

A Series of Vinylidene-, Vinyl-, Carbene- and Carbyneruthenium(II) Complexes with [Ru(PCy₃)₂] and [Ru(PiPr₃)₂] as Molecular Building Blocks

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Dedicated to Professor Michael F. Lappert on the occasion of his 75th birthday

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The hydrido(vinylidene) complexes [RuHCl(=C=CHR)(L)₂] (R = H, *t*Bu, Ph; L = PCy₃, PiPr₃) undergo metathesis reactions in the presence of KX (X = I, NCO, OPh, CH₃CO₂, CF₃CO₂) to give the substitution products [RuHX(=C=CHR)(L)₂] (**6–15**) in good to excellent yields. Treatment of [RuHX(=C=CHR)(L)₂] with HBF₄ in diethyl ether affords the cationic carbyneruthenium(II) derivatives [RuHX(=CCH₂R)(OEt₂)(L)₂][BF₄] (**17, 18, 20, 21**) and [RuH(κ²-O₂CCH₃)(=CCH₂R)(L)₂][BF₄] (**19, 22**). The reactions of [RuHCl(=C=CHR)(L)₂] with MX [X = BF₄, PF₆, BPh₄, B(Ar_f)₄] in acetonitrile lead to the formation of cationic five- and six-coordinate vinylruthenium(II) compounds **26a–d** and **27a–d** of which [Ru(CH=CH₂)(CH₃CN)₂(PCy₃)₂][BPh₄] (**26c**) has been characterized by

X-ray crystallography. The starting material [RuHCl(=C=CHPh)(PiPr₃)₂] reacts with CO to give [RuCl(CH=CHPh)(CO)₂(PiPr₃)₂] (**28**) and with N₂ to produce [RuCl(CH=CHPh)(N₂)(PiPr₃)₂] (**29**). The molecular structure of **29** has been determined. Protonation of [Ru(CH=CH₂)(CH₃CN)₂(PCy₃)₂][X] and [Ru(CH=CHPh)(CH₃CN)₃(PiPr₃)₂][X] with HBF₄ and HB(Ar_f)₄ yields the dicationic carbene-ruthenium(II) complexes [Ru(=CHCH₃)(CH₃CN)₂(PCy₃)₂][X]₂ (**30a,b**) and [Ru(=CHCH₂Ph)(CH₃CN)₃(PiPr₃)₂][B(Ar_f)₄]₂ (**31**), the latter of which eliminates styrene to give [Ru(CH₃CN)₃(PiPr₃)₂][B(Ar_f)₄]₂ (**32**).
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Introduction

In the context of our investigations on the preparation and reactivity of vinylideneruthenium(II) complexes,^[1] we recently reported that the reaction of the five-coordinate hydrido(vinylidene) compound [RuHCl(=C=CH₂)(PCy₃)₂] with acids HA, containing an anion that does *not* coordinate to the metal center, in diethyl ether affords the cationic carbyne(hydrido) complex [RuHCl(=CCH₃)(PCy₃)₂](OEt₂)⁺ instead of the anticipated isomeric carbene derivative [RuCl(=CHCH₃)(PCy₃)₂](OEt₂)⁺.^[2] This cation, as well as the corresponding cations with coordinated water or dimethylaniline instead of diethyl ether, turned out to be a highly efficient catalyst for olefin metathesis, including the cross-olefin metathesis of cyclopentene with methylacrylate to afford multiply unsaturated esters CH₂(C₅H₈)_nCHCO₂Me (*n* = 1–3). The cations [RuHCl(=CCH₃)(PCy₃)₂](S)⁺, however, in the absence of excess HA are rather labile and decompose in solution within 20 min at room temperature. For this reason, we set out to prepare more stable ruthenium carbynes by modifying the coordination sphere and using different ruthenium vinylidenes as the precursors.

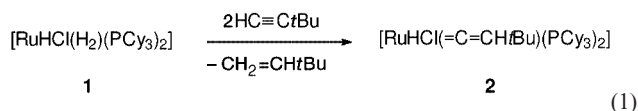
In this paper we report the synthesis of a series of new hydrido(vinylidene) complexes [RuHX(=C=CHR)(PCy₃)₂]

and [RuHX(=C=CHPh)(PiPr₃)₂], their conversion into the corresponding cationic ruthenium carbynes and into neutral as well as cationic vinylruthenium compounds, and also the formation of dicationic, five-coordinate ruthenium carbenes. Some preliminary results have already been communicated.^[3]

Results and Discussion

The hydrido(dihydrogen) complex [RuHCl(H)₂(PCy₃)₂] (**1**), which can be prepared from RuCl₃·3H₂O in high yield,^[2,4] is not only an appropriate starting material for [RuHCl(=C=CH₂)(PCy₃)₂] (**3**) and [RuHCl(=C=CHPh)(PCy₃)₂] (**4**) but also for the *tert*-butylvinylidene counterpart **2** [see Equation (1)]. Treatment of a solution of **1** in CH₂Cl₂ with two equivalents of *t*BuC≡CH at –78 °C leads to the formation of **2** which, after removal of the solvent, was isolated as a brown air-sensitive solid in 72% yield. In contrast to **3** and **4**, compound **2** decomposes slowly in solution even at low temperatures and thus only ¹H and ³¹P NMR spectroscopic data could be obtained. The ¹H NMR spectrum displays the signal for the vinylidene proton as a triplet at δ = 2.87 ppm and the resonance for the hydride, also as a triplet, at δ = –13.89 ppm.

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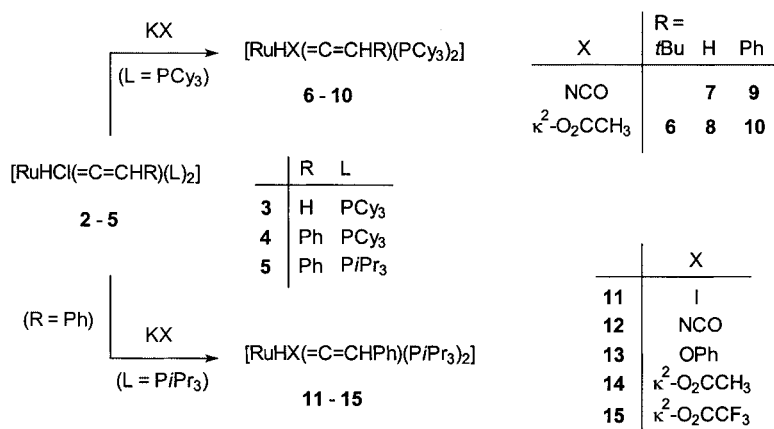


While attempts to replace the chloro ligand in **2** by iodide or isocyanate led to a mixture of products that could not be separated by fractional crystallization, a clean reaction occurs between **2** and excess $\text{CH}_3\text{CO}_2\text{K}$ that affords the acetato derivative **6** in virtually quantitative yield. The characteristic signals for the $=\text{CH}$ and the RuH protons appear in the ^1H NMR spectrum at $\delta = 2.12$ and -12.48 ppm, respectively, and are split into triplets due to ^1H - ^{31}P coupling. The IR spectrum of **6** shows two bands for the asymmetric and symmetric OCO stretching modes at 1635 and 1448 cm^{-1} , respectively, which, in agreement with literature data,^[5] indicate a chelating coordination of the acetate unit.

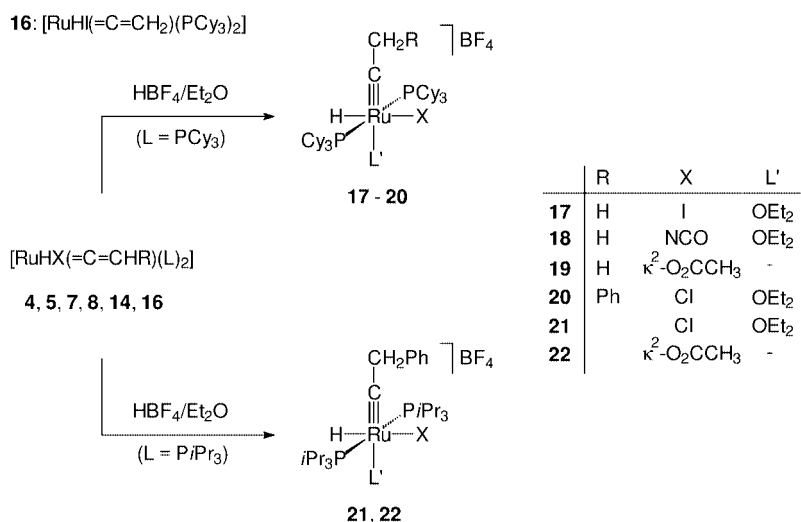
The reactions of compounds **3** and **4**, being significantly more stable than **2**, with both KOCN and $\text{CH}_3\text{CO}_2\text{K}$ in THF proceed cleanly and give the substitution products

7–10 in good to excellent yields. Apart from the elemental analyses, the spectroscopic data support the proposed structure shown in Scheme 1. Since the IR spectra of **7** and **9** display the symmetric $\nu(\text{NCO})$ stretch at 1446 cm^{-1} , we assume that the NCO ligand is *N*-bonded. In case of an *O*-coordination, the corresponding absorption is expected to appear below 1200 cm^{-1} .^[6]

Both the hydrido(vinylidene) complex **5**, containing two triisopropylphosphane ligands, and the compounds **11–15** obtained by salt metathesis with KX in THF (Scheme 1) are considerably more stable than their PCy_3 counterparts. In solution (C_6H_6 or CH_2Cl_2) they do not decompose even after 24 h. In the ^1H NMR spectra of **11–15**, the vinylidene $=\text{CH}$ proton resonates at between $\delta = 4.25$ and 4.40 ppm and the RuH proton at between $\delta = -9.3$ and -13.6 . In the low-field region the ^{13}C NMR spectra of **11–15** display two triplets, one between $\delta = 327$ and 338 ppm and the other between $\delta = 108$ and 110 ppm, which are assigned to the α - and β -carbon atoms of the vinylidene ligand. For the $\text{Ru}(\text{NCO})$ compound **12** and the $\text{Ru}(\kappa^2\text{-O}_2\text{CCR}_3)$ de-



Scheme 1



Scheme 2

derivatives **14** and **15** the positions of the ligand vibrations in the IR spectra are quite similar to those of **7** and **9** and **8** and **10**, respectively, and thus an *N*-linkage for the NCO[−] anion and a chelating coordination mode for the carboxylate unit can be assumed.

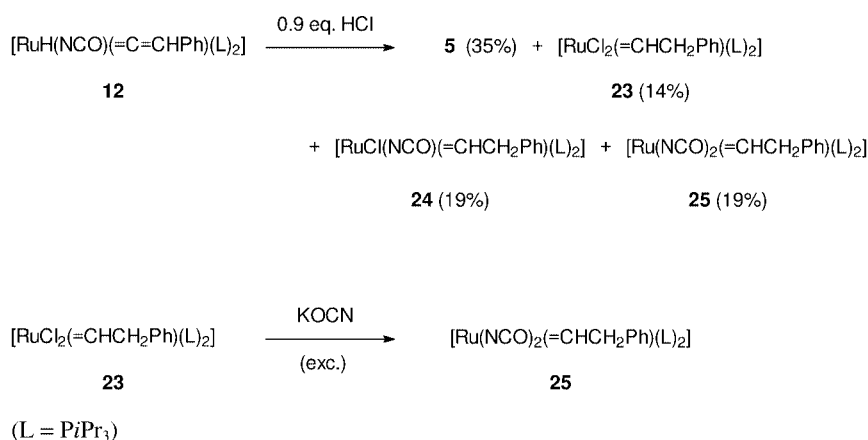
The ruthenium vinylidenes **4**, **5**, **7**, **8**, **14** and **16** are readily protonated with a solution of HBF₄ in diethyl ether at low temperatures to give the six-coordinate cationic carbyne complexes **17–22** in 55–73% yield. The products were isolated as light yellow, moderately air-sensitive solids by precipitation with diethyl ether. While solutions of the acetato derivatives **19** and **22** (see Scheme 2) are stable for about one hour, the related compounds **17**, **18** and **20**, **21** decompose more readily, for example in dichloromethane in ca. 30 min even at 0 °C. Conductivity measurements (in nitromethane) confirm the presence of 1:1 electrolytes. The ¹H NMR spectra of **17** and **18** show a singlet for the methyl protons of the carbyne ligand at δ = 2.51 (**17**) and 2.23 ppm (**18**), while the spectra of **20–22** display the resonance (also a singlet) for the CH₂Ph protons at δ = 3.66–4.03 ppm. The hydride signal appears between δ = −6.41 and −7.46 ppm and is thus shifted downfield by ca. 3–6 ppm compared with the hydrido(vinylidene) precursors. The ¹H NMR spectra of **17**, **18** and **20**, **21** also confirm the coordination of one molecule of diethyl ether which is noteworthy insofar as in the five-coordinate carbyneruthenium complexes [RuCl₂(≡CCH₂R)(PR'₃)₂]⁺ (R = Ph, *t*Bu; R' = Cy, *i*Pr) the position *trans* to the carbyne ligand is not occupied by a solvent molecule.^[7]

Similarly to the chloro derivative [RuHCl(≡CCH₃)-(PCy₃)₂(OEt₂)]BF₄,^[2] the cationic carbyne(hydrido) compounds **17** and **18** also catalyze the ring opening metathesis polymerization (ROMP) of cyclooctene. While for **18**, the rate, the yield of the polymer and the ratio of the *trans*- and *cis*-oriented carbon-carbon double bonds of the polymer are almost identical to the data obtained with the Grubbs catalyst [RuCl₂(=CHPh)(PCy₃)₂], for **17** the results are less good. Under the same conditions (CH₂Cl₂, room temperature, ratio cyclooctene to ruthenium complex = 500:1), the acetato compound **19** is nearly inert in the ROMP of cyclooctene, which is probably due to the coordination number

of six at ruthenium(II). The entering olefin can thus not bind to the metal center and can also not initiate the conversion of the RuH(≡CCH₃) to the active Ru(=CHCH₃) moiety.

Taking into consideration the fact that hydrido(vinylidene)ruthenium compounds [RuHCl(=C=CHR)(PR'₃)₂] react with one equivalent of HCl to give the Grubbs-type carbene complexes [RuCl₂(=CHCH₂R)(PR'₃)₂],^[4] we also attempted to convert the relatively stable isocyanato derivative **12** into the corresponding metal carbene. However, while the dichloro compound **23** was exclusively formed with two equivalents of HCl, the reaction of **12** with HCl in the molar ratio 1:0.9 gave a mixture of four products. Apart from the hydrido(vinylidene) complex **5** three carbene derivatives could be detected, which in the ³¹P NMR spectrum give rise to three singlets at δ = 45.2, 47.0 and 48.3 ppm. The ¹H NMR spectrum of the mixture equally shows three resonances for the carbene Ru=CH proton at δ = 19.06, 19.50 and 19.95 ppm, which are split into triplets due to ¹H-³¹P coupling. While the signals at δ = 45.2 (³¹P) and 19.95 ppm (¹H) belong to the dichloro compound **23**,^[1d,1e] the corresponding resonances at δ = 48.3 (³¹P) and 19.06 ppm (¹H) are assigned to the bis(isocyanato) counterpart **25**, which was prepared from **23** and excess KOCN in THF (see Scheme 3). The mixed ligand RuCl(NCO) species **24** is thus characterized by the signals at δ = 47.0 (³¹P) and 19.50 ppm (¹H). To explain the formation of the unexpected products **23** and **25** in the reaction of **12** with HCl, we assume that the acid attacks both the C=C bond of the vinylidene and the metal, leading to an NCO/Cl exchange and formation of both **5** and HNCO. The starting material **12** can therefore react either with HCl to give **24** or with HNCO to afford **25**. Analogously, the reaction of **5** (generated from **12** and HCl) furnishes **23** (with HCl) and **24** (with HNCO). All attempts to separate the reaction mixture consisting of **5**, **23**, **24** and **25** by fractional crystallization or low-temperature column chromatography failed.

Since the Ru–Cl bond of the hydrido(vinylidene) complexes is quite labile, we were tempted to replace the chloride not only by other anions but also by a neutral Lewis



Scheme 3

base such as acetonitrile. Treatment of a solution of **3** in CH_2Cl_2 with MeCN led, indeed, to a quick change of color from deep red to brown-yellow but afforded, after conventional workup, the cationic vinyl compound $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{NCMe})_2(\text{PCy}_3)_2]\text{Cl}$ instead of a vinylidene complex. Because this compound, even as a solid, is rather unstable, the reaction was repeated in the presence of NaBF_4 or KPF_6 and gave the more stable complexes **26a** and **26b** in about 90% yield (Scheme 4). Salt metathesis with NaBPh_4 and $\text{NaB}(\text{Ar}_f)_4$ [$\text{Ar}_f = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$] in methanol led to the formation of **26c** and **26d**, respectively. Compounds **26a–d** are red-brown or orange-red, only slightly air-sensitive solids, which, in contrast to the analogous chloride, can be stored under argon at room temperature for weeks without decomposition. The composition of **26a–d** has been confirmed by elemental analysis and conductivity measurements. Typical spectroscopic features of **26a–d** are the three resonances for the vinyl protons which, taking **26a** as an example, appear at $\delta = 7.38$, 4.84 and 4.70 ppm. The signal at lowest field is a doublet of doublets with a large *trans*- ^1H - ^1H and a smaller *cis*- ^1H - ^1H coupling and is assigned to the $\text{CH}=\text{CH}_2$ proton. The two other signals are doublets and belong to the methylene protons. The ^{31}P NMR spectra of **26a–d** display a single resonance confirming that the two phosphane ligands are stereochemically equivalent.

The result of the X-ray crystal structure analysis of **26c** is shown in Figure 1. The coordination geometry around the metal center of the cation corresponds to that of a square pyramid with the two phosphanes and the two acetonitriles *trans*-disposed. The atoms C(5) and C(6) of the vinyl ligand (which occupies the apical position) lie in the same plane as the nitrogen and carbon atoms of the MeCN

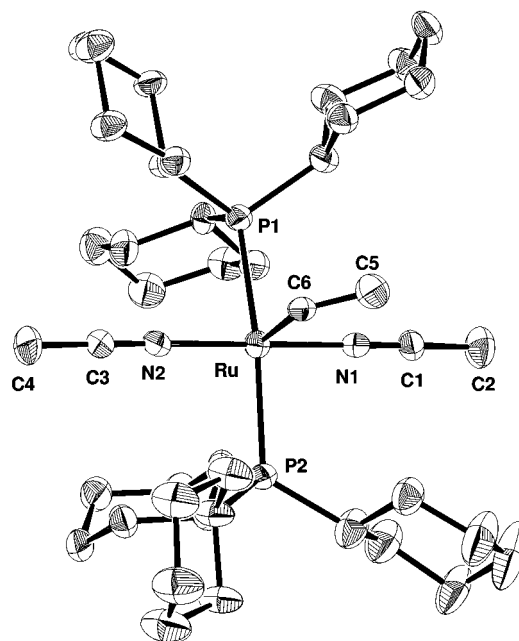
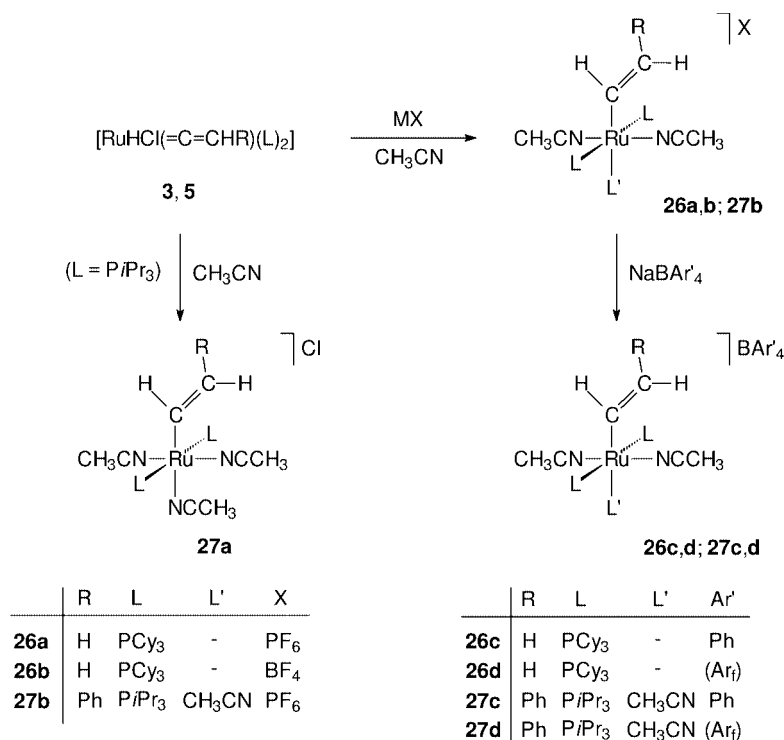


Figure 1. Molecular structure of **26c** (hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: Ru–P(1) 2.3975(13), Ru–P(2) 2.3979(12), Ru–N(1) 2.008(4), Ru–N(2) 2.006(4), Ru–C(6) 2.001(5), C(6)–C(5) 1.340(7), N(1)–C(1) 1.160(6), N(2)–C(3) 1.142(6); P(1)–Ru–P(2) 171.04(4), N(1)–Ru–N(2) 178.05(15), P(1)–Ru–C(6) 92.48(12), P(2)–Ru–C(6) 96.24(12), N(1)–Ru–C(6) 92.35(16), N(2)–Ru–C(6) 89.52(16), Ru–N(1)–C(1) 176.9(4), Ru–N(2)–C(3) 179.0(4), N(1)–C(1)–C(2) 178.7(5), N(2)–C(3)–C(4) 179.0(5), Ru–C(6)–C(5) 129.8(4)

units. In contrast to the nearly linear N(1)–Ru–N(2) axis, the P(1)–Ru–P(2) axis is slightly bent, with the phosphorus atoms pointing away from the $\text{CH}=\text{CH}_2$ moiety.

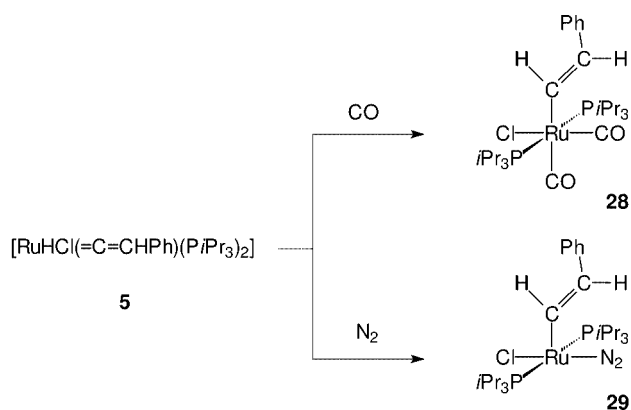


Scheme 4

The distance Ru–C(6) of 2.001(5) Å is relatively short but similar to that in other ruthenium compounds with a Ru–C(sp²) bond.^[8] The Ru–P bond lengths of 2.3975(13) and 2.3979(12) Å lie in the expected range and are nearly identical to those found in five-coordinate carbeneruthenium(II) complexes containing a [Ru(PCy₃)₂] fragment.^[9,10]

The bis(triisopropylphosphane) compound **5** behaves similarly to **3** and reacts with acetonitrile in CH₂Cl₂ to give **27a** (Scheme 4). In the presence of KPF₆, the hexafluorophosphate **27b** is formed, which, upon salt metathesis, affords **27c** and **27d**. The elemental analyses as well as the spectroscopic data of the vinyl complexes **27a–d** confirm that, in contrast to **26a–d**, three acetonitrile ligands are coordinated to the metal center. The smaller cone angle of PiPr₃ (160°) compared to PCy₃ (170°)^[11] probably favors the increase of the coordination number from five to six in the [Ru(PiPr₃)₂] derivatives. An uncharged six-coordinate ruthenium compound of composition [RuCl₂(NCMe)₂(PiPr₃)₂] has recently been prepared by Katayama and Ozawa from [*p*-cymene]RuCl₂ and PiPr₃ in toluene/acetonitrile.^[12] Moreover, Caulton et al. have found that the hydrido(iodo) complex [RuH(=C=CHSiMe₃)(PiBu₂Me)₂] reacts with excess methyl isocyanide to give the substituted vinylruthenium(II) derivative [Ru(CH=CHSiMe₃)(CNMe)₃(PiBu₂Me)₂].^[13]

An intramolecular migration of the hydride to the α -carbon atom of the vinylidene ligand also occurs upon treatment of compound **5** with carbon monoxide. This reaction is accompanied by a quick change of color from olive-green to red and then to pale yellow. The final product is the six-coordinate dicarbonyl complex **28** (Scheme 5), which is probably formed via the corresponding red, monocarbonyl complex [RuCl{(E)-CH=CHPh}(CO)(PiPr₃)₂]. This monocarbonyl compound was previously prepared in our laboratory from [RuHCl(CO)(PiPr₃)₂] and phenylacetylene and shown to react readily with CO to give **28**.^[14]



Scheme 5

Quite unexpectedly, the hydride shift to afford a RuCH=CHPh unit can also be initiated by N₂. Stirring a solution of **5** in pentane under an atmosphere of dinitrogen leads to a smooth change of color from olive-green to red-brown and gives, after low-temperature crystallization and drying the precipitate in a stream of N₂, the insertion product **29**

in 92% isolated yield. In the IR spectrum of **29**, the ν (N₂) stretching mode appears at 2067 cm^{−1} and thus at a similar position as for a [Ru(N₂)(PiPr₃)₃] complex with a tetradentate *N,S,S,N*-bonded chelate ligand.^[15] The ¹H NMR spectrum of **29** displays the two signals for the vinyl protons at δ = 9.50 (RuCH) and 6.37 ppm (=CH) while the resonances for the corresponding carbon atoms appear at δ = 147.5 (RuC) and 130.2 ppm (C=C), respectively.

The formation of **29** from **5** is reversible. If a solution of **29** in benzene is stored at room temperature for ca. 2 h, the ¹H NMR spectrum reveals the presence of **5** and **29** in the ratio of 2:3. After evaporation of the solvent in vacuo, only the hydrido(vinylidene) complex can be detected. The elimination of N₂, accompanied by an α -shift of the RuCH proton from carbon to the metal, also takes place in the thermal reaction of **29**, which has been studied by differential thermal analysis (DTA). The ¹H NMR spectrum of the remaining product is identical to that of **5**. An analogous reversible formation of a vinylmetal compound has also been observed by Bercaw et al. who reacted [(η^5 -C₅Me₅)₂TaH(=C=CH₂)] with CO to give [(η^5 -C₅Me₅)₂Ta(CH=CH₂)(CO)] and regenerated the hydrido(vinylidene) precursor photochemically.^[16]

The proposed structure of the dinitrogen complex **29** has been confirmed crystallographically (see Figure 2). As in the cationic vinyl compound **26c**, the coordination geometry around the metal center is square-pyramidal with the vinyl ligand in the apical position. The bending of the P(1)–Ru–P(2) axis [168.74(3)°] is somewhat more pronounced than in **26c** [171.04(4)°], which could be due to a slightly stronger steric repulsion between the phenyl and the

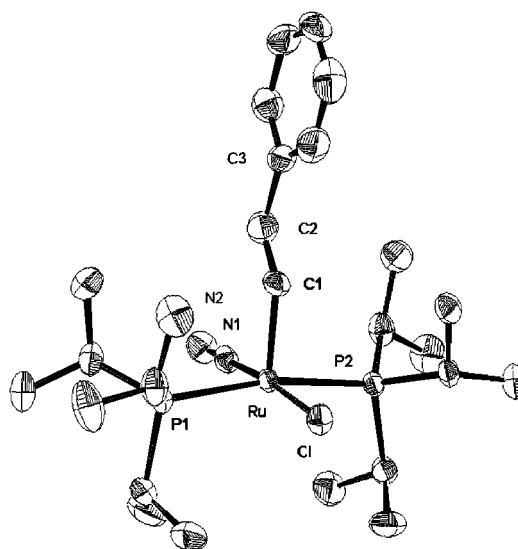


Figure 2. Molecular structure of **29** (hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: Ru–P(1) 2.4021(7), Ru–P(2) 2.4005(7), Ru–N(1) 1.869(5), Ru–Cl 2.3959(19), Ru–C(1) 1.973(3), C(1)–C(2) 1.296(5), N(1)–N(2) 1.088(8); P(1)–Ru–P(2) 168.74(3), N(1)–Ru–Cl 174.13(17), P(1)–Ru–Cl 98.15(9), P(2)–Ru–Cl 93.12(9), N(1)–Ru–P(1) 89.42(17), N(1)–Ru–P(2) 90.59(17), Cl–Ru–P(1) 89.33(4), Cl–Ru–P(2) 89.52(4), Cl–Ru–N(1) 90.63(19), Cl–Ru–C(1) 95.23(11), Ru–N(1)–N(2) 179.2(7), Ru–C(1)–C(2) 135.0(3), C(1)–C(2)–C(3) 125.1(3)

isopropyl groups. The Ru–N(1)–N(2) axis is perfectly linear while in the related complex $[\text{RuHCl}(\text{N}_2)(\text{P}i\text{Pr}_3)_2]$ the bond angle Ru–N–N is $175(2)^\circ$.^[17] The bond lengths Ru–N(1) and N(1)–N(2) are, respectively, 1.869(5) and 1.088(8) Å and thus quite similar to those in $[\text{RuHCl}(\text{N}_2)(\text{P}i\text{Pr}_3)_2]$.

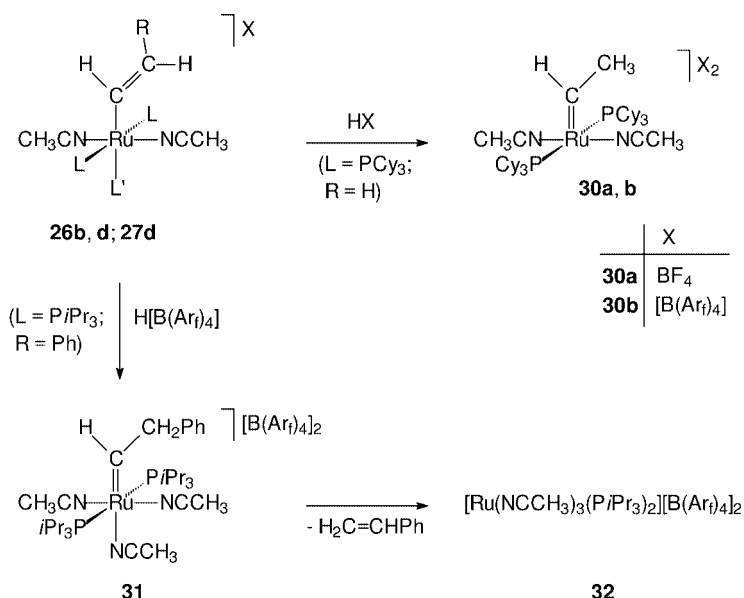
The reactions of the vinyl complexes $[\text{Ru}(\text{CH}=\text{CHR})(\text{NCMe})_n(\text{L})_2]\text{X}$ ($\text{L} = \text{PCy}_3$; $n = 2$; $\text{L} = \text{P}i\text{Pr}_3$; $n = 3$) with strong acids lead to a conversion of the vinyl ligand into a coordinated carbene. While the protonation of **26a** or **26c** with excess HBF_4 in diethyl ether gives a salt-like product with $[\text{Ru}(\text{=CHCH}_3)(\text{NCMe})_2(\text{PCy}_3)_2]^{2+}$ as the cation and different ratios of, respectively, $\text{PF}_6^-/\text{BF}_4^-$ and $\text{BPh}_4^-/\text{BF}_4^-$ as the anion, the reaction of **26b** with HBF_4 affords the bis(tetrafluoroborate) **30a** cleanly in 75% yield (Scheme 6). In a similar way, compound **30b** was prepared on treatment of **26d** with Brookhart's acid $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_f)_4]$.^[18] Both **30a** and **30b** are yellow, moderately air-stable solids, the conductivity of which (in nitromethane) corresponds to that of 1:2 electrolytes. Regarding the spectroscopic data, the most typical features are the signal for the carbene =CH proton at $\delta = 17.70$ (**30a**) and 17.20 ppm (**30b**) in the ^1H NMR spectra and the multiplet for the carbene carbon atom at $\delta = 335.1$ ppm (**30b**) in the ^{13}C NMR spectrum. The single resonance for the phosphorus nuclei in the ^{31}P NMR spectra of **30a** and **30b** suggests that the phosphane ligands are stereochemically equivalent and thus in a *trans* disposition. Attempts to generate the dication $[\text{Ru}(\text{=CHCH}_3)(\text{NCMe})_2(\text{PCy}_3)_2]^{2+}$ from $[\text{RuCl}_2(\text{=CHCH}_3)(\text{PCy}_3)_2]$ by substitution of the chloro ligands for acetonitrile failed.

In contrast to **26d**, the related bis(triisopropylphosphane) compound **27d** reacts with an equimolar amount of $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_f)_4]$ in CH_2Cl_2 at 0°C to give a 1:1 mixture of the dicationic complexes **31** and **32**. Since both compounds are readily soluble in dichloromethane but insoluble in ben-

zene or pentane, they could not be separated by fractional crystallization. The ^1H NMR spectrum of the mixture displays a triplet at $\delta = 17.32$ ppm, assigned to the =CH proton, and a multiplet, which becomes a doublet in off-resonance, at $\delta = 4.22$ ppm for the CH_2Ph protons of the carbene ligand of **31**. In the ^{31}P NMR spectrum, a single resonance for the ^{31}P nuclei of **31** is observed.

Stirring the solution of **31** and **32** for 2 h at room temperature leads to a complete conversion of **31** into the carbene-free complex **32**, which was isolated as a green, moderately air-stable solid in 90% yield. As a by-product, styrene was detected both by ^1H NMR spectroscopy and GC/MS analysis. Since both the ^1H and ^{13}C NMR spectra of **32** show a single set of signals for the protons and carbon atoms of the CH_3CN ligands and since the molecule is diamagnetic, instead of a trigonal-bipyramidal structure a fluxional square-pyramidal geometry is more likely. With regard to the mechanism of the conversion of **31** to **32**, we assume, in agreement with results recently reported by Carmona^[19] and Gimeno^[20] and their co-workers, that the carbene ligand CHCH_2Ph rearranges by an intramolecular 1,2-H shift to styrene. As the bonding of an olefin to a twofold positively charged metal center is, in general, considered to be weak, styrene is eliminated from the intermediate and the five-coordinate complex **32** is formed.

The formation of a metal carbene from a metal vinyl precursor is not without precedence. Casey^[21] and Helquist^[22] et al. showed already in 1982 that neutral cyclopentadienyl-iron compounds with $\text{Fe}-\text{CR}=\text{CH}_2$ as a linkage can be converted with HBF_4 into the corresponding cationic carbene derivatives. Similar transformations of neutral vinyl to monocationic carbene complexes by attack of an electrophile at the β -carbon atom of the vinyl ligand have since been carried by various research groups^[23] including ours.^[24] However, we note that: (1) as far we know there is no report about the preparation of a *dicationic* metal



Scheme 6

carbene from a *monocationic* vinylmetal precursor by protonation, and (2) to the best of our knowledge **30a** and **30b** are the first dicationic five-coordinate carbeneruthenium complexes described as yet.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1**,^[4,25] **3–5**,^[d,25] **16**,^[4,25] and **23**^[d,1e] were prepared as described in the literature. IR spectra were recorded on a Bruker IFS 25 FT-IR infrared spectrometer, and NMR spectra were recorded at room temperature on Bruker AC 200 and AMX 400 instruments, unless otherwise stated. The molar conductivity Λ_M was determined in nitromethane. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer Du Pont 9000. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quadruplet; sept, septet; m, multiplet; vt, virtual triplet; br, broadened signal; $N = {}^3J_{\text{P,H}} + {}^5J_{\text{P,H}}$ or ${}^1J_{\text{P,C}} + {}^3J_{\text{P,C}}$.

Preparation of [RuHCl(=C=CHrBu)(PCy₃)₂] (2): A solution of **1** (177 mg, 0.25 mmol) in CH₂Cl₂ (15 mL) was treated at –78 °C with *tert*-butylacetylene (0.1 mL, 0.82 mmol). After stirring the reaction mixture for 30 s, the solvent was removed in vacuo. A brown solid was obtained, which was washed at –78 °C with pentane (6 mL) and dried in vacuo; yield 143 mg (72%); m.p. 80 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2106$, $\nu(\text{C}=\text{C}) = 1637$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 2.87$ (t, $J_{\text{P,H}} = 3.7$ Hz, 1 H, Ru=C=CH), 2.61–1.20 (m, 66 H, C₆H₁₁), 1.27 (s, 9 H, CCH₃), –13.89 (t, $J_{\text{P,H}} = 17.8$ Hz, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, C₆D₆): $\delta = 39.0$ (s) ppm. C₄₂H₇₇ClP₂Ru (780.5): calcd. C 64.63, H 9.94; found C 63.95, H 9.72.

Preparation of [RuH(κ²-O₂CCH₃)(=C=CHrBu)(PCy₃)₂] (6): A solution of **2** (97 mg, 0.12 mmol) in THF (8 mL) was treated with finely divided potassium acetate (280 mg, 2.85 mmol) and stirred for 20 min at room temperature. The solvent was evaporated in vacuo and the residue was extracted with benzene (10 mL). The extract was dried in vacuo, and the remaining off-white solid was washed twice with pentane (3 mL each) and dried; yield 93 mg (96%); m.p. 50 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2053$, $\nu(\text{OCO}_{\text{asym.}}) = 1635$, $\nu(\text{C}=\text{C}) = 1546$, $\nu(\text{OCO}_{\text{sym.}}) = 1448$ cm^{–1}. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 2.12$ (t, $J_{\text{P,H}} = 3.3$ Hz, 1 H, Ru=C=CH), 1.97–0.87 (m, 66 H, C₆H₁₁), 1.43 (s, 3 H, CH₃CO₂), 0.73 (s, 9 H, CCH₃), –12.48 (t, $J_{\text{P,H}} = 19.6$ Hz, 1 H, RuH) ppm. ¹³C NMR (100.6 MHz, CD₂Cl₂): $\delta = 180.3$ (s, CH₃CO₂), 114.8 (s, Ru=C=CH), 33.4 (vt, $N = 17.8$ Hz, C1 of C₆H₁₁), 32.4 (s, CCH₃), 30.1 (s, C3 or C5 of C₆H₁₁), 29.4 (s, C3 or C5 of C₆H₁₁), 28.2, 28.0 (both vt, $N = 10.2$ Hz, C2,6 of C₆H₁₁), 26.9 (s, C4 of C₆H₁₁), 24.4 (s, CH₃CO₂) ppm; the signal of the Ru=C carbon atom could not be located exactly. ³¹P NMR (162.0 MHz, CD₂Cl₂): $\delta = 38.0$ (s) ppm. C₄₄H₈₀O₂P₂Ru (804.1): calcd. C 65.72, H 10.03; found C 65.62, H 10.19.

Preparation of [RuH(NCO)(=C=CH₂)(PCy₃)₂] (7): A solution of **3** (80 mg, 0.11 mmol) in THF (8 mL) was treated with an excess of finely divided KOCN (400 mg, 4.93 mmol) and stirred for 30 min at room temperature. A gradual change of color from red-brown to brown occurred. The solvent was evaporated in vacuo, the residue was extracted with benzene (10 mL), and the extract was again dried in vacuo. After the oily residue was layered with pentane (5 mL), a brown solid precipitated which was separated from the mother liquor and dried; yield 63 mg (78%); m.p. 42 °C (decomp). IR (KBr): $\nu(\text{NCO}_{\text{asym.}}) = 2219$, $\nu(\text{RuH}) = 2072$, $\nu(\text{C}=\text{C}) = 1612$,

$\nu(\text{NCO}_{\text{sym.}}) = 1446$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 2.66$ (t, $J_{\text{P,H}} = 3.7$ Hz, 2 H, Ru=C=CH₂), 2.47–0.81 (m, 66 H, C₆H₁₁), –18.30 (t, $J_{\text{P,H}} = 18.3$ Hz, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, C₆D₆): $\delta = 43.9$ (s) ppm. C₃₉H₆₉NOP₂Ru (731.0): calcd. C 64.08, H 9.51, N 1.92; found C 63.16, H 9.41, N 2.07.

Preparation of [RuH(κ²-O₂CCH₃)(=C=CH₂)(PCy₃)₂] (8): This compound was prepared as described for **6**, with **3** (74 mg, 0.10 mmol) and potassium acetate (250 mg, 2.55 mmol) as starting materials. Pale brown solid; yield 70 mg (94%); m.p. 50 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2064$, $\nu(\text{OCO}_{\text{asym.}}) = 1601$, $\nu(\text{C}=\text{C}) = 1549$, $\nu(\text{OCO}_{\text{sym.}}) = 1447$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 2.74$ (t, $J_{\text{P,H}} = 3.3$ Hz, 2 H, Ru=C=CH₂), 2.44–1.07 (m, 66 H, C₆H₁₁), 1.94 (s, 3 H, CH₃CO₂), –11.84 (t, $J_{\text{P,H}} = 19.1$ Hz, 1 H, RuH) ppm. ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 330.0$ (t, $J_{\text{P,C}} = 15.3$ Hz, Ru=C=CH₂), 197.7 (s, CH₃CO₂), 84.6 (t, $J_{\text{P,C}} = 3.8$ Hz, Ru=C=CH₂), 33.1 (vt, $N = 17.8$ Hz, C1 of C₆H₁₁), 29.5, 28.9 (both s, C3,5 of C₆H₁₁), 27.6, 27.4 (both vt, $N = 10.2$ Hz, C2,6 of C₆H₁₁), 26.2 (s, C4 of C₆H₁₁), 23.8 (s, CH₃CO₂) ppm. ³¹P NMR (162.0 MHz, C₆D₆): $\delta = 39.4$ (s) ppm. C₄₀H₇₂O₂P₂Ru (748.0): calcd. C 64.23, H 9.70, Ru 13.51; found C 63.70, H 9.00, Ru 13.63.

Preparation of [RuH(NCO)(=C=CHPh)(PCy₃)₂] (9): This compound was prepared as described for **7**, with **4** (133 mg, 0.17 mmol) and KOCN (300 mg, 3.70 mmol) as starting materials. Olive-green solid; yield 92 mg (67%); m.p. 50 °C (decomp). IR (KBr): $\nu(\text{NCO}_{\text{asym.}}) = 2205$, $\nu(\text{RuH}) = 2071$, $\nu(\text{C}=\text{C}) = 1615$, $\nu(\text{NCO}_{\text{sym.}}) = 1446$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 7.15$ –6.76 (m, 5 H, C₆H₅), 4.34 (t, $J_{\text{P,H}} = 3.9$ Hz, 1 H, Ru=C=CH), 2.37–1.17 (m, 66 H, C₆H₁₁), –14.42 (t, $J_{\text{P,H}} = 17.2$ Hz, 1 H, RuH) ppm. ³¹P NMR (C₆D₆, 81.0 MHz): $\delta = 43.1$ (s) ppm. C₄₅H₇₃NOP₂Ru (807.1): calcd. C 66.97, H 9.12, N 1.74; found C 66.80, H 8.89, N 2.07.

Preparation of [RuH(κ²-O₂CCH₃)(=C=CHPh)(PCy₃)₂] (10): This compound was prepared as described for **6**, with **4** (81 mg, 0.10 mmol) and potassium acetate (230 mg, 2.34 mmol) as starting materials. Pale brown solid; yield 68 mg (83%); m.p. 42 °C (dec.). IR (KBr): $\nu(\text{RuH}) = 2099$, $\nu(\text{C}=\text{C}) = 1610$, $\nu(\text{OCO}_{\text{asym.}}) = 1588$, $\nu(\text{OCO}_{\text{sym.}}) = 1446$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 7.29$ –6.92 (m, 5 H, C₆H₅), 4.35 (t, $J_{\text{P,H}} = 3.3$ Hz, 1 H, Ru=C=CH), 2.31–1.07 (m, 66 H, C₆H₁₁), 1.95 (s, 3 H, CH₃CO₂), –10.66 (t, $J_{\text{P,H}} = 19.1$ Hz, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, C₆D₆): $\delta = 40.1$ (s) ppm. C₄₆H₇₆O₂P₂Ru (824.1): calcd. C 67.04, H 9.29; found C 66.20, H 9.25.

Preparation of [RuH(=C=CHPh)(PiPr₃)₂] (11): A solution of **5** (73 mg, 0.13 mmol) in THF (7 mL) was treated with an excess of finely divided KI (250 mg, 1.51 mmol) and stirred for 20 min at room temperature. The solvent was evaporated in vacuo, the residue was extracted with benzene (8 mL), and the extract was again dried in vacuo. After the residue was layered with pentane (5 mL) and the solution stored at –78 °C, a brown solid formed which was washed with small quantities of pentane and dried; yield 71 mg (84%); m.p. 36 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2075$, $\nu(\text{C}=\text{C}) = 1609$ cm^{–1}. ¹H NMR (200 MHz, C₆D₆): $\delta = 7.54$ –6.83 (m, 5 H, C₆H₅), 4.33 (t, $J_{\text{P,H}} = 3.3$ Hz, 1 H, Ru=C=CH), 2.56 (m, 6 H, PCHCH₃), 1.21 (m, 36 H, PCHCH₃), –9.32 (t, $J_{\text{P,H}} = 18.0$ Hz, 1 H, RuH) ppm. ¹³C NMR (50.3 MHz, C₆D₆): $\delta = 326.8$ (t, $J_{\text{P,C}} = 15.3$ Hz, Ru=C=CHPh), 132.8 (s, *ipso*-C of C₆H₅), 128.3, 127.8, 123.9 (all s, C₆H₅), 109.1 (t, $J_{\text{P,C}} = 4.4$ Hz, Ru=C=CHPh), 25.7 (vt, $N = 20.4$ Hz, PCHCH₃), 20.4, 20.3 (both s, PCHCH₃) ppm. ³¹P NMR (81.0 MHz, C₆D₆): $\delta = 51.6$ (s) ppm. C₂₆H₄₉IP₂Ru (651.6): calcd. C 47.93, H 7.58, Ru 15.51; found C 47.75, H 7.30, Ru 15.46.

Preparation of [RuH(NCO)(=C=CHPh)(P*i*Pr₃)₂] (12): This compound was prepared as described for **11**, with **5** (78 mg, 0.14 mmol) and KOCN (250 mg, 3.08 mmol) as starting materials; reaction time 15 min. Dark green solid; yield 77 mg (97%); m.p. 56 °C (decomp). IR (KBr): $\nu(\text{NCO}_{\text{asym.}}) = 2213$, $\nu(\text{RuH}) = 2075$, $\nu(\text{C}=\text{C}) = 1610$, $\nu(\text{NCO}_{\text{sym.}}) = 1464 \text{ cm}^{-1}$. ¹H NMR (200 MHz, C₆D₆): $\delta = 7.20\text{--}6.75$ (m, 5 H, C₆H₅), 4.29 (t, $J_{\text{P,H}} = 3.3 \text{ Hz}$, 1 H, Ru=C=CH), 2.29 (m, 6 H, PCHCH₃), 1.12 (m, 36 H, PCHCH₃), -13.37 (t, $J_{\text{P,H}} = 17.4 \text{ Hz}$, 1 H, RuH) ppm. ¹³C NMR (50.3 MHz, C₆D₆): $\delta = 333.3$ (t, $J_{\text{P,C}} = 14.9 \text{ Hz}$, Ru=C=CHPh), 144.0 (s, NCO), 133.8 (s, *ipso*-C of C₆H₅), 128.2, 126.3, 123.8 (all s, C₆H₅), 110.3 (t, $J_{\text{P,C}} = 3.8 \text{ Hz}$, Ru=C=CHPh), 24.7 (vt, $N = 20.4 \text{ Hz}$, PCHCH₃), 20.2, 20.0 (both s, PCHCH₃) ppm. ³¹P NMR (81.0 MHz, C₆D₆): $\delta = 52.3$ (s) ppm. C₂₇H₄₉NOP₂Ru (566.7): calcd. C 57.22, H 8.71, N 2.47; found C 57.24, H 8.62, N 2.47.

Preparation of [RuH(OPh)(=C=CHPh)(P*i*Pr₃)₂] (13): This compound was prepared as described for **11**, with **5** (209 mg, 0.37 mmol) and KOPh (300 mg, 2.27 mmol) as starting materials; reaction time 10 min. Brown solid; yield 80 mg (35%); m.p. 80 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2058$, $\nu(\text{C}=\text{C}) = 1606 \text{ cm}^{-1}$. ¹H NMR (400 MHz, C₆D₆): $\delta = 7.25\text{--}6.76$ (m, 10 H, C₆H₅ and OC₆H₅), 4.40 (t, $J_{\text{P,H}} = 3.1 \text{ Hz}$, 1 H, Ru=C=CH), 2.16 (m, in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 6 H, PCHCH₃), 1.15, 1.13 (both m, in ¹H{³¹P} both d, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 18 H each, PCHCH₃), -13.59 (t, $J_{\text{P,H}} = 18.3 \text{ Hz}$, 1 H, RuH) ppm. ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 329.6$ (t, $J_{\text{P,C}} = 15.9 \text{ Hz}$, Ru=C=CHPh), 133.6, 129.4, 128.5, 128.1, 123.3, 123.2, 118.0, 116.3 (all s, C₆H₅ and OC₆H₅), 110.4 (t, $J_{\text{P,C}} = 3.8 \text{ Hz}$, Ru=C=CHPh), 24.5 (vt, $N = 19.0 \text{ Hz}$, PCHCH₃), 20.3, 20.2 (both s, PCHCH₃) ppm. ³¹P NMR (162.0 MHz, C₆D₆): $\delta = 50.5$ (s) ppm. C₃₂H₅₄OP₂Ru (617.8): calcd. C 62.21, H 8.81; found C 61.91, H 8.33.

Preparation of [RuH(κ^2 -O₂CCH₃)(=C=CHPh)(P*i*Pr₃)₂] (14): This compound was prepared as described for **11**, with **5** (67 mg, 0.12 mmol) and potassium acetate (250 mg, 2.55 mmol) as starting materials; reaction time 10 min. Orange-red solid; yield 65 mg (92%); m.p. 62 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2021$, $\nu(\text{C}=\text{C}) = 1603$, $\nu(\text{OCO}_{\text{asym.}}) = 1586$, $\nu(\text{OCO}_{\text{sym.}}) = 1449 \text{ cm}^{-1}$. ¹H NMR (400 MHz, C₆D₆): $\delta = 7.25\text{--}6.84$ (m, 5 H, C₆H₅), 4.31 (t, $J_{\text{P,H}} = 3.5 \text{ Hz}$, 1 H, Ru=C=CH), 2.39 (m, in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 6 H, PCHCH₃), 1.82 (s, 3 H, CH₃CO₂), 1.28, 1.25 (both m, in ¹H{³¹P} both d, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 18 H each, PCHCH₃), -10.58 (t, $J_{\text{P,H}} = 18.7 \text{ Hz}$, 1 H, RuH) ppm. ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 335.2$ (t, $J_{\text{P,C}} = 15.3 \text{ Hz}$, Ru=C=CHPh), 181.3 (s, CH₃CO₂), 134.9 (s, *ipso*-C of C₆H₅), 128.3, 123.8, 123.0 (all s, C₆H₅), 108.6 (t, $J_{\text{P,C}} = 3.8 \text{ Hz}$, Ru=C=CHPh), 24.6 (s, CH₃CO₂), 24.4 (vt, $N = 19.0 \text{ Hz}$, PCHCH₃), 20.1, 19.5 (both s, PCHCH₃) ppm. ³¹P NMR (162.0 MHz, C₆D₆): $\delta = 49.1$ (s) ppm. C₂₈H₅₂O₂P₂Ru (583.7): calcd. C 57.61, H 8.98, Ru 17.31; found C 57.99, H 8.73, Ru 17.84.

Preparation of [RuH(κ^2 -O₂CCF₃)(=C=CHPh)(P*i*Pr₃)₂] (15): This compound was prepared as described for **11**, with **5** (153 mg, 0.27 mmol) and CF₃CO₂K (400 mg, 2.63 mmol) as starting materials. The residue was extracted with toluene (9 mL); reaction time 10 min. Red solid; yield 157 mg (91%); m.p. 54 °C (decomp). IR (KBr): $\nu(\text{RuH}) = 2044$, $\nu(\text{C}=\text{C}) = 1628$, $\nu(\text{OCO}_{\text{asym.}}) = 1588$, $\nu(\text{OCO}_{\text{sym.}}) = 1444 \text{ cm}^{-1}$. ¹H NMR (400 MHz, C₆D₆): $\delta = 7.22\text{--}6.85$ (m, 5 H, C₆H₅), 4.24 (t, $J_{\text{P,H}} = 3.5 \text{ Hz}$, 1 H, Ru=C=CH), 2.29 (m, in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 6 H, PCHCH₃), 1.19, 1.16 (both m, in ¹H{³¹P} both d, $J_{\text{H,H}} = 7.0 \text{ Hz}$, 18 H each, PCHCH₃), -11.51 (t, $J_{\text{P,H}} = 18.4 \text{ Hz}$, 1 H, RuH) ppm. ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 338.1$ (t, $J_{\text{P,C}} = 15.3 \text{ Hz}$, Ru=C=CHPh), 163.4 (q, $J_{\text{F,C}} = 36.9 \text{ Hz}$, CF₃CO₂), 133.4 (s, *ipso*-C of C₆H₅), 128.5, 124.0, 123.7 (all s, C₆H₅), 115.2 (q, $J_{\text{F,C}} = 287.3 \text{ Hz}$, CF₃CO₂),

108.9 (t, $J_{\text{P,C}} = 3.8 \text{ Hz}$, Ru=C=CHPh), 24.5 (vt, $N = 20.4 \text{ Hz}$, PCHCH₃), 20.0, 19.5 (both s, PCHCH₃) ppm. ¹⁹F NMR (376.5 MHz, C₆D₆): $\delta = -75.2$ (s) ppm. ³¹P NMR (162.0 MHz, C₆D₆): $\delta = 48.2$ (s) ppm. C₂₈H₄₉F₃O₂P₂Ru (637.7): calcd. C 52.74, H 7.74, Ru 15.85; found C 52.60, H 7.50, Ru 16.80.

Preparation of [RuH(=CCH₃)(OEt₂)(PCy₃)₂]BF₄ (17): A solution of **16** (123 mg, 0.15 mmol) in a 1:1 mixture of CH₂Cl₂ (5 mL) and diethyl ether (5 mL) was treated at -78°C with a 1.6 M solution of HBF₄ in diethyl ether (0.15 mL, 0.24 mmol). After warming the solution to 0 °C the solvent was evaporated in vacuo and the residue was layered with diethyl ether (5 mL). A light yellow solid precipitated, which was filtered, washed with pentane (5 mL) and dried; yield 86 mg (59%); m.p. 45 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 54. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 3.42$ (q, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 4 H, OCH₂CH₃), 2.51 (s, 3 H, Ru=CCH₃), 2.37–1.32 (m, 66 H, C₆H₁₁), 1.15 (t, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 6 H, OCH₂CH₃), -6.87 (t, $J_{\text{P,H}} = 15.3 \text{ Hz}$, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, CD₂Cl₂): $\delta = 55.7$ (s) ppm. C₄₂H₈₀BF₄IOP₂Ru (977.8): calcd. C 51.59, H 8.25; found C 51.45, H 7.98.

Preparation of [RuH(NCO)(=CCH₃)(OEt₂)(PCy₃)₂]BF₄ (18): This compound was prepared as described for **17**, from **7** (45 mg, 0.06 mmol) and a 1.6 M solution of HBF₄ in diethyl ether (0.3 mL, 0.48 mmol). Light yellow solid; yield 39 mg (73%); m.p. 69 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 95. IR (KBr): $\nu(\text{NCO}_{\text{asym.}}) = 2229$, $\nu(\text{RuH}) = 1973$, $\nu(\text{NCO}_{\text{sym.}}) = 1448 \text{ cm}^{-1}$. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 3.42$ (q, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 4 H, OCH₂CH₃), 2.23 (s, 3 H, Ru=CCH₃), 2.30–1.31 (m, 66 H, C₆H₁₁), 1.15 (t, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 6 H, OCH₂CH₃), -7.46 (t, $J_{\text{P,H}} = 16.3 \text{ Hz}$, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, CD₂Cl₂): $\delta = 46.8$ (s) ppm.

Preparation of [RuH(κ^2 -O₂CCH₃)(=CCH₃)(PCy₃)₂]BF₄ (19): A solution of **8** (81 mg, 0.11 mmol) in toluene (5 mL) was treated at 0 °C with a 1.6 M solution of HBF₄ in diethyl ether (0.3 mL, 0.48 mmol) and stirred for 15 min at 0 °C. The solvent was evaporated in vacuo, the remaining light yellow residue was washed with pentane (5 mL) and dried; yield 61 mg (66%); m.p. 60 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 113. IR (KBr): $\nu(\text{RuH}) = 2066$, $\nu(\text{OCO}_{\text{asym.}}) = 1629$, $\nu(\text{OCO}_{\text{sym.}}) = 1448 \text{ cm}^{-1}$. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 2.50\text{--}1.30$ (m, 72 H, C₆H₁₁, Ru=CCH₃ and CH₃CO₂), -7.31 (t, $J_{\text{P,H}} = 17.0 \text{ Hz}$, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, CD₂Cl₂): $\delta = 48.7$ (s) ppm.

Preparation of [RuHCl(=CCH₂Ph)(OEt₂)(PCy₃)₂]BF₄ (20): This compound was prepared as described for **17**, from **4** (93 mg, 0.12 mmol) and a 1.6 M solution of HBF₄ in diethyl ether (0.2 mL, 0.32 mmol). Light yellow solid; yield 75 mg (65%); m.p. 55 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 61. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 7.42\text{--}6.69$ (m, 5 H, C₆H₅), 4.03 (s, 2 H, Ru=CCH₂Ph), 3.44 (q, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 4 H, OCH₂CH₃), 2.83–1.26 (m, 66 H, C₆H₁₁), 1.15 (t, $J_{\text{H,H}} = 7.3 \text{ Hz}$, 6 H, OCH₂CH₃), -6.41 (br. s, 1 H, RuH) ppm. ³¹P NMR (81.0 MHz, CD₂Cl₂): $\delta = 56.0$ (s) ppm. C₄₈H₈₄BClF₄OP₂Ru (962.5): calcd. C 59.90, H 8.80; found C 58.91, H 8.50.

Preparation of [RuHCl(=CCH₂Ph)(OEt₂)(P*i*Pr₃)₂]BF₄ (21): A solution of **5** (56 mg, 0.10 mmol) in a 1:1 mixture of CH₂Cl₂ (3 mL) and diethyl ether (3 mL) was treated at -78°C with a 1.6 M solution of HBF₄ in diethyl ether (0.2 mL, 0.32 mmol). After warming the solution to 0 °C, the solvent was evaporated in vacuo, and the residue was treated with diethyl ether (10 mL). The suspension was stirred for 15 min at 0 °C which led to the precipitation of a light yellow solid. This was separated from the mother liquor, washed with diethyl ether (5 mL) and dried; yield 40 mg (55%); m.p. 60 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 61. ¹H NMR (200 MHz,

CD_2Cl_2): $\delta = 7.41\text{--}7.27$ (m, 5 H, C_6H_5), 3.95 (s, 2 H, $\text{Ru}=\text{CCH}_2\text{Ph}$), 3.43 (q, $J_{\text{H,H}} = 7.3$ Hz, 4 H, OCH_2CH_3), 2.76 (m, 6 H, PCHCH_3), 1.31 (m, 36 H, PCHCH_3), 1.14 (t, $J_{\text{H,H}} = 7.3$ Hz, 6 H, OCH_2CH_3), -6.73 (br. s, 1 H, RuH) ppm. ^{31}P NMR (81.0 MHz, CD_2Cl_2): $\delta = 63.6$ (s) ppm.

Preparation of $[\text{RuH}(\kappa^2\text{-O}_2\text{CCH}_3)(=\text{CCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (22): A solution of **14** (67 mg, 0.11 mmol) in toluene (7 mL) was treated at 0 °C with a 1.6 M solution of HBF_4 in diethyl ether (0.4 mL, 0.64 mmol) and stirred for 15 min at 0 °C. The solution was warmed to room temperature and then concentrated to ca. 1 mL in vacuo. A light yellow solid precipitated, which was separated from the mother liquor, washed with pentane (5 mL, 0 °C) and dried; yield 43 mg (55%); m.p. 48 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 96. IR (KBr): $\nu(\text{RuH}) = 2072$, $\nu(\text{OCO}_{\text{asym.}}) = 1587$, $\nu(\text{OCO}_{\text{sym.}}) = 1465$ cm^{-1} . ^1H NMR (200 MHz, CD_2Cl_2 , 295 K): $\delta = 7.40\text{--}7.18$ (m, 5 H, C_6H_5), 3.90 (s, 2 H, $\text{Ru}=\text{CCH}_2\text{Ph}$), 2.34 (s, 3 H, CH_3CO_2), 2.33 (m, 6 H, PCHCH_3), 1.34 (m, 36 H, PCHCH_3), -6.90 (br. s, 1 H, RuH) ppm. ^1H NMR (200 MHz, CD_2Cl_2 , 263 K): $\delta = -6.75$ (t, $J_{\text{P,H}} = 17.4$ Hz, 1 H, RuH) ppm. ^{31}P NMR (81.0 MHz, CD_2Cl_2 , 295 K): $\delta = 59.1$ (br. s) ppm. ^{31}P NMR (81.0 MHz, CD_2Cl_2 , 263 K): $\delta = 59.0$ (s) ppm. $\text{C}_{28}\text{H}_{53}\text{BF}_4\text{O}_2\text{P}_2\text{Ru}$ (671.5): calcd. C 50.08, H 7.95; found C 49.73, H 7.75.

Reaction of **12 with HCl:** A solution of **12** (87 mg, 0.16 mmol) in benzene (10 mL) was treated with a 0.42 M solution of HCl in benzene (0.33 mL, 0.14 mmol) and stirred for 10 min at room temperature. The solvent was evaporated in vacuo and the red-brown residue was dissolved in C_6D_6 (0.5 mL). The NMR spectra indicated that besides the starting material **12** (13%) a mixture of four products was formed, of which **5** (35%) and $[\text{RuCl}_2(\text{CHCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (**23**, 14%) were identified by comparison with authentic samples.^[1d,1e] The other two products were assumed to be $[\text{RuCl}(\text{NCO})(=\text{CHCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (**24**, 19%) and $[\text{Ru}(\text{NCO})_2(=\text{CHCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (**25**, 19%). Characteristic data for **24**: ^1H NMR (200 MHz, C_6D_6): $\delta = 19.50$ (t, $J_{\text{H,H}} = 5.1$ Hz, $\text{Ru}=\text{CH}$), 4.15 (d, $J_{\text{H,H}} = 5.1$ Hz, CH_2Ph).

Preparation of $[\text{Ru}(\text{NCO})_2(=\text{CHCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (25): A solution of **23** (102 mg, 0.17 mmol) in a mixture of THF (10 mL) and CH_2Cl_2 (3 mL) was treated with finely divided KOCN (150 mg, 1.85 mmol) and stirred for 24 h at room temperature. After evaporation of the solvent in vacuo, the residue was extracted twice with benzene (9 mL each). The combined extracts were dried in vacuo, the remaining violet solid was washed three times with pentane (5 mL each) and dried; yield 98 mg (94%); m.p. 82 °C (decomp). IR (KBr): $\nu(\text{NCO}_{\text{asym.}}) = 2230$, $\nu(\text{NCO}_{\text{sym.}}) = 1450$ cm^{-1} . ^1H NMR (400 MHz, C_6D_6): $\delta = 19.06$ (t, $J_{\text{H,H}} = 5.2$ Hz, 1 H, $\text{Ru}=\text{CH}$), 7.24–7.04 (m, 5 H, C_6H_5), 3.99 (d, $J_{\text{H,H}} = 5.2$ Hz, 2 H, CH_2Ph), 2.14 (m; in $^1\text{H}\{^{31}\text{P}\}$ sept, $J_{\text{H,H}} = 7.0$ Hz, 6 H, PCHCH_3), 0.98 (dvt, $N = 14.0$, $J_{\text{H,H}} = 7.0$ Hz, 36 H, PCHCH_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 319.5$ (br. s, $\text{Ru}=\text{CH}$), 139.9 (s, NCO), 136.6 (s, *ipso*-C of C_6H_5), 127.9, 127.3, 125.9 (all s, C_6H_5), 64.3 (s, CH_2Ph), 22.4 (vt, $N = 20.4$ Hz, PCHCH_3), 18.1 (s, PCHCH_3) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 48.3$ (s) ppm. $\text{C}_{28}\text{H}_{50}\text{N}_2\text{O}_2\text{P}_2\text{Ru}$ (609.7): calcd. C 55.16, H 8.26, N 4.59; found C 54.69, H 8.24, N 4.44.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{NCCH}_3)_2(\text{PCy}_3)_2]\text{PF}_6$ (26a): A solution of **3** (270 mg, 0.39 mmol) in a 1:1 mixture of CH_2Cl_2 and acetonitrile (30 mL) was treated with KPF_6 (250 mg, 1.36 mmol) and stirred for 35 min at room temperature. A gradual change of color from red-brown to light brown occurred. The solvent was evaporated in vacuo and the residue was extracted twice with

CH_2Cl_2 (10 mL each). The combined extracts were dried in vacuo, the remaining brown solid was washed twice with pentane (8 mL each) and dried; yield 307 mg (87%); m.p. 55 °C (dec.). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 69. IR (KBr): $\nu(\text{CN}) = 2253$ cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.38$ (dd, $J_{\text{H,H}} = 15.8$, $J_{\text{H,H}} = 7.9$ Hz, 1 H, $\text{CH}=\text{CH}_2$), 4.84 (d, $J_{\text{H,H}} = 7.9$ Hz, 1 H, *cis*-H of $\text{CH}=\text{CH}_2$), 4.70 (d, $J_{\text{H,H}} = 15.8$ Hz, 1 H, *trans*-H of $\text{CH}=\text{CH}_2$), 2.49 (s, 6 H, CH_3CN), 2.24–1.22 (m, 66 H, C_6H_{11}) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 150.2$ (br. s, RuCH), 125.5 (s, CN), 117.3 (s, $\text{CH}=\text{CH}_2$), 34.3 (vt, $N = 16.2$ Hz, C1 of C_6H_{11}), 29.7 (s, C3,5 of C_6H_{11}), 28.1 (vt, $N = 10.2$ Hz, C2,6 of C_6H_{11}), 26.5 (s, C4 of C_6H_{11}), 5.0 (s, CH_3CN) ppm. ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 22.4$ (s, PCy_3), -144.0 (sept, $J_{\text{F,P}} = 709.4$ Hz, PF_6) ppm. $\text{C}_{42}\text{H}_{75}\text{F}_6\text{N}_2\text{P}_3\text{Ru}$ (916.0): calcd. C 55.07, H 8.25, N 3.06, Ru 11.03; found C 54.89, H 7.81, N 3.06, Ru 10.76.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{NCCH}_3)_2(\text{PCy}_3)_2]\text{BF}_4$ (26b): This compound was prepared as described for **26a**, from **3** (101 mg, 0.14 mmol) and NaBF_4 (250 mg, 2.28 mmol) in a 2:1 mixture of CH_2Cl_2 and acetonitrile (15 mL). Orange-red solid; yield 109 mg (91%); m.p. 52 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 58. IR (KBr): $\nu(\text{CN}) = 2254$ cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.21$ (dd, $J_{\text{H,H}} = 15.6$, $J_{\text{H,H}} = 7.7$ Hz, 1 H, $\text{CH}=\text{CH}_2$), 4.62 (d, $J_{\text{H,H}} = 7.7$ Hz, 1 H, *cis*-H of $\text{CH}=\text{CH}_2$), 4.54 (d, $J_{\text{H,H}} = 15.6$ Hz, 1 H, *trans*-H of $\text{CH}=\text{CH}_2$), 2.39 (s, 6 H, CH_3CN), 2.25–1.10 (m, 66 H, C_6H_{11}) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 148.7$ (br. s, RuCH), 125.6 (s, CN), 117.1 (s, $\text{CH}=\text{CH}_2$), 34.2 (vt, $N = 16.2$ Hz, C1 of C_6H_{11}), 29.7 (s, C3,5 of C_6H_{11}), 28.0 (vt, $N = 9.5$ Hz, C2,6 of C_6H_{11}), 26.5 (s, C4 of C_6H_{11}), 5.0 (s, CH_3CN) ppm. ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 22.5$ (s) ppm. $\text{C}_{42}\text{H}_{75}\text{BF}_4\text{N}_2\text{P}_2\text{Ru}$ (857.9): calcd. C 58.80, H 8.81, N 3.27; found C 58.55, H 8.54, N 3.36.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{NCCH}_3)_2(\text{PCy}_3)_2]\text{BPh}_4$ (26c): A solution of **26a** (450 mg, 0.49 mmol) in methanol (20 mL) was treated with NaBPh_4 (200 mg, 0.58 mmol) and stirred for 15 min at room temperature. An orange-red solid precipitated, which was separated from the mother liquor, washed three times with methanol (10 mL each) and dried in vacuo; yield 416 mg (78%); m.p. 100 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 63. IR (KBr): $\nu(\text{CN}) = 2244$ cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.33\text{--}6.86$ (m, 21 H, $\text{CH}=\text{CH}_2$ and BC_6H_5), 4.70 (d, $J_{\text{H,H}} = 7.3$ Hz, 1 H, *cis*-H of $\text{CH}=\text{CH}_2$), 4.63 (d, $J_{\text{H,H}} = 15.2$ Hz, 1 H, *trans*-H of $\text{CH}=\text{CH}_2$), 2.33 (s, 6 H, CH_3CN), 2.24–1.24 (m, 66 H, C_6H_{11}) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 164.1$ (q, $J_{\text{B,C}} = 49.6$ Hz, *ipso*-C of BC_6H_5), 147.2 (br. s, RuCH), 136.0 (s, CH of BC_6H_5), 125.7 (q, $J_{\text{B,C}} = 3.2$ Hz, *ortho*-C of BC_6H_5), 121.7 (s, BC_6H_5), 117.2 (s, $\text{CH}=\text{CH}_2$), 34.3 (vt, $N = 16.5$ Hz, C1 of C_6H_{11}), 29.8 (s, C3,5 of C_6H_{11}), 28.1 (vt, $N = 10.2$ Hz, C2,6 of C_6H_{11}), 26.5 (s, C4 of C_6H_{11}), 4.8 (s, CH_3CN) ppm; the signal of the CN carbon atom could not be located exactly. ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 23.0$ (s) ppm. $\text{C}_{66}\text{H}_{95}\text{BN}_2\text{P}_2\text{Ru}$ (1090.3): calcd. C 72.71, H 8.78, N 2.57; found C 72.53, H 7.96, N 2.65.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)(\text{NCCH}_3)_2(\text{PCy}_3)_2]\text{B}(\text{Ar}_f)_4$ (26d): A suspension of **26a** (54 mg, 0.06 mmol) in diethyl ether (6 mL) was treated at 0 °C with a solution of $\text{Na}[\text{B}(\text{Ar}_f)_4]$ (55 mg, 0.06 mmol) in diethyl ether (5 mL). After stirring the reaction mixture for 10 min, a white solid precipitated. The solution was filtered and the filtrate dried in vacuo. The remaining red-brown solid was washed three times with pentane (5 mL each) and dried in vacuo; yield 94 mg (96%); m.p. 70 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 78. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.72$ [br. s, 8 H, *ortho*-H of $\text{B}(\text{Ar}_f)_4$], 7.57 [br. s, 4 H, *para*-H of $\text{B}(\text{Ar}_f)_4$], 7.29 (dd, $J_{\text{H,H}} = 15.3$, $J_{\text{H,H}} = 7.6$ Hz, 1 H, $\text{CH}=\text{CH}_2$), 4.70 (dt, $J_{\text{H,H}} = 7.6$, $J_{\text{P,H}} = 2.5$ Hz,

1 H, *cis*-H of CH=CH₂), 4.65 (dt, $J_{\text{H,H}} = 15.3$, $J_{\text{P,H}} = 2.0$ Hz, 1 H, *trans*-H of CH=CH₂), 2.51 (s, 6 H, CH₃CN), 2.25–1.13 (m, 66 H, C₆H₁₁) ppm. ¹³C NMR (100.6 MHz, CD₂Cl₂): $\delta = 161.8$ [q, $J_{\text{B,C}} = 49.9$ Hz, *ipso*-C of B(Ar_f)₄], 147.2 (br. s, RuCH), 134.9 [br. s, *ortho*-C of B(Ar_f)₄], 129.0 [br. q, $J_{\text{F,C}} = 31.5$ Hz, *meta*-C of B(Ar_f)₄], 125.4 (s, CN), 124.7 (q, $J_{\text{F,C}} = 272.4$ Hz, CF₃), 117.5 [m, *para*-C of B(Ar_f)₄], 117.2 (t, $J_{\text{P,C}} = 3.4$ Hz, CH=CH₂), 34.3 (vt, $N = 15.2$ Hz, C1 of C₆H₁₁), 29.8 (s, C3,5 of C₆H₁₁), 28.1 (vt, $N = 9.5$ Hz, C2,6 of C₆H₁₁), 26.4 (s, C4 of C₆H₁₁), 5.0 (s, CH₃CN) ppm. ¹⁹F NMR (376.5 MHz, CD₂Cl₂): $\delta = -62.7$ (s) ppm. ³¹P NMR (162.0 MHz, CD₂Cl₂): $\delta = 22.9$ (s) ppm. C₇₄H₈₇BF₂₄N₃P₂Ru (1634.3): calcd. C 54.39, H 5.36, N 1.71; found C 53.82, H 5.12, N 1.68.

Preparation of [Ru{(E)-CH=CHPh}(NCCH₃)₃(PiPr₃)₂]Cl (27a): A solution of **5** (81 mg, 0.14 mmol) in CH₂Cl₂ (8 mL) was treated with acetonitrile (3 mL, 0.06 mol) and stirred for 10 min at room temperature. The solvent was evaporated in vacuo, the remaining light yellow solid was washed twice with pentane (8 mL each) and dried; yield 87 mg (91%); m.p. 50 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 56. IR (KBr): $\nu(\text{CN}) = 2251\text{ cm}^{-1}$. ¹H NMR (200 MHz, CD₃CN): $\delta = 8.74$ (dt, $J_{\text{H,H}} = 17.2$, $J_{\text{P,H}} = 1.8$ Hz, 1 H, CH=CHPh), 7.15–6.90 (m, 5 H, C₆H₅), 6.43 (dt, $J_{\text{H,H}} = 17.2$, $J_{\text{P,H}} = 1.8$ Hz, 1 H, CH=CHPh), 2.46 (m, 6 H, PCHCH₃), 2.38 (s, 9 H, CH₃CN), 1.26 (m, 36 H, PCHCH₃) ppm. ¹³C NMR (50.3 MHz, CD₃CN): $\delta = 164.2$ (br. s, RuCH), 142.6 (s, *ipso*-C of C₆H₅), 133.8 (s, CH=CHPh), 129.2, 124.3, 123.7 (all s, C₆H₅), 126.9 (s, CN), 24.8 (vt, $N = 17.1$ Hz, PCHCH₃), 19.7 (s, PCHCH₃), 5.3, 5.0 (both s, CH₃CN) ppm. The second signal of the CN carbon atoms is probably covered by the signals of the phenyl carbon atoms. ³¹P NMR (81.0 MHz, CD₃CN): $\delta = 28.8$ (s) ppm. C₃₂H₅₈ClN₃P₂Ru (683.3): calcd. C 56.25, H 8.55, N 6.15; found C 55.89, H 8.05, N 5.56.

Preparation of [Ru{(E)-CH=CHPh}(NCCH₃)₃(PiPr₃)₂]PF₆ (27b): This compound was prepared as described for **26a**, from **27a** (85 mg, 0.12 mmol) and KPF₆ (150 mg, 0.81 mmol) in a 5:3 mixture of CH₂Cl₂ and acetonitrile (8 mL). Orange solid; yield 73 mg (77%); m.p. 36 °C (dec.). Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 66. IR (KBr): $\nu(\text{CN}) = 2260\text{ cm}^{-1}$. ¹H NMR (200 MHz, CD₂Cl₂): $\delta = 8.56$ (d, $J_{\text{H,H}} = 16.8$ Hz, 1 H, CH=CHPh), 7.20–6.89 (m, 5 H, C₆H₅), 6.34 (d, $J_{\text{H,H}} = 16.8$ Hz, 1 H, CH=CHPh), 2.46 (m; in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.4$ Hz, 6 H, PCHCH₃), 2.42 (s, 6 H, CH₃CN), 2.31 (s, 3 H, CH₃CN), 1.27 (dvt, $N = 12.3$, $J_{\text{H,H}} = 7.4$ Hz, 36 H, PCHCH₃) ppm. ¹³C NMR (50.3 MHz, CD₂Cl₂): $\delta = 159.7$ (br. s, RuCH), 141.2 (s, *ipso*-C of C₆H₅), 133.3 (s, CH=CHPh), 128.2, 123.6, 123.1 (all s, C₆H₅), 125.4, 123.3 (both s, CN), 24.1 (vt, $N = 17.1$ Hz, PCHCH₃), 19.1 (s, PCHCH₃), 5.0, 3.3 (both s, CH₃CN) ppm. ³¹P NMR (81.0 MHz, CD₂Cl₂): $\delta = 28.3$ (s, PiPr₃), –144.0 (sept, $J_{\text{F,P}} = 709.4$ Hz, PF₆) ppm. C₃₂H₅₈F₆N₃P₃Ru (792.8): calcd. C 48.48, H 7.37, N 5.30; found C 48.07, H 6.95, N 5.44.

Preparation of [Ru{(E)-CH=CHPh}(NCCH₃)₃(PiPr₃)₂]BPh₄ (27c): This compound was prepared as described for **26c**, from **27b** (230 mg, 0.23 mmol) and NaBPh₄ (200 mg, 0.58 mmol) in methanol (15 mL). Orange-brown solid; yield 162 mg (73%); m.p. 114 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 42. IR (KBr): $\nu(\text{CN}) = 2258\text{ cm}^{-1}$. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 8.48$ (d, $J_{\text{H,H}} = 16.6$ Hz, 1 H, CH=CHPh), 7.35–6.88 (m, 25 H, C₆H₅ and BC₆H₅), 6.30 (d, $J_{\text{H,H}} = 16.6$ Hz, 1 H, CH=CHPh), 2.46 (m; in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.0$ Hz, 6 H, PCHCH₃), 2.24 (s, 6 H, CH₃CN), 2.08 (s, 3 H, CH₃CN), 1.27 (dvt, $N = 12.6$, $J_{\text{H,H}} = 7.0$ Hz, 36 H, PCHCH₃) ppm. ¹³C NMR (100.6 MHz, CD₂Cl₂): $\delta = 164.1$ [q, $J_{\text{B,C}} = 49.5$ Hz, *ipso*-C of BC₆H₅], 140.7 (s, *ipso*-C of C₆H₅), 133.2 (s, CH=CHPh), 136.0, 128.3, 123.7, 123.4, 121.8 (all s, C₆H₅ and

BC₆H₅), 125.7 (q, $J_{\text{B,C}} = 3.1$ Hz, *ortho*-C of BC₆H₅), 24.1 (vt, $N = 17.3$ Hz, PCHCH₃), 19.3 (s, PCHCH₃), 4.9, 3.3 (both s, CH₃CN) ppm. The signals of the CN carbon atoms and of the RuCH carbon atom are probably covered by the signals of the phenyl carbon atoms. ³¹P NMR (162.0 MHz, CD₂Cl₂): $\delta = 28.6$ (s) ppm. C₅₆H₇₈BN₃P₂Ru (967.1): calcd. C 69.55, H 8.13, N 4.35; found C 68.73, H 8.09, N 4.14.

Preparation of [Ru{(E)-CH=CHPh}(NCCH₃)₃(PiPr₃)₂][B(Ar_f)₄] (27d): This compound was prepared as described for **26d**, from **27b** (73 mg, 0.09 mmol) and a solution of Na[B(Ar_f)₄] (77 mg, 0.09 mmol) in diethyl ether (6 mL). Red-brown solid; yield 83 mg (61%); m.p. 70 °C (decomp). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 54. IR (KBr): $\nu(\text{CN}) = 2263\text{ cm}^{-1}$. ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 8.44$ (dt, $J_{\text{H,H}} = 16.6$, $J_{\text{P,H}} = 2.1$ Hz, 1 H, CH=CHPh), 7.73 [br. s, 8 H, *ortho*-H of B(Ar_f)₄], 7.58 [br. s, 4 H, *para*-H of B(Ar_f)₄], 7.21–6.92 (m, 5 H, C₆H₅), 6.28 (d, $J_{\text{H,H}} = 16.6$ Hz, 1 H, CH=CHPh), 2.49–2.40 (m, 12 H, CH₃CN and PCHCH₃), 2.23 (s, 3 H, CH₃CN), 1.25 (m, 36 H, PCHCH₃) ppm. ¹³C NMR (75.5 MHz, CD₂Cl₂): $\delta = 161.8$ [q, $J_{\text{B,C}} = 49.8$ Hz, *ipso*-C of B(Ar_f)₄], 140.6 (s, *ipso*-C of C₆H₅), 134.9 [br. s, *ortho*-C of B(Ar_f)₄], 133.3 (m, CH=CHPh), 128.9 [qq, $J_{\text{F,C}} = 31.5$, $J_{\text{F,C}} = 2.9$ Hz, *meta*-C of B(Ar_f)₄], 128.3, 123.8, 123.5 (all s, C₆H₅), 125.5 (s, CN), 124.7 (q, $J_{\text{F,C}} = 272.6$ Hz, CF₃), 117.6 [m, *para*-C of B(Ar_f)₄], 24.1 (vt, $N = 17.2$ Hz, PCHCH₃), 19.2 (s, PCHCH₃), 5.6, 4.1 (both s, CH₃CN) ppm. The second signal of the CN carbon atoms and the signal of the RuCH carbon atom are probably covered by the signals of the phenyl carbon atoms. ¹⁹F NMR (282.4 MHz, CD₂Cl₂): $\delta = -63.3$ (s) ppm. ³¹P NMR (CD₂Cl₂, 81.0 MHz): $\delta = 29.2$ (s) ppm. C₆₄H₇₀BF₂₄N₃P₂Ru (1511.1): calcd. C 50.87, H 4.67, N 2.78; found C 50.58, H 4.45, N 2.57.

Generation of [RuCl{(E)-CH=CHPh}(CO)₂(PiPr₃)₂] (28): In an NMR tube, a solution of **5** (28 mg, 0.05 mmol) in C₆D₆ (0.5 mL) was cooled to –78 °C. The tube was evacuated in vacuo and then filled with CO. Upon warming to room temperature, a change of color from olive-green to red and finally to pale yellow occurred. The ¹H and ³¹P NMR spectra of the solution revealed that compound **28** was formed in quantitative yield. It was identified by comparison of the NMR spectroscopic data with those of an authentic sample.^[14]

Preparation of [RuCl{(E)-CH=CHPh}(N₂)(PiPr₃)₂] (29): A solution of **5** (68 mg, 0.12 mmol) in pentane (8 mL) was stirred under a nitrogen atmosphere for 2 h at room temperature. A change of color from olive-green to brown occurred and a red-brown solid precipitated. After storing the solution for 12 h at –20 °C, the mother liquor was separated and the remaining red-brown solid dried in a stream of N₂; yield 65 mg (92%); m.p. 34 °C (decomp). IR (KBr): $\nu(\text{N}_2) = 2067\text{ cm}^{-1}$. ¹H NMR (400 MHz, C₆D₆): $\delta = 9.50$ (dt, $J_{\text{H,H}} = 16.6$, $J_{\text{P,H}} = 1.5$ Hz, 1 H, CH=CHPh), 7.39–6.86 (m, 5 H, C₆H₅), 6.37 (dt, $J_{\text{H,H}} = 16.6$, $J_{\text{P,H}} = 1.9$ Hz, 1 H, CH=CHPh), 2.62 (m; in ¹H{³¹P} sept, $J_{\text{H,H}} = 7.2$ Hz, 6 H, PCHCH₃), 1.17, 1.15 (both m; in ¹H{³¹P} both d, $J_{\text{H,H}} = 7.2$ Hz, 18 H each, PCHCH₃) ppm. ¹³C NMR (100.6 MHz, C₆D₆): $\delta = 147.5$ (t, $J_{\text{P,C}} = 10.8$ Hz, RuCH), 138.0 (s, *ipso*-C of C₆H₅), 130.2 (t, $J_{\text{P,C}} = 3.2$ Hz, CH=CHPh), 127.9, 123.2, 123.1 (all s, C₆H₅), 22.5 (vt, $N = 17.8$ Hz, PCHCH₃), 18.8, 18.7 (both s, PCHCH₃) ppm. ³¹P NMR (162.0 MHz, C₆D₆): $\delta = 33.3$ (s) ppm. C₂₆H₄₉ClN₂P₂Ru (588.2): calcd. C 53.10, H 8.40, N 4.76; found C 53.24, H 8.30, N 3.86.

Preparation of [Ru(=CHCH₃)(NCCH₃)₂(PCy₃)₂](BF₄)₂ (30a): A solution of **26b** (275 mg, 0.32 mmol) in CH₂Cl₂ (8 mL) was treated with a 1.6 M solution of HBF₄ in diethyl ether (1.0 mL, 1.60 mmol) at room temperature. A change of color from red to yellow-orange

occurred. The solvent was evaporated in vacuo, the remaining yellow solid was washed three times with pentane (5 mL each) and dried; yield 225 mg (75%); m.p. 55 °C (decomp). Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 99. IR (KBr): $\nu(\text{CN}) = 2275\text{ cm}^{-1}$. ^1H NMR (200 MHz CD_2Cl_2): $\delta = 17.70$ (m, 1 H, $=\text{CHCH}_3$), 2.96 (br.s, 3 H, $=\text{CHCH}_3$), 2.79 (s, 6 H, CH_3CN), 2.53–1.31 (m, 66 H, C_6H_{11}) ppm. ^{31}P NMR (81.0 MHz, CD_2Cl_2): $\delta = 38.0$ (s) ppm. $\text{C}_{42}\text{H}_{76}\text{B}_2\text{F}_8\text{N}_2\text{P}_2\text{Ru}$ (945.7): calcd. C 53.34, H 8.10, N 2.96; found C 53.01, H 7.73, N 3.42.

Preparation of $[\text{Ru}(=\text{CHCH}_3)(\text{NCCH}_3)_2(\text{PCy}_3)_2][\text{B}(\text{Ar}_f)_4]$ (30b): A solution of **26d** (94 mg, 0.06 mmol) in CH_2Cl_2 (8 mL) was treated at 0 °C with a solution of $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_f)_4]$ (58 mg, 0.06 mmol) in CH_2Cl_2 (4 mL). A change of color from red to yellow occurred. After warming the solution to room temperature, the solvent was evaporated in vacuo, and the remaining yellow solid was washed three times with pentane (5 mL each) and dried; yield 130 mg (87%); m.p. 130 °C (decomp). Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 139. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 17.20$ (q, $J_{\text{H,H}} = 5.9$ Hz, 1 H, $=\text{CHCH}_3$), 7.72 [br. s, 16 H, *ortho*-H of $\text{B}(\text{Ar}_f)_4$], 7.57 [br. s, 8 H, *para*-H of $\text{B}(\text{Ar}_f)_4$], 2.87 (d, $J_{\text{H,H}} = 5.9$ Hz, 3 H, $=\text{CHCH}_3$), 2.75 (s, 6 H, CH_3CN), 2.17–1.23 (m, 66 H, C_6H_{11}) ppm. ^{13}C NMR (100.6 MHz, $[\text{D}_6]\text{acetone}$): $\delta = 335.1$ (m, $\text{Ru}=\text{C}$), 163.0 [q, $J_{\text{B,C}} = 49.6$ Hz, *ipso*-C of $\text{B}(\text{Ar}_f)_4$], 135.9 [br. s, *ortho*-C of $\text{B}(\text{Ar}_f)_4$], 130.4 [br. q, $J_{\text{F,C}} = 31.8$ Hz, *meta*-C of $\text{B}(\text{Ar}_f)_4$], 125.7 (q, $J_{\text{F,C}} = 272.1$ Hz, CF_3), 118.8 [m, *para*-C of $\text{B}(\text{Ar}_f)_4$], 48.5 (s, $=\text{CHCH}_3$), 35.3 (vt, $N = 19.1$ Hz, C1 of C_6H_{11}), 30.8 (s, C3, 5 of C_6H_{11}), 28.5 (vt, $N = 10.2$ Hz, C2, 6 of C_6H_{11}), 26.1 (s, C4 of C_6H_{11}), 5.7 (s, CH_3CN) ppm. The signal of the CN carbon atom could not be located exactly. ^{19}F NMR (376.5 MHz, $[\text{D}_6]\text{acetone}$): $\delta = -62.9$ (s) ppm. ^{31}P NMR (162.0 MHz, $[\text{D}_6]\text{acetone}$): $\delta = 41.0$ (s) ppm. $\text{C}_{106}\text{H}_{100}\text{B}_2\text{F}_{48}\text{N}_2\text{P}_2\text{Ru}$ (2498.5): calcd. C 50.96, H 4.03, N 1.12; found C 50.72, H 3.77, N 1.13.

Generation of $[\text{Ru}(=\text{CHCH}_2\text{Ph})(\text{NCCH}_3)_3(\text{P}i\text{Pr}_3)_2][\text{B}(\text{Ar}_f)_4]$ (31): A solution of **27d** (48 mg, 0.03 mmol) in CH_2Cl_2 (5 mL) was treated at 0 °C with a solution of $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_f)_4]$ (32 mg, 0.03 mmol) in CH_2Cl_2 (3 mL). A change of color from red to light green occurred. After stirring the solution for 2 min, it was filtered and the filtrate was dried in vacuo. The ^1H and ^{31}P NMR spectra of the light green residue revealed that it consisted of equal amounts of **31** and **32**. Data for **31**: ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 17.32$ (t, $J_{\text{H,H}} = 5.1$ Hz, 1 H, $=\text{CHCH}_3$), 4.42 (m; in $^1\text{H}\{^{31}\text{P}\}$ d, $J_{\text{H,H}} = 5.1$ Hz, 2 H, CH_2Ph) ppm. ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 51.5$ (s) ppm.

Preparation of $[\text{Ru}(\text{NCCH}_3)_3(\text{P}i\text{Pr}_3)_2][\text{B}(\text{Ar}_f)_4]$ (32): A solution of **27d** (80 mg, 0.05 mmol) in CH_2Cl_2 (6 mL) was treated with a solution of $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{Ar}_f)_4]$ (53 mg, 0.05 mmol) in CH_2Cl_2 (4 mL) and stirred for 2 h at room temperature. The solution was filtered, and the filtrate was dried in vacuo. The remaining green solid was washed twice with pentane (5 mL each) and dried; yield 102 mg (90%); m.p. 68 °C (decomp). Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) = 153. IR (KBr): $\nu(\text{CN}) = 2288\text{ cm}^{-1}$. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.72$ [br. s, 16 H, *ortho*-H of $\text{B}(\text{Ar}_f)_4$], 7.57 [br. s, 8 H, *para*-H of $\text{B}(\text{Ar}_f)_4$], 2.48 (m; in $^1\text{H}\{^{31}\text{P}\}$ sept, $J_{\text{H,H}} = 7.2$ Hz, 6 H, PCHCH_3), 2.40 (s, 9 H, CH_3CN), 1.32, 1.31 (both dvt, $N = 13.5$, $J_{\text{H,H}} = 7.2$ Hz, 18 H each, PCHCH_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 161.8$ [q, $J_{\text{B,C}} = 49.8$ Hz, *ipso*-C of $\text{B}(\text{Ar}_f)_4$], 134.9 [br. s, *ortho*-C of $\text{B}(\text{Ar}_f)_4$], 128.9 [br. q, $J_{\text{F,C}} = 31.8$ Hz, *meta*-C of $\text{B}(\text{Ar}_f)_4$], 127.5 (s, CN), 124.7 (q, $J_{\text{F,C}} = 272.7$ Hz, CF_3), 117.6 [m, *para*-C of $\text{B}(\text{Ar}_f)_4$], 24.0 (vt, $N = 19.1$ Hz, PCHCH_3), 19.0 (s, PCHCH_3), 4.7 (s, CH_3CN) ppm. ^{19}F NMR (376.5 MHz, CD_2Cl_2): $\delta = -62.8$ (s) ppm. ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = 27.9$ (s) ppm.

$\text{C}_{88}\text{H}_{75}\text{B}_2\text{F}_{48}\text{N}_3\text{P}_2\text{Ru}$ (2271.1): calcd. C 46.54, H 3.33, N 1.85; found C 46.65, H 3.35, N 2.31.

X-ray Structure Determination of Compounds 26c and 29: Single crystals of **26c** were grown from CH_2Cl_2 at -20 °C and those of **29** from pentane at -78 °C. Crystal data collection parameters for these structures are presented in Table 1. The data were collected on a Stoe IPDS diffractometer (**26c**) and a Bruker Smart Apex diffractometer (**29**) using monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (SADABS2.0). The structures were solved by direct methods (SHELXS-97).^[26] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method on F^2 using SHELXL-97.^[27] The asymmetric unit of **26c** includes a molecule of dichloromethane, the chloro atoms of which are disordered (ratio of occupancy factors $\text{Cl1}/\text{Cl2}:\text{Cl1}'/\text{Cl2}' = 82:18$). The hydrogen atoms of the vinyl ligand were found in a difference-Fourier synthesis and refined without restraints. The positions of all other hydrogen atoms were calculated according to the ideal geometry and refined by the riding method. The chloro and the nitrogen ligands of **29** are disordered and could be refined anisotropically without restraints (occupancy factor 80:20).

Ref. code MIKMUO (**26c**) and CCDC-215082 (**29**) contain 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].

Table 1. Crystal data for complexes **26c** and **29**

	26c · CH_2Cl_2	29
Empirical formula	$\text{C}_{67}\text{H}_{97}\text{BCl}_2\text{N}_2\text{P}_2\text{Ru}$	$\text{C}_{26}\text{H}_{49}\text{ClN}_2\text{P}_2\text{Ru}$
<i>M</i>	1189.35	588.13
Crystal size (mm)	$0.19 \times 0.16 \times 0.12$	$0.40 \times 0.24 \times 0.12$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> (Å)	12.7193(17)	16.4389(8)
<i>b</i> (Å)	15.482(2)	10.9929(5)
<i>c</i> (Å)	17.447(2)	17.0126(8)
α (°)	88.771(16)	90
β (°)	79.913(15)	105.4450(10)
γ (°)	69.452(15)	90
<i>V</i> (Å ³)	3164.3(7)	2963.3(2)
<i>Z</i>	2	4
<i>D_c</i> (g cm ⁻³)	1.227	1.318
Temperature (K)	173(2)	173(2)
μ (mm ⁻¹)	0.423	0.743
$2\Theta(\text{max})$ (°)	50.06	50.00
No. reflections measured	25291	41784
No. unique reflections	10533 (0.0637)	5210 (0.0291)
(<i>R_{int}</i>)		
No. observed reflections	6204	5026
[<i>I</i> > 2σ(<i>I</i>)]		
Parameters refined	686	331
<i>R₁</i>	0.0495	0.0363
<i>wR₂</i>	0.1280	0.0827
Reflection/parameter ratio	15.4	15.74
Residual electron density	+1.064/−0.948	+1.025/−0.343
(e [−] Å ^{−3})		

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- [1] [1a] H. Werner, A. Stark, M. Schulz, J. Wolf, *Organometallics* **1992**, *11*, 1126–1130. [1b] H. Werner, A. Stark, P. Steinert, C. Grünwald, J. Wolf, *Chem. Ber.* **1995**, *128*, 49–62. [1c] M. Martin, O. Gevert, H. Werner, *J. Chem. Soc., Dalton Trans.* **1996**, 2275–2283. [1d] C. Grünwald, O. Gevert, J. Wolf, P. González-Herrero, H. Werner, *Organometallics* **1996**, *15*, 1960–1962. [1e] J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender, H. Werner, *Eur. J. Inorg. Chem.* **1998**, 1217–1224.
- [2] W. Stüer, J. Wolf, H. Werner, P. Schwab, M. Schulz, *Angew. Chem.* **1998**, *110*, 3603–3606; *Angew. Chem. Int. Ed.* **1998**, *37*, 3421–3423.
- [3] S. Jung, K. Ilg, J. Wolf, H. Werner, *Organometallics* **2001**, *20*, 2121–2123.
- [4] W. Stüer, Dissertation, Universität Würzburg, **1999**.
- [5] [5a] S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.* **1973**, 1912–1920. [5b] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250. [5c] C. Oldham, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, **1987**, Vol. 2, p. 435–459.
- [6] [6a] J. L. Burmeister, E. A. Deardorf, A. Jensen, V. H. Christensen, *Inorg. Chem.* **1970**, *9*, 58–63. [6b] U. Müller, *Z. Anorg. Allg. Chem.* **1973**, *396*, 187–198.
- [7] P. González-Herrero, B. Weberndörfer, K. Ilg, J. Wolf, H. Werner, *Organometallics* **2001**, *20*, 3672–3685.
- [8] T. Daniel, N. Mahr, T. Braun, H. Werner, *Organometallics* **1993**, *12*, 1475–1477.
- [9] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.
- [10] B. Weberndörfer, Dissertation, Universität Würzburg, **2001**.
- [11] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
- [12] H. Katayama, F. Ozawa, *Organometallics* **1998**, *17*, 5190–5196.
- [13] M. Oliván, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 3091–3100.
- [14] H. Werner, M. A. Esteruelas, H. Otto, *Organometallics* **1986**, *5*, 2295–2299.
- [15] D. Sellmann, B. Hautsch, A. Rösler, F. W. Heinemann, *Angew. Chem.* **2001**, *113*, 1553–1555; *Angew. Chem. Int. Ed.* **2001**, *40*, 1505–1507.
- [16] A. van Asselt, B. J. Burger, V. C. Gibson, J. E. Bercaw, *J. Am. Chem. Soc.* **1986**, *108*, 5347–5349.
- [17] J. N. Coalter III, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gérard, E. Clot, O. Eisenstein, *New. J. Chem.* **2000**, *24*, 9–26.
- [18] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920–3922.
- [19] F. M. Aliás, M. L. Poveda, M. Sellin, E. Carmona, *J. Am. Chem. Soc.* **1998**, *120*, 5816–5817.
- [20] M. P. Gamasa, J. Gimeno, B. M. Martín-Vaca, *Organometallics* **1998**, *17*, 3707–3715.
- [21] C. A. Casey, W. H. Miles, H. Takeda, J. M. O'Connor, *J. Am. Chem. Soc.* **1982**, *104*, 3761–3762.
- [22] K. A. M. Kremer, G.-H. Kuo, E. J. O'Connor, P. Helquist, R. C. Kerber, *J. Am. Chem. Soc.* **1982**, *104*, 6119–6121.
- [23] [23a] G. S. Bodner, D. E. Smith, W. G. Hatton, P. C. Heah, S. Georgiou, A. L. Rheingold, S. J. Geib, J. P. Hutchinson, J. A. Gladysz, *J. Am. Chem. Soc.* **1987**, *109*, 7688–7705. [23b] M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, B. Zeier, *Organometallics* **1994**, *13*, 4258–4265. [23c] G. Jia, W. F. Wu, R. C. Y. Yeung, H. Xia, *J. Organomet. Chem.* **1997**, *538*, 31–40. [23d] F. M. Alias, M. L. Poveda, M. Sellin, E. Carmona, E. Gutiérrez-Puebla, A. Monge, *Organometallics* **1998**, *17*, 4124–4126.
- [24] H. Werner, S. Jung, P. González-Herrero, K. Ilg, J. Wolf, *Eur. J. Inorg. Chem.* **2001**, 1957–1961.
- [25] J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab, M. Schulz, *Angew. Chem.* **1998**, *110*, 1165–1167; *Angew. Chem. Int. Ed.* **1998**, *37*, 1124–1126.
- [26] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
- [27] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

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