Reactions of Co-ordinated Ligands. Part 49.[1] Ligand-displacement and Oxidative-addition Reactions of $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$; Crystal Structures of $[Ru(NCMe)\{P(OMe)_3\}(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4Ph_4)][SbF_6]$ and $[Ru\{C(Ph){=}C(Ph)C(\eta^6\text{-}C_6H_5){=}C(Ph)CH_2CH{=}CH_2\}\{P(OMe)_3\}_2][BF_4]$*

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Treatment of the ruthenium(0) complex $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$ with isoprene or cyclohexa-1,3-diene results in the displacement of C_5H_6 and formation of compounds of the type $[Ru\{P(OMe)_3\}(\eta^4\text{-}1,3\text{-diene})(\eta^4\text{-}C_4Ph_4)]$. Although *trans*-penta-1,3-diene reacts similarly to give the η^4-*trans*-penta-1,3-diene complex, the corresponding reaction with *cis*-penta-1,3-diene affords a mixture of both the *trans*- and *cis*-penta-1,3-diene ruthenium complexes. A possible mechanism for this reaction is discussed. Cyclopenta-1,3-diene is also displaced on treatment of $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$ with allyl bromide or 2-methylallyl chloride to give respectively the ruthenium(II) species $[RuBr\{P(OMe)_3\}(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4Ph_4)]$ and $[RuCl\{P(OMe)_3\}(\eta^3\text{-}2\text{-}MeC_3H_4)(\eta^4\text{-}C_4Ph_4)]$. Reaction of these species with $AgBF_4$ in acetonitrile affords the cations $[Ru(NCMe)\{P(OMe)_3\}(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4Ph_4)][BF_4]$ and $[Ru(NCMe)\{P(OMe)_3\}(\eta^3\text{-}2\text{-}MeC_3H_4)(\eta^4\text{-}C_4Ph_4)][BF_4]$. The solid-state structure of the corresponding SbF_6^- salt of the former cation was established by *X*-ray crystallography. The geometry of the molecule is that of a three-legged piano-stool, the allyl group adopting an *endo* configuration. Instead of the expected propeller configuration for the η^4-tetraphenylcyclobutadiene ligand, two of the phenyl rings lie roughly coplanar with the C_4 ring, while the other two are approximately perpendicular to it. Attempts to replace the acetonitrile ligand present in these species by $P(OMe)_3$ failed, however when $AgBF_4$ was added to an acetone solution of $[RuBr\{P(OMe)_3\}(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4Ph_4)]$ followed by addition of $P(OMe)_3$ a yellow cationic species was obtained, which was shown by *X*-ray crystallography to be the ring-opened compound $[Ru\{C(Ph){=}C(Ph)C(\eta^6\text{-}C_6H_5){=}C(Ph)CH_2CH{=}CH_2\}\{P(OMe)_3\}_2][BF_4]$. A mechanism is proposed for this unusual reaction.

In order to rationalise the reactivity of cationic η^4-cyclobutadiene complexes towards nucleophilic reagents we suggested[2] that reaction of $K[BHBu^s_3]$ with $[Ru(PPh_3)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ led to the formation of the labile ruthenium(0) complex $[Ru(PPh_3)(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$, which could be intercepted by displacement of the co-ordinated cyclopenta-1,3-diene with two-electron donor ligands such as CO and $P(OMe)_3$. The discovery[2] that the related trimethyl phosphite-substituted complex $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$ could actually be isolated as an air-sensitive crystalline species provided an opportunity to explore in greater detail displacement reactions of the co-ordinated cyclopenta-1,3-diene. In this paper reactions with a range of 1,3-dienes are described together with the study of the oxidative displacement of η^4-C_5H_6 by allylic halides.

Results and Discussion

Addition of an excess of isoprene or cyclohexa-1,3-diene to a solution of $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)]$ in tetrahydrofuran (thf) resulted in the displacement of cyclopenta-1,3-diene and the formation of the ruthenium(0) complexes (**1**) and (**2**) respectively. These were isolated in good yield by column chromatography followed by recrystallisation, as moderately air-sensitive yellow crystalline materials. From a preparative standpoint it was found that satisfactory yields of (**1**) and (**2**) could also be obtained by simply treating the cation $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ with $K[BHBu^s_3]$ in thf in the presence of the respective 1,3-diene. The new compounds obtained were characterised by elemental analysis, mass and n.m.r. spectroscopy. Although in principle the 1,3-diene could adopt either an *exo* or an *endo* orientation relative to the η^4-C_4Ph_4 ligand, examination of the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**1**) and (**2**) (see Experimental section for details) revealed the presence of only one isomer. From steric considerations one would expect this to adopt the *endo* configuration, however, this needs to be confirmed by *X*-ray crystallography.

A similar reaction between $[Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$, $K[BHBu^s_3]$, and *trans*-penta-1,3-diene afforded a yellow crystalline solid, similar in appearance to (**1**) and (**2**). The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (see Experimental section) indicated that simple displacement of the cyclopentadiene by the penta-1,3-diene had occurred to give (**3**) (Scheme 1). The 1,3-diene ligand was identified as having retained its *trans* configuration, by examination of the ^1H n.m.r. spectrum. In particular, H^1, which resonates at δ 1.95, shows a coupling of

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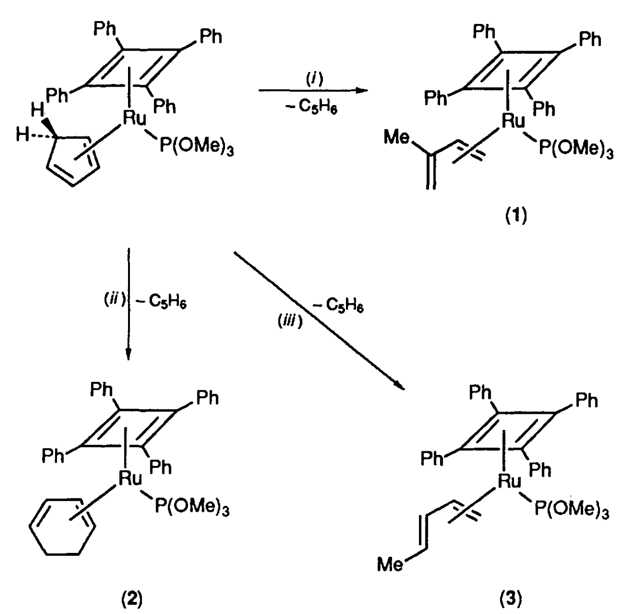
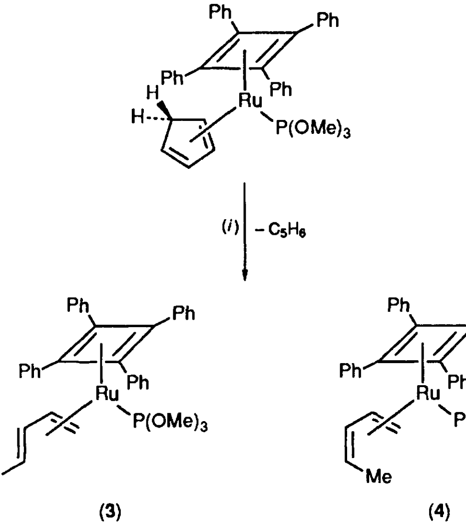
* (Acetonitrile)(η-allyl)(η-tetraphenylcyclobutadiene)(trimethylphosphite) ruthenium hexafluoroantimonate and $[1,2,3(\eta^6),4$-tetraphenylhepta-1,3,6-trien-1-yl)bis(trimethyl phosphite)ruthenium tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



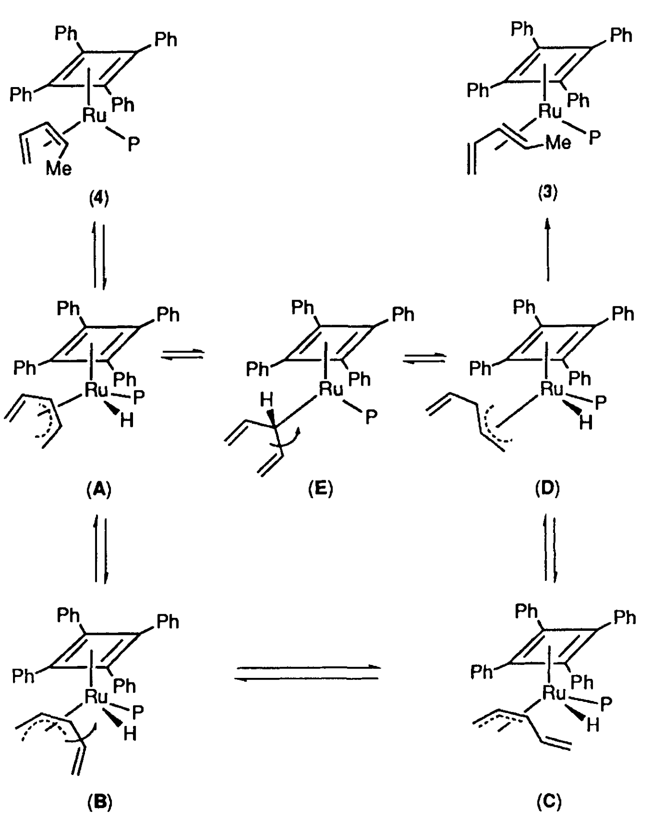
Scheme 1. (*i*) Isoprene; (*ii*) cyclohexa-1,3-diene; (*iii*) *trans*-penta-1,3-diene



Scheme 2. (*i*) + *cis*-penta-1,3-diene

9.3 Hz with H^2, compared to the couplings of H^4 and H^5 with H^3 which were 7.24 and 9.45 Hz respectively.

When the reaction was repeated with *cis*-penta-1,3-diene a yellow crystalline material was again obtained. However, the ^1H n.m.r. spectrum showed it to be a 3:1 mixture of two isomeric compounds, which proved inseparable by column chromatography. The minor isomer was identical (by ^1H and $^{13}C-\{^1H\}$ n.m.r. spectroscopy) with (**3**), while the major isomer (**4**) (Scheme 2) was found to have a *cis*-penta-1,3-diene ligand. This was indicated by the higher-field shift of the methyl group compared to (**3**), and the chemical shift of H^1 (δ 3.7), which clearly indicates that it occupies a *syn* position. When a solution of (**3**) (25%)/(**4**) (75%) was heated in $[^2H_8]$ toluene to 80 °C for 2 h, with the ^1H n.m.r. spectrum being recorded at intervals, an irreversible isomerisation occurred to give a mixture with the composition (**3**) (84%)/(**4**) (16%). In a subsequent experiment, carried out at room temperature, the composition changed from 25% (**3**) and 75% (**4**) to 88% (**3**) and 12% (**4**) over a period of 8 d. There was no evidence of decomposition.



Scheme 3. P = $P(OMe)_3$

The mechanisms discussed for the isomerisation of $[Mo(CO)_2(\eta^4-C_5H_6)(\eta-C_5H_5)][BF_4]^{3,*}$ and the formation of isomers of $[Ru(CO)(\eta^4-C_5H_6)(\eta-C_5H_5)][BF_4]^4$ cannot be in operation here since both require *exo* to *endo* isomerisation, concomitant with *cis*/*trans* isomerisation. A mechanism whereby the isomerisation might occur in this case, is outlined in Scheme 3. An initial oxidative addition ($Ru^0 \longrightarrow Ru^{II}$) of a methyl C–H bond initiated by a η^4 to η^2 slippage of the 1,3-diene would form the η^3-allyl hydride intermediate (**A**) from (**4**).[5–9] The metal must then slip along the carbon chain to form (**B**), such that, when rotation of the non-co-ordinated double bond has occurred, to give (**C**), the metal can again slip along the carbon chain to form (**D**), in which the mutually *cis* orientation of the allylic methylene and hydride groups are maintained. Reductive elimination than allows formation of (**3**). Alternatively the conversion of (**A**) into (**D**) could also arise *via* the 16e σ-allyl complex (**E**). Rotation of the allyl unit *cis* to the hydride group, followed by regeneration of the η^3-allyl bonding mode, then gives (**D**).

Thus, a key step in the isomerisation of compound (**4**) to (**3**) possibly involves an oxidative-addition reaction. This suggested that the complex $[Ru\{P(OMe)_3\}(\eta^4-C_4Ph_4)(\eta^4-C_5H_6)]$ might also undergo oxidative-addition reactions, in which the η^4-cyclopentadiene ligand is displaced. This was confirmed when it was observed that treatment with allyl bromide or 2-methylallyl chloride afforded respectively the yellow crystalline complexes (**5**) and (**6**). Elemental analyses, ^1H and $^{13}C-\{^1H\}$ n.m.r. spectroscopy (see Experimental section) suggested the illust

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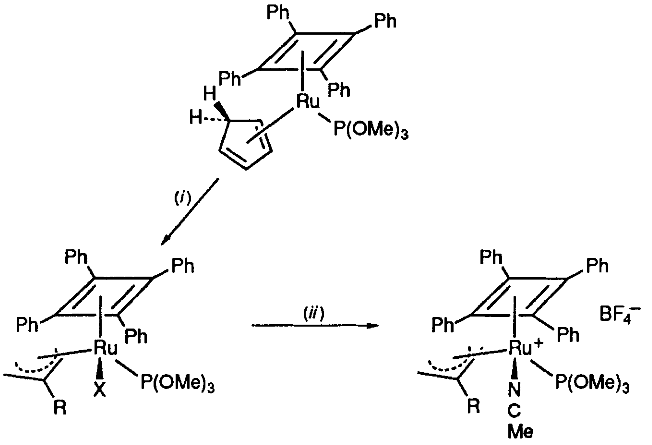
[*] The 'envelope flip' mechanism is also thought to be involved in the thermal isomerisation of $[M(\eta^8-C_8H_8)(\eta^4-C_4H_6)]$ (M = Zr or Hf) and $[Mo(\eta^4-C_4H_6)_3]$ (see R. Benn and G. Schroth, *J. Organomet. Chem.*, 1982, **228**, 71), and in photoisomerisation of $[Co(\eta^4\text{-diene})(\eta-C_5H_5)]$ (see B. Eaton, J. A. King, jun., and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 1359).



(5) R = H, X = Br
(6) R = Me, X = Cl

(7) R = H
(8) R = Me

Scheme 4. (*i*) + Allylic halide, $-C_5H_6$; (*ii*) $AgBF_4$, CH_2Cl_2–MeCN, $-AgX$

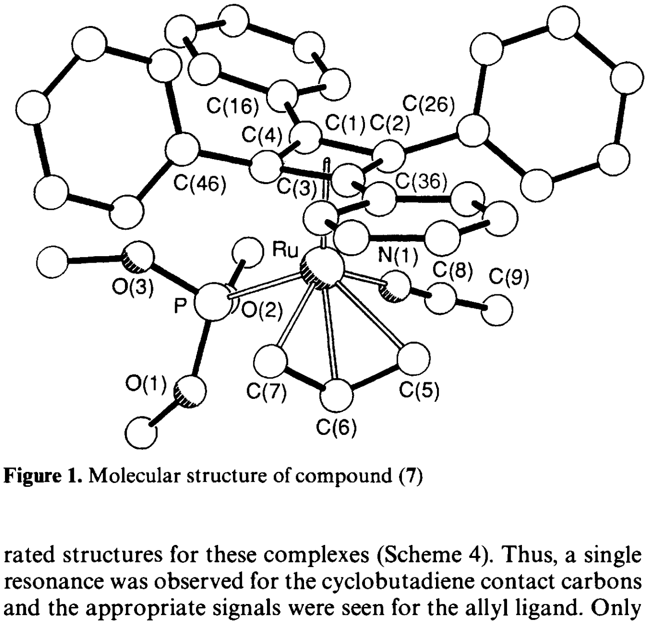


Figure 1. Molecular structure of compound (7)

rated structures for these complexes (Scheme 4). Thus, a single resonance was observed for the cyclobutadiene contact carbons and the appropriate signals were seen for the allyl ligand. Only one isomer was formed in each reaction, and it is suggested from steric considerations that these have an *endo* configuration. Treatment of compounds (**5**) and (**6**) with $AgBF_4$ in CH_2Cl_2–MeCN resulted in an immediate precipitation of AgX, and formation of the yellow crystalline cations (**7**) and (**8**). The structural identity of these cations was confirmed by an *X*-ray crystallographic study with the SbF_6^- salt of (**7**).

Figure 1 shows the molecular structure of the cation, together with the atomic numbering scheme. Fractional atomic coordinates for the non-hydrogen atoms are given in Table 1, bond lengths and angles in Tables 2 and 3. The geometry around the metal is that of a distorted tetrahedron, or so-called 'three-legged piano-stool.' The allyl group adopts an *endo* configuration, and shows the expected variation in the ruthenium–carbon bond lengths for this conformation, with Ru–C(6) being shorter than Ru-C(5) and Ru-C(7). The cyclobutadiene ring is planar to with ± 0.02 Å (Ru lies 1.918 Å from this plane). The C(1)–C(2) bond length of 1.527(16) Å is somewhat longer than the other three bonds in the cyclobutadiene ring [C(2)–C(3) 1.462(17), C(3)–C(4) 1.476(16), and C(4)–C(1) 1.473(17) Å]. There is no obvious reason for this difference, and the rather large estimated standard deviations (e.s.d.s) make it less significant than might appear, but it is interesting that a similar pattern was seen[10] in the solid-state structure of $[Ru(PPh_3)_2(CO)(\eta^4-C_4Ph_4)]$. The most unusual feature of the structure is the arrangement of the phenyl groups around the cyclobutadiene ring. Instead of the usual propeller configuration, as seen,[11] for instance, in $[Ru(NCMe)(\eta^4-C_4Ph_4)(\eta-C_5H_5)][BF_4]$, two of the rings lie roughly coplanar with the cyclobutadiene ring while the other two are close to perpendicular to it. This is evidenced by the interplanar angles between the phenyl rings and the mean plane of the cyclobutadiene ring which are 15.3, 59.7, 8.0, and 76.3°, for those rings attached to C(1), C(2), C(3), and C(4) respectively. It should be noted that there is a slight dishing of the bonds linking the cyclobutadiene ring to the four phenyl rings relative to the C_4 plane; C(16), C(26), C(36), and C(46) lie 0.25, 0.28, 0.23, and 0.42 Å respectively from the ring plane. Figure 2 shows a projection of the molecule down the metal–cyclobutadiene axis. This clearly shows that the ring making the smallest interplanar angle, C(31)—C(36), is that which lies over the allyl group. Indeed, it is this proximity to the allyl ligand which probably forces the phenyl ring to adopt the conformation that it does. Non-bonding distances between the two groups include C(7) • • • C(35) 3.55 Å and C(5) • • • C(31) 3.60 Å. Any significant rotation of the phenyl group would shorten the C(7) • • • C(35) separation, leading to unfavourable interactions. The orientation of the other rings may then follow as a consequence of this; a high degree of twist in C(41)—C(46) and C(21)—C(26) minimising interactions between adjacent rings. It should perhaps be noted that, despite the solid-state geometry, in solution all four phenyl rings are equivalent due to rotation of the cyclobutadiene ring and of the phenyl groups themselves.

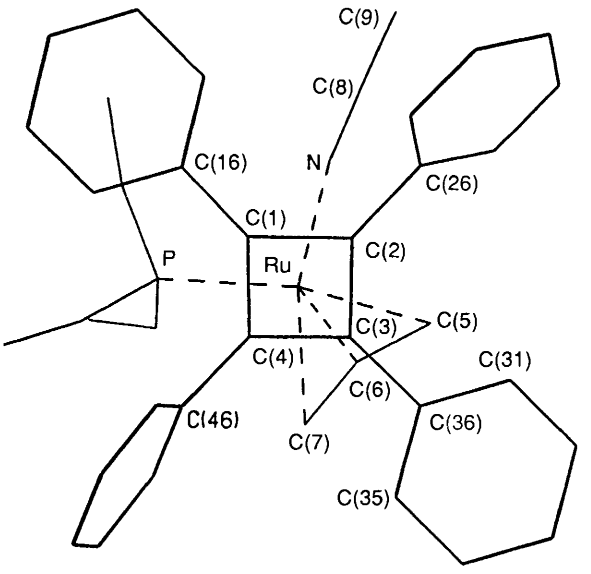


Figure 2. Projection of compound (7) down the metal–cyclobutadiene axis

It was anticipated that complexes similar to (**7**) and (**8**), would be accessible by carrying out the halide-anion abstraction reaction in the presence of other two-electron donor ligands. However, when a CH_2Cl_2 solution of compound (**5**) was treated with $AgBF_4$ in the presence of $P(OMe)_3$ no precipitate of AgBr was observed, and only the starting material could subsequently be isolated. It was then thought that if an acetone adduct analogous to (**7**) and (**8**) was first formed then it might be possible to displace the acetone by $P(OMe)_3$. Thus, an acetone solution of (**5**) was treated with $AgBF_4$, the precipitated AgBr removed by filtration, and a slight excess of $P(OMe)_3$ added. On work-up a cationic yellow powder (**9**) was obtained. The ^1H

Table 1. Atom co-ordinates (× 10^4) for compound (7) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	5 532(1)	10 657(1)	9 482(1)	C(41)	5 448(7)	12 779(4)	8 834(3)
C(1)	7 393(12)	10 920(7)	9 146(5)	C(42)	5 393(6)	13 543(4)	8 587(3)
C(2)	7 407(11)	10 737(7)	9 818(5)	C(43)	6 476(6)	13 956(4)	8 458(3)
C(3)	6 799(11)	11 500(8)	9 936(5)	C(44)	7 614(6)	13 603(4)	8 575(3)
C(4)	6 714(11)	11 658(7)	9 286(5)	C(45)	7 669(6)	12 839(4)	8 821(3)
C(5)	4 546(9)	10 416(6)	10 359(4)	C(46)	6 586(6)	12 426(4)	8 951(3)
C(6)	3 713(9)	10 648(6)	9 914(4)	P	4 643(4)	10 536(3)	8 536(2)
C(7)	3 919(9)	11 434(6)	9 684(4)	O(1)	3 215(10)	10 528(10)	8 552(5)
C(11)	8 490(7)	9 800(4)	8 651(3)	O(2)	4 781(13)	9 728(10)	8 165(8)
C(12)	9 058(7)	9 481(4)	8 143(3)	O(3)	4 982(14)	11 217(10)	8 125(5)
C(13)	9 138(7)	9 932(4)	7 618(3)	C(51)	2 415(19)	10 293(13)	8 083(10)
C(14)	8 650(7)	10 702(4)	7 601(3)	C(52)	5 659(18)	9 205(15)	7 972(11)
C(15)	8 082(7)	11 021(4)	8 109(3)	C(53)	4 567(27)	11 542(18)	7 541(8)
C(16)	8 001(7)	10 569(4)	8 634(3)	N	5 647(9)	9 396(6)	9 497(5)
C(21)	9 425(7)	10 117(4)	10 078(3)	C(8)	5 703(13)	8 703(8)	9 581(7)
C(22)	10 154(7)	9 602(4)	10 418(3)	C(9)	5 818(18)	7 870(10)	9 698(8)
C(23)	9 617(7)	9 121(4)	10 857(3)	C(60)	1 808(17)	7 895(17)	8 617(8)
C(24)	8 351(7)	9 155(4)	10 956(3)	Cl(1)	2 443(11)	8 445(7)	9 202(5)
C(25)	7 621(7)	9 670(4)	10 616(3)	Cl(2)	2 939(16)	7 813(6)	8 066(5)
C(26)	8 158(7)	10 151(4)	10 177(3)	Sb	8 567(1)	6 796(1)	8 667(1)
C(31)	6 885(7)	11 636(4)	11 044(3)	F(1)	10 107(8)	6 439(7)	8 895(4)
C(32)	6 650(7)	12 069(4)	11 567(3)	F(2)	9 250(14)	7 303(8)	7 992(4)
C(33)	6 094(7)	12 818(4)	11 532(3)	F(3)	8 239(15)	5 858(8)	8 278(7)
C(34)	5 773(7)	13 135(4)	10 974(3)	F(4)	7 010(10)	7 183(9)	8 473(5)
C(35)	6 008(7)	12 702(4)	10 451(3)	F(5)	7 928(11)	6 376(7)	9 367(5)
C(36)	6 564(7)	11 953(4)	10 486(3)	F(6)	8 820(12)	7 747(6)	9 070(5)

Table 2. Bond lengths (Å) for compound (7)

Ru–C(1)	2.200(13)	Ru–C(2)	2.174(12)
Ru–C(3)	2.216(12)	Ru–C(4)	2.157(12)
Ru–C(5)	2.263(9)	Ru–C(6)	2.199(10)
Ru–C(7)	2.229(14)	Ru–P	2.327(4)
Ru–N	2.117(11)	C(1)–C(2)	1.527(16)
C(1)–C(4)	1.473(17)	C(1)–C(16)	1.443(14)
C(2)–C(3)	1.462(17)	C(2)–C(26)	1.506(13)
C(3)–C(4)	1.476(16)	C(3)–C(36)	1.463(14)
C(4)–C(46)	1.494(14)	C(5)–C(6)	1.396(19)
C(6)–C(7)	1.432(21)	P–O(1)	1.552(11)
P–O(2)	1.593(17)	P–O(3)	1.508(15)
O(1)–C(51)	1.414(25)	O(2)–C(52)	1.364(29)
O(3)–C(53)	1.401(25)	N–C(8)	1.177(17)
C(8)–C(9)	1.426(21)	C(60)–Cl(1)	1.738(24)
C(60)–Cl(2)	1.742(24)	Sb–F(1)	1.849(9)
Sb–F(2)	1.079(12)	Sb–F(3)	1.829(14)
Sb–F(4)	1.862(11)	Sb–F(5)	1.845(12)
Sb–F(6)	1.849(10)		

n.m.r. spectrum indicated that the molecular formula of the product was, as expected, $[Ru\{P(OMe)_3\}_2(C_3H_5)(C_4Ph_4)][BF_4]$, but the signals observed did not correlate with the expected structure.

Although the trimethyl phosphite groups gave rise to a triplet, characteristic of two equivalent ligands, the signals of the allyl group did not show the expected symmetry. Four groups of signals were observed, with relative integration 1:1:1:2. The central allylic proton showed couplings of 6.2 Hz to the two equivalent protons, and couplings of 17.2 and 10.0 Hz to the remaining two. While a coupling of 10.0 Hz is fairly typical of *trans* vicinal protons in a metal-co-ordinated allyl ligand, the couplings of 6 and 17 Hz are smaller and larger than expected for *cis* and *trans* vicinal protons respectively.

In the $^{13}C-\{^1H\}$ n.m.r. spectrum the allylic CH carbon resonated at 136.6 p.p.m., while the CH_2 carbons appeared at 115.8 and 41.8 p.p.m. The very low-field shifts of the CH and one of the CH_2 carbons, compared with those of (**5**) and (**9**), suggested that the allyl group was no longer η^3 bonded to the metal. However, if (**9**) had the formula $[Ru\{P(OMe)_3\}_2(\sigma\text{-}C_3H_5)(\eta^4\text{-}C_4Ph_4)][BF_4]$ the metal centre would be electron deficient, requiring a further two electrons to attain a stable electronic configuration. A valuable insight into the nature of the bonding in compound (**9**) was provided by the appearance of resonances in the ^{13}C n.m.r. spectrum at 104.0, 102.1, and 94.5 p.p.m., characteristic[12] of a co-ordinated phenyl group, suggesting the partial structure $[Ru(\text{-}CH_2CH{=}CH_2)\{P(OMe)_3\}_2(\eta^6\text{-arene})(C_4Ph_4)][BF_4]$. However, there remained the question as to how the rest of the cyclobutadiene ring was attached to this framework, and for this reason a single-crystal *X*-ray structure determination was carried out.

The structure of the cation (**9**), together with the atomic numbering scheme, is shown in Figure 3. Table 4 lists the fractional atomic co-ordinates for the non-hydrogen atoms; bond lengths and angles are listed in Tables 5 and 6. The tetraphenylcyclobutadiene ring has undergone a ring-opening reaction and formed a butadienyl chain. Of the four original contact carbons [C(4)—C(7)], one, C(7), remains σ bonded to the metal, while the phenyl group attached to C(5) is π bonded to the metal, and the 'terminal' carbon C(4) is substituted by phenyl ring and an allyl group. Interestingly there is a marked pattern of bond alternation between C(4) to C(7) with C(4)–C(5) and C(6)–C(7) [1.337(7) and 1.373(7) Å respectively] displaying significant double-bond character whilst C(5)–C(6) [1.506(6) Å] is comparable with a normal single bond. This chain is, however, still essentially planar with a maximum deviation of 0.05 Å [for C(5)]; C(46), C(56), C(66), and C(76) lie −0.36, 0.25, 0.15, and 0.19 Å from this plane. The electron count at the ruthenium is completed by two trimethyl phosphite ligands.

There would appear to be some strain in the alkenyl chain bridging the arene ring and ruthenium, which is shown, in particular, by the geometry around C(5). This atom is 0.32 Å below the mean plane of the co-ordinated arene ring, and while the C(4)–C(5)–C(56) angle of 11.4(4)° is normal for an sp^2-

Table 3. Bond angles (°) for compound (7)

C(1)–Ru–C(2)	40.9(4)	C(2)–C(3)–C(4)	90.5(9)	C(6)–Ru–N	92.2(5)	Cl(1)–C(60)–Cl(2)	106.8(12)
C(2)–Ru–C(3)	38.9(4)	C(4)–C(3)–C(36)	135.8(11)	P–Ru–N	87.3(3)	F(1)–Sb-F(3)	91.6(6)
C(2)–Ru–C(4)	57.6(4)	Ru–C(4)–C(3)	72.5(7)	Ru–C(1)–C(4)	68.7(7)	F(1)–Sb–F(4)	177.1(5)
C(1)–Ru–C(5)	139.8(4)	C(1)–C(4)–C(46)	131.7(10)	C(2)–C(1)–C(16)	133.4(10)	F(3)–Sb–F(4)	90.7(7)
C(3)–Ru–C(5)	90.8(4)	Ru–C(5)–C(6)	69.3(4)	Ru–C(2)–C(1)	70.5(6)	F(2)–Sb–F(5)	175.1(5)
C(1)–Ru–C(6)	167.5(4)	Ru–C(6)–C(7)	72.3(4)	C(1)–C(2)–C(3)	89.8(9)	F(4)–Sb–F(5)	89.2(5)
C(3)–Ru–C(6)	111.3(4)	Ru–C(7)–C(6)	70.0(4)	C(3)–C(2)–C(26)	136.0(9)	F(2)–Sb–F(6)	86.6(5)
C(5)–Ru–C(6)	36.4(5)	C(1)–C(16)–C(15)	118.1(5)	Ru–C(3)–C(4)	68.1(6)	F(4)–Sb–F(6)	87.0(6)
C(2)–Ru–C(7)	129.2(5)	C(1)–Ru–C(3)	57.1(4)	C(2)–C(3)–C(36)	133.1(10)	C(3)–C(36)–C(31)	120.2(5)
C(4)–Ru–C(7)	93.2(5)	C(1)–Ru–C(4)	39.5(4)	Ru–C(4)–C(1)	71.8(7)	C(4)–C(46)–C(41)	122.7(5)
C(6)–Ru–C(7)	37.7(5)	C(3)–Ru–C(4)	39.4(4)	C(1)–C(4)–C(3)	91.4(9)	Ru–P–O(1)	113.2(5)
C(2)–Ru–P	134.9(3)	C(2)–Ru–C(5)	99.1(4)	C(3)–C(4)–C(46)	130.6(10)	O(1)–P–O(2)	95.7(9)
C(4)–Ru–P	97.6(3)	C(4)–Ru–C(5)	126.6(4)	Ru–C(6)–C(5)	74.3(4)	O(1)–P–O(3)	105.3(8)
C(6)–Ru–P	91.3(4)	C(2)–Ru–C(6)	133.8(4)	C(5)–C(6)–C(7)	114.1(13)	P–O(1)–C(51)	126.9(12)
C(1)–Ru–N	98.7(4)	C(4)–Ru–C(6)	129.0(4)	C(1)–C(16)–C(11)	121.9(5)	P–O(3)–C(53)	137.5(16)
C(3)–Ru–N	126.3(4)	C(1)–Ru–C(7)	132.4(5)	C(2)–C(26)–C(21)	118.5(5)	N(1)–C(8)–C(9)	177.5(17)
C(5)–Ru–N	80.5(5)	C(3)–Ru–C(7)	91.4(5)	C(2)–C(26)–C(25)	121.4(5)	F(1)–Sb–F(2)	90.5(5)
C(7)–Ru–N	128.8(5)	C(5)–Ru–C(7)	63.8(3)	C(3)–C(36)–C(35)	119.8(5)	F(2)–Sb–F(3)	95.0(6)
Ru–C(1)–C(2)	68.7(6)	C(1)–Ru–P	95.3(3)	C(4)–C(46)–C(45)	116.8(5)	F(2)–Sb–F(4)	90.9(6)
C(2)–C(1)–C(4)	88.1(9)	C(3)–Ru–P	136.6(3)	Ru–P–O(2)	120.3(7)	F(1)–Sb–F(5)	89.2(5)
C(4)–C(1)–C(16)	137.5(10)	C(5)–Ru–P	124.6(4)	Ru–P–O(3)	112.5(6)	F(3)–Sb–F(5)	89.9(6)
Ru–C(2)–C(3)	72.1(7)	C(7)–Ru–P	84.7(4)	O(2)–P–O(3)	107.8(8)	F(1)–Sb–F(6)	90.6(5)
C(1)–C(2)–C(26)	131.0(9)	C(2)–Ru–N	90.0(4)	P–O(2)–C(52)	140.7(17)	F(3)–Sb–F(6)	177.3(6)
Ru–C(3)–C(2)	69.0(7)	C(4)–Ru–N	138.1(4)	Ru–N–C(8)	171.8(11)	F(5)–Sb–F(6)	88.5(5)

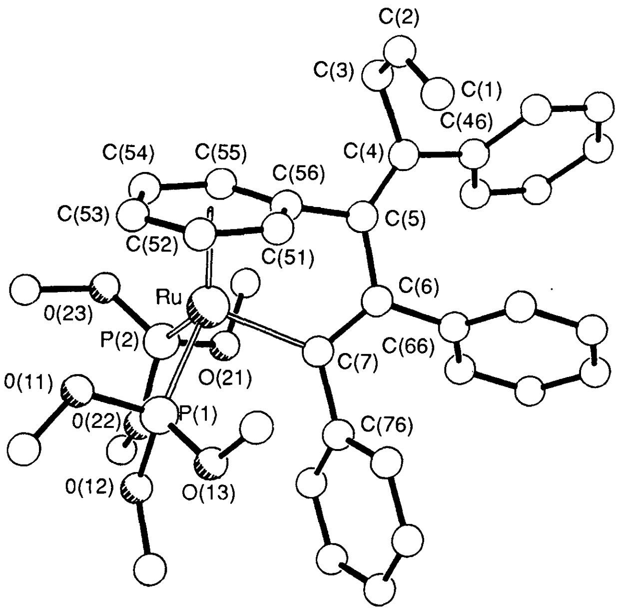


Figure 3. Molecular structure of compound (9)

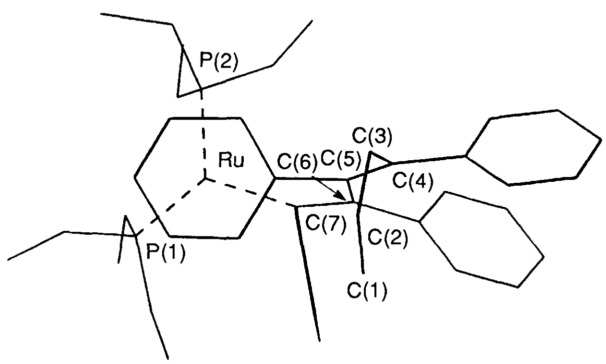
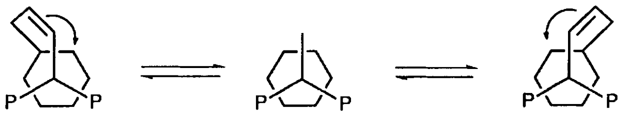


Figure 4. Projection of compound (9) down the metal–arene axis



Scheme 5.

hybridised carbon centre, the other two angles, C(56)–C(5)–C(6) 108.7(4)° and C(4)–C(5)–C(6) 131.9(5)°, are greatly contracted and expanded respectively, from an ideal geometry. This deformation is required, in order to keep C(7) within bonding distance of the metal. As it is, the Ru–C(7) bond length of 2.129(6) Å is longer than Ru–C distances found in other complexes containing an alkenyl chain, and is approximately midway between typical[2,13] bond lengths of σ- and π-bonded carbons. However for C(7) to approach the metal any closer would entail even larger distortion of the geometries around C(5), C(6), and C(7).

The co-ordinated arene ring shows significant asymmetry in the distances to the ruthenium, the Ru atom being displaced towards C(56) in the C(5)–C(56) direction. As might be expected, considering the geometry of the bridging alkenyl chain, C(56) lies closest to the ruthenium [2.189(5) Å] and C(53) furthest away [2.325(6) Å]. This asymmetry is reflected in the bond lengths within the ring, with C(54)–C(55), C(55)–C(56), and C(56)–C(51) being somewhat longer than the other internal bonds (see Table 5).

Figure 4 shows a projection of compound (9) viewed along the metal–arene axis. From this view it is apparent that, in the solid state, the phosphite ligands are inequivalent. However, in solution, the n.m.r. spectra (see Experimental section) indicate that they are equivalent. This equivalencing can be understood in terms of a simple 60° oscillation of the arene ring as illustrated in Scheme 5. Low-temperature $^{31}P-\{^{1}H\}$ n.m.r. spectroscopy at −85 °C failed to effect any change to the spectrum indicating a low activation barrier for this process.

Before discussing the formation of compound (9) it is useful to note that treatment of $[Ru(NCMe)(\eta^4-C_4Ph_4)(\eta-C_5H_5)][BF_4]$ with $K[BHBu^s_3]$ leads to ring opening of the C_4 ring and formation of the η^4(5e) butadienyl complex $[Ru{=}C(Ph)\text{-}\{\eta^3\text{-}C(Ph)C(Ph)CHPh\}(\eta-C_5H_5)]$. It was suggested[2] that this reaction involved a conrotatory ring opening of an intermediate

Table 4. Atom co-ordinates (× 10^4) for compound (**9**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	4 332(4)	3 728(6)	4 413(4)	B	2 853(1)	4 962(1)	2 381(1)
C(2)	4 884(4)	3 042(5)	4 753(3)	F(1)	2 691(1)	5 914(1)	2 743(2)
C(3)	4 880(3)	1 696(5)	4 773(3)	F(2)	2 693(2)	3 958(1)	2 699(1)
C(4)	4 130(3)	1 114(4)	4 359(3)	F(3)	2 413(1)	4 999(2)	1 704(1)
C(41)	3 458(2)	1 497(2)	5 324(2)	F(4)	3 618(1)	4 974(1)	2 379(1)
C(42)	2 986(2)	1 138(2)	5 762(2)	F(1′)	2 347(1)	1 045(2)	2 220(2)
C(43)	2 660(2)	10(2)	5 688(2)	F(2′)	2 789(2)	5 651(2)	1 798(1)
C(44)	2 806(2)	−761(2)	5 176(2)	F(3′)	2 590(1)	4 540(2)	2 594(1)
C(45)	3 278(2)	−402(2)	4 738(2)	F(4′)	2 686(2)	5 613(1)	2 909(1)
C(46)	3 604(2)	727(2)	4 812(2)	P(1)	4 123(1)	1 056(1)	1 047(1)
C(5)	4 007(3)	1 008(4)	3 656(3)	P(2)	4 597(1)	−1 261(2)	2 058(1)
C(51)	4 550(3)	2 373(5)	2 869(3)	O(11)	4 877(3)	1 478(7)	815(3)
C(52)	5 058(4)	2 537(5)	2 433(3)	O(11′)	4 774(5)	875(7)	623(4)
C(53)	5 665(3)	1 750(6)	2 431(3)	O(12)	3 766(5)	36(6)	503(3)
C(54)	5 787(3)	797(5)	2 889(3)	O(12′)	3 332(5)	470(11)	630(4)
C(55)	5 274(3)	589(5)	3 338(3)	O(13)	3 448(4)	1 976(7)	749(4)
C(56)	4 637(3)	1 339(4)	3 309(2)	O(13′)	3 974(6)	2 412(5)	830(5)
C(6)	3 305(3)	625(4)	3 092(3)	O(21)	4 080(4)	−2 028(7)	2 465(3)
C(61)	2 221(2)	1 452(2)	3 567(2)	O(21′)	4 886(4)	−2 080(8)	2 734(4)
C(62)	1 511(2)	1 326(2)	3 747(2)	O(22)	4 166(4)	−1 812(4)	1 326(3)
C(63)	1 112(2)	254(2)	3 627(2)	O(22′)	3 941(4)	−1 977(8)	1 524(7)
C(64)	1 422(2)	−692(2)	3 328(2)	O(23)	5 423(3)	−1 844(7)	2 344(4)
C(65)	2 132(2)	−566(2)	3 149(2)	O(23′)	5 223(3)	−1 434(12)	1 600(4)
C(66)	2 531(2)	506(2)	3 268(2)	C(11)	4 855(6)	1 717(7)	80(3)
C(7)	3 384(3)	464(4)	2 414(4)	C(12)	3 125(6)	238(13)	−126(4)
C(71)	2 155(2)	1 266(3)	1 661(2)	C(13)	3 401(6)	3 142(7)	1 043(5)
C(72)	1 469(2)	1 163(3)	1 128(2)	C(21)	4 373(5)	−2 405(9)	3 186(3)
C(73)	1 282(2)	93(3)	769(2)	C(22)	4 096(6)	−3 085(4)	1 208(6)
C(74)	1 781(2)	−873(3)	944(2)	C(23)	6 005(3)	−1 788(11)	1 930(4)
C(75)	2 467(2)	−770(3)	1 477(2)	Ru	4 507(1)	691(1)	2 226(1)
C(76)	2 654(2)	299(3)	1 835(2)				

Table 5. Bond lengths (Å) for compound (**9**)

C(1)–C(2)	1.296(9)	C(2)–C(3)	1.523(8)
C(3)–C(4)	1.525(7)	C(4)–C(46)	1.499(6)
C(4)–C(5)	1.337(7)	C(5)–C(56)	1.491(8)
C(5)–C(6)	1.506(6)	C(51)–C(52)	1.395(9)
C(51)–C(56)	1.434(7)	C(51)–Ru	2.269(5)
C(52)–C(53)	1.397(9)	C(52)–Ru	2.298(6)
C(53)–C(54)	1.383(9)	C(53)–Ru	2.325(6)
C(54)–C(55)	1.427(9)	C(54)–Ru	2.319(5)
C(55)–C(56)	1.404(7)	C(55)–Ru	2.255(5)
C(56)–Ru	2.189(5)	C(6)–C(66)	1.501(6)
C(6)–C(7)	1.373(7)	C(7)–C(76)	1.502(6)
C(7)–Ru	2.129(6)	P(1)–O(11)	1.587(7)
P(1)–O(11′)	1.590(10)	P(1)–O(12)	1.587(6)
P(1)–O(12′)	1.581(9)	P(1)–O(13)	1.585(8)
P(1)–O(13′)	1.596(6)	P(1)–Ru	2.265(1)
P(2)–O(21)	1.607(7)	P(2)–O(21′)	1.587(8)
P(2)–O(22)	1.569(5)	P(2)–O(22′)	1.579(9)
P(2)–O(23)	1.577(6)	P(2)–O(23′)	1.597(8)
P(2)–Ru	2.243(2)	O(11)–C(11)	1.447(9)
O(11′)–C(11)	1.456(12)	O(12)–C(12)	1.467(10)
O(12′)–C(12)	1.450(11)	O(13)–C(13)	1.448(12)
O(13′)–C(13)	1.447(14)	O(21)–C(21)	1.437(8)
O(21′)–C(21)	1.461(13)	O(22)–C(22)	1.459(7)
O(22′)–C(22)	1.452(13)	O(23)–C(23)	1.459(11)
O(23′)–C(23)	1.435(9)		

η^3-cyclobutenyl to form first the 16-electron η^3(3e)-butadienyl species [Ru-C(Ph)=C(Ph)-{η^2-C(Ph)=CH(Ph)}(η-C_5H_5)], which then collapses to give the 18-electron η^4(5e) complex. It is, therefore, suggested that (**9**) is formed by the sequence of reactions illustrated in Scheme 6. Displacement of acetone from (**F**) by P(OMe)$_3$ would be expected to give the species (**G**). However, this cation most likely undergoes a reversible η^3 to η^1 transformation of the bonding mode of the allyl ligand thus accessing the 16-electron cation (**4**). Since it is known[14–17] that alkyl groups can readily migrate from molybdenum or manganese centres onto cyclopentadienyl or cyclohexa-1,3-diene ligands respectively, it is plausible that the σ-allyl fragment migrates from the ruthenium onto the η^4-tetraphenylcyclobutadiene ring to form the unsaturated cation (**I**), which could then undergo a facile conrotatory ring-opening reaction to form the η^3(3e)-butadienyl cation (**J**). By analogy with our earlier work[2] this species might then have been expected to achieve stability by undergoing a η^3(3e) to η^4(5e) transformation of the bonding mode of the butadienyl chain to form (**K**). However, because the transformation of (**K**) into (**J**) is reversible, greater stability is evidently achieved by conversion of (**J**) into (**L**) *via* rotation about a C–C bond thus allowing one of the benzene rings attached to the butadienyl chain to orientate itself such that η^6 bonding with the ruthenium centre can be achieved thus leading to the formation of the 18-electron cation (**9**).

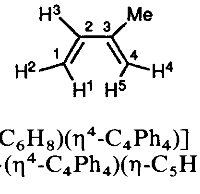
Experimental

The ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} n.m.r. spectra were recorded on JEOL FX 90Q, FX 200, Bruker WM-250 or WH-360 spectrometers as appropriate. Data are given for room-temperature measurements unless otherwise stated, 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$_3$PO$_4$ (85% external) for ^{31}P. Infrared spectra were recorded on a Perkin-Elmer 983G spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled and degassed solvents.

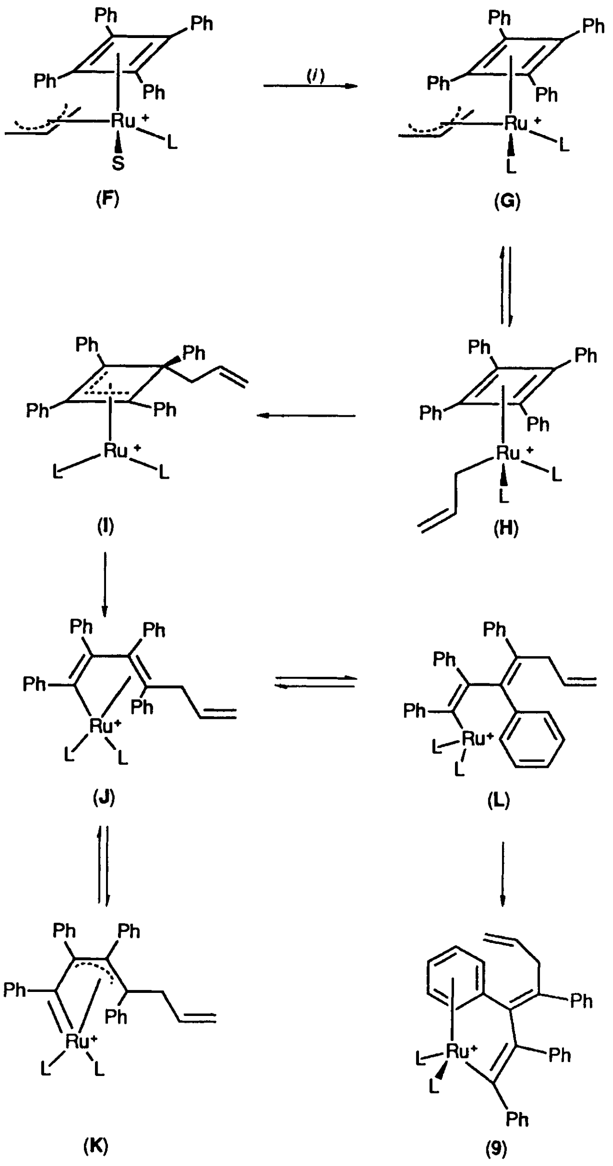
Table 6. Bond angles (°) for compound (**9**)

C(1)–C(2)–C(3)	127.1(5)	C(2)–C(3)–C(4)	115.3(4)
C(3)–C(4)–C(46)	113.9(4)	C(3)–C(4)–C(5)	118.6(5)
C(46)–C(4)–C(5)	125.7(4)	C(4)–C(46)–C(41)	119.3(2)
C(4)–C(46)–C(45)	120.6(2)	C(4)–C(5)–C(56)	119.4(4)
C(4)–C(5)–C(6)	131.9(5)	C(56)–C(5)–C(6)	108.7(4)
C(52)–C(51)–C(56)	118.7(5)	C(51)–C(52)–C(53)	122.1(5)
C(52)–C(53)–C(54)	119.5(6)	C(53)–C(54)–C(55)	120.1(5)
C(54)–C(55)–C(56)	120.3(5)	C(5)–C(56)–C(51)	119.5(5)
C(5)–C(56)–C(55)	121.1(5)	C(51)–C(56)–C(55)	119.0(5)
C(5)–C(6)–C(66)	119.8(4)	C(5)–C(6)–C(7)	118.4(5)
C(66)–C(6)–C(7)	121.6(4)	C(6)–C(66)–C(61)	120.3(2)
C(6)–C(66)–C(65)	119.7(2)	C(6)–C(7)–C(76)	117.5(5)
C(6)–C(7)–Ru	118.1(3)	C(76)–C(7)–Ru	123.8(3)
C(7)–C(76)–C(71)	117.5(2)	C(7)–C(76)–C(75)	122.5(2)
O(11)–P(1)–O(12)	104.8(4)	O(11′)–P(1)–O(12′)	110.3(5)
O(11)–P(1)–O(13)	108.2(4)	O(12)–P(1)–O(13)	95.3(4)
O(11′)–P(1)–O(13′)	94.6(5)	O(12′)–P(1)–O(13′)	101.5(5)
O(11)–P(1)–Ru	106.2(2)	O(11′)–P(1)–Ru	115.2(3)
O(12)–P(1)–Ru	120.9(2)	O(12′)–P(1)–Ru	116.7(3)
O(13)–P(1)–Ru	120.1(3)	O(13′)–P(1)–Ru	115.6(3)
O(21)–P(2)–O(22)	91.3(3)	O(21′)–P(2)–O(22′)	106.3(5)
O(21)–P(2)–O(23)	101.2(4)	O(22)–P(2)–O(23)	110.8(4)
O(21′)–P(2)–O(23′)	105.4(5)	O(22′)–P(2)–O(23′)	94.1(5)
O(21)–P(2)–Ru	112.9(3)	O(21′)–P(2)–Ru	118.2(3)
O(22)–P(2)–Ru	119.2(2)	O(22′)–P(2)–Ru	122.2(3)
O(23)–P(2)–Ru	117.0(3)	O(23′)–P(2)–Ru	106.6(5)
P(1)–O(11)–C(11)	121.2(5)	P(1)–O(11′)–C(11)	120.5(7)
P(1)–O(12)–C(12)	122.8(7)	P(1)–O(12′)–C(12)	124.5(8)
P(1)–O(13)–C(13)	124.4(6)	P(1)–O(13′)–C(13)	123.7(8)
P(2)–O(21)–C(21)	122.0(6)	P(2)–O(21′)–C(21)	121.7(7)
P(2)–O(22)–C(22)	122.6(5)	P(2)–O(22′)–C(22)	122.3(7)
P(2)–O(23)–C(23)	120.6(6)	P(2)–O(23′)–C(23)	120.9(6)
C(7)–Ru–P(1)	97.8(1)	C(7)–Ru–P(2)	90.6(1)
P(1)–Ru–P(2)	92.6(1)		

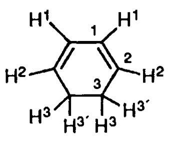
Preparations.—[Ru{P(OMe)$_3$}{η^4-CH$_2$C(Me)CHCH$_2$}(η^4-C$_4$Ph$_4$)] (**1**). To a mixture of [Ru{P(OMe)$_3$}(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)][BF$_4$]^2 (0.20 g, 0.27 mmol) and isoprene (0.5 cm^3, 5 mmol) in tetrahydrofuran (15 cm^3) was added (−78 °C) K[BHBu^s$_3$] (0.27 mmol). After stirring for 30 min at this temperature the mixture was allowed to warm to room temperature, when the volatiles were removed *in vacuo*. The residue was extracted into dichloromethane (2 cm^3) and chromatographed on alumina. Elution with hexane–diethyl ether (1:4) afforded a yellow band which was collected and recrystallised (−78 °C) from hexane to give yellow *crystals* of compound (**1**) (0.12 g, 65%) (Found: C, 66.1; H, 5.6. $C_{36}H_{27}O_3PRu$ requires C, 66.6; H, 5.7%). N.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 7.3—7.1 (m, 20 H, Ph), 3.61 (m, 1 H, H^3), 3.31 [d, 9 H, POCH$_3$, *J*(PH) 11.2], 2.69 [ddd, 1 H, H^2, *J*(H^{2}H^1) 1.71, *J*(H^{2}H^5) 7.81, *J*(HP) 1.71], 2.51 [dd, 1 H, H^4, *J*(H^{4}H^2) 1.7, *J*(HP) 1.7], 1.45 [d, 3 H, Me, *J*(HP) 1.7], 0.56 [ddd, 1 H, H^1, *J*(H^{1}H^2) 1.7, *J*(H^{1}H^3) 9.03, *J*(HP) 15.3], and 0.42 [dd, 1 H, H^5, *J*(H^{5}H^4) 1.71, *J*(HP) 14.7]; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 137.4 (Ph), 129.9 (Ph), 127.7 (Ph), 125.9 (Ph), 98.8 (C^3), 90.37 (C^2), 75.72 (*C*$_4$Ph$_4$), 52.53 [d, POCH$_3$, *J*(CP) 4.6], 39.5 [d, C^4, *J*(CP) 9.19], 37.9 [d, C^1, *J*(CP) 7.66], and 20.3 (Me); ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 172.9 p.p.m. (POMe). Mass spectrum: *m*/*z* 650, [M$^+$]; 582 [*M*$^+$ − C$_5$H$_8$]; and 526, [M$^+$ − P(OMe)$_3$].



[Ru{P(OMe)$_3$}(η^4-C$_6$H$_8$)(η^4-C$_4$Ph$_4$)] (**2**). Similarly, reaction of [Ru{P(OMe)$_3$}(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)][BF$_4$] (0.20 g, 0.27 mmol), cyclohexa-1,3-diene (0.22 g, 2.7 mmol), and K[BHBu^s$_3$] (0.27 mmol) in tetrahydrofuran (15 cm^3) followed by chromatographic work-up gave on recrystallisation (−78 °C) from hexane yellow *crystals* of compound (**2**) (0.15 g, 84%) (Found: C, 67.3; H, 5.7. $C_{37}H_{37}O_3PRu$ requires C, 67.2; H, 5.6%). N.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 7.2—7.0 (m, 20 H, Ph), 3.9 (m, 2 H, H^1), 3.7 (m, 2 H, H^2), 3.27 [d, 9 H, POCH$_3$, *J*(HP) 11.7], 1.64 (m, 2 H, H^3), and 1.39 (m, 2 H, H^3); ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 137.59 (Ph), 129.6 (Ph), 127.52 (Ph), 125.63 (Ph), 88.9 (*C*$_4$Ph$_4$), 75.8 (C^1), 57.7 [d, C^2, *J*(CP) 4.1], 50.8 [d, POCH$_3$, *J*(CP) 2.7], and 23.7 [d, C^3, *J*(CP) 9.6]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 170.0 p.p.m. (POCH$_3$). Mass spectrum: *m*/*z* 582, [*M*$^+$ − P(OMe)$_3$].

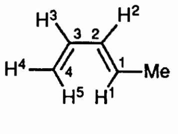


Scheme 6. L = P(OMe)$_3$, solv = acetone. (*i*) + P(OMe)$_3$, −acetone

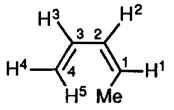


Ru{P(OMe)$_3$}{η^4-*trans*-CH(Me)CHCHCH$_2$}(η^4-C$_4$Ph$_4$)] (**3**). In the same way reaction (−78 °C) of [Ru{P(OMe)$_3$}(η^4-

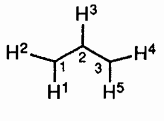
$C_4Ph_4)(\eta$-$C_5H_5)][BF_4]$ (0.20 g, 0.27 mmol), *trans*-penta-1,3-diene (0.4 cm^3, 4 mmol), and K[BHBu$^s{}_3$] (0.27 mmol) in tetrahydrofuran (10 cm^3) gave yellow *crystals* (from hexane, −78 °C) of compound (**3**) (0.08 g, 46%) (Found: C, 67.0; H, 5.6. $C_{36}H_{37}O_3PRu$ requires C, 66.6; H, 5.7%). N.m.r.; ^1H ($C_6D_5CD_3$), δ 7.2—6.9 (m, 20 H, Ph), 4.45 (m, 1 H, H^3), 3.65 (m, 1 H, H^2), 3.13 [d, 9 H, $POCH_3$, *J*(HP) 11.1], 2.65 [d, 1 H, H^4, *J* (H^4H^3) 7.24], 1.95 (m, 1 H, H^1), 1.60 [dd, 3 H, Me, *J*(HP) 1.76, *J*(MeH^1), 6.05], and 0.71 [dd, 1 H, H^5, *J*(H^5H^3) 9.45, *J*(HP) 14.5]; ^{13}C-{^1H} (C_6D_6), δ 138.0 (Ph), 129.0 (Ph), 128.01 (Ph), 125.91 (Ph), 100.96 (C^3), 81.62 (C^2), 74.40 (C_4Ph_4), 58.6 [d, C^1, *J*(CP) 4.8], 51.97 [d, POMe, *J*(CP) 5.49], 38.66 [d, C_4, *J*(CP) 9.8], and 20.15 (Me); ^{31}P-{^1H} (C_6D_6), δ 169.4 p.p.m. (POMe).



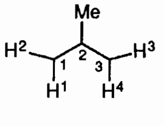
Formation of compound (**3**) *and* [Ru{P(OMe)$_3$}{η^4-*cis*-CH(Me)CHCHCH$_2$}(η^4-C_4Ph_4)] (**4**). A similar reaction using *cis*-penta-1,3-diene (0.4 cm^3, 4 mmol) afforded a yellow crystalline mixture of compounds (**3**) and (**4**) (0.07 g, 40%) (Found: C, 66.5; H, 5.8. $C_{36}H_{37}O_3PRu$ requires C, 66.6; H, 5.7%). N.m.r.: ^1H ($C_6D_5CD_3$) for (**4**), δ 7.2—6.9 (m, 20 H, Ph), 4.5 (m, 1 H, H^3), 3.7—3.55 (m, 2 H, H^1 + H^2), 3.13 [d, 9 H, $POCH_3$, *J*(HP) 11.1], 3.05 (m, 1 H, H^4), 1.95 [dd, 1 H, H^5, *J*(H^5H^3) 12.0, *J*(HP) 12.0], and 1.08 [dd, 3 H, Me, *J*(MeH^1) 6.96, *J*(HP) 2.55]; ^{13}C-{^1H} (C_6D_6) [for (**4**)], δ 137.7 (Ph), 129.0—125.0 (Ph), 101.0 (C^3), 81.6 (C^2), 74.4 (C_4Ph_4), 58.6 [d, C^1, *J*(CP) 4.6], 51.97 [d, POMe, *J*(CP) 4.6], 38.6 [d, C^4, *J*(CP) 10.7], and 20.2 (Me); ^{31}P-{^1H} (C_6D_6), δ 170.9 p.p.m. (POMe). Mass spectrum: *m/z* 650, [M^+]; 582, [$M^+ - C_5H_8$); and 525, (M^+ − P(OMe)$_3$].



[RuBr{P(OMe)$_3$}(η^3-C_3H_5)(η^4-C_4Ph_4)] (**5**). The salt K-[BHBu$^s{}_3$] (0.76 mmol) was added to a stirred (−78 °C) solution of [Ru{P(OMe)$_3$}(η^4-C_4Ph_4)(η-C_5H_5)][BF$_4$] (0.56 g, 0.76 mmol) in tetrahydrofuran (40 cm^3). After stirring at −78 °C for 30 min the mixture was allowed to warm to room temperature, and then recooled to −78 °C. Allyl bromide (0.66 cm^3, 7.6 mmol) was added, the mixture warmed to room temperature, and then stirred for 1 h. Volatiles were removed, the residue extracted into CH_2Cl_2 (3 cm^3), and chromatographed. Elution with diethyl ether–hexane (4:1) afforded a single yellow band. The volume was reduced to 3 cm^3, and the resultant precipitate washed with hexane (2 cm^3) and dried *in vacuo* to give yellow *crystals* of compound (**5**) (0.38 g, 70%) (Found: C, 57.5; H, 5.1. $C_{34}H_{34}BrO_3PRu$ requires C, 58.1; H, 4.9%). N.m.r.: ^1H (C_6D_6), δ 7.55 (m, 8 H, *o*-Ph), 6.98 (m, 12 H, m, *p*-Ph), 5.51 (m, 1 H, H^3), 4.51 (m, 1 H, H^2), 3.99 (m, 1 H, H^4), 3.07 [d, 9 H, POMe, *J*(HP) 10.1], 2.32 (m, 1 H, H^1), and 1.15 (m, 1 H, H^5); ^{13}C-{^1H} (C_6D_6), δ 134.0 (Ph), 130.7 (Ph), 128.1 (Ph), 127.4 (Ph), 88.3 [d, C^2, *J* 3.3], 81.9 (C_4Ph_4), 65.0 (d, C^1, *J* 11.6), 53.4 (d, POMe, *J* 8.3), and 48.8 (d, C^3, *J* 6.6); ^{31}P-{^1H} (C_6D_6), δ 129.3 p.p.m. (POMe).



[RuCl{P(OMe)$_3$}(η^3-CH_2CMeCH_2)(η^4-C_4Ph_4)] (**6**). Similarly prepared to compound (**5**), but using 2-methylallyl chloride and allowing the reaction mixture to stir at room temperature for 20 h, was yellow *crystalline* (**6**) (0.07 g, 39%) (Found: C, 62.6; H, 5.4. $C_{35}H_{36}ClO_3PRu$ requires C, 62.5; H, 5.3%). N.m.r.: ^1H (C_6D_6), δ 7.6—7.5 (m, 8 H, *o*-Ph), 7.1—6.9 (m, 12 H, m, *p*-Ph), 4.18 (m, 1 H, H^2), 3.89 [dd, 1 H, H^1, *J*(H^1H^2) 3.17, *J*(HP) 10.0], 2.98 [d, 9 H, POMe, *J*(HP) 10.0], 2.64 (s, 3 H, Me), 2.38 [d, 1 H, H^3, *J*(HP) 7.08], and 1.27 (s, 1 H, H^4); ^{13}C-{^1H} (C_6D_6), δ 132—124 (Ph), 103.7 [d, C^2, *J*(CP) 3.06], 80.7 (C_4Ph_4), 67.3 [d, C^1, *J*(CP) 13.8], 52.0 [d, POMe, *J*(CP) 9.19], 47.9 [d, C^3, *J*(CP) 6.12], and 19.4 [d, Me, *J*(CP) 3.06]; ^{31}P-{^1H} (C_6D_6), δ 161.0 p.p.m. (POMe).



[Ru(NCMe){P(OMe)$_3$}(η^3-C_3H_5)(η^4-C_4Ph_4)][BF$_4$] (**7**). To compound (**5**) (0.10 g, 0.14 mmol) in CH_2Cl_2 (10 cm^3) was added MeCN (1 cm^3), followed by $AgBF_4$ (0.028 g, 0.14 mmol). After stirring at room temperature for 30 min the precipitated silver bromide was removed by filtration through a Celite plug. Reduction in the volume to 4 cm^3 and addition of diethyl ether (20 cm^3) afforded a pale yellow precipitate which was washed with diethyl ether and dried to give yellow *microcrystals* of compound (**7**) (0.10 g, 94%) (Found: C, 60.2; H, 5.3. $C_{36}H_{37}BF_4NO_3PRu$ requires C, 60.1; H, 5.1%). N.m.r.: ^1H (CD_2Cl_2), δ 7.4—7.0 (m, 20 H, Ph), 5.5 (m, 1 H, H^3), 3.9 (m, 2 H, H^2 + H^4), 3.35 [d, 9 H, POMe, *J*(HP) 10.7], 2.23 [d, 3 H, MeCN, *J*(HP) 1.96], 2.06 [dd, 1 H, H^1, *J*(H^1H^3) 10.5, *J*(HP) 5.86], and 1.03 [d, 1 H, H^5, *J*(H^5H^3) 9.52]; ^{13}C-{^1H} [$(CD_3)_2CO$], δ 131.87 (Ph), 130.04 (Ph), 129.92 (Ph), 128.6 (Ph), 89.9 [d, C^2, *J*(CP) 2.76], 95.0 [d, C_4Ph_4, *J*(CP) 2.75], 64.7 [d, C^1, *J*(CP) 9.63], 53.8 [d, POMe, *J*(CP) 11.0], 52.4 [d, C^3, *J*(CP) 6.88], and 3.28 ($NCCH_3$); ^{31}P-{^1H} (CD_2Cl_2), δ 129.4 p.p.m. (POMe).

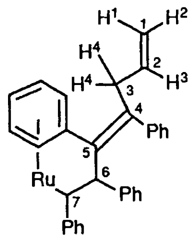
[Ru(NCMe){P(OMe)$_3$}(η^3-CH_2CMeCH_2)(η^4-C_4Ph_4)]-[BF$_4$] (**8**). Similarly, reaction of compound (**6**) (0.08 g, 0.12 mmol) afforded off-white *crystals* of (**8**) (0.08 g, 85%). N.m.r.: ^1H (CD_2Cl_2), δ 7.4—7.1 (m, 20 H, Ph), 4.06 [dd, 1 H, H^2, *J*(H^1H^2) 3.18, *J*(HP) 10.3], 3.80 [dd, 1 H, H^1, *J*(H^1H^2) 3.18, *J*(HP) 3.18], 3.30 [d, 9 H, POMe, *J*(HP) 10.5], 2.38 (s, 3 H, MeCN), 2.33 [d, 3 H, Me, *J*(HP) 2.2], 2.01 [d, 1 H, H^3, *J*(HP) 6.59], and 1.14 (s, 1 H, H^4); ^{13}C-{^1H} (CD_2Cl_2), δ 131.7—128.0 (m, Ph), 108.4 [d, C^2, *J*(CP) 2.75], 84.9 (C_4Ph_4), 66.0 [d, C^1 + C^3, *J*(CP) 12.4], 54.3 [d, POMe, *J*(CP) 11.0], 21.1 [d, Me, *J*(CP) 2.75], and 4.21 ($NCCH_3$); ^{31}P-{^1H} (CD_2Cl_2), δ 128.6 p.p.m. (POMe).

[Ru{C(Ph)=C(Ph)C(η^6-C_6H_5)=C(Ph)CH$_2$CH=CH$_2$}{P-(OMe)$_3$}$_2$][BF$_4$] (**9**). To a solution of compound (**5**) (0.10 g, 0.14 mmol) in acetone (10 cm^3) was added $AgBF_4$ (0.028 g, 0.14 mmol). After stirring for 30 min the precipitated silver bromide was removed by filtration through Celite, and trimethyl phosphite (25 μl, 0.21 mmol) added. After stirring for 1 h the volatiles were removed *in vacuo*, the residue was washed with diethyl ether (2 × 10 cm^3), and redissolved in acetone (2 cm^3). Slow addition of diethyl ether (20 cm^3) afforded pale yellow *crystals* of compound (**9**) (0.09 g, 71%). N.m.r.: ^1H [$(CD_3)_2CO$], δ 7.46—6.25 (m, 20 H, Ph), 5.80 [ddt, 1 H, H^3, *J*(H^1H^3) 17.2, *J*(H^3H^2) 10.0, *J*(H^3H^4) 6.2], 5.09 [ddt, 1 H, H^1, *J*(H^1H^3) 17.2, *J*(H^1H^2) 1.6, *J*(H^1H^4) 1.6], 4.99 [ddt, 1 H, H^2, *J*(H^2H^3) 10.0, *J*(H^2H^1) 1.6, *J*(H^2H^4) 1.6], 3.70 [apparent triplet, 18 H, POMe, *J*(HP) 11.6], and 3.47 [dt, 2 H, H^4, *J*(H^4H^3) 6.2, *J*(H^4H^1) 1.6, *J*(H^4H^2) 1.6]; ^{13}C-{^1H}[$(CD_3)_2CO$], δ 136.6 (C^2), 131.9—124.4 (unco-ordinated Ph + C^4—C^7), 115.8 (C^1), 104.0

Table 7. Structure analysis of compounds (**7**) and (**9**)*

Crystal data		
Complex	(**7**)	(**9**)
Formula	$C_{36}H_{37}F_6NO_3PRuSb\cdot\frac{1}{2}CH_2Cl_2$	$C_{37}H_{43}BF_4O_6P_2Ru$
M	927.25	833.6
Crystal shape and colour	Yellow obloid	Yellow obloid
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$(no. 19)	$P2_1/a$(no. 14)
a/Å	10.867(2)	17.741(7)
b/Å	16.753(3)	11.313(3)
c/Å	22.264(6)	19.462(7)
β/°		104.33(3)
U/Å^3	4 053(2)	3 758(2)
T/K	295	295
Z	4	4
D_c/g cm^{-3}	1.53	1.47
F(000)	1 876	1 712
μ(Cu-K_α)/cm^{-1}	101	48
Data collection and reduction		
Range/°	$0 \leqslant 58$	$0 \leqslant 58$
Maximum, minimum transmission factors	0.325, 0.202	0.453, 0.214
No. unique data	3 083	5 101
No. observed data [$I > 1.5\sigma(I)$]	2 854	4 634
Refinement		
Anisotropic atoms	Ru, C, O, P, N, Sb, F, Cl	Ru, C, O, P, B, F
Isotropic atoms		F
No. least-squares variables	427	498
Final $R(R')$	0.0535 (0.0564)	0.0548 (0.0638)
g	0.0007	0.00 128
Largest final difference features /e Å^{-3}	+ 0.80, −0.50	+ 0.94, −0.90
Crystal faces (distances from origin /mm)	$1\bar{1}1$(0.117)	001(0.125)
	$11\bar{1}$(0.117)	$00\bar{1}$(0.125)
	011(0.0833)	$\bar{1}10$(0.10)
	$0\bar{1}\bar{1}$(0.0833)	$1\bar{1}0$(0.10)
	$0\bar{1}1$(0.0833)	$\bar{1}\bar{1}1$(0.258)
	$01\bar{1}$(0.0833)	113(0.121)
	$\bar{1}00$(0.117)	

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $w^{-1} = \Sigma\sigma_c^2(F_o) = |g|F^2$, $\sigma_c^2(F_o)$ = varience in F_o due to counting statistics, g chosen so as to minimise the variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$.



(Ph), 102.1 [t, Ph, J(CP) 5.6], 94.5 (Ph); 54.1 (POMe), and 41.8 (C^3); ^{31}P-{^1H} [$(CD_3)_2CO$], δ 133.4 p.p.m. (POMe).

Structure Analyses of [Ru(NCMe){P(OMe)$_3$}(η^3-C_3H_5)(η^4-C_4Ph_4)][SbF_6] (**7**) *and* [Ru{C(Ph)=C(Ph)C(η^6-C_6H_5)=C(Ph)-CH_2CH=CH_2}{P(OMe)$_3$}$_2$][BF_4] (**9**).—Crystals of compounds (**7**) and (**9**) were mounted on quartz fibres. Preliminary data on the quality of the crystals and their space groups were obtained by use of oscillation and Weissenberg photographs. Structure solution was by Patterson and difference Fourier methods, and refinement was by block-cascade full-matrix least squares. A numerical absorption correction was applied, in each case, to the data based on the indexed faces of the crystals, and their perpendicular distance from an origin. Calculations were carried on an Eclipse S140 computer using the SHELXTL program package,[18] and the complex neutral scattering factors from ref. 19. Table 7 lists important parameters used in data collection and refinement. In the refinement of the data for compound (**7**) all hydrogen atoms were given idealised geometries with C–H 0.96 Å and with fixed isotropic thermal parameters (equal to 1.2 those of their parent carbon atom), with the exception of those on C(9), whose positions could not be calculated. The phenyl groups were constrained to an idealised D_{6h} geometry. In compound (**9**) the BF_4 group was disordered and was refined as two idealised rigid bodies with occupancies of 0.75 and 0.25. The oxygen atoms of the trimethyl phosphite groups also showed a two-site disorder; these were refined with occupancy factors of 0.60 [O(n)] and 0.40 [O(n')], the P–O and O–C bond lengths being constrained to refined free variables. The hydrogen-atom positions of these ligands were not calculated; all other hydrogen atoms were given idealised geometries.

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

Acknowledgements

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References

1 Part 48, S. G. Bott, L. Brammer, N. G. Connelly, M. Green, N. C. Norman, A. G. Orpen, J. F. Paxton, and C. J. Schaverien, *J. Chem. Soc., Dalton Trans.*, 1990, 1957.

2 M. Crocker, M. Green, A. G. Orpen, H-P. Neumann, and C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, 1984, 1351; M. Crocker, M. Green, K. R. Nagle, A. G. Orpen, H-P. Neumann, C. E. Morton, and C. J. Schaverien, *Organometallics*, 1990, 1422.

3 J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1977, **99**, 4858.

4 M. Crocker, M. Green, C. E. Morton, K. R. Nagle, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1985, 2145.

5 J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Am Chem., Soc.*, 1975, **97**, 3871 and refs. therein.

6 M. Green and R. P. Hughes, *J. Chem. Soc., Dalton Trans.*, 1976, 1907.

7 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.

8 D. B. Jacobson and B. S. Freiser, *J. Am. Chem. Soc.*, 1985, **107**, 72.

9 D. G. Bourner, L. Brammer, M. Green, G. Moran, A. G. Orpen, C. Reeve, and C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, 1985, 1409.

10 B. J. Dunne, B.Sc. Thesis, University of Bristol, 1985.

11 M. Crocker, S. F. T. Froom, M. Green, K. R. Nagle, A. G. Orpen, and D. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1987, 2803.

12 B. E. Mann and B. F. Taylor, '^{13}C NMR Data for Organometallic Compounds,' Academic Press, London, 1981.

13 L. Brammer, M. Crocker, B. J. Dunne, M. Green, C. E. Morton, K. R. Nagle, annd A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 1226.

14 F. W. S. Berfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324.

15 M. Brookhart, W. Lamanna, and A. R. Pinhas, *Organometallics*, 1983, **2**, 638.

16 M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117.

17 P. K. Rush, S. K. Noh, and M. Brookhart, *Organometallics*, 1986, **15**, 1745.

18 G. M. Sheldrick, SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, University of Göttingen, 1983, revision 4.1.

19 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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