Oxidation of Pd(II) with Disilane in a Palladium-Catalyzed Disilylation of Aryl Halides: A Theoretical View

Supporting Information

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1. Complete reference for Gaussian 09

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant ,J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc., Wallingford, CT, 2013.

2. Computational Methods.

All calculations were performed with Gaussian 09 series of programs. Geometry optimizations, vibrational frequency calculations, and natural population analysis (NPA) charge calculations were carried out using the B3LYP functional in gas phase and standard 6-31G(d,p) basis set (LANL2DZ basis set for Pd and I atoms). Harmonic vibrational frequency calculations were performed at the same level of theory for all stationary points to confirm whether they are local minima or transition state structures and to derive the thermochemical corrections for the enthalpies and free energies. When necessary, intrinsic reaction coordinate (IRC) calculations were conducted in order to verify the transition states actually connecting the corresponding two minima. Single-point energy calculations were carried out in N,N-dimethylformamide (DMF) solution using the M06 functional and the SDD basis set for Pd and I, and 6-311++G(d,p) for other atoms with the SMD continuum solvation model. Unless otherwise noted, the Gibbs free energies calculated in DMF solvent (ΔG_{sol}) are used to discuss the energetic profiles presented in this work. All of the three-dimensional diagrams of the molecules were generated with CYLView.

3. Free energies for other possible Pd(0) initial species.

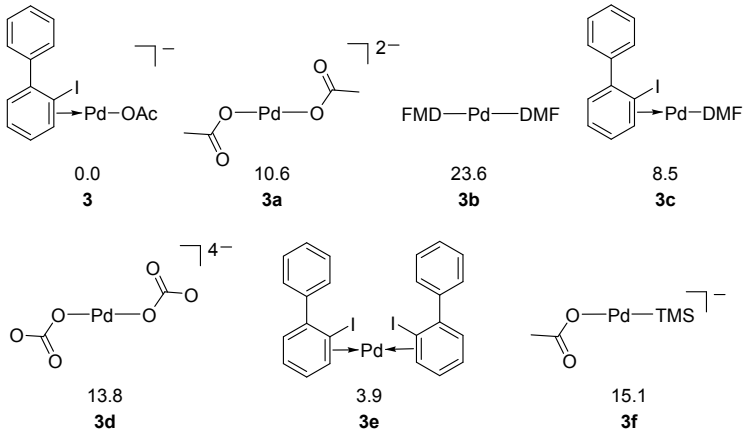

Fig. S1 Some possible Pd(0) initial species. The free energies are given in kcal/mol, where the energy of **3** is the zero energy reference point.

4. Free energies for other possible transition states of oxidative addition of disilane.

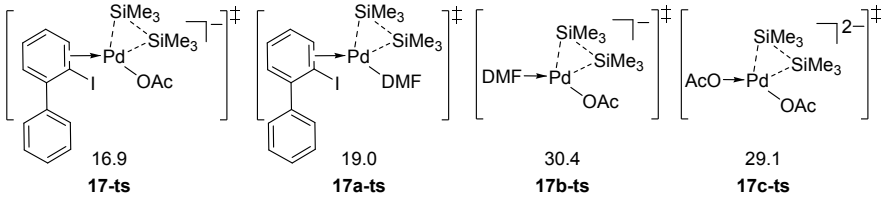

Fig. S2 Some possible transition states for oxidative addition of disilane. The values of free energy are given in kcal/mol, which were calculated using the M06 method in N,N-dimethylformamide.

5. Free-energy profiles for the reductive elimination from 10 to form $AcOSiMe_3$.

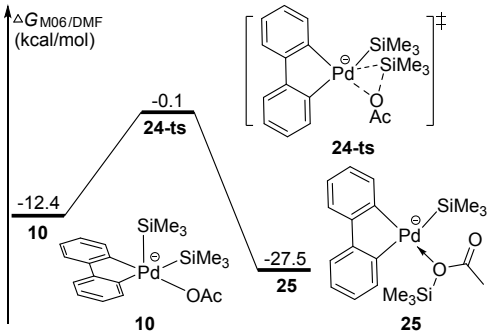

Fig. S3 Free-energy profiles for the reductive elimination from **10** to form $AcOSiMe_3$. The values of free energy are given in kcal/mol, which were calculated using the M06 method in N,N-dimethylformamide.

6. The calculated free energies of the key transition states and intermediates with different methods.

	$\Delta G_{M06/6\text{-}311++G(d,p)//B3LYP\text{-}D3/BSII}$	$\Delta G_{M06/6\text{-}311++G(d,p)//B3LYP/BSI}$
3	0.0	0.0
4-ts	3.2	4.0
17-ts	16.1	16.9
8	-33.3	-33.7
9-ts	-13.1	-10.6
23-ts	-7.4	-8.1

Table S1 The calculated free energies of the key transition states and intermediates, which are related to complex **3** as zero in corresponding calculations. The values of free energy are given in kcal/mol. M06/6-311++G(d,p)//B3LYP-D3/BSII represents geometries were optimized at the B3LYP-D3/BSII level (BSII designates the basis set combination of SDD for Pd and I atoms, and 6-31+G(d,p) for other atoms) by the SMD solvent model using DMF solvent. Then, single-point energy calculations were carried out in DMF using the M06 functional and the SDD basis set for Pd and I atoms, and 6-311++G(d,p) for other atoms. M06/6-311++G(d,p)//B3LYP/BSI indicates geometry optimizations were carried out using the B3-LYP functional in gas phase and standard 6-31G(d,p) basis set (LANL2DZ basis set for Pd and I atoms). Then, single-point energy calculations were carried out in DMF solvent using the M06 functional and the SDD basis set for Pd and I, and 6-311++G(d,p) basis set for other atoms with the SMD continuum solvation model.

7. Absolute calculation energies, enthalpies, and free energies. The values are the free energies given by B3LYP-6-31G(d,p) (LANL12DZ for Pd and I) method.

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	$E_{(solv,M06)}$[4]	IF[5]
1	-474.0818756	0.132107	0.182460	-473.8375277	-
2	-818.5574497	0.181716	0.239935	-818.3794039	
3	-829.4125572	0.167833	0.239984	-830.3528358	
3a	-583.6982455	0.053056	0.112167	-585.0549889	
3b	-623.7922959	0.160839	0.224042	-624.7722416	
3c	-849.3709384	0.218110	0.296353	-850.2046695	
3d	-653.7022652	-0.013950	0.040201	-655.8881425	
3e	-1074.9323847	0.277852	0.368330	-1075.6227934	
3f	-1173.8513726	0.219236	0.297382	-1174.8724787	
4-ts	-829.4106402	0.169165	0.239256	-830.3477644	-80.48
5	-829.4679974	0.171005	0.241335	-830.3962562	

6	-1046.523478	0.217920	0.295191	-1047.3919477	
7-ts	-1046.4891243	0.214073	0.288921	-1047.3630721	-1237.43
8	-817.4222493	0.164676	0.225676	-818.3468095	
9-ts	-1635.9480295	0.374093	0.467565	-1636.717203	-70.69
10	-1635.9546067	0.371205	0.467278	-1636.7171649	
11-ts	-1635.951346	0.371445	0.466365	-1636.7149591	-63.17
12	-1636.000639	0.368566	0.467953	-1636.7563094	
13-ts	-1635.9674172	0.369339	0.466790	-1636.7429696	-100.96
14	-1635.9853403	0.370057	0.467947	-1636.7619203	
15	-1280.6691056	0.332034	0.410942	-1280.2504692	
16-ts	-1635.8634031	0.371360	0.465587	-1636.6346354	-172.03
17-ts	-1647.9476685	0.376029	0.481038	-1648.7317575	-81.23
17a-ts	-1667.9126289	0.423113	0.537353	-1668.5906384	-67.05
17b-ts	-1422.3751109	0.316946	0.408458	-1423.3000708	-71.49
17c-ts	-1402.2807456	0.259573	0.351787	-1403.4297469	-61.84
18	-1173.9093803	0.219727	0.297964	-1174.9153118	
19-ts	-1647.9554155	0.375664	0.481125	-1648.7345637	-185.83
20	-1648.0121771	0.380251	0.483962	-1648.7944554	
21-ts	-1647.9598563	0.380761	0.479100	-1648.744877	-709.66
22	-1647.965609	0.381095	0.483528	-1648.7534879	
23-ts	-1291.4671638	0.317439	0.408312	-1292.1642337	-169.12
24-ts	-1635.9371595	0.372694	0.466659	-1636.699004	-109.41
25	-1635.9756	0.370093	0.467410	-1636.7400394	

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M06 in DMF solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.