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# The first co-ordinatively unsaturated Group 8 allenylidene complexes: insights into Grubbs' *vs.* Dixneuf–Fürstner olefin metathesis catalysts

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The reactions of $[MCl_2(PPh_3)_3]$ with $HC{\equiv}CCPh_2OH$ provided $[MCl_2(=C=C=CPh_2)(PPh_3)_2]$ (M = Ru **1a** or Os **1b**) the first examples of co-ordinatively unsaturated allenylidene complexes of Group 8 metals. The phosphine ligands of **1a** are labile and readily replaced by $PCy_3$ to give $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ **1c**. Heating **1a** with $NaPF_6$ in chloroform gave the known bimetallic salt $[Ru_2(\mu\text{-}Cl)_3(=C=C=CPh_2)_2(PPh_3)_4]PF_6$ **2**·$PF_6$. The reaction of **1a** with carbon monoxide provided $[RuCl_2(=C=C=Ph_2)(CO)(PPh_3)_2]$ **3** which may also be prepared from $[RuCl_2(CO)(dmf)(PPh_3)_2]$ and $HC{\equiv}CCPh_2OH$. The first macrocycle coligated allenylidene complex $[RuCl(=C=C=CPh_2)(PPh_3)([9]aneS_3)]Cl$ **4**·Cl ([9]aneS$_3$ = 1,4,7-trithiacyclononane) was obtained from the reaction of **1a** with [9]aneS$_3$. Alternatively, **4**·$PF_6$ is also obtained by treating $[RuCl_2(PPh_3)([9]aneS_3)]$ sequentially with $NaPF_6$ in acetonitrile followed by $HC{\equiv}CCPh_2OH$. The reaction of **1a** with dppe and $NaPF_6$ yielded the known salt *trans*-$[RuCl(=C=C=CPh_2)(dppe)_2]PF_6$ **5**·$PF_6$. The complex $[RuCl(=C=C=CPh_2)(PCy_3)\{HB(pz)_3\}]$ **6** (pz = pyrazol-1-yl) was obtained from the reaction of **1c** with K[HB(pz)$_3$], whilst the related benzylidene complex $[RuCl(=CHPh)(PCy_3)\{HB(pz)_3\}]$ **7** was obtained similarly from $[RuCl_2(=CHPh)(PCy_3)_2]$ and K[HB(pz)$_3$]. Heating $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-cym})_2]$ (cym = $^iPrC_6H_4Me$-4) with $PCy_3$ and $HC{\equiv}CCPh_2OH$ in refluxing benzene provided a mixture of **1c** and the bimetallic complex $[Ru_2(\mu\text{-}Cl_2)Cl_2(=C=C=CPh_2)(\eta\text{-cym})]$ **8** and other unidentified products. The complex **8** may however be obtained quantitatively from the reaction of **1c** with $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-cym})_2]$. These results suggest that the active species in ring-closure olefin metathesis processes mediated by the allenylidene pre-catalyst $[RuCl(=C=C=CPh_2)(PCy_3)(\eta\text{-cym})]^+$ in non-polar arene solvents may be allenylidene analogues of the Grubbs' alkene metathesis catalyst, *viz.* **1c** and **8**.

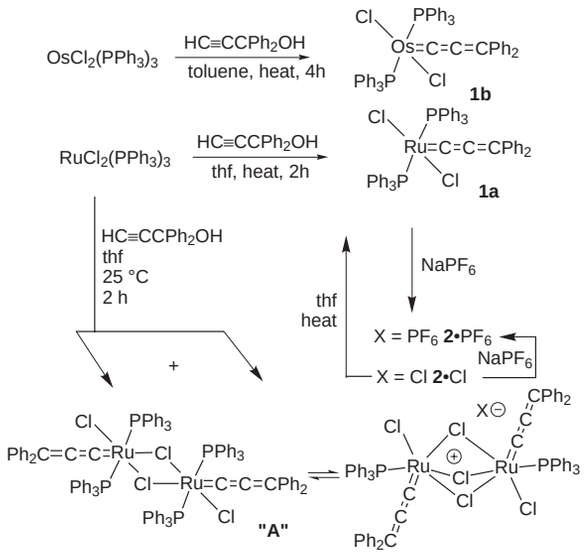
## Introduction

Reviews on the rapidly emerging chemistry of allenylidene complexes of Groups 8[1] and 9[2] reveal noteworthy points of distinction. Most significantly, the rich chemistry of Group 9 allenylidenes developed by Werner centres primarily on neutral co-ordinatively unsaturated examples, typically of the electronically advantageous $d^8$-$ML_4$ square planar geometry. In marked contrast, since the isolation by Selegue[3] of the archetypal complex $[Ru(=C=C=CPh_2)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ all Group 8 examples have been co-ordinatively saturated, in the main cationic,[1b] and of the ubiquitous pseudo-octahedral $d^6$-$ML_6$ geometry. This reflects the more strict adherence to the 18-electron rule by complexes of low-valent metals on moving to the left across the transition series. However, the advent and unprecedented utility of Grubbs' catalysts $[RuCl_2(=CHR)(PR'_3)_2]$ (R = CH=CPh$_2$ or Ph; R′ = Ph or Cy)[4] and the highly successful application of bulky phosphines ($P^iPr_3$, $PCy_3$, $PMeBu^t_2$) within Group 8[5] have made $d^6$-$ML_5$ geometries an increasingly prevalent feature of the organometallic chemistry of ruthenium and osmium. Herein we report the synthesis of the first examples of co-ordinatively unsaturated allenylidene complexes of ruthenium and osmium, *viz*. $[MCl_2(=C=C=CPh_2)(PPh_3)_2]$ (M = Ru or Os), $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ and $[Ru_2(\mu\text{-}Cl)_2Cl_2(=C=C=CPh_2)(PCy_3)(\eta\text{-}MeC_6H_4{}^iPr\text{-}4)]$. These 16-electron complexes are conveniently accessible from commercially available starting materials and serve as versatile precursors to a range of other allenylidene complexes *via* facile ligand addition and/or exchange reactions.

## Results and discussion

The vinylidene complex $[RuCl_2(=C=CHCMe_3)(PPh_3)_2]$ has been shown to result from the reaction of $HC{\equiv}C^tBu$ with $[RuCl_2(PPh_3)_3]$.[6] A related 'parent' vinylidene complex $[RuCl_2(=C=CH_2)(PCy_3)_2]$ was subsequently shown by Grubbs to be accessible *via* the reaction of $[RuCl_2(=CHPh)(PCy_3)_2]$ with allene[4] whilst Katayama and Ozawa[7] showed that this class of complex was capable of catalysing ring-opening metathesis polymerisation of strained bicyclo-olefins. We were prompted by the reports of this and Grubbs' alkylidene analogues[4] to attempt the synthesis of related allenylidene complexes $[RuCl_2(=C=C=CPh_2)(PR_3)_2]$ (R = Ph or Cy). Grubbs' alkylidene complexes ultimately appear to lose their catalytic activity in metathesis processes *via* bimolecular decomposition processes involving alkylidene coupling. In the case of our proposed allenylidene target complexes, the analogous formation and elimination of a hexapentaene appeared unlikely, given that stable binuclear bis(allenylidene) complexes have been reported.[8]

The majority of late transition metal allenylidene complexes[1,2] arise from variants of Selegue's ground-breaking propynol dehydration approach.[3] Fortunately, this strategy has also proven successful here. The reaction of $[RuCl_2(PPh_3)_3]$ with $HC{\equiv}CCPh_2OH$ and $NaPF_6$ in dichloromethane has been previously reported to provide the bimetallic complex $[Ru_2(\mu\text{-}Cl)_3(=C=C=CPh_2)_2(PPh_3)_4]PF_6$. Although no intermediates were identified, it was suggested that the complex $[RuCl_2(=C=C=CPh_2)(PPh_3)_2]$ was a plausible intermediate.[8] We find that when $[RuCl_2(PPh_3)_3]$ is treated with an excess of $HC{\equiv}CCPh_2OH$ in refluxing thf (2 h) the deep red-brown complex $[RuCl_2(=C=C=CPh_2)(PPh_3)_2]$ **1a** may be obtained in high yield. In a similar manner the osmium analogue $[OsCl_2(=C=C=CPh_2)(PPh_3)_2]$ **1b** may be obtained in 98% yield from $[OsCl_2(PPh_3)_3]$, although refluxing toluene is the solvent of choice (Scheme 1). Both complexes **1a** and **1b** may also be recrys-




**Scheme 1**

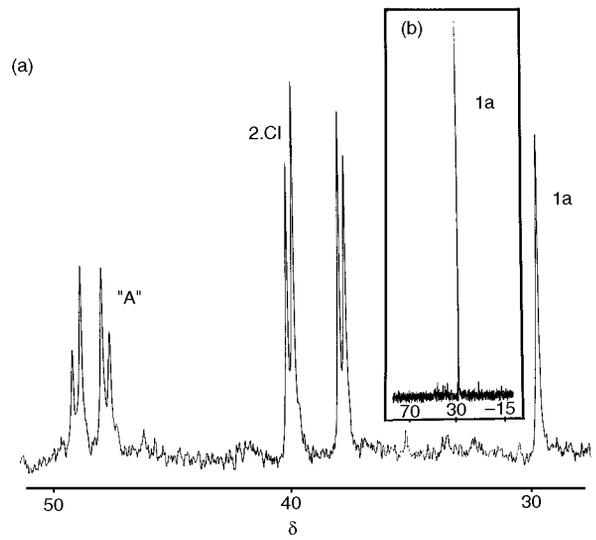



**Fig. 1** $^{31}$P NMR spectra of the products of the reaction of $[RuCl_2(PPh_3)_3]$ with $HC{\equiv}CCPh_2OH$ in thf (a) at room temperature; (b) under reflux.

tallised from mixtures of dichloromethane and methanol, indicating that they are comparatively stable with respect to nucleophilic attack by alcohols. This may be attributed to the neutrality of the complexes which naturally deactivates the π-acidic allenylidene towards nucleophilic attack, in contrast to many cationic ruthenium allenylidene complexes.[1a]

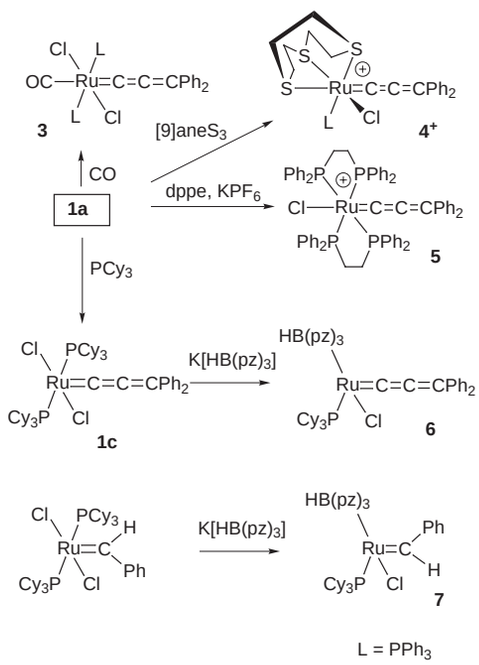
Spectroscopic data for the two complexes are broadly comparable and confirm the mononuclear formulation and stereochemistry. Of particular note are the following observations. (i) Whilst **1b** displays an abundant molecular ion (confirmed by isotopic simulation) in addition to a minor fragment ion due to halide ionisation, the molecular ion for **1a** is very weak relative to the $[M - Cl]^+$ peak. (ii) Low field carbon-13 nuclear magnetic resonances for the metal bound allenylidene carbon nuclei [**1a**, $\delta$ 301.2; **1b**, $\delta$ 266.0] are observed as triplets due to *cis* coupling to two chemically equivalent and mutually *trans* phosphorus nuclei. Whilst this is also consistent with a square-based pyramid with apical allenylidene and *cis*-basal phosphines, such a geometry is highly unlikely on steric grounds, and may also be discounted by the virtual triplet multiplicity of the phenyl resonances for the phosphine substituents. (iii) Characteristic infrared absorptions due to the allenylidene groups are observed for both complexes at 1939 $cm^{-1}$ in solution ($CH_2Cl_2$). The solid state infrared spectra of samples of **1a** crystallised under various conditions reveal three bands of varying intensities in this region (Nujol: 1968, 1929, 1902 $cm^{-1}$) however all such samples on dissolution in dichloromethane give rise to a single absorption (1939 $cm^{-1}$) suggesting that solid state effects are responsible for the splitting observed. This is perhaps not surprising, given that the allenylidene ligand protrudes considerably from the *trans*-$Ru(PPh_3)_2$ double cone, exposing it to packing effects. As noted above, the majority of known ruthenium allenylidene complexes are cationic and are characterised by very intense $\nu$(C=C=C) infrared absorptions. With both neutral and related cationic examples (see below) in hand it becomes clear that there is a very substantial loss of relative intensity for this absorption in neutral complexes, compromising somewhat its diagnostic utility. We have also observed similar though less dramatic behaviour for the complexes $[Ru(=C=C=CPh_2)(PPh_3)_2\{HB(pz)_3\}]^+$ (pz = pyrazol-1-yl) and $[RuCl(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]$.[1b]

The gross mechanism by which complex **1a** forms, *i.e.* metal-mediated propynol dehydration, has considerable precedent.[1,2] The more detailed pathway by which the mononuclear complex **1a** is obtained under thermal conditions, whilst the binuclear salt $[Ru_2(\mu\text{-}Cl)_3(=C=C=CPh_2)_2(PPh_3)_4]PF_6$ **2**·$PF_6$ is reported to form under ambient conditions, calls for comment. We find that if the reaction of $[RuCl_2(PPh_3)_3]$ and $HC{\equiv}CCPh_2OH$ is carried out at room temperature in thf (2 h) three species may be observed [Fig. 1(a), Scheme 1]: small amounts (25%) of **1a** are observed in addition to two compounds which give rise to AB-quartet patterns in the $^{31}P\text{-}\{^1H\}$ NMR spectrum. The first of these corresponds to the chloride salt $[Ru_2(\mu\text{-}Cl)_3(=C=C=CPh_2)_2(PPh_3)_4]Cl$ **2**·Cl [50%: $\delta$ 40.0, 37.8; $J(P_AP_B) = 26.8$ Hz], with the small variation in chemical shift relative to **2**·$PF_6$ [$\delta$ 42.2, 40.8; $J(P_AP_B) = 30$ Hz][8] being attributed to ion-pairing effects. This could be confirmed by anion metathesis with $NaPF_6$ or $KPF_6$. The second compound **A** also giving rise to an AB system [$\delta$ 49.0, 47.7; $J(P_AP_B) = 36.9$ Hz] and formed in 25% yield has yet to be identified unambiguously but possibly also corresponds to a binuclear complex which is however neutral, possessing only two halide bridges {*cf.* $[Ru_2(\mu\text{-}Cl)_2Cl_2(CS)_2(PPh_3)_4]$, see below}. Thus, the presumed intermediacy of **1a** in the formation of **2**·$PF_6$ is not quite as straightforward as might have been initially supposed. Heating isolated **1a** with $KPF_6$ in chloroform provides **2**·$PF_6$, however if $[NH_4][PF_6]$ is employed as the anion source a complex mixture of unidentified products results, presumably *via* allenylidene aminolysis. Furthermore, a solution of **1a** in dichloromethane or chloroform stirred for 2 weeks at room temperature undergoes slow and only partial reversion (*ca.* 50%) to a mixture of **2**·Cl and the unknown binuclear complex **A**. The formation of KCl presumably contributes to the driving force for the formation of $\mathbf{2}^+$ in the presence of $KPF_6$. The reaction of $[RuCl_2(PPh_3)_3]$ and $HC{\equiv}CCMe_2OH$ was also briefly investigated. Under identical conditions to those for the synthesis of **1a** (refluxing thf, 3 h) six inseparable products were observed by $^{31}P$ NMR spectroscopy: the two major products corresponded to analogues of the binuclear salt **2**·Cl [$\delta$ 39.7, 41.9; $J(P_AP_B) = 25.1$] and the neutral binuclear complex **A** [$\delta$ 47.5, 49.8; $J(P_AP_B) = 37.1$ Hz]. The remaining four singlet resonances all occurred sufficiently close to that for **1a** such that unambiguous assignment could not be made. Thus, although the reaction appears to proceed in a similar manner, optimum conditions for the isolation of single products were not established.

It should be noted that parallels exist in the behaviour of formally isoelectronic thiocarbonyl complexes: whilst heating $[OsCl_2(PPh_3)_3]$ with carbon disulfide and an excess of phosphine provides $[OsCl_2(CS)(PPh_3)_3]$ quantitatively,[9] the analogous chemistry based on ruthenium is considerably more complicated by the facile formation of binuclear species with two or three halide bridges.[10] Indeed it is only when thermally forcing

conditions are employed (refluxing xylene) that the mononuclear complex $[RuCl_2(CS)(OH_2)(PPh_3)_2]$ is obtained in useful amounts.[11] Under a variety of milder conditions however, the complexes $[Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_3]$, $[Ru_2(\mu\text{-}Cl)_3(CS)_2(PPh_3)_4]^+$ (analogous to $\mathbf{2}^+$) and $[Ru_2(\mu\text{-}Cl)_2Cl_2(CS)_2(PPh_3)_4]$ could each be isolated. The first of these was presumed to arise from the trapping of transiently formed $[RuCl_2(CS)(PPh_3)_2]$ (isoelectronic with **1a**) by an excess of $[RuCl_2(PPh_3)_3]$. The last of these, $[Ru_2(\mu\text{-}Cl)_2Cl_2(CS)_2(PPh_3)_4]$, is the most likely analogue of complex **A**, which was, however, insufficiently soluble for comparative $^{31}P$ NMR data to be available.[10]

The complex **1a** proves to be a highly versatile synthetic entry point into a range of allenylidene complexes of ruthenium(II) (Scheme 2) by virtue of (i) its co-ordinative unsaturation, (ii)




**Scheme 2**

the lability of one halide and (iii) the lability of one or both phosphine ligands. Carbonylation under very mild conditions ($CH_2Cl_2$, 1 atm) provides the new complex all-*trans*-$[RuCl_2(=C=C=CPh_2)(CO)(PPh_3)_2]$ **3**. Alternatively, we also find that complex **3** may be prepared directly *via* the reaction of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with $HC{\equiv}CCPh_2OH$ in dichloromethane at room temperature. The allenylidene-associated absorption in the infrared spectrum of **3** appears at 1953 $cm^{-1}$ ($CH_2Cl_2$) and is considerably more intense than that of the precursor, although it is highly likely that there is a degree of coupling between the $\nu$(C=C=C) and $\nu$(CO) modes [$\nu$(CO) 2007 $cm^{-1}$]. The increase in intensity may also arise from co-ordination *trans* to a strong π acid (CO). The allenylidene ligand gives rise to three resonances of note in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at $\delta$ 310.7, 198.0 and 163.4 corresponding to the α, β and γ carbons of the allenylidene spine, the former showing coupling to the two *cis* phosphorus nuclei (13.5 Hz). The gross composition was confirmed by the appearance of a molecular ion in the FAB mass spectrum in addition to identifiable fragmentations.

The first example of a macrocycle co-ligated allenylidene complex $[RuCl(=C=C=CPh_2)(PPh_3)([9]aneS_3)]Cl$ **4**·Cl results from the reaction of **1a** with 1,4,7-trithiacyclononane ([9]aneS$_3$). We also find that this chiral complex may be obtained in two steps from the reaction of $[RuCl_2(PPh_3)([9]aneS_3)]$ [12,13] with $KPF_6$ (MeOH) followed by $HC{\equiv}CCPh_2OH$ to provide **4**·$PF_6$. As expected, the chirality at ruthenium results in a complex $^1H$ NMR spectrum due to the 12 different chemical environments of the macrocycle protons.[14] The $^{31}P\text{-}\{^1H\}$ NMR spectrum however consists of a singlet resonance at $\delta$ 34.9 in addition to the characteristic high field $PF_6$ heptet. The most abundant (base) peak in the FAB mass spectrum corresponds to the molecular ion, and is accompanied by assignable fragmentations involving allenylidene dissociation and ethylene eliminations from the macrocycle. The latter is a common feature of the FAB-mass spectra of [9]aneS$_3$ complexes. The reaction of **1a** with dppe and $KPF_6$ in a refluxing 1:1 mixture of tetrahydrofuran and methanol provides the salt $[RuCl(=C=C=CPh_2)(dppe)_2]PF_6$ **5**·$PF_6$. This salt was previously obtained by heating **2**·$PF_6$ with dppe in toluene for 12 h.[8] The formation of **5**·$PF_6$ from the more reactive **1a** is however complete within 4 h at lower temperatures.

Amongst the variants of Grubbs' catalyst, those with bulky $PCy_3$ coligands are found to be the most effective.[4] Accordingly, the reaction of complex **1a** with $PCy_3$ was investigated and found cleanly to provide $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ **1c** in high yield at room temperature. Although the preparation of **1c** must be carried out under anaerobic conditions, once formed the complex appears stable towards aerial oxidation both in solution and in the solid state. The FAB mass spectrum features abundant peaks due to the molecular ion (10%), chloride ionisation (10%) and dissociation of one phosphine (6%). A low-field carbon-13 resonance is observed at $\delta$ 293.6 showing coupling to the two phosphorus nuclei, although this is marginally smaller (7.5 Hz) than that observed for the corresponding resonances of the $PPh_3$ derivatives **1a**, **1b** and **3** (10.8–13.5 Hz).

We have recently described the synthesis of the allenylidene complexes $[Ru(=C=C=CPh_2)(PPh_3)_2\{HB(pz)_3\}]PF_6$ and $[RuCl(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]$ *via* the reactions of $[RuCl(PPh_3)_2\{HB(pz)_3\}]$ [15] with $HC{\equiv}CCPh_2OH$ in the presence or absence, respectively, of $AgPF_6$.[1b] Surprisingly, treating **1a** with $K[HB(pz)_3]$ does not appear ($^{31}P$ NMR) to provide either of these allenylidene complexes. In contrast, the reaction of **1c** with $K[HB(pz)_3]$ gives the complex $[RuCl(=C=C=CPh_2)(PCy_3)\{HB(pz)_3\}]$ **6** in 83% yield. Although a complex reaction does ensue between $[RuCl(=C=C=CPh_2)(PPh_3)\{HB(pz)_3\}]$ and $PCy_3$, **6** which might be anticipated *via* simple phosphine exchange could not be identified ($^{31}P$ NMR) amongst the plethora of products. The related benzylidene complex $[RuCl(=CHPh)(PCy_3)\{HB(pz)_3\}]$ **7** could also be prepared *via* the reaction of $[RuCl_2(=CHPh)(PCy_3)_2]$ with $K[HB(pz)_3]$.† Most notable amongst the characteristic spectroscopic data for **7** are the low field NMR resonances due to the alkylidene proton [$\delta$ 20.06; $J$(PH) = 9.3 Hz] and carbon nuclei [$\delta$ 333.8; $J$(PC) = 14.3 Hz]. The complexes **6** and **7** therefore complement the growing range of '$C_1$' π-acidic ligands multiply bonded to the 'RuCl(PR$_3$){HB(pz)$_3$}' fragment in the complexes $[RuCl(CA)(PR_3)\{HB(pz)_3\}]$ (R = Ph or Cy; CA = CO,[16,17] CS,[17] $CNCMe_3$,[18] C=CHPh[19] or $C{=}C{=}CPh_2$ [1b]).

Dixneuf, Fürstner and co-workers[20] recently showed that an allenylidene salt of ruthenium $[RuCl(=C=C=CPh_2)(PCy_3)(\eta\text{-cym})]PF_6$ (η-cym = $MeC_6H_4{}^iPr$-4) could serve as a pre-catalyst for the ring-closure olefin metathesis of α,ω-dienes. Simultaneously Grubbs[21] showed that his catalysts could be further activated by treatment with $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-cym})_2]$ to provide $[Ru_2(\mu\text{-}Cl)_2Cl_2(=CHR)(PCy_3)(\eta\text{-cym})]$ and $[RuCl_2(PCy_3)(\eta\text{-cym})]$. This prompted us to question whether a complex of the form **1c** or (*in situ*) $[RuCl_2(=C=C=CPh_2)(PCy_3)]$ might be the active species arising from the Dixneuf–Fürstner pre-catalyst. Although arene dissociation could in principle generate the 12-electron species "$RuCl(=C=C=CPh_2)(PCy_3)^+$" (as suggested by recent photochemical studies[22]) this would be unlikely to be particularly long lived unless stabilised by reco-ordination of cymene or the arene solvent. Disproportionation *via* halide transfer could however in principle lead to species akin to Grubbs' binuclear alkylidene complexes, or altern-

† *Note added in proof:* During the processing of this manuscript, Grubbs reported the synthesis of **7** *via* an identical procedure.[26]

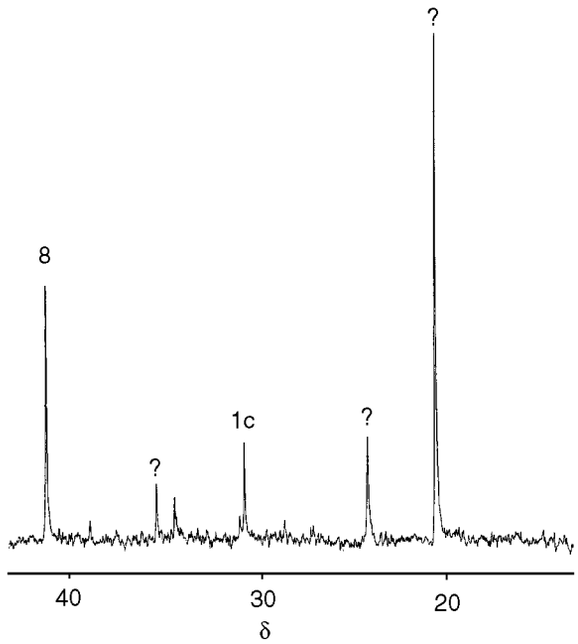
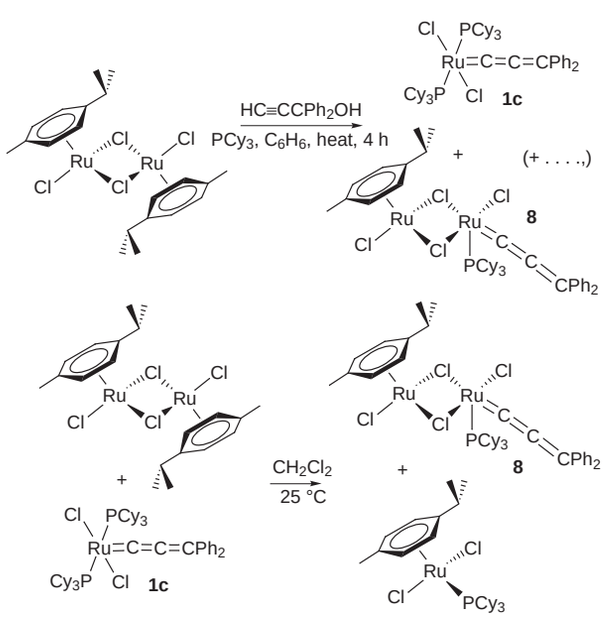



**Fig. 2** $^{31}$P NMR spectra of the products of the reaction of $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$ with $HC{\equiv}CCPh_2OH$ and $PCy_3$ in refluxing benzene.

atively the 14-electron species "$RuCl_2(=C=C=CPh_2)(PCy_3)$" directly observed in the FAB-MS studies above. These neutral species might be more likely to persist and dissolve in the non-polar arene solvent.

The reaction of $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$ with $HC{\equiv}CCPh_2OH$ and $PCy_3$ (stoichiometry 1 : 4 : 6) in refluxing benzene (4 h) was therefore investigated. Amongst the species present in the crude reaction mixture it was apparent ($^{31}$P NMR; Fig. 2) that complex **1c** does indeed form, however in only approximately 2–3% yield. Notably, no $[RuCl_2(PCy_3)(\eta\text{-}cym)]$ ($\delta$ 25.8) was detected. However, two other major products were observed with resonances at $\delta$ 41.1 and 20.3. The first of these was identified as the new binuclear complex $[Ru_2(\mu\text{-}Cl)_2Cl_2(=C=C=CPh_2)(PCy_3)(\eta\text{-}cym)]$ **8** following the unequivocal and high yield synthesis *via* the reaction of **1c** with $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$ (Scheme 3).




**Scheme 3**

Although this reaction was spectroscopically quantitative ($^{31}$P NMR), the complex **8** could only be obtained free from the side-product $[RuCl_2(PCy_3)(\eta\text{-}cym)]$ ($^{31}$P NMR: $\delta$ 25.9) in 73% isolated yield due to sacrificial losses incurred during separation. It also transpires that the phosphine of $[RuCl_2(PCy_3)(\eta\text{-}cym)]$ is sufficiently labile for it also to react with **1c** to provide **8**, however this reaction is considerably slower than that between **1c** and $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$. Furthermore, we find that the binuclear complex **8**, once formed, is stable under ambient conditions in the presence of an excess of $PCy_3$. The formulation of **8** follows from spectroscopic data and by analogy with the complex $[Ru_2(\mu\text{-}Cl)_2Cl_2(=CHPh)(PCy_3)(\eta\text{-}cym)]$ described by Dias and Grubbs.[21] Most notably the allenylidene ligand gives rise to a weak infrared absorption (KBr: 1945 $cm^{-1}$) and a low field doublet resonance [$\delta$ 310.4, $J$(PC) = 15.1 Hz] in the $^{13}$C-{$^1$H} NMR spectrum. The two resonances for the (diastereotopic) methyl constituents of the cymene $^i$Pr group indicate that the molecule does not possess any element of symmetry suggesting the stereochemistry depicted in Scheme 3. The $^{31}$-P{$^1$H} NMR peak at $\delta$ 41.2 is moved approximately 8.3 ppm to low field from the precursor, and a similar low field shift was observed for the conversion of $[RuCl_2(=CHPh)(PCy_3)_2]$ into $[Ru_2(\mu\text{-}Cl)_2Cl_2(=CHPh)(PCy_3)(\eta\text{-}cym)]$.[21] The gross formulation was also confirmed by FAB-mass spectrometry which revealed an intense molecular ion (14%) in addition to fragmentations due to loss of chloride (8%) and also cleavage of the '$RuCl_2(\eta\text{-}cym)$' group (33%), *i.e.* the presumed catalytically active species '$RuCl_2(=C=C=CPh_2)(PCy_3)$'. It is noteworthy in this context that very recently the gas phase alkene metathesis chemistry of the complex $[RuCl_2(=CHPh)(PCy_2C_2H_4NMe_3)]^+$ has been investigated through electrospray ionisation tandem MS experiments.[23]

## Conclusion

Co-ordinatively unsaturated allenylidene complexes of osmium and ruthenium, **1**, are both stable and easily accessible from commercially available starting materials. Their synthetic utility as precursors to a range of other allenylidene complexes of ruthenium has been demonstrated with the synthesis of 16 or 18 electron and mono- or bi-nuclear derivatives. One of these, the binuclear complex $[Ru_2(\mu\text{-}Cl)_2Cl_2(=C=C=CPh_2)(PCy_3)(\eta\text{-}cym)]$ **8**, has been shown also to result from the direct combination of $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$, $PCy_3$ and $HC{\equiv}CCPh_2OH$ under the conditions used for ring closure metathesis of α,ω-diolefins mediated by the Dixneuf–Fürstner pre-catalyst $[RuCl(=C=C=CPh_2)(PCy_3)(\eta\text{-}cym)]^+$. These observations lead us to contend that under these conditions (80 °C, non-polar arene solvent), the Dixneuf–Fürstner pre-catalyst may well provide allenylidene analogues of both class of Grubbs' catalyst, *viz.* **1c** and **8**. Although allenylidene analogues of *both* classes of complex are obtained under these conditions, the higher activity of Grubbs' binuclear catalysts relative to his monometallic precursors[21] suggests that **8** may be the more active catalyst in the Dixneuf–Fürstner system. In this context, preliminary and on-going studies on the ring-closure metathesis of α,ω-diolefins by our isolated and well defined complexes **1c** and **8** indicate similar activities to those of the Grubbs' catalysts.[24] We will report on these promising results subsequently.

## Experimental

### General comments

All experiments were routinely carried out under anaerobic conditions using conventional Schlenk-tube and vacuum line techniques unless otherwise stated. Solvents were distilled from appropriate drying agents and degassed prior to use. The complexes $[RuCl_2(PPh_3)_3]$,[25] $[RuCl_2(=CHPh)(PCy_3)_2]$,[4] $[RuCl_2(PPh_3)([9]aneS_3)]$[13] and $[RuCl_2(CO)(dmf)(PPh_3)_2]$[10a] were prepared according to published procedures; $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}cym)_2]$ was obtained commercially (Aldrich). All other reagents were used as received from commercial sources. Infrared, NMR and FAB-MS data were obtained using a Mattson

Research Series IR spectrometer, JEOL JNM-EX270, and Autospec Q instruments, respectively. Phosphine-associated infrared data are not reported. For phosphine-derived $^{13}C$ NMR resonances "t$^{v}$" denotes a virtual triplet with 'apparent' coupling constants given, indicative of a *trans* bis(phosphine) arrangement. The FAB-mass spectra were obtained from 3-nitrobenzyl alcohol matrices and assignments are denoted by the most intense peak of isotopic envelopes confirmed by simulation; for salts $M^+$ refers to the cationic complex. Microanalytical data were obtained from the Imperial College and University of North London Microanalytical (S.A.C.S.) services. Crystal solvates were confirmed by $^1H$ NMR integration for dichloromethane, however this was not always possible for chloroform solvates due to overlap with phosphine resonances, or adventitious $CHCl_3$ present in the deuteriated NMR solvent. Light petroleum refers to that fraction of boiling range 40–60 °C. The majority of complexes reported could be recrystallised from mixtures of dichloromethane or chloroform and hexane or methanol.

## Preparations

**[RuCl$_2$(=C=C=CPh$_2$)(PPh$_3$)$_2$] 1a.** The complex [RuCl$_2$(PPh$_3$)$_3$] (1.00 g, 1.04 mmol) and HC≡CCPh$_2$OH (0.33 g, 1.59 mmol) were degassed under vacuum and then dissolved under nitrogen in degassed tetrahydrofuran (80 cm$^3$). The mixture was heated with stirring under reflux for 2 h. All solvent was then removed under reduced pressure and the resulting oil dissolved in dichloromethane (10 cm$^3$) to which hexane (60 cm$^3$) was then slowly added. The resulting red-brown precipitate was filtered off, washed with hexane (40 cm$^3$) and dried *in vacuo*. Yield: 0.85 g (92%). Similar yields were obtained when the reaction was carried out on twice the scale: 2.0 g of [RuCl$_2$(PPh$_3$)$_3$] provided 1.65 g (89%) of **1a**. IR: (Nujol) 1968, 1929, 1902 [$\nu$(C=C=C)]; (CH$_2$Cl$_2$) 1939 cm$^{-1}$ [$\nu$(C=C=C)]. NMR (CDCl$_3$, 25 °C): $^1H$, $\delta$ 6.61 [t, 4 H, H$^{3,5}$(C$_6$H$_5$), $J$(HH) = 6.7], 7.05 [d, 2 H, H$^{2,6}$(C$_6$H$_5$), $J$(HH) = 7.2 Hz] and 6.9–7.6 (m, 34 H, C$_6$H$_5$); $^{13}C$-{$^1H$}, $\delta$ 301.2 [t, C$_\alpha$, $J$(PC) = 12.9], 225.4 (s, C$_\beta$), 145.0 (s, C$_\gamma$), 135.0 [t$^{v}$, C$^{2,6}$(PC$_6$H$_5$), $J$(PC) = 5.4], 130.9 [t$^{v}$, C$^1$(PC$_6$H$_5$), $J$(PC) = 21.6], 130.2 [s, C$^4$(PC$_6$H$_5$)], 128.1 [t$^{v}$, C$^{3,5}$(PC$_6$H$_5$), $J$(PC) = 5.4 Hz], 141.5–118.1 (C$_6$H$_5$); $^{31}P$-{$^1H$}, $\delta$ 29.0. FAB-MS: $m/z$ (%) = 851 (12) [M − Cl]$^+$; 696 (2), [M − C$_3$Ph$_2$]$^+$; 660 (2), [M − Cl − C$_3$Ph$_2$]$^+$, 625 (2), [M − 2Cl − C$_3$Ph$_2$]$^+$; 589 (2), [M − Cl − PPh$_3$]$^+$; 553 (12), [M − 2Cl − PPh$_3$]$^+$; 363 (6), [M − 2Cl − C$_3$Ph$_2$ − PPh$_3$]$^+$; and 327 (4), [M − Cl − 2PPh$_3$]$^+$ (Found: C, 63.5; H, 4.5. Calc. for C$_{51}$H$_{40}$Cl$_2$P$_2$Ru·1.25CH$_2$Cl$_2$: C, 63.2; H, 4.3%).

**[OsCl$_2$(=C=C=CPh$_2$)(PPh$_3$)$_2$] 1b.** The complex [OsCl$_2$(PPh$_3$)$_3$] (0.20 g, 0.19 mmol) and HC≡CCPh$_2$OH (0.09 g, 0.43 mmol) were degassed under vacuum, then dissolved under nitrogen in degassed toluene (20 cm$^3$) and the mixture heated under reflux for 3 h. All solvent was then removed and the resulting oil dissolved in dichloromethane (3 cm$^3$) and hexane (40 cm$^3$) slowly added. The brown-red precipitate was filtered off, washed with hexane (20 cm$^3$) and dried *in vacuo*. Yield: 0.19 g (98%). IR: (Nujol) 1986(sh), 1933 [$\nu$(C=C=C)]; (CH$_2$Cl$_2$) 1939 cm$^{-1}$ [$\nu$(C=C=C)]. NMR (CDCl$_3$, 25 °C): $^1H$, $\delta$ 6.95 [t, 4 H, H$^{3,5}$(C$_6$H$_5$), $J$(HH) = 7.9 Hz], 7.22, 7.49, 7.77 (m × 3, 36 H, C$_6$H$_5$); $^{13}C$-{$^1H$}, $\delta$ 266.0 [t, C$_\alpha$, $J$(PC) = 10.8], 210.5 (s, C$_\beta$), 162.1 (s, C$_\gamma$), 135.2 [t$^{v}$, C$^{2,6}$(PC$_6$H$_5$), $J$(PC) = 4.9], 134.4–128.5 [CC$_6$H$_5$ + C$^1$(PC$_6$H$_5$)], 130.1 [s, C$^4$(PC$_6$H$_5$)] and 127.5 [t$^{v}$, C$^{3,5}$(PC$_6$H$_5$), $J$(PC) = 5.4 Hz]; $^{31}P$-{$^1H$}, $\delta$ −14.7. FAB-MS: $m/z$ (%) = 977 (18), [M]$^+$; 941 (5), [M − Cl]$^+$; 750 (2), [M − Cl − C$_3$Ph$_2$]$^+$; 715 (6), [M − PPh$_3$]$^+$; 677 (3), [M − Cl − PPh$_3$]$^+$; and 641 (12), [M − 2Cl − PPh$_3$]$^+$ (Found: C, 66.1; H, 4.4. Calc. for C$_{51}$H$_{40}$Cl$_2$OsP$_2$·1.5C$_7$H$_8$: C, 66.4; H, 4.6%).

**[RuCl$_2$(=C=C=CPh$_2$)(PCy$_3$)$_2$] 1c.** The complex [RuCl$_2$(=C=C=CPh$_2$)(PPh$_3$)$_2$] **1a** (0.80 g, 0.90 mmol) and PCy$_3$ (0.68 g, 2.43 mmol) were degassed under vacuum, then dissolved under nitrogen in degassed dichloromethane (60 cm$^3$) and the mixture stirred for 30 min at room temperature. All solvent was then removed under vacuum and the resulting oil triturated ultrasonically in methanol (20 cm$^3$) to give a brick-red solid which was filtered off, washed with methanol (20 cm$^3$) and hexane (40 cm$^3$) and dried *in vacuo*. Yield: 0.70 g (84%). A further crop could be obtained from the filtrate. Repeating the reaction employing 1.20 g of **1a** provided similar yields, 1.10 g (88%). The phosphine exchange reaction may also be carried out conveniently in diethyl ether suspension. IR: (Nujol) 1969(sh) and 1929 cm$^{-1}$ [$\nu$(C=C=C)]. NMR (CDCl$_3$, 25 °C): $^1H$, $\delta$ 1.22, 1.51, 1.65, 1.91, 2.59 (m × 5, 66 H, Cy), 7.25, 7.33, 7.39, 7.49, 7.72, 8.65 (m × 6, 10 H, C$_6$H$_5$); $^{13}C$-{$^1H$}, $\delta$ 293.6 [t, C$_\alpha$, $J$(PC) = 7.5], 210.0 (s, C$_\beta$), 174.1 (s, C$_\gamma$), 144.5–117.2 (C$_6$H$_5$), 32.7 [t$^{v}$, C$^1$(C$_6$H$_{11}$), $J$(PC) = 8.6], 29.8 [d, C$^{3,5}$(C$_6$H$_{11}$), $J$(PC) = 3.2], 27.8 [m, C$^{2,6}$(C$_6$H$_{11}$)] and 26.5 [C$^4$(C$_6$H$_{11}$)]; $^{31}P$-{$^1H$}, $\delta$ 32.7. FAB-MS: $m/z$ (%) = 922 (10), [M]$^+$; 887 (10), [M − Cl]$^+$; 851 (0.5), [M − 2Cl]$^+$; 644 (6), [M − PCy$_3$]$^+$; 605 (2), [M − PCy$_3$ − Cl]$^+$; 569 (4), [M − PCy$_3$ − 2Cl]$^+$; and 470 (100), [M − PCy$_3$ − C$_3$Ph$_2$] (Found: C, 66.3; H, 8.3. Calc. for C$_{51}$H$_{76}$Cl$_2$P$_2$Ru: C, 66.4; H, 8.3%).

**[Ru$_2$(μ-Cl)$_3$(=C=C=CPh$_2$)(PPh$_3$)$_4$]PF$_6$ 2·PF$_6$.** The mixture of **1a** and dimeric complexes **A** and **2**·Cl obtained from the room temperature reaction of [RuCl$_2$(PPh$_3$)$_3$] and HC≡CCPh$_2$OH in thf (2 h) was treated with an excess (3 equivalents) of KPF$_6$ in a mixture of dichloromethane and methanol (1 : 1) and stirred for 10 h. The solvent was removed and the residue extracted with dichloromethane. The combined extracts were filtered through diatomaceous earth and then freed of volatiles. Inspection of the phosphorus-31 NMR spectrum of the residue indicated that it was the previously reported complex **2**·PF$_6$. $^{31}P$-{$^1H$} NMR (CDCl$_3$, 25 °C): $\delta$ 41.1, 42.4; $J$(P$_A$P$_B$) = 30.0 Hz [*cf.* $\delta$ 40.8, 42.2; $J$(P$_A$P$_B$) = 30 Hz[8]].

**all-*trans*-[RuCl$_2$(=C=C=CPh$_2$)(CO)(PPh$_3$)$_2$] 3.** The complex [RuCl$_2$(CO)(dmf)(PPh$_3$)$_2$] (0.25 g, 0.31 mmol) was stirred with HC≡CCPh$_2$OH (0.10 g, 0.45 mmol) in dichloromethane (50 cm$^3$) at room temperature for 8 h. The solvent volume was reduced under vacuum to *ca.* 10 cm$^3$. The deep pink product was precipitated by addition of light petroleum and was isolated by filtration. The crude product was recrystallised from a mixture of dichloromethane and diethyl ether, from which it was obtained as a dichloromethane hemisolvate. Yield: 0.25 g (87%). IR: (Nujol) 2001 [$\nu$(CO)], 1945 [$\nu$(C=C=C)]; (CH$_2$Cl$_2$) 2007 [$\nu$(CO)], 1953 cm$^{-1}$ [$\nu$(C=C=C)]. NMR (CDCl$_3$, 25 °C): $^1H$, $\delta$ 7.10, 7.31, 7.46, 7.60, 7.74, 7.88 (m × 6, 40 H, C$_6$H$_5$); $^{13}C$-{$^1H$}; $\delta$ 310.7 [t, C$_\alpha$, $J$(PC) = 13.5], 198.0 (C$_\beta$), 194.3 [t, CO, $J$(PC) = 12.4], 163.4 (C$_\gamma$), 142.3 [C$^1$(CC$_6$H$_5$)], 134.4 [t$^{v}$, C$^{3,5}$(PC$_6$H$_5$), $J$(PC) = 5.4], 133.2 [t$^{v}$, C$^1$(PC$_6$H$_5$), $J$(PC) = 23.7], 127.7 [t$^{v}$, C$^{2,6}$(PC$_6$H$_5$), $J$(PC) = 4.3 Hz], 132.4 [C$^4$(CC$_6$H$_5$)], 131.8 [C$^{2,6/3,5}$(CC$_6$H$_5$)], 129.9 [C$^4$(PC$_6$H$_5$)] and 128.9 [C$^{3,5/2,6}$-(CC$_6$H$_5$)]; $^{31}P$-{$^1H$}, $\delta$ 19.0. FAB-MS: $m/z$ (%) = 915 (1), [M]$^+$; 879 (9), [M − Cl]$^+$; 851 (6), [M − Cl − CO]$^+$; 689 (29), [M − C$_3$Ph$_2$ − Cl]$^+$; 653 (4), [M − PPh$_3$]$^+$; 625 (13), [M − C$_3$Ph$_2$ − 2Cl − CO]$^+$; 553 (13), [M − PPh$_3$ − 2Cl − CO]$^+$; and 363 (16), [M − PPh$_3$ − C$_3$Ph$_2$ − 2Cl − CO]$^+$ (Found: C, 65.3; H, 4.3. Calc. for C$_{52}$H$_{40}$Cl$_2$OP$_2$Ru·0.5CH$_2$Cl$_2$: C, 65.9; H, 4.3%).

**[RuCl(=C=C=CPh$_2$)(PPh$_3$)([9]aneS$_3$)]PF$_6$ 4·PF$_6$.** A mixture of [RuCl$_2$(=C=C=CPh$_2$)(PPh$_3$)$_2$] **1a** (0.20 g, 0.25 mmol), 1,4,7-trithiacyclononane (0.050 g, 0.27 mmol), NaPF$_6$ (0.08 g, 0.48 mmol) in dichloromethane (20 cm$^3$) and ethanol (20 cm$^3$) was stirred for 5 h and then freed of solvent under reduced pressure. The residue was extracted with dichloromethane (2 × 10 cm$^3$) and the combined extracts filtered through diatomaceous earth to remove NaCl. The filtrate was diluted with ethanol (20 cm$^3$) and then concentrated slowly under reduced pressure to provide

crystals of the salt. These were filtered off, washed with cold ethanol (5 $cm^3$) and hexane (10 $cm^3$) and dried *in vacuo*. An analytical sample was obtained by recrystallisation of the crude product from a mixture of chloroform and ethanol as a chloroform monosolvate. Yield 0.13 g (62%). IR: ($CH_2Cl_2$) 1947 $cm^{-1}$ [$\nu$(C=C=C)]; (Nujol) 1941 [$\nu$(C=C=C)], 1311, 1282, 1263, 1128, 935, 840 $cm^{-1}$ ($PF_6$). NMR ($CDCl_3$, 25 °C): $^1$H, $\delta$ 0.89, 1.27, 2.30, 2.59, 2.87, 3.21, 3.49 (m × 7, 12 H, $SCH_2$), 7.30, 7.60, 7.76 (m × 3, 25 H, $C_6H_5$); $^{31}$P-{$^1$H}, $\delta$ 34.9. FAB-MS: *m*/*z* (%) = 769 (100), $[M]^+$; 705 (8), $[M - Cl - C_2H_4]^+$; 581 (17), $[M - C_3Ph_2]^+$; 551 (55), $[M - C_2H_4 - C_3Ph_2]^+$; 515 (6), $[M - Cl - C_2H_4 - C_3Ph_2]^+$; and 479 (15), $[M - C_2H_4 - PPh_3]^+$ (Found: C, 47.0; H, 3.7. Calc. for $C_{39}H_{37}ClF_6P_2RuS_3 \cdot CHCl_3$ requires C, 46.5; H, 3.7%).

***trans*-[RuCl(=C=C=CPh$_2$)(dppe)$_2$]PF$_6$ 5·PF$_6$.** Complex **1a** (0.20 g, 0.23 mmol), dppe (0.23 g, 0.58 mmol) and $KPF_6$ (0.08 g, 0.43 mmol) in tetrahydrofuran (10 $cm^3$) and methanol (10 $cm^3$) were heated under reflux for 4 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (3 × 5 $cm^3$). The combined extracts were filtered through diatomaceous earth. The filtrate was diluted with methanol (20 $cm^3$) and then slowly concentrated under reduced pressure to provide red crystals which were filtered off, washed with diethyl ether (10 $cm^3$) and dried *in vacuo*. Yield 0.20 g (70%). The salt was identified by comparison of spectroscopic data [IR (Nujol) 1922 $cm^{-1}$; $^{31}$P-{$^1$H} NMR $\delta$ 38.3] with those previously published [IR (Nujol) 1923 $cm^{-1}$; $^{31}$P-{$^1$H} NMR $\delta$ 37.8].[8]

**[RuCl(=C=C=CPh$_2$)(PCy$_3$){HB(pz)$_3$}] 6.** A mixture of [$RuCl_2$(=C=C=$CPh_2$)($PCy_3$)$_2$] **1c** (0.30 g, 0.32 mmol) and K[$HB(pz)_3$] (0.097 g, 0.38 mmol) in dichloromethane (20 $cm^3$) was stirred for 12 h and then freed of volatiles. The residue was extracted with hexane (3 × 15 $cm^3$), the combined extracts were filtered through diatomaceous earth and the filtrate concentrated to *ca*. 5 $cm^3$ and cooled to −30 °C overnight to provide red crystals. The isolated yield and the obtention of satisfactory elemental microanalytical data were compromised by the high solubility of the product. Yield 0.22 g (83%). A second crop of less pure material (containing small amounts of $PCy_3$ and $OPCy_3$) could be isolated on further cooling of the filtrate. IR ($CH_2Cl_2$): 2479 [$\nu$(BH)] and 1962 $cm^{-1}$ [$\nu$(C=C=C)]. NMR ($CDCl_3$, 25 °C): $^1$H, $\delta$ 0.87, 1.26, 1.42, 1.59, 1.80 (m × 5, 33 H, Cy), 3.1 [s(br), 1 H, BH], 5.40, 5.43, 5.78, 6.06, 6.35, 6.43 (1 H × 6, pz), 7.12–7.91 (m, 12 H, Ph + 2pz) and 8.66 (s, 1 H, pz); $^{31}$P-{$^1$H}, $\delta$ 26.8(br). FAB-MS: *m*/*z* (%) = 820 (72), $[M]^+$; [785 (81), $[M - Cl]^+$; 632 (4), $[M - C_3Ph_2]^+$; 593 (17), $[M - Cl - C_3Ph_2]^+$; 540 (84), $[M - PCy_3]^+$; and 505 (51), $[M - Cl - PCy_3]^+$.

**[RuCl(=CHPh)(PCy$_3$){HB(pz)$_3$}] 7.** The complex [$RuCl_2$(=CHPh)($PCy_3$)$_2$] (0.30 g, 0.36 mmol) was treated as described above for the synthesis of **6** to provide green crystals. Yield 0.19 g (74%). IR (Nujol): 2494 [$\nu$(BH)], 1310, 1253, 1215, 1118, 1049, 888, 851 $cm^{-1}$. NMR ($CD_2Cl_2$, 25 °C): $^1$H, $\delta$ 0.85, 1.21, 1.58, 1.80, 1.96 (m × 5, 33 H, Cy), 5.81, 6.04, 6.24, 6.39, 6.40, 7.57, 7.83, 7.85, 8.54 (1 H × 9, pz), 7.05, 7.48 (m × 2, 5 H, $C_6H_5$) and 20.06 [d, 1 H, Ru=CH, $J$(PH) = 9.3 Hz]; $^{13}$C-{$^1$H}, $\delta$ 333.8 [d, Ru=C, $J$(PC) = 14.3], 150.8 [$C^1(C_6H_5)$], 145.8, 144.6, 143.4 [$C^{3/5}$(pz)], 136.7, 135.5, 133.9 [$C^{5/3}$(pz)], 131.5, 128.5 [$C^{2,3,5,6}(C_6H_5)$], 130.8 [$C^4(C_6H_5)$], 106.1 (2C), 105.3 [$C^4$(pz)], 34.3 [d, $C^1(C_6H_{11})$, $J$(PC) = 16.1], 28.8 [d(br), $C^{3,5}(C_6H_{11})$, $J$(PC) = 12.5], 28.0, 27.7 [d × 2, $C^{2,6}(C_6H_{11})$, $J$(PC) = 8.9, 10.7 Hz] and 26.2 [$C^4(C_6H_{11})$]; $^{31}$P-{$^1$H}, $\delta$ 33.1 (Found: C, 56.5; H, 6.6; N, 11.8. Calc. for $C_{34}H_{49}BClN_6PRu$: C, 56.7; H, 6.9; N, 11.7%).†

**[Ru$_2$(μ-Cl)$_2$Cl$_2$(=C=C=CPh$_2$)(PCy$_3$)(η-cym)] 8.** Complex **1c** (0.16 g, 0.17 mmol) and [$Ru_2$(μ-Cl)$_2$$Cl_2$(η-cym)$_2$] (0.11 g, 0.18 mmol) were dissolved in dichloromethane (10 $cm^3$) and the mixture stirred for 1 h. All solvent was then removed under reduced pressure and propanone (5 $cm^3$) added. The mixture was triturated in an ultrasound bath for 5 min and then the resulting suspension was filtered and the dark brown product washed with cold acetone (2 × 2 $cm^3$) and hexane (10 $cm^3$) and dried *in vacuo*. NB The filtrate and washings contain traces of **8**. Yield: 0.12 g (73%). The reaction was repeated using 0.70 g of **1c** to provide comparable yields: 0.55 g (76%). IR: (KBr) 1945 [$\nu$(C=C=C)], 1619, 1587, 1444, 1363, 1270, 1172, 1114, 1072, 1056, 1027, 1004, 916, 887 and 850; ($CH_2Cl_2$) 1951 $cm^{-1}$ [$\nu$(C=C=C)]. NMR ($CDCl_3$, 25 °C): $^1$H, $\delta$ 1.01, 1.55, 1.75, 1.88, 1.92 (m × 5, 33 H, Cy), 1.14, 1.29 [d × 2, 3 H × 2, CHC$H_3$, $J$(HH) = 6.7], 2.15 (s, 3 H, $C_6H_4CH_3$), 2.75 (h, 1 H, C$H$$CH_3$), 4.92, 5.12, 5.16, 5.49 [d × 4, 4 H, $C_6H_4$, $J$(HH) = 5.7 Hz], 6.68, 6.97, 7.32, 7.56, 8.90 (m × 5, 10 H, $C_6H_5$); $^{31}$P-{$^1$H}, $\delta$ 41.2; $^{13}$C-{$^1$H}, $\delta$ 310.4 [d, $C_\alpha$, $J$(PC) = 15.1], 140.9 [d, $C_\beta$, $J$(PC) = 4.3], 144.8–96.7 (cym + Ph + $C_\gamma$), 36.9 [$t^v$, $C^1(C_6H_{11})$, $J$(PC) = 20.5], 29.4 [$C^{3,5}(C_6H_{11})$], 28.3, 27.5 [d × 2, $C^{2,6}(C_6H_{11})$, $J$(PC) = 8.6, 10.8 Hz], 25.5 [$C^4(C_6H_{11})$], 22.9, 21.4, 18.3 ($CH_3$). FAB-MS: *m*/*z* (%) = 950 (14), $[M]^+$; 913 (9), $[M - Cl]^+$; 758 (0.5), $[M - C_3Ph_2]^+$; and 642 (31), $[M - RuCl_2(cym)]^+$ (Found: C, 54.3; H, 5.9. Calc. for $C_{43}H_{57}Cl_4PRu_2$: C, 54.4; H, 6.1%). The yellow filtrate was diluted with hexane (20 $cm^3$) and then concentrated to *ca*. 5 $cm^3$ and cooled to provide yellow crystals of [$RuCl_2$-($PCy_3$)(η-cym)]. $^{31}$P-{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 25.8.

### Reaction of [Ru$_2$(μ-Cl)$_2$Cl$_2$(η-cym)$_2$] with PCy$_3$ and HC≡CCPh$_2$OH

A suspension of [$Ru_2$(μ-Cl)$_2$$Cl_2$(η-cym)$_2$] (0.10 g, 0.16 mmol), $PCy_3$ (0.14 g, 0.49 mmol) and HC≡$CCPh_2OH$ (0.070 g, 0.32 mmol) in benzene (20 $cm^3$) was heated under reflux for 4 h and then freed of solvent. The residue was washed with hexane (2 × 10 $cm^3$) and then dissolved in $CDCl_3$ and the $^{31}$P-{$^1$H} NMR spectrum measured. The results are shown in Fig. 2, which confirm the presence of complexes **1c** and **8**.

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