

A new class of tethered-arene ruthenium(II) complexes with pendant P and C donor atoms: synthesis of $\eta^6:\eta^1:\eta^1$ phosphonio-azabutadienyl ruthenabicycles via allenylidene intermediates†

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The activation of 1,1-diphenyl-2-propyn-1-ol by complexes $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\eta^2\text{-}P,N\text{-Ph}_2\text{PCH}_2\text{P(=NR)Ph}_2\}]^+$ (**1a–d**) results in the formation of the unusual tethered ($\eta^6\text{-arene}$)–ruthenium(II) derivatives **2a–d**, via an unprecedented imino-phosphorane–allenylidene coupling process.

Since the isolation of the first allenylidene–ruthenium(II) complexes,¹ the development of their chemistry has shown them to form one of the cornerstones of the synthetic applications of carbene–ruthenium complexes. Their applications in both stoichiometric² and catalytic³ organic transformations are among the most appealing in ruthenium-mediated organic synthesis,⁴ featuring a versatile reactivity including nucleophilic, electrophilic as well as cycloaddition reactions. In the context of our studies on the utility of ruthenium(II)–allenylidenes for promoting regio- and stereoselective C–C and C–heteroatom couplings,⁵ we now report a synthetic methodology for unprecedented tethered arene–ruthenium(II) complexes **2** (see Fig. 1). They have been generated from the intramolecular coupling of an iminophosphorane group $\text{Ph}_2\text{P=N-R}_F$ with the allenylidene chain =C=C=CPh_2 and concomitant coordination of one of the terminal phenyl groups to ruthenium. To the best of our knowledge, these complexes represent the first examples of tethered-arene derivatives in which the pendant arm is linked to the metal by both P and C-donor atoms displaying a rare $\eta^6:\eta^1:\eta^1$ coordination mode.⁶

The process takes place by reaction of the iminophosphorane complexes **1a–d** with a 10-fold excess of 1,1-diphenyl-2-propyn-1-ol in dichloromethane at room temperature (ca. 48 h), yielding the bicyclic phosphonio-azabutadienyl–ruthenium(II) derivatives **2a–d** (Scheme 1), which have been isolated as air-stable orange solids in 78–88% yield.⁸ Analytical and spectroscopic data of complexes **2a–d** support the proposed formulation.‡ In particular the ¹H and ¹³C–{¹H} NMR data indicate: (i) the disappearance of the isopropyl and methyl resonances of the *p*-cymene ligand, and (ii) the formation of the Ru–C bond in the azabutadienyl chain as reflected by the appearance of a characteristic low-field doublet of doublets resonance at ca. δ_C 234 ppm [²*J*(CP) = 14.3–18.1 and 1.7–4.5 Hz].⁸

Moreover, the structure of complex **2d** has been determined by a single-crystal X-ray diffraction study (Fig. 2).§ The most remarkable features of the structure are the Ru–C(23) and N(1)–C(23) bond lengths (2.026(10) and 1.297(11) Å, respectively) which are

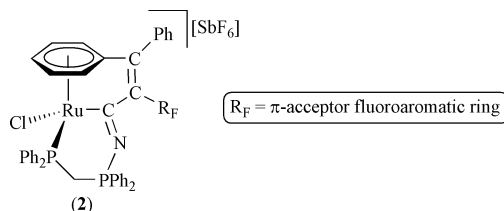


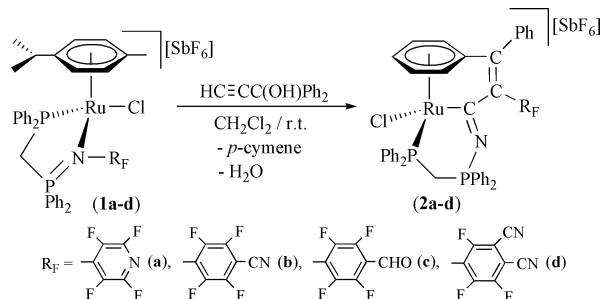
Fig. 1 Structure of the tethered-arene complexes reported in this paper.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b404971c/>

consistent with the presence of single metal–carbon and double nitrogen–carbon bonds, respectively.⁹

Complexes **2a–d** formally result from the coupling of the uncoordinated iminophosphorane unit $\text{Ph}_2\text{P=N-R}_F$ of **1a–d** with the allenylidene chain (resulting from the dehydration of the coordinated propargylic alcohol) with concomitant exchange of the $\eta^6\text{-}p\text{-cymene}$ ligand by one phenyl group of the alkynol. Remarkably, an unusual migration of the fluoroaromatic substituent R_F from the imino group =N-R_F to the C_β atom of the allenylidene chain also takes place.

Although no intermediates could be detected by NMR spectroscopy, the involvement of allenylidene species in this unusual coupling process has been confirmed by using the closely related mesitylene–ruthenium(II) complex **3** as starting material (Scheme 2). Thus, the treatment of **3** with 10 equiv. of $\text{HC}\equiv\text{CC(Ph)}_2$, in CH_2Cl_2 at room temperature generates (ca. 12 h) the diphenylallenylidene derivative **5**. The hemilabile properties of the $\eta^2\text{-}P,N$ -iminophosphorane–phosphine ligand provide the required vacant site for the coordination of the propargylic alcohol.⁷ Complex **5** slowly converts (ca. 10 days) into the phosphonio-



Scheme 1 Activation of 1,1-diphenyl-2-propyn-1-ol by complexes **1a–d**.

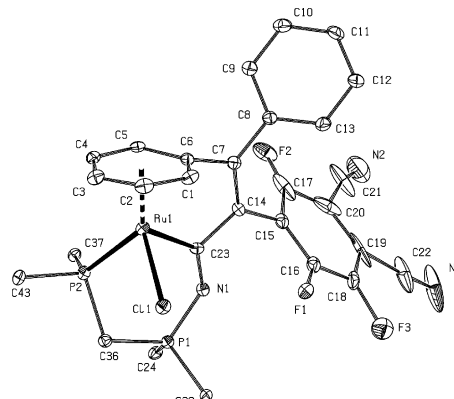


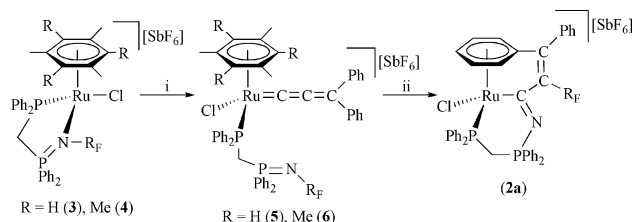
Fig. 2 Molecular structure of **2d**. SbF_6^- anion, hydrogen atoms and phenyl groups of the P,N-ligand have been omitted. Selected bond distances (Å) and angles (°): Ru–Cl(1) 2.399(2); Ru–P(2) 2.302(3); Ru–C(23) 2.026(10); P(1)–N(1) 1.638(6); N(1)–C(23) 1.297(11); C(23)–C(14) 1.490(12); C(14)–C(7) 1.373(13); C(23)–Ru–P(2) 86.7(3); C(23)–Ru–Cl(1) 88.4(2); P(2)–Ru–Cl(1) 90.29(9); Ru–C(23)–N(1) 132.6(7); C(23)–N(1)–P(1) 130.3(7); Ru–C(23)–C(14) 114.1(7); C(23)–C(14)–C(7) 118.1(9).

azabutadienyl metallacycle **2a**, via allenylidene–iminophosphorane coupling and mesitylene–phenyl ring exchange (Scheme 2).

The allenylidene complex **5** could be isolated in 79% yield,[‡] and its structure was confirmed unequivocally by X-ray crystallography (Fig. 3).[¶]

Although the overall mechanism for this coupling reaction is still unknown it seems that the first step, in which the $-\text{Ph}_2\text{P}=\text{N}-\text{R}_\text{F}$ unit is added to the allenylidene chain, depends on the electrophilicity of the C_α atom of the allenylidene ligand. This could explain the observed slower reaction rate in the transformation of the more electron-rich mesitylene vs the *p*-cymene complex (**3** vs **1a**), allowing the isolation of allenylidene **5** in which the electrophilicity of the α -carbon is clearly reduced. In accord with this, the analogous hexamethylbenzene complex **6**[‡] (Scheme 2) remains unchanged under similar reaction conditions. It should be noted that, although the addition of $\text{X}-\text{H}$ ($\text{X} = \text{O}, \text{N}, \text{S}, \text{P}$) bonds to the $\text{C}_\alpha=\text{C}_\beta$ of transition-metal allenylidenes is a well-established transformation which generally yields Fischer-type α,β -unsaturated carbenes² or in some cases azoniabutadienyl species ($\text{X} = \text{N}$),⁸ no $\text{X}-\text{C}$ bond additions to allenylidene chains have been reported to date. This reaction pathway constitutes a novel example of the usefulness of transition-metal allenylidene complexes as building blocks for the preparation of unusual organometallic skeletons.

In summary, a readily accessible route to unprecedented $\eta^6:\eta^1:\eta^1$ tethered-arene–ruthenium(II) complexes, in which the pendant arms involve both P and C donor atoms, is described. The chemistry of transition-metal complexes containing tethered-type ligands is growing rapidly because of their potential contribution to the configurational stability around the metal centre, and for promoting selective stoichiometric and catalytic transformations.^{6,10} Further studies concerning the scope and mechanism of this coupling process, as well as reactivity studies on the new type of tethered-arene–ruthenium(II) complexes **2**, are now under active investigation.



Scheme 2 $\text{R}_\text{F} = p\text{-C}_5\text{F}_4\text{N}$. Reagents and conditions: i, $\text{HC}\equiv\text{CC}(\text{OH})\text{Ph}_2$ (10 equiv.), CH_2Cl_2 , rt; ii, $\text{R} = \text{H}$, CH_2Cl_2 , rt, 10 days.

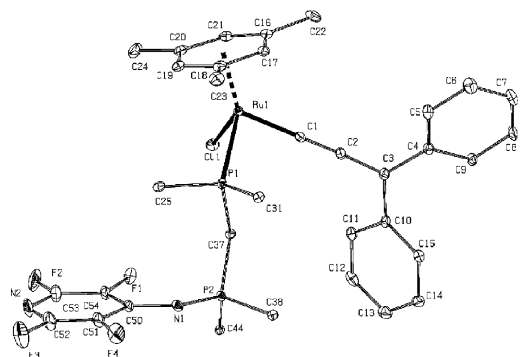


Fig. 3 Molecular structure of **5**. SbF_6^- anion, hydrogen atoms and phenyl groups of the P,N-ligand have been omitted. Selected bond distances (Å) and angles (°): $\text{Ru}-\text{Cl}(1)$ 2.3887(17); $\text{Ru}-\text{P}(1)$ 2.3237(18); $\text{Ru}-\text{C}(1)$ 1.896(7); $\text{C}(1)-\text{C}(2)$ 1.242(9); $\text{C}(2)-\text{C}(3)$ 1.366(10); $\text{P}(1)-\text{C}(37)$ 1.842(6); $\text{C}(37)-\text{P}(2)$ 1.814(6); $\text{P}(2)-\text{N}(1)$ 1.560(6); $\text{N}(1)-\text{C}(50)$ 1.379(9); $\text{C}(1)-\text{Ru}-\text{P}(1)$ 86.0(2); $\text{C}(1)-\text{Ru}-\text{Cl}(1)$ 88.4(2); $\text{P}(1)-\text{Ru}-\text{Cl}(1)$ 89.37(6); $\text{Ru}-\text{C}(1)-\text{C}(2)$ 178.7(6); $\text{C}(1)-\text{C}(2)-\text{C}(3)$ 176.6(8).

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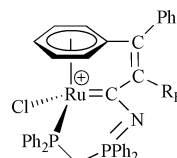
Notes and references

[‡] Compounds **1c–d**, **2a–d**, **5** and **6** have been characterized by NMR spectroscopy and elemental analyses. See ESI.

[§] Crystal data for **2d**: $\text{RuC}_{48}\text{H}_{32}\text{F}_9\text{N}_3\text{P}_2\text{ClSb}$, $M = 1141.98$, orange prism ($0.125 \times 0.075 \times 0.025$ mm), monoclinic, $C2/c$, $a = 39.587(7)$ Å, $b = 12.430(2)$ Å, $c = 20.522(4)$ Å, $\alpha = 90^\circ$, $\beta = 117.306(7)^\circ$, $\gamma = 90^\circ$, $V = 8973(3)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.691$ g cm^{−3}, $\mu(\text{Cu}-\text{K}\alpha) = 9.392$ mm^{−1}, Nonius Kappa CCD diffractometer, Cu–K α radiation ($\lambda = 1.54184$ Å). 54554 reflections collected, 5843 unique ($R_{\text{int}} = 0.095$). $R_1 = 0.0603$; $wR_2 = 0.1392$ both for $I > 2\sigma(I)$. CCDC 236842. See <http://www.rsc.org/suppdata/cc/b4/b404971c/> for crystallographic files in .cif format.

[¶] Crystal data for **5**: $\text{RuC}_{54}\text{H}_{44}\text{F}_{10}\text{N}_2\text{P}_2\text{ClSb}$, $M = 1231.12$, violet prism ($0.25 \times 0.25 \times 0.10$ mm), monoclinic, $P2_1/a$, $a = 16.4727(16)$ Å, $b = 17.1842(17)$ Å, $c = 20.571(2)$ Å, $\alpha = 90^\circ$, $\beta = 112.879(2)^\circ$, $\gamma = 90^\circ$, $V = 5364.9(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.524$ g cm^{−3}, $\mu(\text{Mo}-\text{K}\alpha) = 0.966$ mm^{−1}, Bruker Smart CCD diffractometer, Mo–K α radiation ($\lambda = 0.71073$ Å). 43447 reflections collected, 16052 unique ($R_{\text{int}} = 0.1035$). $R_1 = 0.0728$; $wR_2 = 0.1988$ both for $I > 2\sigma(I)$. CCDC 236843. See <http://www.rsc.org/suppdata/cc/b4/b404971c/> for crystallographic files in .cif format.

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