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Preparation and reactions of some neutral pentamethylcyclopentadienylruthenium vinylidene complexes

Michael I. Bruce,*,†,[a] Ben C. Hall,[a] Natasha N. Zaitseva,[a] Brian W. Skelton[b] and Allan H. White[b]

[a] *Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia*

A synthesis of neutral vinylideneruthenium complexes [RuCl(C=CHR)(PPh_3)(η-C_5Me_5)] (R = Ph, Bu^t or $SiMe_3$) from [RuCl(PPh_3)$_2$(η-C_5Me_5)] and 1-alkynes has been developed. This takes advantage of the presence of two bulky ligands (PPh_3 and C_5Me_5), which results in displacement of one PPh_3 ligand (rather than chloride) and concomitant isomerisation of the 1-alkyne to vinylidene ligands. The vinylidene complexes undergo facile loss of HCl on treatment with NaOMe in the presence of a 2e donor ligand (L) to give the neutral acetylide complexes [Ru(C≡CR)L(PPh_3)(η-C_5Me_5)] [R = Ph, L = PPh_3, CO, O_2 or dppm-*P*; R = Bu^t, L = PPh_3, CO, C_2H_4, dppe-*P*, C_2(PPh_2)$_2$-*P*, S_2, $P(OMe)_3$ or $AsPh_3$]; the complexes [Ru(C≡CBu^t)(L_2)(η-C_5Me_5)] [L_2 = dppm or PPh_2CH=$CHPPh_2$] and [Ru(S_2CC≡CBu^t)(PPh_3)(η-C_5Me_5)] were also obtained. Crystal structure determinations were carried out on eleven of the complexes.

The chemistry of metal vinylidene complexes continues to attract much attention.[1,2] Many early studies of these complexes were made using d^6 and d^8 metal centres, of which the M(PR_3)$_2$(C_5H_5) (M = Fe, Ru or Os; PR_3 = tertiary phosphine or phosphite)[3,4] and MCl(PPr^i_3)$_2$ fragments predominate.[2] Such complexes can easily be obtained from 1-alkynes and the reactions are facilitated by the presence of the electron-rich metal centres. The kinetic stability of the complexes is enhanced by the presence of bulky ligands, such as PPh_3, which offer steric protection to C(1) of the vinylidene ligand. For the Group 8 complexes, co-ordination of the 1-alkyne is followed by isomerisation to the vinylidene, probably by a concerted 1,2-hydrogen shift and formation of the M–C bond.[5] Recently, solid experimental evidence for the latter process has been obtained for an alternative route involving oxidative addition of the 1-alkyne to the metal centre, followed by migration of the metal-bonded hydrogen to C(2).[6]

With the cyclopentadienylruthenium(II) system a variety of complexes containing vinylidene ligands has been obtained. However, until recently, most of these complexes were cationic, of the type [Ru(C=CHR)(PR'_3)$_2$(η-C_5H_5)]$^+$, which were obtained from the precursor chloro complex [RuCl(PR'_3)$_2$(η-C_5H_5)] by ready dissociation of the halide, especially in polar solvents, such as MeOH.[7] Displacement of one of the PR_3 ligands and formation of a neutral complex had not been observed prior to the commencement of this work, although recent publications have described related complexes, such as [RuCl(=C=CHPh){$PPr^i_2CH_2C(O)OMe$-*O*,*P*}(η-C_5Me_5)],[8] [RuCl(=C=$CHCO_2Me$)(PPh_3)(η-C_5H_5)] {obtained from [Ru(PPh_3)(η-C_3H_5)(η-C_5H_5)]},[9] and [RuCl(=C=CHPh)(PPh_3)-{HB($pz)_3$}], which catalysed the dimerisation of 1-alkynes to substituted butenynes.[10] Other neutral vinylideneruthenium(II) complexes are known: these include [$RuCl_2$(=C=CHPh){PPr^i_2-$CH_2C(O)OMe$-*O*,*P*}(*P*-$PPr^i_2CH_2CO_2Me$)][11] and [$RuCl_2$(=C=CHPh)($PPh_2C_2H_4NMe_2$-*N*,*P*)($PPh_2C_2H_4NMe_2$-*P*)],[12] [RuX_2-(=C=CHPh)($EPr^i_2C_2H_4OMe$-*O*,*P*)($PPr^i_2CH_2OMe$-*P*)] [E = P or As; X_2 = Cl_2, Br_2, BrCl or $(CN)_2$],[13,14] and [$RuCl_2$(=C=CHR)-(pnp)] [R = Ph or C_6H_4Me-*p*; pnp = $PrN(C_2H_4PPh_2)_2$].[15,16]

These studies, particularly those carried out with complexes containing hemi-labile ligands, showed that neutral vinylidene complexes could be formed by replacement of donor atoms more weakly attached to the ruthenium than chloride. Replacement of C_5H_5 by the bulky electron-releasing C_5Me_5 ligand has led to many novel discoveries in ruthenium chemistry and we considered that introduction of this ligand might induce dissociation of a bulky PR_3 ligand, such as PPh_3, even though conventional cationic vinylideneruthenium complexes had been obtained with the smaller phosphine PMe_2Ph.[17] This paper describes our studies in this area, and some subsequent reaction of the neutral vinylidene complexes that we have obtained. A preliminary account of some of this work has appeared.[18]

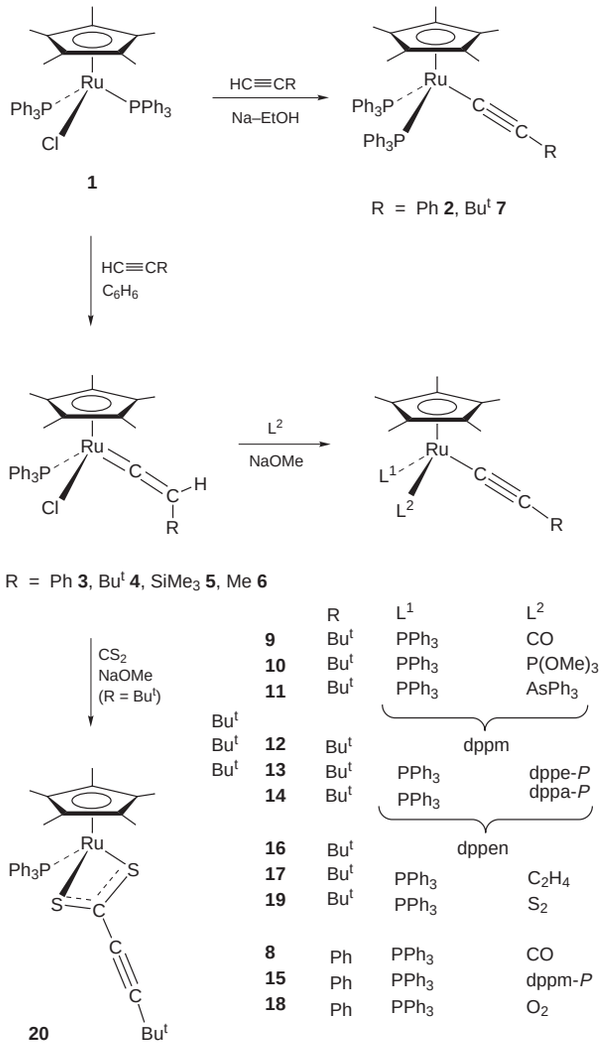
Results

The reaction between [RuCl(PPh_3)$_2$(η-C_5Me_5)] **1**[19,20] and phenylacetylene was carried out in refluxing ethanol in a manner similar to that described for [RuCl(PPh_3)$_2$(η-C_5H_5)] and related complexes.[21] After cooling, addition of metallic sodium to the brown solution resulted in formation of a yellow precipitate, which was characterised as the anticipated phenylethynyl complex [Ru(C≡CPh)(PPh_3)$_2$(η-C_5Me_5)] **2** (Scheme 1) by elemental analysis, IR and NMR spectroscopy (Table 1) and finally by a single-crystal structure determination (see below). The IR spectrum contained ν(C≡C) at 2066 cm^{-1} and the ^{1}H NMR spectrum contained resonances for the C_5Me_5 groups at δ 1.19 and a multiplet for the aromatic protons at δ 7.0–7.5. The ^{13}C NMR spectrum contained resonances for the C_5Me_5 carbons at δ 9.49 (Me) and 93.46 (ring C) and C(1) of the C≡CPh group at δ 122.56. The FAB mass spectrum contained M^+ at *m*/*z* 862, which fragmented by loss of Ph, C_2Ph and PPh_3 groups.

A similar reaction between complex **1** and HC≡CPh in refluxing benzene produced a red solution, from which a red crystalline complex **3** was separated by preparative thin-layer chromatography (TLC) in 67% yield. A small amount of **2** was also obtained. Complex **3** was identified as [RuCl(C=CHPh)(PPh_3)-(η-C_5Me_5)] by means of a crystal structure determination. In the IR spectrum ν(C=C) bands at 1590 and 1606 cm^{-1} were present. Characteristic NMR data included ^{1}H resonances at δ 1.48 (C_5Me_5) and 4.51 (=CH) and ^{13}C NMR signals at δ 9.53 and 112.99 (Me and ring C of C_5Me_5), C(2) at δ 102.34 and the characteristic low field doublet at δ 339.95 for the Ru–C= carbon. The FAB mass spectrum did not contain a molecular ion, but showed [M − Cl]$^+$ and [M − CCHPh]$^+$ at *m*/*z* 600 and 534, respectively.

Complex **3** is a novel and readily available example of a

† E-Mail: mbruce@chemistry.adelaide.edu.au



Scheme 1 dppa = $C_2(PPh_2)_2$, dppen = *cis*-$PPh_2CH{=}CHPPh_2$

neutral vinylidene complex containing a d^6 metal centre. It has important potential as an intermediate in further reactions. The Cl ligand can be replaced by anionic nucleophiles, while the C_5Me_5 and tertiary phosphine ligands render the metal centre extremely electron-rich. As will be shown below and in future accounts, the chemistry of **3** is significantly different from that of related cationic $[Ru(C{=}CHR)(PR'_3)_2(\eta\text{-}C_5H_5)]^+$ complexes which has been extensively developed.

Similar reactions with $HC{\equiv}CBu^t$ and $HC{\equiv}CSiMe_3$ gave the corresponding red or orange neutral vinylidene complexes $[RuCl(C{=}CHR)(PPh_3)(\eta\text{-}C_5Me_5)]$ (R = Bu^t **4** or $SiMe_3$ **5**), the former characterised by the low-field ^{13}C NMR resonance at δ 336.38, the latter by a crystal structure determination (see below). Other spectroscopic data were consistent with these structures and are detailed in the Experimental section. A yellow product was obtained from propyne, but only characterised spectroscopically as $[RuCl(C{=}CHMe)(PPh_3)(\eta\text{-}C_5Me_5)]$ **6**. If the reaction between **1** and $HC{\equiv}CBu^t$ was carried out in more polar solvents, such as ethanol, and the resulting cationic vinylidene was deprotonated with sodium, the anticipated yellow acetylide $[Ru(C{\equiv}CBu^t)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **7** was obtained instead. The IR spectrum of this complex contained a ν(C≡C) band at 2080 cm^{-1}.

The reactivities of these complexes have been probed briefly. As described elsewhere, reactions with phosphite ligands unusually result in displacement of the vinylidene and formation of $[RuCl\{P(OR)_3\}_2(\eta\text{-}C_5Me_5)]$.[22] These reactions contrast with those of the cationic C_5H_5 analogues, which are generally resistant to ligand exchange. We sought milder conditions to preserve the vinylidene or derived ligands and have found that treatment of complexes **3** or **4** with 2e donor ligands (L) in the presence of base (NaOMe) readily afforded the corresponding acetylides $[Ru(C{\equiv}CR)L(PPh_3)(\eta\text{-}C_5Me_5)]$ [R = Ph, L = PPh_3, CO, O_2 or dppm-*P*; R = Bu^t, L = PPh_3, CO, C_2H_4, dppe-*P*, dppa-*P*, S_2, $P(OMe)_3$ or $AsPh_3$] (Scheme 1). Thus, a solution containing **4** and an excess of PPh_3 in methanol was treated with NaOMe, whereupon it changed from red to yellow and rapidly afforded a yellow precipitate of **7**, identified by comparison with the product described above.

The neutral vinylidene complexes were converted into the carbonyl complexes $[Ru(C{\equiv}CR)(CO)(PPh_3)(\eta\text{-}C_5Me_5)]$ (R = Ph **8** or Bu^t **9**) when NaOMe was added to solutions of **3** or **4** whilst passing CO through them. Complex **9** was also obtained by adding $AgPF_6$ to a solution of **4** in acetonitrile which had been saturated with CO. A white precipitate (AgCl) formed. We could not isolate any intermediate such as $[Ru(C{=}CHR)(NCMe)(PPh_3)(\eta\text{-}C_5Me_5)]^+$, but, after filtration, deprotonation with NaOMe afforded yellow **9**. The new complexes are characterised by ν(CO) bands at 1915 and 1928 cm^{-1}, respectively, and ν(C≡C) absorptions at 2095 and 2100 cm^{-1}, respectively. Other typical spectral properties include the C_5Me_5 and Bu^t (if present) resonances in the ^1H and ^{13}C NMR spectra and parent ions which fragment by loss of CO, PPh_3 and C_2R groups. The ^{13}C NMR spectra also contain doublets for the CO groups at δ 206.4 and 207.2, respectively.

The two complexes described above are chiral, although we have not tried to separate the individual enantiomers. However, extension of this reaction to ligands with Group 15 donor atoms allowed the synthesis of several related complexes $[Ru(C{\equiv}CR)L(PPh_3)(\eta\text{-}C_5Me_5)]$, of which we have characterised examples with R = Bu^t, L = $P(OMe)_3$ **10**, $AsPh_3$ **11**, dppm-*P* **12**, dppe-*P* **13**, dppa-*P* **14**, and R = Ph, L = dppm-*P* **15**. Of some interest is the finding that, under the mild reaction conditions, potentially chelating ligands (dppm, dppe) formed complexes in which they are monodentate, in principle allowing the construction of bimetallic species. Not surprisingly, the linear diphosphine $C_2(PPh_2)_2$ (dppa) also acts as a monodentate ligand in **14**. In contrast, the ligand *cis*-$PPh_2CH{=}CHPPh_2$ (dppen) formed $[Ru(C{\equiv}CBu^t)(dppen)(\eta\text{-}C_5Me_5)]$ **16** with expulsion of PPh_3. All of these complexes were identified by microanalysis and from the appropriate spectral properties, of which the most useful were their mass spectra, which contained parent ions which fragmented by loss of C_2R, Ph and PPh_3 groups. In addition, the molecular structures of complexes **9**, **12**, **13** and **16** have been determined by X-ray crystallography (see below).

The ready incorporation of 2e donor ligands under mild conditions at the Ru encouraged us to examine reactions with other ligands capable of π bonding. Examples of neutral complexes of this type are rare in $Ru(PR_3)_2(C_5H_5)$ chemistry, although a wide range of cationic adducts $[Ru(\eta^2\text{-}L)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (L = alkene, alkyne, allene or butadiene) is known.[23–27] The reaction of **4** with ethene in the presence of NaOMe readily afforded $[Ru(C{\equiv}CBu^t)(\eta\text{-}C_2H_4)(PPh_3)(\eta\text{-}C_5Me_5)]$ **17**, obtained as yellow crystals which were characterised by a single-crystal structure determination. The IR spectrum contains ν(C≡C) at 2088 and ν(C=C) at 1570 cm^{-1}, while the ^1H NMR spectrum contains a doublet for the ethylenic protons at δ 1.66. The ^{13}C resonances for the co-ordinated C_2H_4 ligand appear as doublets at δ 39.39 and 51.56; other signals are similar to those found for other complexes described above.

The $\eta^2\text{-}O_2$ complex, first obtained serendipitously during recrystallisation of a sample of **2**, can be made directly by passing oxygen through a solution of **3** while adding NaOMe. The complex $[Ru(C{\equiv}CPh)(\eta^2\text{-}O_2)(PPh_3)(\eta\text{-}C_5Me_5)]$ **18** forms red-orange crystals. The ν(C≡C) and ν(O=O) absorptions are found at 2094 and 914 cm^{-1}, respectively, while the NMR spectrum contains the expected resonances from the C_5Me_5 and Ph groups. There is no parent ion in the mass spectrum: however,

Table 1 Analytical and spectroscopic data

Compound and analysis[a]	Spectroscopic data[b]
2 [Ru(C_2Ph)(PPh_3)$_2$(η-C_5Me_5)]	IR: ν(C≡C) 2066m, 1593s, 1153s, 1086s, 1066s, 1027s, 752s, 737s, 695m, 688s
Yellow, m.p. 186–187 (decomp.)	^{1}H NMR: 1.19 (s, 15 H, C_5Me_5), 7.02–7.57 (m, 35 H, Ph)
C, 75.73 (75.25); H, 6.21 (5.81)	^{13}C NMR: 9.49 (s, $C_5\mathit{Me}_5$), 93.46 (s, C_5Me_5), 113.04 (s, ≡*C*Ph), 122.56 (s, RuC), 126.71–137.67 (m, Ph)
	Mass: 862, M^+; 785, [M − Ph]$^+$; 761, [M − C_2Ph]$^+$; 684, [M − C_2Ph − Ph]$^+$; 600, [M − PPh_3]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$
3 [RuCl(C=CHPh)(PPh_3)(η-C_5Me_5)]	IR: ν(C=C) 1606m, 1590m, 1569m, 1155s, 1092s, 1025s, 766s, 758s, 698m
Red, m.p. 190 (decomp.)	^{1}H NMR: 1.48 (s, 15 H, C_5Me_5), 4.51 (s, 1 H, =CH), 6.8–7.5 (m, 20 H, Ph)
C, 66.80 (67.96); H, 5.62 (5.66)	^{13}C NMR: 9.53 (s, $C_5\mathit{Me}_5$), 102.34 (s, =CH), 112.99 (s, C_5Me_5), 123.88–134.07 (m, Ph), 339.95 [d, *J*(CP) 24.75, RuC]
	Mass: 636, M^+; 600, [M − Cl]$^+$; 534, [M − CCHPh]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 363, [Ru(PPh_3)]$^+$; 237, [Ru(C_5Me_5)]$^+$
4 [RuCl(C=CHBu^t)(PPh_3)(η-C_5Me_5)]	IR: ν(C=C) 1626m, 1229s, 1154s, 1125s, 1094m, 743s, 698m, 680s
Red, m.p. 158 (decomp.)	^{1}H NMR: 0.93 (s, 9 H, CMe_3), 1.41 (s, 15 H, C_5Me_5), 3.38 (s, 1 H, =CH), 7.25–7.68 (m, 15 H, Ph)
C, 65.37 (64.85); H, 6.48 (6.84)	^{13}C NMR: 9.40 (s, $C_5\mathit{Me}_5$), 29.66 (s, $C\mathit{Me}_3$), 32.05 (s, $\mathit{C}Me_3$), 100.93 (s, C_5Me_5), 120.49 (s, =CH), 127.16–134.44 (m, Ph), 336.38 [d, *J*(CP) 24.38, RuC]
(as mono-MeOH solvate)	Mass: 615, M^+; 580, [M − Cl]$^+$; 534, [M − $CCHCMe_3$]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$
5 [RuCl(C=CHSiMe_3)(PPh_3)(η-C_5Me_5)]	IR: ν(C=C) 1609m
Orange, m.p. 138–139 (decomp.)	^{1}H NMR: 0.06 (s, 9 H, $SiMe_3$), 1.41 [d, *J*(HP) 1.34, 15 H, C_5Me_5], 2.91 (s, 1 H, =CH), 7.26–7.54 (m, 15 H, Ph)
C, 62.36 (62.76); H, 6.33 (6.34)	^{13}C NMR: 0.63 (s, $SiMe_3$), 8.65 (s, $C_5\mathit{Me}_5$), 92.33 (s, =CH), 99.41 (s, $C_5\mathit{Me}_5$), 126.88–133.78 (m, Ph), 321.67 (s, RuC)
	Mass: 587, [M − 3Me]$^+$; 559, [M − $SiMe_3$]$^+$; 534, [M − $CCHSiMe_3$]$^+$; 525, [Ru(C_2H)(PPh_3)-(C_5Me_5)]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$
6 [RuCl(C=CHMe)(PPh_3)(η-C_5Me_5)]	IR: ν(C=C) 1586m, 1571m, 1262s, 1184s, 1156s, 1093m, 1027m, 741s, 699m
Yellow, m.p. 180 (decomp.)	Mass: 561, [M − CH_2]$^+$; 534, [M − CCHMe]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 457, [RuCl(PPh_2)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$
7 [Ru(C_2Bu^t)(PPh_3)$_2$(η-C_5Me_5)]	IR: ν(C≡C) 2080m, 1242s, 1157s, 1086m, 1026s, 737s, 696m, 682s
Yellow, m.p. 182 (decomp.)	^{1}H NMR: 1.14 (s, 15 H, C_5Me_5), 1.37 (s, 9 H, CMe_3), 7.02–7.57 (m, 30 H, Ph)
C, 73.95 (74.20); H, 6.18 (6.42)	^{13}C NMR: 9.38 (s, $C_5\mathit{Me}_5$), 30.04 (s, $C\mathit{Me}_3$), 33.01 (s, $\mathit{C}Me_3$), 92.62 (s, C_5Me_5), 99.34 (s, ≡*C*Bu^t), 117.94 (s, RuC), 126.35–137.85 (m, Ph)
	MS (FAB): *m*/*z* 842, M^+; 761, [M − C_2Bu^t]$^+$; 580, [M − PPh_3]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru-(PPh_2)(C_5Me_5)]$^+$; 314, [Ru(C_2Bu^t)(C_5Me_5)]$^+$; 233, [Ru(C_5Me_5)]$^+$
8 [Ru(C_2Ph)(CO)(PPh_3)(η-C_5Me_5)]	IR: ν(C≡C) 2095m; ν(CO) 1915s, 1188s, 1158s, 1092m, 1073m, 1028m, 915s, 759s, 751s, 741s, 697m
Yellow	^{1}H NMR: 1.50 (s, 15 H, C_5Me_5); 7.26–7.57 (m, 15 H, Ph)
C, 69.80 (70.80); H, 5.69 (5.62)	^{13}C NMR: 9.37 (s, $C_5\mathit{Me}_5$), 96.32 (s, C_5Me_5), 103.81 (s, ≡CPh), 123.95 (s, RuC), 127.47–134.11 (m, Ph), 206.44 [t, *J*(CP) 22.7, CO]
9 [Ru(C_2Bu^t)(CO)(PPh_3)(η-C_5Me_5)]	IR: ν(C≡C) 2100m; ν(CO) 1928s, 1911s, 1247s, 1094m, 743s, 697m
Yellow	^{1}H NMR: 0.99 (s, 9 H, CMe_3), 1.60 [d, *J*(HP) 1.43, 15 H, C_5Me_5], 7.25–7.64 (m, 15 H, PPh_3)
C, 69.04 (69.08); H, 6.36 (6.41)	^{13}C NMR: 9.70 (s, $C_5\mathit{Me}_5$), 29.31 (s, $C\mathit{Me}_3$), 32.70 (s, $\mathit{C}Me_3$), 90.50 (s, ≡CBu^t), 118.45 (s, RuC), 127.49–135.32 (m, Ph), 207.23 [d, *J*(CP) 20.9, CO]
	Mass: 608, M^+; 580, [M − CO]$^+$; 527, [M − C_2Bu^t]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)-(C_5Me_5)]$^+$; 342, [Ru(PPh)(C_5Me_5)]$^+$
10 [Ru(C_2Bu^t)(PPh_3){P($OMe)_3$}(η-C_5Me_5)]	IR: ν(C≡C) 2086m; ν(PO) 1030s, 1065s, 740s, 724m, 697m
Yellow	^{1}H NMR: 1.17 (s, 9 H, CMe_3), 1.47 (s, 15 H, C_5Me_5), 3.34 [d, *J*(HP) 10.7, 9 H, OMe], 7.24–7.80 (m, 15 H, Ph)
C, 57.72 (57.86); H, 6.37 (6.39)	^{13}C NMR: 9.58 [d, *J*(CP) 8.9, $C_5\mathit{Me}_5$], 29.50 (s, $C\mathit{Me}_3$), 32.97 [d, *J*(CP) 7.6, $\mathit{C}Me_3$], 51.96 [d, *J*(CP) 5.9, OMe], 93.42 (s, C_5Me_5), 116.80 (s, RuC), 116.86 [d, *J*(CP) 1.81, ≡CBu^t], 126.32–139.22 (m, Ph)
	Mass: 703, M^+; 624, [M − C_2Bu^t]$^+$; 580, [M − P($OMe)_3$]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 441, [M − PPh_3]$^+$
11 [Ru(C_2Bu^t)($AsPh_3$)(PPh_3)(η-C_5Me_5)]	IR: ν(C≡C) 2078m, 1242m, 750m, 741s, 733m, 683m, 667m
Orange	^{1}H NMR: 1.19 (s, 15 H, C_5Me_5), 1.37 (s, 9 H, CMe_3), 7.03–7.57 (m, 30 H, Ph)
C, 65.57 (66.36); H, 6.07 (6.08)	^{13}C NMR: 9.40 (s, $C_5\mathit{Me}_5$), 29.77 (s, $C\mathit{Me}_3$), 32.13 (s, $\mathit{C}Me_3$), 92.48 (s, C_5Me_5), 100.90 (s, ≡CBu^t), 120.50 (s, RuC), 126.29–134.68 (m, Ph)
(as mono-CH_2Cl_2 solvate)	Mass: 884, M^+; 803, [M − C_2Bu^t]$^+$; 725, [M − Ph − C_2Bu^t]$^+$; 668, [Ru($AsPh_3$)(PPh_3)]$^+$; 580, [M − $AsPh_3$]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$
12 [Ru(C_2Bu^t)(dppm)(η-C_5Me_5)]	IR: ν(C≡C) 2078m, 781s, 745m, 739m, 728s
Yellow	^{1}H NMR: 1.15 (s, 15 H, C_5Me_5), 1.48 (s, 9 H, CMe_3), 2.81 (s, 2 H, CH_2), 7.03–7.70 (m, 20 H, Ph)
C, 68.06 (68.70); H, 6.25 (6.05)	^{13}C NMR: 9.41 (s, $C_5\mathit{Me}_5$), 28.04 [t, *J*(CP) 22.9, CH_2], 33.54 (s, $C\mathit{Me}_3$), 92.49 (s, C_5Me_5), 112.40 (s, ≡CBu^t), 113.20 (s, RuC), 125.99–135.26 (m, Ph)
(as mono-CH_2Cl_2 solvate)	Mass: 702, M^+; 621, [Ru(dppm)(C_5Me_5)]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$; 317, [M − dppm]$^+$
13 [Ru(C_2Bu^t)(PPh_3)(dppe-*P*)(η-C_5Me_5)]	IR: ν(C≡C) 2075m, 752s, 737s, 726m, 702m
Yellow	^{1}H NMR: 1.17 (s, 15 H, C_5Me_5), 1.23 (s, 9 H, CMe_3), 2.09 [t, *J*(HP) 3.8, 4 H, CH_2], 6.90–7.52 (m, 35 H, Ph)
C, 72.96 (73.67); H, 6.46 (6.49)	^{13}C NMR: 9.50 (s, $C_5\mathit{Me}_5$), 23.87 (s, CH_2), 29.90 (s, $C\mathit{Me}_3$), 33.22 (s, $\mathit{C}Me_3$), 92.38 (s, C_5Me_5), 92.52 (s, ≡CBu^t), 115.95 (s, RuC), 126.50–138.13 (m, Ph)
	Mass: 978, M^+; 897, [M − C_2Bu^t]$^+$; 716, [M − PPh_3]$^+$; 635, [M − C_2Bu^t − PPh_3]$^+$; 580, [M − dppe]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$
14 [Ru(C_2Bu^t)(PPh_3)(dppa-*P*)(η-C_5Me_5)]	IR: ν(C≡C) 2079m, 739m, 722m, 694s
Yellow	^{1}H NMR: 1.09 (s, 15 H, C_5Me_5), 1.29 (s, 9 H, CMe_3), 6.50–7.73 (m, 35 H, Ph)
C, 70.02 (69.18); H, 5.85 (5.80)	^{13}C NMR: 9.29 (s, $C_5\mathit{Me}_5$), 30.20 (s, $C\mathit{Me}_3$), 33.22 (s, $\mathit{C}Me_3$), 93.07 (s, C_5Me_5), 94.56 (s, ≡CBu^t), 118.02 (s, RuC), 126.59–138.19 (m, Ph)
(as mono-CH_2Cl_2 solvate)	Mass: 974, M^+; 893, [M − C_2Bu^t]$^+$; 712, [M − PPh_3]$^+$; 629, [M − C_2Bu^t − PPh_3]$^+$; 580, [M − dppa]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$

Table 1 (*Contd.*)

Compound and analysis[a]	Spectroscopic data[b]
15 $[Ru(C_2Ph)(PPh_3)(dppm\text{-}P)(\eta\text{-}C_5Me_5)]$ Yellow C, 74.40 (74.45); H, 5.92 (5.84)	IR: ν(C≡C) 2060m, 750s, 746m, 666m ^{1}H NMR: 1.20 (s, 15 H, C_5Me_5), 2.80 [t, *J*(HP) 1.36, 2 H, CH_2], 6.66–7.78 (m, 40 H, Ph) ^{13}C NMR: 10.50 (s, $C_5\mathit{Me}_5$), 30.05 (s, CH_2), 89.40 (s, C_5Me_5), 100.00 (s, ≡CPh), 124.80 (s, RuC), 125.80–136.84 (m, Ph) Mass (FAB): 984, M^+; 723, $[M - PPh_3]^+$; 600, $[M$ − dppm$]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$
16 $[Ru(C_2Bu^t)(dppen)(\eta\text{-}C_5Me_5)]$ Yellow C, 70.81 (70.65); H, 6.00 (6.49)	IR: ν(CO) 2076m; ν(C=C) 1585m, 738s, 713m, 669m ^{1}H NMR: 1.23 (s, 15 H, C_5Me_5), 1.41 (s, 9 H, CMe_3), 6.45 [t, *J*(HP) 6.7, 2 H, =CH], 6.94–7.63 (m, 20 H, Ph) ^{13}C NMR: 10.00 (s, $C_5\mathit{Me}_5$), 30.08 (s, CMe_3), 33.41 (s, $\mathit{C}Me_3$), 92.67 (s, C_5Me_5), 115.49 (s, ≡CBu^t), 118.07 (s, RuC), 126.33–146.90 (m, Ph), 146.78 (s, =CH) Mass: 714, M^+; 633, $[M - C_2Bu^t]^+$; 579, $[M - C_5Me_5]^+$; 317, $[M$ − dppen$]^+$
17 $[Ru(C_2Bu^t)(\eta\text{-}C_2H_4)(PPh_3)(\eta\text{-}C_5Me_5)]$ Yellow C, 62.58 (62.66); H, 6.21 (6.42) (as $1.25CH_2Cl_2$ solvate)	IR: ν(C≡C) 2088m; ν(C=C) 1570s, 749s, 697s, 685s ^{1}H NMR: 0.97 (s, CMe_3), 1.50 (s, 15 H, C_5Me_5), 1.66 [d, *J*(HP) 4.20, 2 H, $=CH_2$], 7.20–7.70 (m, 15 H, Ph) ^{13}C NMR: 9.60 (s, $C_5\mathit{Me}_5$), 30.42 (s, CMe_3), 30.78 (s, $\mathit{C}Me_3$), 39.39 (s, CH_2), 51.56 (s, CH_2), 90.93 (s, C_5Me_5), 105.19 (s, ≡CBu^t), 124.21 (s, RuC), 127.10–136.02 (m, Ph) Mass: 608, M^+; 580, $[M - C_2Bu^t]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$
18 $[Ru(C_2Ph)(\eta\text{-}O_2)(PPh_3)(\eta\text{-}C_5Me_5)]$ Red C, 64.79 (65.02); H, 5.44 (5.38)	IR: ν(C≡C) 2094m; ν(OO) 914m ^{1}H NMR: 1.53 [d, *J*(HP) 1.2, 15 H, C_5Me_5], 6.74–7.45 (m, 20 H, Ph) ^{13}C NMR: 9.03 (s, $C_5\mathit{Me}_5$), 103.90 (s, C_5Me_5), 105.32 (s, ≡CPh), 123.44 (s, RuC), 125.02–134.29 (m, Ph) Mass: 616, $[M - O]^+$; 600, $[M - 2O]^+$; 525, $[M - 2O - Ph]^+$; 513, $[M - 2O - C_2Ph]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$
19 $[Ru(C_2Bu^t)(\eta\text{-}S_2)(PPh_3)(\eta\text{-}C_5Me_5)]$ Khaki-green C, 63.19 (63.35); H, 6.05 (6.06)	IR: ν(C≡C) 2114m; ν(SS) 1248m ^{1}H NMR: 0.91 (s, 9 H, CMe_3), 1.49 [d, *J*(HP) 1.25, 15 H, C_5Me_5], 7.17–7.63 (m, 15 H, Ph) ^{13}C NMR: 8.95 (s, $C_5\mathit{Me}_5$), 29.44 (s, CMe_3), 32.15 (s, $\mathit{C}Me_3$), 101.68 (s, C_5Me_5), 101.72 (s, RuC), 124.67 (s, ≡CBu^t), 126.79–135.38 (m, Ph) Mass: 643, M^+; 562, $[M - C_2Bu^t]^+$; 533, $[M - C_2Bu^t - S]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 381, $[M - PPh_3]^+$
20 $[Ru(S_2CC_2Bu^t)(PPh_3)(\eta\text{-}C_5Me_5)]$ Olive-green C, 62.76 (63.46); H, 5.77 (5.85) (as 0.5MeOH solvate)	IR: ν(C≡C) 2195m; ν(CS) 1288m, 749s, 738m, 706w, 692m ^{1}H NMR: 1.17 (s, 9 H, CMe_3), 1.50 [d, *J*(HP) 1.42, 15 H, C_5Me_5], 7.27–7.50 (m, 15 H, Ph) ^{13}C NMR: 10.54 (s, $C_5\mathit{Me}_5$), 28.89 (s, CMe_3), 30.54 [d, *J*(CP) 8.85, $\mathit{C}Me_3$], 88.03 (s, C_5Me_5), 97.20 (s, ≡CBu^t), 123.0 (s, ≡CCS_2), 127.25–135.62 (m, Ph), 191.80 (s, CS_2) Mass: 656, M^+; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 394, $[M - PPh_3]^+$

[a] Analytical data are given as found (calculated) in %. [b] IR data are given in cm^{-1}; NMR data are given as chemical shift (δ) (multiplicity, *J*/Hz, relative intensity, assignment); mass spectra were obtained using FAB, data are given as *m*/*z*, assignment.

the ion $[M - O]^+$ (*m*/*z* 616) fragments further by loss of O, Ph, C_2Ph and PPh_3 groups.

The sulfur analogue $[Ru(C{\equiv}CBu^t)(\eta^2\text{-}S_2)(PPh_3)(\eta\text{-}C_5Me_5)]$ **19** was formed when S_8 was added to a solution of complex **4** in MeOH, followed by an excess of NaOMe. A grey-green complex was obtained after separation by TLC. It has ν(C≡C) and ν(S=S) at 2114 and 1248 cm^{-1}, respectively. Resonances for the Bu^t, C_5Me_5 and Ph groups were present in the NMR spectra and the parent ion decomposed by loss of S, C_2Bu^t and PPh_3 groups.

The ability of small molecules to co-ordinate to the metal centre is illustrated in a different way in the reaction between complex **4** and CS_2. An olive-green complex was obtained and identified as $[Ru(S_2CC{\equiv}CBu^t)(PPh_3)(\eta\text{-}C_5Me_5)]$ **20** by an X-ray study. Characteristic spectroscopic features include ν(C≡C) and ν(CS) bands at 2195 and 1288 cm^{-1} in the IR spectrum and resonances for the Bu^t, C_5Me_5 and Ph groups in the NMR spectra. The two acetylenic carbons appeared at δ 97.2 and 123.

Molecular structures

Crystal structure determinations were carried out on complexes **2**, **3**, **5**, **9**, **12**, **13** and **16**–**20** which confirmed the structural assignments given above. Major structural parameters are summarised in Tables 2 and 3; Figs. 1–11 are plots of the individual molecules (or cations, for **3** and **5**).

The structure of complex **3** was reported in a communication;[18] that of **5** is very similar. Both contain $RuCl(PPh_3)(C_5Me_5)$ groups in which the bond parameters are similar to those reported in many other related complexes. The Ru–Cl and Ru–P distances fall within the normal ranges, although they are somewhat shorter than those found in $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$,[28–30] probably because of relief of steric strain that occurs in the latter complex. The Ru–C (C_5Me_5) distances range between 2.20 and 2.35(2) Å, again similar to those found in

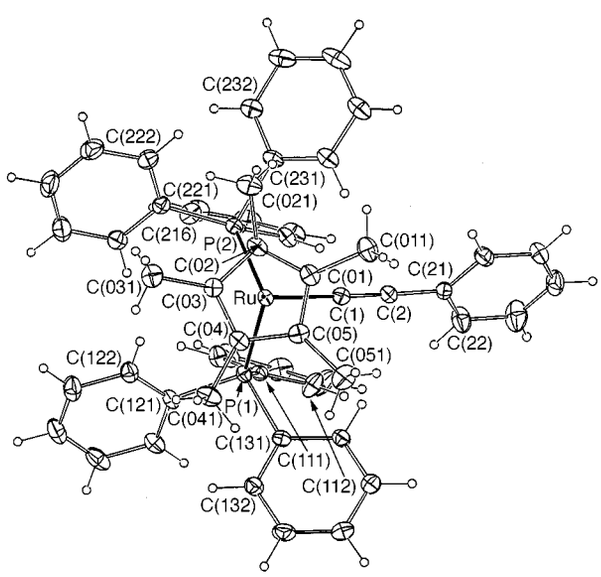


Fig. 1 Molecular projection of $[Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **2** down the Ru–Cp*(centroid) vector. In this and in Figs. 2–9, 20% thermal envelopes are shown for the non-hydrogen atoms, hydrogens having arbitrary radii of 0.1 Å

$Ru{-}C_5H_5$ complexes. Of note are the Ru–C (vinylidene) distances, which at 1.80(1) and 1.84(1) Å, respectively, are shorter than those found in the cationic analogues. This may reflect the increase in back bonding between Ru and the vinylidene compared with that in the cation.

The remaining complexes, like **3** and **5**, adopt the familiar 'piano-stool' structure, with C_2R, L and PPh_3 ligands forming the 'legs' in all except **12**, **16** and **20**, which contain chelating dppm, dppen or $S_2CC_2Bu^t$ ligands, respectively. The geometry

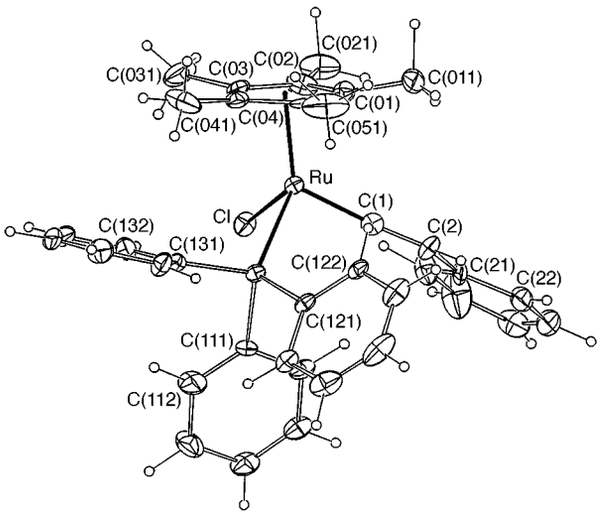


Fig. 2 Molecular projection of [RuCl(C=CHPh)(PPh_3)(η-C_5Me_5)] **3** normal to the Ru–Cp*(centroid) vector

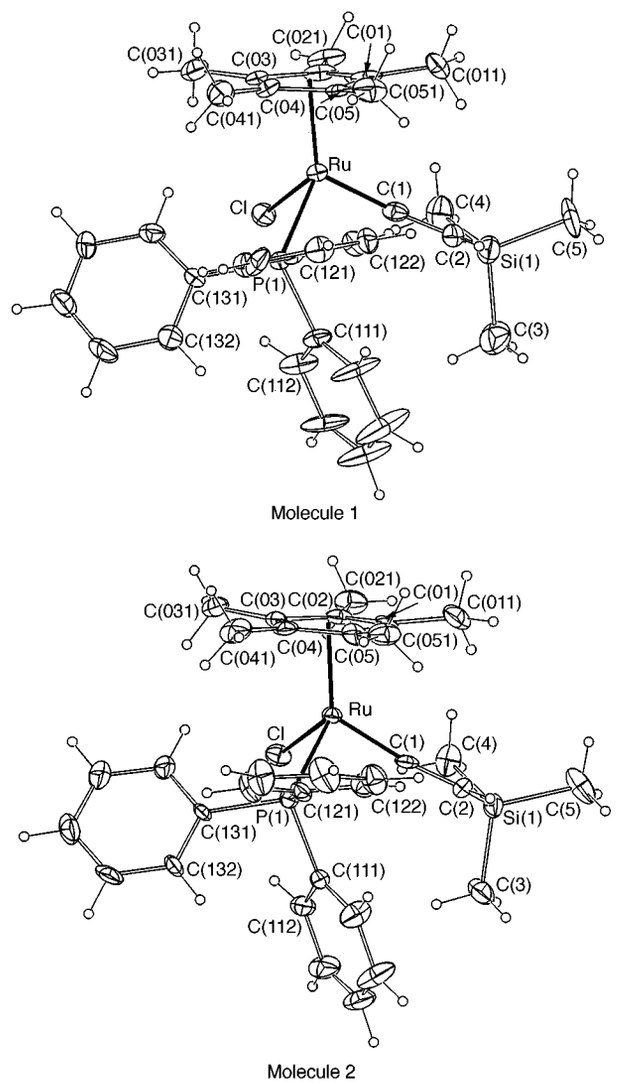


Fig. 3 Molecular projection of molecules 1 and 2 of [RuCl(C=CHSiMe_3)(PPh_3)(η-C_5Me_5)] **5** normal to the Ru–Cp*(centroid) vector

about the ruthenium is pseudo-octahedral, angles between the Ru–L (L = single-atom donor, non-C_5Me_5 ligand) vectors being close to 90° [range 83.3(2) **17** to 95.74(8)° **13**]. Larger excursions are found with **18** and **19**, containing O_2 and S_2 ligands, where small P–Ru–C≡ angles of 80.3(1) and 80.1(1)°, respectively, are

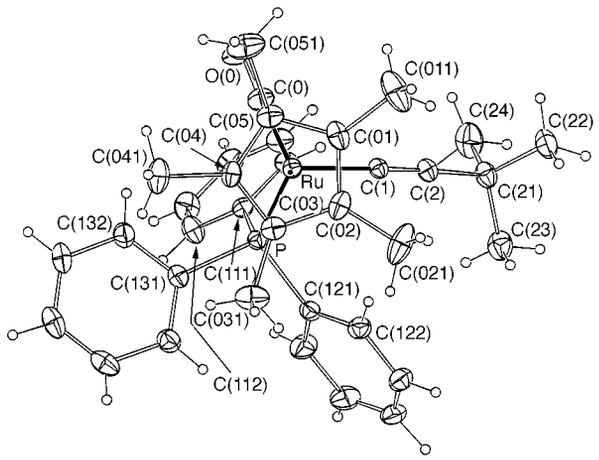


Fig. 4 Molecular projection of [Ru(C_2Bu^t)(CO)(PPh_3)(η-C_5Me_5)] **9** down the Ru–Cp*(centroid) vector

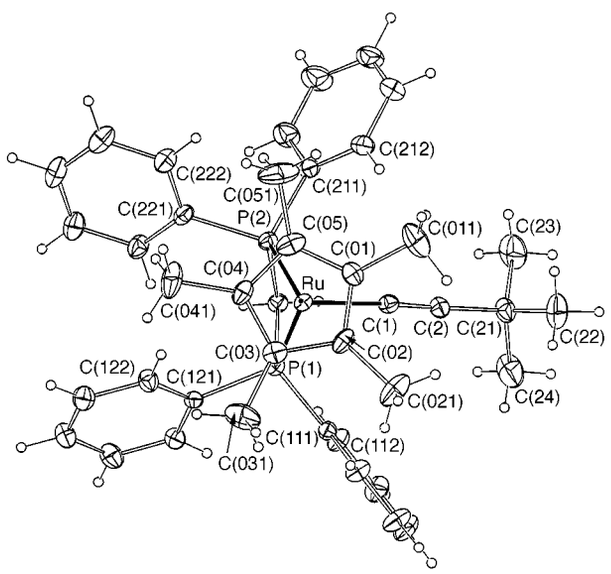


Fig. 5 Molecular projection of [Ru(C_2Bu^t)(dppm)(η-C_5Me_5)] **12** down the Ru–Cp*(centroid) vector

found. In **12** the small bite of the chelating dppm ligands results in a P–Ru–P angle of 70.99(5)°.

The Ru–PPh_3 distances range between 2.267(2) and 2.334(1) Å, the extremes being found for complexes **12** and **19**. For the unidentate phosphine the Ru–P distance is similar, at 2.288(2) Å. With the dppm and dppen complexes **12** and **16** the Ru–P distances are between 2.244(2) and 2.271(2) Å. The Ru–C-(C_5Me_5) distances range between 2.20(3) and 2.311(4) Å, the ruthenium-ring centroids showing similar variability. The Ru–C(1) distances [2.006(4)–2.058(9) Å] may be compared to the value of 2.016(3) Å found in Ru(C≡CPh)(PPh_3)$_2$Cp.[31,32]

The η^2-O_2 ligand in **18** is asymmetrically bound, with Ru–O distances of 2.032(3), 2.048(3) Å. These values are considerably longer than those found in the related cations [Ru(η^2-O_2)(L_2)-(η-C_5Me_5)][BPh_4] [2.023, 2.040(3) (L_2 = dppe);[33] 2.029, 2.035(8) Å (L_2 = dppf) [34]], despite the increased steric hindrance afforded by the PPh_3 and C_5Me_5 ligands in **18**. The O–O separation is 1.363(4) Å, somewhat shorter than the values of 1.398(5) and 1.381(11) Å found in the cationic complexes. For **19** the Ru–S distances are experimentally identical at 2.384(2) Å and the S–S separation is 2.010(2) Å. We are not aware of any comparable η^2-S_2 complex of ruthenium; the Ru–S distance in [Ru(SH)-(CO)(PPh_3)(η-C_5H_5)] is 2.381(3) Å,[35] while in [Ir(η^2-S_2)-(dppe)$_2$]$^+$ the S–S separation is 2.066(6) Å.[36]

The structure of the ethene complex **17** has been reported

Table 2 Bond parameters (lengths in Å, angles in °) for [RuCl(C=CHR)(PPh_3)(η-C_5Me_5)] (R = Ph **3** or $SiMe_3$ **5**)

	3	**5**[a]
Ru–C=	1.80(1)	1.83(1), 1.85(2)
Ru–P	2.305(3)	2.315(4), 2.305(4)
Ru–Cl	2.395(3)	2.397(5), 2.408(4)
Ru–C (Cp*)	2.20–2.35(1)	2.22–2.35(2)
(average)	2.26	2.28
C(1)–C(2)	1.29(2)	1.31(2), 1.29(2)
P–Ru–C(1)	88.4(4)	89.0(4), 87.9(4)
Cl–Ru–C(1)	100.6(4)	99.7(6), 98.1(4)
Cl–Ru–P	89.2(1)	87.4(2), 88.8(1)
Ru–C(1)–C(2)	176(1)	176(1), 173(1)
C(1)–C(2)–Si	—	122(1), 119(1)

[a] Values for two independent molecules given.

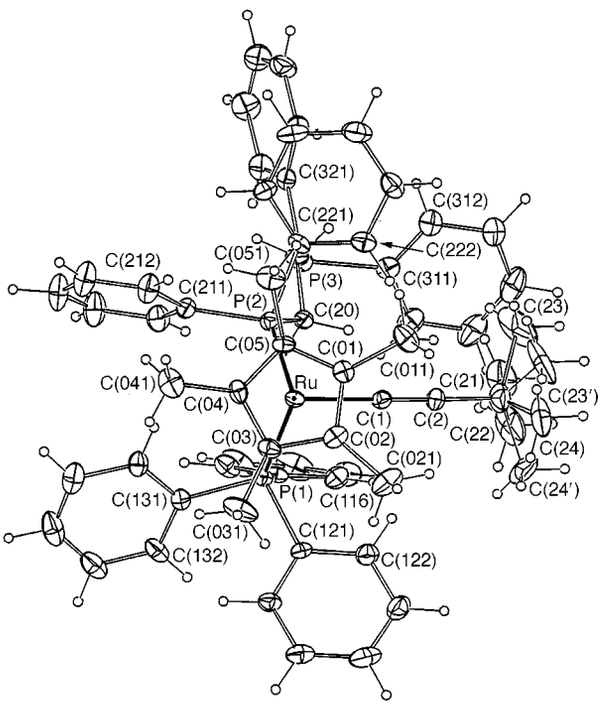


Fig. 6 Molecular projection of [Ru(C_2Bu^t)(dppe)(PPh_3)(η-C_5Me_5)] **13** down the Ru–Cp*(centroid) vector

elsewhere[18] and we note only that the C=C double bond [1.39(1) Å] is parallel to the C_5Me_5 ring plane, with a slightly asymmetric attachment to the metal [Ru–C(1,2) 2.186, 2.170(9) Å]. These values are comparable with Ru–C distances of 2.168(10), 2.194(9) Å found in [RuH(η-C_2H_4)(PPh_3)(η-C_6Me_6)]PF_6,[37] although the C–C separation of 1.410(3) Å in the latter is somewhat longer as a result of reduced back bonding from the cationic metal centre.

The dithiocarboxylate ligand in complex **20** is attached symmetrically by the two S atoms [Ru–S(1,2) 2.35, 2.37(1) Å] and has internal S–C bonds of 1.67, 1.70(4) Å. The alkynyl substituent shows normal geometries, the complex having an overall similarity to [Ru($S_2CC{\equiv}CPh$)(PPh_3)(η-C_5H_5)] in which Ru–S distances of 2.336(3), 2.353(4) Å and thiolate C–S separations of 1.68, 1.71(1) Å were found.[38]

Discussion

The present study describes the formation of neutral vinylidene derivatives of ruthenium, formed by displacement of a bulky PPh_3 ligand from the [$RuCl(PPh_3)_2$(η-C_5Me_5)] precursor by 1-alkynes, with concomitant isomerisation to the vinylidene by 1,2-H shifts. This chemistry contrasts with the normal displacement of chloride that occurs when [$RuCl(PPh_3)_2$(η-C_5H_5)] reacts with 1-alkynes to give cationic [Ru(C=CHR)$(PPh_3)_2$(η-C_5H_5)]$^+$. The latter reaction is also observed with complex **1** in polar solvents and similar studies have been reported with

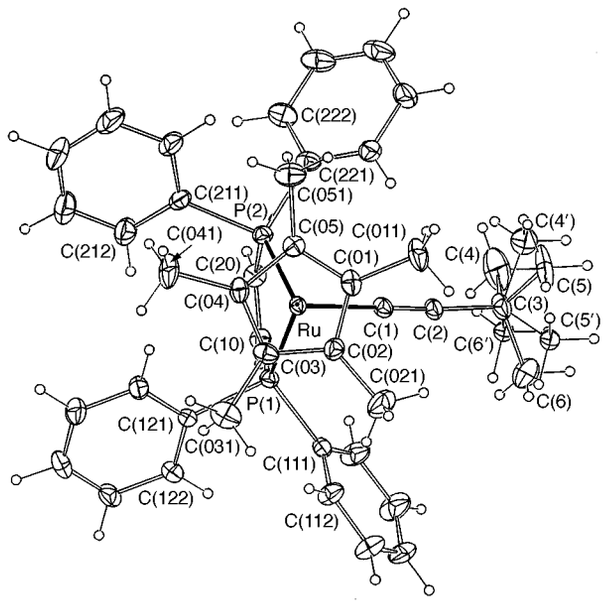


Fig. 7 Molecular projection of [Ru(C_2Bu^t)(dppen)(η-C_5Me_5)] **16** down the Ru–Cp*(centroid) vector

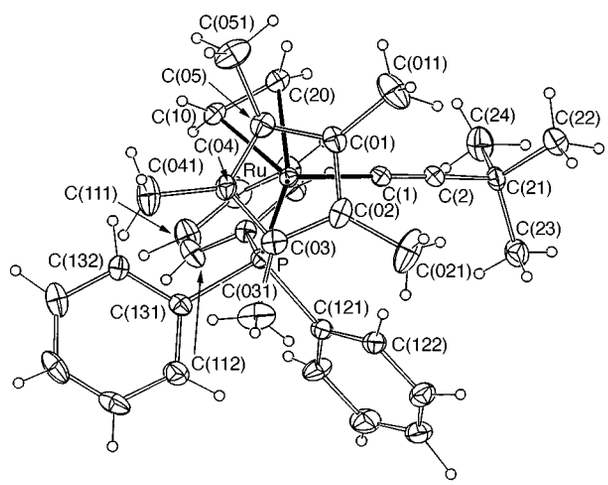


Fig. 8 Molecular projection of [Ru(C_2Bu^t)(C_2H_4)(PPh_3)(η-C_5Me_5)] **17** down the Ru–Cp*(centroid) vector

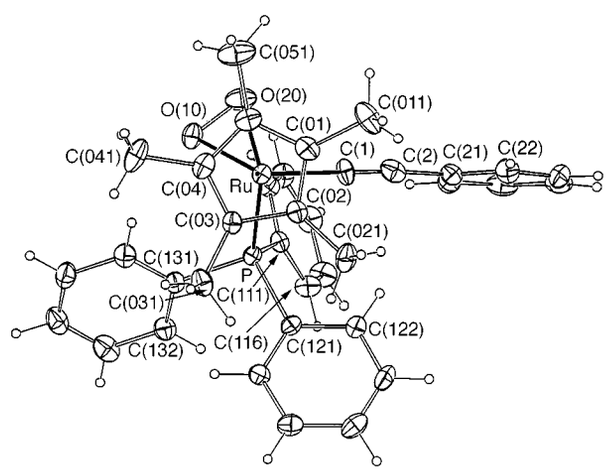


Fig. 9 Molecular projection of [Ru(C_2Ph)(O_2)(PPh_3)(η-C_5Me_5)] **18** down the Ru–Cp*(centroid) vector

Table 3 Selected bond parameters (lengths in Å, angles in °) for ruthenium complexes

Complex	**2**	**9**	**12**	**13**	**16**	**17**	**18**	**19**	**20**
R	Ph	Bu^t	Bu^t	Bu^t	Bu^t	Bu^t	Ph	Bu^t	Bu^t
L^1	PPh_3	PPh_3	dppm	PPh_3	dppen	PPh_3	PPh_3	PPh_3	PPh_3
L^2	PPh_3	CO		dppe-*P*		C_2H_4	O_2	S_2	$S_2C{\equiv}CBu^t$
Ru–C≡	2.006(4)	2.032(3)	2.029(5)	2.058(9)	2.025(8)	2.034(6)	2.022(4)	2.024(5)	—
Ru–P(1)	2.311(1)	2.309(1)	2.267(2)	2.272(2)	2.244(2)	2.300(3)	2.327(1)	2.334(1)	2.303(9)
Ru–L^2	2.313(1)	1.828(4)	2.271(5)	2.288(2)	2.247(2)	2.186(8), 2.170(9)	2.032(3), 2.048(3)	2.383(2), 2.385(2)	2.37(1), 2.350(9)
Ru–C (Cp*)	2.247–2.290(4)	2.223–2.311(4)	2.211–2.257(6)	2.243–2.287(9)	2.215–2.260(8)	2.215–2.292(7)	2.204–2.297(4)	2.206–2.301(7)	2.20–2.23(3)
(average)	2.27	2.26	2.24	2.27	2.24	2.25	2.25	2.26	2.21
C≡C	1.216(6)	1.197(4)	1.186(7)	1.21(1)	1.17(1)	1.189(8)	1.158(5)	1.200(8)	1.17(4)
≡C–R	1.423(5)	1.495(5)	1.495(7)	1.47(2)	1.51(1)	1.490(8)	1.467(5)	1.480(8)	1.52(5)
Other						C=C, 1.39(1)	O=O, 1.363(4)	S=S, 2.010(2)	S–C, 1.70, 1.67(4)
P(1)–Ru–C≡	86.2(1)	84.52(8)	80.6(1)	89.4(2)	82.3(2)	83.3(2)	80.3(1)	80.1(1)	—
P(1)–Ru–L^2	99.56(4)	90.4(1)	70.99(5)	95.74(8)	82.72(8)	84.0(2), 103.6(2)	85.63(9), 103.97(9)	84.72(6), 107.00(7)	93.7(4), 90.6(3)
≡C–Ru–L^2	89.5(1)	91.3(2)	85.3(1)	85.5(1)	87.0(2)	109.4(3), 80.7(3)	118.3(1), 87.6(1)	121.1(2), 81.3(2)	—
Ru–C≡C	173.9(3)	177.6(3)	176.0(4)	171.0(7)	177.3(7)	179.0(5)	172.5(4)	175.4(4)	—
C≡C–R	178.5(5)	174.7(4)	178.4(5)	178.1(9)	173.8(8)	174.1(7)	172.6(4)	177.5(8)	172(4)

For **20**: S(1)–Ru–S(2) 71.4(3), S(1)–C(1)–S(2) 110(2), S–C(1)–C(2) 128, 122(3)°.

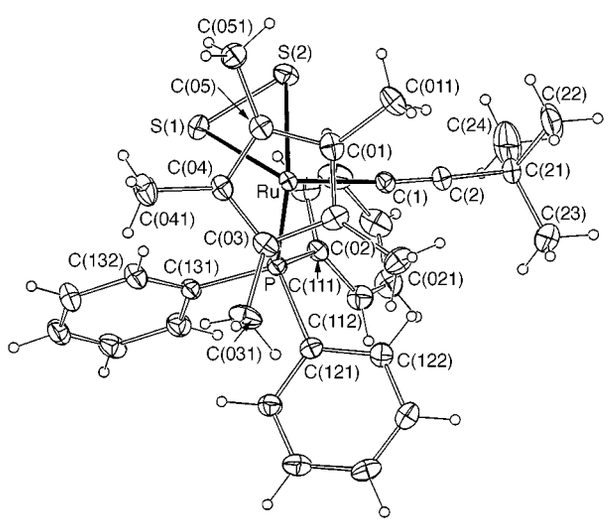


Fig. 10 Molecular projection of $[Ru(C_2Bu^t)(S_2)(PPh_3)(\eta\text{-}C_5Me_5)]$ **19** down the Ru–Cp*(centroid) vector

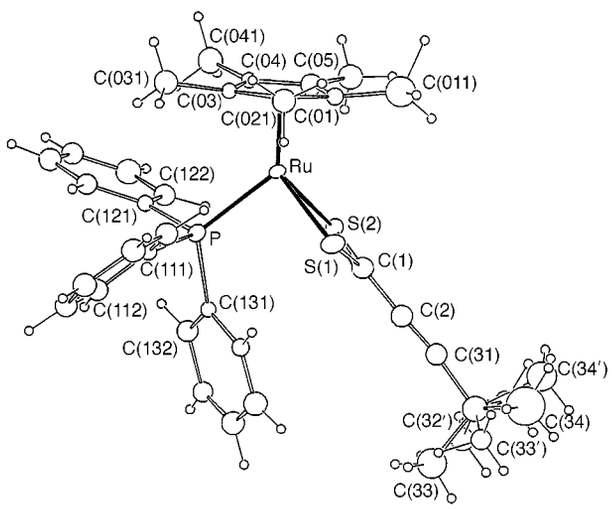
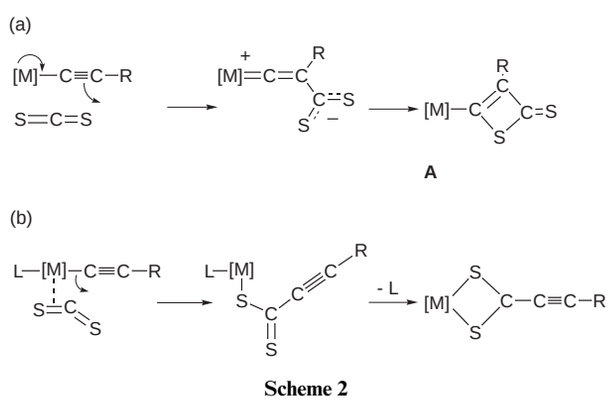


Fig. 11 Molecular projection of $[Ru(S_2CC_2Bu^t)(PPh_3)(\eta\text{-}C_5Me_5)]$ **20** normal to the Ru–Cp*(centroid) vector

precursors having less bulky tertiary phosphine ligands.[17] As mentioned above, structurally related complexes have been prepared using the hemi-labile chelating $PPh_2CH_2CH_2OMe$, when the donor oxygen atom is displaced by the vinylidene.[8]

Very recently, complex **3** has been described by others,[39] who noted the apparent generation of the 16e intermediate $[Ru(C{\equiv}CPh)(PPh_3)(\eta\text{-}C_5Me_5)]$ when it was treated with NEt_3. Our chemistry is similar, a formal base-induced 1,3 elimination of HCl resulting by deprotonation of the vinylidene to the corresponding acetylide. We have no evidence for the formation of the supposed 16e intermediate and prefer to consider that these reactions generate a weakly solvated intermediate (either by MeOH or thf). In the presence of other, stronger 2e donor ligands the solvent is displaced to give $[Ru(C{\equiv}CR)L(PPh_3)(\eta\text{-}C_5Me_5)]$ (R = Bu^t or Ph). In this way we have prepared several complexes where L is carbonyl, tertiary phosphine, arsine or phosphite, olefin, dioxygen or disulfur. X-Ray crystallographic studies of these complexes confirm the assigned structures based on the 'piano stool' arrangement of the three ligands below a capping C_5Me_5 ligand. In cyclopentadienylruthenium chemistry the $\eta^2\text{-}O_2$, $\eta^2\text{-}S_2$ and $\eta^2\text{-}C_2H_4$ ligands are unusual, although during the course of this work



Scheme 2

some other examples have been reported, if not structurally characterised.[40]

Formal addition of CS_2 to the acetylide forming the alkyne dithiocarboxylate ligand has been observed on several previous occasions. Thus, both $[Fe(C{\equiv}CMe)(dppe)(\eta\text{-}C_5H_5)]$[41] and $[Ru(C{\equiv}CC_6H_9)(PMe_3)_2(\eta\text{-}C_5H_5)]$[42] afford the 2*H*-thiete-2-thione complexes [**A**, Scheme 2(a)] by addition of CS_2 to C_β and

subsequent ring closure. A different product is obtained from $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$, when the alkyne dithiolato complex $[Ru(S_2CC{\equiv}CPh)(PPh_3)(\eta\text{-}C_5H_5)]$, analogous to **20**, is formed.[38] This reaction may proceed by initial co-ordination of CS_2 in the η^2 mode, followed by migration of the alkynyl group to the central C atom [Scheme 2(b)]. An alternative mechanism, involving cycloaddition as above, ring opening and rearrangement, which has been advanced for the formation of similar complexes from CS_2 and complexes $[Fe(C{\equiv}CR)L(L')(\eta\text{-}C_5H_5)]$ (L = CO, L′ = PPh_3, R = Ph or Bu^t; LL′ = dppe, R = Ph),[43] requires cleavage of the C–R bond, for which little precedent exists.

Conclusion

The synthesis of neutral vinylideneruthenium complexes by displacement of bulky PPh_3 from the precursor $[RuCl(PPh_3)_2(\eta\text{-}C_5Me_5)]$ contrasts with the chemistry of the related C_5H_5 analogue, which loses chloride and forms the cationic vinylidene complexes. The neutral complexes readily eliminate HCl on treatment with base: in the presence of 2e donor ligands, complexes of the type $[Ru(C_2R)L(PPh_3)(\eta\text{-}C_5Me_5)]$ are formed which, if L ≠ PPh_3, are chiral at the metal centre. In addition to the usual tertiary phosphine, phosphite or arsine ligands, L may be unsaturated hydrocarbon (olefin, alkyne), H_2 or Group 16 donor ligands. These reactions proceed under very mild conditions and offer a novel extension of the already extensive cyclopentadienylruthenium–vinylidene and –acetylide chemistry.

Experimental

General conditions

All reactions were carried out under dry, high-purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled and degassed before use. Elemental analyses were performed by the Canadian Microanalytical Service. Thin-layer chromatography was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation

IR: Perkin-Elmer 1700X FT-IR; 683 double beam, NaCl optics. NMR: Gemini 200 (^{1}H at 199.975 MHz, ^{13}C at 50.289 MHz); Bruker ACP300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz). FAB mass spectrum: VG ZAB 2HF (3-nitrobenzyl alcohol as matrix, exciting gas Ar, gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Starting materials

The compound $RuCl_3{\cdot}xH_2O$ (Johnson Matthey) was used as received. Chemical reagents were laboratory grade and used as received. 1,2,3,4,5-Pentamethylcyclopentadiene was prepared according to the literature procedure;[44] $[RuCl(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **1**[45,46] was obtained by a method similar to that used for the C_5H_5 analogue, as described below.

Preparations

$[RuCl(PPh_3)_2(\eta\text{-}C_5Me_5)]$ 1. The compound $RuCl_3{\cdot}xH_2O$ (500 mg, 2.41 mmol) and C_5Me_5H (655 mg, 4.82 mmol) were dissolved in EtOH (30 cm^3) and heated under reflux for 90 min, after which a solution of PPh_3 (2.525 g, 9.64 mmol) and NaOEt (46 mg of Na in 2 cm^3 of EtOH) in EtOH (40 cm^3) was added dropwise. The solution was then refluxed for 18 h. The orange-yellow precipitate was collected and washed with EtOH (2 × 5 cm^3) and hexane (2 × 5 cm^3) to give $[RuCl(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **1** (1.28 g, 70%), m.p. 270 °C (decomp.).

$[Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ 2. To a suspension of complex **1** (500 mg, 0.628 mmol) in EtOH (60 cm^3) was added phenylacetylene (100 mg, excess) and the mixture refluxed for 2 h, turning brown. At room temperature Na (60 mg, 2.6 mmol) was added, giving a yellow precipitate. The product was collected and washed with cold EtOH and pentane to give yellow $[Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **2** (205 mg, 38%). Recrystallisation (benzene–pentane) gave yellow crystals suitable for X-ray studies.

$[RuCl(C{=}CHPh)(PPh_3)(\eta\text{-}C_5Me_5)]$ 3. Complex **1** (100 mg, 0.126 mmol) and phenylacetylene (15 mg, 0.126 mmol) were dissolved in benzene (30 cm^3). The reaction mixture was refluxed for 30 min, during which time it became red. After removal of solvent, the residue was dissolved in CH_2Cl_2 and separated by preparative TLC to give three bands. The upper yellow band (R_f 0.8) contained $[Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **2** (5 mg, 5%). The second band (R_f 0.65) was recrystallised (CH_2Cl_2–MeOH) to give red crystals of $[RuCl(C{=}CHPh)(PPh_3)(\eta\text{-}C_5Me_5)]$ **3** (55 mg, 67%). The third pink band (R_f 0.4) contained an uncharacterised solid (5 mg).

$[RuCl(C{=}CHBu^t)(PPh_3)(\eta\text{-}C_5Me_5)]$ 4. A mixture of complex **1** (100 mg, 0.126 mmol) and 3,3-dimethylbut-1-yne (100 mg, 1.25 mmol) in benzene (30 cm^3) was heated under reflux for 30 min, the solution becoming deep red. Removal of solvent and separation of a CH_2Cl_2 extract of the residue by preparative TLC (acetone–hexane, 3:7) gave two bands. The upper band (R_f 0.70) was recrystallised (CH_2Cl_2–MeOH) to give red crystals of $[RuCl(C{=}CHBu^t)(PPh_3)(\eta\text{-}C_5Me_5)]$ **4** (60 mg, 78%). The second band (R_f 0.5) was not characterised.

$[RuCl(C{=}CHSiMe_3)(PPh_3)(\eta\text{-}C_5Me_5)]$ 5. A mixture of complex **1** (100 mg, 0.125 mmol) and HC_2SiMe_3 (0.02 g, 0.3 mmol) was heated in refluxing benzene (20 cm^3) for 30 min. Solvent was removed and the residue dissolved in CH_2Cl_2 and separated by preparative TLC (acetone–hexane, 1:4). An orange band (R_f 0.44) gave orange crystals (from hexane) of $[RuCl(C{=}CHSiMe_3)(PPh_3)(\eta\text{-}C_5Me_5)]$ **5** (41 mg, 52%).

$[RuCl(C{=}CHMe)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ 6. Prop-1-yne was passed into a solution of complex **1** (100 mg, 0.126 mmol) in benzene (30 cm^3); after 30 min the solution was golden-yellow. Solvent was removed and the residue dissolved in CH_2Cl_2 and separated (preparative TLC; acetone–hexane, 3:7). The top yellow band (R_f 0.44) contained $[RuCl(C{=}CHMe)(PPh_3)(\eta\text{-}C_5Me_5)]$ **6** (30 mg, 41.5%) which was recrystallised (CH_2Cl_2–MeOH) to give yellow needle-like crystals. The other band was not characterised.

$[Ru(C_2Bu^t)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ 7. (*a*) A mixture of 3,3-dimethylbut-1-yne (100 mg, excess) and complex **1** (500 mg, 0.62 mmol) in EtOH (60 cm^3) was refluxed for 2 h, turning brown. Addition of Na (60 mg, 0.26 mmol) at room temperature gave a yellow precipitate. The product was filtered off and washed with cold EtOH and pentane to give $[Ru(C_2Bu^t)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ **7** (156 mg, 29%). Recrystallisation (benzene–pentane) gave yellow crystals.

(*b*) Sodium methoxide [from Na (92 mg) in MeOH (2 cm^3)] was added to a warm solution containing complex **4** (100 mg, 0.162 mmol) and of PPh_3 (84.9 mg, 0.324 mmol) in MeOH (20 cm^3) when the red solution immediately turned yellow. Cooling in an ice-bath gave a yellow precipitate, which was filtered off to give **7** (100 mg, 73%).

$[Ru(C_2Ph)(CO)(PPh_3)_2(\eta\text{-}C_5Me_5)]$ 8. Carbon monoxide was passed through a solution of complex **3** (100 mg, 0.157 mmol) in MeOH (20 cm^3) for 10 min, after which an excess of NaOMe [from Na (0.092 g) in MeOH (2 cm^3)] was added, resulting in a change from red to yellow. Solvent was removed and the residue chromatographed. The upper yellow band (R_f 0.7) contained yellow $[Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5Me_5)]$ **8** (45 mg, 46%).

[Ru(C_2Bu^t)(CO)(PPh_3)$_2$(η-C_5Me_5)] 9. (*a*) *Using* $AgPF_6$, CO *and* NaOMe. Carbon monoxide was passed into a solution of complex **4** (100 mg, 0.162 mmol) in MeCN (30 cm^3) for 10 min; $AgPF_6$ (41 mg, 0.126 mmol) was then added. Over 3.5 h the solution changed from red through apricot to yellow and contained a white precipitate (AgCl). After filtration, deprotonation with NaOMe [from Na (40 mg) in MeOH (4 cm^3)] gave a dark orange solution. Solvent was removed and the residue separated by preparative TLC (acetone–hexane, 3:7). The upper band (R_f 0.8) was recrystallised (CH_2Cl_2–MeOH) to give fine yellow crystals of [Ru(C_2Bu^t)(CO)(PPh_3)(η-C_5Me_5)] **9** (54 mg, 54%). The lower band ($R_f = 0.55$) was orange and uncharacterised.

(*b*) *Deprotonation with* NaOMe *in the presence of* CO. A solution of complex **4** (100 mg, 0.16 mmol) in MeOH (20 cm^3) was treated with CO as above. After 10 min, NaOMe [excess, from Na (0.92 g) in MeOH (2 cm^3)] was added. On warming to ≈50 °C the solution became yellow. Work-up as above gave a yellow band (R_f 0.8) containing [Ru(C_2Bu^t)(CO)(PPh_3)(η-C_5Me_5)] **9** (40 mg, 41%).

[Ru(C_2Bu^t)(PPh_3){$P(OMe)_3$}(η-C_5Me_5)] 10. An excess of NaOMe was added to a mixture of complex **4** (100 mg, 0.162 mmol) and of trimethyl phosphite (19.8 mg, 0.162 mmol) in MeOH (20 cm^3). Work-up of the resulting yellow solution by preparative TLC (acetone–hexane 3:7) gave a major yellow band (R_f 0.85) which afforded [Ru(C_2Bu^t)(PPh_3){$P(OMe)_3$}-(η-C_5Me_5)] **10** (70 mg, 61%) as a yellow solid.

[Ru(C_2Bu^t)($AsPh_3$)(PPh_3)(η-C_5Me_5)] 11. Orange crystals (from CH_2Cl_2–MeOH) of [Ru(C_2Bu^t)($AsPh_3$)(PPh_3)(η-C_5Me_5)] **11** (55 mg, 40%) were obtained from complex **4** (100 mg, 0.162 mmol) and $AsPh_3$ (50 mg, 0.162 mmol) in MeOH (10 cm^3) after treatment with an excess of NaOMe and work-up as above.

[Ru(C_2Bu^t)(dppm)(η-C_5Me_5)] 12. An excess of NaOMe was added to a mixture of complex **4** (100 mg, 0.162 mmol) and dppm (24.5 mg, 0.324 mmol) in warm MeOH (20 cm^3). The red solution immediately turned yellow; the precipitate which separated on cooling was recrystallised (CH_2Cl_2–MeOH) to give yellow crystals of [Ru(C_2Bu^t)(dppm)(η-C_5Me_5)] **12** (150 mg, 95%).

[Ru(C_2Bu^t)(PPh_3)(dppe-*P*)(η-C_5Me_5)] 13. This complex was prepared in a similar manner to **12** above, from **4** (100 mg, 0.162 mmol) and dppe (124 mg, 0.324 mmol) in MeOH (20 cm^3) with an excess of NaOMe. The yellow precipitate was recrystallised (CH_2Cl_2–MeOH) to give [Ru(C_2Bu^t)(PPh_3)(dppe-*P*)(η-C_5Me_5)] **13** (142 mg, 89%).

[Ru(C_2Bu^t)(PPh_3)(dppa)(η-C_5Me_5)] 14. Similarly, complex **4** (100 mg, 0.162 mmol) and dppa (64 mg, 0.162 mmol) in warm MeOH (20 cm^3), after treatment with an excess of NaOMe, afforded [Ru(C_2Bu^t)(PPh_3)(dppa-*P*)(η-C_5Me_5)] **14** (120 mg, 76%).

[Ru(C_2Ph)(PPh_3)(dppm-*P*)(η-C_5Me_5)] 15. Similarly, a mixture of complex **3** (100 mg, 0.157 mmol) and dppm (60.4 mg, 0.157 mmol) in warm MeOH (20 cm^3) was treated with an excess of NaOMe to give, after work-up and recrystallisation, yellow [Ru(C_2Ph)(PPh_3)(dppm-*P*)(η-C_5Me_5)] **15** (116 mg, 75%).

[Ru(C_2Bu^t)(dppen)(η-C_5Me_5)] 16. The reaction between complex **4** (100 mg, 0.162 mmol) and dppen (64.2 mg, 0.162 mmol) in MeOH (20 cm^3) was carried out in similar fashion. An excess of NaOMe was added to the warm solution, whereupon a yellow precipitate separated. After work-up, [Ru(C_2Bu^t)(dppen)-(η-C_5Me_5)] **16** (110 mg, 94%) was obtained.

[Ru(C_2Bu^t)(η-C_2H_4)(PPh_3)(η-C_5Me_5)] 17. Ethene was passed into a solution of complex **4** (100 mg, 0.162 mmol) in MeOH (20 cm^3) for 20 min. To the red solution an excess of NaOMe (as above) was added and the mixture was warmed on a water-bath. Solvent was removed from the yellow solution until a precipitate formed. After cooling and filtration, recrystallisation (CH_2Cl_2–MeOH) gave yellow crystals of [Ru(C_2Bu^t)(η-C_2H_4)-(PPh_3)(η-C_5Me_5)] **17** (50 mg, 50%).

[Ru(C_2Ph)(O_2)(PPh_3)(η-C_5Me_5)] 18. Oxygen was passed through a solution of complex **3** (100 mg, 0.157 mmol) in MeOH (20 cm^3) for 10 min. Addition of an excess of NaOMe resulted in a change to red-orange. The orange precipitate which separated on cooling was filtered off and recrystallised (C_6H_6–pentane) to give red crystals of [Ru(C_2Ph)(O_2)(PPh_3)-(η-C_5Me_5)] **18** (76 mg, 77%).

[Ru(C_2Bu^t)(S_2)(PPh_3)(η-C_5Me_5)] 19. A mixture of complex **4** (100 mg, 0.162 mmol) and S_8 (10.4 mg, 0.324 mmol) in warm MeOH (20 cm^3) was treated with an excess of NaOMe, when the solution changed to grey-green. Work-up by preparative TLC gave a grey-green band (R_f 0.8) containing [Ru(C_2Bu^t)-(S_2)(PPh_3)(η-C_5Me_5)] **19** (64.1 mg, 62%), which formed khaki-green crystals from CH_2Cl_2–MeOH.

[Ru($S_2CC_2Bu^t$)(PPh_3)(η-C_5Me_5)] 20. Similarly, complex **4** (100 mg, 0.162 mmol) and carbon disulfide (24.4 mg, 0.324 mmol) dissolved in MeOH (20 cm^3), with an excess of NaOMe, gave an olive-green precipitate of [Ru($S_2CC_2Bu^t$)(PPh_3)(η-C_5Me_5)] **20** (51 mg, 48%) on cooling, which was recrystallised from CH_2Cl_2–MeOH as the 0.5MeOH solvate.

Crystallography

Unique room-temperature diffractometer data sets were recorded (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T \approx 295$ K) and used in the full-matrix least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameter forms were refined; (x, y, z, $U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ at convergence are given, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system[47] implemented by S. R. Hall. Data are presented in Table 4.

Abnormal features/variations in procedure. *Complex* **3**. Residuals are quoted for the preferred chirality.

Complex **9**. (x, y, z, $U_{iso})_H$ were refined; the compound is isomorphous with **17** and was refined in the same cell and coordinate setting.

Complex **12**. Crystals were twinned and the structure solved and refined on one deconvoluted component of the reciprocal lattice of the specimen used; nevertheless, overlap between the two components proved a serious problem and one block of *ca*. 500 reflections was refined with a separate scale factor. The lattice is pseudo-symmetric.

Complex **16**. The *tert*-butyl group was rotationally disordered, component populations refining to x, $1 - x$, with $x = 0.85(1)$; isotropic thermal parameter forms were refined for the minor component.

Complex **17**. See above. Compounds **3** and **17** have been reported briefly on a previous occasion; in the present record atom numbering has been adjusted to conform with the common scheme used.

Complex **18**. (x, y, z, $U_{iso})_H$ were refined.

Complex **20**. Data were weak and limited in scope, the consequent refinement difficulties being compounded by rotational disorder in the *tert*-butyl group (site occupancies set at 0.5 after

Table 4 Crystal data and refinement details for the complexes

	2	**3**	**5**	**9**	**12**	**13**	**16**	**17**	**18**	**19**	**20**
Formula	$C_{54}H_{50}P_2Ru$	$C_{36}H_{36}ClPRu$	$C_{33}H_{40}ClPRuSi$	$C_{35}H_{39}OPRu$	$C_{41}H_{46}P_2Ru$	$C_{60}H_{63}P_3Ru$	$C_{42}H_{46}P_2Ru$	$C_{36}H_{43}PRu$	$C_{36}H_{35}O_2PRu$	$C_{34}H_{39}PRuS_2$	$C_{35}H_{39}PRuS_2$
M	862.0	636.2	632.2	607.7	701.8	978.2	713.9	607.8	631.7	643.9	655.9
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
a/Å	17.696(3)	20.473(8)	18.43(1)	9.573(3)	19.352(5)	18.048(8)	22.443(5)	9.308(2)	8.521(6)	18.301(9)	22.75(1)
b/Å	11.937(3)	16.343(6)	14.99(1)	16.706(8)	10.138(4)	12.645(4)	10.089(5)	16.89(2)	17.987(4)	10.371(4)	12.886(3)
c/Å	21.025(4)	9.209(6)	12.526(4)	20.045(7)	19.365(6)	11.768(5)	35.166(2)	20.20(2)	20.003(6)	9.464(4)	25.37(1)
α/°	—	—	69.41(5)	—	—	77.68(3)	—	—	—	116.31(3)	—
β/°	106.44(2)	—	88.86(4)	106.63(3)	108.40(2)	85.14(4)	110.92(3)	104.75(6)	105.53(4)	95.04(3)	111.68(4)
γ/°	—	—	83.70(6)	—	—	80.34(3)	—	—	—	98.66(4)	—
U/Å^3	4260	3081	3221	3072	3605	2583	7437	3072	2954	1567	6913
Z	4	4	4	4	4	2	8	4	4	2	8
D_c/g cm^{-3}	1.34	1.37	1.30	1.31	1.29	1.26	1.27	1.31	1.42	1.36	1.26
F(000)	1792	1312	1312	1264	1464	1024	2976	1272	1304	668	2720
Crystal size/mm	0.40 × 0.13 × 0.23	0.08 × 0.17 × 0.25	0.04 × 0.43 × 0.17	0.32 × 0.65 × 0.45	0.40 × 0.54 × 0.32	0.07 × 0.15 × 0.32	0.12 × 0.45 × 0.40	0.16 × 0.20 × 0.13	0.56 × 0.20 × 0.13	0.45 × 0.16 × 0.45	0.25 × 0.08 × 0.20
*A** (minimum, maximum)	1.07, 1.12	1.05, 1.09	1.08, 1.13	1.15, 1.21	1.16, 1.31	1.03, 1.06	1.05, 1.16	1.06, 1.10	1.08, 1.17	1.21, 1.40	1.05, 1.17
μ/cm^{-1}	4.8	6.7	6.8	5.9	5.5	4.3	5.3	5.8	6.2	7.1	6.4
$2\theta_{max}$/°	50	55	50	60	55	50	50	50	60	50	50
N	7486	3871	11.267	7045	8685	9046	6307	5381	8475	5505	6101
N_o	5324	2329	4585	4969	5548	4713	3400	3126	4974	4673	1652
R	0.037	0.059	0.068	0.036	0.051	0.058	0.047	0.045	0.040	0.051	0.095
R′	0.039	0.057	0.065	0.037	0.055	0.056	0.043	0.042	0.038	0.059	0.113

trial refinement). Anisotropic thermal parameter forms were refined for Ru, P, S only.

CCDC reference number 186/954.

See http://www.rsc.org/suppdata/dt/1998/1793/ for crystallographic files for complex **18** in .cif format.

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