Synthesis and Applications of $RuCl_2(=CHR')(PR_3)_2$: The Influence of the Alkylidene Moiety on Metathesis Activity

Peter Schwab,[†] Robert H. Grubbs,*[,†] and Joseph W. Ziller[‡]

Contribution No. 9116 from the Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Department of Chemistry, University of California, Irvine, California 92717

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Abstract: The reactions of $RuCl_2(PPh_3)_3$ with a number of diazoalkanes were surveyed, and alkylidene transfer to give $RuCl_2(=CHR)(PPh_3)_2$ (R = Me (**1**), Et (**2**)) and $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ (X = H (**3**), NMe_2 (**4**), OMe (**5**), Me (**6**), F (**7**), Cl (**8**), NO_2 (**9**)) was observed for alkyl diazoalkanes $RCHN_2$ and various *para*-substituted aryl diazoalkanes $p\text{-}C_6H_4XCHN_2$. Kinetic studies on the living ring-opening metathesis polymerization (ROMP) of norbornene using complexes **3**−**9** as catalysts have shown that initiation is in all cases faster than propagation (k_i/k_p = 9 for **3**) and that the electronic effect of X on the metathesis activity of **3**−**9** is relatively small. Phosphine exchange in **3**−**9** with tricyclohexylphosphine leads to $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ **10**−**16**, which are efficient catalysts for ROMP of cyclooctene (PDI = 1.51−1.63) and 1,5-cyclooctadiene (PDI = 1.56−1.67). The crystal structure of $RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (**15**) indicated a distorted square-pyramidal geometry, in which the two phosphines are *trans* to each other, and the alkylidene unit lies in the Cl−Ru−Cl plane. The benzylidenes $RuCl_2(=CHPh)(PR_3)_2$ (R = Cy (cyclohexyl) (**10**), Cp (cyclopentyl) (**17**), *i*-Pr (**18**)) are quantitatively available *via* one-pot synthesis with $RuCl_2(PPh_3)_3$, $PhCHN_2$, and PR_3 as reaction components. **10** is an efficient catalyst for metathesis of acyclic olefins: On reaction with excess ethylene, the methylidene complex $RuCl_2(=CH_2)(PCy_3)_2$ (**19**) is formed quantitatively, and various alkylidene compounds $RuCl_2(=CHR)(PCy_3)_3$ (R = Me (**20**), Et (**21**), *n*-Bu (**22**)) are isolated as the kinetic products from the reaction of **10** with an excess of the corresponding terminal or disubstituted olefins. Metathesis of conjugated and cumulated olefins with **10** results in the formation of vinylalkylidene and vinylidene complexes, as shown by the synthesis of $RuCl_2(=CHCH=CH_2)(PCy_3)_2$ (**23**) and $RuCl_2(=C=CH_2)(PCy_3)_2$ (**24**) from 1,3-butadiene or 1,2-propadiene, respectively. Also, functional groups such as −OAc, −Cl, and −OH can be introduced into the alkylidene moiety *via* cross metathesis with the appropriate alkene.

Introduction

Transition-metal-catalyzed C−C bond formation *via* olefin metathesis continues to be of considerable interest and synthetic utility. Initial studies in this area were based on catalytically active mixtures consisting of transition-metal chlorides, oxides, or oxychlorides, cocatalysts such as $EtAlCl_2$ or R_4Sn, and promoters including O_2, EtOH, or PhOH[1] (e.g. $WCl_6/EtAlCl_2$/EtOH 1:4:1).[2] Recent efforts have been directed toward the development of well-defined catalysts. Synthetically useful reactions, including acyclic olefin metathesis,[1,3] ring-opening metathesis polymerization (ROMP),[1,3] alkyne polymerization,[4] carbonyl olefination,[5] acyclic diene metathesis polymerization (ADMET),[6] and ring-closing metathesis (RCM),[7] have been catalyzed by early-transition-metal alkylidenes which were usually generated *via* α-hydrogen abstraction routes,[8] alkylidene transfer from phosphoranes,[9] or ring-opening of cyclopropenes.[10] The latter method was utilized in the synthesis of ruthenium vinylalkylidene complexes of the type $RuCl_2(=CHCH=CPh_2)(PR_3)_2$ (R = Ph (**A**),[11] Cy (**B**)[12]) (Figure 1). In addition to their high activity in ROMP[11−13] and RCM,[7c,d] these complexes show

[†] California Institute of Technology.
[‡] University of California, Irvine.
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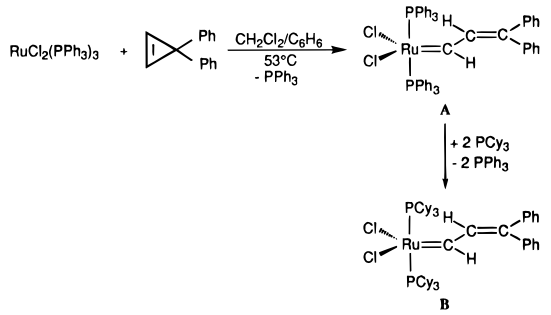


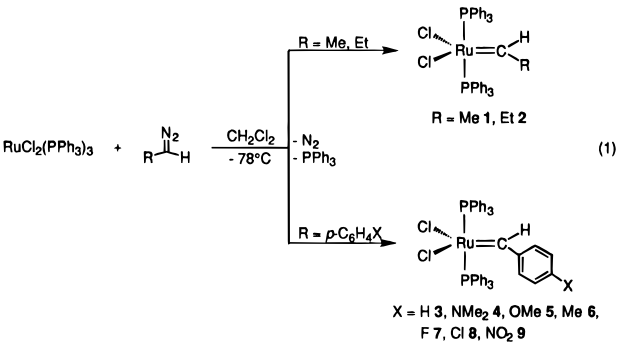
Figure 1. Synthesis of vinylalkylidene complexes **A** and **B**.

a remarkable stability toward functional groups and protic media. However, the multistep synthesis of the cyclopropene and the low initiation rates of the resultant diphenylvinyl alkylidenes are present limitations of **A** and **B**. While previous investigations have explored the influence of the phosphine and anionic ligands,[14] the variation of the alkylidene moiety has not been studied. This prompted us to look for alternative carbene sources among which diazoalkanes are of greatest synthetic utility due to their stability and ease of synthesis.[15] Established by Yates in the early 50's and extensively studied by Herrmann two decades later,[16] diazoalkanes, preferably diaryl diazoalkanes, were frequently used in the synthesis of mainly electron-rich metal carbenes.[17] However, in some cases loss of nitrogen appears to be a limiting factor,[18] and although there are numerous examples of the formation of bridged species [M]−CHR−[M] from $RCHN_2$,[19] it is rare that monoalkyl or aryl diazoalkanes $RCHN_2$ form terminal M=CHR bonds. Our initial studies involved the use of $RuCl_2(PPh_3)_3$,[20] since this compound undergoes PPh_3 displacement in the presence of π-acceptor ligands L, such as CO[20] and CNR,[21] to give octahedral $RuCl_2L_2(PPh_3)_2$ complexes. Furthermore, displacement by acetylenes[22] and 3,3-diphenylcyclopropene[11] yields, after rearrangement, pentacoordinate $RuCl_2(=C=CHR)(PPh_3)_2$ and $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$ complexes. Similar substitution reactions with diazoalkanes were therefore expected to give the desired $RuCl_2(=CHR)(PPh_3)_2$ complexes. Product analogs, such as $RuCl_2(=CHCH=CPh_2)(PR_3)_2$,[11,12] are stable compounds, and there is precedence for CH_2 transfer from diazomethane to ruthenium, as observed in the formation of $RuCl(NO)(=CH_2)(PPh_3)_2$.[23] Reactivity studies of the various alkylidenes will permit a detailed investigation of the general influence of the alkylidene moiety on the metathesis activity and catalyst stability.

Results and Discussion

After a discussion of the synthesis of novel pentacoordinate ruthenium alkylidene complexes $RuCl_2(=CHR)(PPh_3)_2$ (R = alkyl, aryl) and their activity as ROMP catalysts, kinetic studies regarding initiation and propagation rates in living ROMP of norbornene with various *para*-substituted benzylidenes $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ will be examined. We will then focus on the preparation of the corresponding tricyclohexylphosphine analogs $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$. Aspects of catalyst preparation and structure will be discussed followed by a detailed reactivity and kinetic study of olefin metathesis. Finally, the preparation of various substituted alkylidenes *via* acyclic olefin metathesis will be discussed.

Synthesis of $RuCl_2(=CHR)(PPh_3)_2$ *via* Alkylidene Transfer from Diazoalkanes. Our initial investigation involved the reaction of $RuCl_2(PPh_3)_3$ with a series of alkyl-, aryl-, and diaryldiazoalkanes. A spontaneous N_2 evolution at −78 °C indicated a rapid reaction with diazoethane, diazopropane, and variously *para*-substituted aryldiazoalkanes $p\text{-}C_6H_4XCHN_2$ to give $RuCl_2(=CHR)(PPh_3)_2$ (R = Me (**1**), Et (**2**)) and $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ (X = H (**3**), NMe_2 (**4**), OMe (**5**), Me (**6**), F (**7**), Cl (**8**), NO_2 (**9**)), respectively (eq 1). However, no



reaction was observed with diphenyldiazomethane or 9-diazofluorene at room temperature, and diazomethane led to a complex mixture of unidentified products. Complexes **1**−**9** were isolated in 80−90% yield as green air-stable solids. For all of these reactions, transfer of the alkylidene moiety from the diazo compound to ruthenium was clearly indicated by the characteristic downfield-resonances of H_α and C_α of the alkylidene moiety (selected NMR data for **3**−**9** are listed in Table 1).[24] In analogy to the structurally characterized vinylalkylidene $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$ (**A**),[11] these reso-

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Table 1. Selected NMR Data for $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ Complexes[a] **3**−**9** (in ppm) and *J* (in Hz)

compd	X	H_α	J_{HP}	C_α	J_{PC}
3	H	19.56[b]	10.2	310.12	11.4
4	NMe_2	18.30	6.1	309.68	11.4
5	OMe	19.38[b]	8.7	309.20	10.7
6	Me	19.55[b]	9.6	309.17	10.9
7	F	19.24	9.0	307.51	11.4
8	Cl	19.27	9.2	307.34	10.6
9	NO_2	19.47	10.8	313.43	11.2

[a] Spectra were acquired in CD_2Cl_2 unless indicated otherwise. [b] In C_6D_6.

nances appear as triplets due to ^{31}P coupling. These spectroscopic data suggest that the phosphines are mutually *trans* and that the alkylidene unit lies in the P−Ru−P plane. Additionally, the chemical shifts of H_α and C_α in **3**−**9** are downfield compared to **A** (δ H_α 17.94, C_α 288.9 ppm), which might be attributed to reduced conjugation of the alkylidene unit compared to **A**. This phenomenon might also be responsible for the instability of **1**−**9** in solution: In contrast to **A**, **1**−**9** decompose within several hours *via* bimolecular pathways as evidenced by the formation of the corresponding disubstituted olefins RCH=CHR (R = Me, Et, *p*-C_6H_4X).

Kinetic Studies of the Polymerization of Norbornene Catalyzed by $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ Complexes 3−9. Complexes **3**−**9** polymerize norbornene at a rate of ≈150 equiv/h in CH_2Cl_2 at room temperature to give polynorbornene in quantitative yields.[25] All reactions were accompanied by a characteristic color change from green-brown to orange which indicates complete initiation. The resulting polymers are approximately 90% *trans* as determined by ^1H NMR. These results are similar to those obtained with previous systems.[11,3b,26] However, the present catalysts produce *nearly monodispersed polymers* (PDIs = 1.04−1.10, compared to 1.25 for **A**),[27] which is consistent with the measured initiation rates (*vide infra*). As observed for **A**, **3**−**9** fulfill the general criteria for living systems since the propagating alkylidene (^1H NMR: δ 17.79 ppm (dt)) is stable throughout the reaction, and the molecular weights of the polymers display a linear dependence on the [catalyst]/[monomer] ratio.[28] The influence of the *para* substituents in the alkylidene moiety on the metathesis activity was qualitatively assessed. Catalysts **3**−**9** ($RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$, [Ru] = 0.022 M) were treated with norbornene ([mon] = 0.435 M) in CH_2Cl_2 solution. The pseudo-first-order rate constants for initiation and propagation were obtained by integrating the H_α resonances of **3**−**9** vs the corresponding resonance of the propagating alkylidene species and monitoring the decrease of the monomer concentration vs an internal ferrocene standard, respectively. The derived values of k_i and k_p are listed in Table 2. The electronic effect of X in $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ on the initiation rate seems to be relatively small; the initiation rate in the fastest case (X = H (**3**)) was approximately 10 times higher than in the slowest (X = Cl (**8**)). A general trend concerning the electronic influence of the substituents X was not observed. Under similar reaction conditions with $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$ (**A**) as catalyst, observed initiation was <50%. When the consumption of norbornene was complete, uninitiated carbene may be spectroscopically identified. The extrapolated ratio of $k_i/k_p = 6 \times 10^{-3}$ is approximately 1000 times smaller than those observed for complexes **3**−**9**. These results suggest that conjugation seems to decrease k_i, supposedly by lowering the ground state energy of the starting arylidenes **3**−**9** relative to the likely metallacyclobutane intermediate. Although benzylidenes **3**−**9** are better initiators than **A**, their application as metathesis catalysts is similarly limited to ROMP of relatively high-strained cyclic olefins, such as norbornene and cyclobutene derivatives, whose calculated strain energies exceed 10−15 kcal/mol.[29]

Table 2. Determined Initiation and Propagation Rate Constants k_i and k_p in ROMP of Norbornene with $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ Complexes **3**−**9** as Catalysts[a] (k_i and k_p in L/(mol·S))

compd	X	$10^{-3}k_i$	$10^{-3}k_p$	k_i/k_p
3	H	11.5	1.28	9.0
4	NMe_2	3.32	1.28	2.6
5	OMe	3.34	1.28	2.6
6	Me	3.69	1.28	2.9
7	F	6.19	1.28	4.8
8	Cl	1.56	1.28	1.2
9	NO_2	2.91	1.28	2.3

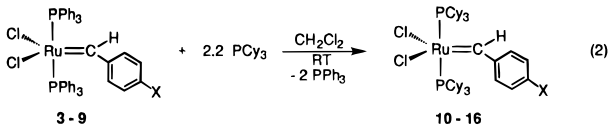
[a] For [Ru] = 0.022 M; [norbornene] = 0.435 M in C_6D_6 at T = 17 °C.

Table 3. Selected NMR Data for $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ Complexes[a] **10**−**16** (in ppm) and *J* (in Hz)

compd	X	H_α	C_α	J_{PC}
10	H	20.02	294.72	7.6
11	NMe_2	18.77	286.13	*b*
12	OMe	19.48	290.90	*b*
13	Me	19.80	293.86	8.3
14	F	19.86	291.52	8.6
15	Cl	19.98	291.46	8.0
16	NO_2	20.71	289.07	7.6

[a] Spectra were acquired in CD_2Cl_2. [b] Broad signal.

Synthesis of $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PR_3)_2$ *via* Phosphine Exchange. In an effort to broaden the synthetic utility of the present benzylidene catalysts, the analogous trialkylphosphine derivatives were prepared by phosphine exchange.[12] Treatment of **3**−**9** with 2.2 equiv of tricyclohexylphosphine at room temperature affords, after workup, $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ (X = H (**10**), NMe_2 (**11**), OMe (**12**), Me (**13**), F (**14**), Cl (**15**), NO_2 (**16**)) as purple (**11** is green) microcrystalline solids in high yields (eq 2). The fully-characterized compounds are



(2)

air-stable in the solid state and do not show any signs of decomposition in solution (CH_2Cl_2 or C_6H_6), even when heated at 60 °C or in the presence of alcohols, amines, or water. Selected solution NMR data for complexes **10**−**16** are listed in Table 3. In contrast to the PPh_3 analogs **3**−**9**, no ^{31}P coupling is observed for the H_α resonances of **10**−**16** in the ^1H NMR. The chemical shifts of these resonances are dependent on the electronic nature of the X substituent.[30] The former observation suggests that the alkylidene moiety is perpendicular to the P−Ru−P plane as in $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**),[12] and

(25) Compare: 2 mg of $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$ (**A**) polymerizes 70 equiv of norbornene in 0.5 mL of a 1:8 CD_2Cl_2/C_6D_6 solvent mixture in 3 h.

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(29) Benson, S. W. *Thermochemical Kinetics—Methods for the Estimation of Thermochemical Data and Rate Parameters*; John Wiley: New York, 1976.

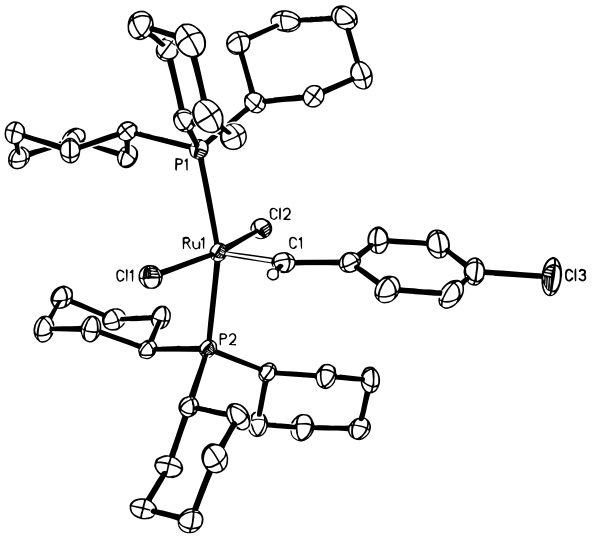
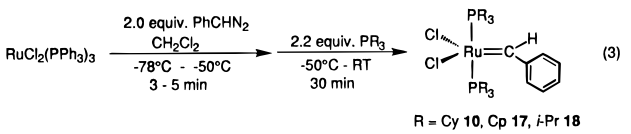


Figure 2. ORTEP plot of $RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (**15**).

the latter observation suggests a high degree of conjugation between the carbene and the aromatic ring of the benzylidene moiety.

X-ray Diffraction Study of $RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (15). Representative of complexes **10**−**16**, the structure of the Cl-substituted benzylidene $RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (**15**) was further confirmed by a single-crystal X-ray diffraction study. An ORTEP drawing of complex **15** is shown in Figure 2, and selected bond lengths and angles are given in Table 4. The analysis reveals distorted square-pyramidal coordination with a nearly linear Cl(1)−Ru−Cl(2) angle (167.61°). The carbene unit is perpendicular to the P1−Ru−P2 plane, and the aryl ligand is only slightly twisted out of the Cl1−Ru−Cl2−C1 plane. The Ru−C1 bond distance is shorter (1.838(3) Å) than in related compounds $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**) [d(Ru−C) = 1.851(21) Å][12] or $[RuCl(=C(OMe)CH=CPh_2)(CO)(P\text{-}i\text{-}Pr_3)_2][BF_4]$ [d(Ru−C) = 1.874(3) Å],[31] respectively.

One-Pot Synthesis of $RuCl_2(=CHPh)(PR_3)_2$. Due to the relative instability of the intermediate $RuCl_2(=CHPh)(PPh_3)_2$ (**3**) in solution, $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) can be synthesized in 75−80% yield from $RuCl_2(PPh_3)_3$. However, if isolation of **3** is avoided, and tricyclohexylphosphine was added at ≈−50 °C shortly after $RuCl_2(PPh_3)_3$ had been treated with phenyldiazomethane, **10** can be obtained in nearly quantitative yield in less than 1 h. The same procedure can also be applied to the synthesis of more soluble derivatives including $RuCl_2(=CHPh)(PR_3)_2$ (R = Cp (**17**), *i*-Pr (**18**)) which exhibit comparable metathesis activity (eq 3).



ROMP Activity of $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ Complexes 10−16. Benzylidenes $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ **10**−**16** are extremely active ROMP catalysts compared to their PPh_3 analogs **3**−**9**. Except for norbornene,[32] ROMP of highly strained monomers including functionalized norbornenes, 7-oxanorbornenes, and variously substituted cyclobutenes was proved to be living and led to polymers with exceptionally narrow molecular weight distributions (PDIs < 1.1).[33] In analogy to $RuCl_2(=CHCH=CPh_2)(PCy)_2$ (**B**),[12,13] complexes **10**−**16** can also polymerize low-strained cycloolefins, such as cyclooctene and 1,5-cyclooctadiene. Although the corresponding polymers are not monodispersed (PDI ≈ 1.50−1.60), these polymerizations proceed more rapidly and with significantly lower polydispersities than with B as catalyst (PDI ≈ 2.50). However, the presence of back-biting in these reactions is responsible for the broader PDIs. Therefore these systems cannot be considered living, even though a propagating alkylidene was observed for ROMP of cyclooctadiene by ^{1}H NMR (δ 18.88 (t)) with **10**. Complex **10** also reacts with cyclooctatetraene in CD_2Cl_2 with complete initiation,[34] but propagation does not occur, and facile back-biting leads to the formation of benzene. The increased activity of **10**−**16** compared to **B** is attributed to a faster initiation rate. Recently developed catalyst mixtures containing $[(cymene)RuCl_2]_2$, a bulky tertiary phosphine, and (trimethylsilyl)diazomethane were found to ROMP cyclooctenes.[35]

Table 4. Selected Bond Lengths and Angles for **15**

bond lengths [Å]			
Ru−C1	1.839(3)	Ru−P1	2.397(1)
Ru−Cl1	2.401(1)	Ru−P2	2.435(1)
Ru−Cl2	2.395(1)		
bond angles [deg]			
Cl1−Ru−P1	87.2(1)	Cl1−Ru−C1	88.7(1)
P1−Ru−C1	97.5(1)	Cl1−Ru−Cl2	167.6(1)
P1−Ru−Cl2	91.5(1)	C1−Ru−Cl2	103.7(1)
Cl1−Ru−P2	90.8(1)	P1−Ru−P2	161.1(1)
C1−Ru−P2	101.2(1)	Cl2−Ru−P2	86.5(1)

Metathesis of Acyclic Olefins. It was recently shown in our laboratory[12,27] that vinylalkylidene $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**) exhibits metathesis activity toward acyclic olefins, e.g., *cis*-2-pentene. Although the turnover numbers were modest compared to the best of the tungsten and molybdenum-based catalysts,[3f,36] this was the first example of acyclic metathesis induced by a ruthenium carbene complex.[3b] However, slow initiation was a present limitation for the general use of **B** as a catalyst.[37] Due to their exceptionally high activity in ROMP, $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ complexes **10**−**16** were expected to be efficient acyclic metathesis catalysts. This was indeed the case, as representatively shown with benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) in the following section.

Synthesis of the Methylidene Complex $RuCl_2(=CH_2)(PCy_3)_2$ (19). Whereas $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**) reacts with ethylene under 100 psi of pressure at 50 °C in CD_2Cl_2 within several hours to reach an equilibrium of **B** and $RuCl_2(=CH_2)(PCy_3)_2$ (**19**) in a ratio of **B:19** = 80:20, benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) is quantitatively converted to the methylidene **19** within a few minutes at room temperature under 14 psi of ethylene (eq 4). Complex **19** is isolated as a red-purple,

(30) For Hammett constants of X, see: Lowry, T. H.; Schueller-Richardson, K. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins Publishers: New York, 1987; p 144.

(31) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258−4265.

(32) $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) polymerized 100 equiv of norbornene within seconds, but polydispersities are much broader (2.0−2.5) than with $RuCl_2(=CHPh)(PPh_3)_2$ (**3**), supposedly due to backbiting and chain transfer as side reactions.

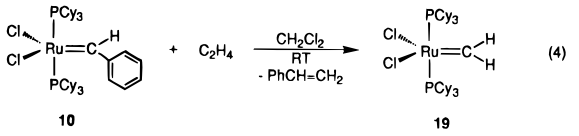
(33) Lynn, D. M.; Maughon, B. R.; Weck, M.; Grubbs, R. H. Unpublished results.

(34) $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**) does not react with cyclooctatetraene.

(35) Schumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127−1128.

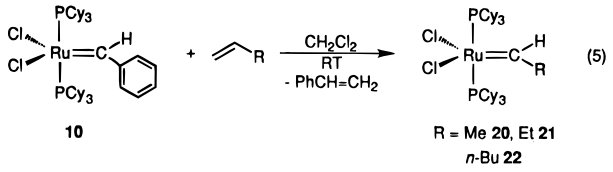
(36) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771−2773.

(37) On reaction of $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**) with 100 equiv of *cis*-2-pentene, the parent catalyst was observed by NMR along with $RuCl_2(=CHR)(PCy_3)_2$ (R = Me and Et) after 1 day.



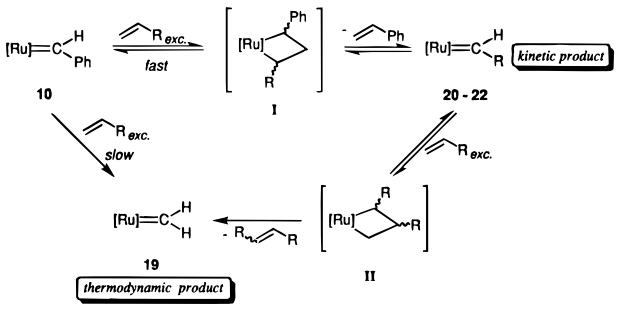
air-stable solid. A pentacoordinate ruthenium center may be inferred from the analytic and spectroscopic data. Methylidene **19** is less stable in solution than benzylidene **10**; decomposition is observed after 12 h in solution (CH_2Cl_2, C_6H_6). The decomposition rate increases, as catalyst solutions are heated. Among all isolated methylidene complexes including RuCl(NO)(=CH_2)(PPh_3)$_2$[23,38] and Ir=CH_2(N($SiMe_2CH_2PPh_2$)$_2$),[39] $RuCl_2$(=CH_2)(PCy_3)$_2$ (**19**) is *the first isolable metathesis-active methylidene complex*. The high activity of **19**, which exhibits a similar stability toward functional groups as benzylidene **10**, was shown in the ROMP of cyclooctene and 1,5-cyclooctadiene[40] and in ring-closing metathesis of diethyl diallylmalonate.[41]

Synthesis of Substituted Alkylidene Complexes *via* Cross Metathesis. The rapid reaction of $RuCl_2$(=CHPh)(PCy_3)$_2$ (**10**) with ethylene to give $RuCl_2$(=CH_2)(PCy_3)$_2$ (**19**) has prompted us to extend our studies to terminal and disubstituted olefins. Although olefin metathesis is an equilibrium process, the kinetic products may be isolated under certain conditions. Indeed, **10** is quantitatively converted to the alkylidenes $RuCl_2$(=CHR)(PCy_3)$_2$ (R = Me (**20**), Et (**21**), *n*-Bu (**22**)) when reacted with a tenfold excess of propene, 1-butene, or 1-hexene, respectively. In each case, an equimolar amount of styrene was formed and spectroscopically identified (eq 5). The isolated compounds **20**−

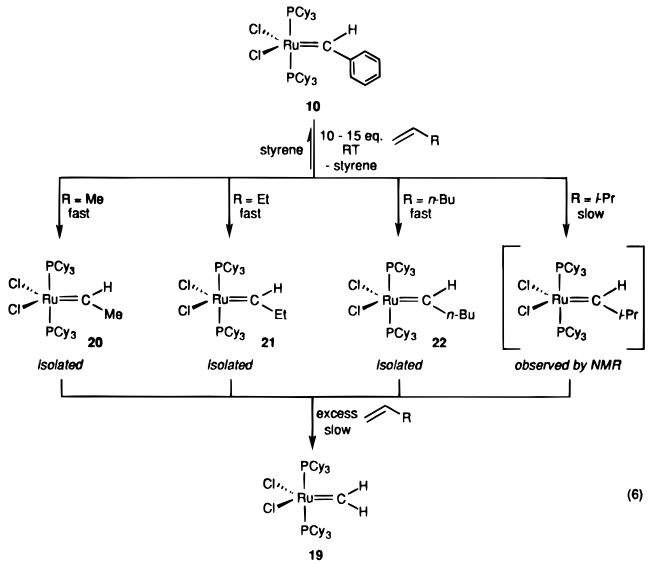


22 are comparable to precursor **10** in stability and solubility and they are reconverted to **10** in the presence of a large excess (30−50 equiv) of styrene. Metathesis of disubstituted olefins *cis*-2-butene and *cis*-3-hexene leads to the formation of $RuCl_2$(=CHR)(PCy_3)$_2$ from benzylidene **10**. However, due to the steric bulk of these olefins, the reactions proceed considerably slower than with the corresponding terminal olefins. No reaction occurred between **10** and 3,3-dimethyl-1-butene, and steric

Scheme 1. Proposed Mechanism for the Formation of $RuCl_2$(=CHR)(PCy_3)$_2$ **20**−**22** and $RuCl_2$(=CH_2)(PCy_3)$_2$ **19**



interaction between the metal fragment and the incoming olefin is also presumed to be responsible for the slow reaction with 20 equiv of 3-methyl-1-butene. The expected alkylidene $RuCl_2$(=CH*i*-Pr)-(PCy_3)$_2$ was identified by NMR, but its concentration remained small and constant throughout the reaction. After 6 h, initiation was complete and methylidene **19** was isolated as the sole reaction product. If alkylidene $RuCl_2$(=CHR)(PCy_3)$_2$ complexes **20**−**22** are not isolated immediately after formation, slow reaction with excess olefin results in the formation of $RuCl_2$(=CH_2)(PCy_3)$_2$ (**19**) within 10−15 h (eq 6). As proposed



in Scheme 1, **10** is likely to react with a terminal olefin to rapidly form a metallacyclobutane intermediate **I**,[42] in which the two substituents (Ph and R) are in the 1,3-position for steric reasons. Productive cleavage of the intermediate metallacycle leads to the formation of alkylidene complexes **20**−**22** as kinetic products. On extended reaction times, $RuCl_2$(=CHR)(PCy_3)$_2$ complexes **20**−**22** undergo a slow reaction with excess olefin to form methylidene **19** presumably through intermediate metallacyclobutane **II**. $RuCl_2$(=CH_2)(PCy_3)$_2$ (**19**) appears to be the thermodynamic product as it will not metathesize α-olefins in dilute conditions.

Kinetic Studies with $RuCl_2$(=CH-*p*-C_6H_4X)(PCy_3)$_2$ Complexes 10−16. The electronic influence of X on the initiation rates of $RuCl_2$(=CH-*p*-C_6H_4X)(PCy_3)$_2$ complexes **10**−**16** was probed by examining the reactions of **10**−**16** with 1-hexene. Clean and quantitative conversion to the pentylidene $RuCl_2$(=CH-*n*-Bu)(PCy_3)$_2$ (**22**) was observed in all cases. Pseudo-

(38) For examples of methylidene complexes, see: (a) Brookhart, M.; Liu, Y. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; Vol. 269, p 251. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577−6578. (c) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98−104. (d) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044−5045. (e) Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408−414. (f) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926−5928. (g) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558−1565. (h) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099−6101. (i) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203−1205. (j) Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 835−837. (k) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760−762. (l) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *11*, 3079−3080. (m) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599−4600. (n) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939−5940.

(39) (a) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708−6710. (b) Fryzuk, M. D.; Gao, X.; Joshi, K.; MacNeil, P. A.; Massey, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10581−10590.

(40) 6.0 μmol of methylidene **19** polymerized 500 equiv of neat cyclooctene or 1,5-cyclooctadiene at room temperature within 80−90 min. Poly-COE: yield ≈ 100%; M_n = 125 kg/mol; PDI(toluene) = 1.40. Poly-COD: yield ≈ 100%; M_n = 59.7 kg/mol; PDI(toluene) = 1.42.

(41) 6.0 μmol of methylidene **19** ring-closed 30 equiv of diethyl diallylmalonate in CD_2Cl_2 at room temperature in 15 min to give 4,4-diethylcyclopentene dicarboxylate quantitatively.

(42) There is abundant evidence that the key step in olefin metathesis consists of the reaction between a transition metal−carbon double bond (M=CHR) and an olefin to give a metallacyclobutane ring, which was first proposed by: Herrison, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

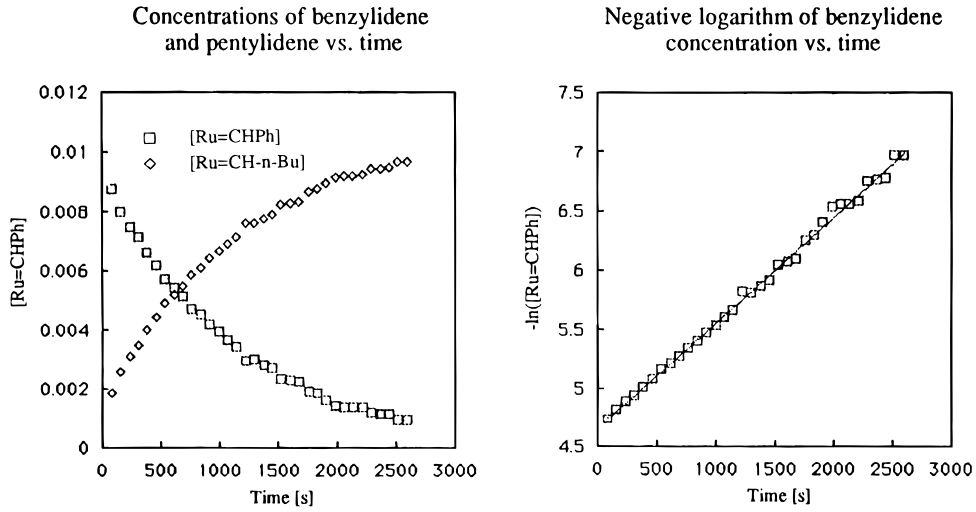


Figure 3. Representative kinetic plots for acyclic metathesis of 1-hexene with $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) as catalyst (T = 0 °C).

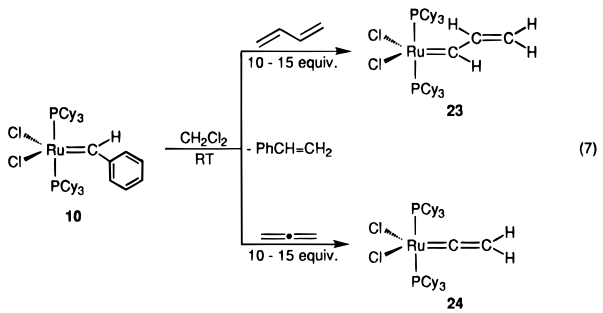
Table 5. Determined Initiation Rate Constants k_i for Acyclic Metathesis of 1-Hexene with $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ Complexes **10**−**16** as Catalysts[a] (k_i in L/(mol·s))

compd	X	$10^{-3}k_i$	compd	X	$10^{-3}k_i$
10	H	2.87	**14**	F	1.21
11	NMe_2	0.31	**15**	Cl	1.37
12	OMe	1.01	**16**	NO_2	1.77
13	Me	2.15			

[a] For [Ru] = 0.01 M; [1-hexene] = 0.32 M in CD_2Cl_2 at T = 0 °C.

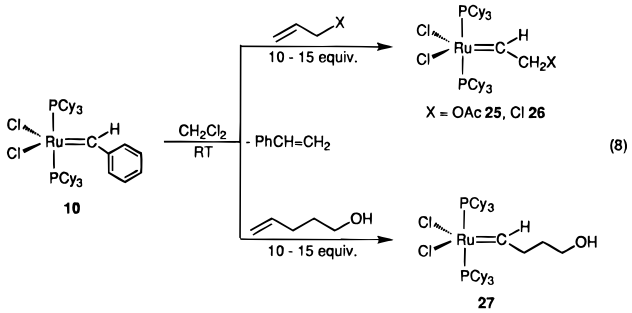
first-order rate constants were measured by integration of the H_α resonances of benzylidenes **10**−**16** vs pentylidene **22**. Representative plots are shown in Figure 3, and rate constants (k_i) are listed in Table 5. As observed for living ROMP of norbornene with $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PPh_3)_2$ catalysts **3**−**9**, the range of k_is among the substituted benzylidenes is approximately an order of magnitude. Although no general trend can be discerned, any perturbation to the aromatic π-system (i.e. X ≠ H) results in a decrease in the initiation rate. $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) initiated approximately 1000 times faster than vinylalkylidene $RuCl_2(=CH\text{-}CH=CPh_2)(PCy_3)_2$ (**B**), which did not completely react to give pentylidene **22** under the above-mentioned conditions.

Metathesis of Conjugated and Cumulated Olefins. Treatment of $RuCl_2(=CHPh)(PCy_3)_2$ (**10**) with a tenfold excess of 1,3-butadiene and 1,2-propadiene resulted in the high-yield formation of vinylalkylidene $RuCl_2(=CHCH=CH_2)(PCy_3)_2$ (**23**) and vinylidene $RuCl_2(=C=CH_2)(PCy_3)_2$ (**24**), respectively (eq 7). The former complex cannot be synthesized *via* ring-opening



of cyclopropene.[27] The spectroscopic data for these complexes are similar to those of related compounds $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$ (**B**)[12] and $RuCl_2(=C=CHt\text{-}Bu)(PPh_3)_2$.[22] In contrast to observations made in the synthesis of $RuCl_2(=CHR)(PCy_3)_2$ (R = Me (**20**), Et (**21**), *n*-Bu (**22**)), no formation of methylidene $RuCl_2(=CH_2)(PCy_3)_2$ (**19**) occurred at extended reaction times, which can be explained by the low activity of **23** and **24** toward their olefinic precursors. However, both complexes exhibit ROMP activity which in the case of **23** was evidenced by comparatively slow polymerization of cyclooctene (PDI = 2.0). Vinylidene **24** rapidly polymerized norbornene, although relatively slow initiation can be inferred by the lack of the characteristic color change, and both compounds are inactive for metathesis of acyclic olefins.

Introduction of Functional Groups *via* Metathesis. Although less active than their early-transition-metal counterparts, ruthenium alkylidenes have broader synthetic utility due to their tolerance of functional groups and protic media. It has been shown in our laboratory that vinylalkylidenes $RuCl_2(=CHCH=CPh_2)(PR_3)_2$ (R = Ph (**A**), Cy (**B**)) react readily with electron-rich olefins, such as vinyl ethers $H_2C=CHOR'$, to yield metathesis-inactive $RuCl_2(=CHOR')(PR_3)_2$.[43] This irreversible reaction has been extensively utilized in our laboratory for the endcapping of growing polymer chains.[44] Electron-deficient olefins are not metathesized by the triphenylphosphine catalyst **A**, and the tricyclohexylphosphine catalyst **B** displays only limited activity toward these substrates. However, the enhanced activity of the present benzylidene catalyst **10** prompted our exploration of this reaction. As shown in eq 8, metathesis of



functionalized olefins catalyzed by benzylidene **10** is not limited to electron-rich olefins, such as allyl acetate, but also includes electron-deficient alkenes, such as allyl chloride. Benzylidene **10** will also undergo efficient metathesis of unprotected en-ols, as shown with 4-penten-1-ol, to generate the corresponding hydroxy alkylidene $RuCl_2(=CH(CH_2)_3OH)(PCy_3)_2$ (**27**) (eq 8). Compounds **25**−**27** were readily isolated and fully characterized.

(43) Pangborn, A. B.; Nguyen, S. T.; Grubbs, R. H. Unpublished results.
(44) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707−4713.

In all cases the alkylidene H_α resonances appeared as triplets due to coupling with the vicinal CH_2 groups. Alkylidenes **25**−**27** are active in ROMP of low-strained olefins, which makes them attractive catalysts for the synthesis of telechelic and other functionalized polymers.

Summary and Conclusions

In this contribution, diazoalkanes have been shown to be an efficient carbene source in the preparation of novel alkylidene complexes of the general type $RuCl_2(=CHR)(PPh_3)_2$ (R = alkyl, aryl). Compared to the vinylalkylidene $RuCl_2(=CHCH=CPh_2)(PPh_3)_2$, these complexes display greater metathesis activity due to faster initiation and produce nearly monodisperse polynorbornene in a living fashion. The corresponding trialkylphosphine derivatives, $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$, are also capable of polymerizing low-strained systems with narrow polydispersities.

The parent benzylidene $RuCl_2(=CHPh)(PCy_3)_2$, which exhibits a remarkable stability toward oxygen and moisture, is generated conveniently and in high yields *via* a one-pot synthesis from $RuCl_2(PPh_3)_3$, phenyldiazomethane and tricyclohexylphosphine. In addition to its high ROMP activity, $RuCl_2(=CHPh)(PCy_3)_2$ is an efficient catalyst for metathesis of acyclic olefins. Under 1 atm of ethylene, $RuCl_2(=CHPh)(PCy_3)_2$ is quantitatively converted to $RuCl_2(=CH_2)(PCy_3)_2$, the first isolable metathesis-active methylidene complex. The benzylidene reacts with excess terminal olefins to yield alkylidenes $RuCl_2(=CHR)(PCy_3)_2$ (R = Me, Et, *n*-Bu) as kinetic products. However, prolonged reaction times result in the formation of the methylidene $RuCl_2(=CH_2)(PCy_3)_2$ as the thermodynamic product.

Comparative kinetic studies of the acyclic metathesis of 1-hexene with $RuCl_2(=CH\text{-}p\text{-}C_6H_4X)(PCy_3)_2$ to give $RuCl_2(=CH\text{-}n\text{-}Bu)(PCy_3)_2$ have shown that the electronic influence of X on the initiation rate is relatively small. Since the highest rates were observed for X = H and Me, it was proposed that k_i depends on conjugative effects of X, which might lower the ground state energy of the starting alkylidene vs the presumed metallacyclobutane intermediate. Supporting this theory, the vinylalkylidene complex $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$, which contains a highly conjugated alkylidene ligand, is a much poorer initiator.

In addition to terminal and disubstituted olefins, $RuCl_2(=CHPh)(PCy_3)_2$ also catalyzes metathesis of conjugated and cumulated olefins, as shown with 1,3-butadiene and 1,2-propadiene, to give vinylalkylidene $RuCl_2(=CHCH=CH_2)(PCy_3)_2$ and vinylidene $RuCl_2(=C=CH_2)(PCy_3)_2$, respectively. The high stability of $RuCl_2(=CHPh)(PCy_3)_2$ toward functional groups was further demonstrated by the introduction of functional groups, such as acetate, halogens, and hydroxyl groups, into the alkylidene moiety *via* metathesis. These alkylidenes give precise control of the polymer end groups in the syntheses of telechelics.

The reasons for the unexpectedly high reactivity of the phenyl substituted carbene relative to all others examined to date are being explored. Independent of the basis for this reactivity, the new catalysts are from $20 - 10^3$ times more active than the previously available complexes **A** and **B**.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox or under an atmosphere of argon. NMR spectra were recorded with either a QE-300 Plus (300.1 MHz ^{1}H; 75.5 MHz ^{13}C), a JEOL GX-400 (399.7 MHz ^{1}H; 161.9 MHz ^{31}P) or a Bruker AM 500 (500.1 MHz ^{1}H; 125.8 MHz ^{13}C; 202.5 MHz ^{31}P; 470.5 MHz ^{19}F) spectrometer.

Materials. Methylene chloride and benzene were passed through columns of activated alumina and stored under argon. Benzene-d_6 and methylene-d_2 chloride were degassed by three continuous freeze−pump−thaw cycles. $RuCl_2(PPh_3)_3$,[20] tricyclohexylphosphine,[45] and the diazoalkanes H_2CN_2,[15a] $MeCHN_2$,[15a] $EtCHN_2$,[15a] $PhCHN_2$,[15b] $p\text{-}C_6H_4NMe_2CHN_2$,[15b] $p\text{-}C_6H_4OMeCHN_2$,[15b] $p\text{-}C_6H_4MeCHN_2$,[15b] $p\text{-}C_6H_4FCHN_2$,[15b] $p\text{-}C_6H_4ClCHN_2$,[15b] and $p\text{-}C_6H_4NO_2CHN_2$[15c] were prepared according to literature procedures. Norbornene was dried over sodium, vacuum transferred, and stored under argon. Cyclooctene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene were dried over CaH_2, distilled, and stored under argon. The following chemicals were obtained from commercial sources and used as received: ethylene, propylene, 1-butene, *cis*-2-butene, 1-hexene, *cis*-3-hexene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 1,3-butadiene, 1,2-propadiene, allyl acetate, allyl chloride, 4-penten-1-ol, diethyl diallylmalonate, triisopropylphosphine, tricyclopentylphosphine, pentane, ether, acetone, and methanol.

$RuCl_2(=CHMe)(PPh_3)_2$ (1). A solution of $RuCl_2(PPh_3)_3$ (417 mg, 0.43 mmol) in CH_2Cl_2 (10 mL) was treated at −78 °C with a −50 °C 0.50 M solution of diazoethane (1.90 mL, 0.93 mmol, 2.2 equiv) in ether. Upon addition of the diazo compound, a color change from orange-brown to green-brown occurred, and slight bubbling was observed. After the cooling bath was removed, the solution was stirred for 3 min and then evaporated to dryness. The oily residue was washed several times with small quantities of ice-cold ether (3-mL portions), and the remaining olive-green solid was dried under vacuum for several hours. Yield = 246 mg (78%). ^{1}H NMR (CD_2Cl_2): δ 18.47 (tq, J_{PH} = 10.2 Hz, $^3J_{HH}$ = 5.1 Hz, Ru=CH), 7.68−7.56 and 7.49−7.36 (both m, $P(C_6H_5)_3$), 2.59 (d, $^3J_{HH}$ = 5.1 Hz, CH_3). ^{13}C NMR (CD_2Cl_2): δ 320.65 (t, J_{PC} = 9.9 Hz, Ru=CH), 134.76 (m, *o*-C of $P(C_6H_5)_3$), 132.06 (m, *ipso*-C of $P(C_6H_5)_3$), 130.38 (s, *p*-C of $P(C_6H_5)_3$), 128.44 (m, *m*-C of $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 29.99 (s, PPh_3). Anal. Calcd for $C_{38}H_{34}Cl_2P_2Ru$: C, 62.99; H, 4.73. Found: C, 63.12; H, 4.61.

$RuCl_2(=CHEt)(PPh_3)_2$ (2). **2** was prepared in analogy to **1**, starting with $RuCl_2(PPh_3)_3$ (502 mg, 0.52 mmol) and a 0.45 M solution of diazopropane (2.56 mL, 1.15 mmol, 2.2 equiv) in ether. An orange-brown, microcrystalline solid was obtained. Yield = 311 mg (81%). ^{1}H NMR (C_6D_6): δ 18.21 (tt, J_{PH} = 10.8, $^3J_{HH}$ = 6.6 Hz, Ru=CH), 7.91−7.86 and 6.97−6.80 (both m, $P(C_6H_5)_3$), 3.11 (dq, $^3J_{HH} = {}^3J_{HH'}$ = 6.6 Hz, CH_2CH_3), 0.79 (t, $^3J_{HH}$ = 6.6 Hz, CH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 320.88 (t, J_{PC} = 10.0 Hz, Ru=CH), 134.36 (m, *o*-C of $P(C_6H_5)_3$), 132.27 (m, *ipso*-C of $P(C_6H_5)_3$), 129.89 (s, *p*-C of $P(C_6H_5)_3$), 128.14 (m, *m*-C of $P(C_6H_5)_3$), 53.20 (s, CH_2CH_3), 29.74 (s, CH_2CH_3). ^{31}P NMR (CD_2Cl_2): δ 30.02 (s, PPh_3). Anal. Calcd for $C_{39}H_{36}Cl_2P_2Ru$: C, 63.42; H, 4.91. Found: C, 62.85; H, 4.81.

$RuCl_2(=CHPh)(PPh_3)_2$ (3). A solution of $RuCl_2(PPh_3)_3$ (2.37 g, 2.47 mmol) in CH_2Cl_2 (20 mL) was treated at −78 °C with a −50 °C solution of phenyldiazomethane (584 mg, 4.94 mmol, 2.0 equiv) in CH_2Cl_2 or pentane (3 mL). A spontaneous color change from orange-brown to brown-green and vigorous bubbling was observed. After the cooling bath was removed, the solution was stirred for 5 min and the solution was then concentrated to ∼3 mL. Upon addition of pentane (20 mL), a green solid was precipitated which was separated from the brown mother-liquid *via* cannula filtration, dissolved in CH_2Cl_2 (3 mL), and reprecipitated with pentane. This procedure was repeated until the mother-liquid was nearly colorless. The remaining gray-green microcrystalline solid was dried under vacuum for several hours. Yield = 1.67 g (89%). ^{1}H NMR (C_6D_6): δ 19.56 (t, J_{PH} = 10.2 Hz, Ru=CH), 7.80−7.64 and 6.99−6.66 (both m, C_6H_5 and $P(C_6H_5)_3$). ^{13}C NMR (CD_2Cl_2): δ 310.12 (t, J_{PC} = 11.4 Hz, Ru=CH), 155.36 (s, *ipso*-C of C_6H_5), 134.91 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 133.97 (d, J_{PC} = 19.6 Hz, *ipso*-C of $P(C_6H_5)_3$), 130.44 (s, *p*-C of $P(C_6H_5)_3$), 130.03, 128.71, and 127.09 (all s, C_6H_5), 128.37 (s(br), *m*-C or *o*-C of $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 30.63 (s, PPh_3). Anal. Calcd for $C_{43}H_{36}Cl_2P_2Ru$: C, 65.65; H, 4.61; P, 7.87. Found: C, 65.83; H, 4.59; P, 7.93.

(45) Preparation of PCy_3, described by Issleib and Brack (Issleib, K.; Brack, A. *Z. Anorg. Allg. Chem.* **1954**, *277*, 258−270), was slightly altered.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4NMe_2)(PPh_3)_2$ (4). A solution of $RuCl_2(PPh_3)_3$ (466 mg, 0.49 mmol) in CH_2Cl_2 (10 mL) was treated at −78 °C with a −50 °C solution of *p*-$C_6H_4NMe_2CHN_2$ (160 mg, 0.98 mmol, 2.0 equiv) in CH_2Cl_2 (3 mL). A spontaneous color change from orange-brown to brown-green and vigorous bubbling was observed. After the cooling bath was removed, the solution was stirred for 10 min and then the solvent was removed under vacuum. The brown residue was dissolved in minimal amounts of CH_2Cl_2 (3 mL), and pentane (20 mL) was added to precipitate a green solid. After cannula filtration, this procedure was repeated until the filtrate was colorless. The remaining olive-green microcrystalline solid was dried under vacuum for several hours. Yield − 317 mg (78%). ^{1}H NMR (CD_2Cl_2): δ 18.30 (t, J_{PH} = 6.1 Hz, Ru=CH), 7.64 (d, $^3J_{HH}$ = 8.7 Hz, *o*-H of $C_6H_4NMe_2$), 7.52−7.49 (m, *o*-H of $P(C_6H_5)_3$), 7.42 (t, $^3J_{HH}$ = 7.5 Hz, *p*-H of $P(C_6H_5)_3$), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, *m*-H of $P(C_6H_5)_3$), 6.32 (d, $^3J_{HH}$ = 8.7 Hz, *m*-H of $C_6H_4NMe_2$), 2.96 (s, $N(CH_3)_2$). ^{13}C NMR (CD_2Cl_2): δ 309.68 (t, J_{PC} = 11.4 Hz, Ru=CH), 152.72 (s, *ipso*-C of $C_6H_4NMe_2$), 135.01 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 133.57 (s, *o*-C or *m*-C of $C_6H_4NMe_2$), 131.86 (s, *p*-C of $P(C_6H_5)_3$), 130.20 (s, *o*-C or *m*-C of $C_6H_4NMe_2$), 128.27 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 127.54 (s(br), *p*-C of $C_6H_4NMe_2$), 110.61 (d, J_{PC} = 21.5 Hz, *ipso*-C of $P(C_6H_5)_3$), 40.30 (s, $N(CH_3)_2$). ^{31}P NMR (CD_2Cl_2): δ 34.84 (s, PPh_3). Anal. Calcd for $C_{45}H_{41}Cl_2NP_2Ru$: C, 65.14; H, 4.98; N, 1.69. Found: C, 65.28; H, 4.97; N, 1.80.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4OMe)(PPh_3)_2$ (5). A solution of $RuCl_2(PPh_3)_3$ (561 mg, 0.59 mmol) in CH_2Cl_2 (12 mL) was treated at −78 °C with a −40 °C solution of *p*-$C_6H_4OMeCHN_2$ (87 mg, 0.59 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL). A spontaneous color change from orange-brown to brown-green and vigorous bubbling was observed. After the cooling bath was removed, the solution was stirred for 5 min and then the solvent was removed under vacuum. The brown-green residue was dissolved in minimal amounts of CH_2Cl_2 (2 mL), and pentane (20 mL) was added and precipitate a brown solid. The brown-green solution was separated *via* cannula filtration and dried under vacuum. The remaining olive-green solid was repeatedly washed with ether (10-mL portions) and dried under vacuum for several hours. Yield = 400 mg (83%). ^{1}H NMR (C_6D_6): δ 19.38 (t, J_{PH} = 8.7 Hz, Ru=CH), 7.85−7.72 and 7.03−6.80 (both m, C_6H_4OMe and $P(C_6H_5)_3$), 6.41 (d, $^3J_{HH}$ = 8.7 Hz, *m*-H of C_6H_4OMe), 3.22 (s, OCH_3). ^{13}C NMR (CD_2Cl_2): δ 309.20 (t, J_{PC} = 10.7 Hz, Ru=CH), 147.42 (s, *ipso*-C of C_6H_4OMe), 135.56 (*pseudo*-t, *m*-C or *o*-C of $P(C_6H_5)_3$), 133.98 (s, *o*-C or *m*-C of C_6H_4OMe), 131.46 (s, *p*-C of $P(C_6H_5)_3$), 130.43 (s, *o*-C or *m*-C of C_6H_4OMe), 128.40 (*pseudo*-t, *m*-C or *o*-C of $P(C_6H_5)_3$), 126.82 (s, *p*-C of C_6H_4OMe), 113.95 (d, J_{PC} = 21.4 Hz, *ipso*-C of $P(C_6H_5)_3$), 55.77 (s, OCH_3). ^{31}P NMR (CD_2Cl_2): δ 32.50 (s, PPh_3). Anal. Calcd for $C_{44}H_{38}Cl_2OP_2Ru$: C, 64.71; H, 4.69. Found: C, 65.23; H, 4.78.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4Me)(PPh_3)_2$ (6). Starting with $RuCl_2(PPh_3)_3$ (350 mg, 0.37 mmol) and *p*-$C_6H_4MeCHN_2$ (48 mg, 0.37 mmol, 1.0 equiv), **6** was synthesized in analogy to **5**. A brown microcrystalline solid was obtained. Yield = 258 mg (87%). ^{1}H NMR (C_6D_6): δ 19.55 (t, J_{PH} = 9.6 Hz, Ru=CH), 7.84−7.63 and 7.02−6.80 (both m, C_6H_4-Me and $P(C_6H_5)_3$), 6.53 (d, $^3J_{HH}$ = 7.8 Hz, *m*-H of C_6H_4Me), 1.68 (s, CH_3). ^{13}C NMR (CD_2Cl_2): δ 309.17 (t, J_{PC} = 10.9 Hz, Ru=CH), 153.34 (s, *ipso*-C of C_6H_5Me), 135.50 (s, *o*-C or *m*-C of C_6H_4OMe), 134.96 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 132.13 (s, *p*-C of $P(C_6H_5)_3$), 130.36 (s, *o*-C or *m*-C of C_6H_4Me), 128.34 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 126.76 (s, *p*-C of C_6H_4Me), 115.23 (d, J_{PC} = 21.4 *ipso*-C of $P(C_6H_5)_3$), 40.92 (s, CH_3). ^{31}P NMR (CD_2Cl_2): δ 31.29 (s, PPh_3). Anal. Calcd for $C_{44}H_{38}Cl_2P_2Ru$: C, 66.00; H, 4.78. Found: C, 65.90; H, 4.75.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4F)(PPh_3)_2$ (7). Starting with $RuCl_2(PPh_3)_3$ (960 mg, 1.00 mmol) and *p*-$C_6H_4FCHN_2$ (272 mg, 2.00 mmol, 2.0 equiv), **7** was synthesized in analogy to **3**. An olive-green microcrystalline solid was obtained. Yield = 716 mg (89%). ^{1}H NMR (CD_2Cl_2): δ 19.24 (t, J_{PH} = 9.0 Hz, Ru=CH), 7.65−7.62 (m, *o*-H of C_6H_4F), 7.50−7.44 and 7.35−7.32 (both m, $P(C_6H_5)_3$), 6.62 (t, $^3J_{HH} = {}^3J_{HF}$ = 8.9 Hz, *m*-H of C_6H_4F). ^{13}C NMR (CD_2Cl_2): δ 307.51 (t, J_{PC} = 11.4 Hz, Ru=CH), 163.27 (d, J_{CF} = 254.3 Hz, *p*-C of C_6H_4F), 152.21 (s, *ipso*-C of C_6H_4F), 134.95 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 134.04 (d, J_{CF} = 19.5 Hz, *m*-C of C_6H_4F), 130.56 (s, *p*-C of $P(C_6H_5)_3$), 130.08 (d, J_{CF} = 8.7 Hz, *o*-C of C_6H_4F), 128.47 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 115.67 (d, J_{PC} = 21.8 Hz, *ipso*-C of $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 31.03 (s, PPh_3). ^{19}F NMR (CD_2Cl_2): δ 45.63 (s, C_6H_4F). Anal. Calcd for $C_{43}H_{35}Cl_2FP_2Ru$: C, 64.18; H, 4.38. Found: C, 64.42; H, 4.42.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PPh_3)_2$ (8). Starting with $RuCl_2(PPh_3)_3$ (350 mg, 0.37 mmol) and *p*-$C_6H_4ClCHN_2$ (111 mg, 0.73 mmol, 2.0 equiv), **8** was synthesized in analogy to **3**. A green microcrystalline solid was obtained. Yield = 246 mg (82%). ^{1}H NMR (CD_2Cl_2): δ 19.27 (t, J_{PH} = 9.2 Hz, Ru=CH), 7.51−7.44, 7.35−7.32, and 6.67−6.63 (all m, C_6H_4Cl and $P(C_6H_5)_3$), 6.86 (d, $^3J_{HH}$ = 8.8 Hz, *m*-H of C_6H_4Cl). ^{13}C NMR (CD_2Cl_2): δ 307.34 (t, J_{PC} = 10.6 Hz, Ru=CH), 153.82 (s, *ipso*-C of C_6H_4Cl), 134.91 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 130.58 (s, *p*-C of $P(C_6H_5)_3$), 128.87, 128.81, and 127.85 (all s, C_6H_4-Cl), 128.48 (s(br), *m*-C or *o*-C of $P(C_6H_5)_3$), 115.90 (d, J_{PC} = 21.7 Hz, *ipso*-C of $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 30.47 (s, PPh_3). Anal. Calcd for $C_{43}H_{35}Cl_3P_2Ru$: C, 62.90; H, 4.30. Found: C, 62.87; H, 4.40.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4NO_2)(PPh_3)_2$ (9). Starting with $RuCl_2(PPh_3)_3$ (604 mg, 0.63 mmol) and *p*-$C_6H_4NO_2CHN_2$ (206 mg, 1.25 mmol, 2.0 equiv), **9** was synthesized in analogy to **3**. A tan microcrystalline solid was obtained. Yield = 398 mg (76%). ^{1}H NMR (CD_2Cl_2): δ 19.47 (t, J_{PH} = 10.8 Hz, Ru=CH), 7.88−7.67, 7.38−7.33, and 7.02−6.71 (all m, $C_6H_4NO_2$ and $P(C_6H_5)_3$). ^{13}C NMR (CD_2Cl_2): δ 313.43 (t, J_{PC} = 11.2 Hz, Ru=CH), 158.40 (s, *ipso*-C of $C_6H_4NO_2$), 148.11 (s, *p*-C of $C_6H_4NO_2$), 135.49 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 132.21 (s, *m*-C of $C_6H_4NO_2$), 130.91 (s, *p*-C of $P(C_6H_5)_3$), 130.72 (s, *o*-C of $C_6H_4NO_2$), 128.86 (m, *m*-C or *o*-C of $P(C_6H_5)_3$), 116.03 (d, J_{PC} = 21.6 Hz, *ipso*-C of $P(C_6H_5)_3$). ^{31}P NMR (CD_2Cl_2): δ 32.27 (s, PPh_3). Anal. Calcd for $C_{43}H_{35}Cl_2NO_2P_2Ru$: C, 62.10; H, 4.24; N, 1.68. Found: C, 62.31; H, 4.66; N, 1.84.

ROMP of Norbornene with 3−9 as Catalysts. Norbornene (59 mg, 0.63 mmol) was dissolved in CH_2Cl_2 (0.7 mL) and treated with solutions of **3**−**9** (6.25 μmol) in CH_2Cl_2 (0.3 mL) at room temperature. The reaction mixtures became viscous within 3−5 min and the color changed from brown-green to orange. The solutions were stirred at room temperature for 1 h, then exposed to air and treated with CH_2Cl_2 (2 mL) containing traces of 2,6-di-*tert*-butyl-4-methylphenol and ethyl vinyl ether. The resulting green solutions were stirred for 20 min and, after filtration through short columns of silica gel, precipitated into vigorously stirred methanol. White, tacky polymers were obtained which were isolated, washed several times with methanol, and dried under vacuum. Yields 95−99%, ≈90% trans, M_n = 31.6−42.3 kg/mol, PDI (toluene) = 1.04−1.10.

Determination of Initiation and Propagation Rates in ROMP of Norbornene with 3−9 as Catalysts. Catalysts **3**−**9** (1.25×10^{-5} mol) were weighed into NMR tubes and dissolved in benzene-d_6 (0.3 mL) to which a ferrocene stock solution in benzene-d_6 (20 μL) was added as an internal standard. These mixtures were treated with solutions of norbornene (23.5 mg, 0.25 mmol, 20 equiv) in benzene-d_6 (250 μL). A ^{1}H NMR routine was started immediately, taking 60 spectra within 40 min, then 200 within 5 h. The initiation rate constants (k_i) were determined by integration of H_α resonances of the initiating and propagating species. The propagation rate constants (k_p) were determined by monitoring the decrease of monomer concentration vs the internal standard. The results are given in Table 2.

$RuCl_2(=CHPh)(PCy_3)_2$ (10). A solution of **3** (242 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) was treated with a solution of tricyclohexylphosphine (190 mg, 0.68 mmol, 2.2 equiv) in CH_2Cl_2 (3 mL) and stirred at room temperature for 30 min. The solution was filtered, and the solvent was removed under vacuum. The residue was repeatedly washed with acetone or methanol (5-mL portions) and dried in vacuo. A purple microcrystalline solid was obtained. Yield = 209 mg (89%). ^{1}H NMR (CD_2Cl_2): δ 20.02 (s, Ru=CH), 8.44 (d, $^3J_{HH}$ = 7.6 Hz, *o*-H of C_6H_5), 7.33 (t, $^3J_{HH}$ = 7.6 Hz, *m*-H of C_6H_5), 2.62−2.58, 1.77, 1.67, 1.46−1.39, and 1.25−1.16 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 294.72 (s, Ru=CH), 153.17 (s, *ipso*-C of C_6H_5), 131.21, 129.49, and 129.27 (all s, C_6H_5), 32.49 (*pseudo*-t, J_{app} = 9.1 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.04 (s, *m*-C of $P(C_6H_{11})_3$), 28.24 (*pseudo*-t, J_{app} = 4.5 Hz, *o*-C of $P(C_6H_{11})_3$), 26.96 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 36.61 (s, PCy_3). Anal. Calcd for $C_{43}H_{72}Cl_2P_2Ru$: C, 62.76; H, 8.82. Found: C, 62.84; H, 8.71.

One-Pot Synthesis of $RuCl_2(=CHPh)(PCy_3)_2$ (10). A solution of $RuCl_2(PPh_3)_3$ (4.0 g, 4.17 mmol) in CH_2Cl_2 (40 mL) was treated at −78 °C with a −50 °C solution of phenyldiazomethane (986 mg, 8.35 mmol, 2.0 equiv) in pentane (10 mL). Upon addition of the diazo compound, an instantaneous color change from orange-brown to green-

brown and vigorous bubbling was observed. After the reaction mixture was stirred at −70 °C to −60 °C for 5−10 min, an ice-cold solution of tricyclohexylphosphine (2.57 g, 9.18 mmol, 2.2 equiv) in CH_2Cl_2 was added *via* syringe. Accompanied by a color change from brown-green to red, the solution was allowed to warm to room temperature and stirred for 30 min. The solution was filtered, concentrated to half of the volume, and filtrated. Methanol (100 mL) was added to precipitate a purple microcrystalline solid, which was filtered off, washed several times with acetone and methanol (10-mL portions), and dried under vacuum for several hours. Yield = 3.40 g (99%).

$RuCl_2(=CH\text{-}p\text{-}C_6H_4NMe_2)(PCy_3)_2$ (11). Starting with **4** (316 mg, 0.38 mmol) and tricyclohexylphosphine (235 mg, 0.84 mmol, 2.2 equiv), **11** was obtained in analogy to **10** as a green microcrystalline solid. Yield: 284 mg (86%). ^{1}H NMR (CD_2Cl_2): δ 18.77 (s, Ru=CH), 8.25−8.14 (s(vbr), *o*-H of $C_6H_4NMe_2$), 6.55 (d, $^3J_{HH}$ = 7.2 Hz, *m*-H of $C_6H_4NMe_2$), 2.97 (s, $N(CH_3)_2$), 2.63−2.61, 1.80−1.67, 1.43−1.41, and 1.21−1.17 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 286.13 (s(br), Ru=CH), 151.28 (s, *ipso*-C of $C_6H_4NMe_2$), 144.80, 134.85, and 110.50 (all s, $C_6H_4NMe_2$), 40.30 (s, $N(CH_3)_2$), 32.54 (*pseudo*-t, J_{app} = 8.2 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.10 (s, *m*-C of $P(C_6H_{11})_3$), 28.36 (m, *o*-C of $P(C_6H_{11})_3$), 27.07 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 34.94 (s, PCy_3). Anal. Calcd for $C_{45}H_{77}Cl_2NP_2Ru$: C, 62.41; H, 8.96; N, 1.62. Found: C, 62.87; H, 9.04; N, 1.50.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4OMe)(PCy_3)_2$ (12). Starting with **5** (171 mg, 0.21 mmol) and tricyclohexylphosphine (130 mg, 0.46 mmol, 2.2 equiv), **12** was obtained in analogy to **10** as a dark-purple microcrystalline solid. Yield = 152 mg (85%). ^{1}H NMR (CD_2Cl_2): δ 19.48 (s, Ru=CH), 8.43 (s(br), *o*-H of C_6H_4OMe), 6.82 (d, $^3J_{HH}$ = 8.6 Hz, *m*-H of C_6H_4OMe), 3.82 (s, OCH_3), 2.64−2.59, 1.78−1.68, 1.46−1.39, and 1.26−1.15 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 290.90 (s(br), Ru=CH), 148.34 (s, *ipso*-C of C_6H_4OMe), 134.91, 132.30, and 128.83 (all s, C_6H_4OMe), 55.81 (s, OCH_3), 32.51 (*pseudo*-t, J_{app} = 9.1 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.06 (s, *m*-C of $P(C_6H_{11})_3$), 28.28 (*pseudo*-t, J_{app} = 5.2 Hz, *o*-C of $P(C_6H_{11})_3$), 27.00 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 35.83 (s, PCy_3). Anal. Calcd for $C_{44}H_{74}Cl_2OP_2Ru$: C, 61.96; H, 8.74. Found: C, 62.36; H, 8.71.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4Me)(PCy_3)_2$ (13). Starting with **6** (416 mg, 0.52 mmol) and tricyclohexylphosphine (321 mg, 1.14 mmol, 2.2 equiv), **13** was obtained in analogy to **10** as a bright-purple microcrystalline solid. Yield = 385 mg (88%). ^{1}H NMR (CD_2Cl_2): δ 19.80 (s, Ru=CH), 8.33 (d, $^3J_{HH}$ = 7.6 Hz, *o*-H of C_6H_4Me), 7.13 (d, $^3J_{HH}$ = 7.6 Hz, *m*-H of C_6H_4Me), 2.08 (s, CH_3), 2.62−2.58, 1.77−1.67, 1.43−1.40, and 1.22−1.17 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 293.86 (t, J_{PC} = 8.3 Hz, Ru=CH), 151.48 (s, *ipso*-C of C_6H_4Me), 140.40 (s, *p*-C of C_6H_4Me), 131.56 and 129.85 (both s, C_6H_4Me), 32.52 (*pseudo*-t, J_{app} = 9.2 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.07 (s, *m*-C of $P(C_6H_{11})_3$), 28.26 (*pseudo*-t, J_{app} = 4.1 Hz, *o*-C of $P(C_6H_{11})_3$), 27.00 (s, *p*-C of $P(C_6H_{11})_3$), 22.39 (s, CH_3). ^{31}P NMR (CD_2Cl_2): δ 36.09 (s, PCy_3). Anal. Calcd for $C_{44}H_{74}Cl_2P_2Ru$: C, 63.14; H, 8.91. Found: C, 63.29; H, 8.99.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4F)(PCy_3)_2$ (14). Starting with **7** (672 mg, 0.84 mmol) and tricyclohexylphosphine (515 mg, 1.84 mmol, 2.2 equiv), **14** was obtained in analogy to **10** as a purple microcrystalline solid. Yield = 583 mg (83%). ^{1}H NMR (CD_2Cl_2): δ 19.86 (s, Ru=CH), 8.52−8.50 (s(br), *o*-H of C_6H_4F), 7.00 (dd, $^3J_{HH} = {}^3J_{HF}$ = 8.8 Hz, *m*-H of C_6H_fF), 2.63−2.59, 1.77−1.68, 1.47−1.40, and 1.26−1.17 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 291.52 (t, J_{PC} = 8.6 Hz, Ru=CH), 162.10 (d, J_{CF} = 254.3 Hz, *p*-C of C_6H_4F), 150.57 (s, *ipso*-C of C_6H_4F), 134.10 (d, J_{CF} = 8.9 Hz, *o*-C of C_6H_4F), 116.00 (d, J_{CF} = 21.3 Hz, *m*-C of C_6H_4F), 32.49 (*pseudo*-t, J_{app} = 9.3 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.05 (s, *m*-C of $P(C_6H_{11})_3$), 28.22 (*pseudo*-t, J_{app} = 5.2 Hz, *o*-C of $P(C_6H_{11})_3$), 26.94 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 36.60 (s, PCy_3). ^{19}F NMR (CD_2Cl_2): δ 45.47 (s, C_6H_4F). Anal. Calcd for $C_{43}H_{71}Cl_2FP_2Ru$: C, 61.41; H, 8.51. Found: C, 61.32; H, 8.59.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (15). Starting with **8** (543 mg, 0.66 mmol) and tricyclohexylphosphine (408 mg, 1.45 mmol, 2.2 equiv), **15** was obtained in analogy to **10** as a purple microcrystalline solid. Yield = 493 mg (87%). ^{1}H NMR (CD_2Cl_2): δ 19.98 (s, Ru=CH), 8.43 (d, $^3J_{HH}$ = 8.7 Hz, *o*-H of C_6H_4Cl), 7.29 (d, $^3J_{HH}$ = 8.7 Hz, *m*-H of C_6H_4Cl), 2.63−2.58, 1.76−1.68, 1.46−1.41, and 1.25−1.17 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 291.46 (t, J_{PC} = 8.0 Hz, Ru=CH), 151.81 (s, *ipso*-C of C_6H_4Cl), 134.64 (s, *p*-C of C_6H_4Cl), 132.56 and 129.51 (both s, *o*-C and *m*-C of C_6H_4Cl), 32.51 (*pseudo*-t, J_{app} = 8.9 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.06 (s, *m*-C of $P(C_6H_{11})_3$), 28.22 (*pseudo*-t, J_{app} = 5.2 Hz, *o*-C of $P(C_6H_{11})_3$), 26.95 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 36.81 (s, PCy_3). Anal. Calcd for $C_{43}H_{71}Cl_3P_2Ru$: C, 60.24; H, 8.35. Found: C, 60.22; H, 8.45.

X-ray Diffraction Study of $RuCl_2(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (15). A maroon prism of **15** was obtained by slow diffusion of hexanes into a concentrated solution of **15** in methylene chloride (0.5 mL) within 24 h. A crystal of the size 0.2 × 0.3 × 0.5 mm was selected, oil-mounted [46] on a glass fiber, and transferred to a Siemens P4 diffractometer, which is equipped with a modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard techniques.[47] Low-temperature (158 K) intensity data were collected *via* a $2\theta-\theta$ scan technique with Mo Kα radiation.

All 7782 data were corrected for absorption[48] and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. Refinement of the model proved the centrosymmetric triclinic space group $P\bar{1}$ to be the correct choice.

All crystallographic calculations were carried out using either the UCLA Crystallographic Computing Package[49] or the SHELXTL Plus program set.[50] The analytical scattering factors[51] for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f'$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from a difference-Fourier map and included with isotropic temperature parameters. Refinement of the model led to convergence with R_F = 3.5%, R_{wF} = 3.6%, and GOF = 1.42 for 726 variables refined against those 6411 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ϱ(max) = 0.52 eÅ^{-3}.

$RuCl_2(=CH\text{-}p\text{-}C_6H_4NO_2)(PCy_3)_2$ (16). Starting with **9** (609 mg, 0.73 mmol) and tricyclohexylphosphine (452 mg, 1.61 mmol, 2.2 equiv), **16** was obtained in analogy to **10** as a red-purple microcrystalline solid. Yield = 527 mg (83%). ^{1}H NMR (CD_2Cl_2): δ 20.71 (s, Ru=CH), 8.64 (d, $^3J_{HH}$ = 8.4 Hz, *o*-H of $C_6H_4NO_2$), 8.13 (d, $^3J_{HH}$ = 8.4 Hz, *m*-H of $C_6H_4NO_2$), 2.63−2.58, 1.73−1.68, 1.47−1.40, and 1.26−1.17 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 289.07 (t, J_{PC} = 7.6 Hz, Ru=CH), 155.93 (s, *ipso*-C of $C_6H_4NO_2$), 145.34 (s, *p*-C of $C_6H_4NO_2$), 131.22 and 125.06 (both s, *o*-C and *m*-C of $C_6H_4NO_2$), 32.57 (*pseudo*-t, J_{app} = 9.2 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.05 (s, *m*-C of $P(C_6H_{11})_3$), 28.16 (*pseudo*-t, J_{app} = 4.1 Hz, *o*-C of $P(C_6H_{11})_3$), 26.88 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 38.11 (s, PCy_3). Anal. Calcd for $C_{43}H_{71}Cl_2NO_2P_2Ru$: C, 59.50; H, 8.25; N, 1.61. Found: C, 59.18; H, 8.25; N, 1.49.

ROMP of Cyclooctene and 1,5-Cyclooctadiene with 10−16 as Catalysts. Complexes **10**−**16** (6.0 μmol) were dissolved in CH_2Cl_2 (0.5 mL) and treated with neat cyclooctene or 1,5-cyclooctadiene (3.0 mmol, 500 equiv) at room temperature. Accompanied by a color change from purple to orange, the reaction mixtures turned viscous within 3−5 min. The solutions were stirred at room temperature for 2.5 h and, upon exposure to air, treated with CH_2Cl_2 (5 mL) containing

(46) The crystal was immersed in a lube-oil additive, which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting pin. Further details were described by: Hope, H. In *Experimental Organometallic Chemistry*: *A Practicum in Synthesis and Characterization*; ACS Symp. Ser. No. 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987.

(47) XSCANS Software Users Guide, Version 2.1, Siemens Industrial Automation, Inc., Madison, WI, 1994.

(48) SHELXTL Empirical Absorption Correction program (see ref 49).

(49) (a) UCLA Crystallographic Computing Package, University of California at Los Angeles, 1981. (b) Strouse, C., University of California at Los Angeles, personal communication.

(50) Sheldrick, G. M. Siemens Analytical X-Ray Instruments, Inc.; Madison, WI, 1990.

(51) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

traces of 2,6-di-*tert*-butyl-4-methylphenol and ethyl vinyl ether. After 20 min, the viscous solutions were filtered through short columns of silica gel and precipitated into vigorously stirred methanol. The resulting polymers were isolated, washed several times with methanol, and dried under vacuum. Cycloocteneamer (white tacky polymers): yields = 95−100%, M_n = 111−211 kg/mol, PDI(toluene) = 1.51−1.63. Polybutadiene (white glue-like polymers): yields = 96−99%, 56−68% cis, M_n = 57.9−63.2 kg/mol, PDI(toluene) = 1.56−1.67.

One-Pot Synthesis of $RuCl_2(=CHPh)(PCp_3)_2$ (17). **17** is obtained in analogy to **10** as a purple microcrystalline solid, using $RuCl_2(PPh_3)_3$ (4.00 g, 4.17 mmol), phenyldiazomethane (986 mg, 8.35 mmol, 2.0 equiv), and tricyclopentylphosphine (2.19 g, 9.18 mmol, 2.2 equiv). Due to the better solubility of **17**, only methanol is used for the washings. Yield = 2.83 g (92%). ^{1}H NMR (CD_2Cl_2): δ 20.20 (s, Ru=CH), 8.47 (d, $^3J_{HH}$ = 7.5 Hz, *o*-H of C_6H_5), 7.63 (t, $^3J_{HH}$ = 7.5 Hz, *p*-H of C_6H_5), 7.36 (t, $^3J_{HH}$ = 7.5 Hz, *m*-H of C_6H_5), 2.68−2.62, 1.81−1.77, 1.62−1.52, and 1.49−1.44 (all m, $P(C_5H_9)_3$). ^{13}C NMR (CD_2Cl_2): δ 300.52 (t, J_{PC} = 7.6 Hz, Ru=CH), 153.38 (s, *ipso*-C of C_6H_5), 130.99, 129.80, and 129.53 (all s, C_6H_5), 35.54 (pseudo-t, J_{app} = 11.2 Hz, *ipso*-C of $P(C_5H_9)_3$), 29.99 and 26.39 (both s, $P(C_5H_9)_3$). ^{31}P NMR (CD_2Cl_2): δ 29.96 (s, PCp_3). Anal. Calcd for $C_{37}H_{60}Cl_2P_2Ru$: C, 60.15; H, 8.19. Found: C, 60.39; H, 8.21.

One-Pot Synthesis of $RuCl_2(=CHPh)(P$*i*$Pr_3)_2$ (18). **18** is obtained in analogy to **17** as a purple microcrystalline solid, using $RuCl_2(PPh_3)_3$ (4.00 g, 4.17 mmol), phenyldiazomethane (986 mg, 8.35 mmol, 2.0 equiv), and triisopropylphosphine (1.79 mL, 9.18 mmol, 2.2 equiv). Yield = 2.26 g (93%). ^{1}H NMR (CD_2Cl_2): δ 20.10 (s, Ru=CH), 8.52 (d, $^3J_{HH}$ = 7.6 Hz, *o*-H of C_6H_5), 7.36 (t, $^3J_{HH}$ = 7.6 Hz, *p*-H of C_6H_5), 7.17 (t, $^3J_{HH}$ = 7.6 Hz, *m*-H of C_6H_5), 2.88−2.85 (m, PC*H*CH_3), 1.19 (dvt, *N* = 13.6 Hz, PCHC*H*$_3$). ^{13}C NMR (CD_2Cl_2): δ 296.84 (s(br), Ru=CH), 152.81 (s, *ipso*-C of C_6H_5), 131.37, 129.54, and 129.20 (all s, C_6H_5), 22.99 (vt, $N = {}^2J_{PC} + {}^4J_{PC}$ = 18.9 Hz, P*C*HCH$_3$), 19.71 (s, PCH*C*H$_3$). ^{31}P NMR (CD_2Cl_2): δ 45.63 (s, P*i*Pr$_3$). Anal. Calcd for $C_{25}H_{48}Cl_2P_2Ru$: C, 51.54; H, 8.31. Found: C, 51.69; H, 8.19.

$RuCl_2(=CH_2)(PCy_3)_2$ (19). A solution of **10** (821 mg, 1.00 mmol) in CH_2Cl_2 (15 mL) was stirred under an atmosphere of ethylene for 15 min at room temperature. The solvent was removed under vacuum, and the residue was repeatedly washed with acetone or pentane (5 mL) and dried under vacuum for several hours. A burgundy microcrystalline solid was obtained. Yield = 745 mg (quantitative). ^{1}H NMR (CD_2Cl_2): δ 18.94 (s, Ru=CH_2), 2.50−2.44, 1.81−1.70, 1.49−1.43, and 1.25−1.23 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 294.71 (t, J_{PC} = 7.6 Hz, J_{CH} = 164.0 Hz (gated decoupled), Ru=CH), 31.05 (*pseudo*-t, J_{app} = 9.6 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.58 (s, *m*-C of $P(C_6H_{11})_3$), 28.20 (*pseudo*-t, J_{app} = 5.3 Hz, *o*-C of $P(C_6H_{11})_3$), 26.94 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 43.74 (s, PCy_3). Anal. Calcd for $C_{37}H_{68}Cl_2P_2Ru$: C, 59.50; H, 9.18. Found: C, 59.42; H, 9.29.

$RuCl_2(=CHMe)(PCy_3)_2$ (20). **20** is obtained in analogy to **19** as a red-purple microcrystalline solid, using **10** (763 mg, 0.93 mmol) and propylene (or 2-butene) as starting materials. Yield = 691 mg (98%). ^{1}H NMR (CD_2Cl_2): δ 19.26 (q, $^3J_{HH}$ = 5.1 Hz, Ru=CH), 2.57 (d, $^3J_{HH}$ = 5.1 Hz, CH_3), 2.59−2.53, 1.87−1.79, 1.57−1.50, and 1.28−1.23 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 316.32 (t, J_{PC} = 7.6 Hz, Ru=CH), 49.15 (s, CH_3), 32.37 (*pseudo*-t, J_{app} = 9.4 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.87 (s, *m*-C of $P(C_6H_{11})_3$), 28.22 (*pseudo*-t, J_{app} = 5.0 Hz, *o*-C of $P(C_6H_{11})_3$), 26.94 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 35.54 (s, PCy_3). Anal. Calcd for $C_{38}H_{70}Cl_2P_2Ru$: C, 59.58; H, 9.27. Found: C, 59.91; H, 9.33.

$RuCl_2(=CHEt)(PCy_3)_2$ (21). **21** is obtained in analogy to **19** as a red-purple microcrystalline solid, using **10** (674 mg, 0.82 mmol) and a tenfold excess of 1-butene (or *cis*-3-hexene) as starting materials. Yield = 616 mg (97%). ^{1}H NMR (CD_2Cl_2): δ 19.12 (t, $^3J_{HH}$ = 5.0 Hz, Ru=CH), 2.79 (dq, $^3J_{HH}$ = 5.0, $^3J_{HH'}$ = 7.1 Hz, C*H*$_2$CH$_3$), 2.55−2.49, 1.84−1.81, 1.54−1.47, and 1.26−1.23 (all m, $P(C_6H_{11})_3$), 1.35 (t, $^3J_{HH'}$ = 7.1 Hz, CH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 322.59 (t, J_{PC} = 9.3 Hz, Ru=CH), 53.48 (s, *C*H$_2$CH$_3$), 32.20 (*pseudo*-t, J_{app} = 8.9 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.85 (s, *m*-C of $P(C_6H_{11})_3$), 29.57 (s, CH_2CH_3), 28.22 (*pseudo*-t, J_{app} = 4.6 Hz, *o*-C of $P(C_6H_{11})_3$), 26.88 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 36.39 (s, PCy_3). Anal. Calcd for $C_{39}H_{72}Cl_2P_2Ru$: C, 60.45; H, 9.37. Found: C, 60.56; H, 9.30.

$RuCl_2(=CH$-*n*$-Bu)(PCy_3)_2$ (22). **22** is obtained in analogy to **19** as a red-purple microcrystalline solid, using (354 mg, 0.43 mmol) and 1-hexene (537 μL, 4.30 mmol, 10 equiv) as starting materials. Yield = 328 mg (95%). ^{1}H NMR (CD_2Cl_2): δ 19.24 (t, $^3J_{HH}$ = 5.1 Hz, Ru=CH), 2.74 (dt, $^3J_{HH}$ = 5.1, $^3J_{HH'}$ = 5.2 Hz, CHC*H*$_2$, 2.56−2.47, 1.82−1.78, 1.70−1.68, 1.54−1.43, 1.26−1.22, and 0.95−0.86 (all m, C*H*$_2$C*H*$_2$C*H*$_3$ and $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 321.13 (t, J_{PC} = 7.6 Hz, Ru=CH), 59.85 (s, CH*C*H$_2$), 32.25 (*pseudo*-t, J_{app} = 9.4 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.90 (s, *m*-C of $P(C_6H_{11})_3$), 28.23 (*pseudo*-t, J_{app} = 5.3 Hz, *o*-C of $P(C_6H_{11})_3$), 26.91 (s, *p*-C of $P(C_6H_{11})_3$), 30.53, 22.94, and 14.06 (all s, *C*H$_2$*C*H$_2$*C*H$_3$). ^{31}P NMR (CD_2Cl_2): δ 36.05 (s, PCy_3). Anal. Calcd for $C_{41}H_{76}Cl_2P_2Ru$: C, 61.32; H, 9.54. Found: C, 61.51; H, 9.71.

Reaction of 8 with 3-Methyl-1-butene and 3,3-Dimethyl-1-butene. In an NMR tube, a solution of **10** (5.0 mg, 6.1 μmol) in methylene-d_2 chloride (0.5 mL) was treated with 10 equiv of 3-methyl-1-butene and 3,3-dimethyl-1-butene (61.0 μmol), respectively. Whereas in the latter case no reaction was observed within 12 h, a gradual color-change from red-purple to orange (within 5 min) indicates that **10** undergoes a reaction with 3-methyl-1-butene. Resonances in the ^{1}H NMR at δ 18.96 (d, $^3J_{HH}$ = 7.5 Hz, Ru=C*H*iPr), 2.27 (m, C*H*CH$_3$), and 1.01 (d, $^3J_{HH}$ = 7.2 Hz, CHC*H*$_3$) may be attributed to the formation of $RuCl_2(=CH$-*i*-Pr$)(PCy_3)_2$). However, the intensity of these signals did not increase in the course of the reaction, and after 10 min, the corresponding resonances of **19** became dominant.

Determination of Initiation Rate Constants in Acyclic Metathesis of 1-Hexene with 10−16 as Catalysts. Catalysts **10**−**16** (6.05 μmol) were placed into NMR tubes and dissolved in methylene-d_2 chloride (550 μL). At 0 °C, 1-hexene (22.7 μL, 0.18 mmol, 30 equiv) was added and a ^{1}H NMR routine (at 0 °C) was started taking 60 spectra within 40 min. The initiation rate constants were determined by integration of the H_α resonances of **10**−**16** and **22**. The results are given in Table 5.

$RuCl_2(=CH$-CH$=CH_2)(PCy_3)_2$ (23). 1,3-Butadiene is slowly bubbled into a solution of **10** (703 mg, 0.85 mmol) in CH_2Cl_2 (15 mL) for 20 s at −20 °C. While the solution is allowed to warm to room temperature, within 10 min, a color change from purple to orange-brown is observed. The solvent was removed under vacuum, the residue repeatedly washed with acetone or pentane (5 mL) and dried under vacuum for several hours. A red-purple microcrystalline solid was obtained. Yield = 627 mg (95%). ^{1}H NMR (CD_2Cl_2): δ 19.06 (d, $^3J_{HH}$ = 10.5 Hz, Ru=CH), 8.11 (ddd, $^3J_{HH}$ = 10.5, $^3J_{HH^{cis}}$ = 9.3, $^3J_{HH^{trans}}$ = 16.8 Hz, C*H*=CH$_2$), 6.25 (d, $^3J_{H^{cis}}$ = 9.3, H^{cis} of CH=C*H*$_2$), 6.01 (d, $^3J_{HH^{trans}}$ = 9.3, H^{trans} of CH=C*H*$_2$), 2.59−2.53, 1.83−1.78, 1.52−1.47, and 1.25−1.21 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 296.00 (t, J_{PC} = 7.6 Hz, Ru=CH), 153.61 (s, CH=*C*H$_2$), 115.93 (s, *C*H=CH$_2$), 32.32 (*pseudo*-t, J_{app} = 8.9 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.82 (s, *m*-C of $P(C_6H_{11})_3$), 28.15 (*pseudo*-t, J_{app} = 5.1 Hz, *o*-C of $P(C_6H_{11})_3$), 26.91 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 36.17 (s, PCy_3). Anal. Calcd for $C_{39}H_{70}Cl_2P_2Ru$: C, 60.61; H, 9.13. Found: C, 60.79; H, 9.30.

$RuCl_2(=C=CH_2)(PCy_3)_2$ (24). **24** is obtained in analogy to **23** as a tan microcrystalline solid, using **10** (413 mg, 0.50 mmol) and 1,2-propadiene as starting materials. Yield = 373 mg (98%). ^{1}H NMR (CD_2Cl_2): δ 3.63 (s, Ru=C=CH_2), 2.71−2.64, 2.05−2.01, 1.81−1.53, and 1.32−1.23 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 327.41 (t, J_{PC} = 17.2 Hz, Ru=*C*=CH$_2$), 99.34 (s, Ru=C=*C*H$_2$), 33.30 (*pseudo*-t, J_{app} = 8.9 Hz, *ipso*-C of $P(C_6H_{11})_3$), 30.41 (s, *m*-C of $P(C_6H_{11})_3$), 28.32 (*pseudo*-t, J_{app} = 5.0 Hz, *o*-C of $P(C_6H_{11})_3$), 27.02 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 35.36 (s, PCy_3). Anal. Calcd for $C_{38}H_{68}Cl_2P_2Ru$: C, 60.14; H, 9.03. Found: C, 60.29; H, 8.91.

$RuCl_2(=CHCH_2OAc)(PCy_3)_2$ (25). A solution of **10** (423 mg, 0.51 mmol) in CH_2Cl_2 (10 mL) was treated with allyl acetate (555 μL, 5.10 mmol, 10 equiv) at −20 °C. While the solution is allowed to warm to room temperature within 10 min, a color change from purple to orange-brown is observed. The solvent was removed under vacuum, and the residue was repeatedly washed with ice-cold methanol (5-mL portions) and dried under vacuum for several hours. A purple microcrystalline solid was obtained. Yield = 342 mg (83%). ^{1}H NMR (CD_2Cl_2): δ 18.90 (t, $^3J_{HH}$ = 4.2 Hz, Ru=CH), 4.77 (d, $^3J_{HH}$ = 3.6 Hz, C*H*$_2$OAc), 2.09 (s, C(O)CH$_3$), 2.53−2.47, 1.81.170, 1.59−1.53, and 1.26−1.22 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 305.76 (t, J_{PC} = 7.6 Hz, Ru=C), 170.41 (s, *C*(O)CH$_3$), 83.19 (s, *C*H$_2$OAc), 32.59 (*pseudo*-t, J_{app} = 8.6 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.94 (s, *m*-C of $P(C_6H_{11})_3$), 28.23 (m, *o*-C of $P(C_6H_{11})_3$), 26.91 (s, *p*-C of $P(C_6H_{11})_3$), 20.91 (s, C(O)-

CH_3). ^{31}P NMR (CD_2Cl_2): δ 36.66 (s, PCy_3). Anal. Calcd for $C_{39}H_{72}Cl_2O_2P_2Ru$: C, 58.05; H, 8.99. Found: C, 58.13; H, 9.07.

$RuCl_2(=CHCH_2Cl)(PCy_3)_2$ (26). **26** is obtained in analogy to **25** as a purple microcrystalline solid, using **10** (583 mg, 0.71 mmol) and allyl chloride (577 μL, 7.08 mmol, 10 equiv) as starting materials. Yield = 552 mg (80%). ^{1}H NMR (CD_2Cl_2): δ 18.74 (t, $^3J_{HH}$ = 4.5 Hz, Ru=CH), 4.43 (d, $^3J_{HH}$ = 4.8 Hz, CH_2Cl), 2.55−2.50, 1.81−1.70, 1.59−1.52, and 1.27−1.23 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 303.00 (t, J_{PC} = 7.8 Hz, Ru=C), 63.23 (s, CH_2Cl), 32.05 (*pseudo*-t, J_{app} = 8.8 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.50 (s, *m*-C of $P(C_6H_{11})_3$), 27.81 (*pseudo*-t, J_{app} = 5.2 Hz, *o*-C of $P(C_6H_{11})_3$), 26.56 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 37.36 (s, PCy_3). Anal. Calcd for $C_{38}H_{69}Cl_3P_2Ru$: C, 57.39; H, 8.74. Found: C, 57.55; H, 8.81.

$RuCl_2(=CH(CH_2)_3OH)(PCy_3)_2$ (27). **27** is obtained in analogy to **25** as a purple microcrystalline solid, using **10** (617 mg, 0.82 mmol) and 4-penten-1-ol (823 μL, 8.2 mmol, 10 equiv) as starting materials. Yield = 459 mg (76%). ^{1}H NMR (CD_2Cl_2): δ 19.20 (t, $^3J_{HH}$ = 4.6 Hz, Ru=CH), 5.46 (s(br), OH), 2.82−2.78, 2.06−2.01, and 1.62−1.58 (all m, $CH_2CH_2CH_2OH$), 2.55−2.51, 1.84−1.81, 1.55−1.52, and 1.26−1.23 (all m, $P(C_6H_{11})_3$). ^{13}C NMR (CD_2Cl_2): δ 305.66 (t, J_{PC} = 7.3 Hz, Ru=C), 62.66 (s, CH_2OH), 33.01 and 30.08 (both s, CH_2CH_2), 32.32 (*pseudo*-t, J_{app} = 8.5 Hz, *ipso*-C of $P(C_6H_{11})_3$), 29.94 (s, *m*-C of $P(C_6H_{11})_3$), 28.28 (*pseudo*-t, J_{app} = 5.3 Hz, *o*-C of $P(C_6H_{11})_3$), 26.91 (s, *p*-C of $P(C_6H_{11})_3$). ^{31}P NMR (CD_2Cl_2): δ 37.06 (s, PCy_3). Anal. Calcd for $C_{40}H_{74}Cl_2P_2ORu$: C, 59.69; H, 9.27. Found: C, 59.51; H, 9.09.

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Supporting Information Available: Tables of crystallographic experimental details, atomic coordinates, interatomic distances and angles, anisotropic displacement coefficients, and H atom coordinate and isotropic displacement coefficients, and structures showing atom numbering (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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