Functional Ruthenium(II) Allenylidene and Diynyl (Arene) Derivatives Formed by Activation of a Diyne *via* a Ru=C=C=C=C=CR_2 Intermediate

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The activation of the diyne HC≡CC≡CC(OSiMe$_3$)Ph$_2$ (**II**) by a variety of RuCl$_2$(PR$_3$)(C$_6$Me$_6$) complexes **1** [PR$_3$ = PMe$_3$(**a**), PMe$_2$Ph (**b**), PMePh$_2$(**c**)], in the presence of the salt NaPF$_6$, selectively leads either to [L$_n$Ru=C(OMe)CH=C=C=CR$_2$]PF$_6$ (**3**), [L$_n$Ru=C=C=C(OR)-CH=CR$_2$]PF$_6$ (**4**–**6**), [L$_n$Ru=C=C=C(NR′$_2$)CH=CR$_2$]PF$_6$ (**7**), or [L$_n$Ru-C≡CC≡CC(OSiMe$_3$)-Ph$_2$]PF$_6$ (**8**), (L$_n$Ru = RuCl(PR$_3$)(C$_6$Me$_6$)). In methanol **1a** leads to the buta-1,2,3-trienyl-carbene complex **3** and the 3-alkenylallenylidene derivative **4a**. In ethanol and 2-propanol the complexes containing the 3-alkenylallenylidene moiety **5a**–**c** and **6a**–**c** are generated from **1a**–**c**. In the presence of HNPh$_2$ the derivatives [L$_n$Ru=C=C=C(NPh$_2$)CH=CPh$_2$]PF$_6$ (**7a**–**c**) are obtained, whereas in the presence of HN^{i}Pr$_2$, NEt$_3$ or, Bu^{t}NH$_2$ and NaPF$_6$ the diynyl derivatives **8a**–**c** are selectively produced. The protonation with HBF$_4$ of the diynyl complexes **8** in the presence of alcohol or diphenylamine is shown to displace the OSiMe$_3$ group and generate (3-alkenylallenylidene)ruthenium derivatives **6**–**7***. The activation of the diyne **II** by complexes **1** and NaPF$_6$ can be rationalized in terms of the formation of the electrophilic penta-1,2,3,4-tetraenylidene intermediate [(C$_6$Me$_6$)(PR$_3$)Cl Ru=C=C=C=C=CPh$_2$]$^+$ (**2**), which is reactive toward weak nucleophiles.

Introduction

Organometallic compounds containing a π-conjugated unsaturated chain have recently attracted interest for their unusual intrinsic properties, such as cumulenyl–metal derivatives,[1] but also for liquid crystal[2] and nonlinear optic[3] properties, such as [MC≡CC≡C]$_n$ polymers,[4] or bis(alkynyl)platinum(II) derivatives,[5] respectively. They also have potential for the synthesis of highly unsaturated molecules.[6,7] Metal–vinylidene M=C=CR$_2$ and their metal–allenylidene M=C=C=CR$_2$ homologs constitute the simplest examples of unsaturated organometallics with a M=C bond. By contrast to the development of the chemistry of vinylidene complexes during the last decade,[8] the allenylidene complexes have not been the source of many chemical discoveries, even if the first examples are known since 1976.[9] However, metal allenylidenes have potential for the access to unusual molecules by ligand transfer to unsaturated molecules by analogy to the chemistry of M=C bond containing complexes,[10] by polymerization of the unsaturated chain by analogy to that of alkenylcarbenes,[11] and by homogeneous catalysis. The first example of the involvement of a M=C=C=CR$_2$ species in catalysis has just been reported for coupling of allylic alcohols with propargylic alcohol derivatives in the presence of the RuCl(PPh$_3$)$_2$(C$_5$H$_5$) catalyst.[12]

Actually the use of metal allenylidenes is limited by the lack of general methods of preparation. They have been obtained *via* (i) transformation of alkenyl-[9a] and alkynylcarbene[13] complexes, and (ii) coordination of a (C)$_3$ skeleton dianion, either [C≡CCR$_2$O]$^{2-}$ [9b,14] or Li$_2$C$_3$-Ph$_2$.[15] The most straightforward method of access to

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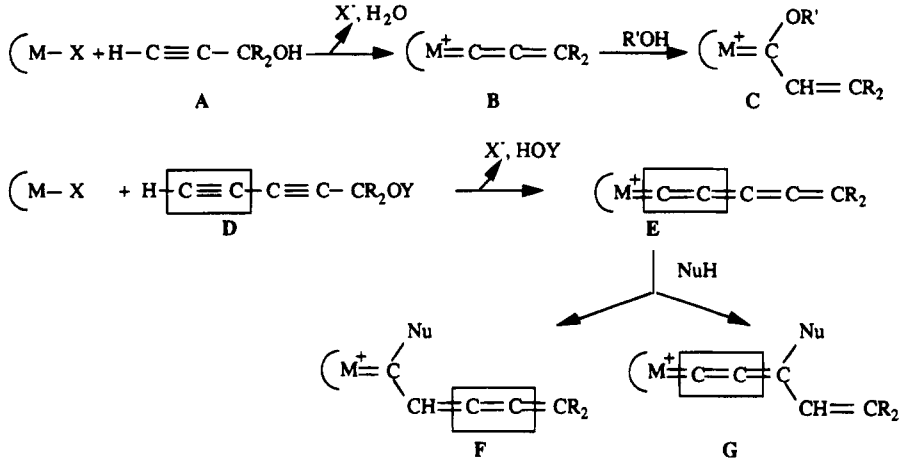
Scheme 1



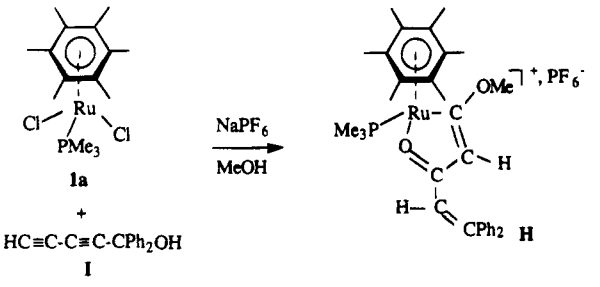
the allenylidene–metal intermediate appears to be the direct dehydration of propargyl alcohol derivatives **A** using ruthenium(II) complexes $RuCl(PMe_3)_2(C_5H_5)$,[16] $RuCl_2(PR_3)(arene)$,[17] $RuCl_2(Ph_2PCH_2PPh_2)_2$,[18a] $RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$,[18b] $N(CH_2CH_2PPh_2)_3RuCl_2$,[18c] $RuCl(PR_3)_2(\eta^5-C_9H_7)$,[19] and $Ru_2(\mu_2\text{-}S^iPr)_2(C_5Me_5)_2$.[20] They are expected to arise from the dehydration of 3-hydroxyvinylidene–metal intermediates[16,21] as it has been shown with rhodium[22] and group 6[14h] derivatives.

The metallacumulenes **B** are thus obtained from propargyl alcohols and easily available ruthenium(II) precursors, and their stability depends on the electron richness of the ruthenium complexes (Scheme 1). They can be isolated with electron-rich ruthenium(II) complexes[16a,18] whereas with the electrophilic precursors $RuCl_2(PR_3)(arene)$ the intermediates **B** are very reactive toward weak nucleophiles and unsaturated carbenes **C** are produced[17] (Scheme 1). This reaction sequence suggested a very simple strategy for the access to higher alkapolyenylidene–metal intermediates. Similar ruthenium(II) precursors should be able to activate diyne derivatives of type **D** containing a leaving group OY to generate the novel penta-1,2,3,4-tetraenylidene–metal reactive species **E** able to produce new cumulenes **F** and functional allenylidenes **G** on addition of weak nucleophiles.

Following our preliminary results[23,24] we report here our first general study based on this strategy of the activation of diyne compounds $HC{\equiv}CC{\equiv}CCR_2OY$ with $RuCl_2(PR_3)(arene)$ complexes and we show a general route to new functional ruthenium allenylidene and diynyl complexes.

Results and Discussion

1. Synthesis of Ruthenium Buta-1,2,3-trienylcarbene Complex 3. The first attempt to activate a diyne with a ruthenium(II) complex was performed with (arene)ruthenium(II) derivative **1a** and the diyne $HC{\equiv}CC{\equiv}CCPh_2OH$ (**I**) in methanol and led to the unexpected formation of a (3-oxopentadienyl)ruthenium complex (**H**)[23] (eq 1). This transformation suggested the formation of a penta-1,2,3,4-tetraenylidene intermediate of type (**E**) *via* dehydration and successive addition of methanol at carbon C_1 and of the released water at carbon C_3.



(1)

In order to decrease the formation of water during the reaction, and thus generate a cumulene, the activation of the diyne $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ (**II**) containing the $OSiMe_3$ leaving group was studied. The reaction of **II** with **1a**, in methanol and in the presence of a slight excess of $NaPF_6$, led, at room temperature, to the formation of two compounds which were separated by fractional precipitation and identified as the first butatrienylcarbene **3** (40%) and 3-alkenylallenylidene–ruthenium **4** (11%) complexes, respectively (Scheme 2). The reaction required the presence of a noncoordinating anion-containing salt ($NaPF_6$) otherwise complex **1a** was

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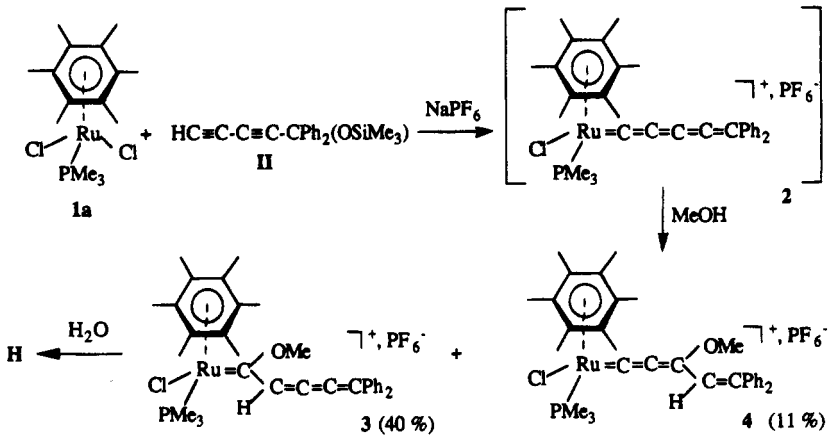
Table 1. ^{13}C NMR Data (δ, ppm) of the [Ru=C_1=C_2=C_3(YR')C_4H=C_5Ph_2] Complexes 4–6

PR_3	compd	YR'	C_1 ($^2J_{PC}$, Hz)	C_2	C_4 ($^1J_{CH}$, Hz)	C_3, C_5
PMe_3	**4**	OMe	233.74 (28.4)	134.05	123.00 (162)	162.55, 161.43
PMe_3	**5a**	OEt	231.20 (28.6)	133.55	123.12 (162)	162.12, 161.13
PMe_{2Ph}	**5b**	OEt	229.93 (28.8)	133.80	123.02 (163)	162.28, 161.40
$PMePh_2$	**5c**	OEt	229.18 (30.3)	132.91	123.04 (163)	162.25, 161.55
PMe_3	**6a**	O^{i}Pr	229.00 (30.5)	131.88	123.67 (163)	161.60, 161.12
PMe_{2Ph}	**6b**	O^{i}Pr	227.99 (28.8)	132.13	123.63 (163)	161.72, 161.40
$PMePh_2$	**6c**	O^{i}Pr	227.11 (30.0)	132.66	123.51 (163)	161.80, 161.71
PMe_3	**7a**	NPh_2	213.04 (33.0)	121.02	123.67 (165)	153.95, 152.10
PMe_{2Ph}	**7b**	NPh_2	210.37 (32.2)	120.68	123.22 (167)	154.92, 150.16
$PMePh_2$	**7c**	NPh_2	210.62 (32.0)	122.75	123.16 (166)	154.98, 150.85

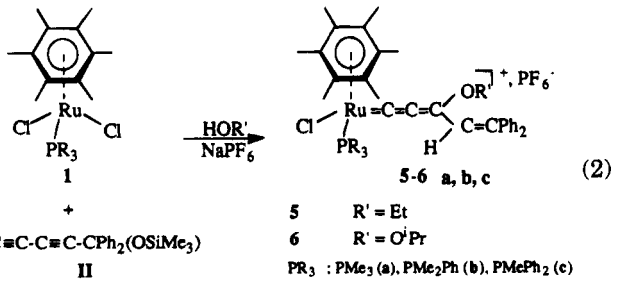
Scheme 2



recovered. The nature of **3** [IR (KBr): $\nu_{C=C=C=C}$: 2080 cm^{-1}] and **4** [$\nu_{C=C=C}$: 1980 cm^{-1}], established by NMR spectroscopy, suggested that the activation of **II** by **1a** proceeded *via* dissociation of the RuCl bond in a polar solvent, coordination of the diyne *via* the terminal C≡CH bond, and "HOSiMe$_3$" elimination to give the cumulene intermediate **2**, analogous to **E**. This cationic heterocumulene **2** is likely to be electrophilic and add methanol either at carbon C_1 and C_3, to give complexes **3** and **4** after protonation at carbon C_2 or C_4, respectively.

Whereas complex **4** is inert toward the addition of water, complex **3** reacts rapidly with water affording the corresponding complex of type **H**.[23] (eq 1, Scheme 2)

2. Preparation of Alkoxyalkenylallenylidene Derivatives 5 and 6. Complex **1a** and $NaPF_6$ also reacted with the diyne **II** in the presence of the bulkier alcohols, ethanol and 2-propanol. Complexes **5a** (45%) and **6a** (57%) were isolated respectively (eq 2). The crude



(2)

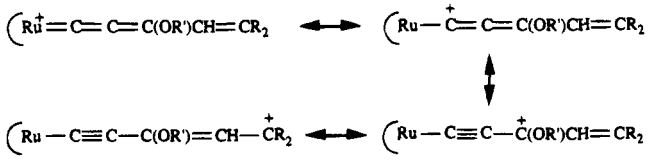
product of the reaction performed in ethanol showed an infrared absorption at 1995 cm^{-1} ($\nu_{C=C=C}$, **5a**) and at 2070 cm^{-1}. The latter absorption disappeared after one crystallization and was likely due to the presence of a small amount of the product analogous to **3** ($\nu_{C=C=C=C}$ 2080 cm^{-1}).

For solubility reasons the reaction of complexes **1b,c** with the diyne **II** and $NaPF_6$ was performed in dichloromethane. After 3 h at room temperature, the red solution had turned into a dark blue one; then an excess of ethanol or 2-propanol was added and the mixture turned immediately violet. The violet allenylidene complexes **5b** (58%), **6b** (49%), **5c** (43%), and **6c** (36%) were isolated (eq 2). The formation of allenylidene complexes **5–6** is consistent with the addition of the alcohol (EtOH or ^{i}PrOH) at carbon (C(3) of the cumulene intermediate **2**. It shows that the steric hindrance of both the PR_3 ligand and alcohol disfavors the addition at carbon C(1) of **2** and the formation of a complex analogous to **3**.

The $^{13}C\{^1H\}$ NMR spectrum of **3** shows a low-field doublet δ 295.13 ppm typical of a carbene (Ru=C) carbon nucleus.[17] Four lines for the C=C=C=C arrangement are observed, and the $^1J_{CH}$ = 172 Hz (δ = 109.79 ppm) and $^2J_{CH}$ = 6.8 Hz (δ = 148.42 ppm) are measured on the undecoupled ^{13}C NMR spectrum. By contrast the ^{13}C NMR spectra of the allenylidene complexes **4–6** show a higher field doublet for the Ru=C carbon nucleus at $\delta \sim 230$ ppm ($^2J_{PC} \approx 30$ Hz) (Table 1). Whereas the C(3) and C(5) singlets are close to each other, the C(4) signal is easily identified from the undecoupled ^{13}C spectrum at $\delta \sim 123$ ppm ($^1J_{CH} \sim 162$ Hz). Thus the chemical shift sequence is $\delta(C_1) > \delta(C_3,C_5) > \delta(C_2) > \delta(C_4)$. The most deshielded signals correspond to the electron-deficient carbon according to the canonical forms (Scheme 3). For the first reported allenylidene–metal complex $(OC)_5W=C_1=C_2=C_3(NMe_2)(Ph)$[9a] the closely related sequence $\delta(C_1) > \delta(C_3) > \delta(C_2)$ was established on the basis of the $^nJ_{WC}$ coupling constants.[25]

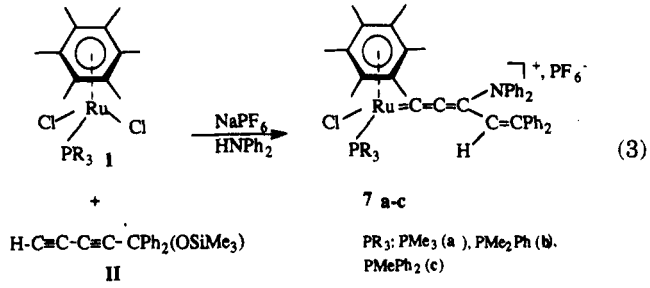
(25) $^nJ_{WC}$ (Hz): ^1J = 102.5; ^2J = 26.9; ^3J = 5 Hz.[9a]

Scheme 3



It is thus likely that the alkenylallenylidene complexes **4**–**6** are stabilized by the presence of an heteroatom electron-releasing group at the electrophilic carbon C(3) as are the Fischer type carbene complexes.

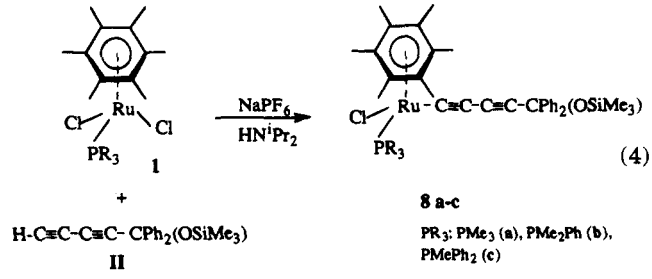
3. Preparation of Ruthenium 3-Amino 3-alkenylallenylidene Complexes 7a–c. As an amino group at C(3) is expected to better stabilize the alkenylallenylidene complexes than an alkoxy group, the addition of amines to the cumulene intermediate **2** was attempted. The diyne **II** was activated by complex **1a** in the presence of $NaPF_6$ and the weak base $HNPh_2$ in dichloromethane. The brown complex **7a** was formed (52%). Analogously from **1b,c** the complexes **7b,c** were isolated in 67% and 81% yield, respectively (eq 3). The complexes **7** show in ^{13}C NMR a chemical shift sequence analogous to that of **5** and **6**, but for C(1) a doublet is observed at slightly higher field than for the complexes **5**–**6** [δ = 213.04 (**7a**), 210.37 (**7b**), 210.62 (**7c**) ppm] (Table 1). This shift is consistent with the electron donating capability of the NPh_2 group.



(3)

It is noteworthy that complexes of type **7** could not be obtained with a more basic secondary amine as another process took place.

4. Preparation of Ruthenium Diynyl Complexes 8. The reaction of **1a** with **II** and $NaPF_6$ but in the presence of HN^iPr_2 (pK_a = 10.96), instead of $HNPh_2$ (pK_a = 0.79), led to the formation of the orange neutral ruthenium diynyl derivative **8a** isolated in 57% yield (eq 4). Similarly, complexes **1b,c** afforded the diynyl



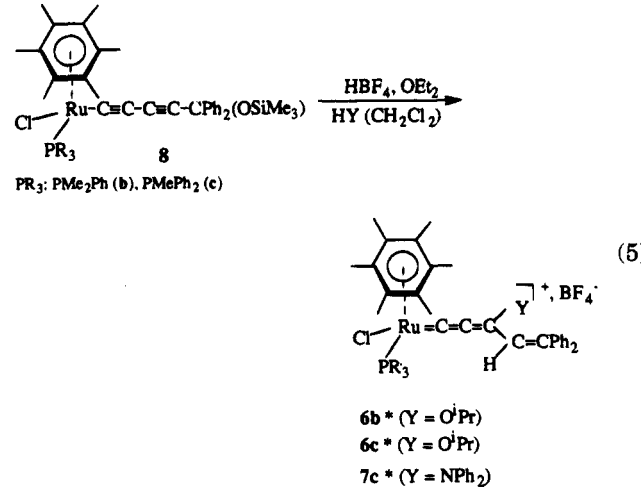
(4)

complexes **8b** (56%) and **8c** (42%). Complexes **8** could also be obtained when another *basic* amine was used. Thus in the presence of the tertiary amine NEt_3 (pK_a = 11.01) complexes **8a** (26%), **8b** (49%), and **8c** (59%) were obtained. The use of the primary amine $^tBuNH_2$ (pK_a = 10.83) led to complexes **8a** (20%), **8b** (23%), and **8c** (25%). HN^iPr_2 appears to be the best compromise.

Thus, the reaction corresponds to the *formal* substitution of one chloride by the "acetylide" expected to be generated by deprotonation of the terminal alkyne **II** with a base. However, the same reaction performed in *the absence of* $NaPF_6$ does not lead to complexes **8** and the starting complex **1** is recovered (92% of **1a**). Complexes **8a-c** show in their infrared spectrum two absorptions at ν ~2185 and ~2025 cm^{-1} typical of C≡C bonds. The ^1H NMR spectrum shows the retention of the $OSiMe_3$ group, and in ^{13}C NMR the RuC_1C_2 chemical shifts [**8a** (δ, ppm): C_1, 121.12 ($^2J_{PC}$ = 39.5 Hz); C_2, 78.28 ($^3J_{PC}$ = 3.9 Hz] are quite consistent with a $RuC_1{\equiv}C_2$ arrangement.

An X-ray diffraction study of a single crystal of **8a** was undertaken. It established that the molecular structure of **8a** contains an almost linear $RuC{\equiv}CC{\equiv}CC(OSiMe_3)Ph_2$ arrangement.[24] However, the quality of the crystal structure (R = 0.076) does not allow significant discussion of the influence of the replacement of the (HC≡C) H atom of **II** by the $Ru(Cl)(PMe_3)(C_6Me_6)$ moiety.[24,27]

5. Synthesis of Alkenylallenylidenes from Ruthenium Diynyl Complexes 8. The facile displacement of a leaving group attached at the C_3 carbon of an alkynyl–metal complex is a well-known process, and for instance, the cationic allenylidenes $[Mn{=}C{=}C{=}CPh_2(CO)_2(C_5H_4Me)]^+$ [29] or $[Ru{=}C{=}C{=}CAr_2(Cl)(Ph_2PCH_2PPh_2)_2]^+$ [18] were prepared by elimination of the OMe group from the corresponding $MC{\equiv}CCR_2OMe$ moiety with an acid and $Ph_3C^+PF_6^-$, respectively. Complexes **8b,c**, in dichloromethane and an excess of 2-propanol, were treated with $HBF_4{\cdot}OEt_2$. Dark blue complexes **6b*,c*** formed immediately and were isolated in 46% and 42% yield, respectively (eq 5). Complex **8c**, in the



(5)

presence of $HNPh_2$, on protonation with $HBF_4{\cdot}OEt_2$

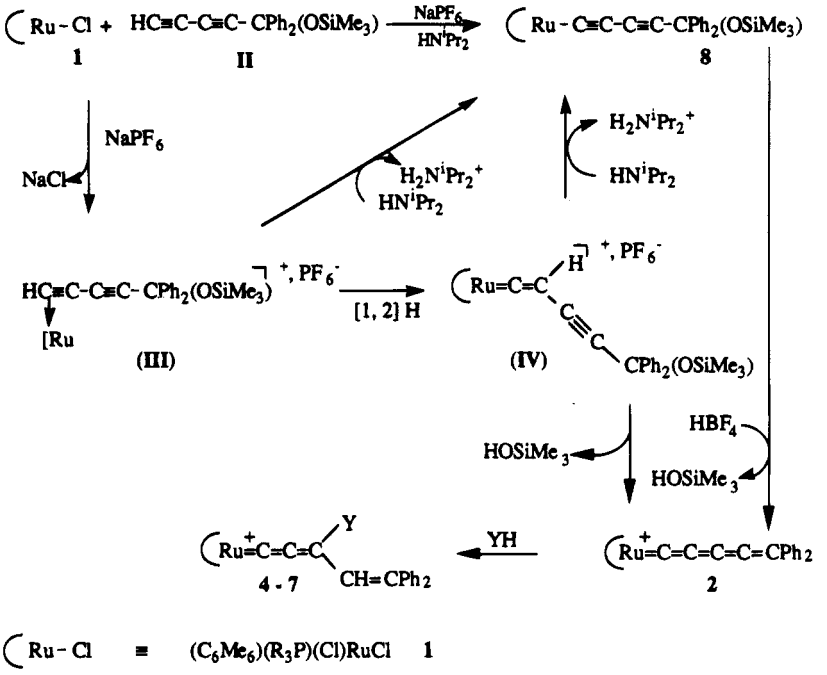
(26) Complex **7b** was also obtained from **1b** by activation of $Me_3Si(C)_4C(OSiMe_3)Ph_2$: Péron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497.

(27) From the X-ray structure of **8a**,[24] the distances (Å) $Ru{-}C_1$ [1.93(3)], $C_1{-}C_2$ [1.26(4)], $C_2{-}C_3$ [1.40(5)], $C_3{-}C_4$ [1.13(6)], $C_4{-}C_5$ [1.53(6)] of the $RuC_1C_2C_3C_4C_5(OSiMe_3)Ph_2$ moiety can be compared with those of *trans*-$Ru(C_1{\equiv}C_2C_3{\equiv}C_4H)_2(CO)_2(PEt_3)_2$:[28] $Ru{-}C_1$, 2.078(2); $C_1{-}C_2$, 1.194(2); $C_2{-}C_3$, 1.386(3); $C_3{-}C_4$, 1.196(3).

(28) Sun, Y.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1992**, *423*, C43; *Organometallics* **1992**, *11*, 4293.

(29) Berke, H.; Huttner, G.; Seyerl, J. v. *Z. Naturforsch.* **1981**, *36b*, 1277.

Scheme 4



afforded complex **7c*** (64%). Complexes **6*** and **7*** contain the same cation as complexes **6** and **7** (eqs 2 and 3) but with a different anion [BF_4^-]. This reaction shows that the $OSiMe_3$ group attached on carbon C_5 is very labile on protonation and that the penta-1,2,3,4-tetraenylidene intermediate **2** can be generated as well from the diynyl complexes **8**. This simple way of access to the alkenylallenylidene was also used to generate *trans*-bis(allenylidene)ruthenium complexes.[30]

6. Mechanism of Activation of the Diyne II. It is likely that the initial steps of selective activation of the diyne **II** include dissociation of the Ru–Cl bond in a polar solvent, which, in the presence of a noncoordinating anion, allows the coordination of the terminal HC≡C bond to give the intermediate **III**. The evidence for this is that there is no reaction, not even the transformation **1** → **8** (Scheme 4), in the absence of $NaPF_6$. Complex **III** is expected to lead to a more stable vinylidene intermediate **IV**. The cationic intermediates **III** and **IV** are much more acidic than the diyne **II**, and consequently, in the presence of a basic amine deprotonation of **III** or **IV** would lead to complex **8**. In the absence of a base (e.g. $HNPh_2$ or ROH) the vinylidene **IV** would lose "$HOSiMe_3$" and give the cumulenylidene intermediate **2**, which on addition of EtOH, ^{i}PrOH, and $HNPh_2$ at the electrophilic carbon C_3 would afford complexes **5**–**7**, respectively. Protonation of **8** with HBF_4·OEt_2 would also generate the cumulene species **2** giving the 3-alkenylallenylidene **6**–**7*** in the presence of HO^{i}Pr and $HNPh_2$.

The formation of the ruthenium(II) cumulenylidene intermediate **2** has just received strong support. The generation of a ruthenium butatrienylidene intermediate has been postulated.[31] Moreover, the isolation and characterization of the first metal pentatetraenylidene complex *trans*-[$(Ph_2PCH_2CH_2PPh_2)_2ClRu$=C=C=C=C=$CPh_2$]$PF_6$, obtained from $(Ph_2PCH_2CH_2PPh_2)_2ClRuC$≡$CC$≡$CCPh_2(OSiMe_3)$, has allowed its transformation into ruthenium allenylidene complexes analogous to **4**–**6** and **7** on addition of alcohol and amine, respectively.[32] The fact that complexes **1** do not lead to stable cumulenylidene derivatives **2** can be understood in terms of the greater electrophilicity and smaller bulk of the $RuCl(PR_3)_2(C_6Me_6)^+$ moiety relative to the $RuCl(PPh_2CH_2CH_2PPh_2)_2^+$ moiety.

Experimental Section

General Procedures. Standard techniques, with Schlenk type equipment for the manipulation of air-sensitive compounds under a blanket of nitrogen, were employed. All solvents were dried (sodium benzophenone ketyl for ether, CaH_2 for pentane and acetonitrile, $Mg(OMe)_2$ for methanol, and P_2O_5 for CH_2Cl_2) and nitrogen-saturated prior to use. The diyne derivative $HC_4CPh_2OSiMe_3$ (**II**) was prepared from HC_4H,[33] and the complexes $RuCl_2(PR_3)(\eta^6\text{-}C_6Me_6)$[34] were obtained by addition of PR_3 to $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ according to previously published procedures.

Instrumentation. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer with KBr disks containing 1–5% of complex. ^{1}H, ^{31}P, and ^{13}C NMR spectra were measured, at the CRMPO Center of the University of Rennes, on a Bruker AC 300 P spectrometer operating at 300.133 MHz for ^{1}H, 75.469 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Elemental analyses were obtained from the Laboratoire d'analyses du CNRS, Vernaison, France.

Preparation of Complexes 3 and 4. A 20 mL volume of dry, twice distilled methanol and then 0.23 g (0.73 mmol) of **II** were added to a mixture of **1a** (0.30 g, 0.73 mmol) and $NaPF_6$ (0.13 g, 0.77 mmol). The mixture, which turned rapidly from orange to violet, was stirred for 1 h at room temperature.

(30) Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem.* **1992**, 104, 664; *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 651.

(31) Lomprey, J. R.; Selegue, J. P. *Organometallics* **1993**, *12*, 616.

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

(33) Brandsma, L. *Preparative acetylenic chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 179.

(34) (a) Bennett, M. A.; Robertson, G. B.; Smith, A. K. *J. Organomet. Chem.* **1972**, *43*, C41. (b) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. (c) Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1982**, *228*, 289. (d) Bennett, M. A.; Latten, J. *Aust. J. Chem.* **1987**, *40*, 841.

Half of the solvent was evaporated, and 0.38 g of a red-violet solid was obtained by filtration on a frit. Its infrared spectrum showed two intense absorptions at 2080 and 1980 cm^{-1}. The product was dissolved in 20 mL of dichloromethane, 10 mL of diethyl ether was first added, and 0.22 g of orange crystals of **3** (40%) (2080 cm^{-1}) was obtained. Further addition of ether led to the crystallization of the deep red crystals of **4** (0.06 g, 11%) (1980 cm^{-1}).

[Ru(C(OMe)CH=C=C=CPh$_2$)(PMe$_3$)(Cl)(η^6-C$_6$Me$_6$)]PF$_6$ (3). IR (KBr): 2080 (s, $\nu_{C=C=C=C}$), 855 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.133 MHz) (δ, ppm): 7.69−7.47 (m, 10 H, Ph), 7.29 (s, 1 H, =CH), 4.51 (s, 3 H, OMe), 2.06 (d, $^4J_{(P,H)}$ = 0.7 Hz, 18 H, C_6Me_6), 1.40 (d, $^2J_{(P,H)}$ = 10.6 Hz, 9 H, PMe_3. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 10.54 (s, PMe_3), −143.45 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 295.13 (d, $^2J_{(P,C)}$ = 21.2 Hz, Ru=C), 166.88, 148.83, (s, *C*=CPh$_2$), 148.42 (s, CH=*C*=, $^2J_{CH}$ = 6.8 Hz), 109.79 (s, HC=, ($^1J_{(C,H)}$ = 172 Hz), 106.47 (s, C_6Me_6), 67.43 (s, OMe), 16.41 (s, C_6Me_6), 16.05 (d, $^1J_{(P,C)}$ = 34.6, PMe_3). Anal. Calcd (found) for $C_{33}H_{41}ClOP_2F_6Ru^1/_2CH_2Cl_2$: C; 49.76 (49.64); H, 5.24 (5.21); Cl, 8.76 (7.89).

[Ru(C=C=C(OMe)HC=CPh$_2$)(Cl)(PMe$_3$)(η^6-C$_6$Me$_6$)]PF$_6$ (4). IR (KBr): 1982 (s, $\nu_{C=C=C}$), 855 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.133 MHz) (δ, ppm): 7.45−7.23 (m, 10 H, Ph), 6.73 (s, 1 H, =CH), 3.94 (s, 3 H, OMe), 2.13 (s, 18 H, C_6Me_6), 1.54 (d, 9 H, $^2J_{(P,H)}$ = 11 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 12.14 (s, PMe_3), −143.45 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 233.74 (d, $^2J_{(P,C)}$ = 28.4 Hz, Ru=C), 162.55, 161.43 (s, C=C=*C*, =*C*Ph$_2$), 141.02, 139.26 (s, Ci (Ph)), 134.05 (s, C=*C*=C), 123.00 (s, =CH, $^1J_{(C,H)}$ = 162 Hz), 109.78 (s, C_6Me_6), 61.85 (s, OMe), 16.80 (s, C_6Me_6), 16.77 (d, $^1J_{(P,C)}$ = 36.9 Hz, PMe_3).

Preparation of Complexes 5a and 6a. A 1 mmol (0.41 g) amount of complex **1a** and of $NaPF_6$ in 20 mL of dry alcohol (ethanol or 2-propanol) were stirred at room temperature, and then compound **II** (3 mmol) was introduced with a syringe. The solution turned rapidly from red to violet, and a violet, product progressively precipitated. After 3 h of stirring, half of the solvent was evaporated and the violet complex was obtained by filtration on a frit. The product was dissolved in 20 mL of dichloromethane, 20 mL of ether was added, and the mixture was kept at room temperature for 2 days. Violet crystals of compounds **5a** and **6a** were formed and isolated by removal of the supernatant through a filter paper tipped cannula.

[Ru(C=C=C(OEt)HC=CPh$_2$)(Cl)(PMe$_3$)(η^6-C$_6$Me$_6$)]PF$_6$ (5a). From 0.41 g (1 mmol) of **1a**, 0.18 g (1 mmol) of $NaPF_6$, 20 mL of ethanol, and 3 mmol of compound **II**, complex **5a** was obtained in 45% yield (0.35 g). IR (KBr): 1995 (s, $\nu_{C=C=C}$), 855 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.48−7.32 (m, 8 H, Ph), 7.23−7.20 (m, 2 H, Ph), 6.74 (s, 1 H, =CH), 4.33 (m, $^3J_{(H,H)}$ = 7.1 Hz, 2 H, CH_2), 2.14 (s, 18 H, C_6Me_6), 1.58 (d, $^2J_{(P,H)}$ = 10.1 Hz, 9 H, PMe_3), 0.94 (t, $^3J_{(H,H)}$ = 7.1 Hz, 3 H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 12.39 (s, PMe_3), −143.49 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 231.20 (d, $^2J_{(P,C)}$ = 28.6 Hz, Ru=*C*), 162.12, 161.13, (s, C=C=*C*, =*C*Ph$_2$), 140.67, 139.49 (s, Ci(Ph)), 123.12 (s, CH=, $^1J_{(C,H)}$ = 162 Hz), 109.60 (d, $^2J_{(P,C)}$ = 2 Hz, C_6Me_6), 71.88 (s, CH_2), 16.81 (s, C_6Me_6), 16.79 (d, $^1J_{(P,C)}$ = 36.9 Hz, PMe_3), 13.71 (s, CH_2Me). Anal. Calcd (found) for $C_{34}H_{43}ClF_6OP_2Ru$: C, 52.34 (52.24); H, 5.55 (5.56).

[Ru(C=C=C(O^{i}Pr)CH=CPh$_2$)(Cl)(PMe$_3$)(η^6-C$_6$Me$_6$)]PF$_6$ (6a). From 0.41 g (1 mmol) of **1a**, 0.18 g (1 mmol) of $NaPF_6$, 20 mL of 2-propanol, and 3 mmol of compound **2**, the violet complex **6a** was obtained in 57% yield (0.45 g). IR (KBr): 1996 (vs, $\nu_{C=C=C}$), 840 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.49−7.32 (m, 8 H, Ph), 7.21−7.18 (m, 2 H, Ph), 6.77 (s, 1 H, =CH), 5.21 (sept, 1 H, $^3J_{(H,H)}$ = 6.2 Hz, OC*H*Me$_2$), 2.15 (s, 18 H, C_6Me_6), 1.55 (d, $^2J_{(P,H)}$ = 11 Hz, 9 H, PMe_3), 1.04 (d, $^3J_{(H,H)}$ = 6.2 Hz, 6 H, OCH*Me*$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 12.47 (s, PMe_3), −143.46 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 229.00 (d, $^2J_{(P,C)}$ = 30.5 Hz, Ru=C), 161.60, 161.12 (s, C=C=*C*, =*C*Ph$_2$), 140.50, 139.55 (s, Ci(Ph)), 131.88 (s, C=*C*=C), 123.67 (s, CH=, $^1J_{(C,H)}$ = 163 Hz), 109.38 (d, $^2J_{(P,C)}$ = 2.3 Hz, C_6Me_6), 80.69 (s, O*C*HMe$_2$), 21.60 (s, OCH*Me*), 21.45 (s, OCH*Me*), 16.85 (d, $^1J_{(P,C)}$ = 36.6 Hz, PMe_3), 16.81 (s, C_6Me_6). Anal. Calcd (found) for $C_{35}H_{45}ClF_6OP_2Ru\cdot{}^1/_2CH_2Cl_2$: C, 50.96 (50.86); H, 5.54 (5.48).

Preparation of Complexes 5b,c, and 6b,c. In a Schlenk tube were successively introduced **1b** or **1c**, $NaPF_6$, 15 mL of dry dichloromethane, and an excess of diyne **II** (4−5 equiv). The reaction mixture was stirred at room temperature for 3 h and turned from orange-red to deep blue. On addition of the alcohol (ethanol or 2-propanol) the solution became violet. After 2 h of stirring the solution was filtered and transfered with a cannula. The solvents were removed under vacuum, and 15 mL of CH_2Cl_2, 30 mL of diethyl ether, and 30 mL of *n*-pentane were successively added. After 24 h at room temperature the complexes **5** or **6** precipitated. The complexes were obtained by removing the supernatent solution with a cannula, washing with diethyl ether, and drying under vacuum.

[Ru(C=C=C(OEt)CH=CPh$_2$)(Cl)(PMe$_2$Ph)(η^6-C$_6$Me$_6$)]PF$_6$ (5b). From 0.24 g (0.51 mmol) of **1b**, 0.11 g (0.65 mmol) of $NaPF_6$, 2 mmol of **II**, and 0.3 mL of ethanol, complex **5b** was obtained in 58% yield (0.25 g). IR (KBr): 1977 (s, $\nu_{C=C=C}$), 840 (vs, ν_{P-F}) cm^{-1}. ^1H NMR ($CDCl_3$, 297 K, 300.134 MHz) (δ, ppm): 7.60−6.95 (m, 15 H, Ph), 6.80 (s, 1 H, CH=), 4.38 (ABX$_3$, $^2J_{(H,H)}$ = 22.5 Hz, $^3J_{(H,H)}$ = 7.1 Hz, 2 H, OCH_2), 1.86 (s, 18 H, C_6Me_6), 1.76 (d, $^2J_{(P,H)}$ = 10.6 Hz, 6H, PMe_2), 0.94 (t, $^3J_{(H,H)}$ = 7.1 Hz, 3 H, CH_2Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 297 K, 121.496 MHz) (δ, ppm): 19.80 (s, PMe_2Ph), −143.94 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 229.93 (d, $^2J_{(P,C)}$ = 28.8 Hz, Ru=C), 162.28, 161.40 (s, C=C=*C*, =*C*Ph$_2$), 140.57, 139.47 (s, Ci(Ph)), 133.88 (s, C=*C*=C), 123.02 (s, CH=, ($^1J_{(C,H)}$ = 162.7 Hz), 109.84 (s, C_6Me_6), 72.01 (s, OCH_2), 16.09 (s, C_6Me_6), 13.71 (s, OCH_2CH_3). Anal. Calcd (found) for $C_{39}H_{45}ClF_6OP_2Ru$: C, 55.62 (55.80); H, 5.38 (5.39).

[Ru(C=C=C(OEt)CH=CPh$_2$)(Cl)(PMePh$_2$)(η^6-C$_6$Me$_6$)]PF$_6$ (5c). From 0.25 g (0.45 mmol) of **1c**, 0.11 g (0.65 mmol) of $NaPF_6$, 2 mmol of **II** and 0.8 mL of ethanol, complex **5c** was obtained in 43% yield (0.185 g). IR (KBr): 1978 (s, $\nu_{C=C=C}$), 839 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.56−7.34 (m, 14 H, Ph), 7.19−7.15 (m, 6 H, Ph), 6.40 (s, 1 H, CH=), 4.15 (ABX$_3$, $^2J_{(H,H)}$ = 22.5 Hz, $^3J_{(H,H)}$ = 7.1 Hz, 2 H, OCH_2), 2.14 (d, $^2J_{(P,H)}$ = 10.7 Hz, 3 H, PMe), 1.86 (s, 18 H, C_6Me_6), 0.80 (t, $^3J_{(H,H)}$ = 7.1 Hz, 3 H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 33.22 (s, $PMePh_2$), −143.80 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 229.18 (d, $^2J_{(P,C)}$ = 30.3 Hz, Ru=C), 162.25, 161.55 (s, C=C=*C*, =*C*Ph$_2$), 140.37, 139.31 (s, Ci(Ph), 132.91 (s, C=*C*=C), 123.04 (s, CH=, $^1J_{(C,H)}$ = 163 Hz), 110.28 (s, C_6Me_6), 71.87 (s, OCH_2), 17.81 (d, $^1J_{(P,C)}$ = 39.1 Hz, P*Me*Ph$_2$), 16.11 (s, C_6Me_6), 13.57 (s, CH_2Me). Anal. Calcd (found) for $C_{44}H_{45}ClF_6OP_2Ru.0.25\ CH_2Cl_2$: C, 57.42 (57.06); H, 5.17 (5.28).

[Ru(C=C=C(O^{i}Pr)CH=CPh$_2$)(Cl)(PMe$_2$Ph)(η^6-C$_6$Me$_6$)]PF$_6$ (6b). From 0.24 g (0.45 mmol) of **1b**, 0.11 g (0.65 mmol) of $NaPF_6$, 2 mmol of **II**, and 0.3 mL of 2-propanol, complex **6b** was obtained in 49% yield (0.21 g). IR (KBr): 1975 (s, $\nu_{C=C=C}$), 838 (vs, ν_{P-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.67−7.56 (m, 3 H, Ph), 7.51−7.21 (m, 12 H, Ph), 6.85 (s, 1 H, CH=), 5.30−5.23 (m, 1 H, OC*H*Me$_2$), 1.88 (s, 18 H, C_6Me_6), 1.82 (d, $^2J_{(P,H)}$ = 9.2 Hz, 3 H, P*Me*), 1.75 (d, $^2J_{(P,H)}$ = 10 Hz, 3 H, P*Me*), 1.08 (d, $^3J_{(H,H)}$ = 5.7 Hz, 3 H, OCH*Me*), 1.06 (d, $^3J_{(H,H)}$ = 5.8 Hz, 3 H, OCH*Me*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 20.10 (s, PMe_2Ph), −143.93 (sept, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 227.99 (d, $^2J_{(P,C)}$ = 28.8 Hz, Ru=C), 161.72, 161.40 (s, C=C=*C*, =*C*Ph$_2$), 132.13 (s, C=*C*=C), 123.63 (s, CH=, $^1J_{(C,H)}$ = 163 Hz), 109.64 (d, $^2J_{(P,C)}$ = 2.3 Hz, C_6Me_6), 80.90 (s, O*C*HMe$_2$), 21.69, 21.49 (s, OCH*Me*), 17.20 (d, $^1J_{(P,C)}$ = 41.4 Hz, PMe), 16.13 (s, C_6Me_6), 13.35 (d, $^1J_{(P,C)}$ = 38.1 Hz, PMe). Anal.

Calcd (found) for $C_{40}H_{47}ClF_6OP_2Ru$: C, 56.11 (56.21); H, 5.53 (5.37); Cl, 4.14 (4.51).

[Ru(C=C=C(O^{i}Pr)CH=CPh$_2$)(Cl)(PMePh$_2$)(η^6-C$_6$Me$_6$)]-PF$_6$ (6c). From 0.24 g (0.45 mmol) of **1c**, 0.11 g (0.65 mmol) of $NaPF_6$, 2 mmol of **II**, and 0.2 mL of 2-propanol, complex **6c** was obtained in 36% yield (0.15 g). IR (KBr): 1978 (s, $\nu_{C=C=C}$), 839 (vs, ν_{P-F}) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.54−7.10 (m, 20 H, Ph), 6.50 (s, 1 H, CH=), 4.96 (sept, $^3J_{(H,H)}$ = 6.2 Hz, 1 H, OC*H*Me$_2$), 2.05 (d, $^2J_{(P,H)}$ = 10.6 Hz, 3 H, PMe), 1.86 (d, $^4J_{(P,H)}$ = 0.7 Hz, 18 H, C$_6$Me$_6$), 0.94 (d, $^3J_{(H,H)}$ = 6.2 Hz, 3 H, OCH*Me*), 0.78 (d, $^3J_{(H,H)}$ = 6.2 Hz, 3 H, OCH*Me*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 34.06 (s, PMe$_3$), −143.51 (sept, PF_6^-). ^{13}C{^{1}H} NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 227.11 (d, $^2J_{(P,C)}$ = 30 Hz, Ru=*C*), 161.80, 161.71 (s, C=C=*C*, =*C*Ph$_2$), 140.23, 139.40 (s, Ci Ph), 133.50 (s, C=*C*=C), 123.51 (s, HC=, $^1J_{(C,H)}$ = 163.1 Hz), 110.09 (d, $^2J_{(P,C)}$ = 2.5 Hz, *C*$_6$Me$_6$), 80.97 (s, O*C*HMe$_2$), 21.51 (s, OCH*Me*), 21.33 (s, OCH*Me*), 18.06 (d, $^1J_{(P,C)}$ = 39.4 Hz, PMe), 16.11 (s, C$_6$*Me*$_6$). Anal. Calcd (found) for $C_{45}H_{49}ClF_6OP_2Ru$: C, 58.86 (58.77); H, 5.38 (5.31); Cl, 3.86 (3.97).

Preparation of Complexes 7a-c. [Ru(C=C=C(NPh$_2$)-HC=CPh$_2$)(Cl)(PMe$_3$)(η^6-C$_6$Me$_6$)]PF$_6$ (7a). A 0.6 mmol (0.25 g) amount of complex **1a** and 0.65 mmol (0.11 g) of $NaPF_6$, 15 mL of dry CH_2Cl_2, and 0.61 mmol of **II** were successively introduced in a Schlenk tube. The mixture was stirred at room temperature and turned rapidly from red to blue. After 1 h of stirring, 0.65 mmol of diphenylamine in 2 mL of dichloromethane was added and the mixture became dark red. After 1 h the solvent was evaporated and the complex was dissolved in 15 mL of dichloromethane and filtered through a filter paper tipped cannula. A 30 mL volume of ether and 30 mL of *n*-pentane were added. The red complex precipitated at room temperature and was isolated by removal of the supernatent solution with a cannula. Dark red complex **7a** was obtained in 53% yield (0.29 g). IR (KBr): 1996 (s, $\nu_{C=C=C}$), 837 (vs, ν_{P-F}) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.133 MHz) (δ, ppm): 7.48−6.76 (m, 20 H, Ph), 6.46 (s, 1 H, =CH), 1.92 (s, 18 H, C$_6$Me$_6$), 1.29 (d, $^2J_{(P,H)}$ = 10.8 Hz, PMe$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 11.10 (s, PMe$_3$), −143.41 (sept, PF_6^-). ^{13}C{^{1}H} NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 213.04 (d, $^2J_{(P,C)}$ = 33 Hz, Ru=C), 153.95, 152.10 (s, C=C=*C*, =*C*Ph$_2$), 123.67 (s, HC=, $^1J_{(C,H)}$ = 165.5 Hz), 121.02 (s, C=*C*=C), 106.59 (d, $^2J_{(P,C)}$ = 2.2 Hz, *C*$_6$Me$_6$), 16.51 (s, C$_6$*Me*$_6$), 16.41 (d, $^1J_{(P,C)}$ = 35.8 Hz, P*Me*$_3$). Anal. Calcd (found) for $C_{44}H_{48}ClF_6NP_2Ru$: C, 58.50 (58.48); H, 5.35 (5.47); N, 1.55 (1.42).

[Ru(C=C=C(NPh$_2$)HC=CPh$_2$)(PMe$_2$Ph)(Cl)(η^6-C$_6$Me$_6$)]-PF$_6$ (7b). From 0.24 g (0.51 mmol) of **1b**, 0.11 g (0.65 mmol) of $NaPF_6$, and 4.3 mmol of **II**, stirring for 4 h, and addition of 0.09 g (0.59 mmol) of $HNPh_2$, stirring for 2 h, 0.33 g (67%) of **7b** was obtained. IR (KBr): 1996 cm^{-1} (s, $\nu_{C=C=C}$), 840 (s, ν_{P-F}) cm^{-1}. ^{31}P{^{1}H}NMR (CD_2Cl_2, 121.496 MHz, 297 K) (δ, ppm): 19.08 (s, PMe$_2$Ph), −143.60 (sept, $^1J_{(P,F)}$= 710 Hz, PF_6^-). ^{1}H NMR (CD_2Cl_2, 300.134 MHz, 297 K) (δ, ppm): 7.48−6.97 (m, 25 H, Ph), 6.55 (s, 1 H, CH=), 1.66 (s, C$_6$Me$_6$), 1.47 (d, $^2J_{(P,H)}$= 10.3 Hz, 6 H, PMe$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.472 MHz, 297 K) (δ, ppm): 210.37 (d, $^2J_{(P,C)}$= 32.2 Hz, Ru=C), 154.92, 150.16 (s, C=C=*C*, =*C*Ph$_2$), 123.22 $^1J_{(C,H)}$ = 167 Hz, CH=), 120.68 (s, C=*C*=C), 106.49 (d, $^2J_{(P,C)}$ = 2.8 Hz, *C*$_6$Me$_6$), 15.55 (s, C$_6$*Me*$_6$), 14.38 (d, $^1J_{(P,C)}$= 38.6 Hz, PMe), 14.13 (d, $^1J_{(P,C)}$= 39.6 Hz, PMe).

[Ru(C=C=C(NPh$_2$)HC=CPh$_2$)(PMePh$_2$)(Cl)(η^6-C$_6$Me$_6$)]-PF$_6$ (7c). From 0.25 g (0.47 mmol) of **1c**, 0.11 g (0.65 mmol) of $NaPF_6$, and 2.6 mmol of **II**, stirring for 4 h, and addition of 0.10 g (0.59 mmol) of $HNPh_2$, stirring for 2 h, the complex **7c** was obtained in 81% yield (0.39 g). IR (KBr): 1995 (s, $\nu_{C=C=C}$), 841 (vs, ν_{P-F}) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.133 MHz) (δ, ppm): 7.58−6.54 (m, 30 H, Ph), 6.33 (s, 1 H, CH=), 1.71 (d, $^2J_{(P,H)}$ = 10.5 Hz, 3 H, PMe), 1.63 (s, 18 H, C$_6$Me$_6$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 35.46 (s, PMePh$_2$), −143.46 (sept, PF_6^-). ^{13}C{^{1}H} NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 210.62 (d, $^2J_{(P,C)}$ = 32.2 Hz, Ru=C), 154.98, 150.86 (s, C=C=*C*, =*C*Ph$_2$), 123.16 (s, HC=, $^1J_{(C,H)}$ =166.4 Hz), 122.75 (s, C=*C*=C), 107.67 (s, *C*$_6$Me$_6$), 17.76 (d, $^1J_{(P,C)}$ = 39.7 Hz, PMe), 15.78 (s, C$_6$*Me*$_6$). Anal. Calcd (found) for $C_{54}H_{52}ClF_6NP_2Ru$: C, 62.07 (61.71); H, 5.10 (5.04); Cl, 3.45 (3.44).

Preparation of Complexes 8a-c. Method A. RuC≡C-C≡CC(OSiMe$_3$)Ph$_2$(Cl)(PMe$_3$)(η^6-C$_6$Me$_6$) (8a). To a mixture of 0.70 mmol (0.29 g) of **1a** and 0.71 mmol (0.12 g) of $NaPF_6$ were successively added 15 mL of dichloromethane, an excess (3 equiv) of **II**, and 1.07 mmol of diisopropylamine. The solution was stirred at room temperature for 2 h and turned from brown to a red color. After evaporation of the solvent and amine, chromatography of the products on an 8 cm alumina column (eluent: dichloromethane, ether, *n*-pentane, 3:1:1) afforded complex **8a**. The pure orange complex was obtained by crystallization after evaporation of the eluent and dissolution in 10 mL of dichloromethane followed by addition of 20 mL of diethyl ether and 20 mL of *n*-pentane. The complex **8a** was obtained in 57% yield (0.27 g). IR (KBr): 2186 (s, $\nu_{C\equiv C}$), 2035 (m, $\nu_{C\equiv C}$) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.56−7.16 (m, 10 H, Ph), 2.05 (s, 18 H, C$_6$Me$_6$), 1.45 (d, $^2J_{(P,H)}$ = 10 Hz, 9 H, PMe$_3$), 0.12 (s, 9 H, OSiMe$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K,121.496 MHz) (δ, ppm): 8.19 (s, PMe$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 121.11 (d, $^2J_{(P,C)}$ = 39.5 Hz, Ru-C), 101.02 (d, $^2J_{(P,C)}$ = 2.8 Hz, *C*$_6$Me$_6$), 86.38, 78.26, 76.75 (s, C≡*CC*≡*C*), 68.31 (s, *C*Ph$_2$), 16.54 (d, $^1J_{(P,C)}$ = 34 Hz, PMe$_3$), 16.37 (s, C$_6$*Me*$_6$), 1.65 (s, OSiMe$_3$). Anal. Calcd (found) for $C_{35}H_{46}ClOPRuSi$: C, 61.97 (61.70), H, 6.83 (6.70), Cl, 5.23 (5.38).

Ru-C≡CC≡CC(OSiMe$_3$)Ph$_2$(Cl)(PMe$_2$Ph)(η^6-C$_6$Me$_6$) (8b). From 1.05 mmol (0.50 g) of **1b**, 1.31 mmol (0.22 g) of $NaPF_6$, 6 mmol of **II**, and 1.14 mmol of HN^{i}Pr$_2$, the complex **8b** was obtained in 56% yield (0.78 g). IR (KBr): 2185 (s, $\nu_{C\equiv C}$), 2033 (m, $\nu_{C\equiv C}$) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.72−7.15 (m, 15 H, Ph), 1.77 (d, $^4J_{(P,H)}$ = 0.7 Hz, 18 H, C$_6$Me$_6$), 1.71 (d, $^2J_{(P,H)}$ = 10.8 Hz, 3 H, PMe), 1.70 (d, $^2J_{(P,H)}$ = 10.4 Hz, 3 H, PMe), 0.14 (s, 9 H, OSiMe$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 297 K, 121.496 MHz) (δ, ppm): 16.73 (s, PMe$_2$Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$, 297 K, 75.469 MHz) (δ, ppm): 121.11 (d, $^2J_{(P,C)}$ = 39.5 Hz, Ru-C), 101.25 (d, $^2J_{(P,C)}$ = 3.2 Hz, *C*$_6$Me$_6$), 78.40 (d, $^3J_{(P,C)}$ = 3.6 Hz, C≡*CC*≡C), 86.73, 76.80 (s, C≡*CC*≡*C*), 68.25 (s, *C*Ph$_2$), 15.68 (s, C$_6$*Me*$_6$), 15.21 (d, $^1J_{(P,C)}$ = 36.7 Hz, PMe), 14.38 (d, $^1J_{(P,C)}$ = 38.9 Hz, PMe), 1.73 (s, OSiMe$_3$); Anal. Calcd (found) for $C_{40}H_{48}ClOPRuSi$: C, 64.89 (64.64); H, 6.53 (6.58); Cl, 4.79 (5.07).

RuC≡CC≡CC(OSiMe$_3$)Ph$_2$(Cl)(PMePh$_2$)(η^6-C$_6$Me$_6$) (8c). From 0.47 mmol (0.25 g) of **1c**, 0.65 mmol (0.11 g) of $NaPF_6$, 2.6 mmol of **II**, and 1.43 mmol of HN^{i}Pr$_2$, the complex **8c** was obtained in 42% yield (0.16 g). IR (KBr): 2189 (s, $\nu_{C\equiv C}$), 2038 (m, $\nu_{C\equiv C}$) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.72−7.14 (m, 20 H, Ph), 1.99 (d, $^2J_{(P,H)}$ = 10.4 Hz, 3 H, PMe), 1.76 (s, 18 H, C$_6$Me$_6$), 0.13 (s, 9 H, OSiMe$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 297 K, 121.496 MHz) (δ, ppm): 31.70 (s, PMePh$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 297 K, 75.469 MHz) (δ, ppm): 120.22 (d, $^2J_{(P,C)}$ = 37.2 Hz, Ru-C), 102.14 (d, $^2J_{(P,C)}$ = 3.2 Hz, *C*$_6$Me$_6$), 78.30 (d, $^3J_{(P,C)}$ = 3 Hz, C≡*CC*≡C), 87.83, 76.68 (s, C≡*CC*≡*C*), 68.37 (s, *C*Ph$_2$), 18.18 (d, $^1J_{(P,C)}$ = 39.5 Hz, PMe), 15.64 (s, C$_6$*Me*$_6$), 1.67 (s, OSiMe$_3$). Anal. Calcd (found) for $C_{45}H_{50}ClOPRuSi$: C, 67.35 (66.88); H, 6.28 (6.41); Cl, 4.42 (4.26).

Method B. Preparation of Complexes 8a-c Using Triethylamine or *tert*-Butylamine. When diisopropylamine in method A was replaced by triethylamine or *tert*-butylamine, an ocher color instantaneously appeared and, after 2.5 h at room temperature, workup as in method A afforded **8a-c**. From 0.61 mmol (0.25 g) of **1a**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.61 mmol (0.08 mL) of NEt_3, complex **8a** was obtained in 26% yield (0.11 g). From 0.53 mmol (0.25 g) of **1b**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.53 mmol (0.07 mL) of NEt_3, the complex **8b** was obtained in 49% yield (0.19 g). From 0.47 mmol (0.25 g) of **1c**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.47 mmol

(0.06 mL) of NEt_3, the complex **8c** was obtained in 59% yield (0.22 g). From 0.61 mmol (0.25 g) of **1a**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.57 mmol (0.06 mL) of $^tBuNH_2$, the complex **8a** was obtained in 20% yield (0.08 g). From 0.53 mmol (0.25 g) of **1b**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.57 mmol (0.06 mL) of $^tBuNH_2$, the complex **8b** was obtained in 23% yield (0.09 g). From 0.47 mmol (0.25 g) of **1c**, 0.65 mmol (0.11 g) of $NaPF_6$, 3 mmol of **II**, and 0.47 mmol (0.05 mL) of $^tBuNH_2$, the complex **8c** was obtained in 25% yield (0.09 g). The complexes **8a-c** were identical to those prepared according to method A on the basis of their IR, ^1H NMR, and ^{31}P NMR spectra.

Preparation of Complexes 6* (X = BF_4^-) from Ruthenium Diynyl Complexes 8. Complex [Ru(C=C=C(O^{i}Pr)-HC=CPh$_2$)(PMe$_2$Ph)(Cl)(η^6-C$_6$Me$_6$)]BF$_4$ (6b*). To a solution of 0.16 mmol (0.12 g) of **8b** in 15 mL of dichloromethane were added successively 1 mL of ^iPrOH and 30 μl of HBF_4·OEt_2. The solution turned immediately from orange to dark blue and was stirred for 2.5 h at room temperature. The solvents were removed, and the solid residue was washed twice with 15 mL of diethyl ether and dissolved in 15 mL of dichloromethane. After addition of 15 mL of diethyl ether and 15 mL of *n*-hexane and after 24 h at room temperature, a violet compound precipitated. The supernatent solution was removed with a cannula, and the solid was washed with ether and dried under vacuum. Complex **7b*** was obtained in 46% yield (60 mg). IR (KBr): 1963 (s, $\nu_{C=C=C}$), 1060 (m, ν_{B-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.63−7.36 (m, 13 H, Ph), 7.22−7.19 (m, 2 H, Ph), 6.83 (s, 1 H, CH=), 5.25 (sept, $^3J_{(H,H)}$ = 6.2 Hz, 1 H, OC*H*Me$_2$), 1.87 (d, $^4J_{(P,H)}$ = 0.5 Hz, 18 H, C$_6$Me$_6$), 1.83 (d, $^2J_{(P,H)}$ = 11.1 Hz, 3 H, PMe), 1.76 (d, $^2J_{(P,H)}$ = 10.7 Hz, 3 H, PMe), 1.06 (d, $^3J_{(H,H)}$ = 6.2 Hz, 3 H, OCH*Me*), 1.04 (d, $^3J_{(H,H)}$ = 6.3 Hz, 3 H, OCH*Me*). Anal. Calcd (found) for $C_{40}H_{47}BClF_4OPRu$: C, 60.20 (60.42), H, 5.94 (6.04).

Complex [Ru(C=C=C(O^{i}Pr)HC=CPh$_2$)(PMePh$_2$)(Cl)-(η^6-C$_6$Me$_6$)]BF$_4$ (6c*). From 0.25 g (0.31 mmol) of **8c**, 1 mL of HO^iPr, and 42.10 μl of HBF_4·OEt_2, 120 mg (42%) of **6c*** was obtained. IR (KBr): 1976 (s, $\nu_{C=C=C}$), 1055 (m, ν_{B-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.55−7.09 (m, 20 H, Ph), 6.50 (s, 1 H, CH=), 4.96 (sept, $^3J_{(H,H)}$ = 6.2 Hz, 1 H, OC*H*Me$_2$), 2.06 (d, $^2J_{(P,H)}$ = 10.6 Hz, 3 H, PMe), 1.86 (d, $^4J_{(P,H)}$ = 0.6 Hz, 18 H, C$_6$Me$_6$), 0.94 (d, $^3J_{(H,H)}$ = 6.2 Hz, 3 H, OCH*Me*), 0.79 (d, $^3J_{(H,H)}$ = 6.3 Hz, 3 H, OCH*Me*). Anal. Calcd (found) for $C_{45}H_{49}BClF_4OPRu$: C, 62.83 (62.82), H, 5.74 (5.61), Cl, 4.12 (4.35).

Complex [Ru(C=C=C(NPh$_2$)HC=CPh$_2$)(PMePh$_2$)(Cl)-(η^6-C$_6$Me$_6$)]BF$_4$ (7c*). From 0.25 g (0.31 mmol) of **8c**, 45 μl of HBF_4. OEt_2, and diphenylamine (0.06 g, 0.35 mmol), 180 mg (64%) of **7c*** was obtained. IR (KBr): 1996 (s, $\nu_{C=C=C}$), 1053 (m, ν_{B-F}) cm^{-1}. ^1H NMR (CD_2Cl_2, 297 K, 300.134 MHz) (δ, ppm): 7.56−6.55 (m, 30 H, Ph), 6.33 (s, 1 H, CH=), 1.71 (d, $^2J_{(P,H)}$ = 10.5 Hz, 3 H, PMe), 1.64 (s, 18 H, C$_6$Me$_6$). Anal. Calcd (found) for $C_{54}H_{52}BClF_4OPRu$: C, 66.77 (65.90), H, 5.40 (5.38); Cl, 3.65 (4.14).

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