Supporting information:

Gas Phase Thermochemistry of Ruthenium Carbene Metathesis Catalysts

*Sebastian Torker, Daniel Merki, and Peter Chen**

Laboratorium für Organische Chemie, ETH Zürich, Switzerland

Data acquisition and processing:

The compounds have been sprayed (3.5 kV) from DCM solutions at tube lense voltages of 85 V (for **1, 3**) and 120 V (for **7**). Flow rates were around 2 µl/min and the capillary temperature was set to 150-170 °C. Kinetic energy distributions were measured in daughter mode at 5 mTorr Ar or norbornene in the 24-pole ion guide and zero pressure in the octopole collision chamber. The FWHM was obtained after fitting with a Gaussian distribution (Figure S1). Ion intensities (Figures S2-S4) of product and parent ions were measured twice (90 µTorr → 30 µTorr and 30 µTorr → 90 µTorr; to average pressure fluctuations) at low resolution by introducing Ar into the collision cell and scaled by mass spectra taken at 47, 57, and 67 eV (for **2, 7** and **4**). Cross-sections (σ) have been calculated according to the following formulas

$$I_R = (I_R + \sum I_P)e^{(-\sigma_{tot} nl)}$$

$$\sigma_P = \sigma_{tot}(I_P / \sum I_P)$$

$$I_0 = I_R + \sum I_P$$

where I_R and I_P are the measured transmitted intensities of the reactant and product ions, n is the gas density, and l is the effective path length (25 cm).[1] Linear zero pressure extrapolation was done with the program CRUNCH,[2] and finally the fitting with L-CID (Figures S5-S7). Every threshold (for example **1** → **2**) was measured three times and every independent experimental cross-section fitted 15 times with L-CID for a given number of rotors. The mean of 45 fits than gave the threshold energy with a confidence interval according to a Gaussian distribution.

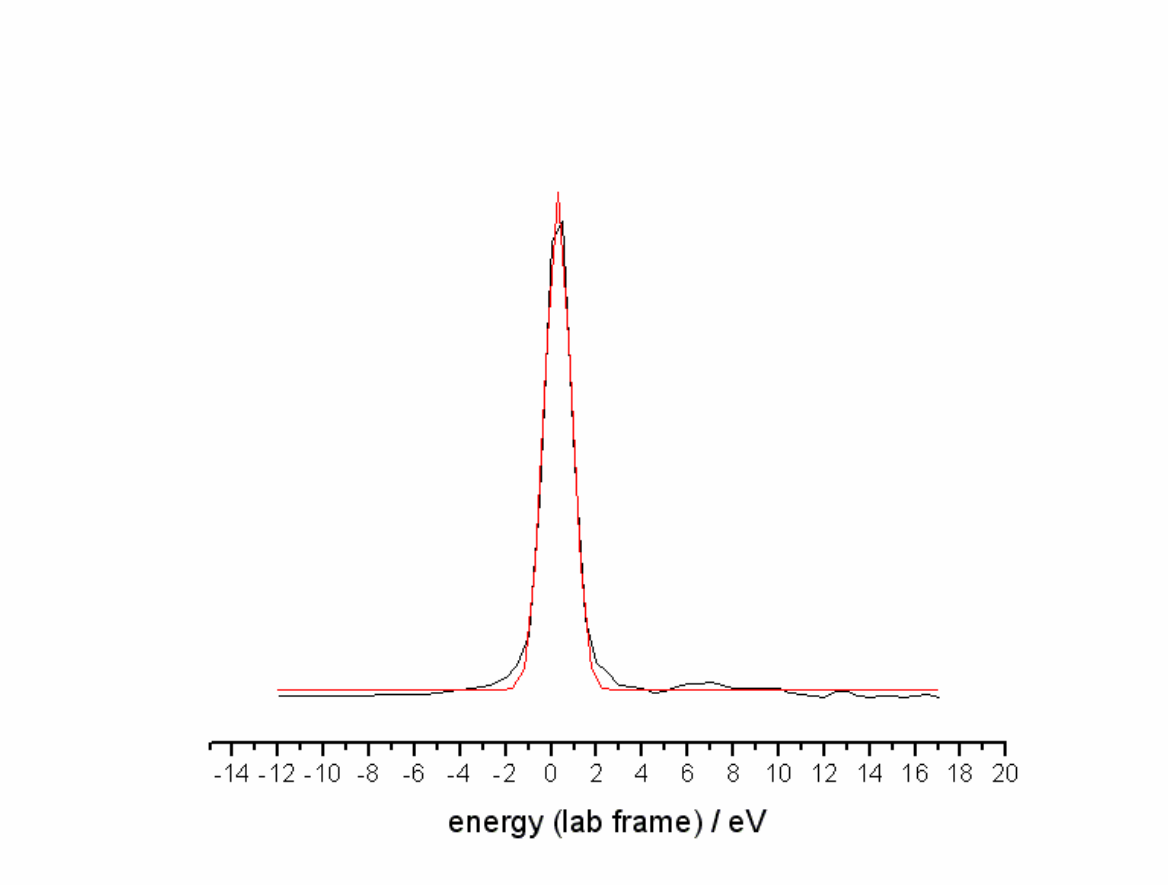


Figure S1. Typical kinetic energy distribution; FWHM = 1.2 – 2.0 eV in lab frame.

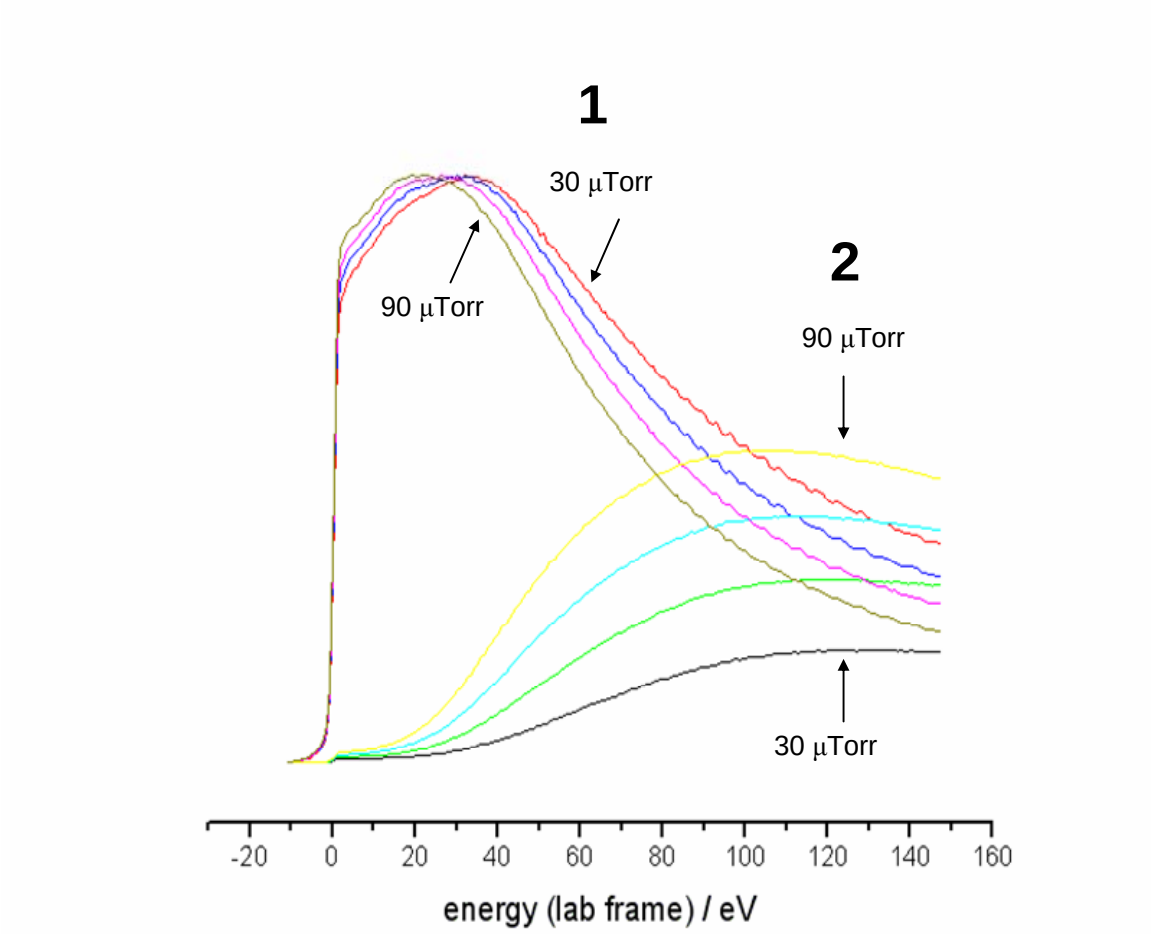


Figure S2. Ion intensities of **1** and **2** as a function of the collision energy at different pressures of Argon in the octopole collision chamber (30, 50, 70, and 90 μTorr). Curves have been scaled to the intensities of the peaks in mass spectra taken at 47 eV.

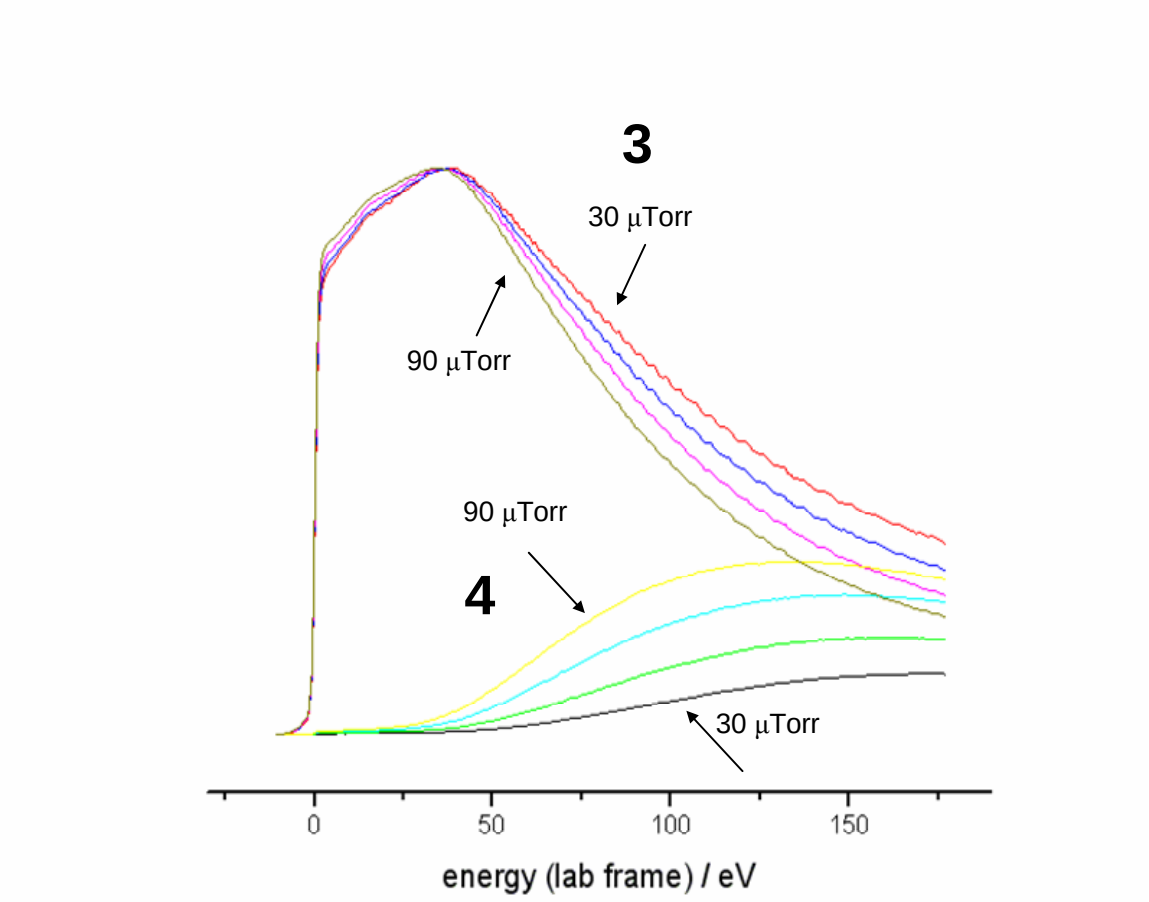


Figure S3. Ion intensities of **3** and **4** as a function of the collision energy at different pressures of Argon in the octopole collision chamber (30, 50, 70, and 90 μTorr). Curves have been scaled to the intensities of the peaks in mass spectra taken at 67 eV.

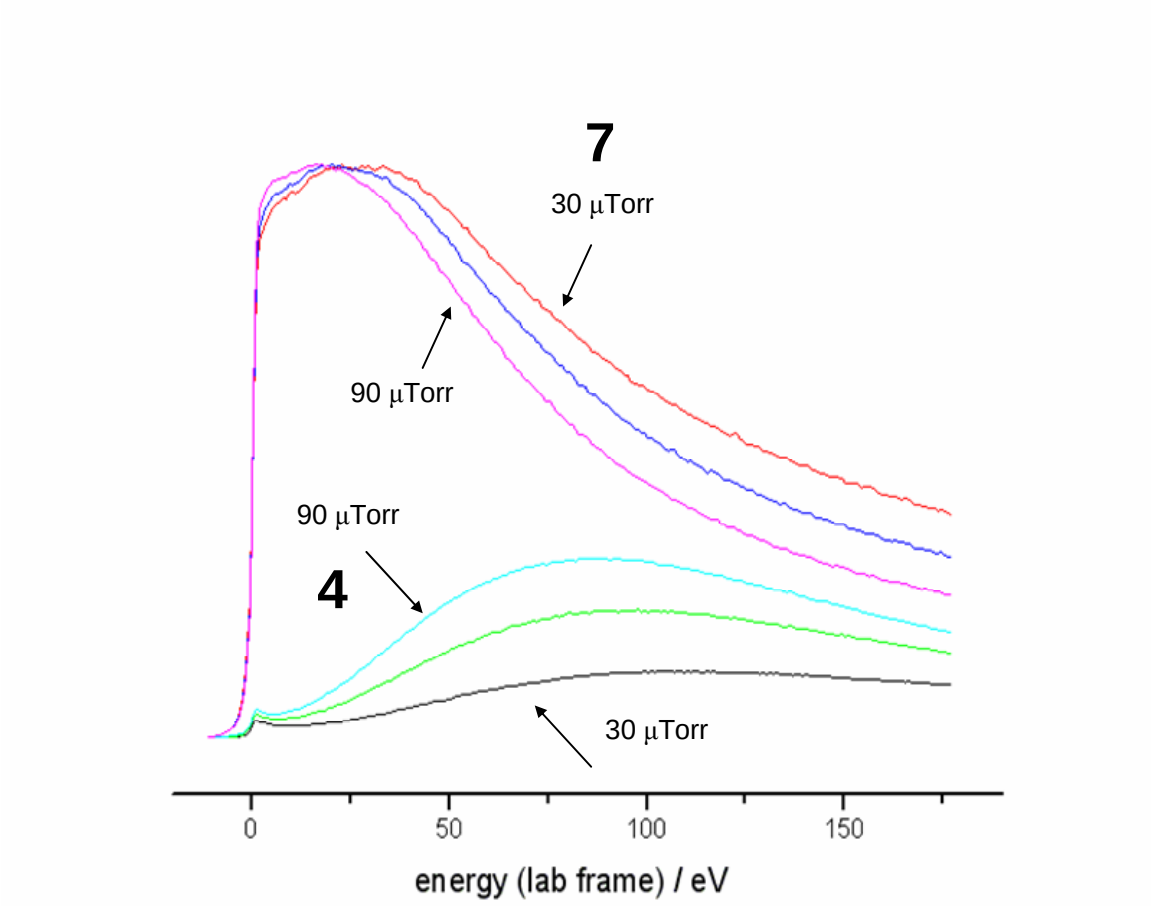


Figure S4. Ion intensities of **7** and **4** as a function of the collision energy at different pressures of Argon in the octopole collision chamber (30, 60, and 90 μTorr). Curves have been scaled to the intensities of the peaks in mass spectra taken at 57 eV.

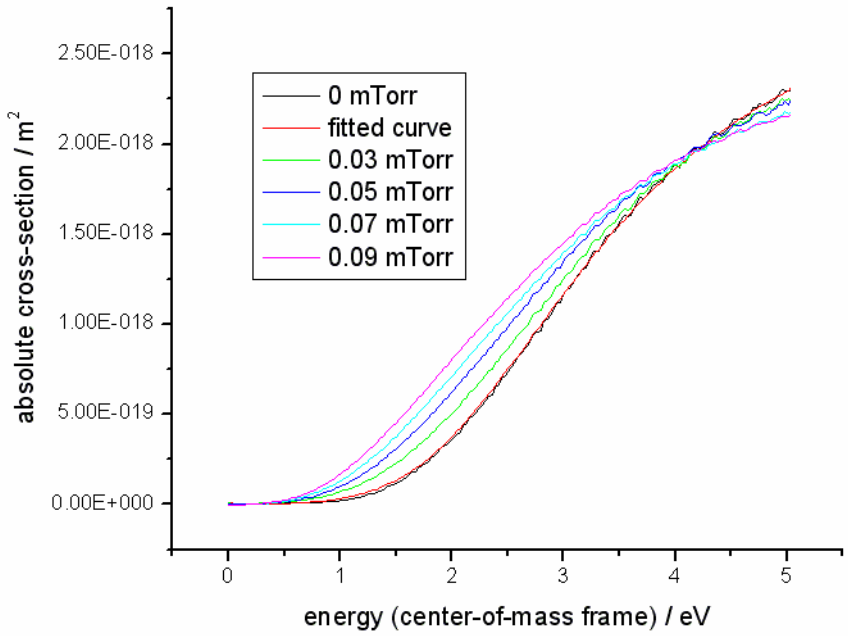


Figure S5. Cross-section and extrapolation to zero pressure for **1** → **2.**

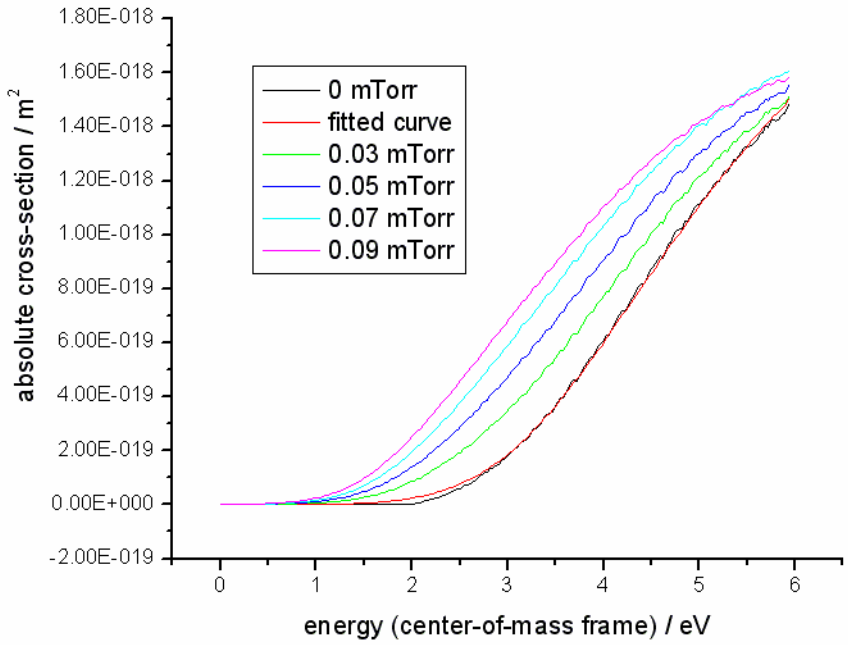


Figure S6. Cross-section and extrapolation to zero pressure for **3** → **4.**

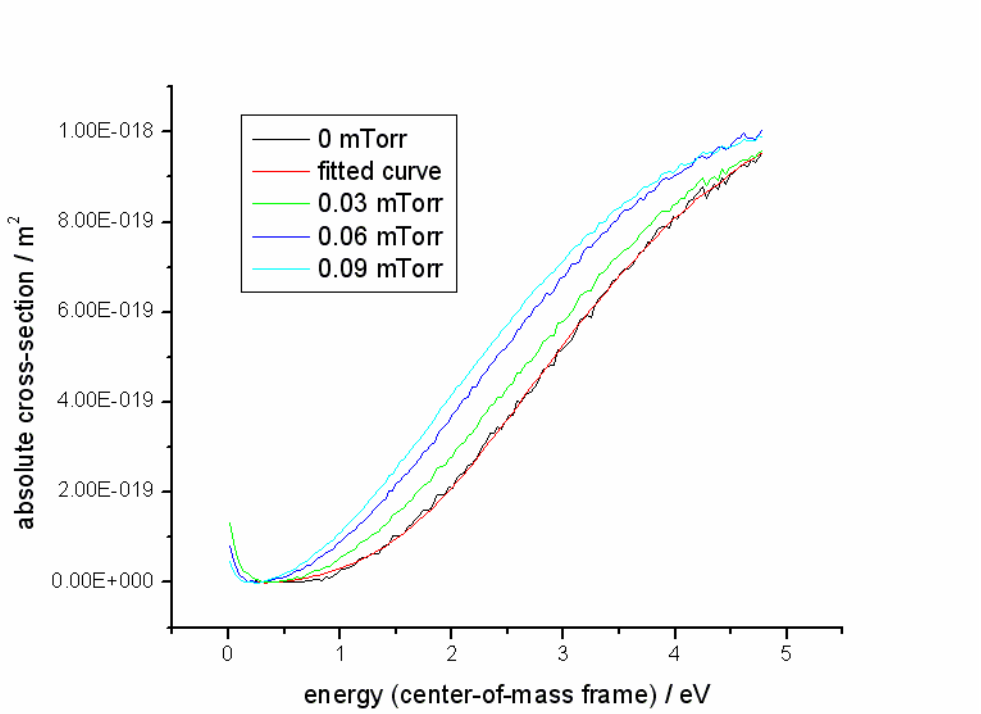


Figure S7. Cross-section and extrapolation to zero pressure for **7** → **4.**

Linear Transit calculations for dissociation (without phosphonium label):

Starting geometries are similar to the ones used by Zhao and Truhlar[3] and Harvey[4]. They took the geometries from crystal structure analogues of **1**[5] (p-Chlorophenyl) and **3**[6] (IMes-ligand). Here we used a crystal structure with the H_2IMes ligand for **3**.[7] The Ru-P distance has been increased in intervals of 0.09 Angstr. [In addition, geometry optimizations at the BP86/ZORA-TZP level of theory (ADF 2006) using the same geometries of Zhao and Truhlar as inputs result in BDE's (without ZPE correction) of 15.4 (**1** → **2**) and 16.6 (**3** → **4**) kcal/mol, which shows the expected order, in contrast to other BP86 values.[3]]

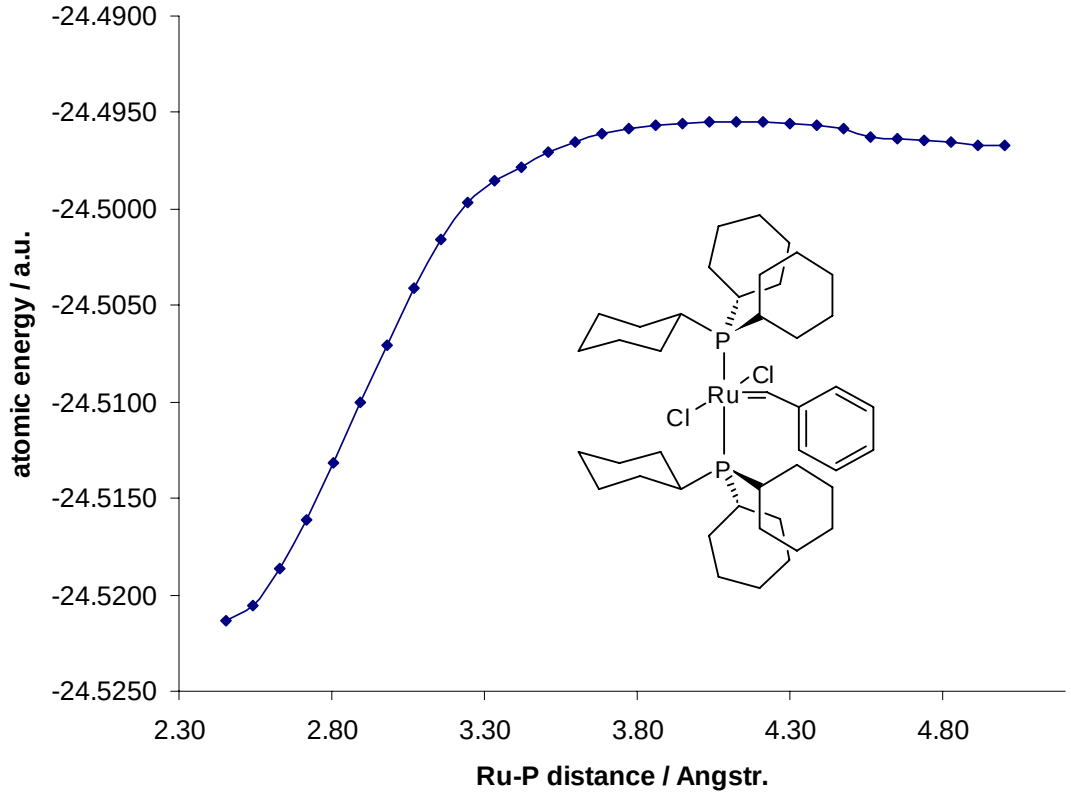


Figure S8. Linear Transit calculation for dissociation **1** → **2** with BP86/ZORA-TZP using ADF 2006 (without phosphonium label).

Coordinates of first point of Linear Transit for Grubbs 1 (= unlabeled 1)

Ru	-0.00323	0.021493	-0.01349
P	2.451341	-0.00677	-0.06726
C	3.124792	1.761111	-0.20095
C	2.618438	2.48283	-1.46969
C	3.29328	3.854849	-1.62912
C	3.083963	4.73343	-0.38804
C	3.542732	4.014583	0.888232
C	2.878453	2.6351	1.047731
C	3.210074	-0.84035	-1.59275
C	4.626659	-0.40369	-2.0245
C	4.994432	-1.02602	-3.38565
C	4.878504	-2.55679	-3.36902
C	3.487357	-3.00074	-2.89518
C	3.132216	-2.38103	-1.53228
C	3.280765	-0.626	1.516437
C	2.775436	-1.99396	2.020664

Coordinates of last point of Linear Transit for Grubbs 1 (corresponds to unlabeled 2)

Ru	-1.15811	-0.09338	-0.13536
P	3.808062	-0.45161	-0.59235
C	4.252559	1.129768	-1.53911
C	4.117695	0.885419	-3.05747
C	4.403087	2.15594	-3.87591
C	3.504232	3.321114	-3.43936
C	3.630574	3.574989	-1.9307
C	3.344576	2.302722	-1.11454
C	5.175797	-1.63256	-1.20661
C	6.62241	-1.12706	-1.37328
C	7.504814	-2.18498	-2.06234
C	7.481054	-3.5225	-1.30757
C	6.043219	-4.02639	-1.11066
C	5.162944	-2.96489	-0.42879
C	4.192936	0.049365	1.198777
C	3.656674	-0.99722	2.200722

C	3.355912	-2.30663	3.410735	C	3.723434	-0.4728	3.645288
C	4.890579	-2.2589	3.413412	C	5.139319	-0.01177	4.022655
C	5.401332	-0.91015	2.887456	C	5.674688	1.023122	3.021743
C	4.822155	-0.58807	1.497496	C	5.618175	0.488835	1.578648
H	4.218679	1.630388	-0.30277	H	5.300312	1.404717	-1.32053
H	1.794032	2.752891	1.210191	H	2.289528	2.007876	-1.25577
H	3.267565	2.146595	1.953415	H	3.472952	2.522078	-0.04393
H	4.639797	3.884079	0.85542	H	4.653141	3.928791	-1.70596
H	3.328821	4.632642	1.77486	H	2.944324	4.378324	-1.61807
H	3.614336	5.692627	-0.5003	H	3.754036	4.232812	-4.00563
H	2.010523	4.975901	-0.29821	H	2.454315	3.075809	-3.67667
H	2.904312	4.359222	-2.52806	H	4.267192	1.945904	-4.94902
H	4.376367	3.709622	-1.79491	H	5.46196	2.442889	-3.74299
H	1.525351	2.617417	-1.40076	H	3.090653	0.538577	-3.26871
H	2.780951	1.870432	-2.3688	H	4.79499	0.081017	-3.38199
H	2.495762	-0.51116	-2.37374	H	4.798906	-1.86301	-2.22316
H	2.129229	-2.70706	-1.22094	H	4.130709	-3.33359	-0.31803
H	3.842196	-2.75822	-0.77478	H	5.544082	-2.79226	0.592014
H	2.731293	-2.69008	-3.63714	H	5.609016	-4.27825	-2.09509
H	3.435139	-4.09921	-2.83071	H	6.040633	-4.95591	-0.51874
H	5.096059	-2.96693	-4.36835	H	8.082684	-4.27565	-1.8412
H	5.64244	-2.97084	-2.6863	H	7.953609	-3.3865	-0.31815
H	4.317112	-0.61951	-4.15719	H	7.139936	-2.34365	-3.09309
H	6.014502	-0.72042	-3.66948	H	8.538475	-1.81325	-2.15035
H	5.365198	-0.72296	-1.27192	H	7.049918	-0.89265	-0.38571
H	4.70327	0.689994	-2.10003	H	6.645885	-0.19312	-1.95458
H	2.913865	0.11884	2.247753	H	3.534449	0.933381	1.306726
H	1.67857	-1.97866	2.075066	H	2.619824	-1.264	1.94463
H	3.06288	-2.79377	1.317427	H	4.254093	-1.92174	2.127305
H	3.003296	-3.29497	3.747046	H	3.374509	-1.25123	4.342552
H	2.96467	-1.56926	4.133168	H	3.023678	0.375333	3.748621
H	5.280375	-3.06865	2.770516	H	5.815529	-0.8859	4.031104
H	5.281287	-2.44646	4.426331	H	5.149768	0.401744	5.044003
H	6.502379	-0.90541	2.841927	H	6.708188	1.307807	3.278121
H	5.110485	-0.11144	3.592215	H	5.068015	1.943886	3.090601
H	5.191055	0.39199	1.161208	H	5.993068	1.251634	0.878575
H	5.196115	-1.33356	0.776627	H	6.297597	-0.37661	1.499933
Cl	-0.02464	0.151862	-2.47355	Cl	-0.75344	1.128321	-2.0974
Cl	0.130506	0.501929	2.407288	Cl	-0.45595	-0.52561	2.062572
C	-0.34726	-1.7588	0.442569	C	-1.87166	-1.71546	-0.72351
C	-0.50795	-3.02016	-0.28787	C	-1.08862	-2.81902	-1.25638
C	-0.774	-4.1769	0.482683	C	-1.76377	-4.01644	-1.5979
C	-0.95057	-5.42185	-0.11698	C	-1.07296	-5.11259	-2.10902
C	-0.86682	-5.54234	-1.50802	C	0.312121	-5.03959	-2.29445
C	-0.6026	-4.40894	-2.28877	C	0.997929	-3.86257	-1.96488
C	-0.42287	-3.16387	-1.69158	C	0.313531	-2.76507	-1.45306
H	-0.46053	-1.90797	1.534662	H	-2.94829	-1.92737	-0.67215
H	-0.83953	-4.07874	1.567114	H	-2.84417	-4.06994	-1.45199
H	-1.15436	-6.29929	0.498251	H	-1.61278	-6.0256	-2.36452
H	-1.00596	-6.51538	-1.98232	H	0.856304	-5.89604	-2.69571

H	-0.53657	-4.50088	-3.37413	H	2.076734	-3.80076	-2.11058
H	-0.21719	-2.27592	-2.29296	H	0.87595	-1.85913	-1.20666
P	-2.31565	0.864213	0.009734	P	-3.09874	0.907	0.403309
C	-2.35443	2.759621	0.032101	C	-2.84599	2.666946	1.07166
C	-1.69629	3.370516	1.287833	C	-1.9832	2.717937	2.352221
C	-1.86841	4.89867	1.309701	C	-1.89158	4.149755	2.907309
C	-1.3154	5.551562	0.035558	C	-1.35632	5.132424	1.85802
C	-1.93438	4.928061	-1.22292	C	-2.20471	5.080968	0.581047
C	-1.77007	3.398274	-1.24735	C	-2.30197	3.653482	0.014792
C	-3.32354	0.485055	-1.54366	C	-4.20599	1.215217	-1.10687
C	-3.43363	-1.01837	-1.869	C	-4.56552	-0.04579	-1.92017
C	-4.01502	-1.22194	-3.27836	C	-5.2554	0.330242	-3.24384
C	-5.37971	-0.53498	-3.43386	C	-6.48624	1.2192	-3.02464
C	-5.29835	0.953512	-3.0644	C	-6.12264	2.465466	-2.20668
C	-4.70382	1.161385	-1.65842	C	-5.45842	2.088518	-0.86982
C	-3.26537	0.419161	1.587197	C	-3.98596	0.067494	1.857066
C	-3.57267	-1.08681	1.726246	C	-4.1483	-1.46213	1.732897
C	-4.07299	-1.41027	3.144566	C	-4.65283	-2.06957	3.053931
C	-5.31608	-0.58202	3.500986	C	-5.95173	-1.41192	3.537726
C	-5.0558	0.91926	3.311124	C	-5.78888	0.110209	3.644886
C	-4.53553	1.239701	1.896373	C	-5.30888	0.719387	2.314821
H	-3.43167	3.009537	0.063513	H	-3.86936	2.989135	1.341682
H	-2.1151	2.932596	2.205774	H	-2.38587	2.049437	3.127441
H	-0.62488	3.112823	1.302739	H	-0.97078	2.343906	2.127059
H	-2.94223	5.14246	1.406285	H	-2.8939	4.479431	3.236047
H	-1.37235	5.314795	2.201029	H	-1.25122	4.153909	3.803399
H	-0.22078	5.409633	0.005899	H	-0.31359	4.866211	1.611274
H	-1.49075	6.639201	0.051493	H	-1.33419	6.155982	2.264451
H	-1.48498	5.363822	-2.12955	H	-1.78776	5.750942	-0.18732
H	-3.01113	5.174788	-1.25796	H	-3.22035	5.454813	0.80546
H	-2.2513	2.990511	-2.14874	H	-2.93896	3.661087	-0.88199
H	-0.69976	3.141942	-1.33181	H	-1.30714	3.317402	-0.3215
H	-2.65673	0.911358	-2.31804	H	-3.49479	1.789082	-1.73284
H	-5.38957	0.724749	-0.91402	H	-6.18826	1.535533	-0.25736
H	-4.64347	2.237639	-1.44138	H	-5.20532	3.003315	-0.31426
H	-4.66405	1.476704	-3.80158	H	-5.42868	3.095236	-2.79034
H	-6.29562	1.419298	-3.11999	H	-7.01858	3.077036	-2.01461
H	-5.75708	-0.65175	-4.4625	H	-6.92701	1.510057	-3.99119
H	-6.11235	-1.03148	-2.77217	H	-7.26099	0.64551	-2.48486
H	-4.10186	-2.2987	-3.4939	H	-5.53245	-0.58598	-3.78863
H	-3.30717	-0.80681	-4.01681	H	-4.52782	0.864326	-3.87893
H	-4.08644	-1.51969	-1.13406	H	-5.23447	-0.69975	-1.33132
H	-2.4445	-1.48885	-1.8002	H	-3.6525	-0.61344	-2.14197
H	-2.4971	0.659884	2.349293	H	-3.22701	0.226245	2.648029
H	-4.35008	-1.37782	0.998204	H	-4.86152	-1.7035	0.923626
H	-2.67917	-1.68481	1.494413	H	-3.18174	-1.91395	1.475001
H	-3.26662	-1.19417	3.866668	H	-3.8697	-1.93976	3.82071
H	-4.29417	-2.48674	3.226961	H	-4.79226	-3.15514	2.931155
H	-5.6331	-0.78648	4.536126	H	-6.25806	-1.83399	4.507798
H	-6.15347	-0.88952	2.848863	H	-6.76454	-1.63902	2.824692

H	-4.30736	1.254522	4.050299	H	-5.05489	0.344405	4.435598
H	-5.97402	1.49577	3.508277	H	-6.73847	0.580667	3.945864
H	-5.32173	1.000474	1.162302	H	-6.08587	0.550622	1.551162
H	-4.3451	2.319257	1.816989	H	-5.20087	1.808515	2.424881

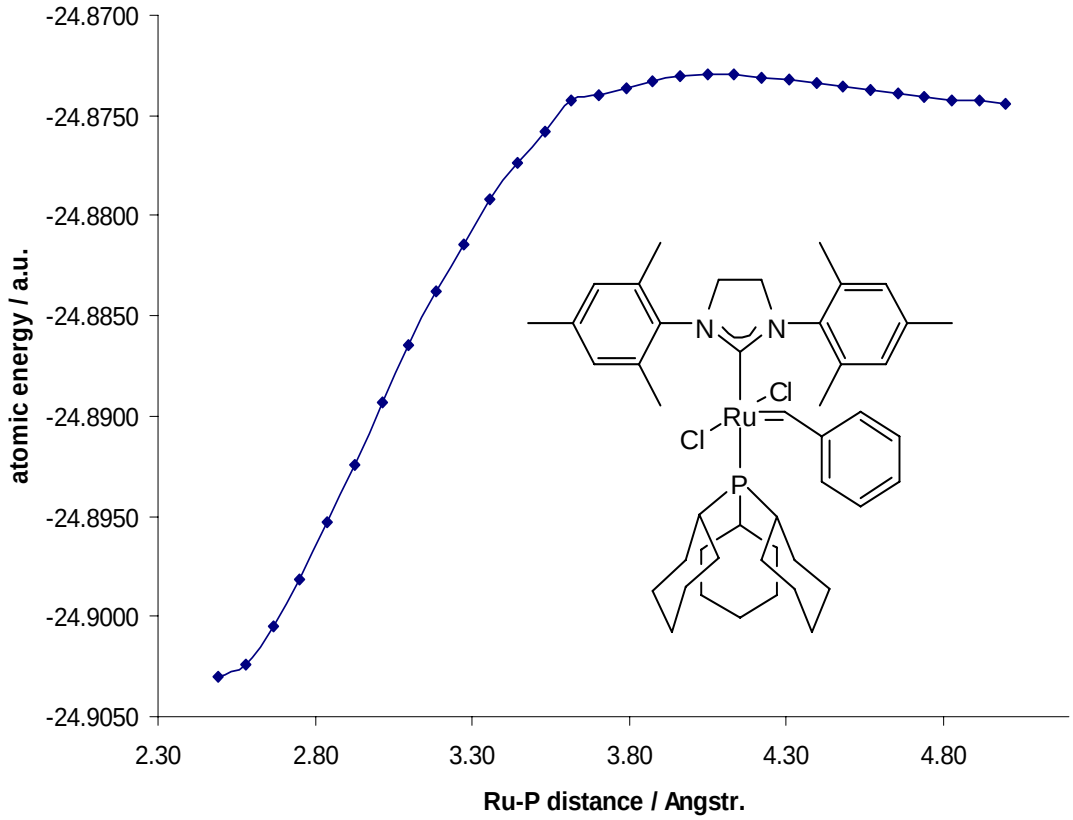


Figure S9. Linear Transit calculation for dissociation **3** → **4** with BP86/ZORA-TZP using ADF 2006 (without phosphonium label).

Coordinates of first point of Linear Transit for Grubbs2 (= unlabeled 3)

Ru	0.026056	0.027374	-0.04206
P	2.519135	0.061882	-0.00947
Cl	-7.8E-05	2.486865	-0.17811
Cl	0.183099	-2.38357	0.519379
C	3.359513	-1.53358	-0.5792
C	2.866243	-2.08145	-1.93456
C	3.45204	-3.47937	-2.19894
C	4.986126	-3.47833	-2.13546
C	5.482642	-2.90991	-0.79874

Coordinates of last point of Linear Transit for Grubbs2 (corresponds to unlabeled 4)

Ru	-1.05713	-0.14174	-0.18972
P	3.9222	0.262794	0.016717
Cl	-0.56446	2.060047	-0.90155
Cl	-0.45431	-2.05586	1.034543
C	5.100058	-0.79826	-1.04482
C	4.996651	-0.42106	-2.5366
C	5.699609	-1.45429	-3.43304
C	7.165273	-1.65371	-3.0188
C	7.278445	-2.01383	-1.52994

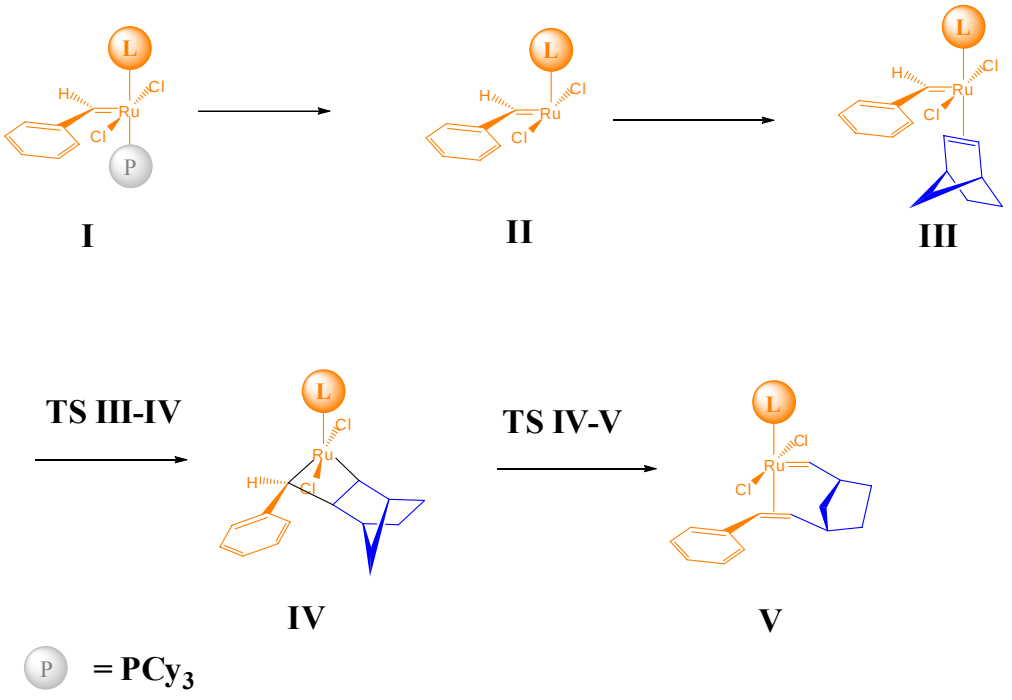
C	4.900267	-1.51092	-0.52615	C	6.575623	-0.97349	-0.63728
H	2.990476	-2.24483	0.184509	H	4.616649	-1.79024	-0.94478
H	1.769618	-2.13992	-1.924	H	3.938187	-0.3243	-2.8238
H	3.15467	-1.40171	-2.75469	H	5.463711	0.565925	-2.69705
H	3.109835	-3.84766	-3.17971	H	5.6396	-1.14265	-4.48883
H	3.054976	-4.1793	-1.44283	H	5.164385	-2.41734	-3.3576
H	5.382835	-2.85977	-2.96057	H	7.724387	-0.71935	-3.20727
H	5.379809	-4.49619	-2.28779	H	7.637294	-2.43239	-3.6393
H	6.583702	-2.86509	-0.78361	H	8.336912	-2.10731	-1.23757
H	5.182588	-3.58921	0.018535	H	6.817198	-3.00342	-1.36096
H	5.25752	-1.14525	0.447921	H	6.655419	-1.2817	0.416091
H	5.28164	-0.81184	-1.28885	H	7.103853	-0.01053	-0.72388
C	3.149786	0.214619	1.768189	C	4.490967	-0.2258	1.759358
C	2.628768	1.487822	2.472535	C	3.813476	0.639213	2.841005
C	3.347591	1.686346	3.818274	C	4.199104	0.184768	4.259198
C	3.194634	0.458076	4.727141	C	3.874329	-1.29794	4.486947
C	3.624914	-0.83363	4.018001	C	4.542351	-2.17352	3.417665
C	2.907962	-1.01675	2.66798	C	4.166499	-1.71661	1.998361
H	4.245166	0.321842	1.650245	H	5.583908	-0.08422	1.842321
H	2.754109	2.379204	1.839114	H	4.084671	1.698197	2.714937
H	1.543017	1.388677	2.647321	H	2.717705	0.574741	2.720629
H	4.420687	1.873803	3.629701	H	5.28184	0.346467	4.410379
H	2.956539	2.584625	4.322843	H	3.682982	0.812638	5.003466
H	2.133378	0.365486	5.012468	H	2.78058	-1.44026	4.434367
H	3.769804	0.594649	5.657893	H	4.190511	-1.61225	5.495008
H	3.430047	-1.70542	4.663801	H	4.260675	-3.2298	3.555123
H	4.71645	-0.81104	3.844386	H	5.639452	-2.12113	3.539946
H	3.2669	-1.93988	2.188443	H	4.68608	-2.34748	1.261376
H	1.825249	-1.15224	2.827338	H	3.085207	-1.8718	1.836821
C	3.312781	1.572143	-0.83589	C	4.483136	2.07648	-0.07837
C	3.29094	1.490774	-2.37745	C	3.861559	2.785137	-1.30271
C	3.657991	2.849156	-3.00007	C	4.080282	4.306538	-1.24092
C	5.027329	3.341847	-2.51122	C	5.566537	4.663192	-1.08568
C	5.08803	3.375603	-0.97772	C	6.187355	3.954179	0.12738
C	4.710551	2.017861	-0.35416	C	5.974454	2.430362	0.058253
H	2.585147	2.35811	-0.54852	H	3.962344	2.494603	0.805098
H	4.018072	0.732305	-2.71963	H	4.318619	2.395629	-2.22843
H	2.301834	1.171053	-2.73545	H	2.785899	2.556626	-1.35857
H	2.883733	3.586833	-2.72554	H	3.517841	4.713991	-0.38166
H	3.646246	2.771819	-4.09899	H	3.663132	4.784453	-2.142
H	5.250109	4.339014	-2.92436	H	5.693084	5.754369	-0.99836
H	5.812348	2.662038	-2.88912	H	6.109432	4.356166	-1.99799
H	6.09365	3.673209	-0.63865	H	7.263351	4.182989	0.196726
H	4.388786	4.144297	-0.60391	H	5.722864	4.342325	1.051733
H	5.465467	1.267329	-0.64022	H	6.52212	2.038623	-0.81574
H	4.749159	2.10672	0.740871	H	6.409808	1.947794	0.947298
C	-0.1987	-0.49291	-1.82587	C	-1.54492	-0.94277	-1.80029
C	-0.20647	0.151206	-3.14494	C	-0.68005	-1.15909	-2.94796
C	-0.17438	1.543727	-3.38519	C	0.544435	-0.47851	-3.15338
C	-0.18376	2.041242	-4.68632	C	1.301959	-0.72035	-4.29665

C	-0.21268	1.170309	-5.78343	C	0.871553	-1.64909	-5.25251
C	-0.23962	-0.21148	-5.56782	C	-0.33547	-2.33409	-5.06527
C	-0.24451	-0.71121	-4.26716	C	-1.1052	-2.08577	-3.93285
H	-0.31847	-1.58892	-1.92134	H	-2.53801	-1.39812	-1.90507
H	-0.13737	2.217266	-2.52771	H	0.872938	0.26341	-2.42441
H	-0.16142	3.120318	-4.85002	H	2.233388	-0.17481	-4.45231
H	-0.21197	1.566914	-6.8005	H	1.471649	-1.83299	-6.14525
H	-0.25828	-0.89911	-6.41493	H	-0.67748	-3.05539	-5.80924
H	-0.2719	-1.78861	-4.09774	H	-2.05394	-2.60544	-3.7883
C	-1.94845	0.051544	0.64864	C	-2.81308	0.330066	0.523852
N	-2.33357	0.277361	1.945476	N	-2.96535	0.813985	1.80528
N	-3.09732	-0.17225	-0.05763	N	-4.04421	0.424752	-0.08273
C	-4.30263	-0.23052	0.795749	C	-5.10034	0.85706	0.857691
C	-3.8028	0.34939	2.104713	C	-4.29396	1.41594	2.025054
H	-4.63972	-1.27294	0.899122	H	-5.72478	-0.00245	1.153384
H	-5.11623	0.351123	0.347605	H	-5.74823	1.605806	0.384384
H	-4.11962	-0.22491	2.98302	H	-4.69107	1.121701	3.004846
H	-4.11352	1.395734	2.243911	H	-4.22569	2.515212	1.991409
C	-3.31568	-0.39389	-1.46265	C	-4.47852	-0.04992	-1.36909
C	-3.62101	0.718864	-2.27161	C	-4.57218	0.864552	-2.43639
C	-4.02566	0.48711	-3.59113	C	-5.09832	0.409499	-3.65143
C	-4.13648	-0.80633	-4.11467	C	-5.53189	-0.91021	-3.82707
C	-3.82467	-1.88748	-3.28202	C	-5.42391	-1.79108	-2.74448
C	-3.42197	-1.71141	-1.95141	C	-4.90442	-1.38584	-1.50795
C	-3.52944	2.121836	-1.72689	C	-4.10778	2.290362	-2.28512
C	-4.55638	-1.02688	-5.54854	C	-6.079	-1.37171	-5.15755
C	-3.13154	-2.90513	-1.07646	C	-4.76769	-2.37609	-0.37628
H	-4.26726	1.34469	-4.22433	H	-5.17011	1.112854	-4.48512
H	-3.91126	-2.90588	-3.67087	H	-5.75239	-2.82727	-2.86103
H	-2.52987	2.327177	-1.31481	H	-3.04924	2.331471	-1.98874
H	-4.25264	2.28819	-0.91231	H	-4.68016	2.822445	-1.50958
H	-3.74264	2.855503	-2.51405	H	-4.23036	2.837823	-3.22766
H	-5.22521	-0.22876	-5.89726	H	-6.76807	-0.62998	-5.58444
H	-5.07296	-1.98795	-5.67341	H	-6.61701	-2.32342	-5.06226
H	-3.67898	-1.03258	-6.21419	H	-5.26754	-1.51728	-5.88712
H	-3.13081	-3.8262	-1.67312	H	-5.03591	-3.38495	-0.71267
H	-2.15846	-2.8139	-0.56979	H	-3.73912	-2.4043	0.010669
H	-3.89597	-3.02755	-0.29236	H	-5.42422	-2.12476	0.470624
C	-1.56837	0.486575	3.152477	C	-2.00922	0.834206	2.885157
C	-1.35046	1.799201	3.621023	C	-1.2793	2.007563	3.165533
C	-0.7949	1.962732	4.899478	C	-0.43644	2.008527	4.28722
C	-0.49045	0.878171	5.725236	C	-0.33071	0.90812	5.141194
C	-0.74092	-0.41119	5.237709	C	-1.11028	-0.22154	4.861295
C	-1.28915	-0.63394	3.96987	C	-1.96084	-0.27906	3.754041
C	-1.74583	3.013338	2.820126	C	-1.42111	3.262764	2.341377
C	0.067328	1.083211	7.114042	C	0.591028	0.930845	6.336962
C	-1.62388	-2.03426	3.528051	C	-2.81596	-1.49778	3.521351
H	-0.62184	2.978334	5.264647	H	0.141242	2.911104	4.502584
H	-0.53093	-1.27587	5.872998	H	-1.06676	-1.08339	5.532272
H	-1.42292	2.93112	1.772811	H	-1.40927	3.052583	1.263933

H	-2.83851	3.15856	2.833634	H	-2.36239	3.784635	2.579582
H	-1.29537	3.916859	3.25007	H	-0.60146	3.958146	2.561412
H	0.128281	2.149199	7.366377	H	0.936187	1.948781	6.557919
H	1.077433	0.657092	7.204927	H	1.479884	0.307288	6.157317
H	-0.56156	0.590063	7.869702	H	0.092908	0.534896	7.233152
H	-1.35864	-2.75655	4.310172	H	-2.77022	-2.16939	4.387513
H	-2.70094	-2.14287	3.324415	H	-3.8689	-1.22937	3.351125
H	-1.09209	-2.30188	2.60124	H	-2.46086	-2.04776	2.637946

Energie surfaces (BP86/ZORA-TZP) – without phosphonium label:

The energy surfaces below for reaction with norbornene have been calculated using BP86/ZORA-TZP (ADF 2006). Geometries for structures **I** and **II** have been described above. Transition states and π-complexes (**III** and **V**) were found by linear transit calculations starting from the metallacyclobutanes **IV** and their nature checked by calculating the frequencies. TS's for the second generation system (Figure S11) are lower in energy then for Grubbs 1 (Figure S10) and also showing a loose transition state for the RCM reaction **V** → **II**.



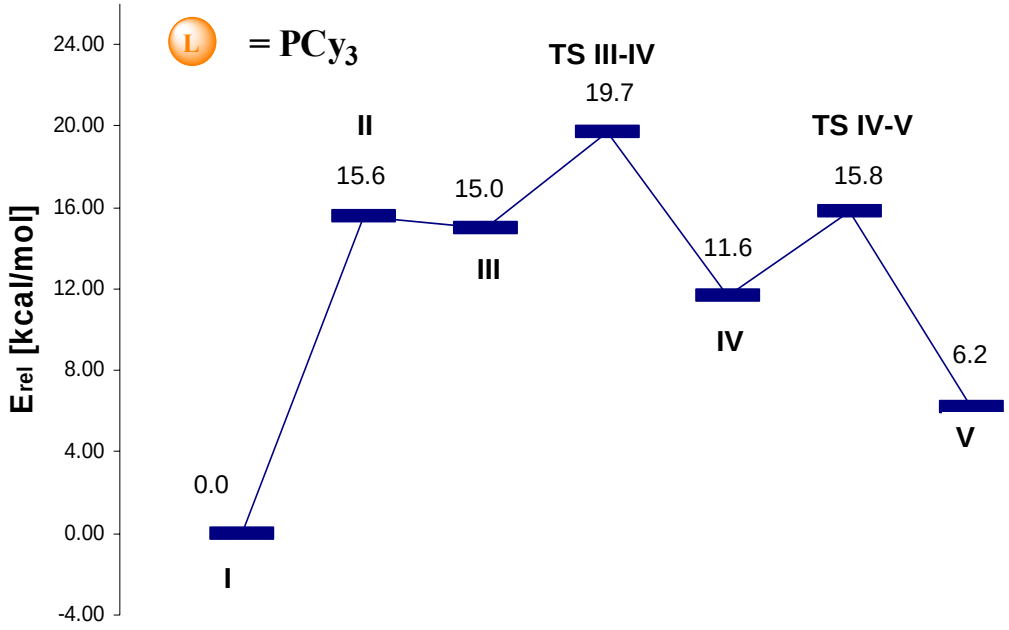


Figure S10. Energy surface without ZPE correction for reaction of first generation catalyst with norbornene at the BP86/ZORA-TZP level of theory using ADF 2006 (without phosphonium label).

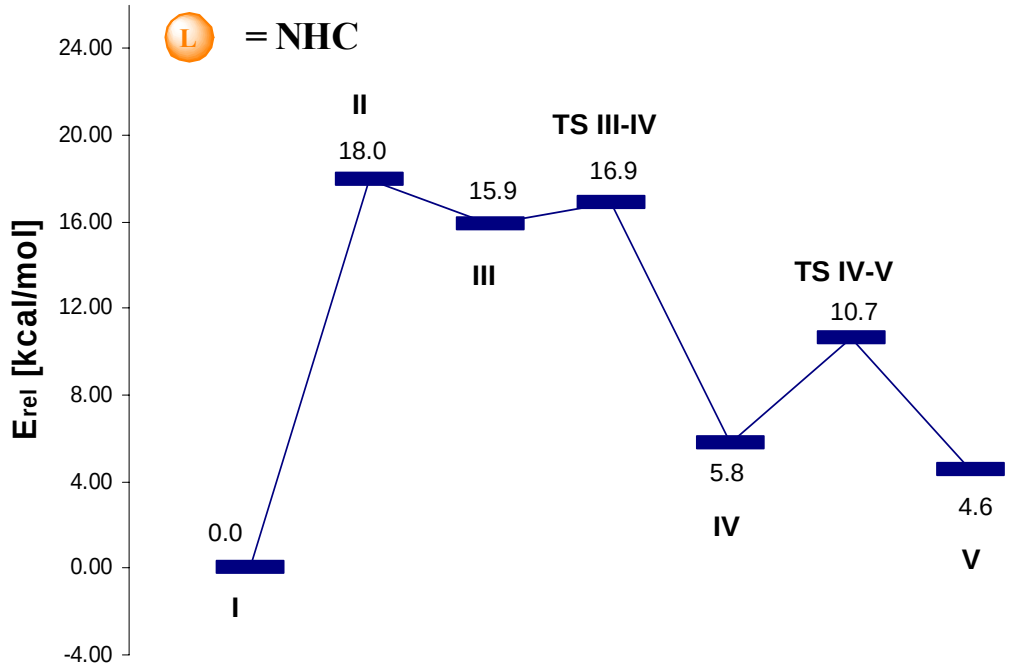


Figure S11. Energy surface without ZPE correction for reaction of second generation catalyst with norbornene at the BP86/ZORA-TZP level of theory using ADF 2006 (without phosphonium label). *Optimizing TS IV-V always gave a second slightly negative frequency which corresponds to twisting of the NHC ring.*

Geometry of unlabeled 5

C	18.59607	7.227297	14.90357
C	18.63259	6.616146	16.17461
C	18.41259	5.225575	16.31713
C	18.03265	4.494656	15.18742
C	17.8963	5.0891	13.92644
C	18.19888	6.447276	13.8059
N	19.08427	7.358097	17.33026
C	18.35002	8.077827	18.23663
N	19.21458	8.511436	19.19798
C	20.57711	7.961868	19.02141
C	20.53673	7.449253	17.58839
Ru	16.36538	8.456566	17.96755
C	15.93414	9.082271	19.6859
C	15.37107	10.32098	20.22225
C	15.35412	11.56776	19.55501
C	14.77279	12.68303	20.15268
C	14.18003	12.58452	21.41889
C	14.19221	11.3617	22.09833
C	14.79315	10.24905	21.51325
C	18.94639	9.231887	20.41521
C	18.59756	8.520428	21.58237
C	18.47495	9.238425	22.77852
C	18.70328	10.61848	22.8442
C	19.06669	11.2858	21.66946
C	19.199	10.6177	20.44623
C	18.37031	7.028503	21.56144
C	18.5368	11.37166	24.14246
C	19.60793	11.3665	19.20363
C	18.61349	4.52083	17.63326
C	17.45826	4.273585	12.73282
C	19.04665	8.648324	14.67543
Cl	16.96459	10.51317	16.75979
Cl	15.88828	6.195054	18.79972
H	15.82124	11.63905	18.57109
H	14.77451	13.63944	19.62677
H	13.71202	13.45912	21.87425
H	13.73504	11.27765	23.08549
H	14.81252	9.295429	22.04337
H	16.00324	8.296972	20.45843
H	21.32944	8.743606	19.1789
H	20.75486	7.156043	19.7508
H	21.00053	8.154446	16.88121
H	21.01186	6.468745	17.46537
H	20.58312	11.0211	18.82468
H	18.87658	11.2222	18.39424
H	19.6959	12.43983	19.41275
H	19.25736	12.36162	21.70115
H	17.48507	11.66315	24.28973

Geometry of unlabeled TS 5-6

C	-0.53663	0.451748	-0.29668
C	1.775411	-0.06201	0.146266
C	2.372454	1.152344	0.561928
Ru	0.588644	1.974763	-0.45413
H	-1.00024	0.403521	0.70372
C	-0.98383	-0.6487	-1.15303
C	-0.56506	-0.88398	-2.48194
C	-1.0439	-1.9842	-3.18926
C	-1.958	-2.86822	-2.60081
C	-2.39265	-2.64583	-1.28981
C	-1.90924	-1.55139	-0.57575
H	0.148284	-0.19398	-2.93404
H	-0.70357	-2.15581	-4.21213
H	-2.3293	-3.72746	-3.16235
H	-3.10475	-3.32835	-0.82339
H	-2.24131	-1.37717	0.448834
H	1.909768	-0.4784	-0.85148
H	3.101095	1.664618	-0.07717
C	1.669997	-0.93465	1.387524
C	3.161941	-1.3347	1.665018
C	3.805151	0.008107	2.140103
C	2.608813	1.01701	2.06181
C	1.447368	0.102002	2.504329
H	0.979918	-1.78345	1.326892
H	3.653844	-1.75592	0.777232
H	3.192488	-2.09775	2.456569
H	4.653716	0.317983	1.514575
H	4.163172	-0.06457	3.177365
H	2.750343	1.950661	2.614639
H	1.610322	-0.32226	3.506438
H	0.477857	0.607083	2.465978
Cl	1.740376	1.534124	-2.58782
Cl	-0.40118	2.727198	1.686466
C	-0.23941	3.734528	-1.20734
N	-1.46676	3.927501	-1.75117
C	-1.7525	5.354359	-2.02435
C	-0.40474	6.025338	-1.77946
N	0.392384	4.94274	-1.16153
H	-2.11392	5.477651	-3.05269
H	-2.53229	5.716059	-1.33931
H	0.074433	6.36028	-2.71072
H	-0.47157	6.884131	-1.10037
C	-2.49629	2.969699	-2.07441
C	-2.48752	2.383341	-3.35615
C	-3.56505	1.565939	-3.71659
C	-4.63843	1.329219	-2.85023
C	-4.61945	1.940828	-1.59244
C	-3.56774	2.770771	-1.1813

H	18.83276	10.75893	25.00469	C	-1.36159	2.635393	-4.32711
H	19.13599	12.29149	24.15132	C	-5.77407	0.419266	-3.25394
H	18.20113	8.696366	23.68782	C	-3.60903	3.431365	0.173371
H	19.31228	6.480155	21.40079	H	-3.56525	1.108002	-4.7091
H	17.95911	6.69033	22.52085	H	-5.45373	1.778221	-0.90482
H	17.67814	6.724681	20.76137	H	-1.25807	3.707084	-4.55944
H	16.40504	3.968979	12.82926	H	-0.39555	2.300418	-3.91941
H	17.55836	4.842504	11.79998	H	-1.54389	2.107264	-5.27125
H	18.05306	3.353665	12.63798	H	-5.9655	0.470775	-4.33424
H	18.15031	6.921794	12.82243	H	-6.70219	0.677212	-2.72694
H	17.84922	3.422702	15.29865	H	-5.53571	-0.62835	-3.01247
H	18.72179	8.998632	13.6875	H	-4.43636	3.026717	0.770067
H	18.65068	9.34151	15.4291	H	-2.66927	3.279438	0.725856
H	20.14742	8.709465	14.69455	H	-3.77214	4.518275	0.08917
H	17.88691	4.883939	18.37497	C	1.736265	5.252217	-0.72177
H	19.62396	4.692568	18.03477	C	2.797674	5.221927	-1.65419
H	18.48109	3.438687	17.51084	C	4.074899	5.596182	-1.21509
C	14.44995	8.406531	16.48386	C	4.316813	6.030043	0.092322
C	14.01626	9.362927	17.37464	C	3.228299	6.120055	0.966502
C	12.68401	8.893619	17.92447	C	1.930381	5.758509	0.58302
C	13.37436	7.332489	16.43576	C	2.587797	4.848124	-3.09898
C	11.70585	9.107215	16.71117	C	5.709295	6.400519	0.5448
C	12.19039	8.039082	15.67969	C	0.784936	5.960531	1.539389
C	12.84009	7.36017	17.8835	H	4.900259	5.564397	-1.93101
H	14.35957	10.39435	17.40868	H	3.382881	6.504014	1.978251
H	15.13365	8.611166	15.6541	H	2.186866	3.82847	-3.19391
H	12.35151	9.35285	18.86178	H	1.886946	5.537366	-3.59535
H	13.67484	6.362613	16.02744	H	3.537901	4.896384	-3.64544
H	10.67387	8.910954	17.0382	H	6.328066	6.738414	-0.29684
H	11.7439	10.13405	16.32089	H	5.686822	7.198803	1.298746
H	11.39855	7.308985	15.45698	H	6.216588	5.535119	0.99932
H	12.51277	8.484789	14.72803	H	1.149914	6.365192	2.491661
H	11.87796	6.8355	17.98619	H	0.257329	5.014484	1.733761
H	13.56674	6.967067	18.60216	H	0.048069	6.673555	1.136963

Geometry of unlabeled 6

C	-0.06129	0.024254	-0.02855
C	1.497732	-0.03353	0.084103
C	2.263718	1.39327	0.159466
Ru	0.48438	1.949311	-0.5563
H	-0.52956	0.099903	0.959513
C	-0.76604	-0.96742	-0.87468
C	-0.329	-1.38959	-2.14753
C	-1.02064	-2.38053	-2.84244
C	-2.16849	-2.96729	-2.29431
C	-2.62387	-2.54867	-1.04061
C	-1.93088	-1.55968	-0.34161

Geometry of unlabeled TS 6-7
(always a second slightly neg. frequency)

C	0.053168	-0.26507	0.021679
C	1.481282	-0.20992	0.14965
C	2.183315	1.839151	0.224941
Ru	0.444409	1.843194	-0.51707
H	-0.49724	-0.19707	0.964827
C	-0.67671	-1.0481	-1.004
C	-0.11992	-1.47982	-2.22479
C	-0.84437	-2.30849	-3.07995
C	-2.13898	-2.72449	-2.74341
C	-2.70973	-2.29172	-1.54324
C	-1.98837	-1.45841	-0.68719

H	0.537658	-0.9066	-2.59994	H	0.873203	-1.13861	-2.51447
H	-0.66604	-2.69371	-3.82608	H	-0.39459	-2.63435	-4.01941
H	-2.705	-3.74299	-2.84354	H	-2.697	-3.38077	-3.41353
H	-3.51765	-2.99628	-0.60273	H	-3.71737	-2.60716	-1.26796
H	-2.28293	-1.24033	0.641407	H	-2.43404	-1.12536	0.252494
H	1.881676	-0.57765	-0.7871	H	2.054952	-0.53996	-0.72131
H	3.005181	1.484295	-0.64675	H	2.970057	1.907615	-0.55015
C	1.950611	-0.62673	1.460703	C	2.13476	-0.46047	1.517202
C	3.474321	-0.90168	1.368892	C	3.68443	-0.45878	1.407953
C	4.107099	0.522104	1.494434	C	4.084638	1.040176	1.577562
C	2.856327	1.445802	1.567689	C	2.712262	1.762051	1.639648
C	1.903856	0.580771	2.413119	C	1.863573	0.749898	2.427217
H	1.354558	-1.50451	1.740333	H	1.74768	-1.40959	1.916869
H	3.749508	-1.41038	0.434175	H	4.026974	-0.88106	0.452478
H	3.783883	-1.55219	2.199423	H	4.116171	-1.07558	2.208589
H	4.762555	0.773152	0.64973	H	4.713269	1.412988	0.75838
H	4.698784	0.617209	2.416639	H	4.632639	1.200724	2.517295
H	3.065264	2.461827	1.923739	H	2.762182	2.77206	2.075915
H	2.319966	0.339789	3.403693	H	2.266146	0.588534	3.439377
H	0.911276	1.027333	2.528509	H	0.809539	1.037887	2.493135
Cl	1.443441	1.453878	-2.7602	Cl	1.553826	1.42132	-2.68687
Cl	-0.62016	2.584295	1.56358	Cl	-0.91328	2.321604	1.486588
C	-0.23653	3.757545	-1.21473	C	-0.19606	3.68824	-1.22388
N	-1.42878	4.002096	-1.81182	N	-1.3909	3.965923	-1.80554
C	-1.62605	5.445311	-2.0789	C	-1.50163	5.372705	-2.25146
C	-0.22831	6.018657	-1.86545	C	-0.14072	5.962353	-1.87909
N	0.462999	4.921417	-1.14968	N	0.551995	4.824391	-1.23145
H	-2.00159	5.593415	-3.0981	H	-1.70073	5.408877	-3.33088
H	-2.36078	5.858406	-1.37227	H	-2.33427	5.867878	-1.73366
H	0.286789	6.231286	-2.81426	H	0.427299	6.300203	-2.757
H	-0.2251	6.930427	-1.25643	H	-0.21715	6.804517	-1.1778
C	-2.48884	3.077468	-2.15273	C	-2.50649	3.081486	-2.06057
C	-2.49203	2.502389	-3.44101	C	-2.54741	2.356815	-3.27123
C	-3.56701	1.676583	-3.79238	C	-3.67872	1.573392	-3.53234
C	-4.6318	1.431132	-2.92002	C	-4.76338	1.515304	-2.65143
C	-4.62077	2.062781	-1.6718	C	-4.71158	2.291496	-1.48906
C	-3.5732	2.899865	-1.2672	C	-3.60638	3.092847	-1.17626
C	-1.39457	2.774436	-4.43694	C	-1.43921	2.43942	-4.28869
C	-5.75646	0.501988	-3.30895	C	-5.95544	0.636485	-2.94638
C	-3.64383	3.598984	0.066118	C	-3.63333	3.95809	0.057925
H	-3.57091	1.220793	-4.78563	H	-3.71199	1.002705	-4.46371
H	-5.45883	1.911616	-0.98632	H	-5.56221	2.28753	-0.80246
H	-1.26356	3.853548	-4.61282	H	-1.25532	3.479736	-4.60007
H	-0.42952	2.380395	-4.08322	H	-0.48886	2.049452	-3.89354
H	-1.62977	2.305839	-5.40059	H	-1.70361	1.865909	-5.18568
H	-5.86928	0.442267	-4.39937	H	-6.14935	0.572717	-4.02556
H	-6.71384	0.826739	-2.87946	H	-6.86247	1.011536	-2.45432
H	-5.55824	-0.51691	-2.94144	H	-5.78136	-0.38885	-2.5846
H	-4.5217	3.257471	0.628662	H	-4.52816	3.742284	0.65484
H	-2.74405	3.406101	0.669572	H	-2.74688	3.778973	0.6825

H	-3.73901	4.689926	-0.05603	H	-3.66373	5.028863	-0.20072
C	1.769502	5.171666	-0.58012	C	1.841269	5.079184	-0.6349
C	2.918075	5.084338	-1.39334	C	2.991635	5.07364	-1.44934
C	4.157513	5.406286	-0.81978	C	4.215684	5.433289	-0.86646
C	4.278229	5.835236	0.504485	C	4.319056	5.81281	0.475159
C	3.108539	5.965286	1.263796	C	3.14991	5.835165	1.246409
C	1.846272	5.656327	0.744561	C	1.901853	5.484048	0.716567
C	2.849191	4.688514	-2.84584	C	2.931191	4.705317	-2.90927
C	5.626123	6.170165	1.099155	C	5.652189	6.191701	1.07725
C	0.613869	5.865616	1.584349	C	0.665535	5.557978	1.574365
H	5.053015	5.330474	-1.44188	H	5.111886	5.427988	-1.4924
H	3.172349	6.333726	2.291195	H	3.201257	6.154049	2.291119
H	2.374502	3.704404	-2.97759	H	2.46958	3.715786	-3.04948
H	2.273774	5.419396	-3.43559	H	2.341056	5.434109	-3.48721
H	3.857598	4.644458	-3.27593	H	3.939776	4.685939	-3.34077
H	6.41858	6.131483	0.341283	H	6.394553	6.40868	0.298631
H	5.627406	7.176535	1.542477	H	5.56292	7.0776	1.721388
H	5.892137	5.464024	1.900183	H	6.052517	5.376554	1.699879
H	0.881726	6.29977	2.555619	H	0.914173	5.932821	2.575205
H	0.086594	4.913763	1.752714	H	0.184482	4.572176	1.676423
H	-0.09579	6.551608	1.096151	H	-0.08651	6.236227	1.142124

Geometry of unlabeled 7

C	0.039358	-0.52785	0.076747
C	1.421321	-0.48455	0.021751
C	2.036619	2.260498	0.424272
Ru	0.499919	1.734349	-0.46579
H	-0.43682	-0.4394	1.055497
C	-0.85997	-1.06148	-0.96787
C	-0.44044	-1.37918	-2.27665
C	-1.30948	-2.00937	-3.16597
C	-2.61308	-2.33858	-2.7743
C	-3.04879	-2.01092	-1.48705
C	-2.18546	-1.36923	-0.59875
H	0.567648	-1.11803	-2.59923
H	-0.9642	-2.2536	-4.17213
H	-3.28362	-2.84676	-3.46959
H	-4.0623	-2.26131	-1.16983
H	-2.52591	-1.1136	0.40656
H	1.913271	-0.72283	-0.92374
H	2.667266	3.007817	-0.08576
C	2.306547	-0.55209	1.255265
C	3.80516	-0.26559	0.934015
C	4.063917	1.203316	1.373089
C	2.640757	1.754009	1.696306
C	1.942721	0.527606	2.293434
H	2.193581	-1.56427	1.677502
H	4.009966	-0.40847	-0.13636

H	4.45742	-0.95765	1.484863
H	4.579274	1.796934	0.606304
H	4.675026	1.242635	2.286941
H	2.692436	2.613076	2.390414
H	2.388463	0.283754	3.270397
H	0.865539	0.678271	2.424292
Cl	1.718078	1.388713	-2.59005
Cl	-1.0343	2.065588	1.421179
C	-0.02981	3.599801	-1.23924
N	-1.20413	3.811263	-1.90359
C	-1.22757	5.099586	-2.63177
C	-0.04939	5.841696	-2.02095
N	0.698318	4.753127	-1.34806
H	-1.09488	4.918454	-3.70926
H	-2.18804	5.607328	-2.48078
H	0.582766	6.33842	-2.76711
H	-0.36073	6.592793	-1.27773
C	-2.35702	2.952906	-2.06525
C	-2.46582	2.120032	-3.19841
C	-3.6575	1.403509	-3.37662
C	-4.73512	1.516081	-2.49403
C	-4.61337	2.397039	-1.41354
C	-3.44747	3.136069	-1.18606
C	-1.38019	2.031059	-4.24092
C	-5.99277	0.705079	-2.69525
C	-3.39236	4.122636	-0.04806
H	-3.74257	0.746852	-4.24602
H	-5.45665	2.529423	-0.73054
H	-1.36356	2.937621	-4.86856
H	-0.38126	1.91263	-3.79905
H	-1.56404	1.179662	-4.90792
H	-6.16104	0.4809	-3.75696
H	-6.8766	1.229968	-2.30855
H	-5.9224	-0.25716	-2.16413
H	-4.35725	4.159291	0.472811
H	-2.61465	3.833573	0.67323
H	-3.16414	5.140034	-0.40205
C	1.891728	5.158686	-0.65216
C	3.099195	5.235236	-1.37352
C	4.232521	5.732518	-0.71561
C	4.190379	6.159643	0.615952
C	2.968415	6.08244	1.296545
C	1.805778	5.594069	0.687686
C	3.186453	4.773962	-2.80588
C	5.429016	6.681675	1.306084
C	0.509201	5.537625	1.456152
H	5.173736	5.791541	-1.26824
H	2.909595	6.424892	2.333224
H	2.816809	3.742061	-2.91192
H	2.579385	5.404733	-3.47403

H	4.223165	4.818758	-3.16186
H	6.175868	7.027584	0.580067
H	5.190065	7.517828	1.977229
H	5.901351	5.897486	1.918074
H	0.64588	5.937664	2.468574
H	0.126273	4.508114	1.536362
H	-0.27766	6.132446	0.96747

References:

[1] Ervin, K.M.; Armentrout, P.B. *J. Chem. Phys.* **1985,** *83*, 166.

[2] This program was kindly provided as an executable by P.B. Armentrout.

[3] Zhao, Y.; Truhlar, D.G. *Organic Lett.* **2007,** *9*, 1967.

[4] Tsipis, A.C.; Orpen, A.G.; Harvey, J.N. *Dalton Trans.* **2005,** 2849.

[5] Schwab, P.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc.* **1996,** *118*, 100.

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

[7] Lehman, Jr., S.E.,; Wagener, K.B. *Organometallics* **2005,** *24*, 1477.