

Tuning Regioselectivity of Palladium-Catalyzed Direct Arylation of Azoles by Metal Coordination

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Supporting Information

Additional Computational Details [S2](#)

Figures and Tables [S2](#)

Cartesian coordinates and energies of species [S6](#)

Additional Computational Details

Orbital populations and compositions were calculated using Mulliken population analysis(MPA)¹ using the *AOMix* program (<http://www.sg-chem.net>).² The fragment molecular orbital analysis and bond order calculations were performed using the same package. Atomic charges were evaluated using the natural population analysis (NPA).³

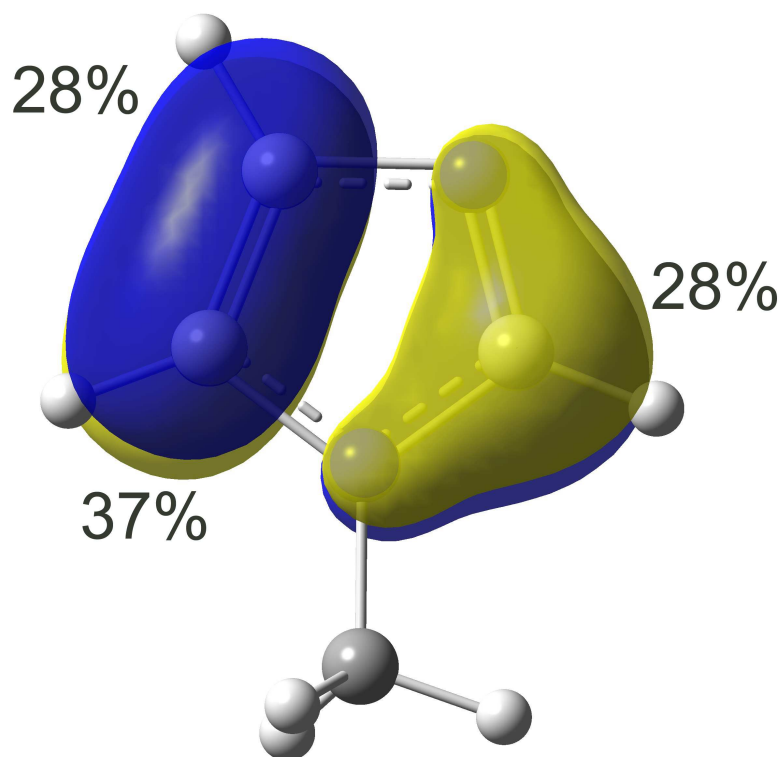


Figure S1. The HOMO of N-methylimidazole (**1**). Isosurface contour value is 0.04 au. MPA-derived atomic contributions (%) of the carbon atoms are shown.

Table S1. Energies and Distortion-Interaction Analysis (kcal mol⁻¹) for CMD TS Structures of Pyridine with and without Coordination to CuCl using the [Pd(C₆H₅)(PMe₃)(OAc)] Catalyst.

Substrate	Position	$\Delta G^\ddagger_{298K}$	$\Delta E^\ddagger$	E_{dist} (PdL) ^b	E_{dist} (ArH)	E_{int}
C₅H₅N	C2	34.8	25.2	16.8	40.7	-32.4
	C3	32.6	23.0	16.2	40.7	-33.9
	C4	34.0	24.4	15.5	41.0	-32.2
[(C₅H₅N)CuCl]^a	C2	25.9	14.2	15.8	36.8	-38.5
	C4	29.4	19.0	15.5	38.7	-35.2
	C5	30.8	20.7	15.1	37.6	-32.0

^aPyridine coordinated to CuCl. ^bDistortion energy (kcal mol⁻¹) for the [Pd(C₆H₅)(PMe₃)(OAc)] catalyst.

Table S2. Energies (kcal mol⁻¹) of CMD TS Structures of N-Methylinidazole (1) with and without Coordination to CuCl using the [Pd(C₆H₅)(PMe₃)(OAc)] Catalyst at the B3LYP/TZVP (SDD for Cu and Pd) Level of Theory.

Substrate	Position	$\Delta G^\ddagger_{298K}$	$\Delta E^\ddagger$
1	C2	27.0	16.6
	C4	29.9	20.5
	C5	25.3	14.7
1.CuCl^a	C2	21.1	8.8
	C4	25.0	13.8
	C5	22.7	12.3

^a N-Methylinidazole coordinated to CuCl.

Table S3. Energies (kcal mol⁻¹) of CMD TS Structures of N-Methylinidazole (1) with and without Coordination to CuCN using the [Pd(C₆H₅)(PMe₃)(OAc)] Catalyst at the B3LYP/TZVP (DZVP for Cu and Pd) Level of Theory.

Substrate	Position	$\Delta G_{298K}^\ddagger$	$\Delta E^\ddagger$
1	C2	26.5	15.9
	C4	29.6	20.2
	C5	25.0	14.3
1.CuCN^a	C2	17.8	5.5
	C4	22.9	11.1
	C5	21.6	10.8

^a N-Methylinidazole coordinated to CuCN.

Table S4. Gibbs Free Energies (kcal mol⁻¹) of CMD TS Structures of Oxazole (2) with and without Coordination to CuCl using the [Pd(C₆H₅)(PMe₃)(OAc)] Catalyst at the B3LYP/TZVP (DZVP for Cu and Pd) Level of Theory in Gas Phase and in Aqueous Solution.

Substrate	Position	$\Delta G_{298K}^\ddagger$ in gas phase	$\Delta G_{298K}^\ddagger$ in aqueous solution	$\Delta E^\ddagger$ in aqueous solution
2	C2	25.3	31.4	20.8
	C4	28.9	36.0	26.1
	C5	23.5	30.3	20.2
2.CuCl^a	C2	15.4	27.6	16.6
	C4	20.3	33.7	22.0
	C5	19.0	29.6	18.9

^a Oxazole coordinated to CuCl.

Table S5. Cu-N Bond Orders and NPA-derived^a Atomic Charges (au) of Cu, Cl, C2 and N3 atoms, and the Net Electron Donation (Δq) from the N-Methylimidazole Ligand to the Cu(L) Fragment.

Species	B(Cu-N)	q(Cu)	q(Cl)	q(C2)	q(N3)	Δq
CuCl	-	+0.645	-0.645	-	-	-
1	-	-	-	+0.150	-0.442	-
1 (deprotonated at C2 position)	-	-	-	-0.084	-0.609	-
1.CuCl	0.52	+0.505	-0.634	+0.198	-0.535	0.129
1.CuCl (deprotonated at C2 position)	0.64	+0.514	-0.703	+0.005	-0.689	0.189
1.Cu⁺	0.68	+0.861	-	+0.208	-0.661	0.139
1.Cu⁺ (deprotonated at C2 position)	0.86	+0.734	-	+0.010	-0.751	0.266

^aNatural population analysis (NPA) charges in the Gaussian 09 implementation (a 3*d*, 4*s*, and 4*p* valence shell for Cu atom)

Absolute electronic energies E (au), Gibbs free energies G (au), energies of frontier orbitals (eV) and Cartesian coordinates for lowest-energy CMD transition states using the [Pd(PMe₃)(Ph)(OAc)] catalyst

1

No imaginary frequencies

E= -265.617336

G= -265.547615 au

HOMO= -6.3928 LUMO= 0.3097 Gap= 6.7025 eV

C	0.227483	1.111992	-0.000012
C	1.500204	0.606044	0.000015
N	1.471324	-0.766997	0.000013
C	0.198553	-1.084576	-0.000011
N	-0.608868	0.016433	-0.000036
C	-2.060338	0.032073	0.000023
H	-0.152378	2.119502	-0.000024
H	2.431153	1.149300	0.000026
H	-0.203337	-2.086190	-0.000021
H	-2.423076	-0.994445	-0.000385
H	-2.442466	0.535934	0.889365
H	-2.442499	0.536643	-0.888898

1.CuCl

No imaginary frequencies

E= -2366.515169

G= -2366.449956 au

HOMO= -5.7969 LUMO= -0.9614 Gap= 4.8355 eV

C	-2.610783	1.142651	-0.000016
C	-1.274918	1.416236	-0.000010
C	-1.470751	-0.738046	-0.000042
N	-2.723810	-0.231393	-0.000050
C	-3.963853	-0.995352	-0.000019
H	-3.472462	1.786744	-0.000015
H	-0.778218	2.370370	-0.000004
H	-1.258595	-1.793759	-0.000062
H	-3.724545	-2.056529	-0.000349
H	-4.549309	-0.766044	0.890283
H	-4.549619	-0.765572	-0.889994
N	-0.569538	0.231194	0.000003
Cu	1.337374	0.015550	0.000016
Cl	3.442598	-0.245747	0.000031

1.Cu⁺

No imaginary frequencies

E= -1905.982708

G= -1905.914473 au

HOMO= -11.1151 LUMO= -7.2141 Gap= 3.9011 eV

C	-1.891606	-0.890154	0.000000
C	-1.381624	0.370998	0.000000
C	0.303815	-1.012030	0.000000
N	-0.815296	-1.751286	0.000000
C	-0.887703	-3.215066	0.000000
H	-2.908068	-1.243329	0.000000
H	-1.903226	1.311764	0.000000
H	1.295555	-1.431555	0.000000

H	0.121535	-3.619221	0.000000
H	-1.411171	-3.556921	0.891212
H	-1.411171	-3.556921	-0.891212
N	0.000000	0.286016	0.000000
Cu	1.209184	1.752779	0.000000

Substrate **1**, CMD TS at the C2 site.

One imaginary frequency: $i1030\text{ cm}^{-1}$

E= -6126.805803

G= -6126.514488 au

HOMO= -5.7602 LUMO= -1.4482 Gap= 4.3120 eV

Pd	-0.439293	0.119734	-0.073521
C	3.506743	1.210759	1.301230
C	2.141620	0.926497	1.233084
C	1.554346	0.514016	0.033978
C	2.364213	0.390878	-1.096908
C	3.726681	0.679349	-1.029816
C	4.303954	1.092007	0.167705
O	-2.655920	-0.217137	-0.084837
C	-3.120856	-1.342657	0.202293
P	-0.880159	2.448013	-0.121800
O	-2.406475	-2.376589	0.443562
H	1.541432	1.028011	2.131023
H	4.339083	0.573760	-1.918509
H	5.363087	1.314619	0.217535
H	3.942824	1.526740	2.242758
H	1.939271	0.050331	-2.033125
C	-4.617112	-1.540015	0.255513
H	-4.884149	-2.177588	1.097622
H	-5.129773	-0.582990	0.320516
H	-4.931286	-2.051031	-0.657533
C	-1.296902	3.172519	1.527550
H	-0.439572	3.075280	2.193768
H	-1.564389	4.227603	1.439114
H	-2.133615	2.621927	1.957450
C	-2.368009	2.840160	-1.141745
H	-3.189991	2.204920	-0.815296
H	-2.643060	3.893075	-1.052262
H	-2.156089	2.609436	-2.186050
C	0.402392	3.602118	-0.773909
H	0.654080	3.318427	-1.795669
H	0.040483	4.632109	-0.760962
H	1.305815	3.521106	-0.171035
H	-1.250566	-2.141780	0.183297
C	0.095346	-2.023895	-0.249921
N	0.290749	-2.412961	-1.521903
C	1.332361	-3.279393	-1.523639
C	1.808994	-3.451984	-0.239679
N	1.034944	-2.664500	0.552701
H	1.687546	-3.749400	-2.427988
C	1.162642	-2.515771	1.989784
H	1.161311	-3.492169	2.477124
H	0.314355	-1.938162	2.351385
H	2.080406	-1.982760	2.243683
H	2.603490	-4.064898	0.153598

Substrate **1**, CMD TS at the C4 site.

One imaginary frequency: $i1025\text{ cm}^{-1}$

E= -6126.798982

G= -6126.509437 au

HOMO= -5.6682 LUMO= -1.1119 Gap= 4.5563 eV

Pd	-0.526941	0.153843	-0.004815
C	2.391426	-2.868691	-0.983228
C	1.501281	-1.796501	-1.043915
C	0.804188	-1.381999	0.092994
C	1.027636	-2.061399	1.293659
C	1.922173	-3.130669	1.356589
C	2.604869	-3.542237	0.216102
O	-2.074358	1.776967	-0.031813
C	-1.751001	2.947275	0.268642
P	-2.329738	-1.391237	-0.141597
O	-0.556519	3.316371	0.538606
H	1.366867	-1.271524	-1.982245
H	2.082839	-3.641230	2.300110
H	3.296611	-4.374991	0.261993
H	2.921559	-3.175168	-1.878584
H	0.511554	-1.756715	2.197770
C	-2.806128	4.027676	0.306931
H	-2.695546	4.654364	-0.580913
H	-3.802822	3.592429	0.314157
H	-2.659926	4.664877	1.178720
C	-3.645752	-0.811384	-1.300659
H	-3.246329	-0.795619	-2.315069
H	-4.522269	-1.461821	-1.267299
H	-3.921948	0.206502	-1.029028
C	-3.244993	-1.613140	1.450511
H	-3.580075	-0.638825	1.806082
H	-4.108852	-2.269829	1.325980
H	-2.574512	-2.040698	2.196316
C	-2.018840	-3.126453	-0.686744
H	-1.310333	-3.600070	-0.008226
H	-2.947092	-3.700692	-0.710852
H	-1.572519	-3.115961	-1.681019
H	0.210254	2.412908	0.326638
C	1.226889	1.485877	-0.056846
C	3.007489	1.806026	-1.259792
N	1.710320	1.743881	-1.352725
H	3.699958	1.998613	-2.066674
C	2.327228	1.403502	0.781374
H	2.393150	1.216828	1.841109
N	3.447977	1.607616	0.028283
C	4.825288	1.626564	0.487911
H	5.482392	1.761143	-0.369977
H	4.991378	2.448826	1.186351
H	5.079433	0.684570	0.975701

Substrate 1, CMD TS at the C5 site.

One imaginary frequency: $i929\text{ cm}^{-1}$

E= -6126.808354

G= -6126.516858 au

HOMO= -5.7865 LUMO= -1.4406 Gap= 4.3460 eV

Pd	-0.409381	0.102972	-0.087150
C	3.419883	1.448750	1.356047
C	2.078020	1.079808	1.248900

C	1.554095	0.615366	0.038542
C	2.406719	0.532742	-1.064402
C	3.745990	0.906805	-0.959138
C	4.258922	1.366654	0.249971
O	-2.615719	-0.354277	-0.081921
C	-3.034306	-1.478525	0.267905
P	-1.040734	2.399348	-0.149450
O	-2.278107	-2.486794	0.506398
H	1.444116	1.158747	2.125816
H	4.391024	0.828443	-1.827170
H	5.300532	1.653503	0.329937
H	3.804834	1.801954	2.306548
H	2.039009	0.159273	-2.011740
C	-4.517442	-1.717126	0.417097
H	-4.719769	-2.213452	1.366503
H	-5.066409	-0.780709	0.353580
H	-4.849460	-2.388154	-0.377825
C	-1.813186	3.008845	1.416449
H	-1.076187	2.985722	2.219497
H	-2.188192	4.028402	1.304030
H	-2.636467	2.346703	1.683841
C	-2.369293	2.678714	-1.402114
H	-3.171040	1.963917	-1.221182
H	-2.757222	3.698138	-1.350336
H	-1.967220	2.498011	-2.399371
C	0.200294	3.705497	-0.543482
H	0.650124	3.492879	-1.513071
H	-0.266321	4.692204	-0.566212
H	0.993918	3.691189	0.202489
H	-1.160117	-2.231600	0.207515
C	0.192002	-2.001660	-0.259707
C	1.912384	-3.421421	-0.320545
N	1.187202	-2.634332	0.501614
H	2.731777	-4.029142	0.034213
C	0.442445	-2.506006	-1.538627
H	-0.120512	-2.288361	-2.434711
N	1.490037	-3.371980	-1.573860
C	1.384771	-2.491421	1.932052
H	2.089481	-3.249170	2.273553
H	1.781254	-1.503780	2.167313
H	0.437550	-2.631026	2.453663

Substrate **1.CuCl**, CMD TS at the C2 site.

One imaginary frequency: $i1076\text{ cm}^{-1}$

E= -8227.720025

G= -8227.430023 au

HOMO= -5.7065 LUMO= -2.0422 Gap= 3.6643 eV

Pd	0.143844	0.230584	-0.665450
C	-4.021670	1.180900	-1.079406
C	-2.663045	0.955349	-1.307097
C	-1.797383	0.683004	-0.244446
C	-2.313619	0.657707	1.051530
C	-3.670482	0.886491	1.278188
C	-4.529319	1.148743	0.215137
O	2.202165	-0.177470	-1.417298
C	2.522454	-1.311958	-1.837722
P	0.624782	2.518697	-0.456263

O	1.761490	-2.340125	-1.780453
H	-2.289648	0.992157	-2.324725
H	-4.053476	0.860867	2.292138
H	-5.582265	1.329760	0.394209
H	-4.678337	1.388707	-1.917001
H	-1.662447	0.459574	1.894493
C	3.894937	-1.521479	-2.429921
H	3.848510	-2.227260	-3.258071
H	4.322663	-0.574725	-2.751856
H	4.538772	-1.952663	-1.659516
C	0.093369	3.585665	-1.864937
H	-0.991703	3.548851	-1.958469
H	0.407184	4.619418	-1.706531
H	0.536863	3.213317	-2.788457
C	2.441522	2.771394	-0.330893
H	2.932543	2.307142	-1.183767
H	2.673909	3.837517	-0.289762
H	2.788052	2.279076	0.578637
C	-0.036230	3.362390	1.037053
H	0.321974	2.826625	1.917098
H	0.316457	4.395193	1.070621
H	-1.124554	3.344633	1.025011
H	0.751493	-2.073651	-1.114136
C	-0.322860	-1.995059	-0.257506
N	-0.134436	-2.163505	1.074571
C	-1.141313	-2.951267	1.555164
C	-1.965830	-3.296618	0.516587
N	-1.448859	-2.698745	-0.597992
H	-1.214300	-3.225734	2.593839
C	-2.010653	-2.770712	-1.937273
H	-2.251440	-3.803952	-2.187288
H	-1.272207	-2.397243	-2.642866
H	-2.909833	-2.156934	-2.005066
H	-2.848246	-3.912579	0.487166
Cu	0.987651	-0.920365	2.011000
Cl	2.076716	0.652609	2.984069

Substrate **1.CuCl**, CMD TS at the C4 site.

One imaginary frequency: $i1068\text{ cm}^{-1}$

E= -8227.711131

G= -8227.421764 au

HOMO= -5.6089 LUMO= -1.6800 Gap= 3.9288 eV

Pd	-0.409226	0.221020	-0.711539
C	2.762020	2.591725	1.059053
C	1.697625	1.705833	0.888942
C	1.075934	1.571126	-0.353196
C	1.533788	2.352103	-1.417641
C	2.599275	3.236843	-1.248056
C	3.217671	3.360315	-0.007767
O	-2.084666	-1.102943	-1.346583
C	-1.861637	-2.221250	-1.861229
P	-1.960389	1.875220	-0.085360
O	-0.695193	-2.730675	-1.994181
H	1.356688	1.122890	1.736757
H	2.941442	3.831123	-2.088194
H	4.041829	4.050560	0.126942
H	3.229824	2.683580	2.033176

H	1.070590	2.271158	-2.394823
C	-3.020657	-3.060397	-2.342451
H	-3.239614	-3.814025	-1.582265
H	-3.904881	-2.444505	-2.489633
H	-2.755833	-3.582081	-3.261216
C	-3.612680	1.128635	0.228552
H	-3.515606	0.437570	1.066712
H	-4.341620	1.904949	0.470014
H	-3.930635	0.566013	-0.646903
C	-2.276965	3.202060	-1.330278
H	-2.614444	2.750031	-2.263116
H	-3.039446	3.896188	-0.970759
H	-1.354138	3.749648	-1.521206
C	-1.609720	2.789967	1.471214
H	-0.673136	3.337143	1.379967
H	-2.423347	3.484362	1.690677
H	-1.522971	2.064120	2.280834
H	0.136724	-2.014808	-1.452298
C	1.175698	-1.419138	-0.734162
C	2.600160	-2.019898	0.841319
N	1.320596	-1.819002	0.613183
H	3.042966	-2.322162	1.776455
C	2.446825	-1.416739	-1.262955
H	2.788313	-1.181361	-2.257049
N	3.329398	-1.794077	-0.281098
C	4.771979	-1.935015	-0.412722
H	5.190969	-2.220464	0.550165
H	5.014511	-2.705888	-1.144851
H	5.214961	-0.988329	-0.721924
Cu	-0.111593	-1.460920	1.838603
Cl	-1.679628	-0.825928	3.156705

Substrate **1.CuCl**, CMD TS at the C5 site.

One imaginary frequency: $i982\text{ cm}^{-1}$

E= -8227.710989

G= -8227.423998 au

HOMO= -5.5114 LUMO= -2.1320 Gap= 3.3794 eV

Pd	-1.401204	-0.247534	-0.020900
C	-0.974574	3.684570	1.676711
C	-1.390654	2.383512	1.388676
C	-0.805514	1.661628	0.345156
C	0.196114	2.270735	-0.411931
C	0.608544	3.572075	-0.125773
C	0.025560	4.283507	0.918452
O	-2.231518	-2.305479	-0.345936
C	-1.840900	-3.264152	0.357975
P	-3.313835	0.583759	-1.130818
O	-0.858447	-3.197081	1.178643
H	-2.177888	1.940956	1.989759
H	1.394289	4.024510	-0.719730
H	0.349117	5.293264	1.139359
H	-1.437804	4.227393	2.493157
H	0.674290	1.735182	-1.222539
C	-2.529361	-4.602147	0.253223
H	-2.740488	-4.990060	1.249876
H	-3.446089	-4.520119	-0.325447
H	-1.854596	-5.308889	-0.234359

C	-4.859819	0.421639	-0.133840
H	-4.793536	1.059723	0.747495
H	-5.736301	0.708530	-0.718409
H	-4.964481	-0.612661	0.192738
C	-3.664515	-0.418700	-2.639477
H	-3.680934	-1.471812	-2.362568
H	-4.618251	-0.132865	-3.087524
H	-2.866349	-0.265790	-3.366171
C	-3.371383	2.321844	-1.739625
H	-2.540228	2.494630	-2.422809
H	-4.312990	2.513843	-2.257418
H	-3.266342	3.009172	-0.901571
H	-0.286578	-2.152532	1.048001
C	0.533074	-1.004511	0.835840
C	2.452478	-0.205308	1.657576
N	1.169766	-0.451216	1.955925
H	3.161477	0.213487	2.352674
C	1.555900	-1.060747	-0.098340
H	1.508853	-1.446170	-1.103558
N	2.729214	-0.563395	0.404745
C	0.540830	-0.194320	3.242280
H	1.310538	0.013252	3.983953
H	-0.128672	0.661984	3.169905
H	-0.023995	-1.072644	3.551912
Cu	4.393162	-0.346177	-0.518444
Cl	6.224138	-0.072238	-1.563879

2

No imaginary frequencies

E= -246.156182

G= -246.123938 au

HOMO= -7.2391 LUMO= -0.5034 Gap= 6.7357 eV

C	-0.594408	-0.966679	0.000000
C	0.753191	-0.876609	0.000000
N	1.119361	0.464844	0.000000
C	0.000000	1.102591	0.000000
O	-1.099916	0.307417	0.000000
H	-1.307305	-1.770765	0.000000
H	1.486578	-1.664787	0.000000
H	-0.168173	2.166492	0.000000

2.CuCl

No imaginary frequencies

C	0.664888	-3.102906	0.000000
C	1.106068	-1.831000	0.000000
C	-1.039995	-1.780822	0.000000
O	-0.706521	-3.076740	0.000000
H	1.132987	-4.069635	0.000000
H	2.110148	-1.446660	0.000000
H	-2.083811	-1.519270	0.000000
N	-0.007888	-0.989353	0.000000
Cu	0.000000	0.932798	0.000000
Cl	0.009547	3.047775	0.000000

Substrate **2**, CMD TS at the C2 site.
One imaginary frequency: $i1059\text{ cm}^{-1}$

E= -6107.345505
 G= -6107.092650 au
 HOMO= -6.2187 LUMO= -1.7889 Gap= 4.4298 eV

Pd	0.401039	-0.033296	-0.032738
C	-3.623567	-0.723490	1.338573
C	-2.244718	-0.517934	1.279359
C	-1.606819	-0.343808	0.050791
C	-2.369275	-0.374054	-1.116660
C	-3.747563	-0.580848	-1.055964
C	-4.378671	-0.761558	0.170718
O	2.623183	0.161574	-0.071267
C	3.156535	1.277779	0.142258
P	0.754204	-2.359623	-0.079146
O	2.508888	2.358497	0.335888
H	-1.678258	-0.478804	2.202756
H	-4.326939	-0.595264	-1.972463
H	-5.449210	-0.921494	0.216766
H	-4.104863	-0.851586	2.301860
H	-1.899096	-0.216366	-2.079979
C	4.663155	1.386948	0.160008
H	4.982814	1.983542	1.014214
H	5.122091	0.401513	0.189917
H	4.987020	1.908823	-0.743078
C	1.593441	-2.962138	1.451218
H	0.932776	-2.824421	2.307268
H	1.857498	-4.018340	1.365855
H	2.495318	-2.371824	1.610306
C	1.934173	-2.817058	-1.421969
H	2.821320	-2.191994	-1.328315
H	2.211530	-3.871499	-1.362046
H	1.473237	-2.620024	-2.390017
C	-0.643893	-3.538885	-0.302013
H	-1.143521	-3.334182	-1.248297
H	-0.282022	-4.568862	-0.295274
H	-1.371330	-3.398043	0.496326
H	1.296282	2.175241	0.179191
C	-0.064173	2.166830	-0.071088
N	-0.510130	2.659235	-1.204525
C	-1.578376	3.464603	-0.895774
C	-1.758027	3.453911	0.451139
O	-0.822120	2.653566	0.998676
H	-2.136299	3.997491	-1.647978
H	-2.451251	3.936516	1.117836

Substrate **2**, CMD TS at the C4 site.

One imaginary frequency: $i1058\text{ cm}^{-1}$

E= -6107.339963
 G= -6107.086868 au
 HOMO= -6.0954 LUMO= -1.5015 Gap= 4.5939 eV

Pd	-0.399138	-0.063702	0.011496
C	3.797561	-0.168186	-0.963145
C	2.411188	-0.025332	-1.023634
C	1.624517	-0.251372	0.106485
C	2.253386	-0.614807	1.299244
C	3.640579	-0.752741	1.360530
C	4.417700	-0.534559	0.227441
O	-2.633670	-0.008156	-0.030445

C	-3.237951	1.061573	0.217265
P	-0.575050	-2.414715	-0.179455
O	-2.658108	2.173121	0.456659
H	1.950031	0.280515	-1.955181
H	4.111122	-1.028800	2.297796
H	5.494758	-0.641539	0.273533
H	4.392962	0.013443	-1.851131
H	1.669852	-0.783955	2.197677
C	-4.748326	1.078703	0.223814
H	-5.095923	1.599667	-0.671017
H	-5.146154	0.066622	0.226870
H	-5.111729	1.634920	1.087680
C	-1.959219	-2.913127	-1.293640
H	-1.725650	-2.609622	-2.314420
H	-2.118787	-3.992928	-1.264950
H	-2.860974	-2.389382	-0.980701
C	-1.000881	-3.240198	1.418498
H	-1.912213	-2.794936	1.817217
H	-1.151780	-4.312752	1.279197
H	-0.195182	-3.081750	2.135448
C	0.851648	-3.404950	-0.798895
H	1.709692	-3.259951	-0.144145
H	0.594764	-4.465204	-0.841940
H	1.126726	-3.058132	-1.794768
H	-1.448182	2.061906	0.305597
C	-0.076874	2.152170	0.042060
C	1.141349	3.602001	-0.993870
N	0.242239	2.720073	-1.225435
H	1.647761	4.255573	-1.685484
C	0.709223	2.801881	0.947840
H	0.823948	2.735480	2.015810
O	1.490777	3.726910	0.322287

Substrate **2**, CMD TS at the C5 site.

One imaginary frequency: $i1020\text{ cm}^{-1}$

E= -6107.347903 G= -6107.095524 au

HOMO= -6.2445 LUMO= -1.7081 Gap= 4.5364 eV

Pd	0.382842	-0.041163	-0.078105
C	-3.670825	-0.520413	1.282987
C	-2.290472	-0.325877	1.220634
C	-1.631946	-0.304219	-0.009336
C	-2.379507	-0.472599	-1.175361
C	-3.759770	-0.663147	-1.112516
C	-4.409849	-0.693124	0.117173
O	2.618948	0.096476	-0.092198
C	3.200354	1.194424	0.072758
P	0.697425	-2.386874	-0.011204
O	2.600534	2.315853	0.193376
H	-1.737178	-0.176738	2.140487
H	-4.325767	-0.782938	-2.029545
H	-5.482044	-0.840075	0.165655
H	-4.166475	-0.531884	2.247419
H	-1.896407	-0.444510	-2.145206
C	4.709104	1.238381	0.132861
H	5.022232	1.718845	1.060802
H	5.128152	0.237120	0.069824
H	5.084056	1.849051	-0.690305

C	1.462682	-2.917502	1.584060
H	0.774135	-2.711580	2.403666
H	1.700827	-3.983173	1.572249
H	2.373720	-2.341608	1.744259
C	1.920377	-2.954762	-1.272617
H	2.817024	-2.342666	-1.183181
H	2.172252	-4.008092	-1.132917
H	1.503771	-2.813988	-2.270214
C	-0.715112	-3.552771	-0.217086
H	-1.176877	-3.397909	-1.191654
H	-0.375485	-4.587014	-0.134703
H	-1.467845	-3.350378	0.543868
H	1.395201	2.177904	0.080826
C	0.005342	2.146018	-0.090538
C	-1.578977	3.522708	0.546870
O	-0.690513	2.648593	1.030577
H	-2.218624	4.025914	1.254620
C	-0.564313	2.813256	-1.149268
H	-0.297138	2.729816	-2.191182
N	-1.559128	3.674416	-0.741662

Substrate **2.CuCl**, CMD TS at the C2 site.

One imaginary frequency: $i1038\text{ cm}^{-1}$

E= -8208.251696 G= -8208.001896 au

HOMO= -6.0015 LUMO= -2.4246 Gap= 3.5770 eV

Pd	0.148832	0.314237	-0.677089
C	-4.045072	0.403361	-1.507018
C	-2.656348	0.519346	-1.574727
C	-1.872912	0.309387	-0.438471
C	-2.498513	0.005722	0.770224
C	-3.887250	-0.106894	0.835873
C	-4.664271	0.092578	-0.300794
O	2.301049	0.459719	-1.193223
C	2.912908	-0.487992	-1.744664
P	0.109064	2.548979	0.000606
O	2.409907	-1.639911	-1.960322
H	-2.194531	0.759759	-2.525828
H	-4.359024	-0.347368	1.781889
H	-5.742897	0.008130	-0.246883
H	-4.639442	0.560301	-2.399960
H	-1.911608	-0.147109	1.668352
C	4.349105	-0.284620	-2.164860
H	4.548668	-0.809177	-3.098157
H	4.575671	0.774803	-2.261221
H	4.996673	-0.713194	-1.396142
C	-0.483256	3.741798	-1.274505
H	-1.523805	3.527116	-1.516258
H	-0.400722	4.767278	-0.908775
H	0.115794	3.632633	-2.178483
C	1.818679	3.086449	0.407807
H	2.474924	2.881358	-0.435225
H	1.831067	4.149851	0.655615
H	2.160672	2.501486	1.262388
C	-0.845765	2.967545	1.513481
H	-0.479175	2.346463	2.331881
H	-0.698331	4.020805	1.761026
H	-1.904600	2.771205	1.357906

H	1.265972	-1.734151	-1.427574
C	0.143065	-2.065494	-0.766554
N	0.110151	-2.428560	0.510609
C	-0.849246	-3.416813	0.641330
C	-1.370350	-3.641619	-0.584419
O	-0.760277	-2.810632	-1.468093
H	-1.081870	-3.879005	1.584316
H	-2.119257	-4.310267	-0.968323
Cu	0.822506	-1.233484	1.839463
Cl	1.415869	0.265324	3.251451

Substrate **2.CuCl**, CMD TS at the C4 site.

One imaginary frequency: $i1064\text{ cm}^{-1}$

E= -8208.245120 G= -8207.994049 au

HOMO= -5.9743 LUMO= -2.0354 Gap= 3.9389 eV

Pd	-0.103655	0.345190	-0.713817
C	3.858045	-0.363862	0.893497
C	2.477525	-0.196593	0.780687
C	1.910659	0.218400	-0.424180
C	2.750757	0.483774	-1.507790
C	4.131139	0.315572	-1.394113
C	4.689213	-0.109123	-0.192645
O	-2.238662	0.659496	-1.237425
C	-2.923351	-0.250405	-1.761973
P	0.037304	2.547230	0.071090
O	-2.496022	-1.434243	-1.977393
H	1.849632	-0.389279	1.643224
H	4.767762	0.519446	-2.247777
H	5.761104	-0.237211	-0.103051
H	4.281327	-0.689335	1.837129
H	2.338536	0.812217	-2.455591
C	-4.354940	0.034971	-2.147076
H	-5.006146	-0.346195	-1.356745
H	-4.519507	1.105277	-2.248722
H	-4.611214	-0.484984	-3.069031
C	-1.636476	3.173996	0.501871
H	-2.020815	2.571137	1.325387
H	-1.580471	4.221938	0.803370
H	-2.300061	3.056199	-0.352044
C	0.703636	3.764978	-1.143984
H	0.102165	3.735412	-2.052524
H	0.681281	4.774802	-0.729381
H	1.730582	3.501147	-1.395340
C	1.009000	2.844354	1.602930
H	2.055541	2.595086	1.439196
H	0.919966	3.891630	1.898825
H	0.606808	2.208543	2.392725
H	-1.348691	-1.575166	-1.502408
C	-0.188661	-1.978362	-0.908146
C	0.530797	-3.470636	0.525965
N	-0.248453	-2.440671	0.443162
H	0.757579	-4.078965	1.384887
C	0.656172	-2.840188	-1.527619
H	1.017610	-2.933041	-2.535806
O	1.113391	-3.784916	-0.640415
Cu	-0.930111	-1.255434	1.794914
Cl	-1.486634	0.227205	3.235032

Substrate **2.CuCl**, CMD TS at the C5 site.

One imaginary frequency: $i1029\text{ cm}^{-1}$

E= -8208.243122 G= -8207.996222 au

HOMO= -5.7833 LUMO= -2.4158 Gap= 3.3674 eV

Pd	-1.444264	-0.197636	0.006566
C	0.194010	3.329726	1.836799
C	-0.517198	2.155907	1.583434
C	-0.450443	1.547112	0.330153
C	0.331970	2.129610	-0.666436
C	1.046089	3.300392	-0.409674
C	0.975813	3.905801	0.840801
O	-2.687869	-2.024494	-0.308827
C	-2.329336	-3.137124	0.149337
P	-3.332711	1.031495	-0.660609
O	-1.213779	-3.346713	0.733894
H	-1.111000	1.717468	2.377363
H	1.662426	3.732545	-1.189427
H	1.531737	4.813874	1.039020
H	0.136101	3.789286	2.817048
H	0.406492	1.672893	-1.646354
C	-3.246651	-4.328173	0.014369
H	-3.425296	-4.762887	0.998758
H	-4.189111	-4.042097	-0.445772
H	-2.756106	-5.091878	-0.591625
C	-4.714078	0.816871	0.543217
H	-4.439694	1.266663	1.497402
H	-5.630561	1.282925	0.175907
H	-4.881682	-0.248827	0.695463
C	-4.017206	0.361427	-2.236218
H	-4.127358	-0.717267	-2.132984
H	-4.982945	0.814625	-2.469057
H	-3.320549	0.564061	-3.049846
C	-3.260200	2.849760	-0.936971
H	-2.533888	3.071762	-1.717948
H	-4.240366	3.228931	-1.232086
H	-2.933433	3.345776	-0.024123
H	-0.504179	-2.344640	0.711931
C	0.426609	-1.321348	0.646773
C	2.246696	-0.666463	1.692358
O	0.964862	-0.921775	1.888963
H	2.848241	-0.337595	2.523112
C	1.495907	-1.287091	-0.203843
H	1.524475	-1.541237	-1.249683
N	2.637499	-0.864047	0.460341
Cu	4.370528	-0.537188	-0.296807
Cl	6.269887	-0.150786	-1.159517

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