Synthesis, Molecular Structure, and C–C Coupling Reactions of Carbeneruthenium(II) Complexes with $C_5H_5Ru(=CRR')$ and $C_5Me_5Ru(=CRR')$ as Molecular Units

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Dedicated to Professor Warren R. Roper on the occasion of his 65th birthday

Abstract: The ethene derivatives $[(\eta^5\text{-}C_5R_5)RuX(C_2H_4)(PPh_3)]$ with R = H and Me, which have been prepared from the η^3-allylic compounds $[(\eta^5\text{-}C_5R_5)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**1**, **2**) and acids HX under an ethene atmosphere, are excellent starting materials for the synthesis of a series of new halfsandwich-type ruthenium(II) complexes. The olefinic ligand is replaced not only by CO and pyridine, but also by internal and terminal alkynes to give (for X = Cl) alkyne, vinylidene, and allene compounds of the general composition $[(\eta^5\text{-}C_5R_5)RuCl(L)(PPh_3)]$ with $L = C_2(CO_2Me)_2$, $Me_3SiC_2CO_2Et$, $C{=}CHCO_2R$, and C_3H_4. The allenylidene complex $[(\eta^5\text{-}C_5H_5)RuCl(=C{=}C{=}CPh_2)(PPh_3)]$ is directly accessible from **1** (R = H) in two steps with the propargylic alcohol $HC{\equiv}CC(OH)Ph_2$ as the precursor. The reactions of the ethene derivatives $[(\eta^5\text{-}C_5H_5)RuX(C_2H_4)(PPh_3)]$ (X = Cl, CF_3CO_2) with diazo compounds $RR'CN_2$ yield the corresponding carbene complexes $[(\eta^5\text{-}C_5R_5)RuX(=CRR')(PPh_3)]$, while with ethyl diazoacetate (for X = Cl) the diethyl maleate compound $[(\eta^5\text{-}C_5H_5)RuCl\{\eta^2\text{-}Z\text{-}C_2H_2(CO_2Et)_2\}(PPh_3)]$ is obtained. Halfsandwich-type ruthenium(II) complexes $[(\eta^5\text{-}C_5R_5)RuCl(=CHR')(PPh_3)]$ with secondary carbenes as ligands, as well as cationic species $[(\eta^5\text{-}C_5H_5)Ru(=CPh_2)(L)(PPh_3)]X$ with L = CO and CN*t*Bu and X = $AlCl_4$ and PF_6, have also been prepared. The neutral compounds $[(\eta^5\text{-}C_5H_5)RuCl(=CRR')(PPh_3)]$ react with phenyllithium, methyllithium, and the vinyl Grignard reagent $CH_2{=}CHMgBr$ by displacement of the chloride and subsequent C–C coupling to generate halfsandwich-type ruthenium(II) complexes with η^3-benzyl, η^3-allyl, and substituted olefins as ligands. Protolytic cleavage of the metal–allylic bond in $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}CH_2CHCR_2)(PPh_3)]$ with acetic acid affords the corresponding olefins $R_2C{=}CHCH_3$. The by-product of this process is the acetato derivative $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCH_3)(PPh_3)]$, which can be reconverted to the carbene complexes $[(\eta^5\text{-}C_5H_5)RuCl(=CR_2)(PPh_3)]$ in a one-pot reaction with R_2CN_2 and Et_3NHCl.

Keywords: C–C coupling · carbene complexes · cyclopentadienyl complexes · olefin complexes · ruthenium

Introduction

Carbeneruthenium(II) complexes of the type $[RuCl_2(=CHR)(PR'_3)_2]$, which were first prepared by Grubbs and co-workers,[1] belong to the most frequently used organometallic compounds, both in organic synthesis and homogeneous catalysis.[2] The best known representative $[RuCl_2(=CHPh)(PCy_3)_2]$[3] is prepared from $[RuCl_2(PPh_3)_3]$ in two steps using phenyldiazomethane as the carbene source.[4] Prior to the early 1990s, this "diazoalkane route", pioneered by Herrmann et al.[5] and Roper et al.,[6] had only rarely been applied, most notably for the preparation of metal carbenes with d^6 and d^8 metal centers.

In the context of our studies on the chemistry of square-planar vinylidene- and allenylidenerhodium(I) complexes *trans*-$[RhCl\{=C(=C)_nRR'\}(P\mathit{i}Pr_3)_2]$ ($n = 1$ and 2),[7] we recently described a synthetic protocol that is also applicable to the corresponding carbenerhodium(I) species *trans*-$[RhCl(=CRR')(L)_2]$, with L being a tertiary phosphane, arsane, or stibane ligand.[8] These compounds are not only the first rhodium(I) complexes bearing a carbene unit that is not stabilized by linkage of the carbene carbon atom to a heteroatom such as O, S, or N,[9] but they are also remarkable insofar as they react with olefins *not* to give cyclopropanes but mono- or trisubstituted ethene derivatives instead.[8, 10]

The rich chemistry offered by the rhodium carbenes *trans*-$[RhCl(=CRR')(L)_2]$[10] and $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$[11] prompted us to extend the diazoalkane route to the prepa-

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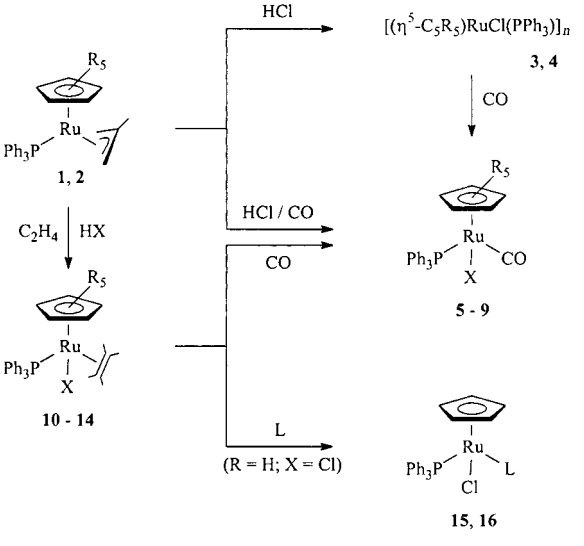
ration of related carbeneruthenium complexes of the half-sandwich-type. Herein, we report the synthesis of a series of compounds $[(\eta^5\text{-}C_5H_5)RuX(=CRR')(PPh_3)]$ and $[(\eta^5\text{-}C_5Me_5)RuX(=CRR')(PPh_3)]$, in which the carbene ligand is not only $C(C_6H_4X)_2$ but also CHPh, $CHSiMe_3$, and CPh{C(O)Ph}, respectively. Moreover, we illustrate that these ruthenium carbenes undergo carbene-plus-methyl, carbene-plus-vinyl, carbene-plus-phenyl, and carbene-plus-hydride coupling reactions leading to new η^3-allyl-, η^3-benzyl-, or olefin(hydrido) metal derivatives. Some preliminary results of this study have already been communicated.[12]

Results and Discussion

Some exploratory studies in $(\eta^5\text{-}C_5H_5)$Ru and $(\eta^5\text{-}C_5Me_5)$Ru chemistry: Following the observation that 16-electron ruthenium compounds of the general composition $[(\eta^5\text{-}C_5Me_5)RuCl(PR_3)]$ are accessible with bulky phosphane ligands[13] as well as with triisopropylstibane,[14] we became interested to find out whether similar triphenylphosphane derivatives $[(\eta^5\text{-}C_5R_5)RuCl(PPh_3)]$ can also be prepared. If treated with diazoalkanes, these could be envisaged as the most appropriate precursors for halfsandwich-type ruthenium carbenes.

The η^3-allyl complexes **1** and **2** (Scheme 1) react with a slight excess of HCl in toluene at $-30\,^\circ C$ to give orange, moderately air-sensitive solids, which analyze as $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)]$ (**3**) and $[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)]$ (**4**), respectively. Both compounds are insoluble in organic solvents and are therefore probably polymeric. The precipitation of **3** and **4** is preceded by a change of color of the toluene solution from yellow to violet, which possibly indicates that a monomeric species is generated in the initial step. The known complex $[(\eta^5\text{-}C_5Me_5)RuCl(P\mathit{i}Pr_3)]$ is violet.[13] Treating a suspension of **3** or **4** in dichloromethane with CO affords the monocarbonyl compounds **5** and **6**, which have previously been prepared by other routes.[15, 16] We note that **5** and **6** can also be obtained by first passing a slow stream of CO through a solution of **1** or **2** in benzene and then adding a solution of HCl in the same solvent. The yields of **5** and **6** are nearly quantitative by using this procedure.



	R
1, 3	H
2, 4	Me

	R	X
5, 10	H	Cl
6, 11	Me	Cl
7, 12	H	O_2CCF_3
8, 13	H	OTos
9, 14	H	OTfl

	L
15	NC_5H_5
16	$C_2(CO_2Me)_2$

Scheme 1. Tos = 4-$MeC_6H_4SO_2$; Tfl = CF_3SO_2.

With **1** and **2** as precursors, it is also possible to prepare the etheneruthenium(II) complexes **10** and **11** (Scheme 1). Addition of a solution of HCl in benzene to a solution of **1** or **2** in benzene or toluene, saturated with ethene, leads to the formation of the halfsandwich-type products, of which **11** could be isolated as a yellow microcrystalline solid in 95% yield. The $(\eta^5\text{-}C_5H_5)$Ru counterpart **10** is extremely labile and smoothly loses the olefinic ligand in the absence of excess C_2H_4. Therefore, **10** has only been characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Typical features of **10** and **11** are the two multiplets at $\delta = 3.53$ and 3.03 ppm (**10**) and $\delta = 2.86$ and 2.56 ppm (**11**) due to the ethene protons in the ^1H NMR spectra, and the singlet at $\delta = 46.2$ ppm (**10**) and $\delta = 47.4$ ppm (**11**) due to the olefinic carbon atoms in the ^{13}C NMR spectra. The chemical shift difference of about 76–77 ppm between the ^{13}C NMR resonances of coordinated and free ethene indicates that in **10** and **11** the degree of back-bonding from Ru to C_2H_4 is moderate;[17] it is possibly less than that in $[(\eta^5\text{-}C_5H_5)RuH(C_2H_4)(PPh_3)]$[18] or $[(\eta^5\text{-}C_5H_5)Ru(C_2H_4)(PPh_3)_2]BF_4$.[19]

The synthetic route developed for **10** and **11** has also been extended to the preparation of other etheneruthenium(II) derivatives of the general composition $[(\eta^5\text{-}C_5H_5)RuX(C_2H_4)(PPh_3)]$ (Scheme 1). Treatment of **1** with CF_3CO_2H, 4-toluenesulfonic acid or trifluoromethanesulfonic acid under an atmosphere of C_2H_4 leads to the formation of the corresponding ethene complexes **12**–**14** in 85–93% yield. The yellow microcrystalline solids are slightly air-sensitive but can be stored under argon for days without decomposition. On the basis of the ^{13}C NMR data, we assume that the back-bonding from the metal to the olefin is somewhat weaker than that in the chloro analogue **10**. This is consistent with the observation that the ethene ligand of **12**–**14** is easily replaced by CO to give the carbonyl complexes **7**–**9** in nearly quantitative yields. We note that the trifluoroacetato and tosylato compounds **7** and **8** have previously been prepared by carbonylation of $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCF_3)(PPh_3)]$ and $[(\eta^5\text{-}C_5H_5)Ru\{\kappa^2\text{-}O_2S(O)CF_3\}(PPh_3)]$, respectively.[20] The related triflate **9** contains a relatively weakly bound CO ligand, as indicated by the position of the CO stretching mode at 1975 cm^{-1}. The ν(CO) band for the chloro derivative **5** is observed at 1958 cm^{-1}.

The ethene ligand of **10** is also displaced by pyridine and $C_2(CO_2Me)_2$. The substitution products **15** and **16** are yellow, moderately air-stable solids, which are readily soluble in benzene and dichloromethane. Their compositions have been confirmed by elemental analysis. Since two sets of resonances for the carbon atoms of the $C_2(CO_2Me)_2$ ligand are seen in the ^{13}C NMR spectrum of **16**, we conclude that rotation about the metal–alkyne axis is significantly hindered on the NMR time scale.

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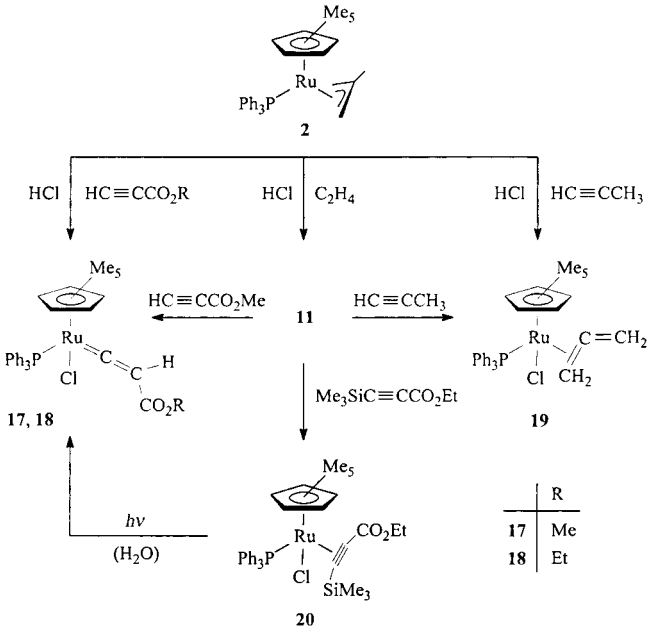
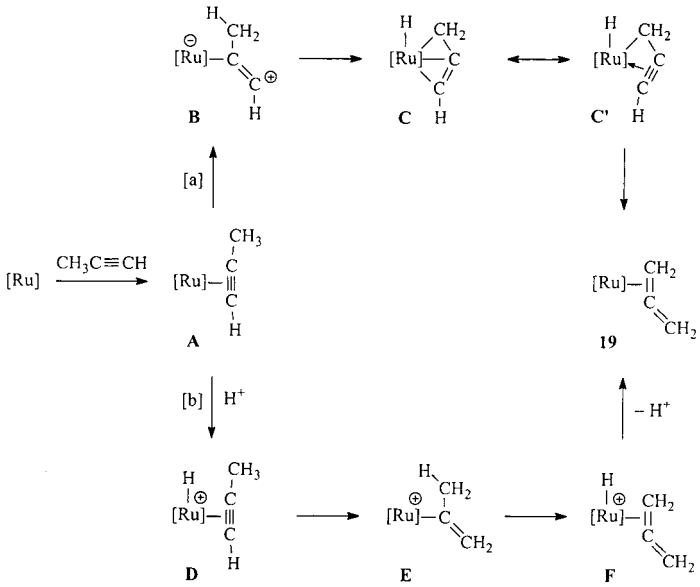
Halfsandwich-type ruthenium(II) complexes with alkyne, allene, vinylidene, and allenylidene ligands: Besides its conversion to **11**, the η^3-allyl compound **2** can also be converted to the vinylidene and allene complexes **17**, **18**, and **19** by treatment with terminal alkynes in the presence of HCl (Scheme 2). The reactions of **2** with HCl and methyl or ethyl



Scheme 2.



Scheme 3. [Ru] = [(η^5-C_5Me_5)RuCl(PPh_3)].

propiolate afford the ruthenium vinylidenes **17** and **18** as yellow or orange solids in moderate yields. Characteristic spectroscopic features of **17** and **18** are the low-field signals at $\delta \approx 333$ and 105 ppm in the ^{13}C NMR spectra due to the α- and β-carbon atoms of the Ru=C=$CHCO_2R$ unit, and the singlet resonances at $\delta = 4.80$ ppm (**17**) and $\delta = 4.61$ ppm (**18**) in the ^1H NMR spectra due to the respective vinylidene CH protons. Compound **17** is also obtained, although together with some other unidentified products, upon treatment of **11** with HC≡CCO_2Me. We note that Bruce et al. recently reported the preparation of **17** starting from [(η^5-C_5Me_5)RuCl(PPh_3)$_2$] as the precursor.[22]

The reactions of **11** with propyne and of **2** with propyne/HCl do not lead to a vinylidene, but rather to the corresponding allene complex **19**, which has been isolated as a yellow solid in 70–75% yield. Quite surprisingly, the ^1H, ^{13}C, and ^{31}P NMR spectra of **19** each show two sets of signals, which may indicate the presence of two rotational isomers. This is supported by measuring the ^1H NMR spectra (in [D_8]toluene) up to 343 K (that is, near to the decomposition temperature), at which a substantial broadening of the CH_2 resonances can be detected. The signals due to the allene protons (which are all resolved) were assigned by determining the cross-peaks in a H,H-COSY spectrum. Since only a broadening and no clear coalescence of the CH_2 signals could be observed in the temperature range 293–343 K, it is conceivable that two distinct dynamic processes take place. The first could be a rotation of the allene ligand about the metal–allene axis,[23] while the second could be a migration of the metal from one C=C bond to the next.[24] Regarding the course of the isomerization of propyne to allene, we assume that in the initial step the expected (but labile) alkyne complex **A** is formed (Scheme 3, path a), which could rearrange via **B** to **C** or **C′** and subsequently by intramolecular reductive elimination to the final product **19**. We note that the structure of the supposed transient **B** is reminiscent of that of the transition state postulated by Silvestre and Hoffmann[25] for the concerted rearrangement of terminal alkynes to vinylidenes, for which, however, a two-step mechanism is also possible.[26] As an alternative to path a, the alkyne compound **A** could be protonated to give **D**, which, via **E** and the allene(hydrido)-metal intermediate **F**, could be converted to **19** (Scheme 3 path b). Precedence for the metal-assisted conversion of alkynes (not only propyne) to allenes stems from previous studies by Richards et al.[27] on six-coordinate rhenium(I) compounds, as well as from our own work on square-planar and halfsandwich-type rhodium(I) and iridium(I) complexes, respectively.[23, 28]

The η-alkyne compound **20** is obtained in excellent yield by treatment of the corresponding ethene derivative **11** with $Me_3SiC{\equiv}CCO_2Et$ (Scheme 2). If a solution of **20** in benzene is irradiated with light from a UV lamp and then the reaction mixture is worked-up by column chromatography on deactivated Al_2O_3, the vinylidene complex **18** can be isolated. Since the photolysis occurs in the absence of water, we conclude that the rearrangement of the coordinated alkyne to the isomeric vinylidene takes place in the initial step, and that this is followed by protolytic cleavage (with traces of HCl from acidic Al_2O_3) of the Si–C bond. Examples of the thermal or photochemical isomerization of silylated alkynes to the corresponding vinylidenes are known,[29] as are instances of the conversion of a :C=C($SiMe_3$)R ligand to a :C=CHR ligand.[29a, 30]

The preparation of **21** (Scheme 4) follows the route developed by Selegue for cationic ruthenium allenylidenes.[31]

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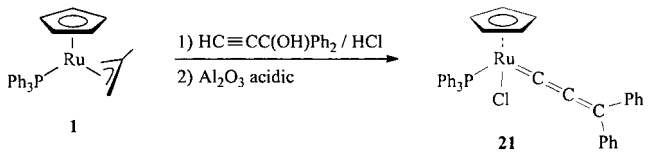
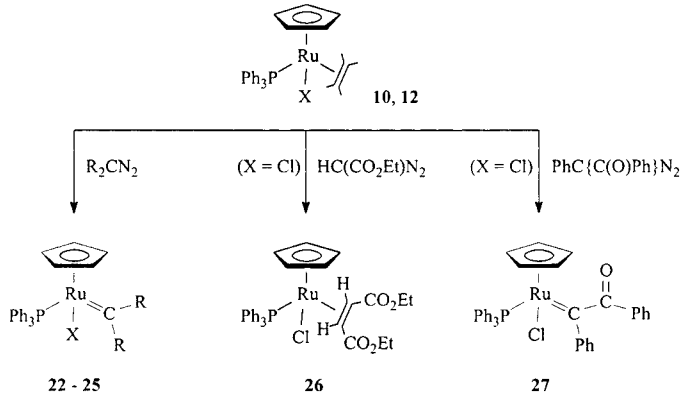


Scheme 4.

We assume that upon treatment of **1** with HCl and the propargylic alcohol $HC{\equiv}CC(OH)Ph_2$ the vinylidene compound $[(\eta^5\text{-}C_5H_5)RuCl\{{=}C{=}CHC(OH)Ph_2\}(PPh_3)]$ is generated initially, which then reacts with acidic Al_2O_3 by elimination of water to give the product. Characteristic data for **21**, which is an orange-red air-stable solid, are the strong $\nu(C{=}C{=}C)$ stretch at 1880 cm^{-1} in the IR spectrum and the low-field ^{13}C NMR signals at $\delta = 273.5$, 223.7, and 140.9 ppm due to the α-C, β-C, and γ-C atoms of the allenylidene unit, respectively. As in the case of $[(\eta^5\text{-}C_5Me_5)RuCl(=C=C=CPh_2)(\kappa P\text{-}i\text{Pr}_2PCH_2CO_2Me)]$,[32] only the resonance of the metal-bonded carbon atom shows a ^{13}C–^{31}P coupling.

Carbeneruthenium(II) complexes of the halfsandwich-type: In our previous studies, which opened the gate to ruthenium carbenes of the halfsandwich-type,[12, 20] the acetato derivative $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCH_3)(PPh_3)]$ was used as the starting material. It reacts with diaryldiazomethanes $RR'CN_2$ under partial opening of the chelate ring to give the intermediates $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}O_2CCH_3)(=CRR')(PPh_3)]$, which are converted to the analogous carbene(chloro) complexes $[(\eta^5\text{-}C_5H_5)RuCl(=CRR')(PPh_3)]$ with either $[HNEt_3]Cl$ or Al_2O_3 in the presence of chloride.[12, 20]

An alternative preparative route is shown in Scheme 5. The ethene complexes **10** (generated in situ from **1**) and **12** react rapidly with diaryldiazomethanes in toluene at room temperature to give the ruthenium carbenes **22**–**25** in 60–80% yield. The properties of the trifluoroacetato derivatives **23**–**25** (such as thermal stability, solubility, and air-sensitivity) are quite



	X	R
22	Cl	C_6H_5
23	O_2CCF_3	C_6H_5
24	O_2CCF_3	4-C_6H_4Cl
25	O_2CCF_3	4-C_6H_4OMe

Scheme 5.

similar to those of the chloro compound **22**, which in the meantime has also been prepared by Baratta et al. from $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and excess Ph_2CN_2 as the precursors.[33] In a similar manner, the related carbene complex $[(\eta^5\text{-}C_5H_5)RuCl(=CPh_2)(PPh_2R)]$ (R = 2-tolyl) has been obtained.[34] Regarding the spectroscopic data of **23**–**25**, the most characteristic feature is the signal due to the carbene carbon atom at $\delta = 332$–340 ppm in the ^{13}C NMR spectra, which is shifted to lower field (by ca. 15 ppm) compared with the corresponding signals of **22** and the $Ru\{=C(4\text{-}C_6H_4Cl)_2\}$ analogue.[20]

In contrast to the reaction with diaryldiazomethanes, compound **10** reacts with two equivalents of ethyl diazoacetate to afford the olefin–ruthenium complex **26** in 82% yield. We assume that a metal carbene complex $[(\eta^5\text{-}C_5H_5)RuCl(=CHCO_2Et)(PPh_3)]$ is formed as an intermediate since this species has been detected upon treatment of a solution of $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCH_3)(PPh_3)]$ with $HC(CO_2Et)N_2$ and Me_2SiCl_2 at low temperature.[35] Diagnostic of the chiral-at-metal compound **26** (which has been independently prepared by Baratta et al.)[35] is the observation of two ^1H NMR resonances due to the olefinic CH protons (which remain unchanged between 273 and 343 K) and of two sets of signals due to the ^{13}C carbon nuclei of the $CHCO_2Et$ units. The chemical shifts of these signals are in good agreement with those for other cyclopentadienylruthenium complexes with diethyl maleate as ligand.[36] We note that with compounds of the general formula $[(\eta^5\text{-}C_5R_5)RuX(PR'_3)_2]$ a stereoselective decomposition of ethyl diazoacetate to diethyl maleate has already been observed.[35]

Compound **10** also reacts quite rapidly with $PhC\{C(O)Ph\}N_2$ (azibenzil). The isolated benzoyl(phenyl)carbene complex **27** is a green, air-stable solid which has a counterpart in cyclopentadienylmanganese chemistry.[37] With regard to the spectroscopic data of **27**, the most remarkable feature is that two signals due to the C_5H_5 carbon atoms and two signals due to the phosphorus atom of the PPh_3 ligand are observed in the ^{13}C and ^{31}P NMR spectra at low temperature. On the basis of ^{31}P variable-temperature NMR measurements, the free enthalpy of activation at the coalescence temperature (293 K at 162.0 MHz) is 37.9 kJ mol^{-1}. To explain the temperature dependence of the NMR spectra, we assume that in solution two rotamers of **27** exist, which differ in the orientation of the two substituents C(O)Ph and Ph about the $Ru-C_{carbene}$ axis. A hindered rotation about an Ru=C axis is not unusual and has also been found for the methylene derivative $[(\eta^5\text{-}C_5R_5)Ru(=CH_2)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)]AsF_6$.[38]

The result of the X-ray crystal structure analysis of **27** is shown in Figure 1. Similarly to $[(\eta^5\text{-}C_5H_5)Mn(=C\{C(O)Ph\}Ph)(CO)_2]$,[39] the molecule has the expected three-legged piano-stool configuration with an $Ru{=}C_{carbene}$ bond length (1.932(7) Å) almost identical to that in **22** (1.92(2) Å)[20] and that in the Fischer-type carbene complex $[(\eta^5\text{-}C_5H_5)RuI\{=C(OEt)Ph\}(CO)]$ (1.934 Å).[40] In contrast to **22**, the plane containing the carbon atoms C6, C7, C10, and C20 is almost perpendicular to the plane of the cyclopentadienyl ring, with the benzoyl group pointing toward the five-membered ring. Due to the strong *trans* influence of the

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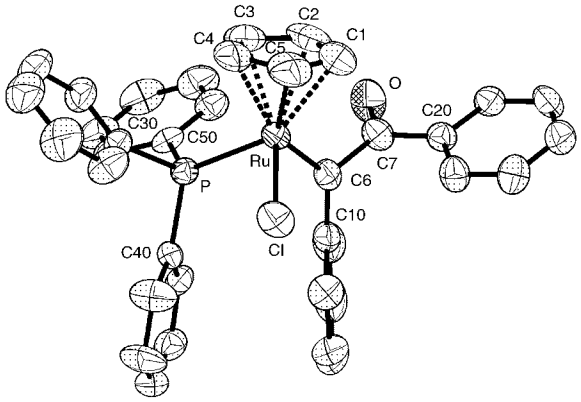
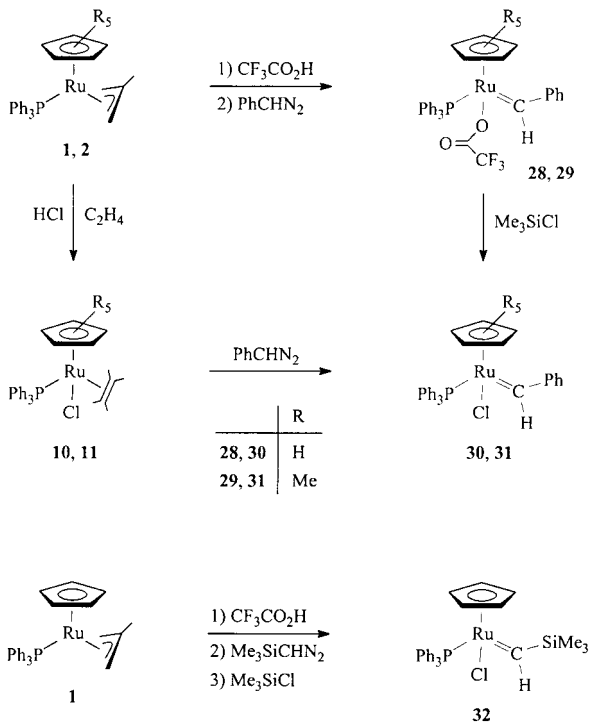


Figure 1. Molecular structure of **27**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Ru–C1 2.288(7), Ru–C2 2.217(7), Ru–C3 2.174(7), Ru–C4 2.290(6), Ru–C5 2.301(6), Ru–C6 1.932(7), Ru–P 2.2997(13), Ru–Cl 2.395(2), C6–C7 1.489(8), C7–O 1.221(6); P-Ru-Cl 91.77(6), P-Ru-C6 93.0(2), Cl-Ru-C6 98.5(2), Ru-C6-C7 115.3(5), C6-C7-O 121.4(5).

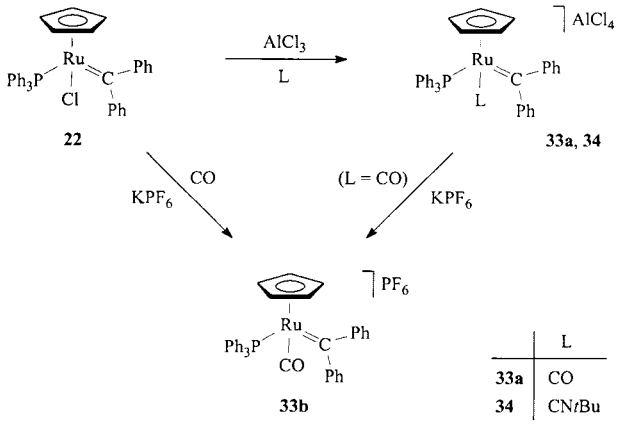
carbene ligand, the C_5H_5 unit is not symmetrically bonded to the metal center, the longest Ru–C4 and Ru–C5 distances being in a *trans* disposition to the carbene carbon atom C6.

While halfsandwich-type rhodium compounds $[(\eta^5\text{-}C_5H_5)Rh(=CR_2)(PR'_3)]$ have hitherto only been prepared with R = aryl,[11] related ruthenium complexes are also accessible with CHPh and $CHSiMe_3$ as carbene ligands. The synthetic routes are summarized in Scheme 6. Stepwise treatment of **1** or **2** first with CF_3CO_2H and then with $PhCHN_2$ gave the phenylcarbeneruthenium(II) compounds **28** and **29** as green solids, each in about 90% yield. These carboxylato derivatives are converted with Me_3SiCl nearly quantitatively to the corresponding carbene(chloro) complexes **30** and **31**, the compositions of which have been determined by elemental analysis and mass spectra. Characteristic spectroscopic features for **28**–**31** are a doublet at $\delta \approx$ 17.25–17.75 ppm due to the carbene CH proton in the ^{1}H NMR spectra, and a low-field resonance at $\delta \approx 303$–314 ppm due to the carbene carbon atom in the ^{13}C NMR spectra. The carbene(chloro) complexes **30** and **31** can also be prepared by substitution of the olefinic ligand in the ethene(chloro) derivatives **10** and **11** with phenyldiazomethane. The trimethylsilylcarbene compound **32** has been obtained in a one-pot reaction from **1**, CF_3CO_2H, Me_3SiCHN_2, and Me_3SiCl, probably via $[(\eta^5\text{-}C_5H_5)Ru(=CHSiMe_3)(\kappa^1\text{-}O_2CCF_3)(PPh_3)]$ as an intermediate. It should be mentioned that quite recently Grubbs et al. reported the preparation of a relative of **28** containing tris(pyrazolyl)borate instead of cyclopentadienyl and diphenylmethylacetate instead of trifluoroacetate as ligands.[41]



Scheme 6.

The conversion of the neutral compound **22** to related cationic complexes of the general formula $[(\eta^5\text{-}C_5H_5)Ru(=CPh_2)(L)(PPh_3)]X$ has also been achieved (Scheme 7). Salts of the corresponding carbene(carbonyl) cation with X = $AlCl_4$ (**33a**) or PF_6 (**33b**) were prepared by treatment of **22** with $AlCl_3$ and KPF_6, respectively, in the presence of CO.



Scheme 7.

Analogously, the isocyanide complex **34** has been obtained. The cationic carbeneruthenium(II) compounds are only moderately air-sensitive and can be stored under argon at room temperature for weeks. Conductivity measurements (in nitromethane) confirm the existence of 1:1 electrolytes. Compared with **22**, the resonances of the carbene carbon atoms in the ^{13}C NMR spectra of **33a** and **34** are shifted by 10–13 ppm to lower field, the trend being similar to that observed for neutral and cationic osmium carbenes with $(\eta^6\text{-}C_6R_6)Os(PPh_3)$ as the molecular unit.[42]

The proposed structure of the carbene(carbonyl) complex **33b** was confirmed by an X-ray diffraction study (Figure 2). Like **27**, the cation of **33b** also has a piano-stool configuration with an $Ru–C_{carbene}$ bond length somewhat longer (by ca. 0.04 Å) than that in the neutral molecules **22** and **27**. Two of the bond angles of the three-legged $RuL^1L^2L^3$ fragment, C1-Ru-C14 (93.3(2)°) and C1-Ru-P (102.0(1)°), are significantly larger than the third one C14-Ru-P (85.5(1)°), which we

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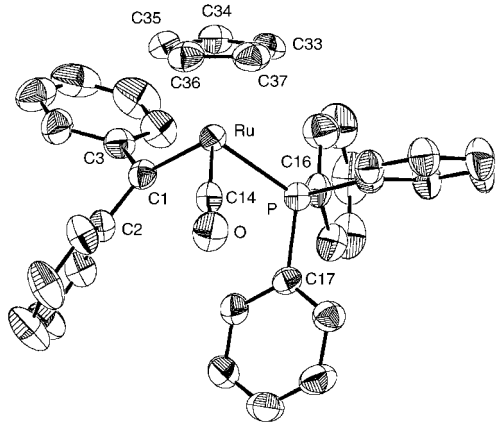
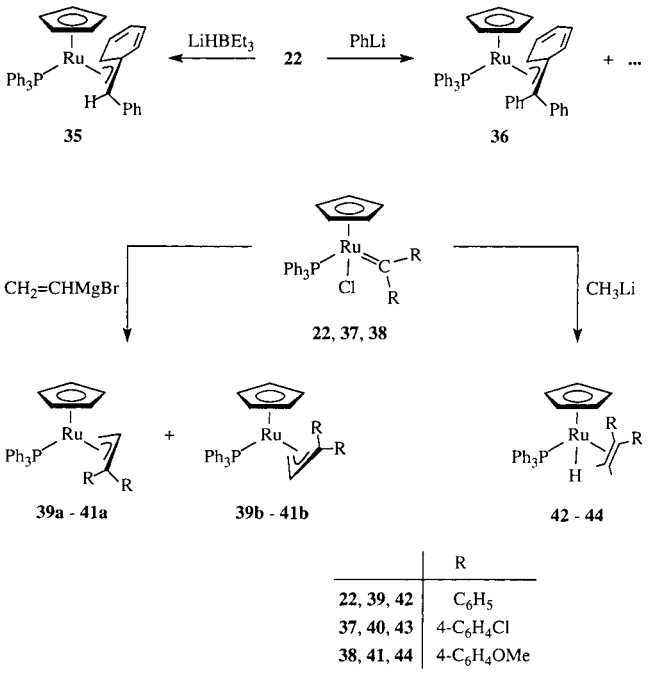


Figure 2. Molecular structure of the cation of **33b**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Ru–C1 1.973(4), Ru–C14 1.860(4), Ru–P 2.363(2), Ru–C33 2.297(5), Ru–C34 2.275(5), Ru–C35 2.234(5), Ru–C36 2.221(5), Ru–C37 2.283(5), C14–O 1.141(5); P-Ru-C1 102.0(1), P-Ru-C14 85.5(1), C1-Ru-C14 93.3(2), Ru-C14-O 174.1(4).

assume is due to the steric demands of the carbene and phosphane ligands. Moreover, a characteristic feature of the structure is that the plane of the carbon atoms C1-C2-C3 is nearly eclipsed in relation to the Ru-C14-O axis, the torsional angle C14-Ru-C1-C2 being only 6.94°. This situation is different to that found in the carbene(chloro) complex, where the plane of the carbene carbon atoms is eclipsed in relation to the Ru–P bond.[20]

C–C Coupling reactions of the halfsandwich-type carbeneruthenium complexes: After investigating the reactivity of vinylidene and allenylidene rhodium complexes of the type *trans*-[RhCl{=C(=C)$_n$RR′}(P*i*Pr$_3$)$_2$] toward organolithium compounds and Grignard reagents,[7, 43] we also became interested in ascertaining the behavior of the ruthenium carbenes [(η^5-C$_5$H$_5$)RuCl(=CRR′)(PPh$_3$)] toward the same type of carbanionic precursors. Treatment of **22** with phenyllithium leads to a mixture of products with the substituted η^3-benzyl complex **36** as the dominating species (Scheme 8). After extraction of the reaction mixture and chromatographic workup, the isolated yellow solid contained about 90% of the coupling product, which was characterized by NMR spectroscopic techniques. Attempts to further purify the product by fractional crystallization or repeated chromatographic separation failed.

An η^3-benzylruthenium(II) derivative, probably having an analogous structure to **36**, was obtained from **22** and LiHBEt$_3$. The yellow, slightly air-sensitive microcrystalline solid with an analytical composition corresponding to **35** was, after chromatographic purification on basic Al$_2$O$_3$, isolated in 63% yield. Particularly diagnostic of the coordination of a substituted η^3-benzyl ligand are the three signals at $\delta = 93.2$, 57.8, and 49.4 ppm in the ^{13}C NMR spectrum of **35**, the chemical shifts of which are similar to those of [(η^5-C$_5$H$_5$)W{η^3-CH(OEt)Ph}(CO)$_2$] and [(η^5-C$_5$H$_5$)Mo{η^3-CH(SnPh$_3$)Ph}(CO)$_2$], respectively.[44] On the basis of a H,C-COSY spectrum, the resonances of the benzylic protons of **35** are assigned to the peaks at $\delta = 2.91$ ppm (H^2) and $\delta = 1.58$ ppm



	R
22, 39, 42	C_6H_5
37, 40, 43	4-C_6H_4Cl
38, 41, 44	4-C_6H_4OMe

Scheme 8.

(H^7). The relatively large ^{1}H–^{31}P coupling constants of both resonances (12.9 and 16.6 Hz) support the assumption that not only H^2 but also H^7 is in an *anti* position with respect to the C^1–C^6 bond. In the ^{13}C NMR spectrum of **36**, the signals due to the benzylic carbon atoms appear at $\delta = 89.2$, 66.6, and 63.8 ppm. The latter is a doublet with nearly the same ^{13}C–^{31}P coupling constant as found for the signal at $\delta = 49.4$ ppm in the spectrum of **35**. By comparing the NMR data of **35** and **36** with those of **39a** and **39b** (see below), we suppose that in both **35** and **36** the η^3-benzyl ligand has an *exo* and not an *endo* configuration with respect to the (η^5-C$_5$H$_5$)Ru(PPh$_3$) fragment. We note that a cationic rhodium complex, isoelectronic to **36** with the η^3-PhCHC$_6$H$_5$ unit in an *exo* position, has been prepared by protonation of [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_3$)] with HBF$_4$.[45] With regard to the mechanism of formation of **35**, we assume that a carbene(hydrido)ruthenium(II) compound [(η^5-C$_5$H$_5$)RuH(=CPh$_2$)(PPh$_3$)] is formed initially, which, after insertion of the carbene unit into the Ru–H bond, generates an Ru–CHPh$_2$ species. Final rearrangement of the diphenylmethyl moiety from η^1 to η^3 would yield the product.

The reactions of **22**, **37**, and **38** with vinyl Grignard reagents lead, in benzene/THF at room temperature, to the displacement of the chloro ligand and formation of the 1,1-diarylallyl complexes **39**–**41** (Scheme 8). These compounds are yellow, moderately air-stable solids, which dissolve readily in benzene or dichloromethane but not in hexane. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **39**–**41** illustrate quite clearly that in each case a mixture of the *exo* (**a**) and *endo* (**b**) isomers is formed, the ratio being approximately 2:1. As a characteristic feature of the *exo* isomers, the ^{1}H NMR spectra display a signal (doublet of doublets of doublets) due to the allyl proton H^3 at the terminal carbon atom at $\delta = 1.37$–1.49 ppm with a much larger ^{1}H-^{31}P coupling constant (16–17 Hz) than that found

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for the *endo* isomers. The characteristic difference in the ^{13}C NMR spectra of **39**–**41** is that the central carbon atom of the allylic group resonates at $\delta = 65-68$ ppm in the case of the *exo* isomers but at $\delta \approx 88$ ppm in the *endo* isomers.

Attempts to separate the isomeric mixture of **39a**/**39b** by low-temperature chromatography and fractional crystallization led to the isolation of single crystals, which, as shown by X-ray crystallography, were composed exclusively of the *exo* isomer **39a**. The results of the structural analysis of **39a** are shown in Figure 3, along with the principal bond lengths and

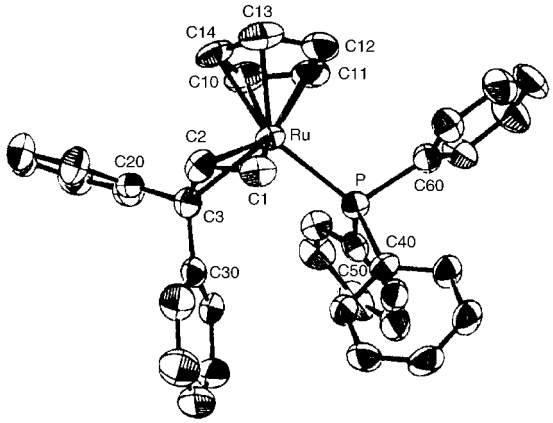


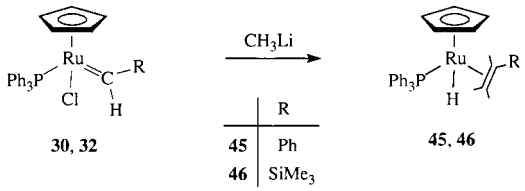
Figure 3. Molecular structure of **39a**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Ru–C1 2.184(7), Ru–C2 2.085(6), Ru–C3 2.243(6), Ru–P 2.329(2), C1–C2 1.399(9), C2–C3 1.420(9); C1-C2-C3 121.7(7), C1-Ru-C2 38.2(3), C2-Ru-C3 38.1(2), Ru-C1-C2 67.1(4), Ru-C3-C2 64.9(3), Ru-C2-C1 74.7(4), Ru-C2-C3 77.0(4).

angles. Although the stereochemistry of **39a** is comparable to that of $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$[46] and $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(CO)]$,[47] compounds which have both been prepared from appropriate $(\eta^5\text{-}C_5H_5)Ru$ precursors and allyl Grignard reagents, an obvious difference is that the bond lengths between the metal and the terminal carbon atoms of the allyl unit in **39a** are unequal. However, the difference (0.06 Å) is much less than that in the related rhenium compound $[(\eta^5\text{-}C_5Me_5)Re\{endo\text{-}\eta^3\text{-}Ph_2CC(Ph)CHCH_3\}(CO)_2]PF_6$ (0.47 Å).[48] As far as we are aware, the only other transition-metal complexes containing Ph_2CCHCH_2 as a η^3-allylic ligand are the osmium derivative $[(\eta^6\text{-mes})OsBr(\eta^3\text{-}Ph_2CCHCH_2)]$[42] and the platinum(II) and palladium(II) compounds $[Pt(\eta^3\text{-}Ph_2CCHCH_2)Cl]_n$[49] and $[Pd(\eta^3\text{-}Ph_2CCHCH_2)(S,S\text{-Chiraphos})]ClO_4$,[50] the structures of which, however, are unknown.

From a mechanistic point of view, the formation of **39**–**41** can best be understood if we assume that a carbene-(η^1-vinyl)metal derivative is generated initially, which, by intramolecular C–C coupling, rearranges to give the products. An alternative pathway, involving addition of the nucleophile to the carbene carbon atom followed by elimination of chloride with a concomitant η^1-to-η^3 rearrangement, could equally be taken into consideration. In this context, we note that Hill et al. recently showed that a carbene and a vinyl unit can also be coupled to give an allyl ligand on the reverse route by treating the vinyl complex $[RuCl(CH{=}CH_2)(CO)(PPh_3)_2]$ with diazomethane as a carbene source.[51] Moreover, in modeling studies in the context of the Fischer–Tropsch synthesis, Maitlis and co-workers illustrated that in the dinuclear rhodium complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)(CH{=}CHR)\}_2]$, the methylene and vinyl ligands couple in acetonitrile in the presence of a one-electron oxidant such as Ag^+ to give the allylic cations $[(\eta^5\text{-}C_5Me_5)Rh(\eta^3\text{-}CH_2CHCHR)(MeCN)]^+$ in good yields.[52] A similar C–C coupling occurs in mononuclear $(\eta^5\text{-}C_5Me_5)Ir$ compounds.[53]

To find out whether the chloro ligand in **22**, **37**, and **38** can be displaced by an alkyl group, as well as by a phenyl or vinyl group, the reactions of the diarylcarbene complexes with methyllithium have been investigated. Treatment of solutions of the respective starting materials with a solution of MeLi in diethyl ether at room temperature, followed by addition of acetone, gave yellow-brown reaction mixtures, from which yellow solids analyzing as $[(\eta^5\text{-}C_5H_5)RuH(CH_2{=}CR_2)(PPh_3)]$ (**42**–**44**) were isolated in 56–72% yields after chromatographic workup. The ^1H NMR spectra of the products display a high-field resonance at $\delta \approx -9.75$ to -9.90 ppm due to the hydridic protons, as well as two well-separated signals at $\delta \approx 3.57-3.90$ and 1.55–1.80 ppm due to the olefinic protons. The $^1H-^{31}P$ coupling constants for the doublets assigned to the Ru–H protons are 35–36 Hz. These data, together with those from the ^{13}C and ^{31}P NMR spectra, leave no doubt that the proposed structure of **42**–**44** shown in Scheme 8 is correct. With regard to the course of formation, it seems conceivable that the initial product of the reaction of **22**, **37**, and **38** with methyllithium is the corresponding carbene(methyl) compound $[(\eta^5\text{-}C_5H_5)RuCH_3(=CR_2)(PPh_3)]$, which, by migratory insertion, yields the 16-electron alkylruthenium intermediate $[(\eta^5\text{-}C_5H_5)Ru(CR_2CH_3)(PPh_3)]$ and then, by β-H shift, yields the hydrido(olefin) complex.

Compounds **30** and **32**, containing a secondary carbene as a ligand, behave analogously to **22**, **37**, and **38** toward MeLi. In toluene/diethyl ether, the reactions proceed as shown in Scheme 9 to give the hydrido(olefin) derivatives **45** and **46** in



Scheme 9.

about 60–70% yield. The spectroscopic data of **45** and **46**, which were isolated as light-yellow or orange, moderately air-sensitive solids, are similar to those of **42**–**44** and thus do not require further comment.

Cleavage of the η^3-benzyl- and η^3-allyl-ruthenium bonds in **35** and **39**–**41** by acetic acid in benzene proceeds slowly at room temperature and affords diphenylmethane and the olefins $R_2C{=}CHCH_3$, respectively, in virtually quantitative yields (Scheme 10). The organometallic product is the acetatoruthenium(II) derivative **47**. The hydrocarbons were identified by comparison of their ^1H NMR data with those of authentic samples.

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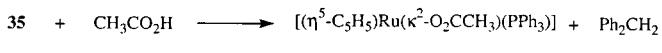
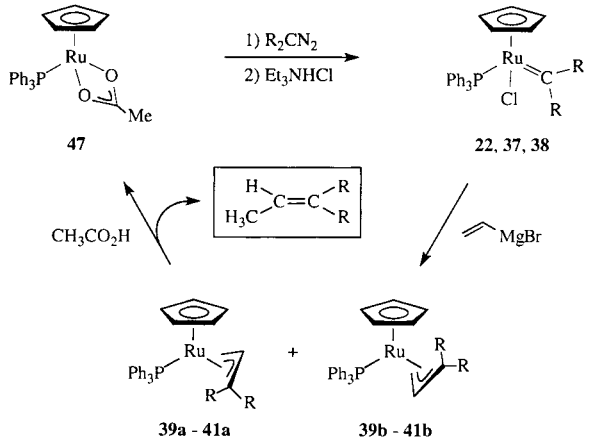


Scheme 10. $R = C_6H_5$, 4-C_6H_4Cl, 4-C_6H_4OMe.

Conclusion

It is now clearly evident that in recent years the "diazoalkane route" has become a powerful method for generating transition-metal carbenes. With regard to ruthenium as the metal center, the formation of Roper's methylidene $[RuCl(=CH_2)(NO)(PPh_3)_2]$,[6b] the Grubbs-type carbene complexes,[4] and the halfsandwich-type compounds reported in this work can be rationalized either in terms of an electrophilic attack of the electron-deficient fragment $[Ru(L)_n]$ $[(L)_n = (NO)Cl(PPh_3)_2$, $Cl_2(PPh_3)_2$ or $(\eta^5\text{-}C_5H_5)Cl(PPh_3)]$ at the diazo carbon atom followed by loss of N_2 or by κ^1-*N*- or κ^2-*N,N*-coordination of the $RR'CN_2$ molecule at the ruthenium center with subsequent metal migration. Since no intermediates could be detected in the reactions of $[(\eta^5\text{-}C_5R_5)RuX(C_2H_4)(PPh_3)]$ (**10**–**12**) with the diazo compounds used here, the exact pathway by which the carbene complexes are generated is open to speculation. We note, however, that in the reaction of *trans*-$[RhCl(C_2H_4)(Sb\textit{i}Pr_3)_2]$ with Ph_2CN_2 leading to *trans*-$[RhCl(=CPh_2)(Sb\textit{i}Pr_3)_2]$, the formation of an intermediate in which the diazoalkane is thought to be κ^2-*N,N*- or κ^2-*N,C*-coordinated has been observed.[21]

The fact that, in contrast to our work on rhodium carbenes,[8] not only diaryldiazomethanes but also $PhCHN_2$ and Me_3SiCHN_2 can be used as carbene sources, places the halfsandwich-type complexes $[(\eta^5\text{-}C_5R_5)RuCl(=CRR')(PPh_3)]$ alongside the Grubbs-type carbenes. The crucial difference between the two classes of compounds, however, is that the cyclopentadienyl derivatives are rather poor catalysts for olefin metathesis compared with their $[RuCl_2(=CRR')(PCy_3)_2]$ counterparts. Despite this disadvantage, the halfsandwich-type complexes are potentially useful for making C–C bonds, with the carbene ligand as one building block and organolithium or Grignard compounds as coupling reagents. Moreover, since the coupling products, in particular the η^3-allylruthenium derivatives **39**–**41**, react with acetic acid by formation of the acetato complex **47** and the olefins $R_2C{=}CHCH_3$, a cyclic process can be created (Scheme 11) whereby the trisubstituted ethene derivatives can be built up from a carbene ligand, a vinyl unit, and a proton in the coordination sphere of ruthenium(II).



Scheme 11.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**, **2**[46] and **37**, **38**[20] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 instruments (abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened signal). IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer, and mass spectra on a Finnigan 90 MAT instrument. Melting points were measured by DTA. Conductivity measurements were carried out in nitromethane with a Schott Konduktometer CG 851.

$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)]_n$ (3): A solution of **1** (215 mg, 0.45 mmol) in toluene (10 mL) was treated at $-30\,^\circ C$ with a 0.30 M solution of HCl in benzene (2.22 mL, 0.67 mmol). A rapid change of color first from yellow to dark violet and then to orange occurred. Upon stirring the solution for about 30 s, an orange solid precipitated, which, after the reaction mixture was warmed to room temperature, was collected by filtration, washed with toluene (2×5 mL) and dried; yield 171 mg (82%); m.p. $135\,^\circ C$ (decomp). The compound is insoluble in all common organic solvents; elemental analysis calcd (%) for $[C_{23}H_{20}ClPRu]_n$ (463.9 for $n = 1$): C 59.55, H 4.35; found: 59.44, H 4.68.

$[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)]_n$ (4): A solution of **2** (366 mg, 0.66 mmol) in toluene (5 mL) was treated at $-78\,^\circ C$ with a 0.05 M solution of HCl in toluene (19.8 mL, 0.99 mmol). A rapid change of color first from yellow to violet and then to orange-yellow occurred. Upon warming to room temperature, an orange solid precipitated, which was collected by filtration, washed with pentane (3×5 mL) and dried; yield 294 mg (83%); m.p. $105\,^\circ C$ (decomp). The compound is insoluble in all common organic solvents; elemental analysis calcd (%) for $[C_{28}H_{30}ClPRu]_n$ (534.0 for $n = 1$): C 62.97, H 5.66; found: C 62.67, H 5.60.

$[(\eta^5\text{-}C_5H_5)RuCl(CO)(PPh_3)]$ (5): A slow stream of CO was passed through a suspension of **3** (15 mg, 0.02 mmol) in CD_2Cl_2 (1 mL) for 5 min at room temperature. A pale yellow solution was formed, which, according to its ^1H and ^{31}P NMR spectra, contained compound **5** as the only detectable species. – An alternative procedure is as follows: A slow stream of CO was passed through a solution of **1** (100 mg, 0.21 mmol) in benzene (5 mL) at room temperature. After 1 min, the solution was treated with a 0.15 M solution of HCl in benzene (2.07 mL, 0.31 mmol) and the mixture was stirred for 2–3 min. The solvent was removed, and the yellow residue was washed with pentane (2×2 mL) and dried; yield 86 mg (89%). Compound **5** was identified by comparison of its NMR and IR spectra with those of an authentic sample.[15]

$[(\eta^5\text{-}C_5Me_5)RuCl(CO)(PPh_3)]$ (6): A slow stream of CO was passed through a suspension of **4** (30 mg, 0.03 mmol) in CD_2Cl_2 (1 mL) for 5 min at room temperature. A pale yellow solution was formed, which, according to its ^1H and ^{31}P NMR spectra, contained compound **6** as the only detectable species. – An alternative procedure is as follows: A slow stream of CO was passed through a solution of **2** (110 mg, 0.20 mmol) in benzene (5 mL) at room temperature. After 1 min, the solution was treated with a 0.05 M solution of HCl in benzene (3.50 mL, 0.18 mmol) and then worked-up as described for **5**. Yellow solid; yield 103 mg (92%). Compound **6** was identified by comparison of its NMR and IR spectra with those of an authentic sample.[16]

$[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}O_2CCF_3)(CO)(PPh_3)]$ (7): A slow stream of CO was passed through a solution of **12** (50 mg, 0.09 mmol) in benzene (1 mL) for 30 s at room temperature. The solvent was removed, and the residue was washed with pentane (2×3 mL) and dried; yield 43 mg (85%). Compound

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7 was identified by comparison of its IR and NMR spectra with those of an authentic sample.[20]

[(η⁵-C_5H_5)Ru(κ¹-$OSO_2C_6H_4$–4-Me)(CO)(PPh_3)] (8): Compound **8** was prepared in the same way as described for **7**, starting from **13** (45 mg, 0.09 mmol) and CO. Yellow microcrystalline solid; yield 54 mg (95%). The compound was identified by comparison of its IR and NMR spectra with those of an authentic sample.[20]

[(η⁵-C_5H_5)Ru(κ¹-OSO_2CF_3)(CO)(PPh_3)] (9): Compound **9** was prepared in the same way as described for **7**, starting from **14** (70 mg, 0.12 mmol) and CO in CH_2Cl_2 (5 mL). Yellow microcrystalline solid; yield 65 mg (90%); m.p. 51 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 1975 cm^{-1} (CO); ^1H NMR (C_6D_6, 400 MHz): δ = 7.44, 7.30, 6.92 (all m, 15H; C_6H_5), 4.36 ppm (s, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 202.9 (d, J(P,C) = 20.1 Hz; CO), 133.8 (d, J(P,C) = 42.3 Hz; *ipso*-C of PC_6H_5), 133.6 (d, J(P,C) = 11.1 Hz; C2,6 of PC_6H_5), 130.9 (d, J(P,C) = 3.0 Hz; C4 of PC_6H_5), 128.8 (d, J(P,C) = 11.1 Hz; C3,5 of PC_6H_5), 119.4 (q, J(F,C) = 319.0 Hz; CF_3), 84.2 ppm (d, J(P,C) = 1.9 Hz; C_5H_5); ^{19}F NMR (C_6D_6, 162.0 MHz): δ = 47.3 ppm (s); elemental analysis calcd (%) for $C_{25}H_{20}F_3O_4PRuS$ (605.5): C 49.59, H 3.33, S 5.30; found: C 50.00, H 3.58, S 4.96.

[(η⁵-C_5H_5)RuCl(C_2H_4)(PPh_3)] (10): A slow stream of ethene was passed through a solution of **1** (160 mg, 0.33 mmol) in benzene (10 mL) at room temperature. After 1 min, the solution was treated with a 0.20 M solution of HCl in benzene (2.50 mL, 0.50 mmol) and stirred for 2 min. The yellow solution was concentrated to about 5 mL in vacuo and then investigated by NMR spectroscopy. If the solvent was completely removed, an orange insoluble residue was obtained, the composition of which corresponded to **3**. Data for **7**: ^1H NMR (C_6D_6, 400 MHz): δ = 7.60, 7.00, 6.90 (all m, 15H; C_6H_5), 4.17 (s, 5H; C_5H_5), 3.53, 3.03 ppm (both m, 2H each; C_2H_4); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 136.5 (d, J(P,C) = 42.3 Hz; *ipso*-C of PC_6H_5), 134.1 (d, J(P,C) = 9.1 Hz; C2,6 of PC_6H_5), 128.5 (d, J(P,C) = 2.0 Hz; PC_6H_5), 83.9 (d, J(P,C) = 2.0 Hz; C_5H_5), 46.2 ppm (s, C_2H_4); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 52.6 ppm (s).

Reaction of [(η⁵-C_5H_5)RuCl(C_2H_4)(PPh_3)] (10) with CO: A slow stream of CO was passed for ca. 30 s through a solution of **10**, which had been generated from **1** (66 mg, 0.14 mmol), a 0.32 M solution (1.07 mL, 0.34 mmol) of HCl in benzene, and toluene (3 mL) saturated with ethene. After the reaction mixture had been stirred for 3 min at room temperature, the solvent was removed in vacuo. The remaining yellow solid was identified by IR and NMR spectroscopy as compound **5**;[15] yield 48 mg (92%).

[(η⁵-C_5Me_5)RuCl(C_2H_4)(PPh_3)] (11): A slow stream of ethene was passed through a solution of **2** (138 mg, 0.25 mmol) in toluene (5 mL) at 0 °C. After 2 min, the solution was treated with a 0.05 M solution of HCl in benzene (4.5 mL, 0.23 mmol) and stirred for a further 2 min. The solvent was removed, and the yellow microcrystalline residue was washed with pentane (2 × 2 mL) and dried; yield 133 mg (95%); m.p. 84 °C (decomp); ^1H NMR (C_6D_6, 400 MHz): δ = 7.74, 7.23, 7.03, 6.93 (all m, 15H; C_6H_5), 2.86 (m; in $^1H\{^{31}P\}$ d, J(H,H) = 7.6 Hz, 2H; C_2H_4), 2.56 (br m, 2H; C_2H_4), 1.21 ppm (d, J(P,H) = 1.4 Hz, 15H; C_5Me_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 136.9, 136.2 (both d, J(P,C) = 9.0 Hz; PC_6H_5), 136.5 (d, J(P,C) = 11.2 Hz; PC_6H_5), 133.9, 133.0 (both d, J(P,C) = 9.0 Hz; PC_6H_5), 132.9 (d, J(P,C) = 41.9 Hz; *ipso*-C of PC_6H_5), 132.4 (d, J(P,C) = 9.6 Hz; PC_6H_5), 131.5 (d, J(P,C) = 5.3 Hz; PC_6H_5), 129.8 (s; PC_6H_5), 129.4 (d, J(P,C) = 7.2 Hz; PC_6H_5), 129.3 (s; PC_6H_5), 128.5 (d, J(P,C) = 12.3 Hz; PC_6H_5), 128.2 (d, J(P,C) = 6.5 Hz; PC_6H_5), 127.9 (br s; PC_6H_5), 127.7 (d, J(P,C) = 8.8 Hz; PC_6H_5), 93.4 (d, J(P,C) = 2.1 Hz; $C_5(CH_3)_5$), 47.4 (s; C_2H_4), 8.3 ppm (s; $C_5(CH_3)_5$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 53.3 ppm (s); elemental analysis calcd (%) for $C_{30}H_{34}ClPRu$ (562.1): C 64.11, H 6.10; found: C 64.17, H 5.79.

[(η⁵-C_5H_5)Ru(κ¹-O_2CCF_3)(C_2H_4)(PPh_3)] (12): A slow stream of ethene was passed through a solution of **1** (174 mg, 0.36 mmol) in toluene (10 mL) at −30 °C. After 2 min, the solution was treated with CF_3CO_2H (28 μL, 0.36 mmol) and, under continuous stirring, was slowly warmed to room temperature. The solvent was removed in vacuo, and the yellow microcrystalline residue was washed with pentane (2 × 5 mL) and dried; yield 191 mg (93%); m.p. 56 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 1690 cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): δ = 7.74, 7.44, 7.03 (all m, 15H; C_6H_5), 4.31 (s, 5H; C_5H_5), 3.71 (dd, J(P,H) = 4.6, J(H,H) = 9.3 Hz, 2H; C_2H_4), 2.76 ppm (m; in $^1H\{^{31}P\}$d, J(H,H) = 9.3 Hz, 2H; C_2H_4); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 163.2 (q, J(F,C) = 35.5 Hz; O_2CCF_3), 135.1 (d, J(P,C) = 43.4 Hz; *ipso*-C of PC_6H_5), 133.9 (d, J(P,C) = 10.1 Hz; C2,6 of PC_6H_5), 130.1 (d, J(P,C) = 1.8 Hz; C4 of PC_6H_5), 126.4 (d, J(P,C) = 9.8 Hz; C3,5 of PC_6H_5), 115.4 (q, J(F,C) = 292.4 Hz; CF_3), 81.2 (s; C_5H_5), 51.5 ppm (s; C_2H_4); ^{19}F NMR (C_6D_6, 376.4 MHz): δ = −74.8 ppm (s); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 52.8 ppm (s); elemental analysis calcd (%) for $C_{27}H_{24}F_3O_2PRu$ (569.5): C 56.94, H 4.25; found: C 57.13, H 4.52.

[(η⁵-C_5H_5)Ru(κ¹-$OSO_2C_6H_4$–4-Me)(C_2H_4)(PPh_3)] (13): A slow stream of ethene was passed through a solution of **1** (84 mg, 0.17 mmol) in toluene (5 mL) at 0 °C. After 2 min, the solution was treated with a 0.68 M solution of *p*-toluenesulfonic acid in THF (0.29 mL, 0.17 mmol) and worked-up as described in the case of **9**. Yellow microcrystalline solid; yield 91 mg (85%); m.p. 64 °C (decomp); ^1H NMR (C_6D_6, 200 MHz): δ = 8.10, 7.50, 7.02, 6.72 (all m, 19H; C_6H_5 and C_6H_4), 4.47 (s, 5H; C_5H_5), 3.81, 3.20 (both br m, 2H each; C_2H_4), 1.89 ppm (s; $C_6H_4CH_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 140.0 (s; *ipso*-C of C_6H_4), 135.2 (d, J(P,C) = 43.3 Hz; *ipso*-C of PC_6H_5), 134.2 (d, J(P,C) = 10.1 Hz; C2,6 of PC_6H_5), 130.1 (d, J(P,C) = 1.0 Hz; C4 of PC_6H_5), 129.3, 127.3 (both s; C_6H_4), 128.7 (d, J(P,C) = 10.1 Hz; C3,5 of PC_6H_5), 126.8 (s; ring-CCH_3), 79.7 (s; C_5H_5), 53.5 (s; C_2H_4), 21.4 ppm (s; $C_6H_4CH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 51.9 ppm (s); elemental analysis calcd (%) for $C_{32}H_{31}O_3PRuS$ (627.7): C 61.23, H 4.98, S 5.11; found: C 60.90, H 4.70, S 5.92.

[(η⁵-C_5H_5)Ru(κ¹-OSO_2CF_3)(C_2H_4)(PPh_3)] (14): A slow stream of ethene was passed through a solution of **1** (104 mg, 0.21 mmol) in toluene (5 mL) at −40 °C. After 2 min, the solution was treated with a solution of CF_3SO_3H (18 μL, 0.21 mmol) in toluene (1 mL) and worked-up as described for **9**. Yellow microcrystalline solid; yield 112 mg (88%); m.p. 45 °C (decomp); ^1H NMR (C_6D_6, 400 MHz): δ = 7.54, 7.42, 7.07 (all m, 15H; C_6H_5), 4.22 (s, 5H; C_5H_5), 3.81, 2.93 ppm (both br m, 2H each; C_2H_4); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 134.6 (d, J(P,C) = 43.9 Hz; *ipso*-C of PC_6H_5), 133.9 (d, J(P,C) = 10.2 Hz; C2,6 of PC_6H_5), 130.4 (d, J(P,C) = 1.6 Hz; C4 of PC_6H_5), 128.6 (d, J(P,C) = 9.9 Hz; C3,5 of PC_6H_5), 80.6 (s; C_5H_5), 54.0 ppm (s; C_2H_4), quartet for CF_3 carbon atom not exactly located; ^{19}F NMR (C_6D_6, 376.4 MHz): δ = −78.2 ppm (s); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 50.0 ppm (s); elemental analysis calcd (%) for $C_{26}H_{24}F_3O_3PRuS$ (605.6): C 51.57, H 3.99, S 5.30; found: C 51.52, H 4.42, S 5.22.

[(η⁵-C_5H_5)RuCl(NC_5H_5)(PPh_3)] (15): Pyridine (2 mL) was added to a solution of **10** generated from **1** (125 mg, 0.26 mmol), a 0.32 M solution of HCl in benzene (1.82 mL, 0.62 mmol), and toluene (3 mL) saturated with ethene. After the reaction mixture had been stirred for 1 h at room temperature, it was worked-up as described for **7**. Orange microcrystalline solid; yield 110 mg (78%); m.p. 78 °C (decomp); ^1H NMR (C_6D_6, 400 MHz): δ = 9.20 (d, J(H,H) = 5.2 Hz, 2H; *ortho*-H of NC_5H_5), 8.53, 7.75, 7.64, 7.00, 6.92 (all m, 18H; C_6H_5 and NC_5H_5), 4.18 ppm (s, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 157.0 (s; *ortho*-C of NC_5H_5), 137.1 (d, J(P,C) = 37.0 Hz; *ipso*-C of PC_6H_5), 134.4 (d, J(P,C) = 10.3 Hz; C2,6 of PC_6H_5), 134.3, 123.0 (both s; NC_5H_5), 131.5 (d, J(P,C) = 2.6 Hz; C4 of PC_6H_5), 127.9 (d, J(P,C) = 9.0 Hz; C3,5 of PC_6H_5), 74.6 ppm (s, C_5H_5); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 50.2 ppm (s); elemental analysis calcd (%) for $C_{28}H_{25}ClNPRu$ (543.0): C 61.93, H 4.64, N 2.58; found: C 61.61, H 5.10, N 2.41.

[(η⁵-C_5H_5)RuCl($MeO_2CC{\equiv}CCO_2Me$)(PPh_3)] (16): An excess of dimethylacetylene dicarboxylate (305 μL, 2.48 mmol) was added to a solution that had been generated from **1** (150 mg, 0.31 mmol), a 0.12 M solution of HCl in benzene (5.20 mL, 0.62 mmol), and toluene (3 mL) saturated with ethene. After the reaction mixture had been stirred for 5 min at room temperature, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (2 mL), and this solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With toluene, an orange fraction was eluted, which was concentrated to dryness in vacuo. The orange solid was washed with diethyl ether (2 × 5 mL) and dried; yield 135 mg (72%); m.p. 102 °C (decomp); IR (CH_2Cl_2): $\tilde{\nu}$ = 1730 (C≡C), 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86, 7.55, 7.18 (all m, 15H; C_6H_5), 5.27 (s, 5H; C_5H_5), 4.03, 3.43 ppm (both br m, 3H each; OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 163.2, 162.7 (both s; CO_2), 133.4 (d, J(P,C) = 48.6 Hz; *ipso*-C of PC_6H_5), 132.0 (d, J(P,C) = 10.0 Hz; C2,6 of PC_6H_5), 130.1 (d, J(P,C) = 2.0 Hz; C4 of PC_6H_5), 127.9 (d, J(P,C) = 10.0 Hz; C3,5 of PC_6H_5), 88.0 (s; C_5H_5), 84.8, 80.8 (both s; C≡C), 52.8, 52.5 ppm (both s; OCH_3); ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = 45.8 ppm (s); elemental analysis calcd (%) for $C_{29}H_{26}ClO_4PRu$ (606.0): C 57.48, H 4.32; found: C 57.27, H 4.82.

[(η⁵-C_5Me_5)RuCl(=C=$CHCO_2Me$)(PPh_3)] (17): A solution of **2** (221 mg, 0.40 mmol) and $HC{\equiv}CCO_2Me$ (143 μL, 1.60 mmol) in toluene (2 mL) was

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treated dropwise at 0 °C with a 0.05 M solution of HCl in benzene (8.0 mL, 0.40 mmol). The solution was warmed to room temperature, stirred for 15 min, and then concentrated to dryness in vacuo. The residue was redissolved in toluene (1 mL), and this solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With toluene/CH_2Cl_2 (1:3), a yellow fraction was eluted, from which the solvent was removed in vacuo. The residue was recrystallized from acetone (1 mL) at −78 °C to give a yellow solid, which was washed with pentane (2 × 2 mL) and dried; yield 26 mg (11 %); m.p. 116 °C (decomp); IR (THF): $\tilde{\nu}$ = 1685 (C=O), 1585 cm^{-1} (C=C); ^1H NMR (C_6D_6, 400 MHz): δ = 7.89, 7.03 (both m, 15H; C_6H_5), 4.80 (s, 1H; =CH), 3.33 (s, 3H; OCH_3), 1.46 ppm (d, J(P,H) = 1.6 Hz, 15H; C_5Me_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 332.5 (d, J(P,C) = 22.8 Hz; Ru=C), 167.3 (s; CO_2), 134.7 (m; PC_6H_5), 132.4 (d, J(P,C) = 9.4 Hz; PC_6H_5), 130.1 (s; PC_6H_5), 104.6 (s; =CH), 103.5 (d, J(P,C) = 2.4 Hz; $C_5(CH_3)_5$), 63.9 (s; OCH_3), 9.5 ppm (d; $C_5(CH_3)_5$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 48.8 ppm (s); elemental analysis calcd (%) for $C_{32}H_{34}ClO_2PRu$ (618.1): C 62.18, H 5.54; found: C 62.39, H 5.87.

[(η⁵-C_5Me_5)RuCl(=C=CHCO$_2$Et)(PPh$_3$)] (18): This compound was prepared as described for **17**, starting from a solution of **2** (225 mg, 0.41 mmol) and HC≡CCO_2Et (167 μL, 1.64 mmol) in toluene (2 mL) and a 0.05 M solution of HCl in benzene (7.4 μL, 0.37 mmol). Orange microcrystalline solid; yield 52 mg (20 %); m.p. 122 °C (decomp); IR (THF): $\tilde{\nu}$ = 1685 (C=O), 1590 cm^{-1} (C=C); ^1H NMR (C_6D_6, 400 MHz): δ = 7.81, 7.77, 7.08, 6.91 (all m, 15H; C_6H_5), 4.61 (s, 1H; =CH), 3.97 (q, J(H,H) = 4.8 Hz, 2H; CH_2CH_3), 1.49 (d, J(P,H) = 1.4 Hz, 15H; C_5Me_5), 0.95 ppm (t, J(H,H) = 4.8 Hz, 3H; CH_2CH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 332.8 (d, J(P,C) = 23.2 Hz; Ru=C), 167.2 (s; CO_2), 134.8, 130.3, 128.4 (all br s, C_6H_5), 105.1 (s; =CH), 103.1 (s; $C_5(CH_3)_5$), 59.2 (s; CH_2CH_3), 14.6 (s; CH_2CH_3), 9.7 ppm (s; $C_5(CH_3)_5$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 49.1 ppm (s); elemental analysis calcd (%) for $C_{33}H_{36}ClO_2PRu$ (632.1): C 62.70, H 5.74; found: C 62.89, H 5.73.

An alternative procedure is as follows: A solution of **20** (110 mg, 0.16 mmol) in benzene (1 mL) in an NMR tube was irradiated with light from a UV lamp for 20 h. Since the ^1H and ^{31}P NMR spectra indicated the formation of a mixture of products, the residue was dissolved in toluene (1 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With toluene/CH_2Cl_2 (1:3), a yellow fraction was eluted, which was concentrated to dryness in vacuo. The residue was dissolved in acetone (1 mL) and this solution was stored at −78 °C for 20 h. An orange solid precipitated, which was identified spectroscopically; yield 11 mg (11 %).

[(η⁵-C_5Me_5)RuCl(η²-CH_2=C=CH_2)(PPh$_3$)] (19): Propyne (1 mL) was condensed into a solution of **2** (160 mg, 0.29 mmol) in toluene (4 mL) at −78 °C. The reaction mixture was then treated with a 0.05 M solution of HCl in toluene (5.8 mL, 0.29 mmol) and warmed to room temperature. After the solution had been stirred for 15 min, the solvent was removed, and the yellow residue was washed with pentane (3 × 2 mL) and dried; yield 125 mg (75 %); m.p. 69 °C (decomp); IR (THF): $\tilde{\nu}$ = 1775 cm^{-1} (C=C=C); ^1H NMR (C_6D_6, 400 MHz): δ = 7.86, 7.65, 7.40, 7.28, 7.02 (all m; C_6H_5), 6.15, 5.96, 2.00, 1.61 (all br s, 1H each; CH_2 of major isomer), 5.91, 4.22, 2.60, 2.29 (all br s, 1H each; CH_2 of minor isomer), 1.38, 1.36 ppm (both s; C_5Me_5); ratio of major to minor isomer = 3:2, assignment according to H,H-COSY spectrum; ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 179.1 (s; C=CH_2), 172.2 (d, J(P,C) = 11.0 Hz; C=CH_2), 136.9–127.5 (m; C_6H_5), 101.8 (d, J(P,C) = 6.5 Hz; CH_2), 97.8 (s; CH_2), 96.9, 96.7 (both d, J(P,C) = 1.8 Hz; $C_5(CH_3)_5$), 22.3 (s; CH_2), 15.0 (d, J(P,C) = 5.2 Hz; CH_2), 8.4, 8.1 ppm (both s; $C_5(CH_3)_5$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 51.0, 48.0 ppm (both s); elemental analysis calcd (%) for $C_{31}H_{34}ClPRu$ (574.1): C 64.86, H 5.97; found: C 64.75, H 5.58.

An alternative procedure is as follows: A slow stream of propyne was passed through a solution of **11** (150 mg, 0.27 mmol) in benzene (4 mL) for 2 min at room temperature. After the solution had been stirred for 10 min, it was worked-up as described above; yield 107 mg (70 %).

[(η⁵-C_5Me_5)RuCl(Me_3SiC≡CCO_2Et)(PPh$_3$)] (20): A solution of **11** (150 mg, 0.27 mmol) in benzene (2 mL) was treated with Me_3SiC≡CCO_2Et (56 μL, 0.29 mmol) and the mixture was stirred for 15 min at room temperature. The solvent was removed in vacuo, and the yellow solid was washed with pentane (2 × 5 mL) and dried; yield 167 mg (88 %); m.p. 96 °C (decomp); IR (THF): $\tilde{\nu}$ = 1830 cm^{-1} (C≡C); ^1H NMR (C_6D_6, 200 MHz): δ = 7.75, 7.09 (both m, 15H; C_6H_5), 3.93 (m, 2H; CH_2CH_3), 1.42 (s, 15H; C_5Me_5), 0.98 (t, J(H,H) = 7.3 Hz, 3H; CH_2CH_3), 0.29 ppm (s, 9H; $SiMe_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 46.0 ppm (s); elemental analysis calcd (%) for $C_{36}H_{44}ClO_2PRuSi$ (604.3): C 61.39, H 6.30; found: C 61.44, H 6.44.

[(η⁵-C_5H_5)RuCl(=C=C=CPh_2)(PPh$_3$)] (21): A solution of **1** (269 mg, 0.56 mmol) and HC≡$CC(OH)Ph_2$ (556 mg, 2.78 mmol) in toluene (10 mL) was treated at −78 °C with a 0.32 M solution of HCl in benzene (0.76 mL, 0.24 mmol). The mixture was warmed to room temperature, stirred for 30 min, and then concentrated to dryness in vacuo. The residue was redissolved in CH_2Cl_2 (2 mL) and chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With CH_2Cl_2, a red fraction was eluted, from which the solvent was removed in vacuo. An orange-red solid was obtained, which was washed with diethyl ether (3 × 5 mL) and dried; yield 40 mg (11 %); m.p. 135 °C (decomp); IR (THF): $\tilde{\nu}$ = 1880 cm^{-1} (C=C=C); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.72, 7.56, 7.47, 7.19 (all m, 25H; C_6H_5), 5.40 ppm (s, 5H; C_5H_5); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 273.5 (d, J(P,C) = 25.4 Hz; Ru=C), 223.7 (s; Ru=C=C), 145.5 (s; *ipso*-C of CC_6H_5), 140.9 (s; Ru=C=C=C), 135.6 (d, J(P,C) = 48.3 Hz; *ipso*-C of PC_6H_5), 135.1 (d, J(P,C) = 10.1 Hz; C2,6 of PC_6H_5), 131.1 (d, J(P,C) = 2.0 Hz; C4 of PC_6H_5), 130.0, 129.8, 129.5 (all s; CC_6H_5), 129.2 (d, J(P,C) = 9.1 Hz; C3,5 of PC_6H_5), 91.9 ppm (s; C_5H_5); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 52.9 ppm (s); elemental analysis calcd (%) for $C_{38}H_{30}ClPRu$ (654.2): C 69.77, H 4.62; found: C 69.70, H 5.01.

[(η⁵-C_5H_5)RuCl(=CPh_2)(PPh$_3$)] (22): A solution of **10**, which was generated in situ from **1** (125 mg, 0.26 mmol), a saturated solution of ethene in toluene (5 mL), and a 0.32 M solution of HCl in benzene (1.82 mL, 0.62 mmol), was treated with a solution of Ph_2CN_2 (60 mg, 0.31 mmol) in toluene (1 mL) and the mixture was stirred for 5 min at room temperature. After the solvent had been removed in vacuo, the residue was washed with diethyl ether (2 × 2 mL) and dried; yield 164 mg (79 %). Compound **22** was identified by comparison of its NMR spectra with those of an authentic sample.[20]

[(η⁵-C_5H_5)Ru(κ¹-O_2CCF_3)(=CPh_2)(PPh$_3$)] (23): A solution of **12** (191 mg, 0.33 mmol) in toluene (5 mL) was treated with Ph_2CN_2 (65 mg, 0.33 mmol) and the mixture was stirred for 5 min at room temperature. The solvent was then evaporated in vacuo, and the remaining green solid was washed with diethyl ether (2 × 2 mL) and dried; yield 144 mg (62 %); m.p. 125 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1} (C=O); ^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.77, 7.23, 7.04, 6.77 (all m, 25H; C_6H_5), 4.66 ppm (s, 5H; C_5H_5); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ = 340.0 (d, J(P,C) = 11.1 Hz; Ru=C), 161.7 (d, J(P,C) = 5.1 Hz; *ipso*-C of CC_6H_5), 135.2 (d, J(P,C) = 43.4 Hz; *ipso*-C of PC_6H_5), 134.0 (d, J(P,C) = 11.0 Hz; C2,6 of PC_6H_5), 130.5 (d, J(P,C) = 2.0 Hz; C4 of PC_6H_5), 128.6 (d, J(P,C) = 9.9 Hz; C3,5 of PC_6H_5), 129.0, 127.3, 125.6 (all s; CC_6H_5), 114.8 (q, J(F,C) = 292.4 Hz; CF_3), 82.5 ppm (d, J(P,C) = 2.0 Hz; C_5H_5), signal of CF_3CO_2 carbon atom not exactly located; ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 42.6 (s); elemental analysis calcd (%) for $C_{38}H_{30}F_3O_2PRu$ (707.7): C 64.49, H 4.27; found: C 64.17, H 4.35.

[(η⁵-C_5H_5)Ru(κ¹-O_2CCF_3){=$C(C_6H_4$-4-Cl)$_2$}(PPh$_3$)] (24): This compound was prepared as described for **23**, starting from **12** (132 mg, 0.23 mmol) and $(4\text{-}ClC_6H_4)_2CN_2$ (61 mg, 0.23 mmol). Green solid; yield 134 mg (75 %); m.p. 131 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1} (C=O); ^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.77, 7.22, 7.01, 6.69 (all m, 23H; C_6H_4 and C_6H_5), 4.70 ppm (s, 5H; C_5H_5); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ = 332.8 (d, J(P,C) = 10.6 Hz; Ru=C), 163.7 (q, J(F,C) = 35.6 Hz; CO_2), 161.1 (s; *ipso*-C of C_6H_4), 135.0 (d, J(P,C) = 47.3 Hz; *ipso*-C of PC_6H_5), 134.1 (d, J(P,C) = 18.1 Hz; C2,6 of PC_6H_5), 130.9 (d, J(P,C) = 2.0 Hz; C4 of PC_6H_5), 128.9 (d, J(P,C) = 10.1 Hz; C3,5 of PC_6H_5), 128.3, 127.9, 125.1 (all s; C_6H_4), 115.0 (q, J(F,C) = 289.9 Hz; CF_3), 84.5 ppm (d, J(P,C) = 2.0 Hz; C_5H_5); ^{19}F NMR (CD_2Cl_2, 188.3 MHz): δ = −75.1 ppm (s); ^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ = 42.1 ppm (s); elemental analysis calcd (%) for $C_{38}H_{28}Cl_2F_3O_2PRu$ (776.6): C 58.77, H 3.63; found: C 58.27, H 3.84.

[(η⁵-C_5H_5)Ru(κ¹-O_2CCF_3){=$C(C_6H_4$-4-OMe)$_2$}(PPh$_3$)] (25): This compound was prepared as described for **23**, starting from **12** (101 mg, 0.18 mmol) and $(4\text{-}MeOC_6H_4)_2CN_2$ (45 mg, 0.18 mmol). Green solid; yield 83 mg (60 %); m.p. 129 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): δ = 8.15, 7.92, 7.62, 7.20, 7.15, 6.83 (all m, 23H; C_6H_4 and C_6H_5), 4.91 (s, 5H; C_5H_5), 3.49, 3.42 ppm (both s; OCH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 161.4 (s; *ipso*-C of C_6H_4), 135.8 (d, J(P,C) = 43.2 Hz; *ipso*-C of PC_6H_5), 134.0 (d, J(P,C) = 11.0 Hz; C2,6 of PC_6H_5), 132.4 (d, J(P,C) = 2.9 Hz; C4 of PC_6H_5), 128.7 (d, J(P,C) = 10.1 Hz;

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C3,5 of PC_6H_5), 129.6, 127.5, 122.6 (all s; C_6H_4), 82.1 (d, $J(P,C) = 2.0$ Hz; C_5H_5), 54.9 ppm (s; OCH_3), signals of the Ru=C and CF_3CO_2 carbon atoms could not be observed; ^{19}F NMR (C_6D_6, 188.3 MHz): $\delta = -74.6$ (s); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 45.2$ ppm (s); elemental analysis calcd (%) for $C_{40}H_{34}F_3O_4PRu$ (767.8): C 62.58, H 4.46; found: C 62.49, H 4.30.

[(η^5-C_5H_5)RuCl{η^2-*Z*-$C_2H_2(CO_2Et)_2$}(PPh_3)] (26): This compound was prepared as described for **22**, starting from **1** (88 mg, 0.18 mmol), a 0.18 M solution of HCl in benzene (1.39 mL, 0.25 mmol), and $HC(CO_2Et)N_2$ (37 μL, 0.36 mmol). Yellow solid; yield 94 mg (82%); m.p. 86 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1692$ cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.72$, 7.63, 7.05, 6.93 (all m, 15H; C_6H_5), 5.02 (s, 5H; C_5H_5), 4.16, 3.94 (both m, 5H; =CH and CH_2CH_3), 3.71 (AB part of ABX spin system, $J(P,H) = 14.2$, $J(H,H) = 9.4$ Hz, 1H; =CH), 1.07 (t, $J(H,H) = 4.0$ Hz; CH_2CH_3), 0.96 ppm (t, $J(H,H) = 4.7$ Hz, 3H; CH_2CH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta =$ 173.9, 173.5 (both s; CO_2), 139.2 (br s; *ipso*-C of PC_6H_5), 132.4 (d, $J(P,C) = 9.6$ Hz; C2,6 of PC_6H_5), 130.4 (s; C4 of PC_6H_5), 128.3 (br s; C3,5 of PC_6H_5), 90.8 (s; C_5H_5), 60.8, 60.4 (both s; CH_2CH_3), 58.3, 51.3 (both s; =CH), 14.6, 14.4 ppm (both s; CH_2CH_3); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta =$ 49.6 ppm (s); elemental analysis calcd (%) for $C_{31}H_{32}ClO_4PRu$ (636.1): C 58.54, H 5.07; found: C 58.27, H 5.17.

[(η^5-C_5H_5)RuCl{=CPhC(O)Ph}(PPh_3)] (27): This compound was prepared as described for **22**, starting from **1** (210 mg, 0.43 mmol), a saturated solution of ethene in toluene (5 mL), a 0.18 M solution of HCl in benzene (3.60 mL, 0.65 mmol), and PhC{C(O)Ph}N_2 (96 mg, 0.43 mmol). Green solid; yield 212 mg (75%); m.p. 117 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1595$ cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz, 293 K): $\delta = 8.32$, 8.13, 7.69, 7.00, 6.52 (all m, 25H; C_6H_5), 4.83 ppm (s, 5H; C_5H_5); ^{13}C NMR ([D_8]toluene, 100.6 MHz, 223 K): $\delta = 293.7$ (m; Ru=C), 207.7 (s; *C*(O)Ph), 162.3, 153.5 (both d, $J(P,C) = 4.5$ Hz; *ipso*-C of CC_6H_5), 137.6–125.3 (br m; C_6H_5), 96.2, 93.2 ppm (both s; C_5H_5); ^{31}P NMR (C_6D_6, 162.0 MHz, 223 K): $\delta = 48.2$, 47.3 ppm (both s); elemental analysis calcd (%) for $C_{37}H_{30}ClOPRu$ (658.1): C 67.53, H 4.59; found: C 67.18, H 4.58.

[(η^5-C_5H_5)Ru(η^1-O_2CCF_3)(=CHPh)(PPh_3)] (28): A solution of **1** (82 mg, 0.17 mmol) in toluene (5 mL) was treated at −40 °C with CF_3CO_2H (13 μL, 0.17 mmol) and then warmed, under continuous stirring, to 0 °C. A change of color from yellow to red occurred. A solution of $PhCHN_2$ (20 mg, 0.17 mmol) in toluene (2 mL) was added dropwise to the reaction mixture at 0 °C, which led to the evolution of a gas (N_2). After about 10 min, the solvent was evaporated in vacuo, and the remaining green solid was washed with pentane (2 × 10 mL) and dried; yield 94 mg (88%); m.p. 100 °C (decomp); MS (FAB): *m*/*z* (I_r): 631 (2.9; [$M^+ - H$]), 519 (29.6; [$M^+ - CF_3CO_2$]), 429 (100; [$C_5H_5RuPPh_3]^+$); IR (C_6H_6): $\tilde{\nu} = 1692$ cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): $\delta = 17.26$ (d, $J(P,C) = 8.0$ Hz, 1H; Ru=CH), 7.77, 7.50, 7.33, 7.20, 7.00 (all m, 20H; C_6H_5), 4.85 ppm (s, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 311.8$ (d, $J(P,C) = 14.0$ Hz; Ru=C), 157.3 (s; *ipso*-C of CC_6H_5), 135.1 (d, $J(P,C) = 45.8$ Hz; *ipso*-C of PC_6H_5), 133.7 (d, $J(P,C) = 10.3$ Hz; C2,6 of PC_6H_5), 130.3 (d, $J(P,C) = 2.6$ Hz; C4 of PC_6H_5), 128.4 (d, $J(P,C) = 9.6$ Hz; C3,5 of PC_6H_5), 129.6, 129.5, 129.2 (all s; CC_6H_5), 115.7 (q, $J(F,C) = 292.4$ Hz; CF_3), 88.5 ppm (d, $J(P,C) = 1.8$ Hz; C_5H_5), signal of CF_3CO_2 carbon atom not exactly located; ^{19}F NMR (C_6D_6, 376.5 MHz): $\delta = -73.7$ ppm (s); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta =$ 52.8 ppm (s); elemental analysis calcd (%) for $C_{32}H_{26}F_3O_2PRu$ (631.6): C 60.85, H 4.15, Ru 16.00; found: C 60.41, H 4.25, Ru 16.58.

[(η^5-C_5Me_5)Ru(η^1-O_2CCF_3)(=CHPh)(PPh_3)] (29): This compound was prepared as described for **28**, starting from **2** (75 mg, 0.14 mmol), CF_3CO_2H (11 μL, 0.14 mmol), and $PhCHN_2$ (17 mg, 0.14 mmol). Light green crystals; yield 88 mg (90%); m.p. 48 °C (decomp); MS (FAB): *m*/*z* (I_r): 702 (2.3; [$M^+ - H$]), 612 (9.4; [$M^+ - CHPh$]); 589 (57.1; [$M^+ - CF_3CO_2$]), 499 (100; [$C_5Me_5RuPPh_3]^+$); IR (C_6H_6): $\tilde{\nu} = 1691$ cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): $\delta = 17.75$ (d, $J(P,H) = 19.6$ Hz, 1H; Ru=CH), 8.02, 7.52, 7.24, 7.12, 7.02 (all m, 20H; C_6H_5), 1.23 ppm (d, $J(P,H) = 1.6$ Hz, 15H; C_5Me_5); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 313.7$ (d, $J(P,C) = 19.1$ Hz; Ru=C), 162.8 (q, $J(P,C) = 35.6$ Hz; O_2CCF_3), 157.3 (d, $J(P,C) = 2.5$ Hz; *ipso*-C of CC_6H_5), 134.4 (d, $J(P,C) = 10.2$ Hz; C2,6 of PC_6H_5), 133.8 (d, $J(P,C) = 40.7$ Hz; *ipso*-C of PC_6H_5), 130.0 (d, $J(P,C) = 2.5$ Hz; C4 of PC_6H_5), 128.3 (d, $J(P,C) =$ 9.5 Hz; C3,5 of PC_6H_5), 129.4, 129.0, 128.9 (all s; CC_6H_5), 116.0 (q, $J(F,C) =$ 292.5 Hz; CF_3), 98.4 (d, $J(P,C) = 2.5$ Hz; $C_5(CH_3)_5$), 10.2 ppm (s; $C_5(CH_3)_5$); ^{19}F NMR (C_6D_6, 376.5 MHz): $\delta = -74.5$ ppm (s); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 55.1$ ppm (s); elemental analysis calcd (%) for $C_{37}H_{36}F_3O_2PRu$ (701.7): C 63.33, H 5.17, Ru 14.40; found: C 62.99, H 4.94, Ru 14.62.

[(η^5-C_5H_5)RuCl(=CHPh)(PPh_3)] (30): A solution of **28** (65 mg, 0.10 mmol) in toluene (5 mL) was treated with Me_3SiCl (13 μL, 0.10 mmol) and the mixture was stirred for 5 min at room temperature. The solvent was then evaporated in vacuo, and the remaining green solid was washed with pentane (2 × 10 mL) at 0 °C and dried; yield 55 mg (96%); m.p. 42 °C (decomp); MS (FAB): *m*/*z* (I_r): 554 (4.6; [M^+]), 519 (25.6; [$M^+ - Cl$]), 429 (100; [$C_5H_5RuPPh_3]^+$); ^1H NMR (C_6D_6, 400 MHz): $\delta = 17.25$ (d, $J(P,H) =$ 8.6 Hz, 1H; Ru=CH), 7.76, 7.64, 7.49, 7.21, 7.07, 6.99, 6.92 (all m, 20H; C_6H_5), 4.86 ppm (s, 5H; C_5H_5); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 52.9$ ppm (s); elemental analysis calcd (%) for $C_{30}H_{26}ClPRu$ (554.0): C 65.04, H 4.73, Ru 18.24; found: C 65.12, H 5.16, Ru 18.54.

An alternative procedure is as follows: A solution of **10** (80 mg, 0.17 mmol) in benzene (10 mL) was treated dropwise with a solution of $PhCHN_2$ (20 mg, 0.17 mmol) in benzene (2 mL) at room temperature. After the reaction mixture had been stirred for 5 min, the solvent was evaporated in vacuo, and the residue was washed with pentane (2 × 5 mL) at 0 °C and dried; yield 82 mg (87%).

[(η^5-C_5Me_5)RuCl(=CHPh)(PPh_3)] (31): This compound was prepared as described for **30**, starting either from **29** (78 mg, 0.11 mmol) and Me_3SiCl (15 μL, 0.11 mmol) or from **11** (97 mg, 0.17 mmol) and a solution of $PhCHN_2$ (20 mg, 0.17 mmol) in benzene (2 mL). Green solid; yield 60 mg (86%) from **29** and 96 mg (90%) from **11**; m.p. 75 °C (decomp); MS (FAB): *m*/*z* (I_r): 624 (16.8; [M^+]), 589 (100; [$M^+ - Cl$]), 499 (57.5; [$C_5Me_5RuPPh_3]^+$); ^1H NMR (C_6D_6, 400 MHz): $\delta = 17.28$ (d, $J(P,H) =$ 12.6 Hz, 1H; Ru=CH), 7.96, 7.65, 7.37, 6.82 (all m, 20H; C_6H_5), 1.27 ppm (d, $J(P,H) = 2.0$ Hz, 15H; C_5Me_5); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 303.5$ (d, $J(P,C) = 21.6$ Hz; Ru=C), 157.7 (d, $J(P,C) = 2.0$ Hz; *ipso*-C of CC_6H_5), 137.8 (d, $J(P,C) = 34.2$ Hz; *ipso*-C of PC_6H_5), 134.7 (d, $J(P,C) = 9.1$ Hz; C2,6 of PC_6H_5), 133.6 (d, $J(P,C) = 8.1$ Hz; C3,5 of PC_6H_5), 129.7 (d, $J(P,C) =$ 3.0 Hz; C4 of PC_6H_5), 128.7, 128.0, 127.6 (all s; CC_6H_5), 99.3 (d, $J(P,C) =$ 3.8 Hz; $C_5(CH_3)_5$), 10.1 ppm (d, $J(P,C) = 3.8$ Hz; $C_5(CH_3)_5$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 56.0$ ppm (s).

[(η^5-C_5H_5)RuCl(=CHSiMe$_3$)(PPh_3)] (32): A solution of **1** (83 mg, 0.17 mmol) in toluene (5 mL) was treated at −40 °C with CF_3CO_2H (13 μL, 0.17 mmol) and then warmed under continuous stirring to 0 °C, whereupon a 2.0 M solution of Me_3SiCHN_2 (86 μL, 0.17 mmol) in toluene (2 mL) was added dropwise. After the evolution of N_2 had ceased, the solution was treated with Me_3SiCl (24 μL, 0.19 mmol) and stirred for 5 min at room temperature. The solvent was then evaporated in vacuo and the residue was extracted with pentane (10 mL). The extract was concentrated to about 1 mL and then stored for 1 h at −60 °C. A green solid precipitated, which was washed twice with small portions of pentane at 0 °C and dried; yield 57 mg (60%); m.p. 51 °C (decomp); MS (FAB): *m*/*z* (I_r): 515 (3.9; [$M^+ - Cl$]), 444 (5.6; [$M^+ - CHSiMe_3$]), 429 (51.6; [$C_5H_5RuPPh_3]^+$); IR (C_6H_6): $\tilde{\nu} = 1692$ cm^{-1} (C=O); ^1H NMR (C_6D_6, 400 MHz): $\delta = 20.46$ (d, $J(P,C) = 18.6$ Hz, 1H; Ru=CH), 7.78–6.86 (br m, 15H; C_6H_5), 4.24 (s, 5H; C_5H_5), 0.14 ppm (s, 9H; $SiMe_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 350.3$ (d, $J(P,C) = 12.7$ Hz; Ru=C), 135.6 (d, $J(P,C) = 47.1$ Hz; *ipso*-C of PC_6H_5), 134.5 (d, $J(P,C) = 9.5$ Hz; C2,6 of PC_6H_5), 130.0 (d, $J(P,C) = 1.9$ Hz; C4 of PC_6H_5), 128.2 (d, $J(P,C) = 10.5$ Hz; C3,5 of PC_6H_5), 75.6 (s; C_5H_5), −0.8 ppm (s; $SiMe_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 50.8$ ppm (s); elemental analysis calcd (%) for $C_{27}H_{30}PRuSi$ (550.0): C 58.96, H 5.51; found: C 59.01, H 5.29.

[(η^5-C_5H_5)Ru(=CPh_2)(CO)(PPh_3)]$AlCl_4$ (33a): A slow stream of CO was passed for 1 min through a solution of **22** (78 mg, 0.12 mmol) in toluene (5 mL). $AlCl_3$ (27 mg, 0.20 mmol) was added and the reaction mixture was stirred for 30 min at room temperature. The solvent was then evaporated in vacuo, the residue was redissolved in CH_2Cl_2 (2 mL), and this solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With CH_2Cl_2, a yellow fraction was eluted, which was concentrated to dryness in vacuo. The yellow-orange solid was washed with benzene (2 × 5 mL) and dried; yield 71 mg (75%); m.p. 86 °C (decomp); $\Lambda =$ 62 cm$^2\,\Omega^{-1}$mol^{-1}; IR (CH_2Cl_2): $\tilde{\nu} = 1985$ cm^{-1} (CO); ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 7.45$, 7.20, 6.84 (all m, 25H; C_6H_5), 5.24 ppm (s, 5H; C_5H_5); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): $\delta = 340.6$ (br s; Ru=C), 201.6 (br s; RuCO), 158.5 (s; *ipso*-C of CC_6H_5), 134.0 (br s; *ipso*-C of PC_6H_5), 133.4 (d, $J(P,C) =$ 10.8 Hz; C2,6 of PC_6H_5), 132.3, 128.9, 128.1 (all br s; CC_6H_5 and PC_6H_5), 129.9 (d, $J(P,C) = 10.9$ Hz; C3,5 of PC_6H_5), 94.4 ppm (s; C_5H_5); ^{31}P NMR (CD_2Cl_2, 162.0 MHz): $\delta = 43.3$ ppm (s); elemental analysis calcd (%) for $C_{37}H_{30}AlCl_4OPRu$ (791.5): C 56.15, H 3.82; found: C 55.70, H 3.50.

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$[(\eta^5\text{-}C_5H_5)Ru(=CPh_2)(CO)(PPh_3)]PF_6$ (33b): A slow stream of CO was passed for 1 min through a solution of **22** (64 mg, 0.10 mmol) in CH_2Cl_2 (5 mL). KPF_6 (37 mg, 0.20 mmol) was added, and the reaction mixture was stirred for 30 min at room temperature and then filtered through Celite. The filtrate was concentrated to dryness in vacuo, and the remaining orange solid was washed with pentane (5 mL) and dried; yield 69 mg (91%); m.p. 235 °C (decomp); $\Lambda = 78\ cm^2\,\Omega^{-1}\,mol^{-1}$; the IR, ^1H, and ^{13}C NMR data were almost identical to those of **33a**; ^{31}P NMR ([D$_6$]acetone, 162.0 MHz): $\delta = -144.1$ (sept, $J(P,F) = 712.8$ Hz; PF_6^-), 43.7 ppm (s; PPh_3); elemental analysis calcd (%) for $C_{37}H_{30}F_6OP_2Ru$ (767.7): C 57.89, H 3.94; found: C 57.80, H 3.93.

An alternative procedure is as follows: A solution of **33a** (71 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) was treated with KPF_6 (165 mg, 0.90 mmol) and the resulting mixture was stirred for 30 min at room temperature. The reaction mixture was filtered through Celite and the filtrate was worked-up as described above to give an orange solid; yield 55 mg (80%).

$[(\eta^5\text{-}C_5H_5)Ru(=CPh_2)(CN\mathit{t}Bu)(PPh_3)]AlCl_4$ (34): A solution of **22** (112 mg, 0.18 mmol) in THF (10 mL) was treated sequentially with CN*t*Bu (29 μL, 0.27 mmol) and $AlCl_3$ (40 mg, 0.30 mmol), and the resulting mixture was stirred for 30 min at room temperature. After removal of the solvent, the residue was worked-up as described for **33a**. Yellow-brown solid; yield 122 mg (80%); m.p. 108 °C (decomp); $\Lambda = 65\ cm^2\,\Omega^{-1}\,mol^{-1}$; IR ($CH_2Cl_2$): $\tilde{\nu} = 2145\ cm^{-1}$ (CN); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.72$, 7.63, 7.41, 7.04 (all m, 25H; C_6H_5), 5.26 (s, 5H; C_5H_5), 1.36 ppm (s, 9H; *t*Bu); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 337.6$ (brs; Ru=C), 163.6 (s; *ipso*-C of CC_6H_5), 146.0 (brs; *C*N*t*Bu), 134.0 (d, $J(P,C) = 49.9$ Hz; *ipso*-C of PC_6H_5), 132.9 (d, $J(P,C) = 10.7$ Hz; C2,6 of PC_6H_5), 131.4, 131.2, 129.0, 128.9 (all brs; CC_6H_5 and PC_6H_5), 127.1 (d, $J(P,C) = 5.3$ Hz; C3,5 of PC_6H_5), 90.6 (s; C_5H_5), 58.3 (s; *C*CH_3), 29.7 ppm (s; C*C*H_3); ^{31}P NMR ($CDCl_3$, 162.0 MHz): $\delta = 43.6$ ppm (s); elemental analysis calcd (%) for $C_{41}H_{39}AlCl_4NPRu$ (846.6): C 58.17, H 4.64, N 1.66; found: C 57.51, H 4.42, N 1.53.

$[(\eta^5\text{-}C_5H_5)Ru(\mathit{exo}\text{-}\eta^3\text{-}PhCHC_6H_5)(PPh_3)]$ (35): A suspension of **22** (130 mg, 0.20 mmol) in benzene (5 mL) was treated with a 1.0 M solution of $LiHBEt_3$ in THF (0.30 mL, 0.30 mmol) and the resulting mixture was stirred for 15 min at room temperature. After evaporation of the solvent in vacuo, the residue was extracted with toluene (2 mL) and the extract was chromatographed on Al_2O_3 (basic, activity grade V, length of column 4 cm) at −40 °C. With toluene, a yellow fraction was eluted, which was concentrated to dryness in vacuo. The remaining yellow solid was washed with pentane (2 × 3 mL) and dried; yield 91 mg (63%); m.p. 85 °C (decomp); ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.87$ (d, $J(H,H) = 8.8$ Hz, 1H; H^6), 7.78, 7.51, 6.98, 6.90 (all m, 5H; C_6H_5), 7.35, 6.70, 6.64 (all m, 1H each; H^{3-5}), 3.64 (s, 5H; C_5H_5), 2.91 (dd, $J(P,H) = 12.9$, $J(H,H) = 5.8$ Hz; H^2), 1.58 ppm (d, $J(P,H) = 16.6$ Hz, 1H; H^7); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta =$ 148.3 (s; *ipso*-C of CC_6H_5), 140.3, 129.4, 129.2, 129.0, 126.0, 123.8, 118.4 (all s; C^{3-6} and CC_6H_5), 137.6 (d, $J(P,C) = 36.5$ Hz; *ipso*-C of PC_6H_5), 135.0 (d, $J(P,C) = 10.3$ Hz; C2,6 of PC_6H_5), 128.5 (s; C4 of PC_6H_5), 127.8 (d, $J(P,C) =$ 10.3 Hz; C2,6 of PC_6H_5), 93.2 (s; C^1), 84.5 (s; C_5H_5), 57.8 ppm (s; C^2), 49.4 (d, $J(P,C) = 6.3$ Hz; C^7), for assignment of protons H^{2-7} and carbon atoms C^{1-7}, see Figure 4; ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 63.6$ ppm (s); elemental analysis calcd (%) for $C_{36}H_{31}PRu$ (595.7): C 72.59, H 5.25; found: C 72.69, H 5.54.

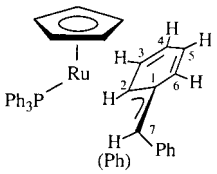

Figure 4. Assignment of protons H^{2-7} and carbon atoms C^{1-7} for compounds **35** and **36**.

$[(\eta^5\text{-}C_5H_5)Ru(\mathit{exo}\text{-}\eta^3\text{-}Ph_2CC_6H_5)(PPh_3)]$ (36): A suspension of **22** (96 mg, 0.15 mmol) in benzene (5 mL) was treated with a 1.8 M solution of PhLi in cyclohexane/diethyl ether (70:30) (0.13 mL, 0.23 mmol) and the mixture was stirred for 15 min at room temperature. The yellow solution was then treated with acetone (5 mL), and the reaction mixture was stirred for 15 min and then concentrated to dryness in vacuo. The residue was extracted with toluene (2 mL) and the extract was chromatographed on Al_2O_3 (basic, activity grade V, length of column 3 cm) at −60 °C. With toluene, a yellow fraction was eluted, from which the solvent was removed. The yellow residue was recrystallized from toluene/pentane but, despite repeating this procedure twice more, small quantities of impurities could not be separated. Data for **37**: ^1H NMR (C_6D_6, 400 MHz): $\delta = 8.21$, 7.92, 7.58, 7.43, 7.13, 6.93, 6.61 (all m, 25H; PC_6H_5 and C_6H_5 at C^7), 6.38, 6.32, 6.22, 6.12 (all m, 4H; H^{3-6}), 3.57 (s, 5H; C_5H_5), 2.41 ppm (m, 1H; H^2); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 152.6-119.3$ (brm, PC_6H_5; C_6H_5 at C^7 and C^{3-6}), 89.2 (s; C^1), 82.3 (s; C_5H_5), 66.6 (s; C^2), 63.8 ppm (d, $J(P,C) =$ 6.1 Hz; C^7); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 58.9$ ppm (s); the assignment of protons H^{2-6} and carbon atoms C^{1-7} is analogous to that in the case of **35**.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-}CH_2CHCPh_2)(PPh_3)]$ (39a,b): A suspension of **22** (146 mg, 0.23 mmol) in benzene (5 mL) was treated with a 0.75 M solution of CH_2=CHMgBr (0.62 mL, 0.47 mmol) in THF and the mixture was stirred for 45 min at room temperature. After evaporation of the solvent in vacuo, the residue was extracted with a 2:1 mixture of pentane/toluene (6 mL). The extract was concentrated to dryness in vacuo, and the remaining yellow solid was washed with pentane (2 × 2 mL) and dried; yield 91 mg (63%); m.p. 82 °C (decomp). According to the ^1H NMR spectroscopic data, the isolated solid consisted of a mixture of two isomers [*exo* (**39a**) and *endo* (**39b**)] in a 2:1 ratio. ^1H NMR for **39a** (C_6D_6, 400 MHz): $\delta = 8.15-6.54$ (brm; C_6H_5), 4.66 (ddd, $J(P,H) = 1.7$, $J(H^1,H^3) = 10.2$, $J(H^1,H^2) = 7.1$ Hz, 1H; H^1), 4.03 (s, 5H; C_5H_5), 3.58 (dd, $J(H^1,H^2) = 7.1$, $J(H^2,H^3) = 0.9$ Hz, 1H; H^2), 1.39 ppm (ddd, $J(P,H) = 16.6$, $J(H^1,H^3) = 10.2$, $J(H^2,H^3) = 0.9$ Hz, 1H; H^3); ^1H NMR for **39b** (C_6H_6, 400 MHz): $\delta = 8.15-6.54$ (brm; C_6H_5), 4.14 (s, 5H; C_5H_5), 3.31 (ddd, $J(P,H) = 13.8$, $J(H^1,H^3) = 11.4$, $J(H^1,H^2) = 7.3$ Hz, 1H; H^1), 3.16 (d, $J(H^1,H^3) = 11.4$ Hz, 1H; H^3), 3.04 ppm (dd, $J(P,H) = 3.0$, $J(H^1,H^2) = 7.3$ Hz, 1H; H^2), for assignment of protons H^{1-3}, see Figure 5; ^{13}C NMR for **39a,b** (C_6D_6, 100.6 MHz): $\delta = 155.3$, 149.9, 149.6 (all s; *ipso*-C of CC_6H_5), 149.3 (d, $J(P,C) = 6.0$ Hz; *ipso*-C of CC_6H_5), 138.6 (d, $J(P,C) =$ 35.2 Hz; *ipso*-C of PC_6H_5), 138.1 (d, $J(P,C) = 36.9$ Hz; *ipso*-C of PC_6H_5),

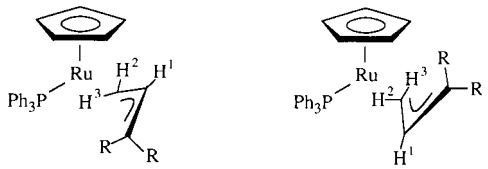

Figure 5. Assignment of protons H^{1-3} for compounds **39a–41a** and **39b–41b**.

134.6, 134.1 (both d, $J(P,C) = 10.5$ Hz; C2,6 of PC_6H_5), 133.4, 130.3, 129.7, 125.0, 124.7, 124.0, 123.7 (all s; CC_6H_5), 128.8, 128.7 (both d, $J(P,C) =$ 1.5 Hz; C4 of PC_6H_5), 128.3–126.8 (brm; CC_6H_5 and C3,5 of PC_6H_5), 88.4 (s; CH of **39b**), 83.2 (d, $J(P,C) = 1.6$ Hz; C_5H_5 of **39b**), 81.8 (s; C_5H_5 of **39a**), 79.1 (s; *C*Ph_2), 76.3 (d, $J(P,C) = 4.9$ Hz; *C*Ph_2), 65.6 (s; CH of **39a**), 37.2 (d, $J(P,C) = 4.7$ Hz; CH_2 of **39a**), 30.9 ppm (s; CH_2 of **39b**); ^{31}P NMR for **39a,b** (C_6D_6, 162.0 Hz): $\delta = 59.8$, 56.2 ppm (both s); elemental analysis calcd (%) for $C_{38}H_{33}PRu$ (621.7): C 73.41, H 5.35; found: C 73.61, H 5.37.

$[(\eta^5\text{-}C_5H_5)Ru\{\eta^3\text{-}CH_2CHC(4\text{-}C_6H_4Cl)_2\}(PPh_3)]$ (40a,b): The isomeric mixture was prepared as described for **39a,b** from **23** (110 mg, 0.16 mmol) and a 1.1 M solution of CH_2=CHMgBr (0.29 mL, 0.32 mmol) in THF. Yellow microcrystalline solid; yield 50 mg (45%); m.p. 91 °C (decomp). According to the ^1H NMR spectroscopic data, the isolated solid consisted of a mixture of two isomers [*exo* (**40a**) and *endo* (**40b**)] in a 2:1 ratio. ^1H NMR for **40a** (C_6D_6, 400 MHz): $\delta = 8.00-6.53$ (brm; C_6H_5 and C_6H_4), 4.45 (ddd, $J(P,H) = 1.7$, $J(H^1,H^3) = 10.1$, $J(H^1,H^2) = 7.1$ Hz, 1H; H^1), 3.98 (s, 5H; C_5H_5), 3.45 (dd, $J(H^1,H^2) = 7.1$, $J(H^2,H^3) = 0.9$ Hz, 1H; H^2), 1.37 ppm (ddd, $J(P,H) = 16.3$, $J(H^1,H^3) = 10.2$, $J(H^2,H^3) = 0.9$ Hz, 1H; H^3); ^1H NMR for **40b** (C_6D_6, 400 MHz): $\delta = 8.00-6.53$ (brm; C_6H_5 and C_6H_4), 4.06 (s, 5H; C_5H_5), 3.30 (m, 1H; H^1), 2.96 ppm (m, 2H; H^2 and H^3); for assignment of protons H^{1-3} see Figure 5; ^{13}C NMR for **40a,b** (C_6H_6, 100.6 MHz): $\delta =$ 153.2, 148.2, 147.7 (all s; *ipso*-C of C_6H_4), 147.6 (d, $J(P,C) = 6.5$ Hz; *ipso*-C of C_6H_4), 138.1 (d, $J(P,C) = 35.7$ Hz; *ipso*-C of PC_6H_5), 137.6 (d, $J(P,C) =$ 37.4 Hz; *ipso*-C of PC_6H_5), 134.5, 134.0 (both d, $J(P,C) = 10.6$ Hz; C2,6 of PC_6H_5), 133.9, 132.4, 132.3, 131.1, 131.0, 130.3, 129.4, 128.5, 128.3, 128.1, 127.7, 126.9 (all s; C_6H_4), 129.0, 128.8 (both d, $J(P,C) = 1.4$ Hz; C4 of PC_6H_5), 127.6, 127.5 (both d, $J(P,C) = 9.0$ Hz; C3,5 of PC_6H_5), 87.5 (s; CH of

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40b), 83.1 (d, J(P,C) = 1.9 Hz; C_5H_5 of **40b**), 81.8 (d, J(P,C) = 1.5 Hz; C_5H_5 of **40a**), 75.3 (s; CAr_2), 68.0 (d, J(P,C) = 5.0 Hz; CAr_2), 64.9 (s; CH of **40a**), 36.3 (d, J(P,C) = 5.2 Hz; CH_2 of **40a**), 32.4 ppm (s; CH_2 of **40b**); ^{31}P NMR for **40a,b** (C_6D_6, 162.0 MHz): δ = 59.0, 54.8 ppm (both s); elemental analysis calcd (%) for $C_{38}H_{31}Cl_2PRu$ (690.6): C 66.08, H 4.52; found: C 66.50, H 4.70.

[(η^5-C_5H_5)Ru{η^3-$CH_2CHC(4\text{-}C_6H_4OMe)_2$}($PPh_3$)] (41a,b): The isomeric mixture was prepared as described for **39a,b** from **24** (100 mg, 0.15 mmol) and a 0.75 M solution of CH_2=CHMgBr (0.38 mL, 0.29 mmol) in THF. Yellow microcrystalline solid; yield 60 mg (57%); m.p. 80 °C (decomp). According to the ^{1}H NMR spectroscopic data, the isolated solid consisted of a mixture of two isomers (*exo* (**41a**) and *endo* (**41b**)) in a 2:1 ratio. ^{1}H NMR for **41a** (C_6D_6, 400 MHz): δ = 7.76–6.16 (br m; C_6H_5 and C_6H_4), 4.68 (ddd, J(P,H) = 1.5, J(H^1,H^3) = 10.2, J(H^1,H^2) = 7.1 Hz, 1H; H^1), 4.09 (s, 5H; C_5H_5), 3.63 (dd, J(H^1,H^2) = 7.1, J(H^2,H^3) = 0.8 Hz, 1H; H^2), 3.36, 3.15 (both s, 3H each; CH_3), 1.49 ppm (ddd, J(P,H) = 16.2, J(H^1,H^3) = 10.3, J(H^2,H^3) = 0.8 Hz, 1H; H^3); ^{1}H NMR for **41b** (C_6D_6, 400 MHz): δ = 7.76–6.16 (br m; C_6H_5 and C_6H_4), 4.20 (s, 5H; C_6H_5), 3.13 (dd, J(P,H) = 3.1, J(H^1,H^2) = 7.1 Hz, 1H; H^2), 3.34, 3.25 ppm (both s, CH_3), signals of H^1 and H^2 probably covered by resonances of CH_3 protons; for assignment of protons H^{1-3}, see Figure 5; ^{13}C NMR for **41a,b** (C_6D_6, 100.6 MHz): δ = 157.7, 157.1, 156.8, 156.7 (all s; C4 of C_6H_4), 148.1, 142.8, 142.3 (all s; *ipso*-C of C_6H_4), 142.2 (d, J(P,C) = 6.1 Hz; *ipso*-C of C_6H_4), 138.8 (d, J(P,C) = 34.3 Hz; *ipso*-C of PC_6H_5), 138.4 (d, J(P,C) = 35.8 Hz; *ipso*-C of PC_6H_5), 134.7, 134.2 (both d, J(P,C) = 10.5 Hz; C2,6 of PC_6H_5), 133.8, 130.9, 130.5, 128.6, 128.3, 127.9, 113.3, 113.2, 112.9, 112.3 (all s; C_6H_4 and C4 of PC_6H_5), 127.5, 127.4 (both d, J(P,C) = 9.0 Hz; C3,5 of PC_6H_5), 88.5 (s; CH of **41b**), 83.1 (s; C_5H_5 of **41b**), 81.7 (s; C_5H_5 of **41a**), 77.2 (s; CAr_2), 69.9 (d, J(P,C) = 4.7 Hz; CAr_2), 66.3 (s; CH of **41a**), 54.9, 54.8, 54.7, 54.6 (all s; CH_3), 36.6 (d, J(P,C) = 4.9 Hz; CH_2 of **41a**), 30.5 ppm (s; CH_2 of **41b**); ^{31}P NMR for **41a,b** (C_6D_6, 162.0 MHz): δ = 59.5, 56.4 ppm (both s); elemental analysis calcd (%) for $C_{40}H_{37}O_2PRu$ (681.8): C 70.47, H 5.47; found: C 69.91, H 5.20.

Reaction of compound 35 with CH_3CO_2H: A solution of **35** (51 mg, 0.09 mmol) in benzene (2 mL) was treated with acetic acid (10 µL, 0.13 mmol) and the mixture was stirred for 3 h at room temperature. After removal of the solvent, the residue was dissolved in a small amount of C_6D_6. The ^{1}H and ^{31}P NMR spectra confirmed the presence of Ph_2CH_2 and the acetatoruthenium complex **47**.[20]

Reaction of the isomeric mixture 39a,b with CH_3CO_2H: A solution of **39a,b** (34 mg, 0.06 mmol) in benzene (2 mL) was treated with acetic acid (9 µL, 0.16 mmol) and the mixture was stirred for 18 h at room temperature. After removal of the solvent, the residue was extracted with pentane (5 mL). The extract was concentrated to ca. 1 mL in vacuo and then chromatographed on Al_2O_3 (neutral, activity grade V, length of column 2 cm). With hexane, an almost colorless fraction was eluted, from which a white solid was isolated. It was characterized as Ph_2C=CHMe by comparison of its ^{1}H NMR spectroscopic data with those of an authentic sample;[54] yield 8 mg (80%). The residue, which was not soluble in pentane, was identified as compound **47** on the basis of its ^{1}H NMR spectrum; yield 22 mg (85%).

Reaction of the isomeric mixture 40a,b with CH_3CO_2H: This was carried out analogously as described for **39a,b**, using **40a,b** (80 mg, 0.12 mmol) and acetic acid (20 µL, 0.36 mmol) as starting materials. After chromatography, the olefin $(4\text{-}ClC_6H_4)_2C$=CHMe[55] was isolated in 90% yield and the acetato complex **47** in 92% yield.

Reaction of the isomeric mixture 41a,b with CH_3CO_2H: This was carried out analogously as described for **39a,b**, using **41a,b** (76 mg, 0.11 mmol) and acetic acid (20 µL, 0.36 mmol) as starting materials. After chromatography, the olefin $(4\text{-}MeOC_6H_4)_2C$=CHMe[54, 56] was isolated in 84% yield and the acetato complex **47** in 88% yield.

[(η^5-C_5H_5)RuH(CH_2=CPh_2)(PPh_3)] (42): A suspension of **22** (160 mg, 0.25 mmol) in toluene (5 mL) was treated with a 1.5 M solution of MeLi in Et_2O (0.33 mL, 0.50 mmol) and the mixture was stirred for 30 min at room temperature. The yellow solution was then treated with acetone (5 mL), stirred for 15 min, and then concentrated to dryness in vacuo. The residue was extracted with toluene (2 mL), and the extract was chromatographed on Al_2O_3 (basic, activity grade V, length of column 5 cm). With toluene, a yellow fraction was eluted, from which the solvent was removed in vacuo. The remaining yellow solid was washed with pentane (5 mL) and dried; yield 100 mg (65%); m.p. 95 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.75, 7.37, 6.91, 6.77 (all m, 25H; C_6H_5), 4.26 (s, 5H; C_5H_5), 3.87 (d, J(H,H) = 1.7 Hz, 1H; one H of CH_2), 1.77 (dd, J(P,H) = 14.0, J(H,H) = 1.7 Hz, 1H; one H of CH_2), −9.79 ppm (d, J(P,H) = 35.0 Hz, 1H; RuH); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 154.0, 150.5 (both s; *ipso*-C of CC_6H_5), 138.9 (d, J(P,C) = 43.3 Hz; *ipso*-C of PC_6H_5), 133.8, 127.5 (both br m; C_6H_5), 128.8 (d, J(P,C) = 1.0 Hz; C4 of PC_6H_5), 126.3, 124.8, 123.8 (all s; CC_6H_5), 87.9 (d, J(P,C) = 2.0 Hz; C_5H_5), 67.3 (s; CPh_2), 26.0 ppm (s; CH_2); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 72.6 ppm (s); elemental analysis calcd (%) for $C_{37}H_{33}PRu$ (609.7): C 72.89, H 5.46; found: C 73.01, H 5.96.

[(η^5-C_5H_5)RuH{CH_2=$C(4\text{-}ClC_6H_4)_2$}(PPh_3)] (43): This compound was prepared as described for **42**, from **37** (80 mg, 0.11 mmol) and a 1.5 M solution of MeLi in Et_2O (0.15 mL, 0.22 mmol). Yellow microcrystalline solid; yield 54 mg (72%); m.p. 129 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.32, 7.13, 6.90, 6.57 (all m, 23H; C_6H_5 and C_6H_4), 4.20 (s, 5H; C_5H_5), 3.57 (d, J(H,H) = 1.7 Hz, 1H; one H of CH_2), 1.56 (dd, J(P,H) = 14.2, J(H,H) = 1.7 Hz, 1H; one H of CH_2), −9.89 ppm (d, J(P,H) = 36.0 Hz, 1H; RuH); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 71.3 (s); elemental analysis calcd (%) for $C_{37}H_{31}Cl_2PRu$ (678.6): C 65.49, H 4.60; found: C 65.57, H 4.62.

[(η^5-C_5H_5)RuH{CH_2=$C(4\text{-}MeOC_6H_4)_2$}(PPh_3)] (44): This compound was prepared as described for **42**, from **38** (92 mg, 0.13 mmol) and a 1.5 M solution of MeLi in Et_2O (0.17 mL, 0.26 mmol). Yellow microcrystalline solid; yield 49 mg (56%); m.p. 118 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.56, 7.14, 6.67 (all m, 19H; C_6H_5 and C_6H_4), 6.40 (d, J(P,H) = 8.0 Hz, 4H; C_6H_4), 4.35 (s, 5H; C_5H_5), 3.89 (d, J(H,H) = 1.2 Hz, 1H; one H of CH_2), 3.28 (s, 6H; OCH_3), 1.76 (dd, J(P,H) = 16.6, J(H,H) = 1.2 Hz, 1H; one H of CH_2), −9.74 ppm (d, J(P,H) = 36.2 Hz, 1H; RuH); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 157.5, 156.5 (both s; *ipso*-C of C_6H_4), 147.1, 143.3 (both s; C4 of C_6H_4OMe), 139.1 (d, J(P,C) = 44.3 Hz; *ipso*-C of PC_6H_5), 135.9 (s; C2,6 of C_6H_4), 135.5 (d, J(P,C) = 10.1 Hz; C2,6 of PC_6H_5), 130.4 (d, J(P,C) = 1.2 Hz; C4 of PC_6H_5), 129.1 (d, J(P,C) = 9.5 Hz; C3,5 of PC_6H_5), 114.6, 114.4 (both s; C_6H_4), 87.7 (d, J(P,C) = 2.0 Hz; C_5H_5), 66.8 (s; CAr_2), 54.8 (s; OCH_3), 25.7 ppm (d, J(P,C) = 4.0 Hz; CH_2); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 72.8 ppm (s); elemental analysis calcd (%) for $C_{39}H_{37}O_2PRu$ (669.8): C 69.94, H 5.57; found: C 70.12, H 5.80.

[(η^5-C_5H_5)RuH(CH_2=CHPh)(PPh_3)] (45): This compound was prepared as described for **42**, from **30** (120 mg, 0.22 mmol) and a 1.6 M solution of MeLi in Et_2O (0.28 mL, 0.44 mmol). The crude product was extracted with pentane (4 × 10 mL), the combined extracts were concentrated to about 5 mL in vacuo, and this solution was then stored for 12 h at −60 °C. The yellow microcrystalline solid was separated from the mother liquor and dried; yield 73 mg (63%); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.80–6.80 (br m, 20H; C_6H_5), 4.35 (s, 5H; C_5H_5), 2.10 (m, 1H; CHPh), 0.95, 0.86 (both m, 1H each; CH_2), −9.84 ppm (d, J(P,H) = 38.3 Hz, 1H; Ru); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 141.0 (s; *ipso*-C of CC_6H_5), 140.8 (d, J(P,C) = 37.2 Hz; *ipso*-C of PC_6H_5), 134.1 (d, J(P,C) = 10.5 Hz; C2,6 of PC_6H_5), 132.4 (d, J(P,C) = 9.5 Hz; C3,5 of PC_6H_5), 131.5 (d, J(P,C) = 2.9 Hz; C4 of PC_6H_5), 129.3, 127.9, 126.9 (all s; CC_6H_5), 84.7 (s; C_5H_5), 22.7 (s; CH_2), 21.4 ppm (d, J(P,C) = 1.9 Hz; CHPh); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 55.2 ppm (s); elemental analysis calcd (%) for $C_{31}H_{29}PRu$ (533.6): C 69.77, H 5.49; found: C 69.45, H 5.31.

[(η^5-C_5H_5)RuH(CH_2=$CHSiMe_3$)(PPh_3)] (46): This compound was prepared as described for **45**, from **32** (115 mg, 0.21 mmol) and a 1.6 M solution of MeLi in Et_2O (0.26 mL, 0.42 mmol). Orange microcrystalline solid; yield 90 mg (68%); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.69, 7.52, 7.02 (all m, 15H; C_6H_5), 4.75 (s, 5H; C_5H_5), 1.41 (dd, J(P,H) = 11.0, J(H,H) = 10.0 Hz, 1H; one H of CH_2), 0.95 (dd, J(P,H) = 5.5, J(H,H) = 10.0 Hz, 1H; one H of CH_2), 0.15 (s, 9H; $SiMe_3$), 0.11 (s, 1H; $CH$$SiMe_3$), −10.43 ppm (d, J(P,H) = 36.8 Hz, 1H; RuH); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 137.7 (d, J(P,C) = 43.9 Hz; *ipso*-C of PC_6H_5), 133.9 (d, J(P,C) = 10.5 Hz; C2,6 of PC_6H_5), 132.4 (d, J(P,C) = 9.5 Hz; C3,5 of PC_6H_5), 131.7 (d, J(P,C) = 2.9 Hz; C4 of PC_6H_5), 83.5 (d, J(P,C) = 2.9 Hz; C_5H_5), 27.2 (d, J(P,C) = 4.8 Hz; CH_2), 22.7 (s, $CH$$SiMe_3$), 1.5 ppm (s, $SiCH_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 77.0 ppm (s); elemental analysis calcd (%) for $C_{28}H_{33}PRuSi$ (529.8): C 63.51, H 6.28; found: C 63.05, H 5.98.

X-ray structure determinations of compounds 27, 33b, and 39a: The X-ray structure determination of **39a** has already been published (Ref. Code ZALVAJ).[12] Single crystals of **27** were grown from toluene/diethyl ether, while those of **33b** were grown from dichloromethane/pentane. Crystal data of **27** (from 25 reflections, $10° < \theta < 15°$): orthorhombic, space group $Pna2_1$ (no. 33); a = 21.218(5), b = 9.501(7), c = 14.87(1) Å, V = 2998(3) Å^3,

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$Z=4$, $\rho_{calcd}=1.458\ g\,cm^{-3}$, $\mu(Mo_{K\alpha})=0.687\ mm^{-1}$, $T=293(2)$ K; crystal size $0.25\times0.20\times0.13$ mm; ω-scan, max $2\theta=58.00^\circ$; 6489 reflections measured, 4117 independent reflections, 2617 regarded as being observed [$I>2\sigma(I)$]; $R=0.0413$, $wR_2=0.0711$; reflection/parameter ratio 11.12; residual electron density $+0.341/-0.303$ e Å^{-3}. Crystal data of **33b** (from 23 reflections, $10^\circ<\theta<13^\circ$): monoclinic, space group $P2_1/c$ (no. 14); $a=14.13(1)$, $b=19.685(8)$, $c=13.20(1)$ Å, $\beta=97.62(5)^\circ$, $V=3640(5)$ Å^3, $Z=4$, $\rho_{calcd}=1.45\ g\,cm^{-3}$, $\mu(Mo_{K\alpha})=0.990\ mm^{-1}$, $T=293(2)$ K; crystal size $0.28\times0.15\times0.13$ mm; ω/θ-scan, max $2\theta=48.00^\circ$; 6526 reflections measured, 6226 independent reflections, 6225 regarded as being observed [$I>2\sigma(I)$]; $R=0.0405$, $wR_2=0.1018$; reflection/parameter ratio 11.90; residual electron density $+0.30/-0.45$ e Å^{-3}. Both crystals were examined on an Enraf-Nonius CAD4 diffractometer; $Mo_{K\alpha}$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4). The intensity data were corrected for Lorentz and polarization effects; minimum transmission was 89.53% for **27** and 96.05% for **33b**. The structures were solved by direct methods (SHELXS-86);[57] atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares (370 parameters for **27**, 523 parameters for **33b**, SHELXL-93).[58] The positions of all hydrogen atoms were calculated according to ideal geometry and were included in the structure factor calculation in the last refinement cycle. The PF_6^- ion of **33b** is disordered. Two independent positions were found and could be refined anisotropically with occupancy factors of 0.50:0.50. The unit cell of **33b** contains a disordered molecule of dichloromethane. Two independent positions were found and could be refined anisotropically with occupancy factors of 0.75:0.25.[59]

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