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Ruthenium Carbene-Based Olefin Metathesis Initiators: Catalyst Decomposition and Longevity

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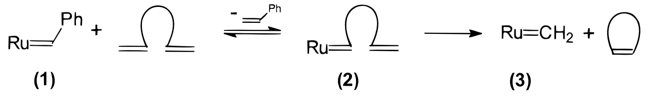
Thermolytic decomposition pathways were studied for several ruthenium carbene-based olefin metathesis catalysts. Substituted carbenes were found to decompose through bimolecular pathways while the unsubstituted carbene was found to decomposed unimolecularly. Implications for ring-closing metathesis are discussed, and the longevity of several ruthenium-based catalysts are compared.

Introduction

In recent years, the use of ruthenium carbene-based olefin metathesis initiators[1] has gained wide acceptance in organic[2] and polymer syntheses.[3] Ruthenium-based catalysts exhibit greater functional group tolerance, as well as greatly enhanced air and water stability, relative to other popular single component catalyst systems based on molybdenum and tungsten.[4] However, thermolytic decomposition limits the usefulness of the ruthenium system in many challenging reactions. Understanding and controlling the decomposition pathways is essential for the increased efficiency of these catalysts.

Although the benzylidene complex $(PCy_3)_2Cl_2Ru{=}CHPh$ (**1**) is used to initiate most metathesis reactions, the propagating species in ring-closing metathesis (RCM)[2,5] is usually either an alkylidene,[6] $(PCy_3)_2Cl_2Ru{=}CHR$ (**2**), where R represents the substrate attached to the catalyst, or the methylidene, $(PCy_3)_2Cl_2Ru{=}CH_2$ (**3**) (Scheme 1), since the original phenyl of the starting carbene is lost in the first turnover. The propylidene, $(PCy_3)_2Cl_2Ru{=}CHCH_2CH_3$ (**4**), and the methylidene (**3**) were chosen as representative catalytic species for these decomposition studies. Since only the methylidene is observed by NMR in a significant quantity during an RCM reaction in progress, the understanding of its stability is critical for designing viable catalyst systems. In this paper, we report NMR studies on several ruthenium carbene complexes, monitoring their rates of decomposition and their ability to carry out RCM under forcing conditions. Our results show which ruthenium catalysts are best suited for RCM and which ligand systems are needed to produce the most viable catalyst.

Scheme 1. Pathway for Ring-Closing Metathesis (RCM)



Experimental Section

All reactions were set up in a nitrogen-filled drybox and carried out with the exclusion of air in Teflon-lined screw-cap NMR tubes. The ethylene generated during the RCM reactions was not vented from the reaction mixture so that all reactions were carried out under equilibrium conditions. All compounds were synthesized as previously reported. The deuterated solvent were purchased from Cambridge Isotope Laboratories. Benzene-d_6 was purified by passing it through a column of LaRoche A-2 alumina and Engelhard Q-5 reactant (supported copper oxide).[7] Methylene chloride-d_2 was dried over calcium hydride for 48 h, degassed by three freeze−pump−thaw cycles, and vacuum transferred into a Schlenk tube.

Typical Decomposition Experiment. In a 0.5 dram vial in a drybox, 13.8 μmol of the corresponding complex was weighed out. Anthracene was added as an internal standard along with 0.60 mL of C_6D_6. The vial was closed and shaken to dissolve the solids. Using a pipet, the solution was then transferred to a screw-cap NMR tube and the cap sealed with electrical tape. The reaction was monitored by ^1H NMR for several half-lives at 55 °C to simulate RCM conditions. Each complex's decomposition was repeated at least two independent times (on different days) to establish reproducibility.

Typical RCM Experiment. In a 0.5 dram vial, 4.1 μmol of the corresponding complex was weighed out in the drybox. C_6D_6 (1.0 mL) was added, and the vial was closed and shaken to dissolve the complex. 4,4-Dicarbethoxy-2-methyl-1,6-heptadiene[5b] (20 μL, 20.4 mg) was then added, the vial was again shaken and the solution transferred via pipet into a screw-cap NMR tube, and the cap was then sealed with electrical tape. Heating typically began 2.5 min after mixing, either using a variable-temperature NMR probe for fast reactions or using a temperature-controlled oil bath for slow reactions. Data were collected until no further significant conversion occurred (over the next day, a few percent ad-

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[1] (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (d) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127. (e) Hashmi, A. S. K. *J. Prakt. Chem.* **1997**, *339*, 195.

[2] Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413 and references therein.

[3] For several reviews, see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Stelzer, F. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 941.

[4] (a) Late transition metals offer greater functional group tolerance. See: Grubbs, R. H. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1829. (b) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.

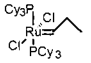
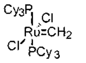
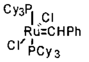
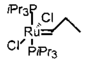
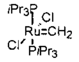
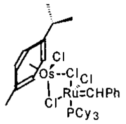
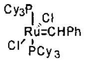
[5] (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310. (c) Kirkland, T. A.; Lynn, D. M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 9904.

[6] For our purposes, we will apply the term alkylidene to signify carbene complexes other than methylidene, $Ru{=}CH_2$, or benzylidene, $Ru{=}CHPh$.

[7] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

10.1021/jo9908703 CCC: $18.00

Table 1. Thermolytic Half-Lives of Complexes

Carbene	Temp	Conc.	Half-Life
 (4)	55 °C	0.023 M	8 hrs
 (3)	55 °C	0.023 M	40 min
 (1)	55 °C	0.023 M	8 days
 (7)	55 °C	0.023 M	10 hrs
 (8)	25 °C	0.039 M	30 min
 (11)	55 °C	0.023 M	30 min
 + CuCl	55 °C	0.023 M	10 min

ditional conversion was often observed but ignored in the cases in which the reaction was otherwise effectively complete in under an hour). Each reaction was repeated at least two independent times (on different days) to confirm reproducibility.

Phosphine Extraction. Freshly made $(P\text{-}i\text{-}Pr_3)_2(Cl)_2Ru{=}CD_2$ (from the reaction of $(P\text{-}i\text{-}Pr_3)_2(Cl)_2Ru{=}CHPh$ and $D_2C{=}CD_2$)[1c] was placed in a J. Young NMR tube in CH_2Cl_2. Decomposition was monitored by ^{31}P NMR until there was no starting species left. An aqueous solution of $P(CH_2OH)_3$[8] and NEt_3 was added. The layers were shaken until the dark brown lower organic layer became tan in color, signifying that most of the metal had been extracted into the aqueous phase. ^{31}P NMR of the organic phase showed free P-*i*-Pr$_3$ along with minor impurities. ^{2}H NMR of the organic phase showed two major signals at 1.8 ppm (1 H) and 1.1 ppm (3.3 H) along with a minor peak for naturally abundant $CDHCl_2$ and three other minor resonances at 6.3, 6.4, and 7.4 ppm.

Results and Discussion

Under standard decomposition conditions (0.023 M in C_6D_6 at 55 °C), the propylidene (**4**) has a half-life of around 8 h while the methylidene (**3**) has a half-life of approximately 40 min (Table 1). For reference, a solution of the benzylidene (**1**) has a half-life of about 8 days.

Attempts to fit the propylidene (**4**) decomposition data to simple rate equations were unsuccessful. The data, covering several half-lives, fit neither first- nor second-order kinetics plots. For the second-order equation, the fitted data were significantly nonlinear at short reaction times but fairly linear at intermediate times.

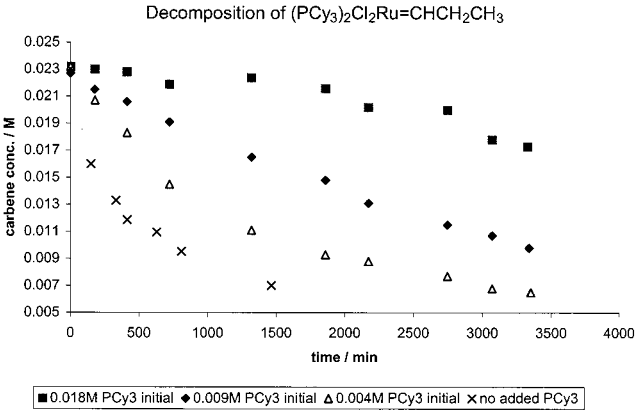


Figure 1. Phosphine dependence of decomposition at 55 °C.

To gain an understanding of the pathway of decomposition, the NMR spectra of the decomposition reaction mixture were examined. The ^{31}P NMR spectrum of the propylidene (**4**) decomposition reaction mixture showed that the predominant product was free PCy_3, but a number of other small unidentifiable phosphine signals also grew in over the course of the decomposition. This multitude of phosphine signals prevented the determination of the discrete inorganic decomposition products. When decomposition was carried out in the presence of excess phosphine, the rate of decomposition slowed significantly (Figure 1). However, because the catalytic activity of the ruthenium system depends on the dissociation of a phosphine ligand,[9] slowing the rate of decomposition with the addition of excess phosphine would also inhibit productive metathesis.

The most notable aspect of the ^{1}H NMR spectrum of the decomposition of propylidene (**4**) was the initial quantitative formation of *trans*-3-hexene (dimerization of the organic fragment of the complex) while there was still a large amount of intact carbene present. Over time, additional olefinic peaks appeared in the spectrum. These were accompanied by the formation of a new quartet carbene signal (19.66 ppm, $J_{HH} = 4.9$ Hz) next to the propylidene (**4**) H_α triplet (19.60 ppm, $J_{HH} = 4.9$ Hz). The presence of minute signals at -7 ppm suggested that *some* of the decomposition products were ruthenium hydrides. These provide a possible explanation for the formation of the new olefins and the new carbene. The hydrides could isomerize the dimerized carbene fragments, the 3-hexene, to 2-hexenes and possibly other olefins. Metathesis of 2-hexenes could form the ethylidene, $(PCy_3)_2Cl_2Ru{=}CHCH_3$ (**5**), which accounts for the quartet carbene signal (coupling to CH_3).[1c]

These observations are consistent with a decomposition mechanism involving dissociation of a phosphine followed by coupling of the two monophosphine species[10,15] (Scheme 2). The buildup of generated free phosphine as the decomposition progresses is expected to inhibit the formation of the monophosphine species and retard the rate of decomposition. This effect would be most significant at low conversion when the greatest changes in phosphine concentration are taking place, which is consistent with the data.

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[8] For the use of tris(hydroxymethyl)phosphine for metal extraction, see: Maynard, H. D.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 4137.

[9] Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

[10] Bimolecular decomposition was observed in early-metal carbene systems. See: (a) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (b) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[11] Chaudret, B.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722.

[12] Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316.

[13] (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Li, C.; Ogasawara, M.; Nolan, S. P.; Caulton, K. G. *Organometallics* **1996**, *15*, 4900.

[14] (a) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484. (b) Kim, S. H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073. (c) Zuercher, W. J.; Scholl, M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 4291.

[15] Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758.

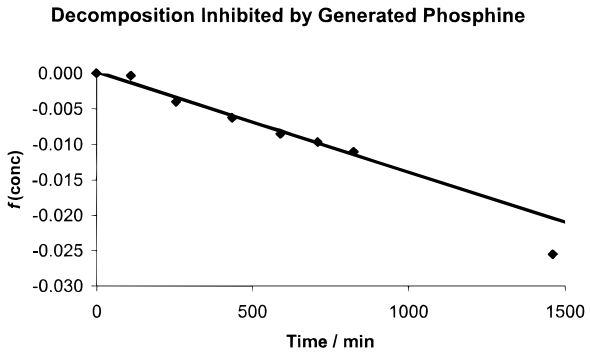
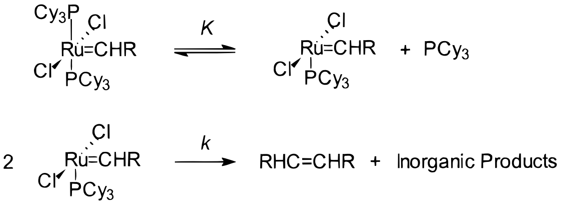


Figure 2. Decomposition data fit of 0.0383 M propylidene (**4**) to mechanism in Scheme 1. The *f*(conc) represents the function of eq 2.

Scheme 2. Proposed Pathway for Alkylidene Decomposition



Assuming a preequilibrium in the first step and the formation of *n* moles of *free* phosphine for every mole of decomposed $(PCy_3)_2Cl_2Ru{=}CHR$ (**2**), the following rate equation was deduced for alkylidene decomposition

$$\frac{d[\text{conc}]_t}{dt} = \frac{Kk}{n^2}\,\frac{[\text{conc}]_t^{\,2}}{([\text{conc}]_0 - [\text{conc}]_t)^2} \qquad (1)$$

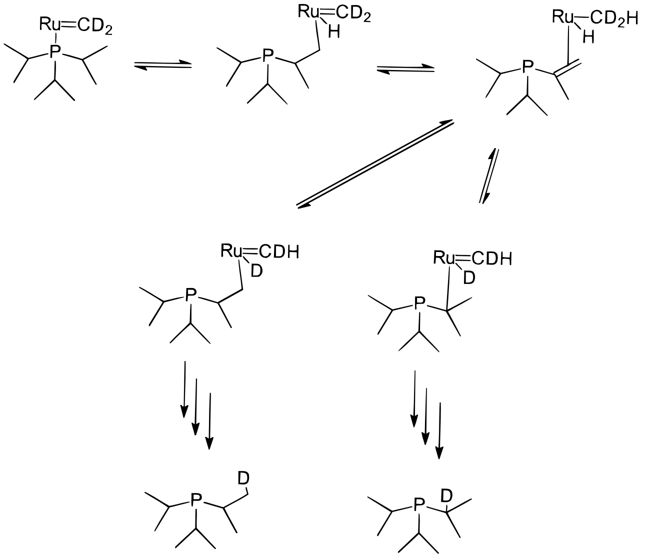
$$f(\text{conc}) = 2([\text{conc}]_0)\text{Ln}\frac{[\text{conc}]_0}{[\text{conc}]_t} + \frac{([\text{conc}]_t - [\text{conc}]_0)([\text{conc}]_t + [\text{conc}]_0)}{[\text{conc}]_t} = \left(\frac{kK}{n^2}\right)t \qquad (2)$$

where $[\text{conc}]_t$ is the concentration of the alkylidene at time *t*, $[\text{conc}]_0$ is the initial alkylidene concentration, *K* is the equilibrium constant for the first step, and *k* is the rate constant for the second step. An integration of eq 1 produced eq 2. Fitting the observed data to eq 2 yielded a fairly good fit at low and intermediate conversion but a poor fit at high conversion (Figure 2). This is presumably because at high conversion the generated free phosphine is consumed by the intractable ruthenium byproducts such that the data does not fit the equation which incorporates the *expected* amount of free phosphine (in other words, *n* is variable over the latter stages of decomposition).

In contrast to the propylidene (**4**), the methylidene (**3**) decomposition data fit a *first-order* kinetics plot, and the presence of excess free phosphine did not effect the rate of decomposition. No ethylene formation was observed by ^{1}H NMR from methylidene decomposition, and while the ^{31}P NMR exhibits many small peaks, the major peaks are free phosphine and an unknown at 34.6 ppm. Attempts to identify this unknown by crystallography were unsuccessful. This unknown is not the phosphine ylide, $Cy_3P{=}CH_2$, which was independently prepared.

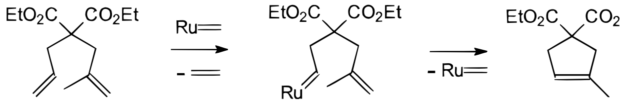
To better understand the decomposition of the methylidene (**3**), the deuterated carbene complex analogue, $(PCy_3)_2Cl_2Ru{=}CD_2$ (**6**), was studied by ^{2}H NMR. The deuterium signal, originally a fairly sharp 19.3 ppm peak corresponding to the carbene, was observed as a broad signal at 2.5 ppm in the decomposition mixture. Since the chemical shift suggests that the carbene fragment becomes a saturated aliphatic product, there is presumed to be either an activation of the phosphine[11] or solvent activation involved in the decomposition pathway. However, similar decomposition products occur in benzene, THF, and methylene chloride. Furthermore, a sample of methylidene-d_2 (**6**) stored as a solid in a drybox for several years also showed some decomposition with the deuterium label partially showing up as a broad signal around 2 ppm. This supports the phosphine activation hypothesis for methylidene decomposition, though solvent activation cannot be excluded as a contributing pathway.

Scheme 3. Proposed Pathway for Deuterium Incorporation into Both Positions on the Triisopropylphosphine



To simplify the investigation of phosphine activation, the triisopropylphosphine analogues of the propylidene and methylidene were synthesized, since this phosphine only has two types of protons. The triisopropylphosphine propylidene, $(P\text{-}i\text{-}Pr_3)_2Cl_2Ru{=}CHCH_2CH_3$ (**7**), exhibited a half-life of approximately 10 h under standard conditions (Table 1). This is not surprising since P-*i*-Pr_3 dissociates slightly less readily than PCy_3[13a] and dissociation is proposed to be the first step toward decomposition. Otherwise, the kinetics were analogous to the PCy_3 case with inhibition by newly generated free phosphine. However, the triisopropylphosphine methylidene, $(P\text{-}i\text{-}Pr_3)_2Cl_2Ru{=}CH_2$ (**8**), was unexpectedly very unstable. It completely decomposed in less than 8 min at 55 °C, and so its decomposition was studied at 25 °C. The half-life of a 0.039 M solution was just over 30 min at 25 °C, and the data fit first-order kinetics fairly well. However, upon the addition of free phosphine the rate of decomposition was *slightly* retarded, though not enough to invoke a phosphine dissociative mechanism, and the data fit neither first- nor second-order kinetics. Decomposition of the deuterated analogue $(PiPr_3)_2Cl_2Ru{=}CD_2$ (**9**) and isolation of the phosphine showed incorporation of the deuterium into *both* the primary and tertiary positions on the isopropyl groups, suggesting an isopropenyl intermediate[12] (Scheme 3) and strongly supporting the

Scheme 4. RCM of 4,4-Dicarbethoxy-2-methyl-1,6-heptadiene by Propagating Methylidene



role of phosphine activation in triisopropylphosphine methylidene (**8**) decomposition, if not necessarily in PCy_3 methylidene (**3**) decomposition.

The metathesis activity of PCy_3 and P-*i*-Pr_3 carbene complexes is similar, with that of the PCy_3 about 10% greater.[9] Both phosphines are fairly bulky (Tolman cone angle of 170° and 160°, respectively) and exhibit similar electronic parameters (20.564 and 20.592 cm^{-1}, respectively) with PCy_3 being slightly larger and slightly more electron donating.[13] It is unclear why the P-*i*-Pr_3 methylidene (**8**) is so much less stable. Since at least some of the possible decomposition pathways involve phosphine activation, perhaps P-*i*-Pr_3 activation proceeds faster than PCy_3 activation in the present system.[11] However, the slight retarding effect of excess phosphine on the P-*i*-Pr_3 methylidene (**8**) decomposition but not on the PCy_3 methylidene (**3**) might invoke a different pathway for decomposition in the P-*i*-Pr_3 case.

To test the effects of methylidene stability on RCM yields, a series of ring-closing metathesis reactions were performed with several different recently developed ruthenium carbene initiators. The RCM substrate chosen was 4,4-dicarbethoxy-2-methyl-1,6-heptadiene,[5b] which allowed for a methylidene propagating species and reacted slowly enough so that the stability of the methylidene was a major factor in the observed conversion (Scheme 4). The ring-closing data is shown in Table 2.

During the course of the RCM reaction for **1** and **10**, the only carbene species observed in significant quantities by ^1H NMR were the corresponding methylidenes. From a study comparing relative rates for the reactions between ruthenium carbenes and various olefins[14a] and earlier work with polycyclizations whereby two distinct products would be formed depending on which olefin the catalyst reacted with first,[14b,c] it can be surmised that initially the catalyst reacts with the less substituted olefin of the diene substrate and then cyclizes to form the methylidene and product. Since the methylidene is the only intermediate observed in significant quantity, we can conclude that its stability is crucial to propagation and longevity.

Due to a combination of respective methylidene stability and propagation rates, the PCy_3-based initiator **1** is significantly better for RCM than the P-*i*-Pr_3-based analogue **10**. The higher temperature data in particular show the significance of methylidene stability. The bimetallic species[15] (**11**) performs metathesis very rapidly but has a very short life span. While the bimetallic methylidene cannot be synthesized,[15] the half-life of the 0.023 M benzylidene solution is only approximately 30 min at 55 °C (the decomposition data fit second-order kinetics). The CuCl-activated reaction[9,15] is even more rapid and even less stable but the high rate of propagation compensates for the rate of decomposition, especially at 55 °C. The benzylidene (**1**) has a half-life of under 10 min under standard conditions in the presence of insoluble CuCl[16] (again the decomposition data fits second-order kinetics).

The salen ligand bound initiator (**12**)[17] is incredibly stable but performs RCM very slowly. The reaction takes months at room temperature but is fairly rapid at 55 °C, and no catalyst decomposition is observed. However, no propagating species were observed and the only carbene species evident in the NMR spectrum was the starting material. The complex also did not react readily with ethylene, 1-hexene, or 3-hexene to generate new carbenes.[18] It would appear that only a small quantity of an active species is generated that performs most of the metathesis while the remaining benzylidene is inactive.

The activity of the bis-dicyclohexylimidazolin-2-ylideneruthenium carbene (**13**) for RCM was also investigated.[19] This is the first reported complex of a new class of ruthenium catalysts containing an imidazolinylene ligand. Despite the extraordinary activity reported for this catalyst, we found very limited reactivity with our substrate under standard conditions. The ring-closing was slow, and the intermediates, which were not observed, are presumed to be unstable. Furthermore, attempts to react the bis-imidazolinylidenebenzylidene complex with ethylene or *trans*-3-hexene to generate, respectively, the methylidene and propylidene analogues, led only to carbene decomposition. Additionally, attempts to synthesize the methylidene and propylidene analogues by adding the imidazolinylidene ligand to the respective phosphine complexes also led only to decomposition. This further supports the hypothesis that the rate of decomposition of the propagating carbenes for this system is quite high with respect to the rate of propagation.

We also examined a recent modification on the Herrmann catalyst developed in our laboratory.[20,21] This monoimidazolinylidenemonophosphine carbene complex (**14**) has been shown to exhibit remarkable activity for the synthesis of tri- and tetrasubstituted olefins through RCM at elevated temperatures. For ring-closing, the activity at room temperature was found to be very slow, but at elevated temperatures we observed fairly rapid activity and high conversion. Furthermore, a methylidene carbene signal was still present in the NMR at the end of the reaction. The marked difference in activity between **13** and **14** seems to be the ability to lose a ligand in order to generate an active species but then to recoordinate the ligand and reform a stable species.[22] Presumably, the imidazolinylidene ligand cannot readily dissociate and

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[16] Reference 15 elaborates on the means by which CuCl speeds up the rate of metathesis. CuCl is known to act as a “phosphine sponge” and either produces a monophosphine initiator or a bimetallic initiator, both of which can rapidly bimolecularly decompose.

[17] Chang, S.; Jones, L., II; Wang, C.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1997**, *17*, 33460.

[18] Heating the salen-catalyst (**12**) under ethylene pressure at 55 °C for several days did result in the formation of some methylidene observed by NMR.

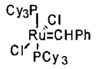
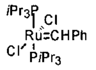
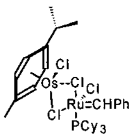
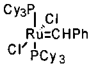
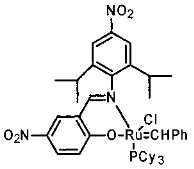
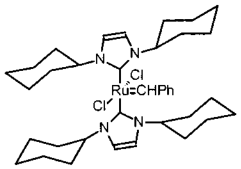
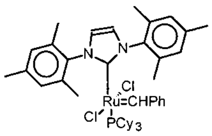
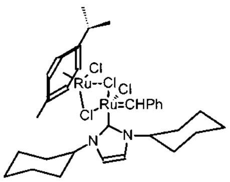
[19] Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490. Also see corrigendum: Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 262.

[20] Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.

[21] Similar work was also carried out independently by another research group: Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.

[22] The mechanism of olefin metathesis with the benzylidene (**1**) and its derivatives involves the dissociation of a phosphine as described in ref 9.

Table 2. Ring-Closing Reactions with 4,4-Dicarbethoxy-2-methyl-1,6-heptadiene and Various Initiators

Carbene	Yield	Time at which reaction progress ceased
 (1)	91 % at 25 °C 80 % at 55 °C	5 days 8 hrs
 (10)	67 % at 25 °C 51 % at 55 °C	2 days 1 hr
 (11)	18 % at 25 °C 18 % at 55 °C	<10 min < 4 min
 + CuCl	55 % at 25 °C 65 % at 55 °C	1.5 hrs 0.5 hrs
 (12)	100 % at 55 °C	2 days, *benzylidene* still present
 (13)	20 % at 25 °C 33 % at 55 °C	4 hrs 3 hrs
 (14)	98% at 55 °C	4 hours, methylidene still present
 (15)	86% at 55 °C	< 15 min

reassociate, and the "naked" complex is allowed to decompose. To further illustrate this difference, we were able to force the mixed ligand complex **14** to react with ethylene, 1-hexene, and 3-hexene to form new observable carbenes, unlike the bis-imidazolinylidene complex **13**.

Finally, we examined another similar metathesis initiator (**15**) recently reported by Herrmann's group.[23] This complex combines an imidazolinylidene ligand with the bimetallic catalyst system to achieve the highest activity so far. However, the lack of a reassociating ligand limits this complex's utility. While it is the fastest metathesis initiator yet, the corresponding propagating species is short-lived and the catalyst cannot take the reaction to completion. Attempts to react it with ethylene to form the corresponding methylidene led only to decomposition, and no new carbene species were observed by NMR.

Conclusion

From these studies, it is concluded that alkylidene decomposition is predominantly second order, requiring phosphine dissociation, while methylidene decomposition is primarily first order. However, the exact nature of the inorganic decomposition products is not known. No bimolecular decomposition product (ethylene) was observed from bis-phosphine methylidenes. However, it has been reported that a ruthenium ethylene complex was observed from the attempted generation of a monophosphine bimetallic methylidene,[15] suggesting that bimolecular decomposition can occur for the methylidenes but is generally slower than their unimolecular decomposition pathway. As a result, bimolecular methylidene decomposition is only observed for monophosphine methylidene complexes. Furthermore, the high instability of monophosphine or mono-L-type-ligand carbene complexes, even the benzylidenes, drastically limits their usefulness as metathesis catalysts.

The first-order decomposition of methylidenes is very

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(23) (a) Herrmann, W. A.; Weskamp, T. *Abstr. Pap. Am. Chem. Soc.* 217:U951, March 21, 1999. (b) Ackermann, L.; Furstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787. (c) Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *582*, 362.

significant in that they are the key propagating species in many ring-closing reactions. The fact that substrates that are difficult to cyclize require high catalyst loadings can now be explained by the unimolecular decomposition of the propagating methylidene catalyst. It is also clear that the choice of phosphine, or phosphine substitute, is critical for effective and stable catalyst systems because even minor alterations in ligand properties can have dramatic consequences. For most applications, the utility of a catalyst is determined by the ratio of the rate of catalysis to the rate of decomposition. Ligand changes that accelerate both processes are not significant improvements in the catalyst system.

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