Comparing Intrinsic Reactivities of the First- and Second-Generation Ruthenium Metathesis Catalysts in the Gas Phase

by **Christian Adlhart** and **Peter Chen***

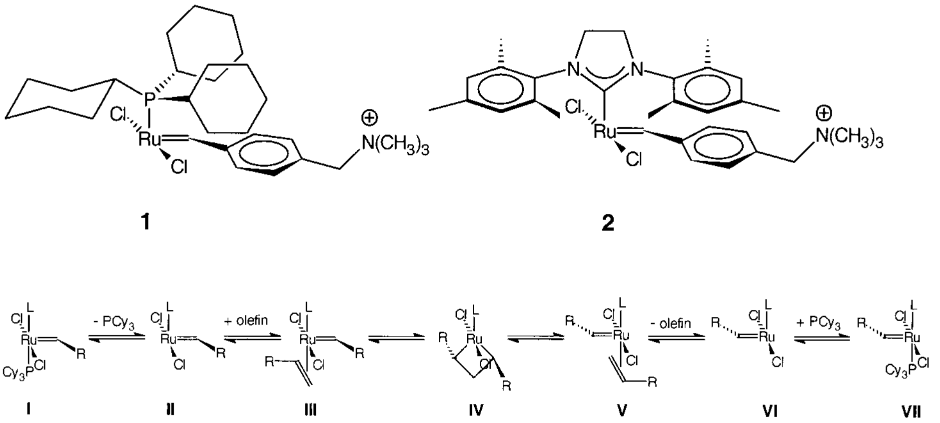
Laboratorium für Organische Chemie, ETH Hönggerberg, HCI G. 209, CH-8093 Zürich

Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

An experimental comparison of the gas-phase reactivity of the 14-electron reactive intermediates produced by phosphine dissociation from the first- and second-generation ruthenium metathesis catalysts, (L)Cl_2Ru=CHR (L = PCy_3 or NHC), supports *Grubbs*'s contention that the second-generation catalysts show hundred-fold higher phenomenological activity despite a slower phosphine dissociation because of a much more-favorable partitioning of the 14-electron active species towards product-forming steps. The gas-phase study finds, in ring-opening metathesis of norbornene as well as acyclic metathesis of ethyl vinyl ether, that the first-generation systems display evidence for a higher barrier above that for phosphine dissociation; the second-generation systems, on the other hand, behave as if there is no significantly higher barrier.

Introduction. – The discovery, and progressive refinement and improvement of olefin-metathesis catalysts [1] makes an understanding of the mechanistic basis for the novel reaction of considerable theoretical as well as practical interest. The ground-breaking discovery of the versatile $(PCy_3)_2Cl_2Ru$=CHPh metathesis catalyst by *Grubbs* and co-workers [2], and others [3], and the subsequent discovery of the 'second-generation' catalysts by *Grubbs* and co-workers [4], *Nolan* and co-workers [5], and *Herrmann* and co-workers [6], in which an N-hetereocyclic carbene (NHC) ligand replaces one phosphine in the first-generation systems, has spurred synthesis of even more varied structural variants [7–9] as well as extensive mechanistic work. Recently, *Grubbs* and co-workers have presented an extensive *in situ* NMR study [10] in which it was concluded that the origin of the greatly increased activity in the second-generation catalysts derived from a more-favorable branching ratio for the competition in which the active carbene complex, (L)Cl_2Ru=CHR (L = PCy_3 or NHC), partitions between entry into the catalytic cycle and rebinding of a phosphine. At about the same time, we reported a gas-phase study [11] comparing the reactivity of a cationized first-generation active species, $(PRCy_2)_2Cl_2Ru$=CH–CH=CMe_2, to that of the activated forms of the Ru-based catalysts from *Hofmann* and co-workers [7], and *Werner* and co-workers [8]. The gas-phase experiments led to the conclusion that the higher activity in solution-phase ring-opening metathesis polymerization (ROMP) of cyclooctene for catalysts from the latter two groups, compared to that of the first-generation *Grubbs* systems, accrued from a more-favorable (reversible) activation step – a better pre-equilibrium. The insights that gas-phase intrinsic reactivity studies on the first-generation *Grubbs*, *Hofmann*, and *Werner* carbene complexes brought for the solution-phase ROMP reactions suggest that a study comparing the first- and second-generation *Grubbs* carbene complexes could be fruitful, especially in conjunction with the *Grubbs*'s kinetic model derived from NMR studies. We report here a gas-phase study of the intrinsic reactivity of (L)$Cl_2Ru{=}CHR$ (L = PCy_3 or NHC), complexes **1** and **2** (*Scheme 1*), respectively, that supports the *Grubbs*'s model by direct observation.

Scheme 1

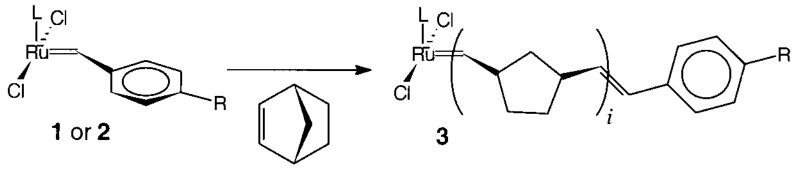


Experimental. – We examined the intrinsic reactivity of the first- and second-generation ruthenium carbene catalyst in the gas phase by electrospray-ionization tandem mass spectrometry ESI-MS/MS. The reactive four-coordinate 14-electron species of the desired catalysts of interest was transferred into the gas phase by electrospray ionization as has been described previously [11–14]. The selected ion was then reacted in the collision cell of the mass spectrometer with either norbornene or ethyl vinyl ether, and analyzed by *m/z* ratio. Electrospray requires charged Ru-carbene complexes; the otherwise neutral complexes were made charged by appending a charged prosthetic group to the benzylidene carbene ligand. In the present experiment, a 4-[(trimethylammonium)methyl] substituent on the benzylidene ligand was found to be convenient. In contrast to our former studies [12], we placed the charge on the carbene moiety for two reasons: as has been demonstrated for the prior first-generation Ru-carbene catalysts [12], as well as for the *Hofmann*-type Ru-carbenes [13], electronic perturbation of the the benzylidene moiety has only a modest influence (approximately one order of magnitude from 4-F to 4-MeO) on the overall reactivity compared that arising from a change of the ligand (up to approximately four orders of magnitude), and, second, the variations made on both catalyst systems are the same, introducing in the ideal case no differential reactivity issues.

Complexes **1** and **2** were synthesized *in situ* by mixing a 10^{-5} M soln. of commercially available [15] (NHC)(PCy_3)$(Cl)_2Ru{=}CHPh$ or $(PCy_3)_2(Cl)_2Ru{=}CHPh$ in CH_2Cl_2 for 15 min with 4-[(trimethylammonium)methyl]styrene. The general procedure has been previously described. The mixture was then electrosprayed at 3.5 kV with a tube-lens potential of 70–90 V on a modified *Finnigan MAT TSQ-700* tandem mass spectrometer. The desired reactive species was mass selected in the first quadrupole upon *m/z*, collided with norbornene in the second octopole ($p_{avg} = 5.36$ mtorr norbornene, *ca.* 2 eV collision energies in the laboratory frame), or ethyl vinyl ether ($p_{avg} = 8.45$ mtorr ethyl vinyl ether, *ca.* 2-eV collision energy, laboratory frame), and then analyzed with the second quadrupole according to *m/z* ratio. To achieve better signal-to-noise ratios, the measurements of peak intensities were performed in the segmented-scan mode. In this mode, the detection quadrupole is scanned over a narrow range, typically 9 amu only, so that more scans could be performed in the same time interval. This was found to be necessary to accurately quantify the weak signals of some of the species. Regions between the peaks were checked independently to ensure that no other significnt products were present. Each intensity measurement was the average of 60 scans. The experiment was furthermore repeated ten times independently for each intensity determination. Statistical error bounds are cited for the 95% confidence level based on a *t*-distribution.

Results. – Gas-phase preparation of the 14-electron complexes, followed by reaction with norbornene in the octopole collision cell produced metal-bound norbornene oligomers **3** in the mass spectrometer (*Scheme 2*).

Scheme 2



The integrated intensities for each species are given in *Table 1* as a fraction of the sum of all oligomers. While absolute rates are dependent on instrument parameters, the relative rates can be directly compared; the rate of the first ring-opening metathesis (ROM) of norbornene by the first-generation complex **1** is arbitrarily chosen as the reference.

Table 1. *Peak Intensities for Norbornene ROM Oligomers for Catalysts* **1** *and* **2**, *Shown with Computed Intensities from a Simple* pseudo-*First-Order Kinetic Fit.* Relative rates for gas-phase ring-opening metathesis of norbornene by complexes **1** and **2** are derived from the fit parameters and are shown normalized to the rate of the first ring-opening by **1**.

	1		**2**	
	Experiment	Fit	Experiment	Fit
I_0/I_{tot}	0.982 ± 0.043	0.9817	0.121 ± 0.004	0.1206
I_1/I_{tot}	0.017 ± 0.001	0.0173	0.402 ± 0.012	0.4022
I_2/I_{tot}	0.001 ± 0.000	0.0009	0.298 ± 0.006	0.2899
I_3/I_{tot}	–	0.0000	0.152 ± 0.004	0.1304
I_4/I_{tot}	–	0.0000	0.025 ± 0.001	0.0429
I_5/I_{tot}	–	0.0000	0.002 ± 0.000	0.0111
k_{first}		1.00 ± 0.05		111 ± 4
$k_{subsequent}$		5.97		66.3
$k_{first}/k_{subsequent}$		0.17		1.67

Conversion of the intensities of the series of peaks comprising complexes **1** or **2** plus norbornene into relative rates for ring-opening metathesis of the first norbornene unit *vs.* ring-opening metathesis of subsequent norbornene units was accomplished with a simple kinetic model by fitting the ratio of the first ring-opening metathesis to each subsequent ring-opening, $k_{first}/k_{subsequent}$, to the integrated peak intensities for the metal-bound norbornene oligomers according to the *pseudo*-first-order kinetic scheme below:

$$\frac{dx_0}{dt} = -k_{first}[x_0]$$

$$\frac{dx_1}{dt} = k_{first}[x_0] - k_{subsequent}[x_1]$$

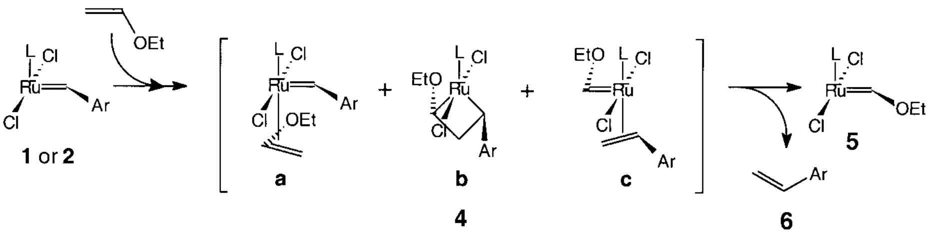
$$\frac{dx_2}{dt} = k_{subsequent}[x_1] - k_{subsequent}[x_2]$$

$$\frac{dx_n}{dt} = k_{subsequent}[x_{n-1}] - k_{subsequent}[x_n]$$

in which x_i is the integrated intensity of the metal-bound norbornene oligomer peak with i norbornene units. The set of linear differential equations was solved in MATLAB [16], producing the fits to the experimental oligomer distributions for the gas-phase ROMP of norbornene, whose intensities are listed in *Table 1* next to the experimental values for comparison. The good fit to the observed integrated intensities supports the assumption that the rate of ring-opening metathesis of norbornene is effectively constant from the second unit up to at least the sixth norbornene unit (which was the highest observable in the mass spectrometer).

When ROMP is done with norbornene, a living polymer is formed and the intermediates **III** to **VI** cannot be distinguished on the basis of m/z. In the case of an acyclic olefin metathesis reaction, the newly formed olefin is released from the π complex **V** and, therefore, **V** and **VI** can now be distinguished from each other by different m/z values. The reaction of ethyl vinyl ether with complexes **1** and **2** is highly exothermic, irreversible, and, therefore, suitable for mechanistic investigations (*Scheme 3*).

Scheme 3



The first-generation catalyst **1** shows little reactivity towards ethyl vinyl ether and surprisingly little tendency to form a π complex with ethyl vinyl ether, even under the low-energy multiple-collision conditions of the experiment, as can be seen in *Table 2*. The low amount of conversion to either π-complex **4** (or isomers of the π complex), or products **5** and **6** is not due to poor reaction conditions; the second-generation catalyst **2** reacts under the same condition, yielding the *Fischer*-type carbene complex **5** and predominantly the species **4**.

Table 2. *Experimental Peak Intensities for the Species Produced by the Gas-Phase Metathesis Reaction of **1** or **2** with Ethyl Vinyl Ether, Normalized to Sum of All Ions.* Each value is the average of ten measurements; the error is given at 95% confidence based on a t distribution.

	1 or **2**	**4**	**6**
1	0.998 ± 0.001	0.0005 ± 0.0003	0.002 ± 0.001
2	0.166 ± 0.009	0.757 ± 0.007	0.077 ± 0.005

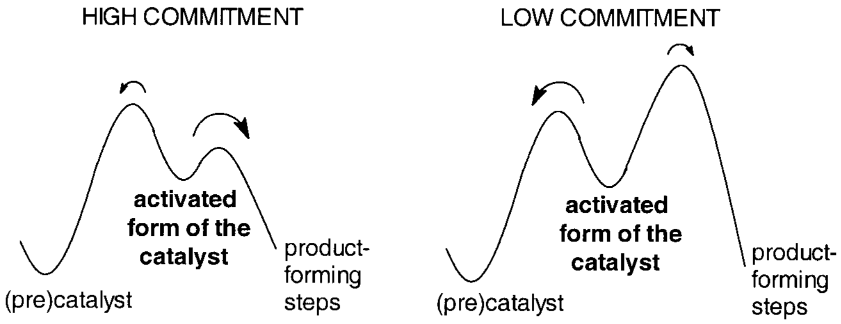
From the mass alone, one cannot assign an unambiguous structure to **4**. Nevertheless, it is highly likely that the intense peak at the m/z ratio corresponding to **4** in the reaction of **2** with ethyl vinyl ether is the π complex **4a**. Crossover experiments in which the related $[(\text{dcpm-}\kappa^2P)(\text{Cl})\text{Ru}{=}\text{CHOR}]^+$ carbenes were complexed with vinyl ethers $H_2C{=}CHOR'$ and then refragmented showed that the most-stable adduct was the π complex rather than the metallocyclobutane [13].

Discussion. – Since the first observation and recognition of homogeneous olefin metathesis by *Calderon*, *Chen*, and *Scott* in 1967 [17], and the validation of the *Chauvin* mechanism [18], the further development of the metathesis chemistry of transition-metal carbene complexes has attracted rapidly increasing interest from both academic and industrial groups. The development of new catalysts, and accompanying characterization of the mechanism and scope of the reaction, has benefited greatly from well-defined compounds synthesized by many groups.

The introduction of the highly active Ru-based catalysts by *Grubbs* and co-workers marked the expansion of the field into a broad range of applications in preparative chemistry. The specific advantages of the Ru catalysts relative to previous systems built around early transition-metal centers were markedly improved tolerance of functional groups in the substrates and very high activity. Continuing exploration of structural space around the 'first-generation' catalysts led to the 'second-generation' systems in which a N-heterocyclic carbene ligand replaces one of the bulky phosphine ligands in the original catalyst. The phenomenological increase in activity by multiple orders of magnitude in ROMP studies raises fundamental questions with the logical target of mechanistic studies being *de novo* catalyst design.

Focusing on the Ru-based systems, the large increase in phenomenological activity by substitution of a N-heterocyclic carbene for a phosphine has been explained by a more-favorable partitioning of the nascent active species between entry into the catalytic cycle and return to the precatalyst (by rebinding of phosphine) (*Scheme 4*) [10]. More generally, the phenomenon is seen in enzyme catalysis, and is termed commitment. While not using this particular terminology, the kinetic analysis from *Grubbs* and co-workers [10], based on NMR investigation of the metathesis of vinyl ethers, is formally identical to the model in enzyme catalysis.

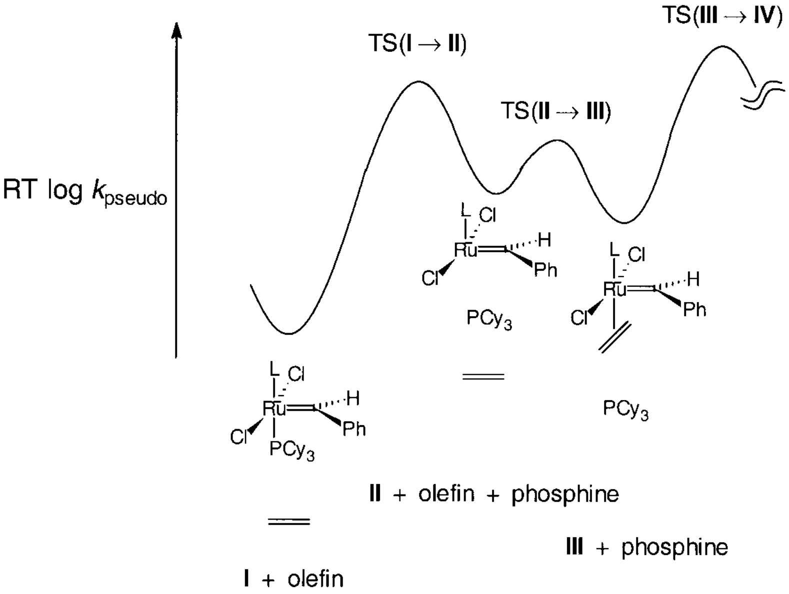
Scheme 4



Interestingly, *Grubbs* found that the activation step, *i.e.*, dissociation of one phosphine ligand, in the second-generation catalysts analogous to **2** is paradoxically *slower* than that for the first-generation systems like **1**. The slower activation, *i.e.*, precatalyst → activated catalyst step, is overcompensated, though, by the much better partitioning to products in the second-generation systems. The commitment issue can be reformulated for the metathesis of norbornene or ethyl vinyl ether as the question: Where is the rate-limiting transition state for the overall reaction **I** → **VII**?

Scheme 5 shows the operational surface, depicted qualitatively, for the first steps of the metathesis reaction. The olefin, norbornene or ethyl vinyl ether, is represented in the diagram by ethylene. Importantly, the vertical scale is $RT \log k_{\text{pseudo}}$, with k_{pseudo} being the *pseudo*-first-order rate in the presence of a large excess of olefin, rather than ΔE, ΔH, or ΔG because one compares, in the same picture, unimolecular steps and bimolecular steps with varying reagent concentrations. For example, the rate of olefin coordination by **II** is accelerated relative to that for phosphine coordination by, among other factors, the much higher concentration of olefin. That rules out **II** → **III** as the rate-limiting step. Because the reaction with norbornene or ethyl vinyl ether is strongly exothermic, the *Hammond* postulate suggests that steps subsequent to structure **IV** are not rate-limiting. Accordingly, for the strongly exothermic metathesis *of a large molar excess* of either norbornene or ethyl vinyl ether, one can already infer *a priori* that either **I** → **II** or **III** → **IV** must be rate-limiting. Which one is it? The *Grubbs* experiment indicates that **III** → **IV** is rate-limiting for **1**, while **I** → **II** is rate-limiting for **2**. This is equivalent to saying that **1** is a low-commitment catalyst, while **2** is a high-commitment one. Because the gas-phase experiment starts with complexes **II**, this question can be treated directly in a mass-spectrometry experiment. The experimental work in the present report confirms the change from low commitment to high commitment going from first- to second-generation Ru catalysts.

Scheme 5



Concomitant with the experimental study of metathesis by Ru complexes, several computational studies on either model or full complexes have appeared, from which an answer to the question posed above can, in principle, be extracted. *Meier* and coworkers [19] reported a molecular-dynamics study of the first-generation catalysts. A DFT treatment of model complexes accompanied the experimental study by *Chen* and co-workers [12]. An extensive evaluation of dissociative *vs.* associative mechanisms with both *cis* and *trans* olefin coordination was reported by *Thiel* and co-workers [20] for both first- and second-generation systems. *Cavallo* has published a full DFT study [21]. Lastly, a QM/MM and full DFT study by *Adlhart* and *Chen* [22] revealed that ligand rotation, ignored in model complexes, is important in near-thermoneutral metathesis reactions. A wealth of detail may be gleaned from the computational studies, but, for the present, one does not yet find a clear prediction for the commitment issue. The calculations by both *Cavallo* and *Thiel* and co-workers do not provide unambiguous support for *Grubbs*'s contention that the difference between first- and second-generation catalysts lies in their commitment. The implications from *Thiel*'s calculation suggests in fact that the contention is incorrect, at least in part. The calculations by *Adlhart* and *Chen* report ΔE rather than ΔG, so they are not directly comparable to the solution-phase reaction, but if one compares the calculations by *Thiel* and co-workers, where ΔG is reported, one sees that the relative stabilities of **III**, **IV**, and **V** analogs are hardly affected by correction to ΔG_{298}, but that all three species are raised relative to the **II** analog by *ca.* 10 kcal/mol. This difference is largely explained by the difference in translational entropy between two molecules *vs.* one, i.e., between (**II** + substrate) and any of the species **III**, **IV**, or **V**. The *Sackur–Tetrode* equation [24] gives an approximate magnitude of the lost translational entropy in the range 30–50 kcal mol^{-1} K^{-1}, which, for a temperature of 298 K, gives a correction of 9–15 kcal/mol. Because the correction for translational entropy is not dependent on particular structures or frequencies, the corresponding correction can be applied qualitatively to the computed ΔE values. Based on the ΔE values from the calculations by *Adlhart* and *Chen*, the estimated ΔG surfaces would then give qualitative support to *Grubbs*'s contention. Given the ambiguity in computational results, an independent experimental determination is desirable.

In general, exothermic ion–molecule reactions occur at the collision rate because attractive electrostatic interactions, *i.e.*, charge/dipole and charge/induced dipole effects, generate a bound adduct for which the transition state for reaction lies below the asymptotic energy in the entrance channel [24]. In contrast to the above-mentioned generalization for ion–molecule reactions, we find a less-than-unit reaction probability per collision for both **1** and **2**. In previous work [12], we had shown that the multiple-collision conditions under which the reactions of **1** and **2** were investigated corresponded to 10^3 to 10^4 collisions with the reagent olefin, *i.e.*, norbornene or ethyl vinyl ether. For neither **1** nor **2** did the reaction with norbornene or ethyl vinyl ether go to completion, meaning that the rates are lower than the collision frequency. Given that we start with the 14-electron complex in both cases, the very exothermic (*ca.* 15 kcal/mol), but nevertheless slow, ion–molecule reaction of **1** and **2** with either norbornene or ethyl vinyl ether means that the rate-limiting transition state cannot lie much lower than the asymptotic energy of the separated 14-electron complexes and either olefinic substrate. The total available energy for **III**, when it is formed in the gas-phase by coordination of the olefinic substrate to the metal center, is necessarily higher than the energy at the incoming asymptote, meaning that **III** will simply dissociate again unless a lower-energy exit channel were available. In solution, this excess energy is rapidly dissipated to the medium, but vibrational relaxation can be made much slower in the gas-phase. Considering both the ROMP of norbornene, listed in *Table 1*, and the acyclic metathesis of ethyl vinyl ether, listed in *Table 2*, one sees that the transition state for the step **III** → **IV** must lie well above the energy of (**II** + olefin) for the first generation catalyst **1** because both the extent of ROMP of norbornene as well as the extent of either π-complex formation or acyclic metathesis of ethyl vinyl ether are very small. On the other hand, the corresponding transition state for **2** must lie very close to the energy of (**II** + olefin), especially for the reaction of ethyl vinyl ether with **2** because both ROMP of norbornene as well as π-complex formation and acyclic metathesis of ethyl vinyl ether are efficient. These conclusions are fully consistent with *Grubbs*'s NMR studies in solution, even though the techniques are completely different.

Conclusions. – We report an gas-phase experimental study of both ROMP and acyclic metathesis by first- and second-generation Ru catalysts. Starting with the 14-electron intermediate, the efficiency of the gas-phase reactions provides clear evidence that the large difference in solution-phase activity between the two systems can be attributed in large part to a difference in catalyst commitment.

REFERENCES

[1] K. J. Ivin, J. C. Mol, 'Olefin Metathesis and Metathesis Polymerization', Academic Press, New York, 1997.

[2] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858.

[3] A. Demonceau, A. F. Noels, E. Saive, A. J. Hubert, *J. Mol. Cat.* **1992**, *76*, 123; A. Mutch, M. Leconte, F. Lefebvre, J.-M. Basset, *J. Mol. Cat. A* **1998**, *133*, 191.

[4] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.

[5] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674.

[6] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1999**, *38*, 2416.

[7] S. M. Hansen, F. Rominger, M. Metz, P. Hofmann, *Chem.–Eur. J.* **1999**, *5*, 557; S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger, P. Hofmann, *Angew. Chem.* **1999**, *111*, 1360; P. Hofmann, M. A. O. Volland, S. M. Hansen, F. Eisenträger, J. H. Gross, K. Stengel, *J. Organomet. Chem.* **2000**, *606*, 88.

[8] W. Stüer, J. Wolf, H. Werner, P. Schwab, M. Schulz, *Angew. Chem.* **1998**, *110*, 3603; P. Gonzalez-Herrero, B. Weberndörfer, K. Ilg, J. Wolf, H. Werner, *Angew. Chem.* **2000**, *112*, 3392.

[9] A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem.–Eur. J.* **2000**, *6*, 1847; D. S. La, E. S. Sattely, J. G. Ford, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **2001**, *123*, 7767.

[10] M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749; M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543.

[11] C. Adhart, M. A. O. Volland, P. Hofmann, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 3306.

[12] C. Hinderling, C. Adlhart, P. Chen, *Angew. Chem., Int. Ed.* **1998**, *37*, 2685; C. Adlhart, C. Hinderling, H. Baumann, P. Chen, *J. Am. Chem. Soc.* **2000**, *122*, 8204.

[13] M. A. O. Volland, C. Adlhart, C. A. Kiener, P. Chen, P. Hofmann, *Chem.–Eur. J.* **2001**, *7*, 4621.

[14] C. Hinderling, D. A. Plattner, P. Chen, *Angew. Chem.* **1997**, *109*, 272; C. Hinderling, D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 10793; D. Feichtinger, D. A. Plattner, *Angew. Chem.* **1997**, *109*, 1796; D. Feichtinger, D. A. Plattner, P. Chen, *J. Am. Chem. Soc.* **1998**, *120*, 7175; C. Hinderling, P. Chen, *Angew. Chem., Int. Ed.* **1999**, *38*, 2253; Y. M. Kim, P. Chen, *Int. J. Mass Spectrom.* **1999**, *185–7*, 871; C. Hinderling, P. Chen, *Int. J. Mass Spectrom. Ion Processes.* **2000**, *195/196*, 377; C. Hinderling, C. Adlhart, P. Chen, *Chimia* **2000**, *54*, 232; C. Adlhart, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 2192.

[15] *Strem Chemicals Inc.*, 7 Mulliken Way, Newburyport, MA 01950-4098, USA.

[16] MATLAB, *The Mathworks Inc*, 3 Apple Hill Drive, Natick MA 01760-2098, USA.

[17] N. Calderon, H. Y. Chen, K. Scott, *Tetrahedron Lett.* **1967**, 3327.

[18] J. L. Herrison, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161; T. J. Katz, *Adv. Organomet. Chem.* **1978**, *16*, 283; N. Calderon, J. P. Lawrence, E. A. Ofstead, *Adv. Organomet. Chem.* **1979**, *17*, 449; R. H. Grubbs, W. Tumas, *Science* **1989**, *243*, 907.

[19] O. M. Aagaard, R. J. Meier, F. Buda, *J. Am. Chem. Soc.* **1998**, *120*, 7174.

[20] S. F. Vyboishchikov, M. Bühl, W. Thiel, *Chem.–Eur. J.* **2002**, *8*, 3964.
[21] L. Cavallo, *J. Am. Chem. Soc.* **2002**, *124*, 8965.
[22] C. Adlhart, P. Chen, *Angew. Chem., Int. Ed.* **2002**, *41*, 4484.
[23] P. W. Atkins, 'Physical Chemistry', 5th edn., Oxford University Press, Oxford, 1994, p. 686.
[24] M. T. Bowers, 'Gas Phase Ion Chemistry', 3 vols., Academic Press, New York, 1979–1984.

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