Metallacumulenes: Activation of Diynes and Formation of New Allenylideneruthenium Complexes. Crystal Structures of *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}CR^1R^2]^+$ and *trans*-$[(Ph_2PCH_2PPh_2)_2Ru({=}C{=}C{=}C(OMe)CH{=}CPh_2)_2]^{2+}$ Derivatives

Daniel Touchard,*[†] Nadine Pirio,[†] Loïc Toupet,[‡] Mohammed Fettouhi,[§]
Lahcène Ouahab,[§] and Pierre H. Dixneuf*[†]

Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Groupe Matière Condensée et Matériaux, URA CNRS 804, and Laboratoire de Cristallochimie, URA CNRS 1495, Campus de Beaulieu, Université de Rennes 1, 35042 Rennes, France

Received June 19, 1995[⊗]

cis-$RuCl_2(Ph_2PCH_2PPh_2)_2$ (**1**) reacts with pentadiynes $XC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ [**2** (X = H) and **3** (X = Bu_3Sn)], but in the presence of $NaPF_6$, to afford *trans*-$(Ph_2PCH_2PPh_2)_2(Cl)RuC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ (**4**). On protonation with HBF_4 complex **4** in methanol leads to allenylidene *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}C(OMe)CH{=}CPh_2]X$ (**5a**) (**a**: X = BF_4) and in dichloromethane to *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}CCH{=}C(Ph)(o\text{-}C_6H_4)]X$ (**6a**) *via* electrophilic *ortho*-substitution within the metallacumulene intermediate $LnRu{=}C{=}C{=}C{=}C{=}CPh_2]X$ (**A**). Alternatively, complex **1** and diyne **2** with $NaPF_6$ afford in one step allenylidenes **5b** (**b**: X = PF_6) in methanol and **6b** in dichloromethane. Bis(diynyl) derivative *trans*-$(Ph_2PCH_2PPh_2)_2Ru[(C{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2]_2$ (**7**), obtained by reaction of **2** with **1** and HN^iPr_2, on protonation with HBF_4 in methanol offered a direct route to the first bis(allenylidene) complex *trans*-$[(Ph_2PCH_2PPh_2)_2Ru({=}C{=}C{=}C(OMe)CH{=}CPh_2)_2](BF_4)_2$ (**8**). The X-ray diffraction studies of two allenylidene complexes **6b** and **8** are reported. The structure of **6b** consists of two different allenylidene cations. That of **8** shows coplanar allenylidene ligands with a strong contribution of a ynyl resonance structure.

Introduction

Metallacumulenes $M{=}(C{=})_nCR_2$ constitute a new class of organometallics containing a carbon-rich unsaturated chain with a M=C linkage. As unsaturated molecules they have potential for the access to metal containing copolymers[1] or for their materials properties.[2] Their M=C bond offers useful applications for both organometallic and organic syntheses, as expected from the richness and versatility of metal–carbene chemistry.[3] This interest provides impetus to the search for a general method of preparation of metallacumulenes containing functionalities. After metal–vinylidene $M{=}C{=}CR_2$ complexes,[4,5] metal–allenylidene $M{=}C{=}C{=}CR_2$ species are the simplest metallacumulenes. They have initially been obtained by $(C_1)OR$ group elimina-

---

[†] URA CNRS 415.

[‡] URA CNRS 804.

[§] URA CNRS 1495.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

(1) (a) Lavastre, O.; Dixneuf, P. H.; Pacreau, A.; Vairon, J. P. *Organometallics* **1994**, *13*, 2500. (b) Carraher, J. E., Jr.; Pittman, C. E., Jr. *Metal-Containing Polymeric Sustems*; Plenum: New York, 1985. (c) Hagihara, N.; Sonogashira, K.; Takashi, K. *Adv. Polym. Sci.* **1980**, *41*, 150. (d) Takahashi, S.; Morimoto, H.; Murata, F.; Kataobe, S.; Sonogashira, K.; Hagihara, N. J. *Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 562. (e) Brefort, J. L.; Corriu, R. J.; Gerbier, PK.; Guérin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, Th. *Organometallics* **1992**, *11*, 2500. (f) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (g) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1984**, 3.

(2) (a) Dhenault, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374*, 339. (b) Yuan, Z.; Stringer, G.; Jobe, I. R.; Kreller, D.; Scott, K.; Koch, L.; Marder, T. B. *J. Organomet. Chem.* **1993**, *452*, 115. (c) Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349. (d) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: Chichester, U.K., 1992. (e) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

(3) (a) Cosset, C.; Del Rio I.; Le Bozec, H. *Organometallics* **1995**, *14*, 1938. (b) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236. (c) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (d) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784.

(4) (a) King, R. B.; Saran, M. S. *Chem. Commun.* **1972**, 1052; *J. Am. Chem. Soc.* **1972**, *95*, 1817. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Antonova, A. B.; Johansson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693.

(5) (a) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5. (d) Bruce, M. I.; Koutsantonis, G. A. *Aust. J. Chem.* **1991**, *44*, 207. (e) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, *3*, 165. (f) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (g) Consiglio, G.; Morandini, F. *Inorg. Chim. Acta* **1987**, *127*, 79. (h) Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976. (i) Morandini, F.; Consiglio, G.; Sironi, A.; Moret, M. *J. Organomet. Chem.* **1988**, *356*, C79. (j) Werner, H.; Stark, A.; Shulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126. (k) Gamasa, M. P.; Gimeno, J.; Martin-vaca, B. M.; Borge, J.; Garcia-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (l) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132. (m) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030.

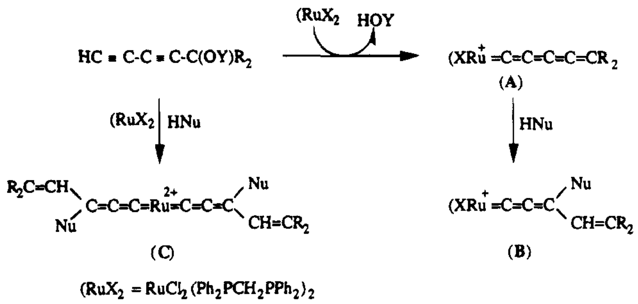
(6) Fischer, E. O.; Kalder, H.-J.; Franck, A.; Köhler, F. H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623.

(7) (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (b) Stein, F.; Duetsch, M.; Noltemeyer, M.; de Meijere, A. *Synlett* **1993**, 486. (c) Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A.K. *Organometallics* **1993**, *12*, 2556. (d) Aumann, R. *Chem. Ber.* **1992**, *125*, 2773.

0276-7333/95/2314-5263$09.00/0

tion of alkenyl[6] and alkynyl[7] carbene derivatives of group 6 metal carbonyls or by addition of a $(C)_3$ skeleton dianion, either $[C{\equiv}CCR_2O]^{2-}$ to metal carbonyls[8] or $Li_2C_3Ph_2$ to Cp_2TiCl_2.[9] The most general method for the access to allenylidenemetal compounds has appeared to consist, since the first evidence given by Selegue,[10] in the activation of propargyl alcohol derivatives which takes place with spontaneous dehydration, essentially by ruthenium(II) complexes.[11-16] Reactive allenylideneruthenium intermediates have also been proposed to arise from prop-2-yn-1-ols to explain dimerization reactions[15] or access to alkenylcarbenes,[16] and they are now classical intermediates in the synthesis of unsaturated carbenes[17] and involved in catalysis.[18] Few examples of allenylidene derivatives of group 6[3a,19] and 7[20] metal, iron,[21] and rhodium[22] complexes have also been obtained from propargyl alcohol derivatives, but these usually require an external reagent or catalyst to promote the dehydration of the 3-hydroxyprop-1-enylidene intermediate. Alternatively, allenylidenes can be produced under mild conditions by activation of conjugated enynes, usually resulting from previous dehydration of propargyl alcohol derivatives, by 1,4 migration of the terminal alkyne hydrogen with $RuCl_2(L)(arene)$ complexes (L = PR_3,[23] $C{\equiv}NR$,[24] or carbene[24]) or $RuCl_2(Ph_2PCH_2PPh_2)_2$.[11d] Recently, new types of bimetallic systems containing a metallacumulene moiety of type $M{\equiv}(C)_nM$ (ReC_3Mn,[25] ReC_4Re[26]) and $M{=}(C{=})_nM$ (ReC_3Mn,[27] ReC_4Re,[25,28] ReC_5Mn,[29] $Fe{=}C_2C_6H_4C_2{=}Fe$[30]) have been produced either by oxidation of $M{-}(C)_n{-}M$ complexes or by methoxide elimination of a $M{-}(C{\equiv}C)_n{-}C(OMe){-}M$ bridge.[31]

Scheme 1



Preliminary study on the activation of a pentadiyne having a leaving group at the C(5) carbon atom, $HC{\equiv}CC{\equiv}C\text{-}CR_2(OY)$[32] or $Me_3SiC{\equiv}C\text{-}C{\equiv}CCR_2(OY)$,[33] by the *electrophilic* complexes $RuCl_2(PR_3)(arene)$ suggested the formation of a metallacumulene intermediate of type $Ru{=}C{=}C{=}C{=}C{=}CR_2$ as a source of new functional allenylideneruthenium complexes. By contrast to the chemistry of *electrophilic* $RuCl_2(PR_3)(arene)$ complexes[16,32,34] the *electron-rich* ruthenium complex $RuCl_2(Ph_2PCH_2Ph_2)_2$ (**1**) is able to activate terminal alkynes and propargyl alcohol compounds to give very stable vinylidenes[51] and allenylidenes.[11c,d] Thus, we have attempted to activate the diyne $XC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ with **1** in order to directly generate the metallacumulene $Ru{=}C{=}C{=}C{=}C{=}CR_2$ intermediate (**A**) toward the formation of functional allenylideneruthenium complexes of type **B** (Scheme 1). Moreover, the presence of two labile chloride groups on the ruthenium atom of **1** could be used for the access to bis(allenylidene) complexes of type **C**. This objective has just been strengthened by the isolation of the first penta-1,2,3,4-tetraenylidene complex$[(Ph_2PCH_2CH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}C{=}C{=}CPh_2]PF_6$ from a diynylruthenium derivative $LnRuC{\equiv}CC{\equiv}CC(OY)Ph_2$.[35]

We report here the full details of the activation of the diynes $HC{\equiv}CC{\equiv}CCR_2(OSiMe_3)$ and $Bu_3Sn\text{-}C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ by $RuCl_2(Ph_2PCH_2PPh_2)_2$ (**1**) following

---

(8) (a) Berke, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624. (b) Berke, H. *Chem. Ber.* **1980**, *113*, 1370. (c) Berke, H.; Härter, P.; Huttner, G.; Seyerl, J. v. *J. Organomet. Chem.* **1981**, *219*, 317. (d) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36 b*, 929. (e) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 695. (f) Berke, H.; Grössmann, U.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1984**, *117*, 3432. (g) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1984**, *117*, 3423. (h) Berke, H.; Härter, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 225. (i) Berke, H.; Huttner, G.; Seyerl, J. v. *Z. Naturforsch.* **1981**, *36b*, 1277. (j) Fischer, H.; Reindl, D.; Roth, G. *Z. Naturforsch.* **1994**, *49b*, 1207.

(9) Binger, P.; Müller, P.; Wenz, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1037.

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

(11) (a) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, 420, 217. (b) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (c) Pirio, N.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18. (d) Touchard, D.; Pirio N.; Dixneuf, P. H., *Organometallics*, in press.

(12) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; Garcia-Granda, S. *Organometallics* **1994**, *13*, 745. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27.

(13) (a) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396. (b) Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994**, *13*, 13.

(14) (a) Braun, T.; Steinert, P.; Werner, H. *J. Organomet. Chem.* **1995**, *488*, 169. (b) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49.

(15) (a) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972. (b) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921. (c) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(16) (a) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1989**, 219. (b) Le Bozec, H.; Pilette, D.; Dixneuf, P. H. *New J. Chem.* **1990**, *14*, 793. (c) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.

(17) Ruiz, N.; Péron, D.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 1095.

(18) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.

(19) (a) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133. (b) Capon, J. F.; Le Berre-Cosquer, N.; Bernier, S.; Pichon, R.; Kergoat, R.; L'Haridon, P. *J. Organomet. Chem.* **1995**, *487*, 201.

(20) (a) Kolobova, N. E.; Ivanov, L.; Zhvanko, O. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 2646. (b) Kolobova, N. E.; Ivanov, L.; Zhvanko, O. S.; Derunov, U. V.; Chechulina, I. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, *11*, 2632.

(21) Nakanishi, S.; Goda, K.-I.; Uchiyama, S.-I.; Otsuji, Y. *Bull. Chim. Soc. Jpn.* **1992**, *65*, 2560.

(22) (a) Werner, H.; Rappert, T. *Chem. Ber.* **1993**, *126*, 669. (b) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721. (c) Baum, M.; Mahr, N.; Werner, H. *Chem. Ber.* **1994**, *127*, 1877.

(23) Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 641.

(24) Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. *Organometallics* **1991**, *10*, 3287.

(25) Weng, W.; Arif, A. N.; Gladysz, J. A. *Angew. Chem., int. Ed. Engl.* **1993**, *32*, 891.

(26) Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802.

(27) Weng, W.; Ramsden, J. A.; Arif, A. N.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824.

(28) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509.

(29) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199.

(30) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634.

(31) For a review see: Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.

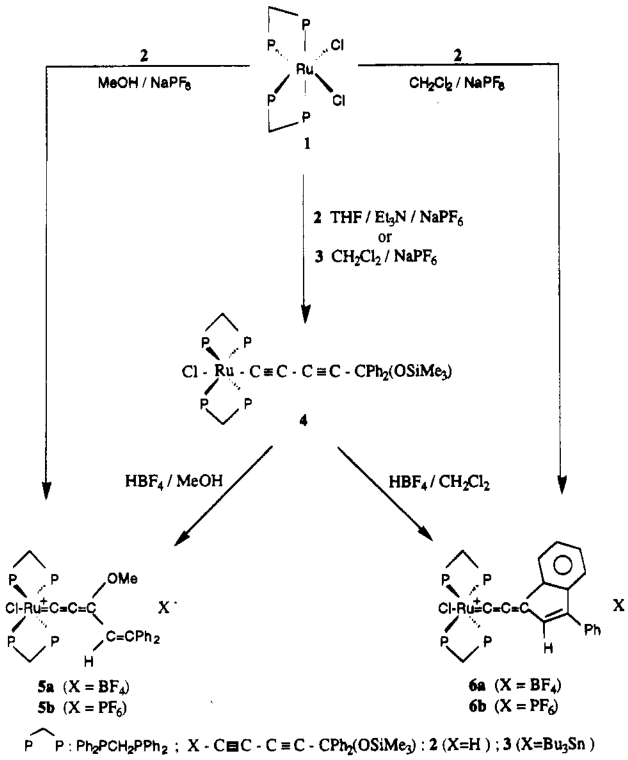
(32) Péron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319.

(33) Péron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497.

(34) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768.

(35) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.

Scheme 2



our initial works[11b,36] and the synthesis of mono-(alkenylallenylidene) and bis(alkenylallenylidene)ruthenium complexes. The present study is based on the X-ray diffraction structural determination of two complexes of types **B** and **C**.

Results and Discussion

1. Synthesis of Allenylideneruthenium Complexes 5a,b. The orange diynylruthenium derivative **4** has first been obtained by two different ways starting from *cis*-$RuCl_2(dppm)_2$ (**1**)[37] (dppm: $Ph_2PCH_2PPh_2$). The first route is based on the Bu_3SnCl elimination by reaction of **1** with $Bu_3SnC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2$ (**3**) in dichloromethane, but it requires the presence of $NaPF_6$. After 16 h at room temperature complex **4** was thus obtained in 30% yield (Scheme 2). The second route is based on the formation of a vinylidene intermediate and its deprotonation, as previously established by the reaction of simple terminal alkyne with $RuCl_2$(diphosphine)$_2$ complexes to produce mono- or bis(alkynyl)-ruthenium derivatives.[38,51] The vinylidene is generated by displacement of one halide ligand of **1**, in a polar solvent and in the presence of $NaPF_6$, and by reaction with $HC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2$ (**2**). Its *in situ* deprotonation by NEt_3 lead to 40% yield of **4**.

The diynylruthenium complex **4** offers the possibility to remove the Me_3SiO leaving group from carbon C(5) and generate the reactive metallacumulene **A**. Complex **4** in methanol was first treated with an excess of $HBF_4{\cdot}OEt_2$, and a violet salt was isolated and identified as the allenylidene **5a** containing a methoxy group and an alkenyl substituent at the C(3) carbon. The formation of the allenylidene **5a** can be easily explained by the initial generation of intermediate **A** followed by addition of methanol at the most accessible and electrophilic carbon C(3). We have shown previously in the structure of the *trans*-$[Cl(Ph_2PCH_2PPh_2)_2Ru{=}C{=}CH_2]^+$ cation,[51] which is expected to be related to that of the intermediate **A**, that the $(Ph_2PCH_2PPh_2)_2Ru$ displays on each side of the plane containing the four phosphorus and the ruthenium atoms four phenyl groups protecting by steric hindrance the C(1) carbon. Thus the addition of methanol at this carbon should be disfavored.

Table 1. ^{13}C NMR Data for $(Ph_2PCH_2PPh_2)_2Ru[{=}C_1{=}C_2{=}C_3R_1R_2]$ Complexes 5, 6, and 8 and $(Ph_2PCH_2PPh_2)_2Ru[C_1{\equiv}C_2C_3{\equiv}C_4CPh_2(OSiMe_3)]$ Derivatives 4 and 7

	δ, ppm		
complex	C1 (^{2}JPC, Hz)	C_2 ($^3J_{PC}$, Hz)	C_3 ($^4J_{PC}$, Hz)
I[a]	306.72 (14.4)	208.95 (2.5)	161.87 (s)
5b	252.76 (13.5)	150.18 (2.2)	155.71 (s)
6b	316.13 (14.6)	234.07 (3.3)	158.82 (2.2)
8	233.68 (14.3)	138.93 (1.6)	164.96 (s)
4	125.97 (15.1)	93.48 (s)	80.24 (s)
7	131.18 (15.2)	96.42 (s)	80.27 (s)

[a] **I** = $[Ru{=}C{=}CPh_2(Cl)(Ph_2PCH_2PPh_2)_2]PF_6$.[11d]

As complex **1** promotes the activation of propargyl alcohols $HC{\equiv}CCAr_2OH$ in the presence of $NaPF_6$, to generate the stable allenylidene *trans*-$[Cl(dppm)_2Ru{=}C{=}C{=}CAr_2]PF_6$[11d] which does not add methanol, the direct formation of the cumulene intermediate **A** was attempted. Complex **1** was reacted with the diyne **2** in methanol and in the presence of $NaPF_6$. After 24 h at room temperature the violet salt **5b** analogous to **5a** was obtained in 65% yield. The nature of **5b** suggests its initial formation *via* the vinylidene intermediate[51] $[Cl(dppm)_2Ru{=}C{=}CH\text{-}C{\equiv}C\text{-}CPh_2(OSiMe_3)]^+$, the precursor of the diynyl derivative **4** on deprotonation. This intermediate on H^+/Me_3SiO^- elimination is expected to release the cumulene intermediate **A**, as in the formation of $[(C_5H_5)(PMe_3)_2Ru{=}C{=}C{=}CR_2]^+$ from $HC{\equiv}CC(OH)Ph_2$ *via* the $[Ru{=}C{=}CHC(OH)Ph_2]^+$ intermediate.[10] Addition of methanol would give **5b** as in the formation of **5a**.

Complexes **5** show a strong absorption $\nu(C{=}C{=}C)$ at $\sim$1950 cm^{-1} in the infrared. The equivalency of the ^{31}P nuclei demonstrates the *trans*-position of the chloride and allenylidene ligands. It is noteworthy that in the ^{13}C NMR spectrum the resonance for the three carbon nuclei of the allenylidene ligand appears at a much lower field as compared to those of **4** [**5b** (δ, ppm): 252.76 (quint, Ru=C(1), $^2J_{PC}$ = 13.5 Hz), 150.18 (quint, Ru=C=*C*(2), $^3J_{PC}$ = 2.2 Hz), and 155.71 (s, Ru=C=C=*C*(3)OMe]. The low-field signal for the C(1) carbon nucleus is typical of a Ru=C= carbon nucleus involved in an allenylidene ligand but takes place at much higher field than that of *trans*-$[Cl(dppm)_2Ru{=}C{=}C{=}CPh_2]PF_6$[11d] [δ = 306.72 ppm, $^2J_{PC}$ = 14.4 Hz]. This is likely due to the presence of the electron-donating OMe group at the C(3) carbon atom (Table 1).

2. Synthesis of Allenylidenes 6a,b. The formation of complexes **5** was first performed in methanol, but the electrophilic intermediate **A** was too reactive toward methanol to be isolated. Thus, a similar reaction was performed in an inert solvent as an attempt to isolate

---

(36) Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 651.

(37) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(38) Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859.

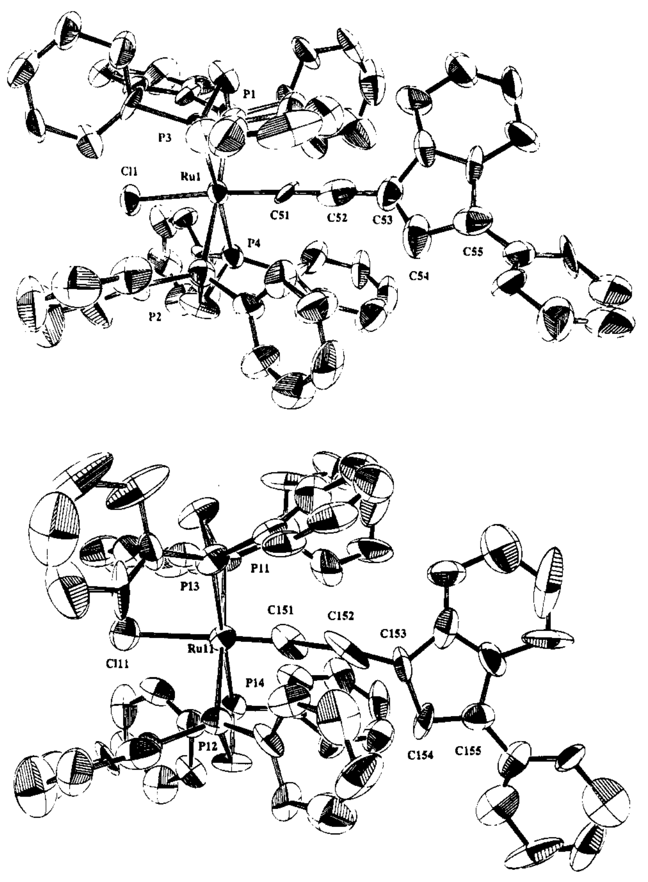
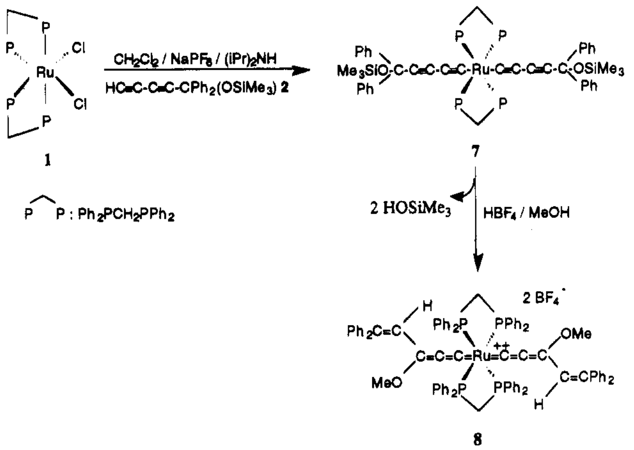


Figure 1. ORTEP diagram for *trans*-[(dppm)$_2$(Cl)Ru=C=C=C(*o*-C_6H_4)-CPh=CH]PF_6 (**6b** (top), **6′b** (bottom)).

A. Complex **4** was dissolved *in dichloromethane* and protonated with $HBF_4 \cdot OEt_2$. The violet complex **6a** was isolated in 30% yield. The analogous derivative **6b** was prepared in better yield (64%) by direct reaction at room temperature (28 h) of **1** with **2** in dichloromethane but in the presence of 1 equiv of $NaPF_6$. The ^{13}C NMR of complexes **6** suggested the presence of an allenylidene $P_4Ru{=}C{=}C{=}C(R^1)(R^2)$ arrangement. However, the structure of **6b** was solved by an X-ray diffraction study (Figure 1). The ^{13}C NMR spectrum of **6b** showed for each allenylidene carbon a quintet signal due to the coupling with four identical ^{31}P nuclei [δ, ppm: 316.13 (quint, Ru=C(1), $^2J_{PC}$ = 14.6 Hz), 234.07 (quint, Ru=C=*C*(2), $^3J_{PC}$ = 3.3 Hz), 158.82 (broad quint, Ru=C=C=*C*(3), $^4J_{PC}$ = 2.2 Hz)]. The undecoupled ^{13}C NMR spectrum of **6b** shows the presence of a proton linked to the C(4) carbon nucleus [δ, ppm: 130.27 (s, $^1J_{CH}$ = 175.6 Hz].

The unexpected formation of complex **6** can be understood in terms of the generation of the cumulene intermediate **A**, either indirectly by protonation of **4** or directly by reaction of **1** and **2** with "$HOSiMe_3$" elimination. The electrophilicity of carbon C(3) was already demonstrated by the selective addition at carbon C(3) of methanol to give complexes **5**. The formation of the metallacumulene **A** is supported by the observation that a diynylruthenium complex analogous to **4** on treatment with $Ph_3C^+PF_6^-$ led to the isolable and characterized cumulene [$(Ph_2PCH_2CH_2PPh_2)_2$(Cl)Ru=C=C=C=C=CPh_2]PF_6 that reacts similarly as the intermediate **A**.[35] The stability of the latter with respect to **A** shows the subtle influence of the dppe with respect to the dppm ligand.

Scheme 3



Thus the nature of **6** indicates that C(3) undergoes an electrophilic substitution at the *ortho* position of one phenyl group, with proton transfer from *ortho* phenyl carbon to carbon C(4). Such a reaction is analogous to the intramolecular electrophilic substitution at an *ortho*-phenyl carbon by a ketene intermediate in the Dötz reaction. It leads to a phenol by proton transfer from the newly C–C-bonded *ortho* carbon to the ketone oxygen.[39]

3. Preparation of the First Bis(allenylidene)ruthenium Complex 8. The direct access to diynylruthenium derivative **4** from **1** and its selective transformation on protonation into **6a** *via* the expected cumulenylidene intermediate **A** led us to consider the possibility to generate the first bis(allenylidene) derivative from a *trans*-bis(diynyl)ruthenium derivative. Indeed a method has been established from precursors *cis*-$RuCl_2(Ph_2P(CH_2)_nPPh_2)_2$ (n = 1 (**1**)[51] or 2[38]) to selectively generate mono(alkynyl) or bis(alkynylruthenium derivatives directly from terminal alkynes, *via* their vinylidene intermediates on deprotonation. Thus complex **1** (0.5 mmol) and an excess of HC≡CC≡$CCPh_2$($OSiMe_3$) (**2**) (2 mmol) were reacted in dichloromethane in the presence of $NaPF_6$ with diisopropylamine (3 mmol). After 4 h at room temperature the yellow *trans*-bis(diynyl)ruthenium derivative **7** was isolated in 24% yield (Scheme 3).

The bis(diynyl) derivative **7** was further reacted in *methanol* with an excess of $HBF_4 \cdot OEt_2$, and a violet complex was immediately formed which was isolated in 76% yield and identified as the *trans*-bis(allenylidene) complex **8** (Scheme 3). The NMR spectra of **8** showed the symmetry of the cation as one line was observed for the four ^{31}P nuclei, and both proton nuclei of each $(Ph_2P)_2CH_2$ group were equivalent as in **7**. In addition both allenylidene groups appeared equivalent in ^{13}C NMR [δ, ppm: one quintet at 233.68 for both Ru=*C*(1) ($^2J_{PC}$ = 14.3 Hz), one broad quintet at 138.93 for Ru=C=*C*(2) ($^3J_{PC}$ = 1.6 Hz), and one singlet for both Ru=C=C=*C*(3) at 164.96] (Table 1). The structure of **8** was established by an X-ray diffraction study (Figure 3).

4. X-ray Diffraction Studies of the Mono(allenylidene) Complex 6b. The molecular structure of **6b** is shown in Figure 1. Experimental crystallographic

---

[39] Fischer, H.; Mühlemeier, J.; Märkl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355.

Table 2. Experimental Crystallographic Data for 6b

formula	$C_{67}H_{54}ClF_6P_5Ru \cdot {}^1\!/_2(CH_2Cl_2) \cdot {}^1\!/_2(C_5H_{12})$
fw	1342.1
cryst	triclinic
space group	$P\bar{1}$
a, Å	13.682(6)
b, Å	22.513(9)
c, Å	23.249(7)
α, deg	112.91(3)
β, deg	96.18(3)
γ, deg	94.43(4)
V, Å^3	6500(2)
Z	4
d_{calc}, Mg m^{-3}	1.27
cryst size, mm	0.12 × 0.18 × 0.25
$2\theta_{max}$, mm	50
diffractometer	CAD-4
Λ (Mo Kα radiation), Å	0.710 69
T, K	293
F(000)	2748
abs coeff μ, cm^{-1}	4.96
scan type	$\omega/2\theta$
no. of rflns read	12 809
no. of unique rflns	4393 ($I > 5\sigma(I)$)
R, R_w	0.076, 0.073

Table 3. Selected Bond Distances (Å) for 6b and 6′b

6b		6′b	
Ru(1)–Cl(1)	2.439(6)	Ru(11)–Cl(11)	2.421(5)
Ru(1)–P(1)	2.351(8)	Ru(11)–P(11)	2.407(7)
Ru(1)–P(2)	2.361(8)	Ru(11)–P(12)	2.381(6)
Ru(1)–P(3)	2.376(6)	Ru(11)–P(13)	2.379(7)
Ru(1)–P(4)	2.385(6)	Ru(11)–P(14)	2.363(7)
Ru(1)–C(51)	1.85(2)	Ru(11)–C(551)	1.67(2)
C(51)–C(52)	1.29(3)	C(151)–C(152)	1.43(3)
C(52)–C(53)	1.39(3)	C(152)–C(153)	1.42(3)
C(53)–C(54)	1.43(4)	C(153)–C(154)	1.50(3)
C(54)–C(55)	1.41(3)	C(154)–C(155)	1.34(3)

Table 4. Selected Bond Angles (deg) for 6b and 6′b

6b		6′b	
Cl(1)–Ru(1)–P(1)	94.1(2)	Cl(11)–Ru(11)–P(11)	85.8(2)
Cl(1)–Ru(1)–P(2)	84.0(2)	Cl(11)–Ru(11)–P(12)	91.5(2)
Cl(1)–Ru(1)–P(3)	94.7(2)	Cl(11)–Ru(11)–P(13)	86.3(2)
Cl(1)–Ru(1)–P(4)	83.5(2)	Cl(11)–Ru(11)–P(14)	94.5(2)
Cl(1)–Ru(1)–C(51)	175.(6)	Cl(11)–Ru(11)–C(151)	176.2(7)
P(1)–Ru(1)–C(51)	88.3(8)	P(11)–Ru(11)–C(151)	96.9(6)
P(2)–Ru(1)–C(51)	93.6(8)	P(12)–Ru(11)–C(151)	85.8(5)
P(3)–Ru(1)–C(51)	90.2(4)	P(13)–Ru(11)–C(151)	92.2(6)
P(4)–Ru(1)–C(51)	91.5(5)	P(14)–Ru(11)–C(151)	87.2(7)
Ru(1)–C(51)–C(52)	179(2)	Ru(11)–C(151)–C(152)	175(1)
C(51)–C(52)–C(53)	177(2)	C(151)–C(152)–C(153)	172(2)
C(52)–C(53)–C(54)	124(2)	C(152)–C(153)–C(154)	126(2)
C(53)–C(54)–C(55)	107(2)	C(153)–C(154)–C(155)	105(2)

data, selected bond distances, bond angles, and positional parameters are given in Tables 2–5, respectively.

The ORTEP plot establishes the presence of an indenylidene group bonded to the end of a metallacumulene and demonstrates the cyclization involving the C(3) and an *ortho* carbon of one phenyl group. This structure shows the steric protection of the C(1) and C(2) carbon atoms by four phenyl groups of the dppm ligand. This protection accounts for the absence of addition of methanol at carbon C(1). The whole structure consists of two allenylideneruthenium complexes **6b** and **6′b** with one molecule of dichloromethane and one of pentane. It shows disordered PF_6 anions. The two allenylideneruthenium cations are not similar and correspond to two different conformers. The main difference between **6b** and **6′b** appears in the orientation of the indenyl plane with respect to the linear P(1)–Ru–P(2) arrangement (Figure 2). The approximative angle of the P(1)–Ru–C plane with respect to the indenyl plane is 10° in **6b** [P(1)–Ru–C(51) and C(57)–C(53)–C(52)] and 28° in **6′b** [P(11)–Ru–C(151) and C(157)–C(153)–C(152)]. In addition, differences in bond distances can be observed; however, it must be noticed that owing to restriction in the programs, it was not possible to include the hydrogen atoms in the calculation and to refine the whole structure in the same set.

5. X-ray Diffraction Study of the Bis(allenylidene) Complex 8. The molecular structure of **8** is shown in Figure 3. Experimental crystallographic data and selected bond distances, bond angles, and positional parameters are given in Tables 6–9, respectively.

Structural characterization of the dication **8** revealed the *trans* positions of two analogous allenylidene groups that are roughly in the same plane and perpendicular to the P_4Ru plane (Figure 3). The C(3′)–C(2′)–C(1′)–Ru–C(1)–C(2)–C(3) arrangement is almost linear, and the molecule is centrosymmetric. The Ru–C(1), C(1)–C(2), and C(2)–C(3) bond lengths in the bis(allenylidene)ruthenium **8** [1.997(7), 1.22(1), 1.39(1) Å] can be compared to those of structurally characterized allenylideneruthenium complexes $[(C_5H_5)(PMe_3)_2Ru{=}C{=}C{=}CPh_2]PF_6$[10] (1.884(5), 1.255(8), and 1.329(9) Å), $[N(CH_2CH_2PPh_2)_3(Cl)Ru{=}C{=}C{=}C(OMe)CH{=}CPh_2]PF_6$[11a] (1.921(5), 1.254(7) and 1.369(7) Å), $[(C_5Me_5)_2(\mu\text{-}S^iPr)_2(Cl)Ru_2{=}C{=}C{=}C(tolyl)_2]OTf$[13b] (1.94(2), 1.24(2), 1.36(2) Å), and $[(\eta^5C_9H_7)(Ph_3P)_2Ru{=}C{=}C{=}C(R^1)(R^2)]PF_6$[12a] (1.889(5), 1.256(7), 1.339(7) Å) and the neutral $(^iPr_2PCH_2CO_2CH_3)_2Cl_2Ru{=}C{=}C{=}CPh_2$[14a] (1.84(1), 1.27(2), 1.34(2) Å). Thus the Ru–C(1) bond of **8** appears very long whereas the C(1)–C(2) bond is short and the C(2)–C(3) long. This observation shows that the C(1)–C(2) bond in **8** has partial triple bond character, possibly due to conjugation with the electron-donating methoxy group at C(3), which is indicated by a short C(3)–O bond (1.292(9) Å). The structural parameters indicate a substantial contribution of the alkynyl mesomeric **B** and **C** forms as shown in Scheme 4 with the positive charge delocalized on C(3) or oxygen atoms.

The formation of the cumulene **8** can be explained by the generation of highly unsaturated *"batonnet"* type cations **I–III** by successive $HOSiMe_3$ elimination and methanol addition (Scheme 5). These intermediates are likely very reactive, but the recent isolation of a $Ru{=}(C{=})_4CR_2$ complex with stabilizing diphosphines[35] suggests that such carbon-rich molecules should be isolated in the near future.

Experimental Section

General Data. All reactions were performed under an argon or nitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Tetrahydrofuran and diethyl ether were distilled over benzophenone ketyl, pentane and hexane over calcium hydride, dichloromethane first over phosphorous pentoxide and then over calcium hydride, and methanol over magnesium. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^1H (300.134 MHz), ^{31}P (121.50 MHz), and ^{13}C (75.469 MHz) NMR spectra were recorded on a Bruker AC 300 P spectrometer at 297 K and referenced to TMS for ^1H and ^{13}C and to 85% H_3PO_4 for ^{31}P. Elemental analysis were

Table 5. Positional Parameters and Their Estimated Standard Deviations for 6b and 6′b

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Ru(1)	0.8389(1)	0.23561(9)	0.92836(8)	3.31(5)	P(13)	0.6483(5)	0.2327(3)	0.3590(3)	4.4(2)
Cl(1)	1.0113(4)	0.2298(3)	0.9113(3)	4.6(2)	P(14)	0.5974(4)	0.2164(3)	0.5511(3)	3.6(2)
P(1)	0.8171(4)	0.3140(3)	0.8863(3)	4.1(2)	C(101)	0.761(2)	0.187(1)	0.3500(9)	5.4(7)
P(2)	0.8650(4)	0.1550(3)	0.9676(3)	3.9(2)	C(102)	0.470(1)	0.244(1)	0.5535(8)	3.9(5)
P(3)	0.7726(4)	0.1809(3)	0.8195(3)	3.9(2)	C(103)	0.819(2)	0.122(1)	0.431(1)	4.7(6)
P(4)	0.9103(4)	0.2874(3)	1.0370(3)	3.7(2)	C(104)	0.889(2)	0.125(1)	0.484(1)	7.0(8)
C(1)	0.746(2)	0.253(1)	0.809(1)	4.7(7)	C(105)	0.914(2)	0.062(1)	0.485(1)	8.9(9)
C(2)	0.950(2)	0.2109(9)	1.041(1)	5.2(7)	C(106)	0.865(2)	0.002(1)	0.442(1)	9(1)
C(3)	0.743(2)	0.380(1)	0.918(1)	5.0(7)	C(107)	0.799(2)	0.001(1)	0.389(1)	7.8(9)
C(4)	0.741(2)	0.403(1)	0.985(1)	8.7(9)	C(108)	0.744(2)	0.059(1)	0.386(1)	5.7(7)
C(5)	0.686(2)	0.457(2)	1.012(2)	13(1)	C(109)	0.890(2)	0.253(1)	0.469(1)	7.2(8)
C(6)	0.626(2)	0.477(2)	0.972(1)	10(1)	C(110)	0.983(2)	0.247(1)	0.439(1)	8.8(9)
C(7)	0.622(2)	0.451(1)	0.907(1)	7.0(8)	C(111)	1.064(2)	0.298(2)	0.479(2)	11(1)
C(8)	0.677(2)	0.397(1)	0.876(1)	6.9(8)	C(112)	1.062(3)	0.345(1)	0.534(1)	12(1)
C(9)	0.915(2)	0.354(1)	0.8690(9)	4.0(6)	C(113)	0.975(2)	0.347(2)	0.561(1)	9(1)
C(10)	0.980(2)	0.315(1)	0.8256(9)	4.3(6)	C(114)	0.891(2)	0.303(1)	0.529(1)	7.0(9)
C(11)	1.063(2)	0.342(1)	0.812(1)	6.0(8)	C(115)	0.423(2)	0.325(1)	0.4892(9)	4.4(6)
C(12)	1.095(2)	0.410(1)	0.842(1)	8.2(9)	C(116)	0.451(2)	0.356(1)	0.453(1)	4.8(6)
C(13)	1.035(2)	0.448(1)	0.885(1)	8(1)	C(117)	0.422(2)	0.422(1)	0.466(1)	7.8(8)
C(14)	0.944(2)	0.419(1)	0.897(1)	5.1(7)	C(118)	0.365(2)	0.448(1)	0.513(1)	10(1)
C(15)	0.770(2)	0.1179(9)	0.991(1)	4.4(6)	C(119)	0.339(2)	0.410(1)	0.546(1)	9(1)
C(16)	0.778(2)	0.101(1)	1.043(1)	6.1(8)	C(120)	0.358(2)	0.350(1)	0.539(1)	5.7(7)
C(17)	0.717(2)	0.072(1)	1.061(1)	7.5(8)	C(121)	0.347(2)	0.192(1)	0.4298(9)	4.0(6)
C(18)	0.617(2)	0.049(1)	1.022(1)	7.9(9)	C(122)	0.282(2)	0.210(1)	0.392(1)	6.3(8)
C(19)	0.606(2)	0.064(1)	0.970(1)	7.2(8)	C(123)	0.199(2)	0.161(1)	0.351(1)	7.5(9)
C(20)	0.673(2)	0.097(1)	0.955(1)	5.6(7)	C(124)	0.185(2)	0.105(1)	0.357(2)	10(1)
C(21)	0.933(2)	0.086(1)	0.925(1)	5.4(7)	C(125)	0.256(2)	0.088(1)	0.394(2)	9(1)
C(22)	0.876(2)	0.030(1)	0.877(1)	6.9(9)	C(126)	0.336(2)	0.132(1)	0.433(1)	6.4(8)
C(23)	0.929(3)	−0.023(1)	0.845(1)	9(1)	C(127)	0.682(2)	0.307(1)	0.3556(9)	3.9(6)
C(24)	1.031(2)	−0.016(2)	0.857(2)	11(1)	C(128)	0.617(2)	0.344(1)	0.3408(9)	5.1(6)
C(25)	1.083(3)	0.037(2)	0.906(2)	14(2)	C(129)	0.644(2)	0.401(1)	0.335(1)	6.3(7)
C(26)	1.037(2)	0.092(1)	0.939(2)	11(1)	C(130)	0.742(2)	0.430(1)	0.354(1)	7.1(8)
C(27)	0.842(2)	0.140(1)	0.7580(9)	4.2(6)	C(131)	0.816(2)	0.398(1)	0.370(1)	7.0(8)
C(28)	0.812(2)	0.136(1)	0.6978(9)	5.6(7)	C(132)	0.786(2)	0.339(1)	0.373(1)	6.6(8)
C(29)	0.858(2)	0.098(1)	0.646(1)	6.9(9)	C(133)	0.561(2)	0.190(1)	0.288(1)	5.0(7)
C(30)	0.937(2)	0.065(1)	0.658(1)	6.4(8)	C(134)	0.602(3)	0.184(2)	0.227(1)	11(1)
C(31)	0.964(2)	0.068(1)	0.718(1)	6.7(8)	C(135)	0.522(3)	0.141(2)	0.169(1)	14(1)
C(32)	0.921(2)	0.107(1)	0.770(1)	5.2(7)	C(136)	0.434(2)	0.138(2)	0.176(2)	13(1)
C(33)	0.663(2)	0.124(1)	0.7955(9)	3.7(6)	C(137)	0.400(3)	0.141(1)	0.231(2)	12(1)
C(34)	0.567(2)	0.146(2)	0.810(1)	8(1)	C(138)	0.472(2)	0.173(1)	0.283(1)	7.6(8)
C(35)	0.484(2)	0.100(1)	0.797(1)	7.7(9)	C(139)	0.677(1)	0.272(1)	0.6192(9)	3.6(6)
C(36)	0.498(2)	0.033(1)	0.767(1)	8.9(9)	C(140)	0.650(2)	0.330(1)	0.663(1)	5.7(8)
C(37)	0.587(2)	0.013(1)	0.749(1)	7.7(9)	C(141)	0.721(2)	0.375(1)	0.711(1)	6.7(8)
C(38)	0.664(2)	0.059(1)	0.768(1)	4.8(7)	C(142)	0.816(3)	0.360(1)	0.719(1)	8(1)
C(39)	0.830(2)	0.320(1)	1.0945(8)	4.5(6)	C(143)	0.841(2)	0.300(1)	0.680(1)	7.2(8)
C(40)	0.831(2)	0.389(1)	1.122(1)	7.1(9)	C(144)	0.773(2)	0.254(1)	0.630(1)	6.3(8)
C(41)	0.767(2)	0.417(1)	1.166(1)	7.6(9)	C(145)	0.588(2)	0.147(1)	0.564(1)	4.7(7)
C(42)	0.705(2)	0.378(1)	1.180(1)	7.0(9)	C(146)	0.629(2)	0.091(1)	0.531(1)	5.3(7)
C(43)	0.705(2)	0.311(1)	1.156(1)	7.8(9)	C(147)	0.619(2)	0.031(1)	0.542(1)	6.9(8)
C(44)	0.777(2)	0.286(1)	1.113(1)	7.2(9)	C(148)	0.573(2)	0.029(1)	0.5894(9)	6.4(7)
C(45)	1.024(1)	0.347(1)	1.0653(9)	4.0(6)	C(149)	0.530(2)	0.088(1)	0.627(1)	7.1(8)
C(46)	1.074(2)	0.356(1)	1.124(1)	7.0(9)	C(150)	0.538(2)	0.1426(9)	0.6131(9)	4.5(6)
C(47)	1.159(2)	0.400(1)	1.151(1)	7.4(8)	C(151)	0.655(1)	0.3035(8)	0.4967(7)	3.2(4)
C(48)	1.196(2)	0.433(1)	1.116(1)	6.9(9)	C(152)	0.676(2)	0.372(1)	0.5336(9)	6.3(6)
C(49)	1.148(2)	0.423(1)	1.056(1)	6.7(9)	C(153)	0.691(2)	0.438(1)	0.577(1)	5.0(7)
C(50)	1.055(2)	0.376(1)	1.0311(9)	4.0(6)	C(154)	0.631(2)	0.468(1)	0.629(1)	5.1(7)
C(51)	0.712(1)	0.242(1)	0.9488(8)	4.0(6)	C(155)	0.672(2)	0.530(1)	0.659(1)	4.7(7)
C(52)	0.624(2)	0.246(1)	0.9638(9)	5.4(7)	C(156)	0.756(2)	0.541(1)	0.628(1)	5.7(7)
C(53)	0.528(1)	0.247(1)	0.9780(9)	4.9(6)	C(157)	0.768(2)	0.484(1)	0.579(1)	5.7(8)
C(54)	0.486(1)	0.210(1)	1.0091(9)	5.9(7)	C(158)	0.839(2)	0.480(1)	0.541(1)	6.7(8)
C(55)	0.386(2)	0.220(1)	1.011(1)	6.3(8)	C(159)	0.906(3)	0.541(1)	0.556(1)	10(1)
C(56)	0.369(1)	0.265(1)	0.977(1)	4.5(7)	C(160)	0.897(4)	0.598(2)	0.613(2)	17(2)
C(57)	0.453(1)	0.282(1)	0.955(1)	4.9(7)	C(161)	0.823(2)	0.604(1)	0.652(1)	9.6(9)
C(58)	0.461(2)	0.320(1)	0.921(1)	6.9(7)	C(162)	0.641(2)	0.577(1)	0.712(1)	5.3(7)
C(59)	0.365(2)	0.342(1)	0.911(1)	7.7(9)	C(163)	0.649(2)	0.645(1)	0.723(1)	5.6(8)
C(60)	0.282(2)	0.327(1)	0.935(1)	7.4(9)	C(164)	0.610(3)	0.691(2)	0.772(1)	13(1)
C(61)	0.278(2)	0.286(1)	0.969(1)	7.7(8)	C(165)	0.570(2)	0.672(1)	0.811(2)	10(1)
C(62)	0.312(2)	0.192(1)	1.039(1)	5.5(7)	C(166)	0.593(2)	0.557(1)	0.752(1)	8(1)
C(63)	0.312(2)	0.125(1)	1.024(1)	6.5(7)	C(167)	0.551(2)	0.605(2)	0.807(1)	11(1)
C(64)	0.243(2)	0.095(2)	1.050(1)	9(1)	P(20)	0.9789(6)	0.2186(4)	0.2383(3)	6.3(2)
C65	0.180(2)	0.134(2)	1.090(1)	10(1)	P(21)	0.6297(8)	0.6024(6)	0.2638(5)	11.3(4)
C(66)	0.191(1)	0.201(1)	1.1034(9)	8.0(8)	F(1)	0.998(2)	0.273(1)	0.216(1)	14.6(8)*
C(67)	0.251(1)	0.229(1)	1.077(1)	8.5(9)	F(1′)	1.077(3)	0.186(2)	0.231(2)	12(1)*
Ru(11)	0.6194(1)	0.22424(9)	0.45478(8)	3.34(4)	F(2)	0.975(2)	0.171(1)	0.167(1)	13.0(7)*
CL(11)	0.5589(5)	0.1110(3)	0.3904(3)	5.0(2)	F(2′)	1.090(2)	0.244(1)	0.256(1)	8.1(8)*
P(11)	0.7810(4)	0.1951(3)	0.4323(3)	4.3(2)	F(3)	0.972(1)	0.1638(9)	0.2617(9)	11.4(6)*
P(12)	0.4569(4)	0.2476(3)	0.4756(3)	3.7(2)	F(4)	1.010(3)	0.263(2)	0.313(2)	9.3(9)*

Table 5. (Continued)

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
F(5)	0.863(3)	0.205(2)	0.220(2)	9.2(9)*	F(12)	0.587(4)	0.650(3)	0.238(3)	18(2)*
F(6)	0.942(2)	0.268(2)	0.297(1)	8.5(9)*	CL(2)	0.932(1)	0.8001(7)	0.3570(7)	7.3(4)*
F(7)	0.707(3)	0.634(2)	0.239(2)	9.3(9)*	CL(3)	0.805(2)	0.810(1)	0.4429(9)	11.4(6)*
F(7′)	0.642(4)	0.555(2)	0.202(2)	15(1)*	C(200)	0.867(5)	0.769(3)	0.380(3)	10(2)*
F8	0.642(3)	0.536(2)	0.269(2)	12(1)*	C(201)	0.781(2)	0.875(1)	0.178(1)	3.9(7)*
F(8′)	0.526(3)	0.586(2)	0.239(2)	13(1)*	C(202)	0.786(3)	0.837(2)	0.208(2)	8(1)*
F(9)	0.553(3)	0.590(2)	0.305(2)	10(1)*	C(203)	0.743(4)	0.810(2)	0.241(2)	10(1)*
F(10)	0.629(3)	0.668(2)	0.319(2)	11(1)*	C(204)	0.780(4)	0.934(3)	0.198(3)	8(2)*
F(11)	0.723(4)	0.606(3)	0.298(3)	19(2)*	C(205)	0.683(6)	0.820(4)	0.265(4)	13(3)*

[a] Starred B values are for atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalnet displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

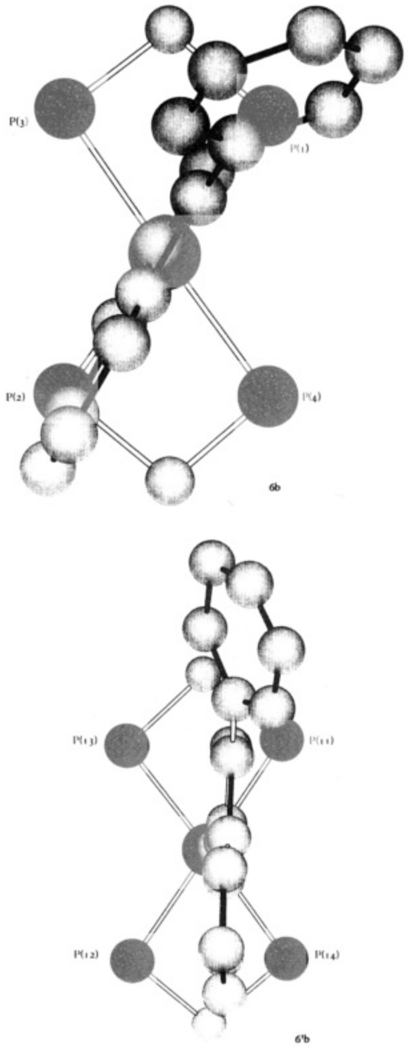


Figure 2. Views of cations **6b** and **6′b** in the C(3)−C(2)−C(1)−Ru axis. The Ph_2P phenyl groups have been omitted. (a) Cation **6b**: approximate angle of the [P(1)−Ru−C(51)] and [C(57)−C(53)−C(52)] planes is 10°. (b) Cation **6′b**: approximate angle of the [P(11)−Ru−C(151)] and [C(157)−C(153)−C(152)] planes is 28°.

performed by the "Service Central de Microanalyse" of CNRS at Vernaison, France. The complex *cis*-$RuCl_2(Ph_2PCH_2PPh_2)_2$ (**1**, $RuCl_2(dppm)_2$) was prepared by the literature method.[37] The pentadiyne derivatives $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ (**2**) and $Bu_3SnC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ (**3**) were prepared from butadiyne[40] according to literature.[41]

Synthesis of *trans*-(dppm)$_2$(Cl)Ru-C≡CC≡CCPh$_2$(OSiMe$_3$) (4). Method A: From Diyne 3. A solution of 1.19 g of $Bu_3SnC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ (**3**) (2.0 mmol) in 60 mL of dichloromethane was added to 470 mg of **1** (0.5 mmol) and 168 mg of $NaPF_6$ (1.0 mmol). The reaction mixture was stirred at room temperature for 16 h. After filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum and the precipitate was washed with pentane. The crude product was filtered on an alumina chromatography column and eluted with diethyl ether. Recrystallization from THF/pentane (10/50) afforded 180 mg of orange crystals of **4** (30%). Anal. Calcd for $C_{70}H_{63}ClOP_4SiRu$: C, 69.56; H, 5.25; Cl, 2.93. Found: C, 69.74; H, 5.28; Cl, 3.01. IR (cm^{-1}, KBr): 2176, 2024 (s, $\nu_{C\equiv C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, δ ppm): 7.49−7.12 (m, 50 H, Ph), 4.95, 4.89 ($ABX_2X'_2$, 4 H, PCH_2P, $^2J_{HAHB} = 14.6$ Hz, $|^2J_{PHA} + {}^4J_{P'HA}| = 8.6$ Hz, $|^2J_{PHB} + {}^4J_{P'HB}| = 8.8$ Hz), 0.01 (s, 9 H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, δ ppm): 149.12 (s, (Ph)*Ci*−C_5), 134.82 (quint, (Ph)Ci−P, $|^1J_{PC} + {}^3J_{P'C}| = 21.5$ Hz), 134.63 (quint, (Ph)Ci−P, $|^1J_{PC} + {}^3J_{P'C}| = 21.6$ Hz), 134.01−126.53 (Ph), 125.97 (quint, Ru*C*≡C, $^2J_{PC} = 15.1$ Hz), 93.48 (s, RuC≡*C*), 80.24, 63.79 (s, RuC≡C*C*≡*C*), 76.51 (s, RuC≡CC≡C*C*), 50.11 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{P'C}| = 20.6$ Hz), 2.03 (s, $OSiMe_3$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, δ ppm): 149.13 (t, (Ph)*Ci*−C_5), $^3J_{CH} = 7.2$ Hz), 50.11 (t quint, PCH_2P,

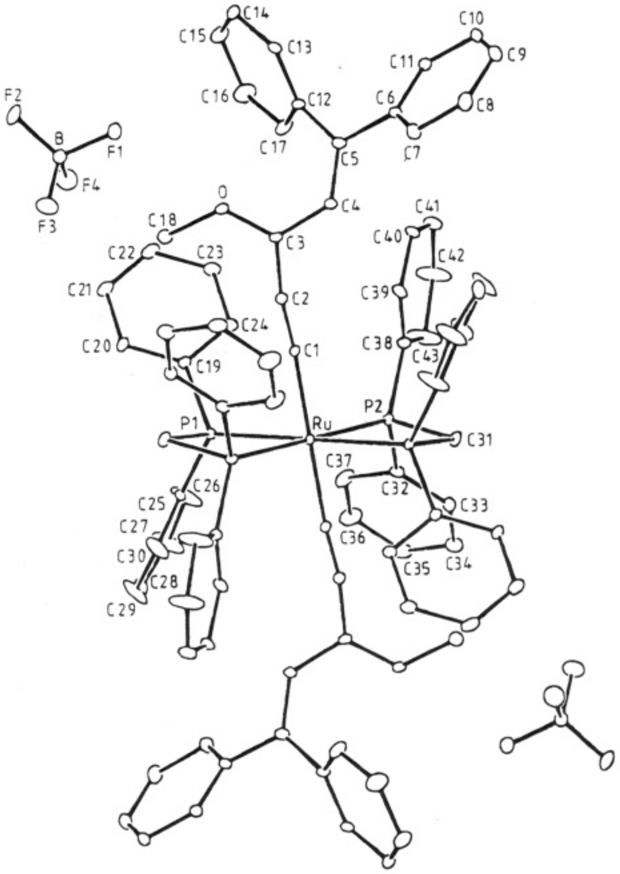


Figure 3. ORTEP diagram for *trans*-[(dppm)$_2$Ru(=C=C=C-(OMe)-CH=CPh$_2$)$_2$](BF$_4$)$_2$ (**8**).

---

[40] Brandsma, L. *Preparative Acetylenic Chemistry* 2nd ed.; Elsevier: Amsterdam, 1988; p 179.

[41] Midland, S. M. M. *J. Org. Chem.* **1975**, *40*, 2250.

Table 6. Experimental Crystallographic Data for 8

formula	$C_{86}H_{72}B_2F_8O_2P_4Ru$
fw	1536.11
cryst	monoclinic
space group	$P2_1/c$
a, Å	16.076(4)
b, Å	11.514(5)
c, Å	20.778(6)
β, deg	103.53(2)
V, Å^3	3739.1
Z	2
d_{calc}, Mg m^{-3}	1.364
cryst size, mm	0.62 × 0.50 × 0.12
$2\theta_{max}$, mm	50
diffractometer	CAD-4
λ (Mo Kα radiation), Å	0.710 73
T, K	293
abs coeff μ, cm^{-1}	5.90
scan type	$\omega/2\theta$
no. of rflns read	6686
no. of unique rflns	2719 ($I > 3\sigma(I)$)
R, R_w	0.058, 0.073

Table 7. Selected Bond Distances (Å) for 8

Ru−P(1)	2.357(2)	C(1)−C(2)	1.22(1)
Ru−P(2)	2.378(2)	C(2)−C(3)	1.39(1)
Ru−C(1)	1.997(7)	C(3)−C(4)	1.45(1)
O−C(3)	1.292(9)	C(4)−C(5)	1.36(1)
O−C(18)	1.46(1)		

Table 8. Selected Bond Angles (deg) for 8

P(1)−Ru−P(2)	71.95(8)	C(1)−C(2)−C(3)	171.4(9)
P(1)−Ru−C(1)	93.3(2)	O−C(3)−C(2)	122.1(9)
P(2)−Ru−C(1)	98.1(2)	O−C(3)−C(4)	117.8(7)
C(3)−O−C(18)	121.3(8)	C(2)−C(3)−C(4)	120.1(7)
Ru−C(1)−C(2)	175.0(7)	C(3)−C(4)−C(5)	123.2(8)

$^1J_{CH}$ = 135.8 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 20.8 Hz), 2.03 (q, OSiMe$_3$, $^1J_{CH}$ = 118.6 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, δ ppm): −6.47 (s, PPh$_2$).

Method B: From Diyne 2. A solution of 0.71 g of HC≡CC≡CCPh$_2$(OSiMe$_3$) (**2**) (2.0 mmol) and 0.56 mL of Et$_3$N (4.0 mmol) in 25 mL of tetrahydrofuran was added to 940 mg of **1** (1.0 mmol) and 336 mg of NaPF$_6$ (2.0 mmol). The reaction mixture was stirred at room temperature for 3 h, and the product was extracted as above. Recrystallization from CH$_2$Cl$_2$/hexane mixture afforded 470 mg of orange crystals of **4** (40%). Anal. Calcd for $C_{70}H_{63}ClOP_4SiRu$: C, 69.56; H, 5.25. Found: C, 69.23; H, 5.15. IR (cm^{-1}, KBr): 2176, 2024 (s, $\nu_{C≡C}$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, δ ppm): −6.47 (s, PPh$_2$).

Synthesis of trans-[(dppm)$_2$(Cl)Ru=C=C=C(OMe)-CH=CPh$_2$]X (X = BF$_4$ (5a), PF$_6$ (5b)). (a) Synthesis of 5a from 4. To a solution of 121 mg of **4** (0.1 mmol) in 20 mL methanol was added 5 equiv of HBF$_4$·Et$_2$O. After 2 h of stirring at room temperature, the solvent was removed under vacuum. The precipitate was washed with diethyl ether and dissolved in 20 mL of dichloromethane. After filtration through a filter-paper-tipped cannula, the precipitation with 60 mL of hexane afforded 50 mg of **5a** (39%) as a red microcrystalline powder. Anal. Calcd for $C_{68}H_{58}BClF_4OP_4Ru$: C, 65.95; H, 4.72. Found: C, 66.27; H, 4.55. IR (cm^{-1}; KBr): 1955 (s, $\nu_{C=C=C}$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, δ ppm): −11.71 (s, PPh$_2$).

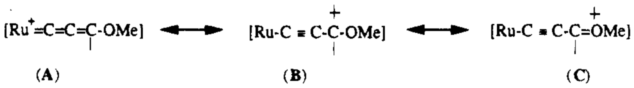
(b) Direct Synthesis of 5b from 1. A solution of 706 mg of HC≡CC≡CCPh$_2$(OSiMe$_3$) (**2**) (2.0 mmol) in 60 mL of methanol was added to 470 mg of **1** (0.5 mmol) and 336 mg of NaPF$_6$ (2.0 mmol). After 24 h of stirring at room temperature and filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum. The precipitate was washed with diethyl ether and dissolved in 20 mL of dichloromethane. After filtration through a filter-paper-tipped cannula, the precipitation with 70 mL of hexane afforded 420 mg of **5b** (65%) as a red microcrystalline powder. Anal. Calcd for $C_{68}H_{58}ClF_6OP_5Ru$: C, 62.99; H, 4.51; Cl, 2.73. Found: C, 62.89; H, 4.71; Cl, 2.42. IR (cm^{-1}, KBr): 1952 (s, $\nu_{C=C=C}$), 838 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, δ ppm): 7.64−6.83 (m, 50 H, Ph), 5.26, 5.09 (ABX$_2$X'$_2$, 4 H, PCH$_2$P, $^2J_{HAHB}$ = 15.4 Hz, $|^2J_{PHA} + {}^4J_{P'HA}|$ = 8 Hz, $|^2J_{PHB} + {}^4J_{P'HB}|$ = 9 Hz), 4.83 (s, 1 H, CH=), 2.35 (s, 3 H, OMe). $^1H\{^{31}P\}$ NMR (300.134 MHz, CD_2Cl_2, δ ppm): 5.27, 5.09 (AB, 4H, PCH$_2$P, $^2J_{HAHB}$ = 15.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, δ ppm): 252.76 (quint, Ru=*C*, $^2J_{PC}$ = 13.5 Hz), 155.71 (broad s, Ru=C=C=*C*), 154.0 (s, CH=*C*Ph$_2$), 150.18 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 2.2 Hz), 141.43 (s, Ph), 139.66 (s, Ph), 133.68−128.36 (Ph), 124.43 (s, *C*H=CPh$_2$), 58.73 (s, OMe), 46.92 (quint, PCH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23.2 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, δ ppm): 124.43

Table 9. Positional Parameters and Their Estimated Standard Deviations for 8

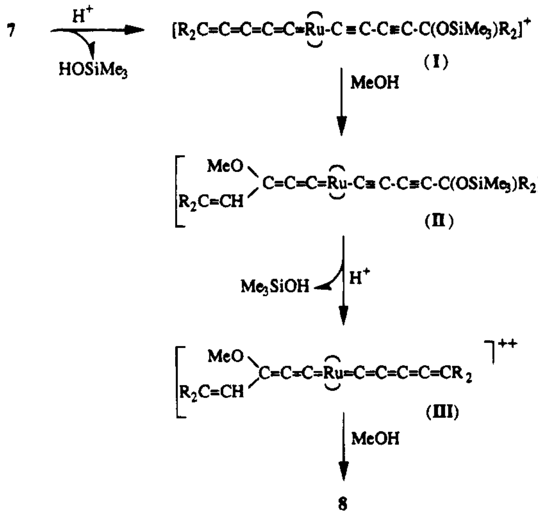
atom	x	y	z	B,[a] Å^2
Ru	0	0	0	2.88(2)
P(1)	−0.0264(1)	0.0811(2)	−0.1070(1)	3.47(5)
P(2)	−0.0539(1)	−0.1494(2)	−0.0776(1)	3.79(5)
O	0.3472(3)	−0.0556(6)	0.0635(3)	5.7(2)
C(1)	0.1243(5)	−0.0231(7)	0.0049(4)	3.2(2)
C(2)	0.2016(5)	−0.0320(7)	0.0123(4)	3.6(2)
C(3)	0.2873(5)	−0.0426(8)	0.0104(5)	4.1(2)
C(4)	0.3119(5)	−0.0371(9)	−0.0522(4)	4.7(2)
C(5)	0.3763(5)	−0.1016(9)	−0.0659(5)	5.1(2)
C(6)	0.4017(5)	−0.076(1)	−0.1302(4)	5.2(2)
C(7)	0.4007(7)	0.034(1)	−0.1526(5)	6.5(3)
C(8)	0.4259(7)	0.056(1)	−0.2116(5)	8.6(4)
C(9)	0.4512(7)	−0.039(2)	−0.2446(5)	10.3(5)
C(10)	0.4511(7)	−0.147(2)	−0.2226(5)	10.7(4)
C(11)	0.4269(6)	−0.170(1)	−0.1635(5)	7.1(3)
C(12)	0.4176(5)	−0.2004(9)	−0.0235(5)	5.0(2)
C(13)	0.5055(6)	−0.207(1(	−0.0057(5)	6.2(3)
C(14)	0.5446(7)	−0.297(1)	0.0370(5)	7.2(3)
C(15)	0.4957(9)	−0.375(1)	0.058(7)	9.3(4)
C(16)	0.4034(9)	−0.370(1)	0.0395(8)	10.4(5)
C(17)	0.3679(7)	−0.280(1)	−0.0015(6)	7.4(3)
C(18)	0.3274(7)	−0.074(1)	0.1279(5)	7.8(3)
C(19)	−0.1014(5)	0.2005(8)	−0.1304(4)	4.2(2)
C(20)	−0.1504(6)	0.213(1)	−0.1932(5)	5.9(3)
C(21)	−0.2085(7)	0.304(1)	−0.2084(6)	8.3(4)
C(22)	−0.2167(7)	0.385(1)	−0.1597(6)	8.3(3)
C(23)	−0.1681(7)	0.372(1)	−0.0973(6)	6.9(3)
C(24)	−0.1101(6)	0.2791(9)	−0.0807(5)	5.1(2)
C(25)	0.0577(5)	0.1157(8)	−0.1487(4)	3.7(2)
C(26)	0.0930(8)	0.213(1)	−0.1476(8)	16.2(4)
C(27)	0.1604(9)	0.242(1)	−0.1743(8)	17.3(5)
C(28)	0.1924(7)	0.180(1)	−0.2061(5)	8.1(3)
C(29)	0.1643(9)	0.075(2)	−0.2078(7)	17.2(6)
C(30)	0.0982(9)	0.034(1)	−0.1764(7)	12.8(4)
C(31)	−0.0808(6)	−0.0518(8)	−0.1498(5)	4.5(2)
C(32)	−0.1540(5)	−0.2226(8)	−0.0759(5)	4.5(2)
C(33)	−0.2241(6)	−0.2190(9)	−0.1260(5)	5.4(3)
C(34)	−0.3008(6)	−0.273(1)	−0.1226(6)	7.5(3)
C(35)	−0.3045(6)	−0.329(1)	−0.0653(6)	7.3(3)
C(36)	−0.2345(8)	−0.339(1)	−0.0156(7)	10.6(4)
C(37)	−0.1579(7)	−0.279(1)	−0.0176(6)	8.9(3)
C(38)	0.0119(5(	−0.2639(9)	−0.0992(4)	4.8(2)
C(39)	0.0922(6)	−0.247(1)	−0.1024(5)	7.0(3)
C(40)	0.1430(6)	−0.334(1)	−0.1198(5)	9.7(4)
C(41)	0.1136(8)	0.561(1)	−0.1371(7)	10.9(4)
C(42)	0.034(1)	0.540(1)	−0.130(1)	17.9(7)
C(43)	−0.022(1)	−0.370(1)	−0.116(1)	17.1(6)
B	0.6776(8)	−0.030(2)	−0.3019(6)	7.5(4)
F1	0.6930(4)	−0.0417(8)	−0.3634(3)	10.3(2)
F2	0.7520(5)	−0.0150(9)	−0.2587(3)	11.6(3)
F3	0.6437(5)	−0.1344(8)	−0.2872(4)	12.3(3)
F4	0.6170(5)	0.0472(7)	−0.3026(4)	11.9(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Scheme 4



Scheme 5



(d, *C*H=CPh$_2$, $^1J_{CH}$ = 163.8 Hz), 58.73 (q, OMe, $^1J_{CH}$ = 148.3 Hz), 46.92 (t quint, PCH$_2$P, $^1J_{CH}$ = 136.3 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 23.4 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, δ ppm): −11.28 (s, PPh$_2$), −143.34 (sept, PF$_6$, $^1J_{PF}$ = 710.9 Hz).

Synthesis of *trans*-[(dppm)$_2$(Cl)Ru=C=C=C(*o*-C$_6$H$_4$)-CPh=CH]X (X = BF$_4$ (6a), PF$_6$ (6b)). (a) Synthesis of 6a from 4. To a solution of 121 mg of **4** (0.1 mmol) in 20 mL of dichloromethane was added 5 equiv of HBF$_4$·Et$_2$O. After 24 h of stirring at 28 °C, the solvent was removed under vacuum. The precipitate was washed with diethyl ether and dissolved in 20 mL of dichloromethane. After filtration through a filter-paper-tipped cannula, the precipitation with 60 mL of pentane afforded 40 mg of **5a** (30%) as a violet microcrystalline powder. Anal. Calcd for C$_{67}$H$_{54}$BClF$_4$Ru·1.5CH$_2$Cl$_2$: C, 61.68; H, 4.31. Found: C, 61.26; H, 4.27. IR (cm^{-1}; KBr): 1934 (s, $\nu_{C=C=C}$). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, δ ppm): −16.62 (s, PPh$_2$).

(b) Direct Synthesis of 6b from 1. A solution of 1.06 g of HC≡CC≡CCPh$_2$(OSiMe$_3$) (**2**) (3.0 mmol) in 60 mL of dichloromethane was added to 470 mg of **1** (0.5 mmol) and 504 mg of NaPF$_6$ (3.0 mmol). After 28 h of stirring at 28 °C and filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum. The precipitate was washed with diethyl ether and dissolved in 30 mL of dichloromethane. After filtration through a filter-paper-tipped cannula, the precipitation with 70 mL of pentane afforded 430 mg of **6b** (64%) as a violet microcrystalline powder. Anal. Calcd for C$_{67}$H$_{54}$ClF$_6$P$_5$Ru·0.5CH$_2$Cl$_2$.0.5C$_5$H$_{12}$: C, 62.60; H, 4.58. Found: C, 62.22; H, 4.40. IR (cm^{-1}, KBr): 1934 (s, $\nu_{C=C=C}$), 838 (s, ν_{PF}). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, δ ppm): 7.72−6.87 (m, 48 H, Ph), 5.44 (d, 1 H, C$_6$H$_4$, $^3J_{HH}$ = 7.3 Hz), 5.39, 5.27 (ABX$_2$X′$_2$, 4H, PCH$_2$P, $^2J_{HAHB}$ = 15.7 Hz, $|^2J_{PHA} + {}^4J_{P'HA}|$ = 7.8 Hz, $|^2J_{PHB} + {}^4J_{P'HB}|$ = 10.2 Hz), 4.52 (s, 1 H, CH=). ^{1}H{^{31}P} NMR (300.134 MHz, CD$_2$Cl$_2$, δ ppm): 5.40, 5.26 (AB, 4 H, PCH$_2$P, $^2J_{HAHB}$ = 15.7 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 316.13 (quint, Ru=*C*, $^2J_{PC}$ = 14.6 Hz), 234.07 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 3.3 Hz), 162.17 (s, CH=*C*Ph), 158.82 (broad quint, Ru=C=C=*C*, $^4J_{PC}$ = 2.2 Hz), 145.50 (s, Ph), 137.78 (s, Ph); 135.35 (s, Ph), 133.56−126.90 (Ph), 122.69, 122.65 (s, Ph), *C*H=CPh masked by signals of phenyl carbon nuclei, 45.98 (quint, PCH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23.6 Hz). ^{13}C NMR with selective decoupling at 4.52 ppm (75.469 MHz, CD$_2$Cl$_2$, δ ppm): 130.27 (s, CH=). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 130.26 (d, *C*H=CPh, $^1J_{CH}$ = 175.6 Hz), 46.00 (t quint, PCH$_2$P, $^1J_{CH}$ = 136.5 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 24.0 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, δ ppm): −16.16 (s, PPh$_2$), −143.37 (sept, PF$_6$, $^1J_{PF}$ = 710.9 Hz).

Synthesis of *trans*-(dppm)$_2$Ru(C≡CC≡CCPh$_2$(OSiMe$_3$))$_2$ (7). A solution of 0.71 g of HC≡CC≡CCPh$_2$(OSiMe$_3$) (**2**) (2.0 mmol) and 420 μL of ^{i}Pr$_2$NH (3.0 mmol) in 60 mL of dichloromethane was added to 470 mg of **1** (0.5 mmol) and 336 mg of NaPF$_6$ (2.0 mmol).The reaction mixture was stirred at room temperature for 4 h. After filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum and the precipitate was washed with *n*-pentane The crude product was filtered with diethyl ether through alumina using a chromatography column. Recrystallization from THF/*n*-pentane afforded 180 mg of yellow crystals of **7** (24%). Anal. Calcd for C$_{90}$H$_{82}$O$_2$P$_4$Si$_2$Ru: C, 73.20; H, 5.60; P, 8.39. Found: C, 73.54; H, 5.45; P, 8.46. IR (cm^{-1}; KBr): 2175, 2020 (s, $\nu_{C\equiv C}$). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, δ ppm): 7.43−7.09 (60 H, Ph), 4.82 (quint, 4 H, PCH$_2$P, $|^2J_{PH} + {}^4J_{P'H}|$ = 8.4 Hz), 0.01 (s, 18H, OSiMe$_3$). ^{1}H{^{31}P} NMR (300.13 MHz, CD$_2$Cl$_2$, δ ppm): 4.82 (s, 4H, PCH$_2$P). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 149.06 (s, Ph); 135.27 (quint, Ph, $|^1J_{PC} + {}^3J_{P'C}|$ = 22.4 Hz), 133.85−126.50 (Ph), 131.18 (quint, Ru*C*≡C, $^2J_{PC}$ = 15.2 Hz), 96.42 (s, RuC≡*C*), 80.27, 64.96 (s, RuC≡*C*C≡*C*), 76.60 (s, RuC≡C-C≡C-*C*), 52.05 (quint, PCH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 21.8 Hz), 2.08 (s, OSiMe$_3$). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 149.06 (t, Ph, $^3J_{CH}$ = 7.2 Hz), 52.06 (t quint, PCH$_2$P, $^1J_{CH}$ = 135.0 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 21.8 Hz), 2.08 (q, OSiMe$_3$, $^1J_{CH}$ = 118.6 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, δ ppm): - 4.21 (s, PPh$_2$).

Synthesis of *trans*-[(dppm)$_2$Ru(=C=C=C(OMe)CH=CPh$_2$)$_2$](BF$_4$)$_2$ (8). To a solution of 90 mg of **7** (0.06 mmol) in 20 mL of methanol was added 10 equiv of HBF$_4$·Et$_2$O. After 2 h of stirring at room temperature, the solution was filtered through a filter-paper-tipped cannula, the solvent was removed under vacuum, and the precipitate was washed with diethyl ether. Recrystallization from CH$_2$Cl$_2$/hexane afforded 70 mg of violet crystals of **8** (76%). Anal. Calcd for C$_{86}$H$_{72}$B$_2$F$_8$O$_2$P$_4$Ru: C, 67.24; H, 4.72; P, 8.06. Found: C, 67.37; H, 4.72; P, 7.55. IR (cm^{-1}; KBr): 1958 (s, $\nu_{C=C=C}$). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, δ ppm): 7.62−7.18 (60 H, Ph), 7.08 (d.m, H, Ph, $^3J_{HH}$ = 8.4 Hz), 6.85 (d m, H, Ph, $^3J_{HH}$ = 8.2 Hz), CH= masked by signal of PCH$_2$P, 5.26 (quint, 4H, PCH$_2$P, $|^2J_{PH} + {}^4J_{P'H}|$ = 8.8 Hz), 2.72 (s, 3H, OMe). ^{1}H {^{31}P} NMR (300.13 MHz, CD$_2$Cl$_2$, δ ppm): CH= masked by signal of PCH$_2$P, 5.27 (s, 4H, PCH$_2$P). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 233.68 (quint, Ru=*C*, $^2J_{PC}$ = 14.3 Hz), 165.58 (s, CH=*C*Ph$_2$), 164.96 (broad s, Ru=C=C=*C*), 140.20 (s, Ph), 138.93 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 1.6 Hz), 138.50 (s, Ph), 133.31−128.72 (Ph), 122.01 (s, *C*H=CPh$_2$), 61.31 (s, OMe), 48.87 (quint, PCH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 26.2 Hz). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$, δ ppm): 140.20 (pseudo q, Ph), 138.50 (pseudo q, Ph), 122.01 (d, *C*H=CPh$_2$, $^1J_{CH}$ = 150.4 Hz), 61.31 (q, OMe, $^1J_{CH}$ = 150.4 Hz), 48.87 (t quint, PCH$_2$P, $^1J_{CH}$ = 136.9 Hz, $|^1J_{PC} + {}^3J_{P'C}|$ = 26.2 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, δ ppm): −9.14 (s, PPh$_2$).

Crystal Structure Analysis of 6b. The sample (prism 0.12 × 0.18 × 0.25 mm) was studied on an automatic diffractometer (CAD-4 Enraf-Nonius) with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta = 1$, t_{max} = 60 s, range *hkl h* 0 to 13, *k* −21 to 21, l −22 to 22, intensity controls without appreciable decay (0.3%)) gave 12 809 reflections from which 4393 were independent (R_{int} = 0.021) with $I > 5\,\sigma(I)$ (Table 2).

After Lorenz and polarization corrections, the structure was solved with a Patterson map which revealed the two Ru atoms. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and Fourier differences. After isotropic refinement (R = 0.12), solvent molecules of pentane and methylene chloride were found, and an absorption correction was made with Difabs.[42] The anions PF$_6^-$ appeared as disordered. The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for Ru, P, Cl, and C atoms; x, y, z, β_{iso} for F atoms; x, y, z, fixed for H atoms; 629 variables and 4393 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2})$ with the resulting R = 0.076, R_w = 0.073, and S_w = 4.42 (residual $\Delta\rho \le 0.84$ e Å^{-3}).

---

(42) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

Atomic scattering factors were from ref 43. All the calculations were performed on a Digital PDP 11/60 computer with the SDP package.[44]

X-ray Structure Determination of 8. Crystal data of **8**, together with details of the X-ray diffraction experiment and subsequent crystallographic calculations, are reported in Table 6. Cell parameters were obtained by least-square refinement of the setting angles for 25 reflections ($2\theta \leq 25°$) on an Enraf-Nonius CAD4 diffractometer. The intensities were corrected for the Lorenz and polarization effects. The structure was solved by direct methods and successive Fourier difference synthesis. Neutral atom scattering factors with anomalous scattering contributions were employed.[43] The pertinent crystallographic parameters for **8** are summarized in Table 6. Tables in the Supporting Information give the H atom coordinates and B values, and bond lengths, bond angles, and anisotropic thermal parameters. All calculations were performed on a MicroVax 3100 using SDP programs.[44]

Acknowledgment. We thank the "Ministère de l'enseignement Supérieur et de la Recherche" for the award of a thesis grant to N.P., the European Union (HCM Programme CHRX-CT94-0501) for financial support, and Alain Daridor for technical assistance.

Supporting Information Available: Tables of bond lengths, bond angles, hydrogen atomic fractional coordinates and B values, and thermal parameters for **6b** and **8** (22 pages). Ordering information is given on any current masthead page.

OM950467W

---

(43) *International Tables for X-Ray Crystallography*; Birmingham, Kynoch Press: Birmingham, U.K., 1974; Vol. IV. Present Distributor: D. Reidel.

(44) B. A. Frenz, and Associates Inc. SDP: Structure Determination Package. College Station, TX, and Enraf-Nonius, Delft, The Netherlands, 1985.