Original Palladium Pincer Complexes Deriving from 1,3–Bis(thiophosphinoyl)indene Proligands: C_{sp3}–H *versus* C_{sp2}–H Bond Activation

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Electronic Supplementary Information

Molecular Orbitals and Z-matrices for complexes **4**, **6** and **8**

Pd complex 4

Molecular orbitals: Hereafter are represented the principal molecular orbitals of **4** involving Pd and C_2: HO–25 and HO–4 display σ interaction between C_2 and Pd; BV+2 displays σ* interaction between C_2 and Pd; HO–22 displays π interaction between C_2 and Pd; HO–1 displays π* interaction between C_2 and Pd.

HO–22

HO–25

HO–4

HO–1

BV+2
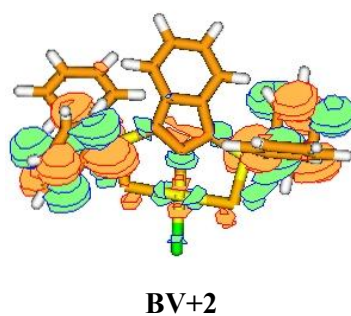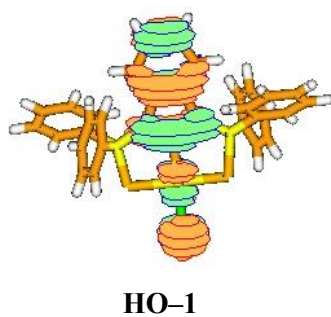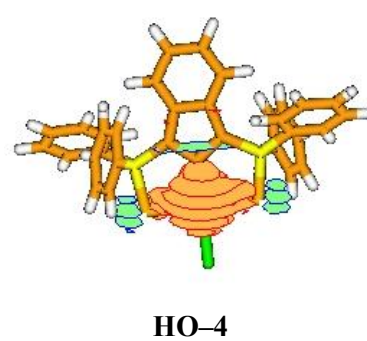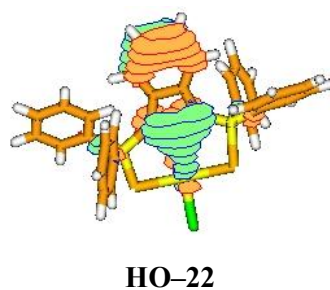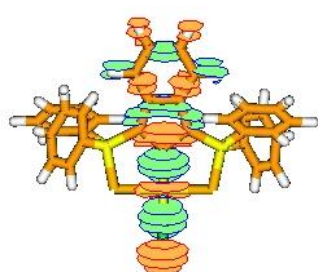
Z-matrix:
63

E=-2224.099090 a.u.

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C	-5.182869	-0.537966	1.316758
C	-5.982905	-1.037581	2.342841
C	-5.396300	-1.581147	3.485242
C	-4.006729	-1.623286	3.601794
P	-2.678893	0.149035	0.147417
S	-2.304143	2.136115	0.520329
Pd	-0.000058	2.144214	-0.000335
S	2.304030	2.136056	-0.520981
P	2.678858	0.149107	-0.147452
C	3.644420	-0.045221	1.426321
C	3.718022	-1.297186	2.049813
C	4.433637	-1.443396	3.235798
C	5.076096	-0.344174	3.807489
C	4.992146	0.904953	3.195345
C	4.274459	1.057680	2.008715
C	-0.000019	0.173263	-0.000069
C	1.131713	-0.675786	-0.105875
C	0.718054	-2.054948	-0.069136
C	-0.718000	-2.054957	0.069669
C	-1.131715	-0.675800	0.106001
C	1.402401	-3.276243	-0.155634
C	0.696761	-4.474638	-0.081558
C	-0.696617	-4.474641	0.082784
C	-1.402303	-3.276252	0.156514
C	3.789893	-0.575629	-1.433337
C	3.203342	-1.121634	-2.580494
C	4.007004	-1.624314	-3.601153
C	5.396565	-1.581947	-3.484579
C	5.983067	-1.037876	-2.342364
C	5.182937	-0.537990	-1.316487

C	-3.644520	-0.045824	-1.426245
C	-3.717777	-1.297910	-2.049531
C	-4.433450	-1.444535	-3.235431
C	-5.076306	-0.345607	-3.807240
C	-4.992699	0.903645	-3.195302
C	-4.274956	1.056788	-2.008760
H	-3.545862	-2.050111	4.488676
H	2.481318	-3.292130	-0.299556
H	1.232102	-5.419042	-0.151650
H	-1.231922	-5.419046	0.153145
H	-2.481222	-3.292138	0.300421
H	2.119978	-1.152083	-2.658089
H	3.546217	-2.051529	-4.487890
H	6.021974	-1.974487	-4.282582
H	7.065501	-1.004215	-2.247614
H	5.640479	-0.119832	-0.424353
H	3.196757	-2.149578	1.623612
H	4.480295	-2.415744	3.719581
H	5.630127	-0.460210	4.735807
H	5.475555	1.768068	3.645770
H	4.173317	2.032778	1.538800
H	-3.196199	-2.150065	-1.623235
H	-4.479840	-2.416974	-3.719057
H	-5.630378	-0.461964	-4.735494
H	-5.476415	1.766536	-3.645827
H	-4.174068	2.031998	-1.539026
H	-5.640493	-0.120198	0.424482
H	-7.065346	-1.004101	2.248106
H	-6.021635	-1.973475	4.283408
H	-2.119793	-1.151160	2.658503
Cl	-0.000098	4.560836	-0.000646

Pd complex 6

Molecular orbitals: Hereafter are represented the principal molecular orbitals of **6** involving Pd and C_2: HO−22 and HO−3 display σ interaction between C_2 and Pd; BV displays σ* interaction between C_2 and Pd; HO−26 displays π interaction between C_2 and Pd; HO−1 displays π* interaction between C_2 and Pd.

HO−26

HO−22

HO−3

HO−1

BV
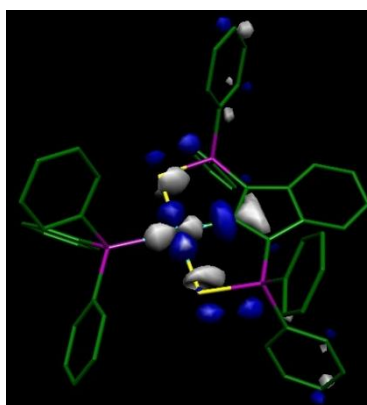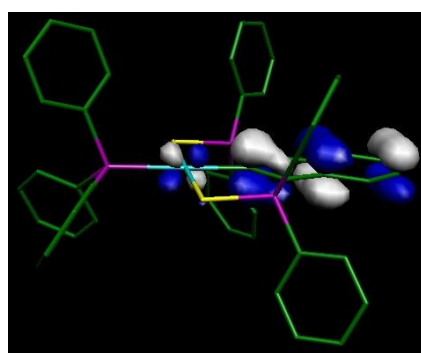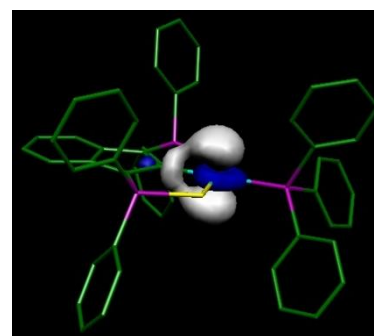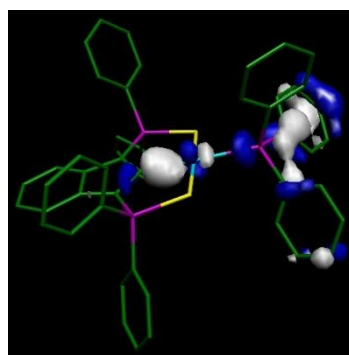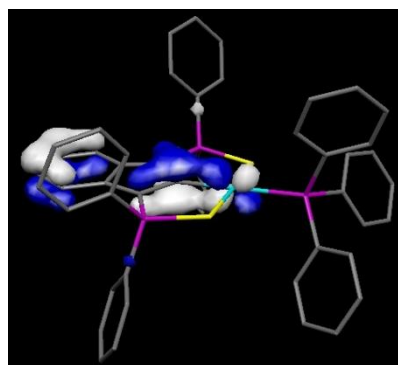
Z-matrix
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E=-2190.236378 a.u.

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C	3.732708	-1.485137	-1.071810		C	5.418173	2.516850	-2.178555
C	4.880229	-2.218304	-0.751857		C	4.745752	1.365382	-1.768957
C	5.341855	-3.208817	-1.617159		C	-1.588903	3.769180	1.439159
C	4.666915	-3.469963	-2.808918		C	-1.022587	5.043056	1.576826
C	3.520949	-2.744363	-3.131402		C	-1.195734	5.753569	2.760892
P	3.066050	-0.126291	-0.001344		C	-1.933652	5.198330	3.808423
C	3.791115	-0.440408	1.676407		C	-2.496099	3.930953	3.671853
C	2.987664	-1.047155	2.649168		C	-2.323180	3.211404	2.489339
C	3.501936	-1.314636	3.917126		H	-4.903897	-2.290146	0.116095
C	4.817034	-0.973525	4.227250		H	-6.977092	-0.947236	0.103642
C	5.619965	-0.360310	3.265684		H	-6.881952	1.527569	0.015749
C	5.110668	-0.091701	1.996789		H	-4.711710	2.704942	-0.059805
Pd	0.653915	-0.002895	-0.024468		H	-0.444601	5.474646	0.763884
C	-1.351341	0.073050	-0.019296		H	-0.753872	6.740404	2.868171
C	-2.152944	1.239161	-0.040905		H	-2.067717	5.756011	4.731395
C	-3.547688	0.876558	-0.010672		H	-3.070977	3.497690	4.485484
C	-3.602945	-0.557565	0.034445		H	-2.754588	2.221208	2.372866
C	-2.240319	-1.028540	0.023523		H	-3.252126	5.034770	-0.292523
C	-4.737920	1.618715	-0.017133		H	-4.051514	6.370517	-2.213201
C	-5.957974	0.954903	0.022401		H	-3.111395	5.982053	-4.478664
C	-6.011959	-0.448124	0.069849		H	-1.370012	4.242139	-4.815325
C	-4.846632	-1.204979	0.074542		H	-0.568895	2.897605	-2.887633
P	-1.320223	2.778531	-0.089159		H	-0.855065	-5.373214	-0.807376
C	-1.865162	3.872126	-1.472072		H	-1.330231	-6.634547	-2.883125
C	-2.843784	4.853890	-1.282421		H	-2.671613	-5.591173	-4.694201
C	-3.291547	5.609176	-2.365633		H	-3.534427	-3.278165	-4.425189
C	-2.763599	5.390054	-3.636465		H	-3.050510	-2.005994	-2.342305
C	-1.786298	4.412354	-3.826346		H	-0.758652	-2.736262	2.850061
C	-1.336975	3.653290	-2.749431		H	-1.612342	-3.986829	4.818388
P	-1.537578	-2.630693	0.060516		H	-3.460193	-5.624345	4.542824
C	-2.128405	-3.662023	1.472968		H	-4.452307	-6.004969	2.298441
C	-1.571257	-3.448316	2.738587		H	-3.599381	-4.763752	0.337919
C	-2.050672	-4.153749	3.838377		H	3.410593	2.540297	1.132496
C	-3.088160	-5.074032	3.682952		H	4.612207	4.566910	0.408225
C	-3.645275	-5.288522	2.424050		H	5.902222	4.565125	-1.718063
C	-3.167210	-4.586195	1.318150		H	5.979464	2.506911	-3.108990
S	0.512792	-2.351989	0.200428		H	4.792011	0.470325	-2.381170
S	0.691859	2.330506	-0.322499		H	1.960340	-1.307068	2.408917
C	-1.934094	-3.612077	-1.445774		H	2.869187	-1.784483	4.665035
C	-1.446088	-4.916374	-1.596714		H	5.214458	-1.178060	5.217721
C	-1.711934	-5.624155	-2.765125		H	6.643916	-0.085230	3.503901
C	-2.464701	-5.035558	-3.783490		H	5.736740	0.401528	1.258873
C	-2.948636	-3.737578	-3.633984		H	5.409014	-2.026165	0.176759
C	-2.682077	-3.020323	-2.467377		H	6.229728	-3.778687	-1.356837
C	4.021136	1.359969	-0.572650		H	5.028677	-4.243656	-3.480766
C	3.976055	2.526072	0.205344		H	2.982110	-2.952234	-4.051553
C	4.654392	3.670824	-0.204634		H	2.137378	-1.218974	-2.497267

Pd complex 8

Molecular orbitals: Hereafter are represented the principal molecular orbitals of **8** involving Pd and C_2: HO–25 and HO–4 display σ interaction between C_2 and Pd; BV displays σ^* interaction between C_2 and Pd; HO–22 displays π interaction between C_2 and Pd; HO displays π^* interaction between C_2 and Pd.

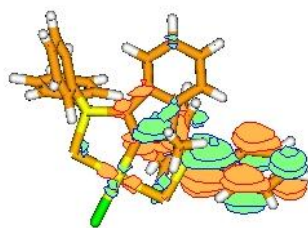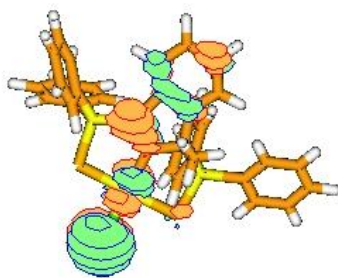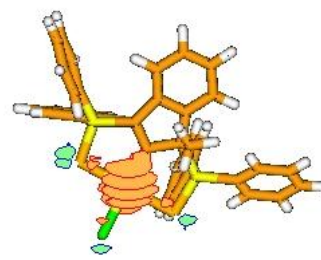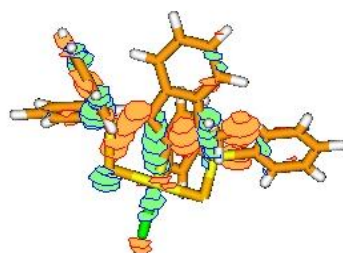**HO–25**   **HO–22**   **HO–4**

HO   **BV**
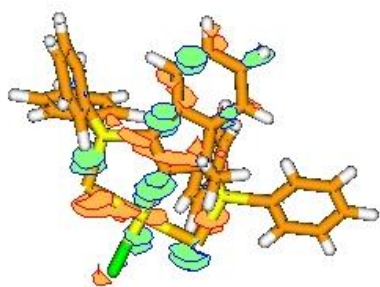
Z-matrix:

67

E=-2263.922150 a.u.

C	-4.842147	2.293341	-0.332268	C	-2.130414	-2.957650	1.699067
C	-4.244977	1.179317	0.273347	C	-2.251912	-3.912716	0.689794
C	-4.862835	0.571041	1.372798	C	-2.464316	-3.510409	-0.627551
C	-6.058038	1.085815	1.870841	C	-2.564691	-2.156378	-0.939956
C	-6.643391	2.201938	1.275069	H	-6.497467	3.661083	-0.305740
C	-6.037039	2.801049	0.171641	H	2.263388	0.170287	2.848036
P	-2.644834	0.572051	-0.400421	H	1.129770	0.639445	4.996906
S	-2.552069	0.854696	-2.423217	H	-1.157064	1.579688	5.043923
Pd	-0.186335	0.757950	-2.525995	H	-2.362286	2.054604	2.919640
S	2.151462	0.485936	-2.573096	H	0.953809	-1.994242	0.778066
P	2.459887	0.136447	-0.570600	H	1.435564	-4.389772	1.174341
C	3.885805	1.114305	0.063491	H	3.581546	-5.373659	0.402226
C	4.689214	0.650127	1.111782	H	5.246129	-3.952931	-0.771891
C	5.721450	1.448901	1.600400	H	4.773824	-1.558572	-1.167730
C	5.954444	2.706721	1.045843	H	4.521814	-0.335700	1.535813
C	5.157069	3.167318	-0.001789	H	6.346624	1.084625	2.410700
C	4.124472	2.374478	-0.496216	H	6.762307	3.325601	1.426260
C	-0.067141	1.024051	-0.591465	H	5.342954	4.142992	-0.441340
C	0.945960	0.646236	0.251757	H	3.511106	2.716076	-1.325597
C	0.573858	0.814466	1.658216	H	-2.115123	-0.867463	2.189347
C	-0.741742	1.333347	1.690466	H	-1.958040	-3.265490	2.726608
C	-1.199506	1.575057	0.273532	H	-2.178056	-4.969750	0.930434
C	1.251310	0.563138	2.852399	H	-2.547160	-4.248481	-1.419784
C	0.610194	0.834991	4.062716	H	-2.712549	-1.836980	-1.967640
C	-0.681016	1.365174	4.091463	H	-4.427859	-0.312006	1.828866
C	-1.361383	1.630488	2.897764	H	-6.535968	0.606029	2.720101
C	2.840493	-1.619265	-0.199848	H	-7.577550	2.597733	1.663459
C	1.897911	-2.419663	0.451786	H	-4.382180	2.742908	-1.207134
C	2.170494	-3.769730	0.669573	Cl	-0.314376	0.449514	-4.867288
C	3.373986	-4.320473	0.234737	C	-1.455776	3.068174	0.003731
C	4.311515	-3.522775	-0.423773	H	-2.280657	3.442713	0.616970
C	4.047913	-2.174496	-0.644007	H	-0.551002	3.624433	0.265392
C	-2.454231	-1.196646	0.072714	H	-1.674388	3.242703	-1.052143
C	-2.228710	-1.599984	1.397365				