Supporting Information

Palladium Catalyzed Electrophilic Substitution of Allyl Chlorides and Acetates via Bis-allylpalladium Intermediates

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¹³C NMR spectra for compounds **25**, **26**, **28-30**, **32-34** and **37-40**

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Computational Details for 47-48

Computational Methods. All geometries were fully optimized employing a Becke-type¹ three-parameter density functional model, B3PW91. This so called hybrid functional includes the exact (Hartree-Fock) exchange, the gradient corrected exchange functional introduced by Becke¹ and the more recent correlation functional of Perdew and Wang². All calculations have been carried out using a valence double- ζ (DZ)+P basis constructed from the LANL2DZ basis³⁻⁵ by adding one set of d-polarization functions to the heavy atoms (exponents: C, 0.63; P, 0.34) and one set of diffuse d-functions for palladium (exponent: 0.0628). All calculations have been conducted by employing the Gaussian 98 program package.⁶

Calculated geometries.

Complex **47a**. E(RB+HF-PW91) = -831.646475889

C1	-1.177915	-2.317037	.233723
C2	-2.177779	-1.277267	.508118
C3	-3.084731	-.789313	-.381100
C4	-4.071425	.268100	-.155009
Pd5	.667342	-1.316167	-.049779
C6	2.614493	-.442372	-1.093099
C7	3.361424	.728797	-.611123
P8	1.133947	-.953580	2.210491
C9	.702564	-1.578628	-2.178612
C10	1.456574	-.402547	-1.890306
H11	-1.397154	-2.895464	-.669667
H12	-.229532	-1.476861	-2.731803
H13	3.151550	-1.393483	-1.043343
H14	1.213392	-2.538692	-2.283501
H15	1.007729	.564329	-2.124977
H16	1.200648	.387285	2.699941
H17	.310965	-1.479394	3.255909
H18	2.385051	-1.387074	2.747462

H19	-1.014983	-2.991140	1.084254
H20	-2.168208	-.857959	1.519362
H21	-3.092796	-1.229527	-1.382830
C22	4.684033	.554586	-.151548
C23	5.440918	1.634815	.311933
C24	4.893455	2.923751	.329088
C25	3.577118	3.112774	-.117674
C26	2.820094	2.033241	-.576408
H27	5.125754	-.443568	-.168321
H28	6.462480	1.470282	.656024
H29	5.480692	3.768847	.688053
H30	3.136350	4.110141	-.102447
H31	1.792153	2.206023	-.895908
C32	-4.975624	.590174	-1.191292
C33	-5.942904	1.587254	-1.035263
C34	-6.036220	2.297542	.168033
C35	-5.145166	1.993636	1.208837
C36	-4.179382	.998643	1.051315
H37	-4.915786	.042354	-2.133558
H38	-6.626623	1.810339	-1.855228
H39	-6.788722	3.075951	.294831
H40	-5.205384	2.541037	2.150503
H41	-3.498493	.789210	1.876213

Complex **47b**. $E(\text{RB+HF-PW91}) = -831.645255817$

C1	-3.043375	-2.501564	.026436
C2	-2.912258	-1.116570	-.228893
C3	-4.026726	-.296685	.057417
C4	-5.214827	-.828222	.567094
C5	-5.326753	-2.203316	.809013
C6	-4.229597	-3.034006	.533818
C7	-1.699601	-.496368	-.765542
C8	-.570864	-1.132331	-1.187553
C9	.649264	-.482566	-1.675823

Pd10	1.991056	-.516479	-.027260
C11	2.270194	.975035	1.559102
C12	1.982312	1.685792	.356788
C13	3.376987	.115539	1.665843
H14	3.503969	-.481269	2.567882
P15	2.530189	-2.753736	-.267724
H16	.501269	.567331	-1.948428
C17	.800113	2.532054	.139997
H18	4.274301	.287414	1.068961
H19	2.836547	1.920225	-.285039
H20	1.511418	.929826	2.341867
H21	2.088110	-3.692622	.715162
H22	2.123894	-3.507568	-1.414306
H23	3.900839	-3.157994	-.277409
H24	1.137934	-1.030825	-2.491416
H25	-.550142	-2.226826	-1.148639
H26	-1.721207	.593192	-.841400
H27	-3.952732	.775683	-.131088
H28	-6.057269	-.167457	.775386
H29	-6.250982	-2.622642	1.206779
H30	-4.301691	-4.106287	.721112
H31	-2.206197	-3.171611	-.168854
C32	-.332425	2.522917	.982798
C33	-1.418488	3.365616	.734942
C34	-1.414019	4.231526	-.367993
C35	-.304275	4.241347	-1.222857
C36	.785889	3.404795	-.968825
H37	-.376734	1.847181	1.836413
H38	-2.278028	3.343139	1.405684
H39	-2.264459	4.885970	-.559033
H40	-.286002	4.905267	-2.087571
H41	1.648046	3.427572	-1.637863

Complex **48a**. E(RB+HF-PW91) = -831.639249423

C1	-.955600	-1.940887	-3.536087
C2	-.965121	-1.975789	-2.185819
C3	.221544	-2.022392	-1.308393
C4	.223149	-2.953480	-.143460
Pd5	.354091	-.024568	-.534378
C6	1.104719	2.189947	-.170645
C7	.251791	3.260538	.361696
P8	-1.165307	-.281683	1.239389
C9	1.881955	.610359	-1.905475
C10	1.152804	1.769770	-1.513279
H11	1.142786	-2.134076	-1.890988
H12	-1.879833	-1.864538	-4.107858
H13	1.817715	.278260	-2.940384
H14	1.930583	1.882595	.476464
H15	2.798389	.341473	-1.374987
H16	.464522	2.211943	-2.235599
H17	-1.654332	.876403	1.920335
H18	-2.422971	-.929067	1.047370
H19	-.759320	-1.024348	2.387375
H20	-1.941939	-1.934689	-1.693547
H21	-.023770	-1.982488	-4.103168
C22	1.430649	-3.181014	.558145
C23	1.486944	-4.025785	1.666574
C24	.330739	-4.680873	2.120889
C25	-.870209	-4.483970	1.430408
C26	-.923811	-3.640161	.312678
H27	2.336060	-2.671610	.222452
H28	2.437054	-4.177761	2.180758
H29	.371345	-5.341922	2.986621
H30	-1.773791	-5.003975	1.752276
H31	-1.865546	-3.543234	-.226571
C32	.531515	3.784230	1.641966
C33	-.246622	4.805080	2.195889
C34	-1.330457	5.332089	1.482472
C35	-1.626737	4.817187	.211444
C36	-.852248	3.794991	-.339610

H37	1.378312	3.387333	2.205114
H38	-.003451	5.192925	3.185574
H39	-1.938298	6.129325	1.910060
H40	-2.472490	5.213795	-.351313
H41	-1.117944	3.400262	-1.320397

Complex **48b**. E(RB+HF-PW91) = -831.637515832

C1	2.965087	-1.480366	.990078
C2	1.919117	-1.220376	.077218
C3	2.233777	-1.302852	-1.300038
C4	3.521416	-1.605891	-1.742467
C5	4.554158	-1.838563	-.819290
C6	4.261746	-1.777467	.547326
C7	.528200	-.877586	.490384
Pd8	.164534	1.207828	.068626
C9	-1.700814	2.213987	-.502527
C10	-1.733832	.923293	-1.103551
C11	.157760	-.983844	1.913069
C12	-.993375	-1.500539	2.400233
C13	-.673341	3.131845	-.783704
H14	-.626528	4.068809	-.230782
P15	2.203275	1.944262	.908327
H16	-.206641	-1.373166	-.153773
H17	-1.204339	-1.493453	3.469559
C18	-2.718981	-.123745	-.803599
H19	-.158637	3.111315	-1.745808
H20	-1.250027	.832553	-2.080485
H21	-2.360656	2.425137	.340400
H22	2.429444	3.323532	1.210341
H23	2.733616	1.406467	2.119850
H24	3.360598	1.739950	.099996
H25	.866513	-.574907	2.640838
H26	-1.746069	-1.939087	1.745717
H27	1.443346	-1.116931	-2.029710
H28	3.724190	-1.663711	-2.812843

H29	5.561248	-2.076698	-1.161540
H30	5.044172	-1.980300	1.280189
H31	2.761475	-1.489308	2.060299
C32	-3.583449	-.084571	.312016
C33	-4.516955	-1.099811	.533081
C34	-4.604827	-2.192019	-.341277
C35	-3.742696	-2.254626	-1.443987
C36	-2.816533	-1.233358	-1.670561
H37	-3.526133	.740229	1.021482
H38	-5.175800	-1.043371	1.400134
H39	-5.331395	-2.984543	-.162645
H40	-3.794726	-3.099314	-2.131394
H41	-2.158437	-1.288761	-2.539648

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