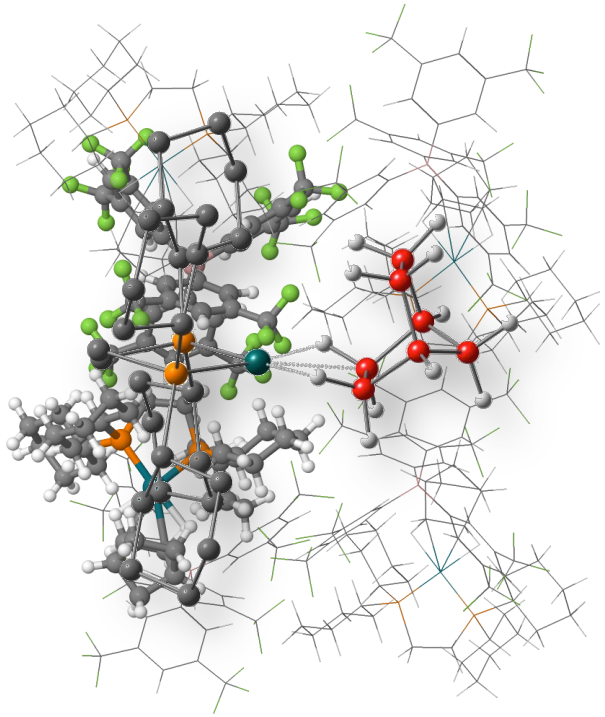
Rhodium(I) Alkane σ-Complexes

Computational Modelling of Organometallic Reactivity in Condensed Phase



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Edinburgh, UK

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University of Oxford, UK

22nd February 2016
CP2K-UK Third Annual Users Meeting
King's College, London

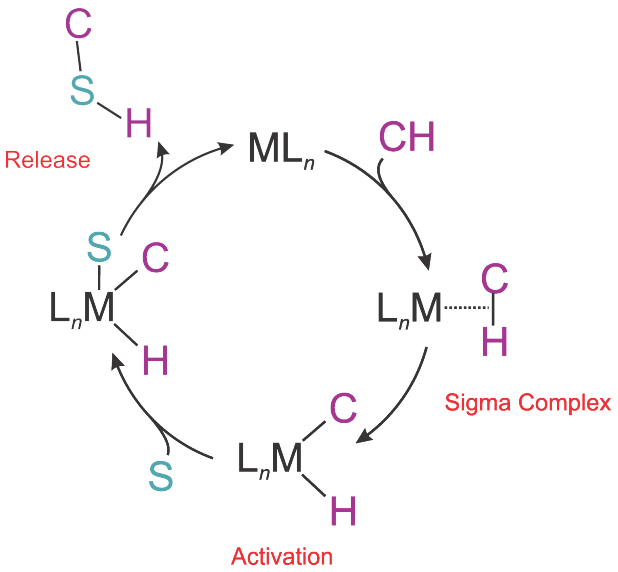
Introduction

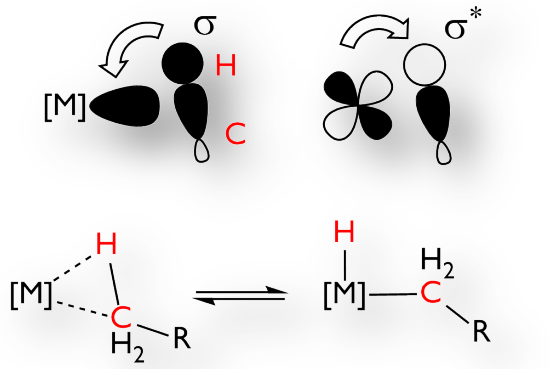
- (Catalytic) C–H bond activation (CHA) important process

  synthesis
  functionalisation of alkanes (petrochemical feedstock)

- σ–Complexes as key intermediates of CHA

  fundamental interest in understanding electronic structure
  catalyst design (activity, selectivity)

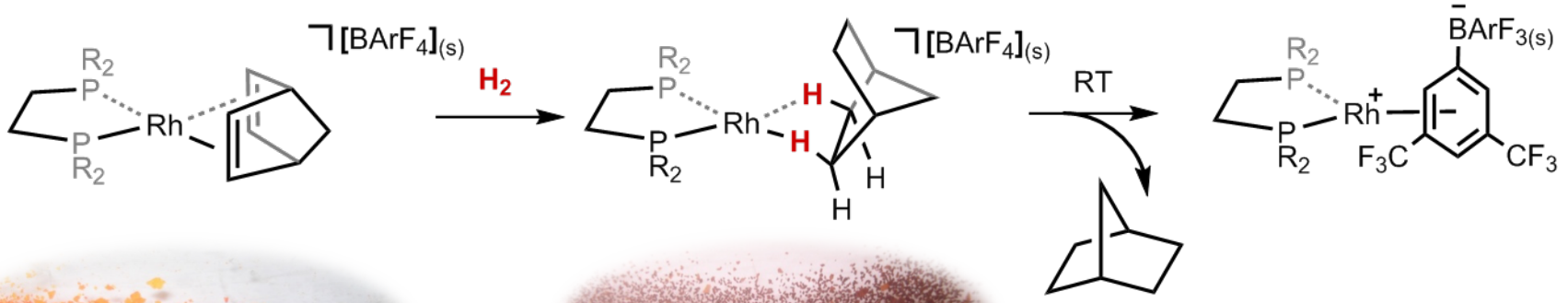


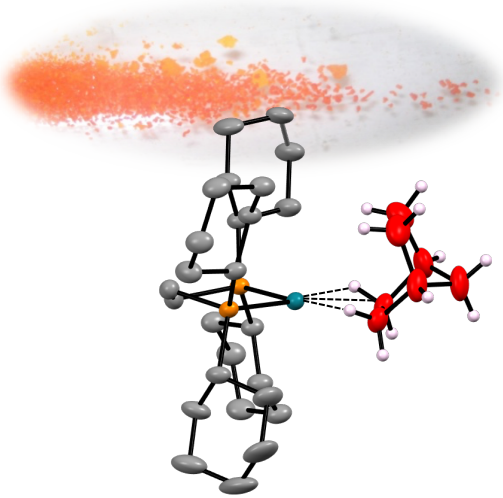


Labinger and Bercaw, *Nature*, **2002**, *417*, 507.

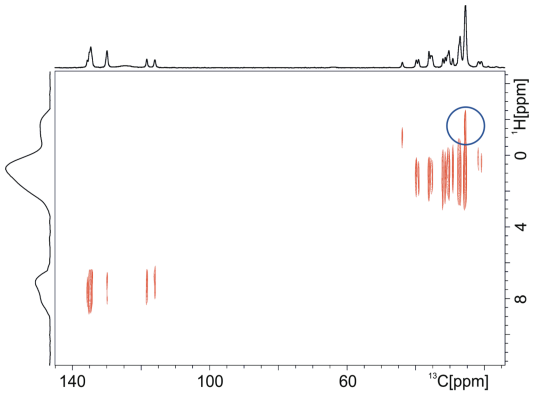
Exploring the Scope of the Solid-Gas Reaction

- vary substituents/phosphine backbone to identify more stable alkane complexes
  - in most cases displacement of NBA by counterion occurs, on varying timescales:





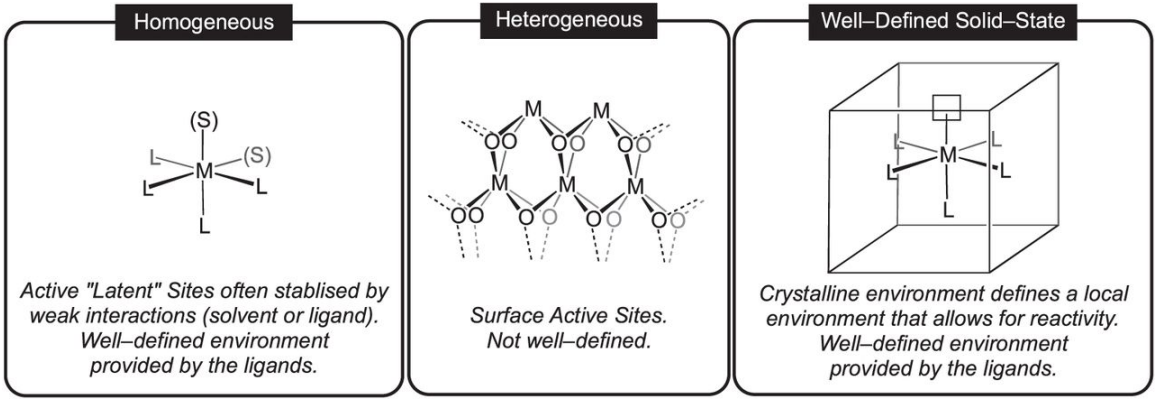
R	Stability (298 K)
^{i}Bu	2-3 hours
^{i}Pr	1 hour
^{i}Pr*	15 minutes
O^{i}Pr	not observed
Cy	**months!!!!**



* $-(CH_2)_3-$ backbone

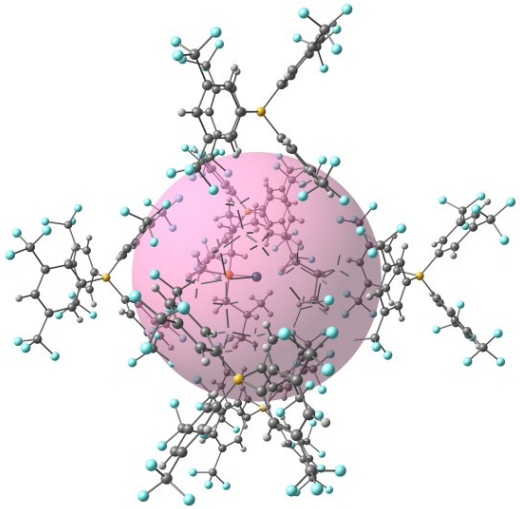
Pike, Thompson, Algarra, Apperley, Macgregor, Weller, *Science*, **2012**, *337*, 1648.
Pike, Chadwick, Rees, Scott, Weller, Krämer, Macgregor, *J. Am. Chem. Soc.*, **2015**, *137*, 820.

Organometallic transformations in the solid-state



Synthesis, reactivity and catalysis using well-defined single-site species

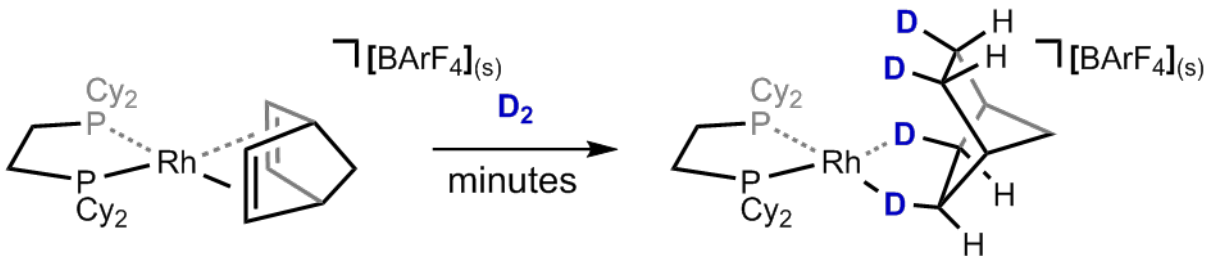
- small structural reorganisation (crystallinity, ~4% vol.)
- rigid porous framework (bulky ligands / anions)
- well-defined channels and voids (diffusion of gases)
- constrained environments allowing for small movements around metal centre



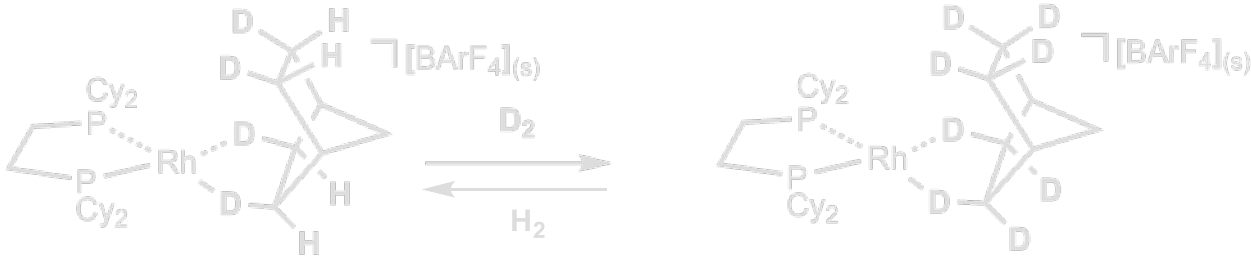
Pike, S. D., Weller, A. S. *Phil. Trans. R. Soc.*, **2015**, *373*, 20140187.

Solid State Reactivity

- with D_2 the alkane σ-complex of the *endo-endo* product is seen exclusively:



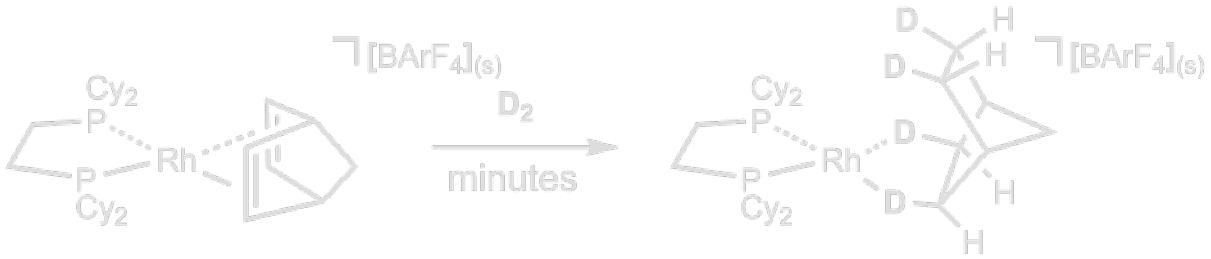
- further reaction (hours) with D_2 leads to d_8-norbornane products:



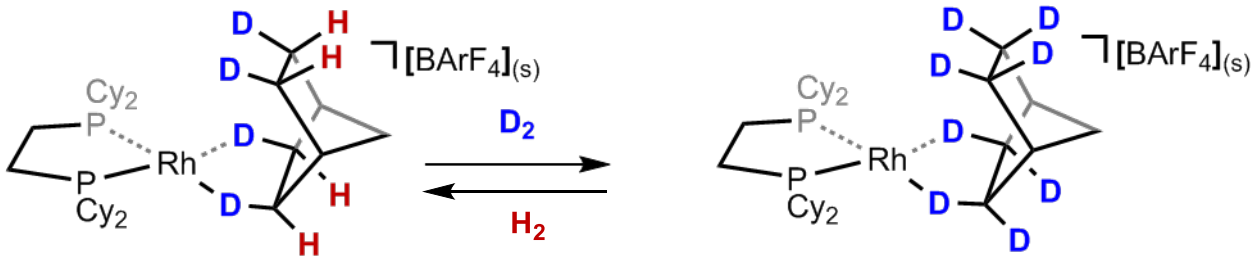
  - C–H/D activation is reversible and selective for the *exo*-positions

Solid State Reactivity

- with D_2 the alkane σ-complex of the *endo-endo* product is seen exclusively:

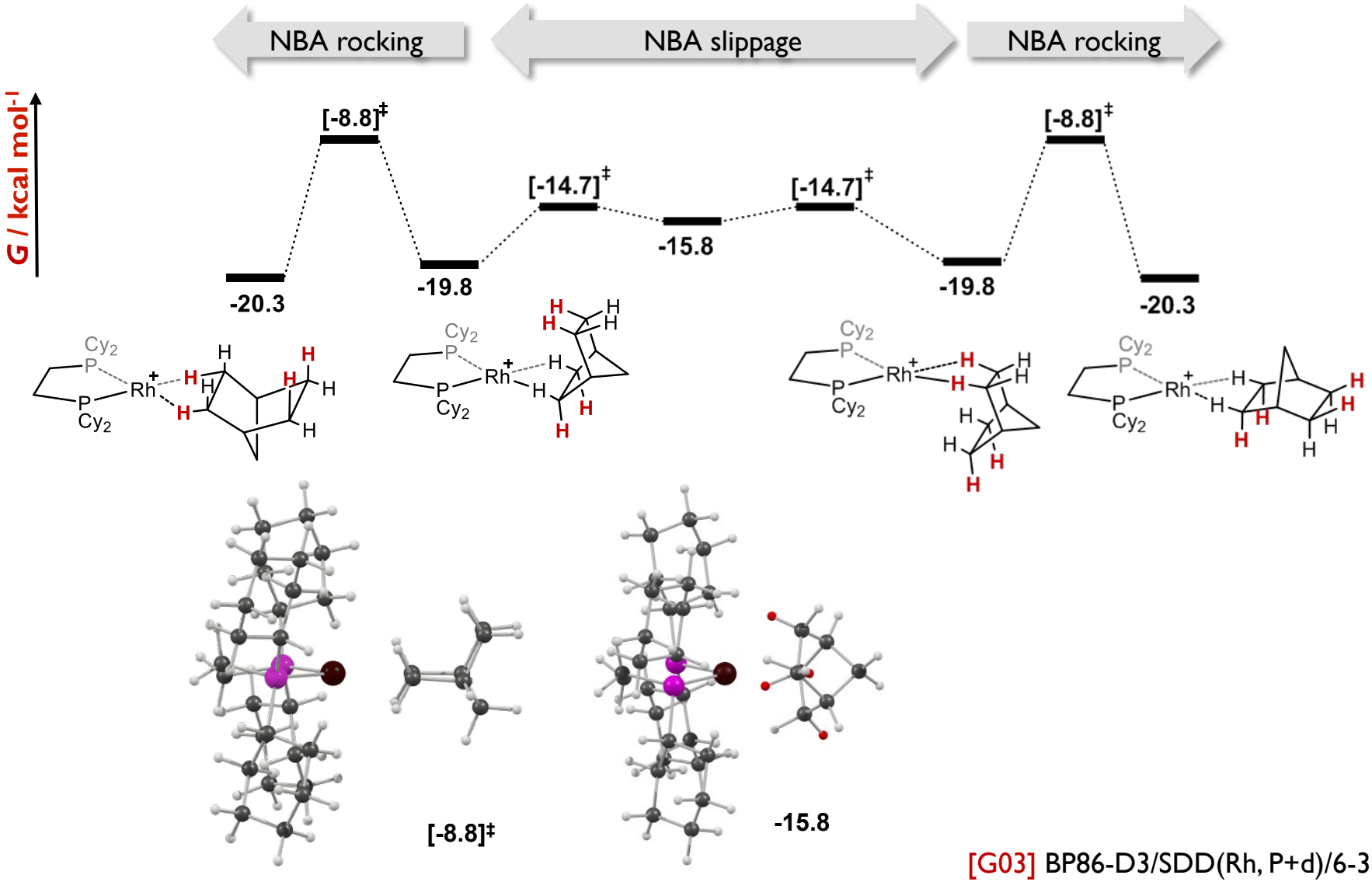


- further reaction (hours) with D_2 leads to d_8-norbornane products:



  - C–H/D activation is reversible and selective for the *exo*-positions
    - implies significant rearrangement of the initially formed ligand (NBA)

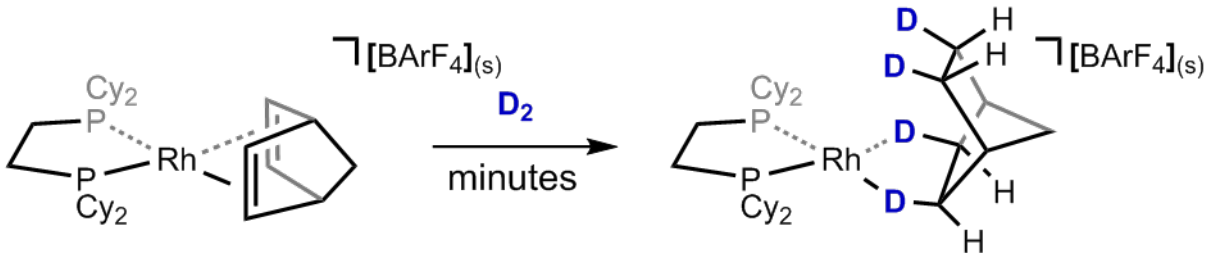
NBA rearrangement: rocking and slipping…



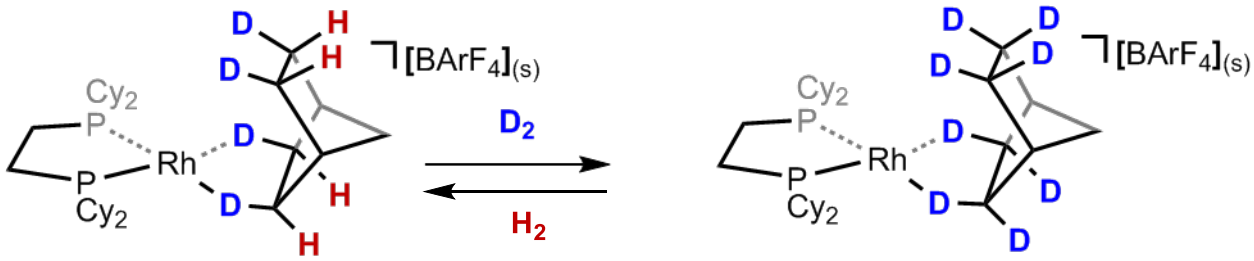
[G03] BP86-D3/SDD(Rh, P+d)/6-31G**

Solid State Reactivity: Summary of Molecular Calculations *vs.* Experiment

✓calculations readily account for the observed *endo-endo* selectivity:

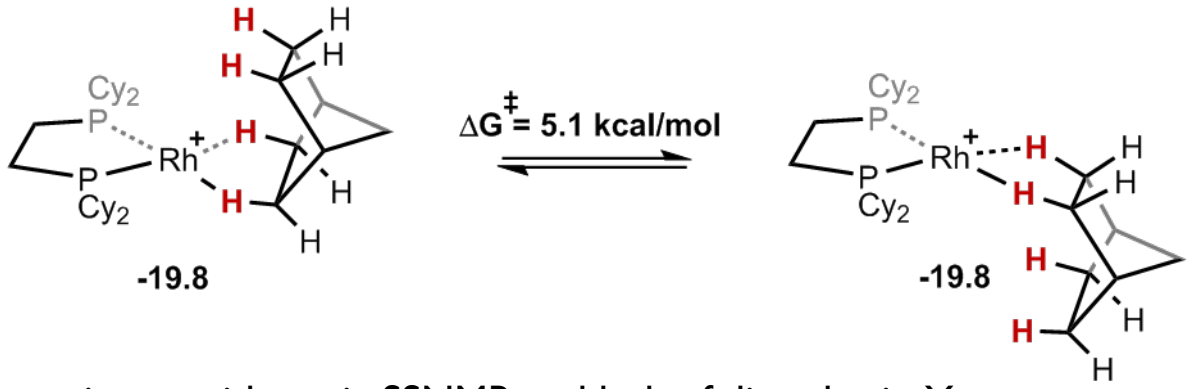


✓ and favour reversible *exo*-C-H activation over *endo*-C-H activation:



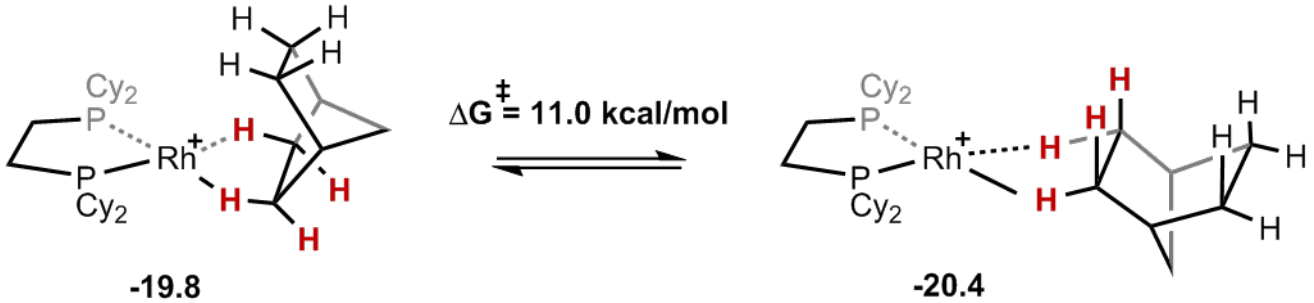
Solid State Reactivity: Summary of Molecular Calculations *vs.* Experiment

- **BUT**: indicate low barriers to reorganisation:



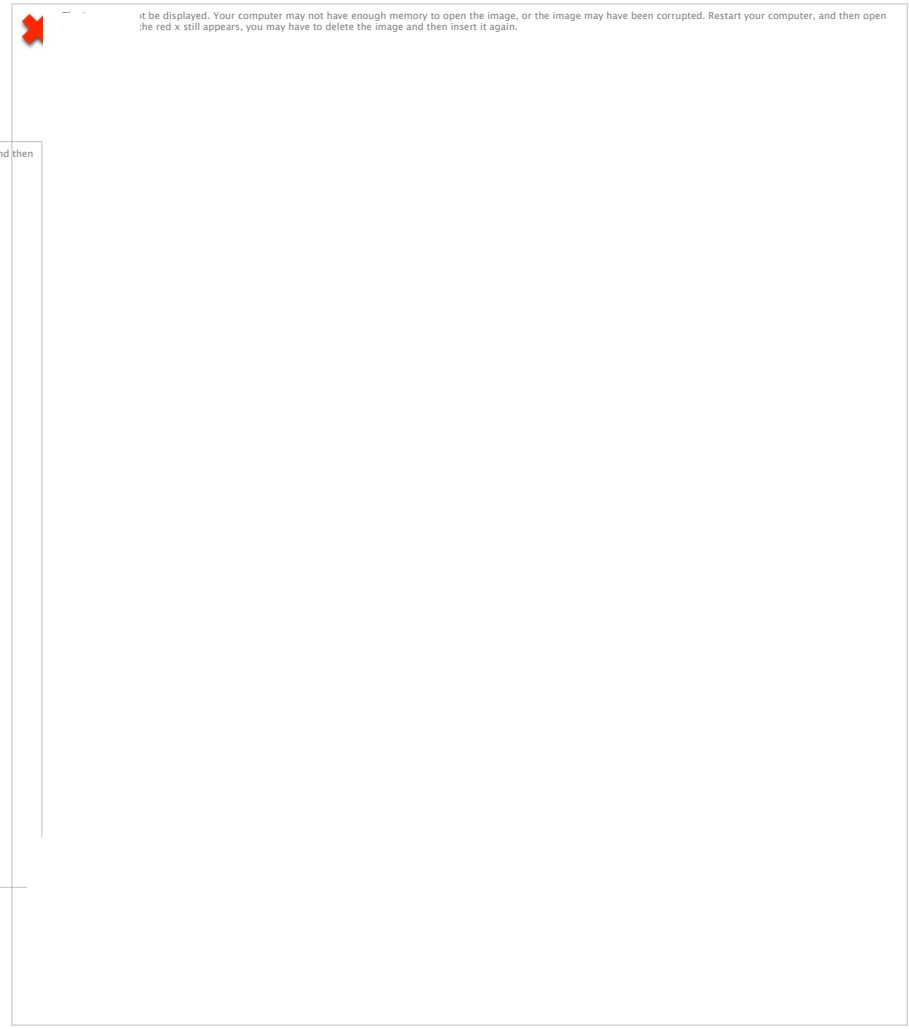
→ inconsistent with static SSNMR and lack of disorder in X-ray

- predict the wrong geometry of the σ-alkane complex!



Cation embedded in cavity

$[Rh(dbpe)(NBA)]^{+}$



Computational Model for Solid Phase

unit cell

+ full unit cell

+ QM (periodic DFT)
+ CP2K
– large system (>600 atoms)
– "spectator" sites

slab model

+ 3x3x4 "block"

+ QM/MM
+ Gaussian
– FF parameters not well-defined
– rigid framework (frozen atoms)

embedded cluster

+ QM cluster embedded in large array of MM atoms
+ QM/MM
+ ChemShell interface
+ surrounding point charges

GEO_OPT Input Sections

```
&FORCE_EVAL
  METHOD QS
  &DFT
    (usual DFT stuff)
    &SCF
      SCF_GUESS ATOMIC
      EPS_SCF 1.0E-7                              (testing)
       &OT ON
         MINIMIZER DIIS
       &END OT
      MAX_SCF 30
      &OUTER_SCF
        MAX_SCF 30
        EPS_SCF 1.0E-7
      &END OUTER_SCF
    &END SCF
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &vdW_POTENTIAL
         DISPERSION_FUNCTIONAL PAIR_POTENTIAL
         &PAIR_POTENTIAL
            TYPE DFTD3                            (Grimme D3)
            PARAMETER_FILE_NAME /work/e338/e338/kraemer/DATA/dftd3.dat
            REFERENCE_FUNCTIONAL PBE
         &END PAIR_POTENTIAL
      &END vdW_POTENTIAL
    &END XC
  &END DFT
  &SUBSYS
    &CELL
      ABC 17.2650 19.2495 19.8297                 (size of cell)
      ALPHA_BETA_GAMMA 88.0526 87.5056 89.1472
      PERIODIC XYZ              (periodic boundary conditions)
    &END CELL
    &TOPOLOGY
      COORDINATE XYZ
      COORD_FILE_NAME input.xyz (external xyz)
      CONNECTIVITY OFF
    &END TOPOLOGY
      &KIND Rh
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q17
      &END
      &KIND C
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q4
      &END
      &KIND P
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q5
      &END
       [...]
  &END SUBSYS
&END FORCE_EVAL

&MOTION
   &GEO_OPT
      OPTIMIZER BFGS
      MAX_DR [bohr] 3.0E-3    (default)
      RMS_DR [bohr] 1.5E-3    (default)
      MAX_FORCE [bohr^-1*hartree] 1.0E-4    (testing)
      RMS_FORCE [bohr^-1*hartree] 3.0E-4    (default)
   &END GEO_OPT
   &PRINT
     &TRAJECTORY
      &EACH
         GEO_OPT 1
      &END EACH
    &END TRAJECTORY
  &END
&END MOTION

&GLOBAL
  PROJECT Rh-dcype-nbd_bulk_opt
  PRINT_LEVEL MEDIUM
  RUN_TYPE GEO_OPT
&END GLOBAL
```

check stress tensor
(< 1 GPa)

VIB_ANALYSIS Input Sections

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&FORCE_EVAL
  METHOD QS
  STRESS_TENSOR ANALYTICAL
  &DFT
    (usual DFT stuff)
    &SCF
      SCF_GUESS RESTART   (in combination with WFN_RESTART_FILE_NAME)
      EPS_SCF 1.0E-8                              (testing)
       &OT ON
         MINIMIZER DIIS
       &END OT
      MAX_SCF 30
      &OUTER_SCF
        MAX_SCF 30
        EPS_SCF 1.0E-8
      &END OUTER_SCF
    &END SCF
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &vdW_POTENTIAL
         DISPERSION_FUNCTIONAL PAIR_POTENTIAL
         &PAIR_POTENTIAL
            TYPE DFTD3                            (Grimme D3)
            PARAMETER_FILE_NAME /work/e338/e338/kraemer/DATA/dftd3.dat
            REFERENCE_FUNCTIONAL PBE
         &END PAIR_POTENTIAL
      &END vdW_POTENTIAL
    &END XC
  &END DFT
  &SUBSYS
    &CELL
      ABC 17.2650 19.2495 19.8297               (size of cell)
      ALPHA_BETA_GAMMA 88.0526 87.5056 89.1472
      PERIODIC XYZ              (periodic boundary conditions)
    &END CELL
    &TOPOLOGY
      COORDINATE XYZ
      COORD_FILE_NAME finalt.xyz (external xyz)
      CONNECTIVITY OFF
    &END TOPOLOGY
      &KIND Rh
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q17
      &END
      &KIND C
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q4
      &END
      &KIND P
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q5
      &END
       [...]
  &END SUBSYS
&END FORCE_EVAL

&VIBRATIONAL_ANALYSIS
   NPROC_REP 64
   DX 0.01
   FULLY_PERIODIC TRUE
   INTENSITIES
    &PRINT
     &PROGRAM_RUN_INFO ON
     &END
     &MOLDEN_VIB
      FILENAME=frequencies.mol
     &END
    &END
&END VIBRATIONAL_ANALYSIS

&GLOBAL
  PROJECT Rh-dcype-nbd_bulk_freq
  PRINT_LEVEL MEDIUM
  RUN_TYPE VIBRATIONAL_ANALYSIS
&END GLOBAL
```

GEO_OPT

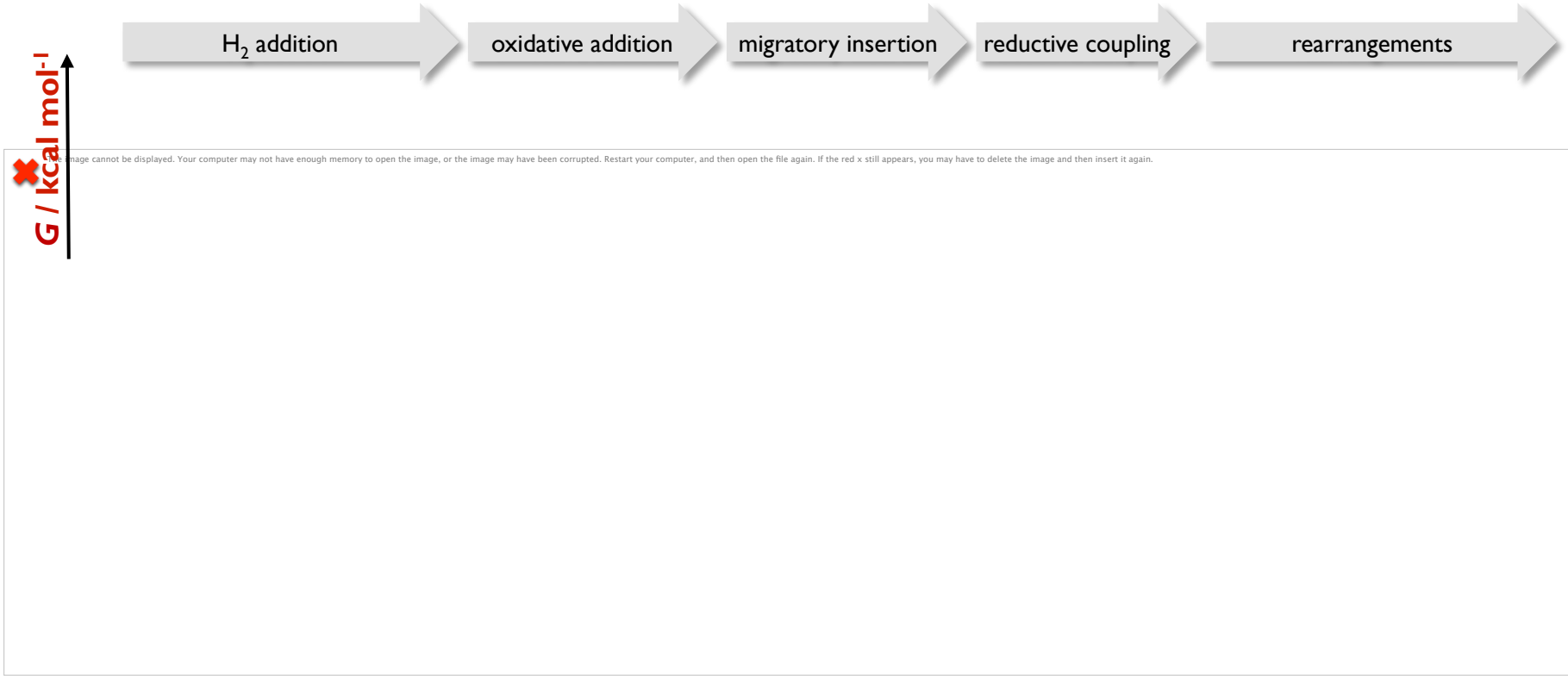
VIB_ANALYSIS

EPS_SCF	MAX_DR	RMS_DR	MAX_FORCE	RMS_FORCE	EPS_SCF	#Imag
10^{-6}	0.00300	0.00150	0.00045	0.00030	10^{-6}	>80
10^{-7}	0.00300	0.00150	0.00045	0.00030	10^{-7}	10
10^{-8}	0.00300	0.00150	0.00045	0.00030	10^{-8}	2
10^{-7}	0.00300	0.00150	0.00045	0.00030	10^{-7}	10
10^{-7}	0.00300	0.00150	0.00010	0.00030	10^{-7}	9
10^{-7}	0.00300	0.00150	0.00010	0.00030	10^{-8}	0

```
VIB|                        NORMAL MODES - CARTESIAN DISPLACEMENTS
VIB|
VIB|                              1                2                3
VIB|Frequency (cm^-1)    -408.337558      -385.206963      -356.051407
VIB|Intensities              0.005867         0.003045         0.005495
VIB|Red.Masses (a.u.)        2.907822         2.843022         2.136175
VIB|Frc consts (a.u.)       -0.000207        -0.000160        -0.000088
```

Hydrogenation in the Solid State

- NBD to NBE @NBD unit cell

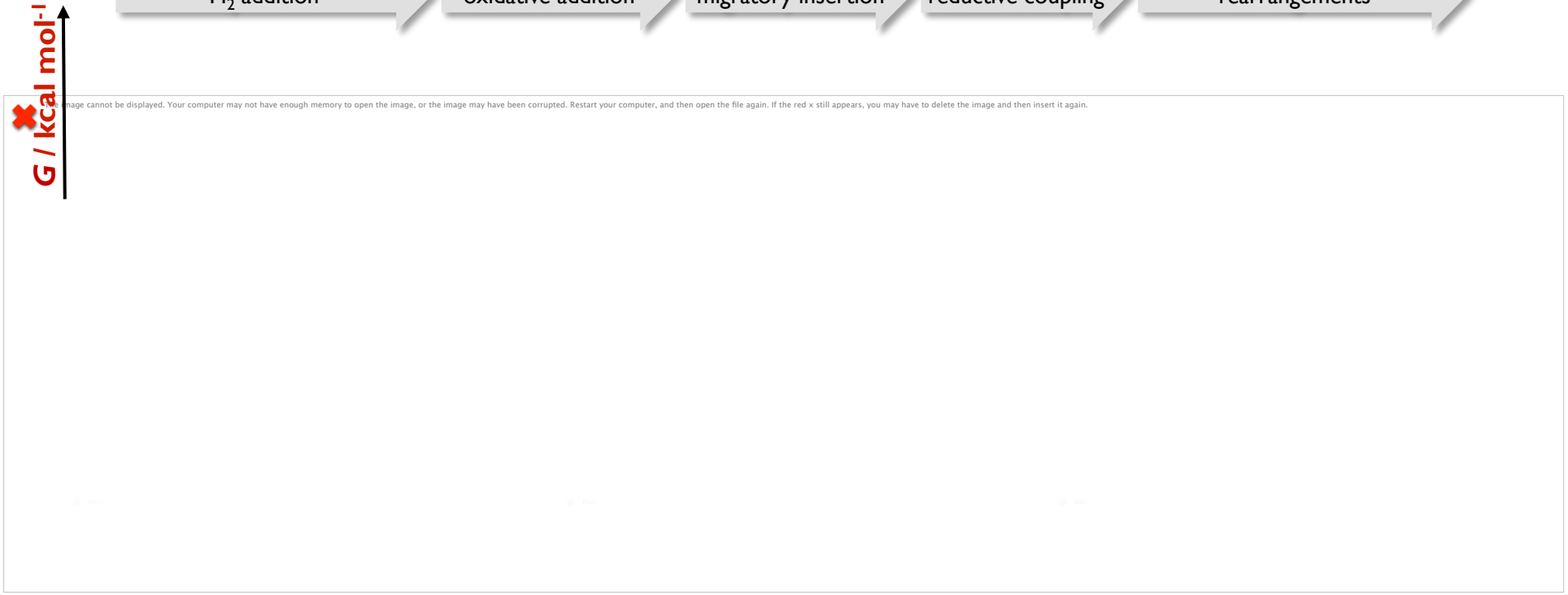


[CP2K] PBE-D3/DZVP-MOLOPT-SR-GTH/GTH-PBE (cutoff 500 Ry)

Hydrogenation in the Solid State

- NBD to NBE @NBD unit cell

H_2 addition → oxidative addition → migratory insertion → reductive coupling → rearrangements



MEP_{oa} **MEP_{mi}** **MEP_{rc}**

BAND Input Sections

```
&FORCE_EVAL
  METHOD QS
  &DFT
    (usual DFT stuff)
    &SCF
      SCF_GUESS ATOMIC
      EPS_SCF 1.0E-6                                  (testing)
       &OT ON
         MINIMIZER DIIS
       &END OT
      MAX_SCF 30
      &OUTER_SCF
        MAX_SCF 30
        EPS_SCF 1.0E-6
      &END OUTER_SCF
    &END SCF
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &vdW_POTENTIAL
         DISPERSION_FUNCTIONAL PAIR_POTENTIAL
         &PAIR_POTENTIAL
            TYPE DFTD3                                (Grimme D3)
            PARAMETER_FILE_NAME /work/e338/e338/kraemer/DATA/dftd3.dat
            REFERENCE_FUNCTIONAL PBE
         &END PAIR_POTENTIAL
      &END vdW_POTENTIAL
    &END XC
  &END DFT
  &SUBSYS
    &CELL
      ABC 17.2650 19.2495 19.8297                     (size of cell)
      ALPHA_BETA_GAMMA 88.0526 87.5056 89.1472
      PERIODIC XYZ                  (periodic boundary conditions)
    &END CELL
    &TOPOLOGY
      COORDINATE XYZ
      COORD_FILE_NAME start.xyz (external xyz)
      CONNECTIVITY OFF
    &END TOPOLOGY
      &KIND Rh
        BASIS_SET DZVP-MOLOPT-SR-GTH
        POTENTIAL GTH-PBE-q17
      &END
       [...]
  &END SUBSYS
&END FORCE_EVAL

&MOTION
   &BAND
      NPROC_REP 48
      BAND_TYPE CI-NEB       (optimizes to TS)
      NUMBER_OF_REPLICA 16
     &CONVERGENCE_CONTROL
        MAX_FORCE [bohr^-1*hartree] 8.0E-4 (testing)
     &END CONVERGENCE_CONTROL
     &OPTIMIZE_BAND
        OPT_TYPE DIIS
          &DIIS
            MAX_STEPS 1000
            N_DIIS 3
          &END DIIS
     &END OPTIMIZE_BAND
     &REPLICA
       COORD_FILE_NAME start.xyz (external xyz)
     &END REPLICA
 !   &REPLICA
 !     COORD_FILE_NAME inter.xyz (external xyz)
 !    &END REPLICA
     &REPLICA
       COORD_FILE_NAME end.xyz (external xyz)
     &END REPLICA
   &END BAND
&END MOTION

&GLOBAL
  PROJECT Rh-dcype-nbd_HH_bulk_ts
  PRINT_LEVEL MEDIUM
  RUN_TYPE BAND
&END GLOBAL
```

DIMER Input Sections

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&FORCE_EVAL
  METHOD QS
  &DFT
    (usual DFT stuff)
    &SCF
      SCF_GUESS RESTART  (in combination with WFN_RESTART_FILE_NAME)
      EPS_SCF 1.0E-7                              (testing)
       &OT ON
         MINIMIZER DIIS
       &END OT
      MAX_SCF 30
      &OUTER_SCF
        MAX_SCF 30
        EPS_SCF 1.0E-7
      &END OUTER_SCF
    &END SCF
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &vdW_POTENTIAL
         DISPERSION_FUNCTIONAL PAIR_POTENTIAL
         &PAIR_POTENTIAL
            TYPE DFTD3                            (Grimme D3)
            PARAMETER_FILE_NAME /work/e338/e338/kraemer/DATA/dftd3.dat
            REFERENCE_FUNCTIONAL PBE
         &END PAIR_POTENTIAL
      &END vdW_POTENTIAL
    &END XC
  &END DFT
  &SUBSYS
    &CELL
      ABC 17.2650 19.2495 19.8297                 (size of cell)
      ALPHA_BETA_GAMMA 88.0526 87.5056 89.1472
      PERIODIC XYZ              (periodic boundary conditions)
    &END CELL
    &TOPOLOGY
      COORDINATE XYZ
      COORD_FILE_NAME start.xyz (external xyz)
    &END TOPOLOGY
[...]
&END FORCE_EVAL
```

```
&MOTION
   &GEO_OPT
      TYPE TRANSITION_STATE
       &TRANSITION_STATE
          METHOD DIMER
           &DIMER
             DR [angstrom] 0.01
             INTERPOLATE_GRADIENT T
             &ROT_OPT
               OPTIMIZER CG
               MAX_ITER
                &CG
                 MAX_STEEP_STEPS 0
                   &LINE_SEARCH
                      TYPE 2PNT
                   &END LINE_SEARCH
                &END CG
              &END ROT_OPT
              &DIMER_VECTOR
                @include 'vector' (external file)
              &END DIMER_VECTOR
           &END DIMER
       &END TRANSITION_STATE
        OPTIMIZER CG
        &CG
          &LINE_SEARCH
            TYPE 2PNT
          &END LINE_SEARCH
        &END CG
        MAX_FORCE 1.0E-4
        MAX_ITER 1000
   &END GEO_OPT
   &PRINT
     &TRAJECTORY
      &EACH
         GEO_OPT 1
      &END EACH
    &END TRAJECTORY
   &END PRINT
&END MOTION
```

```
&GLOBAL
  PROJECT Rh-dcype-nbd_HH_dimer
  PRINT_LEVEL MEDIUM
  RUN_TYPE GEO_OPT
&END GLOBAL
```

“SCAN” Input Sections

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&FORCE_EVAL
  METHOD QS
  &DFT (usual DFT stuff)
    &SCF
      SCF_GUESS ATOMIC
      EPS_SCF 1.0E-5
       &OT ON
         MINIMIZER DIIS
       &END OT
      MAX_SCF 30
      &OUTER_SCF
        MAX_SCF 30
        EPS_SCF 1.0E-5
      &END OUTER_SCF
    &END SCF
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      &vdW_POTENTIAL
         DISPERSION_FUNCTIONAL PAIR_POTENTIAL
         &PAIR_POTENTIAL
            TYPE DFTD3                                  (Grimme D3)
            PARAMETER_FILE_NAME /work/e338/e338/kraemer/DATA/dftd3.dat
            REFERENCE_FUNCTIONAL PBE
         &END PAIR_POTENTIAL
      &END vdW_POTENTIAL
    &END XC
  &END DFT
  &SUBSYS
    &CELL
      ABC 17.2650 19.2495 19.8297
      ALPHA_BETA_GAMMA 88.0526 87.5056 89.1472
      PERIODIC XYZ
    &END CELL
    &COLVAR                          (define collective variable)
      &DISTANCE
        ATOMS 648 307
      &END DISTANCE
      &PRINT
      &END PRINT
   &END COLVAR
      [...]
  &END SUBSYS
&END FORCE_EVAL

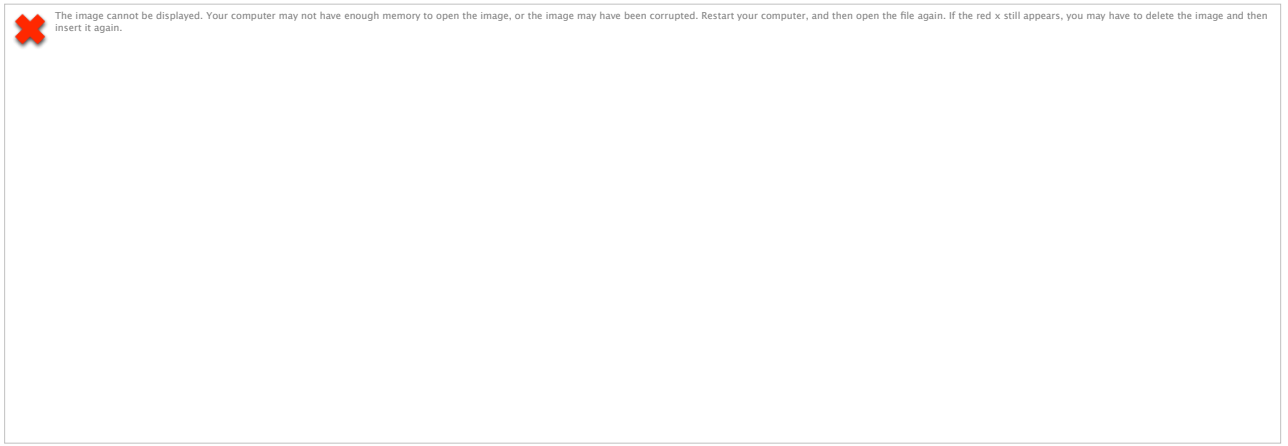
&MOTION
   &CONSTRAINT
      &COLLECTIVE
        COLVAR 1
        INTERMOLECULAR T
          &RESTRAINT
             K=10.0    (force constant for harmonic
                                restraint)
          &END RESTRAINT
        TARGET [angstrom] 2.72
      &END COLLECTIVE
   &END CONSTRAINT
   &GEO_OPT
     OPTIMIZER BFGS
     MAX_FORCE 1.0E-3
   &END GEO_OPT
   &PRINT
     &TRAJECTORY
        &EACH
           GEO_OPT 1
        &END EACH
     &END TRAJECTORY
   &END PRINT
&END MOTION

&GLOBAL
  PROJECT scan
  PRINT_LEVEL MEDIUM
  RUN_TYPE GEO_OPT
&END GLOBAL
```

NBA Rearrangement in the Solid State (@NBA unit cell)

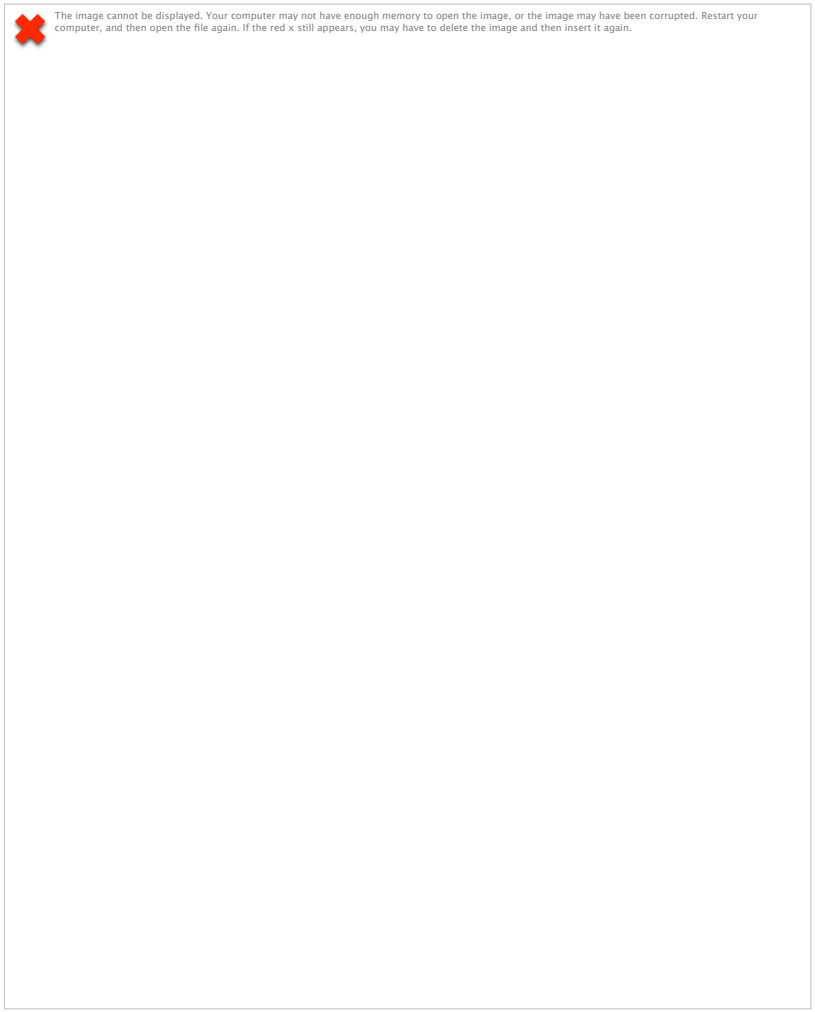
NBA rotation

E / kcal mol^{-1}



MEP$_{rot}$

Non-covalent interactions



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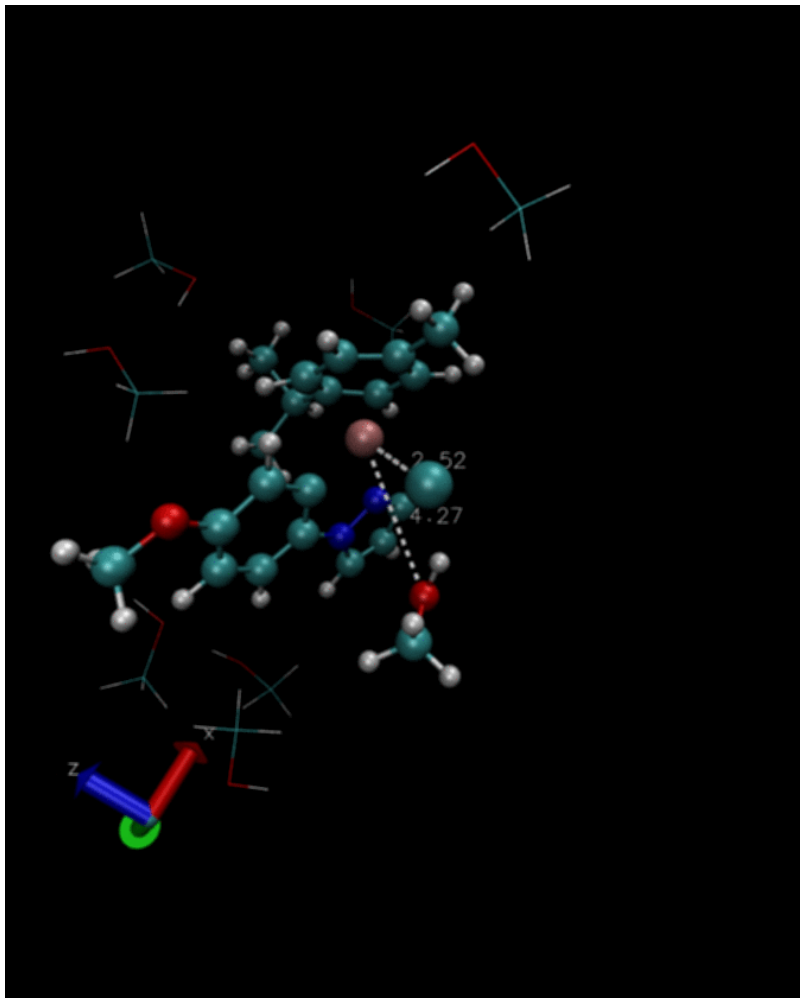
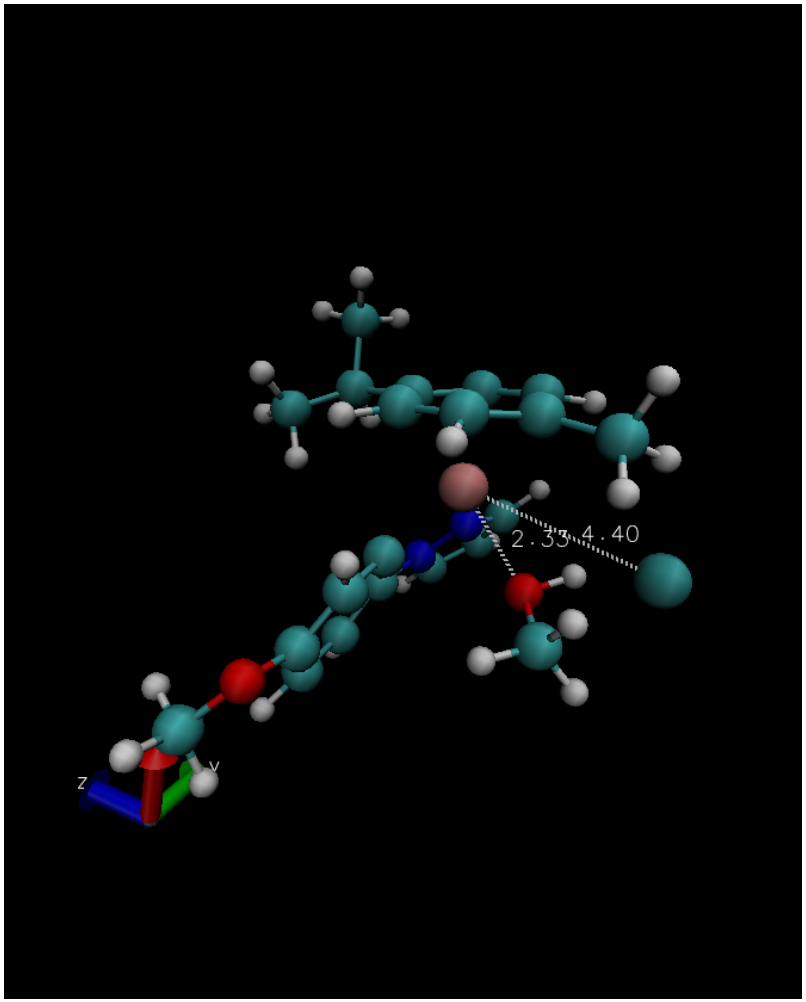
[NCIPLOT]

Ionic Ligand Exchange

The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.





Summary and Outlook

Established protocols for running periodic DFT calculations

Mechanistic study of Hydrogenation steps in Solid Phase

Mapping out H_2 addition PES, substrate rearrangement
Stereoselectivity (*endo*/*endo*)
Considering changes in unit cell

Molecular dynamics

Dynamical behaviour of substrate and cavity

NMR Spectroscopy

Estimate chemical shifts of species in solid phase (impact of crystal environment)

Long-term goal

"*The real test of understanding is prediction*" Roald Hoffmann
Understanding – Prediction – Design

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Thank you for your attention…