Supplementary Information

Accessing and Predicting the Kinetic Profiles of Homogeneous Catalysts from Volcano Plots

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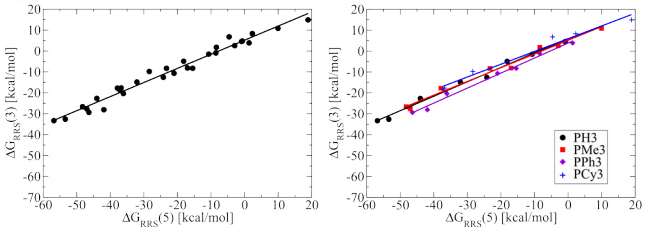
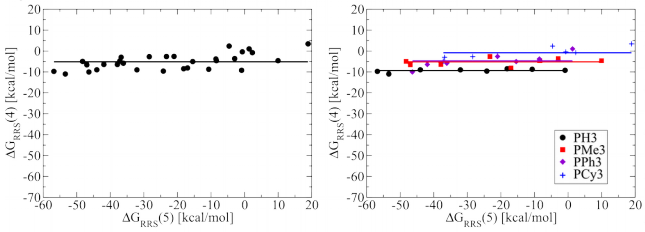
Summary of Linear Scaling Relationships

a) 5 vs. 3:



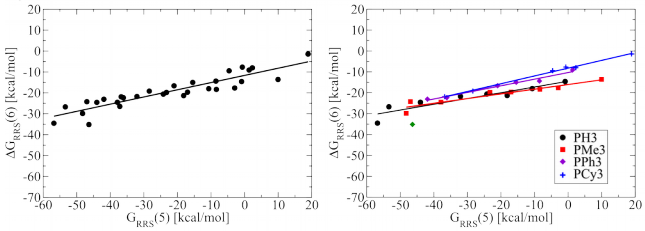
Combined
$\Delta G_{RRS}(3) = 0.67\Delta G_{RRS}(5) + 5$ kcal/mol **$R^2 = 0.97$** **$2\sigma = 5$ kcal/mol**
PH_3:
$\Delta G_{RRS}(3) = 0.69\Delta G_{RRS}(5) + 6$ kcal/mol $R^2 = 0.99$ $2\sigma = 3$ kcal/mol
PMe_3:
$\Delta G_{RRS}(3) = 0.66\Delta G_{RRS}(5) + 5$ kcal/mol $R^2 = 0.98$ $2\sigma = 4$ kcal/mol
PPh_3:
$\Delta G_{RRS}(3) = 0.72\Delta G_{RRS}(5) + 4$ kcal/mol $R^2 = 0.99$ $2\sigma = 3$ kcal/mol
PCy_3:
$\Delta G_{RRS}(3) = 0.61\Delta G_{RRS}(5) + 6$ kcal/mol $R^2 = 0.97$ $2\sigma = 4$ kcal/mol

b) 5 vs. 4:



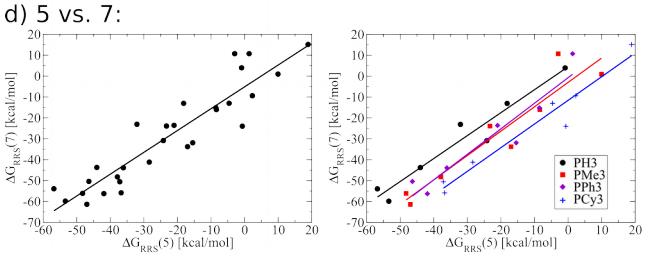
Combined
$\Delta G_{RRS}(4) = -5$ kcal/mol $2\sigma = 8$ kcal/mol
PH_3:
$\Delta G_{RRS}(4) = -9$ kcal/mol **$2\sigma = 2$ kcal/mol**
PMe_3:
$\Delta G_{RRS}(4) = -5$ kcal/mol **$2\sigma = 4$ kcal/mol**
PPh_3:
$\Delta G_{RRS}(4) = -5$ kcal/mol **$2\sigma = 7$ kcal/mol**
PCy_3:
$\Delta G_{RRS}(4) = -1$ kcal/mol **$2\sigma = 6$ kcal/mol**

c) 5 vs. 6:



Combined
$\Delta G_{RRS}(6) = 0.34\Delta G_{RRS}(5) - 12$ kcal/mol $R^2 = 0.83$ $2\sigma = 6$ kcal/mol
PH_3:
$\Delta G_{RRS}(6) = 0.28\Delta G_{RRS}(5) - 14$ kcal/mol **$R^2 = 0.86$** **$2\sigma = 5$ kcal/mol**
PMe_3:
$\Delta G_{RRS}(6) = 0.22\Delta G_{RRS}(5) - 16$ kcal/mol **$R^2 = 0.90$** **$2\sigma = 3$ kcal/mol**
PPh_3:
$\Delta G_{RRS}(6) = 0.32\Delta G_{RRS}(5) - 10$ kcal/mol **$R^2 = 0.98$** **$2\sigma = 2$ kcal/mol**
PCy_3:
$\Delta G_{RRS}(6) = 0.41\Delta G_{RRS}(5) - 8$ kcal/mol **$R^2 = 0.97$** **$2\sigma = 3$ kcal/mol**

d) 5 vs. 7:



Combined
$\Delta G_{RRS}(7) = 1.04\Delta G_{RRS}(5) - 5$ kcal/mol $R^2 = 0.85$ $2\sigma = 18$ kcal/mol
PH_3:
$\Delta G_{RRS}(7) = 1.10\Delta G_{RRS}(5) + 4$ kcal/mol **$R^2 = 0.94$** **$2\sigma = 11$ kcal/mol**
PMe_3:
$\Delta G_{RRS}(7) = 1.17\Delta G_{RRS}(5) - 3$ kcal/mol **$R^2 = 0.89$** **$2\sigma = 18$ kcal/mol**
PPh_3:
$\Delta G_{RRS}(7) = 1.22\Delta G_{RRS}(5) - 1$ kcal/mol **$R^2 = 0.89$** **$2\sigma = 15$ kcal/mol**
PCy_3:
$\Delta G_{RRS}(7) = 1.13\Delta G_{RRS}(5) - 12$ kcal/mol **$R^2 = 0.95$** **$2\sigma = 12$ kcal/mol**

*Figure S1: The scaling relationships between descriptor intermediate **5** and key intermediates are summarized. The scaling relations used to derive the detailed volcano plots shown in Figure S4 and S5 are marked in bold.*

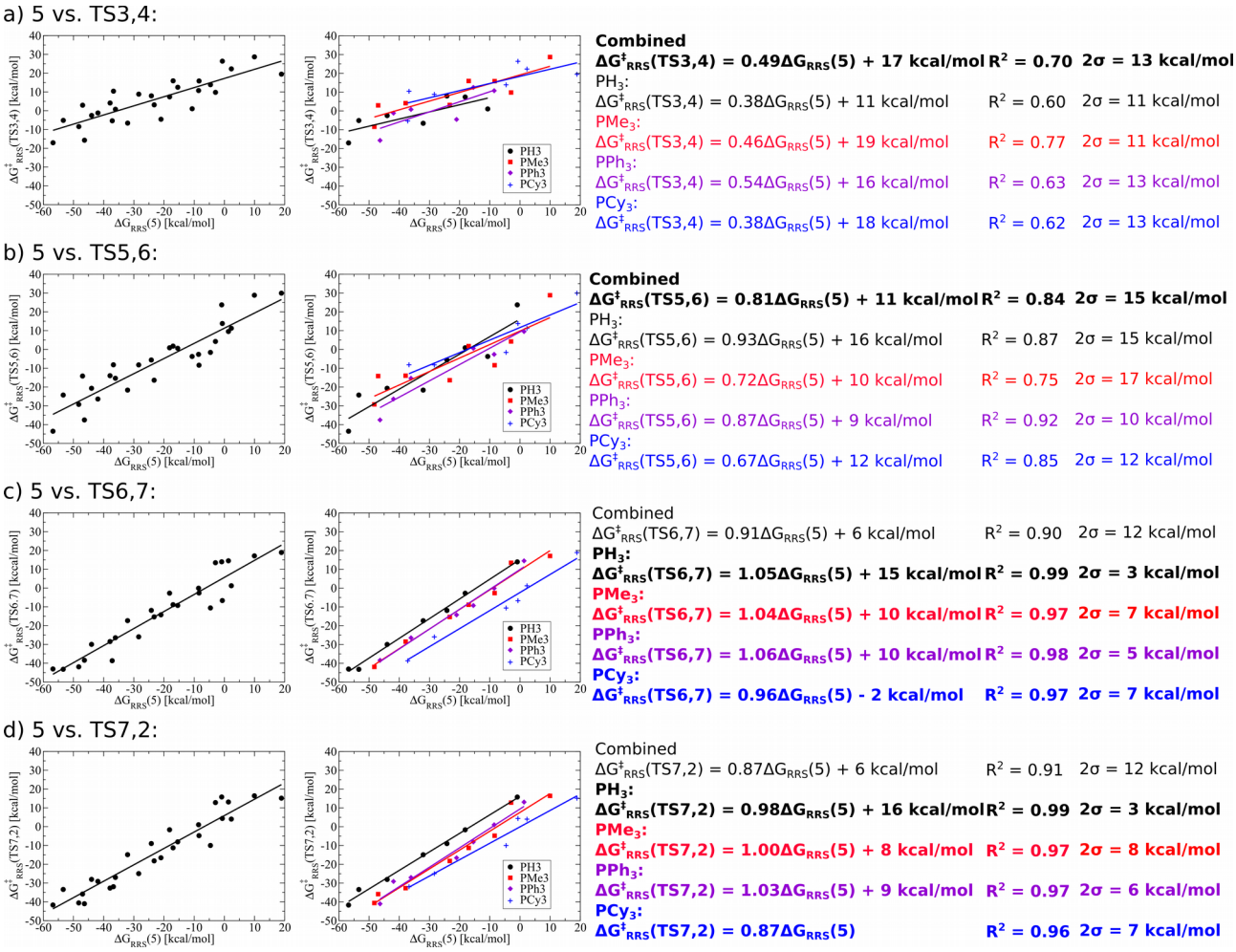


*Figure S2: The scaling relationships between descriptor intermediate **5** and all relevant transition states are summarized. The scaling relationships used to derive the detailed volcano plots shown in Figure S5 are marked in bold.*

Linear Scaling Relations and Volcano Plots

By summarizing the relative activity of a catalyst with respect to a descriptor such as the binding energy of intermediate **5** used in the present study volcano plots offer an intuitive way to compare candidate catalysts. In Figure S 1 and S2 all scaling relationships are summarized. Linear scaling relationships are obtained assuming the reactants as reference

$$G(\mathbf{2}) = G(H_2CCH_2) = G(CO) = G(H_2) = 0kcal/mol \qquad \text{(Equation S1)}$$

while the product's energy corresponds to that of the total reaction.

$$G(Propanal) = -29.6kcal/mol \qquad \text{(Equation S2)}$$

In what follows the procedure will be summarized using the construction of the “combined” volcano shown in Figure 5 in the manuscript as a general example. Thermodynamic volcanoes are constructed by determining the the thermodynamically least favorable or potential determining step (pds) for each region, i.e.

$$\Delta G(pds) = \max[\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}), \Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}), \Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}), \Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}), \Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}), \Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2})] \qquad \text{(Equation S3)}$$

The kinetics determining step (kds) is obtained similarly through:

$$\Delta G^{\ddagger}(kds) = \max[\Delta G^{\ddagger}_{theo}(3 \rightarrow TS3,4), \Delta G^{\ddagger}_{theo}(5 \rightarrow TS5,6), \Delta G^{\ddagger}_{theo}(6 \rightarrow TS6,7), \Delta G^{\ddagger}_{theo}(7 \rightarrow, TS7,2)] \qquad \text{(Equation S4)}$$

“Combined” Thermodynamic Volcano Plots

The eneretics of the individual reaction steps can be estimated from the linear scaling relations summarized below:

$$\Delta G_{RRS}(\mathbf{3}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 5kcal/mol \quad \text{(Equation S5)}$$

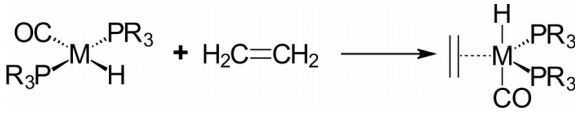
$$\Delta G_{RRS}(\mathbf{4}) = -5kcal/mol \quad \text{(Equation S6)}$$

$$\Delta G_{RRS}(\mathbf{6}) = 0.34_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S7)}$$

$$\Delta G_{RRS}(\mathbf{7}) = 1.04_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S8)}$$

1) Reaction 2→3: Formation of π-Complex

The first reaction step of the hydroformylation reaction comprises the formation of the π-complex **3**.



(Equation S9)

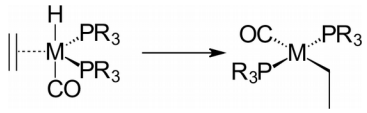
Based on reaction S9 the theoretical reaction free energy ΔG_{theo} for this reaction is then

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -[\Delta G_{RRS}(\mathbf{3}) - (G(\mathbf{2}) + G(H_2CCH_2)] \quad \text{(Equation S10)}$$

With ΔG_{RRS}(**3**) from scaling relation S5 and G(**2**) and G(H_2CCH_2) from equation S1 the theoretical reaction free energy becomes:

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -0.67\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S11)}$$

2) Reaction 3→4: Rearrangement



(Equation S12)

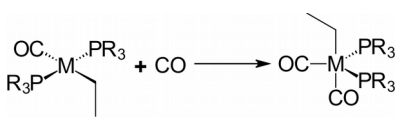
Accordingly the theoretical reaction free energy is given by:

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = -[\Delta G_{RRS}(\mathbf{4}) - \Delta G_{RRS}(\mathbf{3})] \quad \text{(Equation S13)}$$

Inserting the scaling relations from equations S5 and S6 the theoretical reaction free energy becomes:

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 10kcal/mol \quad \text{(Equation S14)}$$

3) **Reaction 4→5: CO Addition**



(Equation S15)

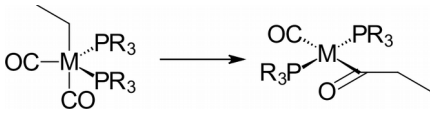
Accordingly ΔG_{theo} is obtained through:

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -[\Delta G_{RRS}(\mathbf{5}) - (\Delta G_{RRS}(4) + G(CO))] \quad \text{(Equation S16)}$$

and by inserting the scaling relation S6 and G(CO) from equation S1 one obtains

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S17)}$$

4) Reaction 5→6: CO Insertion



(Equation S18)

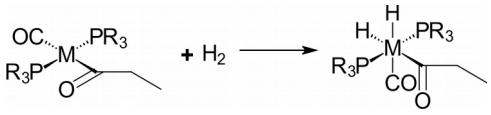
The theoretical reaction free energy is then calculated through

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = -[\Delta G_{RRS}(\mathbf{6}) - \Delta G_{RRS}(\mathbf{5})] \quad \text{(Equation S19)}$$

and inserting the scaling relations for intermediate **6** (equation S7) results in

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = 0.66\Delta G_{RRS}(\mathbf{5}) + 12kcal/mol \quad \text{(Equation S20)}$$

5) Reaction 6→7: H_2 Addition



(Equation S21)

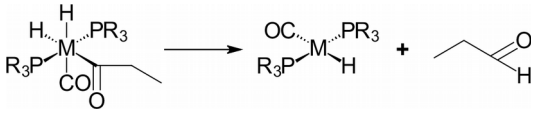
Accordingly the theoretical free energy of this reaction is given by

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -[\Delta G_{RRS}(\mathbf{7}) - (\Delta G_{RRS}(\mathbf{6}) + G(H_2))] \quad \text{(Equation S22)}$$

Inserting the scaling relations S7 and S8 then results in

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -0.70\Delta G_{RRS}(\mathbf{5}) - 7kcal/mol \quad \text{(Equation S23)}$$

6) Reaction 7→2: Reductive Elimination



(Equation S24)

The energetics of the final reductive elimination are obtained through

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = -[(\Delta G(\mathbf{2}) + G(Propanal)) - \Delta G_{RRS}(\mathbf{7})] \quad \text{(Equation S25)}$$

With The scaling relationship S8 and equations S1 and S2 for G(**2**) and G(Propanal) this becomes

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = 1.04\Delta G_{RRS}(\mathbf{5}) + 25kcal/mol \quad \text{(Equation S26)}$$

Based on ΔG_{theo} of the reaction steps the thermodynamics of the hydroformylation reaction can be simulated with respect to the stability of descriptor ΔG_{RRS}(**5**) (see Figure **S3**a). By taking the energetically least favorable steps, i.e. applying equation S3, the resulting volcano shown in Figure 5 of the manuscript is obtained.

“Combined” Kinetic Volcano Plots

The kinetic volcano plots are constructed equivalent to the thermodynamic volcano plots using the thermodynamic scaling relationships summarized in equations S5 to S8 and a set scaling relationships between the binding energy of the transition states and descriptor intermediate **5**.

$$\Delta G^{\ddagger}_{RRS}(\mathbf{TS3,4}) = 0.49\Delta G_{RRS}(\mathbf{5}) + 17kcal/mol \quad \text{(Equation S27)}$$

$$\Delta G^{\ddagger}_{RRS}(\mathbf{TS5,6}) = 0.81\Delta G_{RRS}(\mathbf{5}) + 11kcal/mol \quad \text{(Equation S28)}$$

$$\Delta G^{\ddagger}_{RRS}(\mathbf{TS6,7}) = 0.91\Delta G_{RRS}(\mathbf{5}) + 6kcal/mol \quad \text{(Equation S29)}$$

$$\Delta G^{\ddagger}_{RRS}(\mathbf{TS7,2}) = 0.87\Delta G_{RRS}(\mathbf{5}) + 6kcal/mol \quad \text{(Equation S30)}$$

1) Activation Barrier 3 →TS3,4

$$-\Delta G^{\ddagger}_{theo}(\mathbf{3} \rightarrow \mathbf{TS3,4}) = 0.18\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S31)}$$

2) Activation Barrier 5→ TS5,6

$$-\Delta G^{\ddagger}_{theo}(\mathbf{5} \rightarrow \mathbf{TS5,6}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S32)}$$

3) Activation Barrier 6→ TS6,7

$$-\Delta G^{\ddagger}_{theo}(\mathbf{6} \rightarrow \mathbf{TS6,7}) = -0.57\Delta G_{RRS}(\mathbf{5}) - 18kcal/mol \quad \text{(Equation S33)}$$

4) Activation Barrier 7→ TS7,2

$$-\Delta G^{\ddagger}_{theo}(\mathbf{7} \rightarrow \mathbf{TS7,2}) = 0.17\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S34)}$$

With equations S31 to S34 the activation barriers can be plotted with respect to the stability of the descriptor intermediate **5** (see Figure S3b).

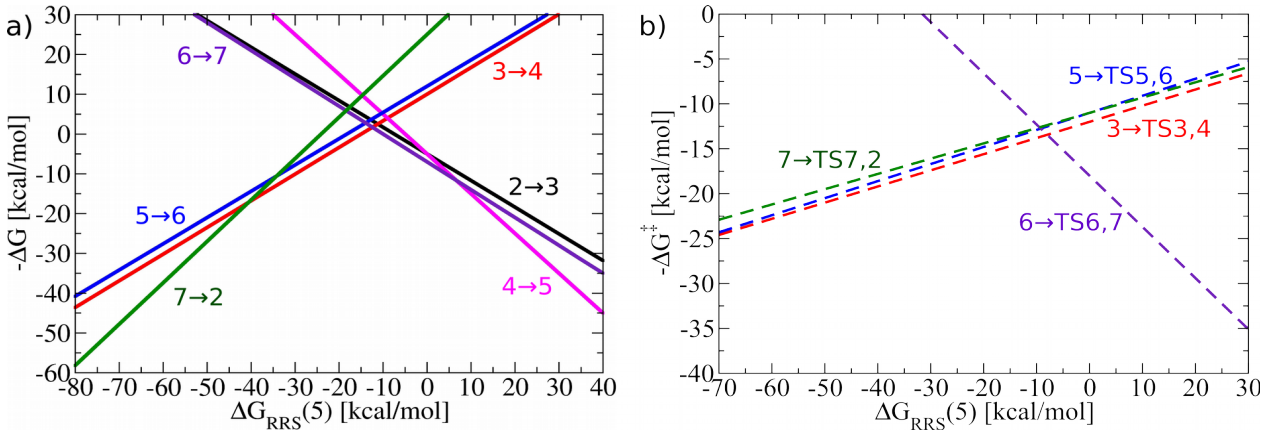


Figure S3: The energetics of the hydroformylation reaction obtained from the "combined" linear scaling relationships with respect to $\Delta G_{RRS}(5)$ simulated reaction profiles are depicted. a) Pure thermodynamic picture b) Pure kinetic picture.

Ligand Resolved Volcano Plots

The ligand resolved volcano plots are constructed equivalently to the “combined” volcano plots. Ligand resolved scaling relationships were only considered in cases where a significant improvement of the standard deviation and/or the correlation coefficient was observed. In all other cases the “combined” scaling relationships were used. The equations used to derive the theoretical reaction free energies and activation barriers are marked in bold in Figure S1 and S2.

1) **Reaction 2→3: Formation of π-Complex**

   a) PH_3

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -0.67\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S35)}$$

   b) PMe_3

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -0.67\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S36)}$$

   c) PPh_3

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -0.67\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S37)}$$

   d) PCy_3

$$-\Delta G_{theo}(\mathbf{2} \rightarrow \mathbf{3}) = -0.67\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S38)}$$

2) **Reaction 3→4: Rearrangement**

   a) PH_3

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 14kcal/mol \quad \text{(Equation S39)}$$

   b) PMe_3

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 10kcal/mol \quad \text{(Equation S40)}$$

   c) PPh_3

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 10kcal/mol \quad \text{(Equation S41)}$$

   d) PCy_3

$$-\Delta G_{theo}(\mathbf{3} \rightarrow \mathbf{4}) = 0.67\Delta G_{RRS}(\mathbf{5}) + 6kcal/mol \quad \text{(Equation S42)}$$

3) **Reaction 4→5: CO Addition**

   a) PH_3

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -\Delta G_{RRS}(\mathbf{5}) - 9kcal/mol \quad \text{(Equation S43)}$$

   b) PMe_3

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S44)}$$

c) PPh_3

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -\Delta G_{RRS}(\mathbf{5}) - 5kcal/mol \quad \text{(Equation S45)}$$

d) PCy_3

$$-\Delta G_{theo}(\mathbf{4} \rightarrow \mathbf{5}) = -\Delta G_{RRS}(\mathbf{5}) - 1kcal/mol \quad \text{(Equation S46)}$$

4) Reaction 5→6: CO Insertion

a) PH_3

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = 0.72\Delta G_{RRS}(\mathbf{5}) + 14kcal/mol \quad \text{(Equation S47)}$$

b) PMe_3

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = 0.78\Delta G_{RRS}(\mathbf{5}) + 16kcal/mol \quad \text{(Equation S48)}$$

c) PPh_3

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = 0.68\Delta G_{RRS}(\mathbf{5}) + 10kcal/mol \quad \text{(Equation S49)}$$

d) PCy_3

$$-\Delta G_{theo}(\mathbf{5} \rightarrow \mathbf{6}) = 0.59\Delta G_{RRS}(\mathbf{5}) + 8kcal/mol \quad \text{(Equation S50)}$$

5) Reaction 6→7: H_2 Addition

a) PH_3

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -0.82\Delta G_{RRS}(\mathbf{5}) - 18kcal/mol \quad \text{(Equation S51)}$$

b) PMe_3

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -0.95\Delta G_{RRS}(\mathbf{5}) - 13kcal/mol \quad \text{(Equation S52)}$$

c) PPh_3

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -0.90\Delta G_{RRS}(\mathbf{5}) - 9kcal/mol \quad \text{(Equation S53)}$$

d) PCy_3

$$-\Delta G_{theo}(\mathbf{6} \rightarrow \mathbf{7}) = -0.72\Delta G_{RRS}(\mathbf{5}) + 4kcal/mol \quad \text{(Equation S54)}$$

6) Reaction 7→2: Reductive Elimination

a) PH_3

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = 1.10\Delta G_{RRS}(\mathbf{5}) + 34kcal/mol \quad \text{(Equation S55)}$$

b) PMe_3

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = 1.17\Delta G_{RRS}(\mathbf{5}) + 27kcal/mol \quad \text{(Equation S56)}$$

c) PPh_3

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = 1.22\Delta G_{RRS}(\mathbf{5}) + 29kcal/mol \quad \text{(Equation S57)}$$

d) PCy_3

$$-\Delta G_{theo}(\mathbf{7} \rightarrow \mathbf{2}) = 1.13\Delta G_{RRS}(\mathbf{5}) + 18kcal/mol \quad \text{(Equation S58)}$$

7) Activation Barrier 3 → TS3,4

a) PH_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{3} \rightarrow \mathbf{TS3,4}) = 0.18\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S59)}$$

b) PMe_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{3} \rightarrow \mathbf{TS3,4}) = 0.18\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S60)}$$

c) PPh_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{3} \rightarrow \mathbf{TS3,4}) = 0.18\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S61)}$$

d) PCy_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{3} \rightarrow \mathbf{TS3,4}) = 0.18\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S62)}$$

8) Activation Barrier 5→ TS5,6

a) PH_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{5} \rightarrow \mathbf{TS5,6}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S63)}$$

b) PMe_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{5} \rightarrow \mathbf{TS5,6}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S64)}$$

c) PPh_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{5} \rightarrow \mathbf{TS5,6}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S65)}$$

d) PCy_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{5} \rightarrow \mathbf{TS5,6}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S66)}$$

9) Activation Barrier 6→ TS6,7

a) PH_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{6} \rightarrow \mathbf{TS6,7}) = -0.77\Delta G_{RRS}(\mathbf{5}) - 29kcal/mol \quad \text{(Equation S67)}$$

b) PMe_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{6} \rightarrow \mathbf{TS6,7}) = -0.82\Delta G_{RRS}(\mathbf{5}) - 26kcal/mol \quad \text{(Equation S68)}$$

c) PPh_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{6} \rightarrow \mathbf{TS6,7}) = -0.74\Delta G_{RRS}(\mathbf{5}) - 20kcal/mol \quad \text{(Equation S69)}$$

d) PCy_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{6} \rightarrow \mathbf{TS6,7}) = -0.55\Delta G_{RRS}(\mathbf{5}) - 6kcal/mol \quad \text{(Equation S70)}$$

10) Activation Barrier 7→ TS7,2

a) PH_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{7} \rightarrow \mathbf{TS7,2}) = 0.12\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S71)}$$

b) PMe_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{7} \rightarrow \mathbf{TS7,2}) = 0.17\Delta G_{RRS}(\mathbf{5}) - 11kcal/mol \quad \text{(Equation S72)}$$

c) PPh_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{7} \rightarrow \mathbf{TS7,2}) = 0.19\Delta G_{RRS}(\mathbf{5}) - 10kcal/mol \quad \text{(Equation S73)}$$

d) PCy_3

$$-\Delta G^{\ddagger}_{theo}(\mathbf{7} \rightarrow \mathbf{TS7,2}) = 0.32\Delta G_{RRS}(\mathbf{5}) - 12kcal/mol \quad \text{(Equation S74)}$$

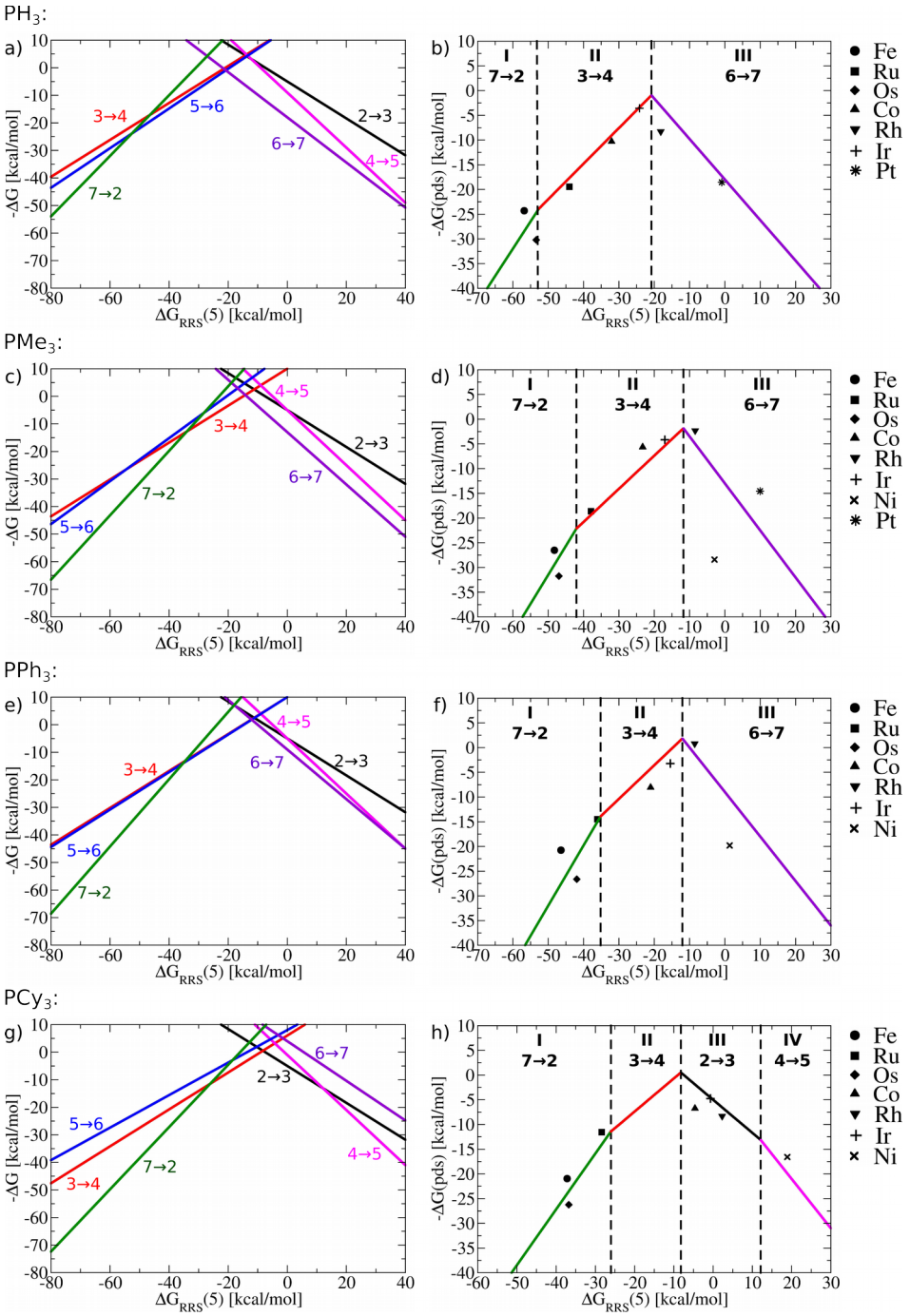


Figure S4: The simulated thermodynamics of the key reaction steps (left row) and ***thermodynamic*** *volcano plots (right row) derived from equations S35 to S58 are depicted.*

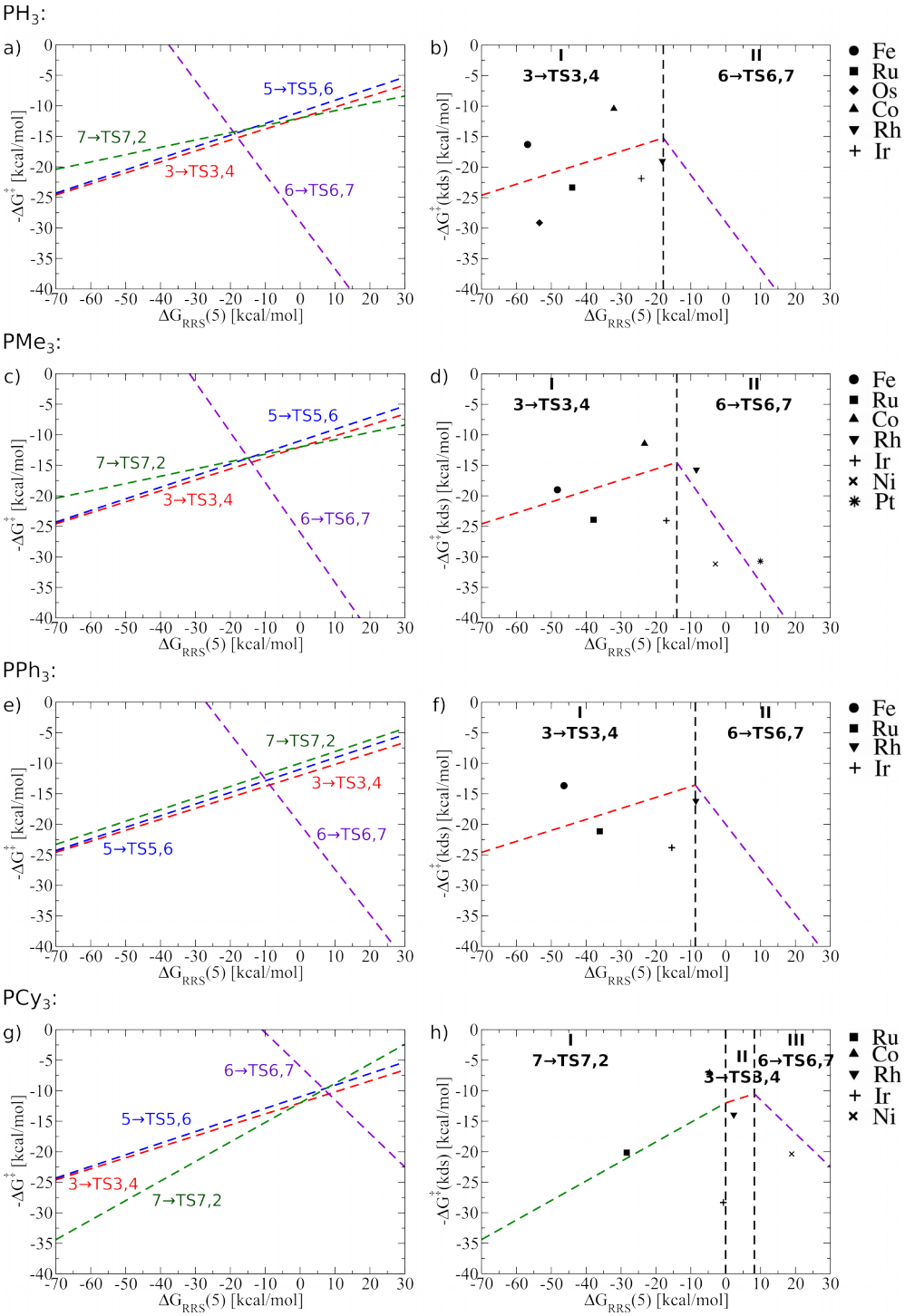


*Figure S5: The activation barriers of key reaction steps with respect to descriptor intermediate ΔG_{RRS}(**5**) (left row) and **kinetic** volcano plots (right row) derived from equations S59 to S74 are depicted.*

Derivation of SAR Kinetic Volcano Plots

a) The peak position of the different ligands is identified from the ligand specific volcano plots shown in Figure S5.

Ligand	Tolman Cone Angle [°]	ΔG_{RRS}(**5**) [kcal/mol]	$-\Delta G^{‡}$(kds) [kcal/mol]
PH_3	87	-17.9	-15.22
PMe_3	118	-14.0	-14.52
PPh_3	145	-8.7	-13.56
PCy_3	179	+8.2	-10.52

b) The peak position is related to the Tolman cone Angle, which ultimately yield a linear equation capable of giving both ΔG_{RRS}(**5**) and $\Delta G^{‡}$(kds) for any other ligand (see Figure S6).

2-Point-Fit

$$\Delta G_{RRS}(\mathbf{5}) = 0.16x - 32kcal/mol \quad \text{(Equation S75)}$$

$$-\Delta G^{‡}(kds) = 0.03x - 18kcal/mol \quad \text{(Equation S76)}$$

4-Point Fit

$$\Delta G_{RRS}(\mathbf{5}) = 0.31x - 49kcal/mol \qquad R^2 = 0.90 \quad \text{(Equation S77)}$$

$$-\Delta G^{‡}(kds) = 0.05x - 20kcal/mol \qquad R^2 = 0.90 \quad \text{(Equation S78)}$$

c) Using the mathematical equations S75 and S76 (2-point fit) or S77 and S78 (4-point fit) where x denotes the Tolman cone angle of other phosphine ligands the peak position of the kinetic volcano for any ligand can be approximated.

Ligand	**2-point fit**		**4-point fit**	
	ΔG_{RRS}(**5**) [kcal/mol]	$-\Delta G^{‡}$(kds) [kcal/mol]	ΔG_{RRS}(**5**) [kcal/mol]	$-\Delta G^{‡}$(kds) [kcal/mol]
PMe_3	-12.8	-14.2	-12.4	-14.2
PCy_3	-3.1	-12.3	+6.5	-11.2
$P(OMe)_3$	-14.6	-14.5	-15.8	-14.8
$P(NMe_2)_3$	-6.6	-13.0	-0.3	-12.3
$P(Mes)_3$	+2.2	-11.3	+16.7	-9.5

d) Using the new peak points, the slopes of the volcanoes are taken from computed linear free energy scaling relationships of computed ligands. This requires only determining the y-intercept for the lines representing the volcano slopes.

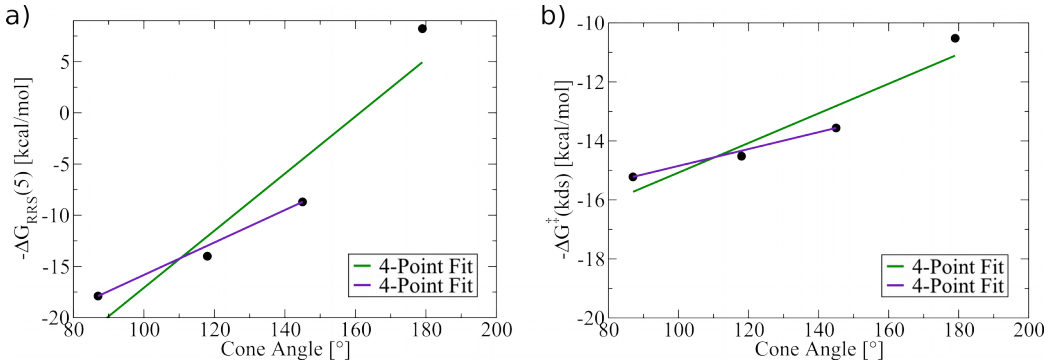


Figure S6: The Dependence of ΔG_{RRS}(5) (a) and $-\Delta G^{‡}$(kds) (b) on the cone angle is summarized for the 4-point and 2-point fit. The 2 point-fit is derived from PH_3 and PPh_3 ligands

a) **P(OMe)$_3$ – 4-Point Fit**

The slopes of the modified modified reaction equations are taken from **PMe$_3$**.

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) + b \quad \text{(Equation S79)}$$

Inserting for $\Delta G^{\ddagger}$(3→TS3,4) and the volcano height -$\Delta G^{\ddagger}$(kds) calculated from Equation S77 and taking the position of the peak ΔG(**5**) from Equation S78 results in

$$(-14.8kcal/mol) = 0.18 * (-15.8kcal/mol) + b \quad \text{(Equation S80)}$$

Thus, b = -12.0 is obtained.

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 12.0kcal/mol \quad \text{(Equation S81)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(6 \rightarrow TS6,7) = -0.82\Delta G(5) + b \quad \text{(Equation S82)}$$

Taking the values for $\Delta G^{\ddagger}$(6→TS6,7) and the volcano height -$\Delta G^{\ddagger}$(kds) from Equations S77 and S78 then results in

$$(-14.8kcal/mol) = -0.82 * (-15.8kcal/mol) + b \quad \text{(Equation S83)}$$

Thus, the modified reaction equation is:

$$-\Delta G^{\ddagger}(6 \rightarrow TS6,7) = -0.82\Delta G(5) - 27.8kcal/mol \quad \text{(Equation S84)}$$

b) P(OMe)$_3$ – 2-Point Fit

The slopes of the new reaction equations are taken from **PH$_3$**.

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) + b \quad \text{(Equation S85)}$$

With $\Delta G^{\ddagger}$(3→TS3,4) and -$\Delta G^{\ddagger}$(kds) from Equations S75 and S76 the resulting reaction equation becomes:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 11.9kcal/mol \quad \text{(Equation S86)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(6 \rightarrow TS6,7) = -0.77\Delta G(5) + b \quad \text{(Equation S87)}$$

Taking the $\Delta G^{\ddagger}$(6→TS6,7) and -$\Delta G^{\ddagger}$(kds) from Equations S75 and S76 results in

$$-\Delta G^{\ddagger}(6 \rightarrow TS6,7) = -0.77\Delta G(5) - 25.7kcal/mol \quad \text{(Equation S88)}$$

c) **P(NMe$_2$)$_3$ – 4-Point Fit**

The slopes are taken from **PPh$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 12.2kcal/mol \quad \text{(Equation S89)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(6 \rightarrow TS6,7) = -0.74\Delta G(5) - 12.5kcal/mol \quad \text{(Equation S90)}$$

d) **P(NMe$_2$)$_3$ – 4-Point Fit**

The slopes are taken from **PPh$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 11.8kcal/mol \quad \text{(Equation S91)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = -0.74\Delta G(5) - 17.9kcal/mol \quad \text{(Equation S92)}$$

e) **P(Mes)$_3$ – 4-Point Fit**

The slopes are taken from **PCy$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 12.5kcal/mol \quad \text{(Equation S93)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = -0.55\Delta G(5) - 0.3kcal/mol \quad \text{(Equation S94)}$$

f) **P(Mes)$_3$ – 2-Point Fit**

The slopes are taken from **PPh$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 11.7kcal/mol \quad \text{(Equation S95)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = -0.74\Delta G(5) - 9.7kcal/mol \quad \text{(Equation S96)}$$

g) **P(Me)$_3$ – 2-Point Fit**

The slopes are taken from **PH$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 11.9kcal/mol \quad \text{(Equation S97)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = -0.77\Delta G(5) - 24.1kcal/mol \quad \text{(Equation S98)}$$

h) **P(Cy)$_3$ – 2-Point Fit**

The slopes are taken from **PPh$_3$**. Following the procedure described for P(OMe)$_3$ one obtains:

3→TS3,4:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = 0.18\Delta G(5) - 11.7kcal/mol \quad \text{(Equation S99)}$$

6→TS6,7:

$$-\Delta G^{\ddagger}(3 \rightarrow TS3,4) = -0.82\Delta G(5) - 14.8kcal/mol \quad \text{(Equation S100)}$$

PBE0-dDsC versus M06

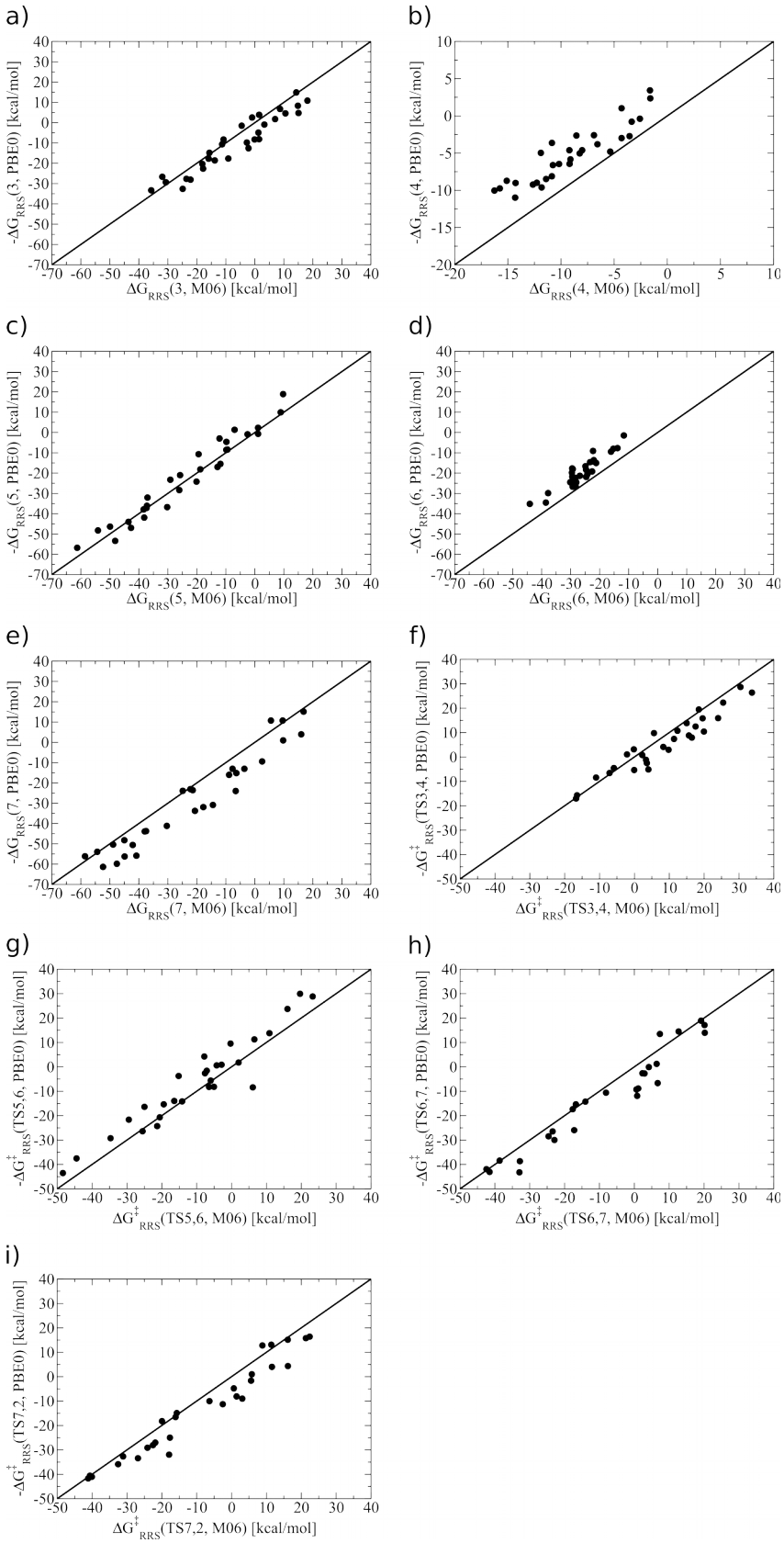


Figure S7: The comparison between binding energies and transition state energies computed with PBE0-dDsC and M06 is depicted.

Computed Free Energies – PBE0-dDsC

Table S1: Computed free energies relative to reference state (2) for each intermediate and transition state. Reported values computed at the PBE0-dDsC/TZ2P//M06/def-SVP level including unscaled free energy corrections from M06/def2-SVP computations and solvation correction in benzene from COSMO-RS (PBE0-dDsC/TZ2P level). Values in kcal/mol.

Catalyst	*Structure 3*	*TS3,4*	*Structure 4*	*Structure 5*	*TS5,6*	*Structure 6*	*TS6,7*	*Structure 7*	*TS7,2*
Fe-PH3	-33.33	-17.04	-9.74	-56.80	-43.52	-34.54	-43.06	-53.92	-41.68
Ru-PH3	-22.66	-2.51	-8.98	-44.01	-20.67	-24.55	-29.97	-43.72	-28.05
Os-PH3	-32.61	-5.13	-10.98	-53.39	-24.27	-26.71	-43.21	-59.82	-33.42
Co-PH3	-14.85	-6.58	-9.01	-32.06	-21.64	-21.75	-17.34	-23.06	-14.91
Rh-PH3	-4.90	7.40	-8.48	-18.15	0.87	-21.34	-2.72	-13.04	-1.64
Ir-PH3	-12.59	7.94	-9.61	-24.20	-5.60	-20.62	-11.89	-30.86	-8.99
Ni-PH3	-1.50	1.05	-8.72	-10.68	-3.74	-18.03	--	--	--
Pt-PH3	4.56	--	-9.23	-0.88	23.72	-14.60	13.97	3.95	15.79
Fe-PMe3	-26.66	-8.43	-4.97	-48.25	-29.24	-29.86	-41.91	-56.13	-40.58
Ru-PMe3	-17.75	4.12	-6.46	-37.89	-13.97	-24.51	-28.47	-48.22	-32.68
Os-PMe3	-27.68	2.95	-6.61	-46.98	-14.15	-24.23	--	-61.35	-35.86
Co-PMe3	-8.29	3.14	-2.64	-23.26	-16.38	-19.80	-15.35	-23.89	-18.22
Rh-PMe3	1.77	15.84	-4.61	-8.40	-8.40	-18.35	-2.63	-16.02	-4.78
Ir-PMe3	-8.14	15.92	-8.11	-16.99	1.77	-19.66	-8.86	-33.77	-11.28
Ni-PMe3	2.56	9.78	-3.63	-2.94	4.24	-17.69	13.48	10.72	12.81
Pt-PMe3	10.85	28.67	-4.61	9.96	28.84	-13.61	17.11	0.96	16.41
Fe-PPh3	-29.37	-15.70	-10.03	-46.37	-37.51	-35.16	-38.41	-50.38	-41.01
Ru-PPh3	-20.35	0.79	-5.84	-36.10	-15.35	-22.34	-26.44	-43.88	-27.01
Os-PPh3	-28.08	-1.18	-6.45	-41.91	-26.38	-23.06	--	-56.24	-29.11
Co-PPh3	-10.67	-4.54	-2.59	-21.01	--	-16.63	-14.25	-23.57	-16.56
Rh-PPh3	-0.94	10.75	-3.81	-8.54	-2.62	-14.38	-0.09	-15.16	1.02
Ir-PPh3	-8.27	12.48	-5.04	-15.45	0.60	-15.01	-9.27	-31.91	-8.08
Ni-PPh3	3.88	--	1.03	1.35	9.54	-9.09	14.51	10.72	13.12
Fe-PCy3	-18.60	-5.35	-4.80	-37.17	--	-26.49	-38.66	-50.56	--
Ru-PCy3	-9.79	8.82	-2.72	-28.38	-8.23	-19.17	-25.95	-41.16	-24.98
Os-PCy3	-17.67	10.42	-2.98	-36.76	-8.17	-21.88		-55.84	-31.95
Co-PCy3	6.77	13.86	2.36	-4.61	-1.58	-9.45	-10.59	-13.02	-10.01
Rh-PCy3	8.33	22.28	-0.78	2.31	11.27	-8.03	1.22	-9.41	4.03
Ir-PCy3	4.75	26.39	-0.38	-0.67	13.80	-7.70	-6.66	-23.97	4.36
Ni-PCy3	14.89	19.47	3.43	18.91	29.94	-1.45	18.92	15.13	15.15

Computed Free Energies – M06

Table S2: Computed free energies relative to reference state (2) for each intermediate and transition state. Reported values computed at the M06/def2-SVP level including unscaled free energy contributions and solvation correction in benzene using the SMD solvation model. Values in kcal/mol.

Catalyst	*Structure 3*	*TS3,4*	*Structure 4*	*Structure 5*	*TS5,6*	*Structure 6*	*TS6,7*	*Structure 7*	*TS7,2*
Fe-PH3	-35.72	-16.73	-15.75	-61.26	-48.36	-38.54	-41.51	-54.34	-41.11
Ru-PH3	-17.84	3.58	-12.27	-43.57	-20.58	-28.06	-22.91	-37.51	-22.53
Os-PH3	-24.88	4.02	-14.31	-48.15	-21.32	-29.30	-32.95	-47.58	-26.83
Co-PH3	-15.66	-7.13	-14.27	-37.01	-29.45	-29.44	-17.66	-22.22	-15.70
Rh-PH3	1.22	11.37	-11.40	-18.79	-2.86	-26.83	2.93	-3.61	5.60
Ir-PH3	-2.18	16.49	-11.82	-20.12	-5.96	-24.22	0.81	-14.46	3.09
Ni-PH3	-4.54	-2.12	-15.10	-19.40	-15.16	-29.27	--	--	--
Pt-PH3	10.55	--	-12.64	-2.52	16.05	-23.30	20.21	16.00	21.32
Fe-PMe3	-31.91	-10.99	-11.89	-54.09	-34.69	-37.77	-42.41	-58.56	-40.61
Ru-PMe3	-15.94	8.29	-10.18	-38.36	-16.43	-30.15	-24.60	-45.00	-31.09
Os-PMe3	-23.59	9.81	-10.76	-42.69	-14.17	-28.73	--	-52.34	-32.52
Co-PMe3	-10.80	-0.16	-8.55	-29.14	-24.97	-29.57	-16.76	-24.87	-19.94
Rh-PMe3	6.99	19.57	-8.01	-9.45	6.11	-24.68	2.32	-8.88	0.66
Ir-PMe3	1.46	24.02	-10.86	-12.89	2.03	-23.96	1.12	-20.65	-2.51
Ni-PMe3	-0.94	5.62	-10.85	-12.18	-7.81	-29.47	7.34	5.55	8.86
Pt-PMe3	18.13	30.43	-9.21	8.93	23.28	-22.01	20.14	9.76	22.41
Fe-PPh3	-30.69	-16.45	-16.26	-49.93	-44.45	-44.08	-38.63	-48.87	-40.05
Ru-PPh3	-18.09	2.26	-9.11	-37.21	-19.44	-28.52	-23.43	-37.97	-21.86
Os-PPh3	-22.17	3.33	-9.19	-38.14	-25.52	-28.42	--	-44.90	-24.10
Co-PPh3	-11.29	-5.88	-6.90	-25.77	--	-24.91	-14.04	-21.41	-16.05
Rh-PPh3	3.28	12.36	-6.57	-9.82	-7.61	-21.81	4.16	-6.38	5.83
Ir-PPh3	-0.08	17.55	-8.24	-11.87	-4.26	-21.22	0.61	-17.76	1.45
Ni-PPh3	1.48	--	-4.30	-6.98	-0.28	-22.28	12.70	9.58	11.41
Fe-PCy3	-13.81	-0.06	-5.37	-37.34	--	-28.29	-32.82	-42.10	--
Ru-PCy3	-2.76	15.64	-3.55	-26.04	-6.45	-22.59	-17.24	-30.35	-17.66
Os-PCy3	-9.15	19.95	-4.30	-30.22	-5.03	-24.64	--	-40.84	-17.91
Co-PCy3	8.68	15.00	-1.60	-9.80	-7.10	-16.09	-8.12	-7.70	-6.32
Rh-PCy3	14.84	25.47	-3.35	1.10	6.56	-15.29	6.40	2.51	11.60
Ir-PCy3	15.05	33.73	-2.58	1.13	10.88	-13.85	6.70	-6.60	16.18
Ni-PCy3	14.28	18.49	-1.63	9.74	19.66	-11.66	19.14	16.80	16.14

Electronic Energies, Free Energies and Solvent Corrections

Table S3: Electronic energies, free energy corrections and solvation corrections of relevant species. Electronic energies and free energy corrections in hartree. Solvation corrections in kcal/mol.

Species	**M06/def2-SVP Electronic Energy**	**M06/def2-SVP Free Energy Correction**	**PBE0-dDsC/TZ2P//M06/def2-SVP Electronic Energy**	**COSMO-RS Solvation Energy**
Ethene	-78.456431	0.029351	-1.408465	-0.98
CO	-113.159931	-0.013993	-0.711247	-0.20
H_2	-1.166532	-0.001440	-0.296529	0.84
Propanal	-192.875378	0.056410	-2.500169	-3.95
Fe-PH3 – 2	-2063.343064	0.033222	-2.779529	-46.91
Fe-PH3 – 3	-2141.877507	0.083659	-4.268259	-44.09
Fe-PH3 – 4	-2141.848904	0.086883	-4.233018	-44.64
Fe-PH3 – 5	-2255.102434	0.093961	-5.043006	-43.16
Fe-PH3 – 6	-2255.065034	0.092764	-5.004162	-44.52
Fe-PH3 – 7	-2256.276915	0.111494	-5.347407	-46.41
Fe-PH3 – TS3,4	-2141.847682	0.084103	-4.242347	-44.34
Fe-PH3 – TS5,6	-2255.082260	0.094342	-5.018219	-45.67
Fe-PH3 – TS6,7	-2256.256707	0.111745	-5.331405	-45.74
Fe-PH3 – TS7,2	-2256.254318	0.109990	-5.327358	-45.81
Ru-PH3 – 2	-894.823931	0.032906	-2.767248	-47.17
Ru-PH3 – 3	-973.329152	0.082624	-4.236939	-45.17
Ru-PH3 – 4	-973.322593	0.084931	-4.216505	-45.76
Ru-PH3 – 5	-1086.550727	0.089259	-5.005218	-43.88
Ru-PH3 – 6	-1086.529141	0.092391	-4.973270	-46.43
Ru-PH3 – 7	-1087.728677	0.108903	-5.314701	-47.85
Ru-PH3 – TS3,4	-973.293237	0.080836	-4.202898	-45.26
Ru-PH3 – TS5,6	-1086.514888	0.090065	-4.964951	-46.32
Ru-PH3 – TS6,7	-1087.704278	0.107764	-5.293036	-46.98
Ru-PH3 – TS7,2	-1087.705829	0.109931	-5.290931	-47.75
Os-PH3 – 2	-890.617774	0.034387	-2.818767	-48.33
Os-PH3 – 3	-969.132331	0.082214	-4.303248	-45.81
Os-PH3 – 4	-969.117426	0.084149	-4.268953	-46.92
Os-PH3 – 5	-1082.351545	0.090430	-5.071826	-44.75
Os-PH3 – 6	-1082.321901	0.090815	-5.026167	-46.97
Os-PH3 – 7	-1083.536359	0.108175	-5.389784	-48.95
Os-PH3 – TS3,4	-969.085592	0.081538	-4.258310	-46.11
Os-PH3 – TS5,6	-1082.308232	0.089860	-5.020587	-47.43
Os-PH3 – TS6,7	-1083.509469	0.104603	-5.363560	-46.55
Os-PH3 – TS7,2	-1083.504738	0.109613	-5.350922	-47.83
Co-PH3 – 2	-2182.367512	0.035154	-2.739198	-5.54
Co-PH3 – 3	-2260.871580	0.087193	-4.195239	-5.76
Co-PH3 – 4	-2260.871959	0.089786	-4.187277	-6.54
Co-PH3 – 5	-2374.087533	0.095189	-4.953787	-7.28
Co-PH3 – 6	-2374.075170	0.094897	-4.934380	-8.97
Co-PH3 – 7	-2375.249586	0.112842	-5.250538	-9.29
Co-PH3 – TS3,4	-2260.855363	0.084558	-4.178696	-6.21
Co-PH3 – TS5,6	-2374.075055	0.094767	-4.934104	-8.95
Co-PH3 – TS6,7	-2375.239539	0.110070	-5.239468	-8.78
Co-PH3 – TS7,2	-2375.238159	0.111800	-5.237325	-8.78
Rh-PH3 – 2	-910.439066	0.033042	-2.673374	-6.13
Rh-PH3 – 3	-988.913483	0.082321	-4.110154	-6.75
Rh-PH3 – 4	-988.937306	0.086036	-4.118991	-7.11
Rh-PH3 – 5	-1102.126863	0.089883	-4.862962	-7.65
Rh-PH3 – 6	-1102.140240	0.090463	-4.865115	-9.85
Rh-PH3 – 7	-1103.289664	0.108912	-5.165649	-10.68
Rh-PH3 – TS3,4	-988.894264	0.079284	-4.087442	-6.80
Rh-PH3 – TS5,6	-1102.100874	0.089295	-4.828750	-9.72
Rh-PH3 – TS6,7	-1103.276655	0.106324	-5.148607	-9.43
Rh-PH3 – TS7,2	-1103.272647	0.106566	-5.146080	-10.08
Ir-PH3 – 2	-904.252976	0.034178	-2.762083	-6.75
Ir-PH3 – 3	-982.732631	0.083272	-4.211149	-7.24

Ir-PH3 – 4	-982.751936	0.087222	-4.209070	-8.04
Ir-PH3 – 5	-1095.943451	0.091584	-4.960995	-8.82
Ir-PH3 – 6	-1095.950219	0.091823	-4.952224	-10.90
Ir-PH3 – 7	-1097.119881	0.109068	-5.281465	-11.50
Ir-PH3 – TS3,4	-982.700163	0.080558	-4.175174	-7.58
Ir-PH3 – TS5,6	-1095.917955	0.088657	-4.925349	-10.76
Ir-PH3 – TS6,7	-1097.093278	0.106798	-5.251933	-9.64
Ir-PH3 – TS7,2	-1097.090597	0.107741	-5.246037	-11.03
Ni-PH3 – 2	-2307.745257	0.035902	-2.339386	-51.76
Ni-PH3 – 3	-2386.228118	0.084456	-3.773390	-50.26
Ni-PH3 – 4	-2386.251043	0.090545	-3.790003	-50.88
Ni-PH3 – 5	-2499.436113	0.094842	-4.523750	-50.40
Ni-PH3 – 6	-2499.453397	0.096393	-4.534386	-52.06
Ni-PH3 – TS3,4	-2386.223676	0.083858	-3.768794	-50.23
Ni-PH3 – TS5,6	-2499.428038	0.093514	-4.510726	-50.81
Pt-PH3 – 2	-919.063342	0.034082	-2.378752	-50.37
Pt-PH3 – 4	-997.564599	0.088123	-3.828453	-50.20
Pt-PH3 – 5	-1110.724239	0.089961	-4.543199	-49.79
Pt-PH3 – 6	-1110.761247	0.093855	-4.565442	-52.00
Pt-PH3 – 7	-1111.883295	0.110563	-4.848687	-52.33
Pt-PH3 – TS5,6	-1110.694213	0.089531	-4.502269	-50.60
Pt-PH3 – TS6,7	-1111.871758	0.105731	-4.829852	-51.10
Pt-PH3 – TS7,2	-1111.870547	0.106282	-4.829062	-50.12
Fe-PMe3 – 2	-2298.895764	0.190557	-7.205914	-46.57
Fe-PMe3 – 3	-2377.430623	0.247478	-8.693625	-41.78
Fe-PMe3 – 4	-2377.398729	0.247489	-8.650338	-47.26
Fe-PMe3 – 5	-2490.649787	0.257383	-9.458710	-44.78
Fe-PMe3 – 6	-2490.622355	0.255952	-9.429109	-44.07
Fe-PMe3 – 7	-2491.838853	0.271350	-9.777630	-47.44
Fe-PMe3 – TS3,4	-2377.395785	0.245990	-8.658549	-44.63
Fe-PMe3 – TS5,6	-2490.619070	0.257584	-9.422823	-48.42
Fe-PMe3 – TS6,7	-2491.810883	0.269115	-9.756620	-45.01
Fe-PMe3 – TS7,2	-2491.809712	0.270815	-9.753414	-46.75
Ru-PMe3 – 2	-1130.372826	0.193467	-7.193008	-48.42
Ru-PMe3 – 3	-1208.878884	0.247035	-8.664012	-43.10
Ru-PMe3 – 4	-1208.869640	0.246984	-8.637108	-48.66
Ru-PMe3 – 5	-1322.095279	0.253782	-9.423449	-46.22
Ru-PMe3 – 6	-1322.081370	0.252960	-9.397396	-48.67
Ru-PMe3 – 7	-1323.290506	0.270457	-9.748003	-49.49
Ru-PMe3 – TS3,4	-1208.837288	0.244066	-8.620680	-46.56
Ru-PMe3 – TS5,6	-1322.061240	0.254686	-9.382716	-48.42
Ru-PMe3 – TS6,7	-1323.253750	0.266208	-9.716328	-46.95
Ru-PMe3 – TS7,2	-1323.268339	0.270454	-9.724045	-48.99
Os-PMe3 – 2	-1126.169928	0.192056	-7.248307	-49.92
Os-PMe3 – 3	-1204.684761	0.242214	-8.728084	-46.90
Os-PMe3 – 4	-1204.668569	0.246471	-8.693733	-50.05
Os-PMe3 – 5	-1317.897900	0.250996	-9.493490	-46.70
Os-PMe3 – 6	-1317.877549	0.252885	-9.453620	-50.15
Os-PMe3 – 7	-1319.101202	0.270945	-9.826776	-50.59
Os-PMe3 – TS3,4	-1204.631513	0.242192	-8.678872	-47.13
Os-PMe3 – TS5,6	-1317.856598	0.255142	-9.440575	-49.67
Os-PMe3 – TS7,2	-1319.068851	0.270182	-9.787009	-49.57
Co-PMe3 – 2	-2417.933890	0.192121	-7.175220	-9.73
Co-PMe3 – 3	-2496.436430	0.250365	-8.627796	-9.45
Co-PMe3 – 4	-2496.434763	0.252291	-8.619750	-10.06
Co-PMe3 – 5	-2609.646755	0.257540	-9.382813	-10.44
Co-PMe3 – 6	-2609.648287	0.258399	-9.376692	-11.36
Co-PMe3 – 7	-2610.826494	0.276112	-9.696553	-11.99
Co-PMe3 – TS3,4	-2496.417188	0.248085	-8.607047	-9.61
Co-PMe3 – TS5,6	-2609.640499	0.257926	-9.369619	-12.08
Co-PMe3 – TS6,7	-2610.810626	0.273175	-9.679583	-12.26
Co-PMe3 – TS7,2	-2610.816225	0.273701	-9.685095	-12.00
Rh-PMe3 – 2	-1146.001459	0.190690	-7.109477	-10.65
Rh-PMe3 – 3	-1224.473342	0.246639	-8.548683	-7.26
Rh-PMe3 – 4	-1224.498610	0.248001	-8.554624	-10.77
Rh-PMe3 – 5	-1337.682572	0.255741	-9.293576	-11.01
Rh-PMe3 – 6	-1337.706086	0.254990	-9.306214	-12.56
Rh-PMe3 – 7	-1338.865766	0.271873	-9.614963	-13.22
Rh-PMe3 – TS3,4	-1224.448986	0.242323	-8.516837	-10.47

Rh-PMe3 – TS5,6	-1337.657782	0.255115	-9.260490	-12.87
Rh-PMe3 – TS6,7	-1338.844621	0.268567	-9.590466	-13.13
Rh-PMe3 – TS7,2	-1338.846969	0.268270	-9.594146	-12.79
Ir-PMe3 – 2	-1139.820591	0.194430	-7.203615	-11.41
Ir-PMe3 – 3	-1218.296495	0.245575	-8.653892	-7.97
Ir-PMe3 – 4	-1218.318318	0.247769	-8.650406	-11.50
Ir-PMe3 – 5	-1331.502555	0.254844	-9.396409	-12.00
Ir-PMe3 – 6	-1331.521578	0.256225	-9.399662	-13.49
Ir-PMe3 – 7	-1332.700804	0.272757	-9.734838	-13.79
Ir-PMe3 – TS3,4	-1218.259073	0.244117	-8.608791	-11.30
Ir-PMe3 – TS5,6	-1331.478716	0.254790	-9.363110	-14.10
Ir-PMe3 – TS6,7	-1332.662529	0.269171	-9.691246	-13.99
Ir-PMe3 – TS7,2	-1332.670345	0.271204	-9.698060	-13.41
Ni-PMe3 – 2	-2543.333044	0.197215	-6.809383	-46.10
Ni-PMe3 – 3	-2621.811800	0.247396	-8.236221	-46.07
Ni-PMe3 – 4	-2621.834404	0.254208	-8.253107	-45.93
Ni-PMe3 – 5	-2735.014166	0.257929	-8.980684	-46.32
Ni-PMe3 – 6	-2735.043128	0.259324	-9.004608	-46.93
Ni-PMe3 – 7	-2736.172300	0.276347	-9.273760	-46.44
Ni-PMe3 – TS3,4	-2621.803235	0.249288	-8.230395	-43.69
Ni-PMe3 – TS5,6	-2735.007387	0.258109	-8.969039	-46.56
Ni-PMe3 – TS6,7	-2736.170792	0.277677	-9.270593	-46.51
Ni-PMe3 – TS7,2	-2736.165597	0.274911	-9.268483	-46.77
Fe-PPh3 – 2	-3447.624629	0.485290	-21.049292	-57.06
Fe-PPh3 – 3	-3526.157429	0.542107	-22.539151	-53.57
Fe-PPh3 – 4	-3526.137202	0.544874	-22.514311	-51.56
Fe-PPh3 – 5	-3639.372621	0.552707	-23.301083	-54.40
Fe-PPh3 – 6	-3639.365823	0.555240	-23.286819	-53.73
Fe-PPh3 – 7	-3640.554400	0.568203	-23.616762	-56.18
Fe-PPh3 – TS3,4	-3526.134315	0.541674	-22.518158	-52.80
Fe-PPh3 – TS5,6	-3639.364894	0.553708	-23.288156	-54.28
Fe-PPh3 – TS6,7	-3640.533471	0.563595	-23.596050	-54.32
Fe-PPh3 – TS7,2	-3640.538155	0.566019	-23.602164	-54.60
Ru-PPh3 – 2	-2279.094302	0.485344	-21.035331	-59.07
Ru-PPh3 – 3	-2357.604435	0.539563	-22.510712	-54.01
Ru-PPh3 – 4	-2357.590499	0.539945	-22.485028	-55.86
Ru-PPh3 – 5	-2470.816600	0.547346	-23.268322	-54.54
Ru-PPh3 – 6	-2470.806169	0.550765	-23.246237	-56.79
Ru-PPh3 – 7	-2472.002669	0.564231	-23.588643	-58.06
Ru-PPh3 – TS3,4	-2357.573133	0.540701	-22.480845	-52.34
Ru-PPh3 – TS5,6	-2470.791375	0.550428	-23.237363	-55.15
Ru-PPh3 – TS6,7	-2471.975174	0.559896	-23.561309	-55.04
Ru-PPh3 – TS7,2	-2471.974821	0.562048	-23.563110	-55.84
Os-PPh3 – 2	-2274.890041	0.483882	-21.089617	-59.90
Os-PPh3 – 3	-2353.408268	0.539703	-22.579462	-54.51
Os-PPh3 – 4	-2353.387577	0.539691	-22.540824	-57.12
Os-PPh3 – 5	-2466.617992	0.550053	-23.336568	-55.04
Os-PPh3 – 6	-2466.600651	0.548202	-23.301349	-57.13
Os-PPh3 – 7	-2467.812283	0.565596	-23.665351	-58.95
Os-PPh3 – TS3,4	-2353.366142	0.538215	-22.537650	-52.91
Os-PPh3 – TS5,6	-2466.595603	0.547776	-23.307209	-56.51
Os-PPh3 – TS7,2	-2467.781831	0.568291	-23.623463	-59.80
Co-PPh3 – 2	-3566.651601	0.489567	-21.005415	-22.71
Co-PPh3 – 3	-3645.150723	0.543614	-22.458683	-21.75
Co-PPh3 – 4	-3645.145013	0.544900	-22.444701	-23.25
Co-PPh3 – 5	-3758.356873	0.552764	-23.207878	-22.99
Co-PPh3 – 6	-3758.357623	0.554884	-23.201013	-24.26
Co-PPh3 – 7	-3759.532838	0.567711	-23.521552	-24.25
Co-PPh3 – TS3,4	-3645.140496	0.542018	-22.447964	-21.34
Co-PPh3 – TS5,6				
Co-PPh3 – TS6,7	-3759.520160	0.566782	-23.506501	-23.79
Co-PPh3 – TS7,2	-3759.523677	0.567087	-23.509933	-24.13
Rh-PPh3 – 2	-2294.714141	0.484461	-20.939168	-23.52
Rh-PPh3 – 3	-2373.190538	0.539011	-22.378450	-21.92
Rh-PPh3 – 4	-2373.207602	0.540379	-22.381549	-23.69
Rh-PPh3 – 5	-2486.393936	0.547600	-23.122739	-23.15
Rh-PPh3 – 6	-2486.416713	0.551267	-23.133207	-24.73
Rh-PPh3 – 7	-2487.571272	0.562452	-23.441749	-25.05
Rh-PPh3 – TS3,4	-2373.173915	0.536854	-22.357818	-21.82

Rh-PPh3 – TS5,6	-2486.390420	0.547601	-23.113047	-23.31
Rh-PPh3 – TS6,7	-2487.555188	0.563167	-23.419533	-24.37
Rh-PPh3 – TS7,2	-2487.552130	0.562764	-23.417266	-24.43
Ir-PPh3 – 2	-2288.531012	0.486960	-21.031142	-24.21
Ir-PPh3 – 3	-2367.011256	0.539991	-22.481139	-22.26
Ir-PPh3 – 4	-2367.026265	0.542001	-22.474671	-24.35
Ir-PPh3 – 5	-2480.210488	0.546522	-23.222848	-23.40
Ir-PPh3 – 6	-2480.230151	0.551273	-23.224057	-25.19
Ir-PPh3 – 7	-2481.404787	0.563450	-23.559525	-25.36
Ir-PPh3 – TS3,4	-2366.981927	0.538759	-22.447060	-22.12
Ir-PPh3 – TS5,6	-2480.200938	0.549091	-23.199249	-23.78
Ir-PPh3 – TS6,7	-2481.374891	0.562831	-23.523621	-24.86
Ir-PPh3 – TS7,2	-2481.375024	0.564309	-23.521511	-25.93
Ni-PPh3 – 2	-3692.050867	0.490316	-20.649328	-47.08
Ni-PPh3 – 3	-3770.527684	0.542413	-22.076120	-46.96
Ni-PPh3 – 4	-3770.543234	0.548743	-22.086276	-47.41
Ni-PPh3 – 5	-3883.728670	0.555987	-22.819068	-47.09
Ni-PPh3 – 6	-3883.753038	0.555978	-22.835191	-47.41
Ni-PPh3 – 7	-3884.883184	0.568923	-23.113023	-47.53
Ni-PPh3 – TS5,6	-3883.718536	0.556527	-22.806542	-47.11
Ni-PPh3 – TS6,7	-3884.880891	0.571606	-23.109763	-47.46
Ni-PPh3 – TS7,2	-3884.879662	0.568324	-23.108397	-47.65
Fe-PCy3 – 2	-3469.296148	0.891861	-27.073779	-48.31
Fe-PCy3 – 3	-3547.805782	0.952402	-28.545587	-47.72
Fe-PCy3 – 4	-3547.789784	0.949856	-28.520910	-47.80
Fe-PCy3 – 5	-3661.026973	0.962170	-29.309398	-48.41
Fe-PCy3 – 6	-3661.011949	0.961581	-29.292361	-48.05
Fe-PCy3 – 7	-3662.220228	0.979868	-29.644346	-48.87
Fe-PCy3 – TS3,4	-3547.780845	0.949377	-28.523181	-46.63
Fe-PCy3 – TS6,7	-3662.199536	0.973977	-29.620758	-48.07
Ru-PCy3 – 2	-2300.769107	0.892532	-27.063564	-51.03
Ru-PCy3 – 3	-2379.260432	0.952376	-28.523823	-48.43
Ru-PCy3 – 4	-2379.258373	0.949065	-28.508209	-49.08
Ru-PCy3 – 5	-2492.475928	0.956847	-29.282711	-48.91
Ru-PCy3 – 6	-2492.474378	0.960791	-29.272810	-48.40
Ru-PCy3 – 7	-2493.672182	0.978262	-29.618760	-50.40
Ru-PCy3 – TS3,4	-2379.224354	0.945618	-28.489572	-47.08
Ru-PCy3 – TS5,6	-2492.447794	0.959933	-29.250125	-51.15
Ru-PCy3 – TS6,7	-2493.644161	0.971138	-29.589821	-48.88
Ru-PCy3 – TS7,2	-2493.650176	0.976475	-29.591094	-50.47
Os-PCy3 – 2	-2296.565533	0.893452	-27.119064	-52.19
Os-PCy3 – 3	-2375.066114	0.952367	-28.592823	-48.42
Os-PCy3 – 4	-2375.056595	0.950576	-28.566070	-49.40
Os-PCy3 – 5	-2488.278600	0.957353	-29.352417	-49.28
Os-PCy3 – 6	-2488.271340	0.958993	-29.330751	-49.03
Os-PCy3 – 7	-2489.483518	0.977381	-29.696493	-51.16
Os-PCy3 – TS3,4	-2375.016944	0.949568	-28.546619	-47.57
Os-PCy3 – TS5,6	-2488.241863	0.960768	-29.306266	-51.79
Os-PCy3 – TS7,2	-2489.443773	0.974178	-29.656988	-50.05
Co-PCy3 – 2	-3588.336120	0.894352	-27.043560	-20.01
Co-PCy3 – 3	-3666.810238	0.955228	-28.475264	-19.42
Co-PCy3 – 4	-3666.824323	0.952918	-28.479089	-19.99
Co-PCy3 – 5	-3780.020900	0.962515	-29.225012	-20.20
Co-PCy3 – 6	-3780.032937	0.964527	-29.233536	-20.95
Co-PCy3 – 7	-3781.206925	0.983908	-29.555150	-21.01
Co-PCy3 – TS3,4	-3666.798838	0.953887	-28.462888	-19.26
Co-PCy3 – TS5,6	-3780.017758	0.963675	-29.219734	-21.21
Co-PCy3 – TS6,7	-3781.200071	0.976390	-29.543867	-20.94
Co-PCy3 – TS7,2	-3781.200147	0.979327	-29.544809	-21.61
Rh-PCy3 – 2	-2316.400137	0.895603	-26.978954	-20.56
Rh-PCy3 – 3	-2394.856483	0.948520	-28.400839	-19.58
Rh-PCy3 – 4	-2394.886702	0.949757	-28.415078	-20.53
Rh-PCy3 – 5	-2508.062328	0.958537	-29.144519	-20.51
Rh-PCy3 – 6	-2508.093363	0.963462	-29.164800	-21.22
Rh-PCy3 – 7	-2509.248826	0.979322	-29.478256	-21.99
Rh-PCy3 – TS3,4	-2394.837625	0.946595	-28.376769	-19.53
Rh-PCy3 – TS5,6	-2508.053491	0.958403	-29.128857	-21.30
Rh-PCy3 – TS6,7	-2509.235905	0.972595	-29.456172	-21.00
Rh-PCy3 – TS7,2	-2509.232251	0.977222	-29.455349	-21.61

Ir-PCy3 – 2	-2310.218773	0.894840	-27.072630	-20.68
Ir-PCy3 – 3	-2388.678533	0.951503	-28.503802	-19.80
Ir-PCy3 – 4	-2388.706785	0.951656	-28.510676	-20.72
Ir-PCy3 – 5	-2501.882288	0.959155	-29.243916	-20.90
Ir-PCy3 – 6	-2501.909413	0.962401	-29.257158	-21.65
Ir-PCy3 – 7	-2503.083825	0.980393	-29.596491	-22.42
Ir-PCy3 – TS3,4	-2388.644554	0.947295	-28.464743	-20.03
Ir-PCy3 – TS5,6	-2501.865283	0.957690	-29.217270	-22.22
Ir-PCy3 – TS6,7	-2503.053269	0.971032	-29.558955	-22.79
Ir-PCy3 – TS7,2	-2503.042438	0.975312	-29.547876	-21.40
Ni-PCy3 – 2	-3713.744336	0.899250	-26.695258	-47.70
Ni-PCy3 – 3	-3792.202063	0.952649	-28.105862	-47.55
Ni-PCy3 – 4	-3792.231242	0.956476	-28.128316	-47.32
Ni-PCy3 – 5	-3905.398269	0.967700	-28.840323	-47.38
Ni-PCy3 – 6	-3905.433170	0.968497	-28.872509	-48.05
Ni-PCy3 – 7	-3906.570016	0.982728	-29.156809	-48.14
Ni-PCy3 – TS3,4	-3792.197851	0.955149	-28.100906	-47.64
Ni-PCy3 – TS5,6	-3905.377917	0.963161	-28.817027	-48.12
Ni-PCy3 – TS6,7	-3906.566817	0.983263	-29.151432	-48.06
Ni-PCy3 – TS7,2	-3906.568171	0.979830	-29.153561	-48.33