Synthesis, Structure, and Reactivity of Cationic Ruthenium(II) Carbene Complexes with Bulky Chelating Bisphosphines: Design of Highly Active Ring Opening Metathesis Polymerization (ROMP) Catalysts

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Complexes of the type $[\{(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2\text{-}\kappa^2P\}XRu{=}CHR]_2(Y)_2$ have been prepared and characterized in solution as well as in the solid state. Parameters governing the ring opening metathesis polymerization (ROMP) activity of these highly active ruthenium catalysts in solution have been assessed. Especially, chloro-bridged dinuclear dicationic ruthenium carbenes with a bis(di-*tert*-butylphosphino)methane ligand and weakly coordinating or noncoordinating anions display extremely high ROMP activity. Comparison of the solution-phase reactivity reported here with high throughput screening results from gas-phase experiments provide further mechanistic insight into the metathesis reaction with these compounds.

Introduction and Background

The introduction of well-defined olefin metathesis ruthenium(II) carbene catalysts (Figure 1) by Grubbs and co-workers[1] has led to a rapid development of these systems in the past decade.[2i,3b,4] Due to the stability and functional group tolerance of these square-pyramidal ruthenium complexes (Figure 1), they have found many applications in organic synthesis and polymer chemistry.[2a,3,5]

Attempts to improve the catalyst performance have aimed toward carbene,[6−8] phosphine,[7,9] or anionic ligand variations,[9,10] phosphine and chloro ligand replacement by chelating Schiff bases,[11] and Lewis acid addition.[12] The activity of homo- and heterobimetallic ruthenium(II) alkylidenes was also assessed.[13] By employing Wanzlick−Arduengo type carbenes instead of the phosphines in the "original" Grubbs type complexes, Herrmann and co-workers[14] set the starting point (**1**) for the development of the "second generation" catalysts

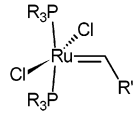

Figure 1.

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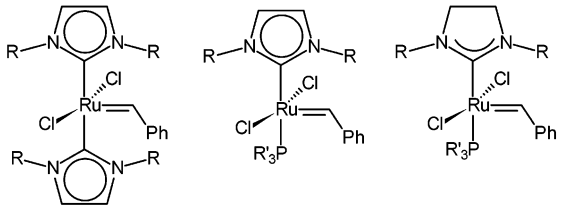


Figure 2. Olefin metathesis catalyst developments by Herrmann (**1, 2**), Nolan (**2**), and Grubbs (**2, 3**).

(**2**,**3**)—a term coined by Grubbs.[4] Independently, Nolan, Herrmann, and Grubbs disclosed the preparation of ruthenium(II) carbene complexes with one phosphine and one Wanzlick−Arduengo type carbene ligand instead of a second phosphine[15,16] (Figure 2). Pyridine as a ligand in these systems was introduced by Grubbs.[17]

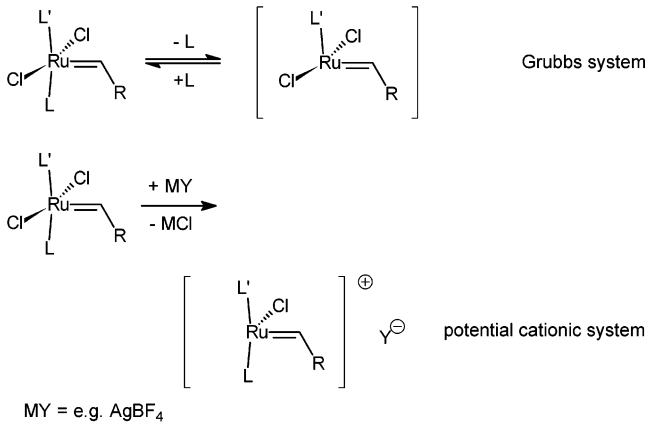
These compounds surpass the "first generation" catalysts in olefin metathesis activity and thus have expanded the scope of possible applications. Recently, Fürstner and co-workers provided a detailed experimental study governing the activity of this class of catalysts;[18a] theoretical background on the mechanism as well as factors governing activity have also been reported by various authors.[18b−h]

Cationic ruthenium allenylidene complexes, a different class of catalysts for olefin metathesis, have been reported by Fürstner and Dixneuf.[19]

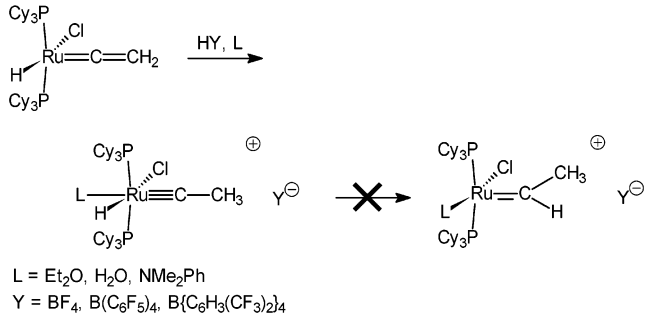
Despite the impressive developments in this field of research, the need to raise catalytic activity in order to decrease catalyst loading remains necessary, especially for applications in polymer chemistry (ring opening metathesis polymerization, ROMP). Given the fact that 14-valence-electron, closed-shell, singlet, neutral d^6-ML_4 systems are proposed to be the active species[9] in Grubbs type complexes and taking into account the cationic nature of many olefin polymerization catalysts, it seemed attractive to synthesize 14-valence-electron cationic ROMP catalysts (Scheme 1).[18b−h,20]

On the basis of a novel synthesis of Grubbs type carbene complexes via protonation of ruthenium vinylidene

Scheme 1



Scheme 2



hydrido precursors, Werner and co-workers had reported the synthesis of carbyne hydrido complexes,[21a] formally isomers of such cationic carbene complexes (Scheme 2).

For specific examples carbyne/carbene isomerism has been described recently.[21b,c] However, for the metathesis-active carbyne complexes shown in Scheme 2, the carbene isomers could not be detected.

In contrast to Werner's results outlined above, our attempts to improve catalytic activity were focused on the use of cis chelating ligands instead of monodentate phosphine or related donor ligands that lead to trans arrangement of these ligands due to large steric bulk. The use of electron-rich chelating ligands was attempted for the following two reasons. First, due to the chelate effect the synthesis and isolation of stable compounds seemed promising. Using the bulky electron-rich chelating ligand bis(di-*tert*-butylphosphino)methane [(*t*-Bu)$_2$PCH$_2$P(*t*-Bu)$_2$, dtbpm)],[22] the synthesis, structure, and ring olefin metathesis activity of the neutral 16-valence-electron complexes (dtbpm-κ^2*P*)Cl_2Ru=CHR had been established by our group (Figure 3).[23−25]

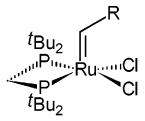


Figure 3.

Second, the trans arrangement of electron-donating phosphorus centers and anionic chloride ligands was expected to facilitate chloride dissociation dramatically. Indeed, the cationic ruthenium carbene complexes can be obtained upon chloride abstraction with suitable Lewis acids, as we have reported previously.[24−27] The

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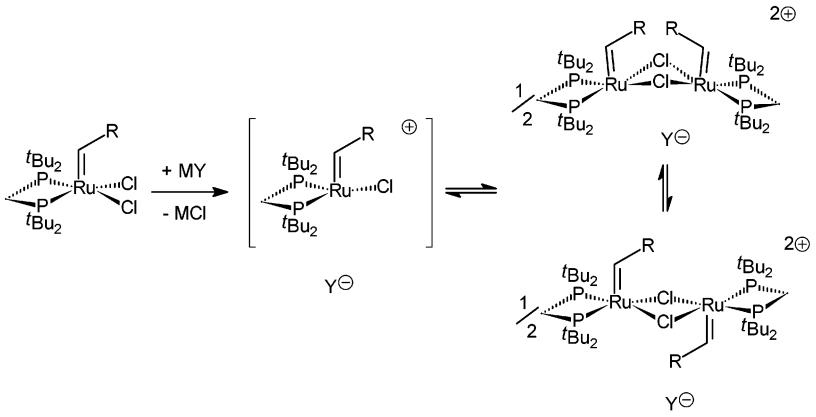
Scheme 3



cations are present as chloro-bridged dimers in solution as well as in the solid state (Scheme 3). In solution these dinuclear dications undergo cis/trans isomerization with respect to the carbene moieties as determined by NMR.[24−26] This cis/trans isomerism is further substantiated by solid-state structures and crossover experiments presented in this report. One of the isomerization pathways is the dissociation into mononuclear cations, which has been proven by crossover[24−27] and trapping[28] experiments.

The dinuclear dications are extremely active homogeneous ROMP catalysts. Presumably, mononuclear 14-valence-electron cations are the metathesis-active species in solution. In an extensive high-throughput gas-phase screening study in collaboration with the Chen group, the parameters governing the intrinsic reactivity of these mononuclear monocations as well as key mechanistic details have been determined.[29−31]

In the present work, the synthesis, structure, and solution-phase ROMP activity of derivatives of these catalysts are reported (Figure 4): effects of varying the bite angle of the chelating ligand, the substituents on the carbene moiety, the coordinating anions, and the noncoordinating counterions have been examined.

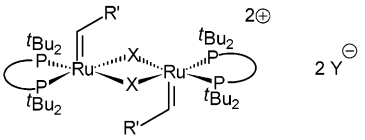


Figure 4.

Results and Discussion

Mechanistic Considerations. To provide an explanation for the parameters governing the catalytic activity of these dicationic complexes, the proposed mechanism for olefin metathesis with these systems needs to be outlined briefly (Scheme 4).

The basis of our mechanistic proposal is the well-accepted Chauvin mechanism.[32] In an initiating step the dinuclear dications **A** dissociate to form the monocations **B** (probably solvent coordinated in solution), which are believed to be the active species on the basis of our crossover and gas-phase studies. In a second equilibrium, these monomeric cationic ruthenium carbene complexes **B** form the olefin π-complex **C**, which is also observable in the gas phase, where formation of the metallacyclobutane **D** is the rate-determining step.[29,30] Product formation (**E**) closes the catalytic cycle.

Four main factors thus seem to govern the overall metathesis rate:[30] (1) the dimer/monomer equilibrium providing the active initiator, (2) the olefin π-complexation at the monomeric 14-valence-electron cation, (3) the barrier of the subsequent rate-determining metallacyclobutane formation (k_2), and (4) in the case of ROMP, "backbiting"[33] of the growing polymer chain hampering further insertions.[7,34]

Factors 1 and 2 may obviously be combined into one "overall" equilibrium, as shown in Scheme 5. However, the two equilibria will be treated separately not only for ease of discussion but also because specifically the

(20) Analogously, cationic metallocenes complexes have proven to be extremely potent catalysts in olefin polymerization: (a) Scheirs, J., Kaminsky, W., Eds. *Metallocene-Based Polyolefins*; Wiley: Chichester, U.K., 2000; Vols. 1 and 2. (b) Ittel, S. D.; Johnson, L. D.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

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(24) Hansen, S. M. Dissertation, Universität Heidelberg, 1999.

(25) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *Angew. Chem.* **1999**, *111*, 1360.

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(28) Hofmann, P.; Volland, M. A. O.; Hansen, S. M.; Eisenträger, F.; Gross, J. H.; Stengel, K. *J. Organomet. Chem.* **2000**, *606*, 88.

(29) Adlhart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 3306.

(30) Volland, M. A. O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem. Eur. J.* **2001**, *7*, 4621.

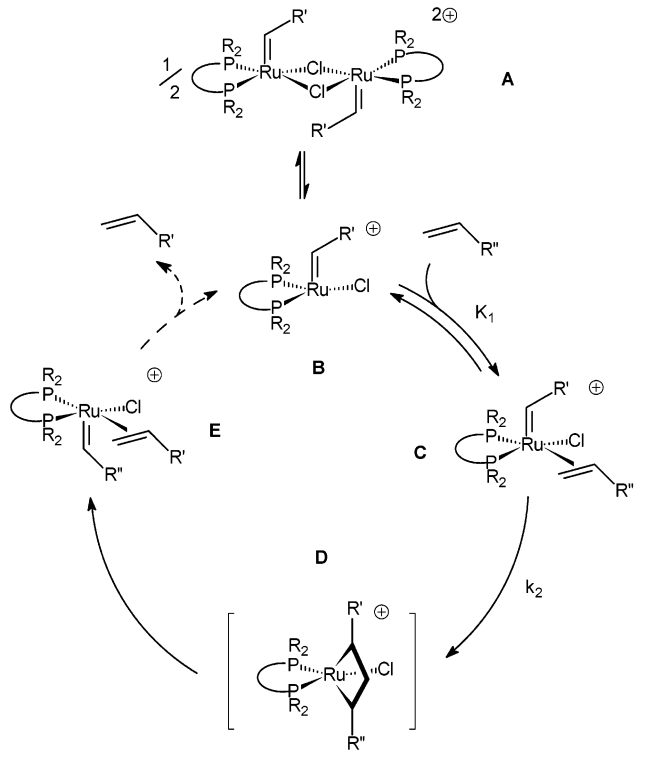
(31) Recently, van Leeuwen and Werner independently reported on neutral carbene complexes with bisphosphines, which show a very low ROMP activity. Addition of trimethylsilyl triflate to these neutral complexes leads to formation of new species, which were not characterized. The reports are incoherent concerning the ROMP activity of these species: (a) Werner, H.; Jung, S.; Gonzáles-Herrero, P.; Ilg, K.; Wolf, J. *Eur. J. Inorg. Chem.* **2001**, 1957. (b) Nieczypor, P.; van Leeuwen, P. W. N. M.; Mol, J. C.; Lutz, M.; Spek, A. L. *J. Organomet. Chem.* **2001**, *625*, 58.

(32) Hérisson, J.-L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

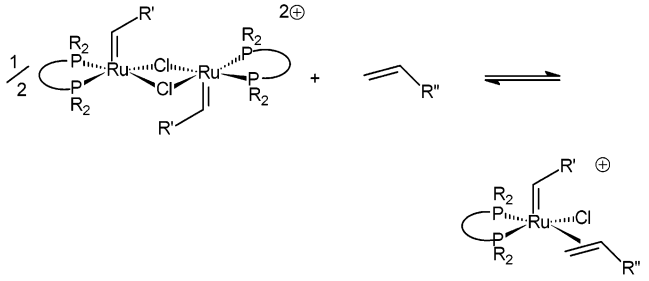
(33) The term "backbiting" indicates a π-complexation of the growing unsaturated polymer chain to the ruthenium center.

(34) Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem.* **1988**, *110*, 2831.

Scheme 4



Scheme 5



π-complexation can be observed in the gas-phase study and thus gives more detailed mechanistic insight.

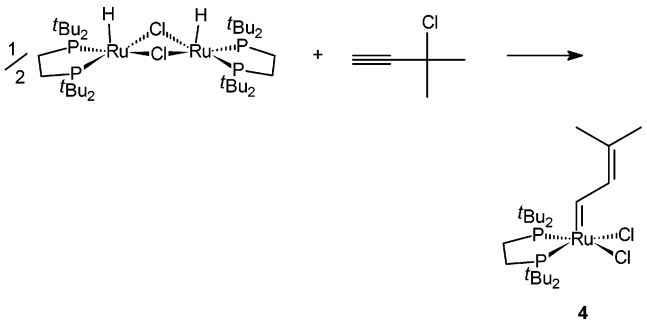
In the following sections, the results of ligand variations upon ROMP activity will be discussed with respect to the mechanism outlined in Scheme 4.

1. (a) Phosphine Bite Angle Variation. To investigate the influence of the P−Ru−P angle on the metathesis activity, the synthesis of complexes with the ethylene-bridged ligand 1,2-bis(di-*tert*-butylphosphino)-ethane ((*t*-Bu)$_2$P(CH$_2$)$_2$P(*t*-Bu)$_2$, dtbpe) was carried out to compare these complexes with the established dtbpm systems.

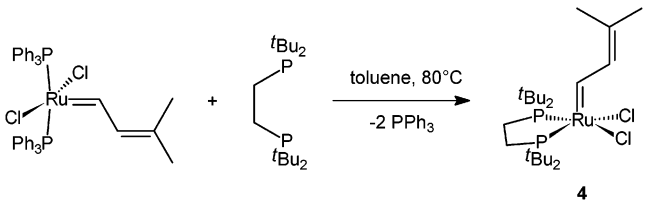
On the basis of the experience with the dtbpm ligand,[25] the neutral complex **4** can be synthesized by treatment of the novel dinuclear dihydride [(dtbpe-κ^2P)-RuH]$_2$(μ_2-Cl)$_2$[35] with propargyl chlorides, as shown in Scheme 6.[36]

We now have developed an alternative and more facile access to dtbpe carbene complexes. Treating the Grubbs type complex (PPh$_3$)$_2$Cl$_2$Ru=CHCH=C(CH$_3$)$_2$[1] with dtbpe leads to the desired complex by simple phosphine exchange[37] (Scheme 7).

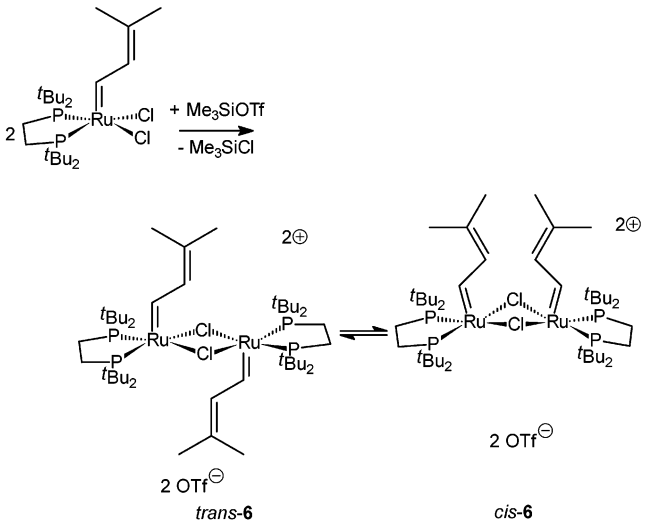
Scheme 6



Scheme 7



Scheme 8



Notably, in the case of dtbpe, the desired carbene complex is formed, whereas in the case of dtbpm, in which the phosphine ligand attacks the carbene moiety, an ylide compound is produced.[23]

Complex **4** has spectroscopic properties very similar to those of the related dtbpm compound (dtbpm-κ^2P)Cl$_2$-Ru=CHCH=C(CH$_3$)$_2$ (**5**). For complex **4**, using CD$_2$Cl$_2$ as the solvent, a characteristic pseudoquartet is observed for Ru=C*H* at δ 16.19 ("q", ^3J(P,H) = 11.5 Hz, ^3J(H,H) = 11.5 Hz) in the ^{1}H NMR spectrum. In comparison to the analogous dtbpm complex **5**,[25] this signal is shifted 0.2 ppm to higher field. The ^{13}C{^{1}H} NMR signal of the carbene carbon atom Ru=*C*H of **4** shows a triplet at δ 298.5 (t, ^2J(P,C) = 13 Hz) and is shifted only 2 ppm to lower field compared to the dtbpm analogue **5**. In the ^{31}P{^{1}H} NMR spectrum of **4**, a singlet is detected at δ 93.6. Interestingly, in complex **4**, the ^{31}P{^{1}H} NMR signal is shifted approximately 60 ppm downfield compared to noncoordinated dtbpe. In the dtbpm complex **5**, on the other hand, the ^{31}P{^{1}H} NMR

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(36) Cf. related synthesis: Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.
(37) Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *J. Organomet. Chem.* **2002**, *641*(1−2), 220.

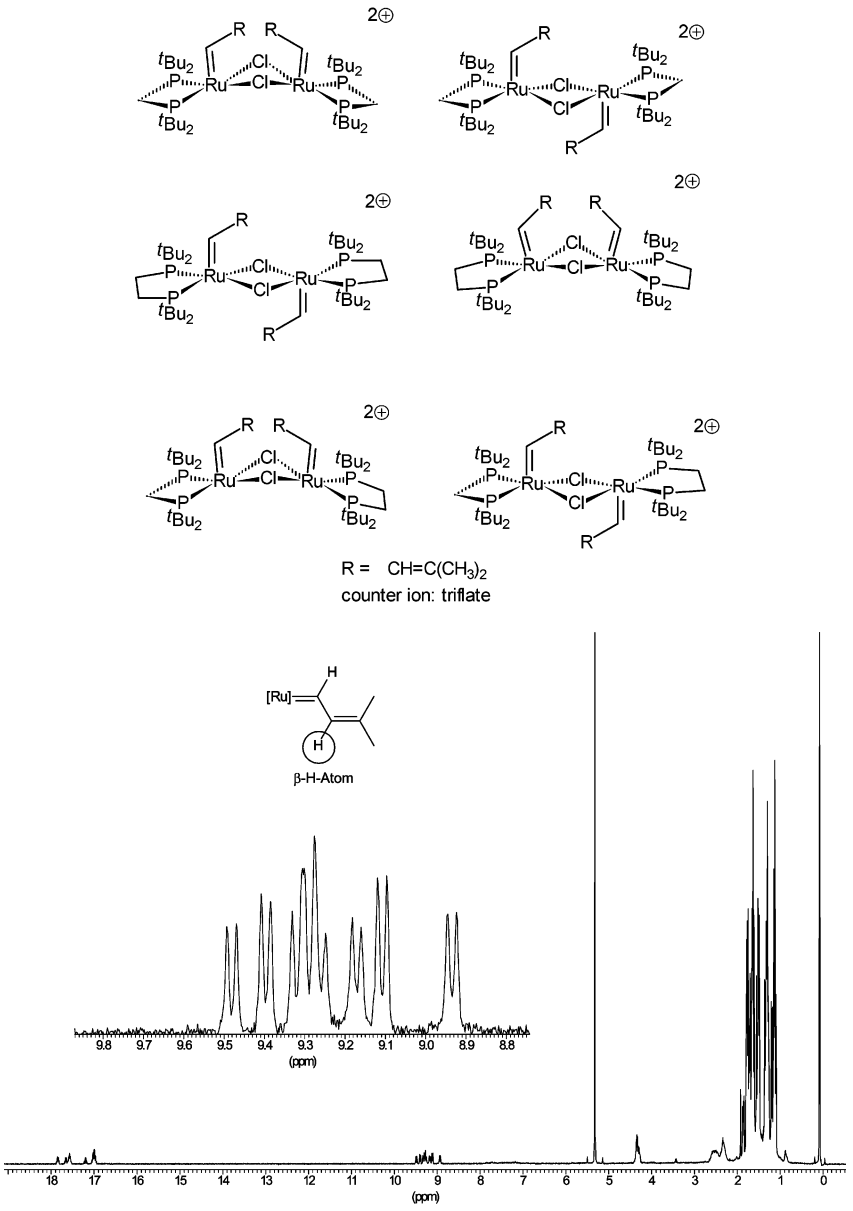

Figure 5. ^{1}H NMR spectrum (500.1 MHz): crossover of [(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**6**) with [(dtbpm-κ^2P)-ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**7**) in CD_2Cl_2 at 298 K. The insert shows eight doublets of β-H atoms of the carbene moieties of the six expected species, proving the presence of [(L-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$^+$ (L = dtbpm, dtbpe) as intermediates in solution as well as the cis/trans isomerism (cf. text).

signal is shifted only about 10 ppm downfield compared to the signal for the noncoordinated ligand dtbpm.

It is noteworthy that the neutral complex **4** shows a very low ROMP activity toward norbornene at ambient temperature in CH_2Cl_2. The related dtbpm complex (dtbpm-κ^2P)Cl_2Ru=CHCH=C$(CH_3)_2$ (**5**) is a modestly active catalyst under the same conditions. This observation for the neutral systems may be interpreted as a ring opening of the strained diphospharuthenacyclobutane, yielding (dtbpm-κ^1P)Cl_2Ru=CHCH=C$(CH_3)_2$ in the initiation step, similar to the initiation of neutral Grubbs carbenes with nonchelating neutral donor ligands. In the dtbpe complex the unstrained diphospharuthenacyclopentane has a much lower tendency for ring opening and thus is a much less active catalyst.

As outlined in Introduction and Background, abstraction of a chloride by an appropriate Lewis acid such as trimethylsilyl triflate (Me_3SiOTf) leads to the formation of chloride-bridged dinuclear dications (Scheme 8). This is a very convenient method for chloride abstraction, since Me_3SiCl is easily removed in vacuo.

The spectroscopic properties of [(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**6**), given in detail in the Experimental Section, are also very similar to those of the dtbpm analogue [(dtbpm-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**7**).[25] One of the possible cis/trans isomerization pathways of **6** has to proceed via mononuclear monocations. Mixing solutions of **6** and **7** should then lead to six species (Figure 5).

This experiment provides very important information about the solution structure. First, if the dinuclear dications (cf. dimeric solid-state structure) were to dissociate completely in solution, no new species should be detected upon mixing solutions of **6** and **7**. Second, the observation of eight signals for the β-hydrogen of the carbene moiety proves (1) formation of mixed dimers, which is only conceivable via short-lived, presumably solvent-coordinated mononuclear cations and

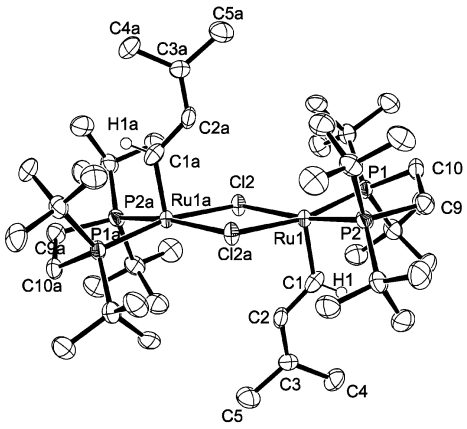

Figure 6. ORTEP plot of [(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**6**) in the solid state. For clarity, the triflate anions and all hydrogen atoms except H1 have been omitted. Displacement ellipsoids are drawn at 50% probability.

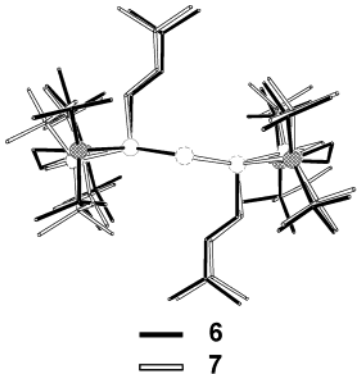

Figure 7. Superimposed solid-state structures of [(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**6**) (solid black sticks) and [(dtbpm-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$_2$$(OTf)_2$ (**7**) (open sticks).[25]

(2) cis and trans isomerism of the dinuclear species. The eight signals belong to *cis*- and *trans*-**6**, *cis*- and *trans*-**7** (due to symmetry, each giving rise to one β-hydrogen resonance) and the mixed dinuclear species *cis*- and *trans*-[(dtbpm-κ^2P)Ru=CHCH=C$(CH_3)_2$(μ-Cl)$_2$(dtbpe-κ^2P)Ru=CHCH=C$(CH_3)_2$](OTf)$_2$ (each giving rise to two β-hydrogen resonances).

It should be noted that complex **6** can be handled in air and is very stable in solution, showing no signs of decomposition (^{1}H and ^{31}P{^{1}H} NMR) in CD_2Cl_2 under argon within 3 weeks at ambient temperature.

Crystals of **6** suitable for X-ray diffraction were grown by very slowly evaporating the solvent from a CH_2Cl_2 solution (Figure 6).When the carbene complexes **6** and **7** are compared with their ligands dtbpe and dtbpm, differences concerning the steric demand around the metal center become obvious (Figure 7). Most notably, the P1−Ru−P2 chelate angle is enlarged by 12°, in a comparison of the dtbpm complex **7** with the dtbpe complex **6**. As a result, the *t*-Bu groups are "pushed" further into the direction of the bridging chloro ligands in complex **6** and shield the metal center even more effectively.

This observation is substantiated by the different olefin complexation constants of the monocationic complexes [(dtbpm-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$^+$ and [(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2$]$^+$ measured in the gas phase.[30]

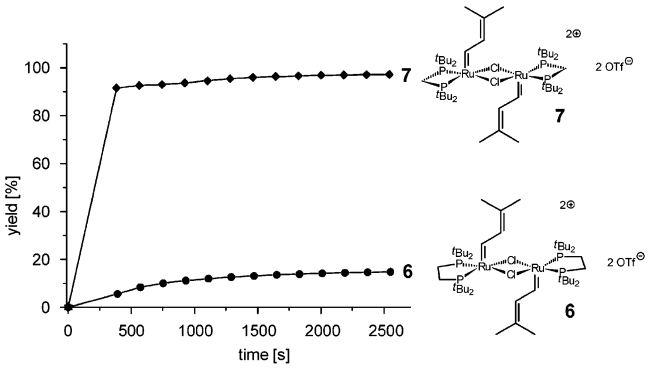

Figure 8. ROMP of cyclooctene (0.5 mL of CD_2Cl_2; 298 K); [COE]:[Ru] = 12 500:1 (=0.008 mol % Ru) under the influence of **6** and **7**.

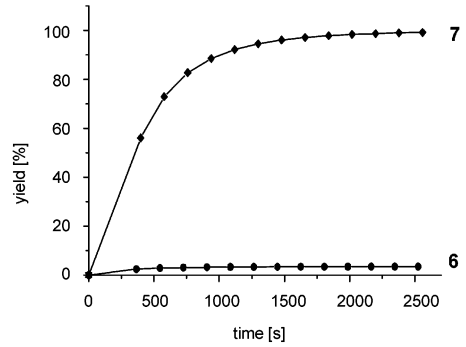

Figure 9. ROMP of 1,5-cyclooctadiene (0.5 mL of CD_2Cl_2; 298 K); [COD]:[Ru] = 1250:1 (=0.08 mol % Ru) under the influence of catalysts **6** and **7**.

Bite Angle Influence on ROMP Activity in Solution. To assess the catalytic activity of these complexes in ring opening metathesis polymerization, the low strain standard test substrates cyclooctene (COE) and 1,5-cyclooctadiene (COD) were employed. Using highly strained norbornene, the differences in activity cannot be assessed for these reactive catalysts. The reaction kinetics, i.e., polymer production, were monitored by NMR as established in the literature.[14,25,39] All kinetic plots in this report for COE and COD, respectively, are presented deliberately according to the same scale and thus allow direct comparison of the data shown in different plots.

Commonly, a cyclooctene-to-ruthenium ratio in the range of 250:1 to 1250:1 is employed for Grubbs ROMP catalysts.[13c] Due to the high activity of the cationic systems in solution, a much lower catalyst loading ([COE]:[Ru] = 12 500:1 = 0.008 mol % Ru) had to be employed in the COE polymerization kinetics reported here.

In full accord with the gas-phase behavior,[30] the ROMP activity in solution is decreased by at least a factor of 10 by enlarging the P−Ru−P angle from 74° (dtbpm systems)[25] to 86° (dtbpe systems) (Figure 8). The same trend is found for the slower ROMP of COD, in which a catalyst loading of 0.08 mol % is necessary (Figure 9).

The gas-phase study[30] had revealed that the overall rate of metathesis of the monocations [(dtbpm-κ^2P)-

(38) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

(39) It should be noted that a high purity of the cycloolefin substrates is crucial to achieve high ROMP rates at these low catalyst loadings.

$ClRu{=}CHCH{=}C(CH_3)_2]^+$ vs $[(dtbpe\text{-}\kappa^2P)ClRu{=}CHCH{=}C(CH_3)_2]^+$ is lowered by a reduced tendency for olefin π-complexation as well as by reduced intrinsic activity, i.e., a higher barrier of the rate-determining step, in the dtbpe case. We assume that dissociation of **6** into active monomers is more facile than dissociation of **7**, due to a larger trans influence of the phosphine ligand in the former and a larger effective steric bulk[38] of dtbpe compared to dtbpm. The preferred formation of active species in the case of complex **6** must then be dramatically overruled by the reduced olefin π-complexation as well as reduced intrinsic activity.

(b) Variation of Phosphine Ligand Bulk. The influence of the steric demand of the phosphine substituents R on metathesis activity has been investigated in the gas phase for R = Cy vs *t*-Bu.[30] In acyclic cross metathesis, the carbene complexes carrying Cy-substituted chelating phosphines reveal a higher overall metathesis rate but a decrease in rate in ROMP reactions, due to backbiting of the growing polymer chain.[30]

To investigate the influence of steric bulk of the phosphine ligand in solution, the synthesis of the complexes was attempted via phosphine substitution. However, the difference in steric bulk of Cy vs *t*-Bu has a significant influence on the tendency of formation of the desired product. As reported, dtbpe readily displaces the monodentate phosphines PPh_3 and PCy_3.[40]

On the other hand, treatment of the Grubbs complex $(PCy_3)_2Cl_2Ru{=}CHPh$ with 1,2-bis(dicyclohexylphosphino)ethane ($Cy_2PCH_2CH_2PCy_2$, dcpe), leads only to formation of traces of the desired complex $(dcpe\text{-}\kappa^2P)Cl_2Ru{=}CHPh$ (**8**), isolated only in sufficient amounts for NMR analysis. Additionally, the undesired product *trans*-$(dcpe\text{-}\kappa^2P)_2RuCl_2$ is formed. The formation of the analogous product $(dtbpe\text{-}\kappa^2P)_2RuCl_2$ (**9**) using the dtbpe ligand is not observed; apparently steric bulk inhibits binding of two such phosphine ligands.

The attractive approach to carbene complexes with Cy-substituted ligands via hydride precursors analogous to $[(dtbpm\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$[23] and $[(dtbpe\text{-}\kappa^2P)RuH]_2(\mu_2\text{-}Cl)_2$[35] failed (Scheme 6), because in the attempted synthesis the known complexes $(dcpm\text{-}\kappa^2P)_2Ru(H)Cl$[41] and $(dcpe\text{-}\kappa^2P)_2Ru(H)Cl$[42] are formed, instead of the chloro-bridged dinuclear systems found for dtbpm and dtbpe (vide supra).

Thus, the difference between Cy- and *t*-Bu-substituted bisphosphines has a drastic influence on the solution-phase ruthenium chemistry described here.

2. Structural Effects of the Carbene Moiety. (a) $[(dtbpm\text{-}\kappa^2P)ClRu{=}CHCH{=}CPh_2]_2(OTf)_2$. Chloride abstraction by treatment of $(dtbpm\text{-}\kappa^2P)Cl_2Ru{=}CHCH{=}CPh_2$ (**10**)[25,26] with an excess of trimethylsilyl triflate leads to formation of $[(dtbpm\text{-}\kappa^2P)ClRu{=}CHCH{=}CPh_2]_2(OTf)_2$ (**11**) in 57% yield.

Suitable crystals for X-ray diffraction were grown by slowly condensing Et_2O onto a solution of **11** in CH_2Cl_2. Surprisingly, and in contrast to all other complexes of this family examined so far, **11** displays a cis arrangement of the carbene moieties in the solid state.

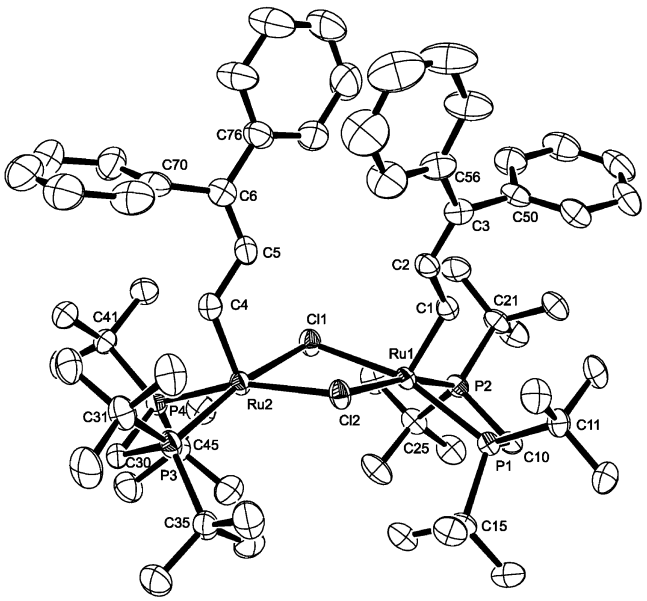

Figure 10. ORTEP plot of $[(dtbpm\text{-}\kappa^2P)ClRu{=}CHCH{=}CPh_2]_2(OTf)_2$ (**11**) in the solid state. For clarity, the triflate anions and all hydrogen atoms are omitted. Displacement ellipsoids are drawn at 50% probability.

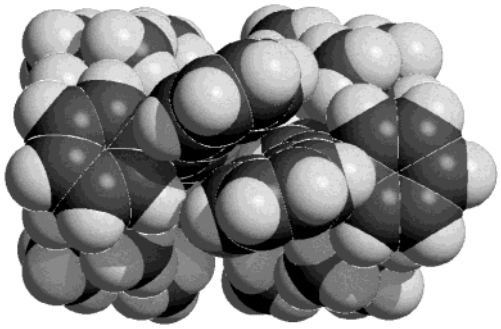

Figure 11. Space-filling model (Schakal, top view) of $[(dtbpm\text{-}\kappa^2P)ClRu{=}CHCH{=}CPh_2]_2(OTf)_2$ (**11**) in the solid state, displaying the nearly parallel arrangement of the phenyl rings of the carbene fragments. The triflate anions are omitted for clarity.

This result corroborates the phenomenon of cis/trans isomerism in solution for these complexes.[24−27]

Due to the large steric bulk of the carbene fragments a trans arrangement of these substituents was expected. Furthermore, the π-systems of these nearly parallel phenyl rings with an average distance of 3.8 Å and an angle between phenyl ring planes of 14.2° should interact repulsively (Figure 10). In general, electron donor substituents on phenyl rings increase this kind of electrostatic repulsion, whereas electron-accepting substituents on phenyl rings lead to decreased electrostatic repulsion.[43] Since the phenyl rings in **11** are in conjugation with the carbene carbons as acceptors, the repulsion between the nearly parallel rings should be small. Packing effects must be responsible for the preference of the cis arrangement in the solid state (Figure 11).

In CD_2Cl_2 solution the analytically pure complex displays two characteristic pseudoquartets for Ru=

(40) Volland, M. A. O.; Straub, B. F.; Gruber, I.; Rominger, F.; Hofmann, P. *J. Organomet. Chem.* **2001**, *617−618*, 288.
(41) Winter, R. F.; Hornung, F. M. *Inorg. Chem.* **1997**, *36*, 6197.
(42) Apparently the wrong NMR solvent (CD_2Cl_2) was given in this paper (cf. ref 41): Mezetti, A.; Del Zotto, A.; Rigo, P.; Pahor, N. B. *J. Chem. Soc., Dalton Trans.* **1989**, 1045.
(43) (a) Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem.* **1995**, *107*, 1092. (b) Vrbanich, J.; Ritchie, G. L. D. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 648.

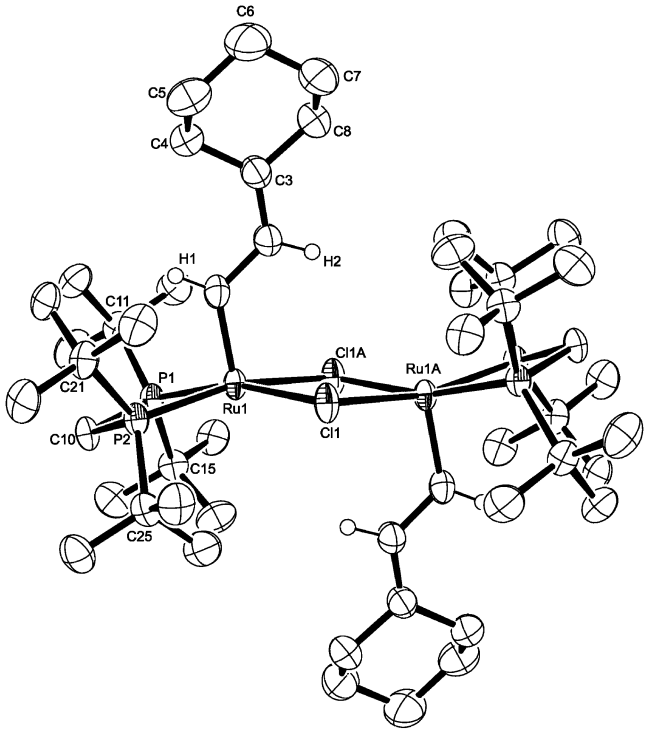

Figure 12. ORTEP plot of [(dtbpm-κ^2*P*)ClRu=CHCH=C$(CH_2)_5$]$_2$$(OTf)_2$ (**13**) in the solid state. For clarity, the triflate anions and all hydrogen atoms except H1 and H2 and have been omitted. Displacement ellipsoids are drawn at 50% probability.

C*H*CH=CPh$_2$ in the ^{1}H NMR spectrum at δ 16.75 and 17.18 with relative intensities of 9:1. Accordingly, the β-H atoms of the carbene moiety (Ru=CHC*H*=CPh$_2$) of the different species show two doublets at δ 9.58 and 10.13 with relative intensities of 1:9. In the ^{31}P{^{1}H} NMR spectrum of **11** two singlets are detected at δ 25.1 and 26.4. These spectroscopic observations are also in accord with the cis/trans isomerism outlined above. Additionally, the analytically pure complex displays very weak signals for a third carbene complex species in the ^{1}H NMR spectrum (cf. the Experimental Section for details). This species is possibly a solvent-coordinated mononuclear monocationic carbene complex[28] that is present in very low concentration and is in equilibrium with the predominant cis and trans species of **11**.

(b) [(dtbpm-κ^2*P*)ClRu=CHCH=C$(CH_2)_5$]$_2$$(OTf)_2$. The neutral precursor complex (dtbpm-κ^2*P*)Cl$_2$Ru=CHCH=C$(CH_2)_5$ (**12**) is prepared by treatment of the dinuclear dihydride [(dtbpm-κ^2*P*)RuH]$_2$(μ_2-Cl)$_2$ with 1-chloro-1-ethynylcyclohexane. Chloride abstraction by addition of trimethylsilyl triflate to a solution of **12** in CH_2Cl_2 leads to formation of the dinuclear dicationic complex [(dtbpm-κ^2*P*)ClRu=CHCH=C$(CH_2)_5$]$_2$$(OTf)_2$ (**13**), which, in CD_2Cl_2 solution, again is present as an equilibrium of cis and trans stereoisomers with respect to the carbene moieties as revealed by NMR.

In the solid state complex **13** displays a trans arrangement of the carbene moieties (Figure 12).

The spectroscopic properties of **13**, which are very similar to those of the closely related compound **7**, are given in detail in the Experimental Section.

Influence of the Carbene Moiety on ROMP Activity: dtbpm Systems. The minor variations of the carbene unit of the complexes **7**, **11**, and **13** expectedly do not have a significant influence on the ROMP activity (Figure 13). Note that, for catalyst **11**, the catalyst loading was lowered to 0.004 mol % Ru. In this case the reaction stops at 75% yield. On the basis of the first data point acquired at t = 625 s with a [COE]:[Ru] ratio of 24 800:1 a remarkable turnover frequency (TOF) of at least 25 s^{-1} at ambient temperature may be derived. The turnover number for cyclooctene in this example is approximately 18 000.

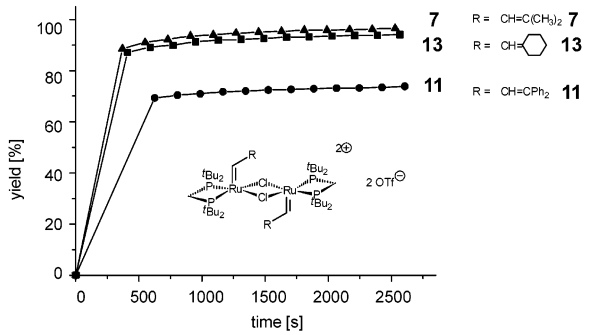

Figure 13. ROMP of cyclooctene (0.5 mL of CD_2Cl_2; 298 K): [COE]:[Ru] = 12 500:1 (=0.008 mol % Ru) under the influence of complexes **7** and **13**. For complex **11**, [COE]:[Ru] = 24 800:1 (=0.004 mol % Ru).

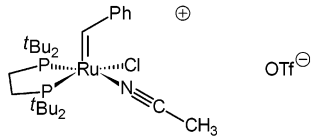

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Figure 14.

(c) [(dtbpe-κ^2*P*)ClRu=CHPh](OTf) (15). With the neutral precursor (dtbpe-κ^2*P*)Cl$_2$Ru=CHPh (**14**)[40] as starting material, a pale green complex of the overall composition [(dtbpe-κ^2*P*)ClRu=CHPh](OTf) (**15**) is obtained analytically pure in 84% yield by chloride abstraction with AgOTf. Attempts to use trimethylsilyl triflate instead of AgOTf for the chloride abstraction were not successful in this case.

In the ^{1}H NMR spectrum in THF-d_8 at 298 K, **15** displays a triplet at δ 17.04 (t, ^3J(P,H) = 12.4 Hz). The ^{31}P{^{1}H} NMR spectrum shows a broad singlet at δ 96.4. When a solution of **15** in either THF-d_8 or CD_2Cl_2 was cooled, various carbene complexes were detected by ^{1}H and ^{31}P{^{1}H} NMR. We assume that these solutions contain chloro-bridged dicationic dimers as well as triflate- and solvent-coordinated species at low temperature. However, addition of acetonitrile leads to clean formation of the adduct complex [(CH$_3$CN)(dtbpe-κ^2*P*)-ClRu=CHPh](OTf) (**16**), which was characterized by NMR at low temperatures (Figure 14).

In the ^{1}H NMR spectrum of **16** in CD_2Cl_2 at 233 K a triplet is found for Ru=C*H* at δ 17.14 (t, ^3J(P,H) = 13.7 Hz) and a singlet for C*H*$_3$CN at δ 2.45. Thus, the coordinated C*H*$_3$CN is shifted downfield by 0.48 ppm compared to noncoordinated C*H*$_3$CN. Two doublets for the inequivalent phosphorus nuclei are detected at δ 87.7 (d, ^2J(P,P′) = 12.4 Hz) and 96.2 (d, ^2J(P,P′) = 12.4 Hz) by ^{31}P{^{1}H} NMR. These spectral data are in accord with the data for the analogous dtbpm complex [(CH$_3$CN)(dtbpm-κ^2*P*)ClRu=CHCH=C$(CH_3)_2$](OTf), which was fully characterized, including a solid-state structure.[28]

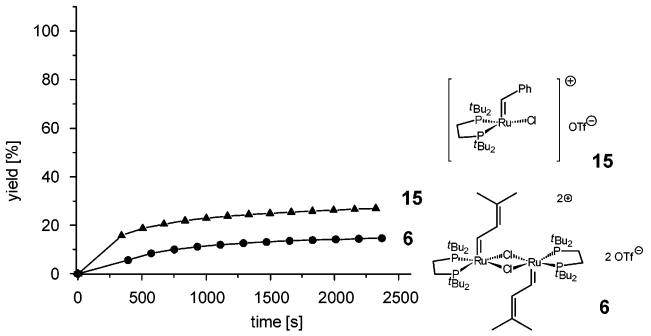


Figure 15. ROMP of cyclooctene (0.5 mL of CD_2Cl_2; 298 K): [COE]:[Ru] = 12 500:1 (=0.008 mol % Ru) under the influence of catalysts **6** and **15**.

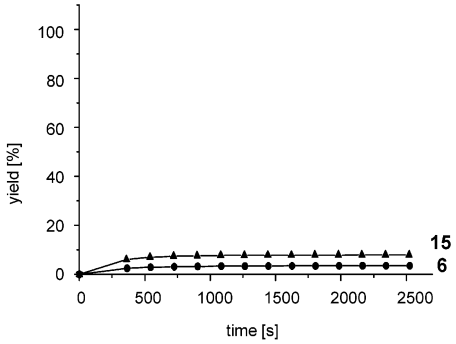


Figure 16. ROMP of 1,5-cyclooctadiene (0.5 mL of CD_2Cl_2; 298 K): [COD]:[Ru] = 1250:1 (=0.08 mol % Ru) under the influence of catalysts **6** and **15**.

Apparently, the steric and electronic properties of the benzylidene ligand inhibit the effective formation of chloro-bridged dinuclear dicationic complexes found for the related compounds with the other carbene substituents studied (vide supra).

Influence of the Carbene Moiety on ROMP Activity: dtbpe Systems. In the gas phase[30] the intrinsic metathesis activity of $[(dtbpe\text{-}\kappa^2P)ClRu{=}CHCH{=}C(CH_3)_2]^+$ is higher than that of $[(dtbpe\text{-}\kappa^2P)ClRu{=}CHPh]^+$. However, in solution the ROMP activity of complex **15** is higher than the activity of **6** (Figures 15 and 16).

This reversal of activity may be explained by the ease of formation of the active species in solution. While complex **15** shows a reduced tendency to form chloro-bridged dinuclear dications, compound **6** in solution is observable by NMR only as the cis and trans chloro-bridged dimers (vide supra). If the catalytically active species are the monomeric cations, a higher concentration of these species is present in the case of **15** than in the case of **6**. As a result, the intrinsically less active complex displays a higher ROMP activity in solution due to this more favorable preequilibrium. This interpretation is corroborated by the small polydispersity index (PDI) of polymers formed under the influence of **15**.[44] A small PDI points to a facile formation of the active species.

In the ROMP of COD, both **6** and **15** show very low activity (Figure 15); as noted previously, the kinetic results are all presented on the same scale—a direct comparison, e.g. with Figure 8, is possible.

(44) Hamilton, J.; Hofmann, P.; Volland, M. A. O. Manuscript in preparation.

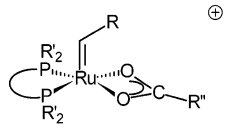
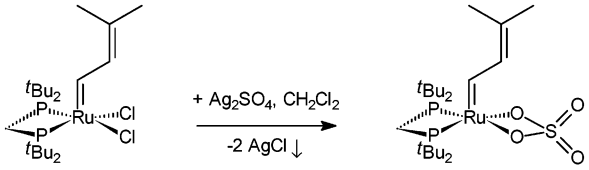


Figure 17.

3. Influence of Coordinating Ions. After having established the importance of the mononuclear carbene species in solution, the coordinating anions X of the complexes $(R'_2P(CH_2)_nPR'_2\text{-}\kappa^2P)X_2Ru{=}CHR$ were varied. In comparison to X = Cl, special emphasis was put on anions which may coordinate in a bidentate fashion, as shown for a carboxylate as an example in Figure 17.

(a) (dtbpm-κ^2P)(SO_4-κ^2O)Ru=CHCH=$C(CH_3)_2$ (17). A bidentate coordination mode of a sulfate is observable in the neutral compound (dtbpm-κ^2P)(SO_4-κ^2O)Ru=CHCH=$C(CH_3)_2$ (**17**), which is obtained as a red-violet powder by treatment of (dtbpm-κ^2P)Cl_2Ru=CHCH=$C(CH_3)_2$ (**5**) with Ag_2SO_4 in CH_2Cl_2 (Scheme 9).

Scheme 9

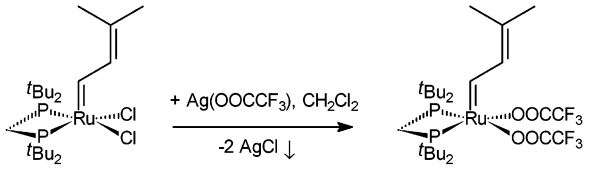


5 **17**

Compound **17** displays no unusual spectroscopic properties. In the solid state the bidentate coordination mode of the sulfate ligand is confirmed by X-ray analysis (cf. the Supporting Information for details).

(b) (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_3)_2$ (18) and (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_2)_5$ (19). Complexes (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_3)_2$ (**18**) and (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_2)_5$ (**19**) are easily synthesized by treatment of the precursor complexes (dtbpm-κ^2P)Cl_2Ru=CHR with $Ag(CF_3COO)$, as shown for **18** in Scheme 10.

Scheme 10



5 **18**

The ^1H NMR spectrum of complex **18** in CD_2Cl_2 at 298 K shows a characteristic doublet of triplets for Ru=C*H* at δ 17.59 (dt, $^3J(P,H) = 8.5$ Hz, $^3J(H,H) = 11.4$ Hz), which is shifted downfield by 1.1 ppm compared to the precursor (dtbpm-κ^2P)Cl_2Ru=CHCH=$C(CH_3)_2$ (**5**). Analogously, the Ru=*C*H signal of **18** in the $^{13}C\{^1H\}$ NMR spectrum is shifted downfield by 14 ppm to δ 310.6 (t, $^2J(P,C) = 6.9$ Hz). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 29.8. Interestingly, the ^{19}F NMR spectrum of **18** in CD_2Cl_2 at 298 K shows only one sharp singlet at δ −76.2. This signal is shifted to δ −75.8 upon lowering the temperature to 213 K. If complex **18** were present in solution as the monocationic $[(dtbpm\text{-}\kappa^2P)(CF_3COO\text{-}\kappa^2O)Ru{=}CHCH{=}C(CH_3)_2]^+$ and anion $(CF_3COO)^-$ and exchange processes were slow on the

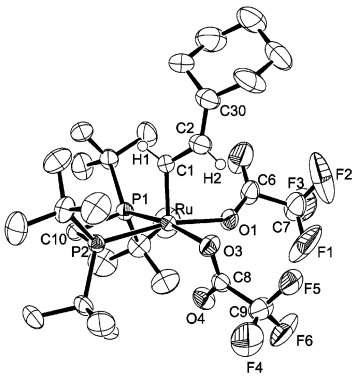


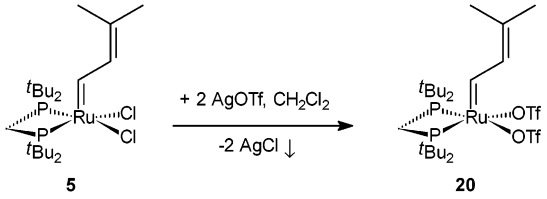
Figure 18. ORTEP plot of (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_2)_5$ (**19**) in the solid state. For clarity, all hydrogen atoms except for H1 and H2 are omitted. Displacement ellipsoids are drawn at 50% probability.

NMR time scale, the ^{19}F NMR spectra should display two signals. However, since only one sharp singlet is detected, probably both $(CF_3COO)^-$ species are coordinated to the Ru center.

This assumption is supported by the solid-state structure of (dtbpm-κ^2P)$(CF_3COO)_2$Ru=CHCH=$C(CH_2)_5$ (**19**) (Figure 18) with both CF_3COO anions coordinated to ruthenium.

(c) (dtbpm-κ^2P)(TfO-κ^1O)$_2$Ru=CHCH=$C(CH_3)_2$ (20). On the basis of the experimental results for the trifluoroacetate ligand, replacement of both chlorides of (dtbpm-κ^2P)Cl_2Ru=CHCH=$C(CH_3)_2$ (**5**) by triflate seemed attractive. In general, triflate coordinates more weakly to the metal center but may still coordinate in a bidentate fashion. The complex (dtbpm-κ^2P)(TfO-κ^1O)$_2$Ru=CHCH=$C(CH_3)_2$ (**20**), in which a monodentate binding mode of two triflates is preferred, is easily accessible by treatment a solution of **5** in CH_2Cl_2 with AgOTf (Scheme 11).[24]

Scheme 11



Complex **20** has spectroscopic properties similar to those of the closely related compounds **18** and **19** (cf. the Experimental Section for details). It is noteworthy that, as in **19**, both anionic ligands are coordinated to the Ru center, as indicated again by the ^{19}F NMR spectra (**20** in CD_2Cl_2: at 298 K, δ −79.1 (s); at 213 K, δ −79.4 (s)) and by the solid-state structure of **20** (Figure 19).

Influence of the Coordinating Ions on ROMP Activity. Complex **17**, containing the bidentate sulfate ligand, has an extremely low ROMP activity even with the highly reactive substrate norbornene. It is reasonable to assume that this is due to a reduced tendency to open a coordination site at the catalytically active Ru center due to the chelate effects of the dtbpm as well as the sulfate ligand.

Complexes **18**−**20** with coordinating monoanionic ligands are also much less reactive than the chloro-

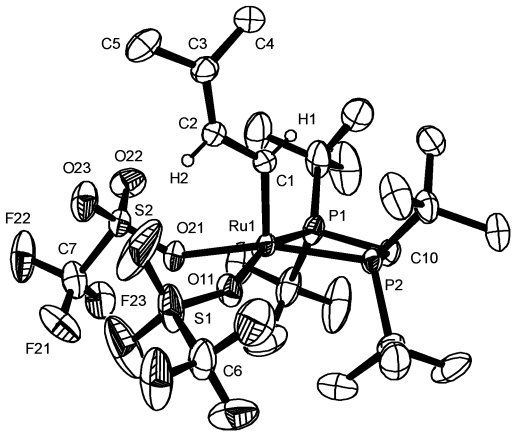


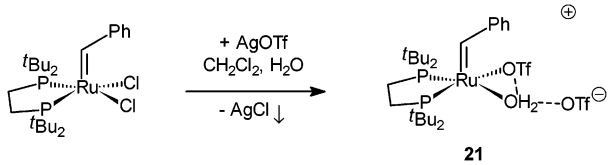
Figure 19. ORTEP plot of (dtbpm-κ^2P)(TfO-κ^1O)$_2$Ru=CHCH=$C(CH_3)_2$ (**20**) in the solid state. For clarity, all hydrogen atoms except for H1 and H2 are omitted. Displacement ellipsoids are drawn at 30% probability.

bridged dicationic dinuclear complexes described above. Most likely, there are two reasons for this observation. First, the compounds **18**−**20** apparently do not dissociate easily to form catalytically active monocations. Second, it was found in the gas phase that [(dtbpm-κ^2P)(TfO)Ru=CHCH=$C(CH_3)_2$]$^+$ has a much lower intrinsic activity than the corresponding chloride derivative [(dtbpm-κ^2P)ClRu=CHCH=$C(CH_3)_2$]$^+$. On the basis of the solution-phase results as well as the gas-phase study, which revealed a decrease of the intrinsic reactivity for [(dtbpm-κ^2P)XRu=CHCH=$C(CH_3)_2$]$^+$ in the order X = Cl > Br > I,[30] the development of catalysts with chloride as the coordinating ion seems most promising.

4. The Water-Coordinated Carbene Complex [(dtbpe-κ^2P)(H_2O-κO)(OTf-κO)Ru=CHPh](OTf) (21). The stability of catalysts toward moisture is of crucial importance for possible applications. We have prepared and fully characterized a water-coordinated cationic carbene complex that shows catalytic activity.

The complex [(dtbpe-κ^2P)(H_2O-κO)(OTf-κO)Ru=CHPh](OTf) (**21**) is obtained by treatment of (dtbpe-κ^2P)Cl_2Ru=CHPh with AgOTf in CH_2Cl_2 in the presence of an excess of water (Scheme 12).

Scheme 12. Synthesis of the Complex [(dtbpe-κ^2P)(H_2O-κO)(OTf-κO)Ru=CHPh](OTf) (21)[a]



[a] Dashed lines indicate hydrogen bridging, as established by a solid-state structure determination (vide infra).

In the ^1H NMR spectrum of **21** in CD_2Cl_2 at 243 K four doublets are observed for the diastereotopic *t*-Bu groups at δ 0.91, 1.11, 1.36, and 1.51. The coordinated H_2O is detected at remarkably low field at 7.26 ppm, and a characteristic triplet is found for Ru=C*H* at 17.23 ppm. In the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at 243 K the two doublets at δ 97.6 ($^2J(P,P') = 12.8$ Hz) and δ 100.9 ($^2J(P,P') = 12.8$ Hz, $P(CH_2)_2P'$) are observed, which is in accord with two inequivalent phosphorus centers.

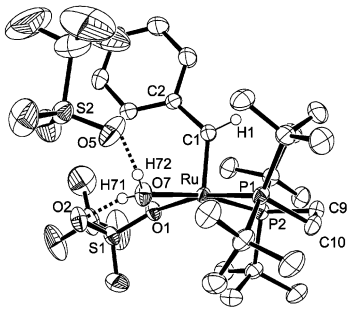


Figure 20. ORTEP plot of [(dtbpe-κ^2P)(H_2O-κO)(OTf-κO)-Ru=CHPh](OTf) (**21**) in the solid state. For clarity, all hydrogen atoms except for H1, H71, and H72 are omitted. Displacement ellipsoids are drawn at 50% probability.

The structural assignment given in Scheme 12 is in agreement with the spectroscopic data in solution as well as the solid-state structure shown in Figure 20.

Hydrogen bridges exist between protons of the coordinated H_2O and the triflates in the solid state, as indicated by the distances O2−O7 = 2.78 Å and O5−O7 = 2.65 Å and the angles O2−H71−O7 = 165° and O5−H72−O7 = 170°.

It should be noted that the ROMP activity of [(dtbpe-κ^2P)(H_2O-κO)(OTf-κO)Ru=CHPh](OTf) (**21**) is also lower than that of the complex [(dtbpe-κ^2P)ClRu=CHPh](OTf) (**15**) in anhydrous solvents. Nevertheless, both complexes are active ROMP catalysts, even in the presence of a large excess of water, as will be reported elsewhere.[44]

5. Noncoordinating Counterions. A pronounced influence of counterions on catalyst activity as well as polymer characteristics is well-established, e.g. in the case of cationic metallocene polymerization catalysts.[45] Therefore, the counterion Y^- influence on the catalyst activity of the cationic carbene complexes [(dtbpm-κ^2P)-ClRu=CHCH=$C(CH_3)_2]_2(Y)_2$ was examined, focusing on noncoordinating anions.

Synthesis of [(dtbpm-κ^2P)ClRu=CHCH=$C(CH_3)_2]_2$-$(BArF)_2$ (**22**) with the borate anion $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$ ($=BArF^-$)[46] was carried out by treating [(dtbpm-κ^2P)-ClRu=CHCH=$C(CH_3)_2]_2(OTf)_2$ (**7**) with NaBArF in a mixture of CH_2Cl_2 and Et_2O. The analytically pure complex **22** was obtained as a reddish brown powder upon repeated recrystallization by slowly condensing hexane onto a solution of **22** in CH_2Cl_2. As expected, the metal fragment of compound **22** shows the same ^1H and $^{31}P\{^1H\}$ spectral data as the metal fragment of its precursor **7**. To confirm complete replacement of the triflate ions by $BArF^-$, a ^{19}F NMR spectrum was measured, which reveals only a singlet at δ −62.7 (BArF) for complex **22** in CD_2Cl_2 at 298 K. No ^{19}F resonance of the triflate of the precursor [(dtbpm-κ^2P)-ClRu=CHCH=$C(CH_3)_2]_2(OTf)_2$ (**7**) at δ −79.1 is detected. The elemental analysis is also in accord with a complete exchange of the anions.

Influence of the Noncoordinating Ions on ROMP Activity. The counterion actually has a small effect on the ROMP activity of catalysts **7** and **22**.

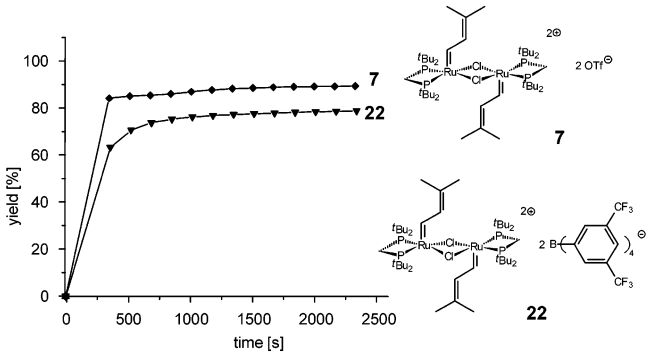


Figure 21. ROMP of cyclooctene (0.5 mL of CD_2Cl_2; 298 K): [COE]:[Ru] = 12 500:1 (=0.008 mol % Ru) under the influence of catalysts **7** and **22**.

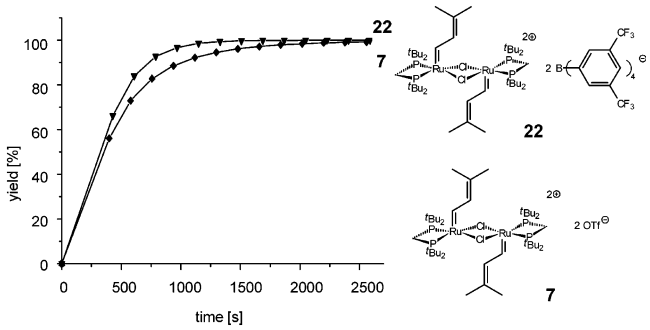


Figure 22. ROMP of 1,5-cyclooctadiene (0.5 mL of CD_2Cl_2; 298 K): [COD]:[Ru] = 1250:1 (=0.08 mol % Ru) under the influence of catalysts **7** and **22**.

In the case of cyclooctene as the substrate, catalyst **7** is slightly more active than **22** (Figure 21). However, using cyclooctadiene as the substrate, the reactivity of **22** is practically the same as that of **7** (Figure 22).

We cannot yet explain this small effect. It should be noted that the counterion also has an influence on polymer characteristics such as tacticity,[47] as will be reported in detail elsewhere.[44]

6. ROMP Activity: Comparison with First- and Second-Generation Grubbs Systems in Solution. So far, the parameters governing the ROMP activity of cationic carbene complexes have been presented. To benchmark their activity against established systems, a comparison with first- and second-generation Grubbs type systems was carried out.

In the gas phase,[29,30] the active species of the first-generation Grubbs catalysts showed a higher metathesis activity than the cationic complexes with chelating phosphines. On the other hand, in solution the cationic complexes are much more active ROMP catalysts for cyclooctene than both first- and second-generation Grubbs systems (Figure 23).

In contrast, the second-generation Grubbs systems are more active in the ROMP of cyclooctadiene (Figure 24).

At this point, we cannot provide a simple and obvious explanation for these changes in activity depending on the substrate. As pointed out in a thorough study by Fürstner,[18] however, the metathesis activity always needs to be evaluated for different substrates: a single catalyst may not be the most suitable for all reactions.

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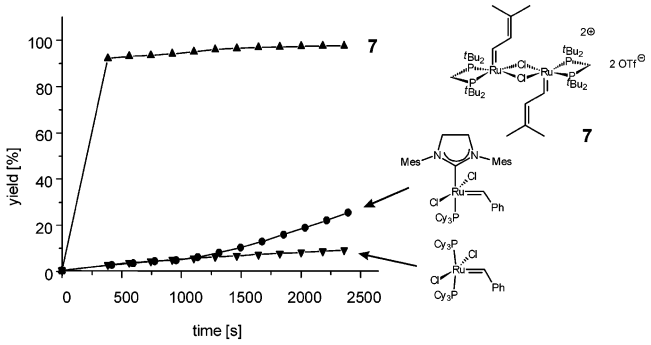

Figure 23. ROMP of cyclooctene (0.5 mL of CD_2Cl_2; 298 K): [COE]:[Ru] = 12 500:1 (=0.008 mol % Ru) under the influence of **7** and first- and second-generation Grubbs catalysts.

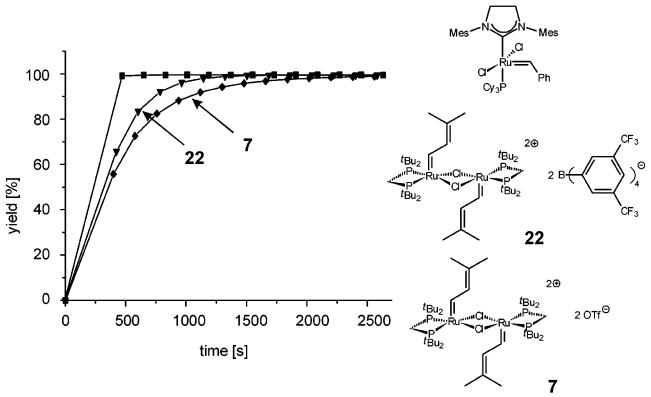

Figure 24. ROMP of 1,5-cyclooctadiene (0.5 mL of CD_2Cl_2; 298 K): [COD]:[Ru] = 1250:1 (=0.08 mol % Ru) under the influence of **7**, **22**, and second-generation Grubbs catalyst.

7. Summary of ROMP Activity of Cationic Carbene Complexes in Solution. The results presented in this study may be summarized as follows.

(1) Enlargement of the bite angle of the chelating bisphosphine ligand in the cationic systems results in a drastic reduction of ROMP activity.

(2) The steric bulk on the phosphine ligands is crucial for the stability and facile accessibility of carbene complexes with chelating bisphosphines. The sterically extremely bulky *t*-Bu substituents are especially favorable.

(3) The carbene moiety of the systems examined in the present study only has a modest influence on the overall ROMP rate. However, comparison of compounds [(dtbpe-κ^2P)ClRu=CHPh](OTf) (**15**) and [(dtbpe-κ^2P)-ClRu=CHCH=$C(CH_3)_2$]$_2$(OTf)$_2$ (**6**) revealed the important influence of the carbene moiety on the preequilibrium forming the catalytically active monomers.

(4) Attempts to replace both chlorides of (dtbpm-κ^2P)Cl_2Ru=CHR by weakly coordinating ligands such as CF_3COO^- and OTf^- result in formation of neutral compounds with a low ROMP activity.

(5) Weakly coordinating to noncoordinating anions Y^- in the systems [(dtbpm-κ^2P)ClRu=CHR]$_2$(Y)$_2$ show a modest influence on the ROMP activity; however, a change in polymer characteristics is observed.

(6) In comparison to neutral Grubbs type catalysts with trans donor ligands, dtbpm cations display a much higher ROMP activity for cyclooctene, whereas the second-generation Grubbs catalyst is slightly more active in ROMP of cyclooctadiene.

Conclusion

In the present study, parameters governing the ROMP activity of complexes of the type [{(*t*-Bu)$_2$P-$(CH_2)_n$P(*t*-Bu)$_2$-κ^2P}XRu=CHR]$_2$(Y)$_2$ have been examined. Along with the gas-phase results, and on the basis of our current mechanistic understanding of the metathesis process with the cationic systems, variations of the substituents on the diphosphinomethane ligands are worth examining. Furthermore, steric and electronic factors of the carbene moiety, facilitating the dimer/monomer equilibrium in solution, are currently being investigated. Additionally, characteristics of the ROM polymers will be determined. The influence of chiral bidentate phosphine ligands is also presently being studied.

Further development of these catalysts seems promising. The cationic dtbpm systems, to the best of our knowledge, belong to the group of most active homogeneous Ru ROMP catalysts currently available.

Experimental Section

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were purchased or prepared according to published procedures: AgOTf (99.995%), $(CH_3)_3Si(OSO_2CF_3)$, Ag_2SO_4, $Ag(CF_3COO)$ (Aldrich), $(PCy_3)_2Cl_2Ru$=CHPh (Strem), (tricyclohexylphosphine)[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)(benzylidene)]-ruthenium dichloride (Strem), 1-chloro-1-ethynylcyclohexane,[49] [(dtbpm-κ^2P)RuH]$_2$(μ_2-Cl)$_2$,[23] $(PPh_3)_2Cl_2Ru$=CHCH=$C(CH_3)_2$,[37] 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe),[48] (dtbpm-κ^2P)-Cl_2Ru=CHCH=$C(CH_3)_2$ (**5**),[23] [(dtbpm-κ^2P)ClRu=CHCH=$C(CH_3)_2$]$_2$(OTf)$_2$ (**7**),[25] (dtbpm-κ^2P)Cl_2Ru=CHCH=CPh_2 (**10**),[25] (dtbpe-κ^2P)Cl_2Ru=CHPh (**14**),[40] [Na][(3,5-$(CF_3)_2C_6H_3)_4$B] (=NaBArF).[46] NMR spectra were recorded using a Bruker DRX 300 or DRX 500 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard. ^{31}P{^{1}H} NMR spectra were calibrated to an external standard (85% H_3PO_4) and ^{19}F NMR spectra to 1,2-difluorobenzene (δ −139.0) as external standard. Abbreviations used are as follows: s = singlet, d = doublet, t = triplet, dt = doublet of triplets, q = quartet, quint = quintet, br = broad signal. Quotation marks indicate a pseudo multiplet. $\Sigma()$ represents the sum of integrated NMR signals over the given range. N = width of the NMR multiplet in Hz. Elemental analyses were carried out at *Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg*.

X-ray Structural Determinations. Frames corresponding to a sphere of data were collected using 0.3° ω scans with a SMART CCD area detector: radiation, Mo Kα; λ = 0.710 73 Å. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space. Structure solution and refinement was carried out with the SHELXTL program system.[50] Crystallographic data for the structure reported here have been deposited as supplementary publications at the Cambridge Crystallographic Data Center (for the CCDC number for each

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compound, see the compound characterization). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

ROMP Kinetics for COE. A representative procedure is described for the complex [(dtbpm-κ^2P)ClRu=CHCH=C$(CH_3)_2]_2$-$(OTf)_2$ (**7**). In a drybox 1.6 mg (1.25 μmol) of [{(dtbpm-κ^2P)-ClRu=CHCH=C$(CH_3)_2]_2(OTf)_2$ (**7**) was dissolved in CD_2Cl_2 (2.5 mL). From this stock solution, 50 μL (0.025 μmol of complex = 0.050 μmol Ru) was transferred via microliter syringe into a 1 mL plastic syringe containing CD_2Cl_2 (0.45 mL). Into an NMR tube degassed cyclooctene (81 μL, 625 μmol) was filled by means of a microliter syringe. The catalyst solution in the plastic syringe was then added to the cyclooctene in the NMR tube, such that thorough mixing was ensured; however, formation of bubbles was avoided. The NMR tube was then sealed with a plastic cap, taken out of the drybox, and tranferred into the NMR spectrometer.

The reaction was monitored in a Bruker DRX 500 spectrometer; spectra were taken every 180 s. To determine the yield, the allylic protons of the cyclooctene (δ 2.15 [br m]) and those of the ROMP polymer (δ 1.95 [br m, trans] and δ 1.99 [br m, cis]) were used. The integral from δ 1.9 to 2.3 in every spectrum was normalized to 1. From the ratio of the integrals of cyclooctene and ROMP poylmer the yield was directly determined. The formation of saturated polymers by possibly competing cationic polymerization may be excluded on the basis of the NMR data of the polymer formed under these conditions, because the ratio of the integrals of the olefinic protons (δ 5.33 [br "t", cis] and δ 5.36 [br s, trans]) to those of the allylic protons (δ 1.95 [br s, trans] and δ 1.99 [br "t", cis]) and the protons in β- and γ-positions (δ 1.30 [br m]) is 2:4:8.

ROMP Kinetics for COD. A representative procedure is described for the complex [(dtbpm-κ^2P)ClRu=CHCH=C$(CH_3)_2]_2$-$(OTf)_2$ (**7**). In a drybox 1.6 mg (1.25 μmol) of [{(dtbpm-κ^2P)-ClRu=CHCH=C$(CH_3)_2]_2(OTf)_2$ (**7**) was dissolved in CD_2Cl_2 (2.5 mL). From this stock solution, 0.5 mL (0.25 μmol of complex = 0.50 μmol of Ru) was transferred into a NMR tube containing degassed 1,5-cyclooctadiene (COD) (77 μL, 625 μmol)). The NMR tube was then sealed with a plastic cap, shaken thoroughly, taken out of the drybox, and transferred into the NMR spectrometer.

The reaction was monitored in a Bruker DRX 500 spectrometer; spectra were taken every 180 s. To determine the yield, the allylic protons of the cyclooctadiene (δ 2.36 [br m]; integration from 2.29 to 2.46 ppm) and those of the ROMP polymer (δ 2.10 [br m]; integration from 2.01 to 2.20 ppm) were used. The sum of both integrals was normalized to 1. From the ratio of both integrals, the yield could be directly determined. For purposes of verification the ratio of the integrals of the olefinic protons of cyclooctadiene (δ 5.57 [br m]) and of the ROMP polymer (δ 5.40 [br m]) was analyzed.

(dtbpe-κ^2P)Cl_2Ru=CHCH=C$(CH_3)_2$ (4). $(PPh_3)_2Cl_2$Ru=CHCH=C$(CH_3)_2$ (243 mg, 0.318 mmol), 1,2-bis(di-*tert*-butylphosphino)ethane (111 mg, 0.349 mmol, 1.1 equiv), and 15 mL of toluene were combined in a Schlenk tube. With stirring, the reaction mixture was heated to 80 °C in an oil bath for 1 h and afterward kept for 1 h at ambient temperature. The reaction mixture was reduced in volume to 2 mL in vacuo. By addition of hexane (15 mL) a red-brown powder was precipitated and separated by cannula filtration. The analogous precipitation procedure was repeated twice with toluene (2 mL)/hexane (15 mL). The remaining solid was then dissolved in CH_2Cl_2 (1 mL) and precipitated with Et_2O (10 mL). Cannula filtration was carried out at −78 °C to reduce loss of product. The remaining red-brown powder was washed twice at ambient temperature with Et_2O (5 mL) and then with hexane (5 mL) and finally dried in vacuo. Yield: 130 mg (73%).

^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.15 ("d", ^3J(P,H) = 11.8 Hz, 18H, C(CH_3)$_3$), 1.45 ("d", ^3J(P,H) = 12.3 Hz, 18H, C(CH_3)$_3$), 1.49 (s, 3H, CH=C(CH_3)CH$_3$), 1.57 (s, 3H, CH=C(CH_3)CH_3), 2.19−2.34 (m, 4H, P(CH_2)$_2$P), 8.73 (d, ^3J(H,H) = 11.5 Hz, 1H, CH=C(CH_3)CH$_3$), 16.19 ("q", ^3J(P,H) = 11.5 Hz, ^3J(H,H) = 11.5 Hz, 1H, Ru=CH). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 298 K, [DEPT-135]): δ 20.7 (s, CH=C(CH_3)CH$_3$, [CH, CH$_3$]), 23.7 ("dd", J(P,C) = 16.6 Hz, J(P′,C) = 14.1 Hz, P(CH_2)$_2$P, [CH_2]), 28.1 (s, CH=C(CH_3)CH_3, [CH, CH$_3$]), 29.3 (s, C(CH_3)$_3$, [CH, CH$_3$]), 30.7 (s, C(CH_3)$_3$, [CH, CH$_3$]), 37.1 (m, N = 31.5 Hz, C(CH_3)$_3$, [C_q]), 38.2 (m, N = 33.2 Hz, C(CH_3)$_3$, [C_q]), 140.6 (s, CH=C(CH_3)CH$_3$, [C_q]), 148.7 (s, CH=C(CH_3)-CH$_3$, [CH, CH$_3$]), 298.5 (t, ^2J(P,C) = 13 Hz, Ru=CH, [CH, CH$_3$]). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 93.6 (P(CH_2)$_2P$). Anal. Calcd for $C_{23}H_{48}Cl_2P_2Ru$: C, 49.46; H, 8.66; P, 11.09. Found: C, 49.42; H, 8.37; P, 11.35. Mp: 218 °C dec.

[(dtbpe-κ^2P)ClRu=CHCH=C$(CH_3)_2]_2(OTf)_2$ (6). In a Schlenk tube (dtbpe-κ^2P)Cl_2Ru=CHCH=C$(CH_3)_2$ (60 mg, 0.107 mmol) in CH_2Cl_2 (5 mL) was treated with $(CH_3)_3Si(OSO_2CF_3)$ (23 μL, 0.119 mmol, 1.1 equiv) at ambient temperature with stirring. After 45 min the reaction mixture was reduced in volume to 1 mL and by addition of Et_2O (5 mL) a red-violet precipitate was formed, which was separated by cannula filtration. The remaining microcrystalline solid was reprecipitated twice from CH_2Cl_2 (0.5 mL) with Et_2O (5 mL) and then washed three times with Et_2O (2 mL) and dried in vacuo to yield a red-violet powder. Yield: 52 mg (72%).

^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.14 ("d", ^3J(P,H) = 13.0 Hz, 25H, C(CH_3)$_3$), 1.20 ("d", ^3J(P,H) = 13.2 Hz, 18H, C(CH_3)$_3$), 1.50 ("d", ^3J(P,H) = 13.2 Hz, 18H, C(CH_3)$_3$), 1.62 ("d", ^3J(P,H) = 13.0 Hz, 25H, C(CH_3)$_3$), 1.70 (s, 4.5H, CH=C(CH_3)-CH$_3$), 1.75 (s, 4.5H, CH=C(CH_3)CH_3), 1.77 (s, 3H, CH=C(CH_3)-CH$_3$), 1.79 (s, 3H, CH=C(CH_3)CH_3), 2.29−2.45 (m, 6H, P(CH_2)$_2$P), 2.45−2.65 (m, 4H, P(CH_2)$_2$P), 9.11 (d, ^3J(H,H) = 11 Hz, 1.4H, CH=C(CH_3)CH$_3$), 9.48 (d, ^3J(H,H) = 11 Hz, 1H, CH=C(CH_3)CH$_3$), 17.02 ("q", ^3J(P,H) = 11 Hz, ^3J(H,H) = 11 Hz, 1.4H, Ru=CH), 17.20 ("q", ^3J(P,H) = 11 Hz, ^3J(H,H) = 11 Hz, 1H, Ru=CH). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 99.7 (s, P(CH_2)$_2P$), 100.2 (s, P(CH_2)$_2P$). Anal. Calcd for $C_{48}H_{96}$-$Cl_2F_6O_6P_4Ru_2S_2$: C, 42.88; H, 7.20. Found: C, 42.74; H, 7.05. Mp: 222 °C dec.

X-ray data: dichroistic brown-violet crystal with dimensions 0.12 × 0.06 × 0.02 mm^3, $C_{48}H_{96}Cl_2F_6O_6P_4Ru_2S_2$, monoclinic crystal system, space group $P2_1/n$, Z = 2, a = 11.2077(2) Å, b = 24.6242(5) Å, c = 11.8961(1) Å, β = 112.924(1)°, V = 3023.80(9) Å^3, ρ(calculated) = 1.48 g cm^{-3}, $2\theta_{max}$ = 43.0°, T = 200(2) K, 25289 reflections measured, 3464 unique (R(int) = 0.1414), 2329 observed ($I > 2\sigma(I)$), μ = 0.82 mm^{-1}, T_{min} = 0.85, T_{max} = 0.98, 334 parameters refined, $R(F)$ = 0.043, $R_w(F^2)$ = 0.070 for observed reflections, residual electron density 0.46 to −0.49 e Å^{-3}. CCDC no. 178694.

(dcpe-κ^2P)Cl_2Ru=CHPh (8). In a Schlenk tube $(PCy_3)_2$-Cl_2Ru=CHPh (200 mg, 0.243 mmol) was dissolved in CH_2Cl_2 (40 mL) at ambient temperature. Within 5 min a solution of 1,2-bis(dicyclohexylphosphino)ethane (dcpe; 100 mg, 0.243 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added dropwise with stirring. After the red solution was stirred for an additional 1 h at ambient temperature, its volume was reduced in vacuo to 2 mL. Upon addition of hexane (15 mL), a green oil was precipitated. After the mother liquor was decanted, the remaining green oil was dissolved in CH_2Cl_2 (2 mL) and reprecipitated by addition of hexane (15 mL). Then the mother liquor was decanted again. This procedure was carried out four times. After it was dried in vacuo, the remaining powder was washed three times with hexane (10 mL), dried again in vacuo, and then suspended in CH_2Cl_2 (1.5 mL). Via cannula filtration, a colorless powder was separated from the green solution containing the product. Volatiles were removed under reduced pressure, and the remaining solid was dried in vacuo. Yield: approximately 10 mg of a green powder.

^{1}H NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 0.9−2.5 (m, Cy H and P(CH_2)$_2$P), 7.48 (t, ^3J(H,H) = 8 Hz, 2H, m-Ar H), 7.69 (t, ^3J(H,H) = 6.9 Hz, 1H, p-Ar H), 8.42 (d, ^3J(H,H) = 6.9 Hz, 2H, o-Ar H), 14.68 (t, ^3J(P,H) = 16.5 Hz, 1H, Ru=CH). ^{31}P{^{1}H}

NMR (202.5 MHz, CD_2Cl_2, 298 K): δ 81.5 (s, $P(CH_2)_2P$). MS (ESI): m/z 635 [(dcpe-κ^2P)ClRu=CHPh$^+$] with correct isotopic pattern.

(dcpe-κ^2P)$_2$RuCl$_2$ (9). For the synthesis and characterization details, cf. Mezzetti et al.[42]

X-ray data: yellow crystal with dimensions 0.24 × 0.23 × 0.16 mm^3, $C_{54}H_{100}Cl_6P_4Ru$, monoclinic crystal system, space group $P2_1/n$, Z = 2, a = 13.1477(1) Å, b = 16.1627(2) Å, c = 14.1525(1) Å, β = 99.990(1)°, V = 2961.84(5) Å^3, ρ(calculated) = 1.33 g cm^{-3}, $2\theta_{max}$ = 51.4°, T = 200(2) K, 21 769 reflections measured, 5128 unique (R(int) = 0.0257), 4375 observed ($I > 2\sigma(I)$), μ = 0.68 mm^{-1}, T_{min} = 0.82, T_{max} = 0.89, 313 parameters refined, $R(F)$ = 0.029, $R_w(F^2)$ = 0.069 for observed reflections, residual electron density 0.61 to −0.65 e Å^{-3}. CCDC no. 178695.

(dtbpm-κ^2P)Cl$_2$Ru=CHCH=CPh$_2$ (10). Synthesis and characterization details are reported elsewhere.[25]

X-ray data: green crystal with dimensions 0.56 × 0.06 × 0.06 mm^3, $C_{32}H_{50}Cl_2P_2Ru$, orthorhombic crystal system, space group $Pnma$, Z = 4, a = 14.6303(14) Å, b = 14.3845(14) Å, c = 15.6793(15) Å, V = 3299.7(5) Å^3, ρ(calculated) = 1.35 g cm^{-3}, $2\theta_{max}$ = 49.4°, T = 298(2) K, 12 334 reflections measured, 2673 unique (R(int) = 0.0595), 1733 observed ($I > 2\sigma(I)$), μ = 0.75 mm^{-1}, T_{min} = 0.83, T_{max} = 0.96, 199 parameters refined, $R(F)$ = 0.040, $R_w(F^2)$ = 0.078 for observed reflections, residual electron density 0.44 to −0.54 e Å^{-3}. CCDC no. 178696.

[(dtbpm-κ^2P)ClRu=CHCH=CPh$_2$]$_2$(OTf)$_2$ (11). In a Schlenk tube (dtbpm-κ^2P)Cl$_2$Ru=CHCH=CPh$_2$ (60 mg, 0.088 mmol) in CH_2Cl_2 (6 mL) was treated with $(CH_3)_3Si(OSO_2CF_3)$ (100 μL, 0.517 mmol, 5.9 equiv) at ambient temperature with stirring. After 1.5 h volatiles were removed in vacuo and the residue was dried in vacuo. The remaining green solid was dissolved in CH_2Cl_2 (6 mL) and treated with 80 μL (0.414 mmol) of $(CH_3)_3Si(OSO_2CF_3)$; this mixture was stirred for 1 h at ambient temperature. Volatiles were again removed, and the remaining solid was dried in vacuo. The solid residue was dissolved in CH_2Cl_2 (1 mL) and precipitated with Et_2O (8 mL), separated by cannula filtration, and then washed twice with THF (2 mL) und three times with pentane (2 mL). The remaining bright green powder was dried in vacuo. Yield: 40 mg (57%).

^{1}H NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 1.06 ("d", ^3J(P,H) = 14.8 Hz, 72H, C(CH_3)$_3$), 1.56−1.60 (m, 8H, C(CH_3)$_3$), 1.67 ("d", ^3J(P,H) = 13.6 Hz, 64H, C(CH_3)$_3$), $\sum$(1.06−1.67) = 144H, 3.76−3.87 (br m, "0.2H", PCH_2P), 4.01−4.15 (m, "0.8H", PCH_2P), 4.17−4.32 (m, 7H, PCH_2P) $\sum$(3.76−4.32) = 8H, 6.80 ("d", J = 7.4 Hz, 7H, Ar H), 7.30−7.33 (m, 22H, Ar H), 7.47−7.52 (m, 5H, Ar H), 7.62 ("quint", J = 4 Hz, 5H, Ar H), 7.73 ("t", J = 7 Hz, "0.5H", Ar H), 7.87 ("d", J = 7.8 Hz, "0.5H", Ar H), $\sum$(6.80−7.87) = 40H, 9.58 (d, ^3J(H,H) = 11.3 Hz, "0.4H", Ph_2C=CH), 9.81 (d, ^3J(H,H) = 10.9 Hz, "0.1H", Ph_2C=CH), 10.13 (d, ^3J(H,H) = 11.2 Hz, "3.5H", Ph_2C=CH), $\sum$(9.58 & 9.81 & 10.13) = 4H, 16.03 (br "q", ^3J(H,H) = 10.9 Hz, ^3J(H,P) = 9.0 Hz, "0.1H", Ru=CH), 16.75 ("q", ^3J(H,H) = 11.3 Hz, ^3J(H,P) = 9.3 Hz, "3.5H", Ru=CH), 17.18 ("q", ^3J(H,H) = 11.3 Hz, ^3J(H,P) = 7.8 Hz, "0.4H", Ru=CH), $\sum$(16.03 & 16.75 & 17.18) = 4H. ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 298 K): δ 25.1 (s, PCH_2P), 26.4 (s, PCH_2P). MS (LR−FAB$^+$): m/z 633.5 ([(dtbpm-κ^2P)ClRu=CHCH=CPh$_2$]$^+$) with correct isotopic pattern. Anal. Calcd for $C_{66}H_{100}Cl_2F_6O_6P_4Ru_2S_2$: C, 50.67; H, 6.44; P, 7.92. Found: C, 50.41; H, 6.66; P, 7.89. mp 212 °C dec.

X-ray data: green needle with dimensions 0.98 × 0.17 × 0.04 mm^3, $C_{74}H_{116}Cl_2F_6O_8P_4Ru_2S_2$, monoclinic crystal system, space group $P2_1/n$, Z = 4, a = 10.9057(2) Å, b = 24.3659(1) Å, c = 31.1378(4) Å, β = 95.773(1)°, V = 8232.19(19) Å^3, ρ(calculated) = 1.38 g cm^{-3}, $2\theta_{max}$ = 51.4°, T = 200(2) K, 61237 reflections measured, 14 157 unique (R(int) = 0.0429), 10 567 observed ($I > 2\sigma(I)$), μ = 0.62 mm^{-1}, T_{min} = 0.87, T_{max} = 0.97, 923 parameters refined, $R(F)$ = 0.039, $R(F)$ = 0.090 for observed reflections, residual electron density 0.67 to −0.65 e Å^{-3}. CCDC no. 178697.

(dtbpm-κ^2P)Cl$_2$Ru=CHCH=C(CH$_2$)$_5$ (12). To a solution of [(dtbpm-κ^2P)RuH]$_2$(μ_2-Cl)$_2$ (362 mg, 0.410 mmol) in toluene (10 mL) was added a solution of 1-chloro-1-ethynylcyclohexane (124 mg, 0.869 mmol, 2.1 equiv) in toluene (2 mL) via cannula with stirring at −78 °C. The reaction mixture was stirred at −78 °C for 1.25 h and then brought to ambient temperature within 1 h and stirred at that temperature for an additional 3 h. The mixture was cooled to −50 °C, and a green microcrystalline precipitate was separated by cannula filtration. The remaining solid was washed twice with cold (0 °C) toluene (2 mL) and three times with hexane (3 mL). Drying in vacuo led to an olive green powder. Yield: 220 mg (46%).

^{1}H NMR (300.1 MHz, THF-d_8, 298 K): δ 1.32 ("d", ^3J(P,H) = 13.7 Hz, 18H, C(CH_3)$_3$), 1.44 (s, 1H, (CH_2)$_5$), 1.49 (s, 1H, (CH_2)$_5$), 1.57 ("d", ^3J(P,H) = 13.7 Hz, 18H, C(CH_3)$_3$), 1.62−1.65 (m, superposed by C(CH_3)$_3$ signal, 4H, (CH_2)$_5$), 1.95−1.99 (m, 2H, (CH_2)$_5$), 2.21 (bs, 2H, (CH_2)$_5$), 4.15 ("quint", ^2J(H,H) = 16.8 Hz, ^2J(H,P) = 9.0 Hz, 1H, PCHHP), 4.35 ("quint", ^2J(H,H) = 16.8 Hz, ^2J(H,P) = 8.7 Hz, 1H, PCHHP), 8.63 (d, ^3J(H,H) = 10.7 Hz, 1H, (CH$_2$)$_5$C=CH), 16.34 ("q", ^3J(H,H) = 10.7 Hz, ^3J(H,P) = 11.2 Hz, 1H, Ru=CH). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8, 298 K, [DEPT-135]): δ 28.0 (s, CH=C(CH_2)$_5$, [CH_2]), 28.9 (s, CH=C(CH_2)$_5$, [CH_2]), 29.1 (s, CH=C(CH_2)$_5$, [CH_2]), 31.6 (s, C(CH_3)$_3$, [CH, CH_3]), 31.9 (s, C(CH_3)$_3$, [CH, CH_3]), 32.7 (s, CH=C(CH_2)$_5$, [CH_2]), 39.0 ("t", J = 3.5 Hz, C(CH$_3$)$_3$, [C_q]), 39.7 ("t", J = 7.5 Hz, C(CH$_3$)$_3$, [C_q]), 40.1 (s, PCH_2P, [CH_2]), 143.3 (s, CH=C(CH_2)$_5$, [C_q]), 147.2 (s, CH=C(CH_2)$_5$, [CH, CH_3]), 293.8 (t, ^2J(C,P) = 13.9 Hz, Ru=CH, [CH, CH_3]). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8, 298 K): δ 25.0 (s, PCH_2P). Anal. Calcd for $C_{25}H_{50}Cl_2P_2Ru$: C, 51.36; H, 8.62. Found: C, 51.04; H, 8.75. Mp: 236−238 °C dec.

X-ray data: red-brown crystal with dimensions 0.37 × 0.24 × 0.12 mm^3, $C_{27}H_{54}Cl_2O_{0.50}P_2Ru$, monoclinic crystal system, space group $P2_1/n$, Z = 4, a = 10.5464(1) Å, b = 19.9661(1) Å, c = 16.1199(1) Å, β = 108.913(1)°, V = 3211.12(3) Å^3, ρ(calculated) = 1.284 g cm^{-3}, $2\theta_{max}$ = 51.2°, T = 200(2) K, 23 365 reflections measured, 5560 unique (R(int) = 0.0255), 4529 observed ($I > 2\sigma(I)$), μ = 0.769 mm^{-1}, T_{min} = 0.83, T_{max} = 0.92, 371 parameters refined, $R(F)$ = 0.026, $R_w(F^2)$ = 0.060 for observed reflections, residual electron density 0.44 to −0.39 e Å^{-3}. CCDC no. 178698.

[(dtbpm-κ^2P)ClRu=CHCH=C(CH$_2$)$_5$]$_2$(OTf)$_2$ (13). In a Schlenk tube (dtbpm-κ^2P)Cl$_2$Ru=CHCH=C(CH$_2$)$_5$ (81 mg, 0.139 mmol) in CH_2Cl_2 (4 mL) was treated with $(CH_3)_3Si(OSO_2CF_3)$ (100 μL, 0.517 mmol, 3.7 equiv) at ambient temperature with stirring. After 1.75 h volatiles were removed under reduced pressure and the residue was dried in vacuo. The remaining green-brown solid was dissolved in CH_2Cl_2 (4 mL) and treated with 90 μL (0.466 mmol) of $(CH_3)_3Si(OSO_2CF_3)$, and this mixture was stirred for 1.5 h at ambient temperature. Volatiles were again removed, and the remaining solid was dried in vacuo. The solid residue was dissolved in CH_2Cl_2 (1 mL) and precipitated with Et_2O (5 mL), separated by cannula filtration, then twice precipitated under analogous conditions (CH_2Cl_2 (1 mL)/Et_2O (5 mL)). The remaining precipitate was dried in vacuo, washed twice with THF (2 mL) and three times with pentane (1.5 mL). The remaining green-brown microcrystalline powder was dried in vacuo. Yield: 84 mg (86%).

^{1}H NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 1.28 ("d", ^3J(P,H) = 14.0 Hz, 36H, C(CH_3)$_3$), 1.31 ("d", ^3J(P,H) = 14.0 Hz, 36H, C(CH_3)$_3$), 1.65 ("d", ^3J(P,H) = 14.0 Hz, 36H, C(CH_3)$_3$), 1.71 ("d", ^3J(P,H) = 14.0 Hz, 36H, C(CH_3)$_3$), 1.78 (br s, superposed by C(CH_3)$_3$ signal, 16H, (CH_2)$_5$), 1.90−1.93 (m, 8H, (CH_2)$_5$), 2.17 (br s, 8H, (CH_2)$_5$), 2.43 (br s, 8H, (CH_2)$_5$), 4.29−4.42 (m, 8H, PCH_2P), 9.13 (d, ^3J(H,H) = 11.2 Hz, "2.3H", (CH$_2$)$_5$C=CH), 9.23 (d, ^3J(H,H) = 11.6 Hz, "1.7H", (CH$_2$)$_5$C=CH), $\sum$(9.13 & 9.23) = 4H, 16.34 ("q", ^3J(H,H) = 11.2 Hz, ^3J(H,P) = 8.8 Hz, 4H, Ru=CH). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 298 K): δ 26.2 (s, PCH_2P), 26.9 (s, PCH_2P). Anal. Calcd for $C_{52}H_{100}Cl_2F_6O_6P_4$-

Ru_2S_2: C, 44.73; H, 7.22; P, 8.87. Found: C, 44.89; H, 7.35; P, 8.69. Mp: 201−203 °C dec.

X-ray data: red-brown crystal with dimensions 0.32 × 0.18 × 0.08 mm^3, $C_{52}H_{100}Cl_2F_6O_6P_4Ru_2S_2$, triclinic crystal system, space group $P\bar{1}$, $Z = 1$, $a = 10.8295(1)$ Å, $b = 13.1531(1)$ Å, $c = 14.1608(2)$ Å, $\alpha = 114.389(1)°$, $\beta = 92.596(1)°$, $\gamma = 112.775(1)°$, $V = 1642.53(3)$ Å^3, ρ(calculated) = 1.41 g cm^{-3}, $2\theta_{max} = 51.0°$, $T = 200$ (2) K, 12 307 reflections measured, 5473 unique (R(int) = 0.0230), 4669 observed ($I > 2\sigma(I)$), $\mu = 0.76$ mm^{-1}, $T_{min} = 0.76$, $T_{max} = 0.94$, 354 parameters refined, $R(F) = 0.029$, $R_w(F^2) = 0.067$ for observed reflections, residual electron density 0.59 to −0.31 e Å^{-3}. CCDC no. 178699.

[(dtbpe-κ^2P)ClRu=CHPh](OTf) (15). In a Schlenk tube (dtbpe-κ^2P)Cl_2Ru=CHPh (150 mg, 0.258 mmol) in CH_2Cl_2 (15 mL) was treated with AgOTf (64 mg, 0.249 mmol, 0.97 equiv). The resulting suspension was vigorously stirred in the dark for 24 h. The resulting colorless precipitate was carefully removed by filtration over Celite and discarded. The mother liquor containing the product was reduced in volume to 1 mL, and a dark green oil was precipitated by addition of hexane (10 mL). The mother liquor was decanted with a cannula and the residue reprecipitated analogously three times from CH_2Cl_2 (1 mL) with hexane (10 mL). Vigorous magnetic stirring in the last of these precipitation steps led to transformation of the precipitated oil into a green powder, which was separated by cannula filtration. This powder was precipitated three times from CH_2Cl_2 (1.5 mL) with Et_2O (15 mL). The microcrystalline powder was washed seven times (30 min stirring in each step) with toluene (5 mL). Subsequent washing with hexane (5 mL) five times and drying in vacuo led to a pale green powder. Yield: 145 mg (84% with respect to AgOTf).

^{1}H NMR (500.1 MHz, THF-d_8, 298 K): δ 1.12 ("d", ^3J(P,H) = 12.8 Hz, 18H, C(CH_3)$_3$), 1.53 ("d", ^3J(P,H) = 13.3 Hz, 18H, C(CH_3)$_3$), 2.51−2.61 (m, 4H, P(CH_2)$_2$P), 7.52 (t, ^3J(H,H) = 7.3 Hz, 2H, *m*-Ar *H*), 7.74 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-Ar *H*), 8.79 (d, ^3J(H,H) = 6.4 Hz, 2H, *o*-Ar *H*), 17.04 (t, ^3J(P,H) = 12.4 Hz, 1H, Ru=C*H*). ^{31}P{^{1}H} NMR (202.5 MHz, THF-d_8, 298 K): δ 96.4 (br s, *P*(CH$_2$)$_2$*P*). Anal. Calcd for $C_{26}H_{46}ClF_3O_3P_2RuS$: C, 44.99; H, 6.68; P, 8.92. Found: C, 44.71; H, 6.67; P, 8.69. Mp: 200 °C dec.

[(CH_3CN-κN)(dtbpe-κ^2P)ClRu=CHPh](OTf) (16). [(dtbpe-κ^2P)ClRu=CHPh](OTf) (**15**; 5.5 mg) was treated with CH_3CN (1 μL) in 0.5 mL of CD_2Cl_2; according to NMR integrals, [Ru]=CHPh:CH_3CN = 1:2.

^{1}H NMR (500.1 MHz, CD_2Cl_2, 233 K): δ 1.07 ("d", ^3J(P,H) = 12.8 Hz, 18H, C(CH_3)$_3$), 1.29 ("d", ^3J(P,H) = 12.8 Hz, 9H, C(CH_3)$_3$), 1.45 ("d", ^3J(P,H) = 13.7 Hz, 9H, C(CH_3)$_3$), 2.00 (s, noncoord CH_3CN), 2.45 (br s, coord CH_3CN), 2.45−2.61 (m, P(CH_2)$_2$P), ∑Int(2.45−2.61) = 7H, 7.62 (t, ^3J(H,H) = 7.3 Hz, 2H, *m*-Ar *H*), 7.86 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-Ar *H*), 8.48 (br s, 2H, *o*-Ar *H*), 17.14 (t, ^3J(P,H) = 13.7 Hz, 1H, Ru=C*H*). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 233 K): δ 87.7 (d, ^2J(P,P′) = 12.4 Hz, P(CH$_2$)$_2$*P*), 96.2 (d, ^2J(P,P′) = 12.4 Hz, *P*(CH$_2$)$_2$P).

(dtbpm-κ^2P)(SO_4-κ^2O)Ru=CHCH=C(CH_3)$_2$ (17). In a Schlenk tube (dtbpm-κ^2P)Cl_2Ru=CHCH=C(CH_3)$_2$ (80 mg, 0.147 mmol) in CH_2Cl_2 (10 mL) was treated with Ag_2SO_4 (49 mg, 0.157 mmol). The reaction mixture was stirred for 22 h in the dark, then additional Ag_2SO_4 (100 mg, 0.320 mmol) was added, and afterward the mixture was stirred for 24 h. The colorless precipitate was removed by filtration over Celite and discarded. The mother liquor was reduced in volume to 1 mL, and addition of pentane (5 mL) led to formation of a red-violet precipitate, which was separated by cannula filtration. The microcrystalline solid residue was precipitated twice from CH_2Cl_2 (1 mL) with pentane (5 mL) and then washed three times with pentane (5 mL). Drying in vacuo yielded a red-violet powder. Yield: 50 mg (60%).

^{1}H NMR (500.1 MHz, CD_2Cl_2, 298 K): δ 1.28 ("d", ^3J(P,H) = 14.1 Hz, 18H, C(CH_3)$_3$), 1.52 ("d", ^3J(P,H) = 13.3 Hz, 18H, C(CH_3)$_3$), 1.64 (s, 3H, CH=C(CH_3)CH$_3$), 1.66 (s, 3H, CH=C(CH$_3$)CH_3), 4.09 ("q", ^2J(H,H) = 16.7 Hz, ^2J(P,H) = 8.7 Hz, 1H, PC*H*HP), 4.28 (dt, ^2J(H,H) = 16.7 Hz, ^2J(P,H) = 9.4 Hz, 1H, PCH*H*P), 8.90 (d, ^2J(H,H) = 10.7 Hz, 1H, C*H*=C(CH$_3$)$_2$), 16.17 ("q", ^3J(P,H) = 10.0 Hz, ^3J(H,H) = 10.7 Hz, 1H, Ru=C*H*). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 298 K): δ 20.9 (s, CH=C(*C*H$_3$)CH$_3$), 28.4 (s, CH=C(CH$_3$)*C*H$_3$), 30.7 (s, C(*C*H$_3$)$_3$), 30.9 (s, C(*C*H$_3$)$_3$), 37.6 ("t", J(P,C) = 5.5 Hz, *C*(CH$_3$)$_3$), 38.6 (t, ^1J(P,C) = 11.1 Hz, P*C*H$_2$P), 39.0 ("t", J(P,C) = 9 Hz, *C*(CH$_3$)$_3$), 142.3 (s, CH=*C*(CH$_3$)$_2$), 143.3 (s, *C*H=C(CH$_3$)$_2$), Ru=CH not observed. ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 298 K): δ 42.9 (*P*CH$_2$*P*). Anal. Calcd for $C_{22}H_{46}O_4P_2RuS$: C, 46.38; H, 8.14; P, 10.87. Found: C, 46.15; H, 8.09; P, 10.81. HRES-MS (FAB+, NBA matrix): calcd for $(C_{22}H_{46}O_4P_2RuS+H)^+$, m/z 571.1714; found, m/z 571.1780 (Δ = +11.7 ppm); isotopic pattern for $(C_{22}H_{46}O_4P_2RuS+H)^+$ m/z (calcd. intensity, found intensity): 565 (15, 17), 566 (4, 6), 567 (6, 9), 568 (36, 38), 569 (43, 46), 570 (57, 62), 571 (100, 100), 572 (27, 30), 573 (58, 60), 574 (15, 17), 575 (4, 5). Mp: 240 °C dec.

X-ray data: violet platelike crystal with dimensions 0.33 × 0.24 × 0.04 mm^3, $C_{24}H_{50}Cl_4O_4P_2RuS$, monoclinic crystal system, space group $P2_1/n$, $Z = 4$, $a = 12.9091(2)$ Å, $b = 17.5107(3)$ Å, $c = 16.3424(3)$ Å, $\beta = 110.345(1)°$, $V = 3463.7(1)$ Å^3, ρ(calculated) = 1.42 g cm^{-3}, $2\theta_{max} = 55.0°$, $T = 200(2)$ K, 34 752 reflections measured, 7933 unique (R(int) = 0. 0730), 5148 observed ($I > 2\sigma(I)$), $\mu = 0.94$ mm^{-1}, $T_{min} = 0.84$, $T_{max} = 0.97$, 347 parameters refined, $R(F) = 0.047$, $R_w(F^2) = 0.097$ for observed reflections, residual electron density 0.82 to −0.67 e Å^{-3}. CCDC no. 178700.

(dtbpm-κ^2P)(CF_3COO)$_2$Ru=CHCH=C(CH_3)$_2$ (18). In a Schlenk tube (dtbpm-κ^2P)Cl_2Ru=CHCH=C(CH_3)$_2$ (81 mg, 0.149 mmol) in CH_2Cl_2 (10 mL) was treated with Ag(CF_3COO) (67 mg, 0.301 mmol, 2.0 equiv) at ambient temperature. After the mixture was stirred for 3 h in the dark, the mother liquor was separated from the colorless precipitate by cannula filtration and then reduced in vacuo to 1 mL in volume. Addition of hexane (15 mL) led to precipitation of a violet powder, which was separated by cannula filtration and reprecipitated twice from CH_2Cl_2 (1 mL) with hexane (15 mL) and then washed twice with Et_2O (5 mL) and dried in vacuo to yield a violet powder. Yield: 57 mg (50%).

^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.29 ("d", ^3J(P,H) = 13.5 Hz, 18H, C(CH_3)$_3$), 1.48 ("d", ^3J(P,H) = 13.7 Hz, 18H, C(CH_3)$_3$), 1.64 (s, 3H, CH=C(CH_3)CH$_3$), 1.72 (s, 3H, CH=C(CH$_3$)CH_3), 3.80 ("q", ^2J(H,H) = 16.9 Hz, ^2J(P,H) = 8.9 Hz, 1H, PC*H*HP), 4.07 (dt, ^2J(H,H) = 16.9 Hz, ^2J(P,H) = 9.4 Hz, 1H, PCH*H*P), 8.64 (d, ^2J(H,H) = 11.4 Hz, 1H, C*H*=C(CH$_3$)$_2$), 17.59 (dt, ^3J(P,H) = 8.5 Hz, ^3J(H,H) = 11.4 Hz, 1H, Ru=C*H*). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 298 K, [DEPT-135]): δ 21.2 (s, CH=C(*C*H$_3$)CH$_3$, [CH, CH$_3$]), 28.1 (s, CH=C(CH$_3$)*C*H$_3$, [CH, CH$_3$]), 30.2 (s, C(*C*H$_3$)$_3$, [CH, CH$_3$]), 30.7 (s, C(*C*H$_3$)$_3$, [CH, CH$_3$]), 36.2 (t, ^2J(P,C) = 13.9 Hz, P*C*H$_2$P, [CH$_2$]), 37.4 ("t", J = 7 Hz, *C*(CH$_3$)$_3$, [C$_q$]), 38.5 ("t", J = 6.9 Hz, *C*(CH$_3$)$_3$, [C$_q$]), 115.4 (weak "d", ^1J(F,C) = 290 Hz, *C*F$_3$, [C$_q$]), 162.8 (weak q, ^2J(F,C) = ca. 36 Hz, CF$_3$*C*O$_2$, [C$_q$]), 141.4 (s, CH=*C*(CH$_3$)$_2$, [C$_q$]), 143.8 (s, *C*H=C(CH$_3$)$_2$, [CH, CH$_3$]), 310.6 (t, ^2J(P,C) = 6.9 Hz, Ru=CH, [CH, CH$_3$]). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 29.8 (*P*CH$_2$*P*). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 298 K): δ −76.2 (s, C*F*$_3$CO$_2$). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 213 K): δ −75.8 (s, C*F*$_3$CO$_2$). IR (KBr): 1702 (s, C=O), 1192 (s, C−F). Anal. Calcd for $C_{26}H_{46}F_6O_4P_2Ru$: C, 44.63; H, 6.63; P, 8.85. Found: C, 44.73; H, 6.58; P, 8.88. Mp: 190 °C dec.

(dtbpm-κ^2P)(CF_3COO)$_2$Ru=CHCH=C(CH_2)$_5$ (19). The synthesis was analogous to that for (dtbpm-κ^2P)(CF_3COO)$_2$Ru=CHCH=C(CH_3)$_2$.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.28 ("d", ^3J(P,H) = 13.5 Hz, 18H, C(CH_3)$_3$), 1.48 ("d", ^3J(P,H) = 13.7 Hz, 18H, C(CH_3)$_3$), 1.61−1.74 (m, 4H, CH=C(CH_2)$_5$), 1.77−1.84 (m, 2H, CH=C(CH_2)$_5$), 2.11 (t, ^3J(H,H) = 6 Hz, 2H, CH=C(CH_2)$_5$), 2.35 (t, ^3J(H,H) = 6 Hz, 2H, CH=C(CH_2)$_5$), 3.81 ("q", ^2J(H,H) = 16.7 Hz, ^2J(P,H) = 9 Hz, 1H, PC*H*HP), 4.07 (dt, ^2J(H,H) = 16.7 Hz, ^2J(P,H) = 9.3 Hz, 1H, PCH*H*P), 8.61 (d, ^3J(H,H) = 11.5 Hz, 1H, C*H*=C(CH$_2$)$_5$), 17.65 (dt, ^3J(P,H) = 8.5 Hz, ^3J(H,H) =

11.5 Hz, 1H, Ru=C*H*). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 30.2 (*P*CH_2P). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1708 (s, C=O), 1195 (s, C−F)). Anal. Calcd for $C_{29}H_{50}F_6O_4P_2Ru$: C, 47.09; H, 6.81. Found: C, 47.00; H, 6.79. Mp (crystal): 182 °C dec.

X-ray data: dark red crystal with dimensions 0.26 × 0.14 × 0.10 mm^3, $C_{29}H_{50}F_6O_4P_2Ru$, orthorhombic crystal system, space group *Pbca*, $Z = 8$, $a = 17.9356(1)$ Å, $b = 19.2490(3)$ Å, $c = 20.2116(3)$ Å, $V = 6977.90(16)$ $Å^3$, ρ(calculated) = 1.41 g cm^{-3}, $2\theta_{max} = 55.0°$, $T = 200(2)$ K, 68 917 reflections measured, 8004 unique (R(int) = 0.1421), 4720 observed ($I > 2\sigma(I)$), μ = 0.60 mm^{-1}, $T_{min} = 0.83$, $T_{max} = 0.92$, 446 parameters refined, $R(F) = 0.044$, $R_w(F^2) = 0.074$ for observed reflections, residual electron density 0.50 to −0.49 e $Å^{-3}$. CCDC no. 178701.

(dtbpm-κ^2*P*)(OTf-κ^1*O*)$_2$Ru=CHCH=C(CH$_3$)$_2$ (20). In a Schlenk tube (dtbpm-κ^2*P*)Cl_2Ru=CHCH=$C(CH_3)_2$ (100 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was treated with AgOTf (95 mg, 0.37 mmol, 2.1 equiv) and stirred vigorously at ambient temperature. After 3 h the dark red mother liquor was separated by cannula filtration and reduced in vacuo to 1 mL in volume. Addition of hexane (5 mL) led to formation of a red-brown precipitate, which was reprecipitated three times from CH_2Cl_2 (1 mL) with hexane (2 mL) and dried in vacuo. Yield: 93 mg (67%).

^1H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.28 ("d", 18H, $C(CH_3)_3$), 1.69 ("d", 18H, $C(CH_3)_3$), 1.75 (s, 3H, CH=$C(CH_3)$-CH_3), 1.78 (s, 3H, CH=$C(CH_3)CH_3$), 3.93 (dt, ^2J(H,H) = 17.0 Hz, ^2J(H,P) = 9.3 Hz, 1H, PCH*H*P), 4.38 (dt, ^2J(H,H) = 17.0 Hz, ^2J(H,P) = 9.9 Hz, 1H, PCH*H*P), 9.40 (d, ^3J(H,H) = 11.3 Hz, 1H, C*H*=$C(CH_3)_2$), 17.46 (dt, ^3J(H,H) = 11.3 Hz, ^3J(H,P) = 9.1 Hz, 1H, Ru=C*H*). ^1H NMR (500.1 MHz, acetone-d_6, 298 K): δ 1.39 ("t", 18H, $C(CH_3)_3$), 1.68 ("t", 1 H, $C(CH_3)_3$), 1.80 (s, 3H, CH=$C(CH_3)CH_3$), 1.95 (s, 3H, CH=$C(CH_3)CH_3$), 4.66 ("m", N = 62.3 Hz, 2H, PCH_2P), 9.19 (d, ^3J(H,H) = 11.2 Hz, 1H, C*H*=$C(CH_3)_2$), 17.62 (dt, ^3J(H,H) = 11.0 Hz, ^3J(H,P) = 8.9 Hz, 1H, Ru=C*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 298 K): δ 22.4 (s, CH=$C(CH_3)CH_3$), 29.1 (s, CH=$C(CH_3)CH_3$), 30.5 (s, $C(CH_3)_3$), 31.5 (s, $C(CH_3)_3$), 37.6 (t, ^1J(H,P) = 14.4 Hz, PCH_2P), 38.8 ("t", N = 14.4 Hz, $C(CH_3)_3$), 39.5 ("t", N = 15.3 Hz, $C(CH_3)_3$), 148.3 (s, *C*H=$C(CH_3)_2$), 148.7 (s, CH=$C(CH_3)_2$), 306.4 (t, ^2J(C,P) = 12.1 Hz, Ru=CH). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 27.0 (s, *P*CH_2P). $^{31}P\{^1H\}$ NMR (202.5 MHz, acetone-d_6, 298 K): δ 31.8 (s, *P*CH_2P). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 298 K): δ −79.1 (s, C*F*$_3$SO$_3$). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 213 K): δ −79.4 (s, C*F*$_3$SO$_3$). HRES-MS (FAB$^+$): calcd for $C_{23}H_{46}F_3O_3P_2RuS^+$, m/z 623.1639; found, m/z 623.1699 (Δ = +9.7 ppm); isotopic pattern for $C_{23}H_{46}F_3O_3P_2RuS^+$ m/z (calcd. intensity, found intensity) 617 (15, 14), 618 (4, 5), 619 (6, 9), 620 (36, 37), 621 (43, 45), 622 (57, 59), 623 (100, 100), 624 (26, 30), 625 (58, 59), 626 (14, 14), 627 (4, 4) Anal. Calcd for $C_{24}H_{46}F_6O_6P_2RuS_2$: C, 37.35; H, 6.01; P, 8.03. Found: C, 37.09; H, 5.97; P, 7.91. Mp: 208 °C dec.

X-ray data: violet crystal with dimensions 0.22 × 0.19 × 0.14 mm^3, $C_{25}H_{48}Cl_2F_6O_6P_2RuS_2$, monoclinic crystal system, space group $P2_1/n$, $Z = 4$, $a = 10.9036(2)$ Å, $b = 18.2631(3)$ Å, $c = 17.0704(3)$ Å, $\beta = 91.135(1)$ °, $V = 3398.62(10)$ $Å^3$, ρ(calculated) = 1.67 g cm^{-3}, $2\theta_{max} = 51.2°$, $T = 233(2)$ K, 24 991 reflections measured, 5845 unique (R(int) = 0.0392), 4322 observed ($I > 2\sigma(I)$), μ = 0.60 mm^{-1}, $T_{min} = 0.81$, $T_{max} = 0.90$, 412 parameters refined, $R(F) = 0.053$, $R_w(F^2) = 0.128$ for observed reflections, residual electron density 1.08 to −1.18 e $Å^{-3}$. CCDC no. 178702.

[(dtbpe-κ^2*P*)(H$_2$O-κ*O*)(OTf-κ*O*)Ru=CHPh](OTf) (21). In a Schlenk tube (dtbpe-κ^2*P*)Cl_2Ru=CHPh (200 mg, 0.344 mmol) was treated with AgOTf (262 mg, 1.02 mmol, 3 equiv) and then suspended in CH_2Cl_2 (5 mL), and this suspension was stirred vigorously for 5 h in the dark. Addition of H_2O (30 μL) was followed by stirring for 12 h in the dark. The colorless precipitate was removed by filtration over Celite. The mother liquor was reduced in volume to 1 mL, and upon cooling the solution for 12 h to −30 °C, a gray-violet powder was formed that was separated by cannula filtration and then washed three times with hexane (5 mL) and dried in vacuo. The yield of this spectroscopically pure product was 135 mg (48%), which was nearly insoluble in CH_2Cl_2 (5 mL). Addition of H_2O (0.1 mL) led to increased solubility, and the solution was passed through a plug of wet (H_2O) Celite and then reduced to 2 mL in volume. Slow condensation of hexane to this solution at ambient temperature led to the formation of gray-violet crystals, which were separated and dried in vacuo for 7 days. Yield: 30 mg (11%).

^1H NMR (300.1 MHz, CD_2Cl_2, 243 K): δ 0.91 ("d", ^3J(P,H) = 11.9 Hz, 9H, $C(CH_3)_3$), 1.11 ("d", ^3J(P,H) = 13.2 Hz, 9H, $C(CH_3)_3$), 1.36 ("d", ^3J(P,H) = 13.7 Hz, 9H, $C(CH_3)_3$), 1.51 ("d", ^3J(P,H) = 13.5 Hz, 9H, $C(CH_3)_3$), 2.04−2.17 (m, 1H, $P(CH_2)_2P$), 2.30−2.46 (m, 1H, $P(CH_2)_2P$), 2.52−2.81 (m, 2H, $P(CH_2)_2P$), ∑Int(2.04−2.81) = 4H, 7.26 (s, 2H, H_2O), 7.69 (t, ^3J(H,H) = 7.8 Hz, 2H, *m*-Ar *H*), 7.94 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-Ar *H*), 8.32 (d, ^3J(H,H) = 7.8 Hz, 2H, *o*-Ar *H*), 17.23 (t, ^3J(P,H) = 12.1 Hz, 1H, Ru=C*H*). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 243 K): δ 97.6 (d, ^2J(P,P′) = 12.8 Hz, $P(CH_2)_2P'$), 100.9 (d, ^2J(P,P′) = 12.8 Hz, $P(CH_2)_2P'$). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3375 (br,w, H_2O). HRES-MS (FAB+): calcd for $(C_{26}H_{46}F_3O_3P_2RuS)^+$ m/z 659.1638, found m/z 659.1649 (Δ = +1.5 ppm), H_2O complex not observable with this method; isotopic pattern for $(C_{26}H_{46}F_3O_3P_2RuS)^+$ m/z (calcd intensity, found intensity) 654 (4, 5), 655 (6, 7), 656 (34, 35), 657 (43, 43), 658 (57, 59), 659 (100, 100), 660 (30, 30), 661 (57, 57), 662 (16, 16), 663 (4, 5). Anal. Calcd for $C_{27}H_{48}F_6O_7P_2RuS_2$: C, 39.27; H, 5.86; P, 7.50. Found: C, 38.98; H, 5.71; P, 7.45. Mp: 232 °C dec.

X-ray data: violet crystal with dimensions 0.29 × 0.16 × 0.14 mm^3, $C_{28}H_{50}Cl_2F_6O_7P_2RuS_2$, monoclinic crystal system, space group $P2_1/c$, $Z = 4$, $a = 10.8739(2)$ Å, $b = 20.0558(3)$ Å, $c = 18.5067(2)$ Å, $\beta = 94.435(1)°$, $V = 4023.94(10)$ $Å^3$, ρ(calculated) = 1.50 g cm^{-3}, $2\theta_{max} = 55.0°$, $T = 200(2)$ K, 40 995 reflections measured, 9201 unique (R(int) = 0.0556), 6802 observed ($I > 2\sigma(I)$), μ = 0.77 mm^{-1}, $T_{min} = 0.76$, $T_{max} = 0.93$, 457 parameters refined, $R(F) = 0.038$, $R_w(F^2) = 0.086$ for observed reflections, residual electron density 0.80 to −0.84 e $Å^{-3}$. CCDC no. 178703.

[(dtbpm-κ^2*P*)ClRu=CHCH=C(CH$_3$)$_2$]$_2$(BArF)$_2$ (22). In a Schlenk tube [Na][(3,5-$(CF_3)_2C_6H_3)_4$B] (=NaBArF) (145 mg, 0.164 mmol, 2.1 equiv) was suspended in CH_2Cl_2 (2 mL) and treated with Et_2O (ca. 1 mL) until a clear solution was obtained, which was transferred by cannula to a second Schlenk tube containing a solution of [(dtbpm-κ^2*P*)ClRu=CHCH=$C(CH_3)_2$]$_2$(OTf)$_2$ (104 mg, 0.079 mmol) in CH_2Cl_2 (2 mL) at ambient temperature. The reaction mixture was stirred for 1 h and then kept 30 min without stirring. The mother liquor was separated by cannula filtration and the colorless residue extracted once with CH_2Cl_2 (2 mL). The combined CH_2Cl_2 solutions were taken to dryness in vacuo. CH_2Cl_2 (1 mL) was added to the residue, and upon addition of hexane (5 mL) a red oil precipitated. The mother liquor was decanted by cannula and discarded. The residue was suspended in CH_2Cl_2 (1 mL) and separated from a colorless residue by cannula filtration. Slow condensation of hexane into this solution at ambient temperature led to formation of a crystalline solid. Recrystallization under analogous conditions was repeated. The remaining crystals were dissolved in CH_2Cl_2 (2 mL), and upon addition of hexane (10 mL) an oil precipitated. The oily residue was treated with hexane, which was removed in vacuo. Repetition of this procedure turned the oil into a reddish brown powder that was washed three times with hexane (3 mL) and subsequently dried in vacuo. Yield: 25 mg (12%).

^1H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 1.23 ("d", ^3J(P,H) = 15.0 Hz, 18H, $C(CH_3)_3$), 1.25 ("d", ^3J(P,H) = 15.0 Hz, 18H, $C(CH_3)_3$), 1.61 ("d", ^3J(P,H) = 14.3 Hz, 18H, $C(CH_3)_3$), 1.66 ("d", ^3J(P,H) = 14.3 Hz, 18H, $C(CH_3)_3$), 1.72 (s, 3H, CH=$C(CH_3)_2$), 1.73 (s, 3H, CH=$C(CH_3)_2$), 1.83 (s, 3H, CH=$C(CH_3)_2$), 1.85 (s, 3H, CH=$C(CH_3)_2$), 3.83−3.97 (m, N = 43.9 Hz, 2H, $P(CH_2)P$), 4.10−4.25 (m, N = 45.3 Hz, 2H, $P(CH_2)P$), 7.56 (s, 10H,

p-B(3,5-$C_6H_3(CF_3)_2)_4^-$), 7.72 (s, 20H, *o*-B(3,5-$C_6H_3(CF_3)_2)_4^-$), 9.14 (d, ^3J(H,H) = 11 Hz, 1H, C*H*=C$(CH_3)_2$), 9.22 (d, ^3J(H,H) = 11 Hz, 1H, C*H*=C$(CH_3)_2$), 17.47−17.58 (m, *N* = 33.4 Hz, 2H, Ru=C*H*). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 298 K): δ −62.7 (s, B(3,5-$C_6H_3(CF_3)_2)_4^-$). No ^{19}F NMR signal of the O_3SCF_3 of the reactant at −79.1 ppm was observed. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 26.0 (s, *P*(CH_2)*P*), 26.9 (s, *P*(CH_2)*P*). Anal. Calcd for $C_{108}H_{116}B_2Cl_2F_{48}P_4Ru_2$: C, 47.26; H, 4.26. Found: C, 47.25; H, 4.31. Mp: 172 °C dec.

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Supporting Information Available: Tables of crystal and intensity collection data, positional and displacement parameters, and all bond distances and bond angles, and figures showing the complete atom-labeling schemes for solid-state structures included in this report. This material is available free of charge via the Internet at http://pubs.acs.org.

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