Preparation of Trifluorophosphaneruthenium(II) Complexes from η^3:η^3-Cyclooctadienediylruthenium(IV) Compounds as Precursors

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Dedicated to Professor Gerhard E. Herberich on the occasion of his 65th birthday

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The dinuclear cyclooctadienediylruthenium(IV) compound $[\{RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) reacts with PCy_3 in 2-propanol under an H_2 atmosphere to give the hydrido(dihydrogen) complex $[RuHCl(H_2)(PCy_3)_2]$ (**2**) in nearly quantitative yield. Treatment of **1** with PCy_3, P*i*Pr$_3$ or P*i*Pr$_2$Ph under argon affords the mononuclear products $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PR_3)]$ (**3**–**5**) by chloride-bridge cleavage. The corresponding compound **6** with PF_3 as phosphane ligand reacts with PCy_3 by nucleophilic attack of PCy_3 at the carbon atom C3 of the dienediyl chain to give the zwitterionic η^2:η^3-alkene(allyl)ruthenium(II) complex $[RuCl_2\{\eta^2{:}\eta^3\text{-}CH_2{=}C(Me){-}CH(PCy_3)(CH_2)_2CHC(Me)CH_2\}(PF_3)]$ (**7**) the crystal and molecular structures of which have been determined. The reaction of **7** with excess PCy_3 in the presence of H_2 affords the five-coordinate hydrido compound $[RuHCl(PF_3)(PCy_3)_2]$ (**8**), which upon treatment with acetylene gives the vinyl derivative $[RuCl(CH{=}CH_2)(PF_3)(PCy_3)_2]$ (**9**). The related cationic carbene complex $[RuCl({=}CHCH_3)(PF_3)(PCy_3)_2]BF_4$ (**10**) is obtained by protonation of **9** with HBF_4 in ether.

Introduction

In the search for coordinatively unsaturated vinylideneruthenium(II) complexes with [Ru(P*i*Pr$_3$)$_2$] and $[Ru(PCy_3)_2]$ as building blocks, we recently discovered that the six-coordinate non-octahedral dihydridoruthenium(IV) compounds $[RuH_2Cl_2(PR_3)_2]$ (R = *i*Pr, Cy) are excellent precursors for the preparation of the target molecules $[RuCl_2({=}C{=}CHR')(PR_3)_2]$.[1] If, however, instead of $[RuH_2Cl_2(PR_3)_2]$ the corresponding hydrido(dihydrogen)ruthenium(II) complexes $[RuHCl(H_2)(PR_3)_2]$ are used as starting materials, the reaction with $HC{\equiv}CR'$ in the presence of Brönsted acids and chloride ions leads to the formation of the Grubbs-type ruthenium carbenes $[RuCl_2({=}CHCH_2R')(PR_3)_2]$.[1,2] Since the reactivity of these species depends on the type of phosphane and since, to the best of our knowledge,[3] complexes of the general composition $[RuCl_2({=}CHCH_2R')(PR_3)(PX_3)]$ with two *different* phosphanes have not been reported in the literature, we were tempted to prepare the respective precursors $[RuHCl(H_2)(PR_3)(PX_3)]$ in order to find out whether they are appropriate starting materials for the synthesis of the desired ruthenium carbenes. While we failed to prepare neutral carbenes $[RuCl_2({=}CHCH_2R')(PR_3)(PX_3)]$, we found in the course of these studies a stepwise synthetic route to ruthenium complexes with $[Ru(PF_3)(PCy_3)_2]$ as a molecular unit. In the present paper we describe details of this route and report on the reactivity of the mixed trifluorophosphane(tricyclohexylphosphane)ruthenium(II) compounds.

Results and Discussion

For the one-pot synthesis of the five-coordinate ruthenium carbenes $[RuCl_2({=}CHCH_2R')(PR_3)_2]$ (R = *i*Pr, Cy), recently developed in our laboratory, polymeric cyclooctadieneruthenium(II) dichloride $[\{(\eta^4\text{-}C_8H_{12})RuCl_2\}_n]$ was used as the starting material.[4] By heating a suspension of this compound in 2-butanol for 6 h at 80 °C, in the presence of PCy_3 and H_2, the hydrido(dihydrogen) complex **2**[5] is formed. Since the conditions for the preparation of **2** with $[\{(\eta^4\text{-}C_8H_{12})RuCl_2\}_n]$ as the precursor are rather severe, we decided to search for another starting material to generate **2**. The compound of choice was the dinuclear cyclooctadienediylruthenium(IV) complex **1**, which was first reported by Porri et al. in 1965[6] and in subsequent studies used as a catalyst for olefin metathesis.[7,8] Both Porri[6a] and others[9,10] have reported that the chloro bridges of **1** can easily be split by hard and soft Lewis bases to yield the mononuclear compounds $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ (L = py, DMSO, CH_3CN, CN*t*Bu, CO, PPh_3, $P(OMe)_3$, PF_3 etc). It was also observed that the reaction of **1** with H_2 (1 bar,

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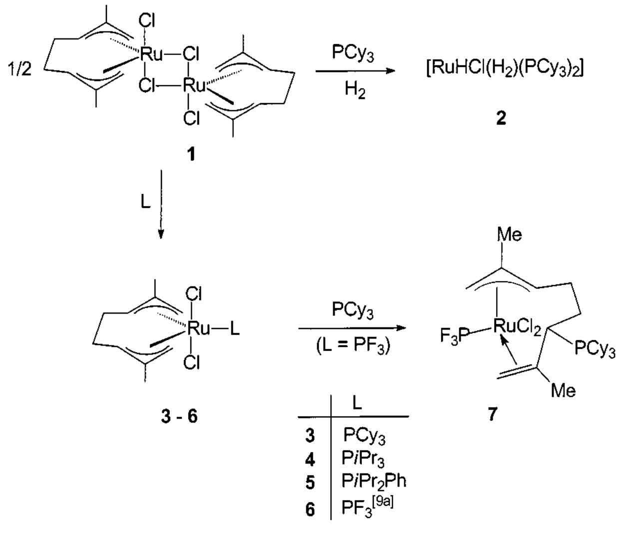
25 °C) in dichloromethane leads quantitatively to the formation of 2,7-dimethylocta-2,6-diene.[6a]

Taking these results into consideration, we treated a suspension of **1** in 2-propanol with PCy_3 and replaced the argon atmosphere by dihydrogen. Upon stirring the suspension under these conditions at ca. 50 °C, an orange solid precipitated which was shown by comparison of the ^1H and ^{31}P NMR spectroscopic data to be **2**.[5] The isolated yield of **2** was 92%. If the reaction of **1** with PCy_3 was carried out in CH_2Cl_2 at −20 °C under argon (i.e., in the absence of H_2 and a hydrogen-transfer reagent such as 2-propanol), the cyclooctadienediylruthenium(IV) complex **3** was formed instead of **2** (Scheme 1). Other bulky tertiary phosphanes such as P*i*Pr_3 and P*i*Pr_2Ph behave analogously and afford the corresponding mononuclear compounds **4** and **5** in 89% and 91% yield, respectively. Compounds **3**−**5** are yellow to brownish solids that are only moderately air-sensitive but thermally quite labile and decompose both in solution and in the solid state at 40−50 °C. The ^1H NMR spectroscopic data of **3**−**5** and the ^{13}C NMR spectroscopic data of **4** and **5** are similar to those of the $Ru(PF_3)$ complex **6**, the crystal and molecular structures of which have been determined crystallographically.[9b] The CH and CH_2 protons H1−H5 of **3**−**5** give rise to five resonances and the carbon atoms C1−C4 to four resonances in the NMR spectra (for assignment see Exp. Sect.), in agreement with the C_2 symmetry of the cyclooctadienediyl ligand.[6b][9b]



Scheme 1

The reactions of **4** and **5** with a slight excess of PCy_3 in the presence of H_2, undertaken with the aim to prepare the mixed-ligand compounds $[RuHCl(H_2)(P$*i*$Pr_2R)(PCy_3)]$ (R = *i*Pr, Ph), led to a mixture of products that could not be separated by fractional crystallization or chromatographic techniques. When the reactions were monitored by ^1H or ^{31}P NMR spectroscopy, the formation of uncoordinated P*i*Pr_3 or P*i*Pr_2Ph was detected. Obviously, PCy_3 replaces the less bulky phosphanes and generates **3**, which upon treatment with PCy_3 and H_2 affords **2**.

In contrast to **4** and **5**, the related PF_3 derivative **6** reacts almost instantaneously with PCy_3, even in the absence of dihydrogen, to yield a single product **7**, the composition of which corresponds to a 1:1 adduct of the two starting materials. The pale-yellow, highly air-sensitive solid is soluble in chloroform and dichloromethane but decomposes in solution at room temperature quite rapidly. Whereas the ^1H and ^{13}C NMR spectra (measured at −50 °C in CD_2Cl_2) are rather complicated, the ^{31}P NMR spectrum displays a doublet at $\delta = 32.5$ for the PCy_3 and a quadruplet of doublets at $\delta = 137.3$ for the PF_3 phosphorus atoms. The rather small ^{31}P-^{31}P coupling constant of 19.3 Hz (for comparison see the data for **8**−**10**) indicate that only one phosphane molecule is coordinated to the metal center while the other is linked to the π-bonded chain-like ligand.

The result of the X-ray crystal structure analysis of **7** is shown in Figure 1. The coordination geometry around ruthenium can best be described as trigonal bipyramidal with the chlorine atoms occupying the apical positions of the bipyramid. The η^2:η^3-alkene(allyl) unit, formed by nucleophilic addition of PCy_3 at the allylic carbon atom C3 of the η^3:η^3-cyclooctadienediyl ligand, occupies two of the equatorial sites, while the third position is occupied by PF_3. In contrast to **6**,[9b] the PF_3 molecule of **7** is not disordered. The carbon atoms C1, C2, C7, C8, C10 and the phosphorus atom P1 lie in one plane, the largest deviation being found for C7 with 0.103(2) Å. Although **7** possesses two centers of chirality, the crystal contains only that pair of enantiomers in which the methyl group at C2 and the PCy_3 moiety are farthest apart. The bond angle between P1, Ru and the midpoint of the line between C7 and C10 is 122.5(2)° and thus deviates only slightly from the ideal value of 120°. The Ru−P1 bond length of 2.178(2) Å is somewhat shorter than in **6** [2.237(3) Å] but almost identical to the $Ru-PF_3$ distances in the octahedral compound $[RuCl_2(PF_3)_2(PPh_3)_2]$ [2.160(2) and 2.180(2) Å].[9b] The olefinic fragment of the zwitterionic $C_{10}H_{16}(PCy_3)$ ligand is unsymmetrically linked to the metal center, the bond lengths Ru−C1 and Ru−C2 pointing to a rather weak coordination compared to other alkeneruthenium complexes.[11] Similar Ru−C olefin distances are found in the compound $[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})]$ which has been prepared from $RuCl_3\cdot3H_2O$ and butadiene.[12]

While we could not convert **7** to the desired hydrido(dihydrogen) complex $[RuHCl(H_2)(PF_3)(PCy_3)]$, treatment of **7** in dichloromethane with excess PCy_3 under a hydrogen atmosphere leads to the formation of the five-coordinate hydridoruthenium(II) compound **8** in 63% isolated yield (Scheme 2). The presence of the hydrido ligand is clearly confirmed by the ^1H NMR spectrum, which displays a signal at high field ($\delta = -24.68$). This signal is split into a doublet of triplets of quadruplets due to the coupling of the RuH proton with the ^{31}P and ^{19}F nuclei of the PCy_3 and PF_3 ligands.

The reactivity of the hydrido(trifluorphosphane)ruthenium(II) complex **8** is similar to that of the corresponding hydrido(carbonyl) derivatives $[RuHCl(CO)(PR_3)_2]$. By passing a slow stream of acetylene through a solution of **8** in

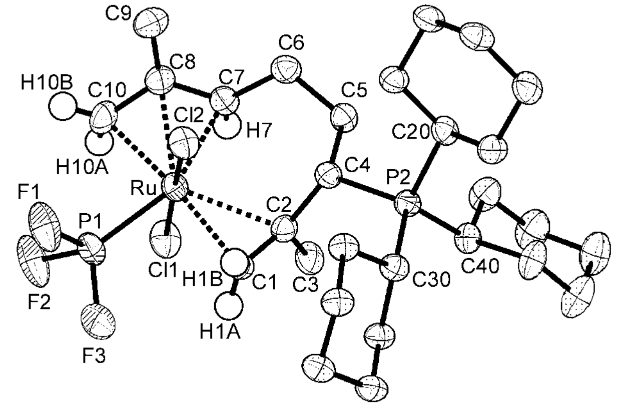
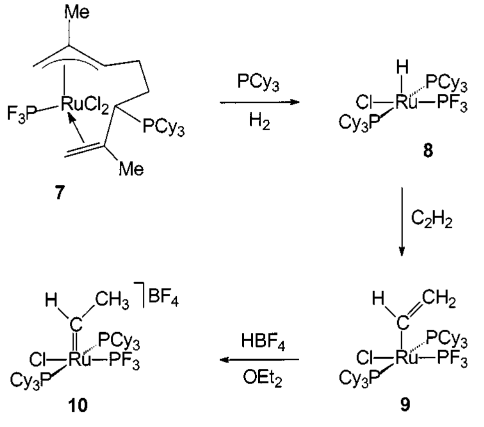


Figure 1. Molecular structure (SCHAKAL plot) of **7**; selected bond lengths [Å] and angles [°]: Ru−P1 2.178(2), Ru−Cl1 2.427(2), Ru−Cl2 2.433(2), Ru−C1 2.228(4), Ru−C2 2.360(4), Ru−C7 2.239(4), Ru−C8 2.246(4), Ru−C10 2.204(4), C1−C2 1.393(5), C2−C4 1.523(5), C7−C8 1.427(5), C8−C10 1.414(6), P2−C4 1.863(4); Cl1−Ru−Cl2 175.6(3), Cl1−Ru−P1 86.5(1), Cl1−Ru−C1 93.7(1), Cl1−Ru−C2 86.8(1), Cl1−Ru−C8 100.5(1), Cl1−Ru−C10 81.3(1), Cl2−Ru−P1 90.6(1), Cl2−Ru−C1 82.9(1), Cl2−Ru−C2 91.9(1), Cl2−Ru−C7 95.6(1), Cl2−Ru−C8 83.7(1), Cl2−Ru−C10 101.8(1), C1−C2−C3 117.5(3), C1−C2−C4 123.0(3), C2−C4−C5 113.1(3), C2−C4−P2 116.6(2), C5−C4−P2 108.7(2), C7−C8−C9 122.0(3), C7−C8−C10 119.6(3)



Scheme 2

hexane, a rapid change of color from yellow to bright-red occurs and, after removal of the solvent, the vinylruthenium(II) compound **9** is obtained in nearly quantitative yield. The ^{31}P NMR spectrum of **9** displays a doublet for the PCy_3 phosphorus atoms at $\delta = 24.3$ and a quadruplet of triplets for the ^{31}P nuclei of coordinated PF_3 at $\delta = 119.2$. Both the ^{31}P-^{31}P and ^{31}P-^{19}F coupling constants of 45.8 Hz and 1241 Hz, respectively, are of the same order of magnitude as for the hydrido complex **8**. The signals for the three vinyl protons of **9** appear in the ^{1}H NMR spectrum at $\delta = 8.51$, 5.37 and 5.10 and are all shifted downfield relative to the related ruthenium carbonyl $[RuCl(CH{=}CH_2)(CO)(PCy_3)_2]$.[13]

In analogy to the structurally related cationic vinylruthenium(II) derivative $[Ru(CH{=}CH_2)(CH_3CN)_2(PCy_3)_2]^+$, which reacts with HBF_4 in ether to generate the dicationic ruthenium carbene $[Ru({=}CHCH_3)(CH_3CN)_2(PCy_3)_2](BF_4)_2$,[14] treatment of **9** with HBF_4 in CH_2Cl_2/OEt_2 gives the monocationic five-coordinate carbene compound **10** in moderate yield. The composition of **10** has been substantiated by elemental analysis and ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy. Typical spectroscopic features of **10** are the signal for the RuCH proton at $\delta = 17.35$ in the ^{1}H NMR spectrum and the multiplet for the carbene carbon atom at $\delta = 326.1$ in the ^{13}C NMR spectrum. Similarly to **9**, the ^{31}P NMR spectrum of **10** exhibits two resonances at $\delta = 49.7$ and 127.1, the splitting of which again corresponds to a doublet and a quadruplet of triplets. It should be noted that solutions of **10** (e.g., in dichloromethane or nitromethane) are stable only below −20 °C for a few hours; at room temperature decomposition occurs. While we failed to identify any Ru-containing decomposition products, the formation of the vinylphosphonium cation $[Cy_3PCH{=}CH_2]^+$ [with resonances for the vinyl protons at $\delta = 6.76$ (dd), 6.35 (dd) and 6.15 (ddd) in the ^{1}H NMR spectrum] could be clearly confirmed.

In summary, the present work illustrates that with the dinuclear η^3:η^3-cyclooctadienediylruthenium(IV) compound **1** as the starting material and the unusual zwitterionic η^3:η^3-alkene(allyl)ruthenium(II) species **7** as an isolated intermediate five-coordinate hydrido-, vinyl- and carbeneruthenium complexes with PF_3 as a supporting ligand can be prepared. In contrast to the neutral ruthenium carbenes $[RuCl_2({=}CHR)(PCy_3)_2]$,[3,15] the cation $[RuCl({=}CHCH_3)(PF_3)(PCy_3)_2]^+$ is catalytically inactive in the ring-opening metathesis polymerization of cyclooctene, probably due to the ease of decomposition to give $[Cy_3PCH{=}CH_2]^+$. In this respect, the properties of the PF_3 derivative **10** are similar to those of the cationic carbene(carbonyl)ruthenium(II) complexes $[RuCl({=}CHCH_2R)(CO)(P\mathit{i}Pr_3)_2]BF_4$ and $[RuCl({=}CHCH_2R)(CO)(PCy_3)_2]BF_4$, the preparation and reactivity of which will be described in a forthcoming publication.

Experimental Section

All operations were carried out under argon using standard Schlenk techniques. The starting materials **1**[6b] and **6**[9a] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and AMX 400 instruments, unless otherwise stated. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; vt, virtual triplet; br, broadened signal; $N = {}^{2}J(PC) + {}^{4}J(PC)$. For assignment of protons and carbon atoms for the π-bonded ligands in compounds **3**−**5** and **7** see Figure 2. Melting and decomposition points were measured by differential thermal analysis (DTA).

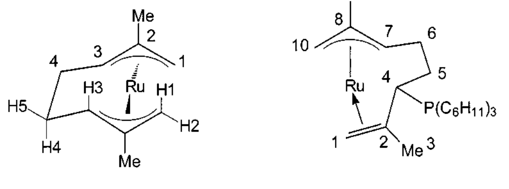


Figure 2. Assignment of proton and carbon atoms for the ligands in compounds **3**−**6** and **7**

Preparation of [RuHCl(H$_2$)(PCy$_3$)$_2$] (2) from 1: A suspension of **1** (510 mg, 0.827 mmol) in 2-propanol (40 mL) was treated with PCy$_3$ (1.86 g, 6.62 mmol) at room temperature. The Schlenk tube was evacuated and the argon atmosphere replaced by H$_2$. The suspension was warmed to ca. 50 °C and, after stirring for 40 min, an orange solid precipitated. This solid was separated from the mother liquor, washed twice with 20 mL portions of 2-propanol and dried. It was identified by comparing the ^{1}H and ^{31}P NMR spectra with those of an authentic sample;[5] yield 1.07 g (92%).

Preparation of [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)(PCy$_3$)] (3): A solution of PCy$_3$ (95 mg, 0.34 mmol) in CH$_2$Cl$_2$ (6 mL) was treated at −20 °C with **1** (104 mg, 0.17 mmol), leading to a change of color from violet to brown-yellow. After stirring the reaction mixture for 5 min, the solvent was evaporated in vacuo. The oily residue was treated with pentane (3 mL) and the suspension irradiated for 1 min in an ultrasound bath. A yellow solid precipitated which was separated from the mother liquor, washed twice with pentane (10 mL) and dried; yield 170 mg (85%); m.p. 46 °C (decomp). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 5.14$ (m, 2 H, H3), 4.69 (d, $^3J_{P,H} = 7.6$ Hz, 2 H, H1 or H2), 3.55 (d, $^3J_{P,H} = 3.2$ Hz, 2 H, H2 or H1), 3.32 (m, 2 H, H4 or H5), 2.64−2.45 (m, 8 H, H5 or H4 and C$_6$H$_{11}$), 2.16 (s, 6 H, Me), 2.20−2.00, 1.83−1.67, 1.40−1.24 (all m, 27 H, C$_6$H$_{11}$). ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$): $\delta = 5.0$ (s). C$_{28}$H$_{49}$Cl$_2$PRu (588.7): calcd. C 57.13, H 8.39; found C 56.89, H 8.28.

Preparation of [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)(P*i*Pr$_3$)] (4): A solution of **1** (101 mg, 0.16 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with P*i*Pr$_3$ (68 μL, 0.51 mmol) at room temperature, leading to a change of color from violet to red-brown. After stirring the reaction mixture for 30 min, the solvent was evaporated in vacuo. The oily residue was treated with pentane (5 mL) which after ca. 10 min led to the formation of a brownish solid. The solid was separated from the mother liquor, washed twice with 10 mL portions of pentane and dried; yield 137 mg (89%); m.p. 51 °C (decomp). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 5.12$ (m, 2 H, H3), 4.81 (d, $^3J_{P,H} = 7.6$ Hz, 2 H, H1 or H2), 3.52 (d, $^3J_{P,H} = 3.2$ Hz, 2 H, H2 or H1), 3.33 (m, 2 H, H4 or H5), 2.82 (m, 3 H, PC*H*CH$_3$) 2.55 (m, 2 H, H5 or H4), 2.17 (s, 6 H, Me), 1.46 (dd, $^3J_{P,H} = 12.0$, $^3J_{H,H} = 7.1$ Hz, 9 H, PCHC*H*$_3$), 1.39 (dd, $^3J_{P,H} = 12.8$, $^3J_{H,H} = 7.1$ Hz, 9 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 124.9$ (s, C2), 108.6 (d, $^2J_{P,C} = 9.1$ Hz, C3), 62.6 (d, $^2J_{P,C} = 5.8$ Hz, C1), 36.2 (s, C4), 28.8 (d, $^1J_{P,C} = 15.8$ Hz, P*C*HCH$_3$), 20.7 (s, Me), 20.1 (d, $^2J_{P,C} = 3.0$ Hz, PCH*C*H$_3$), 17.8 (br. s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 17.7$ (s). C$_{19}$H$_{37}$Cl$_2$PRu (468.5): calcd. C 48.72, H 7.96; found C 48.23, H 7.59.

Preparation of [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)(P*i*Pr$_2$Ph)] (5): This compound was prepared as described for **4**, using **1** (523 mg, 0.85 mmol) and P*i*Pr$_2$Ph (306 mg, 1.80 mmol) as starting materials. Yellow solid; yield 781 mg (91%); m.p. 42 °C (decomp). ^{1}H NMR(400 MHz, CD$_2$Cl$_2$): $\delta = 8.05$ (m, 2 H, Ph), 7.41 (m, 3 H, Ph), 5.14 (m, 2 H, H3), 4.45 (d, $^3J_{P,H} = 8.8$ Hz, 2 H, H1 or H2), 3.46 (d, $^3J_{P,H} = 3.2$ Hz, 2 H, H2 or H1), 3.32 (m, 2 H, H4 or H5), 3.08 (m, 3 H, PC*H*CH$_3$) 2.57 (m, 2 H, H5 or H4), 2.16 (s, 6 H, Me), 1.40 (dd, $^3J_{P,H} = 14.4$, $^3J_{H,H} = 7.2$ Hz, 3 H, PCHC*H*$_3$), 1.32 (dd, $^3J_{P,H} = 13.2$, $^3J_{H,H} = 7.2$ Hz, 3 H, PCHC*H*$_3$), 1.22 (dd, $^3J_{P,H} = 14.0$, $^3J_{H,H} = 7.0$ Hz, 3 H, PCHC*H*$_3$), 1.17 (dd, $^3J_{P,H} = 13.8$, $^3J_{H,H} = 7.0$ Hz, 3 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta = 134.2$ (d, $J_{P,C} = 6$ Hz, Ph), 132.9 (d, $J_{P,C} = 29.2$ Hz, Ph), 129.6 (d, $J_{P,C} = 2$ Hz, Ph), 127.8 (d, $J_{P,C} = 8$ Hz, Ph), 126.0 (s, C2), 108.6 (d, $^2J_{P,C} = 9$ Hz, C3), 63.8 (d, $^2J_{P,C} = 6$ Hz, C1), 36.6 (s, C4), 27.6, 27.2 (both d, $^1J_{P,C} = 19.5$ and 19.9 Hz, P*C*HCH$_3$), 21.0 (s, Me), 19.2, 18.5 (both s, PCH*C*H$_3$), 19.1, 18.5 [both d, $^2J_{P,C} = 2.6$ and 2.7 Hz, PCH*C*H$_3$]. ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 16.9$ (s). C$_{22}$H$_{35}$Cl$_2$PRu (502.5): calcd. C 52.59, H 7.02; found C 53.14, H 6.91.

Preparation of [RuCl$_2${η^2:η^3-CH$_2$=C(Me)CH(PCy$_3$)(CH$_2$)$_2$CHC(Me)CH$_2$}(PF$_3$)] (7): A solution of **6** (112 mg, 0.34 mmol) in toluene (5 mL) was treated dropwise with a solution of PCy$_3$ (106 mg, 0.38 mmol) in toluene (5 mL) at room temperature. A slow precipitation of an orange oil was observed. After stirring the reaction mixture vigorously for 10 min, the oil was partly converted into a yellow solid, the precipitation of which was facilitated by addition of pentane (5 mL) and by cooling the Schlenk tube to −78 °C. The solid was filtered, washed twice with 5 mL portions of pentane (−20 °C) and dried; yield 172 mg (83%); m.p. 62 °C (decomp). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, −50 °C): $\delta = 4.22-4.11$ (m, 2 H, L), 3.54−3.50 (m, 1 H, L), 3.48−3.24 (m, 2 H, L), 2.95 (s, 1 H, L), 2.94−2.72 (m, 1 H, L), 2.60−2.39 (m, 6 H, C$_6$H$_{11}$), 2.19, 1.97−1.60, 1.46−1.30 (all m, 36 H, C$_6$H$_{11}$ and Me of L); L is the abbreviation for the η^2:η^3-alkene(allyl) ligand. ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$, −50 °C): $\delta = 120.6$ (s, C8), 73.2 (s, C2), 72.8 (dq, $^2J_{P,C} = 43.0$, $^3J_{F,C}$ ca. 3 Hz, C7), 59.8 (d, $J_{P,C} = 4.7$ Hz, C1 or C10), 55.5 (s, C10 or C1), 38.2 (d, $J_{P,C} = 21.0$ Hz, C4), 31.5 (d, $^1J_{P,C} = 34.3$ Hz, C$_6$H$_{11}$), 31.1, 24.5 (both d, $J_{P,C} = 9.6$ and 11.5 Hz, C5 and C6), 28.5, 21.5 (both s, C3 and C9), 27.1 (br. s, C$_6$H$_{11}$), 26.7, 26.5 (both d, $J_{P,C} = 11.4$ and 11.5 Hz, C$_6$H$_{11}$), 25.0 (s, C$_6$H$_{11}$). ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta = -17.3$ (d, $^1J_{P,F} = 1362$ Hz, PF$_3$). ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 137.3$ (qd, $^1J_{P,F} = 1362$ Hz, $J_{P,P} = 19.3$ Hz, PF$_3$), 32.5 (d, $J_{P,P} = 19.3$ Hz, PCy$_3$). C$_{28}$H$_{49}$Cl$_2$F$_3$P$_2$Ru (676.6): calcd. C 49.70, H 7.30; found C 50.10, H 7.20.

Preparation of [RuHCl(PF$_3$)(PCy$_3$)$_2$] (8): A solution of **7** (125 mg, 0.19 mmol) in CH$_2$Cl$_2$ (4 mL) was treated with PCy$_3$ (312 mg, 1.11 mmol) and stirred for 2 h under an H$_2$ atmosphere (1 bar). A change of color from yellow to red occurred. After evaporation of the solvent in vacuo, the residue was suspended in acetone (4 mL) and the mixture stirred for 30 min. An orange-yellow solid precipitated, which was separated from the mother liquor, washed with acetone (4 mL) and dried in vacuo; yield 98 mg (63%); m.p. 40 °C (decomp). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 2.63-1.21$ (m, 66 H, C$_6$H$_{11}$), −24.68 (dtq, $^2J_{P^2,H} = 57.8$, $^2J_{P^1,H} = 16.9$, $^3J_{F,H} = 4.4$ Hz, 1 H, RuH); P^1 and P^2 assigned to the phosphorus atoms of PCy$_3$ and PF$_3$, respectively. ^{19}F NMR (188.3 MHz, CD$_2$Cl$_2$): $\delta = -98.1$ (d, $^1J_{P,F} = 1225$ Hz). ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$): $\delta = 128.7$ (qm, $^1J_{F,P} = 1225$ Hz, PF$_3$), 46.8 (d, $^2J_{P,P} = 45.8$ Hz, PCy$_3$). C$_{36}$H$_{67}$ClF$_3$P$_3$Ru (786.4): calcd. C 54.99, H 8.59; found C 54.99, H 8.73.

Preparation of [RuCl(CH=CH$_2$)(PF$_3$)(PCy$_3$)$_2$] (9): A slow stream of acetylene was passed for 10 s through a solution of **8** (88 mg, 0.11 mmol) in hexane (15 mL) at room temperature. A change of color from yellow to bright red occurred. The solvent was then evaporated in vacuo, and the remaining red solid washed with pentane (3 mL) and dried; yield 90 mg (99%); m.p. 88 °C (decomp). ^{1}H NMR (200 MHz, C$_6$D$_6$): $\delta = 8.51$ (m, 1 H, C*H*=CH$_2$), 5.37 (m, 1 H, *cis*-H of CH=C*H*$_2$), 5.10 (dm, $^3J_{H,H} = 13.6$ Hz, 1 H, *trans*-H of CH=C*H*$_2$), 2.85−1.11 (m, 66 H, C$_6$H$_{11}$). ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 153.9$ (br. s, RuCH), 121.8 (br. s, =CH$_2$), 36.2 (vt, $N = 17.4$ Hz, C1 of C$_6$H$_{11}$), 30.8, 30.6 (both s, C3,5 of C$_6$H$_{11}$), 28.3, 28.1 (both s, C2,6 of C$_6$H$_{11}$), 27.0 (s, C4 of C$_6$H$_{11}$). ^{19}F NMR (188.3 MHz, C$_6$D$_6$): $\delta = -6.0$ (d, $^1J_{P,F} = 1241$ Hz). ^{31}P NMR (81.0 MHz, C$_6$D$_6$): $\delta = 119.2$ (qt, $^1J_{F,P} = 1241$, $^2J_{P,P} = 45.8$ Hz, PF$_3$), 24.3 (d, $^2J_{P,P} = 45.8$ Hz, PCy$_3$). C$_{38}$H$_{69}$ClF$_3$P$_3$Ru (812.4): calcd. C 56.18, H 8.56; found C 56.59, H 8.06.

Preparation of [RuCl(=CHCH$_3$)(PF$_3$)(PCy$_3$)$_2$]BF$_4$ (10): A solution of **9** (80 mg, 0.10 mmol) in CH$_2$Cl$_2$ (2 mL) was treated with a 1.6 M solution of HBF$_4$ in ether (0.2 mL, 0.32 mmol) at room temperature. A change of color from red to yellow occurred. The solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 3 mL portions of ether and dried; yield 45 mg (50%); m.p. 108 °C (decomp). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ = 17.35 (br. s, 1 H, Ru=CH), 2.95 (s, 3 H, CH$_3$), 2.70−1.13 (m, 66 H, C$_6$H$_{11}$). ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, −20 °C): δ = 326.1 (m, Ru=CH), 51.0 (s, CH$_3$), 35.1 (br. m, C1 of C$_6$H$_{11}$). 29.5 (s, C3,5 of C$_6$H$_{11}$), 27.2 (m, C2,6 of C$_6$H$_{11}$), 25.5 (s, C4 of C$_6$H$_{11}$). ^{19}F NMR (188.3 MHz, CD$_2$Cl$_2$): δ = −11.6 (d, $^1J_{P,F}$ = 1282 Hz, PF$_3$), −153.5 (br. s, BF$_4$). ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$): δ = 127.1 (qt, $^1J_{F,P}$ = 1282, $^2J_{P,P}$ = 35.6 Hz, PF$_3$), 49.7 (d, $^2J_{P,P}$ = 35.6 Hz, PCy$_3$). C$_{38}$H$_{70}$BClF$_7$P$_3$Ru (900.2): calcd. C 50.70, H 7.84; found C 50.25, H 7.31.

Determination of the X-ray Crystal Structure of 7: Single crystals were grown by cooling a saturated solution of **7** in acetone from 25 °C to −20 °C. Crystal data (from 5000 reflections, 2.49° < Θ < 28.23°): triclinic; space group $P\bar{1}$ (No. 2); a = 9.878(7), b = 13.93(1), c = 14.17(1) Å, α = 87.35(9)°, β = 84.80(9)°, γ = 74.22(9)°; V = 1868(2) Å^3, Z = 2; $d_{\text{calcd.}}$ = 1.410 g cm^{-3}; μ(Mo-K_α) = 0.686 mm^{-1}; crystal size 0.14 × 0.11 × 0.08 mm; IPDS (STOE), Mo-K_α radiation (0.71073 Å), graphite monochromator; T = 173(2) K; Θ-scan, max. 2Θ = 56.46°; 29465 reflections measured, 8456 independent ($R_{\text{int.}}$ = 0.0535), 6042 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. The structure was solved by direct methods (SHELX-97).[16] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares methods using SHELXL-97.[17] The asymmetric unit of **7** includes two molecules of acetone which were refined anisotropically with restraints. The hydrogen atoms H1a, H1b, H6a, H6b, H7, H10a and H10b were found in a difference-Fourier synthesis and refined with fixed temperature factors $U_{\text{eq.}}$ The positions of all other hydrogen atoms were calculated according to an ideal geometry and refined by the riding method. Conventional R = 0.0455 [for 6042 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.1234 for all 8456 located reflections; reflection/parameter ratio 19.90; residual electron density +0.806/−1.074 eÅ^{-3}.

CCDC-175166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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