Supporting Information for

N,N-Chelate-control on the Regioselectivity in Acetate-assisted C-H activation

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1. EXPERIMENTAL

General Procedures. All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[1] NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13 (^{1}H), 100.61 MHz (^{13}C) at ambient temperature unless otherwise stated; chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in hertz (Hz). The electrospray ionisation (ESI) and the fast atom bombardment (FAB) mass spectra were recorded using a micromass Quattro LC mass spectrometer and a Kratos Concept spectrometer with methanol or nitrophenyloctylether as the matrix, respectively. High resolution FAB mass spectra were recorded on Kratos Concept spectrometer (xenon gas, 7 kV) with NBA as matrix. The infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer on solid samples. Melting points (mp) were measured on a Gallenkamp melting point apparatus (model MFB-595) in open capillary tubes and were uncorrected. Elemental analyses were performed on a Carlo Erba CE1108 instrument at the Department of Chemistry, London Metropolitan University. 2-(1-$C_{10}H_7$)-6-(CMe=N(2,6-*i*-$Pr_2C_6H_3$))C_5H_3N was prepared using a procedure similar to that previously reported.[2] (1-$C_{10}H_7$)-6-(CMe$_2$NH(2,6-*i*-$Pr_2C_6H_3$))C_5H_3N and (1-$C_{10}H_7$)-6-(CMe$_2$OH)C_5H_3N were prepared by treating respectively 2-(1-$C_{10}H_7$)-6-(CMe=N(2,6-*i*-$Pr_2C_6H_3$))C_5H_3N or (1-$C_{10}H_7$)-6-(CMeO)C_5H_3N[3] with excess trimethylaluminium at 100 ^{o}C in toluene for 12 hours, followed by addition of water and extraction of the product into dichloromethane. All other chemicals were obtained commercially and used without further purification.

(a) Synthesis of 1

A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen. The flask was then loaded with $Pd(OAc)_2$ (56 mg, 0.25 mmol), 2-(1-$C_{10}H_7$)-6-(CMe=N(2,6-*i*-$Pr_2C_6H_3$))C_5H_3N (102 mg, 0.25 mmol, 1 eq) and the contents dissolved in freshly dsitilled toluene (10 mL). The resultant brown solution was stirred at 60 ^oC for 48 hours. The reaction mixture was then filtered in the air through a thin layer of celite and the celite cake washed thoroughly with dichloromethane and dried under reduced pressure to give **1** as a yellow powder (0.136 g, 95% yield). Recrystallisation from CH_2Cl_2/hexane (1:3 v/v) yields **1** as orangey/yellow plates. Mp: > 270 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 6.6, 6H, CH(CH_3)$_2$), 1.38 (s, 3H, Pd-OC(O)CH_3), 1.39 (d, *J* = 6.6, 6H, CH(CH_3)$_2$), 2.24 (s, 3H, (CH_3)C=N), 3.19 (sept, *J* = 6.6, 2H, C*H*(CH$_3$)$_2$), 7.18-7.27 (m, 4H, Ar/Py-H), 7.45 (t, *J* = 7.6, 1H, Ar/Py-H), 7.54 (d, *J* = 7.6, 1H, Ar/Py-H), 7.72 (d, *J* = 7.8, 1H, Ar/Py-H), 7.80 (d, *J* = 7.6, 1H, Ar/Py-H), 7.90 (d, *J* = 8.0, 1H, Ar/Py-H), 8.01 (t, *J* = 8.1, 1H, Ar/Py-H), 8.14 (d, *J* = 7.6, 1H, Ar/Py-H), 8.39 (d, *J* = 8.1, 1H, Ar/Py-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9 ((*C*H$_3$)C=N), 23.0 (H$_3$*C*-C(O)O), 23.6 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 122.4 (CH), 122.6 (CH), 123.1 (CH), 124.3 (CH), 125.3 (CH), 125.9 (CH), 126.8 (C), 127.1 (CH), 128.7 (CH), 133.2 (C), 134.8 (C), 135.0 (CH) 135.9 (CH), 136.1 (CH), 138.2 (C), 138.5 (C), 140.1 (C), 154.0 (C), 154.8 (C), 169.9 ((CH$_3$)*C*=N), 175.4 (H$_3$C-*C*(O)O). IR (cm^{-1}): 2957 (C-H), 1614 (C=N$_{imine}$), 1582 (COO)$_{asymm}$/C=N$_{pyridine}$), 1369 (COO)$_{symm}$, 1259, 803, 758. FAB MS: *m/z* 570 $[M]^+$, 511 $[M\text{-}OAc]^+$. Anal Calc. for $C_{31}H_{32}N_2O_2Pd$ (570.15): C, 65.20; H, 5.65; N, 4.91. Found: C, 65.01; H, 5.48; N, 5.02%.

(b) Synthesis of 2

A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen. The flask was then loaded with $Pd(OAc)_2$ (51 mg, 0.23 mmol), 2-(1-$C_{10}H_7$)-6-(CMe_2NH(2,6-*i*-$Pr_2C_6H_3$))C_5H_3N (0.102 g, 0.24 mmol, 1.05 eq) and the contents dissolved in toluene (10 mL). The resultant brown solution was stirred at 60 ^oC for 48 hours. The reaction mixture was then filtered in the air through a thin layer of celite and the celite cake washed thoroughly with dichloromethane and dried under reduced pressure to give **2** as a yellow powder (0.126 g, 89%). Recrystallisation from CH_2Cl_2/hexane (1:3 v/v) yields **2** as yellow plates. Mp: > 260 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 0.71 (d, *J* = 6.9, 3H, CH(CH_3)), 1.20 (d, *J* = 6.9, 3H, CH(CH_3)), 1.33 (d, *J* = 6.9, 3H, CH(CH_3)), 1.38 (d, *J* = 6.9, 3H, CH(CH_3)),

1.39 (s, 3H, Pd-OC(O)CH_3), 2.10 (s, 3H, HNC(CH_3)), 2.51 (s, 3H, HNC(CH_3)), 3.43 (sept, *J* = 6.9, 1H, C*H*(CH_3)$_2$), 3.57 (sept, *J* = 6.9, 1H, C*H*(CH_3)$_2$), 7.04 (t, *J* = 4.5, 1H, Ar-*H*), 7.16 (d, *J* = 4.5, 2H, Ar-*H*), 7.24 (d, *J* = 7.9, 1H, Py-*H*), 7.36 (t, *J* = 7.7, 1H, Ar-*H*), 7.53 (t, *J* = 7.7, 1H, Ar-*H*), 7.66 (d, *J* = 7.8, 1H, Ar-*H*), 7.72 (d, *J* = 7.3, 1H, Ar-*H*), 7.91 (t, *J* = 7.9, 1H, Py-*H*), 7.97 (d, *J* = 7.0, 1H, Ar-*H*), 7.98 (s, 1H, (CH_3)$_2$CN*H*), 8.06 (d, *J* = 7.9, 1H, Py-*H*), 8.14 (d, *J* = 7.0, 1H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8 (H_3C-C(O)O), 24.5 (CH(CH_3)$_2$), 24.9 (CH(CH_3)$_2$), 25.8 (CH(CH_3)$_2$), 25.9 (CH(CH_3)$_2$), 26.0 (HNC(CH_3)), 28.3 (HNC(CH_3)), 31.8 (*C*H(CH_3)$_2$), 34.2 (*C*H(CH_3)$_2$), 66.1 (Me$_2$*C*NH), 119.2 (CH), 123.7 (CH), 124.3 (CH), 124.6 (CH), 124.9 (CH), 125.2 (CH), 125.5 (CH), 126.5 (CH), 128.1 (CH), 128.8 (C), 133.4 (CH), 135.2 (C), 136.9 (C), 138.0 (CH), 139.6 (C), 144.6 (C), 144.8 (C), 155.1 (C), 172.1 (C), 178.8 (H_3C-*C*(O)O). IR (cm^{-1}): 2961 (C-H), 2919, 1583 (COO)$_{asymm}$/C=N$_{pyridine}$), 1379 (COO)$_{symm}$, 1327, 985, 803, 767. FAB MS: *m/z* 586 [M]$^+$, 527 [M-OAc]$^+$. Anal Calc. for $C_{32}H_{36}N_2O_2Pd{\cdot}0.5CH_2Cl_2$ (628.16): C, 62.01; H, 5.92; N, 4.45. Found: C, 62.04; H, 6.26; N, 4.44%.

(c) Synthesis of 3

A Schlenk flask equipped with stir bar was evacuated and backfilled with nitrogen. The flask was then loaded with $Pd(OAc)_2$ (88 mg, 0.39 mmol), 2-(1-$C_{10}H_7$)-6-(CMe_2OH)C_5H_3N (0.105 g, 0.4 mmol, 1.03 eq) and the contents dissolved in dry toluene (10 mL). The resultant solution was stirred at 60 °C for 48 hours. The reaction mixture was then filtered in the air through a thin layer of celite and the celite cake washed thoroughly with dichloromtehane and dried under reduced pressure to give **3** as a yellow powder (0.142 g, 83% yield). Recrystallisation from CH_2Cl_2/hexane (1:3 v/v) yields **3** as pale yellow blocks. Mp: > 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 1.73 (s, 3H, Pd-OC(O)CH_3), 1.96 (s, 6H, HOC(CH_3)$_2$), 7.15-7.25 (m, 1H, Ar-*H*), 7.30 (t, *J* = 7.8, 1H, Py-*H*), 7.43 (t, *J* = 8.2, 1H, Ar-*H*), 7.59 (d, *J* = 7.8, 1H, Py-*H*), 7.77 - 7.87 (m, 3H, Ar-*H*), 7.95 (d, *J* = 8.1, 1H, Ar-*H*), 8.04 (d, *J* = 7.8, 1H, Py-*H*), 12.36 (br s,1H, Pd-O*H*C(CH_3)$_2$). FAB MS: *m/z* 427 [M]$^+$, 368 [M-OAc]$^+$. Anal Calc. for $C_{20}H_{19}NO_3Pd$ (427.04): C, 56.15; H, 4.48; N, 3.27. Found: C, 56.21; H, 4.22; N, 2.99%.

2. COMPUTATIONAL DETAILS

Calculations were performed with Gaussian 03, Revision C.02[4] for the BP86, B3P86, B3LYP and BLYP functionals and Gaussian 09, Revision C.02[5] for the B97-D and M06 functionals. The SDD relativistic ECP and associated basis sets were used for Pd[6] and 6-31G** basis sets

were employed for all other atoms.[7] Stationary points were confirmed as either minima or transition states through analytical frequency calculations and transition states were characterised through IRC calculations and subsequent geometry optimisation.

Energies reported in the main text are free energies computed in the gas-phase with the BP86 functional and include a correction for dispersion effects computed using Grimme's DFT-D3 parameter set[8] (i.e. BP86+D). The effects of toluene solvent (PCM approach,[9] UFF radii) are also included with both the solvent and dispersion corrections being calculated with Gaussian 09.

Note that stationary points corresponding to **TS(I-II)**$_{ortho}$ and **II**$_{ortho}$ were located, however upon inclusion of zero-point energy and entropic effects the intermediate moved to higher energy that the preceding acetate displacement transition states and so the *ortho*-C-H activation effectively proceeds in one step on the free energy surface (*cf*. Fig. 4 in the main text).

Table S1 gives that results of test calculations on the functional dependence of the relative energies of ***peri*-1** and ***ortho*-1** as well as **TS(I-III)**$_{peri}$ and **TS(I-III)**$_{ortho}$.

Species	*ortho*-1	TS(I-III)$_{ortho}$
BP86	-0.8	+1.0
BP86+D	+2.2	+3.3
BP86+D(toluene)	+2.3	+1.8
B3P86	-0.9	+2.9
B3LYP	-1.2	+1.3
BLYP	-1.9	+1.3
B97-D	+2.3	+4.7
M06//BP86	+2.2	+6.0

Table S1. Relative Energies of ***ortho*-1** and **TS(I-III)**$_{ortho}$ computed with various functionals. The energies (kcal/mol) are quoted relative to ***peri*-1** and **TS(I-III)**$_{peri}$ respectively.

Which form of **1** corresponds to the lower energy form does depend on the functional employed, although the energy difference between the two isomers is always small. Pure (BP86, BLYP) and hybrid (B3P86, B3LYP) functionals show a small preference (< 2 kcal/mol) for *ortho*-**1**, whereas including a correction for dispersion (B97-D optimisation, or via the BP86+D protocol) or use of the M06 functional favours *peri*-**1** by 1-3 kcal/mol. Functional tests on **TS(I-III)**$_{peri}$ and **TS(I-III)**$_{ortho}$ showed a small kinetic preference of between 1 and 6 kcal/mol for *peri*-C-H activation with all functionals.

Computed Cartesian coordinates (Å) and energies (hartrees) for all species computed with the BP86 functional. Solvent-corrected SCF energies and absolute values for dispersion corrections are also indicated.

(a) Reaction with *N,N*-pyridylarylimine

$\mathbf{1}_{ortho}$

BP86 Energy = -1588.62616290
Enthalpy 0K= -1588.084767
Enthalpy 298K= -1588.049097
Free Energy 298K= -1588.152969
E(PCM) = -1588.63417815
Dispersion = -0.10042148

C	3.33618	-0.51171	1.31600
C	2.91399	0.25810	0.19520
C	3.74797	0.44298	-0.94430
C	5.03328	-0.13286	-0.91014
C	5.48277	-0.86495	0.19434
C	4.63468	-1.05173	1.29327
N	1.57193	0.76775	0.21005
C	1.31191	2.04408	0.37078
C	-0.12108	2.43103	0.37412
N	-0.99025	1.39556	0.20732
C	-2.36008	1.54391	0.21577
C	-2.86738	2.83907	0.48769
C	-1.99347	3.92061	0.64999
C	-0.60412	3.73570	0.57347
Pd	-0.27094	-0.42895	0.03601
C	-2.19534	-0.87005	0.05234
C	-3.05915	0.26463	0.03065
C	-4.48749	0.07960	-0.12507
C	-5.00592	-1.27112	-0.05306
C	-4.10535	-2.37100	0.07582
C	-2.73249	-2.18109	0.08197
C	-5.42601	1.11942	-0.40373
C	-6.78810	0.86343	-0.51736
C	-7.29510	-0.45068	-0.36254
C	-6.40954	-1.49663	-0.15104
O	0.37536	-2.39498	0.03369
C	0.91855	-2.64144	-1.13898
C	1.55565	-4.02387	-1.26240
C	2.35247	3.11140	0.59464
O	0.94409	-1.81955	-2.07924
H	3.35151	2.66683	0.70022
H	2.11754	3.69093	1.50423
H	2.37273	3.82192	-0.25066
H	0.08577	4.57429	0.68914
H	-2.40065	4.91656	0.84976
H	-3.93922	2.99067	0.60967
H	-2.04157	-3.02839	0.12609
H	-4.52546	-3.38278	0.13516
H	-5.07324	2.13338	-0.59931
H	-7.47257	1.68755	-0.74538
H	-8.37050	-0.63914	-0.44067
H	-6.77432	-2.52756	-0.07571
H	2.55783	-4.00239	-0.80026
H	1.66546	-4.29435	-2.32242
H	0.96050	-4.78481	-0.73394
C	3.29535	1.17502	-2.21017
H	5.68864	-0.00732	-1.77875
H	6.48942	-1.29611	0.19591
H	4.98434	-1.62960	2.15543
C	2.44403	-0.70629	2.54341
H	2.28039	1.57297	-2.03700
C	4.22023	2.36545	-2.55509
C	3.19585	0.19656	-3.40473
H	2.81962	0.72722	-4.29750
H	4.18836	-0.21837	-3.65726
H	2.51210	-0.63599	-3.17397
H	3.83246	2.90653	-3.43562
H	4.30895	3.08392	-1.72222
H	5.23932	2.02144	-2.80447
H	1.42466	-0.37498	2.27143
C	2.33027	-2.18772	2.95976
C	2.92949	0.17398	3.71902
H	2.25279	0.07345	4.58564
H	3.94222	-0.12339	4.04495
H	2.97162	1.24116	3.43974
H	1.65134	-2.28360	3.82511
H	1.91825	-2.78738	2.13264
H	3.30559	-2.61126	3.25833

$\mathbf{I}_{ortho}$

BP86 Energy = -1589.04291220
Enthalpy 0K= -1588.489133
Enthalpy 298K= -1588.453017
Free Energy 298K= -1588.559825
E(PCM) = -1589.07499559
Dispersion = -0.09975167

Pd	-0.10571	-0.44807	-0.10522
O	-0.84798	-2.31596	-0.62738
O	1.31493	-1.94169	-0.56814
N	-1.73269	0.70842	0.07870
N	0.77782	1.35248	0.29261
C	-1.52969	2.00377	0.18159
C	-2.63199	3.02185	0.23705
C	-0.11591	2.40406	0.26468
C	0.31865	3.73198	0.32585
C	1.69691	3.99318	0.41888
C	2.58586	2.92149	0.49357
C	2.10961	1.58536	0.46023
C	3.01746	0.44737	0.72776
C	2.70492	-0.39244	1.80257
C	3.59614	-1.41254	2.21356
C	4.79745	-1.59163	1.54481
C	5.14786	-0.77570	0.42878
C	4.24285	0.26378	-0.00735
C	4.59095	1.02473	-1.16272
C	5.79039	0.80419	-1.82767
C	6.69361	-0.19432	-1.37740
C	6.37188	-0.97237	-0.27571
C	0.35672	-2.77822	-0.78209

C	0.60696	-4.20390	-1.15711
C	-3.03522	0.10104	0.00843
H	-3.61616	2.53546	0.23197
H	-2.57114	3.70238	-0.63069
H	-2.54216	3.63977	1.14707
H	-0.40629	4.54862	0.29893
H	2.06265	5.02285	0.46436
H	3.65891	3.08290	0.62252
H	3.34001	-2.03957	3.07257
H	5.50033	-2.36731	1.86790
H	3.89459	1.77722	-1.54656
H	6.03704	1.39867	-2.71291
H	7.63550	-0.35600	-1.91012
H	7.05292	-1.75867	0.06716
H	-0.17811	-4.56046	-1.84076
H	0.57451	-4.82892	-0.24761
H	1.59990	-4.30747	-1.61793
H	1.77932	-0.22535	2.36372
C	-3.61113	-0.39317	1.21197
C	-4.87674	-0.99844	1.11588
C	-5.53037	-1.12974	-0.11641
C	-4.92256	-0.66137	-1.28813
C	-3.65821	-0.04465	-1.26279
C	-2.91311	-0.28386	2.56774
H	-5.35625	-1.37600	2.02453
H	-6.51471	-1.60569	-0.16444
H	-5.43562	-0.77939	-2.24795
C	-3.00861	0.41659	-2.56768
H	-1.92314	0.18105	2.40692
C	-3.70299	0.61948	3.54291
C	-2.66324	-1.68027	3.18354
H	-2.10234	-1.58457	4.12886
H	-3.61144	-2.19619	3.41192
H	-2.08607	-2.32353	2.49890
H	-3.16175	0.71918	4.49900
H	-3.85966	1.63075	3.13070
H	-4.69653	0.19457	3.76596
H	-2.02716	0.86529	-2.32774
C	-2.73774	-0.78477	-3.50439
C	-3.85722	1.49377	-3.28243
H	-2.21765	-0.44600	-4.41653
H	-2.11493	-1.54535	-3.00628
H	-3.67908	-1.26857	-3.81633
H	-3.34301	1.84350	-4.19342
H	-4.83830	1.09300	-3.58914
H	-4.04423	2.36854	-2.63676

TS(I-II) *ortho*

BP86 Energy = -1589.01905033
Enthalpy 0K= -1588.466418
Enthalpy 298K= -1588.430758
Free Energy 298K= -1588.536049
E(PCM) = -1589.05232074
Dispersion = -0.1036834
Nimag=1 (-48.1 cm^{-1})

Pd	-0.07191	-0.39143	-0.26031
O	0.86379	-2.14076	0.11792
O	0.08823	-2.47682	-1.95088
N	1.50803	0.81755	0.23160
N	-0.92467	1.41256	-0.46701
C	1.29129	2.10907	0.06684
C	2.33621	3.16588	0.28668
C	-0.08105	2.48124	-0.31928
C	-0.55826	3.78879	-0.49979
C	-1.91350	3.97440	-0.82058
C	-2.76899	2.86884	-0.91158
C	-2.25431	1.56960	-0.70870
C	-3.01355	0.29669	-0.72104
C	-2.42583	-0.78765	-1.40889
C	-3.03722	-2.07069	-1.41804
C	-4.23868	-2.26053	-0.75771
C	-4.86749	-1.19446	-0.04581
C	-4.24023	0.11185	0.00658
C	-4.85629	1.12519	0.80364
C	-6.05364	0.88606	1.46235
C	-6.68963	-0.38068	1.36994
C	-6.09981	-1.40080	0.63916
C	0.69880	-2.90806	-0.94607
C	1.30413	-4.29007	-0.85948
C	2.78477	0.25441	0.53487
H	3.24056	2.73808	0.73914
H	1.94460	3.96080	0.94387
H	2.61714	3.63712	-0.67231
H	0.11603	4.64258	-0.40152
H	-2.30114	4.98256	-0.99225
H	-3.82655	2.99391	-1.15507
H	-2.55198	-2.87829	-1.97128
H	-4.73266	-3.23797	-0.77677
H	-4.37171	2.09905	0.91537
H	-6.50806	1.67761	2.06599
H	-7.63603	-0.55310	1.89109
H	-6.56946	-2.38854	0.58492
H	1.03265	-4.77191	0.09319
H	2.40416	-4.21367	-0.88772
H	0.96341	-4.90219	-1.70599
H	-1.58788	-0.61200	-2.09903
C	3.78658	0.19847	-0.48069
C	5.00628	-0.40975	-0.13353
C	5.22302	-0.94237	1.14423
C	4.20930	-0.89745	2.11141
C	2.96156	-0.31788	1.82959
C	3.56826	0.69805	-1.91034
H	5.80094	-0.47136	-0.88336
H	6.18633	-1.40277	1.38530
H	4.38936	-1.32749	3.10063
C	1.86179	-0.24584	2.88613
H	2.62887	1.27857	-1.94272
C	4.70399	1.63228	-2.38599
C	3.38842	-0.49279	-2.88403
H	3.22801	-0.12236	-3.91092
H	4.28651	-1.13388	-2.89358
H	2.52242	-1.11725	-2.60959
H	4.46535	2.04098	-3.38207
H	4.86218	2.47753	-1.69499
H	5.66246	1.09413	-2.47709
H	0.89611	-0.16163	2.34925
C	1.78297	-1.50978	3.76496
C	2.02307	1.02389	3.75859
H	0.89923	-1.45177	4.42216
H	1.69543	-2.41859	3.14861
H	2.66422	-1.61538	4.42075
H	1.20105	1.09539	4.49089

H 2.97427 0.99552 4.31744
H 2.02084 1.94680 3.15315

II$_{ortho}$

BP86 Energy = -1589.01939976
Enthalpy 0K= -1588.466296
Enthalpy 298K= -1588.430143
Free Energy 298K= -1588.535279
E(PCM) = -1589.05289757
Dispersion = -0.10386259

Pd -0.14066 -0.34870 -0.23330
O 0.72940 -2.14651 0.03047
O 0.30310 -2.33783 -2.17150
N 1.48919 0.81098 0.28309
N -0.93823 1.46969 -0.35647
C 1.28504 2.11240 0.19468
C 2.33872 3.14819 0.46474
C -0.08660 2.52087 -0.16717
C -0.56127 3.83440 -0.31140
C -1.91241 4.02995 -0.64715
C -2.77226 2.93179 -0.79634
C -2.26146 1.62786 -0.62566
C -2.97895 0.33078 -0.69091
C -2.29593 -0.73228 -1.34279
C -2.84468 -2.04609 -1.37192
C -4.06542 -2.29316 -0.76971
C -4.78282 -1.25508 -0.10154
C -4.22600 0.08380 -0.02649
C -4.93206 1.06848 0.73276
C -6.14779 0.77220 1.32957
C -6.71382 -0.52619 1.21167
C -6.03715 -1.51933 0.52007
C 0.75202 -2.82004 -1.11159
C 1.38615 -4.19383 -1.01813
C 2.76528 0.22269 0.54107
H 3.23658 2.69185 0.90237
H 1.95116 3.91826 1.15319
H 2.63091 3.65686 -0.47153
H 0.11128 4.68538 -0.18085
H -2.29507 5.04435 -0.79103
H -3.82254 3.07321 -1.06126
H -2.29450 -2.82627 -1.90373
H -4.50826 -3.29420 -0.80519
H -4.50155 2.06455 0.86467
H -6.67208 1.54123 1.90481
H -7.67616 -0.74387 1.68447
H -6.45387 -2.52943 0.44965
H 1.04964 -4.72201 -0.11247
H 2.48202 -4.08631 -0.95035
H 1.14151 -4.77828 -1.91598
H -1.48368 -0.51221 -2.05879
C 3.76265 0.22816 -0.48001
C 4.97866 -0.41348 -0.18101
C 5.19614 -1.03458 1.05543
C 4.18615 -1.04811 2.02787
C 2.94314 -0.43884 1.79299
C 3.54610 0.82391 -1.87260
H 5.76838 -0.43172 -0.93861
H 6.15612 -1.51903 1.25985
H 4.36569 -1.54804 2.98366
C 1.84722 -0.42796 2.85607
H 2.59443 1.38498 -1.87298
C 4.66759 1.81401 -2.26361
C 3.40564 -0.29598 -2.93255
H 3.24548 0.14621 -3.93070
H 4.32176 -0.90924 -2.98035
H 2.55455 -0.96165 -2.71429
H 4.43632 2.28436 -3.23403
H 4.79784 2.61385 -1.51495
H 5.63915 1.30343 -2.37337
H 0.87855 -0.34081 2.32391
C 1.79205 -1.72493 3.68638
C 1.98706 0.80940 3.77742
H 0.90741 -1.70737 4.34467
H 1.72041 -2.61176 3.03690
H 2.67474 -1.83872 4.33899
H 1.16806 0.83375 4.51617
H 2.94199 0.77861 4.32970
H 1.96142 1.75605 3.21039

TS(II-III)$_{ortho}$

BP86 Energy = -1589.00660643
Enthalpy 0K= -1588.457125
Enthalpy 298K= -1588.421919
Free Energy 298K= -1588.525271
E(PCM) = -1589.03911842
Dispersion = -0.10165045
Nimag=1 (-112.2 cm^{-1})

Pd -0.08256 -0.36514 -0.09933
O 0.81058 -2.16526 -0.44661
O -0.61762 -2.28891 -2.21241
N 1.62942 0.75538 0.30584
N -0.88811 1.42469 0.02465
C 1.38668 2.04357 0.43744
C 2.43411 3.07121 0.75740
C -0.02664 2.45581 0.27147
C -0.50949 3.76811 0.35591
C -1.89347 3.97051 0.22293
C -2.75315 2.89371 -0.01312
C -2.24031 1.57708 -0.15035
C -2.96251 0.29551 -0.28424
C -2.15274 -0.89195 -0.32157
C -2.70159 -2.14010 0.08893
C -4.02931 -2.23708 0.46967
C -4.91118 -1.13147 0.30585
C -4.39538 0.14851 -0.14865
C -5.35278 1.16146 -0.46337
C -6.71171 0.96348 -0.25600
C -7.19569 -0.25476 0.28775
C -6.30846 -1.28749 0.54298
C 0.34199 -2.74057 -1.53096
C 1.06296 -4.00980 -1.94644
C 2.94367 0.18629 0.37411
H 3.38491 2.59065 1.02476
H 2.10151 3.70945 1.59359
H 2.61262 3.73050 -0.11094
H 0.17042 4.60467 0.52994
H -2.30811 4.97826 0.31572
H -3.82566 3.07120 -0.04877
H -2.06627 -3.02892 0.06119

H	-4.43561	-3.18957	0.82613
H	-5.03778	2.07359	-0.97201
H	-7.41887	1.74894	-0.53972
H	-8.26701	-0.38834	0.46355
H	-6.67004	-2.25571	0.90453
H	1.35823	-4.59844	-1.06568
H	1.98374	-3.73258	-2.48741
H	0.42605	-4.60149	-2.61755
H	-1.35336	-1.16346	-1.23879
C	3.86613	0.39814	-0.69150
C	5.12033	-0.23269	-0.58394
C	5.44622	-1.03506	0.51567
C	4.50752	-1.24815	1.53476
C	3.23293	-0.66029	1.48385
C	3.52981	1.19022	-1.95722
H	5.85255	-0.09604	-1.38598
H	6.43284	-1.50507	0.57498
H	4.76903	-1.88719	2.38270
C	2.21655	-0.86725	2.60557
H	2.56765	1.71076	-1.80516
C	4.59196	2.26560	-2.28041
C	3.33470	0.23263	-3.15785
H	3.05929	0.80116	-4.06235
H	4.26381	-0.32113	-3.37587
H	2.53889	-0.50419	-2.95972
H	4.27395	2.86445	-3.15029
H	4.75970	2.95146	-1.43287
H	5.56437	1.81198	-2.53573
H	1.20663	-0.74730	2.15872
C	2.26910	-2.27696	3.22585
C	2.37031	0.21967	3.69762
H	1.42898	-2.40685	3.92846
H	2.19673	-3.05899	2.45307
H	3.19611	-2.44182	3.80153
H	1.60339	0.09319	4.48065
H	3.36153	0.14981	4.17783
H	2.27152	1.23913	3.28649

III$_{ortho}$

BP86 Energy = -1589.03859656
Enthalpy 0K= -1588.484568
Enthalpy 298K= -1588.448736
Free Energy 298K= -1588.552860
E(PCM) = -1589.07008193
Dispersion = -0.10063638

Pd	-0.21398	-0.37883	0.15890
O	0.51746	-2.35199	0.09903
O	0.15219	-2.37792	-2.14004
N	1.62146	0.79132	0.19932
N	-0.93545	1.44511	0.14602
C	1.37962	2.07983	0.27062
C	2.43425	3.14490	0.38770
C	-0.05346	2.47852	0.25782
C	-0.53112	3.79226	0.36517
C	-1.92300	3.98905	0.41133
C	-2.80311	2.90808	0.30654
C	-2.30151	1.59317	0.12650
C	-3.00886	0.30995	0.02416
C	-2.16148	-0.82787	0.14954
C	-2.70679	-2.11875	0.32580
C	-4.08705	-2.29094	0.34250
C	-4.97212	-1.20325	0.10003
C	-4.43871	0.12778	-0.11243
C	-5.36160	1.14874	-0.48934
C	-6.72614	0.89648	-0.57012
C	-7.24914	-0.38952	-0.27979
C	-6.38020	-1.42215	0.03199
C	0.58139	-2.93809	-1.01164
C	1.15385	-4.31391	-1.16095
C	2.95212	0.24818	0.16686
H	3.43101	2.69919	0.50635
H	2.22531	3.79659	1.25346
H	2.44222	3.78768	-0.51055
H	0.16050	4.63410	0.43416
H	-2.32405	4.99839	0.54176
H	-3.87558	3.07280	0.40196
H	-2.04783	-2.97823	0.48046
H	-4.51383	-3.28594	0.51395
H	-4.99931	2.13306	-0.79031
H	-7.40306	1.69945	-0.87855
H	-8.32700	-0.56791	-0.33359
H	-6.75935	-2.43377	0.21258
H	1.35904	-4.74770	-0.17465
H	2.09010	-4.25497	-1.74174
H	0.45788	-4.95136	-1.72905
H	-0.21601	-1.47801	-1.89542
C	3.73869	0.34155	-1.01650
C	5.00351	-0.28032	-1.00058
C	5.47237	-0.96173	0.12775
C	4.66939	-1.05387	1.27324
C	3.39275	-0.46761	1.31783
C	3.25780	1.02341	-2.30079
H	5.63009	-0.22670	-1.89678
H	6.46357	-1.42566	0.11485
H	5.04114	-1.59203	2.15007
C	2.53534	-0.53390	2.58223
H	2.27913	1.49642	-2.10376
C	4.22717	2.13367	-2.76913
C	3.03896	-0.01241	-3.42963
H	2.65175	0.48249	-4.33658
H	3.98490	-0.51226	-3.69982
H	2.31951	-0.79413	-3.13273
H	3.81896	2.64847	-3.65520
H	4.40443	2.88806	-1.98464
H	5.20841	1.71784	-3.05409
H	1.47619	-0.42433	2.26791
C	2.65002	-1.87623	3.33150
C	2.85889	0.64833	3.52808
H	1.91687	-1.90996	4.15469
H	2.45492	-2.73070	2.66325
H	3.64710	-2.01336	3.78412
H	2.20378	0.62730	4.41566
H	3.90495	0.59151	3.87550
H	2.72726	1.62415	3.03027

1$_{peri}$

BP86 Energy = -1588.62554525
Enthalpy 0K= -1588.083819
Enthalpy 298K= -1588.048378
Free Energy 298K= -1588.151743
E(PCM) = -1588.63417815

Dispersion = -0.10507424

C	-3.17466	-0.50592	-1.19370
C	-2.65877	0.23999	-0.09876
C	-3.37143	0.37572	1.12443
C	-4.64611	-0.21954	1.20320
C	-5.19271	-0.92811	0.12721
C	-4.45649	-1.06998	-1.05602
N	-1.33959	0.80204	-0.21639
C	-1.15049	2.06876	-0.49109
C	0.25689	2.51795	-0.53970
N	1.22158	1.55905	-0.28588
C	2.53822	1.91716	-0.20860
C	2.90559	3.25014	-0.54772
C	1.94636	4.21223	-0.84542
C	0.59313	3.84950	-0.80932
Pd	0.47735	-0.31297	-0.13974
C	2.26098	-1.19242	-0.25898
C	3.47787	-0.48770	0.03211
C	4.69971	-1.26543	0.19453
C	4.70040	-2.66165	-0.08735
C	3.53517	-3.29335	-0.48417
C	2.32096	-2.56425	-0.53613
C	3.59058	0.94966	0.18212
C	4.79184	1.49708	0.66987
C	5.93145	0.71108	0.93096
C	5.89616	-0.64488	0.64865
O	-0.47480	-2.13895	-0.10314
C	-0.78148	-2.50432	1.12836
C	-1.58083	-3.80792	1.18712
C	-2.25952	3.05808	-0.75248
O	-0.48458	-1.86763	2.15499
H	-3.23635	2.55757	-0.70996
H	-2.14126	3.52152	-1.74755
H	-2.25061	3.87111	-0.00580
H	-0.19128	4.58243	-1.00717
H	2.24507	5.23161	-1.10695
H	3.96332	3.50872	-0.60682
H	4.85055	2.56838	0.87950
H	6.83733	1.18070	1.32634
H	6.78699	-1.26844	0.78802
H	1.38914	-3.09187	-0.75814
H	3.53443	-4.36448	-0.71550
H	5.63829	-3.21739	0.02388
H	-2.60697	-3.62386	0.82538
H	-1.62562	-4.17457	2.22239
H	-1.13290	-4.57419	0.53411
C	-2.81078	1.11363	2.34317
H	-5.21488	-0.12642	2.13470
H	-6.18818	-1.37651	0.21285
H	-4.88118	-1.63261	-1.89418
C	-2.39865	-0.66273	-2.50248
H	-1.79209	1.46012	2.09611
C	-3.66595	2.35178	2.70098
C	-2.67808	0.16994	3.56091
H	-2.24163	0.71804	4.41474
H	-3.66465	-0.21075	3.88107
H	-2.02493	-0.68498	3.32272
H	-3.21512	2.89695	3.54845
H	-3.76223	3.05294	1.85433
H	-4.68646	2.05668	3.00257
H	-1.35937	-0.33644	-2.31328
C	-2.32240	-2.13288	-2.96500
C	-2.99124	0.24059	-3.60943
H	-1.70195	-2.20929	-3.87509
H	-1.86470	-2.75247	-2.17833
H	-3.31819	-2.54236	-3.21144
H	-2.40053	0.15519	-4.53839
H	-4.03107	-0.05016	-3.84295
H	-3.00447	1.30304	-3.31008

I_{peri}

BP86 Energy = -1589.04131192
Enthalpy 0K= -1588.487863
Enthalpy 298K= -1588.452462
Free Energy 298K= -1588.557722
E(PCM) = -1589.07377120
Dispersion = -0.10309588

Pd	0.10094	-0.09169	-0.49985
O	-0.50956	-1.79852	-1.50491
O	1.54493	-1.05085	-1.70853
N	-1.57316	0.59666	0.36029
N	0.82415	1.61633	0.37283
C	-1.50904	1.78471	0.91834
C	-2.68383	2.48150	1.54156
C	-0.17192	2.40258	0.91197
C	0.09296	3.68433	1.40920
C	1.40658	4.17673	1.35178
C	2.41271	3.35699	0.84000
C	2.11418	2.05540	0.36417
C	3.20451	1.17958	-0.13228
C	3.99265	1.64475	-1.18714
C	5.06141	0.86733	-1.69742
C	5.34992	-0.36485	-1.13233
C	4.59467	-0.86416	-0.03092
C	3.49932	-0.08325	0.49728
C	2.80037	-0.58002	1.63896
C	3.14077	-1.79996	2.20849
C	4.19695	-2.58103	1.66850
C	4.91156	-2.11599	0.57572
C	0.66924	-1.93879	-2.03548
C	0.97036	-3.05028	-2.98889
C	-2.78487	-0.17257	0.24977
H	-3.57721	1.84426	1.51391
H	-2.90443	3.42132	1.00497
H	-2.46325	2.74525	2.59039
H	-0.71533	4.28768	1.82841
H	1.63974	5.17812	1.72474
H	3.45533	3.68370	0.81948
H	3.76036	2.61108	-1.64781
H	5.65021	1.24531	-2.53813
H	6.17550	-0.97162	-1.51998
H	2.59882	-2.15793	3.08948
H	4.45538	-3.53958	2.12867
H	5.74342	-2.69939	0.16618
H	0.65758	-2.75014	-4.00434
H	0.40453	-3.95255	-2.71216
H	2.05001	-3.25742	-3.00359
H	1.99866	0.01580	2.08528
C	-3.02734	-1.18651	1.21727
C	-4.21118	-1.93337	1.08195
C	-5.10025	-1.70418	0.02393

C	-4.81599	-0.72139	-0.93281
C	-3.65120	0.06392	-0.85518
C	-2.06622	-1.47687	2.37006
H	-4.43722	-2.71028	1.81916
H	-6.01464	-2.29965	-0.06005
H	-5.50917	-0.55990	-1.76441
C	-3.35265	1.09325	-1.94573
H	-1.19777	-0.79988	2.27242
C	-2.72495	-1.20335	3.74207
C	-1.52439	-2.92300	2.28952
H	-2.00194	-1.37549	4.55726
H	-3.09201	-0.16598	3.82233
H	-3.58439	-1.87364	3.91345
H	-0.79683	-3.10329	3.09905
H	-2.33516	-3.66280	2.40076
H	-1.02583	-3.10952	1.32422
H	-2.41396	1.61457	-1.68406
C	-3.11877	0.39750	-3.30809
C	-4.46742	2.15909	-2.05606
H	-4.19512	2.91997	-2.80674
H	-5.42354	1.70973	-2.37406
H	-4.64569	2.67248	-1.09603
H	-2.84749	1.14279	-4.07509
H	-2.31042	-0.34900	-3.24285
H	-4.03039	-0.12076	-3.65152

TS(I-II)$_{peri}$

BP86 Energy = -1589.01138077
Enthalpy 0K= -1588.458460
Enthalpy 298K= -1588.422978
Free Energy 298K= -1588.527742
E(PCM) = -1589.04417895
Dispersion = -0.1058258
Nimag=1 (-80.2 cm^{-1})

Pd	-0.23302	-0.32953	-0.17446
O	0.66972	-2.05426	0.41221
O	-0.43891	-2.44935	-1.45734
N	1.44995	0.79438	0.02906
N	-0.99062	1.52684	-0.60400
C	1.36414	1.99537	-0.50880
C	2.52983	2.93899	-0.62419
C	0.01418	2.42592	-0.90128
C	-0.26388	3.69782	-1.42253
C	-1.60118	4.08019	-1.59905
C	-2.60876	3.21796	-1.16388
C	-2.29238	1.94379	-0.62799
C	-3.35211	1.14990	0.04371
C	-4.09298	1.82299	1.02239
C	-5.06349	1.14968	1.80437
C	-5.30688	-0.19787	1.59263
C	-4.61006	-0.91496	0.57622
C	-3.61320	-0.23702	-0.22349
C	-2.98728	-0.95553	-1.28663
C	-3.31733	-2.28797	-1.53707
C	-4.27069	-2.95730	-0.73259
C	-4.90443	-2.28197	0.30267
C	0.27309	-2.89455	-0.51660
C	0.67230	-4.33928	-0.37731
C	2.66242	0.19435	0.48182
H	3.41994	2.52546	-0.13278
H	2.28445	3.91020	-0.16225
H	2.77343	3.12721	-1.68497
H	0.55305	4.37547	-1.67905
H	-1.84914	5.05138	-2.03647
H	-3.66153	3.50236	-1.22998
H	-3.88667	2.87995	1.22125
H	-5.60727	1.69915	2.57804
H	-6.05230	-0.72897	2.19419
H	-2.83290	-2.81200	-2.36353
H	-4.52169	-4.00153	-0.94192
H	-5.66012	-2.78677	0.91421
H	0.00758	-4.83031	0.35431
H	1.70322	-4.42385	-0.00128
H	0.57269	-4.85289	-1.34414
H	-2.31293	-0.43593	-1.97604
C	3.64721	-0.22637	-0.46352
C	4.80120	-0.84152	0.05424
C	4.97156	-1.04348	1.42999
C	3.97433	-0.64719	2.33214
C	2.79152	-0.03718	1.88543
C	3.48888	-0.08393	-1.97898
H	5.58104	-1.17361	-0.63821
H	5.88412	-1.52047	1.80113
H	4.11550	-0.82296	3.40196
C	1.71110	0.41537	2.86477
H	2.59078	0.52431	-2.18685
C	4.69704	0.63251	-2.62630
C	3.25531	-1.46321	-2.64156
H	4.50855	0.79656	-3.70049
H	4.90174	1.61060	-2.15946
H	5.61660	0.02877	-2.54570
H	3.15101	-1.34657	-3.73361
H	4.10418	-2.14243	-2.45356
H	2.33856	-1.94242	-2.26310
H	0.74481	0.38343	2.32249
C	1.57444	-0.50614	4.09288
C	1.95029	1.88138	3.30528
H	1.14159	2.21855	3.97568
H	2.90500	1.97336	3.85113
H	1.98976	2.57262	2.44590
H	0.69234	-0.20858	4.68390
H	1.44895	-1.55979	3.79548
H	2.44785	-0.43621	4.76391

II$_{peri}$

BP86 Energy = -1589.02429348
Enthalpy 0K= -1588.470520
Enthalpy 298K= -1588.434864
Free Energy 298K= -1588.537510
E(PCM) = -1589.05783639
Dispersion = -0.10990894

Pd	-0.46982	-0.25285	-0.23702
O	0.45742	-2.04567	-0.10074
O	0.78072	-1.86564	-2.33272
N	1.22883	0.82241	0.28282
N	-1.24888	1.63324	-0.18959
C	1.07422	2.12686	0.20713
C	2.15073	3.12334	0.53760
C	-0.27962	2.60668	-0.14058
C	-0.59540	3.95783	-0.34726

C	-1.92749	4.31110	-0.61122
C	-2.91447	3.32360	-0.57759
C	-2.56489	1.97668	-0.31949
C	-3.58695	0.94019	-0.04315
C	-4.69540	1.29935	0.73645
C	-5.60611	0.33023	1.21874
C	-5.39715	-1.01258	0.94265
C	-4.30229	-1.42080	0.12590
C	-3.39974	-0.43276	-0.40877
C	-2.36559	-0.86845	-1.32560
C	-2.23467	-2.24090	-1.63908
C	-3.06451	-3.20670	-1.03467
C	-4.09420	-2.79644	-0.19348
C	0.97164	-2.45403	-1.25107
C	1.83983	-3.69599	-1.12266
C	2.47636	0.18673	0.57568
H	3.02549	2.62376	0.97445
H	1.76893	3.87278	1.25145
H	2.47951	3.66311	-0.36797
H	0.18957	4.71613	-0.31597
H	-2.19214	5.35111	-0.82191
H	-3.96291	3.57393	-0.75590
H	-4.82859	2.34421	1.03420
H	-6.45044	0.64529	1.83807
H	-6.07201	-1.77610	1.34326
H	-1.47712	-2.52747	-2.37382
H	-2.93094	-4.26690	-1.26669
H	-4.78011	-3.53633	0.23417
H	1.47016	-4.37057	-0.33607
H	2.86141	-3.38322	-0.84641
H	1.88454	-4.21718	-2.08950
H	-1.96832	-0.15368	-2.06529
C	3.54678	0.22496	-0.37064
C	4.72102	-0.47340	-0.02844
C	4.83782	-1.17589	1.17671
C	3.76438	-1.21148	2.07769
C	2.55848	-0.54936	1.79821
C	3.48668	0.94103	-1.72325
H	5.56152	-0.46464	-0.72964
H	5.76843	-1.70097	1.41426
H	3.86519	-1.76783	3.01359
C	1.40914	-0.54885	2.80366
H	2.51024	1.45007	-1.81275
C	4.59889	2.01120	-1.85022
C	3.57818	-0.06112	-2.89938
H	4.47546	2.57558	-2.78990
H	4.59846	2.72942	-1.01355
H	5.59763	1.54366	-1.87967
H	3.52725	0.48375	-3.85767
H	4.53765	-0.60647	-2.87999
H	2.75534	-0.79251	-2.87432
H	0.47105	-0.41118	2.22878
C	1.27233	-1.87423	3.57730
C	1.53720	0.64817	3.77824
H	0.68204	0.67079	4.47505
H	2.46110	0.56767	4.37643
H	1.56850	1.61483	3.24639
H	0.35398	-1.85521	4.18789
H	1.21104	-2.73222	2.88903
H	2.11397	-2.04149	4.27145

TS(II-III)$_{peri}$

BP86 Energy = -1589.01076755
Enthalpy 0K= -1588.460032
Enthalpy 298K= -1588.425192
Free Energy 298K= -1588.526854
E(PCM) = -1589.07303781
Dispersion = -0.10525139
Nimag = 1 (-72.3 cm^{-1})

Pd	-0.33774	-0.24195	-0.07592
O	0.62190	-1.96496	-0.63762
O	-0.78239	-1.92399	-2.42591
N	1.41717	0.73884	0.35551
N	-1.10536	1.60529	0.25246
C	1.25010	1.98885	0.71890
C	2.36428	2.87175	1.21108
C	-0.12384	2.51647	0.60236
C	-0.40535	3.87210	0.78514
C	-1.72165	4.31439	0.59283
C	-2.69445	3.39367	0.22696
C	-2.39270	2.01250	0.03496
C	-3.50259	1.06434	-0.26511
C	-4.75907	1.61540	-0.59622
C	-5.95644	0.87562	-0.55082
C	-5.92826	-0.43120	-0.09040
C	-4.68274	-1.07253	0.15638
C	-3.43639	-0.36666	-0.06706
C	-2.23591	-1.16729	-0.10885
C	-2.27345	-2.50696	0.34111
C	-3.47072	-3.11874	0.76307
C	-4.66289	-2.42671	0.60578
C	0.21724	-2.38571	-1.81899
C	1.06769	-3.48893	-2.42322
C	2.70687	0.10082	0.32264
H	3.27911	2.28510	1.36815
H	2.08153	3.36151	2.15795
H	2.58824	3.66654	0.47758
H	0.38844	4.56573	1.06821
H	-1.98525	5.36523	0.74074
H	-3.72355	3.73647	0.13097
H	-4.83494	2.66454	-0.88871
H	-6.90021	1.35736	-0.81997
H	-6.85417	-0.99600	0.05989
H	-1.35332	-3.09609	0.29411
H	-3.46534	-4.15162	1.12246
H	-5.62068	-2.91697	0.81100
H	1.38424	-4.20491	-1.65039
H	1.97950	-3.04017	-2.85232
H	0.51127	-3.99736	-3.22187
H	-1.59909	-1.15432	-1.16723
C	3.59689	0.39351	-0.75020
C	4.83181	-0.28284	-0.75893
C	5.17327	-1.19799	0.24412
C	4.26976	-1.47506	1.27813
C	3.01109	-0.85115	1.33446
C	3.25280	1.35035	-1.89455
H	5.53888	-0.08458	-1.57071
H	6.14536	-1.70020	0.21762
H	4.54470	-2.19378	2.05613
C	2.04370	-1.15677	2.47787
H	2.31949	1.88298	-1.63979
C	4.34785	2.41865	-2.11560

C	2.98074	0.56642	-3.20086
H	4.02535	3.13896	-2.88617
H	4.57162	2.97892	-1.19208
H	5.29157	1.96806	-2.46603
H	2.71838	1.25998	-4.01782
H	3.87419	-0.00085	-3.51331
H	2.14881	-0.14657	-3.07811
H	1.04725	-0.76854	2.18727
C	1.88059	-2.67189	2.72169
C	2.46821	-0.42761	3.77494
H	1.74435	-0.62433	4.58409
H	3.45849	-0.77621	4.11572
H	2.53265	0.66499	3.63349
H	1.10395	-2.84910	3.48505
H	1.58647	-3.19045	1.79519
H	2.81140	-3.13258	3.09413

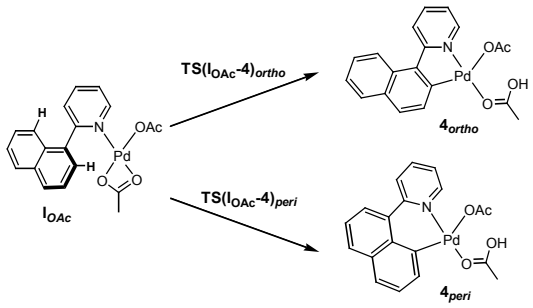
III$_{peri}$

BP86 Energy = -1589.04174300
Enthalpy 0K= -1588.487224
Enthalpy 298K= -1588.451581
Free Energy 298K= -1588.555230
E(PCM) = -1589.07303781
Dispersion = -0.1048092

Pd	-0.44550	-0.27182	0.18960
O	0.51146	-2.13888	-0.06940
O	-0.19714	-2.16073	-2.22478
N	1.39508	0.80216	0.24370
N	-1.16471	1.60257	0.28054
C	1.22296	2.07531	0.49783
C	2.34628	3.04991	0.73390
C	-0.18032	2.54682	0.52561
C	-0.49782	3.88968	0.74247
C	-1.84530	4.28171	0.72106
C	-2.81548	3.33372	0.42515
C	-2.47281	1.97619	0.15462
C	-3.53905	1.01820	-0.20930
C	-4.73452	1.55566	-0.72286
C	-5.88235	0.76974	-0.94497
C	-5.86829	-0.56941	-0.58779
C	-4.67886	-1.18084	-0.10179
C	-3.45057	-0.40965	0.00780
C	-2.24905	-1.11481	0.33549
C	-2.31539	-2.46063	0.71730
C	-3.54142	-3.17429	0.72488
C	-4.69448	-2.55431	0.27689
C	0.48780	-2.67358	-1.20766
C	1.25265	-3.92341	-1.51839
C	2.69994	0.20353	0.12420
H	3.31202	2.52712	0.74299
H	2.21504	3.57181	1.69709
H	2.37451	3.81847	-0.05821
H	0.29431	4.61472	0.93682
H	-2.12827	5.31601	0.93537
H	-3.86704	3.62093	0.43665
H	-4.78697	2.61670	-0.97910
H	-6.78257	1.23015	-1.36133
H	-6.77113	-1.18224	-0.68385
H	-1.40339	-2.99104	1.00650
H	-3.55759	-4.22060	1.04597
H	-5.63847	-3.10506	0.20977
H	1.54531	-4.42853	-0.58942
H	2.16366	-3.64932	-2.07842
H	0.65525	-4.58959	-2.15862
H	-0.66100	-1.34319	-1.87492
C	3.42675	0.34308	-1.09139
C	4.66921	-0.31644	-1.18118
C	5.17336	-1.07643	-0.11966
C	4.43021	-1.20549	1.06123
C	3.17615	-0.58554	1.20867
C	2.91445	1.14521	-2.29108
H	5.25242	-0.22355	-2.10326
H	6.14669	-1.56855	-0.21135
H	4.83072	-1.80008	1.88799
C	2.39170	-0.71305	2.51611
H	1.96063	1.62519	-2.00855
C	3.89890	2.26735	-2.69709
C	2.61998	0.22371	-3.49808
H	3.47521	2.86993	-3.51819
H	4.12470	2.94365	-1.85569
H	4.85736	1.85302	-3.05316
H	2.22309	0.81115	-4.34353
H	3.53686	-0.28264	-3.84538
H	1.87876	-0.55367	-3.24734
H	1.34123	-0.43089	2.30340
C	2.37013	-2.15452	3.06593
C	2.93154	0.27041	3.58263
H	2.33628	0.20287	4.50913
H	3.97993	0.03539	3.83541
H	2.90185	1.31660	3.23352
H	1.70740	-2.21143	3.94591
H	2.00100	-2.86570	2.30952
H	3.36994	-2.48720	3.39326

(b) Reaction with (1-naphthyl)pyridine)

Key Structures:



I_{OAc}

BP86 Energy = -1218.02220376
Enthalpy 0K= -1217.710228
Enthalpy 298K= -1217.685740
Free Energy 298K= -1217.768117
E(PCM) =-1218.03096487
Dispersion =

C	-4.93046	-0.76302	0.71356
C	-3.59615	-0.45194	1.11171
C	-2.79595	0.42067	0.28008
C	-3.36659	0.89540	-0.94041
C	-4.66501	0.56506	-1.30167
C	-5.46108	-0.26117	-0.46407
C	-1.45315	0.72791	0.70368
C	-0.93818	0.15194	1.86950
C	-1.72977	-0.71010	2.66991
C	-3.03467	-0.99754	2.30329
C	-0.59862	1.69247	-0.03891
N	0.67141	1.31524	-0.38447
C	1.51708	2.20522	-0.97129
C	1.11867	3.50926	-1.27721
C	-0.18442	3.91386	-0.95245
C	-1.03831	3.00217	-0.32304
Pd	1.32366	-0.60552	-0.18579
O	2.64437	-0.04090	1.24049
C	3.81643	0.38469	0.79337
O	1.70914	-2.66216	-0.35252
C	0.76405	-2.76221	-1.22527
C	0.46000	-4.06981	-1.90062
O	0.10866	-1.68726	-1.51883
C	4.84323	0.54273	1.91540
O	4.09896	0.61628	-0.39441
H	-5.52676	-1.41944	1.35755
H	-2.76067	1.51134	-1.61113
H	-5.07580	0.93656	-2.24621
H	-6.48548	-0.51105	-0.75849
H	0.08117	0.39657	2.18476
H	-1.30262	-1.13516	3.58338
H	-3.65597	-1.65365	2.92353
H	2.52584	1.81848	-1.16284
H	1.82909	4.18727	-1.75718
H	-0.52637	4.93114	-1.16783
H	-2.04724	3.29075	-0.01725
H	0.68486	-4.90727	-1.22352
H	1.09624	-4.17147	-2.79688
H	-0.59308	-4.09909	-2.21699
H	5.36313	-0.42037	2.05758
H	5.58868	1.29893	1.62893
H	4.36531	0.81274	2.86916

4_{ortho}

BP86 Energy = -1218.04658035
Enthalpy 0K= -1217.735751
Enthalpy 298K= -1217.711765
Free Energy 298K= -1217.792711
E(PCM) = -1218.05294327
Dispersion = -0.05136063

C	4.88646	-1.86734	0.12595
C	3.53818	-1.45688	-0.08617
C	3.14931	-0.09274	0.20231
C	4.13324	0.75266	0.79986
C	5.43493	0.31478	1.01635
C	5.82948	-0.99706	0.65139
C	1.78101	0.29326	-0.07211
C	0.81767	-0.69394	-0.40038
C	1.22316	-2.02846	-0.65921
C	2.55803	-2.38569	-0.54607
C	1.25444	1.66024	-0.11206
N	-0.12462	1.71120	-0.22270
C	-0.77059	2.89342	-0.32643
C	-0.09423	4.11665	-0.33141
C	1.30732	4.09663	-0.27409
C	1.97748	2.87312	-0.17513
Pd	-1.05353	-0.08006	-0.42914
O	-3.02953	0.85632	-0.37607
C	-3.87389	0.79624	0.56537
O	-1.74909	-1.98957	-0.79141
C	-2.35478	-2.67627	0.11845
C	-2.51092	-4.16110	-0.17643
O	-2.79427	-2.23825	1.22681
H	-0.65724	5.05008	-0.40858
H	1.88042	5.02802	-0.32283
H	3.06689	2.84770	-0.19338
H	0.47124	-2.76087	-0.96580
H	2.87720	-3.40928	-0.77795
H	3.85100	1.74423	1.15924
H	6.15674	0.98749	1.49174
H	6.86031	-1.32712	0.81449
H	5.15838	-2.90086	-0.11801
H	-2.45378	-4.35714	-1.25655
H	-3.45984	-4.53273	0.23723
H	-1.69081	-4.70801	0.32116
C	-4.98186	1.82943	0.63724
O	-3.88655	-0.08400	1.51929
H	-1.85713	2.81667	-0.42292
H	-3.23913	-0.97120	1.34739
H	-5.95915	1.32418	0.69332
H	-4.87041	2.41997	1.56222
H	-4.95119	2.49562	-0.23520

TS(I_{OAc}-4)$_{ortho}$

BP86 Energy = -1217.98938035

Enthalpy 0K= -1217.681411
Enthalpy 298K= -1217.657951
Free Energy 298K= -1217.735805
E(PCM) = -1217.99969211
Dispersion = -0.05243082
Nimag = 1 (-115.9cm^{-1})

C	4.93161	-1.56970	-0.64568
C	3.54169	-1.28454	-0.51188
C	3.11705	-0.04872	0.11567
C	4.13787	0.76011	0.70371
C	5.48448	0.43592	0.58820
C	5.89362	-0.71788	-0.12598
C	1.69707	0.24692	0.15197
C	0.77478	-0.81287	-0.09386
C	1.22942	-2.03722	-0.66613
C	2.56803	-2.23248	-0.94500
C	1.11154	1.59845	0.23401
N	-0.25013	1.64562	-0.00577
C	-0.92057	2.81876	-0.04150
C	-0.28150	4.04551	0.15278
C	1.10609	4.04251	0.34753
C	1.79740	2.82737	0.37440
Pd	-1.21178	-0.11002	-0.30016
O	-2.93425	0.80219	-0.93856
C	-3.91561	0.70593	-0.04416
O	-2.15516	-1.92502	-0.38489
C	-1.85919	-2.65218	0.66002
C	-2.72645	-3.88774	0.84043
O	-0.95049	-2.38207	1.49274
H	-0.86147	4.97115	0.12346
H	1.65678	4.98106	0.46397
H	2.88168	2.83669	0.45839
H	0.49602	-2.82075	-0.87241
H	2.90752	-3.15129	-1.43596
H	3.86436	1.60273	1.34021
H	6.23322	1.06793	1.07666
H	6.95744	-0.95406	-0.22705
H	5.22358	-2.49984	-1.14570
H	-3.01593	-4.31133	-0.13248
H	-3.64805	-3.58317	1.36503
H	-2.20263	-4.63476	1.45300
C	-5.26297	1.16353	-0.60743
O	-3.78763	0.28586	1.11258
H	-1.98628	2.72496	-0.26755
H	-0.14569	-1.12214	0.73365
H	-5.68838	0.34908	-1.21856
H	-5.95449	1.38566	0.21792
H	-5.15062	2.04178	-1.26240

4$_{peri}$

BP86 Energy = -1218.03598028
Enthalpy 0K= -1217.725531
Enthalpy 298K= -1217.701526
Free Energy 298K= -1217.782045
E(PCM) = -1218.04337109
Dispersion = -0.0534258

C	-3.27021	-2.82482	-0.47652
C	-3.40118	-1.51213	0.06154
C	-2.27343	-0.59856	0.00353
C	-1.00146	-1.10943	-0.41457
C	-0.92729	-2.39319	-0.95913
C	-2.06670	-3.23785	-1.02333
C	-2.51497	0.78101	0.36739
C	-3.72441	1.13042	0.98412
C	-4.76235	0.19059	1.17186
C	-4.62128	-1.09230	0.66617
C	-1.60566	1.86334	-0.07356
N	-0.28459	1.61129	-0.32969
C	0.49972	2.58720	-0.86497
C	0.03644	3.87098	-1.14055
C	-1.30821	4.16404	-0.86329
C	-2.12133	3.15597	-0.34903
Pd	0.64181	-0.13638	0.11210
O	2.30682	1.01330	0.96668
C	3.47573	1.17266	0.51701
O	1.49645	-1.95306	0.60908
C	2.52706	-2.40756	-0.01493
C	2.91294	-3.84676	0.29694
O	3.23773	-1.77596	-0.86256
H	1.53212	2.30018	-1.06734
H	0.71480	4.61034	-1.57351
H	-1.72409	5.15393	-1.07505
H	-3.18555	3.34142	-0.19506
H	-3.87965	2.15802	1.32656
H	-5.68578	0.49498	1.67414
H	-5.44494	-1.81236	0.73476
H	0.03539	-2.78255	-1.29925
H	-1.97118	-4.23836	-1.45970
H	-4.13654	-3.49487	-0.44612
H	2.20559	-4.30923	0.99837
H	3.93046	-3.86818	0.72104
H	2.94368	-4.42395	-0.64192
C	4.37471	2.22396	1.13915
O	4.01358	0.49365	-0.45558
H	3.49581	-0.46669	-0.67495
H	4.99425	2.70482	0.36693
H	3.77967	2.96879	1.68473
H	5.05956	1.72935	1.84951

TS(I$_{OAc}$-4)$_{ortho}$

BP86 Energy = -1217.98676442
Enthalpy 0K= -1217.679450
Enthalpy 298K= -1217.655951
Free Energy 298K= -1217.733511
E(PCM) = -1217.99613356
Dispersion = -0.05517856
Nimag = 1 (-589.4 cm^{-1})

C	1.19299	3.12612	1.11934
C	1.12000	1.91848	0.38111
N	-0.01756	1.65163	-0.34113
C	-0.93829	2.63866	-0.52087
C	-0.84106	3.88915	0.08794
C	0.21576	4.11212	0.98184
C	2.31340	1.03688	0.28584
C	2.28556	-0.36820	-0.03825
C	3.54961	-1.02121	-0.32831
C	4.77804	-0.31653	-0.18692
C	4.78338	1.01770	0.17923
C	3.55756	1.68578	0.38039

C	1.08226	-1.16003	-0.11028
C	1.16620	-2.48550	-0.58367
C	2.39348	-3.08998	-0.93073
C	3.56919	-2.37516	-0.77310
Pd	-0.78791	-0.25688	-0.46116
O	-1.78431	-2.00895	0.00270
C	-1.55322	-2.32547	1.24312
O	-0.59181	-1.86842	1.93559
O	-2.55831	0.39814	-1.29532
C	-3.55116	0.50925	-0.41937
O	-3.43207	0.46055	0.81251
C	-4.90971	0.69924	-1.10073
C	-2.53787	-3.29590	1.86615
H	-1.78777	2.35107	-1.14495
H	-1.61468	4.63887	-0.09543
H	0.28211	5.03946	1.55916
H	2.02872	3.27466	1.80612
H	3.58398	2.76463	0.55294
H	5.72286	1.57139	0.26924
H	5.71437	-0.84707	-0.39264
H	0.24444	-3.07043	-0.65069
H	2.41136	-4.12315	-1.29200
H	4.53906	-2.83481	-0.99415
H	-2.91101	-4.00836	1.11614
H	-3.39642	-2.70796	2.23306
H	-2.07757	-3.82156	2.71415
H	0.24036	-1.17523	0.89515
H	-5.63255	1.11172	-0.38210
H	-4.83070	1.35157	-1.98459
H	-5.27454	-0.28257	-1.44840

3. CRYSTALLOGRAPHIC STUDIES

Data for **1**, **2** (Fig. S1) and **3** (Fig. S2) were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table S2. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement based on full-matrix least-squares on F^2 employed SHELXTL version 6.10.[10] Hydrogen atoms were included in calculated positions (C-H = 0.95-1.00 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. For compounds **1** and **2**, the SQUEEZE option in PLATON was used to remove disordered solvent molecules (CH_2Cl_2 (**1**), H_2O (**2**)). CCDC reference numbers 912611 - 912613.

Table S2. Crystallographic and data processing parameters for **1**, **2** and **3**

Complex	**1**	**2**	**3**
Formula	$C_{31}H_{32}N_2OPd{\cdot}2CH_2Cl_2$	$C_{32}H_{36}N_2O_2Pd{\cdot}1.5H_2O$	$C_{20}H_{19}NO_3Pd{\cdot}CH_2Cl_2$
M	740.84	614.05	512.69
Crystal size (mm^3)	0.43 x 0.38 x 0.12	0.26 x 0.17 x 0.05	0.28 x 0.17 x 0.11
Temperature (K)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	C2/c
a (Å)	16.649(10)	8.965(2)	30.215(10)
b (Å)	11.043(6)	15.135(5)	11.882(4)
c (Å)	18.579(11)	20.959(7)	12.283(4)
α (°)	90	90	90
β (°)	114.617(10)	90.929(6)	106.179(5)
γ (°)	90	90	90
U ($Å^3$)	3106(3)	2843.6(16)	4235(2)
Z	4	4	8
D_c (Mg m^{-3})	1.585	1.434	1.608
F(000)	1512	1276	2064
μ(Mo-K_α)(mm^{-1})	0.976	0.690	1.150
Reflections collected	23875	21814	16176
Independent reflections	6107	5568	4145
R_{int}	0.1476	0.1215	0.1214
Restraints /parameters	0/331	0/341	0/256
Final *R* indices ($I>2\sigma(I)$)	R1 = 0.0627	R1 = 0.0608	R1 = 0.0748
	wR2 = 0.1406	wR2 = 0.1316	wR2 = 0.1648
All data	R1 = 0.0969	R1 = 0.0895	R1 = 0.1215
	wR2 = 0.1514	wR2 = 0.1406	wR2 = 0.1864
Goodness of fit on F^2 (all data)	0.906	1.028	0.951

Data in common: graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit = $[\Sigma(F_o^2 - F_c^2)2/(n-p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

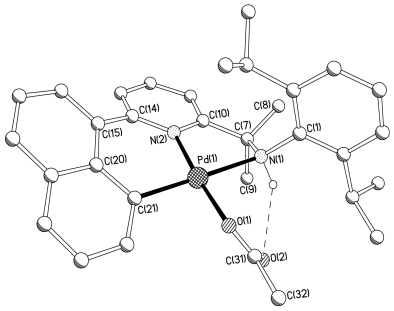


Figure S1 Molecular structure of **2**. Selected bond distances (Å) Pd(1)-C(21), 1.981(5); Pd(1)-N(2), 1.990(4); Pd(1)-N(1), 2.171(4); Pd(1)-O(1), 2.035(4); angles (°) C(21)-Pd(1)-N(2), 93.20(19); N(2)-Pd(1)-N(1), 83.08(15); C(21)-Pd(1)-N(1), 175.11(17); O(1)-Pd(1)-N(1), 93.60(15); O(1)-Pd(1)-C(21), 90.24(18)

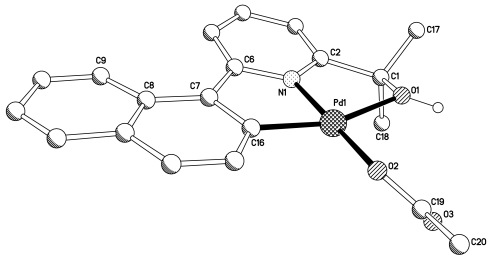


Figure S2 Molecular structure of **3**. Selected bond distances (Å) Pd(1)-C(16), 1.957(7); Pd(1)-N(1), 1.952(6); Pd(1)-O(1), 2.139(5); Pd(1)-O(2), 2.040(5); angles (°) C(16)-Pd(1)-N(1), 82.5(3); O(1)-Pd(1)-N(1), 78.4(2); C(16)-Pd(1)-O(1), 160.2(3); O(2)-Pd(1)-O(1), 105.1(2); O(2)-Pd(1)-C(16), 93.6(3)

Both **2** and **3** have been the subject of single crystal X-ray diffraction studies (Figs. S1 and S2). The structure of **2** shows similar features to that in **1** with the C_{peri},*N*,*N*-ligand again containing both five- and six-membered chelate rings with palladium. The tridentate ligand itself is slightly more twisted than that in **1** [*tors*. N(2)-C(14)-C(15)-C(20) 30.4(8)°] presumably to accommodate for the puckering of the sp^3-CMe_2 moiety. The acetate ligand is again η^1-bound with the pendant oxygen atom undergoing an intramolecular hydrogen bonding interaction with the bound secondary amine hydrogen atom [O(2)···N(1) 2.995(6) Å]. In the X-ray structure of **3** the C_{ortho},*N*,*N*-ligand makes use of two five-membered chelate rings to palladium with the bite angle of the chelate involving O(1) noticeably more acute that with C(16) (78.4(2) *vs.* 82.5(3) °). The non-coordinated oxygen of the O-bound acetate again undergoes hydrogen-bonding in this case intermolecularly with the O-H group of a neighbouring molecule [O(1)···O(3A) 2.588(7) Å] to form a dimeric assembly. In addition, the CH_2Cl_2 molecule of solvation is linked to acetate oxygen O(2) by a C(21)-H(21B)···O(2) hydrogen bond with a C(21)···O(2) distance of 3.074 Å and C(21)-H(21B)…O(2) angle of 158.8 °. The spectroscopic and analytical data further support the structural type.

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