

Communication

# The reaction of ferrocenyl acetylene with $[\text{RuCp}(\text{PR}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ ( $\text{R} = \text{Me}, \text{Ph}, \text{Cy}$ ). Formation of the first allenyl carbene complexes

Eva Růba<sup>a</sup>, Kurt Mereiter<sup>b</sup>, Roland Schmid<sup>a</sup>, Karl Kirchner<sup>a,\*</sup>,  
Herwig Schottenberger<sup>c</sup>

<sup>a</sup> Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

<sup>b</sup> Institute of Mineralogy, Crystallography and Structural Chemistry, Getreidemarkt 9, A-1060 Vienna, Austria

<sup>c</sup> Institute of General Inorganic, and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

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## Abstract

The reaction of  $[\text{RuCp}(\text{PR}_3)(\text{CH}_3\text{CN})_2]\text{PF}_6$ , where  $\text{R} = \text{Ph}$  and  $\text{Cy}$ , with ferrocenyl acetylene ( $\text{HC}=\text{Cfc}$ ) affords the first  $\eta^2$ -allenyl carbene complexes  $[\text{CpRu}(\text{C}(\text{Fc})-\eta^2\text{-CH}=\text{C}=\text{CH}(\text{Fc}))(\text{PR}_3)]\text{PF}_6$ . The new type of C–C bond formation is affected by the strong electronic coupling of the ferrocenyl moiety with the conjugated allenyl carbene unit, which facilitates transient vinylidene formation with subsequent alkyne insertion into the  $\text{Ru}=\text{C}$  double bond. The vinylidene intermediate appears to occur only in the presence of bulky substituents of the phosphine co-ligand. For small  $\text{R} = \text{Me}$ , head-to-tail coupling between two alkyne molecules involving phosphine migration is preferred, giving the more usual  $\eta^3$ -allyl carbene complex  $[\text{CpRu}(\text{C}(\text{Fc})-\eta^3\text{-CHC}(\text{Fc})\text{CHPMe}_3)]\text{PF}_6$ . The X-ray structure of an  $\eta^2$ -allenyl carbene complex is presented. © 2001 Elsevier Science B.V. All rights reserved.

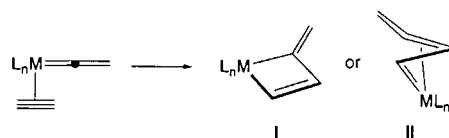
**Keywords:** Ruthenium; Allenyl carbene complexes; C–C bond formation; Vinylidene complexes

## 1. Introduction

Cycloaddition via a metallacyclopentadiene intermediate is a common reaction between acetylenes and coordinatively unsaturated complexes. Interest in such type of reaction has continued since Reppe discovered the tetramerization of acetylene to cyclooctatetraene [1]. For terminal alkynes, another route may proceed via the intermediacy of vinylidene complexes, with subsequent insertion of another alkyne into the metal–carbon double bond of the vinylidene moiety. Such alkylidene metallacyclobutene intermediates **I** (Scheme 1), though extremely rare, may initiate polymerization through ring opening [2]. It is noteworthy that [2 + 2] cycloaddition of an alkyne to a vinylidene species has

been proposed as an intermediate step in the formation of [3]ferrocenophanes containing a cyclopent-3-en-1,2-dione moiety [3].

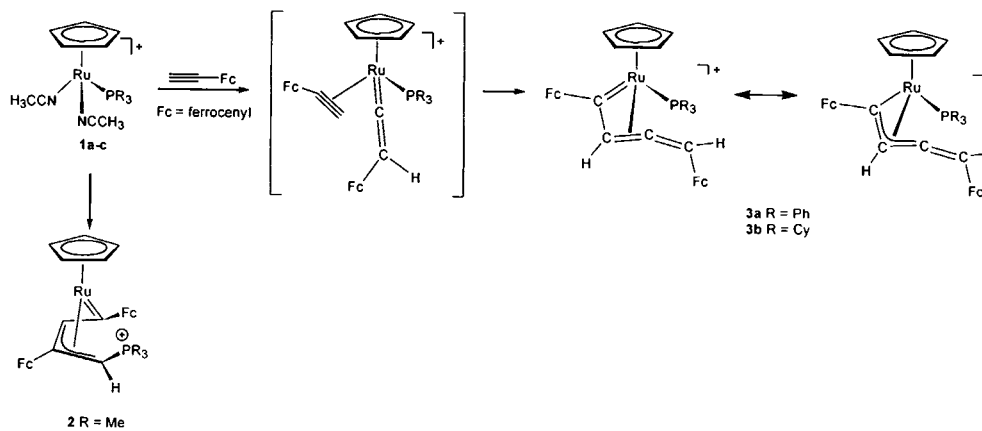
Recently, we encountered a particularly intriguing case when we reacted various terminal alkynes  $\text{HC}=\text{CR}'$  ( $\text{R}' = \text{H}, \text{Ph}, \text{SiMe}_3, n\text{-Bu}$ ) as well as 1,6-heptadiyne, in the presence of  $[\text{RuCp}(\text{PR}_3)(\text{CH}_3\text{CN})_2]^+$  where  $\text{R} = \text{Me}$  (**1a**),  $\text{Ph}$  (**1b**), and  $\text{Cy}$  (**1c**). Instead of oxidative coupling to yield ruthenacyclopentadiene or ruthenacyclopentatriene complexes, i.e. C–C coupling with the  $\text{Ru}-\text{P}$  bond retained, we obtained  $\eta^3$ -allyl carbene complexes involving an extremely facile phosphine migration step



Scheme 1.

\* Corresponding author. Tel.: +43-158-801-15341; fax: +43-158-801-15399.

E-mail address: kkirch@mail.zserv.tuwien.ac.at (K. Kirchner).



Scheme 2.

[4,5]. The outcome of the reaction was independent of the substituents, R' and R, used. The detailed mechanism of this reaction, however, remains obscure and is currently under intensive investigation.

Thus, to study the influence of the substituents further, we here carry out the reaction of the complexes **1a–1c** with a very atypical alkyne, namely ferrocenyl acetylene (HC≡CFc), where a ferrocenyl unit is bonded directly to the alkynyl group. As a result, the novel class of compounds **II** (Scheme 1) becomes available for the first time.

## 2. Results and discussion

The ruthenium complexes **1a–1c** were synthesized as before [6]. Interestingly, the outcome of the reaction with HC≡CFc was found to vary with the substituent of the phosphine ligand. Thus, only with **1a** the allyl carbene complex [CpRu(=C(Fc)-η<sup>3</sup>-CHC(Fc)CHP-Me<sub>3</sub>)]PF<sub>6</sub> (**2**) is formed. In sharp contrast, when HC≡CFc is reacted with **1b** or **1c**, the color of the solution turns immediately dark green giving, on workup, the novel η<sup>2</sup>-allenyl carbene complexes [CpRu(=C(Fc)-η<sup>2</sup>-CH=C=CH(Fc))(PPh<sub>3</sub>)]PF<sub>6</sub> (**3a**) and [CpRu(=C(Fc)-η<sup>2</sup>-CH=C=CH(Fc))(PCy<sub>3</sub>)]PF<sub>6</sub> (**3b**), in 65 and 71% yield, respectively (Scheme 2). Both complexes were characterized by elemental analyses and <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, and <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopies.

The solution <sup>1</sup>H-NMR spectroscopic data for **3a** include resonances at 5.95 (H<sup>2</sup>) and 3.12 ppm (H<sup>4</sup>). The significant upfield shift of the H<sup>4</sup> proton is characteristic of an olefinic hydrogen atom in *anti* position, i.e. pointing towards the metal center. In the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of **3a**, the characteristic resonance of the carbene carbon C<sup>1</sup> is observed at 279.7 ppm (cf. 240–270 ppm in η<sup>3</sup>-allyl and η<sup>2</sup>-vinyl carbene complexes [4,5] and about 270 ppm in metallacyclopentatriene complexes [7]). The carbon resonances of the allenyl chain are observed at 123.1, 66.9, and 30.4 ppm

assignable to C<sup>4</sup>, C<sup>3</sup>, and C<sup>2</sup>, respectively. It is also noteworthy that the <sup>1</sup>H resonances of the ferrocenyl moiety attached to the carbene carbon are significantly down-field shifted relative to that attached to the terminal allenyl carbon (multiplets in the range of 5.49–4.59 and 4.37–4.22, respectively), while the resonances of the unsubstituted Cp rings of the ferrocenyl units are observed at 4.43 and 3.77 ppm. The same trend is reflected in the <sup>13</sup>C{<sup>1</sup>H}-NMR spectra. Note further that the NMR spectra of **3a** and **3b** are very similar. All these findings clearly indicate that the ferrocenyl moiety attached to the carbene carbon is strongly coupled electronically with the conjugated allenyl carbene C4-unit. This is also apparent from the X-ray structure.

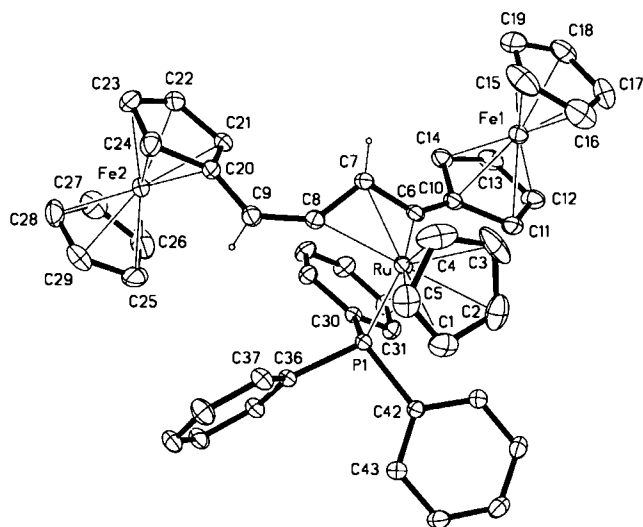


Fig. 1. Structural view of **3a**·CH<sub>2</sub>Cl<sub>2</sub> showing 20% thermal ellipsoids (PF<sub>6</sub><sup>-</sup>, CH<sub>2</sub>Cl<sub>2</sub>, and non-allenyl H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–C(1–5)<sub>av</sub> 2.233(3); Ru–C(6) 1.943(3); Ru–C(7) 2.171(3); Ru–C(9) 2.099(3); Ru–P(1) 2.322(1); C(6)–C(7) 1.415(4); C(7)–C(8) 1.416(4); C(8)–C(9) 1.321(4); C(6)–C(10) 1.403(4); C(9)–C(20) 1.466(4); C(6)–C(7)–C(8) 116.3(2); C(7)–C(8)–C(9) 138.0(3).

The molecular structure of **3a**·CH<sub>2</sub>Cl<sub>2</sub> has been confirmed by X-ray crystallography (Fig. 1). The most notable features are the *exo* orientation of the C(6)–C(7)–C(8) moiety with respect to the phosphine ligand, the distorted *s-trans* structure of the C(6)–C(7)–C(8)–C(9) unit and the short Ru–C(6) bond distance of 1.943(3) Å. The latter value is characteristic of an alkylidene double-bonded to the ruthenium center. The two allenyl carbons, C(7), C(8), are noticeably more apart from the Ru center and asymmetrically bonded (Ru–C(7) = 2.171(3) Å, Ru–C(8) = 2.099(3) Å) while the terminal allenyl carbon, C(9), is not coordinated to the metal center. The complex, therefore, may best be described as an η<sup>2</sup>-allenyl carbene. In addition, a resonance contribution from the allylic structure is obvious from the rather uniform bond distances found for C(6)–C(7) = 1.415(4) Å and C(7)–C(8) = 1.416(4) Å. Thus, π-electron delocalization appears to be substantial. The C(8)–C(9) bond distance of 1.321(4) Å is typical of a non-coordinated C–C double bond. The C–C bond distances linking the two ferrocenyl moieties with the allenyl carbene C4-unit are quite different from one another with C(6)–C(10) being 1.403(4) Å and C(9)–C(20) being 1.466(4) Å. Moreover, the C–C bond distances within the cyclopentadienyl ligand of the ferrocenyl substituent attached to the carbene carbon C(6) are significantly different with C(10)–C(11) and C(10)–C(14) being longer (1.431(4) and 1.450(4) Å, respectively) and C(11)–C(12), C(12)–C(13), and C(13)–C(14) being shorter (1.407(4), 1.406(5), and 1.402(5) Å, respectively), i.e. the one Cp ring attached to the carbene carbon atom is adopting a fulvene-like structure.

The formation of the η<sup>2</sup>-allenyl carbene complexes for the bulky PPh<sub>3</sub> and PCy<sub>3</sub> co-ligands most likely involves a vinylidene complex as the key intermediate (Schemes 1 and 2). It is well known indeed that vinylidene formation is facilitated in the presence of bulky co-ligands [8]. Subsequently, the η<sup>2</sup>-allenyl carbene complex may result from inserting the alkyne into the Ru–C double bond of the vinylidene intermediate [9]. The difference in the allyl and allenyl carbene pathways appears to be rooted in the availability of the vinylidene complex. The unavailability of the vinylidene route in the case of more simple alkynes under experimental conditions, therefore, might be due to a high barrier to vinylidene intermediate formation, which can proceed via either a 1,2 or 1,3 hydrogen shift mechanism. Owing to the conjugation with π-systems, as confirmed by experiment, vinylidene formation seems to be facilitated emphasizing the unique role of the ferrocenyl moiety. Notwithstanding this, complexes **3a** and **3b** appear to be the first examples of η<sup>2</sup>-allenyl carbene complexes as compared to the well-established η<sup>2</sup>-vinyl carbene complexes.

### 3. Experimental

#### 3.1. General procedures

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [10]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [RuCp(PMe<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> (**1a**), [RuCp(PPh<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> (**1b**), and [RuCp(PCy<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> (**1c**) were prepared according to the literature [6]. <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to SiMe<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> (85%).

#### 3.2. [CpRu(=C(Fc)-(η<sup>3</sup>-CHC(Fc)CHPMe<sub>3</sub>)]PF<sub>6</sub> (**2**)

A solution of **1a** (150 mg, 0.319 mM) in CH<sub>3</sub>NO<sub>2</sub> (5 ml) was treated with ferrocenyl acetylene (141 mg, 0.671 mM) and was stirred for 4 h, whereupon the color of the solution turned dark violet. After the volume of the solution was reduced to about 1 ml, Et<sub>2</sub>O (10 ml) was slowly added and a violet microcrystalline precipitate was formed. The solid was collected on a glass frit, washed twice with Et<sub>2</sub>O and dried under vacuum. Yield: 175 mg (80%). Anal. Found: C, 47.64; H, 4.31. Calc. for C<sub>32</sub>H<sub>34</sub>F<sub>6</sub>P<sub>2</sub>Fe<sub>2</sub>Ru: C, 47.61; H, 4.25%. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 5.75 (s, 1H, H<sup>2</sup>); 5.12 (s, 5H, Cp<sub>Ru</sub>); 5.11–5.03 (m, 2H, Fc); 4.85–4.81 (m, 1H, Fc); 5.33 (d, 1H, [*J*<sub>PH</sub>] = 10.80 Hz], H<sup>4</sup>); 4.65–4.57 (m, 3H, Fc); 4.40–4.31 (m, 2H, Fc); 4.29 (s, 5H, Cp<sub>Fe</sub>); 4.23 (s, 5H, Cp<sub>Fe</sub>); 1.20 (d, 9H, [*J*<sub>PH</sub>] = 13.40 Hz], PMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 249.2 (d, [*J*<sub>CP</sub>] = 5.1 Hz], C<sup>1</sup>); 102.1 (d, [*J*<sub>CP</sub>] = 2.5 Hz], C<sup>3</sup>); 92.3 (d, [*J*<sub>CP</sub>] = 2.5], Fc); 82.8 (s, 5C, Cp<sub>Ru</sub>); 78.8 (1C, Fc); 77.2 (1C, C<sup>2</sup>); 74.5 (1C, Fc); 74.2 (1C, Fc); 72.5 (1C, Fc); 72.4 (1C, Fc); 71.5 (s, 5C, Cp<sub>Fe</sub>); 71.3 (1C, Fc); 69.7 (s, 5C, Cp<sub>Fe</sub>); 68.8 (1C, Fc); 68.3 (1C, Fc); 67.2 (1C, Fc); 28.3 (d, [*J*<sub>CP</sub>] = 75.0 Hz], C<sup>4</sup>); 12.2 (d, 3C, [*J*<sub>CP</sub>] = 58.5 Hz], PMe<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 30.2 (PMe<sub>3</sub>); –145.1 ([*J*<sub>PF</sub>] = 707.0 Hz], PF<sub>6</sub>).

#### 3.3. [CpRu(=C(Fc)-η<sup>2</sup>-CH=C=CH(Fc))(PPh<sub>3</sub>)]PF<sub>6</sub> (**3a**)

A solution of **1b** (200 mg, 0.319 mM) and ferrocenyl acetylene (147 mg, 0.701 mM) in CH<sub>2</sub>Cl<sub>2</sub> (4 ml) was stirred at room temperature for 4 h, whereupon the color of the solution turned dark green. The solvent was then removed under vacuum and the remaining green solid was collected on a glass frit, washed with Et<sub>2</sub>O, and dried under vacuum. The crude product was purified by slow diffusion of Et<sub>2</sub>O into a solution of

CH<sub>2</sub>Cl<sub>2</sub>. Yield: 206 mg (65%). Anal. Found: C, 56.79; H, 4.09. Calc. for C<sub>47</sub>H<sub>40</sub>F<sub>6</sub>Fe<sub>2</sub>P<sub>2</sub>Ru: C, 56.82; H, 4.06%. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 7.75–6.60 (m, 15H, PPh<sub>3</sub>); 5.95 (d, 1H, [<sup>5</sup>J<sub>HH</sub> = 3.0 Hz], H<sup>2</sup>); 5.49 (m, 2H, Fc); 5.28 (s, 5H, Cp<sub>Ru</sub>); 5.24 (m, 1H, Fc); 4.59 (m, 1H, Fc); 4.43 (s, 5H, Cp<sub>Fc</sub>); 4.37 (m, 1H, Fc); 4.27 (m, 2H, Fc); 4.22 (m, 1H, Fc); 3.77 (s, 5H, Cp<sub>Fc</sub>); 3.12 (d, 1H, [<sup>5</sup>J<sub>HH</sub> = 3.0 Hz], H<sup>4</sup>). <sup>13</sup>C {<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 279.7 (d, [<sup>2</sup>J<sub>CP</sub> = 9.0 Hz], C<sup>1</sup>); 136.2–127.4 (PPh<sub>3</sub>); 123.1 (d, [<sup>5</sup>J<sub>CP</sub> = 5.0 Hz], C<sup>4</sup>); 89.7 (Cp<sub>Ru</sub>); 85.1 (d, [<sup>4</sup>J<sub>CP</sub> = 5.0 Hz], Fc); 81.8 (Fc); 80.1 (Fc); 78.0 (Fc); 75.9 (Fc); 73.8 (5C, Cp<sub>Fc</sub>); 68.9 (Fc); 68.7 (5C, Cp<sub>Fc</sub>); 68.6 (Fc); 66.9 (1C, C<sup>3</sup>); 65.8 (Fc); 30.4 (d, [<sup>3</sup>J<sub>CP</sub> = 3.0 Hz], C<sup>2</sup>). <sup>31</sup>P {<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 39.3 (PPh<sub>3</sub>); –145.0 (PF<sub>6</sub><sup>–</sup>, [<sup>1</sup>J<sub>PF</sub> = 706 Hz]).

X-ray data for C<sub>48</sub>H<sub>42</sub>Cl<sub>2</sub>F<sub>6</sub>Fe<sub>2</sub>P<sub>2</sub>Ru **3a**·CH<sub>2</sub>Cl<sub>2</sub>: M<sub>r</sub> = 1078.43; monoclinic, space group P2<sub>1</sub>/n, a = 12.220(2) Å, b = 14.509(3) Å, c = 25.300(5) Å, β = 94.87(1)°, V = 4470(1) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.603 g cm<sup>–3</sup>, F(000) = 2176, T = 297(2) K. Of the 52873 reflections collected, 9734 were unique (R<sub>int</sub> = 0.032). R<sub>1</sub> = 0.033 (I ≥ 2σ(I)), R<sub>1</sub> = 0.046 (all data), wR<sub>2</sub> = 0.091 (all data), no. of refined parameters 604. The structure was solved using direct methods and refined by full-matrix least squares on F<sup>2</sup>.

### 3.4. [CpRu(=C(Fc)-η<sup>2</sup>-CH=C=CH(Fc))(PCy<sub>3</sub>)]PF<sub>6</sub> (**3b**)

This compound was prepared analogously to **3a** with **1c** (100 mg, 0.213 mM) and ferrocenyl acetylene (90 mg, 0.447 mM) as starting materials. Yield: 125 mg (71%). Anal. Found: C, 55.84; H, 5.81. Calc. for C<sub>47</sub>H<sub>58</sub>F<sub>6</sub>Fe<sub>2</sub>P<sub>2</sub>Ru: C, 55.81; H, 5.78. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 6.27 (d, 1H, [<sup>4</sup>J<sub>HH</sub> = 3 Hz], H<sup>2</sup>); 5.56 (m, 1H, Fc); 5.54 (s, 5H, Cp<sub>Ru</sub>); 5.42 (m, 1H, Fc); 5.38 (m, 1H, Fc); 5.11 (m, 1H, Fc); 4.52 (m, 1H, Fc); 4.50 (s, 5H, Cp<sub>Fc</sub>); 4.37 (m, 1H, Fc); 4.28 (m, 2H, Fc); 4.16 (s, 5H, Cp<sub>Fc</sub>); 2.98 (d, 1H, [<sup>4</sup>J<sub>HH</sub> = 3 Hz], H<sup>4</sup>); 1.88–0.90 (m, 33H, PCy<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 283.8 (d, [<sup>2</sup>J<sub>CP</sub> = 8.0 Hz], C<sup>1</sup>), 122.0 (d, 1C, [<sup>5</sup>J<sub>CP</sub> = 4.0 Hz], C<sup>4</sup>); 88.2 (Cp<sub>Ru</sub>); 86.6 (Fc); 81.4 (Fc); 79.1 (Fc); 77.6 (Fc); 76.3 (Fc); 73.1 (5C, Cp<sub>Fc</sub>); 69.7 (Fc); 68.9 (5C, Cp<sub>Fc</sub>); 68.7 (d, 1C, [<sup>4</sup>J<sub>CP</sub> = 4.0 Hz], C<sup>3</sup>); 66.7 (Fc); 66.2 (Fc); 37.2 (d, 3C, [<sup>3</sup>J<sub>CP</sub> = 24.0 Hz], Cy<sup>1</sup>); 29.6 (3C, Cy<sup>4</sup>); 29.0 (d, 3C, [<sup>3</sup>J<sub>CP</sub> = 4.0 Hz], Cy<sup>2</sup>); 27.3 (d, [<sup>3</sup>J<sub>CP</sub> = 2.0 Hz], C<sup>2</sup>); 27.2 (3C, Cy<sup>3</sup>); 27.1 (d, 3C, [<sup>3</sup>J<sub>CP</sub> = 4.0 Hz], Cy<sup>2</sup>); 25.8 (3C, Cy<sup>3</sup>). <sup>31</sup>P {<sup>1</sup>H}-NMR (CD<sub>3</sub>CN, 20 °C, δ ppm): 45.1 (PCy<sub>3</sub>); –141.6 (PF<sub>6</sub><sup>–</sup>, [<sup>1</sup>J<sub>PF</sub> = 706 Hz]).

## 4. Supplementary material

Crystallographic data for **3a**·CH<sub>2</sub>Cl<sub>2</sub> have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142969. Copies of this information

may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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(b) M.C. Puerta, P. Valerga, Coord. Chem. Rev. 193 (1999) 977.
- [9] An alternative mechanism to yield  $\eta^2$ -allenyl carbene complexes has been suggested by one reviewer involving the following steps:  
(i) deprotonation of the  $\eta^2$ -HC=CFC ligand to give a  $\sigma$ -C=CFC alkynyl ligand; (ii) insertion of the vinylidene moiety into the alkynyl to yield a neutral  $\eta^3$ -enynyl ligand,  $\text{FcC}\equiv\text{CC}=\text{CHFc}$ ; and (iii) re-protonation to finally afford an  $\eta^2$ -allenyl carbene complex.
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