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Ruthenium Acetylide Oxidation: From Stable Radicals to Allenylidene Synthesis via γ-Elimination of H^+

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Oxidation of ruthenium(II) acetylides *trans*-[Cl(dppe)$_2$Ru−C≡C−CHR$_2$] (R = H, CH$_3$, Ph) leads to cationic radicals of which the stability is found to be highly influenced by the nature of R. This oxidative process leads to a stable cationic radical (R = CH$_3$, H) or to its rearrangement into a neutral radical, *trans*-[Cl(dppe)$_2$Ru−C≡C−C$^•$(R)$_2$] for R = Ph. This unprecedented γ-elimination of a proton provides both the allenylidene *trans*-[Cl(dppe)$_2$Ru═C═C═CR$_2$]PF$_6$ and the vinylidene *trans*-[Cl(dppe)$_2$Ru═C═CH−CHR$_2$]PF$_6$. The allenylidene can be selectively obtained from the acetylide in the presence of a base.

Introduction

Understanding and rationalizing the reactivity of carbon-rich transition metal complexes attract current interest.[1−12] The design, preparations, and applications of metallacumulenes [M]═(C═)$_n$CR$_1$R$_2$ are now well documented;[1−5] ruthenium allenylidenes (n = 3) represent, for instance, valid alternatives to Grubbs' catalysts for olefin metathesis.[4] In parallel, the development of synthetic routes toward metal acetylides has progressed rapidly, and there are constant studies on their properties or chemical reactivity, as they are known to promote carbon coupling reactions as well as catalytic transformations.[6,7] All these carbon-rich species also provide valuable synthons for polymetallic species or metal-containing polymers,[8−10] supramolecular architectures,[11] and molecular switches[12] and are promising in molecular-scaled electronics.[10]

Owing to the increasing demand, i.e., the development of highly efficient selective synthetic methods and new materials, novel compounds need to be processable and characterizable. It is clear that great variation of ligands and metals of different oxidation states is required. Systematic studies of their reactivity and properties will induce more applications. For this purpose, our current research deals with the synthesis, the reactivity, and the electronic properties of acetylides [M]−(C≡C)$_n$−R and cumulenylidenes [M]═(C═)$_n$CR$_1$R$_2$ complexes.[3,5,8] Stimulated by the fact that radical species have been recently proposed as intermediates in metathesis,[13] we recently demonstrated that the reduction of cationic ruthenium cumulenylidenes of the type [Cl(dppe)$_2$Ru═C═C═CR$_2$]PF$_6$ (dppe: Ph$_2$PCH$_2$CH$_2$PPh$_2$) occurs on the carbon chain and that the electron is located at the termini of this chain as a general trend.[5a] By contrast, concerning the oxidation of ruthenium acetylides [Ru]−C≡C−R, a large part of the electron removed originates from the metal[14] (Ru^{II}/Ru^{III}) but little is known on the stability of these oxidation states. Herein, we report our results on the influence of the nature of the acetylide ligand on the oxidation of *trans*-[Cl(dppe)$_2$Ru−C≡C−CHR$_2$] complexes. We have shown that (i) the stability

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(1) (a) Werner, H. *Chem. Commun.* **1997**, 903. (b) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (c) Cardieno, V.; Gamasa, M. P.; Gimeno, J. J. *Eur. J. Inorg. Chem.* **2001**, 571.

(2) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178−180*, 409.

(3) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

(4) (a) Furstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315. (b) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 2249. (c) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 615. (d) Picquet, M.; Touchard, D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **1999**, 141. (e) Osipov, S. N.; Artyushin, O. I.; Kolomiets, A. F.; Bruneau, C.; Picquet, M.; Dixneuf, P. H. *Eur. J. Org. Chem.* **2001**, 3891.

(5) (a) Rigaut, S.; Maury, O.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 373. (b) Touchard, D.; Haquette, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. *Organometallics* **1998**, *17*, 3844.

(6) (a) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2001**, *48*, 71. (b) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79. (c) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.

(7) (a) Hill, H. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 7, pp 411−417. (b) Stang, P. J.; Diederich, F. *Modern Acetylene Chemistry*; VCH: Weinheim, 1995.

(8) (a) Rigaut, S.; Le Pichon, L.; Daran, J.-C.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 1206. (b) Lebreton, C.; Touchard, D.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Inorg. Chim. Acta* **1998**, *272*, 188.

(9) Wong, K. T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259.

(10) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (c) Ward, M. D. *Chem. Ind.* **1996**, *15*, 568. (d) Ziessel, R.; Hissler, M.; El-Gayhouri, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178−180*, 125. (e) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G. *Adv. Organomet. Chem.* **1999**, *43*, 349. (f) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (g) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (h) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (i) Wu, I. Y.; Lin, J. T.; Wen, Y. S. *Organometallics* **1999**, *18*, 320.

(11) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19.

(12) (a) Fillaut, J.-L.; Price, M.; Johnson, A. L.; Perruchon, J. *Chem. Commun.* **2001**, 739. (b) Yam, V. W.-W., Tang, R. P.-L.; Wong, K. M.-C.; Cheung, K.-K. *Organometallics* **2001**, *20*, 4476.

(13) (a) Amir-Ebrahimi, V.; Hamilton, J. G.; Nelson, J.; Rooney, J. J.; Thompson, J. M.; Beaumont, A. J.; Rooney, A. D.; Harding, C. J. *Chem. Commun.* **1999**, 1621.

(14) (a) Koentjoro, O. F.; Rousseau, R.; Low, P. J. *Organometallics* **2001**, *20*, 4502. (b) McGrady, J. E.; Lovell, T.; Stranger, R.; Humphrey, M. G. *Organometallics* **1997**, *16*, 4004. (c) Winter, R. F. *Eur. J. Inorg. Chem.* **1999**, 2121. (d) Winter, R. F.; Hornung F. M. *Organometallics* **1999**, *18*, 4005.

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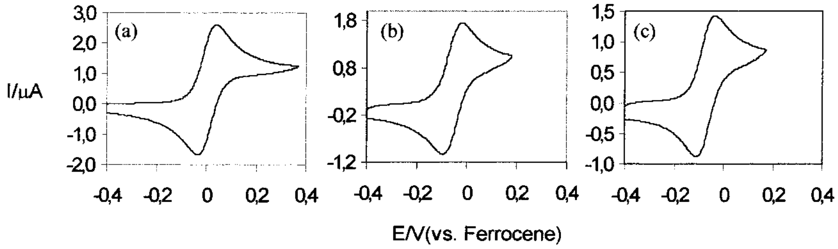
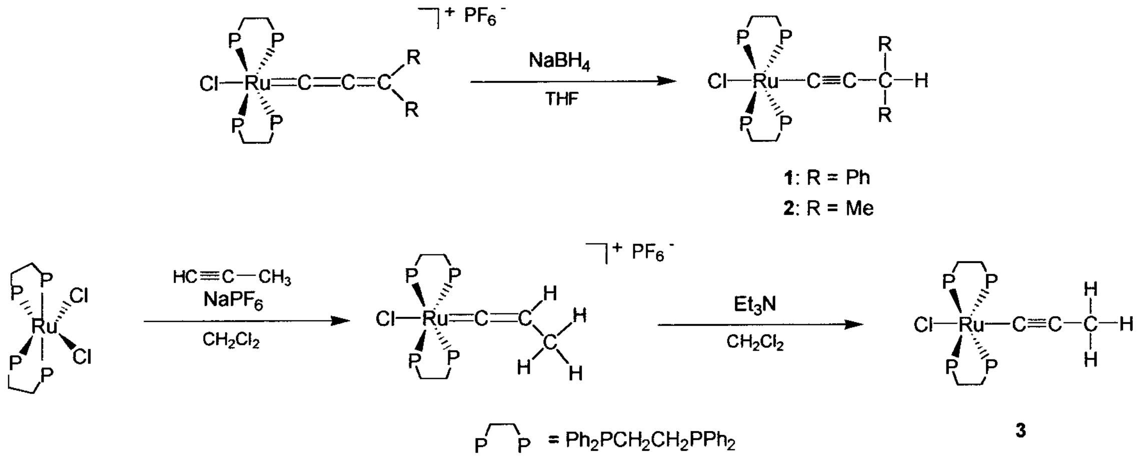


Figure 1. Cyclic voltammetry responses (CH_2Cl_2, Bu_4NPF_6 0.1 M, $\nu = 100$ mV s^{-1}) reported vs internal ferrocene for (a) *trans*-[Cl(dppe)$_2$Ru−C≡C−CHPh$_2$] (**1**), (b) *trans*-[Cl(dppe)$_2$Ru−C≡C−CH(CH$_3$)$_2$] (**2**), and (c) *trans*-[Cl(dppe)$_2$Ru−C≡C−CH$_3$] (**3**).

Scheme 1



of the resulting cationic radical is highly influenced by the nature of R; (ii) stable radical cations are formed when R = CH_3, H; (iii) a rearrangement of these species takes place via an unprecedented γ-elimination of a proton when R = Ph to afford both the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−CHR$_2$]PF$_6$ and the allenylidene *trans*-[Cl(dppe)$_2$Ru=C=C=CR$_2$]PF$_6$; (iv) an advantage of this process can be taken to offer a new route to metal allenylidene species by forcing the deprotonation, e.g., from the alkynyl complexes via oxidation in the presence of pyridine.

Results and Discussion

Nucleophiles are susceptible to add either on the C_α or on the C_γ atom of an allenylidene ligand.[15] Complexes with metal fragments bearing bulky phosphines lead to the regioselective addition on C_γ.[1] Ruthenium(II) *trans*-[Cl(dppe)$_2$Ru−C≡C−CHPh$_2$] (**1**) and *trans*-[Cl(dppe)$_2$Ru−C≡C−CH(CH$_3$)$_2$] (**2**) acetylides were obtained via the selective nucleophilic addition of H^- to the corresponding cationic allenylidenes *trans*-[Cl(dppe)$_2$Ru=C=C=CR$_2$]PF$_6$ (R = Ph, CH$_3$).[5a] These reductions were performed using $NaBH_4$ in THF[16] (Scheme 1), and the deeply colored cationic complexes quickly led to colorless solutions of **1** or **2**. These complexes have been characterized by ^1H, ^{13}C, and ^{31}P NMR and high-resolution mass spectrometry. ^{31}P analysis exhibits one resonance respectively at 51.54 (**1**) and 50.47 (**2**) ppm, showing that the four phosphorus atoms are equivalent and that the Cl atom and alkynyl ligand are in *trans* position. The most characteristic features of the ^1H NMR data are the hydrogen atom on C_γ at 4.77 ppm for **1** (singlet) and 2.43 ppm for **2** (septuplet, $^3J_{CH} = 6.5$ Hz). In addition, characteristic IR vibration stretches are obtained, $\nu_{C\equiv C} = 2085$ (**1**), 2086 (**2**) cm^{-1}. The third acetylide, *trans*-[Cl(dppe)$_2$Ru−C≡C−CH$_3$] (**3**), was obtained from *cis*-[(dppe)$_2$RuCl$_2$] in a propyne atmosphere, with a mild halide abstracting agent (NaPF$_6$) followed by the deprotonation of the resulting vinylidene intermediate with Et$_3$N (Scheme 1). The acetylide structure is supported by the ^1H NMR spectra showing the methyl signal at 1.40 ppm and the FTIR measurement with $\nu_{C\equiv C} = 2110$ cm^{-1}. The singlet observed at 50.46 ppm in ^{31}P NMR reveals the *trans* orientation of the propynyl group and of the chlorine atom.

Cyclic voltammetry (CV) was used to investigate the electrochemical behavior of the three acetylides *trans*-[Cl(dppe)$_2$Ru−C≡C−CHPh$_2$] (**1**), *trans*-[Cl(dppe)$_2$Ru−C≡C−CH(CH$_3$)$_2$] (**2**), and *trans*-[Cl(dppe)$_2$Ru−C≡C−CH$_3$] (**3**) (Figure 1). Complex **1** undergoes a well-defined one-electron reversible oxidation *on the CV scale* ($E° = 0.02$ V vs ferrocene) (Table 1). For complex **2**, an easier one-electron reversible oxidation ($E° = -0.07$ V vs ferrocene) is observed due to the electron releasing effect of the isopropyl group. The oxidation potential of **3** is the same as that of **2** ($E° = -0.07$ V vs ferrocene), showing an analogous acceptor character for the both carbon ligands in **2** and **3**. To a first approximation, these reversible one-electron-step oxidations could be viewed as essentially involving the Ru^{II}/Ru^{III} system.[14]

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[15] (a) Esteruelas, M. A.; Gomez, A. V.; Lopez, A.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

[16] Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. Nucleophilic addition in methanol leads to additional displacement of the chlorine atom by H^- to [H(dppe)$_2$Ru−C≡C−CHR$_2$]: Rigaut, S.; Mousset, F.; Touchard D.; Dixneuf, P. H. Unpublished work.

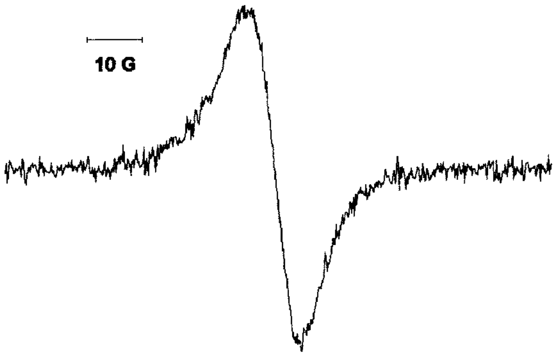

Figure 2. ESR spectra resulting from the oxidation of **1**, $g = 2.0039$.

Table 1. Electrochemistry Data for Complexes 1−5[a]

	$E°_{OX1}$[b]	E_{paOX2}[c]	$E°_{RED}$[b]
$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CHPh_2]$ (**1**)	0.02	1.07	
$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH(CH_3)_2]$ (**2**)	−0.07	1.03	
$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH_3]$ (**3**)	−0.07	0.99	
$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (**4**)	0.99[d]		−1.03
$[Cl(dppe)_2Ru{=}C{=}CH{-}CHPh_2]PF_6$ (**5**)	1.11[d]		−1.93[c,e]

[a] Measurements were performed in CH_2Cl_2 using Bu_4NPF_6 0.1 M, $\nu = 100$ mV s^{-1}. [b] Quasi reversible redox processes $\Delta E_p \approx 60$ mV, $I_{pc}/I_{pa} \approx 1$. Potential are reported in V vs ferrocene. [c] Peak potential of irreversible processes. [d] $\Delta E_p \approx 75$ mV, $I_{pc}/I_{pa} < 1$. [e] $\nu = 400$ mV s^{-1}.

Complexes **1**, **2**, and **3** give a second irreversible oxidation at a much higher potential (not shown) attributed to the Ru^{III}/Ru^{IV} system. Meanwhile, despite the chemical reversibility of the first oxidation observed for compound **1** at a scan rate down to a few mV s^{-1} ($I_{pc}/I_{pa} > 0.95$), we noticed that when a microelectrolysis of the solution was conducted as a pretreatment during several seconds (∼30 s, $E_{applied} = 0.5$ V), the next CV scan showed in the cathodic region two small reduction waves at $E_{pc1} = -1.06$ V and $E_{pc2} = -1.95$ V ($\nu = 400$ mV s^{-1}). As the species responsible for these waves are generated only when a pre-microelectrolysis is performed, this suggests that the initial Ru^{III} species undergoes a slow chemical transformation. By contrast, complexes **2** an **3** do not show this behavior.

Chemical oxidation of acetylides **1**, **2**, and **3** were conducted with 1 equiv of ferrocenium salt $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in methylene chloride. The redox potential of this oxidant is not favorable[17] for **1**, but we assumed that the driving force, i.e., the consecutive chemical reaction observed by the electrochemical analysis, would lead to the total displacement of the equilibrium. After 1 h the reaction was complete and a 1:1 mixture of the well-known ruthenium allenylidene *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (**4**)[5b] along with the vinylidene *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CH\ Ph_2]PF_6$ (**5**) was recovered (Scheme 2). The products were separated by fractional crystallizations, and *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CHPh_2]PF_6$ (**5**) was fully identified by NMR, IR, and high-resolution mass spectroscopies. The characteristic IR vibration stretch for Ru=C=C is observed at 1645 cm^{-1}. ^{31}P NMR analysis exhibits one resonance at 43.78 ppm (s). The ^{1}H NMR shows the signal for the vinylidene proton as a doublet of quintets at 3.35 ppm ($^3J_{HH} = 11.1$ Hz, $^4J_{PH} = 2.7$ Hz) as expected and for the hydrogen atom on C_γ as a doublet at 4.15 ppm ($^3J_{HH} = 11.1$ Hz). In the ^{13}C NMR, a quintet for C_α is observed at 344.35 ppm ($^2J_{PC} = 13$ Hz). CV studies revealed that both **4** and **5** display a reduction wave, a reversible one with $E° = -1.03$ V vs ferrocene for **4** ($E_{pc} \approx -1.06$ V) and an irreversible one with $E_{pc} = -1.93$ V vs ferrocene for **5** ($\nu = 400$ mV s^{-1}). These potentials match those observed after microelectrolysis, confirming that the nature of the products is the same in both experiments. It is noteworthy that their oxidation potential is high and they do not interfere with ferrocenium salt in the oxidation reaction (Table 1).

The reactivities of the *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH(CH_3)_2]$ (**2**) and *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH_3]$ (**3**) complexes were different. Monitoring the oxidation reactions with ^{31}P NMR did not show a following reaction as for **1**, but only the slow appearance of small amounts of *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CH(CH_3)_2]PF_6$ (**6**) and *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CH_3]PF_6$ (**7**) vinylidenes, respectively. To quantitatively evaluate the stability of the oxidized forms arising from **2** and **3**, oxidations were followed after 1 h by reduction with 1 equiv of cobaltocene $[(\eta^5\text{-}C_5H_2)_2Co]$.[17b,18] With complex **2**, 95% of the starting acetylide and 5% of the *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CH(CH_3)_2]PF_6$ (**6**) vinylidene (evaluated via ^{1}H NMR) were recovered (Scheme 2). Compound **6** was unambiguously identified. A characteristic IR vibration stretch is observed at 1647 cm^{-1}($\nu_{=C=C}$). The ^{1}H NMR spectrum shows the vinylidene proton as a doublet of quintets at 2.02 ppm ($^3J_{HH} = 9.7$ Hz, $^4J_{PH} = 2.1$ Hz) and the hydrogen atom on C_γ as a doublet of septuplets at 2.09 ppm ($^3J_{HH} = 9.7$ Hz, $^3J_{HH} = 6.0$ Hz). The same behavior was observed with **3**: oxidation and reduction lead back to 85% of the acetylide and to 15% of the *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CH_3]PF_6$ (**7**) vinylidene complex. The ^{1}H NMR spectrum of **7** presents a broad signal for the vinylidene proton at 2.49 and a doublet at 0.91 ppm ($^3J_{HH} = 6.8$ Hz) for the methyl group. The oxidized species issued from **2** and **3** were then thermally stable, and the formation of **6** and **7** was certainly induced by incorporation of a proton or a hydrogen from the medium by those cationic radicals (vide supra). For complex **3**, it is worth noting that residual water led to partial hydrolysis of the carbon chain to *trans*-$[Cl(dppe)_2Ru(CO)]PF_6$ (**8**), identified by HRMS ($m/z = 961.1402$), via a regioselective cleavage of the $C_\alpha{-}C_\beta$ bond.[19]

The presence of a phenyl group in the alkynyl ligand of **1** led to a cationic radical with a specific reactivity with respect to **2** and **3**. To understand the origin of the odd reactivity of the *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CHPh_2]$ (**1**) complex and the source of the β-hydrogens of the vinylidene complexes, we synthesized the *trans*-[Cl-

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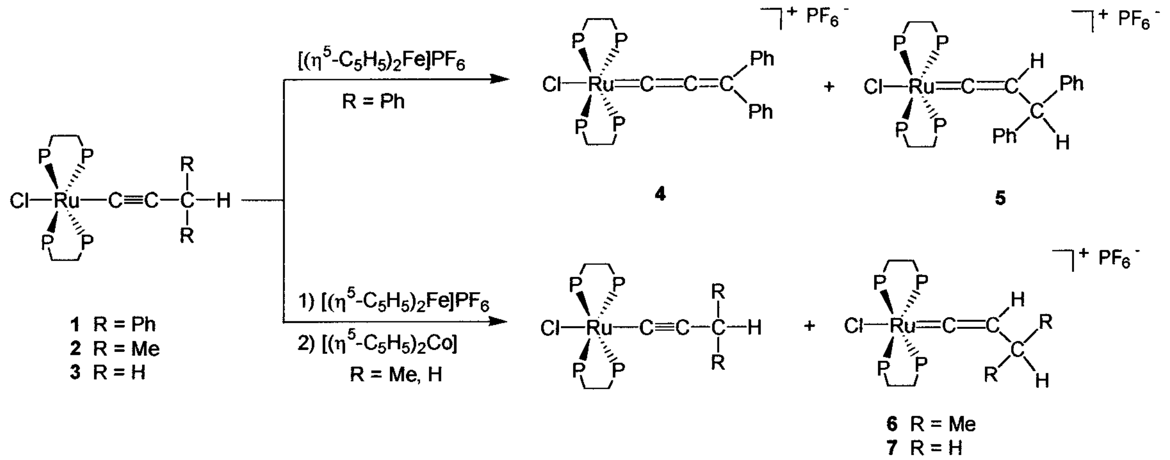
[17] (a) Quantitative prediction assuming totally reversible redox agents leads to a ratio $[\mathbf{1}^+]/[\mathbf{1}]$ of 40/60, see ref b. (b) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

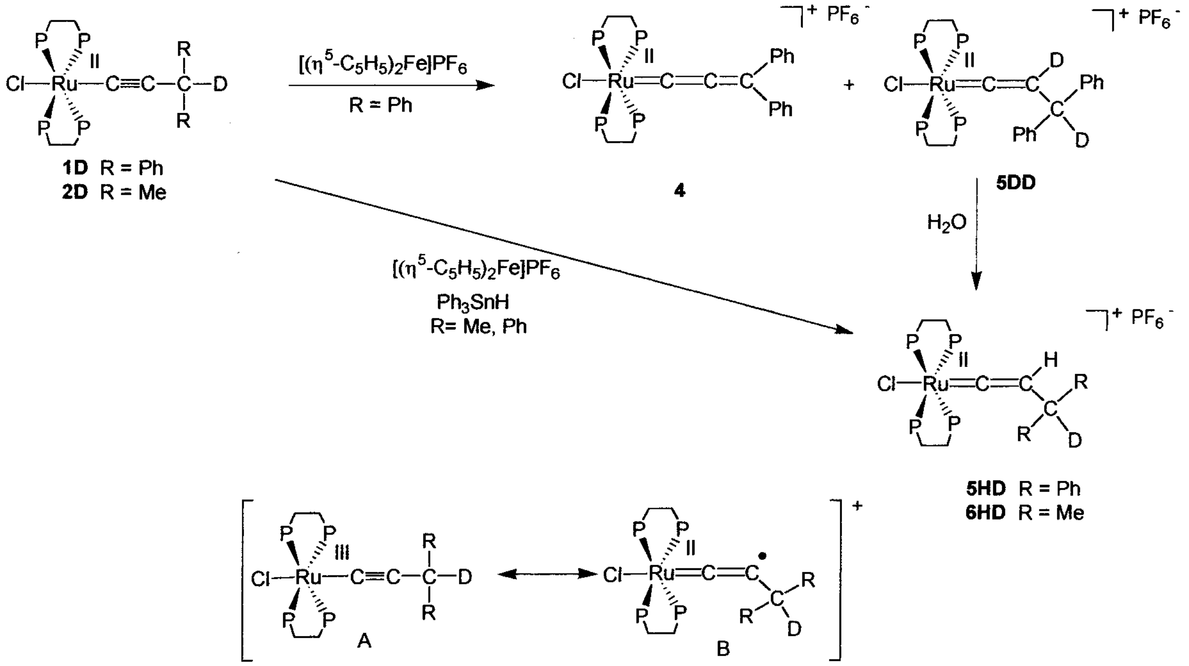
[18] Cobaltocene ($E° = -1.33$ V vs ferrocene) is not able to reduce vinylidene **5** and **6**, which both show an irreversible reduction wave with respectively $E_{pc} = -1.90$ V and -1.97 V (100 mV s^{-1}, V vs ferrocene).

[19] Hydrolysis of metal vinylidenes has already been reported to give carbonyl species and the unsatured hydrocarbon derived from the homologation of vinylidene substituent. See: (a) Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5. (b) Bianchini, C.; Cazares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc* **1996**, *118*, 4585. However in the present case, **7** is not sensitive to hydrolysis on the time scale of the reaction, and **8** then results from the hydrolysis of the radical intermediate.

Scheme 2



Scheme 3



(dppe)$_2$Ru−C≡C−CDPh$_2$] (**1D**) and *trans*-[Cl(dppe)$_2$Ru−C≡C−CD(CH$_3$)$_2$] (**2D**) acetylides deuterated on the C$_\gamma$ position by reduction of the allenylidene compounds with NaBD$_4$. When the oxidation of **1D** was carried out in the same conditions as for **1**, a 1:1 mixture of the allenylidene **4** and the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=C*D*−C*D*Ph$_2$]PF$_6$ (**5DD**) deuterated on the C$_\beta$ and C$_\gamma$ positions was obtained (Scheme 3). Indeed, the ^{1}H NMR spectrum of **5DD** did not show any signal for the hydrogen on both C$_\beta$ and C$_\gamma$ positions. This structure was confirmed by addition of a drop of water to the mixture, which gave fast exchange with the acidic vinylidene hydrogen and afforded *trans*-[Cl(dppe)$_2$Ru=C=C*H*−C*D*Ph$_2$]PF$_6$ (**5HD**). The ^{1}H NMR spectrum shows a quintet at 3.25 ppm ($^4J_{PH} = 2.7$ Hz) indicative of the presence of a proton on C$_\beta$ only coupled with the four phosphorus. The oxidation performed from *trans*-[Cl(dppe)$_2$Ru−C≡C−CD(CH$_3$)$_2$] (**2D**) acetylide leads to the formation of the *trans*-[Cl(dppe)$_2$Ru=C=C*H*−C*D*-(CH$_3$)$_2$]PF$_6$ (**6HD**) vinylidene deuterated only on the C$_\gamma$ position. The ^{1}H NMR signal at 2.01 ppm suggests the presence of one proton on C$_\beta$. No signal is present for a H on C$_\gamma$, while a singlet is observed for the methyl groups at 0.49 ppm. Chemical oxidation reactions of compounds **1D** and **2D** were also carried out with further fast addition of Ph$_3$SnH, which is known as a specific radical quencher by H$^\bullet$ transfer.[20] On the basis of NMR data, these reactions led to the complete disappearance of **1D** and **2D**, and the products formed were the *trans*-[Cl(dppe)$_2$Ru=C=CH−CDPh$_2$]PF$_6$ (**5HD**) and the *trans*-[Cl(dppe)$_2$Ru=C=CH−CD(CH$_3$)$_2$]PF$_6$ (**6HD**) vinylidenes, respectively (Scheme 3).

These results associated with the electrochemical experiments suggest several comments. (i) For **1** (and **1D**) an *intermolecular* hydrogen (deuterium) transfer occurs between two acetylide complexes (or the oxidized forms) to lead to **4** and **5** (**5DD**). (ii) In the case of **2D** and **2**, the small amount of vinylidene observed after oxidation and reduction is the result of incorporation of a hydrogen (or a proton) from the reaction medium. (iii) The trapping reaction with Ph$_3$SnH led to the sole

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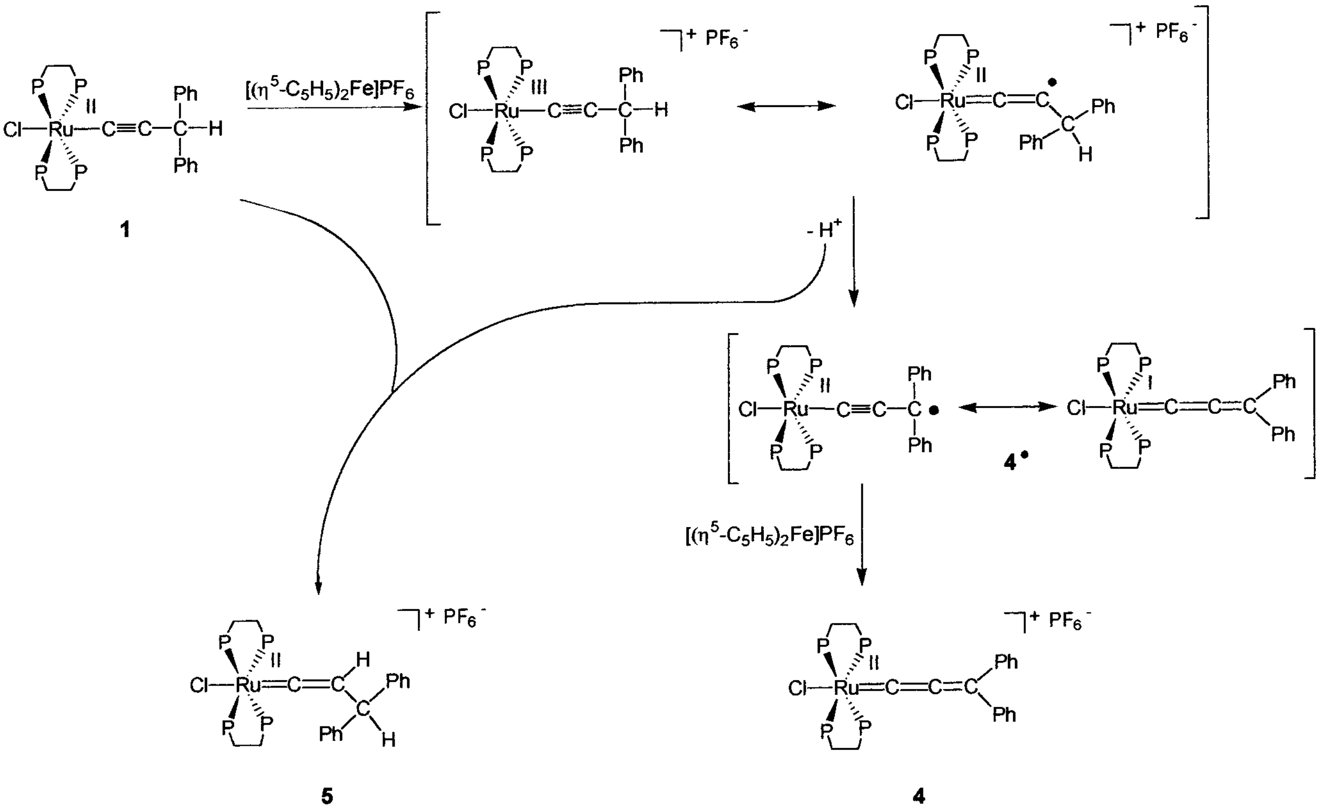
[20] (a) Tanner, D. D.; Diaz, G. E.; Potter, A. *J. Org. Chem.* **1985**, *50*, 2149. (b) Covert, K. J.; Wolczanski, P. T.; Hill, S. A.; Krusic, P. J. *Inorg. Chem.* **1992**, *31*, 66.

Scheme 4



formation of the vinylidenes complex **5HD** or **6HD** and inhibited the intermolecular migration of the deuterium on C_γ. This involves the direct oxidation of starting acetylides as the first step of the mechanism in all cases. Indeed, in this kind of complex, the electron is known to be mostly located on the metal[14] (form **A**, Scheme 3) but a contribution resulting from a metal–carbon π interaction where the single electron is delocalized over the carbon chain (form **B**) cannot be excluded and clarifies the formation of the vinylidenes. (iv) These two last conclusions could be extended to **3**. The weaker steric protection of its carbon chain could explain on one hand the larger amount of vinylidene present after reduction and on the other hand the occurrence of hydrolysis of the chain when traces of water are present, as this feature is not observed for **1** and **2**.

To completely rationalize the formation of **4** and **5** from **1**, the reaction could be related to anodic oxidation of organic compounds such as anilines.[21] Those cationic radicals lead to more stable neutral radicals by losing a proton able to protonate the starting material. Considering the oxidation of **1**, the most appropriate way to form **4** and **5** is the γ-elimination of a proton, which is able to attack another molecule of acetylide to form *trans*-$[Cl(dppe)_2Ru{=}C{=}CH{-}CPh_2H]PF_6$ (**5**) (Scheme 4), as we assume that there is a non-negligible amount of nonoxidized complex in the medium (vide infra). Indeed ruthenium acetylides can be readily protonated to vinylidene;[5b,22] this was verified with complex **1** treated with acids such as $HBF_4{\cdot}Et_2O$ or diluted aqueous HPF_6. On the other hand, the neutral radical *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}Ph_2]$ (**4**$^\bullet$) resulting from the γ-elimination is oxidized by ferrocinium salt to one molecule of the allenylidene *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (**4**) ($E° = -1.03$ V vs ferrocene). This hypothesis is supported by the observation of a broad ESR signal at $g = 2.0039$, when the reaction was carried out in the ESR cavity at 100 K. This can be attributed to the acetylide radical *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}(Ph)_2]$[5b,23] even if the fine structure was not observed at this temperature.[24] It is noteworthy that (i) no stable dimerization of **4**$^\bullet$ was detected as reported for vinylidene oxidation,[25] probably because of the fast following electron transfer and (ii) these results associated with the absence of reaction between **1** and Ph_3SnH rule out the hypothesis of a mechanism involving a hydrogen atom transfer.

The fact that proton elimination does not occur with *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH(CH_3)_2]$ (**2**) and *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH_3]$ (**3**) but only with *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CHPh_2]$ (**1**) could be explained in terms of stabilization of the neutral radical $[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}(R)_2]$ where the single electron is located on the carbon chain.[5a] When R = Ph, the radical $[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}(Ph)_2]$ is highly stabilized by the

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(21) Miras, M. C.; Silber, J. J.; Sereno, L. *Electrochim. Acta* **1988**, *7*, 851.

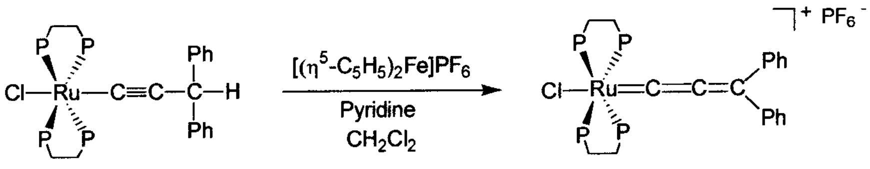
(22) For examples see: (a) Bruce, M. I. *Chem. Rev* **1991**, *91*, 197. (b) Albertin, G.; Antoniutti, S.; Bordignon, E.; Granzotto, M. *J. Oganomet. Chem.* **1999**, *585*, 83. (c) Cardierno, V.; Gamansa, M. P.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1857. (d) Bustello, E, Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2001**, 2391.

(23) The ESR signal of ferrocenium is too broad to be detectable above 78 K. See: Pins, R.; Reinders, F. J. *J. Am. Chem. Soc.* **1969**, *91*, 4929.

(24) It was not possible to observe the coupling at higher temperature when the solution was not frozen because of the fast reaction of the radical with ferrocenium salt present in the medium. We could not observe the Ru^{III} species either.

(25) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910.

Scheme 5



1 **4**

spin delocalization over the phenyl rings. By contrast, the electron-releasing methyl groups of **2** would make the radical $[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}(CH_3)_2]$ very reactive. The transition state for proton elimination is then lowered in the case of **1** with respect to **2** and the formations of **4**$^{\bullet}$ and **4** are likely to occur. As this transition state is too high for oxidized species issued from **2** and **3** (considering the lack of stabilizing groups for $[Cl(dppe)_2Ru{-}C{\equiv}C{-}C^{\bullet}H_2]$), the corresponding cationic radicals are stable.

Finally, it occurred to us that this mechanism could be used to prepare a ruthenium allenylidene complex from an acetylide bearing a hydrogen atom on the C_γ position if the leaving proton can be trapped. We found out that when the oxidation of **1** by ferrocenium salt was conducted in the presence of pyridine, nearly quantitative formation of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (**4**) allenylidene was obtained (Scheme 5). Two equivalents of ferrocenium salt $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ are necessary to complete the transformation, one for the oxidation of the acetylide complex and one for the oxidation of the neutral radical. During the reaction, the pyridine can either trap the proton directly from the cationic radical and/or deprotonate the vinylidene to regenerate the acetylide. This method might be an alternative pathway to obtain allenylidene species from acetylides if propargylic alcohols are not available and when a radical species could be stabilized on C_γ.

In conclusion, we have shown that ruthenium acetylides of the type *trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CHR_2]$ could be easily oxidized and that the stability of the metal-centered cationic radical depends on the nature of the substituents. If the structure is not able to stabilize a neutral radical on the C_γ of the carbon chain (R = H, CH_3), the cationic radical is thermally stable and only reactions with other reagents on C_β could occur depending on the steric protection of the chain. On the contrary, when the formation of a neutral radical can be stabilized at the termini of the chain on C_γ (R = Ph), proton elimination occurs and further oxidation leads to the cationic allenylidene species. A preparative method has been demonstrated based on this principle, and we anticipate that further developments should lead to the generalization of this reaction not only to other chain substituents or metal acetylides but also to longer chains.

Experimental Section

General Comments. The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were freshly distilled under argon using standard procedures. Chromatography and filtration were performed using alumina (Acros, activated neutral 50−200 μm). The EPR spectra were recorded using a EMX-8/2,7 Bruker spectrometer equipped with a Bruker nitrogen temperature controller ER4131VT02. The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a Pt disk, the reference electrode a saturated calomel electrode, and the counter electrode a platinum wire. Ferrocene was used as an internal reference, and all the measurements were carried out in CH_2Cl_2 solution with 0.1 M Bu_4NPF_6 as a supporting electrolyte. Mass spectra were recorded on a Zab SpecETOF FAB$^+$ spectrometer. Elemental analyses were sent out to the Lyon-Villeurbanne CNRS center. *cis*-$[(dppe)_2RuCl_2]$[26] and allenylidene compounds *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CR_2]PF_6$ (R = Ph, CH_3)[5b] were prepared as previously reported.

***trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CHPh_2]$ (1).** In a Schlenk tube, 300 mg of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (0.24 mmol) was introduced with 36 mg of $NaBH_4$ (0.96 mmol), and 20 mL of THF was added using a cannula. The red solution was discolored in 5 min. The solvent was removed under vacuum. The residue was extracted with a 1:1 mixture of CH_2Cl_2/ether (4 × 20 mL) and filtrated. After evaporation, the pale yellow solid was washed with pentane (10 mL), and 230 mg (0.21 mmol) of **1** was recovered (88% yield). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 51.54 (s, PPh_2). ^1H NMR (CD_2Cl_2): δ 7.71−6.86 (m, 50H, Ph), 4.77 (s, 1H, CH), 2.30−2.75 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 145.65−125.95 (Ph), 111.37 (s, $Ru{-}C{\equiv}\mathit{C}{-}$), 105.44 (quint., $Ru{-}\mathit{C}{\equiv}C{-}$, $^2J_{PC}$ = 16 Hz), 49.23 ($Ru{-}C{\equiv}C{-}\mathit{C}H{-}$), 30.95 ($CH_2$, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR: 2085 cm^{-1} ($\nu_{C\equiv C}$). HR-MS FAB$^+$ (*m*/*z*): 1125.2397 ([M + H]$^+$, calcd 1125.2378). Anal. Found for $C_{67}H_{59}P_4ClRu{\cdot}CH_2Cl_2$: C 67.48, H 5.17 (calcd C 67.54, H 5.09).

***trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CDPh_2]$ (1D).** The procedure was identical with that of **1** with 500 mg of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (0.39 mmol), 115 mg of $NaBD_4$ (2.64 mmol), and 40 mL of THF. After evaporation, 339 mg (0.30 mmol) of pale yellow **1D** was recovered (76% yield). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.57 (s, PPh_2). ^1H NMR (CD_2Cl_2): δ 7.90−6.85 (m, 50H, Ph), 2.30−2.75 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.44−127.48 (Ph), 111.36 (s, $Ru{-}C{\equiv}\mathit{C}{-}$), 105.15 (quint., $Ru{-}\mathit{C}{\equiv}C{-}$, $^2J_{PC}$ = 17 Hz), 32.48 (CH_2, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz). IR: 2067 cm^{-1} ($\nu_{C\equiv C}$). HR-MS FAB$^+$ (*m*/*z*): 1125.2433 ([M]$^+$, calcd 1125.2362).

***trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CH(CH_3)_2]$ (2).** The procedure was identical with that of **1** with 200 mg of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}C(CH_3)_2]PF_6$ (0.17 mmol), 26 mg of $NaBH_4$ (0.68 mmol), and 15 mL of THF. The green solution was discolored in 5 min, and 140 mg (0.14 mmol) of **2** as a pale yellow solid was recovered (80% yield). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 50.47 (s, PPh_2). ^1H NMR (CD_2Cl_2): δ 7.86−6.87 (m, 40H, Ph), 2.80−2.50 (m, 8H, CH_2), 2.43 (sept., 1H, CH, $^3J_{CH}$ = 6.5 Hz), 0.90 (d, 6H, CH_3, $^3J_{CH}$ = 6.5 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 138.3−127.18 (Ph), 116.97 (s, $Ru{-}C{\equiv}\mathit{C}{-}$), 96.77 (quint., $Ru{-}\mathit{C}{\equiv}C{-}$, $^2J_{PC}$ = 16 Hz), 31.22 (CH_2, $|^1J_{PC}+^3J_{PC}|$ = 22 Hz), 25.09 ($Ru{-}C{\equiv}C{-}\mathit{C}H{-}$), 24.28 ($CH_3$). IR: 2086 ($\nu_{C\equiv C}$). HR-MS FAB$^+$ (*m*/*z*): 1000.2002 ([M]$^+$, calcd 1000.1986). Anal. Found for $C_{57}H_{55}P_4ClRu{\cdot}CH_2Cl_2$: C 64.38, H 5.38 (calcd C 64.18, H 5.29).

***trans*-$[Cl(dppe)_2Ru{-}C{\equiv}C{-}CD(CH_3)_2]$ (2D).** The procedure was identical with that of **1** with 500 mg of *trans*-[Cl-

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[26] Chaudret, B.; Commengues, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

(dppe)$_2$Ru=C=C=C(CH$_3$)$_2$]PF$_6$ (0.44 mmol), 107 mg of NaBD$_4$ (0.96 mmol), and 40 mL of THF. After evaporation, 350 mg (0.35 mmol) of pale yellow **2D** was recovered (79% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.49 (s, PPh$_2$). ^{1}H NMR (CDCl$_3$): δ 7.86−6.87 (m, 40H, Ph), 2.80−2.50 (m, 8H, CH$_2$), 0.90 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 137.76−126.72 (Ph), 117.24 (s, Ru−C≡*C*−), 96.52 (quint., Ru−*C*≡*C*−, $^2J_{PC}$ = 15 Hz), 31.22 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 31 Hz), 23.98 (CH$_3$). IR: 2084 cm^{-1} ($\nu_{C\equiv C}$). HR-MS FAB$^+$ (*m/z*): 1001.2068 ([M]$^+$, calcd 1001.2049).

trans-[Cl(dppe)$_2$Ru=C=CH−CH$_3$]PF$_6$ (7). In a Schlenk tube, 830 mg of *trans*-[(dppe)$_2$Cl$_2$]PF$_6$ (0.86 mmol) was introduced with 290 mg of NaPF$_6$ (1.72 mmol) and 30 mL of CH$_2$Cl$_2$. The mixture was then placed under a propyne atmosphere and stirred 18 h. The brown solution was filtrated, and the solvent was removed under vacuum. The residue was washed with ether (3 × 15 mL) and dried. A brown solid was recovered (670 mg, 0.60 mmol, 70%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 42.40 (s, PPh$_2$), −143.67 (sept., PF$_6$, $^1J_{PF}$ = 715 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.45−7.05 (m, 40H, Ph), 3.00−2.60 (m, 8H, CH$_2$), 2.49 (m, 1H, CH), 0.91 (d, 3H, CH$_3$, $^3J_{HH}$ = 6.8 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 352.93 (quint., Ru=*C*=*C*−, $^2J_{PC}$ = 17 Hz), 134.13−128.05 (Ph), 99.82 (s, Ru=C=*C*−), 29.03 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz), 4.85 (CH$_3$). IR: 1670 ($\nu_{=C=C}$), 838 (ν_{PF6}) cm^{-1}. HR-MS FAB$^+$ (*m/z*): 973.1752 ([M]$^+$, calcd 973.1764). Cyclic voltammetry: (CH$_2$Cl$_2$, ^{n}Bu$_4$NPF$_6$ 0.1 M, 200 mV s^{-1}, V vs ferrocene): $E_{pa,ox}$ = 1.00 V, $E_{pc,red}$ = − 1.97 V.

trans-[Cl(dppe)$_2$Ru−C≡C−CH$_3$] (3). In a Schlenk tube, 450 mg of *trans*-[Cl(dppe)$_2$Ru=C=CHCH$_3$]PF$_6$ (**7**) (0.40 mmol) was dissolved in 40 mL of CH$_2$Cl$_2$, and 155 μL of Et$_3$N (1.2 mmol) was added using a syringe. The orange solution turned yellow and was stirred 30 min. The mixture was washed with water (2 × 20 mL), dried, and concentrated before filtration on basic alumina (elution with ether). After evaporation, 253 mg (0.26 mmol) of **3** was recovered (65% yield). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 50.46 (s, PPh$_2$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.47−6.83 (m, 40H, Ph), 2.75−2.40 (m, 8H, CH$_2$), 1.40 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 136.74−126.62 (Ph), 103.00 (s, Ru−C≡*C*−), 98.01 (quint., Ru−*C*≡*C*−, $^2J_{PC}$ = 16 Hz), 31.91 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz), 24.28 (CH$_3$). IR: 2110 ($\nu_{C\equiv C}$) cm^{-1}. HR-MS FAB$^+$ (*m/z*): 972.1666 ([M]$^+$, calcd 972.1673). Anal. Found for C$_{57}$H$_{55}$P$_4$ClRu·CH$_2$Cl$_2$: C 63.73, H 4.91 (calcd C 63.61, H 5.05).

Oxidation of _trans_-[Cl(dppe)$_2$Ru−C≡C−CHPh$_2$] (1). In a Schlenk tube, to 200 mg of **1** (0.18 mmol) and 60 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.18 mmol) was added 30 mL of CH$_2$Cl$_2$. The solution was stirred for 1 h at room temperature. The residue was washed with pentane (3 × 20 mL). ^{1}H NMR showed that the residue was a 1:1 mixture of *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ (**4**) and the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−CPh$_2$H]PF$_6$ (**5**). After several fractional crystallizations in a mixture of dichloromethane/pentane, 85 mg of light pink crystals of *trans*-[Cl(dppe)$_2$Ru=C=CH−CPh$_2$H]PF$_6$ (**5**) (0.07 mmol) were isolated (39%). Spectroscopic data for **5**: ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.78 (s, PPh$_2$), −143.63 (sept., PF$_6$, $^1J_{PF}$ = 710 Hz). ^{1}H NMR (CDCl$_3$): δ 7.49−6.43 (m, 50H, Ph), 4.15 (d, 1H, CHPh$_2$, $^3J_{HH}$ = 11.1 Hz), 3.35 (d quint., 1H, =CH, $^3J_{HH}$ = 11.1 Hz, $^4J_{PH}$ = 2.7 Hz), 3.0−2.50 (m, 8H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 344.35 (quint., Ru=*C*=C−, $^2J_{PC}$ = 13 Hz), 143.02−127.08 (Ph), 107.96 (s, Ru=C=*C*−), 45.57 (C=CH−*C*HPh$_2$), 28.75 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz). IR: 1645 ($\nu_{=C=C}$), 837 (ν_{PF6}) cm^{-1}. HR-MS FAB$^+$ (*m/z*): 1125.2367 ([M]$^+$, calcd 1125.2378). Anal. Found for C$_{67}$H$_{60}$P$_5$F$_6$ClRu·CH$_2$Cl$_2$: C 60.01, H 4.67 (calcd C 60.25, H 4.61).

Oxidation of _trans_-[Cl(dppe)$_2$Ru−C≡C−CDPh$_2$] (1D). The procedure was identical with 200 mg of **1D** (0.18 mmol), 60 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.18 mmol), and 30 mL of CH$_2$Cl$_2$. ^{1}H NMR showed that the residue was a 1:1 mixture of *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ (**4**) and the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CD−CPh$_2$D]PF$_6$ (**5D**). Spectroscopic data for **5D**: ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.88 (s, PPh$_2$), −143.60 (sept., PF$_6$, $^1J_{PF}$ = 710 Hz). ^{1}H NMR (CDCl$_3$): δ 7.55−6.39 (m, 50H, Ph), 3.0−2.50 (m, 8H, CH$_2$). No signals were observed at 4.15 and 3.35 ppm. After addition of one drop of water and exchange of the vinylidene proton, *trans*-[Cl(dppe)$_2$Ru=C=CH−CPh$_2$D]PF$_6$ (**5HD**) is obtained. Spectroscopic data for **5HD**: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 43.78 (s, PPh$_2$), −143.63 (sept., PF$_6$, $^1J_{PF}$ = 710 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.52−6.40 (m, 50H, Ph), 3.35 (quint., 1H, =CH, $^4J_{PH}$ = 2.7 Hz), 3.0−2.50 (m, 8H, CH$_2$). No signal was observed at 4.15 ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 344.47 (quint., Ru=*C*=C−, $^2J_{PC}$ = 13 Hz), 143.41−127.40 (Ph), 108.07 (s, Ru=C=*C*−), 45.57 (C=CH−*C*HPh$_2$), 28.23 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 22 Hz).

Oxidation of _trans_-[Cl(dppe)$_2$Ru−C≡C−CDPh$_2$] (1D) and Addition of Ph$_3$SnH. In a Schlenk tube, to 45 mg of **1D** (0.03 mmol) and 10 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.03 mmol) was added 5 mL of CH$_2$Cl$_2$. Via a cannula, 21 mg (0.06 mmol) of Ph$_3$SnH dissolved in 5 mL of CH$_2$Cl$_2$ was further added. The solution was stirred for 1 h at room temperature, and the solvent was evaporated. ^{31}P and ^{1}H NMR analysis showed that the residue contained the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−CPh$_2$D]PF$_6$ (**5HD**).

Oxidation and Reduction of _trans_-[Cl(dppe)$_2$Ru−C≡C−CH(CH$_3$)$_2$] (2). In a Schlenk tube to 39 mg of **2** (0.04 mmol) and 13.5 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.04 mmol) was added 10 mL of CH$_2$Cl$_2$. The solution was stirred 1 h at room temperature, and 7.8 mg (0.04 mmol) of cobaltocene was added to the light green solution. The medium became pale yellow and was evaporated after 15 min. The residue was washed with pentane (3 × 10 mL). ^{1}H NMR showed that the residue contains a 95:5 mixture of the acetylide *trans*-[Cl(dppe)$_2$Ru−C≡C−CH(CH$_3$)$_2$] (**2**) and the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−C(CH$_3$)$_2$H]PF$_6$ (**6**). Spectroscopic data for **6**: ^{31}P{^{1}H} NMR (CDCl$_3$): δ 44.35 (s, PPh$_2$), −143.69 (sept., PF^6, $^1J_{PF}$ = 715 Hz). ^{1}H NMR (CDCl$_3$): δ 7.49−6.95 (m, 40H, Ph), 3.05−2.55 (m, 8H, CH$_2$), 2.09 (d sept., 1H, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.0 Hz), 2.02 (d quint., 1H, =CH, $^3J_{HH}$ = 9.7 Hz, $^4J_{PH}$ = 2.1 Hz), 0.49 (d, 6H, CH$_3$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 348.57 (quint., Ru=*C*=C−, $^2J_{PC}$ = 13 Hz), 133.74−127.97 (Ph), 112.69 (s, Ru=C=*C*−), 29.38 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 30 Hz), 24.70 (CH$_3$), 24.12 (*C*H(CH$_3$)$_2$). IR: 1647 ($\nu_{=C=C}$), 836 (ν_{PF6}) cm^{-1}. HR-MS FAB$^+$ (*m/z*): 1001.2067 ([M]$^+$, calcd 1001.2065). Cyclic voltammetry: (CH$_2$Cl$_2$, ^{n}Bu$_4$NPF$_6$ 0.1 M, 200 mV s^{-1}, V vs ferrocene): $E_{pa,ox}$ = 1.05 V, $E_{pc,red}$ = −1.90 V.

Oxidation of _trans_-[Cl(dppe)$_2$Ru−C≡C−CD(CH$_3$)$_2$] (2D) and Addition of Ph$_3$SnH. In a Schlenk tube to 50 mg of **2D** (0.05 mmol) and 17 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.05 mmol) was added 5 mL of CH$_2$Cl$_2$. Via a cannula, 35 mg (0.06 mmol) of Ph$_3$SnH dissolved in 5 mL of CH$_2$Cl$_2$ was added. The solution was stirred 1 h at room temperature, and the solvent was evaporated. ^{31}P and ^{1}H NMR showed that the residue contains the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−CD(CH$_3$)$_2$]PF$_6$ (**6HD**). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 44.16 (s, PPh$_2$), −145.88 (sept., PF$_6$, $^1J_{PF}$ = 710 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.6−6.80 (m, 40H, Ph), 3.10−2.60 (m, 8H, CH$_2$), 2.01 (br, 1H, =CH), 0.49 (s, 6H, CH$_3$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 348.89 (quint., Ru=*C*=C−, $^2J_{PC}$ = 13 Hz), 134.23−128.38 (Ph), 112.87 (s, Ru=C=*C*−), 29.68 (CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz), 24.80 (CH$_3$). IR: 1652 ($\nu_{=C=C}$), 839 (ν_{PF6}) cm^{-1}.

Oxidation and Reduction of _trans_-[Cl(dppe)$_2$Ru−C≡C−CH$_3$] (3). In a Schlenk tube to 20 mg of **3** (0.02 mmol) and 7.5 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.02 mmol) was added 10 mL of CH$_2$Cl$_2$. The solution was stirred 1 h at room temperature, and 4.5 mg (0.02 mmol) of cobaltocene was added to the light purple solution. The medium became pale yellow and was evaporated after 15 min. ^{1}H NMR showed that the residue contains a 85:15 mixture of the acetylide [Cl(dppe)$_2$Ru−C≡C−CH$_3$] (**3**) and the vinylidene *trans*-[Cl(dppe)$_2$Ru=C=CH−CH$_3$]PF$_6$ (**7**).

[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ (4) via Oxidation. In a Schlenk tube, to 69 mg of **1** (0.061 mmol) and 60 mg of ferrocinium salt [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$ (0.18 mmol) was added 10 mL of CH_2Cl_2. After 1 h at room temperature, 45 μL (0.60 mmol) of pyridine was added. The mixture was stirred overnight, washed with water (2 × 10 mL), and dried. After evaporation, the red residue was washed with pentane (3 × 20 mL). Crystallization (CH_2Cl_2/pentane) afforded 71 mg (0.056 mmol) of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]PF_6$ (**4**) (92%).

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