Monitor the Phosphine Role in the Mechanism of the Palladium catalyzed Benzosiloles Formation from Aryloxyethynyl Silanes

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Computational Details

The buried volume calculations were performed with the SambVca package developed by Cavallo et al.1 The radius of the sphere around the origin placed 2.0 Å below the metal center was set to 3.5 Å, while for the atoms, we adopted the Bondi radii scaled by 1.17, and a mesh of 0.1 Å was used to scan the sphere for buried voxels. The steric maps were evaluated with a development version of the SambVca package.[2,3]

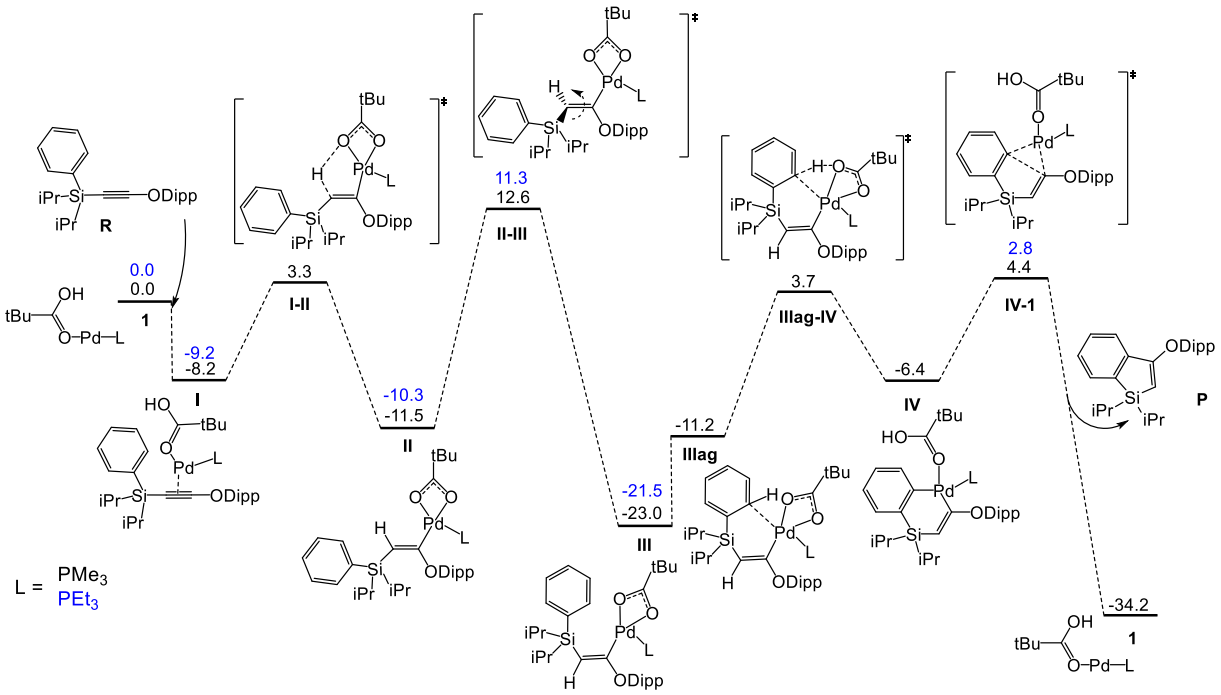


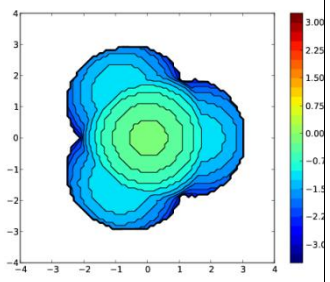
Figure S1. Full reaction pathway for the Pd catalyzed benzosilole formation from aryloxyethynyl silane, using PMe_3 as ligand. Represented the key intermediates using PEt_3 as ligand (M06/cc-pVTZ~sdd//BP86-d3/SVP~sdd Gibbs free energies referred to complex **1** in kcal/mol.

Table S1. Topographic steric maps of PMe_3, PEt_3, PPh_3, $PtBu_3$ and SIMes ligands studied. Iso-contour curves in Å; Pd atom placed at the origin, Pd-C_{NHC} bond set at 2.0 Å and along the z-axis.

PMe_3

V Free	V Buried	V Total	V Exact
136.3	43.2	179.5	179.6
%V_Free	%V_Bur	% Tot/Ex	
75.9	24.1	100	

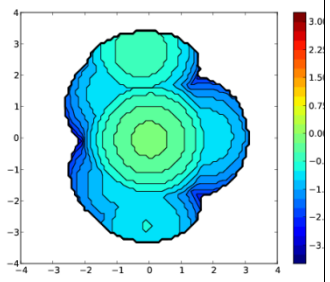
Quadrant	V_f	V_b	V_t	%V_f	%V_b
SE	33.6	11.3	44.9	74.8	25.2
NE	33.6	11.3	44.9	74.8	25.2
NW	34.5	10.3	44.8	77	23
SW	34.6	10.3	44.9	77.1	22.9



PEt_3

V Free	V Buried	V Total	V Exact
130.9	48.6	179.5	179.6
%V_Free	%V_Bur	% Tot/Ex	
72.9	27.1	100	

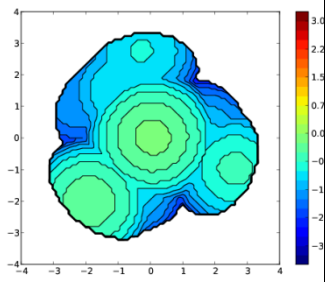
Quadrant	V_f	V_b	V_t	%V_f	%V_b
SE	33.4	11.4	44.9	74.5	25.5
NE	31.8	13	44.9	71	29
NW	32.5	12.3	44.8	72.5	27.5
SW	33.1	11.8	44.9	73.7	26.3



PPh_3

V Free	V Buried	V Total	V Exact
126.7	52.8	179.5	179.6
%V_Free	%V_Bur	% Tot/Ex	
70.6	29.4	100	

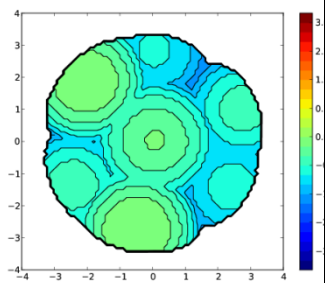
Quadrant	V_f	V_b	V_t	%V_f	%V_b
SE	29.2	15.7	44.9	65	35
NE	32.3	12.6	44.9	72	28
NW	33.3	11.6	44.8	74.2	25.8
SW	31.9	13	44.9	71.1	28.9



$PtBu_3$

V Free	V Buried	V Total	V Exact
113.6	65.9	179.5	179.6
%V_Free	%V_Bur	% Tot/Ex	
63.3	36.7	100	

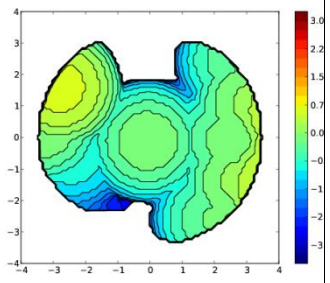
Quadrant	V_f	V_b	V_t	%V_f	%V_b
SE	27.2	17.7	44.9	60.5	39.5
NE	26.7	18.2	44.9	59.4	40.6
NW	30.4	14.5	44.8	67.7	32.3
SW	29.4	15.5	44.9	65.5	34.5



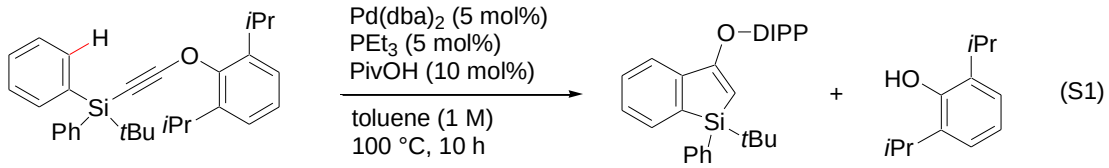
SIMes

V Free	V Buried	V Total	V Exact
111.5	68	179.5	179.6
%V_Free	%V_Bur	% Tot/Ex	
62.1	37.9	100	

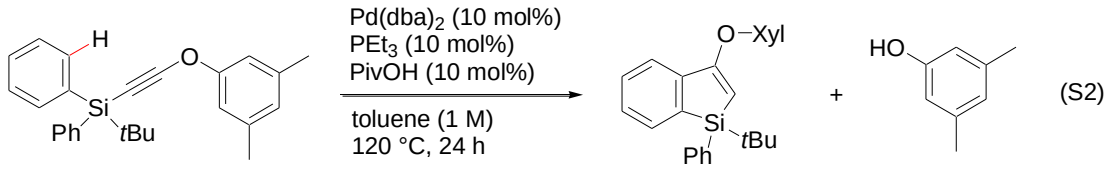
Quadrant	V_f	V_b	V_t	%V_f	%V_b
SE	31.6	13.3	44.9	70.3	29.7
NE	26	18.8	44.9	58	42
NW	28.4	16.5	44.8	63.3	36.7
SW	25.5	19.4	44.9	56.7	43.3



Effect of aryl substituents on oxygen. (eq S1 and S2)[4]



conv. 99% 95% n.d.



conv. 99% 30% 10% (NMR)

Experimentally, sterically bulky ODIPP (DIPP = 2,6-*i*Pr$_2$-C$_6$H$_3$) group inhibits decomposition of substrates to form Ar–OH. Less bulky OXyl (Xyl = 3,5-Me$_2$-C$_6$H$_3$) group cannot inhibit this decomposition sufficiently. This results support the result shown in Figure 3.

(1) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. SambVca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, 1759-1766.

(2) Falivene, L.; Credendino, R.; Poater, A.; Petta, A.; Serra, L.; Oliva, R.; Scarano, V.; Cavallo, L. SambVca 2. A Web Tool for Analyzing Catalytic Pockets with Topographic Steric Maps. *Organometallics* **2016**, *35*, 2286–2293.

(3) Jacobsen, H.; Correa, C.; Poater, A.; Costabile, C.; Cavallo, L. Understanding the M-(NHC) (NHC = N-heterocyclic carbene) bond. *Coord. Chem. Rev.* **2009**, *253*, 687-703.

(4) Minami, Y.; Noguchi, Y.; Hiyama, T. *J. Am. Chem. Soc.* **2017**, *139*, 14013-14016.