Homobinuclear Ru–Ru and heterobinuclear Ru–Rh complexes with alkynyl and vinylidene ligands as molecular units

Helmut Werner, Petra Bachmann, and Marta Martin

Abstract: The chelate complex [$RuCl_2\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2$] (**1**) reacted, in the presence of CF_3SO_3Ag, with 1 equiv of $C_6H_4(C{\equiv}CH)_2$-*p* (**4**) to afford the mononuclear vinylidene compound [$RuCl(C{=}CHC_6H_4$-*p*-$C{\equiv}CH)\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)$ (**3**). From **1** and 0.5 equiv of **4**, the binuclear bis(vinylidene) complex [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*p*-$CH{=}C)RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)_2$ (**6**) was obtained. The related compound [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*-$CH{=}C)RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)_2$ (**7**) was prepared from **1**, 0.5 equiv of $C_6H_4(C{\equiv}CH)_2$-*m* (**5**), and silver triflate. The reaction of **2** or **3** with $[RhCl(P$-*i*-$Pr_3)_2]_2$ (**8**) in the molar ratio of 2:1 yields, by addition of the 14-electron fragment $[RhCl(P$-*i*-$Pr_3)_2]$ to the uncoordinated C—C triple bond, the heterobinuclear complexes [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*/*p*-$C{\equiv}CH)RhCl(P$-*i*-$Pr_3)_2](CF_3SO_3)$ (**9**, **10**) which slowly rearrange at room temperature to give the bis(vinylidene) isomers [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*/*p*-$CH{=}C)RhCl(P$-*i*-$Pr_3)_2](CF_3SO_3)$ (**11**, **12**).

Key words: ruthenium, rhodium, vinylidene complexes, alkyne complexes, phosphine complexes.

Résumé : En présence de CF_3SO_3Ag, le chélate complexe [$RuCl_2\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2$] (**1**) réagit avec un équivalent de $C_6H_4(C{\equiv}C)_2$-*p* (**4**) pour conduire à la formation du composé vinylidène mononucléaire [$RuCl(C{=}CHC_6H_4$-*p*-$C{\equiv}C)\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)_2$ (**3**). À partir de **1** et d'un demi-équivalent de **4**, on obtient le complexe bis(vinylidène) binucléaire [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*p*-$C{=}C)RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)_2$ (**6**). On a préparé le composé apparenté [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*-$C{=}C)RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)_2$ (**7**) en faisant réagir le composé **1** un demi-équivalent de $C_6H_4(C{\equiv}CH)_2$-*m* (**5**) en présence de triflate d'argent. Par le biais d'une addition du fragment à quatorze électrons $[RhCl(P$-*i*-$Pr_3)_2]$ à la triple liaison qui n'est pas coordinée, les réactions des composés **2** ou **3** avec le $[RhCl(P$-*i*-$Pr_3)_2]_2$ (**8**), dans un rapport molaire de 2:1, conduisent aux complexes hétérobinucléaires [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*/*p*-$C{\equiv}C)RhCl(P$-*i*-$Pr_3)_2](CF_3SO_3)_2$ (**9**, **10**) qui se réarrangement lentement à la température ambiante pour conduire aux isomères bis(vinylidènes) [$RuCl\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2(C{=}CHC_6H_4$-*m*/*p*-$C{=}C)RhCl(P$-*i*-$Pr_3)_2](CF_3SO_3)_2$ (**11**, **12**).

Mots clés : ruthénium, rhodium, complexes de vinylidènes, complexes d'alcynes, complexes de phosphines.

[Traduit par la Rédaction]

Introduction

Recently, we (1) described an efficient method for the preparation of the chelate complex [$RuCl_2\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2$] (**1**) using $[(1.5\text{-}C_8H_{12})RuCl_2]_n$ as the starting material. Due to the *hemilabile* coordination mode of the two phosphinoether ligands (for the term hemilabile see ref. 2*a*; for reviews see ref. 2*b*), compound **1** is quite reactive and affords with CO or PhC≡CH by cleavage of one of the Ru—O bonds the corresponding carbonyl and vinylidene complexes, [$RuCl_2(CO)\{\kappa^1(P)$-*i*-$Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}$] and [$RuCl_2(C{=}CHPh)\{\kappa^1(P)$-*i*-$Pr_2PCH_2CH_2OMe\}\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}$], respectively, (3). Moreover, treatment of **1** with terminal alkynes RC≡CH, in the presence of silver triflate, led to the formation of the cationic compounds [$RuCl(C{=}CHR)\{\kappa^2(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2](CF_3SO_3)$ which reacted with base by deprotonation of the vinylidene ligand to give the alkynyl derivatives [$RuCl(C{\equiv}CR)\{\kappa^2$-$(P,O)$-*i*-$Pr_2PCH_2CH_2OMe\}_2$] (1). Since we used in the course of these studies apart from alkynes RC≡CH with *R* = H, Ph, and C_6H_4Me-*p* also the diyne $C_6H_4(C{\equiv}CH)_2$-*m* as a substrate, we isolated a cationic complex with a ligand containing an uncoordinated C≡CH unit in the side chain.

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This paper is dedicated to Professor Brian R. James on the occasion of his 65th birthday, in recognition of his manifold contributions to organometallic chemistry and homogeneous catalysis.

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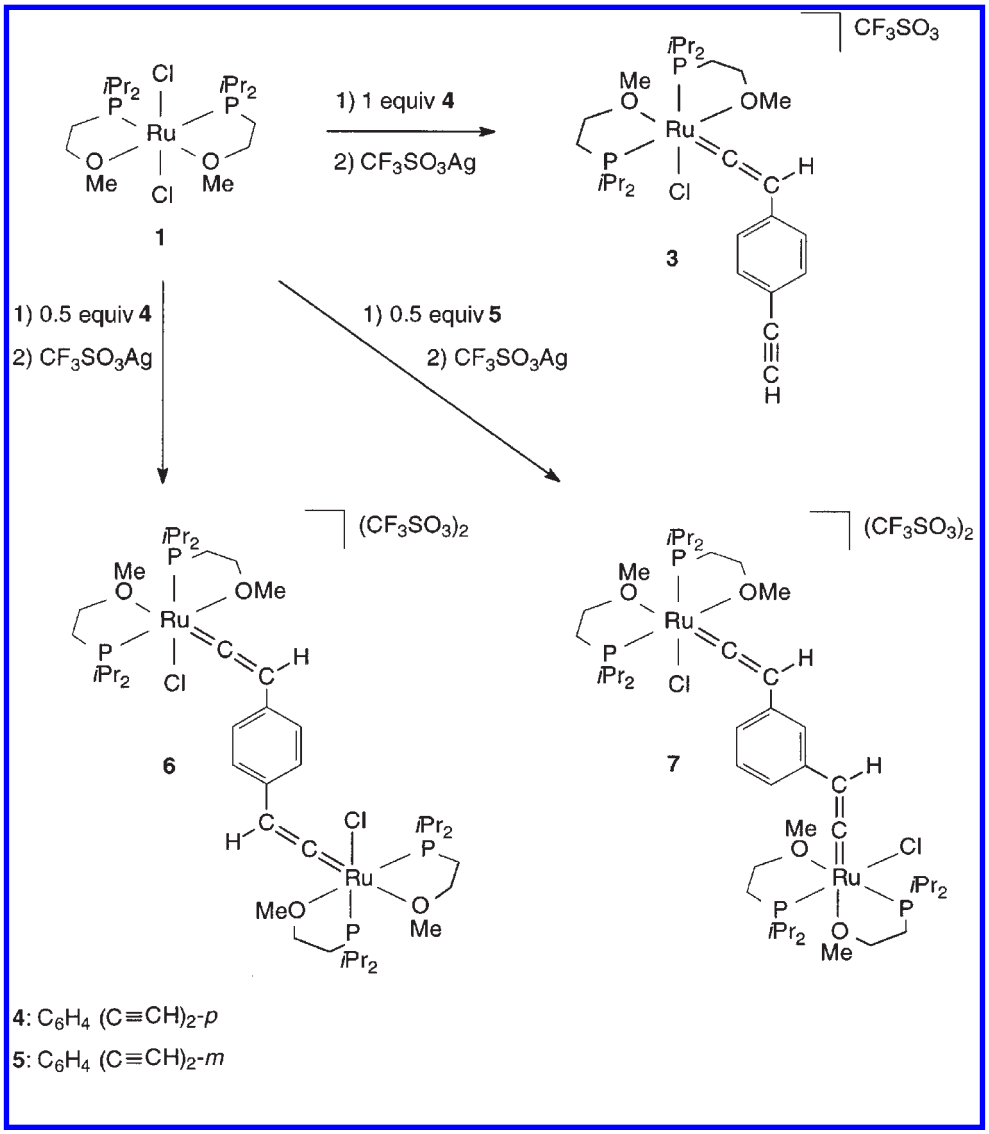
Scheme 1.



Based on this result, the question arose whether this ruthenium cation behaves like an ordinary terminal alkyne and reacts with coordinatively unsaturated precursors to give bimetallic products.

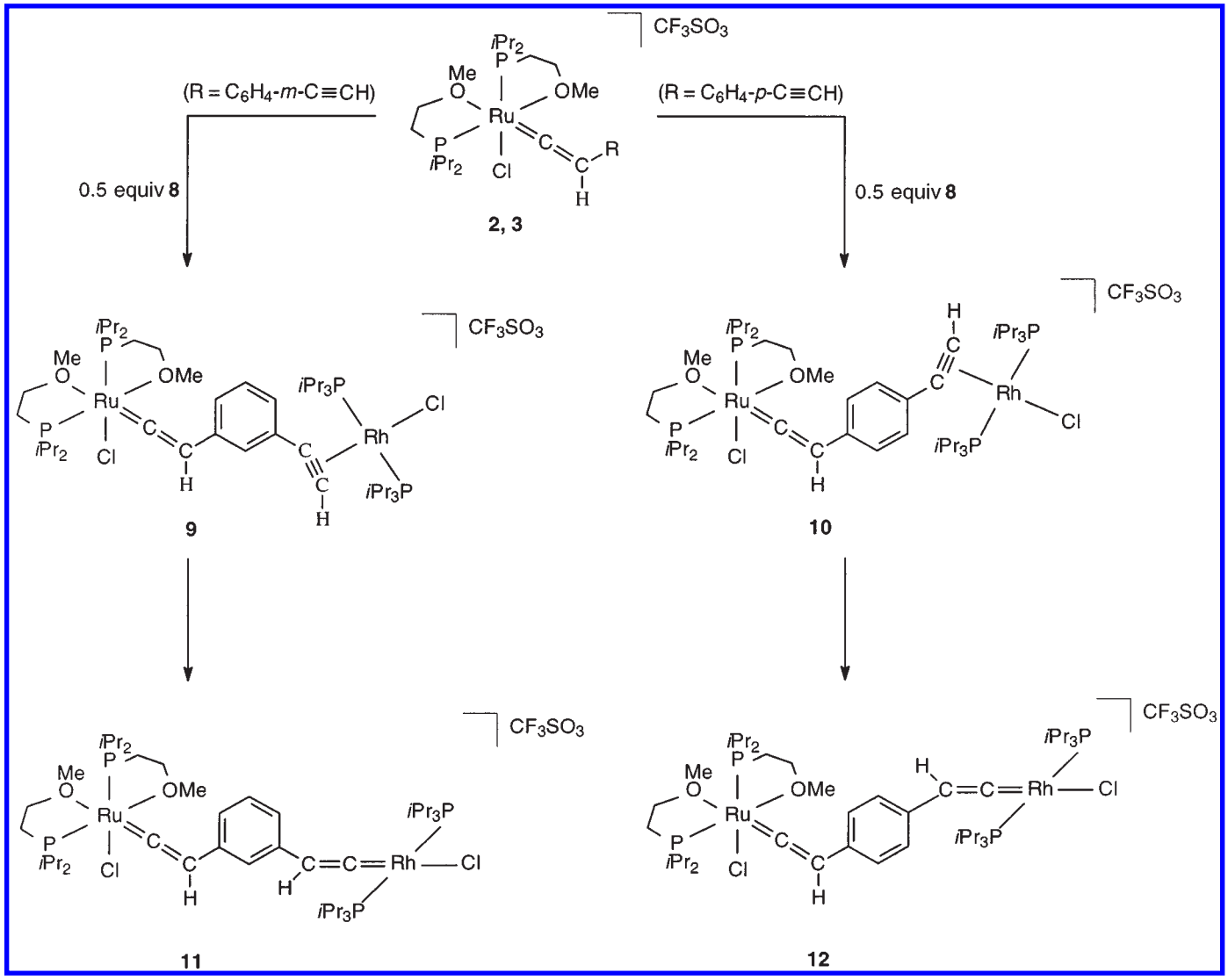
In answering this question, we report in the present paper the synthesis of some homo- and hetero-binuclear Ru–Ru and Ru–Rh complexes, the latter of which revealing different coordination spheres around the two metal centers.

Results and discussion

The preparation of the mononuclear complex **3** (see Scheme 1) followed the route which we had already used for the analogous compound **2** (1). Stepwise treatment of the starting material **1** in acetone with the diyne **4** and silver triflate led, after separation of AgCl, to the formation of a yellow solution from which **3** was isolated in 72% yield. The proposed structure with the *cis*-disposed P-*i*-Pr_2 groups is supported by the ^{31}P NMR spectrum which displays the typical pattern of an AB spin system showing two doublets with a small P—P coupling constant of 24.1 Hz. Further characteristic features are the triplet resonance for the =C*H*R proton in the ^1H NMR spectrum at δ 5.09 and the low-field signals at δ 355.5 and 117.2 in the ^{13}C NMR spectrum which, in agreement with DEPT measurements, are assigned to the α- and β-C atoms of the vinylidene unit. The resonances for the ^{13}C NMR nuclei of the uncoordinated C≡C bond appear as singlets at δ 83.8 and 77.4, respectively.

The reaction of **1** with an equimolar amount of CF_3SO_3Ag but with 0.5 equiv instead of 1 equiv of the diyne **4** led, under the same conditions as used for the preparation of **3**, to the binuclear complex **6** (see Scheme 1). Similarly to **3**, compound **6** is also an orange, only slightly air-sensitive solid which is easily soluble in polar solvents such as acetone or dichloromethane. In contrast to **3**, the IR spectrum of **6** shows no stretching vibrations in the regions at about 3200 and 2100 cm^{-1}, indicating that no C≡CH unit is present. The ^{13}C NMR spectrum of **6** displays the signals for the vinylidene carbon atoms at almost the same positions as found for the mononuclear complex **3**.

Scheme 2.



The starting material **1** reacts not only with **4** but also with the *meta*-isomer **5** of the diyne $C_6H_4(C{\equiv}CH)_2$ in the molar ratio of 2:1 to give the binuclear compound **7**. Due to the related structure of **6** and **7**, it is not surprising that both the chemical properties and the spectroscopic data of the two isomers are in most respects quite similar. The slightly lower symmetry of **7** compared to **6** is indicated, inter alia, by the appearance of a broad multiplet instead of a singlet for the protons of the C_6H_4 fragment and equally by the observation of eight instead of two singlet resonances for the carbon atoms of the phenylene ring. We also note that apart from **6** and **7**, three isomeric binuclear rhodium complexes with the *ortho*-, *meta*-, and *para*-isomers of the bis(vinylidene) unit $C{=}CHC_6H_4CH{=}C$ have been prepared in our laboratory (4).

The uncoordinated alkyne functionality of both **2** and **3** can also be used for the preparation of the mixed-metal ruthenium–rhodium compounds **9**–**12** shown in Scheme 2. The mononuclear precursors react, analogously as terminal alkynes RC≡CH (5), with the dimer $[RhCl(P\text{-}i\text{-}Pr_3)_2]_2$ (**8**) under mild conditions to give the Ru–Rh complexes **9** and **10** as orange microcrystalline solids in ca. 60% yield. In the IR spectra of **9** and **10**, the ν (≡CH) and ν (C≡C) modes appear at significantly lower wave numbers than in the spectra of **2** and **3** which is in agreement with the coordination of the triple bond to the rhodium center. The proposed *trans*-disposition of the two triisopropylphosphine ligands at Rh is supported by the ^{1}H NMR spectra of **9** and **10**, each of which displays two doublets of virtual triplets for the protons of the diastereotopic methyl groups of the P-*i*-Pr_3 units.

Both **9** and **10** slowly rearrange, in toluene at room temperature, to the isomeric species **11** and **12** which are isolated as green, relatively air-stable solids in ca. 70% yield. The ^{13}C NMR spectra of **11** and **12** exhibit in the low-field region two signals for the metal-bound carbon atoms at about δ 355 and 292 which is consistent with the presence of two different carbene-like vinylidene units in the molecule. Another characteristic feature in the ^{31}P NMR spectra of **11** and **12** is the appearance of two doublets for the phosphorus atoms linked to ruthenium and of one doublet for the phosphorus atoms linked to rhodium, the latter showing a rather large Rh—P coupling of ca. 135 Hz. With regard to the course of the rearrangement of **9** and **10** to **11** and **12**, we

failed to find any evidence for the generation of an intermediate containing an alkynyl(hydrido)rhodium moiety RhH(C≡CR)Cl(P-*i*-Pr_3)$_2$ as a building block, and therefore a concerted mechanism is most likely (6). This result is in contrast to that for the isomerization reaction of *trans*-[RhCl(HC≡C*t*Bu)(P-*i*-Pr_3)$_2$] to *trans*-[RhCl(=C≡CH-*t*-Bu)(P-*i*-Pr_3)$_2$] for which a five-coordinate intermediate [RhH(C≡C-*t*-Bu)Cl(P-*i*-Pr_3)$_2$] could not only be detected but even isolated (7).

Experimental

All experiments were carried out under an atmosphere of argon by using standard Schlenk techniques. The starting materials [$RuCl_2${κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$] (**1**) (1), C_6H_4(C≡CH)$_2$-*p* and -*m* (**4**, **5**) (8), [RuCl-(C=CHC_6H_4C≡CH-*m*){κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$](CF_3SO_3) (**2**) (1), and [RhCl(P-*i*-Pr_3)$_2$]$_2$ (**8**) (9) were prepared as described previously. IR spectra were recorded on a PerkinElmer 1420 IR spectrometer and NMR spectra on Bruker AC 200 and WM 400 instruments. Melting points (dec. temp.) were determined by DTA.

Preparation of [RuCl(C=CHC_6H_4-*p*-C≡CH){κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$](CF_3SO_3) (3)

A solution of **1** (262 mg, 0.50 mmol) and **4** (63 mg, 0.50 mmol) in 10 mL of acetone was cooled to 0°C and then treated with CF_3SO_3Ag (128 mg, 0.50 mmol). After the reaction mixture was stirred for 20 min in the dark, the precipitate (AgCl) was separated by filtration through Kieselgur and the filtrate concentrated to ca. 0.5 mL in vacuo. A yellow microcrystalline solid was formed which was washed twice with ether and dried. Yield: 275 mg (72%). IR (KBr) (cm^{-1}): ν(≡CH) 3200, ν(C≡C) 2080, ν(C=C) 1620, 1590. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.37, 7.30 (AB spin system, *J* (HH) = 7.8 Hz, C_6H_4), 5.09 (t, *J* (PH) = 3.2 Hz, =CH), 4.18, 4.13, 4.04, 3.80 (all m, C*H*$_2$OCH$_3$), 3.84, 3.65, (both s, OCH$_3$), 3.10 (s, ≡CH), 2.88, 2.50, 2.40, 2.34, 2.30, 2.00, 1.85 (all m, PC*H*CH$_3$ and PCH$_2$), 1.53–1.29 (br m, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ: 355.5 (dd, *J* (PC) = 18.1 and 15.1 Hz, Ru=C), 132.7, 130.5, 126.5, 119.9 (all s, C_6H_4), 121.4 (q, *J* (FC) = 320.9 Hz, CF_3), 117.2 (s, =*C*HR), 83.8 (s, C≡*C*H), 77.4 (s, *C*≡CH), 72.8, 71.7 (both s, *C*H$_2$OCH$_3$), 63.2, 63.1, 61.7, 61.6 (all s, OCH$_3$), 37.7 (d, *J* (PC) = 33.2 Hz, P*C*HCH$_3$), 29.5 (d, *J* (PC) = 26.0 Hz, P*C*HCH$_3$), 26.6 (d, *J* (PC) = 28.6 Hz, P*C*HCH$_3$), 25.8 (d, *J* (PC) = 20.0 Hz, P*C*HCH$_3$), 25.4 (d, *J* (PC) = 22.0 Hz, PCH$_2$), 23.2 (d, *J* (PC) = 24.0 Hz, PCH$_2$), 20.1, 19.8, 19.7, 19.65, 19.6, 19.5, 19.1, 19.0 (all s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2) δ: 67.9, 56.3 (both d, *J* (PP) = 24.1 Hz). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –78.6 (s). Anal. calcd. for $C_{29}H_{48}ClF_3O_5P_2RuS$: C 45.58, H 6.33, S 4.19; found: C 45.19, H 6.22, S 4.22.

Preparation of [RuCl{κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$(C=CHC_6H_4-*p*-CH=C)RuCl{κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$](CF_3SO_3)$_2$ (6)

The procedure was analogous to that described for **3**, using **1** (262 mg, 0.50 mmol), **4** (31 mg, 0.25 mmol), and CF_3SO_3Ag (128 mg, 0.50 mmol) in 20 mL of acetone as starting materials. An orange microcrystalline solid was obtained. Yield: 298 mg (85%). IR (kBr) (cm^{-1}): ν(C=C) 1600. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.21 (s, C_6H_4), 5.08, 5.06 (both t, *J* (PH) = 3.6 Hz, =CH), 4.19, 4.11, 4.04, 3.77 (all m, C*H*$_2$OCH$_3$), 3.84, 3.82, 3.64 (all s, OCH$_3$), 2.86, 2.48, 2.37, 2.32, 2.20, 2.01, 1.89 (all m, PC*H*CH$_3$ and PCH$_2$), 1.54–1.28 (br m, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ: 355.5 (dd, *J* (PC) = 18.1 and 15.1 Hz, Ru=C), 127.1, 126.3 (both s, C_6H_4), 121.4 (q, *J* (FC) = 320.9 Hz, CF_3), 117.8 (s, =CH), 72.7, 71.7 (both s, *C*H$_2$OCH$_3$), 63.2, 63.1, 61.8 (all s, OCH$_3$), 37.5 (d, *J* (PC) = 33.3 Hz, P*C*HCH$_3$), 28.6, 28.5 (both d, *J* (PC) = 26.0 Hz, P*C*HCH$_3$), 26.6 (d, *J* (PC) = 31.2 Hz, P*C*HCH$_3$), 25.8 (d, *J* (PC) = 20.0 Hz, P*C*HCH$_3$), 25.7 (d, *J* (PC) = 19.0 Hz, PCH$_2$), 23.3 (d, *J* (PC) = 23.6 Hz, PCH$_2$), 20.1, 19.8, 19.75, 19.7, 19.6, 19.2, 19.1, 19.0 (all s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2) δ: 68.1, 56.2 (both d, *J* (PP) = 24.3 Hz). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –78.6 (s). Anal. calcd. for $C_{48}H_{90}Cl_2F_6O_{10}P_4Ru_2S_2$: C 41.11, H 6.47, S 4.57; found: C 41.37, H 6.30, S 4.42.

Preparation of [RuCl{κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$(C=CHC_6H_4-*m*-CH=C)RuCl{κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$](CF_3SO_3)$_2$ (7)

The procedure was analogous to that described for **3**, using **1** (262 mg, 0.50 mmol), **5** (31 mg, 0.25 mmol), and CF_3SO_3Ag (128 mg, 0.50 mmol) in 20 mL of acetone as starting materials. An orange microcrystalline solid was obtained. Yield: 161 mg (46%). IR (KBr) (cm^{-1}): ν(C=C) 1610, 1580. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.22–6.95 (br m, C_6H_4), 5.06, 5.05 (both t, *J* (PH) = 3.7 Hz, =CH), 4.20, 4.12, 4.04, 3.80 (all m, C*H*$_2$OCH$_3$), 3.87, 3.82, 3.65 (all s, OCH$_3$), 2.88, 2.48, 2.42, 2.33, 2.22, 2.03, 1.91 (all m, PC*H*CH$_3$ and PCH$_2$), 1.55–1.28 (br m, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ: 357.4 (dd, *J* (PC) = 19.1 and 15.1 Hz, Ru=C), 129.5, 129.4, 129.3, 127.2, 125.7, 125.5, 123.0, 122.8 (all s, C_6H_4), 121.4 (q, *J* (FC) = 319.9 Hz, CF_3), 117.8, 117.7 (both s, =CH), 72.8, 72.7, 71.7 (all s, *C*H$_2$OCH$_3$), 63.2, 63.1, 61.7 (all s, OCH$_3$), 37.5 (d, *J* (PC) = 31.2 Hz, P*C*HCH$_3$), 29.6, 29.4 (both d, *J* (PC) = 26.3 Hz, P*C*HCH$_3$), 26.7, 26.5 (both d, *J* (PC) = 28.8 Hz, P*C*HCH$_3$), 25.7 (d, *J* (PC) = 20.2 Hz, P*C*HCH$_3$), 25.6 (d, *J* (PC) = 19.6 Hz, PCH$_2$), 23.3 (d, *J* (PC) = 23.0 Hz, PCH$_2$), 20.2, 20.1, 19.7, 19.65, 19.6, 19.1, 19.0, 18.9 (all s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2) δ: 68.0, 56.1 (both d, *J* (PP) = 24.3 Hz). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –78.6 (s). Anal. calcd. for $C_{48}H_{90}Cl_2F_6O_{10}P_4Ru_2S_2$: C 41.11, H 6.47, S 4.57; found: C 41.49, H 6.21, S 4.49.

Preparation of [RuCl{κ^2(*P,O*)-*i*-$Pr_2PCH_2CH_2OMe$}$_2$(C=CHC_6H_4-*m*-C≡CH)RhCl(P-*i*-Pr_3)$_2$](CF_3SO_3) (9)

A solution of **8** (101 mg, 0.11 mmol) in 15 mL of freshly distilled THF was cooled to –60°C and then treated with **2** (160 mg, 0.21 mmol). A characteristic change of color from violet to orange-yellow occurred. After the reaction mixture was warmed to room temperature and stirred for 10 min, the solvent was removed, the remaining orange solid washed three times with 5 mL portions of pentane (–20°C), and dried in vacuo. Yield: 159 mg (62%), mp 114°C (dec.). IR (CH_2Cl_2) (cm^{-1}): ν(≡CH) 3070, ν(C≡C) 1790, ν(C=C) 1570. ^{1}H NMR (200 MHz, CD_2Cl_2) δ: 7.59–6.75 (br m, C_6H_4), 5.10 (t, *J* (PH) = 3.1 Hz, =CH), 4.16, 4.14, 4.02, 3.83 (all m,

CH_2OCH_3), 3.81, 3.67 (both s, OCH_3), 3.71 (d, *J* (RhH) = 2.8 Hz, ≡CH), 2.87, 2.51, 2.37, 2.33, 2.32, 2.10, 1.87 (all m, RuPC*H*CH_3 and PCH_2), 2.74 (m, RhPC*H*CH_3), 1.51–1.39 (br m, RuPCHC*H*$_3$), 1.24 (dvt, *N* = 15.7, *J* (HH) = 7.5 Hz, RhPCHC*H*$_3$), 1.04 (dvt, *N* = 13.8, *J* (HH) = 6.7 Hz, RhPCHC*H*$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ: 66.6, 55.7 (both d, *J* (PP) = 24.0 Hz, RuP), 31.3 (d, *J* (RhP) = 117.7 Hz, RhP). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –78.4 (s). Anal. calcd. for $C_{47}H_{90}Cl_2F_3O_5P_4RhRuS$: C 46.16, H 7.42, S 2.62; found: C 46.09, H 7.35, S 2.26.

Preparation of [RuCl{κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$(C=CHC$_6$H$_4$-*p*-C≡CH)RhCl(P-*i*-Pr$_3$)$_2$](CF$_3$SO$_3$) (10)

The procedure was analogous to that described for **9**, using **3** (153 mg, 0.20 mmol) and **8** (94 mg, 0.10 mmol) as starting materials. An orange microcrystalline solid was obtained. Yield: 147 mg (60%), mp 120°C (dec.). IR (CH_2Cl_2) (cm^{-1}): ν(≡CH) 3070, ν(C≡C) 1780, ν(C=C) 1570. ^{1}H NMR (200 MHz, CD_2Cl_2) δ: 7.65–6.78 (br m, C_6H_4), 5.08 (t, *J* (PH) = 3.0 Hz, =CH), 4.13, 4.11, 4.01, 3.81 (all m, C*H*$_2$OCH$_3$), 3.78, 3.68 (both s, OCH_3), 3.67 (d, *J* (RhH) = 2.7 Hz, ≡CH), 2.87, 2.50, 2.35, 2.34, 2.31, 2.10, 1.88 (all m, RuPC*H*CH_3 and PCH_2), 2.73 (m, RhPC*H*CH_3), 1.49–1.37 (br m, RuPCHC*H*$_3$), 1.23 (dvt, *N* = 15.8, *J* (HH) = 7.3 Hz, RhPCHC*H*$_3$), 1.02 (dvt, *N* = 13.7, *J* (HH) = 6.5 Hz, RhPCHC*H*$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ: 66.2, 55.6 (both d, *J* (PP) = 24.3 Hz, RuP), 31.5 (d, *J* (RhP) = 116.8 Hz, RhP). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –78.6 (s). Anal. calcd. for $C_{47}H_{90}Cl_2F_3O_5P_4RhRuS$: C 46.16, H 7.42, S 2.62; found: C 46.23, H 7.51, S 2.74.

Preparation of [RuCl{κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$(C=CHC$_6$H$_4$-*m*-CH=C)RhCl(P-*i*-Pr$_3$)$_2$](CF$_3$SO$_3$) (11)

A solution of **9** (162 mg, 0.13 mmol) in 15 mL of toluene was stirred for 4 h at room temperature. A change of colour from orange to dark brown occurred. The solvent was removed in vacuo, the remaining residue was dissolved in 2 mL of toluene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column = 7 cm). With toluene, a green fraction was eluted which was evaporated to dryness in vacuo. The green solid was washed twice with 2 mL portions of pentane (0°C) and dried in vacuo. Yield: 113 mg (71%), mp 105°C (dec.). IR (CH_2Cl_2) (cm^{-1}): ν(C=C) 1610, 1570. ^{1}H NMR (200 MHz, CD_2Cl_2) δ: 7.55–6.74 (br m, C_6H_4), 4.80 (t, *J* (PH) = 3.1 Hz, Ru=C=CH), 4.17, 4.15, 4.02, 3.85 (all m, C*H*$_2$OCH$_3$), 3.80, 3.63 (both s, OCH_3), 2.88, 2.48, 2.39, 2.35, 2.31, 2.14, 1.92 (all m, RuPC*H*CH_3 and PCH_2), 2.74 (m, RhPC*H*CH_3), 1.53–1.42 (br m, RuPCHC*H*$_3$), 1.30 (dvt, *N* = 12.8, *J* (HH) = 6.3 Hz, RhPCHC*H*$_3$), the signal of Rh=C=CH could not be exactly located. ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ: 355.3 (dd, *J* (PC) = 17.9 and 14.8 Hz, Ru=C), 292.7 (dt, *J* (RhC) = 59.6, *J* (PC) = 15.5 Hz, Rh=C), 133.8, 130.0 127.3, 122.2 (all s, C_6H_4), 119.6 (q, *J* (FC) = 319.1 Hz, CF_3), 117.9 (s, Ru=C=*C*), 112.2 (dt, *J* (RhC) = 15.3, *J* (PC) = 7.0 Hz, Rh=C=*C*), 62.3, 61.3 (both s, OCH_3), 36.9 (d, *J* (PC) = 31.8 Hz, RuP*C*HCH$_3$), 29.0 (d, *J* (PC) = 24.2 Hz, RuP*C*HCH$_3$), 26.0 (d, *J* (PC) = 28.0 Hz, RuP*C*HCH$_3$), 25.6 (d, *J* (PC) = 24.2 Hz, PCH_2), 25.5 (d, *J* (PC) = 20.5 Hz, PCH_2), 25.4 (d, *J* (PC) = 20.3 Hz, RuP*C*HCH$_3$), 24.0 (vt, *N* = 17.8 Hz, RhP*C*HCH$_3$), 20.4 (s, RhPCH*C*H$_3$), 20.2, 20.1, 19.8, 19.6, 19.5, 19.4, 19.3, 19.1 (all s, RuPCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ: 68.6, 57.7 (both d, *J* (PP) = 24.7 Hz, RuP), 43.2 (d, *J* (RhP) = 135.1 Hz, RhP); ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –77.5 (s). Anal. calcd. for $C_{47}H_{90}Cl_2F_3O_5P_4RhRuS$: C 46.16, H 7.42, S 2.62; found: C 45.99, H 7.50, S 2.27.

Preparation of [RuCl{κ^2(*P,O*)-*i*-Pr$_2$PCH$_2$CH$_2$OMe}$_2$(C=CHC$_6$H$_4$-*p*-CH=C)RhCl(P-*i*-Pr$_3$)$_2$](CF$_3$SO$_3$) (12)

The procedure was analogous to that described for **11**, using **10** (115 mg, 0.09 mmol) in 10 mL of toluene as starting material. A green microcrystalline solid was obtained. Yield: 78 mg (71%), mp 108°C (dec.). IR (CH_2Cl_2) (cm^{-1}): ν(C=C) 1610, 1570. ^{1}H NMR (200 MHz, CD_2Cl_2) δ: 7.53–6.72 (br m, C_6H_4), 4.78 (t, *J* (PH) = 3.0 Hz, Ru=C=CH), 4.21, 4.17, 4.12, 3.97 (all m, C*H*$_2$OCH$_3$), 3.87, 3.67 (both s, OCH_3), 2.78, 2.45, 2.40, 2.36, 2.34, 2.16, 1.97 (all m, RuPC*H*CH_3 and PCH_2), 2.80 (m, RhPC*H*CH_3), 1.51–1.39 (br m, RuPCHC*H*$_3$), 1.32 (dvt, *N* = 12.6, *J* (HH) = 6.2 Hz, RhPCHC*H*$_3$), the signal of Rh=C=CH could not be exactly located. ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ: 355.2 (dd, *J* (PC) = 18.2 and 15.1 Hz, Ru=C), 291.5 (dt, *J* (RhC) = 58.2, *J* (PC) = 15.9 Hz, Rh=C), 134.1, 129.7, 127.2, 122.3 (all s, C_6H_4), 120.2 (q, *J* (FC) = 321.1 Hz, CF_3), 118.3 (s, Ru=C=*C*), 112.4 (dt, *J* (RhC) = 15.4, *J* (PC) = 7.1 Hz, Rh=C=*C*), 62.5, 61.6 (both s, OCH_3), 37.1 (d, *J* (PC) = 31.6 Hz, RuP*C*HCH$_3$), 29.3 (d, *J* (PC) = 24.1 Hz, RuP*C*HCH$_3$), 26.1 (d, *J* (PC) = 28.2 Hz, RuP*C*HCH$_3$), 25.7 (d, *J* (PC) = 24.2 Hz, PCH_2), 25.3 (d, *J* (PC) = 20.5 Hz, PCH_2), 25.2 (d, *J* (PC) = 20.1 Hz, RuP*C*HCH$_3$), 23.7 (vt, *N* = 17.5 Hz, RhP*C*HCH$_3$), 20.3 (s, RhPCH*C*H$_3$), 20.1, 19.9, 19.7, 19.6, 19.5, 19.4, 19.2, 19.1 (all s, RuPCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ: 68.3, 57.6 (both d, *J* (PP) = 24.3 Hz, RuP), 43.7 (d, *J* (RhP) = 135.9 Hz, RhP). ^{19}F NMR (376.5 MHz, CD_2Cl_2) δ: –77.7 (s). Anal. calcd. for $C_{47}H_{90}Cl_2F_3O_5P_4RhRuS$: C 46.16, H 7.42, S 2.62; found: C 46.29, H 7.45, S 2.67.

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