Supporting Information

Air-Stable, Convenient to Handle Pd Based PEPPSI (Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation) Themed Precatalysts of *N/O*-Functionalized N-Heterocyclic Carbenes and its Utility in Suzuki-Miyaura Cross-Coupling Reaction

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The density functional theory calculations were performed on the three transition metal complexes of N-heterocyclic carbenes, namely, *trans*-[1-(benzyl)-3-(N-*t*-butylacetamido)imidazol-2-ylidene]Pd(pyridine)Cl$_2$ (**2**), *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]Pd(pyridine)Cl$_2$ (**3**) and *trans*-[1-(*o*-methoxybenzyl)-3-(*t*-butyl)imidazol-2-ylidene]Pd(pyridine)Br$_2$ (**4**) using GAUSSIAN 03[1] suite of quantum chemical programs.

Input Coordinates for Charge Decomposition Analysis of **2'**, **3'** and **4'**:

Table S1. B3LYP/SDD,6-31G* optimized coordinates of **2'**.

Ground state electronic energy = - 2158.5727952 hartree/particle

O	-3.18681	-3.01404	1.772608
N	1.277695	-1.56344	-0.26092
N	-0.48862	-1.57434	0.975699
N	-3.59052	-1.36321	0.219221
C	0.333479	-0.75488	0.276648
C	1.045846	-2.88563	0.098966
H	1.697705	-3.68365	-0.21805
C	-0.06333	-2.89419	0.878421
H	-0.60335	-3.69306	1.361538
C	2.358269	-1.11917	-1.15974
H	2.379399	-0.0298	-1.08408
H	2.07656	-1.38036	-2.18579
C	3.699643	-1.72421	-0.80532
C	4.310198	-2.64371	-1.66561
H	3.816241	-2.92226	-2.59426
C	5.551556	-3.19977	-1.34543
H	6.016608	-3.91093	-2.02282
C	6.189204	-2.83994	-0.15807
H	7.154582	-3.27073	0.09392
C	5.58481	-1.92069	0.70532
H	6.081155	-1.63376	1.628437
C	4.347725	-1.36308	0.385583
H	3.877485	-0.64323	1.05137
C	-1.67763	-1.14991	1.717924
H	-1.77558	-0.07252	1.57862
H	-1.53691	-1.36888	2.779296
C	-2.91243	-1.93935	1.2377

C	-4.73497	-1.97878	-0.49901
C	-5.16598	-0.9695	-1.57484
H	-5.47625	-0.01999	-1.12314
H	-6.01312	-1.36891	-2.14186
H	-4.35088	-0.7637	-2.27826
O	-4.29425	-3.29953	-1.15899
H	-3.47342	-3.12198	-1.86321
H	-5.13022	-3.74317	-1.71225
H	-3.96012	-4.01306	-0.40184
C	-5.89326	-2.22328	0.485174
H	-5.59232	-2.91799	1.272026
H	-6.75278	-2.64503	-0.0485
H	-6.20704	-1.28161	0.949581
H	-3.15353	-0.55828	-0.2272
C	1.168416	4.13182	0.041553
H	2.089977	3.597852	0.239834
C	1.132881	5.518926	-0.06899
H	2.054796	6.084716	0.016721
C	-0.09188	6.150049	-0.27956
H	-0.1517	7.231517	-0.36336
C	-1.23846	5.363734	-0.3801
H	-2.21604	5.805358	-0.54366
C	-1.12065	3.980925	-0.27453
H	-1.97741	3.326081	-0.37874
Pd	0.190705	1.22081	0.10813
Cl	-1.59722	0.927676	-1.42586
Cl	1.941473	1.391193	1.67422
N	0.061557	3.371357	-0.06313

Table S2. B3LYP/SDD,6-31G* optimized coordinates of **3'**

Ground state electronic energy = - 2103.1995947 hartree/particle

O	-0.06485	2.8512	2.109311
H	-0.30758	1.911097	2.226367
N	1.796834	0.711516	-1.11288
N	0.185318	2.061647	-0.61396
C	0.517455	0.750352	-0.67163
C	1.258975	2.845247	-1.01502
H	1.214265	3.92218	-1.02798
C	2.270405	1.998367	-1.32822
H	3.27794	2.187254	-1.66334
C	2.581134	-0.51019	-1.33736
H	2.883899	-0.53246	-2.38923
H	1.889481	-1.3418	-1.18074
C	3.790483	-0.60814	-0.4286

C	3.641468	-0.55528	0.965517
H	2.653207	-0.42346	1.400383
C	4.757768	-0.66856	1.793162
H	4.632039	-0.62529	2.871629
C	6.031402	-0.83998	1.242128
H	6.898664	-0.92874	1.891006
C	6.185035	-0.89593	-0.14308
H	7.171474	-1.02767	-0.57974
C	5.067671	-0.77663	-0.97368
H	5.190187	-0.8197	-2.05404
C	-1.10085	2.566913	-0.11128
H	-1.65198	1.667228	0.182424
C	-0.90389	3.445391	1.143712
H	-0.38477	4.36786	0.842928
C	-2.28401	3.836855	1.697596
H	-2.13549	4.461453	2.585533
H	-2.80009	2.925117	2.032841
C	-3.132	4.565344	0.64191
H	-4.12153	4.804304	1.050217
H	-2.65669	5.526945	0.397751
C	-3.27446	3.731707	-0.64177
H	-3.82136	4.295473	-1.40709
H	-3.87196	2.833589	-0.42892
C	-1.90591	3.30078	-1.19549
H	-2.02538	2.643442	-2.06419
H	-1.34782	4.186072	-1.53327
C	-2.94481	-2.81622	-0.65154
H	-3.09209	-2.15627	-1.49822
C	-3.76928	-3.91422	-0.42227
H	-4.60316	-4.10419	-1.09014
C	-3.49741	-4.75081	0.659083
H	-4.11974	-5.6185	0.859361
C	-2.4094	-4.4511	1.477352
H	-2.15408	-5.07088	2.330671
C	-1.64021	-3.32643	1.193173
H	-0.80358	-3.03559	1.817211
Pd	-0.64917	-0.80557	-0.25959
Cl	-0.96852	-1.02528	-2.58106
Cl	-0.29908	-0.45286	2.063839
N	-1.8995	-2.5214	0.144839

Table S3. B3LYP/SDD,6-31G* optimized coordinates of **4'**

Ground state electronic energy = - 6287.5150954 hartree/particle

O	2.942783	-1.36995	1.286216
N	0.631592	2.474777	0.300215
N	1.674488	0.759097	-0.52231
C	0.469718	1.168295	-0.04984
C	1.940054	2.86759	0.019913
H	2.300317	3.863046	0.21439
C	2.58786	1.796569	-0.49345
H	3.607891	1.670989	-0.81791
C	-0.39161	3.476084	0.76657
C	-1.66897	2.799867	1.276763
H	-2.19467	2.269603	0.478479
H	-2.33459	3.584047	1.655418
H	-1.45917	2.095941	2.085772
C	-0.72541	4.384579	-0.43195
H	0.162832	4.912887	-0.79592
H	-1.46772	5.133547	-0.13484
H	-1.13626	3.789162	-1.25338
C	0.220891	4.286346	1.926448
H	0.531513	3.623837	2.740921
H	-0.53337	4.977653	2.315337
H	1.081351	4.88868	1.618677
C	1.930974	-0.56999	-1.11667
H	1.258587	-1.2627	-0.60655
H	1.639999	-0.52512	-2.17101
C	3.366348	-1.01458	-0.97996
C	3.847725	-1.4389	0.279789
C	3.288202	-1.83412	2.582648
H	3.577845	-2.89286	2.562713
H	2.38335	-1.70842	3.177785
H	4.105575	-1.24137	3.0142
C	5.165864	-1.88695	0.417411
H	5.538141	-2.21584	1.381117
C	6.007022	-1.91226	-0.69962
H	7.0294	-2.26243	-0.58341
C	5.547754	-1.49863	-1.948
H	6.202937	-1.524	-2.81346

C	4.227904	-1.05333	-2.07632
H	3.854414	-0.7359	-3.04748
C	-3.09303	-2.05957	-1.25813
H	-2.44428	-1.8651	-2.1039
C	-4.16535	-2.94294	-1.34535
H	-4.34362	-3.47605	-2.27361
C	-4.99212	-3.11494	-0.23637
H	-5.84086	-3.79201	-0.27661
C	-4.70604	-2.39953	0.92527
H	-5.31757	-2.49751	1.816364
C	-3.60412	-1.54887	0.940795
H	-3.31742	-1.00205	1.831157
Pd	-1.11966	-0.033	-0.05786
Br	-0.57274	-0.73625	2.279119
Br	-1.51038	0.754184	-2.3978
N	-2.8111	-1.37479	-0.13339

Table S4. Comparison between selected distances [Å] and angles [º] in **2** (X-ray structure)

and **2'** (computed structure).

Parameter	Exp.(**2**)	Calcd.(**2'**)	Parameter	Exp. (**2**)	Calcd. (**2'**)
Pd1-C1	1.957(3)	1.988	N1-C4	1.463(4)	1.474
Pd1-Cl2	2.2913(9)	2.374	N4-C21	1.336(4)	1.347
Pd1-Cl1	2.3026(9)	2.355	N4-C17	1.333(5)	1.347
Pd1-N4	2.089(3)	2.161	C20-C21	1.376(5)	1.392
C1-N1	1.356(4)	1.354	C19-C20	1.355(6)	1.394
C1-N2	1.337(4)	1.355	C18-C19	1.379(6)	1.394
N1-C2	1.385(4)	1.389	C17-C18	1.370(5)	1.392
N2-C3	1.371(4)	1.390	N3-C12	1.328(5)	1.352
N2-C11	1.449(4)	1.464	C10-O1	1.218(4)	1.231
Cl2-Pd1-Cl1	178.14(3)	176.8	Pd1-C1-N2	127.9(2)	126.9
Cl2-Pd1-C1	91.24(9)	89.2	N1-C1-N2	105.1(3)	105.5
Cl1-Pd1-C1	87.62(9)	87.8	Pd1-N4-C21	121.2(2)	121.0
Cl2-Pd1-N4	89.44(8)	91.5	Pd1-N4-C17	120.9(2)	120.4
Cl1-Pd1-N4	91.74(8)	91.4	C1-Pd1-N4	178.63(11)	179.2
Pd1-C1-N1	126.9(2)	127.6			

Table S5. Comparison between selected distances [Å] and angles [º] in **3** (X-ray structure)

and **3'** (computed structure).

Parameter	Exp. (**3**)	Calcd. (**3'**)	Parameter	Exp. (**3**)	Calcd. (**3'**)
Pd1-C1	1.967(4)	1.988	N1-C4	1.466(5)	1.469
Pd1-Cl2	2.3068(10)	2.376	N3-C21	1.343(6)	1.347
Pd1-Cl1	2.3071(10)	2.354	N3-C17	1.352(5)	1.346
Pd1-N3	2.096(3)	2.161	C20-C21	1.409(7)	1.392
C1-N1	1.345(5)	1.354	C19-C20	1.360(8)	1.394
C1-N2	1.343(5)	1.354	C18-C19	1.368(8)	1.393
N1-C3	1.386(6)	1.388	C17-C18	1.376(6)	1.392
N2-C2	1.368(6)	1.388	C12-O1	1.397(6)	1.410
N2-C11	1.496(6)	1.470			
Cl2-Pd1-Cl1	177.74(4)	176.7	Pd1-C1-N2	128.1(3)	127.2
Cl2-Pd1-C1	88.70(11)	90.0	N1-C1-N2	106.4(4)	105.8
Cl1-Pd1-C1	89.07(11)	87.0	Pd1-N3-C21	122.6(3)	120.6
Cl2-Pd1-N3	91.64(9)	91.1	Pd1-N3-C17	119.7(3)	120.8
Cl1-Pd1-N3	90.59(9)	91.8	C1-Pd1-N3	179.66(14)	178.6
Pd1-C1-N1	125.5(3)	126.8			

Table S6. Comparison between selected distances [Å] and angles [º] in **4** (X-ray structure)

and **4'** (computed structure).

Parameter	Exp. (**4**)	Calcd. (**4'**)	Parameter	Exp. (**4**)	Calcd. (**4'**)
Pd1-C1	1.953(9)	1.992	N1-C4	1.498(12)	1.506
Pd1-Br2	2.3929(13)	2.499	N3-C20	1.337(20)	1.346
Pd1-Br1	2.3993(13)	2.501	N3-C16	1.342(12)	1.347
Pd1-N3	2.100(7)	2.160	C19-C20	1.385(14)	1.392
C1-N1	1.359(11)	1.357	C18-C19	1.378(15)	1.394
C1-N2	1.341(12)	1.362	C17-C18	1.354(15)	1.394
N1-C2	1.404(12)	1.382	C16-C17	1.406(14)	1.392
N2-C3	1.365(12)	1.395	C10-O1	1.388(13)	1.355
N2-C8	1.506(11)	1.478			
Br2-Pd1-Br1	173.87(5)	175.9	Pd1-C1-N2	121.1(6)	121.7
Br2-Pd1-C1	86.3(2)	86.5	N1-C1-N2	105.8(8)	105.8
Br1-Pd1-C1	87.6(2)	89.5	Pd1-N3-C20	122.4(6)	120.9
Br2-Pd1-N3	92.58(19)	92.3	Pd1-N3-C16	119.3(6)	120.6
Br1-Pd1-N3	93.5(2)	91.6	C1-Pd1-N3	176.0(3)	177.8
Pd1-C1-N1	133.1(7)	132.4			

[1]. GAUSSIAN 03: Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.