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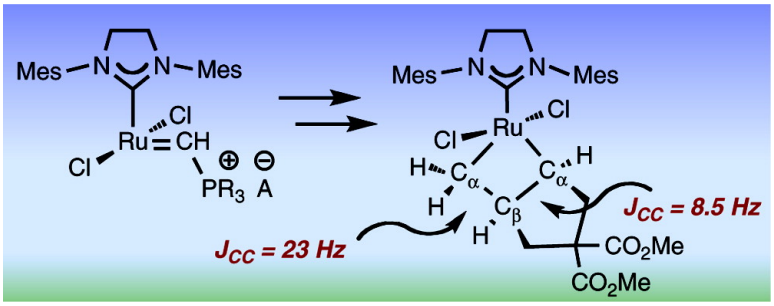

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Generation and Spectroscopic Characterization of Ruthenacyclobutane and Ruthenium Olefin Carbene Intermediates Relevant to Ring Closing Metathesis Catalysis

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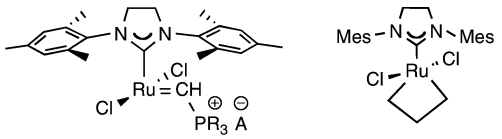
Abstract: The reaction of phosphonium alkylidenes $[(H_2IMes)RuCl_2{=}CHPR_3]^+[A]^-$ (R = C_6H_{11}, A = OTf or $B(C_6F_5)_4$, **1-Cy**; R = *i*-C_3H_7, A = $ClB(C_6F_5)_3$ or OTf, **1-^{i}Pr**) with 1 equiv of ethylene at −78 °C, in the presence of 2−3 equiv of a trapping olefin substrate, yields intermediates relevant to olefin metathesis catalytic cycles. Dimethyl cyclopent-3-ene-1,1-dicarboxylate gives solutions of a substituted ruthenacyclobutane **3** of relevance to ring closing metathesis catalysis. ^{1}H and ^{13}C NMR data are fully consistent with its assignment as a ruthenacyclobutane, but $^1J_{CC}$ values of 23 Hz for the $C_\alpha H_2-C_\beta$ bond and 8.5 Hz for the $C_\alpha H-C_\beta$ bond point to an unsymmetrical structure in which the latter bond is more activated than the former. In contrast, trapping with acenaphthylene leads to an olefin carbene complex (**6**) in which the putative ruthenacyclobutane has opened; this species was also fully characterized by NMR spectroscopy and compared to related species reported previously.

Introduction

Olefin metathesis as catalyzed by ruthenium-based mediators developed by Grubbs[1] and others[2] is one of today's most versatile chemical reactions, with applications in diverse areas of chemistry.[3] Although there is a relatively sophisticated understanding of the mechanism by which these catalysts operate,[4] details concerning the actual structures of key intermediates in the catalytic cycle are still emerging. It is important to determine these details accurately as they inform further catalyst designs aimed at providing more active, longer lived and more selective catalysts.

Of particular interest are the structures of unsaturated olefin−carbene[5,6] and ruthenacyclobutane[7] intermediates. Until recently, direct observation of these species has been hampered by the fact that they are generated in the presence of excess PR_3, produced in the initiation step of the process.[4] Use of weaker, more labile donors such as pyridine[8] has allowed for characterization of olefin−carbene complexes,[5] but an alternative option for circumvention of this issue was provided by the discovery of a related family of catalysts, **1**,[9] in which a 14 electron phosphonium alkylidene serves as the catalyst precursor to metathesis. One metathesis event provides access to the unsaturated intermediates relevant to the Grubbs catalyst systems, and the phosphine is effectively sequestered in the vinylphosphonium byproduct, allowing for direct observation of, for example, the parent ruthenacyclobutane (**2**) intermediate via stoichiometric reactions of **1** with ethylene.



1-Cy: R = C_6H_{11}, A = OTf, $B(C_6F_5)_4$
1-^{i}Pr: R = *iso*-C_3H_7, A = OTf, $ClB(C_6F_5)_3$

2

While this breakthrough provided important insights into the structure of this family of intermediates, it is desirable to obtain structural and spectroscopic data on substituted ruthenacyclobutanes[7c] of more direct relevance to productive metathesis reactions. To this end, we have studied the reactions of catalysts **1** with olefins germane to the ring closing metathesis (RCM) reaction,[10] with a view toward generating and characterizing more complex metathesis intermediates. The efficient generation of substituted

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(2) (a) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791. (b) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 794. (c) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038. (d) Conrad, J. C.; Parnas, H. H.; Snelgrove, J. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2005**, *127*, 11882. (e) Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Arlt, D.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13652.
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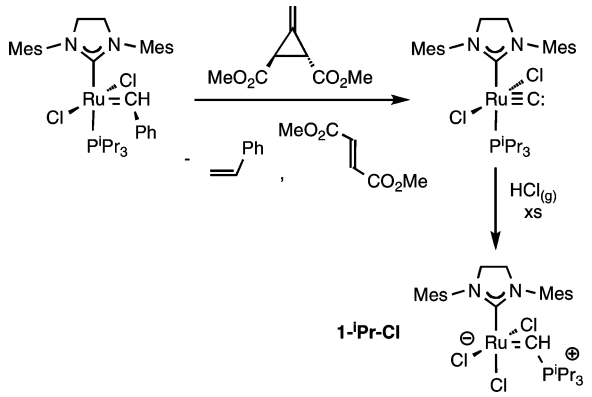
Scheme 1



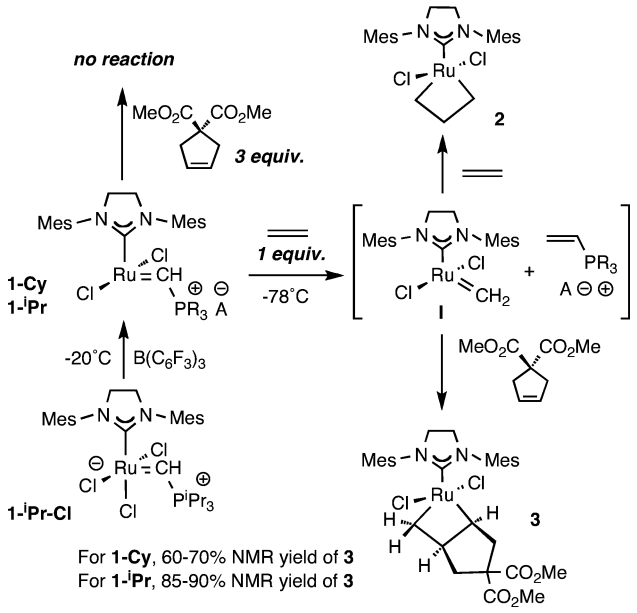
ruthenacyclobutanes of direct relevance to RCM required the introduction of an even more rapidly initiating species than our previously reported tricyclohexylphosphonium alkylidene **1-Cy**. Such a compound was found in the tri-*iso*-propyl-substituted derivative **1-^{i}Pr**.

Results

Complex **1-^{i}Pr** was prepared by the same sequence of reactions as employed for **1-Cy**, starting from the P^{i}Pr$_3$-substituted analogue of the Grubbs generation 2 catalyst (Scheme 1). Conversion to the carbide complex (H$_2$IMes)(Cl)$_2$(P^{i}Pr$_3$)Ru≡C was accomplished smoothly using Heppert's methodology.[11] Protonation of the carbide using gaseous HCl in CH_2Cl_2 triggered formation of the phosphonium alkylidene **1-^{i}Pr−Cl** in which the chloride counteranion coordinates to the Ru center to form the zwitterionic trichloride, analogous to the tricyclohexylphosphonium alkylidene recently reported by Johnson et al.[12] These five-coordinate complexes are characterized by a somewhat larger $^2J_{HP}$ coupling constant for the alkylidene proton (51 Hz for **1-^{i}Pr−Cl**) than is typically observed in the four-coordinate complexes (35−37 Hz).[9] Complex **1-^{i}Pr−Cl** was also characterized by X-ray crystallography; full details are given in the Supporting Information. The Ru−Cl distance for the chloride trans to the NHC ligand (C_{NHC}−Ru−Cl_{trans} = 165.04(9)°) is 2.4619(9) Å, more than 0.1 Å longer than the distances of ∼2.33 Å observed for the chlorides cis to the NHC donor. Zwitterion **1-^{i}Pr−Cl** is more thermally stable than the 14 electron analogues where the anion is weakly coordinating and is conveniently stored in this form prior to activation with, for example, B(C$_6$F$_5$)$_3$[13] (see below).

Compounds **1** rapidly catalyze the RCM of diethyl diallylmalonate at temperatures above 0 °C.[9b] At −60 °C, the catalytic reaction is slowed, but phosphonium alkylidene **1-Cy** reacts slowly with an excess of the diolefin substrate to produce a mixture of products, including [H$_2$C=CHPCy$_3$]$^+$[A]$^-$ (characterized by ^{31}P NMR spectroscopy[9]) the parent, unsubstituted metallacyclobutane, **2**, and a new complex assigned as the ruthenacyclobutane necessarily involved in this RCM reaction, **3** (Et instead of Me). However, even under these conditions, the RCM reaction turns over, producing ethylene and cyclopentene product, and the proportion of **2** rises until, after ∼10 h, it is the dominant ruthenium-containing product in the system; **3** never comprises more than 55−60% of the solution. This observation suggests that the parent, unsubstituted ruthenacyclobutane, is more thermodynamically stable than substituted derivatives and that the presence of free ethylene is detrimental to the generation and stabilization of such compounds.

Scheme 2



To minimize the amount of free ethylene in the system, we developed a route to **3** that begins from the *product* of RCM (dimethyl cyclopent-3-ene-1,1-dicarboxylate); here we use the dimethyl ester to simplify ^{1}H NMR spectra. The chemistry is summarized in Scheme 2. The success of the experiment relies on the fact that, at −78 °C, the RCM product exhibits low reactivity with compounds **1**; for R = Cy, there is no reaction at room temperature, while for R = ^{i}Pr, there is a slow reaction to yield as yet uncharacterized products which effectively stops at low temperatures. Therefore, it is possible to mix the RCM product cyclopentene with **1-Cy** or **1-^{i}Pr** (generated from **1-^{i}Pr−Cl** and B(C$_6$F$_5$)$_3$) prior to the introduction of 1 equiv of ethylene. The ethylene reacts with compounds **1** to form the vinyl trialkylphosphonium salt and, presumably, the 14 electron ruthenium methylidene, **I**, which is not observed.[14] Intermediate **I** is then rapidly trapped by either ethylene to give **2** or cyclopentene to yield **3**. For **1-Cy**, formation of the two products is competitive, despite the excess of the RCM product, suggesting that the rate of the initial reaction of ethylene with **1-Cy** is comparable to the conversion of **I** to **2/3**. **1-^{i}Pr** reacts with ethylene at qualitatively much faster rates than **1-Cy**, probably because of the less sterically bulky phosphonium alkylidene;[15] therefore, use of this faster initiator in this experiment results in a 90% NMR yield of **3**, the remaining 10% comprising mainly

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(14) (a) We failed to detect a phosphonium-substituted ruthenacyclobutane intermediate. Given that the vinyl trialkylphosphonium salts appear to be inert as metathesis substrates, it seems likely that dissociation of this olefin from the putative ruthenacyclobutane to give **I** is facile. Consistent with this is the observation of small amounts of what we currently assign to be a dimer of **I** and **1-^{i}Pr** in addition to **2** in the reaction using **1-^{i}Pr** in Scheme 2. This assignment is based on observations concerning chemical decomposition pathways for compounds **1**[14b] and the observation of minor alkylidene proton resonances in the ^{1}H NMR spectra of **3**. (b) Leitao, E. M.; Piers, W. E. Unpublished results.

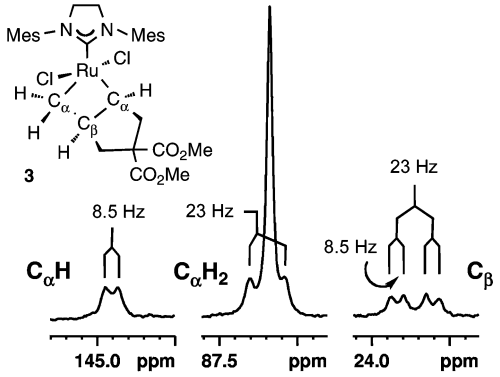


Figure 1. $^{13}C\{^1H\}$ NMR resonances for $C_\alpha H$, $C_\alpha H_2$, and C_β of **3**-$^{13}C_3$ (25%); the singlet at 87.2 ppm is **3**-$^{13}C_1$ since $C_\alpha H_2$ is 99% ^{13}C labeled and C_β is only 25% enriched.

2 plus small amounts of what we assign to be a dimer of **I** and **1**-^{i}**Pr**[14] (vide infra).

The development of this protocol for the generation of highly enriched solutions of **3** has allowed us to comprehensively characterize this species at −60 °C by NMR spectroscopy. Metallaring ^1H NMR signals for **3** were observed at 9.36 ($C_\alpha H$), 6.07, 5.90 (diastereotopic $C_\alpha H_2$), and −2.15 ($C_\beta H$) ppm and are indicative of a ruthenacyclobutane structure (cf. 6.64, $C_\alpha H$, and −2.64, $C_\beta H$, ppm for **2**).[7a,b] An HMQC experiment located the corresponding ^{13}C signals of $C_\alpha H$, $C_\alpha H_2$, and $C_\beta H$ at 144.8, 87.2, and 23.7 ppm, respectively (cf. 94.0 and 2.1 ppm for **2**).[7a,b] This experiment also confirmed that the 6.07 and 5.90 ppm resonances are due to the $C_\alpha H_2$ group since both show a cross-peak to the same carbon at 87.2 ppm.

Although most of the key chemical shifts of **3** are similar to those of **2**, both H_α and C_α of the methine carbon in **3** are shifted significantly downfield in the ^1H and ^{13}C NMR spectra (by 2.72 and 50.8 ppm, respectively) in comparison to **2**. Some downfield shifting is expected upon substitution;[16] for example, in the α-methyl-substituted ruthenacyclobutane derived from **1-Cy** and propene, the $C_\alpha H$ resonances appear at 7.76 ppm (proton) and 120.2 ppm (carbon).[7c] Nevertheless, the magnitude of the perturbations for $C_\alpha H$ in ruthenacyclobutane **3** suggests that they arise from more than simply substitution and that the $C_\alpha H-C_\beta H$ bond is more activated than the $C_\alpha H_2-C_\beta H$ bond, rendering $C_\alpha H$ more carbene-like.

This notion is supported by the observed one bond $^{13}C-^{13}C$ coupling constants in **3**, which were determined by preparing $^{13}C_3$-**3**, labeled selectively in the three metallaring carbons (Figure 1). This sample was generated according to Scheme 2, using ethylene-1,2-$^{13}C_2$ (99%) and dimethyl cyclopent-3-ene-1,1-dicarboxylate-3,4-$^{13}C_2$ (25% ^{13}C enriched in the 3,4 positions; see Supporting Information for the synthesis from acetylene-1,2-$^{13}C_2$).

Most informative is the C_β resonance at 23.7 ppm, which appears as a doublet of doublets, with $^1J_{CC}$ values of 8.5 and 23 Hz (cf. 15 Hz for **2**).[7b] Both coupling constants are reproduced in the $C_\alpha H$ and $C_\alpha H_2$ doublets,[17] and the 8.5 Hz coupling can thus be assigned to the most substituted $C_\alpha C_\beta$ bond. The analogous values for the all-carbon bicyclo[3.2.0]heptane have been calculated by Krivdin[18] to be 31 and 27 Hz (the latter value is for the more substituted CC bond), so the 8.5 Hz coupling is very small in comparison to the all-carbon bicyclic ring system; indeed, this is a very low coupling for any C−C single bond.[19] Interestingly, the average of these two coupling constants is close to the 15 Hz value observed in the symmetrically activated parent ruthenacyclobutane complex **2**. $^1J_{CH}$ values were also extracted from this labeling experiment: 167 Hz for $C_\alpha H$, 163 Hz for the $C_\alpha H_2$ CH bonds, and 157 Hz for $C_\beta H$ (cf. 165 Hz for $C_\alpha H_2$ and 155 Hz for $C_\beta H_2$ in **2**). These coupling constants are quite large compared to those observed in, for example, cyclobutane (134 Hz)[20] but comparable to those observed in parent complex **2** (155−164 Hz). The large magnitude of these coupling constants is likely a consequence of the kite-shaped geometry of the ruthenacyclobutane arising from the C−C→Ru agostic[21] interactions present in these systems. In any case, given their similarity to the $^1J_{CH}$ couplings observed in ruthenium carbene olefin complexes,[5,6] C−H coupling constants do not appear to be a useful metric for distinguishing these two limiting structures.

The skewed C_β to C_α coupling constants in **3** imply a stronger activation of the $C_\alpha H-C_\beta$ bond than the less substituted $C_\alpha H_2-C_\beta$ bond.[22] It suggests that electronic effects are more important than steric factors in dictating the strength of the C−C agostic interactions within ruthenacyclobutanes prone to metathesis activity. Consistent with these data, we have been unable to detect dynamic exchange on the NMR time scale between $C_\alpha H$ and C_β as might be expected on the basis of the observed behavior of **2**, where $C_\alpha H_2$ and $C_\beta H_2$ exchange rapidly on the NMR time scale.[7a,c] Furthermore, the diastereotopic $C_\alpha H_2$ protons in **3** also do not undergo exchange under these conditions. If **3** was predisposed to cleave via path ***b*** in Scheme 3, these two exchange processes would be expected to be rapid and observable; the lack of exchange on the NMR time scale suggests that cleavage via path ***a*** is favored over ***b***. In support of this notion, reaction of **3** with 2 equiv of PMe_3 at low temperature results in rapid formation of the Grubbs-type ruthenium carbene complex **4**[23] (Scheme 3) in essentially quantitative NMR yield (98% against an internal standard);[24] no trace of the PMe_3-stabilized methylidene complex expected via trapping of the cleavage product arising from path ***b*** was detected. A characteristic resonance at 17.74 ppm for the H_α proton exhibits a $^3J_{HP}$ of 3.5 Hz, suggesting alignment of the

(15) The factors influencing the rate of initiation in compounds **1** are poorly understood, but the steric bulk of the PR_3 moiety appears to strongly affect the rate of reaction of the phosphonium alkylidenes with olefins. Preliminary calculations suggest that the barrier to rotation of the phosphonium alkylidene about the Ru=C double bond is quite sensitive to the bulk of the PR_3 unit.

(16) (a) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (b) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.

(17) The $^2J_{CC}$ between the α carbons is unresolved in these spectra.

(18) Krivdin, L. B. *Magn. Reson. Chem.* **2003**, *41*, 885.

(19) (a) Wray, V.; Hansen, P. E. (Webb, C. A., Ed.) *Ann. Rep. NMR Spectrosc.* **1981**, *32*, 789. (b) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177. (c) Even in cyclopropane, where the C−C bonds have high p-character, the coupling constant is 12.4 Hz: Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopic Methods in Organic Chemistry*; Georg Thieme Verlag: New York, 1997.

(20) (a) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175. (b) Kalinowski, H.O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: Chichester, U.K., 1988.

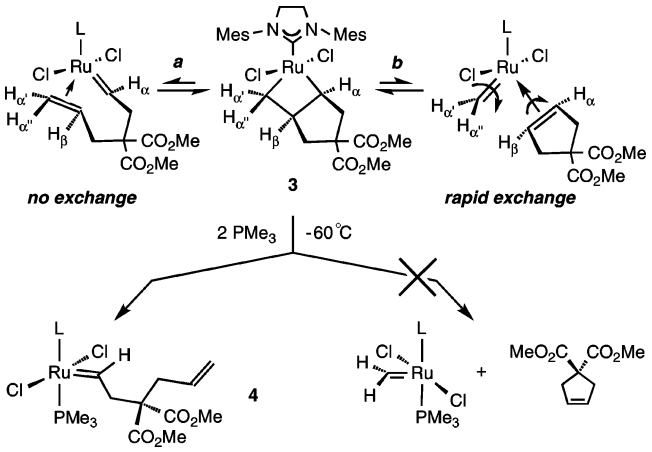
(21) Harvey, B. G.; Mayne, C. L.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 16426.

(22) Some computational studies support this finding: (a) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496. (b) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965.

(23) For related PMe_3 derivatives of Grubbs catalysts, see: Bolton, S. L.; Williams, J. E.; Sponsler, M. B. *Organometallics* **2007**, *26*, 2485.

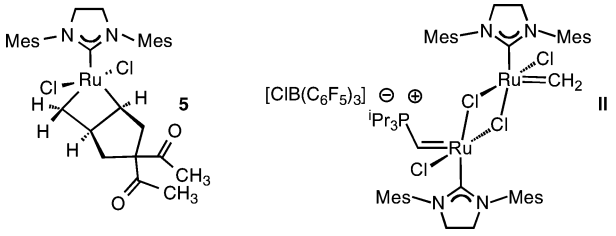
(24) Related species have recently been detected but not thoroughly characterized: P'Pool, S. J.; Schanz, H.-J. *J. Am. Chem. Soc.* **2007**, *129*, 14200.

Scheme 3



carbene ligand[25] with the L−Ru−PMe_3 vector as opposed to the Cl−Ru−Cl vector as is common in Grubbs-type catalysts. Observed C_s symmetry in the ^{1}H NMR spectrum of **4** down to −60 °C supports this assignment, which is likely due to the smaller size of PMe_3 relative to PCy_3. In any case, the ^{13}C and ^{1}H resonances for the terminal vinyl group indicate it is dangling with no interaction with the Ru center.

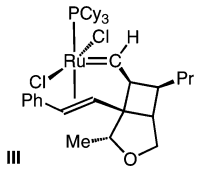
We have also used the methodology in Scheme 2 to trap "$LCl_2Ru{=}CH_2$" (**I**) with other olefins. The generation of another ruthenacyclobutane related to **3** proceeds smoothly with a related cyclopentene featuring 1,1-disubstitution. For example, compound **5** was formed from **1-^{i}Pr** and cyclopent-3-ene-1,1-diacetyl.



When less reactive olefins,[26] such as cyclohexene, *tert*-butyl ethylene, and 1,1-difluoroethylene, were employed as trapping olefins, ruthenacyclobutane products were not observed; here, only **2** and the dimer formed via trapping of **I** by **1-^{i}Pr**[14] were formed. Although dimer **II** has not been comprehensively characterized, the NMR data obtained are consistent with this formulation (see Experimental Section); further studies on these types of dimers are ongoing.[27] Trapping of **I** by ethylene or **1-^{i}Pr** is thus more rapid than its trapping with less reactive olefin substrates. At the other end of the olefin reactivity spectrum, cyclooctene and norbornene undergo facile ROMP reaction with **1-Cy** and **1-^{i}Pr**, even at low temperatures and cannot be used as trapping olefins in this protocol.

Still other olefin substrates give well-defined olefin carbene complexes[5,6] when employed as in Scheme 2. For example, when **1-Cy** is treated with 1 equiv of ethylene in the presence of acenaphthylene, a product, **6**, is generated in >90% NMR yield with ^{1}H and ^{13}C NMR data consistent with an olefin−carbene formulation as opposed to a ruthenacyclobutane (Scheme 4). Specifically, a sharp singlet at 18.13 ppm in the ^{1}H NMR spectrum, accompanied by a resonance at 317.3 ppm in the ^{13}C{^{1}H} NMR trace, is diagnostic for a ruthenium alkylidene moiety. Also identifiable are the resonances for a coordinated vinyl group, the data assigned by 2D correlation spectroscopy (COSY, HMQC) as shown in the Scheme. Unfortunately, although extensive NMR data on **6** were collected, it is not stable above temperatures of −20 °C and could not be isolated for solid state structural characterization.

While the acenaphthylene has clearly undergone ring opening,[28] the data do not allow for assignment of the precise geometry of **6**. On the basis of literature precedent,[5,6] the possible isomers are shown in the scheme: two diastereomeric side-bound isomers related by the face of the vinylic olefin group presented to the ruthenium center (*cis*-chlorides), and a bottom-bound isomer in which the chlorides remain trans disposed (here coordination of the opposite face gives this isomer's enantiomer). In the reaction of Grubbs' generation 2 catalyst with divinyl benzene, an exchanging mixture of side-bound, *cis*-chloride diastereomers was observed in solution, and one was characterized by X-ray crystallography[5] (analogous to the top side-bound isomer depicted in Scheme 4). Conversely, Snapper apprehended a bottom-bound olefin carbene complex **III** by reacting Grubbs generation 1 catalyst with a strained tricyclic cyclobutene substrate.[6]



Thus, precedent exists for both types of isomers. In **6**, we observe only one isomer in solution at all temperatures, with no temperature dependence of the ^{1}H NMR spectrum in ranges where **6** is stable. A comparison of ^{1}H and ^{13}C NMR data for **6** and the Grubbs side-bound isomers shows that the alkylidene proton and carbon resonances for **6** (18.13 and 317.3 ppm) are downfield of those observed in the side-bound species, which resonate at 16.34 and 16.17 and 300.3 and 296.9 ppm, respectively.[5] We observe no NOE correlations between the vinyl protons in **6** and the mesityl methyl or aryl protons of the NHC ligand, as might be expected in a side-bound structure. While these observations circumstantially implicate a bottom-bound structure for **6**, in the absence of more definitive data, we are unable to assign its geometry with a high degree of certainty; nonetheless, it represents another example of the family of olefin carbene intermediates relevant to these catalyst systems.

Conclusions

In summary, we have developed a route from phosphonium alkylidenes **1** to the 14 electron ruthenium carbene complex **I**

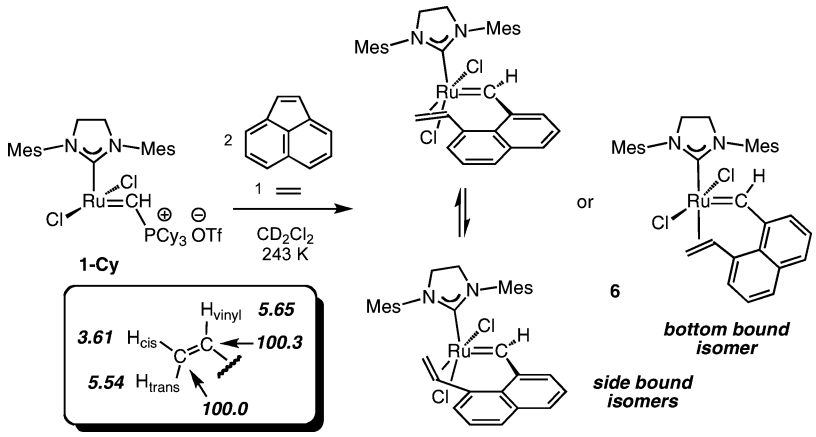
(25) A Karplus-type relationship between the P−Ru−C−H dihedral and $^3J_{PH}$ in Grubbs-type ruthenium carbenes has been noted: (a) Lehman, S. E., Jr.; Wagener, K. B. *Organometallics* **2005**, *24*, 1477. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (c) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511.

(26) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.

(27) Deactivation of ruthenium-based olefin metathesis catalysts via dimerization has been previously observed: (a) Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 3335. (b) Drouin, S. D.; Monfette, S.; Amoroso, D.; Yap, G. P. A., Fogg, D. E. *Organometallics* **2005**, *24*, 4721.

(28) Note that only 1 equiv of the acenaphthylene substrate opens; we do not observe ROMP of this substrate under any conditions explored.

Scheme 4



involving stoichiometric reaction with ethylene. Intermediate **I** is extremely reactive and may be trapped by various olefins to generate stable ruthenacyclobutanes or ruthenium olefin carbene complexes germane to ring opening and/or ring closing metathesis reactions as catalyzed by Grubbs generation 2 catalyst platforms. Examples of both types of intermediates were characterized in detail using low-temperature NMR spectroscopy. The data for ruthenacyclobutane **3** suggest that the C−C bonds of the ring are differentially activated by the ruthenium center, with the more substituted C−C bond being the most weakened in the ground state structure of the compound. This is the opposite to what one would expect for an intermediate crucial in the ring closing metathesis of such substrates, but the influence of external olefin on such a product-forming reaction remains to be studied.

Experimental Section

General procedures and synthetic details concerning the preparation of labeled substrates and starting materials are given in the Supporting Information.

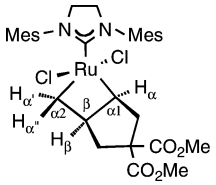
Synthesis of $(H_2IMes)(Cl)_2(P^iPr_3)Ru{\equiv}C$. $(H_2IMes)(Cl)_2(P^iPr_3)Ru{=}CHPh$ (0.740 g, 1.02 mmol) and Feist's dimethyl ester (0.184 g, 1.08 mmol) were placed in a 50 mL flask. Dichloromethane (20 mL) was condensed onto the solids at −78 °C, after which the mixture was warmed to room temperature and stirred for 18 h. During this time, the color went from dark red to light orange/brown. The volatiles were removed under reduced pressure, and the dimethyl fumarate byproduct was sublimed away in vacuo at ca. 50 °C. The residue was washed three times with 20 mL of pentane. The product was purified by passing it through a plug of silica (eluent 50:50 EtOAc/hexanes, material loaded in CH_2Cl_2), from which it elutes as a yellow band. The volatiles were removed in vacuo, and the solid was washed with two 20 mL portions of pentane, after which it was dried in vacuo and isolated: yield 0.540 g (0.830 mmol, 81.7%); ^{1}H NMR (CD_2Cl_2, 300.1 MHz, 300 K) δ 6.98 (s, 2H, Mes C*H*), 6.83 (s, 2H, Mes C*H*), 4.21−4.03 (m, 4H, CH_2CH_2), 2.58 (d septet, $^2J_{HP}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, 3H, ^{i}Pr C*H*), 2.48 (12 H, overlapping inequivalent Mes *ortho* CH_3), 2.29 (s, 3H, Mes *para* CH_3), 2.23 (s, 3H, Mes *para* CH_3), 1.06 (dd, $^3J_{HP}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, 18H, ^{i}Pr CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 300 K) δ 479.6 (s, Ru≡*C*), 212.6 (d, $^2J_{CP}$ = 83 Hz, Ru−*C*(N)$_2$), 139.1, 139.0, 138.7, 138.0, 135.3 (all s, Mes quaternary C, 2 of them overlapped), 129.7, 129.6 (both s, Mes *C*H), 52.4 (br d, $^4J_{CP}$ ∼ 2 Hz, *C*H_2CH_2), 51.6 (br, CH$_2$*C*H$_2$), 22.1 (d, $^2J_{CP}$ = 20 Hz, ^{i}Pr *C*H), 21.4 (s, *para* CH_3), 21.2 (s, *para* CH_3), 20.3 (s, *ortho* CH_3), 19.4 (s, ^{i}Pr *C*H_3), 18.9 (s, *ortho* CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz, 300 K) δ 44.8 (s). Anal. Calcd for $C_{31}H_{47}Cl_2N_2PRu$: C, 57.22; H, 7.28; N, 4.31. Found: C, 57.21; H, 7.17; N, 4.09.

Synthesis of $(H_2IMes)(Cl)_3Ru{=}CHP^iPr_3{\cdot}CH_2Cl_2$, 1-^{i}Pr−Cl. ($H_2$-IMes)(Cl)$_2$($P^iPr_3$)Ru≡C (0.300 g, 0.461 mmol) was put in a 50 mL flask. Dichloromethane (20 mL) was condensed onto the pale yellow solid at −78 °C. To dissolve all of the carbide, the flask was warmed to room temperature, after which it was cooled to −78 °C again, giving a light yellow solution. About 150 mL (∼10−15 equiv) of anhydrous HCl gas was introduced into the flask at −78 °C through the vacuum line. This resulted in a red/brown solution, which turned a greenish yellow color when the reaction mixture was allowed to warm to room temperature. After 3 h of stirring, all the volatiles were removed in vacuo, leaving a green waxy residue. Sonication in pentane yielded a green powder, which was recrystallized by dissolving it in CH_2Cl_2 and carefully layering it with two volumes of pentane, affording large greenish brown/orange prisms (suitable for X-ray diffraction) of the title compound: yield 0.288 g (0.373 mmol, 80.9%); ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 295 K) δ 19.71 (d, $^2J_{HP}$ = 51 Hz, 1H, Ru=C*H*), 7.01 (s, 4H, Mes C*H*), 3.99 (br, 4H, CH_2CH_2), 3.21 (d septet, $^2J_{HP}$ = 15 Hz, $^3J_{HH}$ = 7 Hz, 3H, ^{i}Pr C*H*), 2.47 (br, 12H, *ortho* CH_3), 2.34 (s, 6H, *para* CH_3), 1.19 (dd, $^3J_{HP}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 18H, ^{i}Pr CH_3); ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 227 K) δ 19.62 (d, $^2J_{HP}$ = 50 Hz, 1H, Ru=C*H*), 7.03 (s, 2H, Mes C*H*), 6.97 (s, 2H, Mes C*H*), 4.04−3.83 (m, 4H, CH_2CH_2), 3.11 (m, 3H, ^{i}Pr C*H*), 2.51 (s, 6H, *ortho* CH_3), 2.33 (s, 3H, *para* CH_3), 2.30 (s, 6H, *ortho* CH_3), 2.29 (s, 3H, *para* CH_3), 1.13 (dd, $^3J_{HP}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 18H, ^{i}Pr CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 227 K) δ 274.4 (br, Ru=*C*H), 201.7 (d, $^3J_{CP}$ ∼ 2−3 Hz, Ru-*C*(N)$_2$), 138.95, 138.87, 138.3, 137.3, 137.2, 134.6 (all s, Mes quaternary C), 129.7, 129.1 (both s, Mes *C*H), 51.9 (s, *C*H_2CH$_2$), 51.4 (s, CH$_2$*C*H$_2$), 24.3 (d, $^1J_{CP}$ = 37 Hz, ^{i}Pr *C*H), 21.1 (s, Mes *para* *C*H_3), 20.9 (s, Mes *para* *C*H_3), 20.2 (s, Mes *ortho* *C*H_3), 18.2 (s, Mes *ortho* *C*H_3), 17.6 (d, $^2J_{CP}$ = 3 Hz, ^{i}Pr *C*H_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.8 MHz, 295 K) δ 42.3 (s), (227 K) δ 40.0 (s). Anal. Calcd for $C_{32}H_{50}Cl_5N_2PRu$: C, 49.78; H, 6.53; N, 3.63. Found: C, 49.75; H, 6.29; N, 3.54.

Generation of $[(H_2IMes)(Cl)_2Ru{=}CHP^iPr_3]^+[ClB(C_6F_5)_3]^-$, 1-^{i}Pr. $(H_2IMes)(Cl)_3Ru{=}CHP^iPr_3{\cdot}CH_2Cl_2$ (21 mg, 27 μmol) was dissolved in 0.6 mL of CD_2Cl_2, cooled to −35 °C in the glove box freezer, and added to a cooled vial containing $B(C_6F_5)_3$ (17 mg, 33 μmol). Upon reaction, the color changed from green/brown to light orange/brown. The title compound is only present as the monomer, independent of temperature: ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 285 K) δ 17.77 (d, $^2J_{HP}$ = 35 Hz, 1H, Ru=C*H*), 7.09 (s, 4H, Mes C*H*), 4.23 (s, 4H, CH_2CH_2), 2.61 (d septet, $^2J_{HP}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, 3H, ^{i}Pr C*H*), 2.36 (ps s, 18H, *ortho* and *para* CH_3), 0.99 (dd, $^3J_{HP}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 18H, ^{i}Pr CH_3); ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 213 K) δ 17.72 (d, $^2J_{HP}$ = 35 Hz, 1H, Ru=C*H*), 7.12 (br s, 2H, Mes C*H*), 7.00 (br s, 2H, Mes C*H*), 4.20 (app s, 4H, CH_2CH_2), 2.56 (d septet, $^2J_{HP}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, 3H, ^{i}Pr C*H*), 2.39 (br, 6H, Mes *ortho* CH_3), 2.32 (app s, 6H, overlapping inequivalent Mes *para* CH_3), 2.22 (br, 6H, Mes *ortho* CH_3), 0.91 (dd,

$^3J_{HP}$ = 17 Hz, $^3J_{HH}$ = 7 Hz, 18H, ^{i}Pr CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 285 K) δ 260.1 (br, Ru=*C*H), 187.4 (d, $^3J_{CP}$ = 2 Hz, Ru-*C*(N)$_2$), 141.1, 138.6 (both s, Mes quaternary C), 134.7 (br, Mes quaternary C), 130.7 (s, Mes *C*H), 53.1 (s, *C*H$_2$*C*H$_2$), 21.3 (s, Mes *para* *C*H$_3$), 21.2 (d, $^1J_{CP}$ = 39 Hz, ^{i}Pr *C*H), 19.2 (br, Mes *ortho* *C*H$_3$), 17.7 (d, $^2J_{CP}$ = 3 Hz, ^{i}Pr *C*H$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 213 K) δ 262.3 (br, Ru=*C*H), 186.4 (d, $^3J_{CP}$ = 2 Hz, Ru-*C*(N)$_2$), 139.1, 137.1, 136.1, 132.0 (all br, Mes quaternary C), 130.6 (br, Mes *C*H), 129.4 (br, Mes *C*H), 52.6 (br, *C*H$_2$CH$_2$), 52.2 (br, CH$_2$*C*H$_2$), 21.0 (br, Mes *C*H$_3$), 20.2 (d, $^1J_{CP}$ = 39 Hz, ^{i}Pr *C*H), 19.9 (br, Mes *C*H$_3$), 17.7 (br, Mes *C*H$_3$), 17.2 (d, $^2J_{CP}$ = 2 Hz, ^{i}Pr *C*H$_3$). Note: due to H$_2$IMes fluxional behavior at 213 K, many resonances are broadened and not all Mes quaternary carbons could be located. In addition, some of the Mes quaternary carbons may overlap with the anion resonances. However, most diagnostics in the ^{13}C spectra at both temperatures are the H$_2$IMes carbene resonance at ~187 ppm. In these complexes, this indicates a four-coordinate ruthenium complex with an empty coordination site opposite the H$_2$IMes ligand. ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.8 MHz, 285 K): δ 61.0 (s).

Generation of 3 from 1-Cy. In a typical experiment, [(H$_2$IMes)(Cl)$_2$Ru=CHPCy$_3$]OTf (14 mg, 15 μmol) and dimethyl cyclopent-3-ene-1,1-dicarboxylate (10 mg, 54 μmol) were dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube. The tube was placed in a dry ice/acetone bath and 1 equiv of ethene was added through the septum. The tube was quickly shaken and re-inserted into the cold bath. After ca. 20 h of standing at −78 °C, the sample was inserted into the NMR probe precooled to 223 K, and multinuclear NMR spectroscopy was performed. Typically, the ratio **1-Cy**/**3**/**2** was 25:38:38, that is, a **3**/**2** ratio of ca. 1:1. This ratio did not change much while the sample was in the probe for several hours. Among several experiments, the **3**:**2** ratio varied from 1:1 to 2:1. See below for a superior procedure starting from **1-^{i}Pr**, in which full NMR data for **3** are given.



Generation of 3 from 1-^{i}Pr. In a glove box, dimethyl cyclopent-3-ene-1,1-dicarboxylate (15 mg, 81 μmol) was weighed into an NMR tube and dissolved in 0.1 mL of CD_2Cl_2. (H$_2$IMes)(Cl)$_3$Ru=CHP^{i}Pr$_3$·CH_2Cl_2 (20 mg, 26 μmol) was weighed into a vial and dissolved in 0.5 mL of CD_2Cl_2. B(C$_6$F$_5$)$_3$ (15 mg, 29 μmol) was weighed into a different vial. The vials and the NMR tube were cooled in the glove box freezer (−35 °C). The ruthenium trichloride compound was added to the B(C$_6$F$_5$)$_3$ and shaken to form **1-^{i}Pr**, which was cooled again in the freezer. Then, quickly, the **1-^{i}Pr** solution was added to the NMR tube containing the RCM product, the tube was capped with a septum, brought out of the glove box, and placed in a dry ice/acetone bath. One equivalent of ethene was added through the septum, and the tube was quickly shaken three times, which resulted in a fast color change to red/purple. This procedure results in a reproducible **3**/**2** ratio of 9:1 and with ca. 5% of the ruthenium in the form of the [Ru=CHP^{i}Pr$_3$]$^+$/[Ru=CH$_2$] dimer: ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 213 K) δ 9.36 (app q, 1H, *H*$_\alpha$, $^3J_{H\beta}$ = 7 Hz), 6.92 (s, 1H, Mes C*H*), 6.89 (s, 1H, Mes C*H*), 6.87 (s, 1H, Mes C*H*), 6.85 (s, 1H, Mes C*H*), 6.07 (m, 1H, *H*$_{\alpha''}$, overlapping with H$_2$C=C*H*P byproduct), 5.90 (app dd, 1H, *H*$_{\alpha'}$, $^3J_{H\beta}$ = 9 Hz; $^2J_{H\alpha''}$ = −4.5 Hz), 4.26 (m, 4H, NC*H*$_2$C*H*$_2$N), 3.62 (s, 3H, C*H*$_3$OOC), 3.55 (s, 3H, C*H*$_3$OOC), 2.46 (app s, 6H, overlapping inequivalent Mes C*H*$_3$), 2.40 (s, 3H, Mes C*H*$_3$), 2.39 (s, 3H, Mes C*H*$_3$), 2.31 (app dd, 1H, C*H*H in cyclopentane ring, vicinal to H$_\alpha$), 2.26 (s, 3H, Mes C*H*$_3$), 2.24 (s, 3H, Mes C*H*$_3$), 2.04 (app dd, 1H, CH*H* in cyclopentane ring, vicinal to H$_{\alpha1}$), 1.81 (app dd, 1H, C*H*H in cyclopentane ring, vicinal to H$_\beta$), 1.69 (app dd, 1H, CH*H* in cyclopentane ring, vicinal to H$_\beta$), −2.15 (m, 1H, H$_\beta$); ^{13}C{H$_\alpha$} NMR (CD_2Cl_2, 100.5 MHz, 213 K) δ 213.5 (s, Ru*C*(N)$_2$), 171.9, 169.7 (both s, *C*=O), 144.8 (br s, *C*$_{\alpha1}$H, $^1J_{CH}$ = 167 Hz, $^1J_{CC}$ = 8.5 Hz), 139.2, 138.9, 137.5, 137.34, 137.30, 137.2, 132.4, 132.2 (all s, Mes quaternary C), 128.98, 128.96 (both s, Mes *C*H), 128.9 (app s, 2 overlapping Mes CH), 87.2 (s, *C*$_{\alpha2}$, $^1J_{CH}$ = 163, 163 Hz, $^1J_{CC}$ = 23 Hz), 68.9 (s, O=C*CC*=O), 53.3 (s, *C*H$_3$OOC), 52.9 (s, *C*H$_3$OOC), 52.6 (s, *C*H$_2$CH$_2$), 51.8 (s, CH$_2$*C*H$_2$), 39.8 (s, cyclopentane *C*H$_2$ attached to C$_\alpha$), 26.1 (s, cyclopentane *C*H$_2$ attached to C$_\beta$), 23.7 (s, *C*$_\beta$, $^1J_{CH}$ = 157 Hz), 21.0, 20.9, 19.2, 19.09, 19.05, 19.0 (all s, Mes *C*H$_3$). Notes regarding assignments in ^{1}H **3**: Signals at 6.07 and 5.90 ppm were assigned based on the magnitude of NOESY interactions (mixing time = 0.4 s). H$_\beta$ at −2.15 ppm has a stronger NOESY interaction with the peak at 5.90 ppm than with that at 6.07 ppm. In addition, the peak at 1.69 ppm (assigned by COSY to a cyclopentane CH$_2$ vicinal to H$_\beta$) has a NOESY interaction with the 6.07 ppm peak, which lends support to its assignment as the ruthenacycle C*H*H *anti* to H$_\beta$. In the COSY, H$_\alpha$ couples to peaks at 2.31 and 2.04 ppm, and H$_\beta$ couples to peaks at 1.81 and 1.69 ppm. These four peaks all appear as doublets of doublets in the ^{1}H NMR spectrum and are assigned to the cyclopentane CH$_2$ groups.

Generation of (H$_2$IMes)(Cl)$_2$(PMe$_3$)Ru=C(H)CH$_2$C(CO$_2$Me)$_2$CH$_2$C(H)=CH$_2$, 4. In a J-Young tube, **3** was generated using a procedure similar to that described above. However, in this case, the tube containing the solution of **1-^{i}Pr** and dimethyl cyclopent-3-ene-1,1-dicarboxylate was degassed by three freeze−pump−thaw cycles, after which 1 equiv of ethene was measured with a calibrated bulb and transferred into the tube at −196 °C. The tube was placed in a −78 °C bath, and the contents were allowed to thaw. Careful shaking of the tube at −78 °C resulted in a coloration to red/purple, and ^{1}H NMR analysis indicated a 7:1 ratio of **3**/**2**. Then, again using a calibrated bulb, 2 equiv of PMe$_3$ was measured and transferred into the tube at −196 °C. The tube was placed in a −78 °C bath, and the contents were allowed to thaw. After careful shaking of the tube at −78 °C, the color changed from red/purple to dull orange in the course of several minutes. The tube was inserted into the NMR probe precooled to −60 °C, and multinuclear NMR experiments were performed. The spectra indicated formation of **4** in an NMR yield of 98% from **3**: ^{1}H NMR (CD_2Cl_2, 399.5 MHz, 213 K) δ 17.74 (dt, $^3J_{HP}$ = 3.5 Hz, $^3J_{HH}$ = 5 Hz, 1H, Ru=C*H*), 6.92 (s, 2H, Mes C*H*), 6.85 (s, 2H, Mes C*H*), 5.64 (m, 1H, C(*H*)=CH$_2$), 4.99−4.92 (m, 2H, inequivalent C(H)=C*H*$_2$), 4.08−3.89 (m, 4H, C*H*$_2$C*H*$_2$), 3.58 (s, 6H, C*H*$_3$OOC), 2.48 (s, 6H, Mes *ortho* C*H*$_3$), 2.31 (s, 6H, Mes *ortho* C*H*$_3$), 2.22 (s, 3H, Mes *para* C*H*$_3$), 2.19 (s, 3H, Mes *para* C*H*$_3$), 2.11 (d, $^3J_{HH}$ = 7 Hz, 2H, C*H*$_2$C(H)=CH$_2$), 1.76 (br, 2H, Ru=C(H)C*H*$_2$), 0.83 (d, $^2J_{HP}$ = 10 Hz, 9H, P(C*H*$_3$)$_3$); ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.7 MHz, 213 K) δ 11.9 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.4 MHz, 213 K) δ 303.3 (br, Ru=*C*H), 219.7 (d, $^2J_{CP}$ = 70 Hz, Ru*C*(N)$_2$), 171.0 (s, *C*=O), 139.2, 139.1, 138.2, 137.51, 137.46, 136.9, 136.4 (all s, Mes quaternary C), 133.2 (s, *C*(H)=CH$_2$), 132.7 (s, Mes quaternary C), 129.2 (s, Mes *C*H), 129.1 (s, Mes *C*H), 118.7 (s, C(H)=*C*H$_2$), 57.3 (s, Ru=C(H)*C*H$_2$), 56.3 (s, O=C*CC*=O), 52.4 (s, *C*H$_3$OOC), 51.5 (app s, *C*H$_2$CH$_2$), 51.2 (d, $^4J_{CP}$ = 3 Hz, CH$_2$*C*H$_2$), 38.3 (s, *C*H$_2$C(H)=CH$_2$), 20.9 (s, Mes *para* *C*H$_3$), 20.8 (s, Mes *para* *C*H$_3$), 19.7 (s, Mes *ortho* *C*H$_3$), 18.1 (s, Mes *ortho* *C*H$_3$), 11.2 (d, $^1J_{CP}$ = 30 Hz, P(*C*H$_3$)$_3$).

Generation of 5 from 1-^{i}Pr. The procedure for **3** was followed, except 14 mg (92 μmol, 3.5 equiv) of cyclopent-3-ene-1,1-diacetyl was used instead of dimethyl cyclopent-3-ene-1,1-dicarboxylate. Mixing of **1-^{i}Pr** with the RCM product resulted in a light green solution, indicative of coordination of the RCM product to **1-^{i}Pr**, probably through a carbonyl oxygen. This was confirmed by ^{1}H (δ 19.61, d, $^2J_{HP}$ = 42 Hz, Ru=C*H*) and ^{31}P{^{1}H} (δ 44.3, s) NMR spectroscopy at 213 K, showing quantitative adduct formation. Nevertheless, addition of 1 equiv of ethene at −78 °C and shaking resulted in the formation of the substituted ruthenacyclobutane (red/purple solution), albeit somewhat slower than with the diester RCM product. The ratio substituted/

unsubstituted ruthenacyclobutane is ca. 6:1, with ca. 10% **1-^{i}Pr** (RCM product coordinated) and <5% [Ru=CHP^{i}Pr$_3$]$^+$/[Ru=CH$_2$] dimer: ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 213 K) δ 9.17 (app q, 1H, $C_{\alpha1}H^1$), 6.94 (s, 1H, Mes C*H*), 6.89 (s, 1H, Mes C*H*), 6.86 (s, 1H, Mes C*H*), 6.85 (s, 1H, Mes C*H*), 6.07 (m, 1H, $C_{\alpha2}H^2$, overlapping with H_2C=C*H*P byproduct), 5.92 (app dd, 1H, $C_{\alpha2}H^3$), 4.26 (m, 4H, NCH_2CH_2N), 2.46 (app s, 6H, overlapping inequivalent Mes CH_3), 2.40 (s, 3H, Mes CH_3), 2.38 (s, 3H, Mes CH_3), 2.32 (app dd, 1H, C*H*H in cyclopentane ring, vicinal to H^1), 2.27 (s, 3H, Mes CH_3), 2.24 (s, 3H, Mes CH_3), 1.97 (s, 3H, CH_3C=O), 1.95 (s, 3H, CH_3C=O), 1.81 (app dd, 1H, C*H*H in cyclopentane ring, vicinal to H^4), 1.65 (app dd, 1H, CH*H* in cyclopentane ring, vicinal to H^4), −2.40 (m, 1H, $C_\beta H^4$). One cyclopentane hydrogen not observed, overlapped by other signals: ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 213 K) δ 213.5 (s, Ru*C*(N)$_2$), 205.5 (s, *C*=O), 143.9 (overlapped by H_2C=CHP byproduct, $C_{\alpha1}$H, located by HMQC), 139.1, 138.9, 137.6, 137.5, 137.33, 137.26, 132.5, 132.2 (all s, Mes quaternary C), 129.0, 128.91, 128.86, 128.8 (all s, Mes *C*H), 87.4 (s, $C_{\alpha2}H_2$), 83.7 (s, O=C*C*C=O), 52.6 (s, *C*H$_2$CH$_2$), 51.8 (s, CH$_2$*C*H$_2$), 38.6 (s, cyclopentane *C*H$_2$), 27.1 (s, *C*H$_3$C=O), 26.1 (s, *C*H$_3$C=O), 24.4 (s, cyclopentane *C*H$_2$), 23.3 (s, C_βH), 21.0, 20.9, 19.2, 19.10, 19.05, 19.0 (all s, Mes *C*H$_3$).

Trapping of I with Acenaphthalene To Form 6. [(H_2IMes)-(Cl)$_2$Ru=CHPCy$_3$]OTf (20 mg, 22 μmol) and acenaphthylene (5 mg, 33 μmol) were dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube. The tube was placed in a dry ice/acetone bath, and 1 equiv of ethene was added through the septum. The tube was shaken and inserted in the precooled (234 K) NMR probe. The reaction was allowed to go to completion in the NMR probe, which took ca. 5 h. In the data section below, Np denotes the naphthyl group: ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 234 K) δ 18.13 (s, 1H, Ru=C*H*), 8.20 (app d, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 7.77 (app d, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 7.59 (app d, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 7.34 (app t, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 7.21 (s, 1H, Mes C*H*), 7.16 (app t, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 7.02 (s, 1H, Mes C*H*), 6.98 (s, 1H, Mes C*H*), 6.92 (s, 1H, Mes C*H*), 6.19 (app d, $^3J_{HH}$ = 7 Hz, 1H, Np C*H*), 5.65 (app dd, 1H, H_{vinyl}, $^3J_{Hcis}$ = 9.1 Hz, $^3J_{Htrans}$ = 14.7 Hz), 5.54 (app dd, 1H, H_{trans}, $^2J_{Hcis}$ = 2.8 Hz), 4.30−3.93 (m, 4H, CH_2CH_2), 3.61 (app dd, 1H, H_{cis}), 2.86 (s, 3H, Mes CH_3), 2.70 (s, 3H, Mes CH_3), 2.49 (s, 3H, Mes CH_3), 2.37 (s, 3H, Mes CH_3), 2.28 (s, 3H, Mes CH_3), 1.81 (s, 3H, Mes CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, 245 K) δ 317.3 (s, Ru=*C*H), 210.5 (s, Ru*C*(N)$_2$), 149.7, 146.5, 140.6, 139.93, 139.89, 139.1, 138.8, 137.9, 137.8, 136.1, 133.89 (all s, aromatic quaternary C), 133.86 (s, aromatic *C*H), 131.0 (s, aromatic quaternary C), 130.0, 129.9 (both s, aromatic *C*H), 129.3 (app s, two overlapping Mes *C*H), 129.2, 127.1, 126.3, 126.1, 119.8 (all s, aromatic *C*H), 100.3 (s, H_2C=*C*H), 100.0 (s, H_2C=CH), 52.8 (s, *C*H$_2$CH$_2$), 50.8 (s, CH$_2$*C*H$_2$), 21.3, 21.2, 20.9, 20.5, 18.7, 17.7 (all s, Mes *C*H$_3$).

Trapping of I with 1-^{i}Pr: Generation of II. 1-^{i}Pr was generated as described before, and 0.5 equiv of ethene was introduced at −78 °C. The tube was quickly shaken, affording an orange/brown solution, and inserted in the precooled NMR probe. This generates ca. 60% of dimer, 10−15% of **2**, and 25−30% of **1-^{i}Pr** remains. The dimer is thermally unstable and decomposes above −30 °C. Partial characterization by ^{1}H and ^{31}P NMR spectroscopy was performed, but not all resonances could be unequivocally assigned: ^{1}H NMR (CD_2Cl_2, 399.6 MHz, 213 K) δ 19.79 (d, $^2J_{HP}$ = 43 Hz, 1H, Ru=C*H*), 18.01 (s, 2H, Ru=CH_2), 7.11 (s, 1H, Mes C*H*), 7.02 (br, overlapping Mes C*H*), 7.00 (s, 1H, Mes C*H*), 6.83 (s, 1H, Mes C*H*, overlapping with H*H*C=CHP byproduct), 6.80 (s, 1H, Mes C*H*, overlapping with H*H*C=CHP byproduct), 4.00−3.66 (m, 8H, CH_2CH_2), 2.50 (s, 3H, Mes CH_3), 2.41 (s, 3H, Mes CH_3), 2.36 (s, 3H, Mes CH_3), 2.34 (s, 3H, Mes CH_3), 2.24 (s, 3H, Mes CH_3), 2.15 (s, 3H, Mes CH_3), 2.09 (s, 3H, Mes CH_3), 1.96 (s, 3H, Mes CH_3), 1.89 (s, 3H, Mes CH_3), 1.1 (br, 18H, ^{i}Pr CH_3); ^{31}P-{^{1}H} NMR (CD_2Cl_2, 161.8 MHz, 213 K) δ 43.4 (br).

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Supporting Information Available: General experimental procedures, details on the syntheses of labeled substrates, and crystallographic data for **1-^{i}Pr−Cl** (in .cif format). This material is available free of charge via the Internet at http://pubs.acs.org.

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