New Ruthenium Vinylidene Complexes as Intermediates for the Access to σ-Acetylide and Unsymmetrical *trans*-Diynyl, Alkynyl Metal Complexes. Crystal Structures of $[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}CH_2]PF_6$ and $[(Ph_2PCH_2PPh_2)_2(Cl)RuC{\equiv}CH]$ Complexes

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cis-$RuCl_2(dppm)_2$ (1) (dppm = $Ph_2PCH_2PPh_2$) reacts with acetylene to give *trans*-$(dppm)_2ClRu^+{=}C{=}CH_2$ (3) and with terminal alkynes to give *trans*-$(dppm)_2ClRu^+{=}C{=}CHR$ 4 cations. These vinylidenes 3 and 4 are readily deprotonated using DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to give *trans*-$(dppm)_2ClRuC{\equiv}CH$ (5) and *trans*-$(dppm)_2ClRu\text{-}C{\equiv}CR$ 6. The substitution of chloride from 6 with diyne $HC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2$ and a base gives access to unsymmetrical complexes *trans*-$(dppm)_2(RC{\equiv}CRuC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2)$ 8. These derivatives have been fully characterized by IR, ^1H, $^{13}C\{^1H\}$, ^{13}C, and $^{31}P\{^1H\}$ NMR and single crystal X-ray diffraction for 3 and 5. Complex 3 crystallizes in the orthorhombic space group $Pna2_1$ with $Z = 4$ in a unit cell of dimensions $a = 22.602(3)$ Å, $b = 11.850(2)$ Å, $c = 19.235(6)$ Å with a final R value of 3.9%. Crystals of 5 are monoclinic, space group $I2/a$, with $a = 22.003(2)$ Å, $b = 9.715(1)$ Å, $c = 22.205(3)$ Å, $\beta = 112.38(2)°$ and $Z = 4$, with a final R value of 2.7%.

Introduction

Metal σ-acetylide complexes attract interest as precursors of molecules containing a linear array and delocalizable π systems,[1,2] or polymeric materials,[2] in the search of π interaction through the metal center and new properties.[3] An attractive and convenient way to produce metal σ-acetylide complexes has been shown recently to involve deprotonation of metal vinylidene complexes.[4] Our interest in the activation of terminal alkynes with ruthenium(II) complexes, relevant to both catalysis[5] and the design of new unsaturated organometallics,[6] has already led to evidence for the formation of reactive ruthenium(II) vinylidene species.[7] The difficulty of producing σ-acetylide complexes at more sterically hindered ruthenium(II) centers has led us to look for the generation of new stable vinylidene ruthenium complexes and use them as precursors for σ-acetylide derivatives. We now report (*i*) a general route to $[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}CHR]^+$ cations from $RuCl_2(Ph_2PCH_2PPh_2)_2$ and terminal alkynes and especially to the stable unsubstituted vinylidene (R = H), directly from acetylene, (*ii*) their use for the access to acetylide derivatives *trans*-$(Ph_2PCH_2PPh_2)_2(Cl)RuC{\equiv}CR$ and to unsymmetrical diynyl complexes *trans*-$[(Ph_2PCH_2PPh_2)_2Ru(C{\equiv}CC{\equiv}CCR_2Y)(C{\equiv}CR)$ and (*iii*) the comparative crystal structure studies of closely related complexes $[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}CH_2]PF_6$ and $(Ph_2PCH_2PPh_2)_2(Cl)RuC{\equiv}CH$.

Results and Discussion

1. Synthesis of Ruthenium Vinylidene Complexes. The reaction of *cis*-$RuCl_2(Ph_2PCH_2PPh_2)_2$ (1)[8] in dichloromethane with an excess of acetylene, at 1 atm and room temperature and in the presence of 2 equiv of $NaPF_6$, afforded the orange complex 3 in 92% yield (Scheme I). The structure of 3 corresponds to the *trans*-chloro(vinylidene)ruthenium complex as indicated by NMR (Table I): the equivalence of the four ^{31}P nuclei, the low-frequency resonance as a quintuplet of the (Ru=C) carbon nucleus ($\delta = 340.87$, $^2J_{PC} = 13.2$ Hz), the $=CH_2$ carbon signal as a triplet of quintuplets at δ 91.41 ppm ($^3J_{PC}$ =

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Scheme I

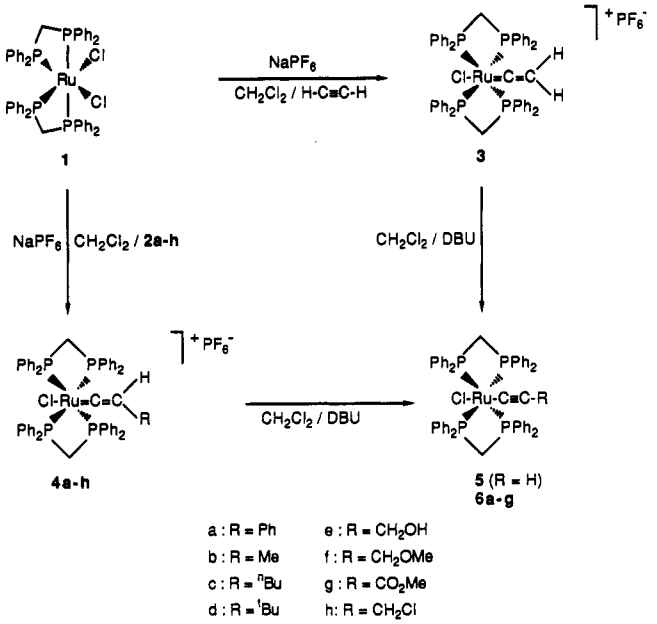

Table I. Selected NMR Data for Vinylidene Compounds 3 and 4[a]

compd no.	$\delta(^{31}P)$, ppm PPh_2	$\delta(^{13}C$ and $^1H)$, ppm Ru=*C* ($^2J_{PC}$, Hz)	Ru=C=*C* ($^3J_{PC}$, $^1J_{CH}$, Hz)	Ru=C=C*H* ($^4J_{PH}$, Hz)
3	−15.14	340.87 (13.2)	91.41 (2.5, 165.6)	2.36 (3.0)
4a	−15.42	336.02 (13.3)	110.75 (153.8)	3.07 (3.1)
4b	−15.09	321.10 (13.3)	100.49 (143.8)	2.57 (2.8)
4c	−15.30	323.18 (13.5)	106.12 (2.0, 155.9)	2.48 (2.8)
4d	−15.02	324.67 (13.3)	117.57 (142.7)	1.80 (2.2)
4e	−15.24	351.41 (13.4)	107.33 (2.2, 160.7)	3.02
4f	−15.27	330.06 (13.5)	104.38 (2.2, 161.3)	2.89
4g	−13.88	346.34 (13.4)	104.35 (1.8, 163.8)	2.98 (2.6)
4h	−16.52	327.05 (13.5)	105.97 (2.4, 163.5)	2.96 (3.0)
I[7a]		360.34	112.30	5.66
II[9]		365.03	114.28	5.85
III[10]		358.90	119.56	5.43
IV[11]		346.2	93.8	4.30
V[4a]		343.9	92.7	3.78

[a] All spectra in CD_2Cl_2 at 297 K. $[(C_6Me_6)(PMe_3)(Cl)Ru{=}C{=}CHPh]PF_6$ (**I**), $[(N(CH_2CH_2PPh_2)_3)(Cl)Ru{=}C{=}CHPh]PF_6$ (**II**), $[(C_5H_5)(PPh_3)_2Ru{=}C{=}CHPh]PF_6$ (**III**), $[(C_5H_5)(PhPMe_2P)_2Ru{=}C{=}CH_2]BF_4$ (**IV**), $[(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2]PF_6$ (**V**).

2.5 Hz, $^1J_{CH}$ = 165.6 Hz). The molecular structure of **3** has been determined by an X-ray diffraction study (Figure 1).

Complex **1** has also been reacted with a variety of terminal alkynes **2a–h** (2 equiv) in the presence of $NaPF_6$ in dichloromethane and *trans*-chloro(vinylidene)ruthenium complexes **4a–h** were readily formed and isolated in 72–87% yield and characterized by NMR (Table I). From phenylacetylene **2a** and *trans*-$RuCl_2(Ph_2PCH_2PPh_2)_2$[8] under similar conditions the same complex **4a** was obtained (80%), but complex **1**[8] was prefered as a precursor for further reactions because of its easiest access.

In ^1H NMR the (=CH) resonance of complexes **4** is at much higher field (δ = 1.83 ppm) than for other ruthenium vinylidene complexes (Table I): $[(C_6Me_6)(PMe_3)(Cl)Ru{=}C{=}CHPh]PF_6$ (**I**) (δ = 5.66 ppm),[7a] $[(N(CH_2CH_2PPh_2)_3)(Cl)Ru{=}C{=}CHPh]PF_6$ (**II**) (δ = 5.85 ppm),[9] $[(C_5H_5)(PPh_3)_2Ru{=}C{=}CHPh]PF_6$ (**III**) (δ = 5.43 ppm),[10] $[(C_5H_5)(PhMe_2P)_2Ru{=}C{=}CH_2]BF_4$ (**IV**) (δ = 4.30 ppm),[11]

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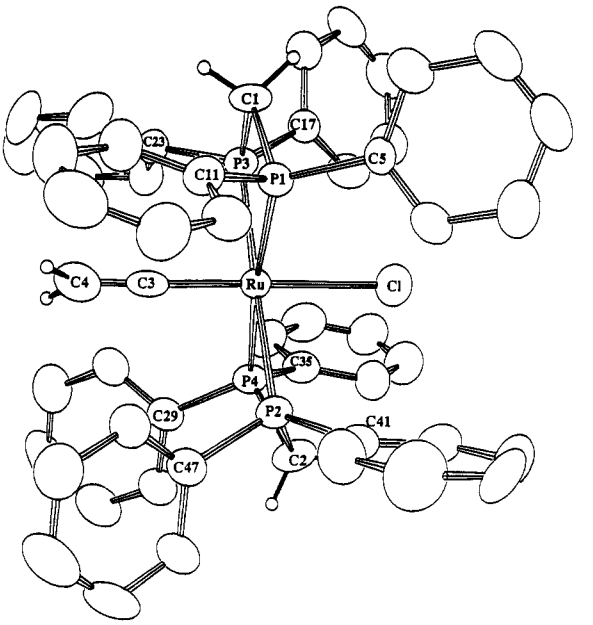

Figure 1. ORTEP diagram for *trans*-$[(dppm)_2(Cl)Ru{=}C{=}CH_2]PF_6$ (**3**).

or $[(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2]PF_6$ (**V**) (δ = 3.78 ppm).[4a] This shielding is thought to be due to the neighborhood of the four phenyl groups of the dppm ($Ph_2PCH_2PPh_2$) ligands in *trans* complexes **3** and **4** (Figure 1).

Although many substituted M=C=CHR complexes have been characterized, very few unsubstituted M=C=CH_2 derivatives are known. $[(C_5H_5)(PMe_3)_2Ru{=}C{=}CH_2]PF_6$ (**V**) has first been obtained from acetylene or with a better selectivity from $HC{\equiv}CSiMe_3$.[4a] $[(C_5H_5)(PhMe_2P)_2Ru{=}C{=}CH_2]BF_4$ (**IV**) has just been prepared by protonation of the corresponding RuC≡CH complex and structurally characterized by Selegue.[11] The latter results from deprotonation with $KOCMe_3$ of the corresponding $Ru(\eta^2\text{-}HC{\equiv}CH)^+$ derivative which also rearranged into the vinylidene complex at 50 °C. It is likely that the steric hindrance of the dppm ligands of **1** makes the $Ru(\eta^2\text{-}HC{\equiv}CH)$ less stable and thus favors the direct formation of the Ru=C=CH_2 complex directly from acetylene. The formally 16-electron Ir=C=CH_2 complex $[N(SiMe_2CH_2PPh_2)_2]Ir{=}C{=}CH_2$ has also been recently prepared by rearrangement the $(\eta^2\text{-}HC{\equiv}CH)Ir$ complex.[12]

The vinylidenes **3**, **4a–h** are stable even in the air and do not react with methanol by contrast with $[(\eta^6\text{-}C_6R_6)Ru(C{=}CHR)Cl(PMe_3)]^+PF_6^-$ intermediates.[7a] The latter were only isolated by protonation of the acetylide,[7a] and methanol immediately adds to give the carbene derivatives $[(\eta^6\text{-}C_6R_6)Ru(=C(OMe)CH_2Ph)Cl(PMe_3)]^+PF_6^-$.[7a] This is expected to be due to the facts that (*i*) the electrophilic carbon C_1 in **4** is sterically hindered by four phenyl groups of the dppm ligands and (*ii*) the $(dppm)_2ClRu^+$ moiety is more electron-releasing than the $(C_6Me_6)(PMe_3)ClRu^+$ moiety, and thus makes the vinylidene less electrophilic.

The activation of propargyl alcohol by complex **1** deserves a special attention as complex **4e** is resistent to dehydration, whereas disubstituted propargyl alcohol derivatives usually lead to allenylidene intermediates **A**[7b,13,14] (Scheme II). The latter adds alcohol at the Ru=C carbon when the metal is electrophilic, to give alkenyl

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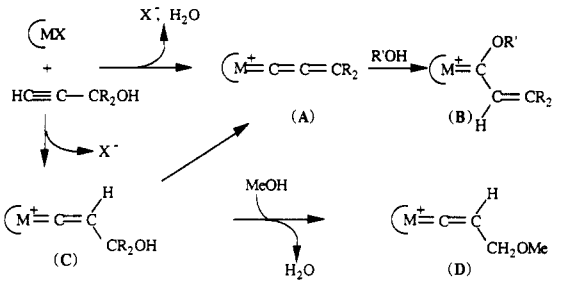
Scheme II



carbene **B** such as that from $[Ru{=}C{=}C{=}CR_2(Cl)(PMe_3)(C_6Me_6)]PF_6$.[7b,14] The intermediate **C** was suggested as a precursor of ruthenium allenylidene complexes **A**[13] and $Mn{=}(C{=}CHCH_2OH)(CO)_2C_5H_5$[15] was obtained on acid- or base-promoted rearrangement of $Mn(\eta^2\text{-}HC{\equiv}CCH_2OH)(CO)_2C_5H_5$. The isolation of the stable complex **4e** confirms that the vinylidene intermediate **C** is the first step of the dehydration process of propynols by ruthenium(II), which takes place when substituents are linked at carbon C(3).[6d]

It is noteworthy that with less sterically hindered and more electrophilic complexes such as $RuCl_2(PR_3)(C_6Me_6)$, addition of a second equivalent of methanol at C_3 of complex of type **B** takes place to give the carbene complex $[(C_6Me_6)(PMe_3)ClRu{=}C(OMe)CH_2CH_2OMe]$.[7b] The hydroxy group of **4e** is very labile. When **4e** is dissolved in methanol, no addition of methanol at carbon C_1 takes place, but after 67 h at room temperature **4e** is transformed into **4f** (60%) corresponding to **D** and to the substitution at C_3 of the hydroxide by the methoxide group. Whether the transformation **C** → **D** involves a direct substitution of the hydroxide at carbon C_3 or an unsubstituted allenylidene complex of type $Ru{=}C{=}C{=}CH_2$, is still a raised question.

2. Synthesis of Ruthenium Acetylide Complexes. The short C=C distance of **3** with a C≡C character (see X-ray structure discussions) was suggestive of a rather strong acidity, and **3** was expected to be readily deprotonated with a base. Complex **3** in dichloromethane was treated with 1 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) at room temperature and the solution turned immediately from orange to yellow. A pale yellow complex was isolated after chromatography on alumina and identified as the acetylide **5** (47%). The similarly treated vinylidenes **4a–g** afforded the corresponding acetylide–ruthenium(II) complexes **6a–g** in 45–65% yields. Attempts at deprotonation of **4** with $NaBH_4$ or $KOCMe_3$ in dichloromethane also produced some amount of complexes **6** but their isolation and purification were not so straightforward as by using DBU.

The acetylide complexes **5** and **6** show in the infrared a C≡C absorption ν = 1935 cm^{-1} for **5** and 2044–2108 cm^{-1} for complexes **6**. The *trans* position of the chloro and acetylide ligands are indicated by the ^{31}P NMR spectra which show only one line; the ^{13}C NMR spectra show two quintuplets for both RuC≡C carbon nuclei (Table II).

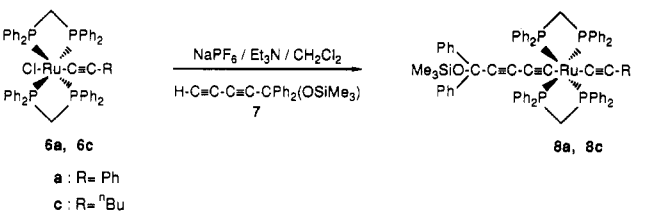
It is noteworthy that the expected formation of the monoacetylides **6** *via* direct chloride substitution of **1** with lithium acetylide or Grignard reagents gave only low yield of **6** and their purification was difficult. However, complex **6a** was obtained in 57% yield directly from **1** in tetrahydrofuran, 2 equiv of phenylacetylene, 2 *equiv of* $NaPF_6$, and 4 equiv of NEt_3. The same reaction performed with **1** and acetylene does not lead to **5**. In addition the formation of the acetylide **6e** derivative of propargyl alcohol cannot be expected from these classical routes. Consequently, the best route to selectively produce *trans*-chloro(acetylide)ruthenium complexes **5** or **6a–g** from **1** appears to be via the deprotonation of the readily available vinylidene with DBU.

Table II. Selected NMR Data for Acetylide Compounds 5 and 6[a]

compd no.	$\delta(^{31}P)$, ppm PPh_2	$\delta(^{13}C)$, ppm RuC≡C ($^2J_{PC}$, Hz)	RuC≡C ($^3J_{PC}$, Hz)
5	−5.38	112.03 (15.3)	97.44
6a	−5.85	122.84 (15.3)	112.55 (1.5)
6b	−5.63	96.69 (15.8)	103.50 (1.2)
6c	−5.58	96.21 (15.6)	109.74
6d	−5.53	91.94 (15.7)	118.39 (1.5)
6e	−5.72	113.43 (15.2)	108.61 (1.3)
6f	−5.47	112.42 (15.4)	106.06 (1.3)
6g	−6.50	141.20 (15.6)	105.74

[a] All spectra in CD_2Cl_2 at 297 K.

Scheme III



3. Synthesis of Unsymmetrical Ruthenium Bis(acetylide) Complexes. The current interest to selectively produce rod-like π conjugated molecules[1] motivates the search for new methods of access and for new systems, especially unsymmetrical molecules. The straightforward access to *trans*-chloro(acetylide)ruthenium derivatives **6** motivated us to attempt the substitution of the remaining chloride of **6** with a different acetylide in order to produce *unsymmetrical* bis(acetylide)metal complexes. When the reaction of **1** with PhC≡CH (**2a**) with a large excess of NEt_3 *and 2 equiv of* $NaPF_6$ was performed in dichloromethane, instead of THF, the formation of the mono(acetylide) **6a** was less selective; a small amount of the bis(acetylide) *trans*-$Ru(C{\equiv}CPh)_2(dppm)_2$ was also formed. We have used these conditions in an attempt to open the access to the (diynyl)(acetylide)ruthenium complex. Complex **6a** and 1 equiv of the pentadiyne **7** were treated in *dichloromethane* with 2 equiv of both NEt_3 *and* $NaPF_6$ at room temperature. This reaction led to the isolation of 28% of the yellow complex **8a**. Similarly **6c** was transformed into 25% of **8c** (Scheme III). Complexes **8** show in the infrared spectrum three C≡C absorption bands [**8a** (KBr) ν 2178 (s), 2077 (m), 2029 (m) cm^{-1}); **6a** (KBr) ν 2075 (m) cm^{-1})]. In the ^{13}C NMR four different quintet resonances are observed for both sets of Ru*C*≡*C* carbon nuclei and are consistent with the coupling with four identical ^{31}P nuclei and the *trans* position of these acetylide linkages.

For the **6** → **8** transformation, both the nature of the solvent (dichloromethane instead of tetrahydrofuran) and the presence of 2 equiv of $NaPF_6$ are *essential*. It is likely that a polar solvent favors the dissociation the Ru–Cl bonds, and the presence of the noncoordinating anion PF_6^- avoids the displacement of the coordinated alkyne (Scheme IV).

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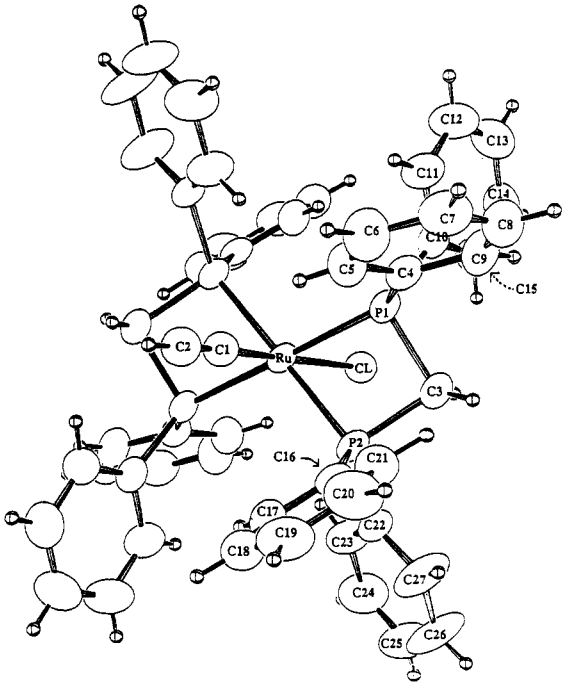
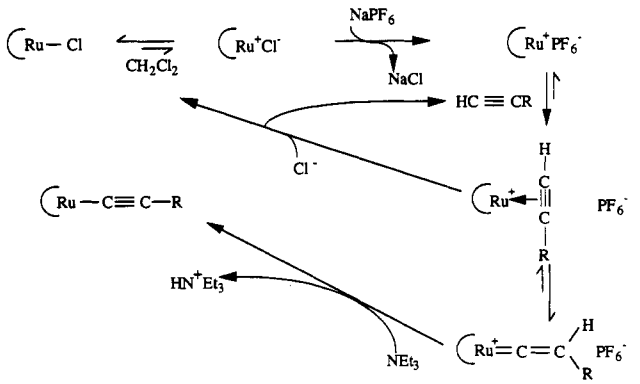


Figure 2. ORTEP diagram for *trans*-(dppm)$_2$(Cl)RuC≡CH (**5**).

Scheme IV



4. X-ray Structure Analysis of *trans*-[(dppm)$_2$(Cl)-Ru=C=CH$_2$]PF$_6$ (3) and *trans*-(dppm)$_2$(Cl)RuC≡CH (5). The isolation of related complexes **3** and **5** containing the simple moieties Ru$^+$=C=CH$_2$ and RuC≡CH, respectively, and differing only by the deprotonation of **3**, motivated the comparative study of their structure. A preliminary account of these structural studies has been reported.[16] An additional interest was the study of new unsubstituted metal vinylidene complexes M=C=CH$_2$ for which the first structures have only recently been prepared by Selegue [(C$_5$H$_5$)(PhMe$_2$P)Ru=C=CH$_2$]$^+$ (**IV**)[11] and Frysuk [N(SiMe$_2$CH$_2$PPh$_2$)$_2$ Ir=C=CH$_2$] (**VI**).[12]

The molecular structures of complexes **3** and **5** are shown in Figures 1 and 2, respectively. Experimental crystallographic data are given in Tables III and VI, and selected bond lengths and angles are contained in Tables IV and V for **3** and Tables VII and VIII for **5**. The structure shows for each molecule an octahedral coordination type for the ruthenium atom, with the apical positions occupied by the chloride and the vinylidene (**3**) or the acetylide (**5**) ligands. The ClRu–C–C linkage is orthogonal to the plane of the four phosphorus atoms and almost linear in both molecules: the Cl–Ru–C and Ru–C–C angles are 178.9(3)° and 178.2(2)° for **3** and 178.3(8)° and 177.0(6)° for **5** (Tables V and VIII).

The Ru–C(3) bond length [1.882(8) Å] in **3** is slightly longer than in related complexes: 1.845(7) Å in[(C$_5$H$_5$)-(PMe$_3$)$_2$Ru(C=CHMe)]$^+$,[17] 1.863(10) Å in [(C$_5$H$_5$)(Ph$_3$P)$_2$-

Table III. Experimental Crystallographic Data for 3

formula	$C_{52}H_{46}ClF_6P_5Ru$, (CH_2Cl_2)
fw	1076.318
cryst	orthorhombic
space group	$Pna2_1$
a, Å	22.602(3)
b, Å	11.850(2)
c, Å	19.235(6)
V, Å^3	5152(2)
Z	4
d_{calc}, Mg m^{-3}	1.39
cryst size, mm	0.15 × 0.23 × 0.32
$2\theta_{max}$, mm	50
diffractometer	CAD-4
λ(Mo Kα radiation), Å	0.710 69
T, K	293
F(000)	2192
abs coeff μ, cm^{-1}	6.15
scan type	$\omega/2\theta$
no. of rflns read	6214
no. of unique rflns	4393 ($I > 3\sigma(I)$)
R; R_w	0.039; 0.037

Table IV. Selected Bond Distances (Å) for 3

Ru–Cl	2.451(2)	Ru–P4	2.388(2)
Ru–P1	2.363(2)	Ru–C3	1.882(8)
Ru–P2	2.378(2)	C3–C4	1.22(1)
Ru–P3	2.374(2)		

Table V. Selected Bond Angles (deg) for 3

Cl–Ru–P1	90.18(8)	P2–Ru–P3	178.77(8)
Cl–Ru–P2	86.00(8)	P2–Ru–P4	70.61(8)
Cl–Ru–P3	93.03(8)	P2–Ru–C3	93.8(3)
Cl–Ru–P4	84.71(8)	P3–Ru–P4	110.07(8)
P1–Ru–P2	107.85(8)	P3–Ru–C3	87.2(3)
P1–Ru–P3	71.98(8)	P4–Ru–C3	94.2(3)
P1–Ru–P4	174.74(8)	Cl–Ru–C3	178.9(3)
P1–Ru–C3	91.0(3)	Ru–C3–C4	178.3(8)

Table VI. Experimental Crystallographic Data for 5

formula	$C_{52}H_{45}ClP_4Ru$
fw	930.36
cryst	monoclinic
space group	$I2/a$
a, Å	22.003(2)
b, Å	9.715(1)
c, Å	22.205(3)
β, deg	112.38(2)
V, Å^3	4389.0(6)
Z	4
d_{calc}, Mg m^{-3}	1.408
cryst size, mm	0.22 × 0.22 × 0.24
$2\theta_{max}$, mm	50
diffractometer	CAD-4
λ(Mo Kα radiation), Å	0.710 69
T, K	293
F(000)	1912
abs coeff μ, cm^{-1}	5.90
scan type	$\omega/2\theta$
no. of rflns read	4281
no. of unique rflns	2267 ($I > 3\sigma(I)$)
R; R_w	0.027; 0.024

Table VII. Selected Bond Distances (Å) for 5

Ru–Cl	2.628(2)	Ru–C1	1.906(9)
Ru–P1	2.354(1)	C1–C2	1.162(9)
Ru–P2	2.318(1)	C2–H2	0.899(0)

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Table VIII. Selected Bond Angles (deg) for 5

Cl–Ru–P1	97.59(5)	P1–Ru–C1	95.8(2)
	82.41(5)		84.2(2)
C1–Ru–P2	94.90(5)	P2–Ru–C1	94.4(2)
	85.10(5)		85.6(2)
P1–Ru–P1	180(0)	Cl–Ru–C1	178.2(2)
P2–Ru–P2	180(0)	Ru–C1–C2	177.0(6)
P1–Ru–P2	71.15(3)	C1–C2–H2	180(0)

Table IX. Comparative Bond Lengths (Å)

M=C=CH$_2$ Complexes.

		M=C	C=CH$_2$
Cl(Ph$_2$PCH$_2$PPh$_2$)$_2$Ru=C=CH$_2$]$^+$PF$_6^-$	**3**	1.882(8)	1.22(1)
(C$_5$H$_5$)(PhMe$_2$P)$_2$Ru=C=CH$_2$]$^+$BF$_4^-$	IV[11]	1.843(10)	1.287(13)
[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]Ir=C=CH$_2$	VI[12]	1.806(4)	1.324(6)

M–C≡CR Complexes

		M–C	C≡C
Cl(Ph$_2$PCH$_2$PPh$_2$)$_2$Ru–C≡CH	**5**	1.906(9)	1.162(9)
(C$_5$H$_5$)(dppe)Ru–C≡CPh	VII[18]	2.009(3)	1.204(5)
(Et$_3$P)$_2$(OC)$_2$Ru–(C≡CH)$_2$	VIII[21]	1.932(2)	1.199(2)

Ru=C=CMePh]$^+$,[18] and 1.843(10) Å in the only recently reported Ru=C=CH$_2$] complex (**IV**)[11] (Table IX).

The C(3)–C(4) bond length in **3** (1.22(1) Å) is surprisingly very short and in the same range as that of a C≡C triple bond [1.20–1.21 Å][19] *e.g.* much shorter than in[(C$_5$H$_5$)(PMe$_3$)$_2$Ru(C=CHMe)]$^+$ (1.313(10) Å),[17] [(C$_5$H$_5$)(Ph$_3$P)$_2$Ru(C=CMePh]$^+$ (1.293(15) Å),[18] (**IV**) (1.287(13))[11] or in [(Ph$_2$PCHMeCH$_2$PPh$_2$)(C$_5$H$_5$)Ru=C=CHMe]$^+$ (1.25(1) Å).[20] This unexpected observation is consistent with a partial sp character for the C(4) terminal carbon of the vinylidene **3**, and may also account for the especially high-field NMR resonance for the =CH$_2$ protons [δ = 2.36 ppm in **3** and 4.30 ppm in (**IV**)[11]] (Table I). However, its significance is reduced by the anomalous thermal motion at C(3) along the bond axis.

The molecular structure of **3** also brings strong evidence for the steric hindrance of the four phenyl groups around the vinylidene ligands and may explain the inertness of the expected electrophilic carbene carbon Ru=C(3) toward addition of alcohol.

The molecular structure of **5** (Figure 2) shows a longer Ru–Cl bond length [2.628(2) Å] with respect to that of **3** [2.451(2) Å]. This suggests a stronger *trans* influence of the C≡CH ligand than of the vinylidene (C=CH$_2$)$^+$ group and/or a π electron withdrawing character of the latter. The most striking features are the significant shortening of the C(1)–C(2) bond length in **5** with respect to that of **3** but also with related M–C≡CH complexes. Especially, the C$_1$–C$_2$ distance of 1.162(2) Å is very short with respect to the C≡C bond length[19] or in Ru(C≡CH)$_2$(CO)$_2$(PEt$_3$)$_2$[21] (Table IX). Along with those of 1.16(4) and 1.14(4) Å observed in [(C$_5$Me$_5$)(Tol-C≡C)Ru(μ_2-SPr^i)]$_2$,[27] complex **5** seems to have one of the shortest observed C≡C bond distances.

Conclusion

It is hoped that this simple method of access via vinylidenes to acetylide and mixed diynyl acetylide complexes, because of the versatile reactivity of the diynyl metal complexes, should open a new route to polyunsaturated organometallics.

Experimental Section

General Considerations. All reactions were performed under an 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 205 FT-IR spectrometer. ^{1}H (300.13 MHz), ^{13}C (75.47 MHz), and ^{31}P (121.50 MHz) NMR spectra were recorded on a Bruker AC 300 P spectrometer at 297 K and referenced to TMS for ^{1}H and ^{13}C and to 85% H$_3$PO$_4$ for ^{31}P. Elemental analyses were performed by the Service Central de Microanalyse of CNRS at Lyon, France. Usually, as observed by NMR, the analytical sample retains dichloromethane.

The complex *cis*-RuCl$_2$(dppm)$_2$ **1** was prepared by literature method.[22] Acetylene and terminal alkynes **2a–h** were commercial and used as received. The pentadiyne derivative **7**[6] was prepared by adaptation of Midland's method[23] from the butadiyne.[24]

Synthesis of the Complex *trans*-[(dppm)$_2$(Cl)Ru=C=CH$_2$]PF$_6$ (3). In a Schlenk tube were successively introduced 470 mg of complex **1** (0.5 mmol), 168 mg of NaPF$_6$ (1 mmol), and 50 mL of dry dichloromethane. The Schlenk tube was connected with acetylene at 1 atm and the solution slowly dissolved a large excess of acetylene (3 mmol) on stirring. The mixture was stirred for 4 h at room temperature. Then, the solution was filtered through a filter-paper-tipped cannula to remove NaCl and NaPF$_6$ in excess. After evaporation of the solvent under vacuum, the orange residue was washed with diethyl ether and dissolved in 20 mL of dichloromethane, and 60 mL of *n*-pentane was slowly added in order to maintain two phases. The orange complex **3** slowly crystallized and 490 mg (92%) was obtained on filtration. Anal. Calcd for C$_{52}$H$_{46}$ClF$_6$P$_5$Ru·CH$_2$Cl$_2$: C, 54.82; H, 4.17; Cl, 9.16; P, 13.34. Found: C, 55.08; H, 4.19; Cl, 9.15; P, 13.46. IR (cm^{-1}; KBr): 1627 (m, $\nu_{C=C}$), 838 (s, ν_{PF}). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, 297 K; δ, ppm): 7.54–7.20 (40 H, Ph), 5.20 (quint, 4H, PCH$_2$P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.6 Hz), 2.36 (quint, 2H, =CH$_2$, $^4J_{PH}$ = 3.0 Hz). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K; δ, ppm): 340.87 (quint, Ru=*C*, $^2J_{PC}$ = 13.2 Hz), 133.95–128.93 (Ph), 91.41 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 2.5 Hz), 46.97 (quint, PCH$_2$P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.3 Hz). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$, 297 K; δ, ppm): 340.86 (quint, Ru=*C*, $^2J_{PC}$ = 13.45 Hz), 91.41 (t quint, Ru=C=*C*, $^1J_{CH}$ = 165.6 Hz, $^3J_{PC}$ = 2.1 Hz), 46.97 (t quint, PCH$_2$P, $^1J_{CH}$ = 136.8 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.4 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$, 297 K; δ, ppm): −15.14 (s, PPh$_2$), −143.87 (sept, PF$_6$, $^1J_{PF}$ = 710.8 Hz).

Synthesis of Vinylidenes *trans*-[(dppm)$_2$(Cl)Ru=C=CHR]PF$_6$ (4a–h). A solution of an excess of terminal alkyne **2** (1.1 mmol) in 50 mL of dry dichloromethane was added to complex **1** (0.5 mmol) and NaPF$_6$ (1.0 mmol). The mixture was stirred for 4 h at room temperature and the solution was filtered through a filter-paper-tipped cannula. Then, the solvent was removed under vacuum and the precipitate was washed with diethyl ether. After dissolution into the smallest volume of dichloromethane (20–25 mL), *n*-pentane (50–70 mL) was slowly added in order to form a biphasic system and crystals of **4** slowly formed. The vinylidenes **4a–h** were characterized by IR, ^{1}H, ^{13}C, and ^{31}P NMR, and elemental analysis. As a typical example, all chemical shifts for dppm groups in ^{1}H and ^{13}C spectra are given for **4a**.

***trans*-[(dppm)$_2$(Cl)Ru=C=CHPh]PF$_6$ (4a).** From 470 mg of **1** (0.5 mmol), 168 mg of NaPF$_6$ (1.0 mmol), and 120 μL of HC≡CPh (1.1 mmol) was isolated 470 mg of red crystals of **4a** (82%). Anal. Calcd for C$_{58}$H$_{50}$ClF$_6$P$_5$Ru: C, 60.45; H, 4.37. Found: C, 60.46; H, 4.36. IR (cm^{-1}; KBr): 1658 (m, $\nu_{C=C}$), 840

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(s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.48–6.73 (43H, Ph), 5.53 (d, 1H, Ph, $^3J_{HH}$ = 7.9 Hz), 5.52 (d, 1H, Ph, $^3J_{HH}$ = 8.5 Hz), 5.30, 5.06 ABX'$_2$X$_2$, 4H, PCH_2P, $^2J_{HAHB}$ = 15.3 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.6 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.8 Hz), 3.07 (quint, 1H, =CH, $^4J_{PH}$ = 3.1 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 336.02 (quint, Ru=*C*, $^2J_{PC}$ = 13.3 Hz), 133.82 (quint, *o*-Ph, $|^2J_{PC} + {}^4J_{PC}|$ = 2.7 Hz), 132.87 (quint, *o*-Ph, $|^2J_{PC} + {}^4J_{PC}|$ = 3.0 Hz), 132.17 (s, *p*-Ph), 132.09, 131.86 (s, *Ph*CH=), 131.79 (s, *p*-Ph), 131.26 (quint, (ipso)Ph, $|^1J_{PC} + {}^3J_{PC}|$ = 12.0 Hz), 130.17 (quint, (ipso)Ph, $|^1J_{PC} + {}^3J_{PC}|$ = 11.8 Hz), 129.56 (quint, *m*-Ph, $|^3J_{PC} + {}^5J_{PC}|$ = 2.1 Hz), 128.93 (quint, *m*-Ph, $|^3J_{PC} + {}^5J_{PC}|$ = 2.4 Hz), 127.70 (s, Ph), 127.63 (s, Ph), 126.61 (s, Ph), 110.75 (m, Ru=C=*C*), 46.35 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.6 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 110.73 (dm, Ru=C=*C*, $^1J_{CH}$ = 153.8 Hz), 46.34 (t quint, PCH_2P, $^1J_{CH}$ = 137.0 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.5 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.42 (s, PPh_2), −143.90 (sept, PF_6, $^1J_{PF}$ = 709.4 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CHMe]PF$_6$ (4b).** From 470 mg of 1 (0.5 mmol) and 168 mg of $NaPF_6$ (1.0 mmol) under HC≡CMe atmosphere was isolated 530 mg of orange crystals of **4b** (97%). Anal. Calcd for $C_{53}H_{48}ClF_6P_5Ru$: C, 58.38; H, 4.44. Found: C, 58.62; H, 4.45. IR (cm^{-1}; KBr): 1659 (m, $\nu_{C=C}$), 838 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.54–7.22 (40 H, Ph), 5.14 (quint, 4H, PCH_2P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.6 Hz), 2.57 (q quint, 1H, =CH, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.8 Hz), 0.49 (d quint, 3H, Me, $^3J_{HH}$ = 7.6 Hz, $^5J_{PH}$ = 0.85 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 321.10 (quint, Ru=*C*, $^2J_{PC}$ = 13.3 Hz), 133.99–128.88 (Ph), 100.49 (broad s, Ru=C=*C*), 46.78 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.2 Hz), 3.24 (broad s, Me). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 100.46 (dm, Ru=C=*C*, $^1J_{CH}$ = 148.8 Hz), 46.78 (t quint, PCH_2P, $^1J_{CH}$ = 136.6 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.5 Hz), 3.24 (qm, Me, $^1J_{CH}$ = 132.0 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.09 (s, PPh_2), −143.83 (sept, PF_6, $^1J_{PF}$ = 712.0 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CH^{n}Bu]PF$_6$ (4c).** From 940 mg of 1 (1.0 mmol), 336 mg of $NaPF_6$ (2.0 mmol), and 253 μL of HC≡C^{n}Bu (2.2 mmol) dissolved in 100 mL of dichloromethane was isolated 820 mg of orange crystals of **4c** (72%). Anal. Calcd for $C_{56}H_{54}ClF_6P_5Ru{\cdot}0.5CH_2Cl_2$: C, 57.76; H, 4.71; Cl, 6.03; P, 13.18. Found: C, 58.54; H, 4.71; Cl, 5.58; P, 13.12. IR (cm^{-1}; KBr): 1627 (m, $\nu_{C=C}$), 838 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.52 to 7.21 (40H, Ph), 5.16, 5.12 (ABX$_4$, 4H, PCH_2P, $^2J_{HAHB}$ = 15.3 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.4 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.7 Hz), 2.48 (t quint, 1H, =CH, $^3J_{HH}$ = 7.9 Hz, $^4J_{PH}$ = 2.8 Hz), 0.94 to 0.26 (unresolved system, 9H, ^{n}Bu). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 323.18 (quint, Ru=*C*, $^2J_{PC}$ = 13.5 Hz), 133.92 to 128.97 (Ph), 106.12 (quint, Ru=C=*C*, $^3J_{PC}$ = 2.0 Hz), 46.71 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.3 Hz), 33.24, 22.22, 19.64 (s, $(CH_2)_3$), 13.75 (s, Me). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 323.24 (m, Ru=*C*), 106.10 (dm, Ru=C=*C*, $^1J_{CH}$ = 155.9 Hz), 46.73 (t quint, PCH_2P, $^1J_{CH}$ = 136.7 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.2 Hz), 33.24 (tm, $(CH_2)_3$, $^1J_{CH}$ = 128.7 Hz), 22.25 (tm, $(CH_2)_3$, $^1J_{CH}$ = 124.4 Hz), 19.64 (tm, $(CH_2)_3$, $^1J_{CH}$ = 132.7 Hz), 13.75 (qm, Me, $^1J_{CH}$ = 126.6 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.30 (s, PPh_2), −143.93 (sept, PF_6, $^1J_{PF}$ = 709.3 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CH^{t}Bu]PF$_6$ (4d).** From 470 mg of 1 (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 135 μL of HC≡C^{t}Bu (1.1 mmol) was isolated 480 mg of orange crystals of **4d** (84%). Anal. Calcd for $C_{56}H_{54}ClF_6P_5Ru$: C, 59.40; H, 4.81. Found: C, 59.17; H, 4.69. IR (cm^{-1}; KBr): 1640 (m, $\nu_{C=C}$), 838 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.48–7.20 (40H, Ph), 5.27, 4.95 (ABX$_4$, 4H, PCH_2P, $^2J_{HAHB}$ = 15.0 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.3 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.7 Hz), 1.80 (quint, 1H, =CH, $^4J_{PH}$ = 2.2 Hz), 0.11 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 324.67 (quint, Ru=*C*, $^2J_{PC}$ = 13.3 Hz), 133.83 to 128.82 (Ph), 117.57 (broad s, Ru=C=*C*), 46.57 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.5 Hz), 32.85 (s, *C*Me$_3$), 31.43 (s, C*Me*$_3$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 324.68 (m, Ru=*C*), 117.60 (dm, Ru=C=*C*, $^1J_{CH}$ = 142.7 Hz), 46.59 (t quint, PCH_2P, $^1J_{CH}$ = 136.8 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.0 Hz), 32.90 (m, *C*Me$_3$), 31.41 (qm, C*Me*$_3$, $^1J_{CH}$ = 126.3 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.02 (s, PPh_2), −143.93 (sept, PF_6, $^1J_{PF}$ = 710.6 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CHCH$_2$OH]PF$_6$ (4e).** From 470 mg of 1 (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 64 μL of HC≡CCH$_2$OH (1.1 mmol) was isolated 480 mg of light brown crystals of **4e** (87%). Anal. Calcd for $C_{53}H_{48}ClF_6OP_5Ru$: C, 57.54; H, 4.37; Cl, 3.20. Found: C, 57.70; H, 4.40; Cl, 3.32. IR (cm^{-1}; KBr): 1655 (m, $\nu_{C=C}$), 839 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.55–7.24 (40H, Ph), 5.22, 5.17 (ABX$_4$, 4H, PCH_2P, $^2J_{HAHB}$ = 15.9 Hz, $|^2J_{PH} + {}^4J_{PH}|$ = 4.9 Hz), 3.02 (m, 1H, =CH), 2.81 (pseudo t, 2H, CH_2), 0.25 (t, 1H, OH, $^3J_{HH}$ = 5.6 Hz). $^1H\{^{31}P\}$ NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 5.22, 5.17 (AB, 4H, PCH_2P, $^2J_{HAHB}$ = 15.7 Hz), 3.01 (t, 1H, =CH, $^3J_{HH}$ = 8.2 Hz). $^1H\{^{31}P\}$ NMR with irradiation at 0.25 ppm (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 2.81 (d, 2H, CH_2, $^3J_{HH}$ = 8.3 Hz) $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 351.41 (quint, Ru=*C*, $^2J_{PC}$ = 13.4 Hz), 134.80–128.96 (Ph), 107.33 (quint large, Ru=C=*C*, $^3J_{PC}$ = 2.2 Hz), 52.16 (s, CH_2), 46.42 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.3 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 351.42 (m, Ru=*C*), 107.33 (d broad s, Ru=C=*C*, $^1J_{CH}$ 160.7 Hz), 52.16 (td, CH_2, $^1J_{CH}$ = 149.2 Hz, $^3J_{CH}$ = 7.4 Hz), 46.41 (t quint, PCH_2P, $^1J_{CH}$ = 137.0 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.4 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.24 (s, PPh_2), −143.41 (sept, PF_6, $^1J_{PF}$ = 711.1 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CHCH$_2$OMe]PF$_6$ (4f) from 1.** From 470 mg of 1 (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 93 μL of HC≡CCH$_2$OMe (1.1 mmol) was isolated 460 mg of light orange crystals of **4f** (82%). Anal. Calcd for $C_{54}H_{50}ClF_6OP_5Ru{\cdot}0.25CH_2Cl_2$: C, 57.08; H, 4.46; Cl, 4.66; P, 13.56. Found: C, 57.22; H, 4.62; Cl, 4.62; P, 13.32. IR (cm^{-1}; KBr): 1655 (m, $\nu_{C=C}$), 836 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.64 to 7.10 (40H, Ph), 5.19 (quint, 4H, PCH_2P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.6 Hz), 2.89 (m, 1H, =CH), 2.72 (d, 2H, CH_2, $^3J_{HH}$ = 8.05 Hz), 2.60 (s, 3H, OMe). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 330.06 (quint, Ru=*C*, $^2J_{PC}$ = 13.5 Hz), 133.96 to 128.91 (Ph), 104.38 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 2.2 Hz), 60.90 (broad quint CH_2, $^4J_{PC}$ = 1.7 Hz), 57.31 (s, OMe), 46.42 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.4 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 330.06 (m, Ru=*C*), 104.37 (dm, Ru=C=*C*, $^1J_{CH}$ = 161.3 Hz), 60.91 (tm, CH_2, $^1J_{CH}$ = 149.6 Hz), 57.31 (qt, OMe, $^1J_{CH}$ = 141.1 Hz, $^3J_{CH}$ = 4.0 Hz), 46.42 (t quint, PCH_2P, $^1J_{CH}$ = 137.1 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.5 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −15.27 (s, PPh_2), −143.90 (sept, PF_6, $^1J_{PF}$ = 710.8 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CHCH$_2$OMe]PF$_6$ (4f) from 4e.** An amount of 276 mg (0.25 mmol) of **4e** dissolved in 300 mL of methanol were stirred during 67 h at room temperature. The solvent was removed and the residue washed with ether and dried. The ^1H and ^{31}P NMR spectra showed the complete transformation of **4e**. The recrystallization in CH_2Cl_2/hexane afforded 170 mg (60%) of orange crystals identified by IR and ^{31}P and ^1H NMR to be an authentical sample of **4f**.

***trans*-[(dppm)$_2$(Cl)Ru=C=CHCO$_2$Me]PF$_6$ (4g).** From 940 mg of 1 (1.0 mmol), 336 mg of $NaPF_6$ (2.0 mmol), and 196 μL of HC≡CCO$_2$Me (2.2 mmol) was isolated 873 mg of orange crystals of **4g** (77%). Anal. Calcd for $C_{54}H_{48}ClF_6O_2P_5Ru$: C, 57.18; H, 4.27. Found: C, 56.98; H, 4.24. IR (cm^{-1}; KBr): 1700 (m, $\nu_{C=O}$), 1608 (m, $\nu_{C=C}$), 839 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ ppm): 8.20–6.70 (40H, Ph), 5.08, 4.97 (ABX$_4$, 4H, PCH_2P, $^2J_{HAHB}$ = 15.2 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.8 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.3 Hz), 2.98 (quint, 1H, =CH, $^4J_{PH}$ = 2.6 Hz), 2.89 (s, 3H, OMe). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ ppm): 346.34 (quint, Ru=*C*, $^2J_{PC}$ = 13.4 Hz), 162.88 (s, C=O), 135.50–127.54 (Ph), 104.35 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 1.8 Hz), 51.75 (s, OMe), 45.81 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.1 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ ppm): 346.21 (m, Ru=*C*), 104.34 (dm, Ru=C=*C*, $^1J_{CH}$ = 163.8 Hz), 51.72 (q, OMe, $^1J_{CH}$ = 147.0 Hz), 45.80 (t quint, PCH_2P, $^1J_{CH}$ = 137.6 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 13.0 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ ppm): −13.88 (s, PPh_2), −143.80 (sept, PF_6, $^1J_{PF}$ = 709.0 Hz).

***trans*-[(dppm)$_2$(Cl)Ru=C=CHCH$_2$Cl]PF$_6$ (4h).** From 470 mg of 1 (0.5 mmol), 168 mg of $NaPF_6$ (1.0 mmol), and 80 μL of HC≡CCH$_2$Cl (1.1 mmol) was isolated 430 mg of orange crystals

of **4h** (76%). Anal. Calcd for $C_{53}H_{47}Cl_2F_6P_5Ru$: C, 56.60; H, 4.21; Cl, 6.30. Found: C, 56.47; H, 4.22; Cl, 6.92. IR (cm^{-1}; KBr): 1644 (w, $\nu_{C=C}$), 838 (s, ν_{PF}). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.57 and 7.30 (40H, Ph), 5.19 (quint, 4H, PCH_2P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.6 Hz), 2.96 (t quint, 1H, =CH, $^3J_{HH}$ = 9.2 Hz, $^4J_{PH}$ = 3.0 Hz), 2.75 (d, 2H, CH_2, $^3J_{HH}$ = 9.3 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 327.05 (quint, Ru=*C*, $^2J_{PC}$ = 13.5 Hz), 133.99–129.01 (Ph), 105.97 (broad quint, Ru=C=*C*, $^3J_{PC}$ = 2.4 Hz), 46.31 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 12.5 Hz), 34.98 (broad s, CH_2). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 327.03 (m, Ru=*C*), 105.97 (dm, Ru=C=*C*, $^1J_{CH}$ = 163.5 Hz), 46.31 (t quint, PCH_2P, $^1J_{CH}$ = 137.1 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 12.4 Hz), 34.99 (td, CH_2, $^1J_{CH}$ = 158.3 Hz, $^2J_{CH}$ = 8.2 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −16.52 (s, PPh_2), −143.90 (sept, PF_6, $^1J_{PF}$ = 711.5 Hz).

Synthesis of Acetylides *trans*-[(dppm)$_2$(Cl)RuC≡CR]PF$_6$ (5, 6a–g). To a solution of a vinylidene **3** or **4** (0.5 mmol) in 40 mL of dry dichloromethane was added 1 equiv of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU). The mixture was stirred at room temperature for 1 h. After filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum. The crude product was dissolved in a minimum amount of tetrahydrofuran and filtered with diethyl ether through alumina using a chromatography column. Recrystallization from a THF/hexane mixture afforded crystals of **5** or **6**. The acetylides **5** and **6a–g** were characterized by IR, ^1H, ^{13}C, and ^{31}P NMR, and elemental analysis. As a typical example, all chemical shifts for dppm groups in ^1H and ^{13}C spectra are given for **6a**.

***trans*-(dppm)$_2$(Cl)RuC≡CH (5).** From 538 mg of **3** (0.5 mmol) was isolated 218 mg of yellow crystals of **5** (47%). Anal. Calcd for $C_{52}H_{45}ClP_4Ru$: C, 67.13; H, 4.88; Cl, 3.81. Found: C, 67.45; H, 5.04; Cl, 4.18. IR (cm^{-1}; KBr): 3292 (m, $\nu_{\equiv CH}$), 1935 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.51 to 7.12 (40H, Ph), 4.97, 4.87 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.2 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.3 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.5 Hz), 0.90 (s, 1H, ≡CH). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 135.74 to 127.69 (Ph), 112.03 (quint, RuC≡C, $^2J_{PC}$ = 15.3 Hz), 97.44 (broad s, RuC≡*C*), 49.79 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.5 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 112.03 (m, RuC≡C), 97.42 (d broad s, RuC≡*C*, $^1J_{CH}$ = 224.6 Hz), 49.79 (t quint, PCH_2P, $^1J_{CH}$ = 135.2 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.38 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CPh (6a) from the Vinylidene 4a.** From 576 mg of **4a** (0.5 mmol) was isolated 320 mg of yellow crystals of **6a** (63%). Anal. Calcd for $C_{58}H_{49}ClP_4Ru$: C, 69.22; H, 4.91; Cl, 3.52. Found: C, 68.61; H, 5.34; Cl, 3.35. IR (cm^{-1}; KBr): 2075 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.54 to 6.07 (45H, Ph), 4.95, 4.89 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.4 Hz, $|^2J_{PH} + {}^4J_{PH}|$ = 4.3 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 137.79 (quint, Ph, $|^1J_{PC} + {}^3J_{PC}|$ = 10.5 Hz), 135.26 (quint, Ph, $|^1J_{PC} + {}^3J_{PC}|$ = 9.6 Hz), 133.99 (quint, Ph, $|^2J_{PC} + {}^4J_{PC}|$ = 3.05 Hz), 133.76 (quint, Ph, $|^2J_{PC} + {}^4J_{PC}|$ = 2.9 Hz), 130.90 (s, Ph), 130.51 (s, Ph), 129.81 (s, Ph), 129.53 (s, Ph), 128.02 (quint, Ph, $|^3J_{PC} + {}^5J_{PC}|$ = 2.4 Hz), 127.98 (quint, Ph, $|^3J_{PC} + {}^5J_{PC}|$ = 2.4 Hz), 127.35 (s, Ph), 122.85 (s, Ph), RuC≡C masked by the signal at 122.85 ppm, 112.55 (broad quint, RuC≡*C*, $^3J_{PC}$ = 1.5 Hz), 50.33 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 122.86 (dt, Ph, $^1J_{CH}$ = 159.3 Hz, $^3J_{CH}$ = 7.9 Hz), 122.84 (quint, RuC≡C, $^2J_{PC}$ = 15.3 Hz), 112.55 (m, RuC≡*C*), 50.34 (t quint, PCH_2P, $^1J_{CH}$ = 135.2 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.85 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CPh (6a) from the Complex 1.** A solution of 220 μL of HC≡CPh (2 mmol) and 558 μL of NEt_3 (4 mmol) in 25 mL of dry tetrahydrofuran was added to 0.94 g of complex **1** (1 mmol) and 3.36 g of $NaPF_6$ (2 mmol). The mixture was stirred at room temperature for 3 h. After filtration through a filter-paper-tipped cannula, the solvent was removed under vacuum. The crude product was dissolved in a minimum amount of THF and filtered with diethyl ether through alumina using a chromatography column. From recrystallization in CH_2Cl_2/hexane was isolated 1.15 g of yellow crystals of **6a** (57%). Anal. Calcd for $C_{58}H_{49}ClP_4Ru{\cdot}0.25CH_2Cl_2$: C, 68.07; H, 4.85. Found: C, 67.91; H, 4.86. IR (cm^{-1}; KBr): 2075 (m, $\nu_{C=C}$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.85 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CMe (6b).** From 545 mg of **4b** (0.5 mmol) was isolated 300 mg of yellow crystals of **6b** (64%). Anal. Calcd for $C_{53}H_{47}ClP_4Ru$: C, 67.41; H, 5.02; Cl, 3.75. Found: C, 67.61; H, 5.18; Cl, 3.69. IR (cm^{-1}; KBr): 2108 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.49 to 6.99 (40H, Ph), 4.88, 4.69 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.2 Hz, $|^2J_{PH} + {}^4J_{PH}|$ = 4.3 Hz), 1.05 (quint, 3H, Me, $^5J_{PH}$ = 1.8 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 136.10 to 127.54 (Ph), 103.50 (quint, RuC≡*C*, $^3J_{PC}$ = 1.2 Hz), 96.69 (quint, RuC≡C, $^2J_{PC}$ = 15.8 Hz), 50.41 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.2 Hz), 6.82 (s, Me). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 103.50 (qm, RuC≡*C*, $^3J_{CH}$ = 9.2 Hz), 96.70 (m, RuC≡C), 50.40 (t quint, PCH_2P, $^1J_{CH}$ = 135.2 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.3 Hz), 6.83 (q, Me, $^1J_{CH}$ = 127.6 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.63 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡C^{n}Bu (6c).** From 566 mg of **4c** (0.5 mmol) was isolated 320 mg of yellow crystals of **6c** (65%). Anal. Calcd for $C_{56}H_{53}ClP_4Ru$: C, 68.19; H, 5.42. Found: C, 68.06; H, 5.50. IR (cm^{-1}; KBr): 2103 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.46–6.99 (40H, Ph), 4.86, 4.73 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.2 Hz, $|^2J_{PH} + {}^4J_{PH}|$ = 4.3 Hz), 1.42 to 0.51 (^{n}Bu). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 136.26 to 127.60 (Ph), 109.74 (s, RuC≡*C*), 96.21 (quint, RuC≡C, $^2J_{PC}$ = 15.6 Hz), 50.38 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.2 Hz), 32.80, 22.72, 22.57 (s, $(CH_2)_3$), 14.22 (s, Me). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 109.73 (m, RuC≡*C*), 96.21 (m, RuC≡C), 50.38 (t quint, PCH_2P, $^1J_{CH}$ = 135.0 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.3 Hz), 32.78 (tm, CH_2, $^1J_{CH}$ = 126.3 Hz), 22.72, 22.61 (tm unresolved, $(CH_2)_2$), 14.21 (q, Me, $^1J_{CH}$ = 124.1 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.58 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡C^{t}Bu (6d).** From 566 mg of **4d** (0.5 mmol) was isolated 320 mg of yellow crystals of **6d** (65%). Anal. Calcd for $C_{56}H_{53}ClP_4Ru$: C, 68.19; H, 5.42. Found: C, 68.18; H, 5.61. IR (cm^{-1}; KBr): 2087 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.75–7.12 (40H, Ph), 4.99, 4.80 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 13.9 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.3 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.5 Hz), 0.31 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 136.99 to 127.90 (Ph), 118.39 (quint, RuC≡*C*, $^3J_{PC}$ = 1.5 Hz), 91.94 (quint, RuC≡C, $^2J_{PC}$ = 15.7 Hz), 50.37 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.7 Hz), 31.81 (s, C*Me*$_3$), 29.65 (s, C*Me*$_3$). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 118.35 (m, RuC≡*C*), 91.93 (quint, RuC≡C, $^2J_{PC}$ = 15.9 Hz), 50.38 (quint, PCH_2P, $^1J_{CH}$ = 135.5 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz), 31.81 (qm, C*Me*$_3$, $^1J_{CH}$ = 125.9 Hz), 29.65 (m, C*Me*$_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.53 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CCH$_2$OH (6e).** From 553 mg of **4e** (0.5 mmol) was isolated 220 mg of yellow crystals of **6e** (45%). Anal. Calcd for $C_{53}H_{47}ClOP_4Ru$: C, 66.29; H, 4.93; Cl, 3.69; P, 12.90. Found: C, 66.13; H, 4.91; Cl, 3.62; P, 12.90. IR (cm^{-1}; KBr): 2094 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.56 to 7.12 (40H, Ph), 4.99, 4.83 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.4 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.3 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.4 Hz), 3.42 (m, CH_2), −0.44 (t, OH, $^3J_{HH}$ = 5.2 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 135.72 to 127.60 (Ph), 113.43 (quint, RuC≡C, $^2J_{PC}$ = 15.2 Hz), 108.61 (broad quint, RuC≡*C*, $^3J_{PC}$ = 1.3 Hz), 54.15 (s, CH_2), 50.19 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 113.45 (m, RuC≡C), 108.61 (tm, RuC≡*C*), 54.16 (td, CH_2, $^1J_{CH}$ = 145.5 Hz, $^2J_{CH}$ = 2.5 Hz), 50.20 (t quint, PCH_2P, $^1J_{CH}$ = 134.7 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.72 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CCH$_2$OMe (6f).** From 560 mg of **4f** (0.5 mmol) was isolated 280 mg of yellow crystals of **6f** (58%). Anal. Calcd for $C_{54}H_{49}ClOP_4Ru$: C, 66.56; H, 5.07; Cl, 3.64. Found: C, 66.56; H, 5.09; Cl, 3.36. IR (cm^{-1}; KBr): 2092 (m, $\nu_{C=C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.54 to 7.10 (40H, Ph), 4.97, 4.86 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.3 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.2 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.3 Hz), 3.31 (broad quint, 2H, CH_2, $^5J_{PH}$ = 1.3 Hz), 2.51 (s, 3H, OMe). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 135.88 to 127.83 (Ph), 112.42 (quint, RuC≡C, $^2J_{PC}$ = 15.4 Hz), 106.06 (broad quint, RuC≡*C*,

$^3J_{PC}$ = 1.3 Hz), 62.95 (s, CH_2), 55.90 (s, OMe), 50.22 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 112.43 (t, quint, RuC≡C, $^3J_{CH}$ = 4.3 Hz, $^2J_{PC}$ = 15.6 Hz), 106.04 (tm, RuC≡C, $^2J_{CH}$ = 6.4 Hz), 62.94 (tq, CH_2, $^1J_{CH}$ = 144.0 Hz, $^3J_{CH}$ = 5.4 Hz), 55.90 (qt, OMe, $^1J_{CH}$ = 144.0 Hz, $^3J_{CH}$ = 5.8 Hz), 50.23 (t quint, PCH_2P, $^1J_{CH}$ = 135.2 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.4 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −5.47 (s, PPh_2).

***trans*-(dppm)$_2$(Cl)RuC≡CCO$_2$Me (6g).** From 566 mg of **4g** (0.5 mmol) was isolated 281 mg of yellow crystals of **6g** (57%). Anal. Calcd for $C_{54}H_{47}ClO_2P_4Ru$: C, 65.62; H, 4.79. Found: C, 65.77; H, 4.81. IR (cm^{-1}; KBr): 2044 (m, $\nu_{C\equiv C}$), 1663 (m, $\nu_{C=O}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.52–7.01 (40H, Ph), 4.83, 4.72 (ABX_4, 4H, PCH_2P, $^2J_{HAHB}$ = 14.1 Hz, $|^2J_{PHA} + {}^4J_{PHA}|$ = 4.3 Hz, $|^2J_{PHB} + {}^4J_{PHB}|$ = 4.6 Hz), 3.08 (s, 3H, OMe). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 152.90 (s, C=O), 134.74–128.02 (Ph), 141.20 (quint, RuC≡C, $^2J_{PC}$ = 15.6 Hz), 105.74 (s, RuC≡C), 50.98 (s, OMe), 49.26 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.6 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 141.30 (m, RuC≡C), 105.70 (m, RuC≡C), 51.07 (q, OMe, $^1J_{CH}$ = 143.0 Hz), 49.29 (t quint, PCH_2P, $^1J_{CH}$ = 137.0 Hz, $|^1J_{PC} + {}^3J_{PC}|$ = 10.3 Hz). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −6.50 (s, PPh_2).

Synthesis of *trans*-Bis(acetylide) Ruthenium Complexes (8a–c). A solution of pentadiyne derivative **7** (1 mmol) and NEt_3 (2 mmol) in 60 mL of dry dichloromethane was added to the acetylide **6a** or **6c** (1 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 *n*-pentane. The crude product was dissolved in a minimum amount of tetrahydrofuran and chromatographed with a mixture of hexane/diethyl ether through alumina using a long column. Recrystallization from CH_2Cl_2/hexane afforded crystals of **8a** or **8c**.

***trans*-(dppm)$_2$Ru(C≡CPh)(C≡CC≡CPh$_2$(OSiMe$_3$)) (8a).** From 1.00 g of **6a** (1 mmol), 353 mg of HC≡CC≡CPh$_2$(OSiMe$_3$) (1 mmol), 168 mg of $NaPF_6$ (1 mmol), and 279 μL of NEt_3 (2 mmol) was isolated 356 mg of yellow crystals of **8a** (28%). Anal. Calcd for $C_{78}H_{68}OP_4SiRu$: C, 73.51; H, 5.38. Found: C, 73.70; H, 5.28. IR (cm^{-1}; KBr): 2178 (s, $\nu_{C\equiv C}$), 2077 (m, $\nu_{C\equiv C}$), 2028 (m, $\nu_{C\equiv C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.48 to 6.22 (55H, Ph), 4.80 (quint, 4H, PCH_2P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.0 Hz), 0.03 (s, 9H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 149.13 to 123.17 (Ph), 132.91 (quint, RuC≡CC≡C, $^2J_{PC}$ = 14.4 Hz), 128.85 (quint, RuC≡C, $^2J_{PC}$ = 15.3 Hz), 115.55 (quint, RuC≡C, $^3J_{PC}$ = 1.5 Hz), 96.26 (s, RuC≡CC≡C), 80.52, 64.55 (s, RuC≡CC≡C), 76.61 (s, RuC≡CC≡CC), 52.07 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 11.0 Hz), 2.04 (s, $OSiMe_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −3.36 (s, PPh_2).

***trans*-(dppm)$_2$Ru(C≡C^{n}Bu)(C≡CC≡CPh$_2$(OSiMe$_3$)) (8c).** From 0.93 g of **6c** (1 mmol), 353 mg of HC≡CC≡CPh$_2$(OSiMe$_3$) (1 mmol), 168 mg of $NaPF_6$ (1 mmol), and 279 μL of NEt_3 (2 mmol) was isolated 314 mg of yellow crystals of **8c** (25%). Anal. Calcd for $C_{76}H_{72}OP_4SiRu$: C, 72.77; H, 5.79. Found: C, 72.49; H, 5.68. IR (cm^{-1}; KBr): 2175 (s, $\nu_{C\equiv C}$), 2098 (m, $\nu_{C\equiv C}$), 2020 (m, $\nu_{C\equiv C}$). ^1H NMR (300.13 MHz, CD_2Cl_2, 297 K; δ, ppm): 7.73 to 7.04 (50H, Ph), 4.76 (quint, 4H, PCH_2P, $|^2J_{PH} + {}^4J_{PH}|$ = 4.1 Hz), 1.55 to 0.61 (9H, ^{n}Bu), 0.00 (s, 9H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 297 K; δ, ppm): 149.26–126.51 (Ph), RuC≡CC≡C masked by signals of phenyls, 113.42 (quint, RuC≡C, $^3J_{PC}$ = 1.2 Hz), 104.17 (quint, RuC≡C, $^2J_{PC}$ = 15.6 Hz), 95.25 (quint, RuC≡CC≡C, $^3J_{PC}$ = 1.2 Hz), 80.81, 63.71 (s, RuC≡CC≡C), 76.66 (s, RuC≡CC≡CC), 52.07 (quint, PCH_2P, $|^1J_{PC} + {}^3J_{PC}|$ = 10.8 Hz), 32.88, 22.63, 14.31 (s, ^{n}Bu), 2.06 (s, $OSiMe_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 297 K; δ, ppm): −3.37 (s, PPh_2).

Crystal Structure Analysis of 3. The sample (prism 0.15 × 0.23 × 0.32 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* 0.15, *k* 0.24, *l* 0.28; intensity controls without appreciable decay (0.1%)) gave 6214 reflections from which 4393 had $I > 3\sigma(I)$.

After Lorenz and polarization corrections, the structure was solved with a Patterson map which revealed the Ru atom. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and Fourier differences. During these calculations, a solvent molecule of methylene chloride was found and after isotropic refinement (R = 0.12), solvent molecules of pentane and methylene chloride were found, and the anion PF6 appeared as disordered. After isotopic refinement (R = 0.09), the whole structure was refined by the full-matrix least-squares 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; 592 variables and 3129 observations; $\omega = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting R = 0.039, R_w = 0.037 and S_w = 2.27 (residual $\Delta\rho \leq 0.82$ e Å^{-3}). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).[25] All the calculations were performed on a Digital Micro VAX 3100 computer with the Mo1EN package (Enraf-Nonius, 1990).[26]

Crystal Structure Analysis of 5. The sample (prism 0.22 × 0.22 × 0.24 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* 0.25, *k* 0.12, *l* −26.26; intensity controls without appreciable decay (0.4%)) gave 4281 reflections from which 2267 independent (R_{int} = 0.011) had $I > 3\sigma(I)$.

After Lorenz and polarization corrections, the structure was solved with direct methods which revealed all the non-hydrogen atoms of the structure except the two acetylenic carbon atoms. These were found after a scale factor refinement and one Fourier difference. After isotropic refinement (R = 0.067) and then anisotropic refinement (R = 0.09), all the hydrogen atoms (including the acetylenic hydrogen atom) may be found in a Fourier difference between 0.27 and 0.14 e Å^{-3}. The whole structure was refined by the full-matrix least-squares techniques (use of F magnitude; x, y, z, β_{ij} for Ru, P, and non-acetylenic C atoms; x, y, z, β_{iso} for Cl and the two acetylenic atoms; x, y, z, fixed for H atoms; 325 variables and 2267 observations; $\omega = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting R = 0.027, R_w = 0.024 and S_w = 1.135 (residual $\Delta\rho \leq 0.18$ e Å^{-3}). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).[25] All the calculations were performed on a Digital Micro VAX 3100 computer with the Mo1EN package (Enraf-Nonius, 1990).[26]

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Supplementary Material Available: For **3** and **5**, lists of bond lengths and angles, least-squares planes, and atomic fractional coordinates and thermal parameters (20 pages). Ordering information is given on any current masthead page.

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