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# A Hybrid Carbocyclic/N-Heterocyclic Carbene Ligand

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# 1. Experimental Details

## *1.1 Materials and Methods*

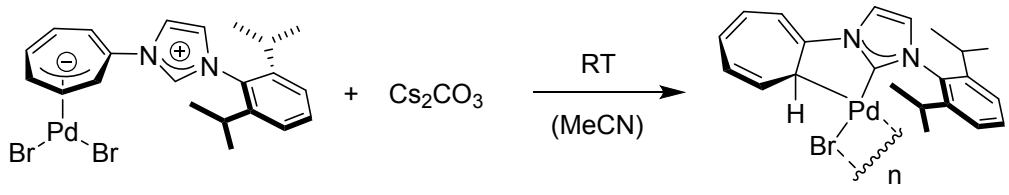
All reactions were performed under Argon (99.996%, *Westfalen*) using standard Schlenk techniques or in a glove box (labmaster 130, *MBraun*). Dry solvents were obtained from an MB-SPS (*MBraun*) and stored over molecular sieves. Chemicals were purchased from commercial suppliers as *ABCR, Sigma Aldrich* and *Fluka* and used without further purification except for caesium carbonate being dried by heating *in vacuo*. Dibromo-$\eta^3$((3-(2,6-diisopropylphenyl)imidazolium-1-yl)cycloheptatrienide) palladium(II) (**1**) was synthesised according to our previously published procedure.[1]

NMR spectra in solution were recorded on a Bruker AVIII 400US and a Bruker DRX500 spectrometer (400.13 MHz for $^{1}$H, 100.61 MHz for $^{13}$C) and chemical shifts are referenced to the solvent residual signals with respect to tetramethylsilane; $^{13}$C-spectra are proton-decoupled. Processing and analysis were performed with the *MestReNova* software package (Version 8.1.4, *Mestrelab Reserach*). $^{1}$H-NMR data are reported as follows: chemical shift in ppm (multiplicity (s = singlet, d = dublet, t = triplet, q = quartet, m = multiplet, virt. = virtual, br. = broad, n. r. = not resolved), coupling constant in Hz, integral, assignment). 2D-NMR spectra (COSY, HSQC, HMBC, NOESY) were used to confirm the peak assignment. Solid state MAS-NMR-spectra were recorded on a Bruker AV300 spectrometer (75.47 MHz for $^{13}$C) with the sample packed in a 4 mm $ZrO_2$-rotor, the rotational frequency of which is given where the spectra are reported. Carbon spectra were measured with cross polarisation technique and signals are referenced to the external standard adamantane with respect to tetramethylsilane.

Elemental analyses were performed by the microanalytical laboratory of the Technische Universität München. ESI mass spectra were recorded on a LTQ TF Ultra (*Thermo Scientific*) with the samples prepared as solution in acetonitrile, FAB mass spectra were recorded on a MAT 90 (*finnigan MAT*) and m/z is reported in atomic units per elementary charge.

## *1.2 Compounds*

### 1.2.1 Bromo [1-(cyclohepta-2,4,6-trien-1,2-diyl-$\kappa C^1$)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II) – **4**




$C_{22}H_{26}Br_2N_2Pd$
584.69 g/mol

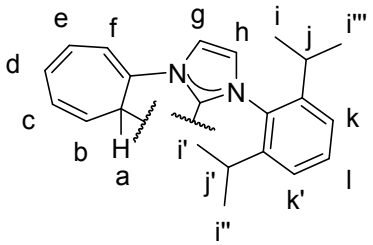
325.82 g/mol

$C_{22}H_{25}BrN_2Pd$
503.69 g/mol

400 mg of **1** (0.684 mmol, 1 eq.) and 223 mg of caesium carbonate (0.684 mmol, 1 eq.) were suspended in 10 mL of acetonitrile and stirred overnight until all of the orange solid was consumed. After concentrating the dark red solution to about half its volume 15 mL of diethyl ether were added to fully precipitate inorganic caesium salts. These were removed by filtration and the filtrate was evaporated *in vacuo*. The crude product was purified by fractioned precipitation (acetone/diethyl ether) which yielded 220 mg of acetonitrile-free **4** (0.437 mmol, 64%) as a pale yellow powder after drying *in vacuo.*

**$^1$H-NMR** (400 MHz, $CD_3CN$, 298 K): δ (ppm) = 7.55 (d, n. r., 1H, H-g), 7.49 (virt. t, $^3J$ = $^3J$ = 7.7 Hz, 1H, H-l), 7.36-7.39 (m, 2H, H-k, H-k'), 7.07 (d, n. r., 1H, H-h), 6.49-6.56 (m, 2H, H-d, H-e), 7.26-7.29 (m, 1H, H-f), 5.90-5.95 (m, 1H, H-c), 5.79-5.84 (m, 1H, H-b), 3.17 (d, $^3J$ = 5.0 Hz, 1H, H-a), 2.54-2.66 (m, 2H, H-j, H-j'), 1.40 (d, $^3J$ = 6.9 Hz, 3H, H-i), 1.30 (d, $^3J$ = 6.9 Hz, 3H, H-i'), 1.17 (d, $^3J$ = 6.9 Hz, 3H, H-i''), 1.14 (d, $^3J$ = 6.9 Hz, 3H, H-i''')

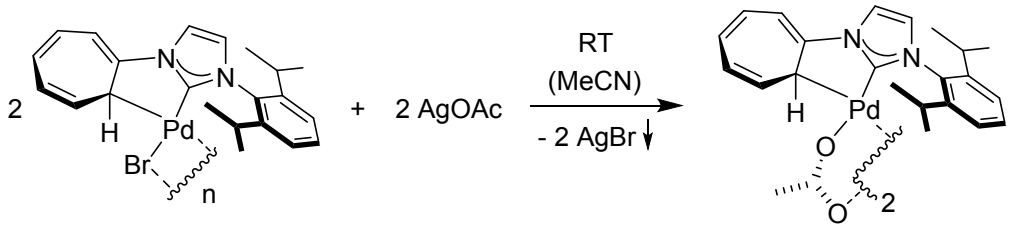
**$^{13}$C-NMR** (100 MHz, $CD_3CN$, 298 K): δ (ppm) = 173.88 (NHC-carbene), 147.18, 147.14, 137.80, 135.52, 134.60, 131.73, 130.52, 128.16, 124.87, 124.77, 124.18, 123.28, 116.54, 106.39, 34.06, 29.32, 29.27, 24.35, 24.28, 24.22, 24.04




**Elemental Analysis** (%): Calcd.: C, 52.45; H, 5.00; N, 5.56; Br, 15.9; Pd, 21.1. Found: C, 52.46; H, 5.03; N, 5.54; Br, 15.7; Pd, 20.9

**ESI-MS** (m/z): 423.14 $(M-Br)^+$, 463.77 $(M-Br+MeCN)^+$

### 1.2.2 Bis-μ-acetato bis{[1-(cyclohepta-2,4,6-trien-1,2-diyl-$\kappa C^1$)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II)} – **5**




$C_{22}H_{25}BrN_2Pd$
503.69 g/mol

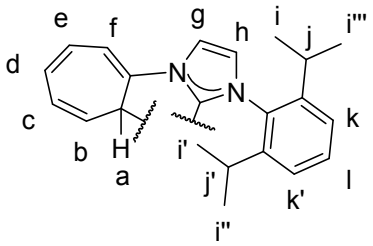
166.91 g/mol

$C_{48}H_{56}N_4O_4Pd_2$
965.79 g/mol

105 mg of **4** (0.208 mmol, 1 eq.) and 36.5 mg of silver acetate (0.219 mmol, 1.05 eq.) were dissolved in 6 mL of acetonitrile together and stirred for 15 min. The solvent was removed *in vacuo* and the residue was extracted with 10 mL of diethyl ether. The extract was concentrated to ca. 3 mL and 8 mL of hexane were added to produce a small amount of dark precipitate which was filtered off. The filtrate was evaporated *in vacuo* and the residue was washed two times with 1.5 mL of hexane. After drying *in vacuo* 74 mg of **5** (0.0766 mmol, 74%) were obtained as a pale yellow powder.

**$^1$H-NMR** (400 MHz, $CD_2Cl_2$, 298 K): δ (ppm) = 7.33 (virt. t, $^3J$ = $^3J$ = 7.8 Hz, 2H, H-l), 7.22 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.5 Hz, 2H, H-k), 7.16 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.5 Hz, 2H, H-k'), 7.12 (d, $^3J$ = 2.1 Hz, 2H, H-g), 7.63 (d, $^3J$ = 2.1 Hz, 2H, H-h), 6.47-6.51 (m, 2H, H-d), 6.38-6.42 (m, 2H, H-e), 5.98-6.02 (m, 4H, H-c, H-f), 5.55-5.59 (m, 2H, H-b), 2.60-2.69 (m, 4H, H-a, H-j), 2.44 (septet, $^3J$ = 6.8 Hz, 2H, H-j'), 1.70 (d, $^3J$ = 6.8 Hz, 6H, H-i), 1.14 (s, 6H, $H_3COO^-$), 1.07 (d, $^3J$ = 6.8 Hz, 12H, H-i', H-i''), 0.95 (d, $^3J$ = 6.8 Hz, 6H, H-i''')

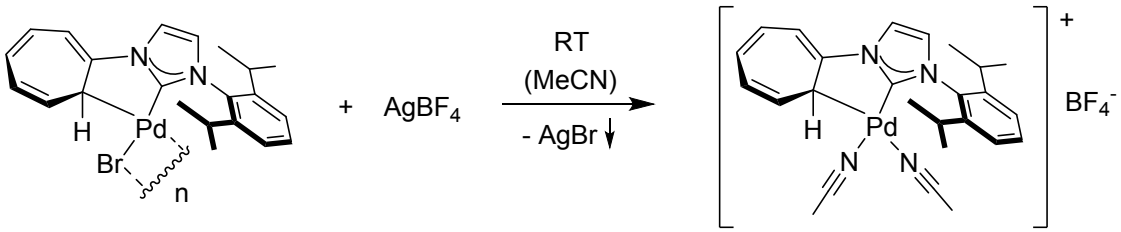
**$^{13}$C-NMR** (100 MHz, $CD_2Cl_2$, 298 K): δ (ppm) = 179.42 ($CH_3COO^-$), 172.68 (NHC-carbene), 146.94, 145.08, 136.84, 134.71, 133.18, 129.70, 128.73, 127.82, 124.65, 124.48, 124.05, 123.02, 115.57, 104.58, 32.50, 29.21, 28.80, 26.51, 25.28, 24.43, 24.26, 24.10




**Elemental Analysis** (%): Calcd.: C, 59.69; H, 5.84; N, 5.80. Found: C, 59.46; H, 5.91; N, 5.71

**FAB-MS** (m/z): 317.1 (½M-OAc-Pd)$^+$, 422.6 (½M-OAc)$^+$, 904.0 (M-OAc)$^+$

### 1.2.3 Diacetonitrile [1-(cyclohepta-2,4,6-trien-1,2-diyl-$\kappa C^1$)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II) tetrafluoroborate – **6**




$C_{22}H_{25}BrN_2Pd$
503.69 g/mol

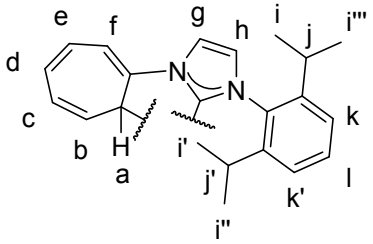
194.67 g/mol

$C_{26}H_{31}BF_4N_4Pd$
592.78 g/mol

A solution of 58.0 mg silver tetrafluoroborate (0.298 mmol, 1 eq.) in 5 mL of acetonitrile was added to a stirred solution of 150 mg of **4** (0.298 mmol, 1 eq.) in 5 mL acetonitrile. After 15 min the white precipitate was removed by filtration and the filtrate was evaporated *in vacuo.* After further drying *in vacuo* 149 mg of **6** (0.251 mmol, 84%) were obtained as a pale orange-yellow solid. Upon extensive drying it partly loses coordinating MeCN.

**$^1$H-NMR** (400 MHz, $CD_3CN$, 298 K): δ (ppm) = 7.65 (d, $^3J$ = 2.2 Hz, 1H, H-g), 7.52 (virt. t, $^3J$ = $^3J$ = 7.8 Hz, 1H, H-l), 7.37-7.41 (m, 2H, H-k, H-k'), 7.17 (d, $^3J$ = 2.2 Hz, 1H, H-h), 6.55-6.63 (m, 2H, H-d, H-e), 6.36-6.38 (m, 1H, H-f), 6.03-6.08 (m, 1H, H-c), 5.57-5.61 (m, 1H, H-b), 3.24 (d virt. t, $^3J$ = 4.8 Hz, $^5J$ = $^5J$ = 1.6 Hz, 1H, H-a), 2.46-2.57 (m, 2H, H-j, H-j'), 1.36 (d, $^3J$ = 6.9 Hz, 3H, H-i), 1.27 (d, $^3J$ = 6.9 Hz, 3H, H-i'), 1.16 (d, $^3J$ = 7.0 Hz, 3H, H-i''), 1.14 (d, $^3J$ = 7.0 Hz, 3H, H-i'''), additional signal: $H_3CCN$ at 1.96 ppm

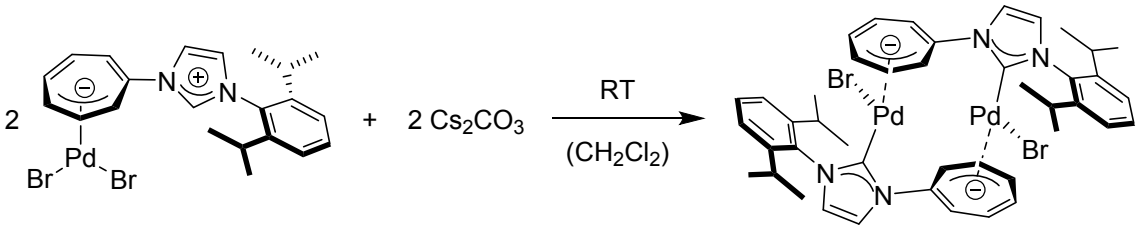
**$^{13}$C-NMR** (100 MHz, $CD_3CN$, 298 K): δ (ppm) = 167.99 (NHC-carbene), 147.15, 147.11, 135.78, 134.96, 132.11, 131.05, 130.85, 128.73, 125.31, 125.07, 124.97, 124.89, 117.40, 107.52, 35.81, 29.31, 29.28, 24.34, 24.30, 24.19, 24.02




**Elemental Analysis** (%): Calcd.: C, 52.68; H, 5.27; N, 9.45. Found: C, 52.47; H, 5.24; N, 9.44

**ESI-MS** (m/z): 423.26 $(M\text{-}BF_4\text{-}2MeCN)^+$, 463.91 $(M\text{-}BF_4\text{-}MeCN)^+$, 506.62 $(M\text{-}BF_4)^+$, 1011.41 $(2M\text{-}2BF_4\text{-}H)^+$

### 1.2.4 Isolation of Bis{Bromo[1-((1,6,7η)-cyclohepta-2,4,6-trien-1,2-diyl)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II)} – **3**




$C_{22}H_{26}Br_2N_2Pd$
584.69 g/mol

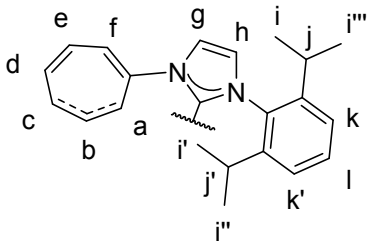
325.82 g/mol

$C_{44}H_{50}Br_2N_4Pd_2$ (byproduct)
1007.38 g/mol

600 mg of **1** (1.03 mmol, 1 eq.) and 334 mg of caesium carbonate (1.03 mmol, 1 eq.) were suspended in 10 mL of dichloromethane and stirred for 2 days. 7 mL of hexane were added to fully precipitate inorganic caesium salts, the solution was filtered and the filtrate evaporated *in vacuo*. After fractioned precipitation from dichloromethane/hexane 250 mg of a brown solid containing ca. 30% **3** were obtained in the first fraction. These were further purified by fractioned precipitation from acetonitrile/diethyl ether yielding 60 mg of **3** (0.0596 mmol, 12%) as an intense red powder.

**$^1$H-NMR** (400 MHz, $CD_3CN$, 233 K): δ (ppm) = 7.73-7.76 (m, 4H, H-f, H-g), 7.44-7.48 (t, $^3J$ = 7.7 Hz, 2H, H-l), 7.26-7.32 (m, 6H, H-h, H-k, H-k'), 6.15-6.20 (m, 2H, H-d), 5.78-5.83 (m, 2H, H-e), 5.63 (virt. t, $^3J \approx {}^3J \approx$ 7.4 Hz, 2H, H-c), 5.07 (d, $^3J \approx$ 7.4 Hz, 2H, H-a), 3.75 (virt. t, $^3J \approx {}^3J \approx$ 7.4 Hz, H-b), 2.52 (septet, $^3J$ =6.5 Hz, 2H H-j'), 2.40 (septet, $^3J$ = 6.3 Hz, 2H H-j), 1.34 (d, $^3J$ = 6.4 Hz, 6H, H-i), 1.22 (d, $^3J$ = 6.4 Hz, 6H, H-i'), 0.98 (d, $^3J$ = 6.7 Hz, 6H, H-i''), 0.88 (d, $^3J$ = 6.5 Hz, 6H, H-i''')

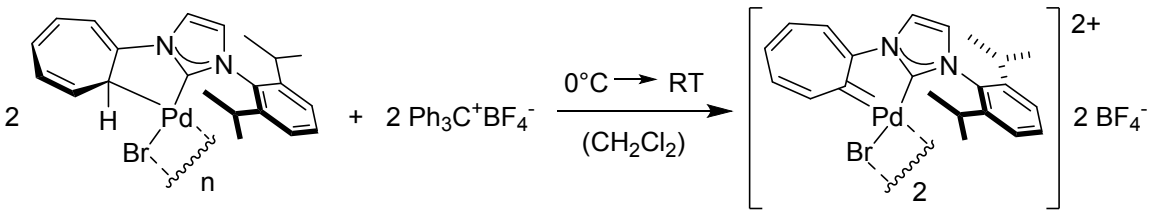
**$^{13}$C-NMR** (100 MHz, $CD_3CN$, 233 K): δ (ppm) = 186.22 (NHC-carbene), 146.88, 145.72, 138.65, 135.62, 130.92, 128.25, 127.46, 125.94, 124.91, 124.07, 122.33, 121.36, 92.46, 81.20, 65.32, 28.80, 28.66, 26.30, 26.17, 22.79, 22.26




**Elemental Analysis** (%): Calcd.: C, 52.45; H, 5.00; N, 5.56. Found: C, 52.66; H, 5.05; N, 5.48

**ESI-MS** (m/z): 423.46 (½M-Br)$^+$, 741.42 (M-Pd-2Br+H$^+$)$^+$, 927.27 (M-Br)$^+$

### 1.2.5 Bis-μ-bromo bis{[1-(cyclohepta-2,4,6-trien-2-yl-1-ylidene-$\kappa C^1$)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II)} tetrafluoroborate – **7**




$C_{22}H_{25}BrN_2Pd$
503.69 g/mol

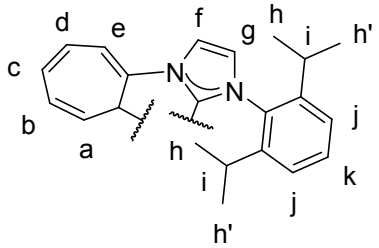
$C_{19}H_{15}BF_4$
330.13 g/mol

$C_{44}H_{48}B_2Br_2F_8N_4Pd_2$
1179.15 g/mol

At 0 °C a solution of 131 mg of triphenylcarbenium tetrafluoroborate (0.397 mmol, 1 eq.) in 5 mL of dichloromethane was slowly added to a stirred solution of 200 mg of **4** (0.397 mmol, 1 eq.) in 5 mL of dichloromethane. The reaction mixture was stirred for 15 min at 0 °C and 60 min at room temperature. The precipitate was collected by filtration and washed with 5 mL of dichloromethane. After drying *in vacuo* 197 mg of **7** (0.167 mmol, 84%) were obtained as a bright yellow powder.

**$^1$H-NMR** (400 MHz, $CD_3CN$, 298 K): δ (ppm) = 10.73 (d, $^3J$ = 10.1 Hz, 2H, H-a), 8.76-8.80 (m, 2H, H-d), 8.68 (d, $^3J$ = 10.1 Hz, 2H, H-e), 8.58-8.62 (m, 2H, H-c), 8.40-8.45 (m, 2H, H-b), 8.11 (d, $^3J$ = 2.3 Hz, 2H, H-f), 7.60 (t, $^3J$ = 7.8 Hz, 2H, H-k) 7.47-7.49 (m, 6H, H-g, H-j), 2.72 (septet, $^3J$ = 6.8 Hz, 4H, H-i), 1.31 (d, $^3J$ = 6.8 Hz, 12H, H-h), 1.20 (d, $^3J$ = 6.8 Hz, 12H, H-h')

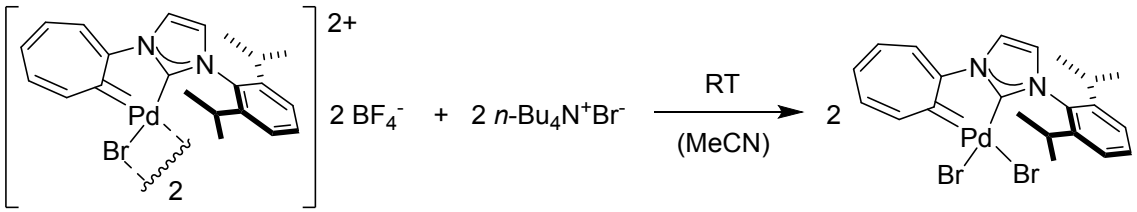
**$^{13}$C-NMR** (100 MHz, $CD_3CN$, 298 K): δ (ppm) = 185.16 (CHT-carbene), 169.59 (NHC-carbene), 167.54, 165.45, 151.83, 147.40, 146.96, 146.78, 134.23, 132.88, 131.88, 127.31, 125.50, 119.21, 29.41, 24.33, 24.09




**Elemental Analysis** (%): Calcd.: C, 44.82; H, 4.10; N, 4.75. Found: C, 44.45; H, 4.07; N, 4.76

**FAB-MS** (m/z): 502.4 (½M-$BF_4$)$^+$, 1004.0 (M-2$BF_4$)$^+$, 1020.8 (M-2Br)$^+$, 1090.8 (M-$BF_4$)$^+$

### 1.2.6 Dibromo [1-(cyclohepta-2,4,6-trien-2-yl-1-ylidene-$\kappa C^1$)-3-(2,6-diisopropylphenyl)imidazol-4-in-2-ylidene] palladium(II) – **8**




$C_{44}H_{48}B_2Br_2F_8N_4Pd_2$ 1179.15 g/mol

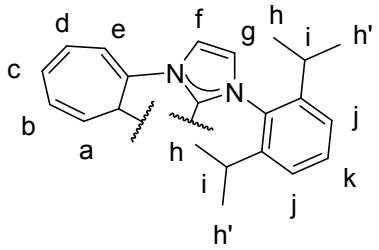
$C_{16}H_{36}BrN$ 322.38 g/mol

$C_{22}H_{24}Br_2N_2Pd$ 582.68 g/mol

A solution of 84.2 mg of tetra-*n*-butylammonium bromide (0.261 mmol, 2.2 eq.) in 5 mL of acetonitrile was slowly added to a stirred solution of 140 mg of **7** (0.119 mmol, 1 eq.) in 3 mL of acetonitrile. The precipitate was collected by filtration, washed with acetonitrile (5 mL) and diethyl ether (5 mL) and dried *in vacuo*. 115 mg of **8** (0.197 mmol, 83%) were obtained as a bright orange, microcrystalline solid.

**$^1$H-NMR** (400 MHz, DMSO-$d^6$, 298 K): δ (ppm) = 10.32 (d, n. r., 1H, H-a), 9.07 (d, $^3J$ = 10.5 Hz, 1H, H-e), 8.80-8.85 (m, 1H, H-d), 8.71 (d, n. r., H-f), 8.61-8.66 (m, 1H, H-c), 8.52-8.57 (m, 1H, H-b), 7.86 (d, n.r., 1H, H-g), 7.49 (t, n. r., 1H, H-k), 7.30 (d, n. r., 2H, H-j), 2.58 (septet, $^3J$ = 6.6 Hz, 2H, H-i), 1.26 (d, $^3J$ = 6.6 Hz, 6H, H-h), 1.11 (d, $^3J$ = 6.6 Hz, 6H, H-h)

**Solid State $^{13}$C-NMR** (75 MHz, 298 K, 12 kHz): δ (ppm) = 191.3 (CHT-carbene), 170.8 (NHC-carbene, overlapping with another signal), 165.1, 150.7, 148.6, 146.5, 144.5, 136.7, 129.0, 124.6, 123.0, 31.0, 29.3, 27.0




**Elemental Analysis** (%): Calcd.: C, 45.35; H, 4.15; N, 4.81. Found: C, 45.27; H, 4.15; N, 5.09

**FAB-MS** (m/z): 502.4 $(M\text{-}Br)^+$

## *1.3 NMR Spectra*

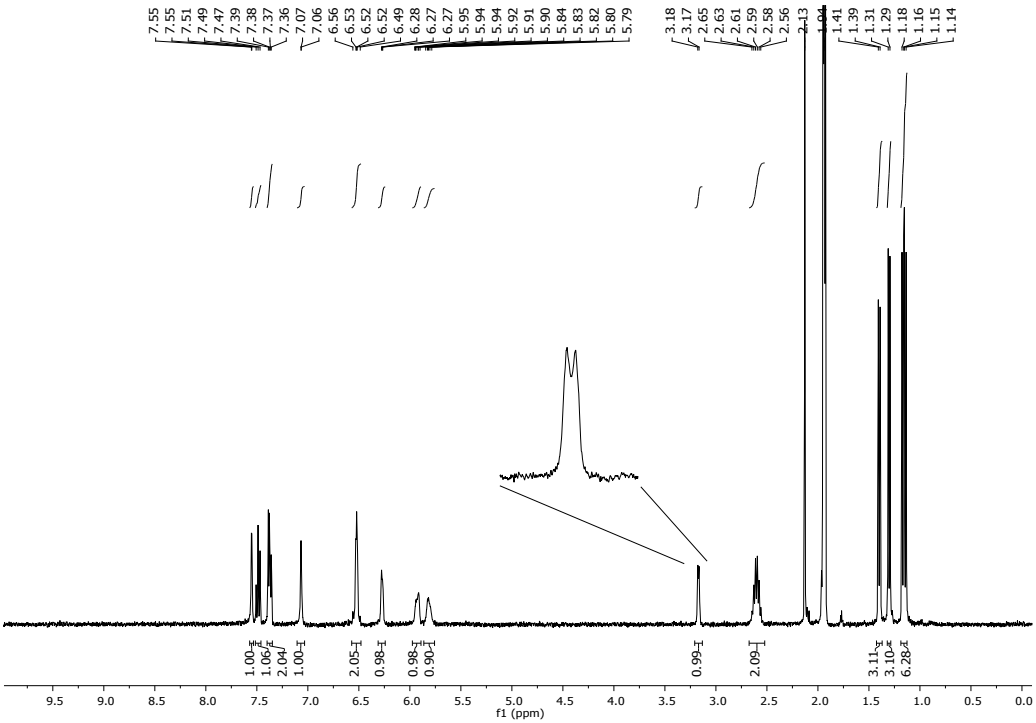



**Figure S1:** $^{1}$H-NMR spectrum of compound **4** in deuterated acetonitrile (where it forms **2**) with an expansion of the signal of the cycloheptatrienyl alkyl-proton. Solvent residual signal at 1.94 ppm and water at 2.13 ppm.

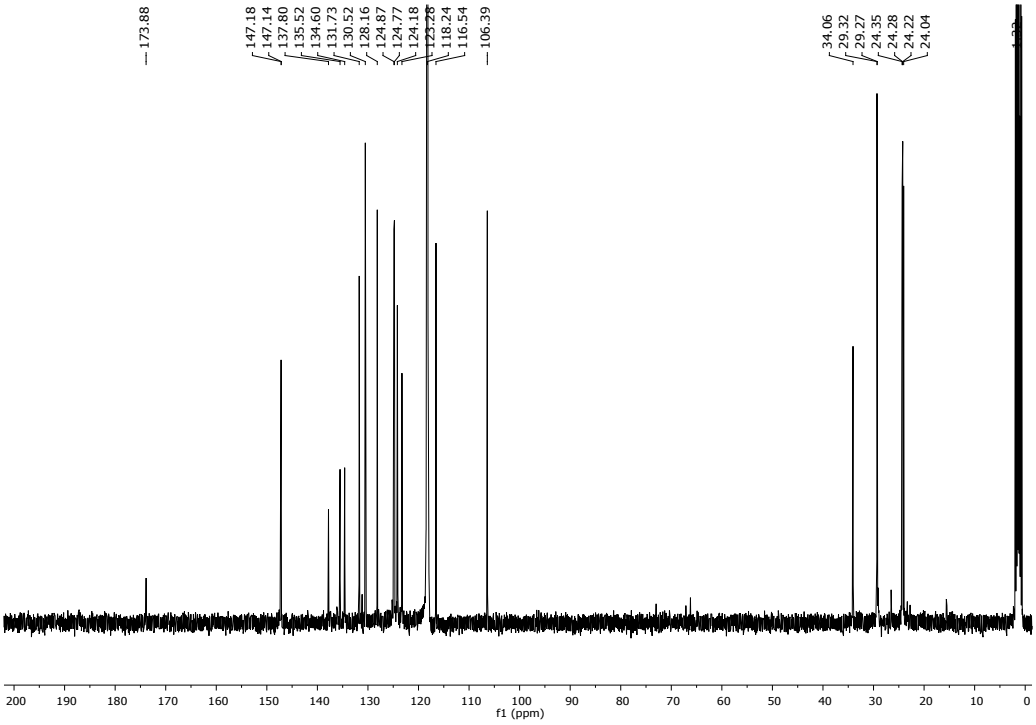



**Figure S2:** $^{13}$C-NMR spectrum of compound **4** in deuterated acetonitrile (where it forms **2**). Solvent signals at 1.32 ppm and 118.24 ppm.

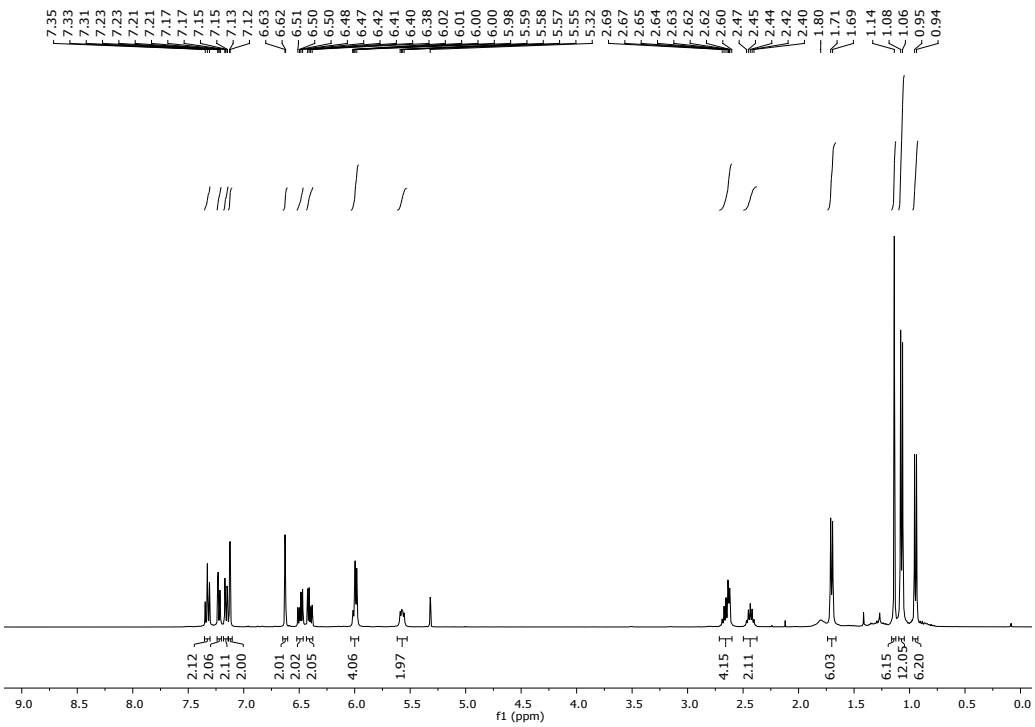



**Figure S3:** $^{1}$H-NMR spectrum of compound **5** in deuterated dichloromethane. Solvent residual signal at 5.32 ppm.

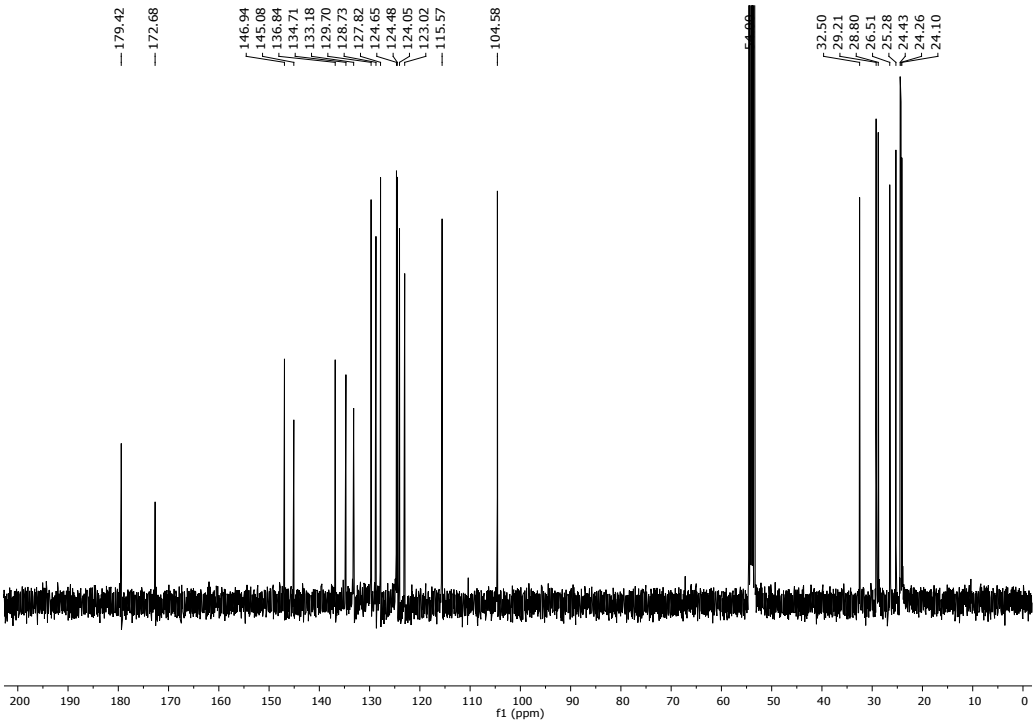



**Figure S4:** $^{13}$C-NMR spectrum of compound **5** in deuterated dichloromethane. Solvent signal at 54.00 ppm.

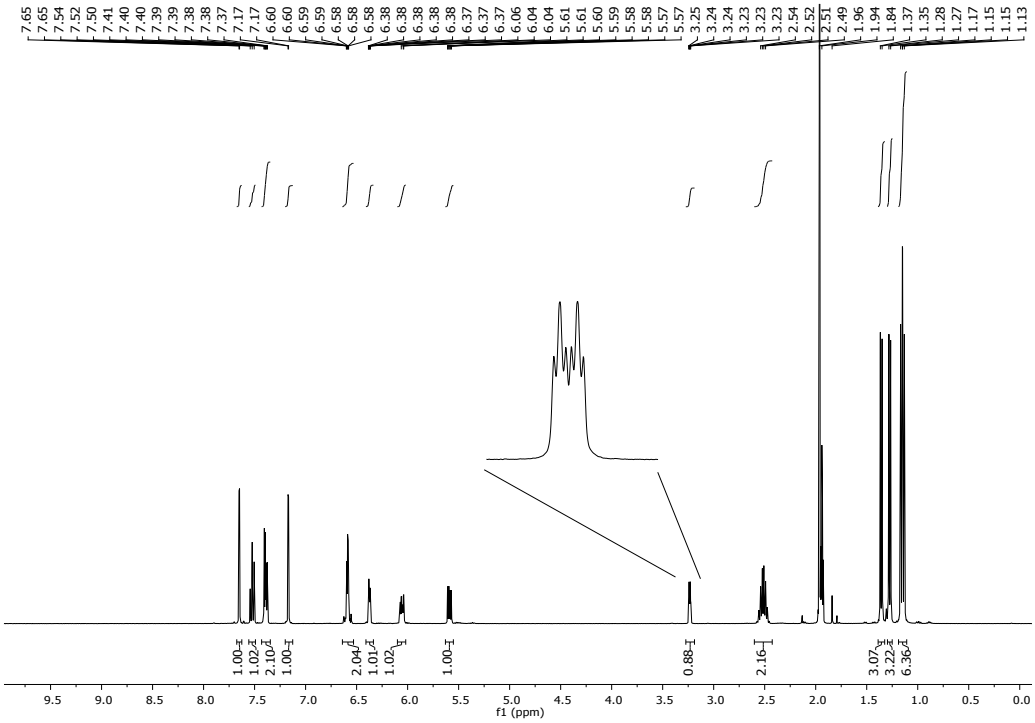



**Figure S5:** $^{1}$H-NMR spectrum of compound **6** in deuterated acetonitrile with an expansion of the signal of the cycloheptatrienyl alkyl-proton. Solvent residual signal at 1.94 ppm, free acetonitrile at 1.96 ppm and coordinating acetonitrile at 1.84 ppm.

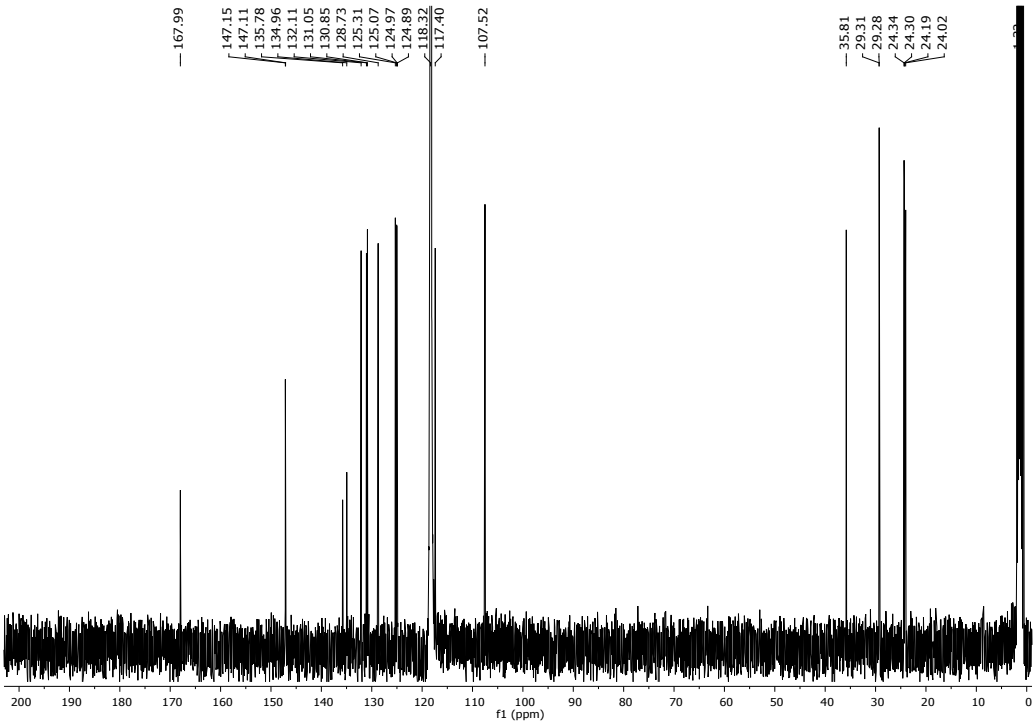



**Figure S6:** $^{13}$C-NMR spectrum of compound **6** in deuterated acetonitrile. Solvent signals at 1.32 ppm and 118.32 ppm.

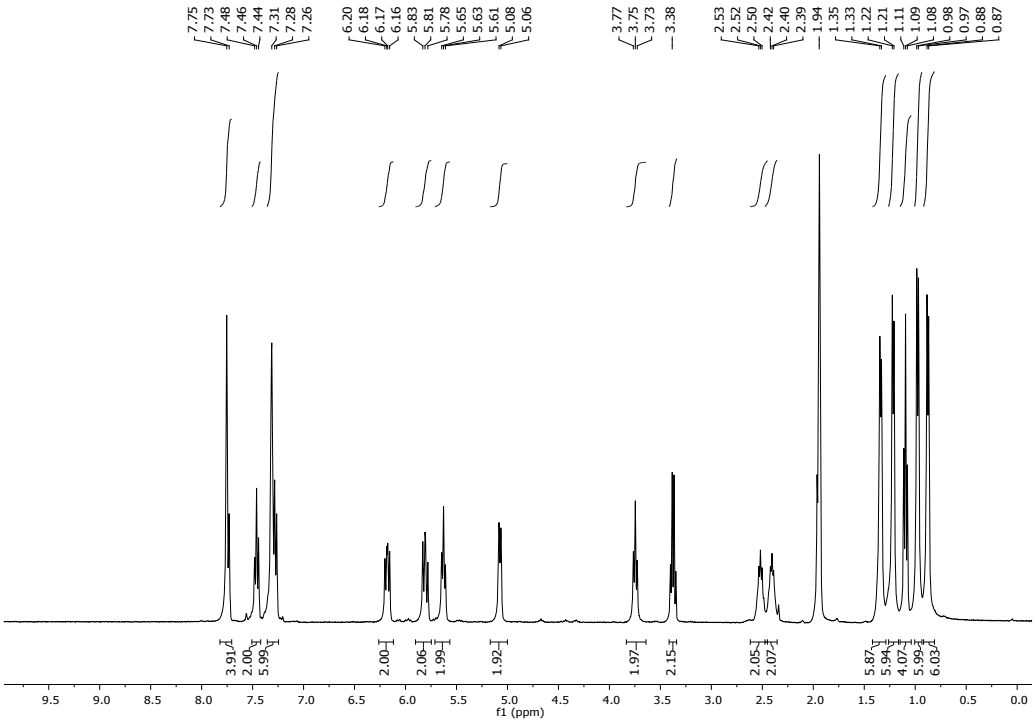



**Figure S7:** $^{1}$H-NMR spectrum of compound **3 (**single crystals) in deuterated acetonitrile at -40 °C. Solvent residual signal at 1.94 ppm.

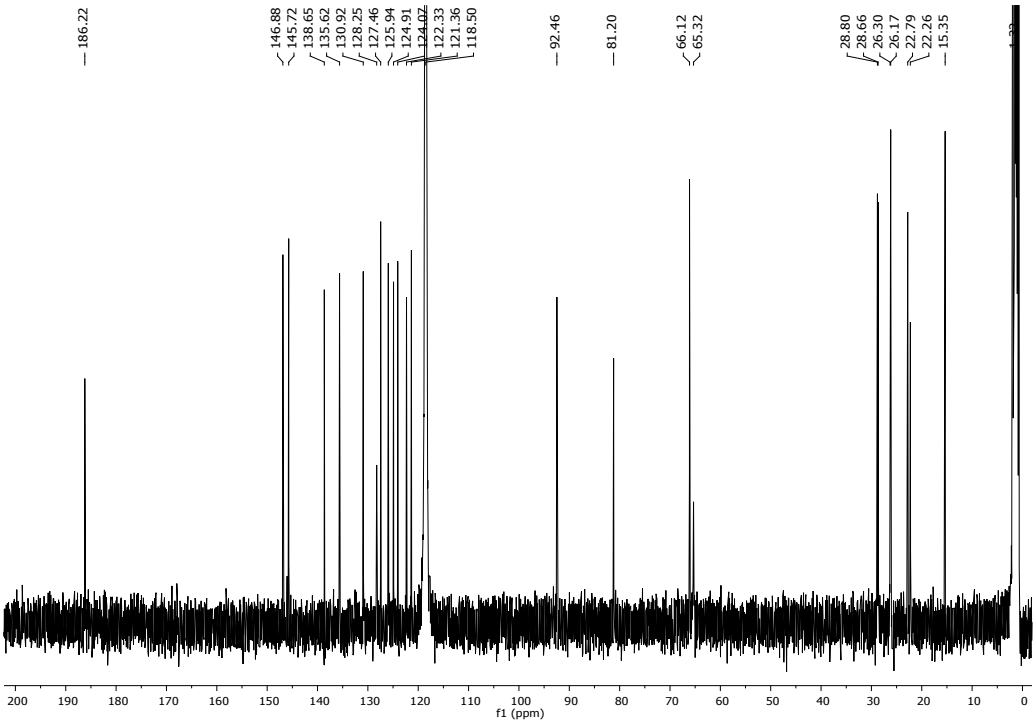



**Figure S8:** $^{13}$C-NMR spectrum of compound **3** (single crystals) in deuterated acetonitrile at -40 °C. Solvent signals at 1.32 ppm and 118.50 ppm.

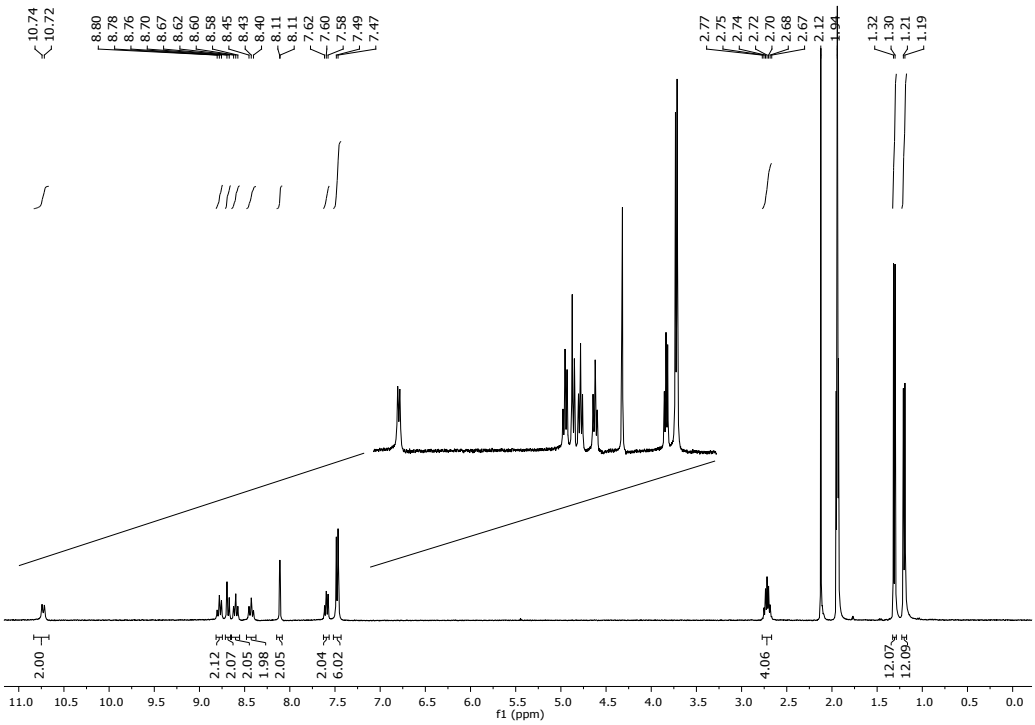



**Figure S9:** $^{1}$H-NMR spectrum of compound **7** in deuterated acetonitrile with an expansion of the 7-11 ppm region. Solvent residual signal at 1.94 ppm and water at 2.12 ppm.

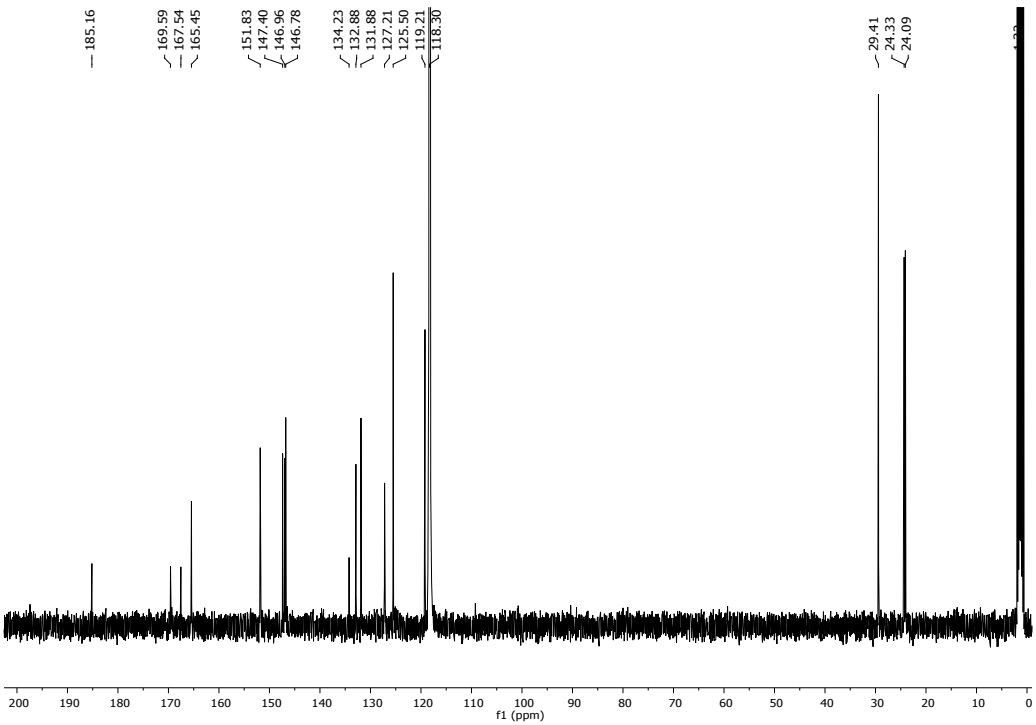



**Figure S10:** $^{13}$C-NMR spectrum of compound **7** in deuterated acetonitrile. Solvent signals at 1.32 ppm and 118.30 ppm.

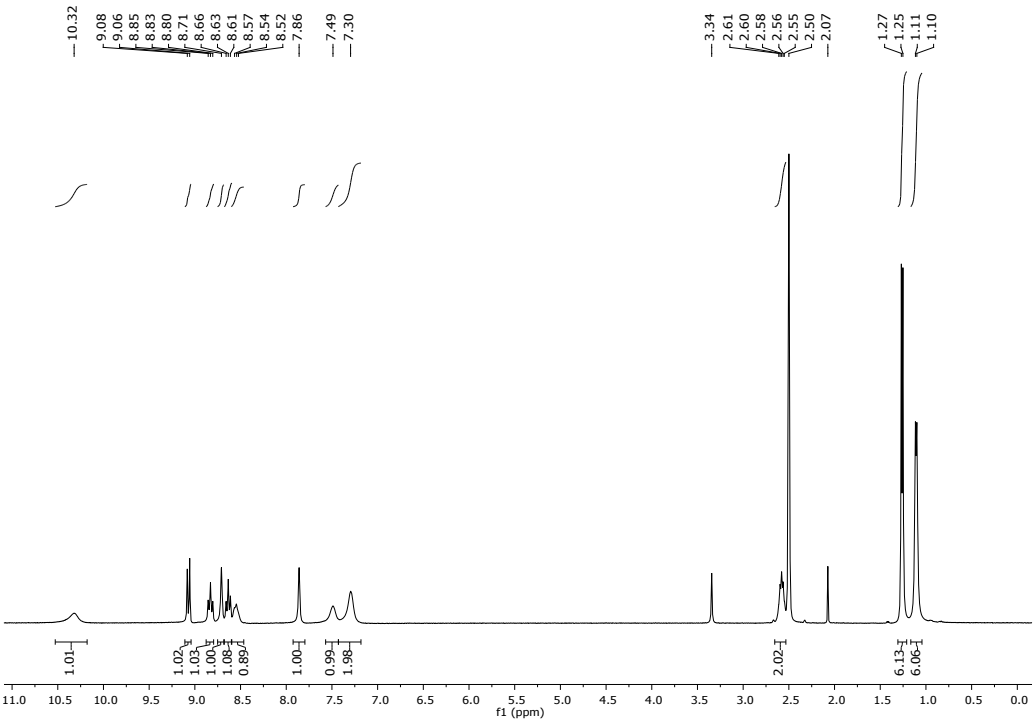



**Figure S11:** $^{1}$H-NMR spectrum of compound **8** in deuterated dimethylsulfoxide at room temperature (for VT data see Figure S14). Solvent residual signal at 2.50 ppm, water at 3.34 ppm and residual acetonitrile at 2.07 ppm.

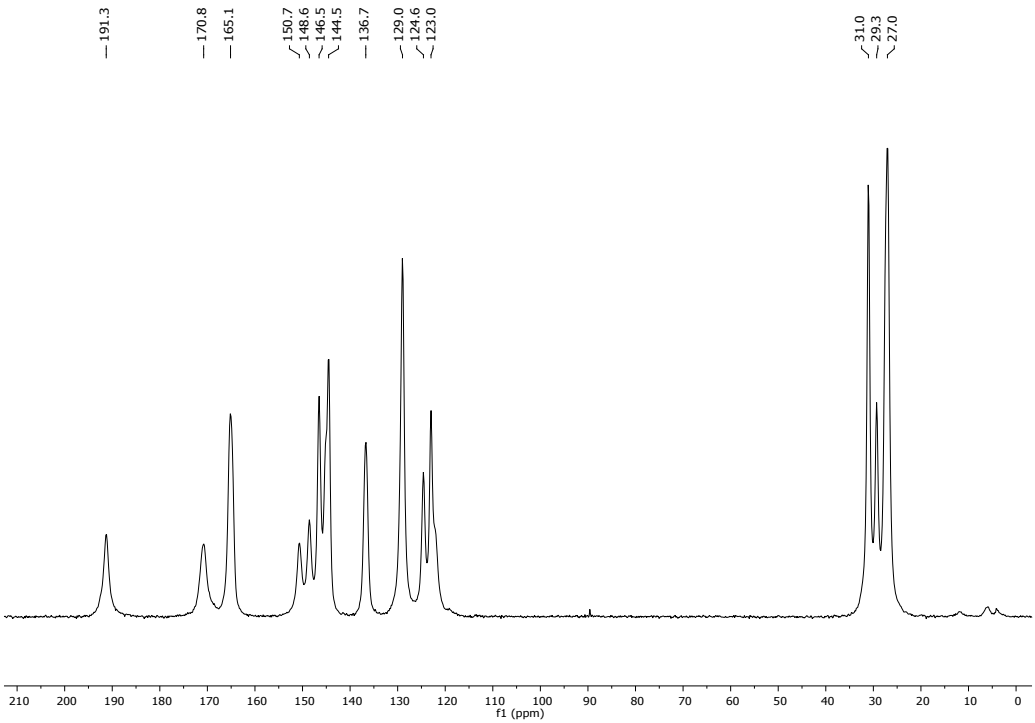



**Figure S12:** Solid state $^{13}$C-NMR spectrum of compound **8** recorded at a rotational frequency of 12 kHz. Sidebands visible between 0 and 15 ppm.

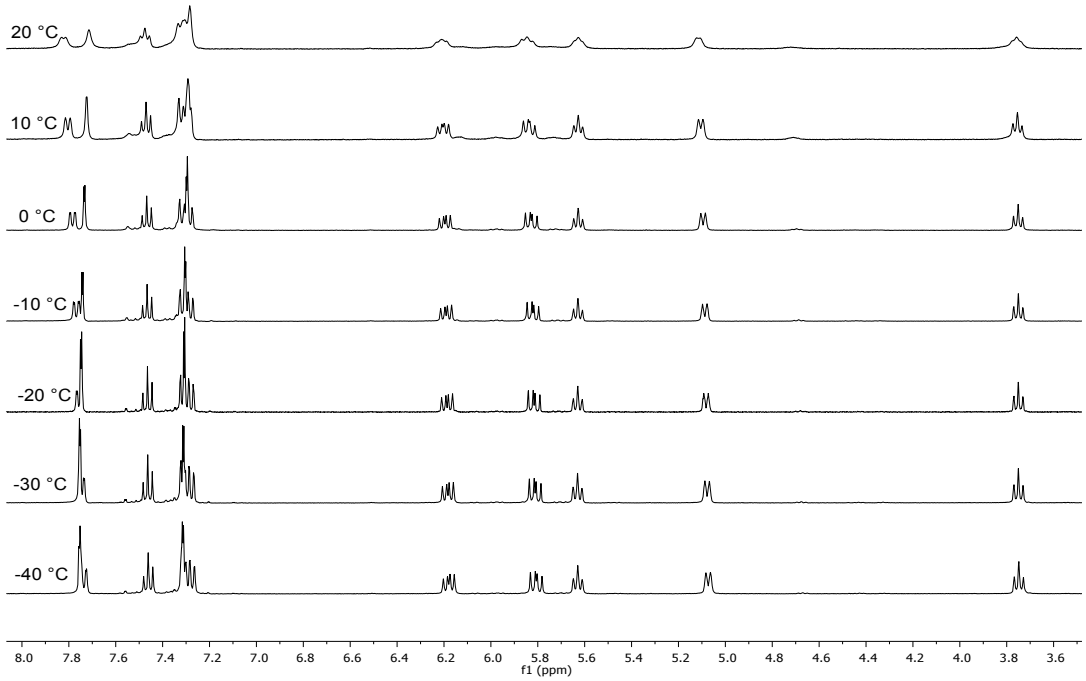



**Figure S13:** Variable temperature $^{1}$H-NMR spectra of compound **3** in deuterated acetonitrile in the 3.5-8 ppm region. Spectra are scaled for a better comparison.

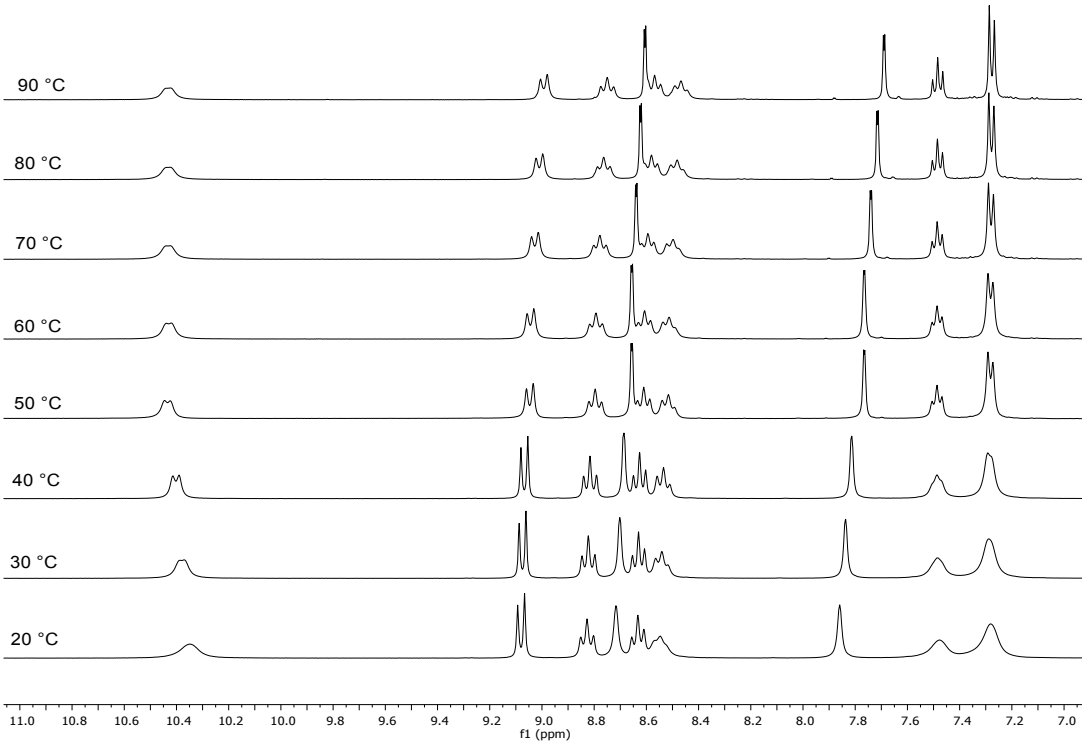



**Figure S3**: Variable temperature $^{1}$H-NMR spectra of compound **8** in deuterated dimethylsulfoxide in the 7-11 ppm region.

## *1.4 Additional Information*

As a by-product of the synthesis of **4** from **1** we could also isolate and characterise complex **3** in which the allyl binding mode of the seven-membered ring is maintained (see Figure S15). This means that besides the desired rearrangement upon intramolecular coordination of the NHC there is a competing dimerisation caused by intermolecular coordination. Furthermore we observed that **3** can slowly be converted to **2** by heating in acetonitrile solution, but as this is accompanied by significant decomposition it is not synthetically beneficial.

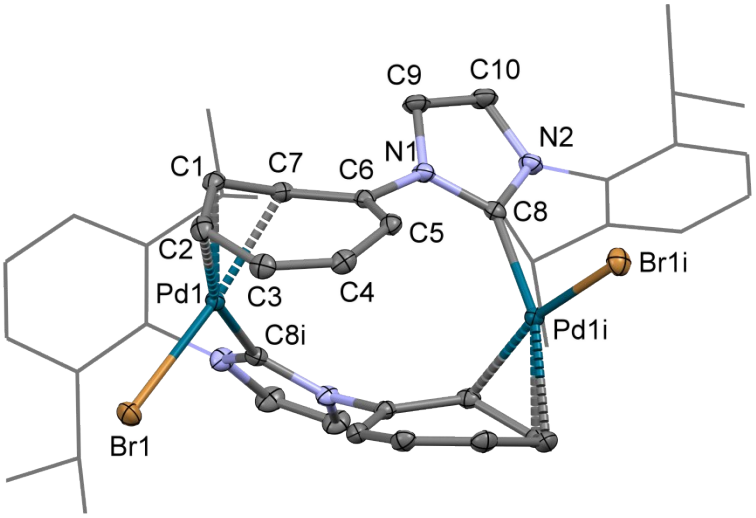
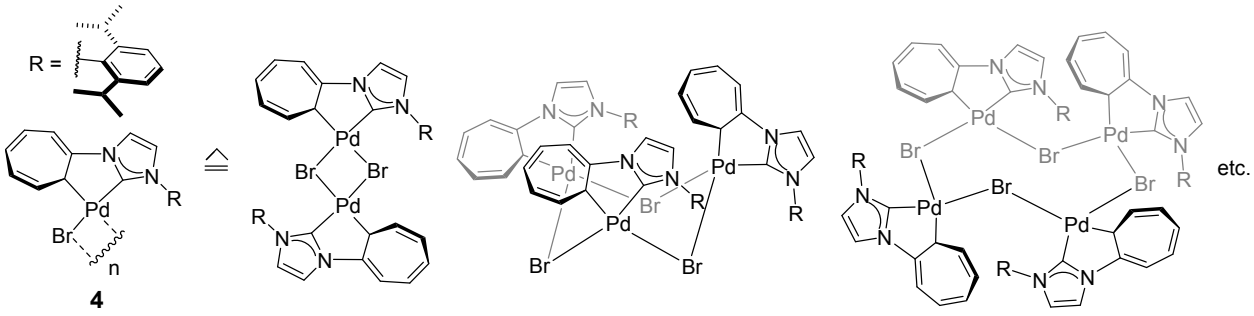



**Figure S15**: Molecular structures of **3** in the solid state with ellipsoids at the 50% probability level. DiPP-groups are simplified as wireframes and hydrogen atoms as well as co-crystallised solvent molecules are omitted for clarity. Selected distances (Å) and angles (°): Pd1—Br1 2.5507(5), Pd1—C1 2.1120(16), Pd1—C2 2.2213(15), Pd1—C7 2.1347(15), Pd1—C8i 2.0559(14), Br1—Pd1—C8i 99.32(4).




**Scheme S1**: Lewis structure representation of possible oligomers of **4** in the solid state.

# 2. Computational Details

## *2.1 Methods*

All quantum chemical calculations were performed using the Gaussian09 software package.[2] The density functional ωB97xD[3] as well as the semi-empirical method PM6[4], the solvent model SMD[5] and the basis sets 6-31G*[6] [7], 6-31+G*[6] [7] [8], LANL2DZ[9] (incl. ECP[9] for metals) were employed as implemented in this software.

All compounds were pre-optimised on the PM6 level of theory if no similar structure optimised on a higher level was available. DFT calculations used the ωB97X-D functional with a double-zeta basis set (6-31G* for non-metals, 6-31+G* (with LANL2DZ-ECP) for Br, LANL2DZ (with ECP) for metals). Starting geometries for the optimisation of transition states were obtained by scans of distances or angles with the same basis set. Calculations of vibrational frequencies were used to determine the nature of stationary points and to evaluate thermodynamic properties as enthalpies and Gibbs free energies. Gibbs free energies were corrected for low vibrations by replacing the entropy contributions of all vibrations lower than 50 $cm^{-1}$ by the contribution of a vibration of 50 $cm^{-1}$ which is 4.82 $\frac{cal}{K \cdot mol}$ in order to account for the inaccuracy of the harmonic oscillator model in case of low energy vibrations.[10] [11] For calculations involving a continuum solvent model the optimisation and frequency calculation were both performed using the solvent model as recommended by Truhlar and Cramer.[11] All reaction data which involve a solvent model are converted to the standard concentration of 1 mol/L for all compounds if not stated otherwise. Pictures of computationally obtained structures were created with CylView (colour code: C, grey; H, white; N, blue; Br, red-brown; Pd, turquoise).[12]

## *2.2 Results*

For the computational modelling of the allyl-to-alkyl rearrangement we employed the DiPP-derivative used in our experimental studies as well as the respective methyl-derivative to check the influence of the steric demand of the NHC-sidearm. The calculations were performed both for an acetonitrile solution using an implicit solvent model and for the gas phase. We started directly after the deprotonation of **1** which produces a free NHC as sidearm of complex $\mathbf{1}_{\mathbf{NHC}}$. The *β*-position represents the minimum both for **1** and for $\mathbf{1}_{\mathbf{NHC}}$ and therefore was chosen as starting point.[1] We also assume that the two bromide ligands remain attached to Pd during the whole course of the rearrangement. We have tried several other species in which one bromide or both are either expelled or replaced by acetonitrile, but the thermodynamic barrier alone for such a substitution was higher than the kinetic barriers of the modelled reaction pathway, so this assumption seems valid and in any way the ancillary ligands cannot be expected to have too great of an influence on a rearrangement of the cycloheptatrienide ring. The results of the computational study are compiled in Table S1 and graphically illustrated for the DiPP-derivative in acetonitrile solution in Figure S16. The half-life of the free NHC compound was estimated according to the Eyring equation for the simplified model of a one-step first order reaction that uses the difference of **TS α-alkyl** to $\mathbf{1}_{\mathbf{NHC}}$**-β** as free energy of activation:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\neq}}{R T}} \qquad T_{\frac{1}{2}} = \frac{ln\, 2}{k}$$

**Table S1**: Calculated Gibbs free energies of stationary points in the allyl-to-alkyl rearrangement from $\mathbf{1}_{\mathbf{NHC}}$ to $\mathbf{2}_{\mathbf{Br}}$ for the methyl- and DiPP-derivative. All data are in kcal/mol and relative to respective β-isomer.

| G_rel. [kcal/mol] | R=Me, gas phase | R=Me, in MeCN | R=DiPP, gas phase | R=DiPP, in MeCN |
|---|---|---|---|---|
| $\mathbf{1}_{\mathbf{NHC}}$**-γ** | 0.41 | 1.38 | 3.55 | 1.90 |
| $\mathbf{1}_{\mathbf{NHC}}$**-β** | 0.0 | 0.0 | 0.0 | 0.0 |
| **TS β-α** | 4.58 | 4.39 | 4.97 | 3.93 |
| $\mathbf{1}_{\mathbf{NHC}}$**-α** | 0.38 | 2.69 | 2.83 | 3.13 |
| **TS NHC-rot** | - | 5.05 | - | 4.97 |
| $\mathbf{1}_{\mathbf{NHC}}$**-α**$_{\mathbf{rot}}$ | - | 3.98 | - | 4.36 |
| **TS α-alkyl** | 12.80 | 7.41 | 15.08 | 7.26 |
| $\mathbf{2}_{\mathbf{Br}}$ | -11.28 | -7.76 | -14.44 | -13.84 |

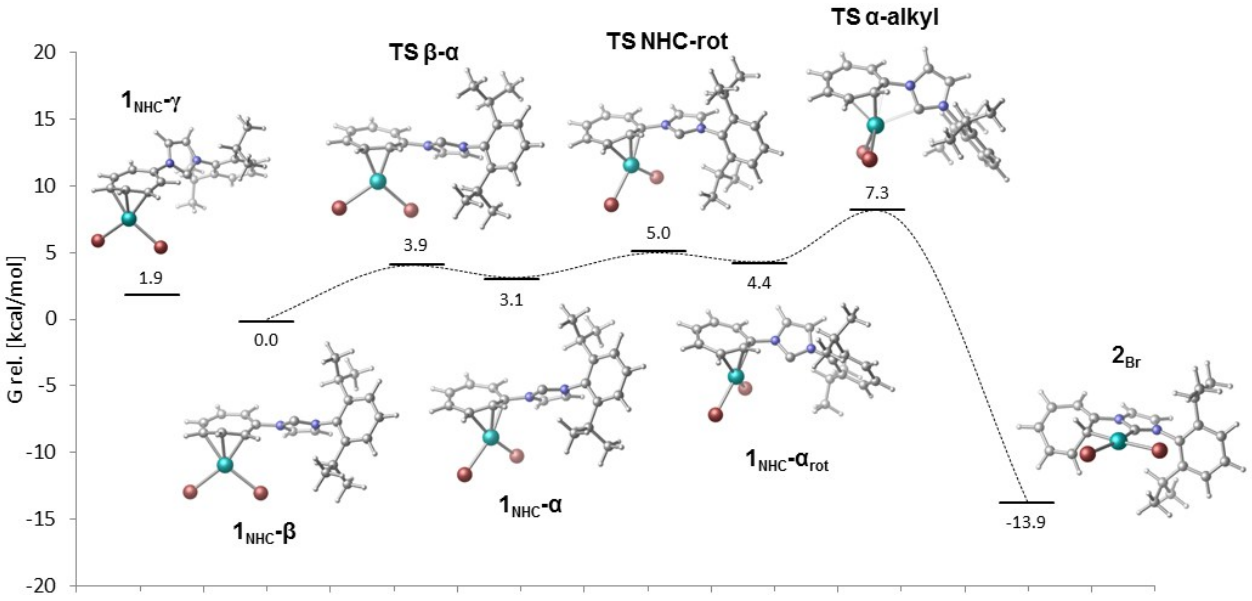



**Figure S16**: Gibbs free energy profile for the rearrangement step of the reaction from **1** to **2a** in acetonitrile. All data are relative to the *β*-isomer.

It can be seen that the *γ*-isomer $\mathbf{1_{NHC}}$-***γ*** is thermodynamically unfavourable in comparison to $\mathbf{1_{NHC}}$-**β**, so the unproductive migration of Pd to the *γ*-position will be ignored here. In addition to the discussion in the main article the detailed profile in Figure S16 shows another transition state **TS NHC-rot** during the rotation of the NHC towards the Pd centre due to steric effects when the cycloheptatrienide ring and the NHC are coplanar. Correspondingly there is a local minimum $\mathbf{1_{NHC}}$-$\mathbf{\alpha_{rot}}$ for the *α*-isomer in which the NHC is already oriented roughly towards Pd. Interestingly, this transition state and local minimum were not found in any of the gas phase calculations. While there are no significant differences between the Me- and DiPP-derivative (except for the Gibbs free energy of the product), the activation barrier for the final reaction step is a lot higher for the gas phase reaction than for the solution model (though still small in absolute terms). Because of the limitations of gas phase calculation and the observed differences to the studies in solution, the solution data must of course be seen as the more reliable model and in the light of the very similar results for both R-groups, the results for the DiPP-derivative in MeCN – which are also closest to the experiment – can be seen as representative and were therefore chosen for the main article. As mentioned there, all barriers are very small, even the final barrier for the actual rearrangement (7.3 kcal/mol relative to $\mathbf{1_{NHC}}$-**β**), so neglecting the minor barriers for the half-life calculation seems valid. The barrier of 7.3 kcal/mol results in a half-life of 25 ns for the free NHC sidearm, before it coordinates to Pd. This value can also serve as estimation for the lifetime of free NHCs in other syntheses of Pd-NHC complexes.

## *2.3 Data*

### 2.3.1 Rearrangement – beta-isomer, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | 0.731184 | 1.378895 | 2.620736 |
| Pd | 1.116369 | -0.045846 | 0.363148 |
| C | 0.488031 | 1.536257 | 1.573027 |
| Br | 3.642989 | -0.397541 | -0.202314 |
| Br | -0.071346 | -2.265264 | -0.245 |
| C | 1.476251 | 2.084472 | 0.721004 |
| H | 2.446614 | 2.256798 | 1.177695 |
| C | -0.686875 | 0.921456 | 1.056479 |
| H | -1.254767 | 0.309654 | 1.750095 |
| C | 1.25723 | 2.796343 | -0.525959 |
| C | -1.471673 | 1.361522 | -0.084717 |
| C | -3.647589 | 0.628174 | 0.806777 |
| H | 2.143578 | 3.288312 | -0.917596 |
| C | 0.115975 | 2.91545 | -1.249169 |
| N | -2.7254 | 0.693849 | -0.204553 |
| C | -1.149422 | 2.267996 | -1.043225 |
| N | -4.627008 | -0.12048 | 0.229011 |
| H | 0.171695 | 3.535979 | -2.140983 |
| C | -3.109397 | -0.001007 | -1.344144 |
| H | -1.919929 | 2.477453 | -1.780969 |
| C | -4.325339 | -0.517352 | -1.069524 |
| H | -2.453995 | -0.115964 | -2.192606 |
| H | -4.972268 | -1.151205 | -1.656584 |
| C | -5.839211 | -0.486841 | 0.923845 |
| H | -5.923442 | -1.575506 | 1.011487 |
| H | -5.787083 | -0.047437 | 1.920295 |
| H | -6.723149 | -0.102308 | 0.40202 |

- N_imag: 0
- E_HF [Hartree]: -688.235945548
- G (corrected) [kcal/mol]: -431778.0915530105

### 2.3.2 Rearrangement – beta-isomer, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | 0.626206 | 1.363899 | 2.639919 |
| Pd | 1.127848 | -0.01805 | 0.363755 |
| C | 0.397496 | 1.526592 | 1.589833 |
| Br | 3.703246 | -0.329699 | -0.207651 |
| Br | 0.089447 | -2.334452 | -0.296394 |
| C | 1.365451 | 2.155328 | 0.775066 |
| H | 2.308278 | 2.381883 | 1.264914 |
| C | -0.732355 | 0.863762 | 1.037522 |
| H | -1.266863 | 0.209757 | 1.718095 |
| C | 1.139855 | 2.86677 | -0.464245 |
| C | -1.540337 | 1.30505 | -0.086585 |
| C | -3.609628 | 0.370203 | 0.869724 |
| H | 1.997811 | 3.429109 | -0.823129 |
| C | -6.9E-4 | 2.944855 | -1.201423 |
| N | -2.791586 | 0.634603 | -0.200625 |
| C | -1.241572 | 2.253353 | -1.017623 |
| N | -4.668889 | -0.229816 | 0.275712 |
| H | 0.029959 | 3.598105 | -2.069991 |
| C | -3.336637 | 0.208535 | -1.407936 |
| H | -2.017742 | 2.485029 | -1.741537 |
| C | -4.529811 | -0.343844 | -1.100967 |
| H | -2.820113 | 0.307907 | -2.350056 |

| | | | |
|---|---|---|---|
| H | -5.276297 | -0.813036 | -1.724522 |
| C | -5.841312 | -0.697181 | 0.994408 |
| H | -5.977356 | -1.771167 | 0.839709 |
| H | -5.694192 | -0.499678 | 2.056409 |
| H | -6.734404 | -0.170264 | 0.646784 |

- N_imag: 0
- E_HF [Hartree]: -688.340858261
- G (corrected) [kcal/mol]: -431843.9938557195

### 2.3.3 Rearrangement – gamma-isomer, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| Pd | -1.458768 | -0.050617 | -0.384702 |
| C | 0.003463 | 0.269676 | -1.956905 |
| C | -0.766282 | -0.905165 | -2.16347 |
| C | 1.312495 | 0.380037 | -1.342918 |
| H | -0.256757 | 1.114341 | -2.588547 |
| C | 1.999443 | -0.535957 | -0.618322 |
| C | 1.577149 | -1.86293 | -0.238867 |
| C | -0.774227 | -1.953317 | -1.207979 |
| C | 0.370522 | -2.437111 | -0.449944 |
| H | 1.775847 | 1.354449 | -1.467348 |
| H | 0.209568 | -3.402269 | 0.023346 |
| H | 2.308836 | -2.415604 | 0.341469 |
| H | -1.521971 | -0.901248 | -2.944781 |
| H | -1.585221 | -2.670101 | -1.300952 |
| N | 3.244143 | -0.11754 | -0.04795 |
| C | 4.376262 | -0.889084 | -0.052454 |
| C | 3.418788 | 1.110845 | 0.580316 |
| C | 4.707227 | 1.139229 | 0.98402 |
| H | 2.610119 | 1.814794 | 0.711073 |
| H | 5.261727 | 1.89239 | 1.523405 |
| N | 5.260779 | -0.073294 | 0.589823 |
| Br | -3.047198 | -1.21039 | 1.306917 |
| Br | -1.504064 | 2.50816 | 0.139012 |
| C | 6.629729 | -0.457393 | 0.846251 |
| H | 7.328195 | 0.256032 | 0.394632 |
| H | 6.82601 | -0.51165 | 1.92304 |
| H | 6.779316 | -1.44184 | 0.401973 |

- N_imag: 0
- E_HF [Hartree]: -688.235224270
- G (corrected) [kcal/mol]: -431777.6786517595

### 2.3.4 Rearrangement – gamma-isomer, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| Pd | 1.423473 | 0.058394 | -0.404696 |
| C | -0.142324 | 0.019444 | -1.938261 |
| C | 0.698246 | 1.158635 | -2.041667 |
| C | -1.452854 | -0.057307 | -1.330547 |
| H | 0.035166 | -0.751499 | -2.683103 |
| C | -2.051706 | 0.814037 | -0.476683 |
| C | -1.484733 | 2.002452 | 0.107717 |
| C | 0.808989 | 2.090248 | -0.98243 |
| C | -0.24252 | 2.51557 | -0.07944 |
| H | -2.02988 | -0.934455 | -1.605139 |
| H | 0.016015 | 3.378989 | 0.528065 |
| H | -2.114497 | 2.509334 | 0.833931 |
| H | 1.411265 | 1.20986 | -2.860456 |
| H | 1.647668 | 2.77759 | -1.049365 |

| | | | |
|---|---|---|---|
| N | -3.36933 | 0.489165 | -0.027746 |
| C | -3.738448 | -0.759132 | 0.405888 |
| C | -4.416047 | 1.405045 | 0.017329 |
| C | -5.484813 | 0.722152 | 0.482431 |
| H | -4.310474 | 2.431678 | -0.29958 |
| H | -6.501943 | 1.034734 | 0.666805 |
| N | -5.049142 | -0.57531 | 0.70762 |
| Br | 3.22041 | 0.901777 | 1.343731 |
| Br | 1.471271 | -2.55375 | -0.089069 |
| C | -5.914557 | -1.620232 | 1.226144 |
| H | -6.313641 | -1.333219 | 2.203075 |
| H | -6.7458 | -1.798702 | 0.537961 |
| H | -5.328554 | -2.533828 | 1.328659 |

- N_imag: 0
- E_HF [Hartree]: -688.337893842
- G (corrected) [kcal/mol]: -431842.6108247815

### 2.3.5 Rearrangement – TS beta-alpha, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.361633 | 1.705205 | -2.038189 |
| Pd | -1.009615 | -0.140432 | -0.17847 |
| C | -0.892134 | 1.724204 | -1.058557 |
| Br | 0.175559 | -2.152752 | 0.988248 |
| Br | -3.581885 | -0.499549 | -0.638492 |
| C | -1.593633 | 2.414512 | -0.031062 |
| H | -2.649598 | 2.556837 | -0.245986 |
| C | 0.450299 | 1.201708 | -0.961892 |
| H | 0.875015 | 0.752482 | -1.855304 |
| C | -1.136021 | 2.934612 | 1.17055 |
| C | 1.35568 | 1.353618 | 0.102446 |
| C | 3.309055 | 0.649304 | -1.21482 |
| H | -1.878512 | 3.449453 | 1.774817 |
| C | 0.15291 | 2.853949 | 1.714978 |
| N | 2.58263 | 0.653068 | -0.049585 |
| C | 1.248817 | 2.146363 | 1.260625 |
| N | 4.365357 | -0.132185 | -0.870449 |
| H | 0.300345 | 3.38488 | 2.653507 |
| C | 3.162544 | -0.105986 | 0.961261 |
| H | 2.143347 | 2.180365 | 1.876196 |
| C | 4.301357 | -0.602931 | 0.43792 |
| H | 2.665558 | -0.290066 | 1.900366 |
| H | 5.034673 | -1.275473 | 0.855945 |
| C | 5.437745 | -0.44568 | -1.786444 |
| H | 5.513288 | -1.527743 | -1.937825 |
| H | 5.20935 | 0.037595 | -2.736596 |
| H | 6.396225 | -0.071299 | -1.408575 |

- N_imag: 1
- E_HF [Hartree]: -688.228840163
- G (corrected) [kcal/mol]: -431773.51449871756

### 2.3.6 Rearrangement – TS beta-alpha, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | 1.366318 | 1.728903 | 2.128019 |
| Pd | 0.927772 | -0.108028 | 0.237952 |
| C | 0.928356 | 1.794978 | 1.134984 |
| Br | -0.185583 | -2.265096 | -0.840733 |
| Br | 3.517074 | -0.638898 | 0.422458 |
| C | 1.613238 | 2.679831 | 0.238062 |

| | | | |
|---|---|---|---|
| H | 2.615935 | 2.949221 | 0.560669 |
| C | -0.423709 | 1.313871 | 1.038899 |
| H | -0.874434 | 0.90725 | 1.938085 |
| C | 1.188173 | 3.21976 | -0.947062 |
| C | -1.24601 | 1.358788 | -0.099483 |
| C | -3.182662 | 0.513154 | 1.164456 |
| H | 1.877658 | 3.890394 | -1.452421 |
| C | -0.042545 | 2.986481 | -1.610274 |
| N | -2.480772 | 0.666325 | -0.009922 |
| C | -1.079037 | 2.156065 | -1.271487 |
| N | -4.277644 | -0.162387 | 0.75494 |
| H | -0.17848 | 3.531224 | -2.541506 |
| C | -3.13414 | 0.091316 | -1.098441 |
| H | -1.913569 | 2.13626 | -1.964865 |
| C | -4.275669 | -0.43165 | -0.608727 |
| H | -2.715255 | 0.059811 | -2.091132 |
| H | -5.070508 | -0.977652 | -1.094401 |
| C | -5.370402 | -0.549616 | 1.630704 |
| H | -5.544354 | -1.626482 | 1.55733 |
| H | -5.102019 | -0.296208 | 2.656312 |
| H | -6.285641 | -0.019072 | 1.352814 |

- N_imag: 1
- E_HF [Hartree]: -688.334719657
- G (corrected) [kcal/mol]: -431839.60191672895

### 2.3.7 Rearrangement – alpha-isomer, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.408172 | 2.229806 | -1.625937 |
| Pd | -0.766266 | -0.024349 | -0.164726 |
| C | -0.881862 | 2.074995 | -0.688529 |
| Br | -3.148812 | -0.367891 | -1.180499 |
| Br | -0.375075 | -2.226959 | 1.150593 |
| C | -1.47313 | 2.754812 | 0.452273 |
| H | -2.458422 | 3.168313 | 0.25475 |
| C | 0.432015 | 1.572503 | -0.8215 |
| H | 0.859483 | 1.435781 | -1.809229 |
| C | -0.967331 | 2.923207 | 1.697915 |
| C | 1.13542 | 1.013514 | 0.281725 |
| C | 3.235955 | 0.841896 | -0.997228 |
| H | -1.571608 | 3.501335 | 2.393641 |
| C | 0.244029 | 2.368886 | 2.241988 |
| N | 2.362541 | 0.347274 | -0.066351 |
| C | 1.118604 | 1.522858 | 1.649491 |
| N | 4.243444 | -0.071605 | -0.937288 |
| H | 0.449235 | 2.617221 | 3.280624 |
| C | 2.810752 | -0.813845 | 0.548853 |
| H | 1.944383 | 1.159085 | 2.255779 |
| C | 4.010751 | -1.081612 | -0.009174 |
| H | 2.193036 | -1.364638 | 1.244896 |
| H | 4.694428 | -1.901875 | 0.149533 |
| C | 5.417503 | 0.00197 | -1.774648 |
| H | 6.329724 | 0.039773 | -1.168057 |
| H | 5.474345 | -0.863126 | -2.445053 |
| H | 5.33973 | 0.913298 | -2.368398 |

- N_imag: 0
- E_HF [Hartree]: -688.235062460
- G (corrected) [kcal/mol]: -431777.706889687

### 2.3.8 Rearrangement – alpha-isomer, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.446947 | 2.145176 | -1.792271 |
| Pd | -0.758433 | -0.011676 | -0.156577 |
| C | -0.928441 | 2.064287 | -0.841145 |
| Br | -3.167687 | -0.613836 | -1.108413 |
| Br | -0.253958 | -2.136523 | 1.296591 |
| C | -1.539761 | 2.815225 | 0.236786 |
| H | -2.521827 | 3.215539 | -5.67E-4 |
| C | 0.390475 | 1.569237 | -0.938356 |
| H | 0.796495 | 1.358245 | -1.921385 |
| C | -1.036956 | 3.094523 | 1.467133 |
| C | 1.127695 | 1.137802 | 0.198844 |
| C | 3.101581 | 0.639497 | -1.209854 |
| H | -1.642972 | 3.726824 | 2.111199 |
| C | 0.191878 | 2.623882 | 2.040693 |
| N | 2.348244 | 0.43666 | -0.082654 |
| C | 1.098533 | 1.761978 | 1.515154 |
| N | 4.149319 | -0.194017 | -1.006284 |
| H | 0.406766 | 2.982706 | 3.043884 |
| C | 2.921499 | -0.485958 | 0.785672 |
| H | 1.947301 | 1.508657 | 2.144721 |
| C | 4.06594 | -0.8885 | 0.193093 |
| H | 2.444626 | -0.798344 | 1.701198 |
| H | 4.813896 | -1.60171 | 0.505579 |
| C | 5.242637 | -0.367663 | -1.946594 |
| H | 6.200986 | -0.217198 | -1.442176 |
| H | 5.218619 | -1.373288 | -2.376546 |
| H | 5.135104 | 0.36871 | -2.743314 |

- N_imag: 0
- E_HF [Hartree]: -688.336158362
- G (corrected) [kcal/mol]: -431841.3043500025

### 2.3.9 Rearrangement – TS NHC-rotation, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.630395 | 1.667001 | -2.141022 |
| Pd | -0.742396 | -0.069916 | -0.164414 |
| C | -1.138481 | 1.811919 | -1.182798 |
| Br | -3.134223 | -1.041559 | -0.758113 |
| Br | 0.195753 | -1.868925 | 1.540966 |
| C | -1.852388 | 2.693553 | -0.281196 |
| H | -2.855202 | 2.955384 | -0.608479 |
| C | 0.24135 | 1.493825 | -1.190452 |
| H | 0.695095 | 1.183918 | -2.124427 |
| C | -1.414343 | 3.233503 | 0.884063 |
| C | 1.009383 | 1.33625 | -0.004523 |
| C | 2.622005 | 0.004872 | -1.307744 |
| H | -2.086954 | 3.915861 | 1.397409 |
| C | -0.180715 | 2.953879 | 1.56054 |
| N | 2.297741 | 0.724607 | -0.179872 |
| C | 0.827139 | 2.112115 | 1.211611 |
| N | 3.880756 | -0.405503 | -1.048561 |
| H | -0.057447 | 3.449596 | 2.520149 |
| C | 3.340393 | 0.726826 | 0.746374 |
| H | 1.610619 | 2.01515 | 1.951152 |
| C | 4.341547 | 0.015248 | 0.189476 |
| H | 3.320138 | 1.224244 | 1.700619 |
| H | 5.327938 | -0.22246 | 0.559012 |
| C | 4.673137 | -1.223638 | -1.950359 |
| H | 5.613184 | -0.718134 | -2.188002 |

| | | | |
|---|---|---|---|
| H | 4.891846 | -2.190035 | -1.487425 |
| H | 4.104213 | -1.381301 | -2.866739 |

- N_imag: 1
- E_HF [Hartree]: -688.332897947
- G (corrected) [kcal/mol]: -431838.940521716

### 2.3.10 Rearrangement – alpha-intermediate, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.591044 | 1.692954 | -2.172046 |
| Pd | -0.720413 | -0.058556 | -0.167051 |
| C | -1.069516 | 1.832032 | -1.229039 |
| Br | -3.088142 | -1.019613 | -0.877767 |
| Br | -0.022148 | -1.706694 | 1.800196 |
| C | -1.715677 | 2.759498 | -0.321795 |
| H | -2.705802 | 3.078145 | -0.637515 |
| C | 0.289712 | 1.449877 | -1.251809 |
| H | 0.723459 | 1.11706 | -2.189256 |
| C | -1.231426 | 3.288506 | 0.832063 |
| C | 1.057394 | 1.269341 | -0.065076 |
| C | 2.494267 | -0.443234 | -1.106209 |
| H | -1.862159 | 4.01443 | 1.339223 |
| C | -0.016437 | 2.944983 | 1.51358 |
| N | 2.324111 | 0.62429 | -0.259521 |
| C | 0.934684 | 2.042834 | 1.157876 |
| N | 3.820354 | -0.688353 | -1.00467 |
| H | 0.126728 | 3.424059 | 2.47867 |
| C | 3.521821 | 1.019314 | 0.334878 |
| H | 1.710144 | 1.855966 | 1.892971 |
| C | 4.467562 | 0.181594 | -0.139776 |
| H | 3.613752 | 1.861955 | 1.000991 |
| H | 5.528849 | 0.130035 | 0.052689 |
| C | 4.504909 | -1.762581 | -1.703229 |
| H | 5.32433 | -1.358318 | -2.303943 |
| H | 4.907056 | -2.484092 | -0.986246 |
| H | 3.788806 | -2.262386 | -2.355661 |

- N_imag: 0
- E_HF [Hartree]: -688.333809681
- G (corrected) [kcal/mol]: -431840.011052923

### 2.3.11 Rearrangement – TS allyl-alkyl, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.591044 | 1.692954 | -2.172046 |
| Pd | -0.720413 | -0.058556 | -0.167051 |
| C | -1.069516 | 1.832032 | -1.229039 |
| Br | -3.088142 | -1.019613 | -0.877767 |
| Br | -0.022148 | -1.706694 | 1.800196 |
| C | -1.715677 | 2.759498 | -0.321795 |
| H | -2.705802 | 3.078145 | -0.637515 |
| C | 0.289712 | 1.449877 | -1.251809 |
| H | 0.723459 | 1.11706 | -2.189256 |
| C | -1.231426 | 3.288506 | 0.832063 |
| C | 1.057394 | 1.269341 | -0.065076 |
| C | 2.494267 | -0.443234 | -1.106209 |
| H | -1.862159 | 4.01443 | 1.339223 |
| C | -0.016437 | 2.944983 | 1.51358 |
| N | 2.324111 | 0.62429 | -0.259521 |
| C | 0.934684 | 2.042834 | 1.157876 |
| N | 3.820354 | -0.688353 | -1.00467 |

| | | | |
|---|---|---|---|
| H | 0.126728 | 3.424059 | 2.47867 |
| C | 3.521821 | 1.019314 | 0.334878 |
| H | 1.710144 | 1.855966 | 1.892971 |
| C | 4.467562 | 0.181594 | -0.139776 |
| H | 3.613752 | 1.861955 | 1.000991 |
| H | 5.528849 | 0.130035 | 0.052689 |
| C | 4.504909 | -1.762581 | -1.703229 |
| H | 5.32433 | -1.358318 | -2.303943 |
| H | 4.907056 | -2.484092 | -0.986246 |
| H | 3.788806 | -2.262386 | -2.355661 |

- N_imag: 1
- E_HF [Hartree]: -688.212757372
- G (corrected) [kcal/mol]: -431765.2903592105

### 2.3.12 Rearrangement – TS allyl-alkyl, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.551193 | 1.062595 | -2.327837 |
| Pd | -0.430419 | -0.044465 | 0.006873 |
| C | -0.818345 | 1.531732 | -1.677748 |
| Br | -1.371809 | 0.068669 | 2.570653 |
| Br | -2.273697 | -1.738386 | -1.425366 |
| C | -1.165961 | 2.78598 | -1.164115 |
| H | -2.194067 | 3.086573 | -1.3519 |
| C | 0.430798 | 0.838769 | -1.600226 |
| H | 0.680654 | 0.120737 | -2.377313 |
| C | -0.361639 | 3.737535 | -0.529456 |
| C | 1.477025 | 1.220612 | -0.678451 |
| C | 1.905469 | -1.013736 | 0.014967 |
| H | -0.834031 | 4.697007 | -0.334712 |
| C | 0.946297 | 3.599928 | -0.083324 |
| N | 2.410324 | 0.165427 | -0.449555 |
| C | 1.739126 | 2.450359 | -0.082832 |
| N | 3.012941 | -1.763857 | 0.197378 |
| H | 1.381156 | 4.466104 | 0.40816 |
| C | 3.793257 | 0.162134 | -0.537234 |
| H | 2.667179 | 2.504452 | 0.481359 |
| C | 4.172575 | -1.072578 | -0.132796 |
| H | 4.36346 | 1.009044 | -0.886764 |
| H | 5.150721 | -1.522971 | -0.054702 |
| C | 3.008428 | -3.129655 | 0.695192 |
| H | 3.601137 | -3.196066 | 1.611135 |
| H | 1.977601 | -3.413368 | 0.908783 |
| H | 3.424349 | -3.806086 | -0.056051 |

- N_imag: 1
- E_HF [Hartree]: -688.327625400
- G (corrected) [kcal/mol]: -431836.586106072

### 2.3.13 Rearrangement – alkyl form, Me-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -1.892639 | -2.197309 | -1.274329 |
| Pd | 0.442186 | -0.251663 | -0.167398 |
| C | -2.379163 | -1.409037 | -0.707679 |
| Br | 2.948614 | -0.115067 | 0.68745 |
| Br | 0.564938 | -2.81534 | -0.247642 |
| C | -3.550173 | -1.740711 | -0.131322 |
| H | -3.881741 | -2.76502 | -0.291653 |
| C | -1.600741 | -0.147239 | -0.732323 |
| H | -1.429349 | 0.134525 | -1.782747 |

| | | | |
|---|---|---|---|
| C | -4.456082 | -0.933574 | 0.675452 |
| C | -2.140822 | 1.041621 | -0.003387 |
| C | 0.120135 | 1.73575 | -0.225537 |
| H | -5.350848 | -1.452119 | 1.018177 |
| C | -4.335735 | 0.357193 | 1.036578 |
| N | -1.189114 | 2.094098 | -0.122454 |
| C | -3.239604 | 1.266234 | 0.738412 |
| N | 0.778169 | 2.91141 | -0.352559 |
| H | -5.12872 | 0.784378 | 1.647592 |
| C | -1.352771 | 3.463038 | -0.172242 |
| H | -3.304101 | 2.2393 | 1.223023 |
| C | -0.109598 | 3.976419 | -0.320436 |
| H | -2.318753 | 3.938337 | -0.122957 |
| H | 0.226828 | 4.99676 | -0.420655 |
| C | 2.205319 | 3.072698 | -0.574079 |
| H | 2.613415 | 3.764209 | 0.168234 |
| H | 2.684965 | 2.09842 | -0.452256 |
| H | 2.378065 | 3.46637 | -1.5809 |

- N_imag: 0
- E_HF [Hartree]: -688.256317368
- G (corrected) [kcal/mol]: -431789.3678987255

### 2.3.14 Rearrangement – alkyl form, Me-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.04826 | -1.980631 | -1.543231 |
| Pd | 0.419392 | -0.251291 | -0.196458 |
| C | -2.437239 | -1.251908 | -0.837668 |
| Br | 2.954331 | -0.253693 | 0.743099 |
| Br | 0.411716 | -2.85184 | -0.262475 |
| C | -3.583039 | -1.594575 | -0.21571 |
| H | -3.992415 | -2.568712 | -0.477887 |
| C | -1.602705 | -0.029728 | -0.773634 |
| H | -1.421539 | 0.313691 | -1.80165 |
| C | -4.386009 | -0.847227 | 0.743786 |
| C | -2.081486 | 1.136066 | 0.031809 |
| C | 0.180036 | 1.764144 | -0.251167 |
| H | -5.254657 | -1.378787 | 1.127286 |
| C | -4.204907 | 0.414304 | 1.183577 |
| N | -1.109332 | 2.164431 | -0.098133 |
| C | -3.132941 | 1.336791 | 0.846591 |
| N | 0.877256 | 2.908701 | -0.389521 |
| H | -4.930265 | 0.804766 | 1.893637 |
| C | -1.224524 | 3.540441 | -0.124351 |
| H | -3.176065 | 2.299275 | 1.351847 |
| C | 0.03179 | 4.007103 | -0.314365 |
| H | -2.169433 | 4.051189 | -0.026623 |
| H | 0.406575 | 5.014275 | -0.415589 |
| C | 2.300019 | 3.027261 | -0.66879 |
| H | 2.754382 | 3.712917 | 0.050278 |
| H | 2.756263 | 2.04261 | -0.568505 |
| H | 2.442306 | 3.414503 | -1.681255 |

- N_imag: 0
- E_HF [Hartree]: -688.356272054
- G (corrected) [kcal/mol]: -431851.75426570605

### 2.3.15 Rearrangement – beta-isomer, DiPP-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.30527 | 0.815315 | -2.849736 |

| | | | |
|---|---|---|---|
| Pd | -2.747759 | -0.026768 | -0.33129 |
| C | -2.207385 | 1.276825 | -1.87038 |
| Br | -5.212407 | -0.590883 | 0.273919 |
| Br | -1.304514 | -1.899686 | 0.758091 |
| C | -3.356062 | 1.850923 | -1.267878 |
| H | -4.284256 | 1.730949 | -1.819359 |
| C | -1.027084 | 1.018727 | -1.125362 |
| H | -0.300287 | 0.354851 | -1.58262 |
| C | -3.372317 | 2.922819 | -0.287349 |
| C | -0.467069 | 1.832045 | -0.058121 |
| C | 1.807598 | 0.965683 | -0.424848 |
| H | -4.34806 | 3.378649 | -0.141482 |
| C | -2.347481 | 3.412854 | 0.453197 |
| N | 0.793338 | 1.356491 | 0.40648 |
| C | -1.007584 | 2.908873 | 0.569145 |
| N | 2.712173 | 0.468178 | 0.464718 |
| H | -2.578454 | 4.253315 | 1.103832 |
| C | 1.049375 | 1.08868 | 1.746643 |
| H | -0.373616 | 3.403144 | 1.301261 |
| C | 2.272532 | 0.524417 | 1.786252 |
| C | 3.899413 | -0.226864 | 0.071204 |
| H | 0.313513 | 1.255576 | 2.516473 |
| H | 2.847938 | 0.120868 | 2.604425 |
| C | 5.11745 | 0.466377 | 0.035152 |
| C | 3.789172 | -1.588336 | -0.247508 |
| C | 4.959746 | -2.258772 | -0.610551 |
| H | 4.91099 | -3.313142 | -0.866332 |
| C | 6.259305 | -0.246076 | -0.332029 |
| H | 7.221229 | 0.255831 | -0.373246 |
| C | 6.180584 | -1.598127 | -0.648961 |
| C | 5.154915 | 1.959863 | 0.318077 |
| H | 4.382625 | 2.172837 | 1.065779 |
| C | 2.438676 | -2.284939 | -0.264574 |
| H | 1.744731 | -1.728768 | 0.37261 |
| H | 7.080348 | -2.138712 | -0.931609 |
| C | 2.48048 | -3.716564 | 0.275894 |
| H | 3.017552 | -4.398627 | -0.395823 |
| H | 2.959953 | -3.759974 | 1.26037 |
| H | 1.454973 | -4.085389 | 0.378743 |
| C | 6.490719 | 2.446973 | 0.886951 |
| H | 6.798462 | 1.858228 | 1.758284 |
| H | 7.292452 | 2.396119 | 0.140582 |
| H | 6.402253 | 3.494837 | 1.19474 |
| C | 4.78574 | 2.737941 | -0.955467 |
| H | 4.758549 | 3.81589 | -0.754474 |
| H | 5.529133 | 2.55378 | -1.741085 |
| H | 3.804442 | 2.425447 | -1.326607 |
| C | 1.851429 | -2.2475 | -1.683497 |
| H | 1.812972 | -1.216426 | -2.048717 |
| H | 2.463139 | -2.843147 | -2.374715 |
| H | 0.83235 | -2.64779 | -1.666638 |

- N_imag: 0
- E_HF [Hartree]: -1115.73954539
- G (corrected) [kcal/mol]: -699906.8215909745

### 2.3.16 Rearrangement – beta-isomer, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | 2.259733 | -1.007794 | -2.817071 |
| Pd | 2.889508 | -0.018101 | -0.379006 |
| C | 2.170476 | -1.386513 | -1.802125 |
| Br | 5.448512 | 0.474797 | 0.092928 |

| | | | |
|---|---|---|---|
| Br | 1.693481 | 2.051251 | 0.711232 |
| C | 3.280172 | -2.0432 | -1.223788 |
| H | 4.176748 | -2.066589 | -1.836944 |
| C | 1.057834 | -0.966384 | -1.024871 |
| H | 0.387946 | -0.264904 | -1.510127 |
| C | 3.26084 | -3.005956 | -0.143759 |
| C | 0.442812 | -1.680185 | 0.081069 |
| C | -1.786136 | -0.755657 | -0.410854 |
| H | 4.197538 | -3.537585 | 0.001803 |
| C | 2.227278 | -3.343709 | 0.673067 |
| N | -0.821134 | -1.152942 | 0.47672 |
| C | 0.926526 | -2.750666 | 0.769642 |
| N | -2.774001 | -0.335205 | 0.421561 |
| H | 2.413391 | -4.146625 | 1.381793 |
| C | -1.204596 | -0.982312 | 1.803937 |
| H | 0.269467 | -3.180623 | 1.520752 |
| C | -2.447605 | -0.458422 | 1.767857 |
| C | -4.02272 | 0.200271 | -0.03481 |
| H | -0.555057 | -1.216158 | 2.633088 |
| H | -3.118016 | -0.150773 | 2.555708 |
| C | -5.116978 | -0.665876 | -0.176835 |
| C | -4.107092 | 1.574714 | -0.303972 |
| C | -5.339649 | 2.07812 | -0.727705 |
| H | -5.438337 | 3.138624 | -0.94343 |
| C | -6.329632 | -0.116239 | -0.600011 |
| H | -7.196763 | -0.760788 | -0.716358 |
| C | -6.441724 | 1.242676 | -0.871974 |
| C | -5.013726 | -2.153966 | 0.117658 |
| H | -3.972184 | -2.382652 | 0.360251 |
| C | -2.913654 | 2.504465 | -0.151198 |
| H | -2.049625 | 1.908118 | 0.15522 |
| H | -7.392469 | 1.652777 | -1.200855 |
| C | -3.1613 | 3.551017 | 0.942173 |
| H | -4.004375 | 4.204463 | 0.687418 |
| H | -3.378769 | 3.073736 | 1.904368 |
| H | -2.273523 | 4.181547 | 1.069156 |
| C | -5.866535 | -2.533445 | 1.335113 |
| H | -5.569508 | -1.960511 | 2.220953 |
| H | -6.930416 | -2.343687 | 1.148855 |
| H | -5.74903 | -3.599007 | 1.563821 |
| C | -5.390489 | -2.994361 | -1.108831 |
| H | -5.237457 | -4.059174 | -0.898888 |
| H | -6.442537 | -2.855685 | -1.384178 |
| H | -4.773163 | -2.726417 | -1.973699 |
| C | -2.553559 | 3.170697 | -1.485172 |
| H | -2.362533 | 2.420239 | -2.260606 |
| H | -3.356916 | 3.828625 | -1.837395 |
| H | -1.648583 | 3.778432 | -1.370597 |

- N_imag: 0
- E_HF [Hartree]: -1115.84287386
- G (corrected) [kcal/mol]: -699972.5055203775

### 2.3.17 Rearrangement – gamma-isomer, DiPP-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| Pd | 3.51289 | -0.264093 | -0.29396 |
| C | 2.234572 | -1.77935 | -1.169839 |
| C | 2.969409 | -1.066333 | -2.153535 |
| C | 0.891866 | -1.513137 | -0.690857 |
| H | 2.582455 | -2.787947 | -0.965482 |
| C | 0.107676 | -0.428543 | -0.896034 |
| C | 0.422232 | 0.768655 | -1.639025 |

| | | | |
|---|---|---|---|
| C | 2.846801 | 0.340676 | -2.281443 |
| C | 1.61314 | 1.109721 | -2.181496 |
| H | 0.498812 | -2.285061 | -0.035594 |
| H | 1.683646 | 2.111724 | -2.596607 |
| H | -0.383274 | 1.494649 | -1.685497 |
| H | 3.795773 | -1.569194 | -2.649525 |
| H | 3.636077 | 0.832191 | -2.843129 |
| N | -1.134183 | -0.385655 | -0.182538 |
| C | -2.324987 | -0.030541 | -0.748685 |
| C | -1.231418 | -0.675542 | 1.174998 |
| C | -2.532737 | -0.515055 | 1.495451 |
| H | -0.367052 | -0.927071 | 1.772662 |
| H | -3.056318 | -0.619114 | 2.432975 |
| N | -3.172336 | -0.126731 | 0.319328 |
| Br | 4.85862 | 1.921533 | 0.045305 |
| Br | 3.549923 | -1.556749 | 1.975256 |
| C | -4.571822 | 0.158625 | 0.24627 |
| C | -5.459347 | -0.886002 | -0.049005 |
| C | -5.005303 | 1.47143 | 0.483686 |
| C | -6.821307 | -0.586285 | -0.105421 |
| C | -6.376307 | 1.7241 | 0.416356 |
| C | -7.276163 | 0.705719 | 0.127457 |
| H | -7.536895 | -1.369423 | -0.336387 |
| H | -6.747561 | 2.729441 | 0.59016 |
| H | -8.340272 | 0.92094 | 0.079075 |
| C | -4.001845 | 2.586541 | 0.731957 |
| H | -3.11922 | 2.141766 | 1.203202 |
| C | -3.551069 | 3.183001 | -0.611122 |
| H | -2.784876 | 3.950643 | -0.451977 |
| H | -3.136013 | 2.400035 | -1.253642 |
| H | -4.40103 | 3.646154 | -1.127972 |
| C | -4.522546 | 3.676313 | 1.673866 |
| H | -5.319568 | 4.269941 | 1.210201 |
| H | -4.912338 | 3.251267 | 2.605305 |
| H | -3.710692 | 4.366634 | 1.926035 |
| C | -4.936269 | -2.277238 | -0.369097 |
| H | -3.99082 | -2.407986 | 0.167868 |
| C | -5.875459 | -3.401424 | 0.078416 |
| H | -6.151735 | -3.298405 | 1.133475 |
| H | -6.797471 | -3.425647 | -0.514745 |
| H | -5.381789 | -4.370351 | -0.053183 |
| C | -4.625372 | -2.377839 | -1.871141 |
| H | -5.540137 | -2.237383 | -2.460366 |
| H | -3.899398 | -1.611835 | -2.161645 |
| H | -4.209064 | -3.363399 | -2.110763 |

- N_imag: 0
- E_HF [Hartree]: -1115.73472923
- G (corrected) [kcal/mol]: -699903.8145654504

### 2.3.18 Rearrangement – gamma-isomer, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| Pd | 3.334236 | -0.424137 | 0.031163 |
| C | 2.032574 | -2.079679 | -0.608734 |
| C | 3.129438 | -1.873309 | -1.48344 |
| C | 0.673053 | -1.611775 | -0.770804 |
| H | 2.118826 | -2.944552 | 0.043082 |
| C | 0.193246 | -0.653114 | -1.605464 |
| C | 0.942235 | 0.201084 | -2.491053 |
| C | 3.316303 | -0.641609 | -2.156223 |
| C | 2.284608 | 0.228768 | -2.686006 |
| H | -0.055507 | -2.10176 | -0.133106 |

| | | | |
|---|---|---|---|
| H | 2.657193 | 1.01372 | -3.338885 |
| H | 0.35968 | 0.95456 | -3.014254 |
| H | 3.939554 | -2.597918 | -1.483551 |
| H | 4.297177 | -0.495766 | -2.600136 |
| N | -1.210155 | -0.381749 | -1.548787 |
| C | -1.899509 | -0.226539 | -0.376108 |
| C | -2.014866 | -0.232853 | -2.675255 |
| C | -3.2589 | 0.015856 | -2.213156 |
| H | -1.637958 | -0.338039 | -3.681386 |
| H | -4.192761 | 0.186897 | -2.72691 |
| N | -3.16164 | 0.01329 | -0.826706 |
| Br | 4.966199 | 1.649003 | 0.028043 |
| Br | 2.713337 | -0.66978 | 2.577961 |
| C | -4.276804 | 0.267249 | 0.037916 |
| C | -5.066073 | -0.814757 | 0.456165 |
| C | -4.546076 | 1.589599 | 0.422282 |
| C | -6.149243 | -0.542557 | 1.295684 |
| C | -5.639635 | 1.812512 | 1.262708 |
| C | -6.434604 | 0.757719 | 1.696229 |
| H | -6.775568 | -1.360365 | 1.642091 |
| H | -5.870034 | 2.825538 | 1.581609 |
| H | -7.28 | 0.950138 | 2.350912 |
| C | -4.767358 | -2.246028 | 0.038632 |
| H | -3.910219 | -2.232844 | -0.640275 |
| C | -5.946042 | -2.864925 | -0.722859 |
| H | -6.838129 | -2.941518 | -0.090099 |
| H | -6.205266 | -2.266255 | -1.603689 |
| H | -5.688734 | -3.875115 | -1.061733 |
| C | -4.378502 | -3.099557 | 1.252652 |
| H | -3.508964 | -2.675051 | 1.766576 |
| H | -5.202157 | -3.164564 | 1.973572 |
| H | -4.125878 | -4.118379 | 0.936636 |
| C | -3.690954 | 2.759613 | -0.038193 |
| H | -2.90526 | 2.373436 | -0.693201 |
| C | -3.002258 | 3.441726 | 1.150579 |
| H | -3.735189 | 3.879685 | 1.838728 |
| H | -2.39167 | 2.727338 | 1.713868 |
| H | -2.3469 | 4.246838 | 0.79878 |
| C | -4.516087 | 3.76326 | -0.853466 |
| H | -4.987382 | 3.278907 | -1.716265 |
| H | -5.306429 | 4.21909 | -0.245373 |
| H | -3.871738 | 4.568563 | -1.224708 |

- N_imag: 0
- E_HF [Hartree]: -1115.83897449
- G (corrected) [kcal/mol]: -699970.6010290451

### 2.3.19 Rearrangement – TS beta-alpha, DiPP-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.685021 | 1.166645 | -2.449721 |
| Pd | -2.495802 | -0.063674 | -0.132628 |
| C | -2.479725 | 1.534536 | -1.447914 |
| Br | -4.804061 | -1.017589 | -0.932573 |
| Br | -1.266157 | -1.573628 | 1.613107 |
| C | -3.493612 | 2.346729 | -0.860097 |
| H | -4.470645 | 2.217888 | -1.318814 |
| C | -1.136789 | 1.342103 | -0.953894 |
| H | -0.444359 | 0.783896 | -1.577758 |
| C | -3.415133 | 3.250961 | 0.180122 |
| C | -0.567722 | 1.907741 | 0.198753 |
| C | 1.628891 | 0.973604 | -0.378076 |
| H | -4.335813 | 3.772641 | 0.428533 |

| | | | |
|---|---|---|---|
| C | -2.297915 | 3.556281 | 0.978392 |
| N | 0.713966 | 1.405863 | 0.547785 |
| C | -1.058415 | 2.956688 | 1.009194 |
| N | 2.610097 | 0.474435 | 0.418197 |
| H | -2.447261 | 4.34736 | 1.710887 |
| C | 1.109828 | 1.15889 | 1.860288 |
| H | -0.359398 | 3.325051 | 1.754647 |
| C | 2.31891 | 0.57258 | 1.778299 |
| C | 3.720786 | -0.276454 | -0.083754 |
| H | 0.466039 | 1.337216 | 2.705813 |
| H | 2.9706 | 0.170927 | 2.537915 |
| C | 4.931161 | 0.379059 | -0.344021 |
| C | 3.541696 | -1.654712 | -0.276614 |
| C | 4.636175 | -2.381405 | -0.750889 |
| H | 4.533403 | -3.449699 | -0.916342 |
| C | 5.99598 | -0.389468 | -0.816109 |
| H | 6.950067 | 0.082474 | -1.030952 |
| C | 5.849302 | -1.75792 | -1.01475 |
| C | 5.038394 | 1.886608 | -0.180574 |
| H | 4.355204 | 2.179775 | 0.624514 |
| C | 2.19088 | -2.309913 | -0.039197 |
| H | 1.621601 | -1.701654 | 0.669969 |
| H | 6.689084 | -2.34225 | -1.38208 |
| C | 2.287805 | -3.712146 | 0.567256 |
| H | 2.683888 | -4.446817 | -0.145818 |
| H | 2.925092 | -3.722115 | 1.459161 |
| H | 1.284496 | -4.037331 | 0.859957 |
| C | 6.439901 | 2.363935 | 0.210959 |
| H | 6.817187 | 1.830191 | 1.090094 |
| H | 7.160543 | 2.228198 | -0.604289 |
| H | 6.415146 | 3.434492 | 0.443539 |
| C | 4.556304 | 2.582264 | -1.463694 |
| H | 4.598688 | 3.672446 | -1.349695 |
| H | 5.192594 | 2.300182 | -2.31172 |
| H | 3.525317 | 2.29258 | -1.69081 |
| C | 1.376243 | -2.328647 | -1.341342 |
| H | 1.297641 | -1.31894 | -1.756147 |
| H | 1.849723 | -2.97882 | -2.089388 |
| H | 0.364616 | -2.692737 | -1.135197 |

- N_imag: 1
- E_HF [Hartree]: -1115.73210751
- G (corrected) [kcal/mol]: -699902.4020415661

### 2.3.20 Rearrangement – TS beta-alpha, DiPP, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.676262 | 1.354916 | -2.483398 |
| Pd | -2.544196 | -0.035432 | -0.208747 |
| C | -2.480854 | 1.652367 | -1.455969 |
| Br | -4.958194 | -0.898433 | -0.866592 |
| Br | -1.574472 | -1.820115 | 1.496142 |
| C | -3.409943 | 2.607506 | -0.923895 |
| H | -4.332993 | 2.692237 | -1.491978 |
| C | -1.154039 | 1.358406 | -0.985918 |
| H | -0.48257 | 0.841406 | -1.663666 |
| C | -3.297336 | 3.412349 | 0.178434 |
| C | -0.620963 | 1.7047 | 0.266537 |
| C | 1.577706 | 0.794149 | -0.353624 |
| H | -4.126995 | 4.085135 | 0.377615 |
| C | -2.229524 | 3.458266 | 1.110322 |
| N | 0.639027 | 1.132973 | 0.589407 |
| C | -1.091954 | 2.697483 | 1.177775 |

| | | | |
|---|---|---|---|
| N | 2.581826 | 0.305275 | 0.412443 |
| H | -2.338177 | 4.193051 | 1.904468 |
| C | 1.056211 | 0.845752 | 1.888308 |
| H | -0.430123 | 2.910745 | 2.01089 |
| C | 2.291795 | 0.32134 | 1.774376 |
| C | 3.801601 | -0.226277 | -0.12383 |
| H | 0.43276 | 0.992972 | 2.755168 |
| H | 2.980376 | -0.053705 | 2.515871 |
| C | 4.89062 | 0.638605 | -0.317728 |
| C | 3.858002 | -1.595527 | -0.420687 |
| C | 5.052666 | -2.095782 | -0.946009 |
| H | 5.129682 | -3.152609 | -1.187332 |
| C | 6.059699 | 0.094257 | -0.853281 |
| H | 6.919367 | 0.733425 | -1.031417 |
| C | 6.140767 | -1.259645 | -1.164506 |
| C | 4.789152 | 2.123262 | -0.002569 |
| H | 3.964903 | 2.260036 | 0.704756 |
| C | 2.674701 | -2.523293 | -0.193349 |
| H | 1.851776 | -1.937746 | 0.225641 |
| H | 7.059732 | -1.664815 | -1.578772 |
| C | 3.013486 | -3.622137 | 0.821331 |
| H | 3.79942 | -4.289065 | 0.446865 |
| H | 3.356165 | -3.192435 | 1.769509 |
| H | 2.126208 | -4.232477 | 1.026419 |
| C | 6.052045 | 2.682868 | 0.660622 |
| H | 6.332418 | 2.10124 | 1.545994 |
| H | 6.905948 | 2.692587 | -0.026148 |
| H | 5.875182 | 3.717335 | 0.976016 |
| C | 4.44386 | 2.912728 | -1.273473 |
| H | 4.318738 | 3.977164 | -1.043039 |
| H | 5.24189 | 2.816745 | -2.02009 |
| H | 3.513423 | 2.547991 | -1.720986 |
| C | 2.177501 | -3.122738 | -1.514661 |
| H | 1.914691 | -2.336944 | -2.231625 |
| H | 2.938783 | -3.763344 | -1.975824 |
| H | 1.284837 | -3.734348 | -1.338999 |

- N_imag: 1
- E_HF [Hartree]: -1115.83622051
- G (corrected) [kcal/mol]: -699968.5760558884

### 2.3.21 Rearrangement – alpha-isomer, DiPP, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.706762 | 1.097584 | -2.599346 |
| Pd | -2.164269 | 0.058843 | -0.11927 |
| C | -2.534161 | 1.550242 | -1.627022 |
| Br | -3.840783 | -1.56333 | -1.286099 |
| Br | -1.551913 | -1.177253 | 2.072557 |
| C | -3.637501 | 2.353729 | -1.132546 |
| H | -4.5657 | 2.204816 | -1.677876 |
| C | -1.181368 | 1.553758 | -1.206067 |
| H | -0.409249 | 1.162058 | -1.860051 |
| C | -3.656148 | 3.234453 | -0.102389 |
| C | -0.822718 | 1.829752 | 0.143245 |
| C | 1.449293 | 1.029935 | -0.380945 |
| H | -4.590897 | 3.761737 | 0.074402 |
| C | -2.597751 | 3.515006 | 0.828634 |
| N | 0.512308 | 1.453875 | 0.519998 |
| C | -1.402635 | 2.891346 | 0.9571 |
| N | 2.437039 | 0.569992 | 0.434608 |
| H | -2.806429 | 4.296077 | 1.556268 |
| C | 0.89863 | 1.244738 | 1.840426 |

| | | | |
|---|---|---|---|
| H | -0.762593 | 3.23238 | 1.766342 |
| C | 2.125666 | 0.691434 | 1.787518 |
| C | 3.494537 | -0.268238 | -0.042888 |
| H | 0.243755 | 1.419552 | 2.677972 |
| H | 2.776824 | 0.325859 | 2.565584 |
| C | 4.740089 | 0.294573 | -0.347207 |
| C | 3.221398 | -1.639517 | -0.175696 |
| C | 4.257354 | -2.45423 | -0.63797 |
| H | 4.083176 | -3.519 | -0.760996 |
| C | 5.74349 | -0.56065 | -0.804844 |
| H | 6.722459 | -0.162312 | -1.054144 |
| C | 5.503402 | -1.922684 | -0.947117 |
| C | 4.944462 | 1.797084 | -0.24355 |
| H | 4.304976 | 2.158493 | 0.569701 |
| C | 1.836456 | -2.201254 | 0.114293 |
| H | 1.321063 | -1.529893 | 0.807336 |
| H | 6.295297 | -2.575788 | -1.305019 |
| C | 1.864956 | -3.576306 | 0.787583 |
| H | 2.208116 | -4.364647 | 0.105262 |
| H | 2.515076 | -3.579304 | 1.670232 |
| H | 0.850015 | -3.830306 | 1.108705 |
| C | 6.384218 | 2.199467 | 0.088297 |
| H | 6.755076 | 1.675279 | 0.97596 |
| H | 7.068521 | 1.987154 | -0.741875 |
| H | 6.435093 | 3.277192 | 0.279952 |
| C | 4.465112 | 2.475645 | -1.53663 |
| H | 4.572606 | 3.564865 | -1.462626 |
| H | 5.059163 | 2.128813 | -2.391286 |
| H | 3.413448 | 2.237755 | -1.725872 |
| C | 0.992428 | -2.237204 | -1.169293 |
| H | 0.970397 | -1.249321 | -1.639066 |
| H | 1.404823 | -2.957818 | -1.888397 |
| H | -0.038219 | -2.521123 | -0.930614 |

- N_imag: 0
- E_HF [Hartree]: -1115.73560047
- G (corrected) [kcal/mol]: -699904.5412214515

### 2.3.22 Rearrangement – alpha-isomer, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.708002 | 0.828551 | -2.769476 |
| Pd | -2.43032 | 0.009627 | -0.126802 |
| C | -2.454984 | 1.349342 | -1.850309 |
| Br | -4.565725 | -1.295637 | -1.022439 |
| Br | -2.173918 | -1.008577 | 2.279154 |
| C | -3.338151 | 2.452308 | -1.527905 |
| H | -4.230255 | 2.50104 | -2.146656 |
| C | -1.143726 | 1.101744 | -1.382389 |
| H | -0.489531 | 0.4681 | -1.97156 |
| C | -3.183714 | 3.417822 | -0.585618 |
| C | -0.719446 | 1.471483 | -0.078905 |
| C | 1.550863 | 0.605584 | -0.530011 |
| H | -3.949155 | 4.188622 | -0.544039 |
| C | -2.142576 | 3.525759 | 0.396862 |
| N | 0.546468 | 0.938332 | 0.337631 |
| C | -1.111437 | 2.677435 | 0.637938 |
| N | 2.52289 | 0.178633 | 0.316906 |
| H | -2.208134 | 4.387584 | 1.055837 |
| C | 0.891919 | 0.732704 | 1.669192 |
| H | -0.454865 | 2.936909 | 1.463881 |
| C | 2.151101 | 0.248474 | 1.656044 |
| C | 3.797143 | -0.313088 | -0.11838 |

| | | | |
|---|---|---|---|
| H | 0.20165 | 0.898313 | 2.480674 |
| H | 2.80547 | -0.065249 | 2.454828 |
| C | 4.87019 | 0.582725 | -0.221712 |
| C | 3.922552 | -1.68105 | -0.410388 |
| C | 5.170206 | -2.14131 | -0.836489 |
| H | 5.300195 | -3.191181 | -1.082875 |
| C | 6.102449 | 0.073855 | -0.641596 |
| H | 6.954085 | 0.743121 | -0.729434 |
| C | 6.251556 | -1.273081 | -0.948785 |
| C | 4.726537 | 2.060531 | 0.105405 |
| H | 3.679623 | 2.255517 | 0.353831 |
| C | 2.735782 | -2.627513 | -0.317121 |
| H | 1.957023 | -2.135632 | 0.273511 |
| H | 7.215501 | -1.650237 | -1.278897 |
| C | 3.07959 | -3.941755 | 0.391748 |
| H | 3.774654 | -4.553676 | -0.194587 |
| H | 3.530084 | -3.760588 | 1.373995 |
| H | 2.167444 | -4.530864 | 0.539537 |
| C | 5.570751 | 2.439073 | 1.329194 |
| H | 5.289011 | 1.842916 | 2.204682 |
| H | 6.639058 | 2.280097 | 1.139947 |
| H | 5.425999 | 3.496949 | 1.576987 |
| C | 5.078294 | 2.934567 | -1.105022 |
| H | 4.902671 | 3.991386 | -0.873412 |
| H | 6.131875 | 2.824839 | -1.387688 |
| H | 4.463185 | 2.670002 | -1.972541 |
| C | 2.156769 | -2.889902 | -1.714503 |
| H | 1.881473 | -1.951414 | -2.207695 |
| H | 2.887497 | -3.406231 | -2.349188 |
| H | 1.260158 | -3.517238 | -1.647085 |

- N_imag: 0
- E_HF [Hartree]: -1115.83761632
- G (corrected) [kcal/mol]: -699969.379895558

### 2.3.23 Rearrangement – TS NHC-rotation, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.776615 | 1.657981 | -2.441915 |
| Pd | -2.175971 | 0.044952 | -0.229389 |
| C | -2.655453 | 1.853769 | -1.379955 |
| Br | -3.76978 | -1.483081 | -1.711514 |
| Br | -1.612518 | -1.493007 | 1.845911 |
| C | -3.805314 | 2.473686 | -0.756711 |
| H | -4.695356 | 2.496674 | -1.380224 |
| C | -1.314554 | 1.836322 | -0.938325 |
| H | -0.529856 | 1.68506 | -1.670321 |
| C | -3.886968 | 3.04877 | 0.470826 |
| C | -0.960451 | 1.770458 | 0.442516 |
| C | 1.175967 | 0.766033 | -0.236676 |
| H | -4.83056 | 3.521328 | 0.731687 |
| C | -2.883587 | 3.061119 | 1.494602 |
| N | 0.408723 | 1.410019 | 0.703244 |
| C | -1.655372 | 2.479961 | 1.50431 |
| N | 2.326042 | 0.527548 | 0.436334 |
| H | -3.168166 | 3.561127 | 2.416853 |
| C | 1.075357 | 1.537892 | 1.920527 |
| H | -1.122949 | 2.563205 | 2.44268 |
| C | 2.292076 | 0.982684 | 1.747797 |
| C | 3.439379 | -0.181534 | -0.123474 |
| H | 0.670059 | 2.006867 | 2.800322 |
| H | 3.124402 | 0.871436 | 2.425941 |
| C | 4.514843 | 0.551265 | -0.647126 |

| | | | |
|---|---|---|---|
| C | 3.417757 | -1.584933 | -0.106187 |
| C | 4.519633 | -2.255191 | -0.643784 |
| H | 4.533423 | -3.341935 | -0.646037 |
| C | 5.595431 | -0.163613 | -1.169522 |
| H | 6.44506 | 0.375373 | -1.58007 |
| C | 5.598715 | -1.553946 | -1.169836 |
| C | 4.535495 | 2.071528 | -0.643439 |
| H | 3.57021 | 2.42597 | -0.271092 |
| C | 2.257572 | -2.373857 | 0.480447 |
| H | 1.485678 | -1.674227 | 0.810877 |
| H | 6.447344 | -2.092946 | -1.581608 |
| C | 2.704778 | -3.17561 | 1.709402 |
| H | 3.453564 | -3.931999 | 1.444419 |
| H | 3.139746 | -2.518837 | 2.471732 |
| H | 1.845881 | -3.690962 | 2.154813 |
| C | 5.617041 | 2.598044 | 0.309084 |
| H | 5.469035 | 2.21493 | 1.325106 |
| H | 6.617644 | 2.297227 | -0.024364 |
| H | 5.58947 | 3.69315 | 0.34955 |
| C | 4.715449 | 2.640718 | -2.055844 |
| H | 4.653033 | 3.734766 | -2.03069 |
| H | 5.690336 | 2.371553 | -2.478614 |
| H | 3.937077 | 2.270477 | -2.732378 |
| C | 1.612162 | -3.285601 | -0.569675 |
| H | 1.279765 | -2.708749 | -1.440314 |
| H | 2.30795 | -4.058491 | -0.918043 |
| H | 0.735804 | -3.784441 | -0.141144 |

- N_imag: 1
- E_HF [Hartree]: -1115.83503344
- G (corrected) [kcal/mol]: -699967.538782685

### 2.3.24 Rearrangement – alpha-intermediate, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | 2.888792 | -2.607087 | -1.190643 |
| Pd | 2.161413 | -0.038917 | -0.257656 |
| C | 2.755919 | -2.177286 | -0.201704 |
| Br | 3.572721 | 0.407205 | -2.468916 |
| Br | 1.860231 | 2.401466 | 0.733924 |
| C | 3.915002 | -2.282523 | 0.657543 |
| H | 4.812132 | -2.639308 | 0.15842 |
| C | 1.413896 | -1.964626 | 0.16915 |
| H | 0.627376 | -2.307602 | -0.495569 |
| C | 4.003272 | -2.035881 | 1.992294 |
| C | 1.044597 | -1.137547 | 1.276097 |
| C | -1.083974 | -0.474072 | 0.230465 |
| H | 4.961352 | -2.242643 | 2.462889 |
| C | 3.008685 | -1.462425 | 2.850455 |
| N | -0.358282 | -0.82979 | 1.336986 |
| C | 1.760295 | -1.028855 | 2.533455 |
| N | -2.339417 | -0.362412 | 0.734986 |
| H | 3.323288 | -1.285415 | 3.875532 |
| C | -1.149462 | -0.939046 | 2.479604 |
| H | 1.223601 | -0.508433 | 3.320156 |
| C | -2.40743 | -0.639948 | 2.094876 |
| C | -3.49196 | -0.044031 | -0.057075 |
| H | -0.77263 | -1.243604 | 3.442817 |
| H | -3.333825 | -0.60709 | 2.64777 |
| C | -4.177284 | -1.091942 | -0.691936 |
| C | -3.903445 | 1.29341 | -0.152746 |
| C | -5.037169 | 1.570372 | -0.9213 |
| H | -5.383207 | 2.596369 | -1.013333 |

| | | | |
|---|---|---|---|
| C | -5.299105 | -0.764573 | -1.45709 |
| H | -5.844342 | -1.552502 | -1.969614 |
| C | -5.727034 | 0.55332 | -1.570856 |
| C | -3.729267 | -2.540862 | -0.579067 |
| H | -2.899646 | -2.588626 | 0.131543 |
| C | -3.168581 | 2.421881 | 0.552839 |
| H | -2.286421 | 2.002068 | 1.044061 |
| H | -6.604208 | 0.788969 | -2.167049 |
| C | -4.048842 | 3.052232 | 1.639519 |
| H | -4.942085 | 3.517589 | 1.20572 |
| H | -4.376715 | 2.302171 | 2.368096 |
| H | -3.492089 | 3.828851 | 2.17679 |
| C | -4.847191 | -3.438088 | -0.033455 |
| H | -5.215029 | -3.069541 | 0.930938 |
| H | -5.696614 | -3.489422 | -0.724666 |
| H | -4.472673 | -4.457966 | 0.111255 |
| C | -3.210923 | -3.05944 | -1.926772 |
| H | -2.839759 | -4.085629 | -1.821995 |
| H | -4.005995 | -3.062343 | -2.681993 |
| H | -2.390986 | -2.435385 | -2.299019 |
| C | -2.675776 | 3.477957 | -0.444129 |
| H | -2.028256 | 3.028611 | -1.205267 |
| H | -3.511596 | 3.971564 | -0.953889 |
| H | -2.100241 | 4.250368 | 0.079174 |

- N_imag: 0
- E_HF [Hartree]: -1115.83528553
- G (corrected) [kcal/mol]: -699968.1468393905

### 2.3.25 Rearrangement – TS allyl-alkyl, DiPP-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -3.325454 | -2.360285 | 0.059482 |
| Pd | -1.539983 | -0.287208 | 0.350455 |
| C | -3.231482 | -1.48299 | -0.574424 |
| Br | -1.247946 | -2.348938 | 2.116729 |
| Br | -1.715159 | 2.194209 | 1.394343 |
| C | -4.383188 | -0.690049 | -0.728032 |
| H | -5.194908 | -0.943505 | -0.050447 |
| C | -1.985195 | -1.392449 | -1.273754 |
| H | -1.358951 | -2.275891 | -1.368581 |
| C | -4.648562 | 0.320968 | -1.645496 |
| C | -1.602502 | -0.181448 | -1.976244 |
| C | 0.497311 | -0.083472 | -0.919863 |
| H | -5.662143 | 0.715701 | -1.630267 |
| C | -3.767505 | 0.95088 | -2.523319 |
| N | -0.178271 | -0.056309 | -2.101029 |
| C | -2.392073 | 0.776689 | -2.614128 |
| N | 1.766626 | 0.20195 | -1.288 |
| H | -4.180036 | 1.760764 | -3.120023 |
| C | 0.631865 | 0.262634 | -3.177571 |
| H | -1.843312 | 1.526683 | -3.179799 |
| C | 1.873751 | 0.417986 | -2.660173 |
| C | 2.867638 | 0.271726 | -0.37102 |
| H | 0.268742 | 0.334651 | -4.190686 |
| H | 2.818091 | 0.64618 | -3.129602 |
| C | 3.713992 | -0.841528 | -0.276139 |
| C | 3.034924 | 1.431912 | 0.398622 |
| C | 4.150571 | 1.477981 | 1.237172 |
| H | 4.317756 | 2.356306 | 1.85162 |
| C | 4.813954 | -0.744077 | 0.576302 |
| H | 5.49445 | -1.583635 | 0.678326 |
| C | 5.036927 | 0.411327 | 1.3146 |

| | | | |
|---|---|---|---|
| C | 3.370694 | -2.140777 | -0.987758 |
| H | 2.839135 | -1.89303 | -1.913177 |
| C | 2.038502 | 2.579579 | 0.327127 |
| H | 1.040299 | 2.150497 | 0.187241 |
| H | 5.895569 | 0.470368 | 1.978362 |
| C | 2.345278 | 3.494752 | -0.867958 |
| H | 3.333153 | 3.961362 | -0.757051 |
| H | 2.331817 | 2.946111 | -1.815887 |
| H | 1.593719 | 4.289358 | -0.92971 |
| C | 4.600076 | -2.965086 | -1.383809 |
| H | 5.324624 | -2.367531 | -1.949038 |
| H | 5.109661 | -3.380272 | -0.506604 |
| H | 4.292328 | -3.812212 | -2.006888 |
| C | 2.41434 | -2.96628 | -0.108789 |
| H | 2.114893 | -3.88457 | -0.628184 |
| H | 2.908619 | -3.249521 | 0.82767 |
| H | 1.509386 | -2.409124 | 0.155771 |
| C | 1.960424 | 3.392774 | 1.620632 |
| H | 1.7892 | 2.740436 | 2.481553 |
| H | 2.867412 | 3.988425 | 1.794021 |
| H | 1.106974 | 4.073983 | 1.560787 |

- N_imag: 1
- E_HF [Hartree]: -1115.71468465
- G (corrected) [kcal/mol]: -699892.2859609164

### 2.3.26 Rearrangement – TS allyl-alkyl, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -3.510971 | 1.864033 | 0.972627 |
| Pd | -1.61584 | 0.153184 | -0.199616 |
| C | -3.286893 | 0.843875 | 1.270196 |
| Br | -1.887533 | -1.589973 | -2.287454 |
| Br | -1.89536 | 2.762258 | -1.402967 |
| C | -4.369271 | -0.044916 | 1.289929 |
| H | -5.288606 | 0.348373 | 0.862514 |
| C | -1.950748 | 0.647474 | 1.738088 |
| H | -1.370276 | 1.512644 | 2.049417 |
| C | -4.459035 | -1.318348 | 1.857058 |
| C | -1.415698 | -0.663562 | 2.028892 |
| C | 0.625156 | -0.254904 | 0.889784 |
| H | -5.449688 | -1.765868 | 1.854353 |
| C | -3.438986 | -2.101881 | 2.384663 |
| N | 0.012529 | -0.676344 | 2.029877 |
| C | -2.069122 | -1.837985 | 2.39234 |
| N | 1.937744 | -0.417052 | 1.18089 |
| H | -3.727784 | -3.081349 | 2.756453 |
| C | 0.904651 | -1.109373 | 2.998729 |
| H | -1.419236 | -2.659974 | 2.683731 |
| C | 2.132712 | -0.936116 | 2.458021 |
| H | 0.591977 | -1.476945 | 3.963894 |
| H | 3.11874 | -1.121296 | 2.856056 |
| C | 3.001704 | -0.095217 | 0.274046 |
| C | 3.491586 | 1.219313 | 0.256325 |
| C | 3.504723 | -1.104322 | -0.559928 |
| C | 4.507943 | 1.517421 | -0.654129 |
| C | 4.527016 | -0.759037 | -1.447288 |
| C | 5.020729 | 0.539272 | -1.498806 |
| H | 4.901425 | 2.52874 | -0.705058 |
| H | 4.936879 | -1.516423 | -2.109973 |
| H | 5.810159 | 0.791033 | -2.201307 |
| C | 2.936959 | 2.303381 | 1.167014 |
| H | 2.269052 | 1.832337 | 1.894109 |

| | | | |
|---|---|---|---|
| C | 4.046768 | 3.007561 | 1.957174 |
| H | 4.718441 | 3.570676 | 1.299079 |
| H | 3.607998 | 3.718671 | 2.666548 |
| H | 4.649145 | 2.290264 | 2.525897 |
| C | 2.106784 | 3.312141 | 0.362002 |
| H | 1.272011 | 2.82422 | -0.154356 |
| H | 1.691491 | 4.078189 | 1.027966 |
| H | 2.726276 | 3.817329 | -0.389288 |
| C | 2.982854 | -2.531793 | -0.516577 |
| H | 2.181959 | -2.583034 | 0.226216 |
| C | 2.383491 | -2.951894 | -1.864443 |
| H | 1.564475 | -2.285427 | -2.157485 |
| H | 3.139128 | -2.942676 | -2.658713 |
| H | 1.981793 | -3.969812 | -1.795648 |
| C | 4.083539 | -3.503171 | -0.070268 |
| H | 4.501186 | -3.210963 | 0.89984 |
| H | 3.6776 | -4.516822 | 0.025245 |
| H | 4.903606 | -3.536106 | -0.797364 |

- N_imag: 1
- E_HF [Hartree]: -1115.82972113
- G (corrected) [kcal/mol]: -699965.2452354624

### 2.3.27 Rearrangement – alkyl form, DiPP-group, gas phase

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -3.133572 | -0.052753 | 1.793925 |
| Pd | -0.991428 | -0.680782 | -0.276788 |
| C | -3.453961 | 0.570027 | 0.962776 |
| Br | -2.686736 | -2.605491 | -0.194277 |
| Br | 1.084746 | -2.271238 | -0.517858 |
| C | -4.622637 | 1.240011 | 1.056776 |
| H | -5.241364 | 1.073404 | 1.938143 |
| C | -2.610899 | 0.591759 | -0.282674 |
| H | -3.22979 | 0.285254 | -1.135248 |
| C | -5.151818 | 2.161452 | 0.074086 |
| C | -2.177336 | 2.016895 | -0.485513 |
| C | -0.022573 | 1.055581 | -0.201566 |
| H | -6.23242 | 2.301806 | 0.077962 |
| C | -4.43224 | 2.955189 | -0.763191 |
| N | -0.785371 | 2.183198 | -0.32978 |
| C | -2.991912 | 3.039817 | -0.819019 |
| N | 1.229173 | 1.532079 | 0.014641 |
| H | -4.980802 | 3.675229 | -1.368941 |
| C | -0.030676 | 3.333391 | -0.188359 |
| H | -2.565894 | 3.998754 | -1.112966 |
| C | 1.237089 | 2.921679 | 0.026459 |
| C | 2.413141 | 0.783555 | 0.328206 |
| H | -0.458823 | 4.32108 | -0.232697 |
| H | 2.148465 | 3.470257 | 0.202262 |
| C | 3.34605 | 0.558226 | -0.68891 |
| C | 2.605133 | 0.362125 | 1.647654 |
| C | 3.807198 | -0.279189 | 1.945186 |
| H | 3.984214 | -0.636624 | 2.955928 |
| C | 4.539511 | -0.069538 | -0.338904 |
| H | 5.286838 | -0.262538 | -1.103331 |
| C | 4.770294 | -0.482988 | 0.966756 |
| C | 3.066938 | 0.949894 | -2.129555 |
| H | 2.006665 | 1.208424 | -2.205555 |
| C | 1.551727 | 0.55094 | 2.725661 |
| H | 0.694595 | 1.067379 | 2.284908 |
| H | 5.700144 | -0.985826 | 1.218381 |
| C | 2.07523 | 1.427766 | 3.870831 |

| | | | |
|---|---|---|---|
| H | 2.924898 | 0.95591 | 4.379088 |
| H | 2.405697 | 2.406077 | 3.502328 |
| H | 1.288418 | 1.589328 | 4.61683 |
| C | 3.886855 | 2.183466 | -2.532805 |
| H | 3.653228 | 3.044779 | -1.895865 |
| H | 4.961888 | 1.983233 | -2.44476 |
| H | 3.678285 | 2.462152 | -3.572495 |
| C | 3.301531 | -0.222526 | -3.089534 |
| H | 2.972835 | 0.051205 | -4.099166 |
| H | 4.36336 | -0.49195 | -3.149176 |
| H | 2.733769 | -1.097249 | -2.756768 |
| C | 1.039535 | -0.80442 | 3.230641 |
| H | 0.668846 | -1.40948 | 2.397382 |
| H | 1.836628 | -1.366678 | 3.732812 |
| H | 0.22553 | -0.655324 | 3.949953 |

- N_imag: 0
- E_HF [Hartree]: -1115.76377570
- G (corrected) [kcal/mol]: -699921.8127929296

### 2.3.28 Rearrangement – alkyl form, DiPP-group, in MeCN

- Optimised geometry (xyz) [Å]:

| | | | |
|---|---|---|---|
| H | -2.986596 | 0.254694 | 1.919119 |
| Pd | -1.023215 | -0.67608 | -0.215568 |
| C | -3.362332 | 0.753889 | 1.02874 |
| Br | -2.815844 | -2.559433 | -0.158069 |
| Br | 0.96299 | -2.430739 | -0.318102 |
| C | -4.533316 | 1.424846 | 1.094373 |
| H | -5.112342 | 1.372398 | 2.016075 |
| C | -2.586326 | 0.650191 | -0.255846 |
| H | -3.260724 | 0.307644 | -1.051392 |
| C | -5.089858 | 2.244311 | 0.037098 |
| C | -2.123222 | 2.040161 | -0.583807 |
| C | 0.005993 | 1.047278 | -0.259096 |
| H | -6.167331 | 2.399226 | 0.060481 |
| C | -4.380744 | 2.962405 | -0.878462 |
| N | -0.727446 | 2.178068 | -0.47403 |
| C | -2.94086 | 3.042314 | -0.970382 |
| N | 1.271554 | 1.498253 | -0.105539 |
| H | -4.938681 | 3.639795 | -1.52228 |
| C | 0.061591 | 3.314604 | -0.45217 |
| H | -2.520061 | 3.974106 | -1.343068 |
| C | 1.319737 | 2.88389 | -0.22146 |
| C | 2.443976 | 0.749498 | 0.255581 |
| H | -0.336132 | 4.307651 | -0.588382 |
| H | 2.2498 | 3.420301 | -0.116579 |
| C | 3.374865 | 0.443195 | -0.743642 |
| C | 2.645953 | 0.444901 | 1.607595 |
| C | 3.833531 | -0.20485 | 1.949003 |
| H | 4.02312 | -0.459322 | 2.988493 |
| C | 4.553754 | -0.192969 | -0.351394 |
| H | 5.303056 | -0.438677 | -1.09918 |
| C | 4.781591 | -0.51676 | 0.981265 |
| C | 3.140864 | 0.784579 | -2.205985 |
| H | 2.133302 | 1.199213 | -2.306215 |
| C | 1.634533 | 0.799677 | 2.685536 |
| H | 0.79692 | 1.323567 | 2.215641 |
| H | 5.706069 | -1.010806 | 1.267769 |
| C | 2.236764 | 1.751385 | 3.727027 |
| H | 3.065914 | 1.280846 | 4.268501 |
| H | 2.615018 | 2.665895 | 3.255941 |
| H | 1.476206 | 2.037147 | 4.462745 |

| | | | |
|---|---|---|---|
| C | 4.129669 | 1.854241 | -2.687624 |
| H | 4.050708 | 2.769575 | -2.089904 |
| H | 5.16348 | 1.493991 | -2.621068 |
| H | 3.930509 | 2.113164 | -3.734077 |
| C | 3.202826 | -0.468429 | -3.087433 |
| H | 2.945455 | -0.21548 | -4.122963 |
| H | 4.208225 | -0.906359 | -3.092788 |
| H | 2.500045 | -1.225556 | -2.723294 |
| C | 1.066533 | -0.464238 | 3.341964 |
| H | 0.641875 | -1.134276 | 2.586034 |
| H | 1.846363 | -1.013365 | 3.884069 |
| H | 0.281656 | -0.198626 | 4.06014 |

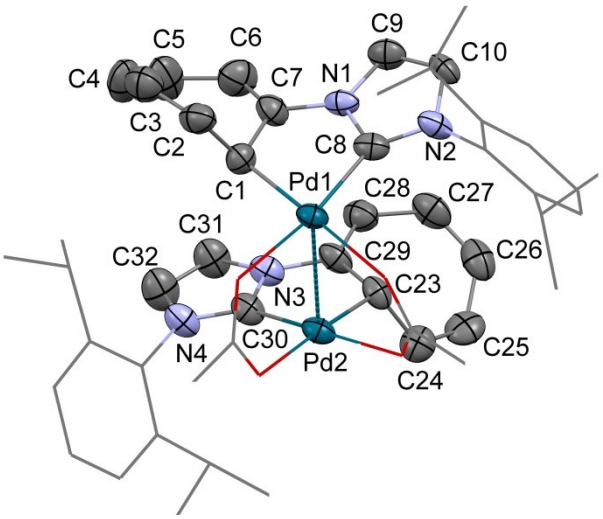
- N_imag: 0
- E_HF [Hartree]: -1115.86682679
- G (corrected) [kcal/mol]: -699986.3471249286

# 3. Crystallographic Details

## *3.1 General*

Data were collected on a single crystal X-ray diffractometer equipped with a CCD detector (APEX II, *κ*-CCD), a fine-focus sealed tube with $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a Triumph monochromator using the APEX II software package (**3**, **5**) or with a CMOS detector (APEX III, *κ*-CMOS), an IMS microsource (**8**) or a TXS rotating anode (**7**) with $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a Helios optic using the APEX III software package.[13,14] The crystals were fixed on the top of a kapton micro sampler with perfluorinated ether, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[15] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[15] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using the APEX III software in conjunction SHELXL-2014 and SHELXLE.[13] [16,17,18] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)}$ = 1.5·$U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å and $U_{iso(H)}$ = 1.2·$U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL-97 weighting scheme.[17] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[19] A split layer refinement was used to treat with disordered anion/solvent molecules and additional SIMU, DELU and SAME restraints were employed to stabilise the refinement of the layers. **3** contains disordered diethyl ether on a special position and **7** contains disordered dichloromethane on a special position which both were treated as a diffuse contribution to the overall scattering without specific atom positions using the PLATON/SQUEEZE procedure.[20] **5** contains huge voids filled with toluene and hexane which are disordered and partly on mixed positions; two toluene positions could be properly refined, for the rest (12 positions in the asymmetric unit) the PLATON/SQUEEZE procedure had to be employed. [20] Images were created with Mercury.[21]

### *3.2 Compound 5 (CCDC 1510764)*




Crystals were obtained by slow evaporation of a solution in dichloromethane/hexane (1:1) and simultaneous diffusion of toluene into it.

diffractometer operator C. Jandl
scanspeed 20-60 s per frame
dx 80 mm
3105 frames measured in 11 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

| | |
|---|---|
| $2(C_{48}H_{56}N_4O_4Pd_2)\cdot C_7H_8$ | |
| $M_r$ = 2023.67 | $D_x$ = 1.149 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Melting point: ? K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 22.183 (3) Å | Cell parameters from 9724 reflections |
| $b$ = 38.918 (5) Å | θ = 2.4–26.0° |
| $c$ = 29.113 (4) Å | μ = 0.65 mm$^{-1}$ |
| β = 111.441 (8)° | $T$ = 100 K |
| $V$ = 23394 (6) Å$^3$ | Fragment, yellow |
| $Z$ = 8 | 0.49 × 0.28 × 0.23 mm |
| $F$(000) = 8336 | |

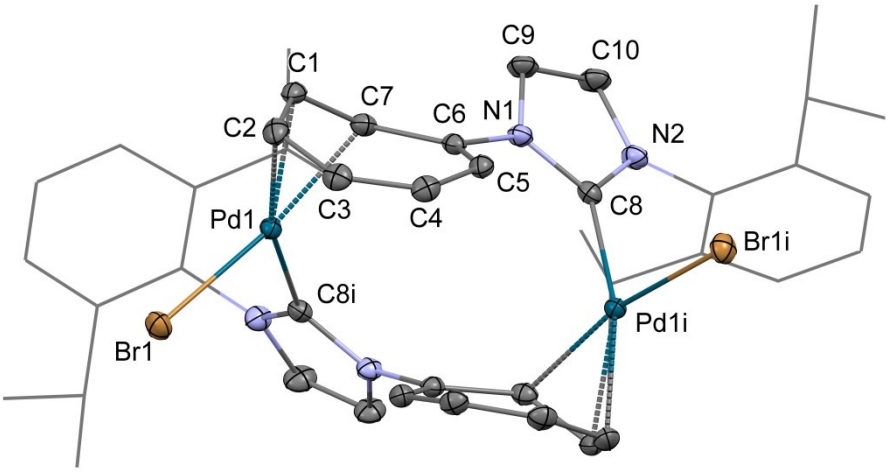
*Data collection*

| | |
|---|---|
| Apex II CCD diffractometer | 41325 independent reflections |
| Radiation source: fine-focus sealed tube | 23974 reflections with $I > 2\sigma(I)$ |
| Triumph monochromator | $R_{int} = 0.112$ |
| Detector resolution: 16 pixels $mm^{-1}$ | $\theta_{max} = 25.0°$, $\theta_{min} = 0.9°$ |
| phi– and ω–rotation scans | $h = -26 \quad 25$ |
| Absorption correction: multi-scan | $k = -46 \quad 46$ |
| $T_{min} = 0.575$, $T_{max} = 0.745$ | $l = -34 \quad 34$ |
| 241128 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.078$ | H-atom parameters constrained |
| $wR(F^2) = 0.213$ | $W = 1/[\Sigma^2(FO^2) + (0.069P)^2 + 198.9685P]$ WHERE $P = (FO^2 + 2FC^2)/3$ |
| $S = 1.05$ | $(\Delta/\sigma)_{max} = 0.037$ |
| 41325 reflections | $\Delta\rho_{max} = 1.40$ e $Å^{-3}$ |
| 2321 parameters | $\Delta\rho_{min} = -1.17$ e $Å^{-3}$ |
| 237 restraints | Extinction correction: none |
| 0 constraints | Extinction coefficient: - |
| Primary atom site location: intrinsic phasing (SHELXT) | |

## *3.3 Compound 3 (CCDC 1510762)*




Crystals were obtained by slow diffusion of diethyl ether into a solution in acetonitrile.

Diffractometer operator C. Jandl
scanspeed 1 s per frame
dx 40 mm
3579 frames measured in 9 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

| | |
|---|---|
| $C_{44}H_{50}Br_2N_4Pd_2$ | |
| $M_r$ = 1007.48 | $D_x$ = 1.461 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Melting point: ? K |
| Hall symbol: -C 2yc | Mo *K*α radiation, λ = 0.71073 Å |
| *a* = 17.4798 (14) Å | Cell parameters from 9543 reflections |
| *b* = 16.3475 (13) Å | θ = 2.4–30.0° |
| *c* = 17.1405 (14) Å | μ = 2.56 mm$^{-1}$ |
| β = 110.780 (3)° | *T* = 100 K |
| *V* = 4579.3 (6) Å$^3$ | Fragment, dark red |
| *Z* = 4 | 0.33 × 0.24 × 0.20 mm |
| *F*(000) = 2016 | |

*Data collection*

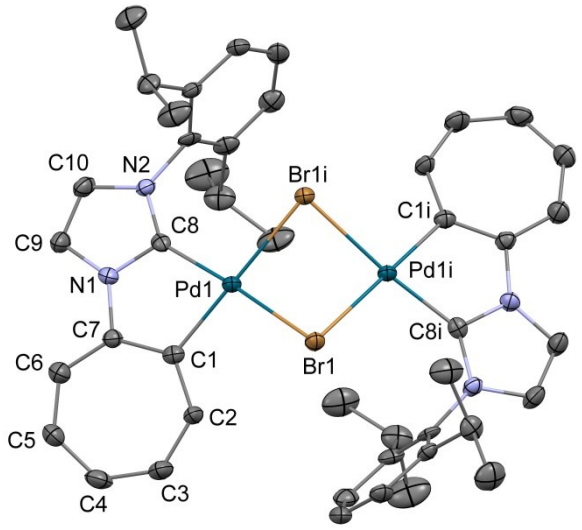
| | |
|---|---|
| Bruker APEX-II CCD diffractometer | 5676 independent reflections |
| Radiation source: fine-focus sealed tube | 5184 reflections with i > 2σ(i) |

| | |
|---|---|
| Triumph optic monochromator | $R_{int}$ = 0.025 |
| Detector resolution: 16 pixels mm$^{-1}$ | $\theta_{max}$ = 28.3°, $\theta_{min}$ = 1.8° |
| phi– and ω–rotation scans | *h* = −23  23 |
| Absorption correction: multi-scan | *k* = −21  21 |
| $T_{min}$ = 0.693, $T_{max}$ = 0.746 | *l* = −22  22 |
| 69130 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.017 | H-atom parameters constrained |
| $wR(F^2)$ = 0.043 | W = 1/[$\Sigma^2$(*F*O$^2$) + (0.0195*P*)$^2$ + 5.7318*P*] WHERE *P* = (*F*O$^2$ + 2*F*C$^2$)/3 |
| *S* = 1.05 | $(\Delta/\sigma)_{max}$ = 0.002 |
| 5676 reflections | $\Delta\rho_{max}$ = 0.69 e Å$^{-3}$ |
| 239 parameters | $\Delta\rho_{min}$ = −0.35 e Å$^{-3}$ |
| 0 restraints | Extinction correction: none |
| 0 constraints | Extinction coefficient: - |
| Primary atom site location: intrinsic phasing (SHELXT) | |

### *3.4 Compound 7 (CCDC 1510763)*




Crystals were obtained by slow evaporation of a solution in dichloromethane and simultaneous diffusion of diethyl ether into it.

Diffractometer operator C. Jandl
scanspeed 20 s per frame, shutterless mode
dx 50 mm
2590 frames measured in 6 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

| | |
|---|---|
| $C_{44}H_{48}Br_2N_4Pd_2 \cdot 2(BF_4) \cdot 2(CH_2Cl_2)$ | |
| $M_r$ = 1348.94 | $D_x$ = 1.606 Mg m$^{-3}$ |
| Orthorhombic, *Pccn* | Melting point: ? K |
| Hall symbol: -P 2ab 2ac | Mo *K*α radiation, λ = 0.71073 Å |
| *a* = 16.011 (3) Å | Cell parameters from 9173 reflections |
| *b* = 24.099 (4) Å | θ = 2.5–26.6° |
| *c* = 14.460 (2) Å | μ = 2.33 mm$^{-1}$ |
| *V* = 5579.4 (16) Å$^3$ | *T* = 100 K |
| *Z* = 4 | Fragment, yellow |
| *F*(000) = 2672 | 0.37 × 0.16 × 0.13 mm |

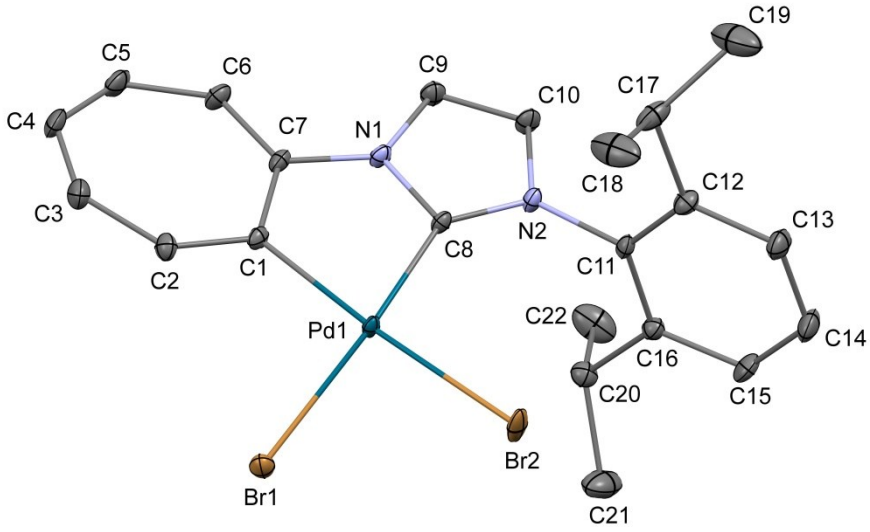
*Data collection*

| | |
|---|---|
| Bruker Photon CMOS diffractometer | 5105 independent reflections |
| Radiation source: TXS rotating anode | 4648 reflections with $I > 2\sigma(I)$ |
| Helios optic monochromator | $R_{int} = 0.050$ |
| Detector resolution: 16 pixels $mm^{-1}$ | $\theta_{max} = 25.4°$, $\theta_{min} = 2.5°$ |
| phi– and ω–rotation scans | $h = -19 \quad 19$ |
| Absorption correction: multi-scan | $k = -29 \quad 29$ |
| $T_{min} = 0.523$, $T_{max} = 0.745$ | $l = -17 \quad 17$ |
| 140795 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | H-atom parameters constrained |
| $wR(F^2) = 0.090$ | $W = 1/[\Sigma^2(FO^2) + (0.0083P)^2 + 34.1708P]$ WHERE $P = (FO^2 + 2FC^2)/3$ |
| $S = 1.21$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 5105 reflections | $\Delta\rho_{max} = 1.10$ e $Å^{-3}$ |
| 357 parameters | $\Delta\rho_{min} = -0.95$ e $Å^{-3}$ |
| 174 restraints | Extinction correction: none |
| 0 constraints | Extinction coefficient: - |
| Primary atom site location: intrinsic phasing (SHELXT) | |

### *3.5 Compound 8 (CCDC 1510761)*




Crystals were grown by slow diffusion of diethyl ether into a solution in acetonitrile (also possible by performing the reaction under 1.2.6 in an NMR tube without stirring).

Diffractometer operator C. Jandl
scanspeed 2-30 s per frame
dx 34 mm
3552 frames measured in 15 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

*Crystal data*

| | |
|---|---|
| $C_{22}H_{24}Br_2N_2Pd$ | |
| $M_r$ = 582.63 | $D_x$ = 1.838 Mg m$^{-3}$ |
| Monoclinic, *Cc* | Melting point: ? K |
| Hall symbol: C -2yc | Mo *K*α radiation, λ = 0.71073 Å |
| *a* = 12.9980 (9) Å | Cell parameters from 9888 reflections |
| *b* = 11.2086 (8) Å | θ = 2.4–30.6° |
| *c* = 14.9044 (10) Å | μ = 4.69 mm$^{-1}$ |
| β = 104.191 (3)° | *T* = 100 K |
| *V* = 2105.2 (3) Å$^3$ | Fragment, red-orange |
| *Z* = 4 | 0.25 × 0.24 × 0.18 mm |
| *F*(000) = 1144 | |

*Data collection*

| | |
|---|---|
| Bruker Photon CMOS | 6080 independent reflections |

| | |
|---|---|
| diffractometer | |
| Radiation source: IMS microsource | 5991 reflections with $I > 2\sigma(I)$ |
| Helios optic monochromator | $R_{int} = 0.041$ |
| Detector resolution: 16 pixels $mm^{-1}$ | $\theta_{max} = 30.0°$, $\theta_{min} = 2.4°$ |
| phi– and ω–rotation scans | $h = -18 \quad 18$ |
| Absorption correction: multi-scan | $k = -15 \quad 15$ |
| $T_{min} = 0.653$, $T_{max} = 0.746$ | $l = -20 \quad 20$ |
| 67398 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.015$ | $W = 1/[\Sigma^2(FO^2) + (0.0155P)^2 + 0.7753P]$ WHERE $P = (FO^2 + 2FC^2)/3$ |
| $wR(F^2) = 0.037$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.08$ | $\Delta\rho_{max} = 0.80$ e $Å^{-3}$ |
| 6080 reflections | $\Delta\rho_{min} = -0.84$ e $Å^{-3}$ |
| 249 parameters | Extinction correction: none |
| 2 restraints | Extinction coefficient: ? |
| 0 constraints | Absolute structure: Flack (1983) |
| Primary atom site location: intrinsic phasing (SHELXT) | Absolute structure parameter: 0.040 (4) |
| Secondary atom site location: difference Fourier map | |

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