

Synthesis of ruthenium acetylides: new building blocks for molecular electronics

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Abstract

Several ruthenium(II) mono(acetylides) *trans*-[Cl(dppe)₂Ru-(C≡C)_n-R] (*n* = 1–4; R = SiMe₃, H) and bis(acetylide) *trans*-[(dppe)₂Ru(-(C≡C)₂-R)₂] (R = SiMe₃, 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)₂Ru-(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.

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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 cumulenylenes [M]=(C)_n=CR₁R₂ [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 cumulenenic species.

Previous studies showed that dppe (1,2-bis(diphenylphosphino)ethane) is an excellent ligand to stabilize carbon rich species such as allenylidenes *trans*-[Cl(dppe)₂Ru=C=C=CR₁R₂]⁺ and acetylides *trans*-[Cl(dppe)₂Ru-C≡C-R]. For steric and electronic reasons, the bulky ruthenium [RuCl(dppe)₂]⁺ moiety protects C α from nucleophilic attack [12,13]. We previously reported new bimetallic complexes using the new *trans*-[ClRu(dppe)₂-C≡C-C≡C-SiMe₃] 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 [Cl₂Ru(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]) [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, SiMe₃; *n* = 1, 2; *m* = 1–4), and we show how to control synthesis and deprotection. In addition, we report homocoupling of the mono(tri-yne) *trans*-[ClRu(dppe)₂-C≡C-C≡C-

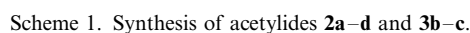
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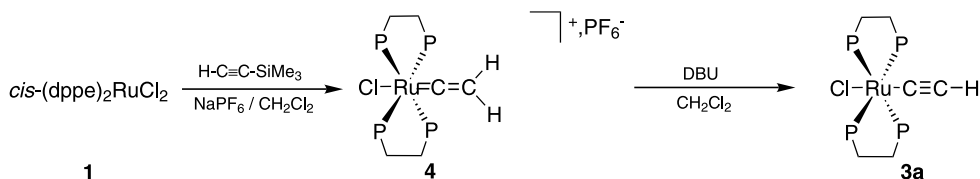
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2. Results and discussion

2.1. Ruthenium mono-acetylide complexes

It is also of note that either the mono-substitution with $\text{H}-(\text{C}\equiv\text{C})_2-\text{SiMe}_3$, in the presence of a non-coordinating salt, or the protonation of the resulting ruthenium diyne **2b** did not lead to the vinylidene



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

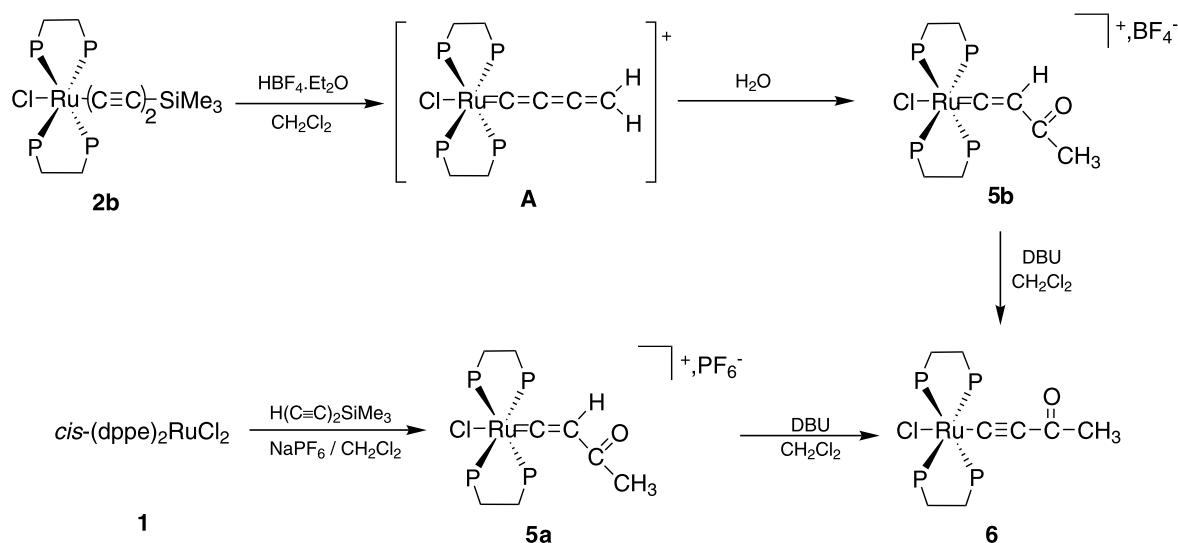
complex *trans*-[Cl(dppe)₂Ru=C=C(H)–C≡C–SiMe₃]⁺ nor to the isolation of *trans*-[Cl(dppe)₂Ru=C=C=C=CH₂]⁺. We observed that when the diyne complex **2b** reacted with a strong acid such as HBF₄·Et₂O in methylene chloride, a blue colour appeared before the solution turned rapidly to orange. The orange 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 ¹H-NMR spectrum showed up the vinylidene proton as a quintet (δ = 3.49 ppm, ⁴J_{PH} = 2.5 Hz) and the ¹³C-NMR spectrum, the low field quintet for C_α (δ = 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≡C)₂–SiMe₃ on **1** in the presence of NaPF₆. 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 ν(C≡C) was observed at 2001 cm^{−1} and also ν(CO) at 1603 cm^{−1}. Characteristic ¹³C-NMR chemical shifts for the C_α (δ = 153.5 ppm, ²J_{PC} = 15 Hz) and CO (δ = 180.6 ppm) were observed. Previous attempts to protonate

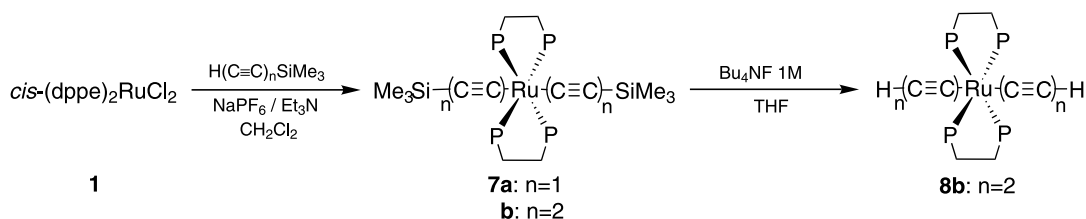
ruthenium diynes such as *trans*-[ClRu(dppe)₂–C≡C–C≡C–Ph] [22] or [CpRu(PPh₃)₂–C≡C–C≡C–H] [19] led to the same results and conclusions especially concerning a butatrienyldiene species. So far, this kind of intermediate has been isolated only with a complex of iridium [23].

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) containing *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≡C)₂–SiMe₃ in the presence of NaPF₆ and Et₃N in CH₂Cl₂. After purification by column chromatography **7b** was obtained in good yield (77%). The ³¹P-NMR spectra shows a singlet at δ = 53.57 ppm proving the *trans* position of the two carbon chains. In the ¹H-NMR spectrum, we observe the presence of two equivalent trimethylsilyl groups at δ = 0.21 ppm, and finally, the symmetric structure of **7b** is proved by the presence of

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

Scheme 4. Synthesis of bis(acetylide)s **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 structure was identified in particular with the disappearance of the trimethylsilyl group and the appearance of a signal for the terminal hydrogen ($^1\text{H-NMR}$). As the resulting complex is poorly soluble and of limited stability, $^{13}\text{C-NMR}$ could not be obtained.

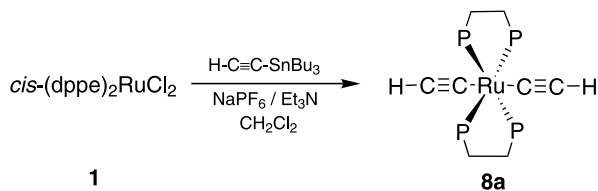
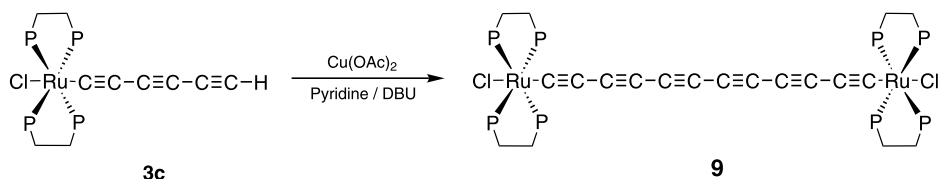
2.3. Coupling of acetylide ligands: preparation of carbon-rich bridged bimetallic complexes

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

actions are the result of an odd reactivity of **2b** and **3b** involving butatrienylidene intermediates (vide infra).

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 be unsuccessful to obtain a C_8 bridge. By contrast, under the conditions of the Eglinton recipe ($\text{Cu}(\text{OAc})_2$, 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 $^1\text{H-}$ and $^{31}\text{P-NMR}$ (one singlet $\delta = 47.58$ ppm), IR (three $\text{C}\equiv\text{C}$ vibration band at 2113, 2053, and 1946 cm^{-1}), HR-MS (FAB) data. These spectroscopic data confirmed the acetylide form of the complex rather than the mesomeric cumulenic form. Due to the low solubility, the $^{13}\text{C-NMR}$ 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 $\text{RuC}_{12}\text{Ru}^+$ and the dication $\text{RuC}_{12}\text{Ru}^{++}$. No reductions were observed prior to solvent limits. The first oxidation was observed at $E_1^\circ = -0.05\text{ V}$ versus ferrocene and the second one at $E_2^\circ = 0.18\text{ V}$ versus ferrocene. The split of the two oxidations (230 mV) show a substantial coupling between the metal centres ($K_c = \exp(\Delta E^\circ F/RT) = 10^4$) [11a] as the oxidations should present high metal character. It is noteworthy that the first oxidation is much easier than the oxidation of an alkynyl ruthenium ($E^\circ = 0.13\text{ V}$ vs. ferrocene for **2b**). This result is certainly attributable to the delocalisa-

Scheme 5. Alternative synthesis of complex **8a**.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 $(C_5Me_5)Re(NO)-(PPh_3)-(C\equiv C)_6-(PPh_3)(NO)Re(C_5Me_5)$ a separation of 190 mV for the two poorly reversible oxidation processes ($K_c = 1.7 \times 10^3$). 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 μ m). 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 ($-78^\circ C$) of $Me_3Si-(C\equiv C)_n-SiMe_3$ in THF. The solution was stirred for 1 h at $-78^\circ C$ 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*- $[Cl(dppe)_2Ru-C\equiv C-SiMe_3]$ (**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 ($CDCl_3$): δ 52.43 (s., PPh_2). 1H -NMR ($CDCl_3$): δ 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 ($CDCl_3$): δ 146.89 (quint., $Ru-C\equiv C$, $^2J_{PC} = 14$ Hz), 138.12–127.05 (Ph), 120.07 (s., $Ru-C\equiv C$), 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*- $[Cl(dppe)_2Ru-C\equiv C-C\equiv C-SiMe_3]$ (**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 ($CDCl_3$): δ 49.09 (s., PPh_2). 1H -NMR ($CDCl_3$): δ 7.46–6.97 (40H, Ph), 2.65 (m., 8H, PCH_2CH_2P), 0.19 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): δ 133.56–127.12 (Ph, $Ru-C\equiv C$ masked by the phenyls), 96.27 (s., $Ru-C\equiv C$), 95.53 (s., $Ru-C\equiv C-C\equiv C$), 66.83 (s., $Ru-C\equiv C-C\equiv C$), 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*- $[Cl(dppe)_2Ru-C\equiv C-C\equiv C-C\equiv C-SiMe_3]$ (**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 ($CDCl_3$): δ 48.36 (s., PPh_2). 1H -NMR ($CDCl_3$): δ 7.46–6.96 (40H, Ph), 2.64 (m., 8H, PCH_2CH_2P), 0.21 (s., 9H, $SiMe_3$). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): δ 133.56–127.20 (Ph, $Ru-C\equiv C$ masked by the phenyls), 94.86 (s., $Ru-C\equiv C$), 92.34 (s., $Ru-C\equiv C-C\equiv C$), 76.95 (s., $Ru-C\equiv C-C\equiv C$), 68.34 (s., $Ru-(C\equiv C)_2-C\equiv C$), 47.25 (s., $Ru-(C\equiv C)_2-C\equiv C$), 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)₂Ru–C≡C–C≡C–C≡C–C≡C–SiMe₃] (**2d**)

The general procedure with 1.1 ml of MeLi (1.76 mmol), 485 mg of Me₃Si–(C≡C)₄–SiMe₃ (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). ³¹P{¹H}-NMR (CDCl₃): δ 47.58 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.47–7.00 (40H, Ph), 2.64 (m., 8H, PCH₂CH₂P), 0.19 (s., 9H, SiMe₃). ¹³C{¹H}-NMR (CDCl₃): δ 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., PCH₂CH₂P, ¹J_{PC}+³J_{PC}=23 Hz), 0.34 (s., SiMe₃). IR (cm^{−1}, KBr): 2104, 2070, 2039 and 1963 (s) (ν_{C≡C}). Anal. Found for C₆₃H₅₇ClP₄SiRu: 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 Bu₄NF (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 C₅H₁₂.

4.2.1. *trans*-[Cl(dppe)₂Ru–(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 Bu₄NF (1.1 mmol) led to 0.88 g of **3b** (95% yield). ³¹P{¹H}-NMR (CDCl₃): δ 49.00 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.46–6.99 (40H, Ph), 2.66 (m., 8H, PCH₂CH₂P), 1.28 (s., 1H, ≡C–H). ¹³C{¹H}-NMR (CDCl₃): δ 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, PCH₂CH₂P). IR (cm^{−1}, KBr): 3264 (ν_{CH}), 2102 (ν_{C≡C}). Anal. Found for C₅₆H₄₉ClP₄Ru: C, 68.76; H, 4.97. Calc.: C, 68.47; H, 5.03%.

4.2.2. *trans*-[Cl(dppe)₂Ru–(C≡C)₃–H] (**3c**)

The general procedure with 1.08 g of **2c** in 75 ml of THF (1 mmol) of Bu₄NF (1.1 mmol) led to 0.9 g of complex **3c** (90% yield). ³¹P{¹H}-NMR (CDCl₃): δ 48.88 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.37–6.93 (40H, Ph), 2.57 (m., 8H, PCH₂CH₂P), 1.68 (s., 1H, ≡CH). ¹³C{¹H}-NMR (CDCl₃): δ 135.16–127.05 (Ph, Ru–C≡ masked by the phenyls), 94.27, 72.34, 66.69, 59.62, 59.11, 30.52 (quint., PCH₂CH₂P, ¹J_{PC}+³J_{PC}=23 Hz). IR (cm^{−1}, KBr): 3295 (ν_{CH}); 2132, 2079 and 1964 (ν_{C≡C}). Anal. Found for C₅₈H₄₉ClP₄Ru: 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)CH₃] [PF₆] (**5a**)

A solution of 245 mg of H–C≡C–C≡C–SiMe₃ (2 mmol) in 100 ml of CH₂Cl₂ was added to 968 mg of **1** (1 mmol) and 360 mg of NaPF₆ (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 Et₂O. Crystallisation in a CH₂Cl₂–C₅H₁₂ mixture led to 1.03 g of **5a** (90% yield). ³¹P{¹H}-NMR (CD₂Cl₂): δ 41.27 (s., PPh₂), −144.1 (sept., J_{PF}=711 Hz, PF₆). ¹H-NMR (CD₂Cl₂): δ 7.50–7.08 (40H, Ph), 3.39 (quint., 1H, ⁴J_{PH}=2.3 Hz, Ru=C=CH), 2.87 (m., 8H, PCH₂CH₂P), 1.45 (s., 3H, CH₃). ¹³C{¹H}-NMR (CD₂Cl₂): δ 340.43 (quint., ²J_{PC}=12 Hz, Ru=C), 191.47 (s., CO), 134.27–128.17 (Ph), 112.61 (s., Ru=C=C), 30.04 (s., CH₃), 29.22 (quint., ¹J_{PC}+³J_{PC}=23 Hz, PCH₂CH₂P). IR (cm^{−1}, KBr): 1570 (ν_{C=C}), 738 (ν_{PF}). Anal. Found for C₅₆H₅₂ClF₆OP₅Ru: 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)CH₃] [BF₄] (**5b**)

To a solution of 527 mg of **2b** (0.5 mmol) in 50 ml of CH₂Cl₂, 90 μl of a solution of HBF₄·Et₂O in Et₂O was added. After 1 h at r.t., the solvent was evaporated and the residue washed with Et₂O. Crystallisation in a CH₂Cl₂–C₅H₁₂ mixture led to 473 mg of **5b** (87% yield). ³¹P{¹H}-NMR (CDCl₃): δ 41.15 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.42–6.99 (Ph), 3.49 (quint., 1H, ⁴J_{PH}=2.5 Hz, Ru=C=CH), 2.85 (m., 8H, PCH₂CH₂P), 1.43 (s., 3H, CH₃). ¹³C{¹H}-NMR (CDCl₃): δ 340.42 (quint., ²J_{PC}=13 Hz, Ru=C), 191.23 (s., CO), 134.27–128.16 (Ph), 112.61 (s., Ru=C=C), 30.03 (s., CH₃), 29.21 (quint., ¹J_{PC}+³J_{PC}=23 Hz, PCH₂CH₂P). IR (cm^{−1}, KBr): 1567 (ν_{C=C}). Anal. Found for C₅₆H₅₂ClF₄OP₄Ru: 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)–CH₃] (**6**)

To a solution of 1.15 g of **5a** (1.00 mmol) in 100 ml of CH₂Cl₂, 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 C₅H₁₂, dissolved in THF, and purified by column chromatography (Al₂O₃, Et₂O as solvent). Crystallisation in a CH₂Cl₂–C₅H₁₂ mixture led to 800 mg of **6** (80% yield). ³¹P{¹H}-NMR (CDCl₃): δ 48.65 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.46–6.99 (40H, Ph), 2.72 (m., 8H, PCH₂CH₂P), 1.54 (s., CH₃). ¹³C{¹H}-NMR (CDCl₃): δ 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., CH₃), 30.91 (quint., ¹J_{PC}+³J_{PC}=22 Hz, PCH₂CH₂P). 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*)₂Ru-(C≡C-C≡C-SiMe₃)₂] (**7b**)

In a Schlenk tube containing 775 mg of **1** (0.80 mmol) and 537 mg (3.20 mmol) of NaPF₆, a solution of H-C≡C-C≡C-SiMe₃ (3.20 mmol), 800 μ l (6.40 mmol), and 100 ml of CH₂Cl₂ was added. After 22 h at r.t., the solution was filtered and the solvent evaporated. The residue was washed with C₅H₁₂. After purification by column chromatography on neutral alumina, eluted with a mixture CH₂Cl₂-Et₂O (1:1), 700 mg of **7b** was obtained (77% yield). ³¹P{¹H}-NMR (CDCl₃): δ 53.57 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.31–6.98 (40H, Ph), 2.56 (m., 8H, PCH₂CH₂P), 0.21 (s., 18H, CH₃). ¹³C{¹H}-NMR (CDCl₃): 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, PCH₂CH₂P), 1.1 (s., CH₃). 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 C₆₆H₆₆ClP₄RuSi₂: C, 69.27; H, 5.77. Calc.: C, 69.51; H, 5.83%.

4.7. Preparation of *trans*-[(*dppe*)₂Ru-(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 Bu₄NF (1 M in THF) was added. The reaction medium was stirred for 2 h after evaporation, the residue was chromatographed on neutral alumina (elution with a mixture (1:1) CH₂Cl₂-Et₂O), and 95 mg of **8b** was obtained (94% yield). ³¹P{¹H}-NMR (CDCl₃): δ 53.50 (s., PPh₂). ¹H-NMR (CDCl₃): δ 7.34–6.96 (40H, Ph), 2.58 (m., 8H, PCH₂CH₂P), 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*)₂Ru-(C≡C)₆-Ru(*dppe*)₂Cl] (**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 μ l 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 Et₂O and dried. After extraction with 1 l of CH₂Cl₂, 0.453 g of complex **9** was obtained (90% yield). ³¹P{¹H}-NMR (CDCl₃): δ 47.58. ¹H-NMR (CD₂Cl₂): δ 7.45–6.96 (80H, Ph), 2.60 (m., 16H, PCH₂CH₂P). 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 C₁₁₆H₉₆Cl₂P₈Ru₂: C, 68.93; H, 4.77. Calc.: C, 69.29; H, 4.81%.

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References

- [1] (a) J. Manna, K.D. John, M.D. Hopkins, Adv. Organomet. Chem. 38 (1995) 79; (b) P.J. Stang, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995; (c) P.J. Low, M.I. Bruce, Adv. Organomet. Chem. 48 (2001) 71.
- [2] M.I. Bruce, Chem. Rev. 98 (1998) 2797.
- [3] S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861.
- [4] (a) I. Manners, Chem. Rev. 99 (1999) 1515; (b) N. Matsumi, Y. Chujo, O. Lavastre, P.H. Dixneuf, Organometallics 20 (2001) 2423; (c) K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, Chem. Commun. (1998) 643; (d) J.L. Lewis, P.R. Raithby, W.-Y. Wong, J. Organomet. Chem. 556 (1998) 219.
- [5] (a) P.J. Stang, Chem. Eur. J. 4 (1998) 19; (b) P.J. Stang, B. Olenyuk, Acc. Chem. Res. 30 (1997) 502.
- [6] J.-L. Fillaut, M. Price, A.L. Johnson, J. Perruchon, Chem. Commun. (2001) 739.
- [7] (a) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. (1999) 43, 349; (b) S.K. Hurst, M.G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B.L. Davies, Organometallics 21 (2002) 2024; (c) T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, Organometallics 19 (2000) 5235.
- [8] (a) V.W.-W. Yam, R.P.-L. Tang, K.M.-C. Wong, K.-K. Cheung, Organometallics 20 (2001) 4476; (b) V.W.-W. Yam, K.M.-C. Wong, N.J. Zhu, J. Am. Chem. Soc. 124 (2002) 6506.
- [9] S. Rigaut, L. Le Pichon, J.-C. Daran, D. Touchard, P.H. Dixneuf, Chem. Commun. (2001) 1206.
- [10] S. Rigaut, J. Massue, D. Touchard, J.-L. Fillaut, S. Golhen, P.H. Dixneuf, Angew. Chem. Int. Ed. Engl. 41 (2002) 4513.
- [11] For selected examples see: (a) F. Paul, C. Lapinte, Coord. Chem. Rev. (1998) 178–180, 431; (b) R. Ziesel, M. Hissler, A. El-Gayhoury, A. Harriman, Coord. Chem. Rev. (1998) 178–180, 1251; (c) P.F.H. Schab, M.D. Levin, J. Michl, Chem. Rev. 99 (1999) 1863; (d) R. Dembinski, S. Szafert, P. Haquette, T. Lis, J.A. Gladysz, Organometallics (1999) 18, 5438–5440; (e) C. Hartbaum, H. Fischer, J. Organomet. Chem. (1999) 578, 186–192; (f) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. (2000) 122, 810–822; (g) M.I. Bruce, B.D. Kelly, B.W. Skelton, A.H. White, J. Organomet. Chem. 604 (2000) 150; (h) F.J. Fernandez, O. Blacque, M. Alfonso, H. Berke, Chem. Commun. (2000) 1266–1267; (i) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. (2000) 122, 1949–1962; (j) P. Siemen, U. Gubler, C. Bosshard, P. G nter, F. Diederich, Chemistry 7 (2001) 1333; (k) N.Y. Choi, M.C.W. Chan, M. Peng, K.-K. Cheung, C.-M. Che, Chem. Commun. (2000) 1259.

- [12] D. Touchard, P.H. Dixneuf, *Coord. Chem. Rev.* 178–180 (1998) 409.
- [13] (a) S. Rigaut, O. Maury, D. Touchard, P.H. Dixneuf, *Chem. Commun.* (2001) 373;
(b) D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, *Organometallics* 17 (1998) 3844;
(c) N. Pirio, D. Touchard, P.H. Dixneuf, *Chem. Commun.* (1991) 980;
(d) S. Rigaut, F. Monnier, F. Mousset, D. Touchard, P.H. Dixneuf, *Organometallics* 21 (2002) 2657;
(e) R.F. Winter, *Eur. J. Inorg. Chem.* (1999) 2121.
- [14] (a) C. Lebreton, D. Touchard, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, *Inorg. Chem. Acta* 272 (1998) 188;
(b) Y. Zhu, O. Clot, M.O. Wolf, G.P.A. Yap, *J. Am. Chem. Soc.* 120 (1998) 1812.
- [15] (a) G. Xu, T. Ren, *Organometallics* 20 (2001) 2400;
(b) K.T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee, *Chem. Commun.* (2000) 2259.
- [16] A. Sakurai, M. Akita, Y. Moro-oka, *Organometallics* 18 (1999) 3241.
- [17] (a) T.B. Peters, J.C. Bohling, A.M. Arif, J.A. Gladysz, *Organometallics* 18 (1999) 3261;
(b) W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, *Inorg. Chem.* 40 (2001) 3263.
- [18] O.F. Koentjoro, R. Rousseau, P.J. Low, *Organometallics* 20 (2001) 4502.
- [19] M.I. Bruce, P. Hinterding, E.R.T. Tiekink, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 450 (1993) 209.
- [20] (a) Y. Sun, N.J. Taylor, A.J. Carty, *J. Organomet. Chem.* 423 (1992) C43;
(b) Y. Sun, N.J. Taylor, A.J. Carty, *Organometallics* 11 (1992) 4293.
- [21] L. Dahlenburg, A. Weiß, M. Bock, A. Zahl, *J. Organomet. Chem.* 541 (1997) 465.
- [22] P. Haquette, D. Touchard, L. Toupet, P.H. Dixneuf, *J. Organomet. Chem.* 565 (1998) 63.
- [23] K. Ilg, H. Werner, *Chem. Eur. J.* 8 (2002) 2812.
- [24] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, *Organometallics* 16 (1997) 3640.
- [25] B. Chaudret, G. Commengues, R. Poilblanc, *J. Chem. Soc. Dalton Trans.* (1984) 1635.
- [26] Y. Rubin, S.S. Lin, C.B. Knobler, J. Anthony, A.M. Boldi, F. Diederich, *J. Am. Chem. Soc.* 113 (1991) 6943.
- [27] W. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 117 (1995) 11922.