Articles

Amphoteric Allenylidene Ruthenium Complexes and the First Dinuclear Ruthenium Species with a Bis-alkenyl Carbyne Bridging Ligand

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Cationic ruthenium(II) allenylidenes *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)R]BF$_4$ (R = Ph, CH$_3$) can be deprotonated to generate neutral alkenyl acetylide metal *trans*-[Cl(dppe)$_2$Ru−C≡C−C(=CH$_2$)R] or protonated with HBF$_4$·Et$_2$O to lead to dicationic ruthenium(II) carbynes *trans*-[Cl(dppe)$_2$Ru≡C−CH=C(CH$_3$)R](BF$_4$)$_2$. The latter reaction was applied to transform a conjugated bis-allenylidene bridged diruthenium complex, *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)-*p*-C$_6$H$_4$−(CH$_3$)C=C=C=Ru(dppe)$_2$Cl](BF$_4$)$_2$, into the first bis-alkenyl carbyne ruthenium species *trans*-[Cl(dppe)$_2$Ru≡C−CH=C(CH$_3$)-*p*-C$_6$H$_4$−(CH$_3$)C=HC−C≡Ru(dppe)$_2$Cl](BF$_4$)$_4$.

Introduction

Allenylidene metal species [M]=C=C=CR^{1}R^2 and even cumulenylidenes have been largely developed since Selegue's 1982 breakthrough showing their direct synthesis from readily available propargylic alcohols.[1] Their design, preparation, and applications are now well documented.[2−9] Ruthenium(II) allenylidenes correspond to their most representative group showing interest for both innovative stoichiometric reactions[2,3] and catalysis.[5,6] For instance, [(*p*-cymene)RuCl(=C=C=CPh$_2$)-PCy$_3$)]$^+$X$^-$ precursors represent a valid alternative to alkylidene ruthenium catalysts for olefin metathesis.[5] These carbon-rich complexes are also valuable synthons for advanced architectures for molecular-scaled electronics due to the association of stable redox systems with carbon-rich systems.[9,10] By contrast, the synthesis of Fischer type carbyne complexes has always been a more laborious process.[11−16] Actually, ruthenium car-

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bynes are very scarce,[13−15] unlike their osmium analogues,[16] despite their interest as catalysts in olefin metathesis.[14c,15b] Synthetic routes usually involve the conversion of coordinated carbenes such as vinylidenes[14] and allenylidenes.[15]

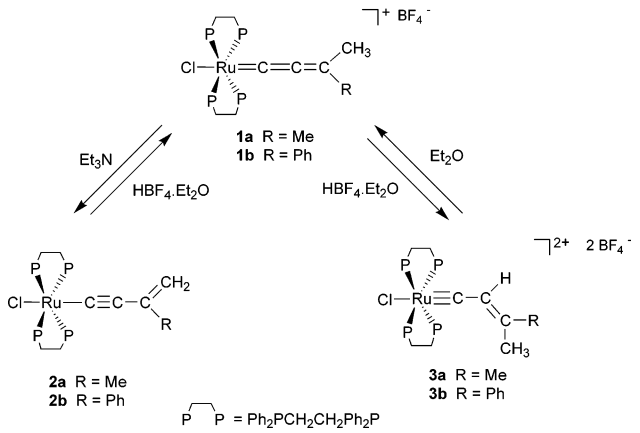
We recently reported that cationic allenylidenes *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_2$R$_1$)R$_2$]BF$_4$ (dppe = 1,2-bis(diphenylphosphino)ethane) react with a ruthenium acetylide complex as a route to rich bimetallic complexes via an original coupling reaction.[9a] This process involves as an initial step the easy deprotonation of the allenylidene complex on the δ carbon. The deprotonation/protonation study of ruthenium allenylidene now reveals (i) the amphoteric properties of ruthenium allenylidenes *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)R]BF$_4$, (ii) that protonation of these ruthenium allenylidenes provides alkenyl carbyne ruthenium species without decoordination of any ligand, and (iii) that the protonation of a conjugated bimetallic complex with a bis-allenylidene bridge offers a route to the first bis-carbyne ruthenium species. The objective of this paper is to report these new aspects of the chemistry of ruthenium allenylidene complexes.

Results and Discussion

Allenylidene species display an extensive reactivity.[2,3] Nucleophiles usually add either on the C$_\alpha$ or on the C$_\gamma$ atom of the allenylidene ligand.[17] However, allenylidene ruthenium complexes with metal fragments bearing electron-releasing bulky phosphines lead to the regioselective addition on C$_\gamma$ for steric and electronic reasons.[7,18] These observations were recently rationalized with computational studies.[7d] They also suggested that the HOMO localization would favor orbital-controlled addition on the C$_\beta$ atom. An additional feature of allenylidene reactivity consists in the deprotonation on a δ carbon to produce a ruthenium alkenyl acetylide by action of a weak base.[19] This should be a general characteristic for allenylidene with a −CHR^{1}R^2 group on the C$_\gamma$ carbon atom.

To verify the possible amphoteric behavior of allenylidenes, we used *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)R]-BF$_4$ (R = Ph, CH$_3$) complexes[9] (Scheme 1). Deprotonations of **1a**,**b** were performed using Et$_3$N in CH$_2$Cl$_2$. The deeply colored cationic complexes quickly led to pale yellow solutions of **2a**,**b**. After column chromatography to eliminate ammonium salts, these complexes were fully characterized. The ^{31}P analysis displays one resonance respectively at 50.60 (**2a**) and 50.91 (**2b**) ppm,

Scheme 1



showing that the four phosphorus atoms remain equivalent and that the chlorine atom and alkynyl ligand are in a *trans* orientation. The most characteristic features of the ^{1}H NMR data are the two coupled ethylenic hydrogen atoms on C$_\delta$. For **2b** the doublets are observed at 5.26 and 4.74 ppm with $^2J_{HH}$ = 2.2 Hz. In addition, characteristic IR vibration stretches are observed: $\nu_{C\equiv C}$ = 2049 (**2a**), 2041 (**2b**) cm^{-1} and $\nu_{C=C}$ = 1586 (**2a**), 1557 (**2b**) cm^{-1}. These alkenyl acetylides are easily protonated in the presence of 1 equiv of HBF$_4$·Et$_2$O to regenerate the allenylidene species **1a**,**b**.

By attempting to protonate ruthenium alkenyl acetylides **2a**,**b** to obtain ruthenium allenylidenes **1a**,**b**, with a slight excess of acid (1.2 equiv), we observed in addition to **1a**,**b** the formation of a small amount of a thermally stable product. When protonations were carried out starting from the allenylidene complexes **1a**,**b** with a large excess of HBF$_4$·Et$_2$O, the formation of the same products identified as alkenyl carbynes (**3a**,**b**) was observed. Such a ruthenium allenylidene protonation reaction was recently reported in two other examples leading to alkenyl carbynes [ClRu≡C−CH=CPh$_2$-(κ^2-*P*,*O*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)(κ^2-*P*-Cy$_2$PCH$_2$CH$_2$OCH$_3$)]-(BF$_4$,PF$_6$)$_2$[15a] and [Cp*(dippe)Ru≡C−CH=CPh$_2$]-(B(Ar$_F$)$_4$)$_2$.[15c] The latter was the only one obtained without decoordination of any ligand.

For example, total conversion to **3a** was obtained from **1a** with the addition of 3 equiv of HBF$_4$·Et$_2$O, and from the alkenylmetal acetylide **2a** with 4 equiv. A large excess of acid was necessary in order to displace the equilibrium. The carbyne structure of **3a** is supported by NMR evidence. The ^{1}H NMR spectrum shows a complex signal at δ = 6.19 ppm attributed to the β hydrogen. Interestingly, the two methyl groups are quite different: one is observed at 1.68 ppm and the other one at −0.11 ppm. The latter high-field chemical shift is rather surprising and is likely due to the shielding of the dppe ligands in close proximity of a *cis* methyl group with respect to the ruthenium. This is also supported by a NOESY experiment showing a correlation feature between the aromatic protons of the dppe ligand and those of the methyl group. Furthermore, another correlation is also observed between the proton at 6.19 ppm and those of the other methyl group at 1.68 ppm, corroborating this attribution. The ^{31}P NMR shows a singlet for the four equivalent phosphorus atoms at higher field than for allenylidenes (δ = 36.53 ppm vs 42.2 ppm), showing the free rotation of the carbon chain

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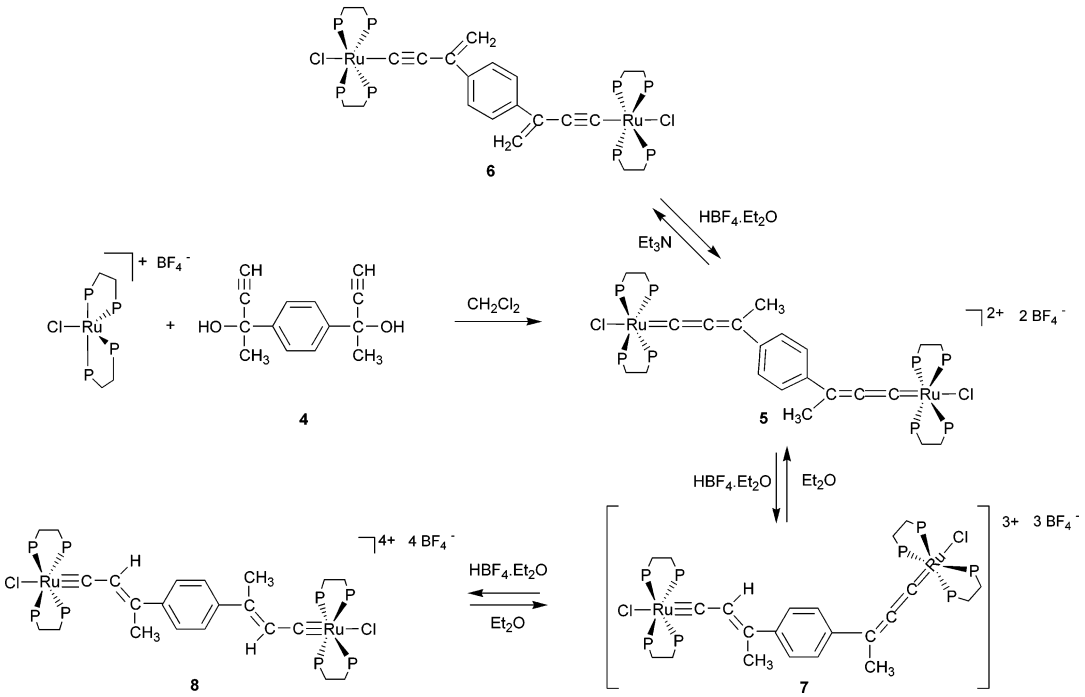
Scheme 2



along the Ru≡C−CH axis. The chemical shift of the C_α carbon is located at $\delta = 307.74$ ppm (quintet, $^2J_{PC} = 13$ Hz), that of C_γ at $\delta = 199.65$ ppm, and that of C_β at $\delta = 129.94$ ppm. They are consistent with the ethylenic bond and with Valerga's and Werner's observations.[15a,c] IR spectroscopy confirms the disappearance of the characteristic vibration stretch for the allenylidene species ($\nu_{=C=C=C} = 1958$ cm^{-1}), but we were unable to assign a characteristic carbyne vibration stretch. Similar experimental and spectroscopic observations were obtained for **3b**. In that case, they are consistent with an *E* configuration of the double bond as expected for steric reasons, and the Z methyl group also resonates at high field ($\delta = 0.42$ ppm). In addition, UV−vis studies showed a significant 60 nm shift of the metal to a ligand charge transfer band (MLCT) from $\lambda_{max} = 482$ nm for the allenylidene **1b** to 426 nm for the carbyne **3b** as a consequence of the conjugation change. In the case of **3a**, a similar blue shift ($\lambda_{max} = 420$ nm for **1a**) is observed but difficult to determine accurately since the band is shifted in the UV range and is overlapped by high-energy absorptions.

Not unexpectedly, these protonations can be easily reversed. Our attempts to isolate a stable salt of the alkenyl carbyne ruthenium failed. The β proton is very acidic, and addition of a very weak base such as acetone to a solution of **3a**,**b**, and even of diethyl ether to wash the solid, leads to the regeneration of the allenylidene compounds. Interestingly, this protonation reaction does not apply to allenylidenes such as *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]BF$_4$. This behavior can be attributed to the steric interactions in the resulting carbyne and to the electron-withdrawing effect of the second phenyl group, which decreases the nucleophilic character of C_β.

The application of this protonation reaction to bis-allenylidene species was attractive as an attempt to prepare the first bis-alkenyl carbyne ruthenium complex bridging two ruthenium moieties. The allenylidene **5** with two methyl groups was prepared using the same strategy of activation of the derivative **4**, with two propargylic alcohol functionalities, as that leading to *trans*-[Cl(dppe)$_2$Ru=C=C=CH-*p*-C$_6$H$_4$−CH=C=C=Ru(dppe)$_2$Cl](PF$_6$)$_2$ (Scheme 2).[7c] This compound, **5**, was fully characterized on the basis of its NMR, IR, UV−vis, and HR-MS (FAB) data. The double deprotonation of **5**, with Et$_3$N, readily yielded the expected bis-alkenylmetal acetylide **6** (Scheme 2). Characteristic features similar to those of **2a** and **2b** were observed. The protonation reaction was carried out with various amounts of acid in order to observe mono- and bis-protonated species. Three new signals were observed, using ^{31}P NMR monitoring, at $\delta = 38.73$, 37.07, and 36.70 ppm. Progressively, increasing the acid amount first led to the predominance of the signals at $\delta = 38.73$ and 36.70 ppm and then to their disappearance to the benefit of that at 37.07 ppm. We then ascribed the latter to the bis-protonated species **8** with two equivalent metal centers. By analogy, the two other signals are those of the monoprotonated species **7** with $\delta = 38.73$ ppm for the allenylidene moiety and $\delta = 36.70$ ppm for the carbyne moiety. Unfortunately it was not possible to isolate this species generated with 1 equiv of acid, likely because of a fast proton exchange between the various protonation sites, producing a mixture of the three compounds in equilibrium. The protonation was complete with 6 equiv of acid and gives exclusively the bis-carbyne **8**. Not surprisingly, the other spectroscopic features are very close to those observed for **3b**, including for ^{1}H NMR the β hydrogen signal at $\delta = 6.10$ ppm and the methyl group at $\delta = 0.39$ ppm. The UV−vis spectra of **8** also shows a blue shift of the broad MLCT band from $\lambda_{max} = 589$ nm for the blue allenylidene **5** to $\lambda_{max} = 496$ nm for the red bis-carbyne species **8**, which is larger than that of the monometallic species. It is of note that complex **6** displays no absorption band in the visible range, as observed for monometallic acetylides **2b** and **2a**. Therefore, the three characterized forms of the bimetallic complex, or of the monometallic

complexes, with three very different types of absorption in the visible range are again a demonstration that a slight variation in the structure of the chain of ruthenium(II) carbon-rich complexes induces significant modifications of the properties of the molecule.[9] Any reversible reaction (or interaction) that will induce a modification of the conjugation of the carbon bridge makes them good candidates for the design of new sensors or switches.[20]

In conclusion, we have shown that electron-rich allenylidenes of the type *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)R]BF$_4$ (R = Ph, CH$_3$) can be easily deprotonated on the δ carbon to alkenyl acetylide metal complexes and protonated to generate new alkenyl carbyne ruthenium complexes. The protonation of a conjugated bis-allenylidene ruthenium complex allowed the isolation of the first bis-alkenyl carbyne ligand bridging two ruthenium moieties.

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). Mass spectra were recorded on a Zab SpecETOF FAB$^+$ spectrometer. *cis*-[(dppe)$_2$-RuCl$_2$],[21] [(dppe)$_2$RuCl]BF$_4$,[22] and allenylidene compounds *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)R]BF$_4$ (R = Ph, CH$_3$)[9a] (**1a**,**b**) were prepared as previously reported.

***trans*-[Cl(dppe)$_2$Ru−C≡C−C(CH$_3$)=CH$_2$] (2a).** In a Schlenk tube containing 570 mg of *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)$_2$]BF$_4$ (0.52 mmol), 40 mL of CH$_2$Cl$_2$ and 0.5 mL of Et$_3$N were added. The green mixture turned to pale yellow and was stirred for 1 h at room temperature. The solution was then concentrated, and the product was purified by column chromatography over Al$_2$O$_3$ (elution with diethyl ether). After evaporation, the pale yellow solid was washed with pentane (10 mL), and 408 mg (0.41 mmol) of **2a** was recovered (78% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.60 (s, PPh$_2$). ^{1}H NMR (CDCl$_3$): δ 7.72−6.92 (m, 40H, Ph), 4.59 (m, 1H, CH), 4.39 (d, 1H, CH, $^2J_{HH}$ = 3.0 Hz), 2.64 (m, 8H, CH$_2$), 1.57 (s, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 137.16−126.49 (Ph), 132.05 (Ru−C≡C−*C*), 120.64 (quint., Ru−*C*≡C−, $^2J_{PC}$ = 16 Hz), 116.10 (s, Ru−C≡*C*−), 110.68 (s, =CH$_2$), 30.81 (CH$_2$, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz), 24.55 (CH$_3$). IR: 2049 cm^{-1} ($\nu_{C\equiv C}$), 1586 cm^{-1} ($\nu_{C=C}$). HR-MS FAB$^+$ (*m*/*z*): 998.1842 ([M]$^+$, calcd 998.1830). Anal. Found for C$_{57}$H$_{53}$P$_4$ClRu: C 69.01, H 5.47 (Calcd: C 68.57, H 5.35).

***trans*-[Cl(dppe)$_2$Ru−C≡C−C(Ph) CH$_2$] (2b).** In a Schlenk tube containing 600 mg of *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)-Ph]BF$_4$ (0.52 mmol), 40 mL of CH$_2$Cl$_2$ and 0.5 mL of Et$_3$N were added. The red mixture turned to pale yellow and was stirred for 1 h at room temperature. The solution was then concentrated, and the product was purified by column chromatography over Al$_2$O$_3$ (elution with diethyl ether). After evaporation, the pale yellow solid was washed with pentane (10 mL), and 454 mg (0.43 mmol) of **2b** was recovered (82% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.91 (s, PPh$_2$). ^{1}H NMR (CDCl$_3$): δ 7.72−6.90 (m, 45H, Ph), 5.26 (d, 1H, CH, $^2J_{HH}$ = 2.2 Hz), 4.74 (d, 1H, CH, $^2J_{HH}$ = 2.2 Hz), 2.66 (m, 8 H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141.72−126.46 (Ph), 135.80 (Ru−C≡C−*C*), 124.51 (quint., Ru−*C*≡C−, $^2J_{PC}$ = 15 Hz), 114.60 (s, Ru−C≡*C*−), 112.21 (s, =CH$_2$), 30.61 (CH$_2$, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz). IR: 2041 cm^{-1} ($\nu_{C\equiv C}$), 1557 cm^{-1} ($\nu_{C=C}$). HR-MS FAB$^+$ (*m*/*z*): 1060.2001 ([M]$^+$, calcd 1060.1986). Anal. Found for C$_{57}$H$_{53}$P$_4$ClRu: C 70.41, H 5.40 (Calcd: C 70.22, H 5.23).

***trans*-[Cl(dppe)$_2$Ru≡C−CH=C(CH$_3$)$_2$](BF$_4$)$_2$ (3a).** In an NMR tube containing 17 mg of *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)$_2$]BF$_4$ (0.016 mmol) in 0.5 mL of CD$_2$Cl$_2$, 7 μL of HBF$_4$·Et$_2$O (3 equiv) was added. The green solution turned to yellow. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 36.53 (s, PPh$_2$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.58−7.14 (m, 40H, Ph), 6.19 (m, 1H, CH), 3.30 (m, 8H, CH$_2$), 1.68 (m, (*E*)-CH$_3$), −0.11 (s, (*Z*)-CH$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 307.74 (quint., Ru≡*C*, $^2J_{PC}$ = 13 Hz), 199.65 (Ru≡C−HC=*C*), 134.28−127.93 (Ph), 129.94 (s, Ru≡C−*C*H), 28.99 (CH$_2$, $|^1J_{PC} + {}^3J_{PC}|$ = 22 Hz), 28.37 ((*E*)-CH$_3$), 27.65 ((*Z*)-CH$_3$).

***trans*-[Cl(dppe)$_2$Ru≡C−CH=C(CH$_3$)Ph](BF$_4$)$_2$ (3b).** In an NMR tube containing 8 mg of *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)Ph]BF$_4$ (0.009 mmol) in 0.5 mL of CD$_2$Cl$_2$, 5 μL of HBF$_4$·Et$_2$O (4 equiv) was added. The red solution turned to yellow. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 36.85 (s, PPh$_2$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.80−7.00 (m, 45H, Ph), 6.09 (m, 1H, CH), 3.33 (m, 8H, CH$_2$), 0.42 (s, CH$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 323.05 (Ru≡*C*), 184.67 (Ru≡C−HC=*C*), 138.11−129.89 (Ph), 125.45 (Ru≡C−*C*H), 28.59 (CH$_2$, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz), 23.49 (CH$_3$).

HC≡C−(OH)C(CH$_3$)-*p*-C$_6$H$_4$-(CH$_3$)C(OH)−C≡CH (4). In a Schlenk tube, 40 mmol of acetylene was dissolved in 40 mL of THF at −78 °C. Then, 30 mmol of ^{n}BuLi (solution 1.6 M in hexane, 18.75 mL) was slowly added. The mixture was stirred for 30 mn at −78 °C. In another tube, 2.03 g (12.5 mmol) of *p*-diacetobenzene was dissolved in 10 mL of THF and added with a cannula to the solution. The mixture was stirred overnight at room temperature before hydrolysis with 10 mL of a saturated NH$_4$Cl solution. The crude product was extracted with diethyl ether (4 × 50 mL), washed with water (3 × 20 mL), and dried. Further purification was achieved by chromatography over silica gel (10% diethyl ether in pentane) to afford 2.09 g of **4** (9.8 mmol) in 78% yield. ^{1}H NMR (CDCl$_3$): δ 7.54 (s, 4H, C$_6$H$_4$), 6.09 (s, 2H, OH), 3.52 (s, 2H, C≡CH), 1.62 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 146.11 (Cq phenyl), 125.35 (CH phenyl), 89.65 (C≡*C*H), 75.42 (C−OH), 68.52 (*C*≡CH), 34.41 (s, CH$_3$). IR: 2132 cm^{-1} ($\nu_{C\equiv C}$) = cm^{-1}. HR-MS EI (*m*/*z*): 214.0990 ([M]$^+$, calcd 214.0994).

***trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)-*p*-C$_6$H$_4$−(CH$_3$)C=C=C=Ru(dppe)$_2$Cl](BF$_4$)$_2$ (5).** In a Schlenk tube containing 500 mg of [(dppe)$_2$RuCl]BF$_4$ (0.5 mmol) and 54 mg of HC≡C−(OH)C(CH$_3$)-*p*-C$_6$H$_4$−(CH$_3$)C(OH)−C≡CH (0.25 mmol), 40 mL of CH$_2$Cl$_2$ was added. The solution was stirred for 10 days at room temperature. After evaporation, the residue was washed with diethyl ether (3 × 20 mL). Further crystallization in a dichloromethane/pentane mixture, led to 310 mg of dark blue crystals (56%) of **5**. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 40.06 (s, PPh$_2$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.30−7.02 (m, 80H, Ph), 6.59 (s, 4H, C$_6$H$_4$), 2.98 (m, 16H, CH$_2$), 1.55 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 329.29 (C$_\alpha$), 223.98 (s, C$_\beta$), 161.01 (s, C$_\gamma$), 134.11−128.31 (Ph), 32.43 (CH$_3$), 29.32 (m, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz, CH$_2$). IR: 1940 cm^{-1} ($\nu_{=C=C=C}$). HR-MS FAB$^+$ (*m*/*z*): 2131.3837 ([M^{2+},BF$_4^-$]$^+$, calcd 2131.3837). Anal. Found for C$_{118}$H$_{106}$P$_8$Cl$_2$-Ru$_2$B$_2$F$_8$: C 63.27, H 5.16 (Calcd: C 63.88, H 4.82).

***trans*-[Cl(dppe)$_2$Ru−C≡C−C(=CH$_2$)-*p*-C$_6$H$_4$−(CH$_2$=)C−C≡C−Ru(dppe)$_2$Cl] (6).** In a Schlenk tube containing 250 mg of **5** (0.13 mmol.), 40 mL of CH$_2$Cl$_2$ and 0.5 mL of Et$_3$N were added. The blue mixture turned to pale yellow and was stirred for 1 h at room temperature. The solution was then concentrated, and the product was purified by column chromatography over Al$_2$O$_3$ (elution with diethyl ether). After evaporation, the pale yellow solid was washed with pentane (10 mL), and 170 mg (0.08 mmol) of **6** was recovered (74% yield). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.16 (s, PPh$_2$). ^{1}H NMR (CDCl$_3$): δ 7.71−6.84 (m, 84H, Ph), 5.13 (d, 2H, CH, $^2J_{HH}$ = 2.0 Hz), 4.66 (d, 2H, CH, $^2J_{HH}$ = 2.0 Hz), 2.62 (m, 16H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 140.31−125.98 (Ph), 135.93 (Ru−C≡C−*C*), 124.20 (Ru−*C*≡C), 114.87 (s, Ru−C≡*C*−), 112.80 (s, =CH$_2$), 30.56 (CH$_2$, $|^1J_{PC} + {}^3J_{PC}|$ = 22 Hz). IR: 2047 cm^{-1}

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($\nu_{C\equiv C}$), 1572 cm^{-1} ($\nu_{C=C}$). HR-MS ESI (*m*/*z*): 2043.3723 ([M + H]$^+$ calcd 2043.3621). Anal. Found for $C_{118}H_{104}P_8Cl_2Ru_2 \cdot CH_2Cl_2$: C 67.12, H 5.01 (Calcd: C 67.17, H 5.02).

***trans*-[Cl(dppe)$_2$Ru≡C−CH=C(CH$_3$)-*p*-C$_6$H$_4$-(CH$_3$)C=CH−C≡Ru(dppe)$_2$Cl](BF$_4$)$_4$ (8).** In an NMR tube containing 8 mg of **5** (0.009 mmol) in 0.5 mL of CD_2Cl_2, 10 μL of $HBF_4 \cdot Et_2O$ (8 equiv) was added. The blue solution turned to yellow. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.07 (s, PPh_2). ^1H NMR (CD_2Cl_2): δ 7.65−7.15 (m, 84H, Ph), 6.10 (m, 2H, CH), 3.33 (m, 16H, CH_2), 0.39 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 314.13 (Ru≡*C*), 182.35 (Ru≡C−HC=*C*), 140.90−127.32 (Ph), 128.41 (Ru≡C−*C*H), 28.14 (CH_2, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz), 23.56 (CH_3).

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