Vinylidene, Vinyl, and Carbene Ruthenium Complexes with Chelating Diphosphanes as Ligands

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Dedicated to Professor Wolfgang Kiefer on the occasion of his 60th birthday

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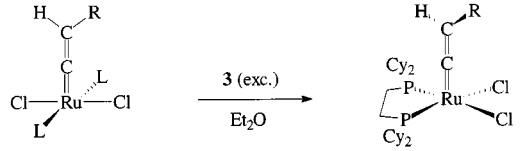
The ruthenium vinylidenes $[RuCl_2(=C=CHR)(PR'_3)_2]$ (**1**, **2**) react with 1,2-$C_2H_4(PCy_2)_2$ (**3**) to give the chelate complexes $[RuCl_2(=C=CHR)(\kappa^2\text{-}\mathbf{3})]$ (**4**, **5**) by displacement of the two monodentate phosphane ligands. In contrast, the reaction of the hydrido compound $[RuHCl(=C=CH_2)(PCy_3)_2]$ (**6**) with excess **3** proceeds by migration of the hydride to the Cα carbon atom of the vinylidene unit and affords the six-coordinate vinyl complex *trans*-$[RuCl(CH=CH_2)(\kappa^2\text{-}\mathbf{3})_2]$ (**7**). Protonation of **7**, followed by addition of NH_4PF_6, yields the cationic ruthenium carbene *trans*-$[RuCl(=CHCH_3)(\kappa^2\text{-}\mathbf{3})_2]PF_6$ (**8**), together with small quantities of the hydrido compound $[RuH(\kappa^2\text{-}\mathbf{3})_2]PF_6$ (**9**). The Grubbs catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ (**10**) reacts with both **3** and $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$ (**11**), also by ligand substitution, to give the corresponding chelate complexes $[RuCl_2(=CHPh)(\kappa^2\text{-}\mathbf{3})]$ (**12**) and $[RuCl_2(=CHPh)(\kappa^2\text{-}\mathbf{11})]$ (**13**); the latter has been characterized by X-ray crystal structure analysis.

Introduction

Recently, we reported that the reaction of the hydrido compound $[RuHCl(=C=CH_2)(PCy_3)_2]$ with acids HA, having a non-coordinating anion A^- such as BF_4^- or $B(Ar_f)_4^-$ [Ar_f = 3,5-$C_6H_3(CF_3)_2$], affords, in the presence of a donor solvent S, the six-coordinate carbyne(hydrido) complexes $[RuHCl(\equiv CCH_3)(PCy_3)_2(S)]A$ instead of the anticipated five-coordinate vinylideneruthenium derivatives $[RuCl(=C=CH_2)(PCy_3)_2(S)]A$.[1] Although the carbyne(hydrido) cations are highly efficient catalysts for the ring-opening metathesis polymerization (ROMP) of cyclooctene as well as for the cross-olefin metathesis of cyclopentene with methylacrylate, their lifetime is rather limited and significantly shorter than that of the corresponding ruthenium carbene $[RuCl_2(=CHCH_3)(PCy_3)_2]$.[2,3] This unfavorable aspect prompted us to prepare five-coordinate vinylideneruthenium complexes with chelating diphosphanes as ligands, which, we hoped, would be more suitable starting materials for the synthesis of stable cationic ruthenium carbynes. In this context it has to be mentioned that during the progress of this work, Hofmann et al. described the preparation and structural characterization of the carbeneruthenium compounds $[RuCl_2(=CHR)\{\kappa^2\text{-}tBu_2P(CH_2)_nPtBu_2\}]$ (n = 1 and 2) which, in the presence of trimethylsilyl triflate, catalyze the ring-opening metathesis polymerization (ROMP) of strained cycloolefins such as cyclooctene or norbornene.[4,5]

Results and Discussion

The reaction of the dichlororuthenium compound **1**[6] with an excess of the sterically demanding diphosphane **3** in ether results in the displacement of the two monodentate phosphane ligands and the formation of the chelate complex **4**, which precipitated as a yellow solid and was isolated in 94% yield (Scheme 1). The synthesis of the related complex **5** could only be achieved using **2** as the starting material since the bis(tricyclohexylphosphane)ruthenium counterpart $[RuCl_2(=C=CHPh)(PCy_3)_2]$[6,7] does not react with **3** by substitution of the PCy_3 units. The yield of **5** is relatively low (31%) due to the formation of an insoluble (probably polymeric) by-product. Both **4** and **5** are quite stable in the solid state but slowly decompose in solution. The ^1H NMR spectra of **4** and **5** display a triplet at δ = 3.26 (**4**) and 4.62 (**5**), which is assigned to the =C*H*R proton of the vinylidene ligand. The ^{13}C NMR spectra show the resonance for the Cα carbon atom of the Ru=C=CHR unit at δ = 353.0 (**4**) and 355.4 (**5**), the low-field chemical shift



	L	R
1	PCy_3	*t*Bu
2	$PiPr_3$	Ph

	R
4	*t*Bu
5	Ph

Scheme 1

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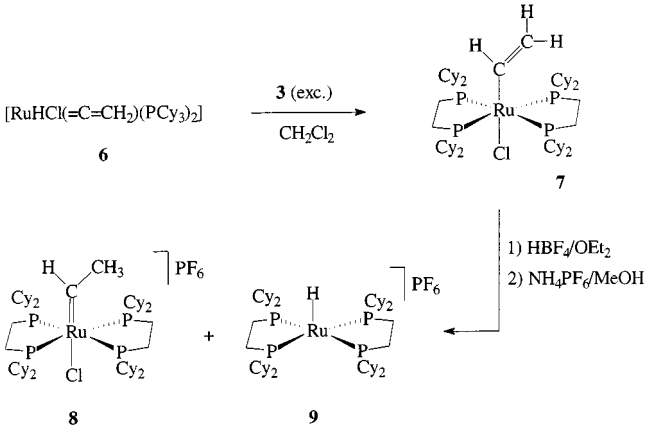
being in good agreement with the data observed for other mononuclear ruthenium vinylidenes.[6–8]

The most important feature of the NMR spectroscopic data of **4** and **5**, however, is the appearance of *two* signals at δ = 74.9, 73.5 (**4**) and 76.9, 74.5 (**5**) in the ^{31}P NMR spectra that are part of an AB system. The conclusion is that the chelating five-coordinate vinylidene complexes do not possess any plane of symmetry and, as found in the crystal structure of **1**,[6] the C–R bond lies parallel to one of the Ru–Cl bonds. Moreover, the rotation around the Ru=C=C axis must be significantly hindered, possibly due to the steric requirements of the four cyclohexyl groups.

Both **4** and **5** can be protonated with $HBF_4{\cdot}OEt_2$. While the protonation of **4** requires only one equivalent of the acid, the corresponding reaction of **5** requires an excess. In both cases a mixture of two products is formed of which one, according to the ^1H and ^{31}P NMR spectroscopic data, is the expected cationic ruthenium carbyne. Unfortunately, all attempts to separate the two compounds by fractional crystallization failed. The protonation is reversible and thus, upon addition of ether to a solution of the products in CH_2Cl_2, the ruthenium vinylidenes **4** and **5** are regenerated.

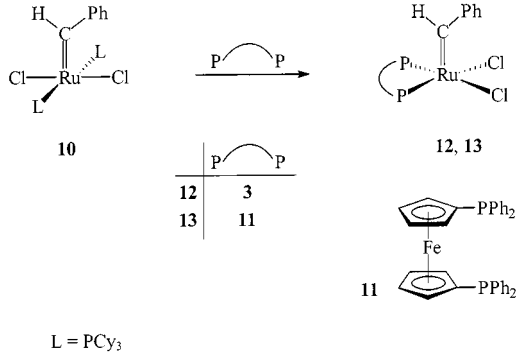
In contrast to **1**, which upon treatment with **3** affords the vinylidene compound **4**, the reaction of the chloro(hydrido) derivative **6** with a sixfold excess of **3** gives the vinylruthenium(II) complex **7** in 75% isolated yield (Scheme 2). A similar conversion of a RuH(=C=CHR) to a Ru(CH=CHR) moiety was recently reported by Caulton et al. who prepared the cationic vinyl compound [Ru(CH=CHSiMe$_3$)(CNMe)$_3$(P*t*Bu$_2$Me)$_2$]I from [RuHI(=C=CHSiMe$_3$)(P*t*Bu$_2$Me)$_2$] and methyl isocyanide.[9] With regard to the structure of **7**, we assume that the two chelating diphosphane ligands are *trans* disposed which is consistent with the single resonance in the ^{31}P NMR spectrum at δ = 53.2.

In analogy to the five-coordinate vinyl complex [Ru(CH=CH$_2$)(CH$_3$CN)$_2$(PCy$_3$)$_2$]BF$_4$, which reacts with HBF_4 in ether to generate the dicationic ruthenium carbene [Ru(=CHCH$_3$)(CH$_3$CN)$_2$(PCy$_3$)$_2$](BF$_4$)$_2$,[10] treatment of **7** with ethereal HBF_4, followed by addition of NH_4PF_6, gives the monocationic, six-coordinate carbene compound **8** in moderate yield. The hydrido complex **9** is formed (yield 10%) as a by-product; it was previously obtained by Winter and Hornung from [RuCl$_2$(DMSO)$_4$], **3** and NH*i*Pr$_2$ in the presence of NH_4PF_6.[11] Typical spectroscopic features of **8** are the signal for the RuC*H* proton at δ = 16.48 in the ^1H NMR spectrum and the multiplet for the carbene carbon atom at δ = 342.9 in the ^{13}C NMR spectrum; the latter appears as a singlet after $^{13}C\{^{31}P\}$ decoupling. Similarly to **4** and **5**, the ^{31}P NMR spectrum of **8** displays two resonances at δ = 80.3 and 78.9, corresponding to an AB system, which illustrates that the PCy$_2$ units are pairwise inequivalent.



Scheme 2

In order to compare the reactivity of the five-coordinate ruthenium vinylidenes **1** and **2** with that of related ruthenium carbenes, the Grubbs catalyst **10** was also treated with **3** as well as with 1,1′-bis(diphenylphosphanyl)ferrocene (**11**). In both cases the monodentate PCy$_3$ ligands are readily displaced and the chelate compounds **12** and **13** (Scheme 3) are isolated in nearly quantitative yield. Both **12** and **13** can be stored under argon for weeks without decomposition, and they are also significantly more stable in solution than their vinylidene counterparts **4** and **5**. The ^1H NMR spectra of **12** and **13** show the expected triplet resonance for the Ru=C*H*Ph proton at δ = 14.68 (**12**) and 17.18 (**13**), while the signal for the carbene carbon atom is observed in the ^{13}C NMR spectra at δ = 282.6 (**12**) and 364.3 (**13**). Consistent with the results obtained by Hofmann and co-workers,[4,5] the ruthenium carbenes **12** and **13** are inactive in the ROMP of cyclooctene, but become good catalysts for olefin metathesis upon addition of trimethylsilyl triflate.



Scheme 3

The molecular structure of **13** is shown in Figure 1. In contrast to the ruthenium vinylidene [RuCl$_2$(=C=CHPh)(PCy$_3$)$_2$][7] and the related ruthenium carbenes [RuCl$_2$(=CHCH=CMe$_2$)(κ^2-*t*Bu$_2$PCH$_2$P*t*Bu$_2$)][4] and [RuCl(=CHPh)(κ^2-*t*Bu$_2$PCH$_2$CH$_2$-P*t*Bu$_2$)],[5] the geometry around the metal center is not square-pyramidal but distorted trigonal-bipyramidal. The P1–Ru–Cl2 axis, connecting the ligand atoms in the apical positions, is somewhat bent [167.23(5)°] which could be due to the steric hindrance between the two phenyl rings containing the carbon atoms C30–C35 and C2–C7. While the angle C1–Ru–P2 is near to 90°, the two other bond angles in the basal plane of the molecule are considerably larger [123.93(14)° and 146.96(5)°, respectively]. Owing to the che-

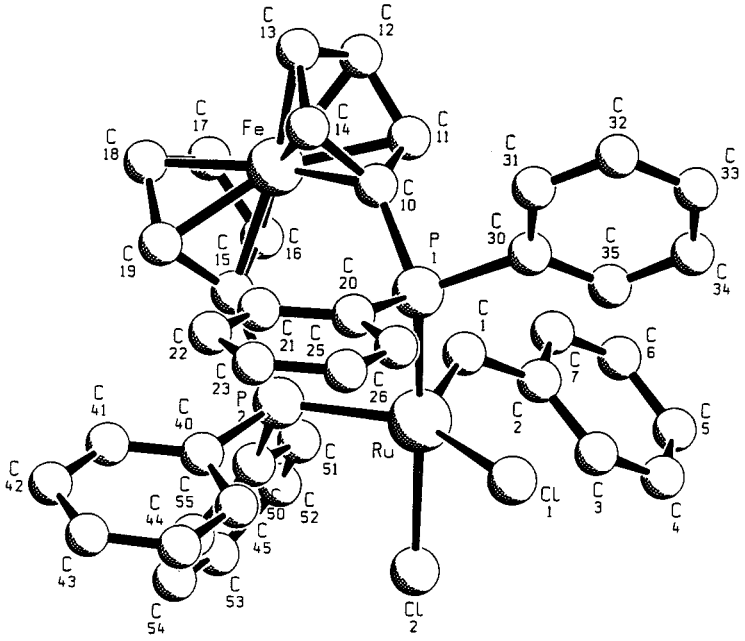


Figure 1. Molecular structure (SCHAKAL plot) of **13**; four of the five phenyl rings are reduced in size and the hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru−C1 1.860(5), Ru−P1 2.3151(14), Ru−P2 2.2718(12), Ru−Cl1 2.3949(13), Ru−Cl2 2.4115(14), C1−C2 1.470(7); P1−Ru−P2 95.32 (5), P1−Ru−C1 90.46(16), P1−Ru−Cl1 84.07(5), P1−Ru−Cl2 167.23(5), P2−Ru−C1 89.07(14), P2−Ru−Cl1 146.96(5), P2−Ru−Cl2 87.13(5), Cl1−Ru−Cl2 86.93(5), C1−Ru−Cl1 123.93(14), C1−Ru−Cl2 102.09(16), Ru−C1−C3 125.3(4)

lating coordination of **11**, the cyclopentadienyl rings are not parallel to each other, the two planes C10−C11−C12−C13−C14 and C15−C16−C17−C18−C19 forming a dihedral angle of 37.7(3)°. The Ru−C1 bond length [1.860(5) Å] is almost identical to that of the Hofmann compounds [$RuCl_2(=CHCH=CMe_2)(\kappa^2$-$t Bu_2PCH_2Pt Bu_2)$] [1.858(2) Å][4] and [$RuCl_2(=CHPh)(\kappa^2$-$t Bu_2PCH_2CH_2Pt Bu_2)$] [1.836(3) Å][5] and differs only slightly from that of the bis(tricyclohexylphosphane) complexes [$RuCl_2(=CH$-p-$C_6H_4Cl)(PCy_3)_2$] [1.839(3) Å][2] and [$RuCl(CN)(=CHCH_3)(PCy_3)_2$] [1.810(6) Å].[12] The Ru−P distances of **13** are in the expected range and that is also true for the Ru−Cl bond lengths.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1**,[6] **2**,[7] **3**,[13] **6**,[3] and **10**[2] were prepared as described in the literature. Compound **11** was a product from Aldrich. − NMR: Bruker AC 200 and AMX 400 [dvt = doublet of virtual triplets; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$]. − MS: Finnigan 90 MAT. − Melting points determined by DTA.

Preparation of [$RuCl_2(=C=CHt Bu)(\kappa^2$-3)] (4): A solution of **1** (1.13 g, 1.39 mmol) in 60 mL of ether was treated with **3** (878 mg, 2.08 mmol) and stirred for 7.5 h at room temperature. A yellow solid precipitated, which was separated from the mother liquor, washed with ether (2 × 10 mL) and recrystallized from CH_2Cl_2/pentane (1:10) (−20 °C); yield 884 mg (94%); m.p. 174 °C (dec.). − IR (KBr): ν(C=C) = 1648 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.26 [t, J(PH) = 3.8 Hz, 1 H, =C*H*R], 2.59−1.26 (br. m, 48 H, CH_2 and C_6H_{11}), 1.20 (s, 9 H, CCH_3). − $^{13}C\{^1H,^{31}P\}$ NMR (100.6 MHz, $CDCl_3$): δ = 353.0 (Ru=C), 118.9 (=*C*HR), 40.2, 39.9, 39.3, 38.3 (CH of C_6H_{11}), 33.1 (CCH_3), 32.1 (CCH_3), 30.4, 30.0, 29.9, 29.6, 28.8, 28.7, 28.2, 27.7, 27.5, 27.4, 26.9, 26.1, 26.0 (CH_2 of C_6H_{11}), 21.5, 20.1 (CH_2 of **3**). − $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 74.9, 73.5 (AB system, J = 13.5 Hz). − $C_{32}H_{58}Cl_2P_2Ru$ (676.7): calcd. C 56.97, H 8.64; found C 56.60, H 8.22.

Preparation of [$RuCl_2(=C=CHPh)(\kappa^2$-3)] (5): A solution of **2** (347 mg, 0.58 mmol) in 20 mL of ether was treated with **3** (438 mg, 1.04 mmol) and stirred for 2.5 h at room temperature. A pink solid slowly precipitated which was separated from the mother liquor, washed with ether (2 × 10 mL) and suspended in 8 mL of CH_2Cl_2. A color change from pink to yellow occurred upon stirring this suspension for 4.5 h at room temperature. The suspension was filtered to remove the insoluble by-product, the filtrate was concentrated to ca. 3 mL in vacuo and 20 mL of ether was added. A greenish-yellow precipitate was formed which was recrystallized from CH_2Cl_2/ether (1:10) (−20 °C): yield 127 mg (31%); m.p. 128 °C (dec.). − IR (KBr): ν(C=C) = 1626 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20, 7.02 (both m, 5 H, C_6H_5), 4.62 [t, J(PH) = 3.5 Hz, 1 H, =C*H*Ph], 2.69−0.90 (br. m, 48 H, CH_2 and C_6H_{11}). − $^{13}C\{^1H,^{31}P\}$ NMR (100.6 MHz, $CDCl_3$): δ =355.4 (Ru=C), 128.5, 127.9, 126.8, 125.9 (all C_6H_5), 112.3 (=*C*HPh), 40.9, 40.0, 39.5, 38.0 (CH of C_6H_{11}), 30.2, 30.0, 29.3, 28.9, 28.6, 28.4, 27.5, 27.2, 27.1, 27.0, 26.9, 26.6, 26.0, 25.9, 25.5, 25.4 (CH_2 of C_6H_{11}), 22.3, 20.4 (CH_2 of **3**). − $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 76.9, 74.5 (AB system, J = 15.3 Hz). − $C_{34}H_{54}Cl_2P_2Ru$ (696.8): calcd. C 58.61, H 7.81; found C 58.25, H 7.44.

Preparation of *trans*-[$RuCl(CH=CH_2)(\kappa^2$-3)$_2$] (7): A solution of **6** (350 mg, 0.48 mmol) in 25 mL of CH_2Cl_2 was treated with a solution of **3** (1.21 g, 2.85 mmol) in 15 mL of CH_2Cl_2 and stirred for 1 h at room temperature. The solvent was evaporated in vacuo, and the off-white solid was washed with pentane (2 × 10 mL) and dried: yield 365 mg (75%); m.p. 54 °C (dec.). − IR (KBr): ν(C=C) = 1528 cm^{-1}. − ^1H NMR (300 MHz, CD_2Cl_2): δ = 6.74 (m,

1 H, RuCH), 4.67 [d, *J*(HH) = 7.2 Hz, 1 H, one H of CH_2 *cis* to =CH], 3.91 [d, *J*(HH) = 15.3 Hz, 1 H, one H of CH_2 *trans* to =CH], 2.43−1.14 (br. m, 96 H, CH_2 of **3** and C_6H_{11}). − $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 146.8 (m, RuCH), 120.1 (m, $=CH_2$), 39.3, 35.5 (both m, CH of C_6H_{11}), 30.5, 29.9, 29.6, 29.1, 28.0, 27.7, 27.4, 27.3, 26.1, 26.0 (all s, CH_2 of C_6H_{11}), 18.0 (m, CH_2 of **3**). − $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 53.2 (s). − $C_{54}H_{99}ClP_4Ru$ (1008.8): calcd. C 64.29, H 9.89; found C 64.13, H 9.88.

Preparation of *trans*-[RuCl(=CHCH$_3$)(κ^2-3)$_2$]PF$_6$ (8): A solution of **7** (309 mg, 0.31 mmol) in 20 mL of CH_2Cl_2 was treated at −78 °C with 0.4 mL of a 1.6 M solution of HBF_4 (0.64 mmol) in ether. After stirring the solution 30 min. at −78 °C, the solvent was evaporated in vacuo and the residue washed with ether (2 × 10 mL). The brownish yellow solid, which according to the ^1H NMR spectrum consists of a mixture of the BF_4^- salts of the cations $[RuCl(=CHCH_3)(\kappa^2\text{-}\mathbf{3})_2]^+$ and $[RuH(\kappa^2\text{-}\mathbf{3})_2]^+$, was suspended in 15 mL of methanol and the suspension was treated dropwise with a solution of NH_4PF_6 (340 mg, 2.09 mmol) in 10 mL of methanol. Stirring the reaction mixture for 25 min. at room temperature led to the formation of a pink precipitate of **8**, which was separated from the mother liquor, washed with methanol (2 × 15 mL) and dried: yield 111 mg (39%). From the mother liquor and the combined washings a yellow solid slowly precipitated which was identified as $[RuH(\kappa^2\text{-}\mathbf{3})_2]PF_6$ (**9**) by comparison with reference data.[11]

8: m.p. 92 ° C (dec.). − Λ(CH_3NO_2) = 53.4 cm$^2\Omega^{-1}$ mol^{-1}. − ^1H NMR (400 MHz, CD_2Cl_2): δ = 16.48 [m; in $^1H\{^{31}P\}$: q, *J*(HH) = 6.0 Hz, 1 H, =CH], 2.94 [d, *J*(HH) = 6.0 Hz, 3 H, CH_3], 2.81, 2.66, 2.44−0.90 (all m, 96 H, CH_2 and C_6H_{11}). − $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 342.9 [quin, *J*(PC) = 14.5 Hz, Ru=C], 49.5 (s, CH_3), 39.9 [d, *J*(PC) = 21.6 Hz, CH of C_6H_{11}], 38.0 [d, *J*(PC) = 24.2 Hz, CH of C_6H_{11}], 37.6 [d, *J*(PC) = 22.9 Hz, CH of C_6H_{11}], 37.5 [d, *J*(PC) = 25.4 Hz, CH of C_6H_{11}], 29.9, 29.4, 29.3 (all s, CH_2 of C_6H_{11}), 28.9 [d, *J*(PC) = 2.6 Hz, CH_2 of C_6H_{11}], 28.6 [d, *J*(PC) = 6.4 Hz, CH_2 of C_6H_{11}], 28.5 [d, *J*(PC) = 5.1 Hz, CH_2 of C_6H_{11}], 27.8−27.1 (m, CH_2 of C_6H_{11}), 26.7 [d, *J*(PC) = 11.4 Hz, CH_2 of C_6H_{11}], 26.4, 26.2, 26.1 (all s, CH_2 of C_6H_{11}), 20.0, 19.4 [both dd, *J*(PC) = 29.2 and 8.9 Hz, CH_2 of **3**]. − $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 80.3, 78.9 (AB system, *J* = 21.8 Hz), −144.4 [sept, *J*(PF) = 710.7 Hz, PF_6^-]. − $C_{54}H_{100}ClF_6P_5Ru$ (1154.8): calcd. C 56.17, H 8.73; found C 55.88, H 8.27.

Preparation of *trans*-[RuCl$_2$(=CHPh)(κ^2-3)] (12): A solution of **10** (202 mg, 0.25 mmol) in 8 mL of CH_2Cl_2 was treated with a solution of **3** (129 mg, 0.31 mmol) in 5 mL of CH_2Cl_2 and stirred for 3.5 h at room temperature. The solvent was evaporated in vacuo, the remaining greenish solid was washed with pentane (3 × 10 mL) and ether (2 × 8 mL) and then dried: yield 160 mg (92%); m.p. 76 °C (dec.). − ^1H NMR (400 MHz, CD_2Cl_2): δ = 14.68 [t, *J*(PH) = 16.1 Hz, 1 H, =C*H*Ph], 8.41, 7.70−7.34 (both m, 5 H, C_6H_5), 2.30−0.86 (m, 48 H, CH_2 and C_6H_{11}). − $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 292.6 [t, *J*(PC) = 16.5 Hz, Ru=C], 148.7 (s, *ipso*-C of C_6H_5), 131.5, 130.5, 128.8 (all s, C_6H_5), 38.1, 36.3 (both m, CH of C_6H_{11}), 30.1, 28.8, 28.4, 28.2 (all s, CH_2 of C_6H_{11}), 27.5−26.5 (m, CH_2 of C_6H_{11}), 26.4, 26.0 (both s, CH_2 of C_6H_{11}), 20.1 [dd, *J*(PC) = 20.4 and 16.5 Hz, CH_2 of **3**]. − $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 81.7 (s). − $C_{33}H_{54}Cl_2P_2Ru$ (684.7): calcd. C 57.89, H 7.95; found C 57.65, H 7.57.

Preparation of *trans*-[RuCl$_2$(=CHPh)(κ^2-11)] (13): A solution of **10** (492 mg, 0.60 mmol) in 15 mL of CH_2Cl_2 was treated with a solution of **11** (398 mg, 0.72 mmol) in 10 mL of CH_2Cl_2 and stirred for 7 h at room temperature. The solvent was evaporated in vacuo, the remaining olive-green solid was washed with acetone (2 × 5 mL) and pentane (2 × 6 mL) and then dried: yield 430 mg (88%); m.p. 176 °C (dec.). − ^1H NMR (200 MHz, CD_2Cl_2): δ = 17.18 [t, *J*(PH) = 18.2 Hz, 1 H, =C*H*Ph], 7.88−7.02 (br. m, 25 H, C_6H_5), 4.78, 4.59, 4.47, 4.36 (all s, 8 H, C_5H_4). − $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 364.3 [t, *J*(PC) = 21.0 Hz, Ru=C], 150.5 (s, *ipso*-C of C_6H_5), 135.7, 133.5 [both t, *J*(PC) = 5.1 Hz, C_6H_5], 132.7, 131.0, 130.7, 129.6, 129.5 (all s, C_6H_5), 127.9, 127.2 [both t, *J*(PC) = 5.1 Hz, C_6H_5], 74.6 [t, *J*(PC) = 5.1 Hz, C_5H_4], 74.5 (s, C_5H_4), 72.5 [t, *J*(PC) = 5.1 Hz, C_5H_4], 69.3 (s, C_5H_4). − $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 50.9 (s). − MS (FAB): *m*/*z* = 816 [M$^+$]. − $C_{41}H_{34}Cl_2FeP_2Ru$ (816.5): calcd. C 60.31, H 4.20, Ru 12.38; found C 59.95, H 4.64, Ru 11.77.

Determination of the X-ray Crystal Structure of 13: Single crystals were grown upon cooling of a saturated solution of **13** in CH_2Cl_2 from 25 °C to −20 °C. Crystal data (from 5000 reflections, 2.34° < Θ < 25.00°): triclinic; space group $P2_1/c$ (No. 14); *a* = 13.998(2), *b* = 14.7459(16), *c* = 20.125(3) Å, β = 98.417(18)°; *V* = 4109.3(10) Å^3, *Z* = 4; $d_{calcd.}$ = 1.593 g·cm^{-3}; μ(Mo-K_α) = 1.220 mm^{-1}; crystal size 0.18 × 0.18 × 0.12 mm; IPDS (STOE), Mo-K_α radiation (0.71073 Å), graphite monochromator; *T* = 173(2) K; -scans, max. 2θ = 50.00°; 32351 reflections measured, 7226 independent ($R_{int.}$ = 0.0530), 4891 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-97).[14] Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares on F^2 (SHELXL-97).[15] The positions of all hydrogen atoms were calculated according to ideal geometry and refined by using the riding method. The asymmetric unit includes two molecules of CH_2Cl_2 which were refined anisotropically with restraints. One of them was found to be disordered and two positions were refined with occupancy factors of 0.85 and 0.15, respectively. Conventional *R* = 0.0403 [for 4891 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.1041 for all 7226 located reflections; reflection/parameter ratio 14.5; residual electron density +0.121/−0.067 eÅ^{-3}.

Crystallographic data (excluding structure factors) for **13** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159684. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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