

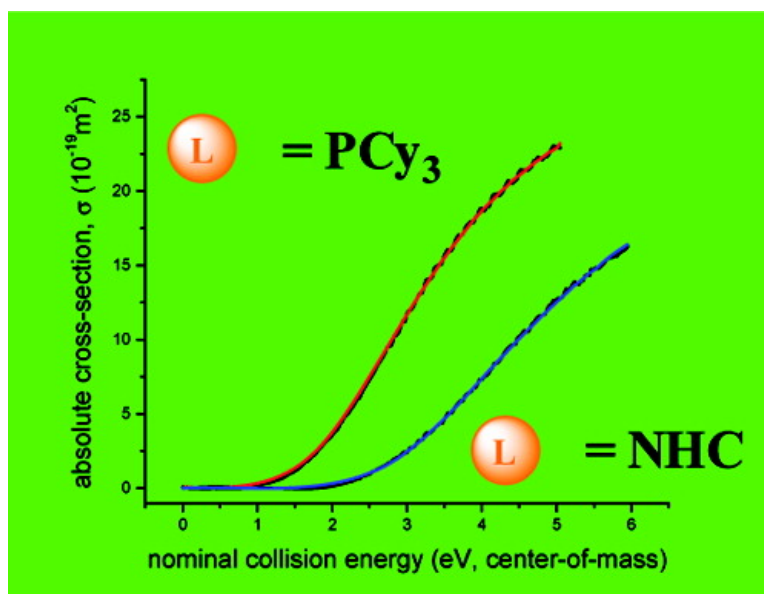
Article

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## Gas-Phase Thermochemistry of Ruthenium Carbene Metathesis Catalysts

Sebastian Torker, Daniel Merki, and Peter Chen\*

Laboratorium für Organische Chemie, ETH Zürich, Wolfgang-Pauli-Strasse 10,  
CH-8093 Zürich, Switzerland

Received October 24, 2007; E-mail: peter.chen@org.chem.ethz.ch

**Abstract:** Quantitative energy-resolved collision-induced dissociation cross-sections by tandem ESI-MS provide absolute thermochemical data for phosphine binding energies in first- and second-generation ruthenium metathesis catalysts of 33.4 and 36.9 kcal/mol, respectively. Furthermore a study of the ring-closing metathesis in the second-generation system to liberate norbornene by forming the 14-electron reactive intermediate from the intramolecular  $\pi$ -complex gives an estimate of the olefin binding energy to the 14-electron complex of around 18 kcal/mol, assuming a loose transition state. The results reported here are in remarkably good agreement with the latest DFT calculations using the M06-L functional.

### Introduction

Quantitative thermochemistry of organometallic complexes involved in homogeneous catalysts is central to clear mechanistic thinking and catalyst design and, at the same time, uncommon because many of the experimental approaches, for example, reaction calorimetry, fail for solutions where the catalysts themselves may be part-per-thousand to part-per-million components in a complex reaction system with many other complexes and substrates simultaneously present in much higher concentrations. We have in recent years prepared the active species in catalytic cycles by a combination of chemical synthesis, electrospray ionization, and gas-phase ion–molecule reactions in a tandem mass spectrometer.<sup>1</sup> In many cases, the gas-phase chemistry resembled the reactions in solution, providing experimental data for mechanistic models and quantum chemical studies. Among the reactions we have investigated with these techniques is the olefin metathesis reaction,<sup>2</sup> catalyzed by ruthenium carbene complexes.<sup>3</sup> While the mass spectrometric experiments proved informative, specifically with respect to the reactivity of the 14-electron reactive intermediate, the methods and the analysis suffered from the inability of the experiment to produce absolute activation energies and reaction thermochemistry for the elementary steps observed in the mass spectrometer.

We report here the experimental measurement of the activation energies for phosphine dissociation and ring-closing metathesis for cationized Grubbs first and second-generation catalysts, **1** and **3**, in the gas phase, by deconvolution of the

energy-resolved collision-induced dissociation cross-sections of electrosprayed ruthenium carbene complexes. The gas-phase energetics are consistent with the most recent quantum chemical calculations as well as solution-phase results if one factors in observed trends in solvation.

### Experimental Section

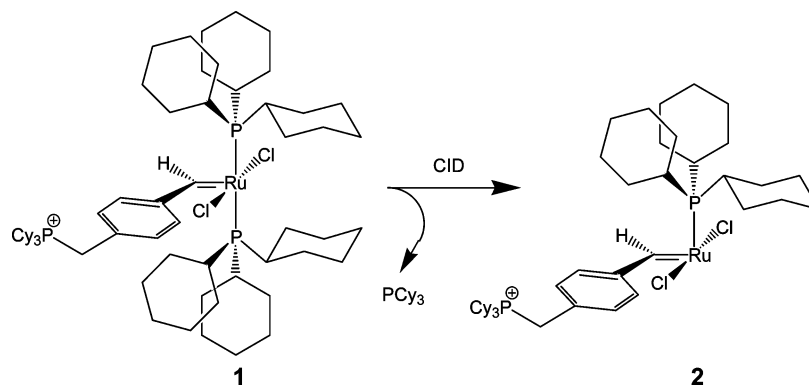
**General Remarks.** Unless otherwise stated, all manipulations were carried out under an argon atmosphere on a vacuum line using standard Schlenk techniques. The solvents were dried by distillation from the following drying agents prior to use and were transferred under N<sub>2</sub>: diethyl ether (Na/K), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), acetonitrile (CaH<sub>2</sub>). 1,2-Dichlorobenzene was deoxygenated by N<sub>2</sub> bubbles and dried with molecular sieves (3 Å). Low-resolution ESI-MS measurements were done on a Finnigan MAT TSQ Quantum mass spectrometer. NMR measurements are reported for a Varian Mercury XL 300 (<sup>1</sup>H: 300 MHz, <sup>31</sup>P: 121 MHz) spectrometer. Chemical shifts ( $\delta$ -values) are reported in ppm with respect to Me<sub>4</sub>Si ( $\delta = 0$  ppm), used as an internal standard for <sup>1</sup>H NMR, and an 85% aqueous H<sub>3</sub>PO<sub>4</sub> solution, used as an external standard for <sup>31</sup>P NMR. Coupling constants (*J*) are given in hertz. <sup>31</sup>P NMR spectra were proton broad-band-decoupled. The multiplicities of peaks are denoted by the following abbreviations: s: singlet, d: doublet, dd: double doublet, m: multiplet.

**Syntheses. Tricyclohexyl(4-vinylbenzyl)phosphonium Chloride.**<sup>4</sup> Tricyclohexylphosphine (0.99 g, 3.53 mmol) was dissolved in acetonitrile (4 mL) in a Teflon-valve sealed bomb, and 4-vinylbenzyl chloride (0.54 g, 3.55 mmol) was added. The reaction mixture was stirred at 80 °C for 3 days. The solvent was removed *in vacuo*, the pale yellow sticky residue was dissolved in chloroform (2 mL), and diethyl ether (15 mL) was added dropwise to force precipitation. In the beginning, a sticky precipitate was formed at the bottom, and after a few minutes of stirring, a fine white powder also precipitated. This powder was separated by decantation followed by filtration and was dried *in vacuo* for 4 h: 0.92 g (67%). (The sticky residue was analyzed separately and it turned out to be mostly the same as the white powder, but it was not used any further.)

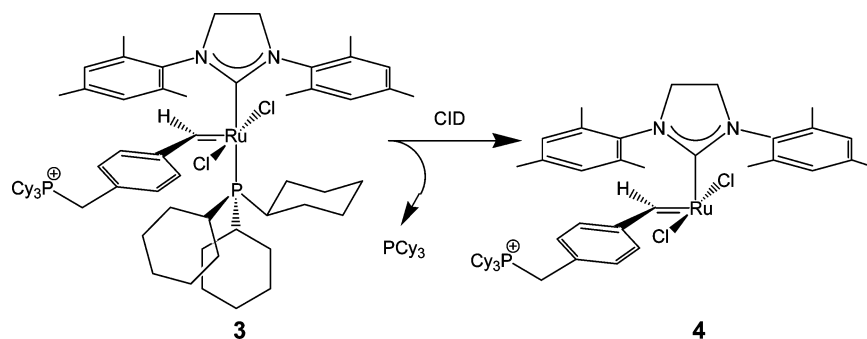
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Scheme 1



Scheme 2



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.38$  (s, 4H, HAR), 6.67 (dd,  $J = 17.6$  Hz, 11.0 Hz, 1H, olefinic), 5.75 (d,  $J = 17.7$  Hz, 1H, olefinic), 5.28 (d,  $J = 10.8$  Hz, 1H, olefinic), 4.36 (d,  $J = 14.4$  Hz, 2H), 2.74 (q,  $J = 6.0$  Hz, 3H, HCy), 1.88 (m, 15H, HCy), 1.37 (m, 15H, HCy).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta = 29.8$  (s, 1P). MS (ESI,  $\text{CH}_2\text{Cl}_2$ ): 397 (100,  $\text{M}^+$ ), 830 (9,  $[\text{2M}^+ + \text{Cl}^-]^+$ ), 117 (6,  $[\text{M}^+ - \text{PCy}_3]^+$ ).

$[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(p\text{-CH}_2\text{PCy}_3\text{Ph})]^+\text{Cl}^-$ , **1**. Grubbs first generation catalyst (100 mg, 0.12 mmol) and tricyclohexyl(4-vinylbenzyl)phosphonium chloride (40 mg, 0.09 mmol) were dissolved in dichloromethane (6 mL). This mixture was allowed to stir at room temperature for 20 min. The solvent was removed *in vacuo*, and the formed styrene was coevaporated with 1,2-dichlorobenzene ( $7 \times 2$  mL) to shift the equilibrium. Furthermore dichloromethane ( $2 \times 2$  mL) was added to remove residual 1,2-dichlorobenzene, and the residue was dried *in vacuo* overnight. After dissolving in dichloromethane (1 mL), diethyl ether (15 mL) was added dropwise to force precipitation. The mixture was filtered, and the purple solid was dried *in vacuo*: 68 mg (64%).

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 20.02$  (s, 1H, carbene), 8.53 (s, 2H, HAR), 7.47 (s, 2H, HAR), 4.19 (d,  $J = 13.8$  Hz, 2H), 2.69 (m, 9H, HCy), 1.84 (m, 45H, HCy), 1.28 (m, 45H, HCy).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 37.1$  (s, 2P, phosphine), 27.9 (s, 1P, phosphonium). MS (ESI,  $\text{CH}_2\text{Cl}_2$ ): 836 (100,  $[\text{M}^+ - \text{PCy}_3]^+$ ), 1118 (55,  $\text{M}^+$ ), 383 (41,  $[\text{stilbene derivative}]^{2+}$ ).

$[(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CH}(p\text{-CH}_2\text{PCy}_3\text{Ph})]^+\text{Cl}^-$ , **3** was prepared from Grubbs second generation catalyst (51 mg, 0.06 mmol) and tricyclohexyl(4-vinylbenzyl)phosphonium chloride (21 mg, 0.05 mmol) according to the above procedure which yielded a dark purple, fine powder after drying *in vacuo* overnight: 39 mg (67%). The product was not as clean as **1** due to the higher metathesis activity of second generation systems and thus giving a considerable amount of stilbene side products. The quality however was sufficient for MS experiments where the ions were totally separated.

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , only downfield region):  $\delta = 19.22$  (s, 1H, carbene).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 30.5$  (s, 1P, phosphine), 27.8 (s, 1P, phosphonium). MS (ESI,  $\text{CH}_2\text{Cl}_2$ ): 862 (100,  $[\text{M}^+ - \text{PCy}_3]^+$ ), 1144 (35,  $\text{M}^+$ ), 384 (34,  $[\text{carbene}]^+$ ).

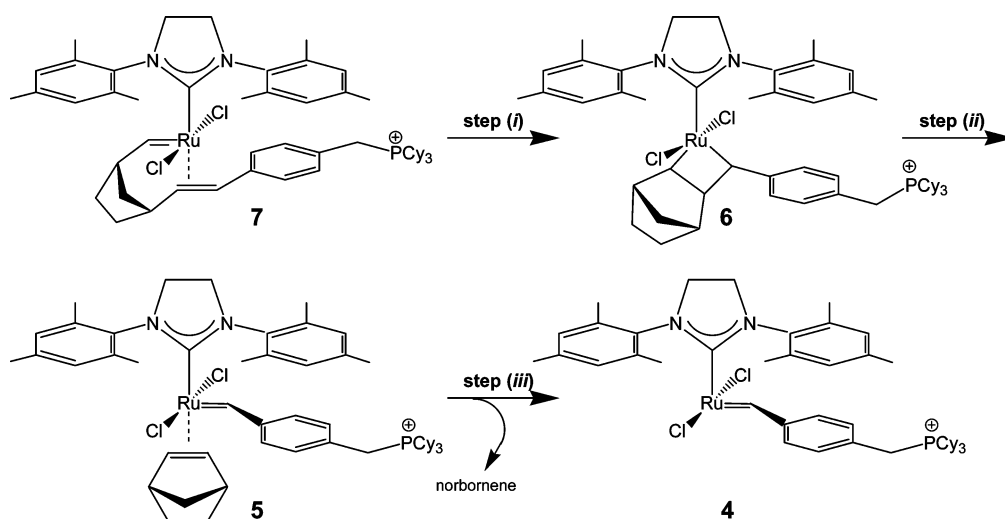
**T-CID Experiments.** Dilute solutions ( $10^{-5}$  mol/L) of the charged complexes in  $\text{CH}_2\text{Cl}_2$  were freshly prepared in a glovebox. All measurements were performed on a Finnigan MAT TSQ-700 tandem mass spectrometer modified by replacement of the transfer octopole in the original triple quad instrument with a long radiofrequency 24-pole ion guide, which was run at gas pressures of 5 mTorr argon or norbornene for thermalization to the 70 °C manifold temperature or reaction. No external field is applied, and the ions move through the ion guide because of a weak longitudinal potential induced by the space charge from the continuous beam of incoming ions. The principle significance of this modification is the achievement of a well-defined, narrow distribution of the ions' kinetic and internal energies. The ions were selected in the first quadrupole and then injected into the octopole collision cell where they undergo CID with Argon at low pressures (30, 50, 70, and 90  $\mu\text{Torr}$ ) before mass analysis in the second quadrupole. The instrument has been described previously.<sup>5c</sup>

## Results

Collision-induced dissociation (CID) of electrosprayed complexes<sup>5</sup> provides access to two of the important elementary reactions in olefin metathesis: the initial dissociation of the phosphine ligand to produce the key 14-electron intermediate (Schemes 1 and 2), and ring-closing metathesis of a carbene complex with a pendant olefinic moiety (Scheme 3). Daughter-ion spectra produced by CID of mass-selected parent ions are shown in Figures 1–4. The suitability of a given CID process for the subsequent energy-resolved CID cross-section measurements can be read off of the spectra in Figures 1–4 in a straightforward manner. The present deconvolution procedure, implemented in the L-CID program,<sup>6</sup> can handle one or two

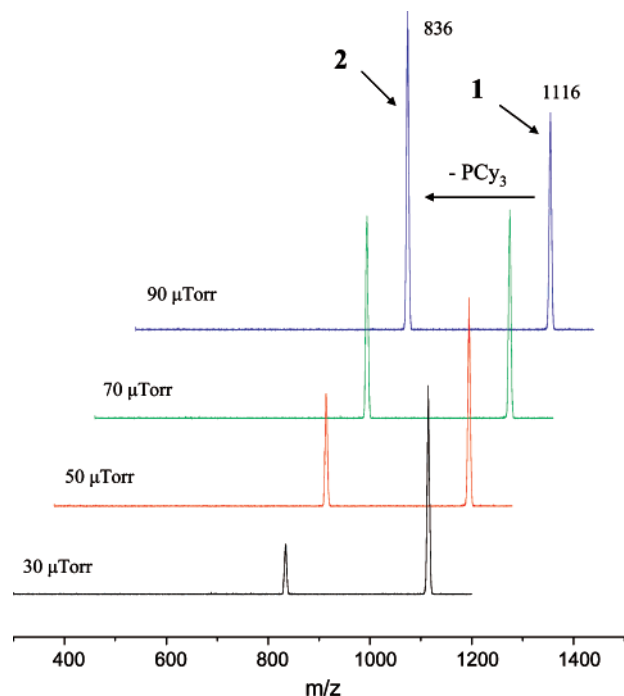
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Scheme 3

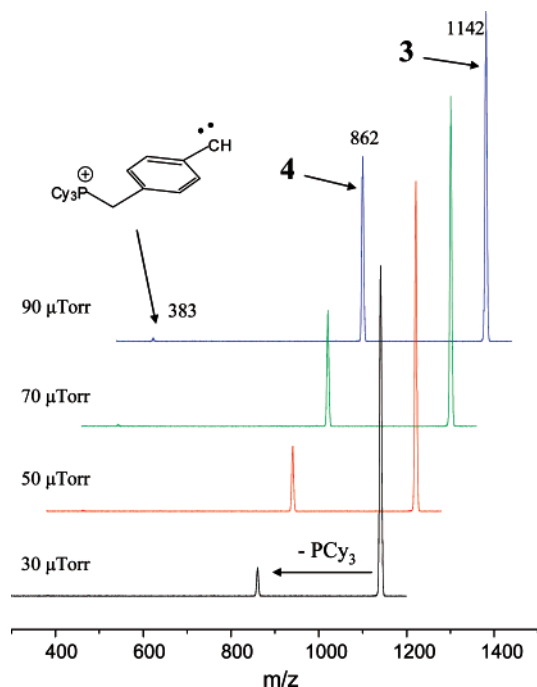


parallel dissociation channels. Moreover, there should be no major loss processes other than the CID process under investigation. In an important control experiment with the bis (dicyclohexylethyl) analog of **1**, only loss of PCy<sub>2</sub>Et was seen upon CID, indicating that the PCy<sub>3</sub> lost from **1** was one of the ligands on ruthenium and not a loss of the charge label from the carbene moiety. The CID curves at progressively lower collision gas pressure are shown in the Supporting Information. Extrapolation to zero pressure and deconvolution with L-CID produces the energy-dependent cross-sections depicted in Figures 5 and 6. As had been discussed in our previous work,<sup>6</sup> the deconvolution itself cannot distinguish between a tight and loose transition state. In the cases examined thus far, either assumption can yield a statistically acceptable fit. Nevertheless, as will be seen below, chemical arguments usually do lead to

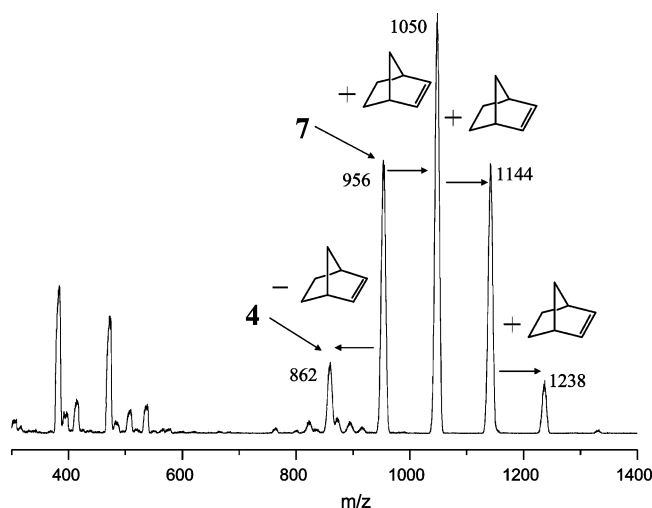
an unambiguous transition state model. It should also be noted that L-CID requires as input the number of free rotors in the molecule. While the number of free rotors is relatively easy to ascertain for the N-heterocyclic carbene (NHC) ligand, the same cannot be said for tricyclohexylphosphine in a metathesis catalyst because of strongly hindered rotations.<sup>7</sup> Accordingly, we performed a sensitivity analysis in which the number of rotors was run from zero up to the number that would include all groups that could formally rotate around a single bond. We observed that there is a modest difference in the deconvoluted  $E_0$  as the number of rotors increases from zero to moderate values, such as 6 for ions as large as the metathesis catalysts, but even that small effect of additional rotors diminishes rapidly as the number of rotors is further increased. Almost no dependence on the number of rotors is observed with a tight transition state assumption. The end effect is a minor increase



**Figure 1.** Daughter spectra of **1** ( $m/z = 1116$ ) at a collision offset of  $-25$  eV at different pressures of xenon (30, 50, 70, and 90  $\mu\text{Torr}$ ) in the octopole collision chamber. Comparable spectra are obtained with argon at collision energies of about  $-100$  eV.



**Figure 2.** Daughter spectra of **3** ( $m/z = 1142$ ) at a collision offset of  $-25$  eV at different pressures of xenon (30, 50, 70, and 90  $\mu\text{Torr}$ ) in the octopole collision chamber. Comparable spectra are obtained with argon at collision energies of about  $-100$  eV.



**Figure 3.** Mass spectrum after spraying compound **3** from DCM ( $m/z = 1142$ ) and reaction at 5.7 mTorr of norbornene in the 24-pole ion guide.

in the uncertainty bounds for  $E_0$ . The final results for the three reactions in Schemes 1–3 are listed in Table 1, along with fitting parameters and assumptions. For the dissociative activation reaction of the first-generation catalyst,  $\mathbf{1} \rightarrow \mathbf{2} + \text{PCy}_3$ , we take  $E_0$  for the loss of tricyclohexylphosphine to be  $1.45 \pm 0.1$  eV, or  $33.4 \pm 2.3$  kcal/mol for a loose transition state. The comparable reaction for the second-generation system,  $\mathbf{3} \rightarrow \mathbf{4} + \text{PCy}_3$ , shows  $E_0 = 1.60 \pm 0.1$  eV, or  $36.9 \pm 2.3$  kcal/mol, also for the loose transition state. The comparable dissociation energies, assuming tight transition states, are 0.84 and 0.96 eV, respectively. The error bounds contain the uncertainty of the fit due to the statistical scatter of the data points and day-to-day fluctuations in calibration and operation of the mass spectrometers. One accordingly can claim with confidence that, although the listed ranges of the two dissociation energies just overlap, the difference between them,  $\sim 0.15$  eV or  $\sim 3.5$  kcal/mol, is real and can be reproduced. Comparable measurements published for copper complexes clearly show the ability to distinguish reliably between dissociation thresholds that differ by 0.1 eV.<sup>8</sup> For the ring-closing metathesis, or backbiting reaction,  $\mathbf{7} \rightarrow \mathbf{4} + \text{norbornene}$ , the CID was only clean enough for a reliable fit in the case of the second-generation catalyst, shown in Scheme 3. Side reactions in the first-generation system increased the number of significant channels beyond what L-CID could reliably handle. The measured threshold energy is  $E_0 = 1.45$  or  $0.79 \pm 0.1$  eV ( $33.4$  or  $18.2 \pm 2.3$  kcal/mol) depending on whether the transition state is modeled as loose or tight.

An approximation to the reaction coordinate by means of a linear synchronous transit at the BP86/ZORA-TZP level of theory using ADF 2006 showed neither credible evidence for a reverse barrier in the dissociation reaction nor any indication of a rate-determining development of an intramolecular agostic interaction in the reaction,  $\mathbf{1} \rightarrow \mathbf{2} + \text{PCy}_3$ , which suggests strongly that the dissociation of a phosphine should be treated with a loose transition state as has been argued in other reports.<sup>9</sup> The energy profiles, as well as the coordinates and energies along the dissociation path, are given in the Supporting Information.

## Discussion

Olefin metathesis presented a broad range of mechanistic problems, of which many have been addressed using a variety of experimental and computational methods.<sup>2</sup> It is generally agreed now that the initial ligand exchange of the tricyclohexylphosphine for the olefin substrate, the initiation step in catalysis, occurs by way of a dissociative mechanism via a 14-electron intermediate ruthenium carbene complex. The best current quantum chemical calculations support this mechanism.<sup>10</sup> The strongest experimental evidence comes from the series of kinetic and NMR experiments by Grubbs and co-workers in which the enthalpies, and more importantly, the entropies of activation were measured.<sup>11</sup> A key recognition from that work was, that despite being strong  $\sigma$ -donors, the NHC-ligands in the second-generation catalysts do not labilize a tricyclohexylphosphine in the trans position when the corresponding first-generation system is taken as a reference. Effectively, the conclusion is that the first- and second-generation catalysts operate by similar mechanisms but with different rate-determining steps.<sup>12</sup> For a simple, near-thermoneutral cross-metathesis, the ligand exchange, olefin for phosphine, is rate-limiting in the second-generation catalysts, whereas the rate-determining step in the first-generation catalysts occurs later within the sequence of reactions defining the metathesis itself. The recognition matters a great deal in attempts to design stereo-, regio-, or chemoselectivity into a catalytic metathesis reaction. Our chemoselective catalyst for alternating copolymerization of two different cyclic olefins was built on a first-generation chassis for precisely this reason.<sup>13</sup> Under these circumstances, the amount of quantitative data on the elementary steps in olefin metathesis is surprisingly small, the paucity being attributable to technical difficulties in doing detailed kinetic and thermochemical experiments on low-abundance intermediates in a catalytic cycle. The activation parameters from Grubbs are the only extant experimental data.

Being able to directly manipulate in the gas phase some of the reactive intermediates in homogeneous catalytic cycles, we believed that it should be possible to obtain quantitative kinetic and thermochemical data for key elementary steps in the olefin metathesis reaction by means of energy-resolved CID cross-section measurements. Unfortunately, the deconvolution of the experimental curves had not been possible for species of the size and complexity of the first- and second-generation ruthenium metathesis catalysts, but we have recently produced a deconvolution program, L-CID,<sup>6</sup> which is generally applicable to the treatment of CID thresholds for organometallic ions of the size and structural complexity commonly found in homogeneous catalysis.

Application of L-CID to the energy-resolved CID cross-section curves produced the activation energies for phosphine loss from both the first- and second-generation ruthenium metathesis catalysts, which, in the case of no reverse barrier, correspond to the ligand binding energies. While the data analysis itself can be done for either a loose or a tight transition state, one would expect a loose transition state for a simple

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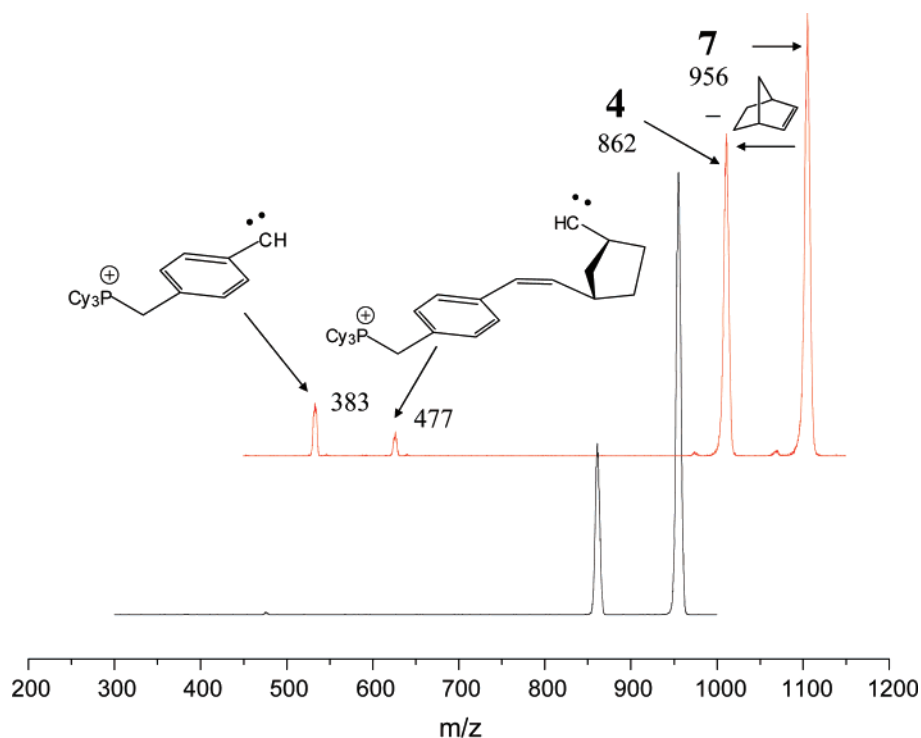
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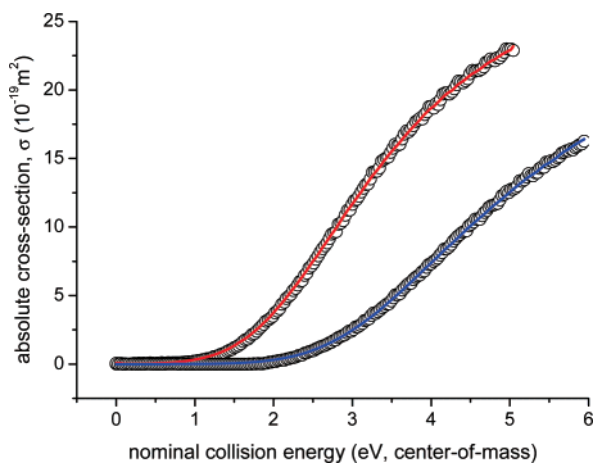
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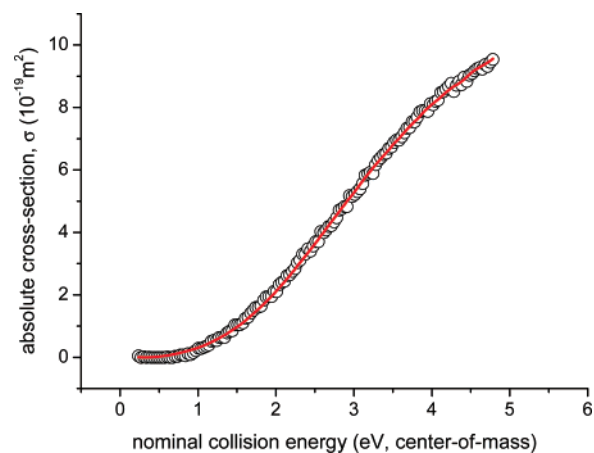


**Figure 4.** Daughter spectrum of **7** ( $m/z = 956$ ) at a collision offset of  $-60$  (bottom) and  $-120$  eV (top) at a pressure of  $90 \mu\text{Torr}$  of argon in the octopole collision chamber. The latter energy was the highest energy taken for the fit. It is evident that new dissociation channels open at the highest energies. At lower collision energies used in the deconvolution of the threshold, only negligible amounts of second and third channel products (cleavage of the C–Ru bond;  $m/z = 383$  and  $477$ ) are formed.



**Figure 5.** Energy-dependent cross-section curves after extrapolation to zero pressure and deconvolution with L-CID for processes **1**  $\rightarrow$  **2** (red) and **3**  $\rightarrow$  **4** (blue).

ligand dissociation. Grubbs entropies of activation also indicate a loose transition state. We nevertheless considered the possibility that there could be an intramolecular formation of an agostic bond, either preceding or synchronous with phosphine departure, which could lead to a rate-determining transition state that would be tight. We had been alerted to the possibility of an intramolecular agostic bond by structural distortions in the X-ray structures of many of the ruthenium carbene complexes.<sup>13</sup> The reaction coordinate, approximated by a linear synchronous transit, showed no evidence for the incipient formation of an agostic bond, and there was furthermore no evidence for a reverse barrier along the energy profile, all of which indicates that the treatment of the phosphine departure via a loose transition state is very likely to be correct. The threshold energies



**Figure 6.** Energy-dependent cross-section curve after extrapolation to zero pressure and deconvolution with L-CID for process **7**  $\rightarrow$  **4**.

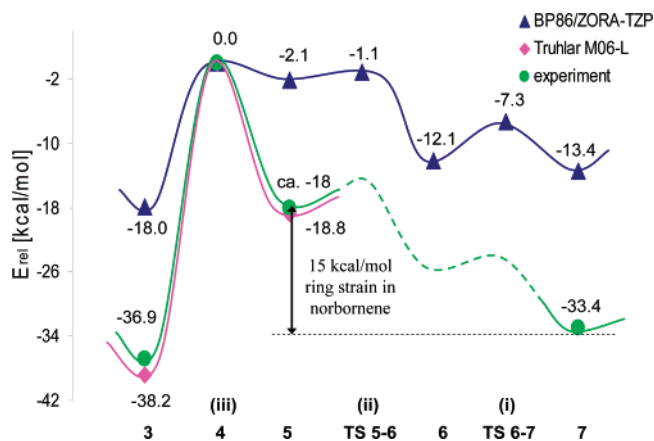
for phosphine dissociation from the first- and second-generation complexes were found to be 33.4 and 36.9 kcal/mol, respectively. Both values are systematically higher than the values reported by Grubbs for the same process in the solution-phase reaction.<sup>11</sup> In that previous work, it was reported that the initiation rate, in which the dissociation of tricyclohexylphosphine plays the dominant role, is dependent on the solvent, showing a marked dependence on the dielectric constant of the solvent. The increasing dissociation rate as the medium is made more polar was rationalized by the greater polarity of the 14-electron intermediate relative to its 16-electron precursor. It is therefore no surprise that the threshold energies for dissociation in the gas phase are higher than in the solution-phase reaction. Interestingly, the difference in activation energies for phosphine

**Table 1.** Threshold Energies ( $E_0$ ) after Deconvolution with L-CID. Values Arise from Three Different Experimental Data Sets and 15 Fits per Number of Rotors.  $\Delta$ -Values Represent a 95% Confidence Interval with Respect to a Gaussian Distribution.  $\alpha'$ -Values Cover a Huge Range within the Limit for the TS-model (5000–5600 for loose TS and 0–495 for tight TS)

	TS-model	rotors	$E_0$ (eV)	$\Delta E_0$ (eV)	$\nu_{\text{eff}}$ ( $\text{cm}^{-1}$ )	$\Delta \nu_{\text{eff}}$ ( $\text{cm}^{-1}$ )
1 → 2	loose	0	1.43	0.03	956	57
		2	1.45	0.04	972	26
	tight	13	1.53	0.05	988	17
		0	0.84	0.01	985	21
		2	0.84	0.02	980	23
3 → 4	loose	13	0.85	0.01	980	18
		0	1.53	0.04	923	51
		6	1.58	0.05	951	46
		8	1.60	0.05	963	37
	tight	18	1.63	0.06	978	24
		0	0.95	0.02	977	24
		6	0.96	0.02	984	21
		8	0.96	0.02	973	28
7 → 4	loose	18	0.96	0.02	973	24
		0	1.38	0.04	523	24
		6	1.45	0.04	529	20
		8	1.43	0.06	533	25
	tight	0	0.78	0.02	539	29
		6	0.79	0.02	547	29
		8	0.80	0.02	549	33

loss between the first- and second-generation catalysts is independent of whether the reaction occurs in the gas phase or in toluene.

Several quantum chemical calculations have examined the loss of tricyclohexylphosphine from the first- and second-generation catalysts, with the reported dissociation energies being uniformly lower than the values from our gas-phase experiment.<sup>14</sup> The very low values from truncated model compounds are likely unrepresentative of the situation for the fully elaborated, complicated ligands in the experimental systems, but, more fundamentally, it has been claimed that the usual DFT methods systematically underestimate the phosphine binding,<sup>10</sup> at least for the ruthenium carbene complexes. Given the previously mentioned solvent dependence of the phosphine binding, one would expect the gas-phase values to be higher than those reported by Grubbs in solution. The typical DFT calculation, however, produces values for the gas-phase which are lower than those measured in solution, which strongly suggests that these calculations are an unreliable guide to the absolute thermochemistry of this class of organometallic complexes. Interestingly, Zhao and Truhlar have reported a new density functional, M06-L, which has been designed to better handle the medium-range correlation energy.<sup>10</sup> It is claimed that this treatment is particularly well-suited to dissociation energies in organometallic complexes. Application of the M06-L density functional, with a triple- $\zeta$  quality basis set and counterpoise correction, to the first- and second-generation ruthenium carbene complexes produces tricyclohexylphosphine dissociation energies of 34.2 and 38.2 kcal/mol, respectively, which are in remarkable agreement with the measurements in the present report. Figure 7 shows the bond dissociation energy of unlabeled



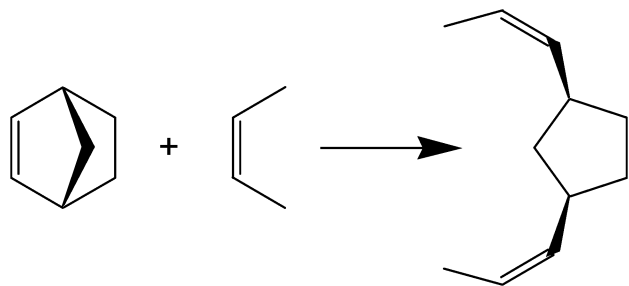
**Figure 7.** Energetic surface of the reaction of the second generation Grubbs catalyst **3** with norbornene relative to the 14-electron complex **4**. Green points correspond to experimental values based on loose transition state assumptions for both CIDs (**3** → **4** and **7** → **4**). The dashed line gives the region that is not accessible by this experiment at this time. Truhlar's energy of **3** is based on M06-L/TZQ-CP, and the complex **5** shows the binding energy of ethylene with M06-L/DZQ. Geometries of the BP86 surface are given in the Supporting Information.

**3** calculated with BP86/ZORA-TZP using ADF 2006 (geometries are given in the Supporting Information) in comparison with the experimental value based on a loose transition state assumption, together with Truhlar's value for the phosphine binding energy of 38.2 kcal/mol. The subsequent steps along the reaction for the overall metathesis reaction with norbornene from **4** → **7** require a more detailed examination. Again, full DFT energies at the BP86/ZORA-TZP level of theory have been calculated for comparison with the experiment. This common level of theory does show the qualitatively correct orders of stability, but the errors in absolute energies are very large.

The energy-resolved CID cross-section curve in Figure 6 depicts the threshold for a composite reaction which amounts to a ring-closing metathesis culminating in the loss of the cyclic olefin product, in this case, norbornene. All of the reliable computational evidence indicates that the resting state is the  $\pi$ -bound intramolecular olefin complex, and the experimentally observable product is the 14-electron complex resulting from dissociation of norbornene. There are several steps between these two points, and the question may be rightly asked as to which step is rate-determining. The answer to the question determines whether one takes the deconvoluted  $E_0$  for a loose versus a tight transition state. The candidates for the rate-determining step are (i) formation of the metallacyclobutane from the intramolecular  $\pi$ -complex, **7** → **6**, (ii) cleavage of the metallacyclobutane to a carbene complex with coordinated norbornene, **6** → **5**, or (iii) dissociation of the coordinated norbornene, **5** → **4**. Both i and ii would have tight transition states, whereas iii would have a loose one. The bulk of the ring strain incurred in step i. One can also reason that, starting from the metallacyclobutane, **6**, going backward to the ring-opened intramolecular  $\pi$ -complex, **7**, should have a lower activation energy than the step going forward to coordinated norbornene, **5**. This application of the Hammond Postulate suggests that step i cannot be rate-limiting, which is likely to be legitimate given that both the forward and reverse reaction of **6** are of the same type. Given that the strain release upon ring-opening of norbornene, as defined by the homodesmotic equation in Scheme 4, comes out to 15 kcal/mol,<sup>15</sup> one can accordingly consider the consequences of the

(14) (a) Cavallo, L.; *J. Am. Chem. Soc.* **2002**, *124*, 8965. (b) see reference 6. (c) See reference 7. (d) See reference 8. (e) van Rensburg, W. J.; Steynberg, P. J.; Kirk, M. M.; Meyer, W. H.; Forman, G. S. *J. Organomet. Chem.* **2006**, *691*, 5312. (f) Jordaán, M.; van Helden, P.; Sittert, C. G. C. E.; Vosloo, H. C. M. *J. Mol. Catal. A: Chemical* **2006**, *254*, 145. (g) Forman, G. S.; McConnell, A. E.; Toozee, R. P.; van Rensburg, W. J.; Meyer, W. H.; Kirk, M. M.; Dwyer, C. L.; Serfontein, D. W. *Organometallics* **2005**, *24*, 4528.

Scheme 4



two remaining choices. If one were to assume that step ii is rate-limiting, i.e., the step in which the metallacyclobutane, **6**, is cleaved to a  $\pi$ -bound norbornene complex, **5**, then a tight transition state would be appropriate. The 18 kcal/mol threshold energy extracted by L-CID would be just enough to account for the strain in either the metallacyclobutane, **6**, or the bound norbornene relative to intramolecular  $\pi$ -complex, **7**. The assumption of rate-limiting step ii would also place a bound on the ligand binding energy of norbornene to the 14-electron complex, **4**. Consider that a rate-limiting step ii would necessarily mean that the transition state for dissociation of norbornene from the 16-electron complex, **5**, cannot lie more than 18 kcal/mol above the intramolecular  $\pi$ -complex. At the same time, the assumption means that the  $\pi$ -complex, **5**, cannot lie below the intramolecular  $\pi$ -complex, **7**, because, were that to be the case, then the former and not the latter would be the resting state, and the overall reaction by which norbornene is lost from this resting state by CID would proceed necessarily by way of a loose transition state. The two conditions mean that an assumption of a rate-limiting step ii would constrain the ligand binding energy of norbornene to the 14-electron carbene complex to be less than 18 kcal/mol. The other choice, rate-limiting step iii via a loose transition state, would place the transition state for dissociation of norbornene 33 kcal/mol above the intramolecular  $\pi$ -complex, **7**. The transition states for steps i and ii are constrained to lie below this limit, but this is not a difficult condition to meet. If we were to neglect the small energy difference between a ruthenium benzylidene and a ruthenium alkylidene, then the difference in energy between the intramolecular  $\pi$ -complex, **7**, and the norbornene complex, **5**, is principally the 15 kcal/mol strain of norbornene relative to a monocyclic reference. This would place the ligand binding energy of norbornene to the 14-electron carbene complex around 18 kcal/mol, or perhaps slightly higher.

There is no *a priori* reason in the experiment itself that favors one or the other transition states, i.e., step ii or step iii, but both

(15) (a) Lebedev, B.; Smirnova, N.; Kiparisova, Y.; Makovetsky, K. *Makromol. Chem.* **1992**, *193*, 1399. The heat of polymerization of norbornene has been measured to be about 62.2 kJ/mol (~15 kcal/mol), which is essentially determined by strain release. (b) Khoury, P. R.; Goddard, J. D.; Tam, W. *Tetrahedron* **2004**, *60*, 8103. The total ring strain in norbornene has been determined to be 19.2 kcal/mol and 6.2 kcal/mol in cyclopentane (slightly less in substituted cyclopentanes), which gives a strain release after RÖMP of norbornene of slightly more than 13 kcal/mol (19.2–6.2).

have the same consequence in that it is clear from the reaction in which a ring-closing metathesis of the intramolecular  $\pi$ -complex, **7**, goes to the 14-electron complex, **4**, and norbornene, that the ligand binding energy of a  $\pi$ -bound olefin is very significantly less than that of tricyclohexylphosphine. This is consistent with the great difficulty in observing the olefin  $\pi$ -complexes in ruthenium-catalyzed metathesis reactions. The relative binding energies are furthermore important in judging the extent to which phosphine binding and (re)dissociation is kinetically important during turnover of metathesis catalysts.<sup>16</sup> Considering the considerable dependence of the phosphine binding energy with solvent polarity, and, presumably, a comparable but not necessarily parallel dependence in the olefin binding energies, it would not be unexpected that the extent of intervention of phosphine ligands in multiple turnovers is a delicate balance determined by concentrations, solvents, temperature, and other conditions. The solution-phase experiment, as well as computational studies, indicate a rate-limiting phosphine dissociation, i.e., step iii is rate-determining with a loose transition state, for the second-generation system. Accordingly, the experiment indicates that the olefin binding energy to the 14-electron, second-generation ruthenium carbene complex should be slightly more than 18 kcal/mol, which can be compared to Zhao and Truhlar's computed binding energy of 18.8 kcal/mol for ethylene. One would expect norbornene to bind somewhat more strongly than ethylene because of the pyramidalization in the strained olefin, so the degree of agreement here is again more than satisfactory.

## Conclusions

Mass spectrometric methods lead to the experimental determination of the phosphine binding energy in first- and second-generation ruthenium metathesis catalysts. An experimental study of a gas-phase ring-closing metathesis sets bounds on the binding energy of the olefinic substrate to the 14-electron active species. The absolute binding energies agree remarkably well with the latest DFT calculations using a density functional specifically suited to organometallic thermochemistry.

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**Supporting Information Available:** Data acquisition and processing (kinetic energy distribution, scaled ion intensities as a function of the collision energy and pressure, cross-section curves at different pressures and extrapolation to zero pressure). Linear transit calculations for **1**  $\rightarrow$  **2** and **3**  $\rightarrow$  **4** and minimum geometries of **1** and **3** as well as of the end points at Ru–P distances of 5.00 Å. Furthermore, energy surfaces of the reaction of unlabeled **1** and **3** with norbornene at the BP86/ZORA-TZP level of theory using ADF 2006. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.