The Sensitive Balance between Five-Coordinate Carbene and Six-Coordinate Carbyne Ruthenium Complexes Formed from Ruthenium Vinylidene Precursors†

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The reaction of the dichloro(vinylidene)ruthenium compounds $[RuCl_2(=C=CHR)L_2]$ (R = Ph or *t*Bu and L = PCy_3 or P*i*Pr$_3$) (**1a**−**d**) with $[H(OEt_2)_2]BAr_f$ (BAr_f^- = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) resulted in the attack of the proton at the C_β carbon atom of the vinylidene ligand and afforded the corresponding cationic, five-coordinate carbyneruthenium complexes $[RuCl_2(\equiv CCH_2R)L_2]BAr_f$ (**2a**−**d**) in almost quantitative yields. The protonation of the carboxylato derivatives $[RuCl(\kappa^2\text{-}O_2CR)(=C=CHPh)(PiPr_3)_2]$ [R = H (**3a**), CH_3 (**3b**), or Ph (**3f**)] with $[H(OEt_2)_2]BAr_f$ led to the formation of the five-coordinate cyclic carbene complexes $[RuCl\{=C(CH_2Ph)OC(O)R\}(PiPr_3)_2]BAr_f$ [R = H (**6a**), CH_3 (**6b**), or Ph (**6f**)], which are formed via nucleophilic attack of the carboxylato ligand to a cationic carbyneruthenium intermediate. The protonation of the related vinylidene compounds $[RuCl(\kappa^2\text{-}O_2CR)(=C=CHPh)(PiPr_3)_2]$ [R = CH_2F (**3c**), CHF_2 (**3d**), CF_3 (**3e**), $C_6H_4NO_2$-4 (**3g**), $C_6H_4NO_2$-2 (**3h**), C_6F_5 (**3i**), and $C_6H_3(NO_2)_2$-2,4 (**3j**)] with $[H(OEt_2)_2]BAr_f$ gave an equilibrium mixture of the carbyne $[RuCl(\kappa^2\text{-}O_2CR)(\equiv CCH_2Ph)(PiPr_3)_2]BAr_f$ (**5c**−**e**, **5g**−**j**) and the isomeric, cyclic carbene complexes $[RuCl\{=C(CH_2Ph)OC(O)R\}(PiPr_3)_2]BAr_f$ (**6c**−**e**, **6g**−**j**). The position of this equilibrium significantly depends on the basicity of the carboxylato ligand. The six-coordinate cyclic carbene complexes $[Ru(\kappa^2\text{-}O_2CR^1)\{=C(CH_2Ph)OC(O)R^2\}(PiPr_3)_2]BAr_f$ [$R^1 = R^2 = CHF_2$ (**7a**), CF_3 (**7b**); $R^1 = CF_3$, R^2 = H (**7c**)] were obtained on protonation of the precursors $[Ru(\kappa^1\text{-}O_2CR^1)(\kappa^2\text{-}O_2CR^2)(=C=CHPh)(PiPr_3)_2]$ (**4a**−**c**) with $[H(OEt_2)_2]BAr_f$. Both **7a** and **7b** undergo a fluxional process in solution resulting in a κ^1/κ^2 interconversion of the carboxylato groups. The crystal and molecular structures of **2b, 5e**, and **6a** were determined by X-ray crystallography.

Introduction

In the last two decades, transition-metal complexes containing carbynes as ligands have received a great deal of attention not only because of their unusual type of bonding but also due to their growing application in organic synthesis and alkyne metathesis.[1] After Fischer et al. reported in 1973 the preparation and structural characterization of the first representatives of metal carbynes,[2] various synthetic routes to compounds with a metal−carbon triple bond have been developed which include the conversion of coordinated carbenes, vinylidenes, allenylidenes, and even alkynyls to corresponding CR units.[3,4]

We have recently shown that the reaction of the vinylidene(hydrido) complex $[RuHCl(=C=CH_2)(PCy_3)_2]$ with acids HA having a noncoordinating anion A^-, in the presence of a donor solvent S, yields the six-coordinate ruthenium carbynes $[RuHCl(\equiv CCH_3)(PCy_3)_2(S)]A$ (S = Et_2O, H_2O, $PhNMe_2$) instead of the anticipated five-coordinate ruthenium vinylidenes $[RuCl(=C=CH_2)(PCy_3)_2(S)]A$.[5] These cationic ruthenium carbynes turned out to be highly efficient catalysts for

† Dedicated to Professor Akio Yamamoto on the occasion of his 70th birthday.

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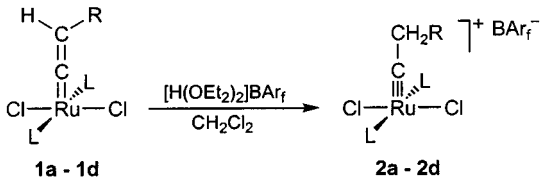
Scheme 1



	L	R
a	PCy_3	Ph
b	P*i*Pr_3	Ph
c	PCy_3	*t*Bu
d	P*i*Pr_3	*t*Bu

olefin metathesis, including the cross-olefin metathesis of cyclopentene with methylacrylate to afford multiply unsaturated esters $CH_2(C_5H_8)_nCHCO_2Me$ (n = 1−3). The cations $[RuHCl(\equiv CCH_3)(PCy_3)_2(S)]^+$, however, are rather labile and decompose in solution within 20 min at room temperature. For this reason, we set out to prepare more stable ruthenium carbynes in particular by using different ruthenium vinylidenes as precursors.

In this paper we report the synthesis of five-coordinate ruthenium carbyne complexes of the general composition $[RuCl_2(\equiv CCH_2R)L_2]BAr_f$ ($BAr_f^- = [B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) as well as a detailed study on the protonation of a series of vinylideneruthenium compounds containing carboxylato ligands. This work led to the observation of an equilibrium between isomeric carbene and carbyne metal complexes for which there is no precedence. Some preliminary results have already been communicated.[6]

Results and Discussion

Cationic Carbyne Complexes with $[RuCl_2(PR_3)_2]$ as a Molecular Unit. The ruthenium vinylidenes **1a**−**d**[7] were readily protonated with $[H(OEt_2)_2]BAr_f$ in dichloromethane to give the five-coordinate, cationic carbyne complexes **2a**−**d** in almost quantitative yields (Scheme 1). The products were isolated as pale yellow or beige, moderately air-stable solids by precipitation with pentane. Although the protonation could also be carried out with CF_3SO_3H or HBF_4, the BAr_f salts were easier to handle and obtained solvent-free in analytically pure form. While solutions of **2a** and **2b** (R = Ph) in chloroform (if rigorously dried) are stable for days at room temperature, solutions of **2c** and **2d** (R = *t*Bu) in $CHCl_3$ decompose in less than 24 h to give $[HL]^+BAr_f^-$ (L = PCy_3 or P*i*Pr_3) and some unidentified ruthenium-containing species. Compound **2d** must be prepared at low temperature due to its reduced stability.

Since it is known that in some cases the reaction of vinylidene transition-metal complexes with strong acids proceeds via the initial protonation at the metal center and the generation of a hydridometal species as an intermediate,[8] we also attempted to detect such a hydrido(vinylidene)ruthenium(II) cation $[RuHCl_2(=C=CHR)(PR_3)_2]^+$ in the course of the reaction of **1a**−**d** with $[H(OEt_2)_2]BAr_f$. However, due to the almost instantaneous formation of the cationic carbyne complexes even at low temperatures, these experiments failed. We note that although $[H(OEt_2)_2]BAr_f$ has been used as the acid for protonation, the isolated products **2a**−**d** do not contain an ether molecule, which is in contrast to the related cationic carbynes $[RuHCl(\equiv CCH_3)(PCy_3)_2(S)]^+$, where a solvent molecule is coordinated to attain the coordination number six for ruthenium(II).

The formation of **2a**−**d** is reversible. The cationic carbyne complexes are readily deprotonated even by weak bases such as NEt_3 to give the parent metal vinylidenes. Moreover, donor solvents such as acetone, THF, or alcohols also deprotonate **2a**−**d** to regenerate **1a**−**d**. Owing to this behavior, we were unable to carry out detailed studies about the reactivity of **2a**−**d** and could not prepare new ruthenium carbenes by reaction of the cationic ruthenium carbynes with nucleophiles.

The composition and configuration of complexes **2a**−**d** were confirmed not only by elemental analyses but also by NMR spectroscopy and the X-ray crystal structure analysis of **2b**. The ^1H NMR spectra (in $CDCl_3$) of the cationic carbynes display a characteristic triplet at δ 4.5 (R = Ph) or 3.3 (R = *t*Bu), which is assigned to the two protons of the CH_2R group. The ^{13}C NMR spectra of **2a**−**d** show the resonance of the C_α atom of the carbyne ligand as a triplet at δ 310 (R = Ph) or 317 (R = *t*Bu) and the signal of the CH_2 carbon atom as a singlet at δ 62 (R = Ph) or 72 (R = *t*Bu), respectively.

Complex **2b** crystallizes with two formula units and one molecule of dichloromethane in the asymmetric unit. The structure of one of the two independent cations is shown in Figure 1. The coordination geometry around the ruthenium center is distorted square-pyramidal with the carbyne carbon atom at the apical and the phosphorus and chloro atoms at the basal positions. The axes P1−Ru1−P2 and Cl1−Ru1−Cl2 are significantly bent and pointing away from the Ru1−C1 unit. The coordination geometry is nearly identical to that of the parent vinylidene complex **1b**, the only noticeable difference being the more pronounced bending of the P1−Ru1−P2 axis in **2b** than in **1b** [169.17(3)°].[7a] The most remarkable feature of the structure, however, is the distance Ru1−C1 [ca. 1.66 Å], which is among the shortest metal−carbon bond lengths found for transition-metal carbynes.[3,9] Only a few compounds containing a Cr≡CR or Mn≡CR bond possess metal−carbon distances slightly below 1.70 Å, while the Os−C distances found in osmium carbyne complexes lie in the range 1.71−1.78 Å.[4b,g,10]

Catalytic Activity of 2a−d in Olefin Metathesis. The carbyne complexes **2a** and **2b** are good catalyst

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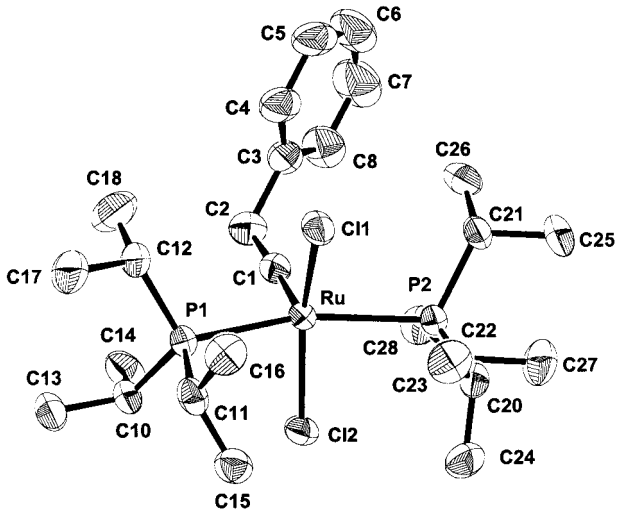
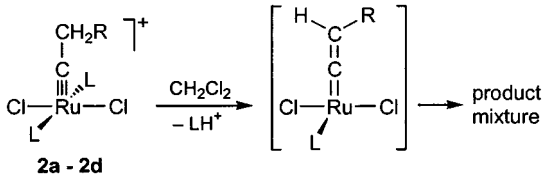


Figure 1. Molecular structure (ORTEP diagram) of one of the two independent cations of **2b**·1/2CH_2Cl_2. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Ru−C1 1.660(5), Ru−Cl1 2.3288(14), Ru−Cl2; 2.3218(14), Ru−P2 2.4749(17), Ru−P1 2.4541(16), C1−C2 1.481(7); C1−Ru−Cl2 100.98(17), C1−Ru−Cl1 101.58(17), Cl2−Ru−Cl1 157.44(6), C1−Ru−P1 97.17(16), Cl2−Ru−P1 88.25(5), Cl1−Ru−P1 88.77(5), C1−Ru−P2 102.26(16), Cl2−Ru−P2 85.69(5), Cl1−Ru−P2 89.73(5), P1−Ru−P2 160.42(5), C2−C1−Ru 176.9(4), C1−C2−C3 113.2(4).

Scheme 2



precursors for the ring-opening metathesis polymerization (ROMP) of cyclooctene. Solutions of cyclooctene and compounds **2a** or **2b** (1 mol %, 10 mM) in CH_2Cl_2 became viscous within ca. 6 h at 20 °C, and the complete consumption of the monomer took place after 20 h. During the catalysis, the only detectable ruthenium-containing species is the carbyne complex **2a** or **2b**, the concentration of which decreases only slightly after 6 h. The phosphonium salt $[HL]^+BAr_f^-$ (L = P*i*Pr$_3$ or PCy_3) can also be detected by NMR. This finding suggests that the formation of the catalytically active compound involves the elimination of one of the phosphine ligands of **2a,b** and that the 14-electron vinylidene complex, depicted in Scheme 2, is the real catalyst in the observed ROMP of cyclooctene. Compounds **2c** and **2d** exhibit a significantly lower catalytic activity in this process, which could be due to their reduced stability.

Six-Coordinate Vinylideneruthenium Compounds with Carboxylato Ligands. The preparation of a series of vinylideneruthenium(II) complexes containing carboxylato ligands was achieved by treatment of the starting material **1b** with RCO_2M, where M is Na, Tl, or Et_3NH, respectively (Scheme 3). However, both the conditions required for these reactions and the composition of the products significantly depend on the nature of the carboxylate.

The monosubstituted derivatives **3a** and **3b** with the relatively electron-rich formato and acetato ligands are formed exclusively from **1b** and an excess of RCO_2Na in THF. In contrast, the synthesis of compounds with the fluorinated carboxylates $CH_{3-n}F_nCO_2^-$ (n = 1−3) requires the use of the corresponding thallium salts. While the complete conversion of **1b** to **3c** occurs by stirring a solution of equimolar amounts of the dichloro complex, CH_2FCO_2Na, and CF_3SO_3Tl in THF for 5 days, treatment of **1b** with an excess of CH_2FCO_2Na leads, even after 12 days, only to partial conversion of **1b** to **3c**. Similar results were obtained if solutions of **1b** were treated with an excess of either CHF_2CO_2Na or CF_3CO_2Na in THF; in the latter case, a mixture of the mono- and the bis(carboxylato) complexes **3e** and **4b** was isolated together with some unreacted starting material.

The best method to prepare compounds **3d** and **3e** consists of the slow addition of a solution of CHF_2CO_2Tl or CF_3CO_2Tl in THF to a solution of **1b** in the same solvent. Under these conditions, the excess of the carboxylate in solution is minimized, and thus the formation of the disubstituted derivatives **4a** and **4b** occurs only to a small extent. Complex **3f** has been obtained by using 1 equiv of $PhCO_2H$ in the presence of Et_3N, while compounds **3g**−**j** containing substituted benzoates as ligands are prepared from **1b** and an excess of the corresponding sodium carboxylate in THF. The disubstituted complexes **4a** and **4b** are formed in ca. 80−85% yield upon treatment of **1b** with 2.5 equiv of CHF_2CO_2Tl or CF_3CO_2Tl, respectively, whereas the mixed bis(carboxylate) **4c** is generated by ligand exchange from **4b** and excess HCO_2Na.

Evidence for the chelating coordination of the respective RCO_2^- ligand in the monocarboxylato complexes is provided by the IR spectra of **3a**−**d**, **3f**, and **3g**, which display an absorption of medium intensity at around 1580−1520 cm^{-1}. This is assigned, according to reference data,[11] to the asymmetric ν(OCO) stretching frequency. While a corresponding absorption could not be observed in the IR spectra (in Nujol) of **4a** and **4b,** the presence of a unidentate carboxylato ligand in these compounds is indicated by the appearance of a ν_{as}(OCO) band at 1691 and 1701 cm^{-1}, respectively. The IR spectrum of the mixed complex **4c** shows an absorption at 1701 cm^{-1} arising from the unidentate trifluoroacetato and a second one at 1550 cm^{-1} arising from the chelating formato ligand. With regard to the NMR data, the most characteristic feature is the low-field signal for the C_α carbon atom of the vinylidene ligand in the ^{13}C NMR spectra at δ ca. 350 for **3a**−**j** and at δ ca. 360 for **4a**−**c**, which is in good agreement with the chemical shifts observed for other mononuclear vinylideneruthenium complexes.[7,12]

To confirm the coordination mode of the carboxylato ligands in compounds **4a** and **4b**, a variable-temperature (VT) ^{19}F NMR study has been carried out. The results illustrate not only that these complexes are

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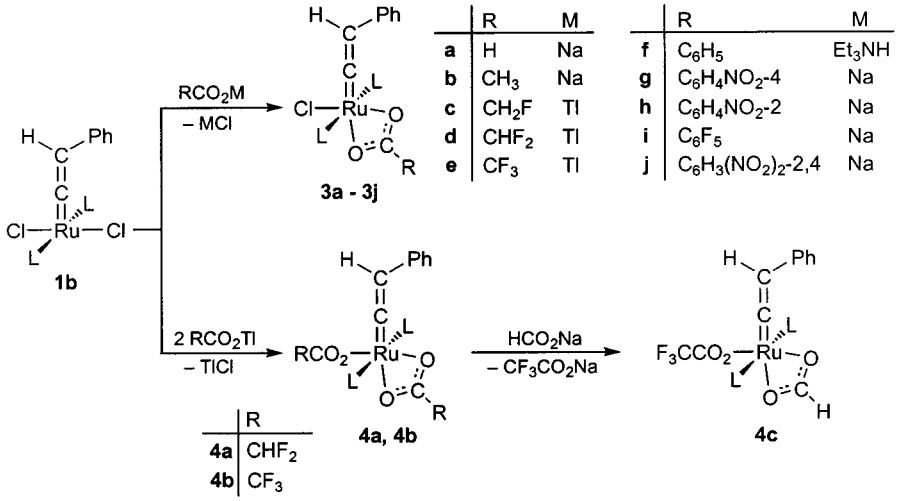
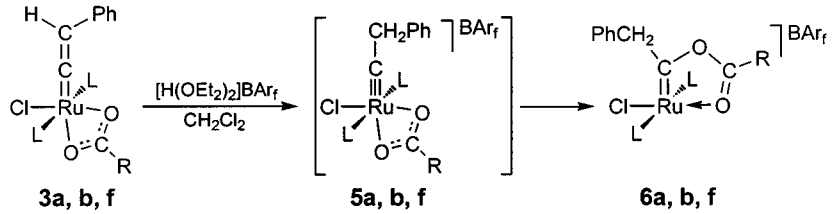
Scheme 3[a]



[a] L = P*i*Pr$_3$.

Scheme 4[a]



[a] L = P*i*Pr$_3$.

indeed six-coordinate with one unidentate and one bidentate carboxylate but also that in solution an interchange of the bonding mode between the two RCO_2^- units occurs. Thus, at 190 K, the $^{19}F\{^1H\}$ NMR spectrum of **4a** in CD_2Cl_2 displays two singlets at δ −123.2 and −126.1, which coalesce at 215 K and give rise at 293 K to one resonance at δ −124.5. Similarly, in the ^{19}F NMR spectrum of **4b** in CD_2Cl_2 at 180 K two broad singlets of equal intensity appear at δ −74.14 and −74.63, which coalesce at 200 K and give rise at 290 K to one singlet resonance at δ −74.75. By using the Eyring equation,[13] approximate values of $\Delta G^{\ddagger} = 9.1$ (**4a**) and 8.9 (**4b**) kcal mol^{-1} were calculated for the free activation energy of these exchange processes at the coalescence temperature. In contrast, analogous VT NMR measurements revealed that the mixed complex **4c**, containing one chelating formato and one monodentate trifluoroacetato ligand, is *not* fluxional in solution, probably due to the more favorable coordination ability of the formato compared to the trifluoroacetato moiety.

The formato compounds **3a** and **4c** undergo a decarboxylation reaction leading to the hydrido(vinylidene)-ruthenium derivatives [RuHCl(=C=CHPh)(P*i*Pr$_3$)$_2$] and [RuH(κ^2-O$_2$CCF$_3$)(=C=CHPh)(P*i*Pr$_3$)$_2$], which have been identified by their ^{1}H NMR spectra.[7b,14] The elimination of CO_2 takes place even at room temperature with the consequence that solutions of **3a** and **4c** always contain small amounts of the corresponding hydrido complex. If solutions of **3a** or **4c** in toluene containing 2 equiv of P*i*Pr$_3$ are stirred at 60 °C, complete decarboxylation of the HCO_2^- unit is achieved within 9 h (for **3a**) and 28 h (for **4c**), respectively. The generation of the hydrido-(vinylidene) compounds is always accompanied by the formation of small amounts of byproducts which could not be exactly identified.

Carbyne and Carbene Ruthenium Complexes from Carboxylato(vinylidene) Precursors. Similarly as described for the formation of **2a**−**d** (see Scheme 1), the reaction of the carboxylato compounds **3a**−**j** with [H(OEt$_2$)$_2$]BAr$_f$ affords cationic complexes, which can be isolated as the BAr$_f$ salts in good to excellent yields. While the analytical composition of these ionic products corresponds in all cases to that of an 1:1 adduct of the parent ruthenium vinylidene **3a**−**j** and HBAr$_f$, their nature depends quite remarkably on the basicity of the carboxylato ligand.

Protonation of [RuCl(κ^2-O$_2$CR)(=C=CHPh)(P*i*Pr$_3$)$_2$], where R = H, CH$_3$, C$_6$H$_5$. The protonation of compounds **3a**, **3b**, and **3f** containing the relatively electron-rich formato, acetato, or benzoato ligand leads to the formation of the cyclic carbene complexes **6a**, **6b**, and **6f**, which are the result of a nucleophilic attack of the carboxylato ligand to the C_α carbon atom of the initially generated ruthenium carbynes **5a**, **5b**, and **5f**, respectively (Scheme 4). For R = H, CH_3, and C_6H_5, these carbyne derivatives could not be detected by spectroscopic means.

The fact that the protonation takes place at the C_β carbon atom of the vinylidene ligand was confirmed by the ^{1}H and ^{13}C NMR data of **6a**, **6b**, and **6f**. In the ^{1}H NMR spectra, the resonance of the CH_2Ph protons appears as a somewhat broadened singlet (the broadening probably being due to unresolved coupling with the

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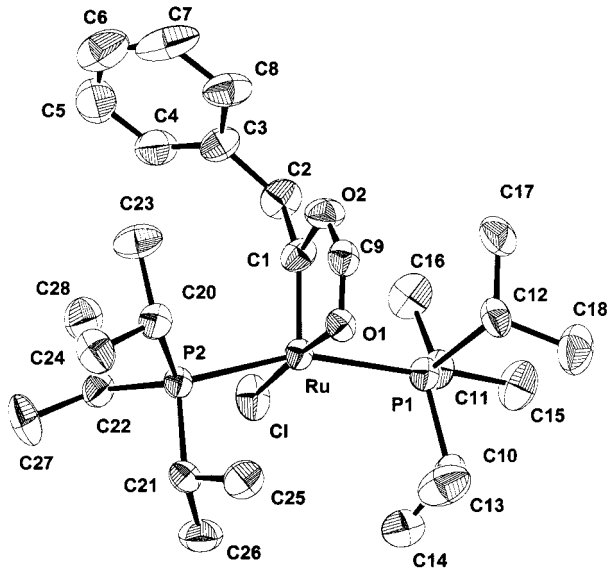
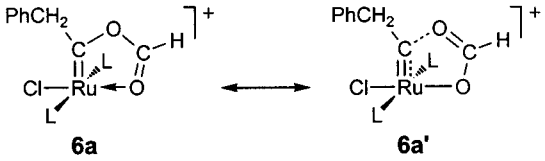


Figure 2. Molecular structure (ORTEP diagram) of the cation of **6a**. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Ru−C1 1.787(7), Ru−Cl 2.3306(17), Ru−O1 2.108(4), Ru−P1 2.4291(19), Ru−P2 2.4569(19), O1−C9 1.211(8), O2−C9 1.309(8), C1−O2 1.453(7), C1−C2 1.521(10); C1−Ru−O1 79.6(2), C1−Ru−Cl 105.5(2), C1−Ru−P1 97.2(2), C1−Ru−P2 103.4(2), Cl−Ru−O1 174.93(14), P1−Ru−P2 159.11(6), Cl−Ru−P1 88.36(6), Cl−Ru−P2 89.55(6), O1−Ru−P1 91.42(12), O1−Ru−P2 88.85(12), Ru−C1−C2 135.6(5), Ru−C1−O2 117.0(5), C2−C1−O2 107.2(6), C1−O2−C9 111.2(5), O1−C9−O2 122.3(6), Ru−O1−C9 109.9(4), C1−C2−C3 117.1(6).

^{31}P nuclei) at δ ca. 5.0, which is about 0.5 ppm downfield compared with the carbyne complexes **2a** and **2b**. Moreover, the signal of the HCO_2 proton of **6a** is a singlet and not a triplet, as was observed in the case of the parent vinylidene compound **3a**. The ^{13}C NMR spectra of **6a**, **6b**, and **6f** display a triplet at about δ 287, which is typical for a metal-coordinated carbene. Another typical feature is that the solid-state IR spectra of **6a**, **6b**, and **6f** do not show any bands assignable to a chelating carboxylato ligand.

The single-crystal X-ray structure analysis of **6a** (Figure 2) confirmed the formation of a metal carbene. The coordination geometry around the ruthenium center is distorted square-pyramidal with the carbene carbon at the apical position and the chlorine, the oxygen, and the two phosphorus atoms at the basal positions. In contrast to the Cl−Ru−O1 axis, which is almost linear, the P1−Ru−P2 axis is significantly bent, both phosphorus atoms pointing away from the Ru−C1 unit. An analogous square-pyramidal configuration has been found for the carbeneruthenium complexes $[RuCl_2(=CHCH_2Ph)(P\textit{i}Pr_3)_2]$[15] and $[RuCl_2(=CHR)(PCy_3)_2]$ (R = 4-C_6H_4Cl, $CH=CPh_2$)[16] as well as for the related vinylidene derivatives $[RuCl_2(=C=CHPh)L_2]$ (L = $P\textit{i}Pr_3$, PCy_3).[7] Compared with $[RuCl_2(=CHCH_2Ph)(P\textit{i}Pr_3)_2]$ and $[RuCl_2(=CHR)(PCy_3)_2]$, the bond length Ru−C1 in **6a** is rather short, whereas the distance C1−O2 is ca. 0.07−0.15 Å longer than in Fischer-type ruthenium carbenes containing a Ru=C(OR)R′ moiety.[9] The plane of the chelate ring formed by Ru, C1, O2, C9, and O1 (main deviation from planarity 0.017 Å) lies essentially perpendicular to the plane containing the ruthenium and phosphorus atoms, which probably minimizes the steric repulsion between the ring atoms and the isopropyl groups.

Scheme 5[a]



[a] L = P*i*Pr$_3$.

Regarding the rather long C1−O2 distance of 1.453(7) Å, we assume that the $p_\pi(O)\rightarrow p_\pi(C)$ bond component usually present in alkoxycarbene metal complexes is strongly reduced in **6a** and that the C1−O2 bond is relatively weak. This interpretation is supported by the short Ru−C1 distance, which reflects some *carbyne* character for the metal-to-carbon bond. Therefore, for an adequate description of the bonding in **6a**, also the resonance form **6a′** should be considered as indicated in Scheme 5. This resonance form would represent an intermediate stage between a five-membered chelate ring and a separated Ru(κ^1-O_2CH)($\equiv CCH_2Ph$) unit. We note in this context that the distances C9−O2 of 1.309(8) Å and C9−O1 of 1.211(8) Å in **6a** are slightly shorter or longer, respectively, than the average C−O and C=O distances in carboxylic esters (1.336 and 1.196 Å).[17]

The formation of Fischer-type carbene complexes via attack of a nucleophile on a metal-bonded carbyne is a well-established reaction.[3,18] The conversion of the Ru(κ^2-O_2CR)($\equiv CR'$) fragment into the cyclic carbene Ru{=C(R′)OC(O)R}, which occurs during the formation of **6a**, **6b**, and **6f**, represents a particular variant of this reaction with the nucleophile being already present in the starting material. However, to the best of our knowledge, this kind of rearrangement had not been observed before. Recently, Esteruelas et al. reported that the related carbyneosmium complexes $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CR)(P\textit{i}Pr_3)_2]BF_4$, with R = $CH=C(CH_3)_2$, $CH_2\textit{t}Bu$, and CH_3, are kinetically stable and do not rearrange to a cyclic osmium carbene.[19] There exist some similarities, however, between **6a**, **6b**, and **6f** and the compounds $[(\eta^5\text{-}C_5H_5)Ru\{C(=CHCO_2CH_3)OC(O)CH_3\}(PPh_3)]$,[20] $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)(acetone)(P\textit{i}Pr_3)_2]BF_4$,[21] and $[RuCl\{C(=CHPh)OC(O)CH_2CH_3\}(CO)(PPh_3)_2]$,[22] which all contain a five-membered Ru−C−O−C−O ring generated by nucleophilic attack of a metal-bonded carboxylate to the C_α carbon atom of a vinylidene ligand.

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(19) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949−4959.
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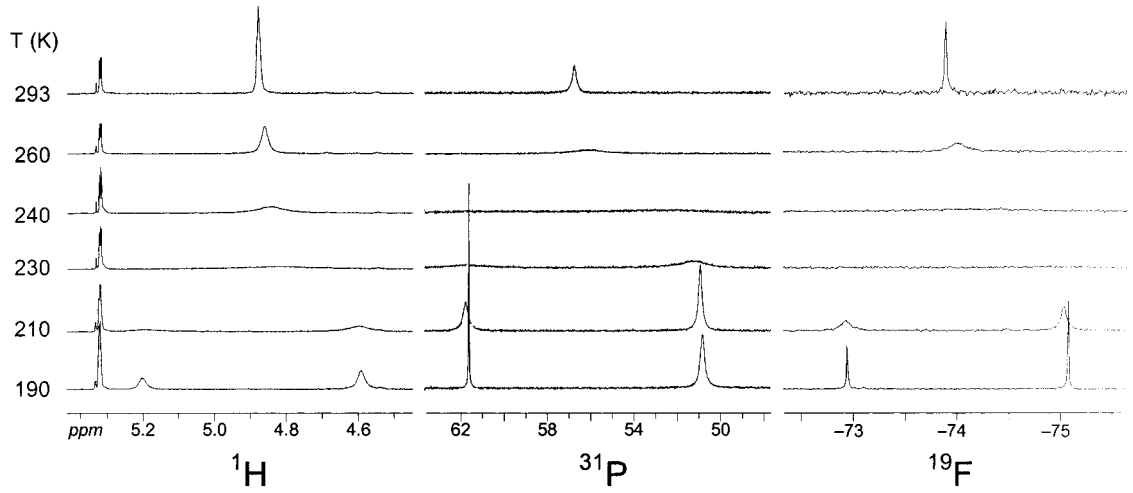
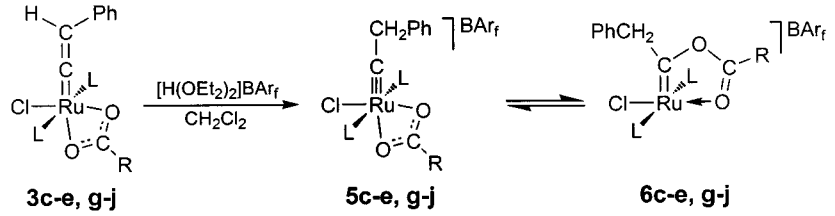


Figure 3. Variable-temperature ^{1}H (resonance of the CH_2Ph protons), ^{31}P, and ^{19}F NMR spectra for the equilibrium between **5e** and **6e**.

Scheme 6[a]



[a] L = P*i*Pr$_3$.

Since also in these compounds relatively short Ru−C$_\alpha$ and relatively long C$_\alpha$−O bond distances have been encountered, it has been assumed that the Ru{C(=CHR)OC(O)R′} unit represents an intermediate stage between a five-membered chelate ring and a Ru(κ^1-O$_2$CR)(=C=CHR′) fragment, the carbonyl group of the carboxylato ligand being en route to nucleophilic attack to the C$_\alpha$ vinylidene carbon atom. The complex [RuCl{=C(CH$_2$Ph)OC(O)CH$_3$}(CO)(P*i*Pr$_3$)$_2$]BF$_4$ with the same carbene ligand as in **6b** had previously been described but was not structurally characterized.[21]

Protonation of Vinylideneruthenium Compounds Containing Electron-Poor Carboxylato Ligands. Following the observation that the interaction of the formato ligand with the C$_\alpha$ carbon atom in **6a** is relatively weak, we wondered what the behavior of the starting materials containing a carboxylato ligand with an electron-withdrawing substituent R toward [H(OEt$_2$)$_2$]BAr$_f$ is. We took into consideration that those substituents could disfavor the nucleophilic attack at the Ru≡C unit and could thus allow the isolation (or at least the spectroscopic characterization) of six-coordinate carbyneruthenium complexes.

The protonation of compounds **3c**−**e** and **3g**−**j**, which all contain a relatively electron-poor carboxylato ligand, furnishes always an equilibrium between the respective carbyne **5** and the isomeric, cyclic carbene **6** (see Scheme 6). The existence of this equilibrium was established by VT NMR measurements. As an example, the ^{1}H, ^{31}P, and ^{19}F NMR spectra of the product obtained by protonation of **3e** (R = CF$_3$) with [H(OEt$_2$)$_2$]BAr$_f$ in CD$_2$Cl$_2$ at different temperatures are shown in Figure 3. At 190 K, the ^{1}H NMR spectrum displays two broad signals at δ 5.20 and 4.59 in the approximate ratio of 1:2. The comparison of the chemical shifts of these signals with those of the CH$_2$ protons of the metal carbynes **2a** and **2b** on one side and the metal carbenes **6a**, **6b**, and **6f** on the other allows us to assign the more intense resonance at δ 4.59 to the carbyne **5e** and the other at δ 5.20 to the carbene **6e**. These two signals coalesce at 225 K and, by raising the temperature to 290 K, give rise to a singlet at δ 4.88. The ^{19}F NMR spectrum displays at 190 K two sharp singlets at δ −72.9 and −75.1, which correspond to the fluorine atoms of the CF$_3$ group of **6e** and **5e**, respectively. These signals coalesce at 230 K and at 290 K give rise to one singlet resonance at δ −73.9. Similarly, the ^{31}P NMR spectrum shows at 200 K two singlets at δ 61.7 (**5e**) and 50.8 (**6e**), which coalesce at 250 K and at 290 K exhibit a broad signal at δ 56.7.

In the same way as described for **5e**/**6e**, VT ^{1}H, ^{31}P, and, if possible, ^{19}F NMR measurements established the existence of equilibria between the respective carbene and carbyne complexes containing carboxylato ligands RCO$_2^-$ with CH$_2$F, CHF$_2$, C$_6$F$_5$, or various substituted phenyl groups R. Well below the coalescence temperature, in the ^{1}H NMR spectra the resonances for the CH_2Ph protons appear (in CD$_2$Cl$_2$) invariably in a very narrow range at around δ 4.5 for the carbyne complexes **5** and at around δ 5.0 for the cyclic carbenes **6**. This result allowed in all cases the unequivocal identification of the isomers **5** and **6**. The complete set of ^{13}C NMR data could be obtained for the major isomers **6c**, **5d**, and **6g**−**i** as well as for both **5j** and **6j** at low temperatures (see Experimental Section). In these spectra, the resonance for the carbene carbon atom always appears as a triplet between δ 284.4 and 286.8, and that is at almost the same chemical shift as found for the isolated

Table 1. Parameters for the Equilibria between the Carbyne Complexes 5 and the Isomeric Cyclic Carbenes 6[a]

	R	pK_a of RCO_2H	x_5	x_6	T_c	$\Delta G^{\ddagger}_{5\to6}$	$\Delta G^{\ddagger}_{6\to5}$	ΔG_0
a	H	3.75	0	1.00				
b	CH_3	4.76	0	1.00				
c	CH_2F	2.59	0.10	0.90	280	13.1	14.3	1.2
d	CHF_2	1.34	0.88	0.12	240	12.0	11.1	−0.9
e	CF_3	0.23	0.65	0.35	225	10.6	10.3	−0.3
f	C_6H_5	4.19	0	1.00				
g	$C_6H_4NO_2$-4	3.41	<0.05	>0.95				
h	$C_6H_4NO_2$-2	2.16	<0.05	>0.95				
i	C_6F_5	1.52	0.05	0.95	270	12.4	14.0	1.6
j	$C_6H_3(NO_2)_2$-2,4	1.42	0.35	0.65	270	12.5	12.8	0.3

[a] x denotes the relative concentration of the complexes **5** and **6**; T_c in K; ΔG in kcal mol^{-1}.

ruthenium carbenes **6a**, **6b**, and **6f**. In contrast, the signal for the carbyne carbon atom of **5d** and **5j** is observed at δ 330.0 and 330.8, respectively. It should be mentioned that the complete set of ^{13}C NMR data for compounds **5e** and **6e** could not be obtained because at the temperature required for the decoalescence of the respective signals (below 243 K) the carbyne complex **5e** already precipitates from the solution.

As anticipated, the isomers **5** and **6** differ in their free energies and their relative amounts at the equilibrium. The latter were determined by the integration of the signals of the CH_2 protons and, for the products with the carboxylates $CH_{3-n}F_nCO_2^-$ (n = 1−3) as ligands, also by integrating the corresponding resonances of the fluorine atoms in the ^{19}F NMR spectrum. The difference in the free energy ΔG_0 between the two isomers was calculated by using the Boltzmann equation.[13] Moreover, on the basis of the method reported by Shanan-Atidi and Bar-Eli,[23] the VT NMR measurements also allowed the determination of the free energies of activation $\Delta G^{\ddagger}_{5\to6}$ and $\Delta G^{\ddagger}_{6\to5}$ at the temperature of coalescence T_c. Table 1 summarizes the parameters for the equilibria between the isomers **5** and **6**. The pK_a values of the corresponding carboxylic acids RCO_2H in aqueous solution, which reflect the electron-withdrawing character of the group R, are also included in order to provide a basis for the discussion of the observed differences.

Figure 4 illustrates the relation between the basicity of the carboxylato ligand and the relative amount of the isomers **5** and **6**. For the two equilibria **5g**/**6g** and **5h**/**6h**, the concentration of the respective carbyne complex was very low and, therefore, it was not possible to determine with good accuracy both the ratio between the two isomers and the temperature of coalescence.

To analyze the data shown in Table 1 and Figure 4, it is convenient to consider two separate series of compounds: that with the acetato (**b**−**e**) and that with the benzoato ligands (**f**−**j**). For the first series with **c**−**e**, the coalescence temperature and the activation energies $\Delta G^{\ddagger}_{5\to6}$ and $\Delta G^{\ddagger}_{6\to5}$ increase with the basicity of the carboxylate $CH_{3-n}F_nCO_2^-$. This means that both the chelating coordination of the substituted acetate and the formation of the cyclic carbene are energetically more favored if the basicity of the anionic ligand increases. In other words, the more basic carboxylates form

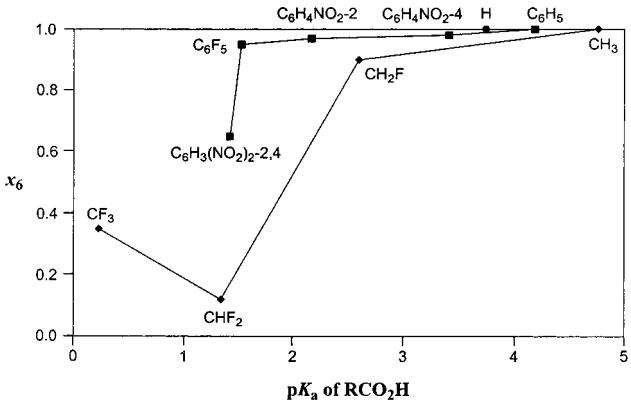


Figure 4. Relative concentration of the cyclic carbene **6** (x_6) versus pK_a of RCO_2H.

stronger Ru−O and C−O bonds, which is in agreement with the expected tendency. However, the relative amount of **5** and **6** indicates that with increasing basicity of the anion $CH_{3-n}F_nCO_2^-$ the formation of the cyclic carbene with one Ru−O and one C−O bond is favored *to a greater extent* than that of the carbyne with two Ru−O bonds. The only deviation from this tendency is found for the equilibrium **5d**/**6d** (R = CHF_2), for which we have no explanation. With regard to the second series (**f**−**j**), it appears that the substituted benzoates form stronger Ru−O and C−O bonds than the fluorinated acetates having a comparable basicity and thus prefer in all cases the formation of the cyclic carbene **6**.

The product isolated as a solid is in most cases the pure major isomer. Addition of pentane to a dichloromethane solution containing both isomers leads to the precipitation of the deeply colored carbene complexes **6c** (orange), **6g** (dark green), **6h**, **6i** (both dark violet), and **6j** (olive-green) and of the yellow carbyne **5e**. For R = CHF_2, an orange solid is obtained, which contains both **5d** and **6d** according to the solid-state IR spectrum (see Experimental Section). However, a pure sample of yellow **5d** has been obtained by slow crystallization from a solution in dichloromethane at −78 °C.

The result of the X-ray crystal structure analysis of **5e** is shown in Figure 5. The diagram reveals that the ruthenium center possesses a distorted octahedral coordination sphere with a significant bending of the C1−Ru−O1 axis. Both the Cl1−Ru−O2 and P1−Ru−P2 axes with the bond angles of, respectively, 161.45(9)° and 169.94(4)° are bent away from the Ru−C1 unit. The four-membered ring Ru−O1−C70−O2 is exactly planar and lies almost perpendicular to the P1−Ru1−P2 plane. However, the most noteworthy structural feature is that the trifluoroacetato ligand is unsymmetrically coordinated. While the Ru−O2 distance [2.133(3) Å] corresponds to a Ru−O single bond, the distance Ru−O1 [2.336(3) Å] is considerably longer. Moreover, the small bite of the trifluoroacetato ligand accounts for the O1−Ru−O2 angle of 58.56(11)°. A similar coordination geometry for ruthenium and a related bonding situation of the trifluoroacetato ligand have been found in the enynylruthenium(II) compound [Ru{C(=CHPh)(C≡CPh)}(κ^2-O_2CCF_3)(CO)(PPh_3)$_2$], where the bond lengths Ru−O1 and Ru−O2 are 2.353 and 2.234 Å, respectively.[24] The angle Ru−C1−C2 of 173.0(4)° is nearly linear, as expected for a sp-hybridized

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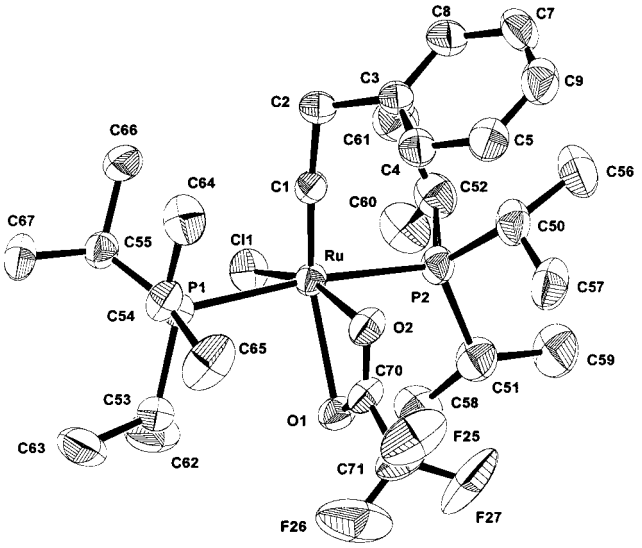
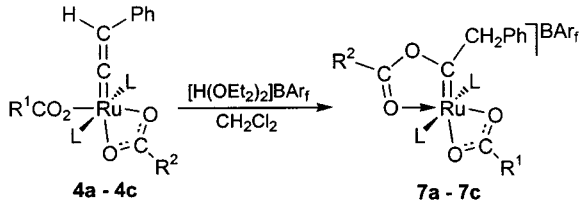


Figure 5. Molecular structure (ORTEP diagram) of the cation of **5e**. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Ru−C1 1.660(4), Ru−Cl 2.3143(11), Ru−O1 2.336(3), Ru−O2 2.133(3), Ru−P1 2.4823(11), Ru−P2 2.4922(11), C1−C2 1.489(6), C2−C3 1.524(7), O1−C70 1.244(5), O2−C70 1.253(5); C1−Ru−O1 154.74(16), C1−Ru−O2 96.18(16), C1−Ru−Cl 102.35(15), C1−Ru−P1 95.06(14), C1−Ru−P2 93.40(14), O1−Ru−O2 58.56(11), O1−Ru−Cl 102.90(8), O1−Ru−P1 86.58(8), O1−Ru−P2 88.09(8), O2−Ru−Cl 161.45(9), O2−Ru−P1 92.23(9), O2−Ru−P2 92.26(9), Cl−Ru−P1 85.23(4), Cl−Ru−P2 87.66(4), P1−Ru−P2 169.94(4), Ru−C1−C2 173.0(4), C1−C2−C3 110.9(4), Ru−O1−C70 84.8(2), Ru−O2−C70 93.8(3), O1−C70−O2 122.9(4).

Scheme 7[a]



	R^1	R^2
a	CHF_2	CHF_2
b	CF_3	CF_3
c	CF_3	H

[a] L = P*i*Pr$_3$.

carbyne carbon atom. We also note that the distance Ru−C1 of 1.660(4) Å is almost identical to that of the carbynedichloro complex **2b** (see above).

Protonation of Vinylideneruthenium Complexes Containing Two Carboxylato Ligands. The protonation of compounds **4a**−**c** with $[H(OEt_2)_2]BAr_f$ in dichloromethane proceeds at low temperature to give the six-coordinate carbene complexes **7a**−**c** in 75−99% yield (Scheme 7). They were isolated as pale yellow (**7b**) or orange (**7a**, **7c**) microcrystalline solids by precipitation with pentane. The formation of **7c** involves the nucleophilic attack of the formato ligand to the C_α carbon atom of a metal carbyne intermediate and also the change of coordination mode of the trifluoroacetato ligand from mono- to bidentate. The ^{1}H NMR spectra of **7a**−**c** show the signal of the CH_2 protons at δ 5.07, 5.24, and 5.04, respectively, and that is at almost the same chemical shift as found for the corresponding five-coordinate carbene complexes **6d**, **6e**, and **6a**, having the same Ru{=C(CH_2Ph)OC(O)R} unit. The ^{13}C NMR spectra of **7a**−**c** display a low-field resonance at about δ 295−331, which is assigned to the carbene carbon atom and is thus in agreement with the proposed structure.

A variable-temperature ^{19}F NMR study revealed that both **7a** and **7b** are fluxional in solution. The ^{19}F{^{1}H} NMR spectrum of **7a** shows at 200 K two singlets at δ −123.7 and −125.4, which correspond to two different difluoroacetate groups. By comparing these chemical shifts with those of the CHF_2CO_2 group of the carbyne **5d** (δ −126.7) and the carbene **6d** (δ −123.0), it is possible to assign the signal at δ −125.4 to the chelating difluoroacetato ligand and that at δ −123.7 to the difluoroacetate group generating the five-membered ring. The two signals coalesce at 255 K, and by raising the temperature to 290 K a somewhat broadened singlet is observed at δ −124.9. Similarly, the ^{19}F{^{1}H} NMR spectrum of **7b** displays at 180 K two singlets at δ −74.3 for the Ru(κ^2-O_2CCF_3) and at δ −72.5 for the Ru,C-bonded CF_3CO_2 unit. These signals coalesce at 240 K and at 290 K give rise to a singlet at δ −73.4. Using the Eyring equation,[13] approximate values $\Delta G^{\ddagger} = 11.2$ (**7a**) and 10.5 (**7b**) kcal mol^{-1} were calculated for the activation energies of the exchange processes at the coalescence temperature. Unlike **7a** and **7b**, complex **7c** is *nonfluxional* in solution.

As already discussed for compounds **2a**−**d**, also the formation of complexes **5**/**6** and **7** is reversible. The carbene and carbyne metal cations react either with 1 equiv of NEt_3 in dichloromethane or with a coordinating solvent such as THF to regenerate the parent metal vinylidenes. With the noteworthy exception of compound **6f** (R = Ph), which is stable in dichloromethane or chloroform solution at room temperature for at least 24 h, all the other complexes of the series **5**/**6** decompose within ca. 2 h to afford the salt [HP*i*Pr$_3$]BAr_f together with some unidentified ruthenium-containing species. We note that none of the carbene and carbyne complexes of the series **5**/**6** and **7** are catalytically active in ROMP of cyclooctene.

Conclusions

The work presented in this paper has shown that, by using $[H(OEt_2)_2]BAr_f$ as the proton source, neutral five- or six-coordinate vinylidene complexes of the general composition $[RuCl_2(=C=CHR)(L)_2]$ (**2**), $[RuCl(\kappa^2\text{-}O_2CR)(=C=CHPh)(P{i}Pr_3)_2]$ (**3**), and $[Ru(\kappa^1\text{-}O_2CR^1)(\kappa^2\text{-}O_2CR^2)(=C=CHPh)(P{i}Pr_3)_2]$ (**4**) can be protonated at the C_β carbon atom of the vinylidene ligand. The observation that in all cases the protonation is reversible and that only very weak bases are needed to deprotonate the cationic species illustrates the weak basic character of the =CHR vinylidene unit.

The type of products resulting from the protonation critically depends on the anionic ligands present in the starting material. While the reaction of the dichloro complexes **1** with $[H(OEt_2)_2]BAr_f$ affords exclusively the five-coordinate ruthenium carbynes $[RuCl_2(\equiv CCH_2R)L_2]BAr_f$ (**2**), the protonation of the monocarboxylato

(24) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M. B.; New, L. *Polyhedron* **1985**, *4*, 1119−1130.

derivatives **3** leads predominantly to an equilibrium mixture of the six-coordinate carbyne complex [RuCl(κ^2-O_2CR)(≡CCH_2Ph)($PiPr_3$)$_2$]BAr_f (**5**) and the isomeric five-coordinate cyclic carbene [RuCl{=$C(CH_2Ph)OC(O)R$}($PiPr_3$)$_2$]BAr_f (**6**). The position of this equilibrium depends on the basicity of the carboxylato ligand, thereby the more basic carboxylates favoring the formation of the cyclic ruthenium carbene **6** versus the isomeric ruthenium carbyne **5**. The six-coordinate carbene complexes [Ru(κ^2-O_2CR){=$C(CH_2Ph)OC(O)R$}($PiPr_3$)$_2$]BAr_f (**7a** and **7b**), obtained by protonation of the corresponding biscarboxylato compounds **4a** and **4b**, undergo a fluxional process in solution which leads to an exchange of the bonding mode between the two carboxylato ligands. This process is closely related to the equilibrium reaction between **5** and **6**, and in fact the activation energies found for the dynamics of **7a** and **7b** are very similar to those of the equilibria **5d**/**6d** and **5e**/**6e**. The result that the protonation of the mixed biscarboxylate **4c** gives exclusively the chelate complex [Ru(κ^2-O_2CCF_3){=$C(CH_2Ph)OC(O)H$}($PiPr_3$)$_2$]BAr_f (**7c**), in which the more basic formate forms the cyclic carbene unit, is in agreement with the observed tendency.

Experimental Section

General Considerations. All experiments were carried out under an atmosphere of argon using Schlenk techniques. The starting materials **1a**−**d**[7] and [H(OEt_2)$_2$]BAr_f[25] were prepared as previously described. CH_2FCO_2Na was a product from Aldrich. CHF_2CO_2Tl and CF_3CO_2Tl were obtained upon treatment of CHF_2CO_2H (ABCR) and CF_3CO_2H (Riedel-deHaën) with Tl_2CO_3 in THF. The sodium benzoates 2-$NO_2C_6H_4CO_2Na$, 4-$NO_2C_6H_4CO_2Na$, 2,4-$(NO_2)_2C_6H_3CO_2Na$, and $C_6F_5CO_2Na$ were prepared from the corresponding benzoic acids (Aldrich) and Na_2CO_3 in THF. Technical grade solvents were dried by standard procedures and distilled under argon before use. $CDCl_3$ was dried over Al_2O_3 (basic, activity grade I), and C_6D_6 as well as CD_2Cl_2 over 4 Å molecular sieves. NMR spectra were recorded on Bruker AC 200 or AMX 400 instruments usually at 293 K, unless otherwise indicated. Chemical shifts are referred to TMS (^{1}H and ^{13}C{H}), 85% H_3PO_4 (^{31}P{^{1}H}), or $CFCl_3$ (^{19}F{^{1}H}). Abbreviations: app = apparent, vt = virtual triplet, dvt = doublet of virtual triplets, $N = {}^3J_{PH} + {}^5J_{P'H}$ for ^{1}H NMR and $N = {}^1J_{PC} + {}^3J_{P'C}$ for ^{13}C{H} NMR data. The ^{13}C{H} NMR resonances of the BAr_f^- anion are not given. The ^{1}H and ^{19}F NMR data for the equilibria between compounds **5** and **6** include fractional integrated values for some of the signals, which are referred to the integrated values of the signals arising from the BAr_f^- anion. IR spectra were recorded on a Bruker IFS 25 spectrophotometer. Melting points were determined by DTA.

Preparation of [$RuCl_2$(≡CCH_2Ph)(PCy_3)$_2$]BAr_f (2a). To a solid mixture of **1a** (254 mg, 0.30 mmol) and [H(OEt_2)$_2$]BAr_f (308 mg, 0.30 mmol) was added CH_2Cl_2 (8 mL). After the suspension was stirred for 5 min, an orange-yellow solution was obtained. The solution was concentrated to ca. 4 mL in vacuo, and upon addition of pentane (20 mL) a pale yellow solid precipitated. The mother liquor was decanted, and the remaining solid was washed with pentane (5 mL) and dried: yield 519 mg (99%); mp 141 °C dec. Anal. Calcd for $C_{76}H_{85}BCl_2F_{24}P_2Ru$: C, 53.72; H, 5.04. Found: C, 53.48; H, 4.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (br m, 8H, *ortho*-H of Ar_f), 7.53 (br m, 4H, *para*-H of Ar_f), 7.40 (m, 3H, C_6H_5), 7.09 (m, 2H, C_6H_5), 4.51 (t, $^4J_{PH}$ = 2.9 Hz, 2H, CH_2Ph), 2.85 (m, 6H, C*H* of C_6H_{11}), 1.93−1.10 (br m, 60H, CH_2 of C_6H_{11}). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 309.7 (t, $^2J_{PC}$ = 4.4 Hz, Ru≡C), 130.2, 130.1, 128.7, 126.4 (all s, C_6H_5), 62.3 (s, *C*H_2Ph), 33.8 (vt, N = 10.2 Hz, C1 of C_6H_{11}), 30.3 (s, C3, C5 of C_6H_{11}), 27.5 (vt, N = 6.4 Hz, C2, C6 of C_6H_{11}), 25.8 (s, C4 of C_6H_{11}). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 55.4 (s).

Preparation of [$RuCl_2$(≡CCH_2Ph)($PiPr_3$)$_2$]BAr_f (2b). This complex was prepared as described for **2a**, starting from **1b** (143 mg, 0.24 mmol) and [H(OEt_2)$_2$]BAr_f (243 mg, 0.24 mmol). Pale yellow solid: yield 331 mg (95%); mp 118 °C dec. Anal. Calcd for $C_{58}H_{61}BCl_2F_{24}P_2Ru$: C, 47.75; H, 4.21. Found: C, 47.48; H, 4.02. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71 (br m, 8H, *ortho*-H of Ar_f), 7.53 (br m, 4H, *para*-H of Ar_f), 7.40 (br m, 3H, C_6H_5), 7.16 (m, 2H, C_6H_5), 4.49 (t, $^4J_{PH}$ = 2.7 Hz, 2H, CH_2Ph), 3.06 (m, 6H, PC*H*CH_3), 1.30 (dvt, N = 15.7, $^3J_{HH}$ = 7.3 Hz, 36H, PCHCH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 310.0 (t, $^2J_{PC}$ = 5.1 Hz, Ru≡C), 130.3, 130.2, 129.2, 125.9 (all s, C_6H_5), 62.4 (s, *C*H_2Ph), 24.6 (vt, N = 10.8 Hz, P*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 62.6 (s).

Preparation of [$RuCl_2$(≡CCH_2tBu)(PCy_3)$_2$]BAr_f (2c). This complex was prepared as described for **2a**, starting from **1c** (216 mg, 0.27 mmol) and [H(OEt_2)$_2$]BAr_f (268 mg, 0.27 mmol). Beige solid: yield 337 mg (96%); mp 132 °C dec. Anal. Calcd for $C_{74}H_{89}BCl_2F_{24}P_2Ru$: C, 52.93; H, 5.34. Found: C, 52.61; H, 5.06. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73 (br m, 8H, *ortho*-H of Ar_f), 7.56 (br m, 4H, *para*-H of Ar_f), 3.33 (t, $^4J_{PH}$ = 3.3 Hz, 2H, CH_2*t*Bu), 2.88 (br, 6H, C*H* of C_6H_{11}), 2.18−1.42 (br m, 60H, CH_2 of C_6H_{11}), 1.17 (s, 9H, CCH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 317.0 (t, $^2J_{PC}$ = 3.8 Hz, Ru≡C), 72.3 (s, *C*H_2*t*Bu), 38.7 (s, *C*CH_3), 34.2 (vt, N = 10.1 Hz, C1 of C_6H_{11}), 30.8 (s, C*C*H$_3$), 30.4 (s, C3, C5 of C_6H_{11}), 27.4 (vt, N = 5.1 Hz, C2, C6 of C_6H_{11}), 25.7 (s, C4 of C_6H_{11}). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 52.9 (s).

Preparation of [$RuCl_2$(≡CCH_2tBu)($PiPr_3$)$_2$]BAr_f (2d). To a solid mixture of **1d** (101 mg, 0.18 mmol) and [H(OEt_2)$_2$]BAr_f (173 mg, 0.17 mmol) was added CH_2Cl_2 (2.5 mL) at −78 °C. After the suspension was stirred and allowed to warm to −20 °C, a brown solution was obtained. Addition of pentane (15 mL) led to the precipitation of a beige solid, which was separated from the mother liquor, washed with pentane (3 × 10 mL), and dried in vacuo: yield 224 mg (89%); mp 102 °C dec. Anal. Calcd for $C_{56}H_{65}BCl_2F_{24}P_2Ru$: C, 46.75; H, 4.55. Found: C, 46.68; H, 4.25. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73 (br m, 8H, *ortho*-H of Ar_f), 7.55 (br m, 4H, *para*-H of Ar_f), 3.31 (t, $^3J_{PH}$ = 3.5 Hz, 2H, CH_2*t*Bu), 3.11 (m, 6H, PC*H*CH_3), 1.41 (dvt, N = 15.3, $^3J_{HH}$ = 7.3 Hz, 36H, PCHCH_3), 1.19 (s, 9H, CCH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 278 K): δ 317.7 (t, $^2J_{PC}$ = 3.8 Hz, Ru≡C), 72.2 (s, *C*H_2*t*Bu), 38.8 (s, *C*CH_3), 30.9 (s, C*C*H$_3$), 24.9 (vt, N = 10.8 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 58.9 (s).

Preparation of [RuCl(κ^2-O_2CH)(=C=CHPh)($PiPr_3$)$_2$] (3a). A solution of **1b** (693 mg, 1.16 mmol) in THF (25 mL) was treated with HCO_2Na (780 mg, 11.47 mmol), and the resulting suspension was stirred for 22 h at room temperature. The solvent was removed, and the residue was extracted with diethyl ether (2 × 20 mL). The combined extracts were evaporated in vacuo to give an orange solid, which was washed with pentane (2 × 5 mL) at −78 °C and dried: yield 543 mg (77%); mp 77 °C dec. Anal. Calcd for $C_{27}H_{49}ClO_2P_2Ru$: C, 53.68; H, 8.18. Found: C, 53.49; H, 8.18. IR (Nujol): ν(C=C) 1615, ν_{as}(OCO) 1570 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.56 (t, $^4J_{PH}$ = 1.8 Hz, 1H, HCO_2), 7.15 (m, 4H, C_6H_5), 6.89 (m, 1H, C_6H_5), 4.92 (t, $^4J_{PH}$ = 3.3 Hz, 1H, =C*H*Ph), 2.67 (m, 6H, PC*H*CH_3), 1.27, 1.22 (both dvt, N = 13.2, $^3J_{HH}$ = 6.9 Hz, 18H, PCHCH_3). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 351.0 (t, $^2J_{PC}$ = 14.6 Hz, Ru=C), 174.1 (s, HCO_2), 133.6 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.6, 125.4, 124.3 (all s, C_6H_5), 110.5 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 22.9 (vt, N = 9.5 Hz, P*C*HCH$_3$), 19.8, 19.6 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 25.3 (s).

Preparation of [RuCl(κ^2-O_2CCH_3)(=C=CHPh)($PiPr_3$)$_2$] (3b). This complex was prepared as described for **3a**, starting from **1b** (819 mg, 1.38 mmol) and $CH_3CO_2Na{\cdot}3H_2O$ (400 mg, 2.94 mmol). Orange microcrystalline solid: yield 789 mg (82%); mp 128 °C dec. Anal. Calcd for $C_{28}H_{51}ClO_2P_2Ru$: C, 54.40; H, 8.32. Found: C, 54.49; H, 8.03. IR (Nujol): ν(C=C) 1610, ν_{as}-

(OCO) 1553 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.17 (m, 4H, C_6H_5), 6.88 (m, 1H, C_6H_5), 4.93 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 2.67 (m, 6H, PC*H*CH_3), 1.72 (s, 3H, CH_3CO_2), 1.27 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 350.8 (t, $^2J_{PC}$ = 14.6 Hz, Ru=C), 183.1 (s, CH_3CO_2), 134.0 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.6, 125.4, 124.1 (all s, C_6H_5), 111.3 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 24.0 (s, *C*H_3CO_2), 22.9 (vt, *N* = 9.5 Hz, P*C*HCH$_3$), 19.8, 19.7 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 25.6 (s).

Preparation of [RuCl(κ^2-O_2CH_2F)(=C=CHPh)(P*i*Pr$_3$)$_2$] (3c). A solution of **1b** (453 mg, 0.76 mmol) in THF (20 mL) was treated with both CH_2FCO_2Na (80 mg, 0.80 mmol) and CF_3SO_3Tl (284 mg, 0.80 mmol) and then stirred for 5 days at room temperature. The solvent was removed, and the residue was extracted with pentane (2 × 5 mL). The combined extracts were evaporated in vacuo to give a beige solid, which was washed with methanol (3 × 5 mL) at −60 °C and purified by recrystallization from pentane at −78 °C: yield 304 mg (63%); mp 121 °C dec. Anal. Calcd for $C_{28}H_{50}ClFO_2P_2Ru$: C, 52.86; H, 7.92. Found: C, 53.12; H, 7.81. IR (Nujol): ν(C=C) 1614, ν_{as}(OCO) 1578 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.17 (m, 4H, C_6H_5), 6.87 (m, 1H, C_6H_5), 4.91 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 4.38 (d, $^2J_{FH}$ = 47.5 Hz, 2H, CH_2F), 2.62 (m, 6H, PC*H*CH$_3$), 1.23 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 352.0 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C), 178.1 (d, $^2J_{FC}$ = 20.3 Hz, CH_2FCO_2), 133.4 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.7, 125.5, 124.5, 124.4 (all s, C_6H_5), 111.1 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 79.1 (d, $^1J_{FC}$ = 183.1 Hz, CH_2F), 23.0 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.7, 19.6 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ 25.1 (s). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_6D_6): δ −227.1 (s).

Preparation of [RuCl(κ^2-O_2CHF_2)(=C=CHPh)(P*i*Pr$_3$)$_2$] (3d). A solution of CHF_2CO_2Tl (308 mg, 1.03 mmol) in THF (50 mL) was added dropwise to a stirred solution of **1b** in THF (10 mL) over a period of 1 h. After the resulting suspension was stirred for 3.5 h at room temperature, the solvent was removed and the residue was extracted with pentane (25 + 5 mL). Partial evaporation of the solvent from the combined extracts to ca. 8 mL led to the precipitation of an orange solid, which was washed with pentane (2 × 5 mL) at −78 °C and dried: yield 472 mg (71%); mp 110 °C. Anal. Calcd for $C_{28}H_{49}ClF_2O_2P_2Ru$: C, 51.41; H, 7.55. Found: C, 51.17; H, 7.68. IR (Nujol): ν(C=C) 1602, ν_{as}(OCO) 1571 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.15 (m, 4H, C_6H_5), 6.88 (m, 1H, C_6H_5), 5.32 (t, $^2J_{FH}$ = 53.7 Hz, 1H, CHF_2), 4.91 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 2.61 (m, 6H, PC*H*CH$_3$), 1.22 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 352.8 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C), 171.6 (t, $^2J_{FC}$ = 27.9 Hz, CHF_2CO_2), 132.9 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.7, 125.5, 124.6 (all s, C_6H_5), 111.1 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 106.8 (t, $^1J_{FC}$ = 249.2 Hz, CHF_2), 22.9 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.7, 19.6 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ 24.9 (s). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_6D_6): δ −125.1 (s).

Preparation of [RuCl(κ^2-O_2CCF_3)(=C=CHPh)(P*i*Pr$_3$)$_2$] (3e). A solution of CF_3CO_2Tl (432 mg, 1.36 mmol) in THF (30 mL) was added dropwise to a stirred solution of **1b** (809 mg, 1.36 mmol) in THF (10 mL) over a period of 30 min. After the resulting suspension was stirred for 30 min, the solvent was removed in vacuo and the residue was extracted with pentane (2 × 15 mL). Evaporation of the solvent from the combined extracts led to the formation of an oil, which, after drying in vacuo for 4 h, gave a dark brown solid: yield 866 mg. The solid contained approximately 84% of **3e**, 8% of **1b**, and 8% of **4b**. Complex **3e** could not be purified by either recrystallization or chromatography. Spectroscopic data for **3e**: IR (Nujol): ν(C=C) 1615 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.17 (m, 4H, C_6H_5), 6.87 (m, 1H, C_6H_5), 4.93 (t, $^4J_{PH}$ = 3.3 Hz, 1H, =C*H*Ph), 2.57 (m, 6H, PC*H*CH$_3$), 1.20 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 353.7 (t, $^2J_{PC}$ = 15.3 Hz, Ru=C), 164.8 (q, $^2J_{FC}$ = 39.4 Hz, CF_3CO_2), 132.5 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.8, 125.6, 124.8 (all s, C_6H_5), 111.1 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 22.9 (vt, *N* = 9.5 Hz, P*C*HCH$_3$), 19.6, 19.5 (both s, PCH*C*H$_3$), signal of *C*F_3CO_2 not observed. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 25.8 (s). ^{19}F NMR (188.3 MHz, C_6D_6): δ −74.91 (s).

Preparation of [RuCl(κ^2-O_2CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] (3f). A solution of **1b** (345 mg, 0.58 mmol) in THF (5 mL) was treated with $PhCO_2H$ (73 mg, 0.60 mmol) and Et_3N (100 μL, 0.72 mmol). After the resulting solution was stirred for 5 h at room temperature, the solvent was removed in vacuo and the remaining residue was extracted with pentane (30 mL). Partial evaporation of the solvent from the extract to ca. 8 mL led to the precipitation of an orange solid, which was washed with cold pentane (2 × 5 mL) and dried: yield 304 mg (77%); mp 138 °C dec. Anal. Calcd for $C_{33}H_{53}ClO_2P_2Ru$: C, 58.27; H, 7.85. Found: C, 58.39; H, 7.75. IR (Nujol): ν(C=C) 1608, ν_{as}(OCO) 1524 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 8.21, 7.31, 7.23 (all m, 2H each, C_6H_5), 7.10 (m, 3H, C_6H_5), 6.91 (m, 1H, C_6H_5), 4.99 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 2.68 (m, 6H, PC*H*CH$_3$), 1.25 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 351.0 (t, $^2J_{PC}$ = 15.3 Hz, Ru=C), 177.5 (s, Ph*C*O_2), 134.0 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C, C_6H_5 of vinylidene), 133.0, 132.2, 128.8, 128.6, 125.4, 124.2 (all s, C_6H_5), 111.1 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 22.9 (vt, *N* = 9.5 Hz, P*C*HCH$_3$), 19.8, 19.7 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ 25.3 (s).

Preparation of [RuCl(κ^2-$O_2CC_6H_4NO_2$-4)(=C=CHPh)-(P*i*Pr$_3$)$_2$] (3g). A solution of **1b** (367 mg, 0.62 mmol) in THF (20 mL) was treated with 4-$NO_2C_6H_4CO_2Na$ (212 mg, 1.12 mmol) and stirred for 16 h at room temperature. A red suspension was obtained, from which the solvent was removed in vacuo. The residue was extracted with dichloromethane (10 mL), and the extract was evaporated in vacuo. After the remaining residue was treated with methanol (8 mL), a yellow-orange solid precipitated, which was filtered, washed with methanol (3 × 5 mL), and recrystallized from dichloromethane/pentane: yield 358 mg (80%); mp 159 °C. Anal. Calcd for $C_{33}H_{52}ClNO_4P_2Ru$: C, 54.65; H, 7.23; N, 1.93. Found: C, 54.37; H, 6.97; N, 1.90. IR (Nujol): ν(C=C) 1615, ν_{as}(NO_2) 1548, ν_{as}(OCO) 1522 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.89, 7.69 (AB system, $^3J_{HH}$ = 8.8 Hz, 4H, C_6H_4), 7.26 (m, 4H, C_6H_5), 6.94 (m, 1H, C_6H_5), 4.99 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 2.65 (m, 6H, PC*H*CH$_3$), 1.23 (m, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 352.0 (t, $^2J_{PC}$ = 15.3 Hz, Ru=C), 175.1 (s, $C_6H_4CO_2$), 150.1 (s, C4 of C_6H_4), 133.5 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 129.3, 128.7, 125.5, 124.5, 123.8 (all s, C_6H_5 and C_6H_4), 111.1 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 22.9 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 19.7, 19.6 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ 25.2 (s).

Preparation of [RuCl(κ^2-$O_2CC_6H_4NO_2$-2)(=C=CHPh)-(P*i*Pr$_3$)$_2$] (3h). This complex was prepared as described for **3g**, starting from **1b** (304 mg, 0.51 mmol) and 2-$NO_2C_6H_4CO_2$-Na (145 mg, 0.77 mmol). Yellow-orange solid: yield 181 mg (49%); mp 162 °C dec. Anal. Calcd for $C_{33}H_{52}ClNO_4P_2Ru$: C, 54.65; H, 7.23; N, 1.93. Found: C, 54.17; H, 6.88; N, 1.91. IR (Nujol): ν(C=C) 1615, ν_{as}(NO_2) 1539 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 8.15 (m, 1H, C_6H_4), 7.30 (m, 4H, C_6H_5), 6.95 (m, 1H, C_6H_5), 6.77 (m, 1H, C_6H_4), 6.60 (m, 2H, C_6H_4), 5.01 (t, $^4J_{PH}$ = 3.5 Hz, 1H, =C*H*Ph), 2.66 (m, 6H, PC*H*CH$_3$), 1.28, 1.22 (both dvt, *N* = 13.2, $^3J_{HH}$ = 7.0 Hz, 18H each, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 352.6 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C), 172.2 (s, $C_6H_4CO_2$), 151.3 (s, C2,6 of C_6H_4), 133.4 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 132.9, 131.1, 129.8, 128.8, 125.7, 124.4, 122.5, 122.4 (all s, C_6H_5 and C_6H_4), 111.0 (t, $^3J_{PC}$ = 3.8 Hz, =*C*HPh), 22.9 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.8, 19.7 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ 25.2 (s).

Preparation of [RuCl(κ^2-$O_2CC_6F_5$)(=C=CHPh)(P*i*Pr$_3$)$_2$] (3i). A solution of **1b** (313 mg, 0.53 mmol) in THF (20 mL) was treated with $C_6F_5CO_2Na$ (182 mg, 0.78 mmol) and stirred for 30 h at room temperature. A red-orange suspension was obtained, from which the solvent was evaporated in vacuo. The residue was extracted with pentane (15 mL), and the extract was brought to dryness in vacuo. After the residue was treated

with methanol (8 mL), a red-orange solid precipitated, which was washed with cold methanol (2 × 5 mL) and recrystallized from pentane at −78 °C: yield 360 mg (89%); mp 132 °C. Anal. Calcd for $C_{33}H_{48}ClF_5O_2P_2Ru$: C, 51.46; H, 6.28. Found: C, 51.57; H, 5.96. IR (Nujol): ν(C═C) 1610 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.21 (m, 4H, C_6H_5), 6.89 (m, 1H, C_6H_5), 4.99 (t, $^4J_{PH}$ = 3.5 Hz, 1H, ═C*H*Ph), 2.73 (m, 6H, PC*H*CH$_3$), 1.27 (m, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 352.4 (t, $^2J_{PC}$ = 15.2 Hz, Ru═C), 168.3 (br m, $C_6F_5CO_2$), 133.1 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.2, 125.6, 124.6 (all s, C_6H_5), 111.0 (t, $^3J_{PC}$ = 3.8 Hz, ═*C*HPh), 22.9 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 19.7, 19.6 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ 25.3 (s). ^{19}F{^{1}H} NMR (376.4 MHz, C_6D_6): δ −139.0 (m, 2F, C_6F_5), −148.5 (m, 1F, C_6F_5), −160.9 (m, 2F, C_6F_5).

Preparation of [RuCl{κ^2-O$_2$CC$_6$H$_3$(NO$_2$)$_2$-2,4}(═C═CHPh)(P*i*Pr$_3$)$_2$] (3j). This compound was prepared as described for **3g**, starting from **1b** (311 mg, 0.52 mmol) and 2,4-$(NO_2)_2C_6H_4CO_2Na$ (142 mg, 0.63 mmol). Orange microcrystalline solid: yield 275 mg (68%); mp 146 °C dec. Anal. Calcd for $C_{33}H_{51}ClN_2O_6P_2Ru$: C, 51.46; H, 6.67; N, 3.64. Found: C, 50.55; H, 6.14; N, 3.45. IR (Nujol): ν(C═C) 1611, ν_{as}(OCO) 1569, ν_{as}(NO$_2$) 1550, 1539 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.85 (d, J_{HH} = 8.5 Hz, 1H, H6 of C_6H_4), 7.34 (m, 4H, H3,5 of C_6H_5 and H3,5 of C_6H_4), 7.23 (m, 2H, H2,6 of C_6H_5), 6.97 (m, 1H, H4 of C_6H_5), 5.01 (t, $^4J_{PH}$ = 3.5 Hz, 1H, ═C*H*Ph), 2.63 (m, 6H, PC*H*CH$_3$), 1.26, 1.21 (both dvt, *N* = 13.2, $^3J_{HH}$ = 7.0 Hz, 18H each, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 353.4 (t, $^2J_{PC}$ = 15.3 Hz, Ru═C), 170.0 (s, $C_6H_4CO_2$), 150.2, 149.3 (both s, C2,4 of C_6H_4), 132.9 (br m, *ipso*-C of C_6H_5), 132.1, 128.8, 125.9, 125.7, 124.7, 124.5, 118.2 (all s, C_6H_5 and C_6H_4), 111.0 (t, $^3J_{PC}$ = 3.8 Hz, ═*C*HPh), 22.9 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 19.8, 19.6 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ 25.2 (s).

Preparation of [Ru(κ^1-O$_2$CCHF$_2$)(κ^2-O$_2$CCHF$_2$)(═C═CHPh)(P*i*Pr$_3$)$_2$] (4a). A solution of **1b** (502 mg, 0.85 mmol) in THF (20 mL) was treated with CHF_2CO_2Tl (572 mg, 1.91 mmol) and stirred for 3 days at room temperature. A white solid of TlCl precipitated, and the color of the solution changed from violet to orange. The solvent was removed in vacuo, and the residue was extracted with pentane (25 + 5 mL). The combined extracts were concentrated to ca. 8 mL in vacuo, and the solution was stored for 12 h at −78 °C. Orange crystals precipitated, which were washed with pentane (−78 °C) and dried: yield 462 mg (77%). Since the product slowly decomposes in solution, forming an unidentified insoluble yellow solid, it could not be purified by recrystallization. Therefore, no satisfactory elemental analyses were obtained. Data for **4a**: IR (Nujol): ν(C═C) 1622, ν_{as}(OCO) 1691, 1675 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.20 (m, 4H, C_6H_5), 6.89 (m, 1H, C_6H_5), 6.07 (t, $^4J_{PH}$ = 3.5 Hz, 1H, ═C*H*Ph), 5.52 (t, $^2J_{FH}$ = 54.6 Hz, 2H, CHF_2), 2.27 (m, 6H, PC*H*CH$_3$), 1.17 (dvt, *N* = 13.2, $^3J_{HH}$ = 7.0 Hz, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 359.3 (t, $^2J_{PC}$ = 15.3 Hz, Ru═C), 169.6 (t, $^2J_{FC}$ = 26.7 Hz, CHF_2CO_2), 133.1 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.3, 125.6, 124.7 (all s, C_6H_5), 113.0 (t, $^3J_{PC}$ = 4.4 Hz, ═*C*HPh), 107.3 (t, $^1J_{FC}$ = 250.5 Hz, CHF_2), 23.3 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.5 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6): δ 27.1 (s). ^{19}F{^{1}H} NMR (376.4 MHz, C_6D_6): δ −123.5 (s).

Preparation of [Ru(κ^1-O$_2$CCF$_3$)(κ^2-O$_2$CCF$_3$)(═C═CHPh)(P*i*Pr$_3$)$_2$] (4b). A solution of **1b** (595 mg, 1.00 mmol) in acetone (25 mL) was treated with CF_3CO_2Tl (790 mg, 2.49 mmol) and stirred for 20 h at room temperature. The solvent was removed in vacuo, the residue was extracted with pentane (25 mL), and the extract was concentrated in vacuo to ca. 3 mL. An orange solid precipitated, which was washed with pentane (2 × 5 mL) at −78 °C and dried: yield 647 mg (86%); mp 105 °C dec. Anal. Calcd for $C_{30}H_{48}F_6O_4P_2Ru$: C, 48.06; H, 6.45. Found: C, 47.75; H, 6.12. IR (Nujol): ν_{as}(OCO) of κ^1-O$_2$CCF$_3$ 1701, ν(C═C) 1614 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.15 (m, 4H, C_6H_5), 6.87 (m, 1H, C_6H_5), 6.05 (t, $^4J_{PH}$ = 3.3 Hz, 1H, ═C*H*Ph), 2.22 (m, 6H, PC*H*CH$_3$), 1.12 (dvt, *N* = 13.2, $^3J_{HH}$ = 6.9 Hz, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 362.1 (t, $^2J_{PC}$ = 15.3 Hz, Ru═C), 163.5 (q, $^2J_{CF}$ = 38.1 Hz, CF_3CO_2), 132.2 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.9, 125.8, 125.2 (all s, C_6H_5), 114.3 (q, $^1J_{CF}$ = 288.5 Hz, CF_3CO_2), 113.0 (t, $^3J_{PC}$ = 3.8 Hz, ═*C*HPh), 23.3 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.3 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 27.8 (s). ^{19}F NMR (188.3 MHz, C_6D_6): δ −74.2 (s).

Preparation of [Ru(κ^1-O$_2$CCF$_3$)(κ^2-O$_2$CH)(═C═CHPh)(P*i*Pr$_3$)$_2$] (4c). A solution of **4b** (323 mg, 0.43 mmol) in THF (15 mL) was treated with HCO_2Na (186 mg, 2.74 mmol) and stirred for 5.5 h at room temperature. The reaction mixture was then worked up as described for **4b**. Orange crystals (containing 1/3 molecule of pentane per formula unit) were obtained after recrystallization from pentane at −78 °C: yield 213 mg (72%); mp 58 °C dec, Anal. Calcd for $C_{30.67}H_{53}F_3O_4P_2Ru$: C, 52.19; H, 7.57. Found: C, 52.25; H, 7.54. IR (Nujol): ν_{as}(OCO) of κ^1-O$_2$CCF$_3$ 1701, ν(C═C) 1617, ν_{as}(OCO) of κ^2-O$_2$CH 1550 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.41 (t, $^4J_{PH}$ = 1.8 Hz, 1H, *H*CO$_2$), 7.19 (m, 4H, C_6H_5), 6.87 (m, 1H, C_6H_5), 5.98 (t, $^3J_{PH}$ = 3.3 Hz, 1H, ═C*H*Ph), 2.26 (m, 6H, PC*H*CH$_3$), 1.16 (dvt, *N* = 13.2, $^3J_{HH}$ = 6.9 Hz, 18H, PCHC*H*$_3$), 1.15 (dvt, *N* = 12.9, $^3J_{HH}$ = 7.1 Hz, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 359.0 (t, $^2J_{PC}$ = 15.3 Hz, Ru═C), 174.5 (s, HCO_2), 161.4 (q, $^2J_{FC}$ = 36.9 Hz, CF_3CO_2), 133.3 (t, $^4J_{PC}$ = 2.5 Hz, *ipso*-C of C_6H_5), 128.7, 125.6, 124.6 (all s, C_6H_5), 112.4 (t, $^3J_{PC}$ = 4.4 Hz, ═*C*HPh), 23.2 (vt, *N* = 8.9 Hz, P*C*HCH$_3$), 19.5 (s, PCH*C*H$_3$), 19.4 (s, PCH*C*H$_3$), signal of CF_3CO_2 not observed. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 27.5 (s). ^{19}F NMR (188.3 MHz, C_6D_6): δ −73.74 (s).

Preparation of [RuCl{═C(CH$_2$Ph)OC(O)H}(P*i*Pr$_3$)$_2$]BAr$_f$ (6a). A solid mixture of **3a** (157 mg, 0.26 mmol) and $[H(OEt_2)_2]BAr_f$ (260 mg, 0.26 mmol) was treated with dichloromethane (3 mL), and the resulting dark red solution was stirred for 5 min at room temperature. Additon of pentane (25 mL) led to the precipitation of a red microcrystalline solid, which was separated from the mother liquor, washed with pentane (5 mL), and dried: yield 376 mg (98%); mp 100 °C dec. Anal. Calcd for $C_{59}H_{62}BClF_{24}O_2P_2Ru$: C, 48.26; H, 4.26. Found: C, 48.02; H, 4.23. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.24 (s, 1H, HCO_2), 7.72 (br m, 8H, *ortho*-H of Ar$_f$), 7.54 (br m, 4H, *para*-H of Ar$_f$), 7.39 (m, 5H, C_6H_5), 5.00 (s, 2H, C*H*$_2$Ph), 2.93 (m, 6H, PC*H*CH$_3$), 1.25, 1.16 (both dvt, *N* = 14.6, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 286.9 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 170.0 (s, HCO_2), 130.8, 129.9, 128.8, 128.5 (all s, C_6H_5), 60.5 (s, *C*H$_2$Ph), 23.2 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 19.0, 18.6 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 48.0 (s).

Preparation of [RuCl{═C(CH$_2$Ph)OC(O)CH$_3$}(P*i*Pr$_3$)$_2$]BAr$_f$ (6b). This complex was prepared as described for **6a**, starting from **3b** (172 mg, 0.28 mmol) and $[H(OEt_2)_2]BAr_f$ (282 mg, 0.28 mmol). Red microcrystalline solid: yield 389 mg (92%); mp 101 °C dec. Anal. Calcd for $C_{60}H_{64}BClF_{24}O_2P_2Ru$: C, 48.61; H, 4.35. Found: C, 48.50; H, 4.38. IR (Nujol): ν(C═O) 1633 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73 (br m, 8H, *ortho*-H of BAr$_f$), 7.56 (br m 4H, *para*-H of BAr$_f$), 7.38 (m, 5H, C_6H_5), 4.96 (s, 2H, C*H*$_2$Ph), 2.68 (s, 3H, CH_3CO_2), 2.33 (br m, 6H, PC*H*CH$_3$), 1.22 (dvt, *N* = 14.6, $^3J_{HH}$ = 7.3 Hz, 18H, PCHC*H*$_3$), 1.14 (dvt, *N* = 14.2, $^3J_{HH}$ = 6.9 Hz, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 253 K): δ 287.0 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 182.6 (s, CH_3CO_2), 131.3, 129.8, 128.7, 128.3 (all s, C_6H_5), 60.3 (s, *C*H$_2$Ph), 23.3 (vt, *N* = 10.7 Hz, P*C*HCH$_3$), 19.0, 18.6 (both s, PCH*C*H$_3$), 18.0 (s, *C*H$_3$CO$_2$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 47.1 (s).

Preparation of [RuCl{═C(CH$_2$Ph)OC(O)CH$_2$F}(P*i*Pr$_3$)$_2$]BAr$_f$ (6c). A solid mixture of **3c** (121 mg, 0.19 mmol) and $[H(OEt_2)_2]BAr_f$ (184 mg, 0.18 mmol) was treated with dichloromethane (3 mL) at −78 °C. The resulting suspension was stirred for 10 min and then allowed to warm to room temperature. Addition of pentane (20 mL) led to the precipitation of an orange solid, which was separated from the mother

liquor and washed with small quantities of pentane (0 °C). It was recrystallized from dichloromethane/pentane and dried: yield 242 mg (89%); mp 95 °C dec. The NMR data indicated that in solution (CD_2Cl_2) both isomers **6c** and **5c** (molar ratio 9:1) are present. Anal. Calcd for $C_{60}H_{63}BClF_{25}O_2P_2Ru$: C, 48.03; H, 4.23. Found: C, 47.90; H, 4.04. IR (Nujol): ν(C═O) 1632 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 233 K): δ 7.72 (br m, 8H, *ortho*-H, BAr_f), 7.55 (br m, 4H, *para*-H, BAr_f), 7.37 (m, 5H, C_6H_5), 5.62 (d, $^2J_{FH}$ = 45.2 Hz, 1.8H, CH_2F of **6c**), 4.97 (s, 1.8H, CH_2Ph of **6c**), 4.81 (d, $^2J_{FH}$ = 46.4 Hz, 0.2H, CH_2F of **5c**), 4.53 (s, 0.2H, CH_2Ph of **5c**), 2.54 (m, 0.6H, PC*H*CH_3 of **5c**), 2.35 (m, 5.4H, PC*H*CH_3 of **6c**), 1.24, 1.13 (both dvt, N = 14.4, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHCH_3). $^{13}C\{^1H\}$ NMR of **6c** (50.3 MHz, CD_2Cl_2, 243 K): δ 285.4 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 178.6 (d, $^2J_{CF}$ = 22.9 Hz, CH_2FCO_2), 131.0, 129.9, 128.7 (all s, C_6H_5), 76.5 (d, $^1J_{FC}$ = 189.4 Hz, CH_2FCO_2), 60.5 (s, CH_2Ph), 23.4 (vt, N = 10.8 Hz, PCHCH$_3$), 19.0, 18.5 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 233 K): δ 49.7 (s, **5c**), 47.6 (s, **6c**). $^{19}F\{^1H\}$ NMR (376.4 MHz, CD_2Cl_2, 233 K): −62.5 (s, 24F, CF_3 of Ar_f), −229.9 (s, 0.1F, CH_2F of **5c**), −233.1 (s, 0.9F, CH_2F of **6c**).

Preparation of [RuCl(κ^2-O_2CCHF_2)(≡CCH_2Ph)(P*i*Pr_3)$_2$]-BAr_f (5d). Following the procedure described for the preparation of **6c**, treatment of **3d** (193 mg, 0.29 mmol) and $[H(OEt_2)_2]$-BAr_f (293 mg, 0.29 mmol) with dichloromethane (3 mL) at −78 °C finally led to an orange-red microcrystalline solid, which consisted of a mixture of **5d** and **6d**. If a solution of this solid in dichloromethane (3 mL) was stored at −78 °C for 6 days, yellow crystals of **5d** were obtained: yield 421 mg (96%); mp 82 °C dec. The NMR data indicated that in solution (CD_2Cl_2) both isomers **5d** and **6d** (molar ratio ca. 8:1) are present. Anal. Calcd for $C_{60}H_{62}BClF_{26}O_2P_2Ru$: C, 47.46; H, 4.12. Found: C, 47.20, 4.32. IR for **5d** (Nujol): ν_{as}(OCO) 1584 cm^{-1}, for the mixture **5d/6d** an additional ν(C═O) band at 1643 cm^{-1} is observed. ^1H NMR (400 MHz, CD_2Cl_2, 190 K): δ 7.73 (br m, 8H, *ortho*-H of Ar_f), 7.53 (s, 4H, *para*-H of Ar_f), 7.36 (m, 5H, C_6H_5), 6.58 (t, $^2J_{FH}$ = 51.6 Hz, 0.1H, CHF_2 of **6d**), 5.84 (t, $^2J_{FH}$ = 52.5 Hz, 0.9H, CHF_2 of **5d**), 5.01 (s, 0.2H, CH_2Ph of **6d**), 4.55 (s, 1.8H, CH_2Ph of **5d**), 2.48 (br m, PC*H*CH_3 of **5d**), 2.34 (br m, PC*H*CH_3 of **6d**), 1.22 (br m, PCHCH_3 of **5d**), 1.08 (br m, PCHCH_3 of **6d**). $^{13}C\{^1H\}$ NMR of **5d** (50.3 MHz, CD_2Cl_2, 243 K): δ 330.0 (t, $^2J_{PC}$ = 7.6 Hz, Ru≡C), 174.7 (t, $^2J_{CF}$ = 29.2 Hz, CHF_2CO_2), 129.9, 129.7, 128.9, 125.6 (all s, C_6H_5), 105.1 (t, $^1J_{CF}$ = 247.8 Hz, CHF_2CO_2), 64.1 (s, CH_2Ph), 24.3 (vt, N = 10.2 Hz, PCHCH$_3$), 19.9, 18.3 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 193 K): δ 51.1 (s, **6d**), 49.7 (s, **5d**). $^{19}F\{^1H\}$ NMR (376.4 MHz, CD_2Cl_2, 193 K): −62.3 (s, 24F, CF_3 of Ar_f), −123.0 (s, 0.2F, CHF_2 of **6d**), −126.7 (s, 1.8F, CHF_2 of **5d**).

Preparation of [RuCl(κ^2-O_2CCF_3)(≡CCH_2Ph)(P*i*Pr_3)$_2$]-BAr_f (5e). This complex was prepared following the procedure described for **6c**, starting from $[H(OEt_2)_2]BAr_f$ (268 mg, 0.27 mmol) and the mixture containing 84% of **3e**, 8% of **1b**, and 8% of **4b** (181 mg, 0.27 mmol of Ru). The crude product was purified by recrystallization from dichloromethane (2 mL) at −78 °C to give yellow crystals: yield 347 mg (99% based on initial content of complex **3e** in the starting material); mp 97 °C dec. The NMR data indicated that in solution (CD_2Cl_2) both isomers **5e** and **6e** (molar ratio ca. 2:1) are present. Anal. Calcd for $C_{60}H_{61}BClF_{27}O_2P_2Ru$: C, 46.91; H, 4.00. Found: C, 46.58, 3.78. ^1H NMR (400 MHz, CD_2Cl_2, 193 K): δ 7.73 (br m, 8H, *ortho*-H of Ar_f), 7.53 (s, 4H, *para*-H of Ar_f), 7.36 (m, 5H, C_6H_5), 5.20 (br s, 0.7H, CH_2Ph of **6e**), 4.59 (br s, 1.3H, CH_2Ph of **5e**), 2.62 (br m, PC*H*CH_3 of **6e**), 2.48 (br m, PC*H*CH_3 of **5e**), 1.21 (m, 36H, PCHCH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 253 K): δ 130.4, 130.3, 129.7, 128.6 (all s, C_6H_5), 64.9 (s, CH_2Ph), 24.8 (vt, N = 10.2 Hz, PCHCH$_3$), 19.6, 19.0 (both s, PCHCH_3), signals for Ru═C, CF_3CO_2, and CF_3CO_2 not exactly located. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 193 K): δ 61.6 (s, **5e**), 50.8 (br, **6e**). $^{19}F\{^1H\}$ NMR (376.4 MHz, CD_2Cl_2, 193 K): δ −62.7 (s, 24F, CF_3 of Ar_f), −72.9 (s, 1.1F, CF_3CO_2 of **6e**), −75.1 (s, 2.9F, CF_3CO_2 of **5e**).

Preparation of [RuCl{═C(CH_2Ph)OC(O)Ph}(P*i*Pr_3)$_2$]-BAr_f (6f). This complex was prepared as described for **6c**, starting from **3f** (162 mg, 0.24 mmol) and $[H(OEt_2)_2]BAr_f$ (238 mg, 0.24 mmol). Purple microcrystalline solid: yield: 345 mg (95%); mp 111 °C dec. Anal. Calcd for $C_{65}H_{66}BClF_{24}O_2P_2Ru$: C, 50.55; H, 4.31. Found: C, 50.53; H, 4.43. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (m, 2H, C_6H_5), 7.70 (m, 9H, *ortho*-H of Ar_f, C_6H_5), 7.53 (m, 8H, *para*-H of Ar_f, C_6H_5), 7.39 (m, 3H, C_6H_5), 5.10 (s, 2H, CH_2Ph), 2.42 (m, 6H, PC*H*CH_3), 1.28, 1.19 (both dvt, N = 14.4, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHCH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 287.4 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 177.4 (s, PhCO_2), 138.1, 131.7, 130.6, 130.4, 130.0, 128.9, 128.6, 121.6 (all s, C_6H_5), 60.5 (s, CH_2Ph), 23.8 (vt, N = 10.8 Hz, PCHCH$_3$), 19.3, 18.9 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 47.1 (s).

Preparation of [RuCl{═C(CH_2Ph)OC(O)$C_6H_4NO_2$-4}-(P*i*Pr_3)$_2$]BAr_f (6g). This complex was prepared as described for **6c**, starting from **3g** (94 mg, 0.13 mmol) and $[H(OEt_2)_2]$-BAr_f (124 mg, 0.12 mmol). Dark green microcrystalline solid: yield 182 mg (93%); mp 106 °C dec. Anal. Calcd for $C_{65}H_{65}$-$BClF_{24}NO_4P_2Ru$: C, 49.12; H, 4.12; N, 0.88. Found: C, 48.90; H, 4.02; N, 0.92. IR (Nujol): $\nu_{as}(NO_2)$ 1537 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2, 243 K): δ 8.43, 8.26 (AB system, $^3J_{HH}$ = 8.4 Hz, 4H, C_6H_4), 7.72 (br m, 8H, *ortho*-H of Ar_f), 7.53 (br m, 4H, *para*-H of Ar_f), 7.43 (m, 5H, C_6H_5), 5.09 (s, 2H, CH_2Ph), 2.33 (m, 6H, PC*H*CH_3), 1.26, 1.12 (both dvt, N = 14.6, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHCH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 243 K): δ 285.8 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 175.8 (s, $C_6H_4CO_2$), 152.4 (s, C4 of C_6H_4), 132.0, 131.4, 129.9, 128.8, 128.4, 125.6, 125.3 (all s, C_6H_5 and C_6H_4), 60.3 (s, CH_2Ph), 23.4 (vt, N = 10.2 Hz, PCHCH$_3$), 19.1, 18.5 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 243 K): δ 48.2 (s).

Preparation of [RuCl{═C(CH_2Ph)OC(O)$C_6H_4NO_2$-2}-(P*i*Pr_3)$_2$]BAr_f (6h). This complex was prepared as described for **6c**, starting from **3h** (60 mg, 0.08 mmol) and $[H(OEt_2)_2]BAr_f$ (83 mg, 0.08 mmol). Dark violet microcrystalline solid: yield 113 mg (85%); mp 93 °C dec. Anal. Calcd for $C_{65}H_{65}BClF_{24}NO_4P_2Ru$: C, 49.12; H, 4.12; N, 0.88. Found: C, 48.85; H, 4.27; N, 0.92. IR (Nujol): $\nu_{as}(NO_2)$ 1550 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2, 243 K): δ 7.87 (m, 2H, C_6H_4), 7.73 (br m, 10H, *ortho*-H of Ar_f and C_6H_4), 7.55 (br m, 4H, *para*-H of Ar_f), 7.42 (m, 5H, C_6H_5), 5.06 (s, 2H, CH_2Ph), 2.38 (m, 6H, PC*H*CH_3), 1.31, 1.11 (both dvt, N = 14.6, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHCH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 243 K): δ 284.9 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 173.8 (s, $C_6H_4CO_2$), 150.4 (s, C2 of C_6H_4), 138.6, 132.7, 131.4, 130.1, 128.8, 124.6, 113.2 (all s, C_6H_5 and C_6H_4), 60.5 (s, CH_2Ph), 23.3 (vt, N = 10.2 Hz, PCHCH$_3$), 19.1, 18.6 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 243 K): δ 49.1 (s).

Preparation of [RuCl{═C(CH_2Ph)OC(O)C_6F_5}(P*i*Pr_3)$_2$]-BAr_f (6i). This complex was prepared as described for **6c**, starting from **3i** (277 mg, 0.36 mmol) and $[H(OEt_2)_2]BAr_f$ (359 mg, 0.36 mmol). Dark violet microcrystalline solid: yield 552 mg (94%); mp 106 °C dec. The NMR data indicated that in solution (CD_2Cl_2) both isomers **6i** and **5i** (molar ratio ca. 19:1) are present. Anal. Calcd for $C_{65}H_{61}BClF_{29}O_2P_2Ru$: C, 47.77; H, 3.76. Found: C, 47.59; H, 3.78. ^1H NMR (400 MHz, CD_2Cl_2, 233 K): δ 7.72 (s, 8H, *ortho*-H of Ar_f), 7.55 (s, 4H, *para*-H of Ar_f), 7.39 (m, 5H, C_6H_5), 5.09 (s, 1.9H, CH_2Ph of **6i**), 4.54 (br s, 0.1H, CH_2Ph of **5i**), 2.56 (br m, PC*H*CH_3 of **5i**), 2.35 (m, PC*H*CH_3 of **6i**), 1.28, 1.11 (both dvt, N = 14.6, $^3J_{HH}$ = 7.3 Hz, 18H each, PCHCH_3). $^{13}C\{^1H\}$ NMR of **6i** (100.6 MHz, CD_2Cl_2, 243 K): δ 286.7 (t, $^2J_{PC}$ = 5.1 Hz, Ru═C), 170.4 (s, $C_6F_5CO_2$), 131.3, 130.3, 128.8, 128.5 (all s, C_6H_5), 60.9 (s, CH_2Ph), 23.6 (vt, N = 10.2 Hz, PCHCH$_3$), 19.2, 18.7 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 233 K): δ 49.2 (br s, **5i**), 48.4 (s, **6i**). ^{19}F NMR (376.4 MHz, CD_2Cl_2, 243 K, data for **6i**): δ −62.6 (s, 24F, CF_3 of Ar_f), −131.7 (m, 2F, C_6F_5), −135.6 (m, 1F, C_6F_5), −156.3 (m, 2F, C_6F_5).

Table 2. Crystallographic Data for 2b·1/2CH_2Cl_2, 5e, and 6a

	2b•1/2CH_2Cl_2	**5e**	**6a**
formula	$C_{58.50}H_{62}BCl_3F_{24}P_2Ru$	$C_{60}H_{61}BClF_{27}O_2P_2Ru$	$C_{59}H_{62}BClF_{24}O_2P_2Ru$
M	1501.25	1536.36	1468.36
cryst size, mm	0.20 × 0.15 × 0.15	0.21 × 0.19 × 0.15	0.25 × 0.20 × 0.20
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	18.693(4)	18.882(3)	20.287(4)
b, Å	18.878(4)	15.5787(14)	15.739(2)
c, Å	21.200(4)	22.468(3)	20.271(5)
α, deg	105.11(3)	90	90
β, deg	113.66(3)	91.405(17)	92.52(1)
γ, deg	90.36(3)	90	90
V, Å^3	6563(2)	6607.3(14)	6466(2)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.519	1.544	1.508
T, K	173(2)	173(2)	193(2)
μ, mm^{-1}	0.515	0.444	0.443
scan method	*ϕ*	*ϕ*	*ω*/*θ*
2*θ*(max), deg	50	50	50
total no. of rflns	51560	62685	11694
no. of unique rflns	21786 [*R*(int) = 0.0639]	11647 [*R*(int) = 0.0701]	11351 [*R*(int) = 0.0325]
no. of obsd rflns ($I > 2\sigma(I)$)	11 834	7096	6414
no. of rflns used for refinement	21786	11647	11351
no. of params refined	1879	972	877
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0460, wR2 = 0.1032[a]	R1 = 0.0470, wR2 = 0.1121[a]	R1 = 0.0678, wR2 = 0.1293[a]
R indices (all data)	R1 = 0.0931, wR2 = 0.1152[a]	R1 = 0.0825, wR2 = 0.1270[a]	R1 = 0.1377, wR2 = 0.1649[a]
resid electron density, e A^{-3}	1.213/−0.912	0.633/−1.108	0.585/−0.508

[a] $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.0000P]$ (**2b**·1/2CH_2Cl_2), $w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.0000P]$ (**5e**), $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 15.0489P]$ (**6a**), where $P = [F_o^2 + 2F_c^2]/3$.

Preparation of [RuCl{=C(CH$_2$Ph)OC(O)C$_6$H$_3$(NO$_2$)$_2$-2,4}(P*i*Pr$_3$)$_2$]BAr$_f$ (6j). This complex was prepared as described for **6c**, starting from **3j** (105 mg, 0.14 mmol) and [H(OEt$_2$)$_2$]BAr$_f$ (134 mg, 0.13 mmol). Olive-green microcrystalline solid: yield 199 mg (92%); mp 107 °C dec. The NMR data indicated that in solution (CD_2Cl_2) both isomers **6j** and **5j** (molar ratio ca. 2:1) are present. Anal. Calcd for $C_{65}H_{64}BClF_{24}N_2O_6P_2Ru$: C, 47.77; H, 3.95; N, 1.71. Found: C, 47.60; H, 3.85; N, 1.69. ^{1}H NMR (400 MHz, CD_2Cl_2, 223 K): *δ* 8.64 (d, $^4J_{HH}$ = 2.0 Hz, 0.65H, H3 of C_6H_3 for **6j**), 8.58 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.0 Hz, 0.65H, H5 of C_6H_3 for **6j**), 8.50 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.0 Hz, 0.35H, H5 of C_6H_3 for **5j**), 8.39 (d, $^4J_{HH}$ = 2.0 Hz, 0.35H, H3 of C_6H_3 for **5j**), 8.32 (d, $^3J_{HH}$ = 8.5, 0.35H, H6 of C_6H_3 for **5j**), 8.15 (d, $^3J_{HH}$ = 8.5, 0.65H, H6 of C_6H_3 for **6j**), 7.72 (s, 8H, *ortho*-H of Ar$_f$), 7.53 (s, 4H, *para*-H of Ar$_f$), 7.41 (m, 5H, C_6H_5), 5.05 (s, 1.3H, CH_2Ph of **6j**), 4.54 (s, 0.7H, CH_2Ph of **5j**), 2.50 (br m, 2.1H, PC*H*CH$_3$ of **5j**), 2.34 (br m, 3.9H, PC*H*CH$_3$ of **6j**), 1.30 (dvt, *N* = 14.6, $^3J_{HH}$ = 7.0 Hz, 11.7H, PCHC*H*$_3$ of **6j**), 1.23 (m, 12.6H, PCHC*H*$_3$ of **5j**), 1.09 (dvt, *N* = 14.4, $^3J_{HH}$ = 7.4 Hz, 11.7H, PCHC*H*$_3$ of **6j**). ^{13}C NMR (100.3 MHz, CD_2Cl_2, 243 K): *δ* 330.8 (br m, Ru≡C of **5j**), 284.5 (br m, Ru=C of **6j**), 173.6, 172.8 (both s, $C_6H_3CO_2$ of **5j** and **6j**), 151.8, 150.7, 150.5, 150.2 (all br s, C2 and C4 of C_6H_3 for **5j** and **6j**), 134.3, 133.1, 131.3, 130.3, 130.0, 129.0, 128.6, 127.6, 125.9, 118.8, 117.9 (all s or br s, C_6H_5 and C1, C3, C5, C6 of C_6H_3 for **5j** and **6j**), 64.2 (s, *C*H$_2$Ph of **5j**), 60.7 (s, *C*H$_2$Ph of **6j**), 25.1 (br m, P*C*HCH$_3$ of **5j**), 23.6 (vt, *N* = 10.2 Hz, P*C*HCH$_3$ of **6j**), 19.9, 19.0 (both s, PCH*C*H$_3$ of **5j**), 19.1, 18.6 (both s, PCH*C*H$_3$ of **6j**). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 223 K): *δ* 50.2 (br s, **5j**), 49.4 (s, **6j**).

Preparation of [Ru(*κ*^{2}-O$_2$CCHF$_2$){=C(CH$_2$Ph)OC(O)-CHF$_2$}(P*i*Pr$_3$)$_2$]BAr$_f$ (7a). This complex was prepared as described for **6c**, starting from **4a** (235 mg, 0.33 mmol) and [H(OEt$_2$)$_2$]BAr$_f$ (327 mg, 0.32 mmol). Orange solid: yield 505 mg (99%); mp 52 °C dec. Anal. Calcd for $C_{62}H_{63}BClF_{28}O_4P_2Ru$: C, 47.19; H, 4.02. Found: C, 46.75; H, 4.07. IR (Nujol): *ν*(C=O) 1638, ν_{as}(OCO) 1591 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): *δ* 7.73 (br m, 8H, *ortho*-H of Ar$_f$), 7.57 (br m, 4H, *para*-H of Ar$_f$), 7.45 (m, 5H, C_6H_5), 6.15 (t, $^2J_{HF}$ = 52.2 Hz, 2H, CHF_2), 5.07 (s, 2H, CH_2Ph), 2.04 (m, 6H, PC*H*CH$_3$), 1.19 (dvt, *N* = 14.6, $^3J_{HH}$ = 7.3 Hz, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 243 K): *δ* 296.1 (t, $^2J_{PC}$ = 5.1 Hz, Ru=C), 173.6 (br t, CHF_2CO_2), 130.4, 129.9, 129.0, 128.6 (all s, C_6H_5), 104.5 (br t, CHF_2CO_2), 57.6 (s, *C*H$_2$Ph), 24.1 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 18.7 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): *δ* 45.9 (s). ^{19}F{^{1}H} NMR (188.3 MHz, CD_2Cl_2): *δ* −63.2 (s, 24F, CF_3 of Ar$_f$), −124.9 (s, 4F, CHF_2).

Preparation of [Ru(*κ*^{2}-O$_2$CCF$_3$){=C(CH$_2$Ph)OC(O)CF$_3$}-(P*i*Pr$_3$)$_2$]BAr$_f$ (7b). This compound was prepared and purified as described for **5e**, starting from **4b** (185 mg, 0.25 mmol) and [H(OEt$_2$)$_2$]BAr$_f$ (240 mg, 0.24 mmol). Pale yellow crystals: yield 319 mg (83%); mp 108 °C dec. Anal. Calcd for $C_{62}H_{61}BF_{30}O_4P_2Ru$: C, 46.14; H, 3.81. Found: C, 45.86; H, 3.73. IR (Nujol): *ν*(C=O) 1691 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K): *δ* 7.75 (br m, 8H, *ortho*-H of Ar$_f$), 7.58 (br m, 4H, *para*-H of Ar$_f$), 7.46 (m, 5H, C_6H_5), 5.27 (s, 2H, CH_2Ph), 2.18 (br m, 6H, PC*H*CH$_3$), 1.25 (dvt, *N* = 15.3, $^3J_{HH}$ = 7.3 Hz, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 253 K): *δ* 331.0 (t, $^2J_{PC}$ = 5.7 Hz, Ru=C), 130.3, 130.2, 130.0, 126.7 (all s, C_6H_5), 113.3 (q, $^1J_{FC}$ = 287.2 Hz, CF_3CO_2), 65.4 (s, *C*H$_2$Ph), 25.2 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 18.9 (s, PCH*C*H$_3$), signal of CF_3CO_2 not observed. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 253 K): *δ* 56.5 (s). ^{19}F NMR (376.4 MHz, CD_2Cl_2, 253 K): *δ* −62.6 (s, 24F, CF_3 of Ar$_f$), −73.4 (br s, 6F, CF_3CO_2).

Preparation of [Ru(*κ*^{2}-O$_2$CCF$_3$){=C(CH$_2$Ph)OC(O)H}-(P*i*Pr$_3$)$_2$]BAr$_f$ (7c). This complex was prepared and purified as described for **5e**, starting from **4c** (102 mg, 0.15 mmol) and [H(OEt$_2$)$_2$]BAr$_f$ (151 mg, 0.15 mmol). Orange solid: yield 175 mg (75%); mp 84 °C dec. Anal. Calcd for $C_{61}H_{62}BF_{27}O_4P_2Ru$: C, 47.39; H, 4.04. Found: C, 47.16, 3.97. ^{1}H NMR (200 MHz, $CDCl_3$): 8.05 (s, 1H, HCO_2), 7.70 (br m, 8H, *ortho*-H of Ar$_f$), 7.52 (br m, 4H, *para*-H of Ar$_f$), 7.43 (m, 5H, C_6H_5), 5.04 (s, 2H, CH_2Ph), 1.97 (m, 6H, PC*H*CH$_3$), 1.16 (dvt, *N* = 14.1, $^3J_{HH}$ = 7.1 Hz, 18H, PCHC*H*$_3$), 1.15 (dvt, *N* = 14.8, $^3J_{HH}$ = 7.1 Hz, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 253 K): *δ* 295.4 (t, $^2J_{PC}$ = 5.1 Hz, Ru=C), 172.2 (s, HCO_2), 165.7 (q, $^2J_{FC}$ = 39.4 Hz, CF_3CO_2), 130.5, 129.9, 128.9, 128.6 (all s, C_6H_5), 112.7 (q, $^1J_{FC}$ = 284.7 Hz, CF_3CO_2), 64.4 (s, *C*H$_2$Ph), 24.0 (vt, *N* = 10.2 Hz, P*C*HCH$_3$), 19.1, 18.4 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): *δ* 44.0 (s). ^{19}F NMR (188.3 MHz, $CDCl_3$): *δ* −62.8 (s, 24F, CF_3 of Ar$_f$), −75.3 (s, 3F, CF_3CO_2).

ROMP of Cyclooctene with Complexes 2a−d as Catalyst Precursors. A sample of **2a**−**d** (6 *μ*mol) was dissolved

in CD_2Cl_2 (550 μL) and treated in an NMR tube with cyclooctene (0.6 mmol, 100 equiv). The polymerization was followed by ^{1}H NMR spectroscopy. Total consumption of the monomer was observed after 20 h with **2a** and **2b** as precatalyst, and the reaction was accompanied by the formation of a brownish viscous solution. The ^{13}C NMR spectra of the polymers revealed with regard to the configuration at the double bonds a trans/cis ratio of 78:22 (**2a**) or 73:27 (**2b**). In the case of **2c** and **2d**, a conversion of only 50 or 10%, respectively, of cyclooctene to the polymer was observed.

X-ray Structural Analysis of 2b·1/2CH$_2$Cl$_2$, 5e and 6a. Single crystals of **2b**·1/2CH_2Cl_2 and **5e** were grown from dichloromethane at −20 °C, and those of **6a** from chloroform at −20 °C. The data were collected from a shock-cooled crystal protected by an oil drop on a Stoe IPDS diffractometer (**2b**·1/2CH_2Cl_2, **5e**) or an Enraf-Nonius CAD4 diffractometer (**6a**) using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data collection parameters are summarized in Table 2. Intensity data were corrected by Lorentz and polarization effects, and for **6a** an *Lp* and empirical absorption correction were applied (Ψ-scan method, minimum transmission 91.35%). The structure of **2b**·1/2CH_2Cl_2 was solved by direct methods, and the structures of **5e** and **6a** were solved by the Patterson method (SHELXS-97).[26] Atomic coordinates and anisotropic displacement parameters were refined by full matrix least-squares against F_0^2 (SHELXL-97).[27] The CH_2Cl_2 molecule in **2b**·1/2CH_2Cl_2 was found disordered over two independent positions and refined anisotropically with restraints on *U*(*ij*) (DELU, SIMU) and occupancy factors 50:50; also eight of the CF_3 groups of the BAr_f anions of **2b**·1/2CH_2Cl_2 were found rotationally disordered and refined in the same way with the following occupancy factors: 69:40 (F1−F3), 83:17 (F7−F9), 75:25 (F16−F18), 80:20 (F7A−F9A), 50:50 (F10A−F12A), 80:20 (F13A−F16A), 85:15 (F16A−F18A), 65:35 (F19A−F21A). The CF_3 group of the trifluoroacetato ligand of **5e** and three of the CF_3 substituents on the BAr_f anion were also found rotationally disordered with the occupancy factors 78:22 (F25−F27), 66:36 (F4−F6), 78:22 (F7−F9), and 56:44 (F22−F24). The hydrogen atoms H2A, H2B, and H9 of **6a** were found in a differential Fourier synthesis and refined isotropically by setting the displacement parameter to 120% of the equivalent isotropic *U* value of C2 and C9; one CF_3 group of the BAr_f anion of **6a** was found rotationally disordered with occupancy factors of 80:20 (F16−F18).

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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