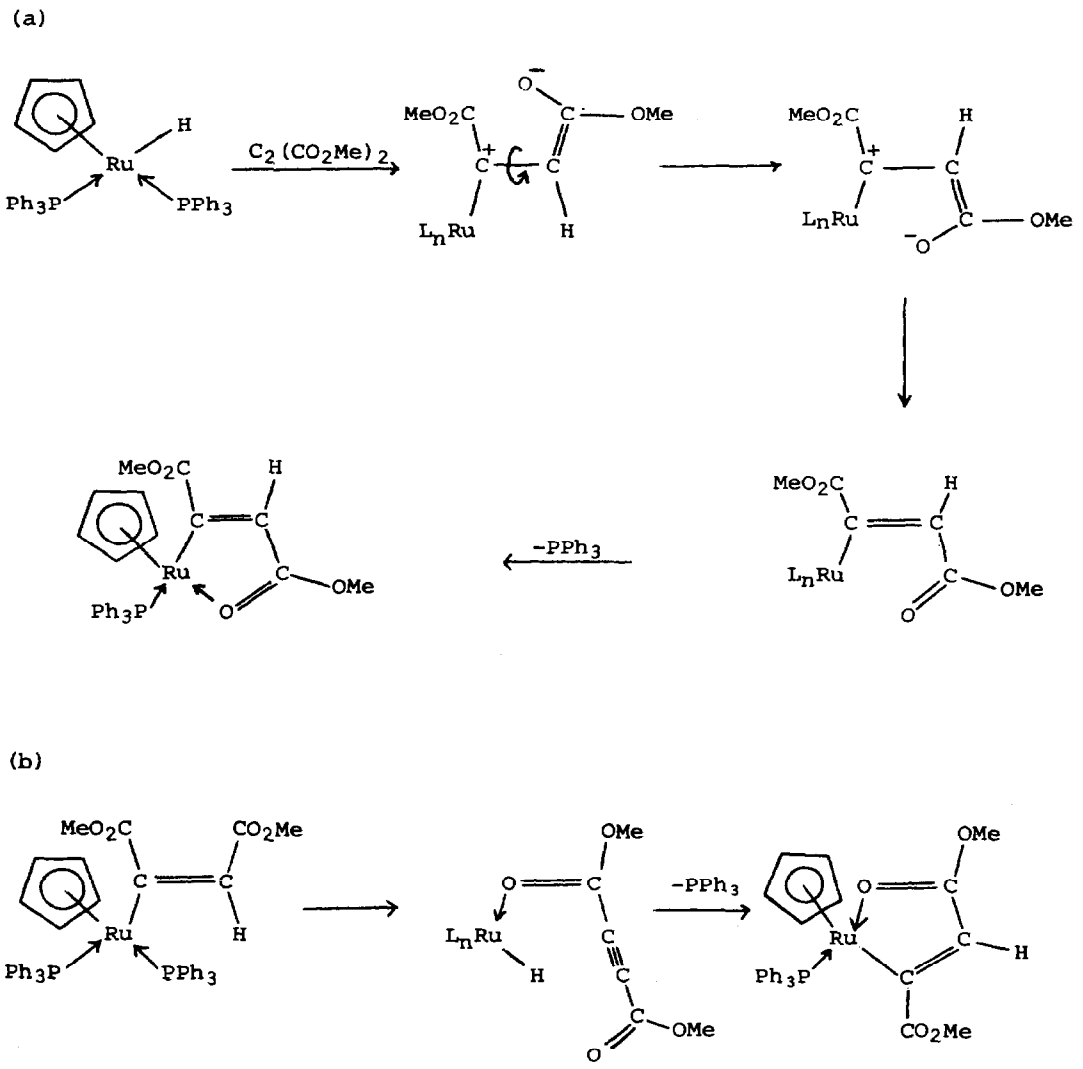
coordinated by CO (Ru(1)–C(6), 1.832(7) Å), PPh_3 (Ru(1)–P(1) 2.298(2) Å) and C_5H_5 ligands (Ru(1)–C(cp) 2.261(6)–2.279(6), av. 2.270 Å), all distances being within the ranges normally found for complexes containing these ligands [9]. The vinyl ether ligand has the *E* configuration, that is, the ruthenium atom is *trans* to the phenyl group. The Ru(1)–C(7) bond length (2.103(6) Å) is similar to those found in the butadienyl complexes $Ru\{C(CF_3)=C(CF_3)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (2.05 Å) [10] and $Ru\{C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (2.082(5) Å) [11], and the vinyl derivative $Ru\{C(CO_2Me)=CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ (2.08(1) Å) [12]. The C(7)–C(8) distance is 1.335(8) Å, and angles at C(7) and C(8) range between 116.3(5) and 130.6(6)°; these two carbons are coplanar with Ru(1), O(1) and C(9). The largest angle, C(7)–C(8)–C(9), is probably a result of an intramolecular interaction between C(14) and O(1), which are only 2.896 Å apart.

Although the structural study allows the geometry of the vinyl ligand to be determined, the differences in chemical shift between the isomers are small, and in the cases of **2** and **4**, much less than the change in chemical shift brought about by substituting Ph by CO_2Me. Consequently it is not possible to make any definitive statements about the individual isomers of these complexes. Neither was it possible to use the criterion applied recently to the complexes $Fe\{C(OMe)=CHR\}(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (R = H or Me) [13], in which the magnitude of the coupling between the vinylic hydrogen and the ^{31}P nucleus can be used to distinguish the *cis* and *trans* isomers. Ruthenium has long been known to be a poorer transmitter of spin–spin coupling effects than iron, and while this coupling is observed in several cases, it does not serve to establish the stereochemistry of the components of the isomeric mixtures.

Interestingly, the methoxy(ethyl)carbene-iron complex was deprotonated stereospecifically to the *Z* isomer [13]; presumably it is the bulk of the $Ru(L)(PPh_3)(\eta\text{-}C_5H_5)$ (L = CO or PPh_3) moiety which results in the differing stereochemistry found in our studies.

Formation of a chelate vinyl ether complex

Our earlier studies showed that one of the PPh_3 ligands of an $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ moiety could be displaced easily by the carbonyl oxygen of a methoxycarbonyl group attached to the β-carbon of a suitable ligand. Thus, the complex $Ru\{C(CO_2Me)=CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ was readily converted to the chelate complex $Ru\{(CO_2Me)=CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)$ on heating [14]. We have found that a similar reaction occurs on heating **7** for a short time in refluxing chloroform. The solution, originally yellow, deepens in colour to orange; an almost quantitative yield of the chelate complex $Ru\{C(OMe)=CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)$ (**12**) was obtained. This compound was identified by the characteristic shift of the ν(CO) band at 1691 cm^{-1} in **7** to 1549 cm^{-1} in **12** as a result of coordination to the ruthenium. The vinylic proton resonates at δ 5.06 ppm, and now has a 2 Hz coupling to ^{31}P. It is interesting to find that although **7** exists as a 3/1 mixture of *E* and *Z* isomers, the yield of **12** is almost quantitative, showing that there must be a facile isomerisation pathway available, since it is only the *Z* isomer which can chelate. A similar observation was made in the case of the bis(methoxycarbonyl)vinyl complex mentioned above, and the same explanation can be applied to **7**, namely, a reduction in C=C bond order by electron withdrawal onto the CO_2Me group (Scheme 1a). Alternatively, a mechanism involving β-hydrogen abstraction can be



SCHEME 1

invoked (Scheme 1b): further work is necessary to clarify the course of these reactions.

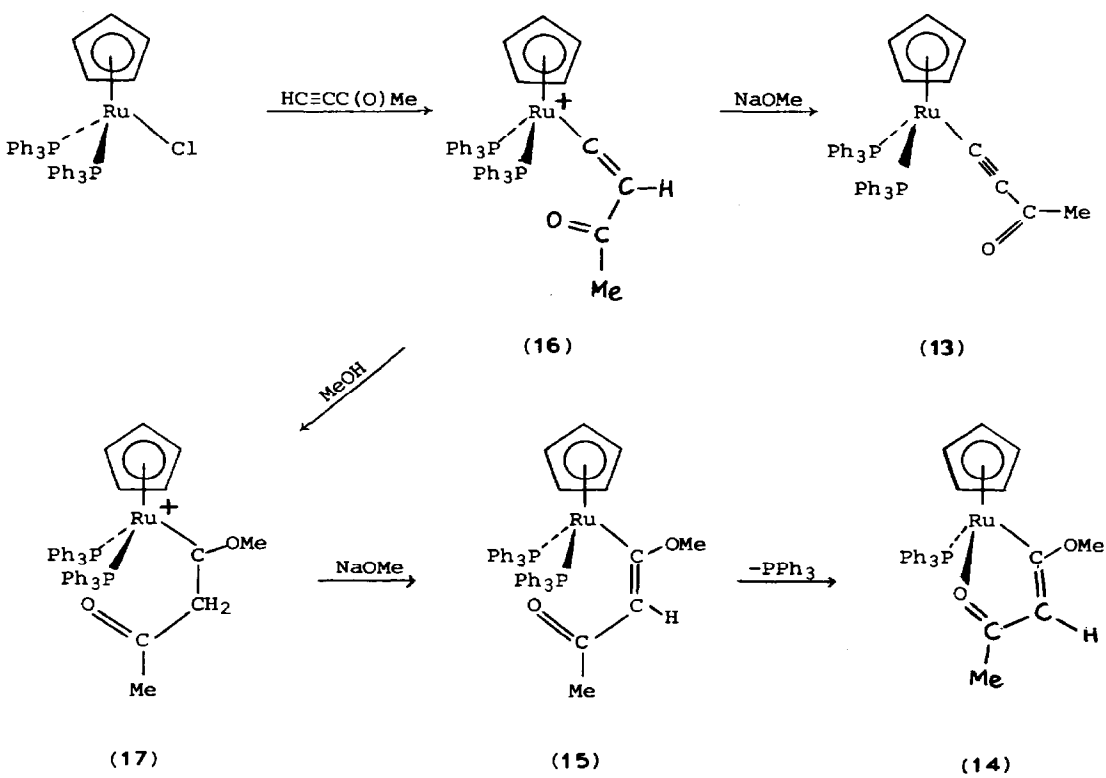
Reaction of 3-butyn-2-one with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in methanol

The reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and 3-butyn-2-one (ethynyl methyl ketone) in methanol afforded an orange solution, which on treatment with NaOMe gave yellow crystals. Chromatography separated the product into two fractions, shown to contain the acetylide $Ru[C{\equiv}CC(O)Me](PPh_3)_2(\eta\text{-}C_5H_5)$ (**13**), and a cyclic vinyl ether derivative, $Ru[C(OMe){=}CHC(O)Me](PPh_3)(\eta\text{-}C_5H_5)$ (**14**). Complex **13** was the expected product from this reaction on the basis of earlier studies [15], and was identified by IR bands at 2048, 2011 (ν(C≡C)) and 1602 cm^{-1} (ν(CO)), ^1H NMR resonances at δ 1.98, 4.39 and 7.4 ppm assigned to Me, C_5H_5 and Ph protons,

respectively, and a parent ion cluster centred on m/z 758 in the mass spectrum.

The vinyl ether complex **14** was shown from microanalytical data and by ^1H NMR spectroscopy to contain only one PPh_3 ligand. In addition, resonances at δ 1.75, 3.60, 4.57 and 5.85 ppm could be assigned to Me, OMe, C_5H_5 and CH protons, respectively, while in the ^{13}C NMR spectrum, the α-carbon has the relatively high chemical shift of 271.6 ppm; it is coupled to only one ^{31}P nucleus. The mass spectrum contained a parent ion cluster centred on m/z 528. Further examination of the solution from which **13** and **14** were isolated showed a third complex, identified as $Ru[C(OMe)=CHCOMe](PPh_3)_2(\eta\text{-}C_5H_5)$ (**15**), was present, but gradually changed on standing for several hours to **14**. Complex **15** could be identified from characteristic ^1H NMR resonances at δ 1.95, 3.02, 4.32 and 6.02 ppm, assigned to Me, OMe, C_5H_5 and CH protons; these decayed with the phenyl resonance at δ 7.4 ppm, and concomitantly with the increase in intensity of the resonances due to **14**. At the same time, a signal at δ 7.32 ppm from free PPh_3, also appeared. These changes are all consistent with the displacement of a coordinated PPh_3 by the carbonyl group of the acyl vinyl ether ligand in **15**, a reaction similar to that described above in the conversion of **7** to **12**.

Scheme 2 summarises the various steps that occur in the reaction of HC≡CCOMe with $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, and the subsequent deprotonation steps. Initial formation of a vinylidene complex **16** is followed by a slow addition of methanol to form the carbene complex **17**. This reaction is faster than those observed with related methyl- or phenyl-vinylidene complexes, because after as short a period as 75

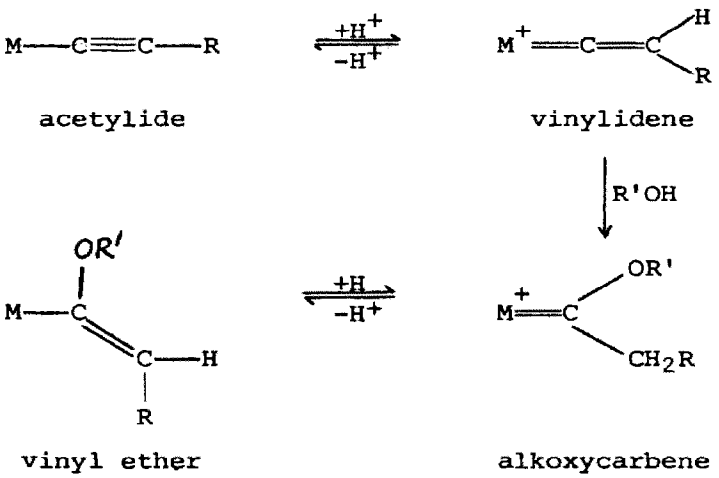


SCHEME 2

minutes, addition of sodium to the solution affords not only the expected acetylide **13**, but also the vinyl ether **15**. Spontaneous cyclisation of the latter affords **14** and free PPh_3.

Conclusion

In summary it is useful to recall the relationship between various η^1-carbon bonded ligands first pointed out by Davison and coworkers [16]. As can be seen from Scheme 3, the vinyl ether complexes described above occupy a position intermediate between the alkoxycarbene and vinylidene derivatives, and can be converted to either by appropriate reagents. Further studies of the chemistry of these reactive complexes will be described elsewhere.



SCHEME 3

Experimental

All reactions were carried out under a nitrogen atmosphere, and the oxidative sensitivity of the vinyl ether complexes made it advisable to perform as much as possible of the succeeding isolation procedure with exclusion of oxygen.

Solvents were dried and distilled under nitrogen before use. Spectra were obtained with Perkin–Elmer 457 or 683 double grating (IR), Bruker WP 80 (^{1}H NMR, δ(ppm) at 80 MHz; ^{13}C NMR δ(ppm) at 20.1 MHz), and AEI-GEC MS 3074 (mass; 70 eV ionising energy, 8 kV accelerating potential) instruments.

The alkoxy(alkyl)carbene complexes were obtained in the course of earlier work [1], or as described below. 3-Butyn-2-one was used as received from Aldrich Chemical Co. Microanalyses were by the Canadian Microanalytical Service, Vancouver, B.C., V6T 1K6.

Preparation of $[Ru\{C(OEt)CH_2CO_2Me\}(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$

A suspension of $Ru(C{\equiv}CCO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (500 mg, 0.65 mmol) in ethanol (30 ml) was treated with $HPF_6 \cdot OEt_2$ (36 drops, excess). Light yellow

crystals precipitated immediately. The product was collected and recrystallised from dichloromethane/methanol to give [Ru{C(OEt)CH_2CO_2Me}(PPh_3)$_2$(η-C_5H_5)]PF_6 (332 mg, 53%), m.p. 159°C(dec.). (Found: C, 57.9; H, 4.5. $C_{47}H_{45}F_6O_3P_3Ru$ calcd.: C, 58.5; H, 4.7%). Infrared (Nujol): ν(C=O) 1732s(br) cm^{-1}, ν(C–O) 1271m cm^{-1}, ν(P–F) 839s(br) cm^{-1}; other bands at 1587w, 1575s, 1337(sh), 1312w, 1170w, 1089m, 1051w, 1011(sh), 999w, 940w, 829(sh), 753(sh), 744m, 721w, 697m cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 1.30, m, 3H, CH_2CH_3; 3.47, s, 3H, CO_2Me; 3.80, m, 2H, CH_2CH_3; 4.55, s, 2H, CH_2CO_2Me; 4.90, s, 5H, C_5H_5; 7.40, m, 30H, Ph.

Preparation of [Ru{C(OMe)CH_2Ph}(dppm)(η-C_5H_5)]Cl

A mixture of RuCl(dppm)(η-C_5H_5) (1.00 g, 1.71 mmol) and PhC≡CH (1.4 g, excess) was heated in refluxing methanol (50 ml) for 3 h, after which time solvent was removed. Addition of light petroleum to a dichloromethane extract of the residue afforded after recrystallisation (MeOH) yellow crystals of [Ru{C(OMe)CH_2Ph}(dppm)(η-C_5H_5)]Cl (876 mg, 71%), m.p. 164–165°C. (Found: C, 67.9; H, 5.0, $C_{39}H_{37}ClOP_2Ru$ calcd.: C, 65.0; H, 5.2%). Infrared (Nujol): ν(C–O) 1230m cm^{-1}; other bands at 1598w, 1544(sh), 1539m, 1435m, 1328w, 1309w, 1182w, 1173w, 1155w, 1142w, 1101m, 1092m, 1084m, 1072w, 1068w, 1023m, 1011w, 1002w, 972s, 885m, 858w, 818w, 786s, 772m, 765m, 765w, 750s, 732s, 721s, 714s, 694s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 3.93, s, 3H, Me; 4.77, m, 2H, PCH_2P; 5.11, s, 5H, C_5H_5; 6.65, ABq, 2H, CH_2; 7.27, m, 25H, Ph.

Preparation of vinyl ether complexes

(a) From [Ru{C(OMe)CH_2Ph}(PPh_3)$_2$(η-C_5H_5)]PF_6 (1). On addition of sodium methoxide solution (sodium 50 mg, 2 mg atom, in methanol, 15 ml), to a stirred suspension of **1** (300 mg, 0.31 mmol) in methanol (30 ml), a fine yellow powder was precipitated. After 2 h this was collected and identified as Ru[C(OMe)=CHPh](PPh_3)$_2$(η-C_5H_5) (**2**) (225 mg, 88%) m.p. 137–139°C (Found: C, 72.1; H, 5.0. $C_{50}H_{44}OP_2Ru$ calcd.: C, 72.9; H, 5.4%). Infrared (Nujol): ν(C=C) 1592m, 1588(sh), 1570w, 1541s; ν(CO) 1251w cm^{-1}; other bands at 1433s, 1310w, 1197w, 1187w, 1183(sh), 1156w, 1088s, 1070w, 1041s, 1030(sh), 1000w, 919w, 893w, 830w, 796m, 770w, 750m, 738m, 696vs cm^{-1}. ^{1}H NMR: δ(C_6H_6) 3.37, s, 3H, CH_3; 4.52, s, 5H, C_5H_5; 6.03, s, 1H, =CH; 7.0–7.5, m, 35H, Ph. ^{13}C NMR: δ(C_6D_6) 59.1, s, CH_3; 84.6, s, =CH; 86.2, s, C_5H_5; 123.0–143.2, m, Ph; 193.1, t, J(PH) 7.5 Hz, RuC.

In a 'one-pot' synthesis of **2**, RuCl(PPh_3)$_2$(η-C_5H_5) (1.0 g, 1.38 mmol), phenylacetylene (200 mg, 2.0 mmol) and NH_4PF_6 (250 mg, 1.53 mmol) in methanol (50 ml) were heated at reflux point for 22 h. Upon cooling sodium (200 mg) was added and the solution refluxed briefly to give Ru[C(OMe)=CHPh](PPh_3)$_2$(η-C_5H_5) (**2**) (970 mg, 85%) as a yellow powder.

(b) From [Ru{C(OMe)Et}(PPh_3)$_2$(η-C_5H_5)]PF_6 (3). A mixture of **3** (100 mg, 0.11 mmol) and sodium (50 mg, 2 mg atom, in methanol 15 ml) was heated at reflux point for 1 h. After cooling and filtering under anaerobic conditions, the solution was further cooled (−10°C) to precipitate Ru[C(OMe)=CHMe](PPh_3)$_2$(η-C_5H_5) (**4**) (74 mg, 88%) as a yellow powder, m.p. 130°C (dec.). Infrared (Nujol): ν(C=C) 1580s, 1563s; ν(CO) 1188m cm^{-1}; other bands at 1432s, 1318m, 1160(sh), 1152w, 1106m, 1091(sh), 1088s, 1070w, 1053s, 1040(sh), 1028w, 1009w, 1002(sh), 1000w, 877m, 860(sh), 830w, 798m, 750m, 740s, 698vs, 681m cm^{-1}. The infrared spectrum

was virtually identical to that of **2**. The complex proved highly unstable preventing further characterization.

(c) From [Ru{C(OMe)CH$_2$CO$_2$Me}(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$. A suspension of the alkoxycarbene complex (300 mg, 0.32 mmol) in MeOH (30 ml) was treated with a NaOMe solution (0.2 g of Na in MeOH, 20 ml). Light yellow crystals precipitated after 1 min and were collected and recrystallised from dichloromethane/methanol to give Ru[C(OMe):CHCO$_2$Me](PPh$_3$)$_2$(η-C$_5$H$_5$) (**7**) (204 mg, 78%), m.p. 141°C. (Found: C, 67.65; H, 5.35. $C_{46}H_{42}O_3P_2Ru$ calcd.: C, 68,6; H, 5.3%). Infrared (Nujol): ν(C=O) 1691m cm^{-1}; ν(C=C) 1494s cm^{-1}; ν(C–O) 1150s, 1049s cm^{-1}; other bands at 1479w, 1432w, 1421w, 1378m, 1366(sh), 1203m, 1187m, 1181(sh), 1087m, 1062m, 953w, 894m, 832w, 812w, 799w, 758(sh), 752m, 749(sh), 710w, 700m, 696m, 679(sh) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) (major isomer) 2.49, s, 3H, CO$_2$Me; 3.69, s, 3H, OMe; 4.37, s, 5H, C$_5$H$_5$; 5.43, s, 1H, =CH; (minor isomer) 3.13, s, 3H, CO$_2$Me; 3.54, s, 3H, OMe; 4.25, s, 5H, C$_5$H$_5$; 5.78, s, 1H, =CH; (both isomers) 7.19, m, 30H, Ph. Intensity ratio major/minor 3/1.

(d) From [Ru{C(OEt)CH$_2$CO$_2$Me}(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$. The alkoxycarbene complex (170 mg, 0.18 mmol) was converted to Ru[C(OEt)=CHCO$_2$Me](PPh$_3$)$_2$(η-C$_5$H$_5$) (**8**), light yellow crystals (113 mg, 78%), m.p. 143°C, as in (c) above. (Found: C, 68.3; H, 5.3. $C_{47}H_{44}O_3P_2Ru$ calcd.: C, 68.85, H, 5.4%). Infrared (Nujol): ν(C=O) 1692s cm^{-1}, ν(C=C) 1495s cm^{-1}, ν(C–O) 1149s, 1049s cm^{-1}; other bands at 1481w, 1432w, 1421w, 1415(sh), 1262w, 1203m, 1187w, 1182w, 1088m, 1062m, 1012w, 998w, 992(sh), 953m, 894m, 832m, 811m, 798m, 757(sh), 751m, 749(sh), 740(sh), 710w, 700w, 692s, 678(sh) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) (major isomer) 3.70, s, 3H, CO$_2$Me; 4.38, s, 5H, C$_5$H$_5$; (minor isomer) 3.53, s, 3H, CO$_2$Me; 4.25, s, 5H, C$_5$H$_5$; (both) 7.22, m, 30H, Ph. Intensity ratio major/minor 3/1.

(e) From [Ru{C(OMe)CH$_2$Ph}(CO)(PPh$_3$)(η-C$_5$H$_5$)]PF$_6$. Similarly, Ru[C(OMe)=CHPh](CO)(PPh$_3$)(η-C$_5$H$_5$) (**9**) was obtained as light yellow crystals (35 mg, 60%), m.p. 187°C (dec.), from the alkoxycarbene complex (73 mg, 0.1 mmol) (Found: C, 67.0; H, 5.15. $C_{33}H_{29}O_2PRu$ calcd.: C, 67.2; H, 4.95%). Infrared (Nujol): ν(CO) 1935s, 1923s cm^{-1}, ν(C=C) 1552m cm^{-1}, ν(C–O) 1265m, 1091m cm^{-1}; other bands at 1594w, 1574m, 1481w, 1441w, 1436s, 1199w, 1183w, 1071m, 1060(sh), 1028w, 1009(sh), 998w, 952m, 901w, 849(sh), 838w, 830(sh), 805m, 799(sh), 758(sh), 750m, 727w, 700(sh), 693s, 685(sh) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) (major isomer) 3.53, s, 3H, Me; 4.94, s, 5H, C$_5$H$_5$; 5.98, s, 1H, =CH; (minor isomer) 2.93, s, 3H, Me; 5.03, s, 5H, C$_5$H$_5$; 5.96, s, 1H, =CH; (both) 7.36, m, 20H, Ph. ^{13}C NMR: δ(CDCl$_3$) 55.17, 57.80, s, 2 × Me; 87.95, s, C$_5$H$_5$; 111.58, s, =CH; 123–138, m, Ph; 177.44, 178.32, 179.12, 179.78, d, 2 × Ru–C=; 204.44, 205.54, 206.63, d, 2 × CO. Intensity ratio major/minor 8/7.

(f) From [Ru{C(OEt)CH$_2$Ph}(CO)(PPh$_3$)(η-C$_5$H$_5$)]PF$_6$. Upon mixing a suspension of the alkoxycarbene complex (130 mg, 0.17 mmol) in methanol (50 ml) with a sodium methoxide solution (sodium, 50 mg, 2 mg atom, in methanol 15 ml) a yellow powder precipitated. After 30 min this was collected and identified as Ru[C(OEt)=CHPh](CO)(PPh$_3$)(η-C$_5$H$_5$) (**6**) (90 mg, 86%) m.p. 226–228°C (Found: C, 67.9; H, 5.1; *M*, (mass spectrometry), 604. $C_{34}H_{31}O_2PRu$ calcd.: C, 67.7; H, 5.2%, *M*, 604). Infrared (CHCl$_3$): ν(CO) 1938vs; ν(C=C) (Nujol) 1593w, 1572m, 1551s; ν(C–O) 1263m cm^{-1}; other bands at 1633s, 1340w(br), 1198w, 1182w, 1157w, 1109w, 1088s, 1059s, 1025w, 1007(sh), 997s, 990m, 907w, 892w, 841(sh), 832m, 797s, 753(sh), 746s, 730w, 692(sh), 688s, 659w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$)

0.4–1.5, m, 3H, CH_3; 3.5–4.2, m, 2H, CH_2; 4.92, 4.98, 5.03, 3 × s, 5H, C_5H_5; 5.92, s, br, 1H, CH; 7.0–7.5, m, 15H, Ph.

(g) From [Ru{C(OPr^i)CH$_2$Ph}(CO)(PPh$_3$)(η-C$_5$H$_5$)]PF$_6$. Ru[C(OPr^i)=CHPh](CO)(PPh$_3$)(η-C_5H_5) was prepared similarly from {Ru[C(OPr^i)CH$_2$Ph](CO)(PPh$_3$)(η-C_5H_5)}PF_6 (**10**) (250 mg, 0.33 mmol) as light yellow crystals (130 mg, 64%) m.p. 187°C. (Found: C, 67.35; H, 5.1. $C_{35}H_{33}O_2PRu$ calcd.: C, 68.05; H, 5.4%). Infrared (Nujol): ν(CO) 1932s, 1922s cm^{-1}, ν(C=C) 1552s cm^{-1}, ν(C–O) 1264m, 1091s cm^{-1}; other bands at 1593s, 1573m, 1489w, 1479m, 1441w, 1434s, 1325w, 1311w, 1200w, 1182m, 1158w, 1108w, 1071s, 1029m, 1010w, 998m, 951s, 901w, 836m, 832(sh), 802s, 749s, 728m, 700(sh), 693vs cm^{-1}. ^1H NMR: δ($CDCl_3$) 1.12, d, *J*(HH) 6.1Hz, 1.37, d, *J*(HH) 6.1Hz, 6H each, Me; 4.64, m, 2H, C*H*CMe$_2$; 4.82, d, *J*(HP) 1.2Hz, 1H, =CH; 5.03, s, 10H, C_5H_5; 7.35, m, 20H, Ph. ^{13}C NMR: δ($CDCl_3$) 22.54, s, 23.20, s, 2 × Me; 72.59, s, *C*HMe$_2$; 88.10, s, C_5H_5; 88.76, s, =CH; 127–135, m, Ph; 174.69, d, *J*(CP) 16.2Hz, RuC; 206.08, d, *J*(CP) 22Hz, CO.

(h) From [Ru{C(OMe)CH$_2$Ph}(dppm)(η-C$_5$H$_5$)]Cl. A suspension of [Ru{C(OMe)CH$_2$Ph}(dppm)(η-C_5H_5)]Cl (300 mg, 0.417 mmol) in methanol (10 ml) was treated with excess of NaOMe in methanol. A yellow solid precipitated after five minutes. Stirring was continued for 90 minutes, and the solid collected and washed (MeOH). Recrystallisation (CH_2Cl_2/MeOH) afforded yellow crystals of Ru[C(OMe)=CHPh](dppm)(η-C_5H_5) (**11**) (250 mg, 88%), m.p. 148–153°C (dec.) (Found: C, 68.7; H, 5.3; *M* (mass spectrometry) 684. $C_{39}H_{36}OP_2Ru$ calcd.: C, 68.5; H, 5.3%. *M*, 684). Infrared (Nujol): ν(C=C) 1538m cm^{-1}; other bands at 1595w, 1574w, 1435s, 1100m, 1092m, 1027w, 999w, 938m, 786m, 732s, 702s, 689s cm^{-1}. ^1H NMR: δ($CDCl_3$) (major isomer) 2.75, s, 3H, OMe; 5.05, s, 5H, C_5H_5; (minor isomer) 2.91, s, 3H, OMe; 4.48, s, 5H, C_5H_5; (both) 4.74, m, 2H, CH_2; 7.33, m, 25H, Ph; vinyl protons not located. Intensity ratio major/minor 4/1.

Cyclisation of Ru{C(OMe)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (7)

Complex 7 (188 mg, 0.23 mmol) was heated in refluxing $CHCl_3$ for 1 h, at which time the colour of the solution had deepened to orange. After evaporation and extraction of the residue with dichloromethane, methanol was added to the filtered solution. Concentration afforded orange crystals of Ru{C(OMe)=CHC(O)OMe}(PPh$_3$)(η-C_5H_5) (**12**) (118 mg, 93%) m.p. 135–136°C. (Found: C, 62.05; H, 4.95. $C_{46}H_{42}O_3P_2Ru$ calcd.: C, 61.9; H, 5.0%). Infrared (Nujol): ν(CO) 1549m, 1195s; other bands at 1585w, 1572w, 1412m, 1138m, 1099w, 1091w, 1088w, 1049w, 835w, 807w, 761w, 752w, 745w, 695m, 690m cm^{-1}. ^1H NMR: δ($CDCl_3$) 3.29, s, 3H, OMe; 3.61, s, 3H, OMe; 4.39, s, 5H, C_5H_5; 5.06, d, *J*(HP) 2H, =CH; 7.30, m, 15H, Ph.

Reaction of RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$) with 3-butyn-2-one

A mixture of RuCl(PPh$_3$)$_2$(η-C_5H_5) (300 mg, 0.41 mmol), NH_4PF_6 (75 mg, 0.46 mmol), and 3-butyn-2-one (50 mg, 0.74 mmol) in methanol (90 ml) was heated at reflux point until an orange solution formed. On cooling, a sodium methoxide solution (sodium, 50 mg, 2 mg atom, in methanol, 10 ml) was added and the mixture taken to dryness, washed with water (3 × 30 ml), and the residue extracted with chloroform (50 ml). After warming for 4 d (35–40°C), preparative TLC (7/10 diethyl ether/cyclohexane) yielded two major products: (i) Ru[C(OMe)=

CHC(O)Me](PPh$_3$)(η-C$_5$H$_5$) (**14**, $R_f = 0.9$) was isolated from dichloromethane/hexane under anaerobic conditions as a yellow powder (32 mg, 15%) m.p. 134–138°C (Found: C, 63.7; H, 5.4%, *M* (mass spectrometry), 528. $C_{28}H_{27}O_2PRu$ calcd.: C, 63.8; H, 5.2%, *M*, 528). Infrared (Nujol): ν(CO) 1308s cm^{-1}; other bands at 1720m(br), 1583w, 1572w, 1212w, 1190m, 1180m, 1167m, 1149w, 1133m, 1100w, 1090m, 1070w, 1028w, 998w, 977m, 929w, 798(sh), 781m, 757m, 747w, 739m, 721w, 696s, 692s, 681w, 642w cm^{-1}. ^{1}H NMR: δ(C$_6$D$_6$) 1.75, d, *J*(PH) 1.5Hz, 3H, CH$_3$; 3.60, s, 3H, OCH$_3$; 4.57, s, 5H, C$_5$H$_5$; 5.85, s, 1H, =CH; 7.2–7.7, m, 15H, Ph. ^{13}C NMR: δ(C$_6$D$_6$) 23.0, s, CH$_3$; 59.4, s, OCH$_3$; 78.7, s, C$_5$H$_5$; 112.5, s, =CH; 127.3–138.0, m, Ph; 201.8, s, CO; 271.6, d, *J*(CP) 14Hz, RuC.

(ii) Ru(C≡CCOMe)(PPh$_3$)$_2$(η-C$_5$H$_5$) (**13**, $R_f = 0.3$), was isolated as yellow microcrystals from dichloromethane/methanol (46 mg, 15%) m.p. 213–216°C (Found: C, 70.6; H, 5.2, *M* (mass spectrometry), 758. $C_{45}H_{38}OP_2Ru$ calcd.: C, 71.3; H, 5.1%, *M*, 758). Infrared (CH$_2$Cl$_2$): ν(C≡C) 2048vs, 2011vs; ν(C=O) 1602vs cm^{-1}; other bands at (Nujol) 1437s, 1346w, 1218m, 1206(sh), 1192(sh), 1184w, 1151w, 1097s, 1089s, 1071w, 1029w, 1009s, 1001w, 978w, 862w, 833m, 811m, 757m. 742s, 696vs cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 1.98, s, 3H, Me; 4.39, s, 5H, C$_5$H$_5$; 7.4, m, 30H, Ph.

In another reaction, RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$) (150 mg, 0.21 mmol) and 3-butyn-2-one (200 mg, 2.9 mmol) were reacted in MeOH (30 ml) for 75 minutes at 30–35°C. The mixture was filtered into NaOMe solution (50 mg Na in 10 ml MeOH), which resulted in the precipitation of yellow crystals (90 mg). These were identified by ^{1}H NMR spectroscopy as a 3/5 mixture of Ru(C≡CCOMe)(PPh$_3$)$_2$(η-C$_5$H$_5$) (**13**) (22%, ^{1}H NMR as described above) and Ru[C(OMe)=CHCOMe](PPh$_3$)$_2$(η-C$_5$H$_5$) (**15**) (34%, ^{1}H NMR: δ(CDCl$_3$) 1.95, s, 3H, Me; 3.02, s, 3H, OMe; 4.32, s, 5H, C$_5$H$_5$; 6.06, t, *J*(PH) 1Hz, 1H, =CH; 7.4, m, 30H, Ph). Upon standing in CDCl$_3$ (48 h, 35°C) the spectrum of **13** remains unchanged, while **15** loses PPh$_3$ to give Ru[C(OMe)=CHC(O)Me](PPh$_3$)(η-C$_5$H$_5$) (**14**) (^{1}H NMR: δ(CDCl$_3$) 1.65, d, *J*(PH) 1.5Hz, 3H, Me; 3.73, s, 3H, OMe; 4.49, s, 5H, C$_5$H$_5$; 5.62, d, *J*(PH) 1.5Hz, =CH; 7.3, m, Ph). A sharp singlet also appeared at δ 7.32 and is assigned to free PPh$_3$.

Protonation of Ru[C(OMe)=(CHPh)](PPh$_3$)$_2$(η-C$_5$H$_5$) (2)

A solution of **2** in CDCl$_3$ within an NMR tube showed resonances at δ 3.15 (CH$_3$), 4.33 (C$_5$H$_5$), and 5.66 (=CH), which disappeared on addition of HPF$_6$ · OEt$_2$ with concomitant formation of peaks at δ 3.49 (CH$_3$), 4.84 (C$_5$H$_5$), and 5.06 (CH$_2$) due to [Ru{C(OMe)CH$_2$Ph}(PPh$_3$)$_2$(η-C$_5$H$_5$)]PF$_6$ (**1**).

*Crystal structure of **10***

Yellow air-stable crystals of **10** suitable for X-ray analysis were obtained from CHCl$_3$/MeOH. A crystal of dimensions 0.52 × 0.15 × 0.24 mm was attached to a glass fibre with epoxy resin. Lattice parameters were determined at 22°C by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf–Nonius CAD4 four-circle diffractometer, employing graphite-monochromated Mo-K_α X-radiation.

Crystal data. $C_{35}H_{33}O_2PRu$, mol. wt. 617.65, monoclinic, space group $P2_1/c$; *a* 10.337(5), *b* 15.161(4), *c* 18.714(5) Å, β 90.83(3)°; D_m 1.40, D_c 1.40 g cm^{-3} for $Z = 4$; *U* 2927(6) Å^3; *F*(000) 1272, μ(Mo-K_α) 5.76 cm^{-1}, λ(Mo-K_α) 0.7107 Å.

A total of 2596 unique reflections in the range $1.3 < \theta < 20°$ were collected, of

which 2240 with $I > 2.5\sigma(I)$ were considered observed and used in the subsequent calculations.

Solution and refinement. The ruthenium atom was located using the direct methods routine of SHELX [17]; all other non-hydrogen atoms were located by subsequent Fourier difference maps. Subsequent refinement of all positional parameters proceeded using anisotropic thermal parameters for Ru, P, cyclopentadienyl C, and C(16), C(17), isotropic thermal parameters for all other atoms, with the cyclopentadienyl and phenyl rings refined as rigid groups (C–C 1.42, 1.395 Å,

TABLE 1

POSITIONAL PARAMETERS FOR NON-HYDROGEN ATOMS IN Ru{C(OPr^i)=CHPh}-(CO)(PPh_3)(η-C_5H_5) (Ru, $\times 10^5$; other atoms, $\times 10^4$)

	x	*y*	*x*
Ru(1)	18307(5)	43589(4)	23449(3)
P(1)	2919(1)	4719(1)	3384(1)
C(1)	2588(5)	3009(4)	2041(4)
C(2)	1639(5)	2890(4)	2575(4)
C(3)	437(5)	3194(4)	2294(4)
C(4)	642(5)	3503(4)	1587(4)
C(5)	1972(5)	3388(4)	1431(4)
O(6)	−81(5)	5769(4)	2677(3)
C(6)	683(7)	5243(4)	2546(3)
C(7)	3059(5)	5182(4)	1755(3)
C(8)	4329(6)	5039(4)	1709(3)
H(8)	4716(50)	4454(36)	1960(28)
C(10)	6612(4)	5455(3)	1580(2)
C(11)	7608(4)	5940(3)	1273(2)
C(12)	7343(4)	6505(3)	700(2)
C(13)	6081(4)	6585(3)	434(2)
C(14)	5085(4)	6100(3)	741(2)
C(9)	5350(4)	5535(3)	1314(2)
O(1)	2590(4)	5925(3)	1411(2)
C(15)	1442(6)	5853(4)	952(4)
C(16)	935(7)	6767(5)	876(5)
C(17)	1789(8)	5440(6)	247(4)
C(19)	3317(4)	6102(2)	4363(2)
C(20)	3536(4)	6979(2)	4556(2)
C(21)	3491(4)	7641(2)	4037(2)
C(22)	3227(4)	7425(2)	3325(2)
C(23)	3008(4)	6547(2)	3131(2)
C(18)	3053(4)	5886(2)	3650(2)
C(25)	5627(4)	4946(2)	3461(2)
C(26)	6900(4)	4640(2)	3476(2)
C(27)	7148(4)	3734(2)	3476(2)
C(28)	6123(4)	3135(2)	3462(2)
C(29)	4851(4)	3442(2)	3447(2)
C(24)	4603(4)	4347(2)	3447(2)
C(31)	843(3)	4196(3)	4214(2)
C(32)	240(3)	3865(3)	4821(2)
C(33)	983(3)	3561(3)	5398(2)
C(34)	2330(3)	3588(3)	5369(2)
C(35)	2933(3)	3919(3)	4763(2)
C(30)	2190(3)	4223(3)	4185(2)

TABLE 2

SELECTED BOND LENGTHS (Å) FOR Ru{C(OPr^i)=CHPh}(CO)(PPh_3)(η-C_5H_5)

Bond	Distance	Bond	Distance
Ru(1)–P(1)	2.298(2)	Ru(1)–C(6)	1.832(7)
Ru(1)–C(7)	2.103(6)	Ru(1)···C(8)	3.039
Ru(1)–C(cp)(av.)	2.270	P(1)–C(18)	1.841(4)
P(1)–C(24)	1.833(4)	P(1)–C(30)	1.844(4)
C(6)–O(6)	1.151(7)	C(7)–C(8)	1.335(8)
C(7)–O(1)	1.381(7)	C(8)–C(9)	1.498(7)
C(8)–H(8)	1.07(5)	O(1)–C(15)	1.459(7)
C(15)–C(16)	1.488(9)	C(15)–C(17)	1.50(1)

TABLE 3

SELECTED BOND ANGLES (deg) FOR Ru{C(OPr^i)=CHPh}(CO)(PPh_3)(η-C_5H_5)

Angle		Angle	
P(1)–Ru(1)–C(7)	90.5(2)	C(6)–Ru(1)–C(7)	94.1(3)
P(1)–Ru(1)–CT[a]	127.4(–)	C(6)–Ru(1)–CT[a]	127.8(–)
C(7)–Ru(1)–CT[a]	118.8(–)	C(18)–P(1)–Ru(1)	115.8(1)
C(24)–P(1)–Ru(1)	115.8(1)	C(30)–P(1)–Ru(1)	112.8(1)
C(18)–P(1)–C(24)	102.2(2)	C(18)–P(1)–C(30)	101.7(2)
C(24)–P(1)–C(30)	102.8(2)	Ru(1)–C(6)–O(6)	176.8(6)
O(1)–C(7)–Ru(1)	121.1(4)	C(8)–C(7)–Ru(1)	122.7(5)
C(7)–C(8)–H(8)	117.0(3)	O(1)–C(7)–C(8)	116.3(5)
C(7)–C(8)–C(9)	130.6(6)	H(8)–C(8)–C(9)	111.0(3)
O(1)–C(15)–C(16)	105.6(6)	C(7)–O(1)–C(15)	119.4(5)
O(1)–C(15)–C(17)	110.1(6)	O(1)–C(15)–H(15)	99.6(3)
H(15)–C(15)–C(17)	108.2(4)	H(15)–C(15)–C(16)	119.1(4)
C(16)–C(15)–C(17)	113.0(7)		

[a] CT ≡ centroid of cyclopentadienyl ring.
Equation of plane for Ru(1), O(1), C(7), C(8), H(8), C(9) is $0.1772x + 0.5444y + 0.8199z = 7.4981$
Atom deviations (Å) from this plane:
Ru(1) 0.0046, O(1) −0.0037, C(7) −0.0081, C(8) 0.0206, H(8) −0.0134, C(9) 0.0001.

respectively). Hydrogens were placed in calculated positions (C–H 1.08 Å) and refined with a common thermal parameter, with the exception of H(8), which was allowed to refine freely. Final convergence gave $R = 0.0388$, $R_w = 0.0436$. The largest residual electron density was 0.65 eÅ^{-3} associated with the PPh_3 ligand near atoms C(33) and C(34).

The atomic coordinates are listed in Table 1, and selected bond lengths and angles are given in Tables 2 and 3. Tables of thermal parameters structure factor tables are available from the authors.

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Note added in proof. The conformational properties of complexes $MR(L)(PPh_3)(\eta\text{-}C_5H_5)$ have been rationalised recently (S.G. Davies and J.I. Seeman, Tetrahedron Letters, 25 (1984) 1845); while most complexes described above have properties consistent with the rules elaborated by Davies and Seeman, some (notably **7** and **8**) appear to have somewhat greater steric freedom.