Table S1: Initial (default) EVB parameters. See Fig. 4 in the main text for the definition and atom numbering in the different VB states.

i. Partial atomic charges of the reacting part (in fraction of an elementary charge) in the different VB states for calculating electrostatic interactions by $E_{elec} = 332 \frac{q_i q_j}{r_{ij}} \left(1 - e^{-4r_{ij}^2}\right)$.

	Cl(1)	H(3,4,5)	C(2)	Cl(6)
State I	-0.168	0.200	-0.438	-0.994
State II	-0.994	0.200	-0.438	-0.168

ii. Bond parameters for the covalent bonds of the reacting part in the different VB states. All bonds are Morse bonds, where $E_{bond} = D(1 - e^{-\beta(r-r_0)})^2$.

	D (kcal mol^{-1})	r_0 (Å)	β, (Å^{-1})
C-Cl	79	1.82	0.8
C-H	100.4	1.10	2.0

iii. Angle parameters for the bending of the adjacent covalent bonds in the reacting part in the different VB states, where $E_{angle} = K_\theta (\theta - \theta_0)^2$, and no bond-angle coupling is activated.

	K_θ, (kcal rad^{-2} mol^{-1})	Θ (rad)
H-C-H, H-C-Cl	50	1.911
Cl-C-Cl	17	3.142

iv. VdW parameters for atom pairs in the reactive part, which are bonded in one of the VB states. Here, $E_{VDW} = \frac{A}{r^{12}} - \frac{B}{r^6} + Ce^{-\beta \cdot r}$, and A and B are zero.

	C (kcal mol^{-1})	β (A^{-1})
Cl$^-$---C	69999	4
Cl$^-$---H	12000	3.6

v. VdW parameters for atom pairs in the reactive part, which are never bonded in any VB state. Here, $E_{VDW} = \frac{A}{r^{12}} - \frac{B}{r^6}$, and B is zero.

	A (kcal·mol^{-1}·A^{12})
Cl$^-$---Cl	1000000

vi. Screening term to account for the inductive interaction between the Cl⁻---C atom pair, using the relationship $E_{screen} = -166 \frac{\sqrt{\alpha}}{r^4}$.

	α (A^8)
Cl⁻---C	0.6

vii. Gas-phase shifts of 13.96 kcal/mol were applied to both state 1 (α_1) and 2 (α_I), and the initial value of the mixing term (H$_{12}$) before parameter refinement was 50 kcal/mol.

Table S2: Final (refined) EVB parameters. See Fig. 4 in the main text for the definition and atom numbering in the different VB states.

i. Partial atomic charges of the reacting part (in fraction of an elementary charge) in the different VB states. $E_{elec} = 332 \frac{q_i q_j}{r_{ij}} \left(1 - e^{-4.5 r_{ij}^2}\right)$

	Cl(1)	H(3,4,5)	C(2)	Cl(6)
State I	-0.180	0.183	-0.382	-0.987
State II	-0.987	0.183	-0.382	-0.180

ii. Bond parameters for the covalent bonds of the reacting part in the different VB states. All bonds are Morse bonds, where $E_{bond} = D(1 - e^{-\beta(r-r_0)})^2$.

	D (kcal mol⁻¹)	r$_0$ (Å)	β (Å⁻¹)
C-Cl	80	1.806	1.650
C-H	100.4	1.093	1.740

iii. Angle parameters for the bending of the adjacent covalent bonds in the reacting part in the different VB states. After parameter refinement, bond-angle coupling was activated between the H-C-Cl angle and the C-Cl bond, through the relationship $\Phi_{ba} = \begin{cases} 1, r \le r_0 \\ 2e^{-\beta(r-r_0)} - e^{-2\beta(r-r_0)}, r > r_0 \end{cases}$, such that now $E_{angle} = K_\theta (\theta - \theta_0)^2 \Phi_{ba}$.

	K$_\theta$ (kcal rad⁻² mol⁻¹)	Θ (rad)
H-C-Cl	25.4	1.907
H-C-H	35.5	1.914
Cl-CCl	17	3.142

iv. VdW parameters for atom pairs in the reactive part, where $E_{VDW} = \frac{A}{r^{12}} - \frac{B}{r^6}$.

	A (kcal mol^{-1} Å^{12})	B (kcal mol^{-1} Å^6)
Cl$^-$---C	119246	235
Cl$^-$---H	75848	120
Cl$^-$---Cl	126247162	8306

v. After refinement, gas-phase shifts of -1.05 kcal/mol were applied to both state 1 (α_1) and 2 (α_1). Additionally, the best form for the mixing term (see main text) was found to be $H_{12} = A \exp(-\mu(r_{12} - r_{26})^2)$, where r_{12} and r_{26} are the distances between atoms 1 and 2, and 2 and 6, respectively. Here, A=37 kcal/mol and α=1.45.