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# Synthesis of ruthenium acetylides: new building blocks for molecular electronics

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**Abstract**

Several ruthenium(II) mono(acetylides) *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_n$–R] ($n = 1$–4; R = SiMe$_3$, H) and bis(acetylide) *trans*-[(dppe)$_2$Ru(–(C≡C)$_2$–R)$_2$] (R = SiMe$_3$, H) were selectively obtained and could be used as a new set of building blocks for rigid rod-like structures and further assemblies. Especially, the oxidative coupling of *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_3$–H] with Cu(OAc)$_2$ led to the formation of the first Ruthenium(II) binuclear species with 12 carbon atoms between the remote metals. This compound shows two reversible redox processes.


*Keywords:* Acetylide; Bimetallic complexes; Bridging ligand; Poly-ynes; Ruthenium complexes

## 1. Introduction

The chemistry of metal complexes containing alkynyl and higher poly-ynyl ligands is now well established [1]. This metal acetylide linkage has proven to be useful to obtain carbon rich complexes with an extended π-conjugation. They are of interest in organic synthesis, to achieve metal cumulenylidenes [M]=(C)$_n$=CR$_1$R$_2$ [2], and to prepare liquid crystals [3], metal containing polymers [4], supramolecular architectures [5], molecular switches [6], ONL active [7] or luminescent [8] materials. Their contribution is also essential for the building of molecular wires constituted of bimetallic complexes allowing through bridge exchange of electron between the remote metals [9–11]. The design of later motivate the selective easy to perform synthesis of new alkynyl and bis(alkynyl) metal complexes. Indeed, one can imagine many potential of expansion especially with the creation of new molecular models obtained by combination of multiples acetylides moieties or by reaction with cumulenic species.

Previous studies showed that dppe (1,2-bis(diphenyphosphino)ethane) is an excellent ligand to stabilize carbon rich species such as allenylidenes *trans*-[Cl(dppe)$_2$Ru=C=C=CR$_1$R$_2$]$^+$ and acetylides *trans*-[Cl(dppe)$_2$Ru–C≡C–R]. For steric and electronic reasons, the bulky ruthenium [RuCl(dppe)$_2$]$^+$ moiety protects C$_\alpha$ from nucleophilic attack [12,13]. We previously reported new bimetallic complexes using the new *trans*-[ClRu(dppe)$_2$–C≡C–C≡C–SiMe$_3$] acetylide as a precursor [9,10]. Also, a Ru(II) containing bis(acetylide) bridge has been found to enhance the ground state electronic communication between terminal ferrocenyl groups [14]. Therefore, the synthesis of mono and bis(poly-yne) complexes using the [Cl$_2$Ru(dppe)$_2$] precursor would led, via substitution of one or two chlorine atoms, to a new set of building blocks for rigid rod-like structure such as oligometallaynes ([M]–(C≡C)$_{n-}$)$_m$–[M] [15]. We wish now to fully account our synthetic work on these ruthenium mono and bis(acetylide) *trans*-[Cl$_{2-n}$Ru(dppe)$_2$](–(C≡C)$_m$–R)$_n$ (R = H, SiMe$_3$; $n = 1, 2$; $m = 1$–4), and we show how to control synthesis and deprotection. In addition, we report homocoupling of the mono(triyne) *trans*-[ClRu(dppe)$_2$–C≡C–C≡C–

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C≡C–H] that lead to a new poly-yne bimetallic complex with a $C_{12}$ carbon rich bridge which is the first ruthenium complex with such an extended structure and furthermore with a reversible redox behaviour. To date, only three main systems were reported bearing such a long sp carbon chain spanning two metals, $FeC_{12}Fe$ [16], $PtC_{12}Pt$ [17], and $ReC_{12}Re$ 11f. The bridge of the platinum and the rhenium species were, respectively extended up to $C_{16}$ and $C_{20}$ successfully. The rhenium system was the only one electrochemically studied, and it did not show two distinct reversible redox systems for $n > 6$.

## 2. Results and discussion

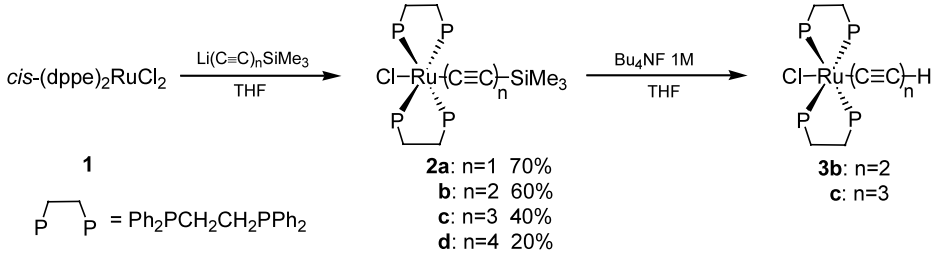
Recently, ruthenium poly-ynes have been studied by us and others [1c,12,18] as stable redox systems. Interestingly, only few protected or terminal acetylides $[RuL_x](-C\equiv C-C\equiv C-R)_n$ (R = H, $SiMe_3$; $n = 1, 2$) are available such as the $[CpRu(PPh_3)_2](-C\equiv C-C\equiv C-R)_n$ [19] (R = H, $SiMe_3$; $n = 1$), $[Ru(CO)_2(PEt_3)_2](-C\equiv C-C\equiv C-R)_n$ [20] (R = H, $SiMe_3$; $n = 2$), and $[Cl_{2-n}Ru(dppm)_2](-C\equiv C-C\equiv C-R)_n$ ($R = SiMe_3$; $n = 1, 2$) [21] moieties. The new protected mono-acetylide ruthenium complexes we describe here were formed using the classical reaction of preformed poly-yne reagents with metal centres, and more specifically of the poly-yne anions $Li(C\equiv C)_nSiMe_3$ with the metal halide complex *cis*-$[RuCl_2(dppe)_2]$ (**1**). Bis-substitution was selectively obtained on deprotonation of the vinylidene intermediates from 1-alkynes and **1** in the presence of a non-coordinating salt and a base.

### 2.1. Ruthenium mono-acetylide complexes

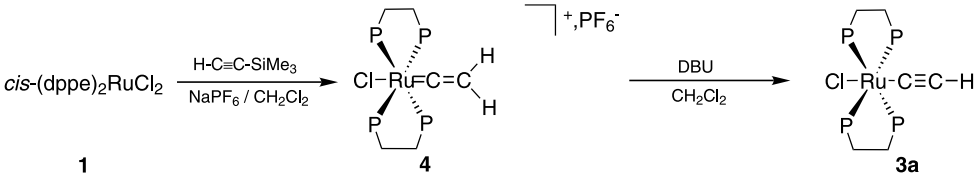
The pale yellow acetylide ruthenium complexes *trans*-$[Cl(dppe)_2Ru-(C\equiv C)_n-SiMe_3]$ (**2a–d**) ($n = 1-4$) were achieved via addition of a slight excess (1.5 equivalents) of the suitable lithium-acetylide $Li-(C\equiv C)_n-SiMe_3$, previously obtained by slow addition of MeLi (1.6 M in $Et_2O$) to $Me_3Si-(C\equiv C)_n-SiMe_3$ in THF at −78 °C, to suspension of **1** in THF (Scheme 1). The mixture was stirred for 18 h at room temperature. After purification through neutral alumina, the pure acetylide complexes **2a–d** were obtained. They were fully characterized on the basis of their NMR, IR, UV–vis and HR-MS (FAB) data. The *trans* structure of complexes **2a–d** was evidenced by $^{31}$P-NMR showing a singlet for the four equivalent phosphorus nuclei. The carbon chain was identified via $^{13}$C-NMR showing the presence of singlets for all the $C_{sp}$ carbons, excepted the carbon bonded to the metal, when observed, that shows a quintet ($^2J_{PC} = 15$ Hz) at lower field. In the $^1$H-NMR spectra, the presence of a singlet ($\delta \approx 0$ ppm) confirmed the presence of the trimethylsilyl group. The infrared spectroscopy also showed characteristic triple bond vibrations between 2175 and 1970 $cm^{-1}$.

The deprotection procedure of complexes **2a–d** led to the isolation of a terminal acetylide complex only in the case of **2b** and **2c**. The protected acetylide complexes were dissolved in dry THF and 1.2 equivalents of $Bu_4NF$ (1 M in THF) was added. After 1 h at room temperature, the solvent was evaporated and the residue purified by column chromatography on neutral alumina to yield to **3b** (95%) or **3c** (90%). The structures of complexes **3b–c** were fully determined. The disappearance of the trimethylsilyl group in NMR spectroscopy, the appearance of a signal for the terminal hydrogen ($^1$H-NMR), and a new signal for the corresponding terminal carbon atom ($^{13}$C-NMR) are the most striking features. Concerning **2a**, a treatment with a large excess of $Bu_4NF$ failed to remove the silyl group, as well as the use of a methanolic solution of KOH or $K_2CO_3$. Two reasons can be proposed to account for this unexpected behaviour: (i) the steric hindrance of the $[(dppe)_2RuCl]^+$ moiety; and (ii) a higher vinylidene character of **2a** owing to the donor effect of the dppe ligands (the chemical shift for $C_\alpha$ in $^{13}$C-NMR is $\delta = 146.89$ ppm for **2a** and $\delta = 123.17$ for **3b**). It is worth mentioning that **3a** was previously obtained starting directly from $H-C\equiv C-SiMe_3$ or from acetylene and complex **1** [24]. Deprotonation of the vinilydene intermediate **4** obtained then led to **3a** (Scheme 2) showing that desilylation takes place before the acetylide formation likely via an activated $\eta^2$-complex.

It is also of note that either the mono-substitution with $H-(C\equiv C)_2-SiMe_3$, in the presence of a non-coordinating salt, or the protonation of the resulting ruthenium diyne **2b** did not lead to the vinylidene




Scheme 1. Synthesis of acetylides **2a–d** and **3b–c**.



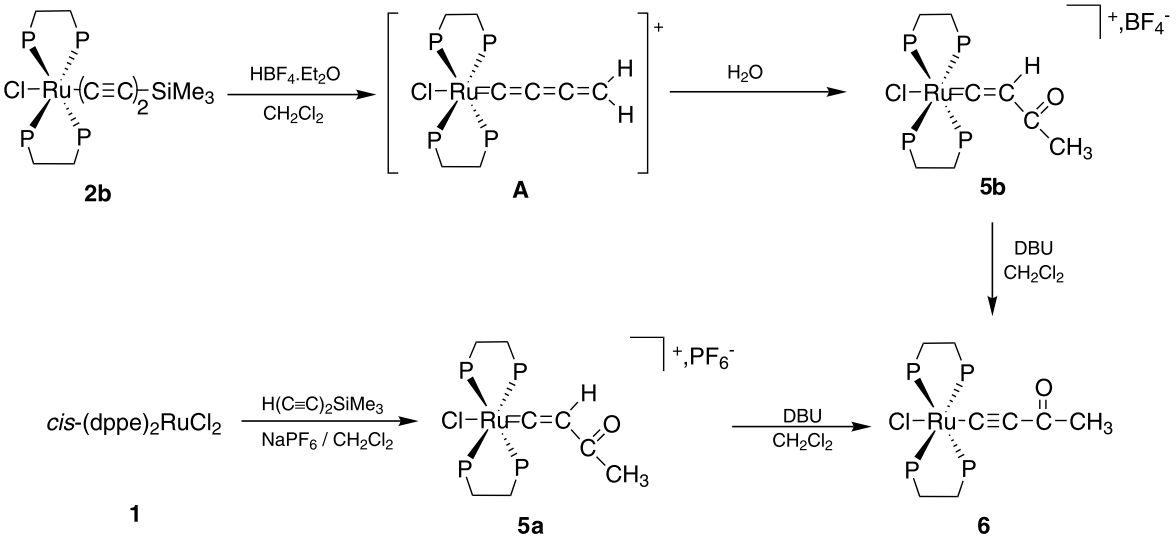

Scheme 2. Alternative synthesis of complex **3a**.

complex *trans*-$[Cl(dppe)_2Ru{=}C{=}C(H){-}C{\equiv}C{-}SiMe_3]^+$ nor to the isolation of *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}C{=}CH_2]^+$. We observed that when the diyne complex **2b** reacted with a strong acid such as $HBF_4{\cdot}Et_2O$ in methylene chloride, a blue colour appeared before the solution turned rapidly to orange. The orange product was identified as the vinylidene **5b** (Scheme 3). A vinylidene characteristic vibration stretch was observed at 1567 $cm^{-1}$ in the IR spectra. The $^1$H-NMR spectrum showed up the vinylidene proton as a quintet ($\delta = 3.49$ ppm, $^4J_{PH} = 2.5$ Hz) and the $^{13}$C-NMR spectrum, the low field quintet for $C_\alpha$ ($\delta = 340.4$ ppm, $^2J_{PC} = 13$ Hz). This reaction can be explained via protonation and desilylation forming the blue cumulene intermediate [**A**]. The following addition of residual water on the electrophilic carbon lead to **5b**. The analogue vinylidene **5a** was obtained by direct addition of $H{-}(C{\equiv}C)_2{-}SiMe_3$ on **1** in the presence of $NaPF_6$. The non-coordinating salt allows the formation of the 16 electron species which activates the terminal alkyne certainly to also form [**A**], via proton migration, before adding water. Deprotonations of both vinylidenes **5a**–**b** were easily carried out in the presence of DBU in methylene chloride, and led to the sole complex **6**. The typical IR absorption $\nu(C{\equiv}C)$ was observed at 2001 $cm^{-1}$ and also $\nu(CO)$ at 1603 $cm^{-1}$. Characteristic $^{13}$C-NMR chemical shifts for the $C_\alpha$ ($\delta = 153.5$ ppm, $^2J_{PC} = 15$ Hz) and CO ($\delta = 180.6$ ppm) were observed. Previous attempts to protonate ruthenium diynes such as *trans*-$[ClRu(dppe)_2{-}C{\equiv}C{-}C{\equiv}C{-}Ph]$ [22] or $[CpRu(PPh_3)_2{-}C{\equiv}C{-}C{\equiv}C{-}H]$ [19] led to the same results and conclusions especially concerning a butatrienylidene species. So far, this kind of intermediate has been isolated only with a complex of iridium [23].

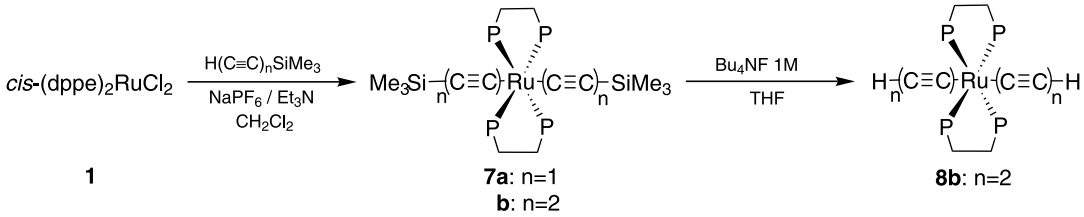
### 2.2. Ruthenium bis-acetylides complexes

Attempt to perform the double substitution of the two chlorine atoms using the poly-ynyl lithium derivatives in order to obtain Ru(II) contening *trans*-bis(acetylide) ligands were unsuccessful, even using a large amount of the anion. We have then applied another strategy, i.e. the deprotonation of the vinylidene intermediates obtained from 1-alkyne and **1** in the presence of a non-coordinating salt.

This procedure, previously described to obtain **7a** [24], was successful to produce **7b** (Scheme 4). The precursor **1** was reacted with four equivalents of $H{-}(C{\equiv}C)_2{-}SiMe_3$ in the presence of $NaPF_6$ and $Et_3N$ in $CH_2Cl_2$. After purification by column chromatography **7b** was obtained in good yield (77%). The $^{31}$P-NMR spectra shows a singlet at $\delta = 53.57$ ppm proving the *trans* position of the two carbon chains. In the $^1$H-NMR spectrum, we observe the presence of two equivalent trimethylsilyl groups at $\delta = 0.21$ ppm, and finally, the symmetric structure of **7b** is proved by the presence of




Scheme 3. Synthesis of complex **6** via a butatrienylidene intermediate.



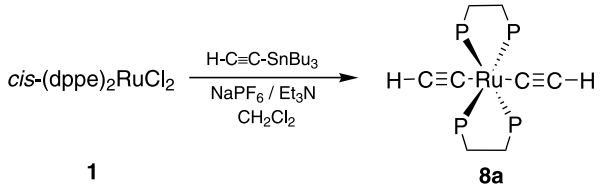

Scheme 4. Synthesis of bis(acetylides) **7a**–**b** and **8b**.

only four signals for the four pairs of carbon atoms of the two chains.

As observed for the mono(acetylide) **2a**, complex **7a** could not be desilylated, probably for the same reasons. Meanwhile, **8a** was previously obtained by another method using tributyl stannyl acetylide [24] (Scheme 5). In contrast, the bis(diyne) complex **8b** could be obtained by the simple action of $Bu_4NF$ on **7b**, under the conditions used for the formation of **3b** (Scheme 4). The structures was identified in particular with the disappearance of the trimethylsilyl group and the appearance of a signal for the terminal hydrogen ($^1$H-NMR). As the resulting complex is poorly soluble and of limited stability, $^{13}$C-NMR could not be obtained.

### 2.3. Coupling of acetylide ligands: preparation of carbon-rich bridged bimetallic complexes

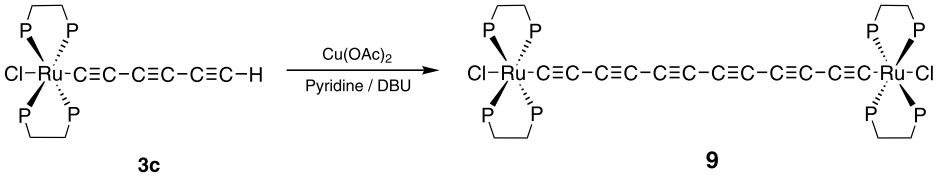
Metal acetylides are potential building blocks for further assemblies such as bimetallic molecular wire or oligometallaynes. Indeed, novel interesting binuclear complexes *trans*-[Cl(dppe)$_2$Ru=C=C=C–CH=C(CH$_2$)–C≡C–(dppe)$_2$RuCl]PF$_6$ [9] and *trans*-[Cl(dppe)$_2$Ru=C=C=C(R$_2$)–C(R$_1$)=C(CH$_3$)–C≡C–(dppe)$_2$RuCl]BF$_4$ [10] with seven conjugated carbons between the remote ruthenium moieties were recently built using **2b** or **3b**. The precursor was reacted, respectively with [FeCp$_2$]PF$_6$ as an oxidant or associated with a selected allenylidene *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_2$R$_1$)R$_2$]BF$_4$. These reactions are the result of an odd reactivity of **2b** and **3b** involving butatrienylidene intermediates (vide infra).




Scheme 5. Alternative synthesis of complex **8a**.

Thus, attempts to make use of the triyne **3c** were undertaken in order to possibly reach a binuclear complex with 12 conjugated carbons. Only a limited number of complexes with a $C_{12}$ chain have been described so far, $FeC_{12}Fe$ [16], $PtC_{12}Pt$ [17], and $ReC_{12}Re$ [11f]. One route to obtain such compounds is the symmetric oxidative coupling of terminal or protected acetylides. In the case of the diyne **3b**, several methods such as Eglinton or Hay coupling appeared to by unsuccessful to obtain a $C_8$ bridge. By contrast, under the conditions of the Eglinton recipe (Cu(OAc)$_2$, pyridine, DBU), the diyne **3c** reacted to form the poorly soluble bimetallic compound **9** with 12 carbon atoms between the remote metals (Scheme 6). This complex was isolated as a thermally stable powder and characterized on the basis of its $^1$H- and $^{31}$P-NMR (one singlet $\delta = 47.58$ ppm), IR (three C≡C vibration band at 2113, 2053, and 1946 cm$^{-1}$), HR-MS (FAB) data. These spectroscopic data confirmed the acetylide form of the complex rater than the mesomeric cumulenic form. Due to the low solubility, the $^{13}$C-NMR spectra could not be obtained and all attempts to obtain crystals have been unsuccessful.

The $RuC_{12}Ru$ complex **9** bears two redox active end groups. Cyclic voltametry analysis shows two successive reversible oxidation waves corresponding to the radical cation $RuC_{12}Ru^+$ and the dication $RuC_{12}Ru^{++}$. No reductions were observed prior to solvent limits. The first oxidation was observed at $E_1^\circ = -0.05$ V versus ferrocene and the second one at $E_2^\circ = 0.18$ V versus ferrocene. The split of the two oxidations (230 mV) show a substantial coupling between the metal centres ($Kc = \exp(\Delta E^\circ F/RT) = 10^4$) [11a] as the oxidations should present high metal character. It is noteworthy that the first oxidation is much easier that the oxidation of an alkynyl ruthenium ($E^\circ = 0.13$ V vs. ferrocene for **2b**). This result is certainly attributable to the delocalisa-




Scheme 6. Synthesis of the bimetallic $RuC_{12}Ru$ **9**.

tion of the charge on both metals. For comparison, Gladysz's group [11f] found for $(C_5Me_5)Re(NO)(PPh3)–(C\equiv C)_6–(PPh3)(NO)Re(C_5Me_5)$ a separation of 190 mV for the two poorly reversible oxidation processes ($Kc = 1.7 \times 10^3$). In our case, The larger separation of the redox processes is attributable to a higher resonance energy or Coulombic repulsion and/or a higher structural distortion associated with the introduction of the second charge. The singly oxidized compounds (mixed valence) should then be stable and possible to isolate for further studies.

## 3. Conclusion

A rational synthesis has been developed to obtain ruthenium terminal but also protected mono-acetylides and bis(acetylides). These systems offer potential to reach valuable models for new one dimensional wire like arrangements. Especially, the first ruthenium binuclear complex with a $C_{12}$ bridge showing a reversible redox behaviour was obtained. Further investigations will lead to novel surprising and exciting compounds with extended carbon network especially using bis(acetylides).

## 4. Experimental

The reactions were carried out under an inert atmosphere using the Schlenk techniques. Solvents were freshly distilled under Ar using standard procedures. Chromatography and filtration were performed using alumina (Acros activated neutral 50–200 μm). The electrochemical studies were carried out under Ar 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 Pt wire. Ferrocene was used as an internal reference and 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 determined at the Villeurbanne CNRS service central d'analyses. The precursors, *cis*-$[(dppe)_2RuCl_2]$ [25], $Me_3Si–(C\equiv C)_3–SiMe_3$ [26], $Me_3Si–(C\equiv C)_4–SiMe_3$ [27], $H–(C\equiv C)_3–SiMe_3$ [11f] were prepared as previously reported.

### 4.1. General procedure for complexes **2a–d**

A 1.6 M commercial solution of MeLi in $Et_2O$ was added dropwise to a cooled solution (−78 °C) of $Me_3Si–(C\equiv C)–_nSiMe_3$ in THF. The solution was stirred for 1 h at −78 °C and then 2 h at room temperature (r.t.). This solution was then added to a suspension of *cis*-$(dppe)_2RuCl_2$ in THF. The reaction medium was stirred overnight at r.t. After filtration the solvent was removed in vacuo. The crude product was washed with $C_5H_{12}$, dissolved in a mixture of $THF–CH_2Cl_2$ (50/50), and purified via column chromatography ($Al_2O_3$, $Et_2O$ as eluant).

#### 4.1.1. *trans*-[Cl(dppe)$_2$Ru–C≡C–SiMe$_3$] (**2a**)

The general procedure with 1 ml of MeLi (1.6 mmol), 500 mg of $Me_3Si–C\equiv C–SiMe_3$ (3 mmol) in 20 ml of dry THF and 968 mg of **1** (1 mmol) in 40 ml of THF led to 720 mg of complex **2a** (70% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 52.43 (s., $PPh_2$). $^1H$-NMR ($CDCl_3$): $\delta$ 8.09–6.81 (40H, Ph), 2.73 and 2.59 (m., 8H, $PCH_2CH_2P$), −0.08 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 146.89 (quint., Ru–*C*≡C, $^2J_{PC} = 14$ Hz), 138.12–127.05 (Ph), 120.07 (s., Ru–C≡*C*), 31.08 (quint., $PCH_2CH_2P$, $|^1J_{PC} + {}^3J_{Pc}| = 24$ Hz), 1.30 (s., $SiMe_3$). IR ($cm^{-1}$, KBr): 1991.3 ($\nu_{C\equiv C}$). HRMS-$FAB^+$ (*m*/*z*): 1030.1929 ($[M]^+$, Calc.: 1030.1925). Anal. Found for $C_{57}H_{57}ClP_4RuSi$: C, 66.80; H, 5.70. Calc.: C, 66.43; H, 5.57%.

#### 4.1.2. *trans*-[Cl(dppe)$_2$Ru–C≡C–C≡C–SiMe$_3$] (**2b**)

The general procedure with 1.875 ml of MeLi (3 mmol), 660 mg of $Me_3Si–C\equiv C–C\equiv C–SiMe_3$ (3.4 mmol) in 40 ml of dry THF and 1.936 g of **1** (2 mmol) in 60 ml of THF led to 1.266 g of complex **2b** (60% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 49.09 (s., $PPh_2$). $^1H$-NMR ($CDCl_3$): $\delta$ 7.46–6.97 (40H, Ph), 2.65 (m., 8H, $PCH_2CH_2P$), 0.19 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 133.56–127.12 (Ph, Ru–*C*≡C masked by the phenyls), 96.27 (s., Ru–C≡*C*), 95.53 (s., Ru–C≡C–*C*≡C), 66.83 (s., Ru–C≡C–C≡*C*), 30.67 (quint., $PCH_2CH_2P$, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz), 0.02 (s., $Si(CH_3)_3$. IR ($cm^{-1}$, KBr): 2175 (m), 2103 (s) and 1999 (m) ($\nu_{C\equiv C}$). HR-MS$FAB^+$ (*m*/*z*): 1054.1916 ($[M]^+$, Calc.: 1054.1925). Anal. Found for $C_{59}H_{57}ClP_4SiRu$: C, 67.08; H, 5.50. Calc.: C, 67.20; H, 5.45%.

#### 4.1.3. *trans*-[Cl(dppe)$_2$Ru–C≡C–C≡C–C≡C–SiMe$_3$] (**2c**)

The general procedure with 2.53 ml of MeLi (4.05 mmol), 1 g of $Me_3Si–C\equiv C–C\equiv C–C\equiv C–SiMe_3$ (4.6 mmol) in 95 ml of THF and 2.60 g of **1** (2.69 mmol) in 80 ml of THF led to 1.16 g of complex **2c** (40% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 48.36 (s., $PPh_2$). $^1H$-NMR ($CDCl_3$): $\delta$ 7.46–6.96 (40H, Ph), 2.64 (m., 8H, $PCH_2CH_2P$), 0.21 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 133.56–127.20 (Ph, Ru–*C*≡C masked by the phenyls), 94.86 (s., Ru–C≡*C*), 92.34 (s., Ru–C≡C–*C*≡C), 76.95 (s., Ru–C≡C–C≡*C*), 68.34 (s., Ru–(C≡C)$_2$–*C*≡C), 47.25 (s., Ru–(C≡C)$_2$–C≡*C*), 30.52 (quint., $PCH_2CH_2P$, $|^1J_{PC} + {}^3J_{PC}| = 23$ Hz), 0.37 (s., $SiMe_3$). IR ($cm^{-1}$, KBr): 2113 (s) and 1973 (s) ($\nu_{C\equiv C}$). Anal. Found

for $C_{61}H_{57}ClP_4SiRu$: C, 68.00; H, 5.39. Calc.: C, 67.93; H, 5.33%.

#### 4.1.4. *trans*-[Cl(dppe)$_2$Ru–C≡C–C≡C–C≡C–C≡C–SiMe$_3$] (**2d**)

The general procedure with 1.1 ml of MeLi (1.76 mmol), 485 mg of $Me_3Si$–$(C\equiv C)_4$–$SiMe_3$ (2.0 mmol) in 40 ml of THF and 1.14 g of **1** (1.18 mmol) in 40 ml of THF led to 265 mg of complex **2d** (20% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 47.58 (s., $PPh_2$). $^1$H-NMR ($CDCl_3$): $\delta$ 7.47–7.00 (40H, Ph), 2.64 (m., 8H, $PCH_2CH_2P$), 0.19 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 135.49–127.70 (Ph, Ru–*C*≡C masked by the phenyls), 94.80, 90.70, 82.12, 77.61, 67.64, 54.98 and 48.08 (C≡C), 30.66 (quint., $PCH_2CH_2P$, $|^1J_{PC}+{}^3J_{PC}| = 23$ Hz), 0.34 (s., $SiMe_3$). IR (cm$^{-1}$, KBr): 2104, 2070, 2039 and 1963 (s) ($\nu_{C\equiv C}$). Anal. Found for $C_{63}H_{57}ClP_4SiRu$: C, 68.19; H, 5.01. Calc.: C, 68.62; H, 5.21%.

### 4.2. General procedure for complexes **3b–c**

In a Schlenk tube containing complex **2** dissolved in THF, 1.1 equivalent of a commercial solution of $Bu_4NF$ (1 M in THF) was added. The reaction medium was stirred for 1 h. After solvent evaporation the residue was washed with water, dried and washed with $C_5H_{12}$.

#### 4.2.1. *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_2$–H] (**3b**)

The general procedure with 1.05 g of **2b** in 50 ml of THF (1 mmol) 1.1 ml of $Bu_4NF$ (1.1 mmol) led to 0.88 g of **3b** (95% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 49.00 (s., $PPh_2$). $^1$H-NMR ($CDCl_3$): $\delta$ 7.46–6.99 (40H, Ph), 2.66 (m., 8H, $PCH_2CH_2P$), 1.28 (s., 1H, ≡C–H). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 135.61–127.12 (Ph), 123.17 (quint., $^2J_{PC} = 16$ Hz, Ru–*C*≡), 94.46 (s., Ru–C≡*C*), 74.51 (s., Ru–C≡C–*C*≡), 50.89 (s., Ru–C≡C–C≡*C*), 30.57 (quint., $|^1J_{PC}+{}^3J_{PC}| = 23$ Hz, $PCH_2CH_2P$). IR (cm$^{-1}$, KBr): 3264 ($\nu_{CH}$), 2102 ($\nu_{C\equiv C}$). Anal. Found for $C_{56}H_{49}ClP_4Ru$: C, 68.76; H, 4.97. Calc.: C, 68.47; H, 5.03%.

#### 4.2.2. *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_3$–H] (**3c**)

The general procedure with 1.08 g of **2c** in 75 ml of THF (1 mmol) of $Bu_4NF$ (1.1 mmol) led to 0.9 g of complex **3c** (90% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 48.88 (s., $PPh_2$). $^1$H-NMR ($CDCl_3$): $\delta$ 7.37–6.93 (40H, Ph), 2.57 (m., 8H, $PCH_2CH_2P$), 1.68 (s., 1H, ≡CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 135.16–127.05 (Ph, Ru–*C*≡ masked by the phenyls), 94.27, 72.34, 66.69, 59.62, 59.11, 30.52 (quint., $PCH_2CH_2P$, $|^1J_{PC}+{}^3J_{PC}| = 23$ Hz). IR (cm$^{-1}$, KBr): 3295 ($\nu_{CH}$); 2132, 2079 and 1964 ($\nu_{C\equiv C}$). Anal. Found for $C_{58}H_{49}ClP_4Ru$: C, 68.81; H, 4.77. Calc.: C, 69.22; H, 4.91%.

### 4.3. Preparation of *trans*-[(dppe)$_2$(Cl)Ru=C=CH(CO)CH$_3$] [$PF_6$] (**5a**)

A solution of 245 mg of H–C≡C–C≡C–$SiMe_3$ (2 mmol) in 100 ml of $CH_2Cl_2$ was added to 968 mg of **1** (1 mmol) and 360 mg of $NaPF_6$ (2 mmol). The mixture was stirred for 24 h at r.t. After filtration of the solution, evaporation of the solvent, the residue was washed with $Et_2O$. Crystallisation in a $CH_2Cl_2$–$C_5H_{12}$ mixture led to 1.03 g of **5a** (90% yield). $^{31}P\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 41.27 (s., $PPh_2$), −144.1 (sept., $J_{PF} = 711$ Hz, $PF_6$). $^1$H-NMR ($CD_2Cl_2$): $\delta$ 7.50–7.08 (40H, Ph), 3.39 (quint., 1H, $^4J_{PH} = 2.3$ Hz, Ru=C=C*H*), 2.87 (m., 8H, $PCH_2CH_2P$), 1.45 (s., 3H, $CH_3$). $^{13}C\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 340.43 (quint., $^2J_{PC} = 12$ Hz, Ru=*C*), 191.47 (s., *C*O), 134.27–128.17 (Ph), 112.61 (s., Ru=C=*C*), 30.04 (s., $CH_3$), 29.22 (quint., $|^1J_{PC}+{}^3J_{PC}| = 23$ Hz, $PCH_2CH_2P$). IR (cm$^{-1}$, KBr): 1570 ($\nu_{C=C}$), 738 ($\nu_{PF}$). Anal. Found for $C_{56}H_{52}ClF_6OP_5Ru$: C, 58.95; H, 4.71. Calc.: C, 58.67; H, 4.57%.

### 4.4. Preparation of *trans*-[(dppe)$_2$(Cl)Ru=C=CH(CO)CH$_3$] [$BF_4$] (**5b**)

To a solution of 527 mg of **2b** (0.5 mmol) in 50 ml of $CH_2Cl_2$, 90 μl of a solution of $HBF_4{\cdot}Et_2O$ in $Et_2O$ was added. After 1 h at r.t., the solvent was evaporated and the residue washed with $Et_2O$. Crystallisation in a $CH_2Cl_2$–$C_5H_{12}$ mixture led to 473 mg of **5b** (87% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 41.15 (s., $PPh_2$). $^1$H-NMR ($CDCl_3$): $\delta$ 7.42–6.99 (Ph), 3.49 (quint., 1H, $^4J_{PH} = 2.5$ Hz, Ru=C=C*H*), 2.85 (m., 8H, $PCH_2CH_2P$), 1.43 (s., 3H, $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 340.42 (quint., $^2J_{PC} = 13$ Hz, Ru = *C*), 191.23 (s., *C*O), 134.27–128.16 (Ph), 112.61 (s., Ru=C=*C*), 30.03 (s., $CH_3$), 29.21 (quint., $|^1J_{PC}+{}^3J_{PC}| = 23$ Hz, $PCH_2CH_2P$). IR (cm$^{-1}$, KBr): 1567 ($\nu_{C=C}$). Anal. Found for $C_{56}H_{52}ClF_4OP_4Ru$: C, 62.01; H, 4.87. Calc.: C, 61.81; H, 4.82%. HR-MSFAB$^+$ (*m*/*z*): 1001.1718 ([M$^+$], Calc. 1001.1713).

### 4.5. Preparation of *trans*-[(dppe)$_2$(Cl)Ru–C≡C–(CO)–CH$_3$] (**6**)

To a solution of 1.15 g of **5a** (1.00 mmol) in 100 ml of $CH_2Cl_2$, 598 μl of DBU (4.00 mmol) was added. After 1 h at r.t. and evaporation of the solvent, the residue was washed with $C_5H_{12}$, dissolved in THF, and purified by column chromatography ($Al_2O_3$, $Et_2O$ as solvent). Crystallisation in a $CH_2Cl_2$–$C_5H_{12}$ mixture led to 800 mg of **6** (80% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 48.65 (s., $PPh_2$). $^1$H-NMR ($CDCl_3$): $\delta$ 7.46–6.99 (40H, Ph), 2.72 (m., 8H, $PCH_2CH_2P$), 1.54 (s., $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 180.66 (s., CO), 153.52 (quint., $^2J_{PC} = 15$ Hz, Ru–*C*≡C), 136.13–127.66 (Ph), 120.94 (s., Ru–C≡*C*), 31.84 (s., $CH_3$), 30.91 (quint., $|^1J_{PC}+{}^3J_{PC}| = 22$ Hz, $PCH_2CH_2P$). IR (cm$^{-1}$, KBr):

2001 ($\nu_{C\equiv C}$). Anal. Found for $C_{56}H_{51}ClOP_4Ru$: C, 66.87; H, 4.96. Calc.: C, 67.23; H, 5.14%.

### 4.6. Preparation of trans-[(dppe)$_2$Ru–(C≡C–C≡C–SiMe$_3$)$_2$] (7b)

In a Schlenk tube containing 775 mg of **1** (0.80 mmol) and 537 mg (3.20 mmol) of $NaPF_6$, a solution of H–C≡C–C≡C–$SiMe_3$ (3.20 mmol), 800 μl (6.40 mmol), and 100 ml of $CH_2Cl_2$ was added. After 22 h at r.t., the solution was filtered and the solvent evaporated. The residue was washed with $C_5H_{12}$. After purification by column chromatograpy on neutral alumina, eluted with a mixture $CH_2Cl_2$–$Et_2O$ (1:1), 700 mg of **7b** was obtained (77% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 53.57 (s., $PPh_2$). $^1H$-NMR ($CDCl_3$): $\delta$ 7.31–6.98 (40H, Ph), 2.56 (m., 8H, $PCH_2CH_2P$), 0.21 (s., 18H, $CH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 136.32–129.01 (Ph), 131.8 (quint., $^2J_{PC} = 15$ Hz, Ru–*C*≡C), 100.2 (s., Ru–C≡*C*), 95.24 (s., Ru–C≡C–*C*≡C), 69.1 (s., Ru–C≡C–C≡*C*), 31.5 (quint., $|^1J_{PC} + {}^3J_{PC}| = 24$ Hz, $PCH_2CH_2P$), 1.1 (s., $CH_3$). IR ($cm^{-1}$, KBr): 2166 (m), 2109 (s) and 1993 (m) ($\nu_{C\equiv C}$). HR-MSFAB$^+$ (*m*/*z*): 1140.2709 ([$M^+$], Calc. 1140.2715). Anal. Found for $C_{66}H_{66}ClP_4RuSi_2$: C, 69.27; H, 5.77. Calc.: C, 69.51; H, 5.83%.

### 4.7. Preparation of trans-[(dppe)$_2$Ru–(C≡C–C≡C–H)$_2$] (8b)

In a Schlenk tube containing 114 mg of **7a** (0.1 mmol) in 30 ml of THF, 0.3 ml (0.3 mmol) of $Bu_4NF$ (1 M in THF) was added. The reaction medium was stirred for 2 h after evaporation, the residue was chromatographied on neutral alumina (elution with a mixture (1:1) $CH_2Cl_2$–$Et_2O$), and 95 mg of **8b** was obtained (94% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 53.50 (s., $PPh_2$). $^1H$-NMR ($CDCl_3$): $\delta$ 7.34–6.96 (40H, Ph), 2.58 (m., 8H, $PCH_2CH_2P$), 1.41 (s., 2H, C≡CH). IR ($cm^{-1}$, KBr): 2112 (s) and 1971 (m) ($\nu_{C\equiv C}$).

### 4.8. Preparation of trans-[Cl(dppe)$_2$Ru–(C≡C)$_6$–Ru(dppe)$_2$Cl] (9)

To a solution of 0.503 g of **3c** (0.5 mmol) and 0.1 g of Copper(II) acetate (0.5 mmol) in 40 ml of Py, 75 μl of DBU (0.5 mmol) was added. The solution was stirred for 3 h at r.t. After evaporation of the solvent, the residue was washed with $Et_2O$ and dried. After extraction with 1 l of $CH_2Cl_2$, 0.453 g of complex **9** was obtained (90% yield). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 47.58. $^1H$-NMR ($CD_2Cl_2$): $\delta$ 7.45–6.96 (80H, Ph), 2.60 (m., 16H, $PCH_2CH_2P$). IR ($cm^{-1}$, KBr): 2113, 2053 and 1946 ($\nu_{C\equiv C}$). HR-MSFAB$^+$ (*m*/*z*): 2011.2971 ([M+H]$^+$, Calc. 2011.2955). Anal. Found for $C_{116}H_{96}Cl_2P_8Ru_2$: C, 68.93; H, 4.77. Calc.: C, 69.29; H, 4.81%.

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