Articles

Novel Ruthenium Allenylidene and Mixed Alkynyl Allenylidene Complexes: Crystal Structure of *trans*-[$(Ph_2PCH_2CH_2PPh_2)_2Ru(C{\equiv}CPh)(=C=C=CPh_2)]PF_6$†

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cis-$RuCl_2(dppe)_2$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with propargylic alcohols, $HC{\equiv}CCR^1R^2OH$, and $NaPF_6$ to give a variety of allenylidene complexes *trans*-[$(dppe)_2(Cl)Ru^+{=}C{=}C{=}CR^1R^2]PF_6$ (**6**). The subtitution of the chloride from vinylidene *trans*-[$(dppe)_2(Cl)Ru{=}C{=}CHR$] cations, in the presence of a base, by a variety of propargylic alcohols constitutes the easiest way to selectively produce complexes containing both the alkynyl and the allenylidene groups, *trans*-[$(dppe)_2Ru(C{\equiv}CR)(=C=C=CR^1R^2)]PF_6$ (**7**, **8**). These derivatives have been fully characterized by IR, ^1H, ^{13}C, and ^{31}P NMR. Single-crystal X-ray diffraction is determined for **7c** (R = R^1 = R^2 = Ph). Complexes **7** react with strong nucleophiles such as NaOMe or $NaBH_4$ to form exclusively unsymmetrical bis(acetylide) complexes by addition of H^- or MeO^- on the carbon C(3) of the allenylidene ligand. Cyclic voltammetry of complexes **6** and **7** shows the marked influence of the terminal groups of the allenylidene ligands on the reduction of the ruthenium(II) center.

Introduction

Carbon-rich organometallics are attracting interest for their potentiality to provide liquid crystal,[1] nonlinear optical,[2] mixed-valence, or conducting[3] properties. New trends are emerging such that they can be successfully used as precursors for the building of carbon-rich networks,[4] multitopic organometallics, and dendrimers[5] and for the selective access to a variety of metal-containing oligomers[6] and polymers[7] with conjugated bridges. One of the best ways to build carbon-rich metal complexes derives from the activation of the best carbon-rich organic molecules: functional alkynes and polyynes. Recently, terminal polyynes have proved their efficiency

† Dedicated to Professor Akira Nakamura on the occasion of his 60th birthday.

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(1) (a) Takahashi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K. *J. Chem. Soc., Chem. Commun.* **1984**, 3. (b) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087. (c) Altmann, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 569. (d) Altmann, M.; Enkelmann, V.; Lieser, G.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 726. (e) Oriol, L.; Serrano, J. L. *Adv. Mater.* **1995**, *7*, 248.

(2) (a) Dhenaut, C.; Ledoux, I.; Samuel, D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374*, 339. (b) Whittall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 5, 1935. (c) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. In *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J., Kajar, F., Prasad, P., Ulrich, D., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1991, p 391. (d) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245. (e) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 21. (f) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: Chichester, U.K., 1992; p 115. (g) Fyfe, H. B.; Mlekuz, M.; Stringer, G.; Taylor, N. J.; Marder, T. B. In *Inorganic and Organometallic Polymers With Special Properties*; NATO ASI Series E; Laine, R. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. 206, p 331.

(3) (a) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J.-M.; Marczinke, B. *J. Phys. Chem.* **1994**, *98*, 7798. (b) Seesler, J. L.; Wang, B.; Harrimman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. (c) Harrimman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461. (d) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 595. (e) Grosshenny, V.; Harrimman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 1100. (f) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921. (g) Constable, E. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 407.

(4) (a) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 3, 1073. (b) Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3, 3823. (c) Bunz, U. H. F.; Wiegelmann-Kreiter, J. E. C. *Chem. Ber.* **1996**, *129*, 9, 785. (d) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (e) Diederich, F. *Nature* **1994**, *369*, 149. (f) Diederich, F. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, Eds.; VCH: Weinheim, Germany, 1995; p 443. (g) Bunz, U. H. F. *Synlett* **1997**, 1117. (h) Faust, R.; Diederich, F.; Gramlich, V.; Seiler, P. *Chem. Eur. J.* **1995**, *1*, 111. (i) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (j) Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (k) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Riceunto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. (l) Keegstra, M. A.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 774.

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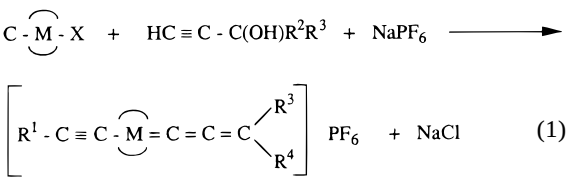
to generate highly unsaturated organometallic systems via their formation of vinylidene−metal intermediates.[8]

Besides the vinylidene−metal derivatives M=C=CHR,[9] the next carbon-rich metallacumulene members, the allenylidenes M=(C=)$_2$CR$_2$,[10] are known since 1976 with the contribution of Fischer et al.[11] and Berke.[12] However, the development of metal allenylidene complex chemistry has taken its roots in Selegue's discovery that a ruthenium(II) complex could activate the prop-2-yn-1-ol HC≡CCPh$_2$OH, dehydrate it, and generate a stable ruthenium allenylidene complex [Ru=C=C=CPh$_2$(PMe$_3$)$_2$C$_p$](PF$_6$).[13] Since this discovery many metal allenylidene derivatives have been produced using this method such as derivatives of ruthenium[14−18] and iron,[19] group 6 and 7 metal carbonyl derivatives,[11,12,20−22] and rhodium and iridium derivatives.[23,24] The same method is now directed toward the building of bimetallic systems with allenylidene ligands[25] or bridges.[25−27]

Whereas a few mixed alkynyl vinylidene derivatives have been produced,[28] only a few examples of the homologues, mixed alkynyl allenylidene metal complexes, are known[27,29,30] despite their potential to create a C−C bond, by carbon-rich ligand coupling, or their interest to build linear conjugated organometallics and offer the dual donor (alkynyl)−acceptor (allenylidene) functionalities. We now report, following our initial result,[29] new metal allenylidene complexes and a straightforward route to *trans*-ruthenium alkynyl allenylidene complexes according to eq 1, based on the direct



(1)

activation of functional prop-2-yn-1-ols with alkynylmetal precursors. The X-ray structure of *trans*-[Ru(C≡CPh)(=C=C=CPh$_2$)(dppe)$_2$]PF$_6$ and a set of nucleophilic additions to the allenylidene ligands are also presented.

(5) (a) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199. (b) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. (c) Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. *Organometallics* **1997**, *16*, 2024. (d) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (e) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 4, 634. (f) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411. (g) Davies, S. J.; Johnson, B. F. G.; Khan, D. J.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (h) Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *470*, 153. (i) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *487*, 139. (j) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646. (k) Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **1996**, 871. (l) Jutzi, P.; Batz, C.; Neumann, B.; Stammler, H.-G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2118. (m) Astruc, D. *New J. Chem.* **1992**, *16*, 305.

(6) (a) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530.

(7) (a) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319. (b) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237. (c) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603.

(8) (a) Touchard, D.; Haquette, P.; Guesmi, S.; Le Pichon L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 3640. (b) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *17*, 1184.

(9) (a) King, R. B.; Saron, M. S. *J. Chem. Soc., Chem. Commun.* **1972**, 1052; *J. Am. Chem. Soc.* **1972**, *95*, 1817. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Kolobova, N. E.; Ivanov, L.; Zhoanho, O. S.; Derunov, V. V.; Chechulina, I. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1982**, *11*, 2632.

(10) (a) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, in press. (b) Le Bozec, H.; Dixneuf, P. H. *Russ. Chem. Rev.* **1995**, *44*, 801. (c) Dixneuf, P. H.; Bruneau, C. In *Organic Synthesis via Organometallics*; OSM5, Helmchen, C., Vieneg, Eds.; 1997; p 1.

(11) Fischer, E. O.; Kalder, H. J.; Franck, A.; Köhler, F. H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 5, 623.

(12) Berke, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624.

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

(14) (a) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Richard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (b) Ruiz, N.; Péron, D.; Sinbandith, S.; Dixneuf, P. H.; Baldoli, C.; Maiorana, S. *J. Organomet. Chem.* **1997**, *553*, 213.

(15) (a) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980. (b) Pirio, N.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18. (c) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. See also ref 10a.

(16) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Davies, S. G.; McWally, J. P.; Smallbridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. See also reviews in ref 9a,c.

(17) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; Garcia-Granda, S. *Organometallics* **1994**, *13*, 745. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E.; Borge, J.; Garcia-Granda, S.; Perez-Carreno, E. *Organometallics* **1996**, *15*, 2137. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lopez-Gonzales, M. C.; Borge, J.; Garcia-Granda, S. *Organometallics* **1997**, *16*, 4453. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; Garcia-Granda, S. *Organometallics* **1997**, *16*, 3178. (f) Gamasa, M. P.; Gimeno, J.; Gonzales-Bernardo, C.; Borge, J.; Garcia-Granda, S. *Organometallics* **1997**, *16*, 2483. (g) Touchard, D.; Pirio, N.; Toupet, L.; Fettouhi, M.; Ouahab, L.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 5263. (h) Lomprey, J. R.; Selegue, J. P. *Organometallics* **1993**, *12*, 616.

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

(19) Nakanishi, S.; Goda, K. I.; Uchiyoma, S. I.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2560.

(20) (a) Berke, H. *Chem. Ber.* **1980**, *113*, 1370. (b) Berke, H.; Härter, P.; Hutter, G.; Seyerl, J. V. *J. Organomet. Chem.* **1981**, *219*, 317. (c) Fischer, H.; Roth, G.; Reindl, D.; Troll, C. *J. Organomet. Chem.* **1993**, *454*, 133. (d) Fischer, H.; Reindl, D.; Roth, G. *Z. Naturforsch.* **1994**, *49b*, 1207. (e) Roth, G.; Fischer, H. *J. Organomet. Chem.* **1996**, *507*, 125. (f) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139.

(21) Duetsch, M.; Stein, F.; Lackman, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051.

(22) Tamm, M. *Organometallics* **1997**, *16*, 1418 and references therein.

(23) (a) Windmüller, B.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *502*, 147. (b) Werner, H.; Laubender, M.; Wiedemann, R.; Windmuller, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1237. (c) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495. (d) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561. (e) Werner, H.; Wiedemann, R.; Laubender, M.; Wolf, J.; Windmuller, B. *J. Chem. Soc., Chem. Commun.* **1996**, 1413 and cited references.

(24) (a) Esteruelas, M. A.; Oro, L. A.; Schrikel, J. *Organometallics* **1997**, *16*, 796. (b) Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Modrego, J.; Onate, E. *Organometallics* **1997**, *16*, 5826. (c) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373.

(25) (a) Touchard, D.; Guesmi, S.; Bouchaib, M.; Haquette, P.; Daridor, A.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2579. (b) Capon, J. F.; Le Berre-Cosquer, N.; Leblanc, B.; Kergoat, R. *J. Organomet. Chem.* **1996**, *508*, 31.

(26) (a) Xia, H. P.; Jia, G. *Organometallics* **1997**, *1*, 16. (b) Jia, G.; Xia, H. P.; Wu, W. F.; Sang Ng, W. *Organometallics* **1996**, *15*, 3634. (c) Xia, H. P.; Wu, W. F.; Sang Ng, W.; Williams, I. D.; Jia, G. *Organometallics* **1997**, *16*, 2940.

(27) (a) Guesmi, S.; Touchard, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1996**, 2773. (b) Lebreton C.; Touchard, D.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Inorg. Chim. Acta*, **1998**, in press.

(28) (a) Albertin, G.; Antonuitti, S.; Bordignon, E.; Cazzaro, F.; Ianelli, S.; Pellizi, G. *Organometallics* **1995**, *14*, 4114. (b) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561.

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

(30) Werner, H. *J. Chem. Soc., Chem. Commun.* **1997**, 903 and cited references.

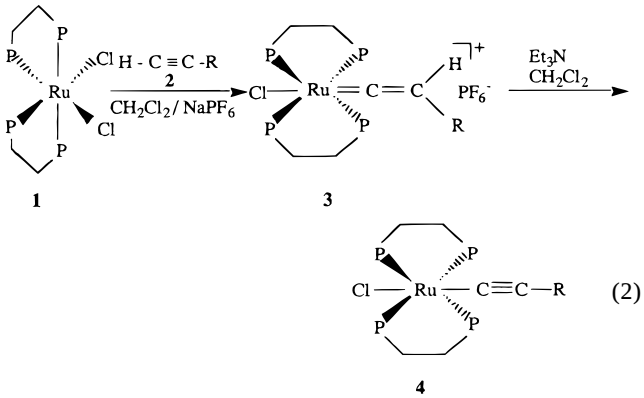
Table 1. Selected NMR Data (δ) for Compounds 6−8

	X	Y	$^{13}P\{^1H\}$	$^{13}C\{^1H\}$[a] C_1	C_2	C_3	C'_1	C'_2
6a	Cl	$=C=C=CPh_2$	37.98	308.58	215.91	161.46		
6b	Cl	$=C=C=C(CH_3)_2$	42.13	319.9	201.76	175.08		
6c	Cl	$=C=C=CHPh$	39.91	321.07	218.99	154.05		
6d	Cl	$=C=C=C(p\text{-}PhOMe)_2$	39.23	288.4	193.4	160.1		
6e	Cl	$=C=C=C(p\text{-}PhF)_2$	38.0	305.9	215.1	156.9		
6f	Cl	$=C=C=C(p\text{-}PhCl)_2$	39.45	308.33	220.81	156.49		
6g	Cl	$=C=C=CH(p\text{-}PhNMe_2)$	43.75	265.7	169.4	147.9		
6h	Cl	$=C=C=CHCH=CHPh$	40.98	312.98	220.26	153.83		
6i	Cl	$=C=C=CHCH=CHPhNO_2$	39.92	322.77	237.06	152.4		
6j	Cl	$=C=C=CHCH=CH\text{-}p\text{-}PhNMe_2$	43.72	268.9	181.08	159.7		
7a	$-C\equiv CH$	$=C=C=CPh_2$	43.7	318.85	213.25	161.93	111.24	128.68
7b	$-C\equiv C^nBu$	$=C=C=CPh_2$	43.7	316.6	216.4	160.5	101.3	128.68
7c	$-C\equiv CPh$	$=C=C=CPh_2$	43.85	316.57	213.23	162.29	120.04	128.68
7d	$-C\equiv C\text{-}p\text{-}PhNO_2$	$=C=C=CPh_2$	44.06	316.3	209.0	163.38		137.95
7e	$-C\equiv C\text{-}p\text{-}PhOMe$	$=C=C=CPh_2$	43.60	315.7	214.3	161.61	117.1	121.39
7f	$-C\equiv C\text{-}p\text{-}PhNO_2$	$=C'=C=CH\text{-}p\text{-}PhNMe_2$	49.65	264.65	163.67	142.65	139.23	144.64
7g	$-C\equiv CPh$	$=C=C=C(p\text{-}PhOMe)_2$	45.22	294.22	189.99	161.46	120.52	125.35
8	$-C\equiv C\text{-}p\text{-}PhNO_2$	$=C=C=CHCH=CH\text{-}p\text{-}PhNMe_2$	50.13	260.58	169.41	150.12	139.77	125.35

[a] $(R^2)(R^1)C_3=C_2=C_1=Ru-C'_1\equiv C'_2-R$.

Results and Discussion

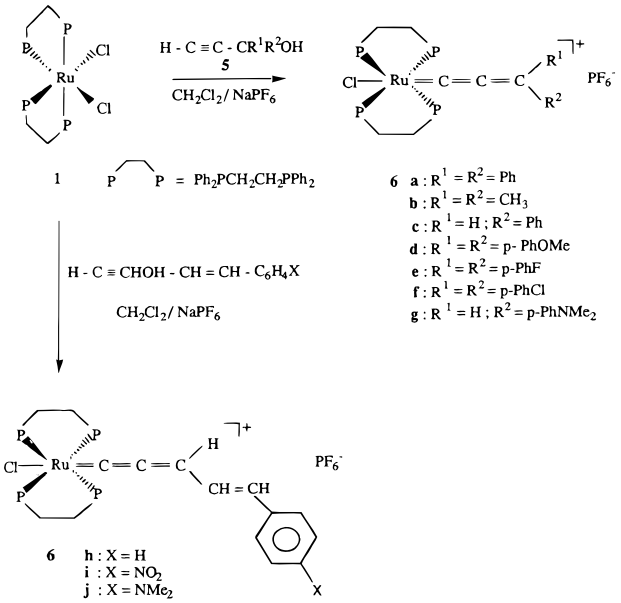
1. Preparation of Ruthenium Allenylidene Complexes. The activation of a variety of terminal alkynes **2** with the *cis*-$RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$ precursor **1** in a polar solvent (CH_2Cl_2) and in the presence of a noncoordinating salt $NaPF_6$ has recently been shown to provide an easy route to a set of vinylidene−metal complexes **3** in high yields (~90%).[8a] This activation does not require the initial generation of the 16 electron intermediate $[RuCl(dppe)_2]^+PF_6^-$,[27a,31] which is in situ generated. These vinylidenes are very acidic and can be easily deprotonated to generate the neutral alkynylruthenium derivatives **4**[8a] (eq 2). This two-step transformation **1** → **3** → **4** can be performed in one pot in the presence of NEt_3 and constitutes the best way to build a ruthenium(II)−alkynyl bond. The easy in situ generation of the active 16 electron $[RuCl(dppe)_2]PF_6$ species led us to study the activation of propargylic alcohols $HC\equiv CCR^1R^2(OH)$ (**5**).



(2)

The reaction of 1,1-diphenyl-prop-2-yn-1-ol (**5a**) with the complex **1** in dichloromethane and in the presence of $NaPF_6$ leads to the isolation of the deep red allenylidene ruthenium complex **6a** in 85% yield (Scheme 1). Several disubstituted **6b**,**d**,**e**,**f** and secondary allenylidenes **6c**,**g** were prepared under the same conditions from the corresponding propynols **5** and **1** in 60−85% yields. The similar activation of the conjugated alkynes $HC\equiv CCHOHCH=CHC_6H_4X$ (**5**) (X = H (**h**), NO_2 (**i**), NMe_2 (**j**)) by **1**-$NaPF_6$ produced the secondary long chain allenylidenes **6h**−**j** (Scheme 1). It is noteworthy that the allenylidenes **6a**−**j** are stable toward the addition of methanol on C_1 carbon. This is likely due to the steric hindrance of the dppe ligands and the electron-donating capability of the $Ru(dppe)_2$ moiety.

Scheme 1

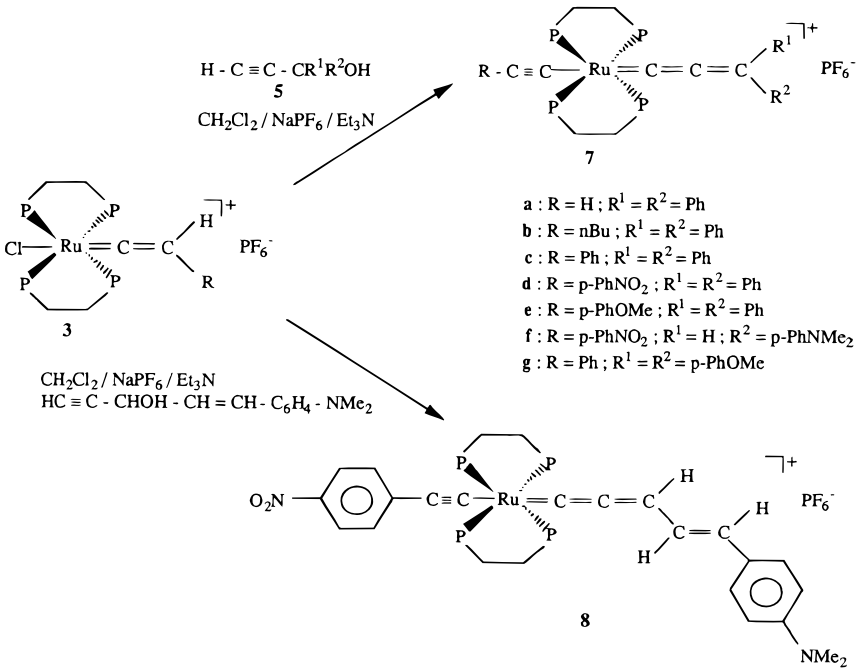


The similar activation of the conjugated alkynes $HC\equiv CCHOHCH=CHC_6H_4X$ (**5**) (X = H (**h**), NO_2 (**i**), NMe_2 (**j**)) by **1**-$NaPF_6$ produced the secondary long chain allenylidenes **6h**−**j** (Scheme 1). It is noteworthy that the allenylidenes **6a**−**j** are stable toward the addition of methanol on C_1 carbon. This is likely due to the steric hindrance of the dppe ligands and the electron-donating capability of the $Ru(dppe)_2$ moiety.

The allenylidenes **6a**−**j** are easily characterized by infrared ($\nu(C=C=C)$ = 1920−1959 cm^{-1}) and by their ^{13}P and ^{13}C NMR spectra showing the equivalency of the four phosphorus nuclei and thus the relative trans position of the chloride and allenylidene ligands (Table 1). The low-field ^{13}C signal for the Ru=C carbon nucleus appears as a quintet at δ = 265−320 ppm with a $^2J_{PC}$ of approximately 14 Hz and a quintet at δ = 169−237 ppm with a small $^3J_{PC}$ (2−3 Hz) for the Ru=C=*C* carbon nucleus. The secondary allenylidenes **6h**−**j** show analogous spectroscopic properties. The drastic effect of the *p*-NMe_2 group (**6j**) on the same carbon nuclei C_1 and C_2 leads to a significant shielding (δ = 268.9 and 181.1 ppm) (Table 1).

(31) Chin, B.; Lough, A. J.; Morris, R. H.; Sheitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.

Scheme 2



2. Synthesis of Ruthenium Alkynyl Allenylidene Complexes. The attempts to generate ruthenium mixed alkynyl allenylidene complexes from the *cationic* complexes **6**, by displacement of the chloride ligand, failed. The presence of a chloride group attached to the ruthenium in *neutral* complexes **4** offers the possibility to displace it in order to generate the 16 electron intermediate and activate propagylic alcohols **5** to produce ruthenium mixed alkynyl allenylidene complexes. The reaction of **4c** (R = Ph) in the presence of $NaPF_6$ and $HC{\equiv}CCPh_2OH$ led to a mixture of **6a** and the expected **7c** (Scheme 2). This showed a competition between the breaking of the Ru−Cl and the Ru−C≡C−Ph bonds. By contrast, the reaction of the vinylidene **3c** with a solution of $HC{\equiv}CCPh_2OH$ in CH_2Cl_2 and in the presence of $NaPF_6$ and triethylamine led to a better selectivity, and after recrystallization pure **7c** complex was obtained (64% yield). Thus the better selectivity is obtained when the alkynyl complex **4** is *in situ* generated by deprotonation of the vinylidene **3**. The presence of an excess of NEt_3 may give a $[R_3NRu{-}C{\equiv}CR(dppe)_2]^+$ intermediate as a *relay* before the NEt_3 displacement by the propynol. Such an amine−ruthenium complex was isolated in the case of NH_3, and the ammonia ligand could be easily displaced by L = CO and PR_3 ligands.[32] The structure of **7c** was established by an X-ray diffraction study (Figure 1). A variety of ruthenium mixed alkynyl allenylidene derivatives **7a**−**g** were prepared by following this procedure from precursors **3** (Scheme 2).

These complexes **7a**−**g** are characterized in infrared by the presence of two typical absorptions at 1949−2100 cm^{-1} for $\nu(C{\equiv}C)$ and 1919−1959 cm^{-1} for $\nu(C{=}C{=}C)$. ^{31}P NMR spectra show the equivalency of the four phosphorus nuclei for the trans position of the acetylide and allenylidene groups. ^{13}C NMR spectra show the presence of a low-field quintet signal for the Ru=C carbon nucleus at δ = 260−318 ppm, a signal at δ = 163−216 ppm for Ru=C=*C*, and a singlet at δ = 142−163 ppm for the Ru=C=C=*C* carbon nuclei (Table 1).

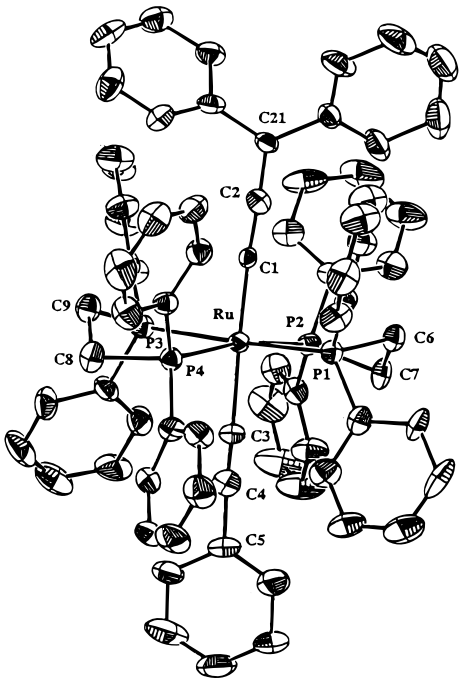


Figure 1. ORTEP diagram for *trans*-$[(dppe)_2Ru(C{\equiv}CPh)(=C=C=CPh_2)]PF_6$ (**7c**).

The shift of the ^{13}C signal for the allenylidene (=C=C=CPh_2) Ru=C(1) carbon nucleus for complexes 7**a**−**e** remains in the narrow range of δ = 315−318 ppm, showing that the terminal group on the alkyne has almost no effect on this Ru=C carbon nucleus (Table 1). The study of **7f**,**g** shows that only the substituent on the allenylidene ligands affects the Ru=C carbon nucleus shift. The $Ru(dppe)_2$ moiety appears to cut electronic influence from one end of the molecule to the other trans ligand (Table 1).

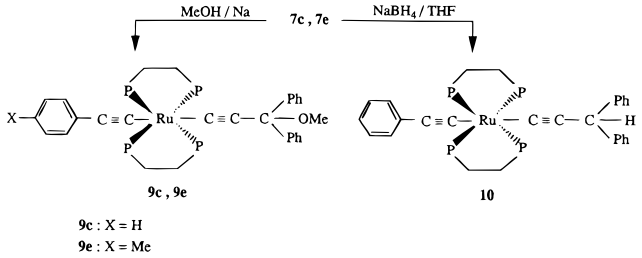
(32) Touchard, D.; Guesmi, S.; Le Pichon, L.; Daridor, A.; Dixneuf, P. H. *Inorg. Chim. Acta*, **1998**, in press.

Table 2. Cyclic Voltammetry of Complexes *trans*-[Ru(X)(Y)(dppe)$_2$]PF$_6$ (6, 7)[a]

	X	Y	$E_{1/2}$ (mV) *b*	$E_{1/2}$ (mV) *c*	$E_a - E_c$ (mV)		
trans-**1**	Cl	Cl	+17			86	
4c	Cl	−C≡CPh	+825, −52		130	83	
4e	Cl	−C≡C-*p*-PhNO$_2$	−132			82	
6a	Cl	=C=C=CPh$_2$		−1057			81
6d	Cl	=C=C=C(*p*-PhOMe)$_2$		−1235			80
6e	Cl	=C=C=C(*p*-PhF)$_2$		−1048			82
6f	Cl	=C=C=C(*p*-PhCl)$_2$		−974			81
7c	−C≡CPh	=C=C=CPh$_2$	+740	−1016		120	81
7d	−C≡C-*p*-PhNO$_2$	=C=C=CPh$_2$		−964			81
7e	−C≡C-*p*-PhOMe	=C=C=CPh$_2$	+535	−1053		89	79

[a] Cyclic voltammograms were recorded at 20 °C in dichloromethane, with ^{n}BuNPF$_6$ (0.1 M) as electrolyte, potentials in V vs ferrocenium/ferrocene, at a scan rate of 200 mV/s. [b] Oxidative wave. [c] Reduction wave.

Scheme 3



The activation of the unsaturated alkyne HC≡CCHOHCH=CHC$_6$H$_4$NMe$_2$ with the vinylidene **3** containing an electron-withdrawing group *p*-C$_6$H$_4$NO$_2$ on the alkynyl ligand led to the almost linear trans derivative **8** with a withdrawing group on the alkyne and a donor group linked at the end of the allenylidene ligand. The high-field signal δ = 260.58 ppm for the Ru=C carbon nucleus of **8** compared to that of **6j** (δ = 268.9 ppm) proves that only the donating group linked to the allenylidene has an influence on the Ru=C chemical shift.

It was shown during the synthesis of **7** that these complexes are stable in the presence of methanol by contrast to more electrophilic allenylidene complexes.[14a] The inhibition of the addition of methanol at the carbon C_1 of allenylidene **6** or **7** is likely due to the steric protection of this carbon by the two dppe ligands.

By contrast with a stronger nucleophile such as sodium methoxide, complexes **7c**,**e** react to give the yellow diacetylides **9c**,**e** by addition of MeO$^-$ to the electrophilic carbon C(3) (Scheme 3). This reaction provides another method to obtain unsymmetrical bis(alkynyl)metal complexes.

Complex **7c** reacted with sodium borohydride in THF, and pale yellow unsymmetrical bis(alkynyl) derivative **10** was isolated in 87% yield, resulting also from the addition of the hydride to the C_3 carbon (Scheme 3).

3. Electrochemical Study. The ruthenium allenylidene complexes were studied by cyclic voltammetry and by *voltammetry at a rotating electrode* in order to appreciate the dual influence of both trans ligands and groups on the reduction of the cationic ruthenium derivatives. The voltamograms were recorded at 20 °C in dichloromethane (^{n}Bu$_4$NPF$_6$, 0.1 M) between −1.4 and +1.0 V with a scan rate of 200 mV/s. Half-wave potentials measured, with reference to the ferrocenium/ferrocene couple potential, were collected in Table 2. Voltammograms at a platinum rotating electrode show for **4c** two anodic waves ($E_{1/2}$ = −52 mV, reversible; $E_{1/2}$ = +825 mV, partially reversible), whereas those for **7c** show a cathodic wave ($E_{1/2}$ = −1016 mV, reversible) and an anodic wave ($E_{1/2}$ = +740 mV, partially reversible). All compounds **6** and **7** show a cathodic wave corresponding to a reversible redox system Ru^{II}/Ru^{I} (wave b). As observed in Table 2, an electron-withdrawing group on the allenylidene ligand (*p*-Cl, **6f**) and on the alkynyl group (*p*-NO$_2$, **7d**) favors the reduction and, on the contrary, an electron-donating group (*p*-OMe, **6d**) disfavors the reduction. For the ruthenium alkynyl allenylidene derivatives **7c**−**e** their reduction is easier than that of derivatives **6**. Neutral alkynyl compound **4c** is more easily oxidized than cationic alkynyl allenylidene compounds **7c**,**e**. These waves (a) are corresponding to a redox system Ru^{III}/Ru^{II}. As observed in Table 2, an electron-donating group on the alkynyl group (*p*-OMe **7e**) favors the oxidation in contrast to **7d**. For **4c**, a second anodic wave (+825 mV) is observed and corresponds to the redox system Ru^{IV}/Ru^{III}.

Table 3. Experimental Crystallographic Data for 7c

formula	$RuC_{77}H_{67}P_5F_6Cl_4$
fw	1504.117
cryst syst	monoclinic
space group	*Pn*
a, Å	15.404(6)
b, Å	20.120(7)
c, Å	11.542(5)
β, deg	93.60(9)
V, Å^3	3570(2)
Z	2
F_{000}	1540.0
d_{calc}, g cm^{-3}	1.3391
μ, cm^{-1}	5.399
diffractometer	Philips PW-1100
radiation	Mo Kα
scan technique	$\omega/2\theta$
no. of ind reflns	6300
no. of obsd. reflns	5435 ($I \geq 2\sigma(I)$)
R, R_w[a]	0.064, 0.075
cryst decay	no

[a] Structure determination and refinement unit weight assigned to every reflection [$R = \Sigma(|F_o| - |F_c|)$].

4. X-ray Structure Analysis of *trans*-[(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$Ru(C≡CPh)(=C=C=CPh$_2$)]PF$_6$ (7c). The molecular structure of **7c** is shown in Figure 1. Experimental crystallographic data and selected bond distances, bond angles, and positional parameters are given in Tables 3 and 4 and the Supporting Information, respectively. Complex **7c** revealed the trans position of the two carbon chains lying roughly in the same plane and perpendicular to the P$_4$Ru plane. The C(5)−C(4)−C(3)−Ru−C(1)−C(2) arrangement is almost linear. The

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7c

Bond Lengths			
Ru−C$_1$	2.11(1)	Ru−P$_4$	2.414(4)
Ru−C$_3$	1.91(1)	C1−C$_2$	1.14(2)
Ru−P$_1$	2.396(4)	C3−C$_4$	1.28(2)
Ru−P$_2$	2.405(3)	C4−C$_5$	1.35(2)
Ru−P$_3$	2.408(4)		
Angles			
C1−Ru−C$_3$	172.7(4)	P$_2$−Ru−P$_4$	170.0(1)
Ru−C$_3$−C$_4$	173.9(9)	P$_1$−Ru−P$_3$	175.2(1)
C$_3$−C$_4$−C$_5$	177(1)	P$_1$−Ru−P$_2$	82.3(1)
Ru−C$_1$−C$_2$	176(1)	P$_3$−Ru−P$_4$	82.3(1)

Ru−C(3), C(3)−C(4), and C(4)−C(5) bonds are longer than those in ruthenium allenylidene complexes [(C$_5$H$_5$)(PMe$_3$)$_2$=C=C=CPh$_2$]PF$_6$[13] (1.884(5), 1.255(8), and 1.339(9) Å) and [(η^5-C$_9$H$_7$)(Ph$_3$P)$_2$Ru=C=C=CR^{1}R^2]PF$_6$[17] (1.889(5), 1.256(7), and 1.339(7) Å) and comparable to those in the vinylallenylidene [N(CH$_2$CH$_2$PPh$_2$)$_3$(Cl)Ru=C=C=C(OMe)CH=CHPh$_2$]PF$_6$[33] (1.921(5), 1.254(7), and 1.369(7) Å. For the alkynyl chain the Ru−C(3) and C(3)−C(4) bonds (1.91(1) and 1.28 Å) can be compared with those of analogous ruthenium alkynyl complexes [Cl(Ph$_2$PCH$_2$PPh$_2$)$_2$RuC≡CH][34] (1.906(9) and 1.162(9) Å) and [(C$_5$H$_5$)(dppe)RuC≡CPh][35] (2.009(3) and 1.204(5) Å). The structure of **7c** shows a long Ru−C(1) bond and one of the shortest observed C≡C bond distances.

Experimental Section

General Data. All reactions were performed under argon or nitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded on a Nicolet 205FT-IR spectrometer. ^{1}H (300.13 MHz), ^{31}P (121.50 MHz), and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AC300P spectrometer at 297 K and referenced to TMS for ^{1}H and ^{13}C and to 86% H$_3$PO$_4$ for ^{31}P. Elemental analyses were performed by the "Service Central d'Analyses du CNRS", Vernaison, France. The syntheses of complex *cis*-(dppe)$_2$RuCl$_2$ (**1**) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)[36] and of propargyl alcohols **5**[37] were performed by literature methods.

Synthesis of Allenylidenes *trans*-[(dppe)$_2$(Cl)Ru=C=C=CR^{1}R^2]PF$_6$ (6a−j). A solution of an excess of propargyl alcohol **5** (1 mmol) in 50 mL of dichloromethane was added to **1** (0.5 mmol) and NaPF$_6$ (1 mmol) in a Schlenk tube. After 12 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. After dissolution in a minimum of dichloromethane and slow addition of hexane, to form a biphasic system, crystals of **6** were obtained.

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CPh$_2$]PF$_6$ (6a).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 210 mg of HC≡CCPh$_2$OH (1.0 mmol), 538 mg of deep red crystals of **6a** (85%) was isolated. Anal. Calcd for C$_{67}$H$_{58}$ClF$_6$P$_4$Ru: C, 63.44; H, 4.61. Found: C, 63.17; H, 4.59. IR (cm^{-1}, KBr): 1925 (s, $\nu_{C=C=C}$), 841 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 7.67−6.69 (50H, Ph), 3.01, 2.81 (m, 8H, PCH$_2$CH$_2$P). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 308.58 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 215.91 (m, Ru=C=C), 161.46 (m, Ru=C=C=C), 145.3−127.2 (Ph), 27.6 (t m, PCH$_2$-CH$_2$P, $^1J_{CH}$ = 137 Hz). ^{13}C{^{1}H} NMR (δ, ppm): 308.57 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 215.9 (quint, Ru=C=C, $^3J_{PC}$ = 2.5 Hz), 161.4 (quint, Ru=C=C=C, $^4J_{PC}$ = 1.4 Hz), 27.68 (quint, PCH$_2$-CH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 37.98 (s, PPh$_2$), −143.89 (sept, PF$_6$, $^1J_{PF}$ = 711 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=C(CH$_3$)$_2$]PF$_6$ (6b).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 100 μL of HC≡CC(CH$_3$)$_2$OH (1.0 mmol), 469 mg of green crystals of **6b** (82%) was isolated. Anal. Calcd for C$_{57}$H$_{54}$ClF$_6$P$_5$Ru: C, 59.82; H, 4.76. Found: C, 59.77; H, 4.67. IR (cm^{-1}, KBr): 1959 (s, $\nu_{C=C=C}$), 839.4 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 7.36−6.99 (40H, Ph), 2.95, (m, 4H, PCH$_2$−), 2.70 (m, 4H, −CH$_2$P), 1.26 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 319.9 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 201.76 (quint, Ru=C=C, $^2J_{PC}$ = 2.4 Hz), 175.08 (s, Ru=C=C=C), 133.7−127.8 (Ph), 35.74 (s, CH$_3$), 29.14 (quint, PCH$_2$CH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 42.13 (s, PPh$_2$), −143.64 (sept, PF$_6$, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CHPh]PF$_6$ (6c).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 132 mg of HC≡CCHPhOH (1.0 mmol), 459 mg of red crystals of **6c** was isolated. Anal. Calcd for C$_{61}$H$_{54}$ClF$_6$P$_5$Ru: C, 61.44; H, 4.56. Found: C, 61.17; H, 4.53. IR (cm^{-1}, KBr): 1935 (s, $\nu_{C=C=C}$), 838.9 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 9.44 (quint, 1H, =CH, $^5J_{PH}$ = 3 Hz), 7.58−6.78 (45H, Ph), 2.99 (m, 8H, PCH$_2$CH$_2$P). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 321.07 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 218.99 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 154.05 (s, Ru=C=C=C), 143−127.9 (Ph), 29.18 (quint, PCH$_2$CH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 39.91 (s, PPh$_2$), −143.47 (sept, PF$_6$, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=C(*p*-PhOMe)$_2$]PF$_6$ (6d).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 270 mg of HC≡CC(*p*-PhOMe)$_2$OH (1.0 mmol), 458 mg of red crystals of **6d** (69%) was isolated. Anal. Calcd for C$_{69}$H$_{62}$ClF$_6$O$_2$P$_5$Ru: C, 62.38; H, 4.66. Found: C, 62.36; H, 4.35. IR (cm^{-1}, KBr): 1930 (s, $\nu_{C=C=C}$), 839.2 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 7.26−6.71 (48H, Ph), 3.87 (s, 6H, OMe), 3.01 (m, 4H, PH$_2$−), 2.86 (m, 4H, CH$_2$P). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 288.4 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 193.4 (s, Ru=C=C), 160.1 (s, Ru=C=C=C), 163.45−114.49 (Ph), 56.1 (s, OCH$_3$), 27.7 (quint, PCH$_2$CH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 39.23 (s, PPh$_2$), −143.59 (sept, PF$_6$, $^1J_{PF}$ = 709 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=C(*p*-PhF)$_2$]PF$_6$ (6e).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 244 mg of HC≡CC(p-PhF)$_2$OH (1.0 mmol), 469 mg of red crystals of **6e** was isolated (72%). Anal. Calcd for C$_{67}$H$_{56}$ClF$_8$P$_5$Ru: C, 61.69; H, 4.33. Found: C, 61.79; H, 4.47. IR (cm^{-1}, KBr): 1923.7 (s, $\nu_{C=C=C}$), 838.9 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 7.29−6.69 (48H, Ph), 3.05 (m, 4H, PCH$_2$−), 2.86 (m, 4H, −CH$_2$P). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 305.9 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 215.1 (s, Ru=C=C), 156.9 (s, Ru=C=C=C), 166.8−116.6 (Ph), 27.9 (quint, PCH$_2$CH$_2$P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K, δ, ppm): 38.0 (s, PPh$_2$), −143.5 (sept, PF$_6$, $^1J_{PF}$ = 709 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=C(*p*-PhCl)$_2$]PF$_6$ (6f).** From 484 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 277 mg of HC≡CC(*p*-PhCl)$_2$OH (1.0 mmol), 448 mg of red crystals of **6f** (67%) was isolated. Anal. Calcd for C$_{67}$H$_{56}$Cl$_3$F$_6$P$_5$Ru: C, 60.17; H, 4.22. Found: C, 59.36; H, 4.25. IR (cm^{-1}, KBr): 1920.8 (s, $\nu_{C=C=C}$), 835.8 (s, PF$_6$). ^{1}H NMR (300.133 MHz, CD$_2$-

(33) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217.
(34) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132.
(35) Bruce, M. I.; Humphrey, H. G.; Snow, H. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.
(36) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.
(37) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988.

Cl_2, 297 K, δ, ppm): 7.28−6.59 (48H, Ph), 3.05 (m, 4H, PCH_2−), 2.82 (m, 4H, −CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 308.33 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 220.81 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 156.49 (quint, Ru=C=C=C, $^4J_{PC}$ = 2 Hz), 143.37−128.4 (Ph), 27.85 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 39.45 (s, PPh_2), −141.96 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CH(*p*-PhNMe$_2$)]PF$_6$ (6g).** From 484 mg of **1** (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 175 mg of HC≡CCHOH(*p*-$PhNMe_2$) (1.0 mmol), 383 mg of blue crystals of **6g** (62%) was isolated. Anal. Calcd for $C_{63}H_{59}ClF_6NP_5Ru$: C, 61.24; H, 4.81. Found: C, 61.35; H, 5.05. IR (cm^{-1}, KBr): 1953.8 (s, $\nu_{C=C=C}$), 839.9 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.69 (s, 1H, Ru=C=C=CH), 7.31−6.99 (44H, Ph), 3.13 (s, 6H, NMe_2), 2.89 (m, 4H, PCH_2−), 2.77 (m, 4H, −CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 265.71 (d quint, Ru=C, $^2J_{PC}$ = 14 Hz, $^3J_{CH}$ = 5 Hz), 169.43 (s, Ru=C=C), 147.87 (d, =CH, $^1J_{CH}$ = 160 Hz), 155.45−113.7 (Ph), 40.84 (q, NMe_2, $^1J_{CH}$ = 138 Hz), 29.60 (t m, PCH_2CH_2P, $^1J_{CH}$ = 132 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm): 265.7 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 169.4 (s, Ru=C=C), 147.9 (s, Ru=C=C=C), 40.8 (s, NMe_2), 29.61 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.75 (s, PPh_2), −143.67 (sept, PF_6, $^1J_{PF}$ = 713 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CH(*trans*-CH=CHPh)]PF$_6$ (6h).** From 484 mg of **1** (1.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 158 mg of *trans*-HC≡CCHOH(CH=CHPh) (1.0 mmol), 481 mg of deep red crystals (79%) of **6h** was isolated. Anal. Calcd for $C_{63}H_{56}ClF_6P_5Ru$: C, 62.1; H, 4.63. Found: C, 61.87; H, 4.73. IR (cm^{-1}, KBr): 1944 (s, $\nu_{C=C=C}$), 838.80 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 8.9 (d quint, 1H, Ru=C=C=CH, $^5J_{PH}$ = 2 Hz, $^3J_{HH}$ = 11 Hz), 7.71 (d, 1H, =CHPh, $^3J_{HH}$ = 15 Hz), 7.70−6.77 (45H, Ph), 5.38 (d.d., 1H, C*H*=CHPh, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 11 Hz), 2.80 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 312.92 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 220.25 (quint, Ru=C=C, $^3J_{PC}$ = 2 Hz), 154.42 (d m, =CHPh, $^1J_{CH}$ = 157 Hz), 153.83 (d m, Ru=C=C=, $^1J_{CH}$ = 164 Hz), 136.63 (m, Ph), 136.59 (d, −*C*H=CHPh, $^1J_{CH}$ = 160 Hz), 135.12−126.91 (Ph), 29.35 (t m, PCH_2CH_2P, $^1J_{CH}$ = 135 Hz. $^{13}C\{^1H\}$ NMR (δ, ppm): 312.96 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 220.26 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 154.43 (s, =CHPh), 153.83 (s. large, Ru=C=C=*C*H), 136.68 (s, Ph), 136.59 (s, −*C*H=CHPh), 134.06−127.94 (Ph), 29.36 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 40.98 (s, PPh_2), −143.47 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CH(*trans*-CH=CHpPhNO$_2$)]PF$_6$ (6i).** From 484 mg of **1** (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 203 mg of *trans*-HC≡CCHOH(CH=CHpPhNO$_2$) (1.0 mmol), 423 mg of deep red crystals (67%) of **6i** was isolated. Anal. Calcd for $C_{63}H_{55}ClF_6O_2NP_5Ru{\cdot}0.5CH_2Cl_2$: C, 58.40; H, 4.32. Found: C, 58.32; H, 4.53. IR (cm^{-1}, KBr): 1936 (s, $\nu_{C=C=C}$), 838 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 9.26 (d quint, 1H, Ru=C=C=CH, $^5J_{PH}$ = 2 Hz, $^3J_{HH}$ = 11 Hz), 7.75 (d, 1H, =CHPhNO$_2$, $^3J_{HH}$ = 15 Hz), 8.08−6.70 (44H, Ph), 5.38 (d d, 1H, C*H*=CHPhNO$_2$, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 11 Hz), 2.84 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 322.8 (m, Ru=C), 237.1 (m, Ru=C=C) 152.34 (d d, Ru=C=C=CH, $^1J_{CH}$ = 165 Hz, $^3J_{CH}$ = 7 Hz), 148.9−125.9 (Ph), 138.55 (d large, C*H*=CHPhNO$_2$, $^1J_{CH}$ = 161 Hz), 128.86 (d d, =CHPh$_2$NO$_2$, $^1J_{CH}$ = 164 Hz, $^3J_{CH}$ = 6 Hz), 29.28 (t m, PCH_2CH_2P, $^1J_{CH}$ = 133 Hz. $^{13}C\{^1H\}$ NMR (δ, ppm): 322.77 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 237.06 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 152.4 (s, Ru=C=C=C), 138.55 (s, −*C*H=CHPh), 128.85 (s, =CHPhNO$_2$), 29.27 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 39.92 (s, PPh_2), −143.41 (sept, PF_6, $^1J_{PF}$ = 713 Hz).

***trans*-[(dppe)$_2$(Cl)Ru=C=C=CH(*trans*-CH=CHpPhNMe$_2$)]PF$_6$ (6j).** From 484 mg of **1** (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 201 mg of *trans*-HC≡CCHOH(CH=CHpPhNMe$_2$) (1 mmol), 385 mg of green crystals (61%) of **6j** was isolated. Anal. Calcd for $C_{65}H_{61}ClF_6NP_5Ru$: C, 61.88; H, 4.87. Found: C, 61.43; H, 4.61. IR (cm^{-1}, KBr): 1958 (s, $\nu_{C=C=C}$), 841.3 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.73 (d, 1H, Ru=C=C=CH, $^3J_{HH}$ = 12 Hz), 7.41−6.81 (44H, Ph), 6.80 (d. 1H, =CHPhNMe$_2$, $^3J_{HH}$ = 9 Hz), 5.68 (m, 1H, −C*H*=CHPhNMe$_2$), 3.15 (s, 6H, NMe_2), 2.79 (m, 8H, PCH_2CH_2P). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 268.95 (m, Ru=C), 180.9 (m, Ru=C=C), 159.7 (d m, Ru=C=C=CH, $^1J_{CH}$ = 160 Hz), 150.21 (d m, CH=, $^1J_{CH}$ = 159 Hz), 154.8−126.7 (Ph), 113.3 (d d, $^1J_{CH}$ = 138 Hz), 29.8 (t m, PCH_2CH_2P, $^1J_{CH}$ = 137 Hz. $^{13}C\{^1H\}$ NMR (δ, ppm): 268.95 (quint, Ru=C, $^2J_{PC}$ = 17 Hz), 181.08 (s large, Ru=C=C), 159.75 (s large, Ru=C=C=C), 150.18 (s, CH=), 113.31 (s, CHpPhNMe$_2$), 40.59 (s, NMe_2), 29.76 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.72 (s, PPh_2), −143.53 (sept, PF_6, $^1J_{PF}$ = 709 Hz).

Synthesis of Allenylidene Alkynyl *trans*-[(dppe)$_2$(C≡CR)Ru=C=C=CR^{1}R^2]PF$_6$ (7a−h). A solution of propargyl alcohol **5** (1 mmol) and triethylamine (2 mmol) in 50 mL of dichloromethane was added to complex **3** (0.5 mmol) and $NaPF_6$ (1 mmol). After 18 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. The compound, dissolved in dichloromethane, was washed with 30 mL of water three times to eliminate the ammonium salt. After drying with $MgSO_4$, evaporation of the solvent, dissolution in a minimum of dichloromethane, and slow addition of hexane, to form a biphasic system, crystals of **7** were obtained.

***trans*-[(dppe)$_2$(C≡CH)Ru=C=C=CPh$_2$]PF$_6$ (7a).** From 551 mg of **3a**, 168 mg of $NaPF_6$, 208 mg of HC≡$CCPh_2OH$, and 280 μL of Et_3N, 383 mg of violet crystals (61%) of **6j** was isolated. Anal. Calcd for $C_{69}H_{59}F_6P_5Ru$: C, 65.87; H, 4.73. Found: C, 65.58; H, 4.75. IR (cm^{-1}, KBr): 3252 (m, $\nu_{C\equiv H}$), 1949.5 (m, $\nu_{C\equiv C}$), 1919 (s, $\nu_{C=C=C}$), 842 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.58−6.62 (50H, Ph), 3.17 (quint, 1H, ≡CH, $^4J_{PH}$ = 3 Hz), 2.92 (m, 4H, PCH_2−), 2.74 (m, 4H, −CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 318.85 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 213.25 (s large, Ru=C=C), 161.93 (s, Ru=C=C=C) 144.2−127.53 (Ph), 128.68 (obtained by 2D correlation, d, ≡CH, $^1J_{CH}$ = 166 Hz), 111.24 (quint, Ru−C≡, $^2J_{PC}$ = 17 Hz), 29.11 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.7 (s, PPh_2), −143.6 (sept, PF_6, $^1J_{PF}$ = 711 Hz).

***trans*-[(dppe)$_2$(C≡C^{n}Bu)Ru=C=C=CPh$_2$]PF$_6$ (7b).** From 580 mg of **3b**, 168 mg of $NaPF_6$, 208 mg of HC≡$CCPh_2OH$, and 280 μL of Et_3N, 420 mg of violet crystals (64%) of **7b** was isolated. Anal. Calcd for $C_{73}H_{67}F_6P_5Ru{\cdot}0.5CH_2Cl_2$: C, 65.06; H, 5.05. Found: C, 65.22; H, 5.14. IR (cm^{-1}, KBr): 2100 (m, $\nu_{C\equiv H}$), 1919 (s, $\nu_{C=C=C}$), 838 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.63−6.71 (50H, Ph), 2.94 (m, 4H, PCH_2), 2.78 (m, 4H, −CH_2P), 2.42 (m, 2H, ≡CCH_2), 1.45 (m, 2H, −CH_2CH_2), 1.35 (m, 2H, −CH_2CH_2), 0.91 (t., 3H, −CH_3, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 316.6 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 216.4 (s large, Ru=C=C), 160.5 (s, Ru=C=C=C), 144.7−126.5 (Ph), 101.3 (quint, Ru−C≡, $^2J_{PC}$ = 17 Hz), 29.37 (t m, PCH_2CH_2P, $^1J_{CH}$ = 139 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm): 316.7 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 216.43 (s, Ru=C=C), 160.53 (s, Ru=C=C=C) 101.34 (quint, Ru−C≡, $^2J_{PC}$ = 17 Hz), 31.89 (s, ≡CCH_2), 29.39 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz), 23.99 (s, −CH_2CH_2−) 22.87 (s, −CH_2CH_2−), 14.12 (s, CH_3). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.7 (s, PPh_2), −143.62 (sept, PF_6, $^1J_{PF}$ = 713 Hz).

***trans*-[(dppe)$_2$(C≡CPh)Ru=C=C=CPh$_2$]PF$_6$ (7c).** From 590 mg of **3c**, 168 mg of $NaPF_6$, 208 mg of HC≡$CCPh_2OH$, and 280 μL of Et_3N, 460 mg of blue crystals (69%) of **7c** was isolated. Anal. Calcd for $C_{75}H_{63}F_6P_5Ru$: C, 67.52; H, 4.76. Found: C, 67.37; H, 4.67. IR (cm^{-1}, KBr): 2065 (m, $\nu_{C\equiv C}$),

1920.5 (s, $\nu_{C=C=C}$), 839.1 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.67−6.76 (55H, Ph), 2.99 (m, 4H, PCH_2-), 2.82 (m, 4H, $-CH_2P$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 316.57 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 213.23 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 162.29 (s, Ru=C=C=C), 144.7−126.2 (Ph), 120.04 (quint, Ru−C≡, $^2J_{PC}$ = 17 Hz), 29.70 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.85 (s, PPh_2), −143.96 (sept, PF_6, $^1J_{PF}$ = 709 Hz).

***trans*-[(dppe)$_2$(C≡C-*p*-PhNO$_2$)Ru=C=C=CPh$_2$]PF$_6$ (7d).** From 619 mg of **3e**, 208 mg of $NaPF_6$, 208 mg of HC≡$CCPh_2$-OH, and 280 μL of Et_3N, 393 mg of deep-red crystals (57%) was isolated. Anal. Calcd for $C_{75}H_{62}F_6NO_2P_5Ru\cdot CH_2Cl_2$: C, 62.34; H, 4.36. Found: C, 62.18; H, 4.31. IR (cm^{-1}, KBr): 2069 (m, $\nu_{C\equiv C}$), 1920 (s, $\nu_{C=C=C}$), 839 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 8.15−6.71 (54H, Ph), 2.94 (m, 8H, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 316.3 (quint, Ru=C, $^2J_{PC}$ = 13 Hz), 209.00 (s, Ru=C=C), 163.38 (s, Ru=C=C=C), 144.95−127.34 (Ph), 137.95 (s, Ru−C≡C), 29.0 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 44.06 (s, PPh_2), −143.63 (sept, PF_6, $^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(C≡C-*p*-PhOCH$_3$)Ru=C=C=CPh$_2$]PF$_6$ (7e).** From 604 mg of **3d**, 168 mg of $NaPF_6$, 208 mg of HC≡$CCPh_2OH$, and 280 μL of Et_3N, 423 mg of violet crystals (62%) was isolated. Anal. Calcd for $C_{76}H_{65}F_6OP_5Ru\cdot 0.5CH_2Cl_2$: C, 65.32; H, 4.73. Found: C, 65.63; H, 4.74. IR (cm^{-1}, KBr): 2079 (m, $\nu_{C\equiv C}$), 1919 (s, $\nu_{C=C=C}$), 839 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.66−6.75 (54H, Ph), 3.84 (s, OCH_3), 2.97 (m, 4H, PCH_2-), 2.79 (m, 4H, $-CH_2P$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 315.75 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 214.23 (s large, Ru=C=C), 161.66 (s, large, Ru=C=C=C), 158.3−112.9 (Ph), 121.43 (t m, Ru−C≡C, $^3J_{CH}$ = 8 Hz), 117.12 (quint, Ru−C≡, $^2J_{PC}$ = 18 Hz), 55.72 (q, OCH_3, $^1J_{CH}$ = 144 Hz), 29.65 (t m, PCH_2CH_2P, $^1J_{CH}$ = 137 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm): 315.75 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 214.33 (quint, Ru=C=C, $^3J_{PC}$ = 3 Hz), 161.61 (quint, Ru=C=C=C, $^4J_{PC}$ = 2 Hz), 158.38−113.98 (Ph), 121.39 (quint, Ru−C≡C, $^3J_{PC}$ = 2 Hz), 117.05 (quint, Ru−C≡, $^2J_{PC}$ = 18 Hz), 55.68 (s, OCH_3), 29.64 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 43.60 (s, PPh_2), −143.97 (sept, PF_6,$^1J_{PF}$ = 710 Hz).

***trans*-[(dppe)$_2$(C≡C-*p*-PhNO$_2$)Ru=C=C=CH-*p*-PhNMe$_2$)]-PF$_6$ (7f).** From 613 mg of **3e**, 168 mg of $NaPF_6$, 175 mg of HC≡CCHOH-*p*-$PhNMe_2$, and 280 μL of Et_3N, 390 mg of blue crystals (58%) was obtained. Anal. Calcd for $C_{71}H_{63}F_6N_2O_2P_5$-Ru: C, 63.35; H, 4.72. Found: C, 63.28; H, 4.67. IR (cm^{-1}, KBr): 2059 (m, $\nu_{C\equiv C}$), 1954.1 (s, $\nu_{C=C=C}$), 839 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 8.11−6.30 (48H, Ph), 7.39 (quint, =CH, $^5J_{PH}$ = 2 Hz), 3.22 (s, 6H, NMe_2), 2.75 (m, 8H, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 297 K, δ, ppm): 264.65 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 163.67 (s, Ru=C=C), 142.65 (s, Ru=C=C=C), 156.64−113.34 (Ph), 144.64 (s, ≡C−), 139.23 (quint, Ru−C, $^2J_{PC}$ = 17 Hz), 41.34 (s, NMe_2), 31.21 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 49.65 (s, PPh_2), −143.59 (sept, PF_6,$^1J_{PC}$ = 710 Hz).

***trans*-[(dppe)$_2$(C≡CPh)Ru=C=C=C(*p*-PhOMe)$_2$]PF$_6$ (7g).** From 590 mg of **3c** (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), 270 mg of HC≡CC(*p*-$PhOMe)_2OH$ (1.0 mmol), and 280 μL of Et_3N (2 mmol), 439 mg of violet crystals (63%) was obtained. Anal. Calcd for $C_{77}H_{67}F_6O_2P_5Ru\cdot CH_2Cl_2$: C, 63.33; H, 4.70. Found: C, 63.28; H, 4.93. IR (cm^{-1}, KBr): 2050 (m, $\nu_{C\equiv C}$), 1925 (s, $\nu_{C=C=C}$), 838 (s, PF_6). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.20−6.70 (53H, Ph), 3.90 (s, 6H, OMe), 2.91 (m, 8H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 294.22 (quint, Ru=C, $^2J_{PC}$ = 14 Hz), 189.99 (quint, Ru=C=C, $^3J_{PC}$ = 2 Hz), 161.46 (s large, Ru=C=C=C), 163.71−114.52 (Ph), 125.35 (s, Ru−C≡C), 120.52 (quint, Ru−C≡, $^2J_{PC}$ = 18 Hz), 56.15 (s, OCH_3), 29.74 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 45.22 (s, PPh_2), −143.62 (sept, PF_6,$^1J_{PC}$ = 710 Hz).

***trans*-[(dppe)$_2$(C≡C-*p*-PhNO$_2$)Ru=C=C=CH(*trans*-CH=CH-*p*-PhNMe$_2$)]PF$_6$ (8).** From 613 mg of **3e**, 168 mg of $NaPF_6$, 201 mg of *trans*-HC≡CCHOH(CH=CH-*p*-$PhNMe_2$), and 280 μL of Et_3N, 404 mg of red crystals (59%) was obtained. Anal. Calcd for $C_{73}H_{65}F_6N_2O_2P_5Ru$: C, 63.89; H, 4.77. Found: C, 63.79; H, 4.94. IR (cm^{-1}, KBr): 2057.8 (m, $\nu_{C\equiv C}$), 1959.1 (s, $\nu_{C=C=C}$), 840 (s, PF_6). ^1H NMR (300.133 MHz, $CDCl_3$, 297 K, δ, ppm): 8.10−6.84 (50H, Ph, Ru=C=C=CH, Ru=C=C=C−C=CH), 5.96 (t, Ru, C=C=C−CH=, $^3J_{PC}$ = 13 Hz), 3.21 (s, 6H, NMe_2), 2.69 (m, 8H, PCH_2CH_2P). ^{13}C (75.47 MHz, $CDCl_3$, 297 K, δ, ppm): 260.78 (m, Ru=C), 169.41 (s large, Ru=C=C), 161.71 (d m, Ru=C=C=CH*C*H=, $^1J_{CH}$ = 150 Hz), 150.12 (d d, Ru=C=C=C, $^1J_{CH}$ = 160 Hz, $^3J_{CH}$ = 7 Hz), 155.87−123.81 (Ph), 139.77 (quint, Ru−C≡, $^2J_{PC}$ = 16 Hz), 113.85 (d m, Ru=C=C=CHCH=*C*, $^1J_{CH}$ = 162 Hz), 40.82 (q, NMe_2, $^1J_{CH}$ = 138 Hz), 30.97 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 23 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm) 260.78 (quint, Ru=C, $^2J_{PC}$ = 15 Hz): 169.41 (s, large, Ru=C=C), 161.71 (s, Ru=C=C=C*H*C*H*=, 150.12 (s, Ru=C=C=C), 139.77 (quint, Ru−C≡, $^2J_{PC}$ = 16 Hz), 113.85 (s, Ru=C=C=CH−CH=*C*), 40.82 (s, NMe_2), 30.97 (t m, PCH_2CH_2P, $^1J_{CH}$ = 132 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 50.13 (s, PPh_2), −143.54 (sept, PF_6,$^1J_{PF}$ = 709 Hz).

Synthesis of Mixed Bis(alkynyl) *trans*-[(dppe)$_2$Ru-(C≡CPhX)(C≡CCPh$_2$OMe)] (9c,e). To a solution of 666 mg of **7c** (0.5 mmol) in 50 mL of MeOH was added a solution of 115 mg of Na in 10 mL of MeOH. After 2 h of stirring at room temperature, a pale yellow powder precipitate. The solution was eliminated and the residue washed with methanol. After drying, the crude product was recrystallized in a dichloromethane−hexane mixture to give 409 mg of pale yellow crystals of **9c** (67%). Anal. Calcd for $C_{76}H_{66}OP_4Ru$: C, 74.80; H, 5.45. Found: C, 74.75; H, 5.59. IR (cm^{-1}, KBr): 2068.1 (s, $\nu_{C=C=C}$), 2031.5 (s, $\nu_{C=C=C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 8.03−6.36 (55H, Ph), 3.09 (s, 3H, OCH_3), 2.49 (m, 4H, PCH_2-), 2.0 (m, 4H, $-CH_2P$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 52.19 (q, OCH_3, $^1J_{CH}$ = 148 Hz), 32.14 (t m, PCH_2CH_2P, $^1J_{CH}$ = 133 Hz), $^{13}C\{^1H\}$ NMR (δ, ppm): 147.09−122.99 (Ph), 133.35 (quint, Ru−C≡, $^2J_{PC}$ = 16 Hz), 121.04 (quint, Ru−C≡, $^2J_{PC}$ = 15 Hz), 115.13 (s, ≡C−), 113.31 (s, ≡C−), 82.54 (s, $COCH_3$), 52.20 (s, OCH_3), 32.14 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 57.06 (s, PPh).

9e. From 681 mg of **7e**, 431 mg of **9e** was obtained (69%). Anal. Calcd for $C_{77}H_{68}P_4Ru\cdot 0.5CH_2Cl_2$: C, 71.93; H, 5.38. Found: C, 71.47; H, 5.12. IR (cm^{-1}, KBr): 2076 (s, $\nu_{C\equiv C}$), 2031.2 (s, $\nu_{C\equiv C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 8.09−6.36 (54H, Ph), 3.78 (s, 3H, OCH_3), 3.15 (s, 3H, OCH_3), 2.55 (m, 4H, PCH_2-), 2.05 (m, 4H, $-CH_2P$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K, δ, ppm): 55.19 (q, OCH_3, $^1J_{CH}$ = 143 Hz), 51.9 (q, OCH_3, $^1J_{CH}$ = 142 Hz). $^{13}C\{^1H\}$ NMR (δ, ppm): 155.49−112.52 (Ph), 128.31 (quint, Ru−C≡, $^2J_{PC}$ = 16 Hz), 121.35 (quint, Ru−C≡, $^2J_{PC}$ = 15 Hz), 114.45 (s, ≡C−), 111.93 (s, ≡C−), 82.28 (s, $-CPh_2OMe$), 55.17 (s, OCH_3), 51.89 (s, OCH_3), 31.81 (quint, PCH_2CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 56.76 (s, PPh_2).

Synthesis of Bis*(*alkynyl) Complex *trans*-[(dppe)$_2$Ru-(C≡CPh)(C≡CCHPh$_2$)] (10). To a solution of 666 mg of **7c** (0.5 mmol) in 50 mL of THF was added 95 mg (2.5 mmol) of $NaBH_4$. After 1 h of stirring at room temperature, the solution was filtered and purified on a short alumina chromotography column. The residue was recrystallized in a THF/hexane mixture. A total of 517 mg of yellow crystals (87%) was obtained. Anal. Calcd for $C_{75}H_{64}P_4Ru$: C, 75.68; H, 5.42. Found: C, 76.08; H, 5.49. IR (cm^{-1}, KBr): 2063.1 ($\nu_{C=C=C}$). ^1H NMR (300.133 MHz, CD_2Cl_2, 297 K, δ, ppm): 7.88−6.63 (55H, Ph), 4.77 (s, 1H, $-CHPh_2$), 2.61 (m, 4H, PCH_2-), 2.37 (m, 4H, $-CH_2P$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K,

δ, ppm): 146.08−123.04 (Ph), 133.55 (quint, Ru−C≡, $^2J_{PC}$ = 15 Hz), 115, 28 (s, ≡C−), 114.48 (s, ≡C−), 114.04 (quint, Ru−C≡, $^2J_{PC}$ = 15 Hz), 49.04 (s, $CHPh_2$), 31.85 (quint, PCH_2-CH_2P, $|^1J_{PC} + {}^3J_{P'C}|$ = 24 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K, δ, ppm): 55.68 (s, PPh_2).

Crystal Structure Analysis of 7c. A single crystal of 0.42 × 0.20 × 0.16 mm was selected for the structure determination. The determination of the cell constants and the intensity data collection were carried at room temperature. Unit cell dimensions were determined by least-squares refinement of 25 accurately centered reflections. Pertinent crystal data and data collection parameters can be found in Table 3. The data collection was limited up to θ = 26° because no significant intensity was observed above this limit. In addition, only 5435 reflections of the 6300 measured were considered as observed. The structure was solved by Patterson methods and Fourier synthesis. An empirical absorption correction[38] was applied after the isotropic refinement. Maximum and minimum corrections applied were 1.155 and 0.891, respectively (mean 0.986). The refinement was made in the mixed mode, anisotropic for all non-H-atoms and isotropic for H-atoms (a total of 837 parameters were refined; data-to-parameter ratio = 6.49). The final Fourier difference map showed a largest differential peak and hole of 0.60 and −0.58 e/Å^3, respectively. Scattering factors and anomalous dispersion factors were taken from the literature.[39] All calculations were performed on a Alpha Station-200 computer by using the following programs: XRAY 80 system[40] and DIRDIF.[41] The most significant bond lengths and angles are indicated in Table 4. The molecule is represented in Figure 1.

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Supporting Information Available: Tables of bond lengths and angles, torsion angles, positional parameters, and displacement parameters for **7c** (34 pages). Ordering information is given on any current masthead page.

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(38) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1987**, *39*, 158.

(39) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(40) Stewart, J. M., Ed. *The X-ray System of Crystallographic Programs*; University of Maryland: College Park, MD, 1978.

(41) Berskens, P.; Bosman, W. P.; Doesburg, H. H.; Gould, R. O.; Van den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Parthasarati, V.; Bruins Slot, H. J.; Haltiwanger, R. C.; Smits, J. M. M. *Dirdif System*; Crystallography Toernooivel: Nijmegen, The Netherlands, 1984.