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Suzuki–Miyaura cross-coupling reaction catalyzed by [R_3Si-IPr]Pd complexes: a computational study

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Details of Quantum Chemical Calculations

All quantum chemical calculations were performed at the DFT B3LYP level of theory with Lanl2DZ basis set (for Pd atoms) and 6-31G(d) basis set (for atoms of other elements), using GAUSSIAN16 C.01 program package and assuming a singlet ground state for all computed species. Calculations included geometry optimization and vibrational analysis of reactants, intermediates, transition states, and products to obtain optimized structures and activation energies. All energies discussed in this study include zero-point energy correction. To incorporate solvent effects, we used the integral equation formation of polarizable continuum model (IEF-PCM) and EtOH as the solvent (dielectric constant 24.55 was assumed).

Supporting Information 1: Details for Gaussian16 input

Here we present a "root section" line for Gaussian16 input used in this study. Ethanol solvent is assumed by using polarizable continuum model (PCM).

For Intermediate molecules

#p opt freq b3lyp/genecp scrf=(iefpcm,solvent=ethanol)

For Transition States

#p opt=(calcfc,ts) freq b3lyp/genecp scrf=(iefpcm,solvent=ethanol)

ECP input, put at the bottom of input file (between ---)

Pd 0

LanL2DZ

****

C N H Cl Si 0

6-31G*

****

Pd 0

LanL2DZ

For molecular coordinate of each compound, see .xyz files.

Supporting information 2: Other thermochemical properties

Table S1: Enthalpies changes in the whole reaction (in kcal mol^{-1}).

		1	**2**	**3**	**4**	**5**	**6**	**7(H)**
Oxidative Addition	**Pd^0**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	I1	-10.04	-9.83	-11.16	-9.94	-10.00	-10.01	-10.05
	TS1	-2.18	-1.80	-3.06	-1.64	-2.05	-2.09	-1.82
	I2	-17.64	-16.75	-18.13	-16.21	-16.86	-17.05	-16.17
Transmetalation	**I3**	-40.63	-39.38	-40.57	-35.87	-38.63	-35.34	-43.87
	TS2	-36.50	-36.12	-36.92	-34.67	-34.83	-34.22	-40.05
	I4	-47.08	-45.43	-46.53	-44.50	-44.44	-44.28	-48.83
	TS3	-31.91	-29.44	-32.13	-30.74	-29.66	-29.25	-34.31
	I5	-33.76	-33.44	-33.74	-31.85	-32.72	-32.24	-36.31
	TS4	-27.42	-26.63	-27.58	-25.44	-25.84	-25.67	-29.52
	I6	-42.83	-40.35	-42.86	-40.93	-41.11	-40.68	-44.41
Reductive Elimination	**I7**	-43.61	-43.09	-44.38	-42.66	-40.83	-43.19	-43.73
	TS5	-39.82	-38.13	-40.01	-38.58	-38.78	-38.95	-38.96
	Pd^0	-62.81	-62.81	-62.81	-62.81	-62.81	-62.81	-62.81
Activation	**Pd^{II}**	15.40	17.37	15.17	17.00	17.80	18.17	13.28
	I8	-9.71	-8.30	-9.92	-8.44	-8.22	-7.84	-11.10
	TS6	15.39	15.19	15.22	16.33	16.35	16.23	15.44
	I9	-20.35	-18.47	-20.58	-19.14	-19.32	-19.48	-18.76

Table S2: Gibbs energy changes in the whole reaction (in kcal mol^{-1}).

		1	2	3	4	5	6	7(H)
Oxidative Addition	**Pd^0**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	I1	1.23	0.76	0.30	1.87	1.19	1.14	1.03
	TS1	9.15	8.25	8.35	10.48	9.14	9.33	8.72
	I2	-6.97	-5.41	-6.69	-4.74	-5.66	-6.01	-4.08
Transmetalation	**I3**	-11.70	-9.81	-11.59	-5.61	-8.04	-5.68	-15.26
	TS2	-6.66	-7.72	-7.15	-5.37	-4.93	-4.70	-10.62
	I4	-25.99	-26.56	-26.89	-25.02	-23.95	-24.84	-28.05
	TS3	-10.63	-8.14	-11.49	-7.18	-6.72	-8.26	-13.99
	I5	-12.48	-12.58	-13.17	-12.19	-10.98	-11.89	-14.77
	TS4	-6.65	-6.75	-6.97	-3.84	-4.43	-4.42	-9.88
	I6	-23.87	-21.87	-24.67	-22.59	-21.48	-21.62	-26.50
Reductive Elimination	**I7**	-39.05	-37.05	-39.12	-38.48	-34.49	-39.46	-39.65
	TS5	-34.91	-32.77	-34.22	-33.13	-32.63	-33.25	-35.09
	Pd^0	-69.96	-69.96	-69.96	-69.96	-69.96	-69.96	-69.96
Activation	**Pd^{II}**	28.04	30.60	29.08	30.65	32.91	31.30	26.58
	I8	0.42	1.62	-0.24	2.68	2.70	1.36	0.05
	TS6	25.86	25.03	26.41	27.63	27.56	27.29	25.61
	I9	-13.21	-10.18	-12.47	-10.22	-10.04	-11.28	-10.77

Table S3: Imaginary frequencies in each transition state (in cm^{-1}).

	1	2	3	4	5	6	7(H)
TS1	201.96*i*	210.91*i*	209.89*i*	204.09*i*	207.04*i*	206.82*i*	214.99*i*
TS2	65.91*i*	83.63*i*	80.77*i*	80.82*i*	81.34*i*	82.01*i*	68.21*i*
TS3	46.81*i*	45.78*i*	38.42*i*	37.83*i*	32.37*i*	27.63*i*	66.87*i*
TS4	274.69*i*	273.53*i*	275.71*i*	274.84*i*	272.70*i*	273.04*i*	268.42*i*
TS5	259.44*i*	242.15*i*	260.09*i*	256.65*i*	259.37*i*	257.57*i*	251.36*i*
TS6	324.55*i*	320.18*i*	324.48*i*	321.46*i*	318.91*i*	322.31*i*	326.49*i*

Supporting Information 3: Optimized geometries

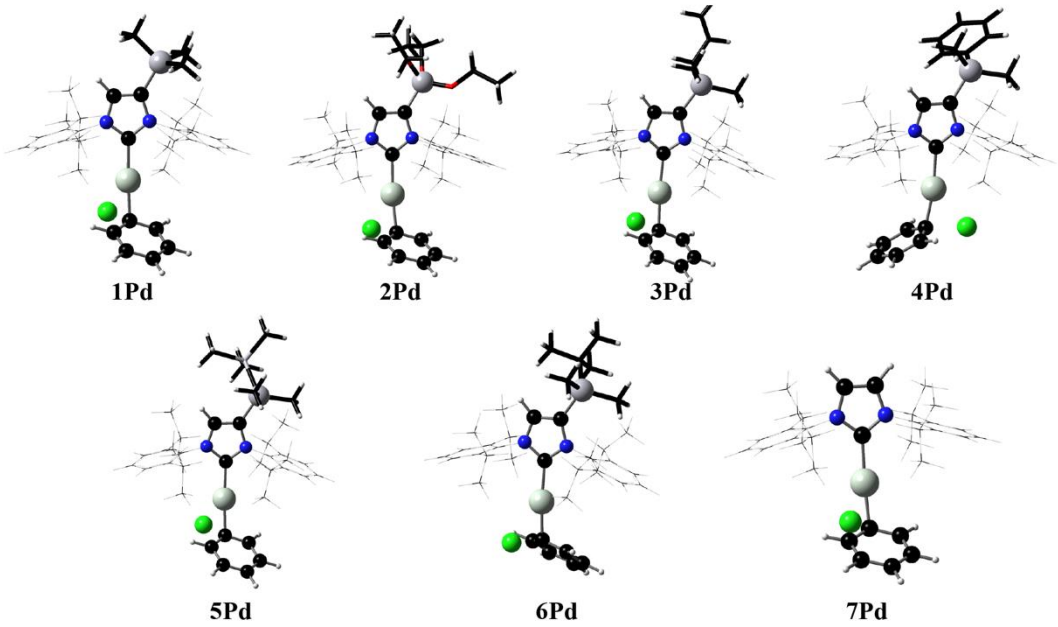

Figure S1: Difference in optimized geometries of the **TS1** (generated starting from the pre-catalysts **1Pd**-**7Pd**).

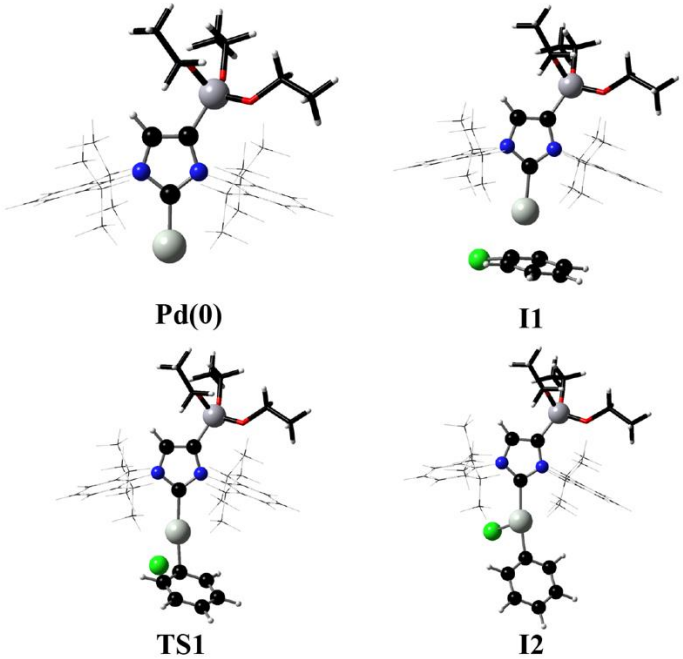

Figure S2: Optimized geometries of the species involved in the oxidative addition step.

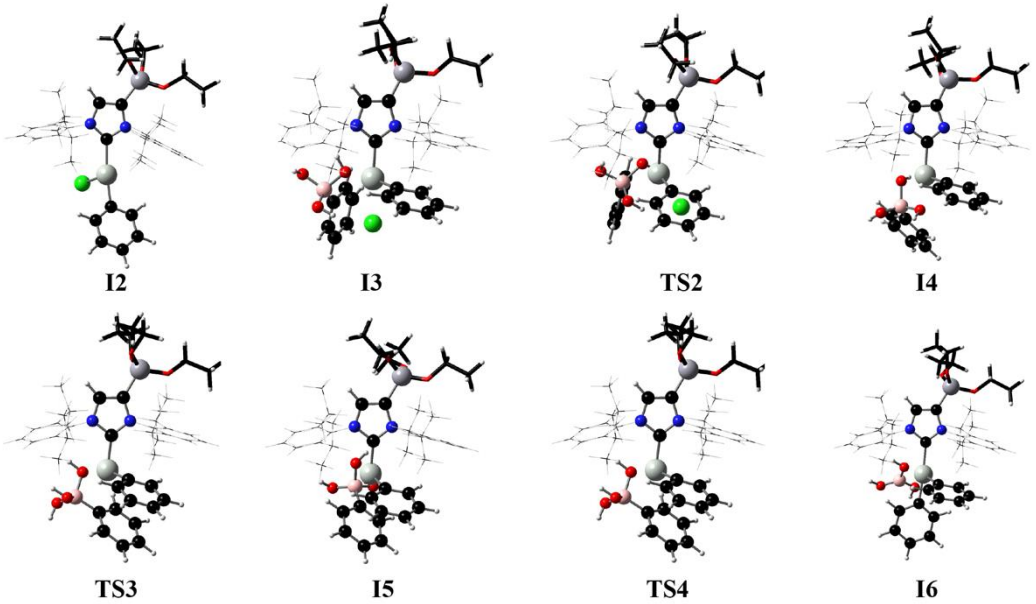

Figure S3: Optimized geometries of the species involved in the transmetalation step.

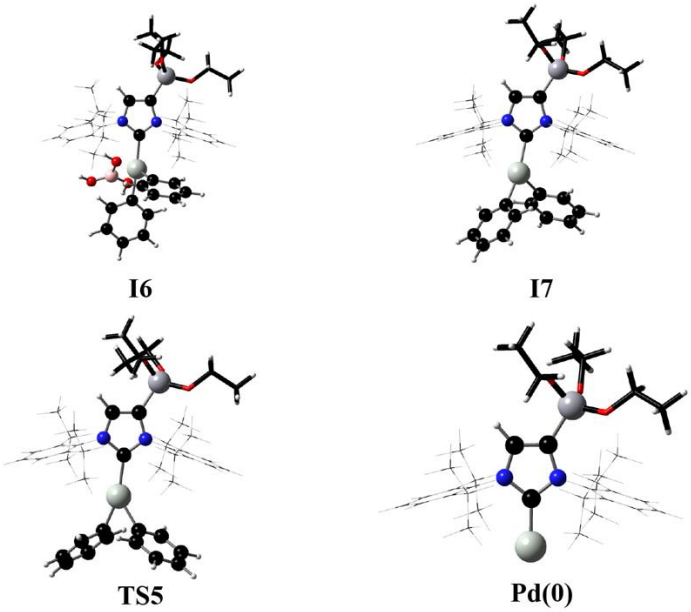

Figure S4: Optimized geometries of the species involved in the reductive elimination step.

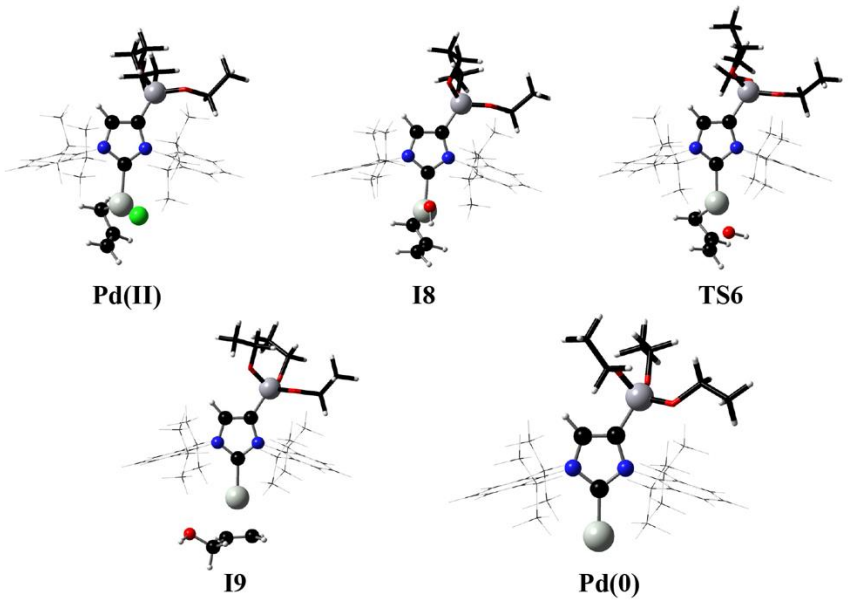

Figure S5: Optimized geometries of the species involved in the pre-catalyst activation step.