Organometallics **2005,** *24,* 3111−3117 3111

Efficient One-Pot Synthesis of α,*β*-Unsaturated Carbyne Complexes *fac*-[RuX_3{≡CC(H)=CR_2}(dppf)] (X = Cl, Br; R = Aryl, Alkyl; dppf = 1,1′-Bis(diphenylphosphino)ferrocene)

Victorio Cadierno,* Josefina Díez, Sergio E. García-Garrido, and José Gimeno*

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

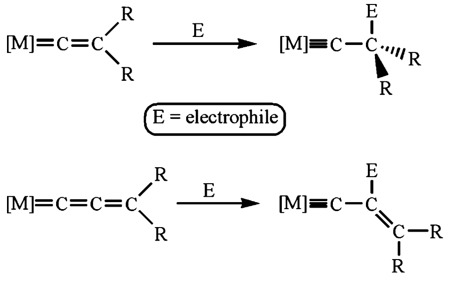
Received March 18, 2005

Alkenyl-carbyne complexes *fac*-[RuX_3{≡CC(H)=CR_2}(dppf)] (X = Cl, Br; R = Ph, ^{i}Pr or CR_2 = $C_{13}H_8$) (**2a**−**c**, **3a**−**c**) have been prepared by reaction of the bis(allyl)-ruthenium(II) derivative [Ru(η^3-2-$C_3H_4Me)_2$(dppf)] (**1**) with the appropriate propargylic alcohol HC≡CCR_2(OH) in the presence of 3.5 equiv of the corresponding hydrogen halide HX. The structure of compounds *fac*-[$RuCl_3${≡CC(H)=CR_2}(dppf)] (R = Ph (**2a**) and ^{i}Pr (**2c**)) has been confirmed by X-ray crystallography. Structural parameters within the alkenyl-carbyne chain in **2a**,**c** suggest an important contribution of the zwitterionic vinylidene canonical form *fac*-[$RuCl_3$-{=C=C(H)-CR_2}(dppf)]. Formation of complexes **2**,**3a**−**c** involves the 1,3-addition of HX to the corresponding dinuclear allenylidene intermediates [{RuX(μ-X)(=C=C=CR_2)(dppf)}$_2$]. Such allenylidene complexes, i.e., [{RuX(μ-X)(=C=C=CR_2)(dppf)}$_2$] (X = Cl, Br; R = Ph or CR_2 = $C_{13}H_8$) (**4a**,**b**, **5a**,**b**), have been prepared and characterized by treatment of *fac*-[RuX_3{≡CC(H)=CR_2}(dppf)] (X = Cl, Br; R = Ph or CR_2 = $C_{13}H_8$) (**2a**,**b**, **3a**,**b**) with 1 equiv of $AgSbF_6$, via halide abstraction and concomitant deprotonation of the alkenyl-carbyne chain.

Introduction

After Fischer and co-workers reported in 1973 the preparation and structural characterization of the first examples of transition metal carbyne complexes, namely, [MX(≡CR)$(CO)_4$] (M = Cr, Mo, W; X = Cl, Br, I; R = Me, Ph),[1] the chemistry of this class of compounds has been largely developed not only because of their unusual type of bonding but also due to their growing applications in organic synthesis.[2] Among the most useful synthetic routes for the preparation of carbyne complexes,[2] the addition of electrophiles to the nucleophilic C_β of coordinated vinylidene and allenylidene ligands is now well established (see Chart 1).[3,4] In particular, when allenylidene complexes are used as starting materials, α,β-unsaturated alkenyl-carbynes [M]≡C−C(E)=CR_2 are readily generated.

Chart 1



In contrast to the high number of osmium-carbyne complexes reported to date,[5] those of ruthenium are much less numerous[6] despite some of them having proven to be active catalysts in olefin metathesis.[6b,e,i,m] In particular, ruthenium alkenyl-carbynes are very scarce. Thus, until now, the only examples described in the literature are (see Chart 2) [RuCl{≡CC(H)=CPh_2}-{κ^2(*P*,*O*)-$Cy_2P(CH_2)_2OMe$}{κ^1(*P*)-$Cy_2P(CH_2)_2OMe$}]-[BF_4, PF_6] (**A**),[6f] [Ru{≡CC(H)=C(R)Ph}(η^5-C_5Me_5)(dippe)]-

---

* To whom correspondence should be addressed. E-mail: jgh@uniovi.es (J.G.); vcm@uniovi.es (V.C.).

(1) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 564.

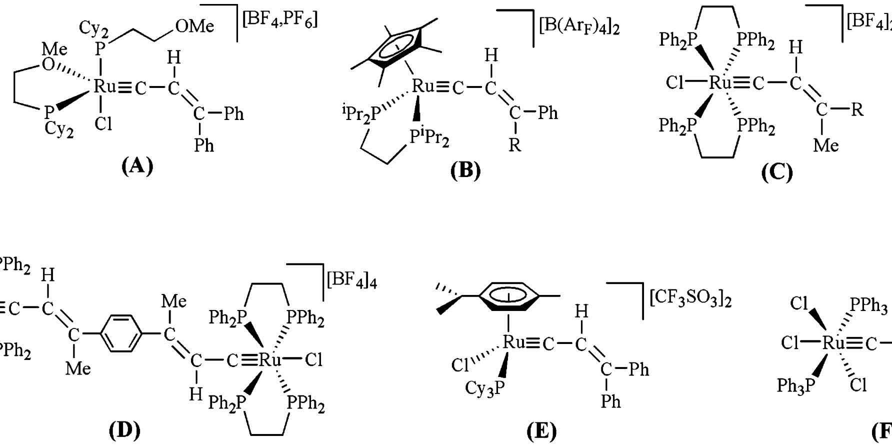
(2) For general reviews on the chemistry of transition metal carbyne complexes see: (a) Kim H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. In *Carbyne Complexes*; VCH: Weinheim, Germany, 1988. (c) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (d) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281. (e) Schrock, R. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2541, and references therein.

(3) For reviews on the chemistry of transition metal vinylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (d) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193−195*, 977. (e) Selegue, J. P. *Coord. Chem. Rev.* **2004**, *248*, 1543. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627. (g) Werner, H. *Coord. Chem. Rev.* **2004**, *248*, 1692. (h) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703.

(4) For reviews on the chemistry of transition metal allenylidene complexes see: (a) Le Bozec, H.; Dixneuf, P. H. *Russ. Chem. Bull.* **1997**, *44*, 801. (b) Werner, H. *Chem. Commun.* **1997**, 903. (c) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (d) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178−180*, 409. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (f) Werner, H.; Ilg, K.; Lass, R.; Wolf, J. *J. Organomet. Chem.* **2002**, *661*, 137. (g) Winter, R. F.; Záliš, S. *Coord. Chem. Rev.* **2004**, *248*, 1565. (h) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **2004**, *248*, 1585. (i) Fischer, H.; Szesni, N. *Coord. Chem. Rev.* **2004**, *248*, 1659.

10.1021/om050204u CCC: \$30.25

Chart 2

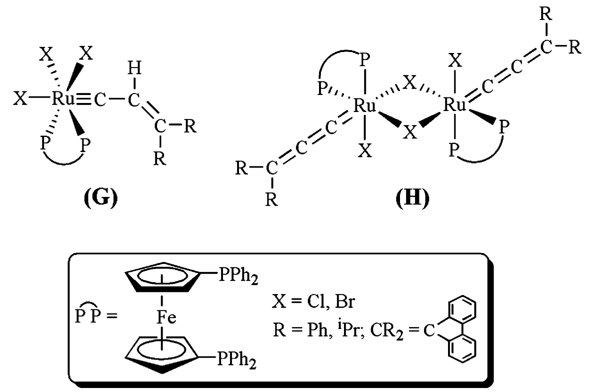


$[\mathrm{B(Ar_F)_4}]_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane; R = H, Ph; $\mathrm{Ar_F} = 3,5\text{-}\mathrm{C_6H_3(CF_3)_2}$) (**B**),[6g] *trans*-$[\mathrm{RuCl\{{\equiv}CC(H){=}C(R)Me\}(dppe)_2}][\mathrm{BF_4}]_2$ (dppe = bis(diphenylphosphino)ethane; R = Me, Ph) (**C**),[6k] *trans*-$[\mathrm{Cl(dppe)_2Ru\{{\equiv}CC(H){=}C(Me)}\text{-}p\text{-}\mathrm{C_6H_4{-}C(Me){=}C(H)C{\equiv}\}RuCl(dppe)_2}][\mathrm{BF_4}]_4$ (**D**),[6k] $[\mathrm{RuCl\{{\equiv}CC(H){=}CPh_2\}}(\eta^6\text{-}p\text{-cymene})(\mathrm{PCy_3})][\mathrm{CF_3SO_3}]_2$ (**E**),[6m,7] and *mer,trans*-$[\mathrm{RuCl_3\{{\equiv}CC(H){=}CMe_2\}(PPh_3)_2}]$ (**F**).[6h]

With the exception of complex **F**, which has been obtained by reacting $[\mathrm{RuHCl(PPh_3)_3}]$ with an excess of 3-chloro-3-methyl-1-butyne ($\mathrm{HC{\equiv}CC(Cl)Me_2}$),[6h] the rest of alkenyl-carbynes **A**−**E** have been generated by protonation of the corresponding allenylidene derivatives. This synthetic methodology requires that these starting materials have to be available.

In the present paper we report a straightforward and efficient synthetic approach to novel neutral alkenyl-carbyne ruthenium complexes *fac*-$[\mathrm{RuX_3\{{\equiv}CC(H){=}CR_2\}(dppf)}]$ (**G**) (dppf = 1,1′-bis(diphenylphosphino)ferrocene)[8] (see Chart 3), which avoids the use of isolated allenylidenes as starting materials. They have been prepared in a one-pot manner by reacting the bis(allyl)-ruthenium(II) complex $[\mathrm{Ru}(\eta^3\text{-}2\text{-}\mathrm{C_3H_4Me})_2(\mathrm{dppf})]$ (**1**)[9] with propargylic alcohols in the presence of HCl or HBr. The process involves the initial formation of dinuclear allenylidene species $[\{\mathrm{RuX}(\mu\text{-X})(\mathrm{{=}C{=}C{=}CR_2})(\mathrm{dppf})\}_2]$ (**H**), via HX-promoted releasing of the η^3-allyl units from **1**,[10] which react in situ with HX to give the alkenyl-carbyne derivatives **G**. The synthesis of these dinuclear metallacumulenes by treatment of *fac*-$[\mathrm{RuX_3\{{\equiv}CC(H){=}CR_2\}(dppf)}]$ (**G**) with $\mathrm{AgSbF_6}$ is also reported.

Chart 3



---

(5) For recent examples see: (a) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Oñate, E. *Organometallics* **2001**, *20*, 1545. (b) Wen, T. B.; Zhou, Z. Y.; Jia, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1951. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283. (d) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (e) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332. (f) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491. (g) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681. (h) Wen, T. B.; Ng, S. M.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Shek, L.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *J. Am. Chem. Soc.* **2003**, *125*, 884. (i) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (j) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (k) Wen, T. B.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Organometallics* **2003**, *22*, 5217. (l) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946. (m) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 3021. (n) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858. (o) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787. (p) Wen, T. B.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Williams, I. D.; Jia, G. *Eur. J. Inorg. Chem.* **2004**, 2837.

(6) (a) Baker, L. J.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **1998**, *551*, 247. (b) Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421. (c) González-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3266. (d) Coalter, J. N., Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925. (e) González-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672. (f) Jung, S.; Brandt, C. D.; Werner, H. *New J. Chem.* **2001**, *25*, 1101. (g) Bustelo, E.; Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903. (h) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757. (i) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *J. Chem. Soc., Dalton Trans.* **2002**, 318. (j) Conrad, J. C.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 3634. (k) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980. (l) Beach, N. J.; Jenkins, H. A.; Spivak, G. J. *Organometallics* **2003**, *22*, 5179. (m) Castarlenas, R.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4524. (n) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Eur. J. Inorg. Chem.* **2004**, 469.

(7) P. H. Dixneuf and co-workers have recently demonstrated that the dicationic alkenyl-carbyne $[\mathrm{RuCl\{{\equiv}CC(H){=}CPh_2\}}(\eta^6\text{-}p\text{-cymene})(\mathrm{PCy_3})][\mathrm{CF_3SO_3}]_2$ (**E**) is a key intermediate in the intramolecular transformation of the diphenylallenylidene complex $[\mathrm{RuCl({=}C{=}C{=}CPh_2)}(\eta^6\text{-}p\text{-cymene})(\mathrm{PCy_3})][\mathrm{CF_3SO_3}]$ into the indenylidene derivative $[\mathrm{RuCl}(3\text{-phenylinden-1-ylidene})(\eta^6\text{-}p\text{-cymene})(\mathrm{PCy_3})][\mathrm{CF_3SO_3}]$, the latter showing an extremely high catalytic activity in ROMP. See ref 6m and (a) Bassetti, M.; Centola, F.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 4459. We note that related ruthenium indenylidene complexes of type $[\mathrm{RuCl_2(L)(L')}(3\text{-phenylinden-1-ylidene})]$ (L = L′ = $\mathrm{PCy_3}$, $\mathrm{PPh_3}$; L = *N*-heterocyclic carbene, L′ = $\mathrm{PCy_3}$, $\mathrm{PPh_3}$), resulting from the corresponding diphenylallenylidenes, have been widely used as robust and efficient catalysts for olefin RCM and ROMP reactions. See for example: (b) Dragutan, V.; Dragutan, I.; Verpoort, F. *Platinum Met. Rev.* **2005**, *49*, 33, and references therein.

(8) For reviews on the coordination chemistry of dppf and related ferrocenyl-phosphine ligands see: (a) Gan, K. S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Material Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; p 3. (b) Bandoli, G.; Dolmella, A. *Coord. Chem. Rev.* **2000**, *209*, 161. (c) Colacot, T. J. *Platinum Met. Rev.* **2001**, *45*, 22.

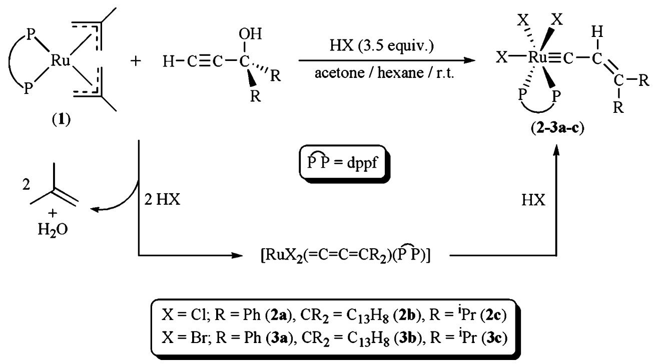
(9) Smith, D. C., Jr.; Cadoret, J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Can. J. Chem.* **2001**, *79*, 626.

Results and Discussion

Synthesis and Characterization of the Alkenyl-Carbyne Complexes *fac*-[RuX$_3${≡CC(H)═CR$_2$}-(dppf)] (X = Cl, Br; R = Ph, ^{i}Pr or CR$_2$ = C$_{13}$H$_8$) (2a–c, 3a–c). Dehydration of propargylic alcohols HC≡CC(OH)R$_2$ upon coordination to an unsaturated metal center is probably the most general synthetic approach to allenylidene complexes [M]═C═C═CR$_2$.[4,11] We have recently reported that the treatment of the readily available bis(allyl)-ruthenium(II) derivative [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**)[9] with 2 equiv of hydrogen halides HX (X = Cl, Br) effectively delivers the unsaturated ruthenium(II) fragments [RuX$_2$(dppf)], via releasing of 2-methylpropene, which can be readily trapped in the presence of isocyanides, affording complexes *trans,cis,-cis*-[RuX$_2$(CNR)$_2$(dppf)].[10d] On the basis of these results we wondered about the possibility of using the highly reactive species [RuX$_2$(dppf)] as suitable starting materials for the preparation of five-coordinate allenylidene-ruthenium(II) complexes [RuX$_2$(═C═C═CR$_2$)(dppf)] by trapping them with propargylic alcohols.[12,13]

However, we have found that the treatment of dichloromethane or acetone solutions of complex [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**) with 1,1-diphenyl-2-propyn-1-ol, 9-ethynyl-9-fluorenol, or 3-isopropyl-4-methyl-1-pentyn-3-ol, in the presence of 2 equiv of HX, leads instead to complicated reaction mixtures containing the desired allenylidene derivatives and the alkenyl-carbyne complexes *fac*-[RuX$_3${≡CC(H)═CR$_2$}(dppf)] (**2a**–**c**, **3a**–**c**) along with several unidentified species. The presence in these mixtures of both alkenyl-carbyne and allenylidene species strongly suggests that a rapid 1,3-addition of a HX molecule to the allenylidene intermediates [RuX$_2$(═C═C═CR$_2$)(dppf)] has occurred. This has been assessed by performing the reactions with a slight excess of HX (3.5 equiv), which leads to the selective formation of the alkenyl-carbynes *fac*-[RuX$_3${≡CC(H)═CR$_2$}(dppf)] (**2a**–**c**, **3a**–**c**) (see Scheme 1).

Scheme 1



Compounds **2a**–**c** and **3a**–**c**, which are only slightly soluble in polar organic solvents, have been isolated as air-stable orange solids in 92–97% yield. They have been characterized by elemental analyses and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy (details are given in the Experimental Section). Key spectroscopic features are as follows: (i) (IR) the presence of a typical ν(C═C) absorption band in the range 1540–1574 cm^{-1}, (ii) (^{31}P{^{1}H} NMR) the appearance of a singlet signal at 19.15–22.27 ppm, in accord with the proposed *fac* stereochemistry and the chemical equivalence of the phosphorus nuclei of the dppf ligand, (iii) (^{1}H NMR) a singlet (**2b**,**c** and **3c**) or triplet (**2a** and **3a**,**b**; $^4J_{HP}$ = 3.7–4.0 Hz) resonance at 3.59–4.33 ppm assigned to the olefinic ═CH hydrogen, and (iv) (^{13}C{^{1}H} NMR) characteristic low-field resonances for the carbynic Ru≡C$_\alpha$ and olefinic C$_\beta$═C$_\gamma$ carbon nuclei which appear in the ranges 292.45–298.52, 130.13–138.95, and 151.19–175.75 ppm, respectively.[14] These chemical shifts compare well with those previously observed in the related alkenyl-carbyne complexes **A**–**F** (see Chart 2). We note also that the Ru≡C$_\alpha$ carbon resonance appears in all cases as a triplet due to the coupling with the two equivalent phosphorus nuclei of the dppf ligand. The relatively low values of the $^2J_{CP}$ coupling constant (15.8–16.9 Hz) clearly reveal that the alkenyl-carbyne chain is located in a *cis* disposition with respect to both phosphorus atoms of the diphosphine.

The proposed stereochemistry for complexes **2a**–**c** and **3a**–**c** has been unequivocally confirmed by X-ray diffraction studies on *fac*-[RuCl$_3${≡CC(H)═CPh$_2$}(dppf)] (**2a**) and *fac*-[RuCl$_3${≡CC(H)═C^{i}Pr$_2$}(dppf)] (**2c**). ORTEP plots are shown in Figure 1; selected bond distances and angles are listed in Table 1. In both molecules the ruthenium atom is in a slightly distorted octahedral environment with the three chloride ligands disposed in a mutually *fac* arrangement. The carbyne unit is located *trans* to one of the chloride ligands and is bound to ruthenium in a nearly linear fashion (Ru–C(35)–C(36) = 171.1(5)° (**2a**) and 175.86(18)° (**2c**)). Bond lengths within the metalla-carbyne unit are very similar in both structures: Ru–C(35) of 1.731(6) Å (**2a**) vs 1.717(2) Å (**2c**); C(35)–C(36) of 1.390(8) Å (**2a**) vs 1.398(3) Å (**2c**); C(36)–C(37) of 1.343(9) Å (**2a**) vs 1.356(3) Å (**2c**). These values can be compared to those previously reported for the related alkenyl-carbyne complexes [Ru{≡CC(H)═CPh$_2$}(η^5-C$_5$Me$_5$)(dippe)][B(Ar$_F$)$_4$]$_2$ and *mer,-trans*-[RuCl$_3${≡CC(H)═CMe$_2$}(PPh$_3$)$_2$] (**B** and **F** in Chart 2).[6g,h] It is interesting to note that in both cases the C(35)–C(36) and C(36)–C(37) bond lengths are quite similar (ca. ±0.05 Å) despite the fact that the former corresponds to a single C–C bond and the latter to a C═C bond. This seems to indicate an important contri-

---

(10) It is well-known that η^3-allyl groups act as labile ligands, generating free coordination sites in acidic media. See for example: (a) Braterman, P. S. In *Reactions of Coordinated Ligands*: Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, p 103. (b) Ratovelomanana-Vidal, V.; Genêt, J. P. *J. Organomet.* Chem. **1998**, *567*, 163, and references therein. (c) Cadierno, V.; Crochet, P.; Díez, J.; García-Garrido, S. E., Gimeno, J. *Organometallics* **2003**, *22*, 5226. (d) Cadierno, V.; Crochet, P.; Díez, J.; García-Garrido, S. E.; Gimeno, J. *Organometallics* **2004**, *23*, 4836.

(11) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(12) A related synthetic methodology has been successfully applied for the preparation of the five-coordinate vinylidene complexes [RuCl$_2${═C═C(H)R}(P^{i}Pr$_3$)$_2$] (R = Ph, ^{t}Bu) by reacting [Ru(η^3-2-C$_3$H$_4$-Me)$_2$(COD)] (COD = 1,5-cyclooctadiene) with P^{i}Pr$_3$ (2 equiv), HCl (2 equiv), and the corresponding terminal alkyne HC≡CR (R = Ph, ^{t}Bu). Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190.

(13) To the best of our knowledge, only three examples of 16-electron allenylidene-ruthenium(II) complexes have been reported, i.e., [RuCl$_2$(═C═C═CPh$_2$)(PCy$_3$)(L)] (L = PCy$_3$, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) and [RuCl(═C═C═CPh$_2$)(PCy$_3$)(DMSO)$_2$][CF$_3$SO$_3$] (DMSO = dimethyl sulfoxide). (a) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187. (b) Abdallaoui, I. A.; Sémeril, D.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 577.

(14) No signal could be experimentally observed for the Ru≡C carbon nuclei in complexes **2c** and **3c** despite trials with long acquisition periods due to their low solubility in common deuterated solvents.

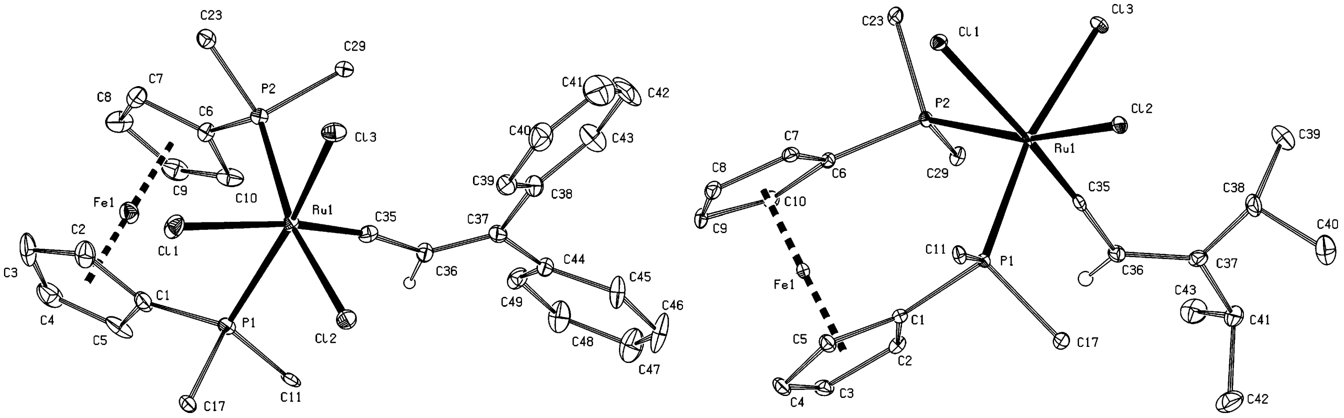


Figure 1. ORTEP-type views of the structure of *fac*-[RuCl$_3${≡CC(H)=CPh$_2$}(dppf)] (**2a**; on the left) and *fac*-[RuCl$_3${≡CC(H)=C^i-Pr$_2$}(dppf)] (**2c**; on the right) showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity (except that on C(36)). Thermal ellipsoids are drawn at the 20% (**2a**) or 30% (**2c**) probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 2a and 2c[a]

2a		**2c**	
	Bond Distances		
Ru–P(1)	2.4157(19)	Ru–P(1)	2.4185(5)
Ru–P(2)	2.3977(18)	Ru–P(2)	2.3824(5)
Ru–Cl(1)	2.4836(18)	Ru–Cl(1)	2.5130(5)
Ru–Cl(2)	2.4432(17)	Ru–Cl(2)	2.3966(5)
Ru–Cl(3)	2.3919(18)	Ru–Cl(3)	2.4442(5)
Ru–C(35)	1.731(6)	Ru–C(35)	1.717(2)
C(35)–C(36)	1.390(8)	C(35)–C(36)	1.398(3)
C(36)–C(37)	1.343(9)	C(36)–C(37)	1.356(3)
Fe–C*	1.6381(10)	Fe–C*	1.6419(3)
Fe–C**	1.6441(10)	Fe–C**	1.6418(3)
	Bond Angles		
P(1)–Ru–P(2)	103.07(6)	P(1)–Ru–P(2)	102.492(18)
P(1)–Ru–Cl(1)	80.94(6)	P(1)–Ru–Cl(1)	97.189(18)
P(1)–Ru–Cl(2)	86.48(6)	P(1)–Ru–Cl(2)	85.349(17)
P(1)–Ru–Cl(3)	164.61(6)	P(1)–Ru–Cl(3)	168.800(18)
P(2)–Ru–Cl(1)	97.71(6)	P(2)–Ru–Cl(1)	80.298(17)
P(2)–Ru–Cl(2)	168.73(6)	P(2)–Ru–Cl(2)	164.953(19)
P(2)–Ru–Cl(3)	85.15(6)	P(2)–Ru–Cl(3)	87.553(18)
Cl(1)–Ru–Cl(2)	89.62(6)	Cl(1)–Ru–Cl(2)	86.032(17)
Cl(1)–Ru–Cl(3)	85.11(6)	Cl(1)–Ru–Cl(3)	89.307(18)
Cl(2)–Ru–Cl(3)	86.97(6)	Cl(2)–Ru–Cl(3)	86.013(17)
P(1)–Ru–C(35)	91.1(2)	P(1)–Ru–C(35)	85.58(7)
P(2)–Ru–C(35)	85.92(19)	P(2)–Ru–C(35)	90.79(7)
Cl(1)–Ru–C(35)	171.8(2)	Cl(1)–Ru–C(35)	171.04(7)
Cl(2)–Ru–C(35)	87.96(19)	Cl(2)–Ru–C(35)	102.71(7)
Cl(3)–Ru–C(35)	102.6(2)	Cl(3)–Ru–C(35)	89.38(7)
Ru–C(35)–C(36)	171.1(5)	Ru–C(35)–C(36)	175.86(18)
C(35)–C(36)–C(37)	130.2(6)	C(35)–C(36)–C(37)	122.8(2)
C*–Fe–C**	179.53(7)	C*–Fe–C**	178.67(2)

[a] C* and C** denote the centroids of the cyclopentadienyl rings C(1), C(2), C(3), C(4), C(5) and C(6), C(7), C(8), C(9), C(10), respectively.

bution of the vinylidene-type canonical form **B** to the structure of alkenyl-carbynes **2a**–**c** and **3a**–**c** (see Figure 2).[15] A high contribution of a vinylidene-type canonical form has been previously proposed by Valerga and co-workers for the alkenyl-carbyne complex [Ru{≡CC(H)=CPh$_2$}(η^5-C$_5$Me$_5$)(dippe)][B(Ar$_F$)$_4$]$_2$.[6g]

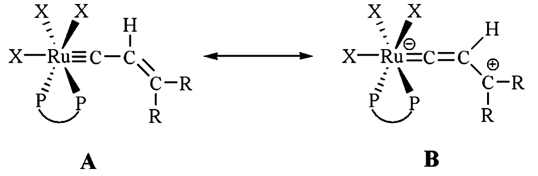


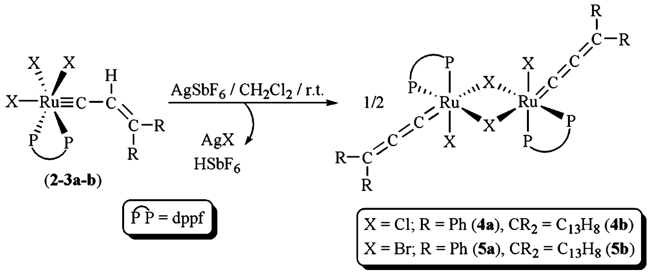
Figure 2. Canonical forms of alkenyl-carbynes **2a**–**c** and **3a**–**c**.

Synthesis and Characterization of Dinuclear Allenylidene Complexes [{RuX(μ-X)(=C=C=CR$_2$)(dppf)}$_2$] (X = Cl, Br; R = Ph or CR$_2$ = C$_{13}$H$_8$) (4a,b, 5a,b). Although all attempts to isolate allenylidene intermediates [RuX$_2$(=C=C=CR$_2$)(dppf)] by reacting [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**) with 1-alkyn-3-ols in the presence of 2 equiv of HX failed, these metallacumulenic species have been obtained using the alkenyl-carbyne complexes *fac*-[RuX$_3${≡CC(H)=CR$_2$}(dppf)] as starting materials. Thus, we have found that the treatment of dichloromethane solutions of complexes **2a**,**b** and **3a**,**b** with 1 equiv of AgSbF$_4$ generates the dinuclear allenylidene compounds [{RuX(μ-X)(=C=C=CR$_2$)(dppf)}$_2$]

---

[15] This fact should be also reflected in a longer Ru–C(35) bond length in comparison to simple (no α,β-unsaturated) ruthenium-carbynes [Ru]≡CR. Nevertheless, the values reported in the literature for this type of complex fall in a broad range (from 1.66 to 1.88 Å; see ref 6), preventing precise conclusions.

Scheme 2



(**4a**,**b**, **5a**,**b**) via halide abstraction and concomitant deprotonation of the alkenyl-carbyne chain (see Scheme 2).[16,17]

Complexes **4a**,**b** and **5a**,**b**, isolated as violet air-stable solids in 93−98% yield, have been characterized by standard analytical and spectroscopic (IR and ^{1}H, ^{31}P-{^{1}H}, and ^{13}C{^{1}H} NMR) techniques (details are given in the Experimental Section). Moreover, their dinuclear nature has been confirmed by FAB-MS, which shows the presence of peaks corresponding to the loss of one halide ligand from the parent ion ($[M^+ - X]$).[18] The spectroscopic data obtained for **4a**,**b** and **5a**,**b** are in agreement with the presence of two equivalent allenylidene chains. Thus, the IR spectra (KBr) exhibit a broad and strong ν(C=C=C) absorption band (asymmetric stretching vibration) at ca. 1930 cm^{-1}, and the ^{13}C{^{1}H} NMR spectra display the characteristic low-field doublet of doublet ($^2J_{CP} = {}^2J_{CP'} = 13.8$−$18.9$ Hz) resonance for the carbenic Ru=C$_\alpha$ atom at 300.30−316.28 ppm. The $^2J_{CP}$ values observed clearly reveal that the allenylidene groups are located in a *cis* disposition with respect to both phosphorus nuclei of the dppf ligands. The spectra also show two singlet signals in the ranges δ_C 218.03−228.35 and 153.66−159.74 ppm corresponding to the β- and γ-carbon nuclei, respectively, as expected for their sp and sp^2 character. All these data are comparable to those previously reported in the literature for other allenylidene-ruthenium(II) complexes.[4,13,18] We also note that, in accord with the proposed structure, the ^{31}P{^{1}H} NMR spectra display a typical AB pattern (δ_P 43.03−49.08 ppm; $^2J_{PP} = 25.3$−28.3 Hz) indicating that (i) both dppf ligands are equivalent and (ii) phosphorus atoms within each dppf ligand are inequivalent.[19]

Apparently, the formation of the coordinatively saturated dinuclear species [{RuX(μ-X)(=C=C=CR$_2$)(dppf)}$_2$] vs the corresponding 16-electron allenylidenes [RuX$_2$(=C=C=CR$_2$)(dppf)] is a thermodynamically favored process. Moreover, the involvement of these dinuclear allenylidenes as the actual intermediate species in the generation of alkenyl-carbynes *fac*-[RuX$_3${≡CC(H)=CR$_2$}(dppf)] (**2a**−**c**, **3a**−**c**) from the reactions of [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**) with propargylic alcohols and 2 equiv of HX has been assessed by comparison of the ^{31}P{^{1}H} NMR spectra of **4a**,**b** and **5a**,**b** with those obtained from the corresponding reaction mixtures. In agreement with this, the treatment of dichloromethane solutions of allenylidenes **4a**,**b** and **5a**,**b** with hydrogen halides HX (X = Cl, Br) regenerates the alkenyl-carbynes **2a**,**b** and **3a**,**b** quantitatively.

Conclusions

In this paper we have described an efficient, straightforward, and stereoselective synthetic route for the preparation of novel alkenyl-carbyne ruthenium complexes *fac*-[RuX$_3${≡CC(H)=CR$_2$}(dppf)] (**2a**−**c**, **3a**−**c**). This synthetic methodology involves the use of the readily available bis(allyl)-ruthenium(II) derivative [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**) as starting material. Thus, complex **1** reacts with propargylic alcohols in the presence of an excess of hydrogen halides HX (X = Cl, Br), leading to the α,β-unsaturated carbynes in a one-pot manner. To the best of our knowledge, only the neutral alkenyl-carbyne *mer,trans*-[RuCl$_3${≡CC(H)=CMe$_2$}(PPh$_3$)$_2$] (**F**; see Chart 2), serendipitously obtained by reacting [RuHCl(PPh$_3$)$_3$] with an excess of 3-chloro-3-methyl-1-butyne (HC≡CC(Cl)Me$_2$), has been previously reported.[6h] We note also that, in comparison with the classical two-step methodology, namely, preparation and isolation of an allenylidene precursor and its subsequent protonation, the synthetic route reported here is much more simple and efficient. It is proposed that formation of alkenyl-carbynes **2a**−**c** and **3a**−**c** proceeds via 1,3-addition of HX to dinuclear allenylidene intermediates [{RuX(μ-X)(=C=C=CR$_2$)(dppf)}$_2$]. Remarkably, these metallacumulenic species can be also easily prepared from *fac*-[RuX$_3${≡CC(H)=CR$_2$}(dppf)] through abstraction of one halide ligand and concomitant deprotonation of the alkenyl-carbyne chain. Although the chemistry of allenylidene-ruthenium(II) complexes has been the subject of special attention during the last years due to the wealth of their applications in stoichiometric and catalytic reactions,[4a,c−e,g,h] the allenylidene derivatives described here [{RuX(μ-X)(=C=C=CR$_2$)(dppf)}$_2$] belong to the limited series of dinuclear complexes containing halide-bridged ligands.[18]

Experimental Section

Synthetic procedures were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compound [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**), which was prepared by following the method reported in the literature.[9] Infrared spectra were recorded on a Perkin-

---

(16) It is known that the hydrogen atom on the β-carbon of alkenyl-carbyne complexes is highly acidic, being easily deprotonated even with weak bases such as diethyl ether or acetone. See refs 6f,g.

(17) (a) Allenylidene complexes **4a**,**b** and **5a**,**b** are also generated in the reaction of carbyne complexes **2a**,**b** and **3a**,**b** with Et$_3$N. Nevertheless, we were unable to isolate **4a**,**b** and **5a**,**b** in pure form by this route since all attempts to separate the ammonium salts [Et$_3$NH]X (X = Cl, Br), formed as byproducts in these reactions, failed (chromatographic workup leads to extensive decompositions). (b) One of the referees directed our attention to the formulation of allenylidene complexes **4a**,**b** and **5a**,**b** as cationic dimers containing three halide-bridged ligands [Ru$_2$(μ-X)$_3$(=C=C=CR$_2$)$_2$(dppf)$_2$][X]. Conductance measurements at room temperature allow discarding this formulation. Λ_M values of acetone solutions (ca. 10^{-3} mol dm^{-3}) of complexes **4a**,**b** and **5a**,**b** are in all cases <30 Ω^{-1} cm^2 mol^{-1} (typical values for 1:1 electrolytes fall in the range 100−140 Ω^{-1} cm^2 mol^{-1}).

(18) The dinuclear allenylidene-ruthenium(II) complexes containing halide-bridged ligands [{Ru(=C=C=CR$_2$)(PPh$_3$)$_2$}$_2$(μ-Cl)$_3$][PF$_6$] (R = Ph, *o*-C$_6$H$_4$Cl, *o*-C$_6$H$_4$F) and [Na]$_4$[{RuCl(μ-Cl)(=C=C=CPh$_2$)(TPPMS)$_2$}$_2$] (TPPMS = Ph$_2$P(*o*-C$_6$H$_4$SO$_3$Na) are known: (a) Touchard, D.; Guesmi, S.; Bouchaib, M.; Haquette, P.; Daridor, A.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2579. (b) Saoud, M.; Romerosa, A.; Peruzzini, M. *Organometallics* **2000**, *19*, 4005.

(19) We note that all these NMR spectroscopic data are comparable to those recently reported by us for the dimeric species [{RuX(μ-X)(CO)(dppf)$_2$}$_2$] (X = Cl, Br), which present the same arrangement of the two metallic units. See ref 10c.

Elmer 1720-XFT spectrometer. FAB mass spectra were recorded using a VG-Autospec spectrometer operating in positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper.

Synthesis of *fac*-[RuCl$_3${≡CC(H)=CR$_2$}(dppf)] (R = Ph (2a), CR$_2$ = C$_{13}$H$_8$ (2b), R = ^{i}Pr (2c)). To a solution of [Ru(η^3-2-C_3H_4Me)$_2$(dppf)] (**1**) (0.765 g; 1.0 mmol) in 120 mL of a mixture of acetone/hexane (1:5) were added HCl (3.5 mL of a 1.0 M solution in diethyl ether; 3.5 mmol) and the corresponding propargylic alcohol (2 mmol). The reaction mixture was then stirred at room temperature for 24 h. The orange precipitate formed during the reaction was collected by filtration, washed with hexane (10 × 10 mL), and dried in vacuo. **2a**: yield 93% (0.886 g). Anal. Calcd for $FeRuC_{49}H_{39}Cl_3P_2$: C, 61.75; H, 4.12. Found: C, 62.11; H, 4.35. IR (KBr, cm^{-1}): ν 1572 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.29 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.14 (t, 1H, $^4J_{HP}$ = 4.0 Hz, =CH), 4.62, 4.68, 4.73, and 5.60 (br, 2H each, C_5H_4), 6.70−8.10 (m, 30H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 73.29 (br, 2C, CH of C_5H_4), 75.53 and 76.76 (br, CH of C_5H_4), 77.41 (d, $^1J_{CP}$ = 55.6 Hz, C of C_5H_4), 126.70−138.25 (m, C_{arom} and CH_{arom}), 136.83 (s, =C$_\beta$H), 175.75 (s, =C$_\gamma$), 298.52 (t, $^2J_{CP}$ = 15.8 Hz, Ru≡C$_\alpha$) ppm. **2b**: yield 96% (0.913 g). Anal. Calcd for $FeRuC_{49}H_{37}Cl_3P_2$: C, 61.88; H, 3.92. Found: C, 62.23; H, 4.23. IR (KBr, cm^{-1}): ν 1570 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.27 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.33 (s, 1H, =CH), 4.62, 4.69, 4.76, and 5.61 (br, 2H each, C_5H_4), 6.75−9.50 (m, 28H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 73.42 (br, 2C, CH of C_5H_4), 75.81 and 76.65 (br, CH of C_5H_4), 76.83 (d, $^1J_{CP}$ = 54.2 Hz, C of C_5H_4), 120.20−142.50 (m, C_{arom} and CH_{arom}), 136.64 (s, =C$_\beta$H), 165.13 (s, =C$_\gamma$), 292.45 (t, $^2J_{CP}$ = 16.9 Hz, Ru≡C$_\alpha$) ppm. **2c**: yield 97% (0.858 g). Anal. Calcd for $FeRuC_{43}H_{43}Cl_3P_2$: C, 58.36; H, 4.90. Found: C, 58.53; H, 5.08. IR (KBr, cm^{-1}): ν 1573 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.06 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.09 and 1.20 (br, 6H each, CH(C*H*$_3$)$_3$), 2.82 and 3.38 (m, 1H each, C*H*(CH$_3$)$_3$), 3.59 (s, 1H, =CH), 4.25, 4.57, 4.72, and 5.49 (br, 2H each, C_5H_4), 6.85−8.10 (m, 20H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.66 and 23.10 (s, CH(*C*H$_3$)$_3$), 31.51 and 32.00 (s, *C*H(CH$_3$)$_3$), 73.83 (br, 2C, CH of C_5H_4), 75.43 and 76.97 (br, CH of C_5H_4), 77.82 (d, $^1J_{CP}$ = 51.7 Hz, C of C_5H_4), 126.00−136.10 (m, C_{arom} and CH_{arom}), 130.13 (s, =C$_\beta$H), 152.14 (s, =C$_\gamma$) ppm. Ru≡C not observed.

Synthesis of *fac*-[RuBr$_3${≡CC(H)=CR$_2$}(dppf)] (R = Ph (3a), CR$_2$ = C$_{13}$H$_8$ (3b), R = ^{i}Pr (3c)). Complexes **3a**−**c**, isolated as orange solids, were prepared as described for **2a**−**c** starting from [Ru(η^3-2-C_3H_4Me)$_2$(dppf)] (**1**) (0.765 g, 1.0 mmol), HBr (3.5 mL of a 1.0 M solution in diethyl ether; 3.5 mmol), and the corresponding propargylic alcohol (2 mmol). **3a**: yield 94% (1.021 g). Anal. Calcd for $FeRuC_{49}H_{39}Br_3P_2$: C, 54.17; H, 3.62. Found: C, 54.35; H, 3.94. IR (KBr, cm^{-1}): ν 1574 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.15 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 3.99 (t, 1H, $^4J_{HP}$ = 3.7 Hz, =CH), 4.62, 4.69, 4.75, and 5.70 (br, 2H each, C_5H_4), 6.60−8.20 (m, 30H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 74.25, 75.15, 77.08, and 77.40 (br, CH of C_5H_4), 78.67 (d, $^1J_{CP}$ = 52.2 Hz, C of C_5H_4), 125.40−141.90 (m, C_{arom} and CH_{arom}), 138.95 (s, =C$_\beta$H), 175.34 (s, =C$_\gamma$), 296.61 (t, $^2J_{CP}$ = 16.4 Hz, Ru≡C$_\alpha$) ppm. **3b**: yield 92% (0.998 g). Anal. Calcd for $FeRuC_{49}H_{37}Br_3P_2$: C, 54.27; H, 3.44. Found: C, 54.56; H, 3.71. IR (KBr, cm^{-1}): ν 1570 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 20.40 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.28 (t, 1H, $^4J_{HP}$ = 3.9 Hz, =CH), 4.68, 4.71, 4.80, and 5.70 (br, 2H each, C_5H_4), 6.10−9.70 (m, 28H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 73.98, 74.49, 76.97, and 77.25 (br, CH of C_5H_4), 78.26 (d, $^1J_{CP}$ = 53.3 Hz, C of C_5H_4), 120.20−143.00 (m, C_{arom} and CH_{arom}), 136.01 (s, =C$_\beta$H), 165.12 (s, =C$_\gamma$), 296.15 (t, $^2J_{CP}$ = 16.4 Hz, Ru≡C$_\alpha$) ppm. **3c**: yield 93% (0.947 g). Anal. Calcd for $FeRuC_{43}H_{43}Br_3P_2$: C, 50.71; H, 4.26. Found: C, 50.96; H, 4.41. IR (KBr, cm^{-1}): ν 1540 (C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.47 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.12 and 1.23 (br, 6H each, CH(C*H*$_3$)$_3$), 2.73 and 3.41 (m, 1H each, C*H*(CH$_3$)$_3$), 3.63 (s, 1H, =CH), 4.29, 4.60, 4.76, and 5.53 (br, 2H each, C_5H_4), 6.95−8.15 (m, 20H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 20.71 and 22.15 (s, CH(*C*H$_3$)$_3$), 30.56 and 31.05 (s, *C*H(CH$_3$)$_3$), 71.57 (br, 2C, CH of C_5H_4), 73.60 and 76.02 (br, CH of C_5H_4), 77.27 (d, $^1J_{CP}$ = 55.2 Hz, C of C_5H_4), 125.05−136.25 (m, C_{arom} and CH_{arom}), 136.27 (s, =C$_\beta$H), 151.19 (s, =C$_\gamma$) ppm. Ru≡C not observed.

Synthesis of [{RuCl(μ-Cl)(=C=C=CR$_2$)(dppf)}$_2$] (R = Ph (4a), CR$_2$ = C$_{13}$H$_8$ (4b)). $AgSbF_6$ (0.176 g, 0.5 mmol) was added, at room temperature, to a solution of complexes *fac*-[RuCl$_3${≡CC(H)=CR$_2$}(dppf)] (**2a**,**b**; 0.5 mmol) in 20 mL of dichloromethane. The reaction mixture was stirred, at room temperature and in the absence of light, for 30 min. The AgCl formed was then filtered off over Kieselguhr and the solvent removed under reduced pressure to afford a violet solid, which was washed with diethyl ether (3 × 50 mL) and vacuum-dried. **4a**: yield 93% (0.426 g). Anal. Calcd for $Fe_2Ru_2C_{98}H_{76}Cl_4P_4$: C, 64.21; H, 4.18. Found: C, 64.53; H, 4.23. IR (KBr, cm^{-1}): ν 1934 (C=C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 46.36 and 49.05 (d, $^2J_{PP}$ = 28.3 Hz) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.10−4.30 (m, 16H, C_5H_4), 7.20−7.70 (m, 60H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 72.10, 72.20, 72.79, and 73.50 (d, $^2J_{CP}$ = 4.6 Hz, CH of C_5H_4), 75.94, 76.13, 76.34, and 76.45 (d, $^3J_{CP}$ = 8.7 Hz, CH of C_5H_4), 80.17 and 80.91 (d, $^1J_{CP}$ = 45.0 Hz, C of C_5H_4), 127.25−145.25 (m, C_{arom} and CH_{arom}), 159.00 (s, C$_\gamma$), 218.03 (s, C$_\beta$), 312.04 (dd, $^2J_{CP}$ = 16.5 and 16.5 Hz, Ru=C$_\alpha$) ppm. MS (FAB): *m/z* 1797 [M$^+$ − Cl], 881 [1/2M$^+$ − Cl]. **4b**: yield 98% (0.448 g). Anal. Calcd for $Fe_2Ru_2C_{98}H_{72}Cl_4P_4$: C, 64.35; H, 3.97. Found: C, 64.72; H, 4.16. IR (KBr, cm^{-1}): ν 1934 (C=C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.17 and 49.08 (d, $^2J_{PP}$ = 28.0 Hz) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.22−4.54 (m, 16H, C_5H_4), 6.90−7.90 (m, 56H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 71.53, 71.99, 73.44, and 73.87 (d, $^2J_{CP}$ = 4.7 Hz, CH of C_5H_4), 75.64, 75.80, 76.11, and 76.64 (d, $^3J_{CP}$ = 8.5 Hz, CH of C_5H_4), 78.78 and 80.38 (d, $^1J_{CP}$ = 54.3 Hz, C of C_5H_4), 121.50−165.15 (m, C_{arom} and CH_{arom}), 153.66 (s, C$_\gamma$), 227.37 (s, C$_\beta$), 300.30 (dd, $^2J_{CP}$ = 13.8 and 13.8 Hz, Ru=C$_\alpha$) ppm. MS (FAB): *m/z* 1793 [M$^+$ − Cl], 879 [1/2M$^+$ − Cl].

Synthesis of [{RuBr(μ-Br)(=C=C=CR$_2$)(dppf)}$_2$] (R = Ph (5a), CR$_2$ = C$_{13}$H$_8$ (5b)). Complexes **5a**,**b**, isolated as violet solids, were prepared as described for **4a**,**b** starting from *fac*-[RuBr$_3${≡CC(H)=CR$_2$}(dppf)] (**3a**,**b**; 0.5 mmol) and $AgSbF_6$ (0.176 g, 0.5 mmol). **5a**: yield 93% (0.467 g). Anal. Calcd for $Fe_2Ru_2C_{98}H_{76}Br_4P_4$: C, 58.53; H, 3.81. Found: C, 58.31; H, 3.70. IR (KBr, cm^{-1}): ν 1926 (C=C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.59 and 48.79 (d, $^2J_{PP}$ = 25.3 Hz) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.06−4.55 (m, 16H, C_5H_4), 6.85−7.95 (m, 60H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 71.89, 72.31, 72.74, and 74.12 (d, $^2J_{CP}$ = 5.1 Hz, CH of C_5H_4), 75.71, 76.22, 76.36, and 76.64 (d, $^3J_{CP}$ = 7.5 Hz, CH of C_5H_4), 80.45 and 80.91 (d, $^1J_{CP}$ = 54.2 Hz, C of C_5H_4), 122.00−165.50 (m, C_{arom} and CH_{arom}), 159.74 (s, C$_\gamma$), 218.70 (s, C$_\beta$), 312.82 (dd, $^2J_{CP}$ = 18.9 and 18.9 Hz, Ru=C$_\alpha$) ppm. MS (FAB): *m/z* 1931 [M$^+$ − Br], 925 [1/2M$^+$ − Br]. **5b**: yield 96% (0.482 g). Anal. Calcd for $Fe_2Ru_2C_{98}H_{72}Br_4P_4$: C, 58.65; H, 3.62. Found: C, 58.91; H, 3.85. IR (KBr, cm^{-1}): ν 1932 (C=C=C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.03 and 48.49 (d, $^2J_{PP}$ = 25.5 Hz) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.01−4.40 (m, 16H, C_5H_4), 6.55−7.95 (m, 56H, H_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 72.02, 72.60, 73.44, and 74.90 (d, $^2J_{CP}$ = 5.8 Hz, CH of C_5H_4), 75.84, 76.19, 76.36, and 77.02 (d, $^3J_{CP}$ = 8.2 Hz, CH of C_5H_4), 79.63 and 80.52 (d, $^1J_{CP}$ = 55.8 Hz, C of C_5H_4), 122.00−165.45 (m, C_{arom} and CH_{arom}), 154.37 (s, C$_\gamma$), 228.35 (s, C$_\beta$), 316.28 (dd, $^2J_{CP}$ = 18.5 and 18.5 Hz, Ru=C$_\alpha$) ppm. MS (FAB): *m/z* 1927 [M$^+$ − Br], 923 [1/2M$^+$ − Br].

X-ray Crystal Structure Determination of Complexes 2a and 2c. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into saturated solu-

Table 2. Crystal Data and Structure Refinement Details for 2a and 2c

	2a	**2c**
chemical formula	$C_{49}H_{39}Cl_3P_2FeRu$	$C_{43}H_{43}Cl_3P_2FeRu\cdot C_2H_4Cl_2$
fw	953.01	983.94
T (K)	223(2)	100(2)
wavelength (Å)	0.71073	1.54178
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cryst size, mm	0.25 × 0.20 × 0.15	0.22 × 0.13 × 0.12
a, Å	11.512(3)	16.6808(1)
b, Å	15.153(4)	13.6309(1)
c, Å	27.063(6)	18.8276(1)
α, deg	90	90
β, deg	93.156(6)	98.265(1)
γ, deg	90	90
Z	4	4
V, Å^3	4714.1(19)	4236.45(5)
ρ_{calcd}, g cm^{-3}	1.343	1.543
μ, mm^{-1}	0.897	9.493
F(000)	1936	2008
θ range, deg	1.51 to 30.59	2.68 to 70.62
index ranges	$-12 \leq h \leq 16$ $-21 \leq k \leq 21$ $-36 \leq l \leq 38$	$-18 \leq h \leq 20$ $-16 \leq k \leq 15$ $-20 \leq l \leq 21$
completeness to θ_{max}	97.4%	92.3%
no. of data collected	39 831	20 532
no. of unique data	11 423 (R_{int} = 0.1654)	7503 (R_{int} = 0.0308)
no. of params/restraints	505/0	676/0
refinement method	full-matrix least-squares on F^2	
goodness of fit on F^2	0.849	1.036
weight function (a, b)	0.0592, 0	0.0338, 1.7542
R1[a] [$I > 2\sigma(I)$]	0.0806	0.0255
wR2[a] [$I > 2\sigma(I)$]	0.1471	0.0632
R1 (all data)	0.2146	0.0278
wR2 (all data)	0.1833	0.0645
largest diff peak and hole, e Å^{-3}	0.755 and −1.343	0.556 and −0.551

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

tions of complexes **2a** and **2c** in dichloromethane or 1,2-dichloroethane, respectively. **2c** was obtained as solvated crystals that contained one 1,2-dichloroethane molecule per molecular unit. The most relevant crystal and refinement data are collected in Table 2. Diffraction data for **2a** were recorded on a Bruker Smart CCD diffractometer using Mo Kα radiation. Diffraction data for **2c** were recorded on a Bruker Smart 6k CCD area-detector three-circle diffractometer using Cu Kα radiation. In both cases, the data were collected using 0.3° wide ω scans with a crystal-to-detector distance of 40 mm. The diffraction frames were integrated using the SAINT package[20] and corrected for absorption with SADABS.[21]

The software package WINGX was used for space group determination, structure solution, and refinement.[22] The structures were solved by Patterson interpretation and phase expansion using DIRDIF.[23] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[24] During the final stages, all non-hydrogen atoms for **2a** and **2c** were refined with anisotropic displacement parameters. The H atoms for **2a** were geometrically located, and their coordinates were refined riding on their parent atoms. The H atoms for **2c** were located by difference maps and refined isotropically. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are shown in Table 2) with $\sigma(F_o^2)$ from counting statistics and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[25] Geometrical calculations were made with PARST.[26] The crystallographic plots were made with PLATON.[27]

Acknowledgment. We are indebted to the Ministerio de Ciencia y Tecnología (MCyT) of Spain (Project BQU2003-00255) for financial support. S.E.G.G and V.C. thank the MCyT for the award of a Ph.D. grant and a "Ramón y Cajal" contract, respectively.

Supporting Information Available: Tables and a CIF file giving crystallographic data for complexes **2a** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050204U

---

(20) *SAINT*, version 6.02; Bruker Analytical X-ray Systems; Madison, WI, 2000.

(21) Sheldrick, G. M. *SADABS*: *Empirical Absorption Program*; University of Göttingen: Göttingen, Germany, 1996.

(22) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(23) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1999.

(24) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(25) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (Present distributor: Kluwer Academic Publishers: Dordrecht, The Netherlands).

(26) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(27) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2005.