Supplemental material

for

*A computational study on possible active species in nickel(II) catalysed
1-butene dimerisation in [BMIM]⁺[AlCl₄]⁻ ionic liquid solution*

by

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5.1 Activation energies

The activation energies for butene insertion are collected in Table 1 of the main paper. This section provides additional information on zero-point vibrational energies, free energies of activation, dispersion-corrected values, effect of COSMO on the activation energies, and a comparison of the BP with the B3LYP functional.

Table 1: Zero-point vibrational energy corrected gas phase activation energies $\Delta E_{3 \rightarrow 4}^\ddagger$ in kcal/mol, BP/TZVP level; cf. Table 1 of the main paper.

Pathway	L = 2x PPh ₃	L = PPh ₃	L, L' = PPh ₃ , AlCl ₄ ⁻	L = AlCl ₄ ⁻	L = 2x AlCl ₄ ⁻
<u>a</u>	13.2	9.3	13.0	19.1	19.3
<u>b</u>	10.5	9.6	11.7	20.5	20.9
<u>c</u>	13.0	11.4	12.8	20.5	19.8
<u>d</u>	14.3	12.0	11.8	22.4	23.3

Table 2: Gas phase free energies of activation $\Delta E_{3 \rightarrow 4}^\ddagger$ in kcal/mol for T = 25 °C and p = 1 bar, BP/TZVP level; cf. Table 1 of the main paper.

Pathway	L = 2x PPh ₃	L = PPh ₃	L, L' = PPh ₃ , AlCl ₄ ⁻	L = AlCl ₄ ⁻	L = 2x AlCl ₄ ⁻
<u>a</u>	13.0	11.0	11.6	19.9	19.8
<u>b</u>	10.7	11.2	10.4	21.3	21.7
<u>c</u>	12.3	13.3	12.1	20.5	19.9
<u>d</u>	14.0	13.5	11.0	23.1	23.9

Table 3: Dispersion-corrected gas phase activation energies $\Delta E_{3 \rightarrow 4}^\ddagger$ in kcal/mol, BP-D3/TZVP level.

Pathway	L = 2x PPh ₃	L = PPh ₃	L, L' = PPh ₃ , AlCl ₄ ⁻	L = AlCl ₄ ⁻	L = 2x AlCl ₄ ⁻
<u>a</u>	16.5	7.5	16.5	21.3	21.1
<u>b</u>	12.6	9.6	17.0	23.1	23.3
<u>c</u>	16.9	10.0	14.1	22.5	22.1
<u>d</u>	17.0	12.1	12.7	23.5	24.4

Table 4: Solvation-corrected activation energies $\Delta E_{3 \rightarrow 4}^\ddagger$ in kcal/mol, BP(COSMO)/TZVP//BP/TZVP level (i.e., single-point COSMO ($\epsilon = 12$) calculations have been performed on BP/TZVP optimised geometries).

Pathway	L = 2x PPh ₃	L = PPh ₃	L, L' = PPh ₃ , AlCl ₄ ⁻	L = AlCl ₄ ⁻	L = 2x AlCl ₄ ⁻
<u>a</u>	12.6	7.9	13.0	17.9	18.0
<u>b</u>	10.2	8.5	11.6	19.8	19.8
<u>c</u>	13.6	10.2	12.0	19.7	19.5
<u>d</u>	14.3	11.4	11.3	22.0	22.5

Table 5: Effect of DFT functional on activation energies $\Delta E_{3a \rightarrow 4a}^\ddagger$ (in kcal/mol) of the linear insertion pathway **a**; TZVP basis set, BP/TZVP geometries.

Pathway	L = 2x PPh ₃	L = PPh ₃	L, L' = PPh ₃ , AlCl ₄ ⁻	L = AlCl ₄ ⁻	L = 2x AlCl ₄ ⁻
BP	13.2	8.5	12.9	18.8	19.2
B3LYP	13.8	8.2	12.3	18.1	18.6

5.2 Ligand exchange energy levels: BP vs. B3LYP functional

Figure 1 compares the relative energies of the various catalyst compositions at the BP/TZVP (cf. Figure 3 of the main paper) and the B3LYP/TZVP levels, using optimized BP geometries.

Figure 1: Relative energies of catalyst compositions **3a** in kcal/mol; (R, R' = butene, butyl) calculated with two different functionals. BP: solid lines, cf. Figure 3 of the main paper; B3LYP: dashed lines. BP optimized geometries and the COSMO correction have been used throughout. The energy of **3a₃** is set to zero for each functional.

Table 6: Relative energies (kcal/mol) of catalyst compositions at various levels of theory, cf. Figure 3 of the main paper and Figure 1 of the SI for "pure" BP(COSMO) and B3LYP(COSMO)//BP(COSMO) energies. The energy of species **3a₃** is set to zero at each level of theory. ZPVE = zero-point vibrational energy; G = free energy correction from standard (gas-phase) formulae (including ZPVE); G' = as G, but without translational and rotational degrees of freedom. ZPVE and free energy corrections have been obtained from BP/TZVP geometries without COSMO (gas phase). TZVP basis set.

Level / Species	3a₁	3a₂	3a₄	3a₅
BP(COSMO)	3.1	1.9	9.0	9.8
BP(COSMO) + ZPVE(gas)	4.6	1.5	8.0	9.2
BP(COSMO) + G(gas)	7.4	-12.5	-7.5	4.8
BP(COSMO) + G'(gas)	6.2	5.6	11.3	5.9
B3LYP(COSMO)//BP(COSMO)	7.2	2.8	6.2	6.1

5.3 Geometries optimized at the BP/TZVP level of theory

Visualisations of optimized geometries (BP/TZVP level) are shown in the Figures, cartesian coordinates can be found at the end of this document. The Tables provide additional details on selected bond lengths.

Figure 2: Optimized insertion product geometries **4b** for diphosphine catalyst **4b₂** (left) and the singly bonded AlCl_4 -catalyst **4b₄** (right) at the BP/TZVP-level, cf. Figure 4 of the main text.

Figure 3: Optimized insertion step geometries for the diphenylphosphine catalyst at BP/TZVP-level; educts **3a₁**, **3b₁** (first row); transition states **a₁**, **b₁** (second row); transition states **c₁**, **d₁** (third row).

Figure 4: Optimized insertion step geometries for the monophosphine catalyst at BP/TZVP-level; educts **3a₂**, **3b₂** (first row); transition states **a₂**, **b₂** (second row); transition states **c₂**, **d₂** (third row).

Figure 5: Optimized insertion step geometries for the heteroleptic catalyst at the BP/TZVP-level; educts **3a₃**, **3b₃** (first row); transition states **a₃**, **b₃** (second row); transition states **c₃**, **d₃** (third row).

Figure 6: Optimized insertion step geometries for the mono- AlCl_4 catalyst at the BP/TZVP-level; educts $3\mathbf{a}_4$, $3\mathbf{b}_4$ (first row); transition states $\mathbf{a}_4$, $\mathbf{b}_4$ (second row); transition states $\mathbf{c}_4$, $\mathbf{d}_4$ (third row).

Figure 7: Optimized insertion step geometries for the bis- AlCl_4 catalyst at BP/TZVP-level; educts $3a_5$, $3b_5$ (first row); transition states a_5 , b_5 (second row); transition states c_5 , d_5 (third row).

Table 7: Important bond lengths for all calculated states in Å.

Pathway	r(C ₁ -Ni)	r(C ₃ -Ni)	r(C ₁ -C ₂)	r(Ni-H ₁)	r(Ni-H ₂)	r(C ₂ -C ₃)
3a₁	2.09	1.97	1.39	1.87	-	-
3b₁	2.11	2.04	1.39	1.87	-	-
a₁	1.99	2.15	1.44	-	2.10	2.12
b₁	1.98	2.12	1.44	-	2.01	2.12
c₁	2.02	2.16	1.43	-	2.06	2.20
d₁	1.99	2.26	1.43	-	-	2.17
3a₂	2.02	1.97	1.40	1.62	-	-
3b₂	2.02	1.99	1.40	1.64	-	-
a₂	1.92	2.05	1.47	1.74	-	1.90
b₂	1.89	2.05	1.47	1.72	-	1.89
c₂	1.91	2.11	1.48	1.76	-	1.85
d₂	1.88	2.13	1.50	1.77	-	1.78
3a₃	2.04	1.96	1.40	1.74	-	-
3b₃	2.02	2.00	1.40	1.81	-	-
a₃	1.97	2.03	1.43	-	1.96	2.11
b₃	1.93	2.06	1.45	-	1.95	2.10
c₃	1.97	2.06	1.44	-	1.91	2.14
d₃	1.93	2.12	1.44	-	1.92	2.12
3a₄	1.99	1.91	1.41	2.01	-	-
3b₄	2.00	1.93	1.41	1.90	-	-
a₄	1.94	2.05	1.46	-	1.94	1.95
b₄	1.90	2.07	1.46	-	1.92	1.95
c₄	1.93	2.09	1.45	-	1.91	1.98
d₄	1.90	2.12	1.46	-	1.87	1.97
3a₅	2.00	1.91	1.41	2.01	-	-
3b₅	2.00	1.93	1.41	1.87	-	-
a₅	1.93	2.05	1.45	-	1.93	1.96
b₅	1.91	2.07	1.45	-	1.91	1.94
c₅	1.93	2.09	1.45	-	1.91	1.96
d₅	1.91	2.12	1.45	-	1.88	1.96

Table 8: Bond length changes from ground state to transition state for all calculated states in Å.

Pathway	$\Delta r(\text{C}_1\text{-Ni})$	$\Delta r(\text{C}_3\text{-Ni})$	$\Delta r(\text{C}_1\text{-C}_2)$
3a₁→a₁	-0.10	+0.18	+0.05
3a₁→b₁	-0.10	+0.15	+0.05
3b₁→c₁	-0.09	+0.12	+0.04
3b₁→d₁	-0.12	+0.22	+0.04
3a₁→a₁	-0.10	+0.08	+0.07
3a₁→b₁	-0.13	+0.08	+0.07
3b₁→c₁	-0.11	+0.12	+0.08
3b₁→d₁	-0.14	+0.14	+0.10
3a₁→a₁	-0.07	+0.07	+0.03
3a₁→b₁	-0.11	+0.10	+0.05
3b₁→c₁	-0.05	+0.06	+0.04
3b₁→d₁	-0.09	+0.12	+0.04
3a₁→a₁	-0.05	+0.14	+0.05
3a₁→b₁	-0.09	+0.16	+0.05
3b₁→c₁	-0.07	+0.16	+0.04
3b₁→d₁	-0.10	+0.19	+0.05
3a₁→a₁	-0.07	+0.14	+0.04
3a₁→b₁	-0.09	+0.16	+0.04
3b₁→c₁	-0.07	+0.16	+0.04
3b₁→d₁	-0.09	+0.19	+0.04

5.4 Cartesian coordinates of optimised geometries

Optimised cartesian coordinates (xyz file format) of all reactants and transition states and associated total energies can be found in the attached archive XYZ-GEOMETRIES.zip for both the BP/TZVP and BP-D3/TZVP levels.