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$$>SiH_2 + RCH{=}CH_2 \rightarrow >SiH(CH_2)_2R \qquad (3)$$

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Olefin Metathesis of a Ruthenium Carbene Complex by Electrospray Ionization in the Gas Phase**

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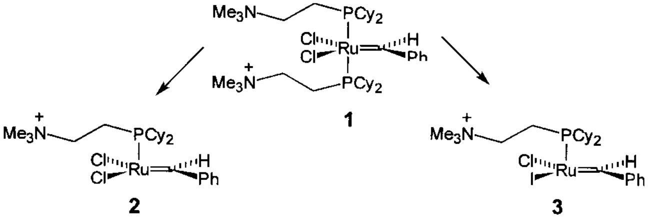
We report the direct mass spectrometric observation of an olefin metathesis reaction[1] of an acyclic alkene and the ring-opening metathesis (ROM) of cycloalkenes in the gas phase by the water-soluble ruthenium benzylidene complex **1** developed by Grubbs et al.[2] Besides constituting the first observation of olefin metathesis in the gas phase by a complex that performs the same reaction in solution, the mass spectrometric study finds and quantifies intramolecular π complexation of the penultimate double bond in the growing oligomeric chain to the metal center, and provides surprising evidence that, except for a large increase in the absolute rates, the gas phase reactions of a [RuCl$_2$(=CHPh)(PR$_2$R')$_2$] complex closely parallel the corresponding reactions in solution.

The electrospray ionization[3, 4] tandem mass spectrometric (ESI-MS/MS) experiment was performed in a modified TSQ-7000 mass spectrometer (Finnigan MAT) as described in our reports on gas-phase C–H activation[5] by [CpIr(PMe$_3$)(CH$_3$)]$^+$, oxo-transfer reactions[6] by [O=Mn^V(salen)]$^+$ (salen = *N,N'*-bis(salicylidene)ethylenediamine dianion), the Ziegler–Natta polymerization[7] of α-olefins by [Cp$_2$ZrR]$^+$, and reversible hydrogenation of olefins[8] by [Rh(PMe$_3$)$_2$]$^+$. Complex **1** was synthesized as described by Grubbs et al.[2] A 10^{-5} M solution of the diiodide salt of **1** in CH$_2$Cl$_2$ was then electrosprayed. Ions were thermalized with about 10 mTorr inert gas in the first octopole region (Scheme 1).



Scheme 1. Reactions of **1** in the mass spectrometer. Cy = cyclohexyl.

Under relatively mild desolvation conditions, that is with a tube lens potential of 44 V in front of the first octopole, the mass spectrum consisted of signals due to the dication **1**, the monocation **2**, which was formed by the loss of one phosphane ligand from **1**, and a second monocation **3** with a mass that indicated that one of the chloride ligands in **2** had been replaced with an iodide. The use of the dichloride salt of **1** instead of the diiodide eliminated **3**. As the tube lens potential was increased stepwise to 150 V, first the intensity of the peak due to **2** increased at the expense of that for **1**, and then decreased with the loss of the second phosphane (the phosphane appears in the mass spectrum because it carries the charge on its side chain), loss of trimethylamine, and loss of HCl. These fragments are consistent with the assumed structure. When 1-butene was used as the thermalization gas, a new signal with the mass corresponding to the ruthenium propylidene product **4** (loss of styrene) appeared in the spectrum as a result of an olefin metathesis reaction. Moreover, when either **1** or **2** was mass-selected in the first quadrupole, and then allowed to react with 1-butene in the second octopole, the only metathesis product we obtained in both cases was **4** (Figure 1). Complex **3** exhibited considerably lower reactivity with alkenes in comparable experiments.[9]

With cyclobutene[10] or norbornene, the new complexes **5a** ($n = 1$) and **6** ($n = 1$) were formed predominately. Their masses correspond to the adducts of **2** with the cycloalkenes, as expected for ROM products. Collision-induced dissociation (CID) of **5a** ($n = 1$) or **6** ($n = 1$) led to loss of the cycloalkene mass,[11] presumably reforming **2** (Scheme 2). Closer exami-

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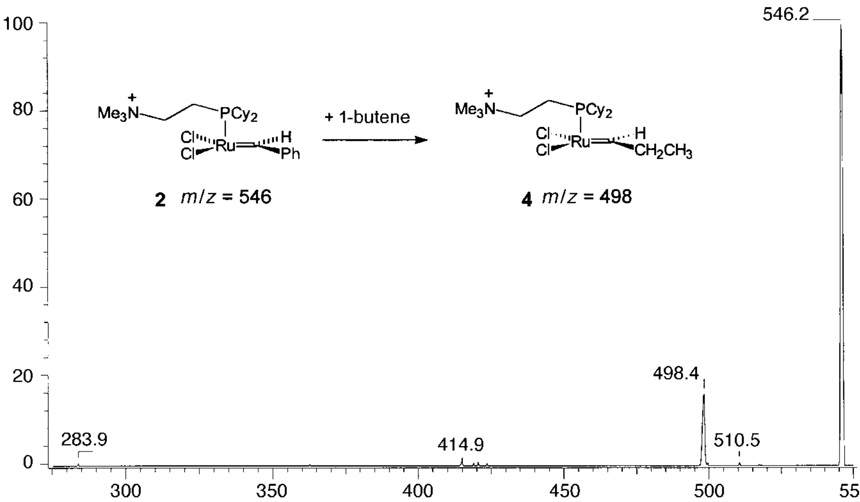
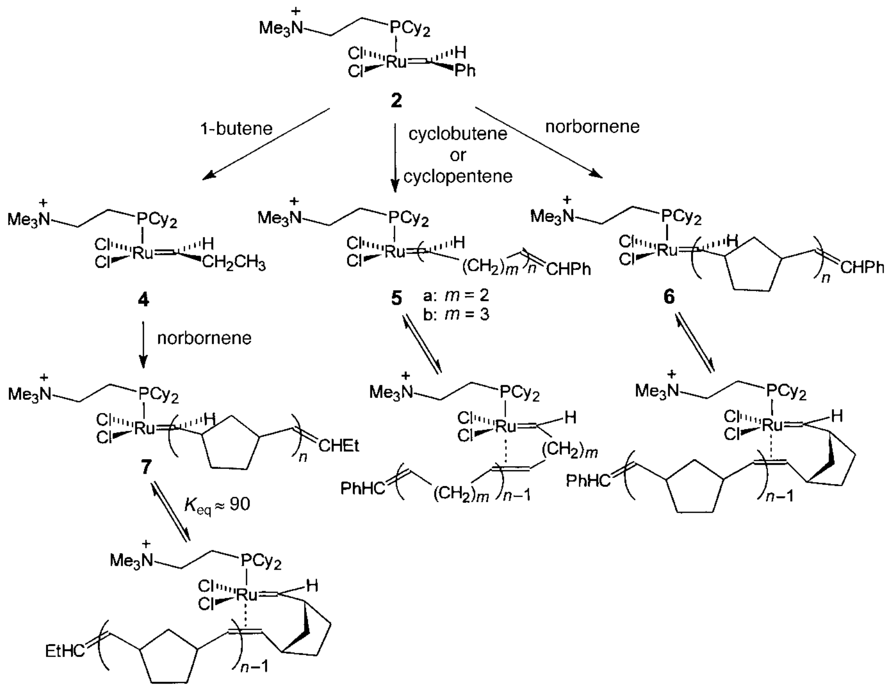


Figure 1. Daughter-ion spectrum of a dilute solution of **1** in CH_2Cl_2: Electrospray ionization was followed by desolvation, collisional removal of one phosphane ligand, and thermalization in octopole 1, mass-selection of the ion at $m/z = 546$ in quadrupole 1, reaction with 1-butene in octopole 2, and mass analysis in quadrupole 2.



Scheme 2. Reactions of **2** in the mass spectrometer.

nation of the mass spectrum produced when **2** was allowed to react with cyclobutene in the first octopole revealed a smaller peak at the mass expected for **5a** ($n = 2$), thus indicating that a second molecule of cyclobutene had added. This prompted a comparison of 1-butene with cyclobutene, cyclopentene, and norbornene, in which **2** was mass-selected in the first quadrupole and then collided with the alkenes (10 mTorr) in the octopole collision cell. These experiments gave product distributions from which the relative rates (Table 1) were extracted by kinetic modeling of the multiple additions of the cycloalkenes.[12] Addition of up to three cycloolefin units was established; the last adducts were observed in a segmented-scan mode. In order to probe the electronic influence of an alkyl versus aryl residue on the ROM reaction, **4**, generated in the first octopole by reaction of **2** and 1-butene, was mass-selected and then collided with norbornene in the collision cell under the same conditions.

Several mechanistic points can be made from the data, even without the more thorough thermochemical measurements (by CID reaction thresholds[13]) that are possible with the present instrument.[5] Electrospray ionization of medium-to-large organometallic complexes has been reported,[14, 15] but has not been combined systematically[16] with the broad range of ion–molecule reaction techniques available for mechanistic work on small gas phase organometallic ions.[17] Other workers investigating ion–molecule reactions have observed olefin metathesis with several simple metal carbenes,[18] for example $[Mn{=}CH_2]^+$, $[Fe{=}CH_2]^+$, and $[Co{=}CH_2]^+$. Most of the metatheses have been observed with deuterated ethylene. The present result constitutes, however, the first instance in which a solution-phase olefin metathesis catalyst has been shown to effect the same reaction in the gas phase.

Absolutely critical to the significance of the experiment is the extent to which the gas-phase and solution-phase reactions resemble each other: many features that appear in solution-phase metathesis reactions (or at least the trends) also appear in the gas-phase reactions. Dissociation of one phosphane ligand from complex **1** is a prerequisite for metathesis

Table 1. Relative rate constants, normalized to the **2**→**4** reaction.[a]

Reaction	Relative rates (relative intensities)		
	$k_{0\to1,\,\text{rel}}$	$k_{1\to2,\,\text{rel}}$	$k_{2\to3,\,\text{rel}}$
2 + 1-butene→**4**	1.0 (0.150)	NA	NA
2 + cyclopentene→**5b**	0.01 (0.0015)	–	–
2 + cyclobutene→**5a**	13 (4.86)	0.03 (0.0151)	–
2 + norbornene→**6**	15 (7.32)	0.01 (0.00678)	–
4 + norbornene→**7**	9 (2.53)	0.1 (0.0238)	0.1 (0.000154)

[a] Extracted by kinetic modeling of the peak intensities for the addition of the first, second, and third alkene units to either **2** or **4** to form **4**–**7**. The peak intensities, given in parentheses, are relative to the intensity of either **2** or **4** in the respective daughter-ion spectrum. (NA = not applicable; – indicates not observed).

1433-7851/98/3719-2686 $ 17.50+.50/0

reactions both in the gas phase and in solution,[19] as evidenced by the presence of products like **4** and the complete absence of metathesis products containing two of the phosphane ligands. The gas-phase ion **2** shows no metathesis reactivity with carbonyl compounds, which agrees with the behavior observed in solution.[20] The metathesis product of the reaction of **2** with 1-butene is the ruthenium–propylidene complex **4**, and not the alternative ruthenium–methylene complex. Within the signal-to-noise ratio of about 100:1 in a normal scan spectrum (10000:1 can be achieved in segmented-scan mode), the other possible product is absent. We believe that this represents a kinetic preference in the metathesis reaction which becomes evident because of reaction under nonequilibrating conditions. Precisely the same kinetic preference was reported by Grubbs et al.[21] in the reaction of $[RuCl_2(=CHPh)(PCy_3)_2]$ with 1-butene in solution; studies showed that this initially forms the propylidene complex before equilibrating to the thermodynamically favored methylene complex. As is evident in Table 1, ROM of the first cycloalkene unit is much easier than subsequent additions, which is entirely consistent with the observation by Grubbs et al.[21] that the ruthenium–benzylidene complexes in ROMP reactions in solution showed rates of initiation much greater than the subsequent rates of propagation (the ratio k_i/k_p is 9 for norbornene at 17 °C.)

The gross trends in the relative rates in the present work are rationalized by invoking an intramolecular π complex between the metal center and the penultimate double bond, once at least one cycloalkene unit has added to either **2** or **4**. Exactly this type of π complex[22] has been observed for ruthenium[23] and tungsten[24] carbene complexes by X-ray crystallography, and, furthermore, has been proposed to explain the *cis* selectivity[25] in ROMP as well as relative rates in both ROMP[26]and ADMET[27] reactions. We can interpret the reactivity pattern of **2** with 1-butene, cyclobutene, cyclopentene, and norbornene by assuming that addition of further cycloalkene units to the uncomplexed metal center is in competition with intramolecular π complexation. Patton and McCarthy[26] have suggested that this π complex precedes the metallocyclobutane on the reaction coordinate for the reverse reaction (loss of cycloolefin with regeneration of **2**). We propose that cyclobutene and norbornene exhibit the highest rates because the short and/or rigid spacer in **5a** or **6** disfavors π complexation. The longer, more flexible methylene chain in **5b**, on the other hand, favors intramolecular π complexation; it inhibits further addition and facilitates the loss of cyclopentene. In this picture, the apparent rate for the reaction **2**→**5b** is so low because the ROM of cyclopentene is easily reversible, not because it is intrinsically slow. The second and subsequent ROM additions are always slower than the first because the reactions going from $n=0$ to $n=1$ for all of the entries in Table 1 lack the preequilibria that slow the subsequent additions. The benzylidene complex **2** is more reactive, presumably on electronic grounds, than the propylidene complex **4** in the addition of the first norbornene unit. However, in the next addition, **6** ($n=1$) is slower than **7** ($n=1$) even though the only structural difference (an aryl versus an alkyl residue at the end of the chain) is remote from the metal center. The reduced reactivity of **6** ($n=1$) versus **7** ($n=1$) most likely stems from the better donor properties of a styryl group relative to a simple olefin. This property facilitates π complexation and thus adds a less favorable preequilibrium to the overall rate of the next addition. Lastly, we can take the reduction in the rate for adding one more norbornene unit between **4** and **7**, as the equilibrium constant for intramolecular complexation ($K_{eq} \sim 90$ or $\Delta G_{diss.} \approx 3\,kcal\,mol^{-1}$ at 70 °C). This is possible because the electronic influence of the alkylidene ligands in **4** and **7** should be comparable. We are currently working on generalizing this kinetic method for determining the equilibrium constant so that we can explore systematically the steric and electronic effects on the complexation.

The absolute rate is the exception to the overall similarity of the gas phase and solution-phase reactions. As in the case of the Ziegler–Natta polymerization by unsolvated metallocene cations,[7] the olefin metathesis and ROM reactions reported here are accelerated by up to a factor of about 10^4 relative to the reactions in solution described by Grubbs and co-workers.[21] The gas-phase second-order rate constant was estimated by comparing measured product yields for reaction in the second octopole to the computed number of total collisions (reactive and nonreactive). These values were obtained from a Monte–Carlo simulation of ion transmission through a "high-pressure" octopole.[7] The model was validated by comparison of the computed versus measured ion residence time in the octopole collision cell.[28] While the absence of any external preequilibria[29] with solvent molecules or free phosphane, as well as the absence of ion-pairing effects, certainly contribute, the rate acceleration can be attributed at least in part to the ion dipole or ion-induced dipole interaction common to all ion–molecule reactions. These interactions can provide up to $10\,kcal\,mol^{-1}$ towards passage over an activation barrier for a bimolecular reaction.[30] The rate increase is not large enough to render the metathesis reactions of **2** diffusion-controlled as evidenced by the solution-phase reactivity differences which are still displayed in the gas-phase reactions. An increase in absolute rates that nevertheless preserves relative rates, as observed for the metathesis reaction, differs from the result in the typical organic ion–molecule reactions,[30] for example S_N2 or proton-transfer reactions. This result occurs presumably because of the absence of large changes in charge distribution along the metathesis reaction coordinate, despite the fact that the molecule is charged.

Lastly, in the ROM reaction of **2** and **4** with the cycloalkenes, one could have been worried that the complexes with masses corresponding to **5a**–**7** might be *intermolecular* π complexes rather than ROM products. Two lines of argument indicate, however, that they are in fact ROM products: a) The reaction of **2** and an acyclic olefin, 1-butene, in the mass spectrometer clearly involves an olefin metathesis. It would be curious, then, if ROM did not occur for cycloalkenes whose metathesis rates are typically not too dissimilar from those for acyclic alkenes.[31] b) The relative rates in Table 1 are consistent with a ROM reaction. Moreover, Patton and McCarthy[26] state that norbornene is more readily lost from an intermolecular π complex than is cyclopentene, which is precisely the opposite from the ordering in the present work.

Further investigations on the selectivity and thermochemistry of the reaction are planned. Applications of this method to anionic molybdenum and tungsten carbene ROMP catalysts,[32] for which the catalytically active species are not well-characterized, will also be explored.

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Gemini Surfactants as New, Low Molecular Weight Gelators of Organic Solvents and Water[**]

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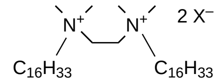
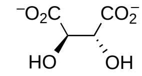
During the last decade a number of reports have described the solution-state self-assembly of small molecules into elongated aggregates such as rods, ribbons, helices, or tubules. When these structures are sufficiently long and entangled they may entrap the solvent molecules in a network and lead to the formation of gels.[1] Although the organization of the aggregates has rarely been elucidated at the molecular level,[2] it is generally agreed that the process of aggregate elongation in water or in organic solvents arises from one or more of several factors: the presence of chiral centers often induces helicity and decreases the crystallinity observed for racemates;[1] directional attractive interactions such as hydrogen bonding[3] or face-to-face $\pi-\pi$ aromatic stacking[4] help generate linear arrays of molecules. In gemini[5] (dimeric) surfactants, covalent connections between charged head groups were also shown to promote the formation of wormlike micelles and tubules in water.[6, 7] Herein we show that head-group connection also allows gemini surfactants to gel organic solvents upon their assembly into aggregates similar to those formed in water.

Compounds **1**–**5** consist of dimers of cetyltrimethylammonium ions (CTA) with various counterions. Compounds **1** and **2** form gels in chlorinated solvents (CH_2Cl_2, $CHCl_3$, $Cl_2CHCHCl_2$) that remain unchanged after several months. At temperatures above 40 °C the solutions are completely transparent and fluid. They become translucent and viscous upon standing for several hours at 25 °C. The solvent thickening is so efficient that a gel as dilute as 10 mM (gel point for $CHCl_3$) in a 1 cm diameter test tube can be turned upside down without any flow. This means that one molecule of **1** entraps about 1200 molecules of $CHCl_3$. At concentrations lower than the gel point a gel phase separates, and leaves a layer of free solvent.

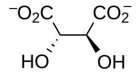


1 – 5

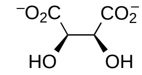
1 : 2X⁻ = L-tartrate
2 : 2X⁻ = D-tartrate
3 : 2X⁻ = *meso*-tartrate
4 : 2X⁻ = L-malate
5 : 2X⁻ = 2 Br⁻



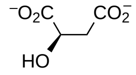
L-tartrate



D-tartrate



meso-tartrate



L-malate

When warm solutions of **1** and **2** are mixed in equimolar proportions no gel forms, and the racemate partially precipitates. The *meso* derivative **3** is poorly soluble in chlorinated solvents, and does not form gels either. Thus, for this system, chirality seems essential for gel formation. The gels are easily disrupted upon the addition of alcohols (5–10% volume%) which suggests that hydrogen bonding also plays a role in gel cohesion. The importance of hydrogen bonds is supported further by the fact that **4**, which lacks one of the hydroxyl groups of **1**, does not form gels with organic solvents. Nevertheless, the residual quantities of water[8] contained in a freshly opened bottle of solvent are necessary to partially solvate the polar groups. In anhydrous solvents **1** and **2** tend to crystallize instead of forming gels.

The most probable structure for these gels is thus an entangled network of long fibers with polar groups at the core of the aggregate, and nonpolar hydrocarbon chains in contact with the solvent, like in an inverted long micelle, or in an inverted ribbon.[9] Yet, hydrogen bonding and chirality are not sufficient to explain the formation of the fibers, and head-group connection between the ammonium ions also plays a critical role. Indeed, the monomeric form $(CTA)_2$-L-tartrate is freely soluble in chlorinated solvents, and does not form gels. In water, hydrophobic effects dominate the process of surfactant aggregation. Short and rigid covalent connections enforce proximity between charged head groups that would otherwise repulse each other. The result is a change in the spontaneous curvature of the water–surfactant interface, as under the screening effect of salt[10] or of a hydrophobic counterion.[11] In nonpolar media the aggregation is directed by electrostatic forces. A possible effect of head-group connections is the reciprocal bridging of bisanions and biscations, a prerequisite to the assembly of a noncovalent polymeric material.[12]

The texture of the gels were examined with transmission electron microscopy (TEM). The images revealed very regular and long helical fibers (Figure 1A). The pitch is 130 nm for a fiber with a width of 20 nm and a length exceeding one micron. The L-tartrate **1** gives exclusively right-handed helices, and its enantiomer **2** gives left-handed helices. These helices are strongly entangled, and sometimes pack into parallel domains. Although the TEM images do not show the inner structure of the helices, their thickness indicate that they are superstructures, probably consisting of stacked rods or ribbons.

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