Reactions of Co-ordinated Ligands. Part 51.[1] The Reactions of σ,η³(5e)-Butadienylruthenium Complexes [Ru{=C(Ph)-η³-C(Ph)C(Ph)CR(Ph)}(η-C_5H_5)](R = H or CHO) with $P(OMe)_3$, PhC≡CPh, H^+ and Aryldiazonium Cations; Crystal Structure of [Ru{C(O)C(Ph)=C(Ph)-η²-(*Z*)-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)]‡

Mark Crocker, Barry J. Dunne, Michael Green*,† and A. Guy Orpen
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, and Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK

Treatment of the σ,η³(5e)-butadienyl complex [Ru{=C(Ph)-η³-C(Ph)C(Ph)C(Ph)CHO}(η-C_5H_5)] **1** with $P(OMe)_3$ affords the acyl complex [Ru{C(O)C(Ph)=C(Ph)-η²-(*Z*)-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)], structurally identified by single-crystal X-ray diffraction. This reaction involves an apparent 1,5-hydrogen shift from the aldehydic carbon to the former alkylidene carbon. Reaction of the related complex [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] **2** with diphenylacetylene gives [Ru(η⁵-*endo*-C_6Ph_6H)(η-C_5H_5)], whereas reaction of **2** with the electrophilic reagent HBF_4·Et_2O affords the 1,3-diene cationic complex [Ru{η⁴-(*E*,*Z*)-CH(Ph)=C(Ph)C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)][BF_4]. In contrast, protonation of the adduct formed between **2** and $P(OMe)_3$, the complex [Ru{C(Ph)=C(Ph)-η²-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)], gives the isomeric cation [Ru{η⁴-(*Z*,*Z*)-CH(Ph)=C(Ph)-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)][BF_4]. An attempt to convert **2** into a 17e cation by oxidation with *p*-nitrobenzenediazonium tetrafluoroborate leads instead to formation of the aryldiazenido complex [Ru{C(Ph)=C(Ph)-η²-C(Ph)=CH(Ph)}(*p*-$NO_2C_6H_4N_2$)(η-C_5H_5)]. The mechanisms of these reactions are discussed.

Recently[2,3] we described relatively simple synthetic routes to the cationic η⁴-bonded tetraphenylcyclobutadiene complexes [RuL(η⁴-C_4Ph_4)(η-C_5H_5)][BF_4] (L = CO or MeCN), and in exploring their reactivity towards sources of 'H^-' have observed ring-opening reactions leading to the formation and structural characterisation of the first examples of σ,η³(5e)-butadienyl complexes [Ru{=C(Ph)-η³-C(Ph)C(Ph)C(Ph)-CHO}(η-C_5H_5)] **1** and [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}-(η-C_5H_5)] **2**. These molecules are interesting both from the standpoint of structure and reactivity. Their reactivity might be expected to be associated with the metal–carbon double bond and also with the ability of these species to behave as masked or latent co-ordinately unsaturated σ,η²(3e)-butadienyl complexes. Indeed the reaction of **2** with $P(OMe)_3$ or PPh_3 affords[3] the complexes [Ru{C(Ph)=C(Ph)-η²-C(Ph)=CH(Ph)}L(η-C_5-H_5)] **3** [L = $P(OMe)_3$] or **4** (L = PPh_3). In this paper are described further studies of the reactivity of the unusual species **1** and **2**. Some aspects of this work have been previously reported.[4]

Results and Discussion

In view of the reactivity shown by the σ,η³(5e) complex [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] **2** towards donor ligands the related aldehyde-substituted complex [Ru-{=C(Ph)-η³-C(Ph)C(Ph)C(Ph)CHO}(η-C_5H_5)] **1** was treated with trimethyl phosphite. Stirring a solution of **1** and $P(OMe)_3$ in CH_2Cl_2 for 6 d at room temperature resulted in the formation of a deep yellow solution, chromatography of which afforded a yellow crystalline solid **5** in 41% yield. Elemental analysis and mass spectrometry of the product showed it to be a 1:1 adduct of **1** and $P(OMe)_3$, whilst significantly an IR spectrum showed the absence of a band attributable to an aldehyde group. That the CHO group present in **1** was no longer intact was further indicated by the absence in the ^{13}C NMR spectrum of **5** of a resonance in the range δ 200–180. The structural identity of **5** was established by a single-crystal X-ray diffraction study (see Tables 1–3). As is shown in Fig. 1, the ruthenium atom forms part of a six-membered RuC_5 ring. The metal is co-ordinated to η⁵-C_5H_5 and $P(OMe)_3$ ligands and to an acyl ligand formally derived from penta-2,4-dien-1-one. This ligand binds to ruth-

Table 1 Bond lengths (Å) for compound **5**

Ru–P	2.240(4)	Ru–C(1)	2.215(9)
Ru–C(2)	2.183(11)	Ru–C(5)	2.040(12)
Ru–C(61)	2.275(13)	Ru–C(62)	2.336(13)
Ru–C(63)	2.291(13)	Ru–C(64)	2.236(12)
Ru–C(65)	2.238(11)	P–O(1)	1.594(9)
P–O(2)	1.564(9)	P–O(3)	1.585(9)
C(1)–H(1)	1.042(94)	C(1)–C(11)	1.502(14)
C(1)–C(2)	1.429(17)	C(2)–C(21)	1.510(14)
C(2)–C(3)	1.494(17)	C(3)–C(31)	1.514(13)
C(3)–C(4)	1.340(16)	C(4)–C(41)	1.480(14)
C(4)–C(5)	1.515(15)	C(5)–O(5)	1.213(13)
C(61)–C(62)	1.413(19)	C(61)–C(65)	1.369(19)
C(62)–C(63)	1.389(18)	C(63)–C(64)	1.421(18)
C(64)–C(65)	1.411(21)	O(1)–C(71)	1.407(17)
O(2)–C(81)	1.458(18)	O(3)–C(91)	1.435(17)

† *Present address:* School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY.

η-Cyclopentadienyl[(4,5-η)-1-oxo-2,3,4,5-tetraphenylpenta-2,4-dien-1-yl-κ*C*¹](trimethyl phosphite)ruthenium.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 2 Bond angles (°) for compound **5**

P–Ru–C(1)	*82.1(3)*	P–Ru–C(2)	108.4(3)	H(1)–C(1)–C(2)	113.2(53)	C(11)–C(1)–C(2)	130.5(10)
C(1)–Ru–C(2)	37.9(4)	P–Ru–C(5)	82.1(4)	C(1)–C(11)–C(12)	115.1(5)	C(1)–C(11)–C(16)	124.9(5)
C(1)–Ru–C(5)	101.0(4)	C(2)–Ru–C(5)	78.1(4)	Ru–C(2)–C(1)	72.3(6)	Ru–C(2)–C(21)	120.4(7)
P–Ru–C(61)	92.6(4)	C(1)–Ru–C(61)	132.1(5)	C(1)–C(2)–C(21)	126.1(10)	Ru–C(2)–C(3)	108.8(7)
C(2)–Ru–C(61)	151.1(5)	C(5)–Ru–C(61)	125.5(4)	C(1)–C(2)–C(3)	115.2(10)	C(21)–C(2)–C(3)	109.0(9)
P–Ru–C(62)	113.0(3)	C(1)–Ru–C(62)	104.1(4)	C(2)–C(21)–C(22)	120.3(5)	C(2)–C(21)–C(26)	119.3(4)
C(2)–Ru–C(62)	115.7(5)	C(5)–Ru–C(62)	152.2(4)	C(2)–C(3)–C(31)	115.8(9)	C(2)–C(3)–C(4)	120.7(10)
C(61)–Ru–C(62)	35.7(5)	P–Ru–C(63)	147.8(3)	C(31)–C(3)–C(4)	123.4(10)	C(3)–C(31)–C(32)	119.2(5)
C(1)–Ru–C(63)	105.6(4)	C(2)–Ru–C(63)	95.0(4)	C(3)–C(31)–C(36)	120.8(5)	C(3)–C(4)–C(41)	126.6(9)
C(5)–Ru–C(63)	125.3(4)	C(61)–Ru–C(63)	58.7(5)	C(3)–C(4)–C(5)	111.2(10)	C(41)–C(4)–C(5)	122.1(9)
C(62)–Ru–C(63)	34.9(4)	P–Ru–C(64)	141.6(4)	C(4)–C(41)–C(42)	121.9(4)	C(4)–C(41)–C(46)	118.0(4)
C(1)–Ru–C(64)	135.8(5)	C(2)–Ru–C(64)	108.0(5)	Ru–C(5)–C(4)	116.1(7)	Ru–C(5)–O(5)	123.9(8)
C(5)–Ru–C(64)	93.7(5)	C(61)–Ru–C(64)	59.0(5)	C(4)–C(5)–O(5)	120.0(10)	Ru–C(61)–C(62)	74.5(7)
C(62)–Ru–C(64)	59.7(5)	C(63)–Ru–C(64)	36.6(5)	Ru–C(61)–C(65)	70.9(7)	C(62)–C(61)–C(65)	111.3(13)
P–Ru–C(65)	105.1(4)	C(1)–Ru–C(65)	164.2(5)	Ru–C(62)–C(61)	69.8(8)	Ru–C(62)–C(63)	70.8(7)
C(2)–Ru–C(65)	144.0(5)	C(5)–Ru–C(65)	94.0(4)	C(61)–C(62)–C(63)	106.0(11)	Ru–C(63)–C(62)	74.3(8)
C(61)–Ru–C(65)	35.3(5)	C(62)–Ru–C(65)	60.3(5)	Ru–C(63)–C(64)	69.6(7)	C(62)–C(63)–C(64)	108.2(12)
C(63)–Ru–C(65)	60.9(5)	C(64)–Ru–C(65)	36.8(5)	Ru–C(64)–C(63)	73.9(7)	Ru–C(64)–C(65)	71.7(7)
Ru–P–O(1)	118.1(4)	Ru–P–O(2)	114.8(4)	C(63)–C(64)–C(65)	108.3(12)	Ru–C(65)–C(61)	73.8(7)
O(1)–P–O(2)	106.3(5)	Ru–P–O(3)	119.5(4)	Ru–C(65)–C(64)	71.5(6)	C(61)–C(65)–C(64)	106.2(12)
O(1)–P–O(3)	97.2(5)	O(2)–P–O(3)	97.7(5)	P–O(1)–C(71)	120.7(9)	P–O(2)–C(81)	124.4(9)
Ru–C(1)–H(1)	100.9(41)	Ru–C(1)–C(11)	118.6(7)	P–O(3)–O(91)	121.0(8)		
H(1)–C(1)–C(11)	112.4(49)	Ru–C(1)–C(2)	69.8(5)				

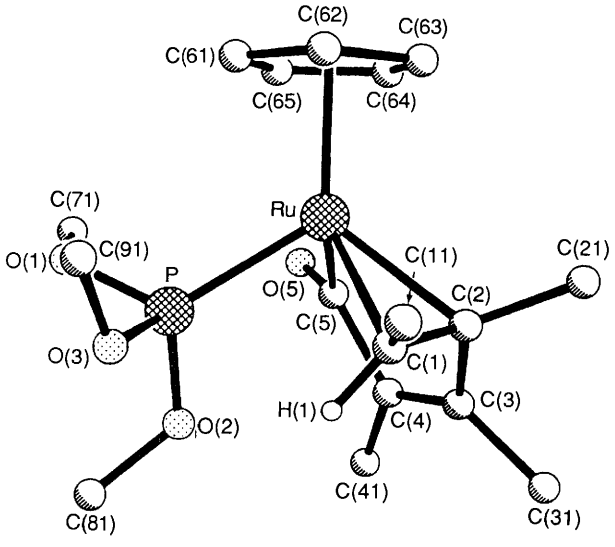
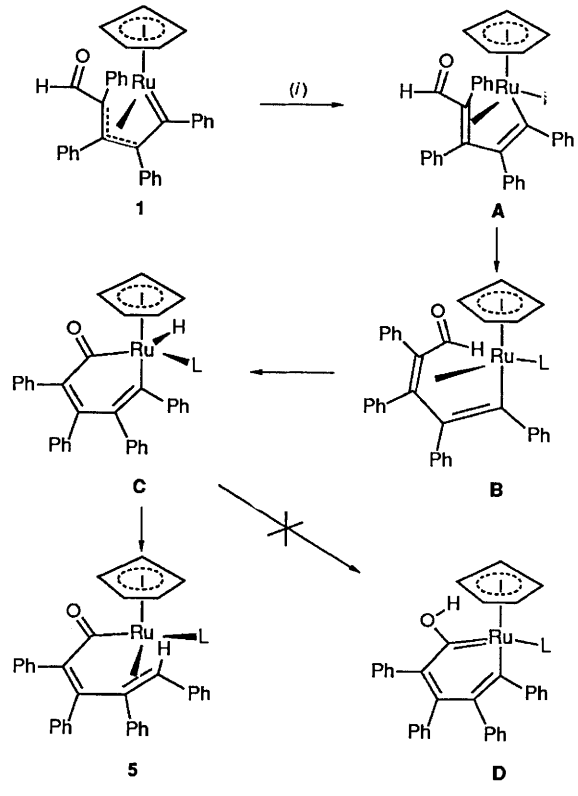


Fig. 1 Molecular structure of compound **5** with the labelling scheme; only the *ipso* carbons of the phenyl rings are shown, for clarity

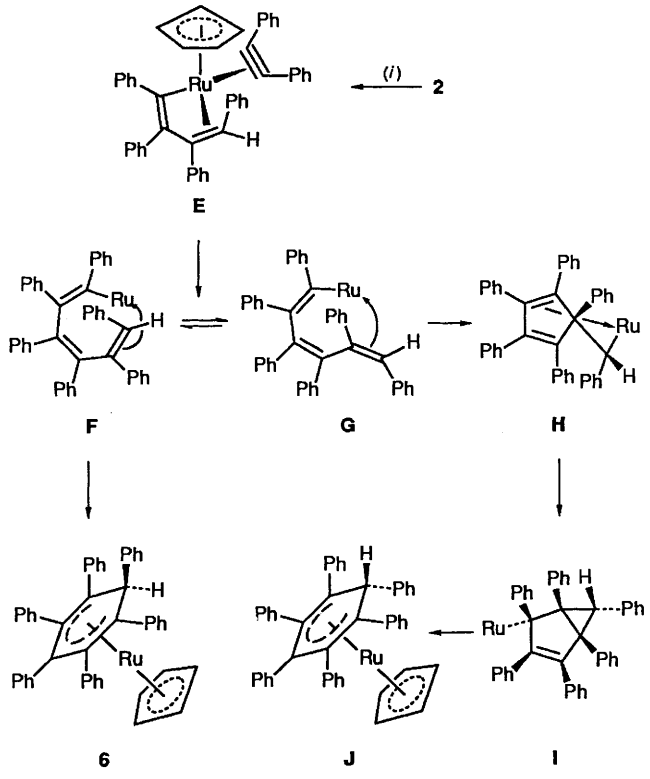


Scheme 1 L = $P(OMe)_3$. (*i*) + $P(OMe)_3$

enium through σ-acyl and η^2-terminal C=C double-bond interactions, thereby completing the formal 18e count at the metal centre. The η^2-vinylic moiety is bonded to the metal atom at Ru–C distances of 2.215(9) and 2.183(11) Å for Ru–C(1) and Ru–C(2) respectively. The carbon atom C(1) carries a phenyl ring and a hydrogen atom as substituents, the latter having undergone transfer from the formyl group present in **1**. Lengthening of the C(1)–C(2) olefinic bond arising from co-ordination to the metal is reflected in the bond distance of 1.429(17) Å, whilst the remaining C(2)–C(3), C(3)–C(4) and C(4)–C(5) distances of 1.494(17), 1.340(16) and 1.515(15) Å indicate a localised single, double, single C–C bond structure around the remainder of the C_5 chain. The Ru–C(5) and C(5)–O(5) distances of 2.040(12) and 1.213(13) Å respectively are broadly similar to those observed in other ruthenium acyl derivatives. Thus, compound **5** contains a σ,η^2(3e)-pentadienyl system, the formation of which involves an apparent 1,5-hydrogen shift, transfer occurring from the aldehydic carbon to the former alkylidene carbon. This rearrangement can be understood if it is assumed that there is a parallel with the formation of **3** on reaction of $P(OMe)_3$ with [Ru{=C(Ph)-η^3-C(Ph)C(Ph)CH-(Ph)}(η-C_5H_5)].[3] Thus it is suggested that compound **1** reacts with $P(OMe)_3$ *via* an associative process to give the kinetically controlled product [Ru{C(Ph)=C(Ph)-η^2-C(Ph)=C(Ph)CHO}-{$P(OMe)_3$}(η-C_5H_5)] **A** (Scheme 1) in which the formyl substituent points away from the ruthenium centre. Isomerisation by a ring-flip process[3,5] can then generate the corresponding isomer **B** where the CHO group points towards the metal centre, the aldehydic hydrogen now being placed in proximity to the ruthenium centre. A σ,η^2(3e) to σ(1e) transformation of the bonding mode of the butadienyl complex **B** can then provide the vacant co-ordination site needed to allow the formation of **C**

Table 3 Atomic coordinates ($\times 10^4$) for compound **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	548(1)	1260(1)	1543(1)	C(31)	2242	−361	3377
P	−667(3)	1639(2)	2497(2)	C(4)	85(11)	14(5)	2440(7)
C(1)	2021(10)	1215(6)	2898(7)	C(42)	−1683(7)	−794(4)	2276(4)
C(12)	3075(7)	2043(4)	3977(5)	C(43)	−2470	−1179	2690
C(13)	3981	2521	4264	C(44)	−2296	−1197	3675
C(14)	4825	2686	3691	C(45)	−1336	−831	4247
C(15)	4764	2374	2833	C(46)	−550	−446	3833
C(16)	3858	1895	2546	C(41)	−723	−428	2848
C(11)	3013	1730	3118	C(5)	−487(12)	461(5)	1636(7)
C(2)	2081(11)	641(6)	2378(7)	O(5)	−1494(8)	328(4)	1087(5)
C(22)	2846(6)	43(4)	1130(5)	C(61)	−56(13)	2047(7)	465(8)
C(23)	3854	−238	807	C(62)	1309(13)	2046(6)	677(8)
C(24)	5125	−167	1321	C(63)	1669(12)	1460(5)	394(7)
C(25)	5388	186	2158	C(64)	529(14)	1112(7)	8(8)
C(26)	4380	467	2481	C(65)	−546(14)	1487(7)	68(8)
C(21)	3109	395	1967	O(1)	−2019(8)	1954(4)	2017(6)
C(3)	1364(11)	96(5)	2730(7)	O(2)	−946(7)	1159(4)	3249(5)
C(32)	2250(8)	−994(4)	3114(5)	O(3)	−132(8)	2197(4)	3206(6)
C(33)	3058	−1421	3700	C(71)	−2967(14)	1611(8)	1377(11)
C(34)	3858	−1216	4549	C(81)	−1761(15)	1292(9)	3913(9)
C(35)	3850	−583	4812	C(91)	309(15)	2775(6)	2869(11)
C(36)	3042	−155	4226				



Scheme 2 Cyclopentadienyl ligands omitted for clarity. (*i*) + PhC_2Ph

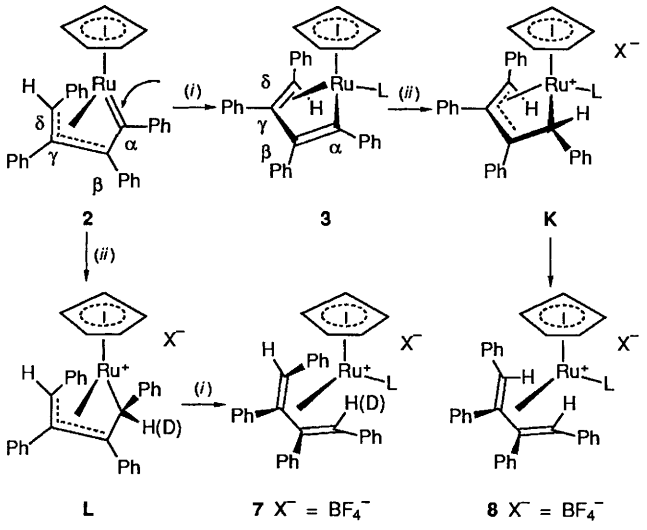
via an oxidative addition reaction ($Ru^{II} \longrightarrow Ru^{IV}$) of the proximal CHO group. In principle **C** could undergo a 1,3 hydrogen shift to form the ruthenabenzene derivative **D**, however this does not occur, instead a reductive elimination reaction competes to form **5**.

Since butadienyl complexes have been implicated[6,7] in the oligomerisation of alkynes at mononuclear centres, it was also of obvious interest to test further the idea that σ,η^3(5e)-butadienyls can behave as masked or latent co-ordinatively unsaturated σ,η(3e)-butadienyl species by treating **2** with diphenylacetylene. Refluxing a solution of **2** and an excess of PhC_2Ph in tetrahydrofuran (thf) resulted in a change in colour from purple to yellow-orange. Column chromatography of the reaction mixture afforded yellow-orange crystals of **6**. Elemental analysis and a mass-spectrum showed that the molecule had the molecular formula $[Ru(C_6Ph_6H)(C_5H_5)]$. Comparison of the ^1H and ^{13}C-$\{^1H\}$ NMR spectra of **6** with that of the previously[8] prepared complex $[Ru(\eta^5\text{-}exo\text{-}C_6Ph_6H)(\eta\text{-}C_5H_5)]$ showed that **6** was the corresponding *endo* isomer.

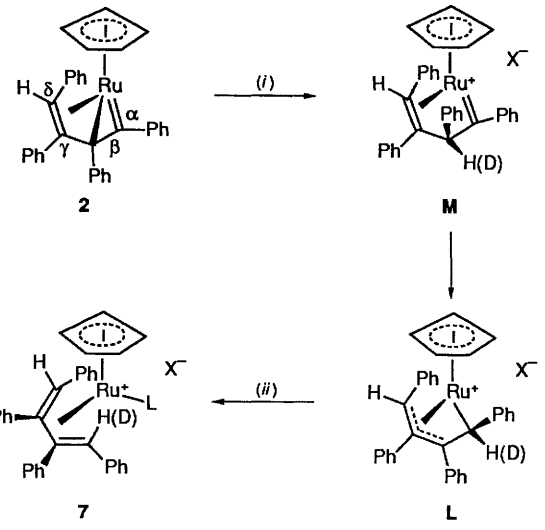
A possible mechanism for the formation of compound **6** is shown in Scheme 2. Initial co-ordination of the alkyne to the metal centre might be expected to lead to the formation of the η^3(3e)-butadienyl alkyne complex **E**. Insertion of the alkyne into the ruthenium σ bond could then result in the formation of a 16-electron hexatrienyl species which, as is illustrated, can adopt two conformations **F** and **G**. Ring closure of **F** leads directly to the observed product **6**. However, hexatrienyl **G** *via* consecutive intramolecular insertion reactions generating successive ruthenium-substituted methylcyclopentadienyl and bicyclo[3.1.0]hexane intermediates [similar to those implicated[7] in the reactions of alkynes with vinylpalladium(II) species] would lead[9,10] to a cyclohexadienyl species **J** containing the hydrogen substituent in an *exo* position relative to the metal, rather than the observed *endo* isomer. Although the formation of the *endo* isomer **6** might be taken as evidence for the first reaction path, the observation[2] that in the reaction of **2** with $P(OMe)_3$ the initially formed adduct undergoes stereomutation of the end CHPh group introduces an element of uncertainty into this conclusion.

Having established the scope of donor ligand-promoted σ,η^3(5e) to σ,η^2(3e) transformations the reactivity of the σ,η^3(5e)-butadienyl complex **2** towards electrophiles was next examined. It was realised that treatment of **2** with a source of protons was likely to lead to a co-ordinatively unsaturated species, which might be unstable. Indeed, treatment of **2** in dichloromethane as solvent with HBF_4·Et_2O led to decomposition. To avoid this difficulty the reaction of **2** with HBF_4·Et_2O in the presence of $P(OMe)_3$ was studied, it being argued that the trimethyl phosphite would act as a proton carrier, and that the liberated $P(OMe)_3$ might then stabilise the initial product of protonation by co-ordination.

Addition of excess of $P(OMe)_3$ to a solution of compound **2** in CH_2Cl_2 cooled to −78 °C, followed by immediate addition of 1 equivalent of HBF_4·Et_2O, did not result in any visible change in the colour of the solution. However, warming the mixture to room temperature led to a rapid change from purple to yellow. Crystallisation of the product from dichloromethane–diethyl ether afforded pale yellow crystals of compound **7** in essentially quantitative yield. Elemental and NMR spectral



Scheme 3 L = $P(OMe)_3$, X^- = BF_4^- or $CF_3SO_3^-$. (*i*) +$P(OMe)_3$; (*ii*) +$[PH(OMe)_3][BF_4]$ or $[PD(OMe)_3][CF_3SO_3]$



Scheme 4 L = $P(OMe)_3$, X^- = BF_4^- or $CF_3SO_3^-$. (*i*) +$[PH(OMe)_3][BF_4]$ or $[PD(OMe)_3][CF_3SO_3]$; (*ii*) +$P(OMe)_3$

analysis showed **7** to be a cationic species, containing η-C_5H_5, $P(OMe)_3$ and η^4-bonded diene ligands. Of particular interest relating to this latter structural feature was the stereochemistry of the 1,3-diene substituents. Hydrogen-1 and ^{13}C-$\{^1H\}$ NMR spectra (see Experimental section) indicated[11] that the diene was unsymmetrically substituted, four ^{13}C resonances being observed for the diene carbons, whilst the ^1H spectrum contained resonances due to olefinic protons at δ 5.66 [d, 1 H, *J*(HP) 1.4] and 3.76 [d, 1 H, *J*(HP) 15.1]. From the chemical shifts of these protons and the magnitudes of the observed phosphorus couplings, the resonance at δ 5.66 is ascribed to a proton in a *syn* position, whilst that at δ 3.76 corresponds to a proton in the *anti* position. When the protonation reaction was carried out with CF_3SO_3D instead of HBF_4·Et_2O the triflate analogue of **7** was formed, and examination of the ^1H and ^2D NMR spectra showed that deuterium had been incorporated exclusively into the *anti* position of the 1,3-diene cation.

Before interpreting these observations it is clearly important to consider also the result of protonation of the adduct [Ru{C(Ph)=C(Ph)-η^2-(*Z*)-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)] **3**, which is formed on reaction of $P(OMe)_3$ with **2**. Protonation occurred readily on treatment of **3** with HBF_4·Et_2O in dichloromethane at −78 °C. Crystallisation of the resultant reaction mixture afforded, in addition to some decomposed material, a cream crystalline solid **8**. Hydrogen-1 and ^{13}C-$\{^1H\}$ NMR spectra of the material revealed the presence of η-C_5H_5 and $P(OMe)_3$ ligands, as well as a symmetrical η^4-coordinated 1,3-diene. This latter structural feature was inferred from the presence of two resonances at δ 102.5 (s, *C*Ph) and 68.8 [d, *C*H(Ph), *J*(CP) 7.7 Hz] in the ^{13}C-$\{^1H\}$ NMR spectrum of **8**, and a two-proton doublet at δ 2.87 [C*H*(Ph), *J*(HP) 16.3 Hz] in the ^1H NMR spectrum consistent with the presence of a *Z,Z*-CH(Ph)=C(Ph)C(Ph)=CH(Ph) ligand, *i.e.* both hydrogens in an *anti* position.

In considering explanations for these observations the most likely reaction path for the formation of compound **8** from **3** involves delivery of the proton onto C_α *via* the inside face of the molecule. As is illustrated in Scheme 3 such a process would lead to initial formation of the intermediate **K**, which would be expected to collapse to give **8**. In the case of direct protonation of the σ,η^3(5e)-butadienyl complex **2** there are two distinct reaction pathways which are consistent with the incorporation of the deuterium into the inside, *i.e. anti* position, and formation of the *E,Z*-1,3-diene cation **7**. The simpler explanation is shown in Scheme 3, and involves either direct attack on C_α from the inside face or initial attack on ruthenium followed by migration onto C_α, both processes affording the 16e species **L**, which is then captured by $P(OMe)_3$ to give **7**. The second and more complex pathway to compound **7** relates to an alternative valence description of **2** which depicts this molecule as a vinyl-substituted η^2-vinyl complex. As is shown in Scheme 4, proton attack could alternatively occur from the inside face on C_β to give the cationic alkylidene intermediate **M**, which then *via* migration of the hydrogen on the inside face of the molecule to C_α affords **L**, which is captured by $P(OMe)_3$. It is not possible at present to distinguish between these two alternative mechanisms.

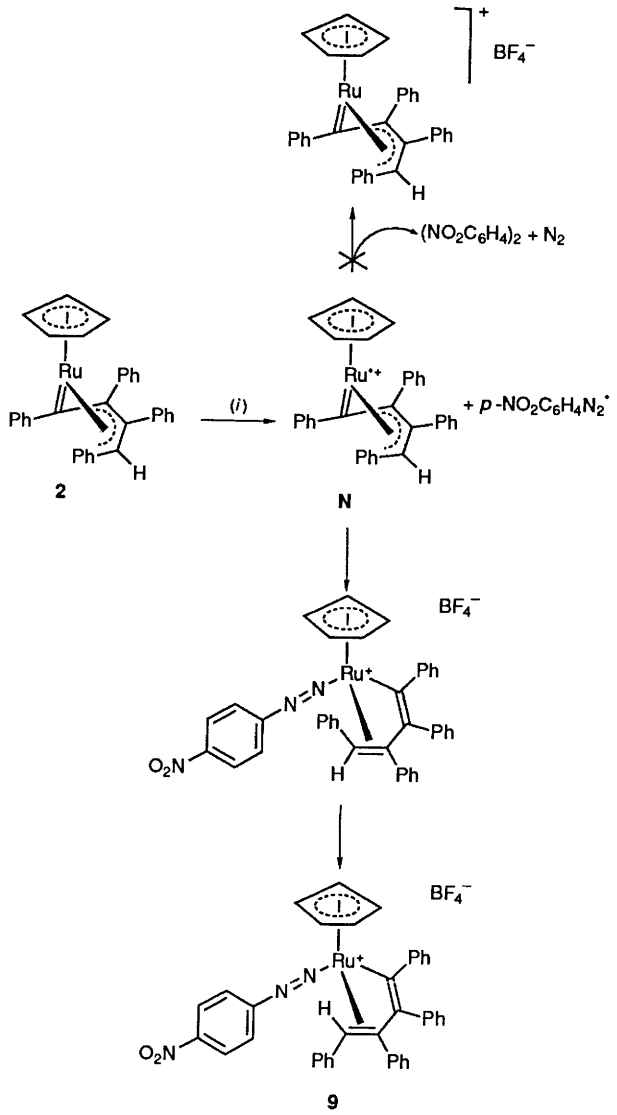
Finally, attention was focused on the ease with which ferrocene and ruthenocene can be oxidised to 17e cations. Since compound **2** can be pictured as an analogue of ruthenocene where one of the η^5-C_5H_5 ligands is replaced by a σ,η^3(5e)-butadienyl ligand, an attempt was made to oxidise **2** with *p*-nitrobenzenediazonium tetrafluoroborate. At room temperature in dichloromethane as solvent the red crystalline cationic compound **9** was formed in essentially quantitative yield. However, the elemental analysis, IR and the NMR spectra of **9** clearly showed that the compound was a 1:1 adduct of **2** and [*p*-$NO_2C_6H_4N_2$][BF_4], which can best be formulated as a cation containing σ,η^2(3e)-butadienyl and linear (3e) aryldiazenido ligands. Regarding the butadienyl chain, the ^1H NMR spectrum showed a signal for the C*H*Ph proton at δ 5.34, which is at lower field than that exhibited by **2** (δ 4.02), implying that in the formation of **9** stereomutation also occurs on the end carbon of the C_4 chain.

Thus, it is likely that in the reaction between compound **2** and [*p*-$NO_2C_6H_4N_2$][BF_4] an initial one-electron-transfer reaction occurs to form the 17e cation **N**. However, instead of the *p*-$NO_2C_6H_4N_2^{\bullet}$ radical losing N_2 and the resultant aryl radical dimerising, recombination of the 17-electron cation **N** (Scheme 5) with *p*-$NO_2C_6H_4N_2^{\bullet}$ evidently competes with the resultant formation of **9**.

Experimental

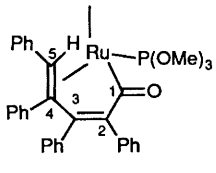
The ^1H, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectra were recorded on JEOL FX 90 Q, FX 200, Bruker WM-250 or W-360 spectrometers as appropriate. Data are given for room-temperature measurements, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference $SiMe_4$ for ^{13}C and ^1H, and H_3PO_4 (85% external) for ^{31}P. Infrared spectra were recorded on a Perkin-Elmer 983 G spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled and degassed solvents.

Reaction of [Ru{=C(Ph)-η^3-C(Ph)C(Ph)C(Ph)CHO}(η-C_5-

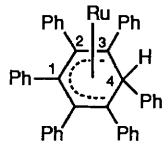


Scheme 5 (*i*) $+[p\text{-}NO_2C_6H_4N_2][BF_4]$, CH_2Cl_2

$H_5)$] **1** *with Trimethyl Phosphite.*—A solution of compound **1** (0.06 g, 0.11 mmol) and $P(OMe)_3$ (0.03 g, 0.24 mol) in CH_2Cl_2 (8 cm^3) was stirred at room temperature for 6 d, during which time the colour changed from deep blue-green to deep yellow. The volatile material was removed *in vacuo* and the residue dissolved in the minimum of CH_2Cl_2–hexane (1:1). Chromatography on alumina and elution with ethyl acetate afforded a yellow band which on collection and recrystallisation (CH_2Cl_2–hexane, −78 °C) afforded yellow *crystals* of [Ru{C(O)C(Ph)=C(Ph)-η²-(*Z*)-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)] **5** (0.03 g, 41%) (Found: C, 65.6; H, 5.2. $C_{37}H_{35}O_4PRu$ requires C, 65.8; H, 5.2%), $\nu_{CO}(CH_2Cl_2)$ 1598w cm^{-1}. NMR (C_6D_6): ^1H, δ 7.52–6.69 (m, 20 H, Ph), 4.82 [d, 5 H, C_5H_5, *J*(HP) 0.7], 4.20 [d, 1 H, C*H*Ph, *J*(HP) 12.2] and 3.17 [d, 9 H, P(OMe), *J*(HP) 11.5]; ^{13}C-{^1H}, δ 242.3 [d, C^1, *J*(CP) 20.2], 165.6 (C^2), 152.9–125.2 (Ph), 93.6 (C_5H_5), 90.3 (C^3), 81.7 (C^4), 59.0 [d, C^5, *J*(CP) 9.2] and 51.7 [d, P(OMe), *J*(CP) 3.7 Hz].



Reactions of [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] **2**.—(*a*) *Diphenylacetylene.* A solution of [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] (0.125 g, 0.24 mmol) and diphenylacetylene (0.20 g, 1.12 mmol) in tetrahydrofuran (10 cm^3) was refluxed for 36 h. Volatiles were removed, and the resultant orange-red oil extracted into CH_2Cl_2–hexane (1:3) (4 cm^3) and chromatographed. Elution with the same solvent combination afforded an orange band which on recrystallisation (hexane, −78 °C) afforded yellow-orange *crystals* of [Ru(η⁵-*endo*-C_6Ph_6H)(η-C_5H_5)] **6** (0.04 g, 24%) (Found: C, 80.0; H, 4.5. $C_{47}H_{36}Ru$ requires C, 80.5; H, 5.1%). NMR ($CDCl_3$); ^1H, δ 7.56–6.82 (m, 30 H, Ph), 4.98 (s, 5 H, C_5H_5) and 4.49 (s, 1 H, C*H*Ph); ^{13}C-{^1H}, δ 146.9–123.2 (Ph), 102.7 (C^1), 98.8 (C^2), 82.9 (C_5H_5), 58.1 (C^4) and 48.2 (C^3). The mass spectrum showed peaks at *m/z* 701 (3, *P*), 625 (78, *P* − Ph), 535 (48, C_6Ph_4H) and 534 (100%, C_6Ph_4).



(*b*) *Protonation.* To a solution of compound **2** (0.136 g, 0.26 mmol) in CH_2Cl_2 (8 cm^3) cooled to −78 °C, $P(OMe)_3$ (0.10 g, 0.8 mmol) was added, followed immediately by HBF_4·Et_2O (0.3 mmol). After stirring for 15 min at this temperature no reaction was apparent. On warming to room temperature the colour changed from purple to yellow. Removal of the solvent *in vacuo* and recrystallisation (0 °C) from CH_2Cl_2–Et_2O (1:1) afforded yellow *crystals* of [Ru{η⁴-(*E*,*Z*)-CH(Ph)=C(Ph)C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)][BF_4] **7** (0.14 g, 93%) (Found: C, 58.6; H, 5.0. $C_{36}H_{36}BF_4O_3PRu$ requires C, 58.8; H, 4.9%). NMR: ^1H[$(CD_3)_2CO$], δ 7.36–6.88 (m, 20 H, Ph), 5.82 (s, 5 H, C_5H_5), 5.66 [d, 1 H, H (*syn*), *J*(HP) 1.4], 3.76 [d, 1 H, H (*anti*), *J*(HP) 15.1] and 3.54 [d, 9 H, P(OMe), *J*(HP) 11.5]; ^{13}C-{^1H} (CD_2Cl_2), δ 139.3–127.3 (Ph), 105.6 (*C*Ph), 94.0 (*C*Ph), 90.9 (C_5H_5), 70.3 [d, *C*HPh, *J*(CP) 6.1], 60.3 [d, *C*HPh, *J*(CP) 4.5] and 55.0 [d, P(OMe), *J*(CP) 9.2 Hz]; ^{31}P-{^1H}[$(CD_3)_2CO$], δ 131.9 (POMe).

Protonation of [Ru{C(Ph)=C(Ph)-η²-C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)] **3**.—To a solution of compound **3** (0.11 g, 0.17 mmol) in CH_2Cl_2 (8 cm^3), HBF_4·Et_2O (0.20 mmol) was added at −78 °C. After stirring for 30 min at this temperature the reaction mixture was allowed to warm slowly to room temperature. The volume of the solvent was then reduced *in vacuo* to 5 cm^3. Addition of Et_2O (2 cm^3) resulted in the precipitation of a small amount of a brown solid. The supernatant liquid was decanted and cooled (−78 °C) to afford cream *crystals* of [Ru{η⁴-(*Z*,*Z*)-CH(Ph)=C(Ph)C(Ph)=CH(Ph)}{$P(OMe)_3$}(η-C_5H_5)][BF_4] **8** (0.04 g, 30%) (Found: C, 58.5; H, 4.6. $C_{36}H_{36}BF_4O_3PRu$ requires C, 58.8; H, 4.9%). NMR [$(CD_3)_2CO$]: ^1H, δ 7.12 (m, 20 H, Ph), 5.85 (s, 5 H, C_5H_5), 3.79 [d, 9 H, P(OMe), *J*(HP) 11.5] and 2.87 [d, 2 H, C*H*Ph, *J*(HP) 16.3]; ^{13}C-{^1H}, δ 139.8–127.7 (Ph), 102.5 (*C*Ph), 90.5 (C_5H_5), 68.8 [d, *C*HPh, *J*(CP) 7.7] and 56.1 [d, P(OMe), *J*(CP) 9.2 Hz]; ^{31}P-{^1H}, δ 130.1 (POMe).

Reaction of [Ru{=C(Ph)-η³-C(Ph)C(Ph)CH(Ph)}(η-C_5H_5)] *with p-Nitrobenzenediazonium Tetrafluoroborate.*—To a solution of compound **2** (0.10 g, 0.19 mmol) in CH_2Cl_2 (10 cm^3) cooled to −78 °C, [p-$NO_2C_6H_4N_2$][BF_4] (0.045 g, 0.19 mmol) was added and the mixture stirred at this temperature for 15 min. After this time no reaction was apparent and so the mixture was allowed to warm to room temperature, whereupon it rapidly turned red-brown. Stirring was continued for 15 min and diethyl ether (35 cm^3) then added, affording red *crystals* of compound **9** (0.133 g, 92%) (Found: C, 61.3; H, 3.9; N, 4.7. $C_{39}H_{30}BF_4N_3O_2Ru$ requires C, 61.6; H, 4.0; N, 5.5%);

ν(Nujol) 1608m and 1594m cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 8.31 [d, 2 H, *o*-H of $C_6H_4NO_2$, *J*(HH) 9.0], 7.68 [d, 2 H, *m*-H of $C_6H_4NO_2$, *J*(HH) 9.0 Hz], 7.41–7.08 (m, 20 H, Ph), 5.85 (s, 5 H, C_5H_5) and 5.34 (s, 1 H, C*H*Ph); ^{13}C-{^1H}, δ 150.4–122.9 (Ph, $C^{1,2}$), 90.4 (C_5H_5), 80.2 (C^4) and 71.0 (C^3).

Structure Determination of Compound **5**.—*Crystal data.* $C_{37}H_{35}O_4PRu$, M = 675.7, monoclinic, space group $P2_1/c$, a = 10.627(6), b = 21.198(12), c = 14.448(6) Å, β = 103.03(4)°, U = 3171(3) $Å^3$, Z = 4, D_c = 1.42 g cm^{-3}, λ = 0.710 69 Å, μ = 5.7 cm^{-1}, F(000) = 1392, T = 295 K. Crystal faces [distances from origin in mm] (100) [0.05], (100) [0.05], (010) [0.056], (010) [0.056], (001) [0.18], (021) [0.157].

Diffraction measurements were made with a Nicolet four-circle P3m diffractometer using graphite-monochromated X-radiation on a single crystal (approximate dimensions 0.4 × 0.1 × 0.1 mm) mounted in a thin-walled glass capillary under N_2. Cell dimensions were determined from the setting angle values of 22 centred reflections with 2θ in the range 19–21°. A total of 4299 diffracted intensities (including checks) were measured in a unique quadrant of reciprocal space for 4.0 < 2θ < 50.0° by ω–2θ scans of width 2.0° + $\Delta_{\alpha_1\alpha_2}$; only reflections with count rates > 5 s^{-1} were measured for 2θ > 40°. Three check reflections (200, 080, 002) remeasured after every 50 ordinary data showed no decay and *ca.* 1% variation over the period of data collection, an appropriate correction was therefore applied. Of the 3897 non-check intensity data collected, 3552 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these 2472 with $I > 1.5\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of the indexed crystal faces; maximum and minimum transmission coefficients were 0.95 and 0.93 respectively. Lorentz and polarisation corrections were applied. The structure was solved by heavy-atom (Patterson and Fourier difference) methods, and refined by blocked-cascade least squares against F. All non-hydrogen atoms except the phenyl carbons were assigned anisotropic displacement parameters. Phenyl ring carbons and H(1) were assigned refined isotropic displacement parameters. Phenyl rings were constrained to planarity with C–C 1.395 Å and C–C–C 120°; H(1) was refined without positional constraints. All other (methyl) hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å. Refinement of the 233 least-squares variables converged smoothly to residual indices R = 0.084, R' = 0.072, S = 1.60.* Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$. Here $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and g = 0.0003 was chosen to minimise the variation in S as a function of F_o. Final difference electron-density maps showed no features outside the range +0.7 to −0.9 e $Å^{-3}$. Table 3 reports the positional parameters for the non-hydrogen atoms.

All calculations were made with programs of the SHELXTL [12] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref. 13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, where $\Delta = F_o - F_c$ and N_o, N_v are the numbers of observations and variables respectively.

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