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Gas-Phase Energetics of Reductive Elimination from a Palladium(II) N-Heterocyclic Carbene Complex

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Abstract: Energy-resolved collision-induced dissociation experiments using tandem mass spectrometry are reported for an phenylpalladium N-heterocyclic carbene (NHC) complex. Reductive elimination of an NHC ligand as a phenylimidazolium ion involves a barrier of 30.9(14) kcal mol⁻¹, whereas competitive ligand dissociation requires 47.1(17) kcal mol⁻¹. The resulting threecoordinate palladium complex readily undergoes reductive C–C coupling to give the phenylimidazolium π complex, for which the binding energy was determined to be 38.9(10) kcal mol⁻¹. Density functional calculations at the M06-

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L//BP86/TZP level of theory are in very good agreement with experiment. In combination with RRKM modeling, these results suggest that the rate-determining step for the direct reductive elimination process switches from the C–C coupling step to the fragmentation of the resulting σ complex at low activation energy.

Introduction

The formation of C-C bonds under mild conditions by palladium-catalyzed cross-coupling reactions has become widely used in organic synthesis.^[1] The archetypal catalytic cycle involves a Pd⁰ species that undergoes oxidative addition, transmetalation, and reductive elimination (Scheme 1). However, the exact mechanism is still poorly understood, mainly because the transmetalation and successive reductive elimination are generally too fast to be studied individually.^[2] Only recently were the solution-state kinetics for reductive elimination of two isolable cis-diaryl palladium(II) complexes reported.^[3] Cavell et al.^[4] showed that also N-heterocyclic carbene (NHC) hydrocarbyl palladium(II) complexes can readily decompose by concerted reductive elimination of hydrocarbyl imidazolium ions, in contrast with the common view of NHCs as mere spectator ligands.^[5] This reactivity parallels biaryl formation if one envisages the in-



Scheme 1. Simplified palladium-catalyzed C-C cross-coupling cycle.

volvement of an imidazolium-2-yl palladium(II) resonance structure (Scheme 2). The superior catalytic activity found for NHC-based precursors, which is usually attributed to the strong σ -donor properties of NHCs, may alternatively stem from the thus-generated low-coordinate Pd⁰ species.

Here we report on the use of electrospray tandem mass spectrometry (ESI-MS)^[6] to study the gas-phase reactivity of a palladium NHC complex. Energy-resolved collision-induced dissociation (CID) experiments are reported for the reductive elimination of an imidazolium species and for competitive ligand dissociation (cf. Scheme 2). The three-coordinate complex generated on loss of an NHC can still undergo reductive elimination, and we present a model to describe the energy dependence for such sequential-reaction

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Scheme 2. Resonance structures for cationic palladium NHC complexes, and associated fragmentation reactivity.

cross sections. The experimental results are complemented by a detailed computational study, which indicates that the direct reductive elimination channel proceeds via a σ complex, whose fragmentation becomes rate-limiting at low activation energy. Additionally, we evaluated several density functionals for accurate reproduction of the gas-phase reaction barriers, a validation of importance for our ongoing mechanistic research on the palladium-catalyzed C–C coupling cycle.

Results and Discussion

Gas-phase reactivity: Treatment of iodo-bridged dimeric palladium complex 1 with 1,3-dimethyl-1*H*-imidazol-2-ylidene silver iodide [(NHC)AgI] in acetonitrile generated cationic complex 2a, as observed at m/z 471 by ESI-MS (Scheme 3). The only other intense signal corresponded to



Scheme 3. Formation and gas-phase reactivity of complexes **2a,b** (NHC = 1,3-dimethyl-1*H*-imidazol-2-ylidene). Inset: calculated (red bars) and experimental isotope pattern (blue) of **2a**.

the analogous palladium complex **2b** (m/z 637), in which the original triphenylphosphine ligand is not replaced by a third NHC group.^[7] The identity of these ions is corroborated by their isotope patterns (see inset Scheme 3 and the Supporting Information) and gas-phase reactivities. On collisional

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activation with argon, **2a,b** underwent reductive elimination of 1,3-dimethyl-2-phenyl-1*H*-imidazolium (**3**, m/z 173) and competitive decomplexation of one N-heterocyclic carbene (**2a**) or the triphenylphosphine ligand (**2b**) to give tricoordinate palladium complex **4** at m/z 375. Density functional calculations (see below) indicated that **4** can undergo rather facile reductive C-C coupling to give the more stable phenylimidazolium π complex **4**- π , so that both species are accessible at high energy. By either increasing the tube lens voltage to 175 V or using 30 V source collision-induced dissociation (CID), **4/4-\pi** was generated in the spray and was confirmed to eliminate **3** selectively on CID.

CID threshold measurements: Energy-resolved reaction cross sections were acquired on a customized Finnigan MAT TSQ-700 (see Experimental Section). The zero-pressure extrapolated cross sections are shown in Figure 1; Table 1 summarizes the fitting results for deconvolution with L-CID^[8] (see the Supporting Information for details and results with other transition-state models). Collision of 2a with xenon gas was carried out to monitor the reductive elimination of **3** (Figure 1A, green diamonds) and competitive NHC ligand dissociation giving $4/4-\pi$ (red circles). Above a collision energy E_{CM} of about 5 eV, the experimental cross section for formation of 3 rises more steeply at the expense of that of 4/ 4- π , which indicates the occurrence of sequential reductive elimination of 3 from 4.^[9] Therefore, we performed twochannel fits of the primary reaction cross sections up to $E_{\rm CM}$ = 4.5 eV, and then simulated the reaction cross sections over the full collision-energy range (solid lines in Figure 1 A). Thanks to the physically realistic treatment of the collisional activation in L-CID,^[8] the simulated curves reliably reflect the primary reaction cross sections in the absence of the sequential reductive elimination. Thus, the difference between the simulated and experimental cross section for formation of $4/4-\pi$ (red solid line vs. red circles) affords an estimate of the cross section for sequential conversion of 4 to 3 (Figure 1B).

To fit the sequential CID threshold curve^[10] with L-CID, we implemented the following model (see the Supporting Information): the collisional activation was treated for 2a with the previously fitted parameters for the primary reaction giving 4. The primary reaction barrier was then subtracted and the remaining internal energy scaled to account for the energy partitioning on NHC ligand dissociation. Finally, the fitting procedure was performed with the degrees of freedom and number of free rotors for 4. As the sequential reaction sets in at energies where the primary reaction cross section has not yet leveled off, the kinetic shift was treated with the appropriate overall rate equation. In this way, all aspects of the sequential reaction are treated except for the additional internal energy broadening due to the primary NHC dissociation. Whereas the extra assumptions made are realistic, the model is less rigorous than that for fitting of the primary reaction cross sections, and therefore we find it more appropriate to list the barrier with only two significant digits and without confidence interval.

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Figure 1. Cross sections and L-CID fits for A) reductive elimination of **3** from **2a** (green diamonds) and competitive ligand dissociation to give **4**/ **4-** π (red circles), fitted up to 4.5 eV center-of-mass frame collision energy (dotted vertical line). B) Sequential reductive elimination of **3** from **4**, derived as the difference between fitted and experimental cross sections for formation of **4**/**4-** π . C) Dissociation of **3** from **4**- π .

The sequential formation of **3** was also studied separately by generating $4/4-\pi$ in the spray at 60.0 V tube-lens voltage, presumably affording the more stable $4-\pi$ on thermalization (see below), which was then subjected to CID threshold measurements (Figure 1C). Argon was used as the collision gas to allow working at higher laboratory-frame energies, so that the CID threshold region would not overlap with the region in which the ion beam is truncated.

DFT calculations: Quantum-chemical calculations were performed to confirm the nature of the observed species and their reactivities, in particular with respect to the transition-

Table 1. L-CID fitting results $[\text{kcal}\,\text{mol}^{-1}]$ for reaction of $2\,a$ to give 3 and $4/4 \text{-} \pi^{[a]}$

Process	TS model	$d^{[b]}$	DoF ^[c]	Rotors	E_0^{\ddagger}
$2a \underbrace{\overset{3+(\mathrm{NHC})_2\mathrm{Pd}^0}{4/4-\pi+\mathrm{NHC}}}_{4/4-\pi+\mathrm{NHC}}$	tight loose	2 1	165	6	30.9(14) 47.1(17)
$[2a \rightarrow 4] \\ \rightarrow 3 + (NHC)Pd^0$	[loose] loose ^[a]	[1] 2	[165] 120	[6] 4	[47.1] 37
$4-\pi \rightarrow 3 + (\text{NHC}) \text{Pd}^0$	loose	1	120	4	38.9(10)

[a] The primary NHC dissociation (in brackets) was treated with fixed parameters from the two-channel fit up to 4.5 eV, and the remaining excess internal energy was corrected for this ligand loss; see main text. [b] Reaction-path degeneracy. [c] Degrees of freedom.

state model to use (i.e., tight when an intramolecular rearrangement is rate-limiting, or loose when product dissociation is), and to assess the performance of various density functionals for the system studied. We will discuss the results for the following density functionals: B3PW91; the one-parameter mPW1K^[11] designed for improved kinetics^[12] and used with some success in transition-metal chemistry;^[13] and M06-L,^[14] which was designed to accurately describe main-group and transition-metal thermochemistry, kinetics, and nonbonding interactions at a reasonable computational cost. The first two density functionals were employed for optimizations and energy calculations in Gaussian,^[15] whereas energies for the last-named functional were evaluated in ADF.^[16]

The M06-L//BP86/TZP potential-energy diagram for the reactivity of 2a is shown in Figure 2 and the calculated relative energies are listed in Table 2. We will first discuss the formation of *trans*-4 and the sequential reductive elimination of 3 (upper profile in Figure 2), because three experimental values are available, namely, the binding energies of an NHC ligand in 2a and of 3 in $4-\pi$, as well as the sequential reductive elimination barrier. Thereafter, we will focus on direct reductive elimination from 2a.

Ligand dissociation from 2a and sequential reductive elimination: A loose transition-state model should be appropriate for the fragmentation of 2a into trans-4 and an NHC ligand.^[17] The experimental dissociation energy of 47.1(17) kcalmol⁻¹ is well reproduced by both M06-L and mPW1K (45.8 and 44.4 kcalmol⁻¹, respectively, Table 2), whereas B3PW91 underestimates it at 39.7 kcalmol⁻¹. According to our calculations, the resulting trans-4 isomerizes to cis-4 along the way to reductive C-C coupling to give complex 4- π , in which the product 3 is still *ipso,ortho* π -coordinated to the (NHC)Pd⁰ fragment (see Figure 2).^[18] All three methods give very similar results for the transition states and intermediates involved in the reductive elimination reaction. Specifically, the barrier for reductive C-C coupling (4-TS, 14.6 kcalmol⁻¹ at M06-L) is rather low, so that when NHC ligand dissociation is induced by a harsh tube lens setting, most likely the initially generated trans-4 is sufficiently activated to rearrange to the more stable $4-\pi$.

(NHC)Pd (NHC)Pd (NHC)Pd (NHC)Pd $(NHC)_2Pd$ $(NHC)_2Pd$

Figure 2. Mo6-L//BP86/TZP potential-energy diagram, including selected optimized geometries with C···C and Pd···H distances in angstrom; other hydrogen atoms are omitted for clarity. Dashed arrows denote dissociation reactions without reverse activation barriers.

Table 2. Calculated relative energies $[kcalmol^{-1}]$ for reaction of *trans*-4 to give 3 (top) and for reaction of 2a to *trans*-4 and 3 (bottom).

Method	trans-4 \rightarrow	4-TSx	cis-4	4-TS	4-π ^[a]	3+(NHC)Pd	4-π –	• 3 + (NHC)Pd ^[a]
M06-L ^[b]	0.0	11.2	8.7	14.6	-6.1 (-5.7)	32.8		38.9 (38.5)
mPW1K ^[c]	0.0	12.6	8.3	16.8	-7.7 (-8.5)	22.3		30.0 (30.8)
B3PW91 ^[c]	0.0	11.0	8.2	15.9	-6.3 (-7.5)	23.2		29.6 (30.6)
	$2a\!\rightarrow\!$	trans-4	+NHC	2-TS	2-π ^[a]	2-TS2	2-σ	$3+(NHC)_2Pd$
M06-L ^[b]	0.0	45	.8	23.6	12.1 (14.2) 13.3	7.3	28.7
mPW1K ^[c]	0.0	44	.4	30.2	12.1 (12.8) 21.4	9.6	22.8
B3PW91 ^[c]	0.0	39	.7	27.3	10.9 (10.7) 17.6	6.2	18.3

[a] Values for *ortho,meta* π -coordinated complexes **4-\pib** and **2-\pib** are given in parentheses. [b] ADF M06-L energy evaluations of BP86/TZP geometries, including Gaussian mPW1K/SDD(d) zero-point energy corrections. [c] Gaussian SDB-cc-pVTZ single-point energies, including zero-point energy corrections of SDD(d) geometries.

On collisional activation, $4-\pi$ can again interchange with *trans/cis-4*, but this does not affect the measured barrier according to the Curtin–Hammett principle. The dissociation of **3** from $4-\pi$, which was thus experimentally determined to require 38.9(10) kcalmol⁻¹ by using a loose TS model, is exactly matched by M06-L, whereas both mPW1K and B3PW91 underestimate it by about 9 kcalmol⁻¹. Finally, the measured sequential reaction barrier of 37 kcalmol⁻¹ corresponds reasonably well with the M06-L energy of [**3**+ (NHC)Pd] relative to *trans-***4** (32.8 kcalmol⁻¹), but is again underestimated by mPW1K and B3PW91 by about 14 kcalmol⁻¹.

Thus, the M06-L density functional gives best agreement with the experimental barriers, mainly because of its superior performance for dissociation energies,^[6e,f] which can be attributed to the improved treatment of medium-range noncovalent interactions.^[14] We note that of all 69 density functionals screened with ADF,^[16] only PW91 and M06 also

Table 3. BP86/TZP (NHC)_nPd–3 bond analyses [kcalmol⁻¹] and fragment Hirshfeld charges for 4- π , 2- π , and 2- σ .

	4-π	2-π	2-σ
$\Delta E_{ m Pauli}$	118.8	171.7	21.7
$\Delta V_{ m elstat}$	-92.5	-127.6	-21.7
$\Delta E_{ m oi}$	-64.9	-99.7	-16.6
$\Delta E_{ m int}{}^{[a]}$	-38.5	-55.6	-16.6
$\Delta E_{\rm prep}(3)$	4.9	13.7	0.9
$\Delta E_{\rm prep}(L_n Pd)$	2.1	32.5	1.4
$\Delta E_{\rm Net}^{[b]}$	-31.5	-9.3	-14.6
$q(L_nPd)$	0.243	0.434	0.118
[a] $\Delta E_{\rm int} = \Delta E_{\rm Pauli}$ +	$-\Delta V_{\text{elstat}} + \Delta E_{\text{oi}}.$	$[b] \Delta E_{\rm Net} = \Delta E_{\rm int} + \Sigma \Delta E$	$E_{\rm prep} = E_{\rm complex} -$
$\Sigma E_{\text{for an example}}$			

-31.5 vs. -9.3 kcal mol⁻¹), mainly because of the large preparation energy that is required to deform the preferably linear (NHC)₂Pd fragment to its bent geometry in **2-** π (C-Pd-C=103.94°). This strain is released when the two frag-

agree within 5 kcal mol^{-1} for the two direct dissociation reactions, but these underestimate the sequential reaction barrier by 10–12 kcal mol⁻¹.

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Direct reductive elimination from 2a: Reductive C-C coupling in four-coordinate palladium complex 2a (Figure 2, bottom) initially affords the expected *ipso,ortho* π complex 2- π .^[18] At this point, it is instructive to compare the Pd--phenyl bonding in 4- π and 2- π , as analyzed with ADF,^[16] in terms of fragments 3 their and $(NHC)_n Pd^0$ (*n*=1, 2; Table 3). The Hirshfeld charges^[19] on the formally neutral (NHC),Pd⁰ fragments of $4-\pi$ (0.243) and 2- π (0.434) indicate strong backdonation to the phenylimidazolium fragment, especially in 2- π , reflecting increasing electron-richness of these d10 Pd species with the number of strong σ-donor NHC ligands. This trend is paralleled by the extent of Cipso-Cortho bond elongation (1.440 Å in $4-\pi$ and 1.468 Å in **2-** π versus 1.408 Å in 3) and the interaction energies $\Delta E_{\rm int} = -38.5,$ **(4-**π: $2-\pi$: $-55.6 \text{ kcal mol}^{-1}$ at BP86/TZP). However, the net π -coordination strength in $4-\pi$ is much larger than in 2- π (ΔE_{Net} =

ments partially separate to give intermediate 2- σ (C-P-C 171.30°), which features end-on σ coordination of the Pd atom with both an acidic imidazolium methyl H and a phenyl *ortho*-H atom of 3. The near-linearity of the Pd-(NHC)₂ fragment in 2- σ and the recovered phenyl aromaticity result in a very small preparation energy, compensating for the much weakened interaction energy and making 2- σ more stable than 2- π .

For the experimental barrier of 30.9 kcal mol⁻¹ for reductive elimination of 3 from 2a a tight TS model was initially assumed, that is, that the C-C coupling barrier (2-TS) would be rate-determining. This is supported by both mPW1K and B3PW91, which also reproduce the experimental barrier well (Table 2; 30.2 and 27.3 kcalmol⁻¹, respectively). Then again, as was the case for $4-\pi$, these density functionals presumably underestimate the energy for dissociation into $3+(NHC)_2Pd$, so that in reality it may be very similar to the C-C coupling barrier. M06-L gives a C-C coupling barrier that is even 5.1 kcalmol⁻¹ below the dissociation energy of 28.7 kcalmol⁻¹, but the latter is much lower than that obtained from fitting the experimental data with a loose TS model (44.3(16) kcalmol⁻¹, see the Supporting Information). At first sight, M06-L thus surprisingly seems to fail, but the situation may be more complicated. The threshold curves were fitted by assuming unimolecular first-order kinetics, which is a valid approximation for a multistep reaction only if one step is much slower than all the others. However, for the reductive elimination from 2a the "tight" C–C coupling to $2-\pi$ becomes rate-limiting at high collision energies, as the rate of the only slightly less favorable "loose" elimination of 3 increases more rapidly with increasing excess energy.^[20,21] Moreover, in the intermediate regime where both steps are slow on the experimental timescale, the overall reaction does not obey pseudo-first-order kinetics. Only few reactant ions will undergo both C-C coupling and subsequent elimination before reaching the detector, leading to a much larger kinetic shift than for a singlestep first-order reaction. Thus, a loose TS model is inappropriate in cases where rearrangement precedes fragmentation with an activation barrier that is comparable to the dissociation energy.

Transition-state switching: To probe the role of such switching of the rate-limiting transition state^[20] in the reductive elimination from **2a**, we extracted the rate constants for this reaction and the competitive ligand dissociation from the L-CID fits (Figure 3, thick green and red curve, respectively). The RRKM^[21] rate constants for the individual steps were calculated in CRUNCH^[22] by using the M06-L relative energies with mPW1K zero-point energy corrections, frequencies, and rotational constants (see Supporting Information for details). As a control, we also calculated the RRKM rate constant k_{diss} for NHC ligand dissociation from **2a** and found fair agreement with the corresponding first-order rate constant derived from experiment (thin and thick red curve, respectively). For the reductive elimination from **2a**, the less stable intermediate **2-** π will rapidly interconvert with **2-** σ



Figure 3. Experimentally derived (thick solid lines) and M06-L based rate constants for reductive elimination (green) and NHC ligand dissociation (red) from **2a**. The individual RRKM rate constants for rearrangement of **2a** to **2-** σ (blue long dashes) and vice versa (cyan dots), as well as for subsequent elimination of **3** from **2-** σ (black dashes) are also included.

and can thus be ignored to simplify the overall reaction kinetics. In Figure 3, the individual RRKM rate constants are plotted against the collision energy for the tight C–C coupling of **2a** (k_{C-C} , blue long dashes), the net reverse process from **2-σ** (k_{C-C} , cyan dots), and the loose elimination of **3** from **2-σ** (k_{elim} , black dashes). Indeed, k_{C-C} rises less steeply than k_{elim} and is already the smaller of the two from a collision energy of 1.3 eV.

Next, to evaluate the kinetic shift we derived the overall rate equation for the multistep reductive elimination from 2a. For each set of individual RRKM rate constants, the formation of **3** within the detection time window (ca. $60 \,\mu$ s) was calculated and converted back to an apparent firstorder rate constant k_{app} for comparison with the experimentally derived rate constant (Figure 3, thin and thick green curves, respectively). The apparent rate constant has its onset just after that of the loose dissociation and is considerably smaller than both individual rate constants k_{C-C} and k_{elim} up to 1.85 eV; at higher excess energy k_{app} follows the profile of the tight C-C coupling step. As a result, the profile of k_{app} resembles that for a tight TS model but with a barrier height slightly above that of the loose step, in reasonable agreement with the rate constant extracted from the L-CID fits (thick green curve).^[23] In other words, in this case it is appropriate to fit the CID data with a tight TS model, but this gives an upper bound to the dissociation energy rather than the barrier for the preceding rearrangement. Hence, the M06-L results for the direct reductive elimination of 3 from 2a are not at variance with the experimentally determined threshold. More generally, this RRKM modeling illustrates how CID thresholds for multistep reac-

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tions are affected when the barrier for rearrangement approaches the final product dissociation energy.

Conclusion

A phenylpalladium(II) N-heterocyclic carbene complex was studied by CID threshold measurements to provide quantitative gas-phase thermochemical data for reductive elimination and ligand dissociation. The analogous three-coordinate complex readily undergoes reductive C-C coupling to give a π complex, for which the product binding energy was also determined. Our results complement recent solution-state evidence^[4] that NHCs are not always mere spectator ligands, but can be reductively eliminated as imidazolium salts. Quantum chemical calculations show that the barrier for reductive C-C coupling is similar to the energy required for dissociation of the produced 1,3-dimethyl-2-phenyl-1H-imidazolium, which supposedly leads to transition-state switching. An RRKM treatment showed that in this case one should fit the energy-resolved CID data with a "tight" TS model, but then actually obtains an upper bound to the dissociation energy. The M06-L density functional reproduces the experimental energetics well, which is an important validation for our ongoing investigations of the cross-coupling mechanism.

Experimental Section

General procedures: Solvents were distilled from the appropriate drying agents.^[24] Starting materials were synthesized and handled under inert atmosphere by standard Schlenk techniques or in a glove box. Their structure and purity was confirmed by ¹H and, where applicable, ³¹P NMR spectroscopy on Varian Mercury 300 MHz instruments. Iodide-bridged palladium dimer **1** was prepared in two steps in 84% overall yield from bis(triphenylphosphine)palladium(II) dichloride following the procedures of Grushin and Alper.^[25] 1,3-Dimethyl-1*H*-imidazol-2-ylidene silver iodide [(NHC)AgI] was prepared from 1-methyl-1*H*-imidazole according to literature procedures.^[26,27]

Tris(1,3-dimethyl-1*H*-imidazol-2-ylidene)phenylpalladium(II) iodide (2a): Fresh stock solutions of 2a in dry acetonitrile were prepared in a glove box by dissolving 1 (1.7 mg, 1.5 µmol) and [(NHC)AgI] (3 mg, 4.5 µmol) in acetonitrile (0.50 mL). The produced dark brown precipitate was removed by filtration through cotton wool and washed with acetonitrile (2×0.50 mL). For the ESI-MS studies, the clear colorless filtrate was diluted to approximately 50 µm. Stock and spray solutions were stored at -35 °C in the glove box. For the qualitative MS measurements on a Thermo Finnigan TSQ Quantum tandem mass spectrometer, optimal ESI settings were a spray rate of 5 µLmin⁻¹ at 5 kV spray voltage, heating the capillary at 170 °C at 35 V capillary voltage, and 25 V tube lens voltage; CID experiments were conducted with 0.5 mTorr argon.

CID threshold measurements: Energy-resolved CID threshold measurements were performed on a customized Finnigan MAT TSQ-700 tandem mass spectrometer, whose original transfer octapole was replaced by a long radio-frequency 24-pole ion guide to thermalize the ions with 5 mTorr argon to the manifold temperature of 70 °C. The previously reported design^[28] was improved to extend the ion transmission range below m/z 200. Specifically, rods instead of plates were used for the poles to lower the capacitance and hence allow for higher radio frequencies, in combination with a movable thermalization chamber that was positioned somewhat closer to the skimmer to improve the background vacuum in

the first mass-selection quadrupole.^[29] The ion guide is operated without an external longitudinal field; ions move through it because of a weak longitudinal potential induced by the space charge from the continuous beam of incoming ions. Thus, a well-defined near-Gaussian distribution of the ions' kinetic and, presumably, internal energies is achieved (Figure 4), which is required for subsequent deconvolution of the crosssection curves.



Figure 4. Distribution of ion kinetic energies in the laboratory frame, determined for ion 2a by retarding potential measurements after the gasfilled 24-pole ion guide; the Gaussian fit (red line) has a full width at half-maximum of 1.71 eV.

For the CID threshold measurements, the parent ion was mass-selected in the first quadrupole and allowed to react with xenon or argon (30-110 µTorr) in the octapole collision cell. Intensities of the reactant and product ions were recorded as a function of the collision offset voltage. An ICL^[30] script was developed to sample all species in an interleaved fashion rather than individually, which suppresses discrepancies between the ion intensity curves due to variations in experimental conditions. The script also monitors the collision gas pressure as measured by a hot-cathode gauge, allowing for improved zero-pressure extrapolations. The ion intensities were converted to cross sections according to Ervin et al., [31] extrapolated to zero collision-gas pressure, and fitted with L-CID.^[8] For cases where the nature of the rate-limiting reaction step was uncertain, both tight and loose transition states (i.e., with or without reverse activation barrier) were considered. Methyl groups were taken as free rotors and a reaction-path degeneracy of two was used for the C-C coupling steps.^[32] Further details of the experimental setup, data acquisition and processing, and L-CID deconvolution are contained in the Supporting Information.

Computational methods: Density functional theory (DFT) calculations were performed with the Gaussian suite^[15] employing the B3PW91 and mPW1K^[11] density functionals. Geometry optimizations were performed with the Stuttgart/Dresden effective-core potential and associated basis set^[34] for palladium and the Cartesian Dunning 95 full double-zeta basis set^[34] with additional d polarization functions for main-group elements, which we abbreviate as SDD(d). The Geometry DIIS algorithm^[35] was applied in combination with an ultrafine integration grid and tight SCF and geometry convergence criteria. The nature of each stationary point was confirmed by a frequency analysis; for the transition states, the vibrational mode of the imaginary frequency corresponded to the expected reaction coordinate. Subsequent single-point energies were calculated with the SDB-cc-pVTZ basis set,^[36] to which the SDD(d) zero-point energy corrections were added.^[37]

Additionally, density functionals were screened with the Amsterdam Density Functional (ADF) suite.^[16] Geometries were reoptimized with the BP86 density functional using an all-electron Slater-type basis set of triple-zeta quality with added polarization functions (TZP), where relativistic effects were treated with the scalar zeroth-order regular approximation (ZORA). The integration accuracy was set to 6.0, and geometry convergence criteria were used of 2×10^{-5} on the energy and 3×10^{-4} on

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the gradients. Subsequent single-point calculations with the keywords MetaGGA and HartreeFock^[16] afforded energy evaluations for 69 density functionals, including Truhlar's M06 suite,^[14] to which the Gaussian mPW1K/SDD(d) zero-point energy corrections were added.^[37,38]

Bond analyses in terms of the separate fragments were performed with ADF^[16] by using the BP86/TZP results. According to the extended transition-state model,^[39] the net bond energy ΔE_{Net} can be decomposed into four contributions: the preparation energy ΔE_{prep} needed to deform each fragment from its equilibrium geometry to that in the complex; the steric interactions between the fragments due to Pauli repulsion (ΔE_{Pauli}) and electrostatic attraction (ΔV_{elstat}); and the orbital interaction energy ΔE_{oi} ; the last three are usually summed to give the total interaction energy ΔE_{int} . Furthermore, the net transfer of electron density between the fragments is indicated by their Hirshfeld charges.^[19]

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