Supplementary Material: Intramolecular Transfer of Pd Catalyst on Carbon–Carbon Triple Bond and Nitrogen–Nitrogen Double Bond in Suzuki–Miyaura Coupling Reaction

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1. The product ratio of 5a to 4a and 5a as a function of conversion of 1a.

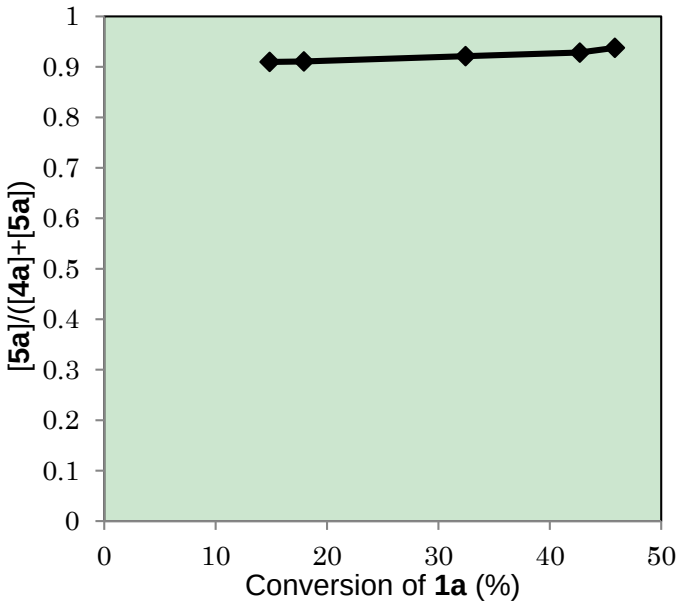

Figure. S1 The product ratio of **5a** to **4a** and **5a** as a function of conversion of **1a** in Suzuki-Miyaura coupling reaction of **1a** with **2** in in the presence of 5.0 mol% of **3**, KOH (4.5 equiv.)/18-crown-6 (8.0 equiv.) in THF ($[\mathbf{1a}]_0 = 1.60 \times 10^{-2}$ M) and water (THF/water = 26.7/1, v/v) at rt.

2. Estimation of product ratio of 4b to 5b by ^{1}H NMR spectra

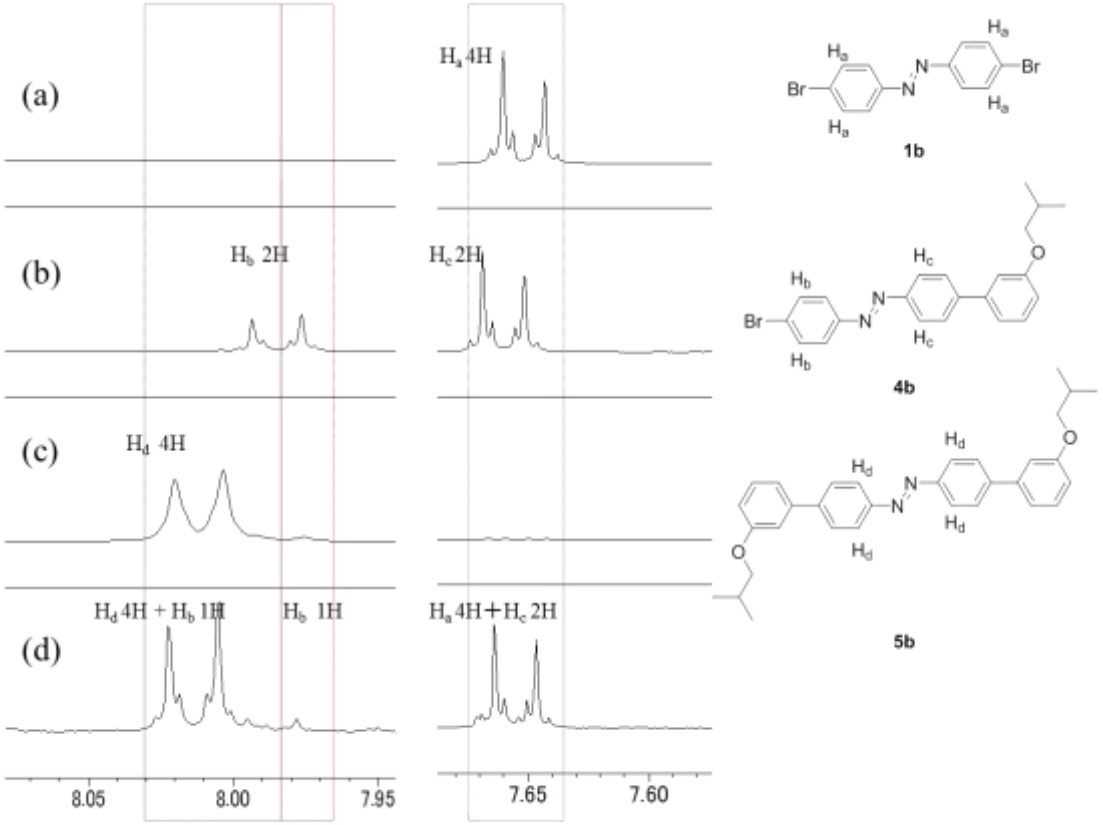

Figure S2. ^{1}H NMR spectra of (a) **1b**, (b) **4b**, (c) **5b**, and (d) products obtained by the reaction of **1b** with 1.05 equiv of **2** in the presence of 5.0 mol% of **3** and KOH (4.5 equiv)/18-crown-6 (8.0 equiv) at room temperature in THF ($[\mathbf{1b}]_0 = 1.60 \times 10^{-2}$ M) and water (THF/water = 16.7/1, v/v) for 24 h ($CDCl_3$ at 25 °C).

3. Computational details.

Density functional theory (DFT) calculations were performed using Gaussian 09 program package [S1]. Geometry optimizations and vibrational analyses of all local equilibrium were performed using Truhlar's metahybrid M06 functional [S2] together with effective core potentials (ECPs) with the SDD basis sets [S3,S4] for Pd, and 6-31G(d) basis sets for the other atoms. All stationary points were characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima). The values of electronic energies (ΔE) were evaluated by single-point energy calculations using M06 functional together with ECPs with SDD basis sets for Pd, and 6-311++G(d,p) basis sets for the other atoms, and shown in kcal/mol unless otherwise noted. The calculated geometries are shown in Figures S4–S5. Cartesian coordinates and energies of the computed structures are listed in 7. Appendix.

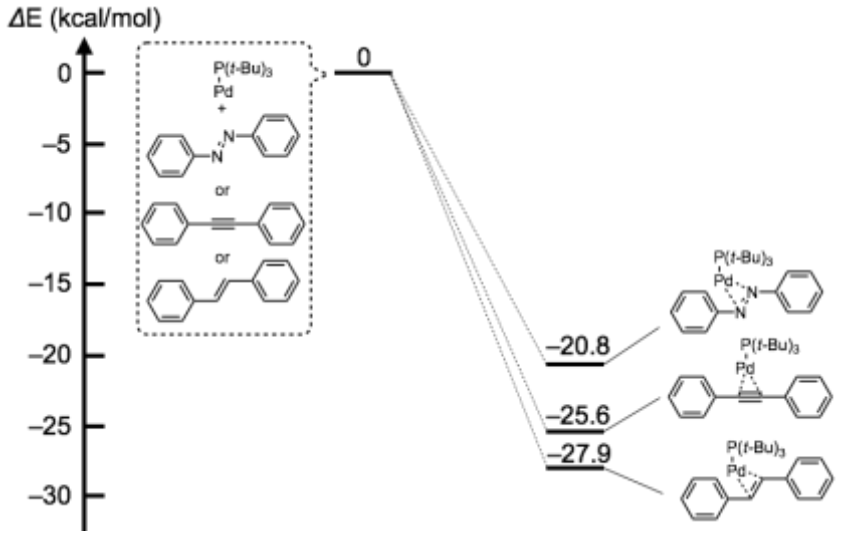

Figure. S3. Theoretical energy diagram on a complexation of diphenylacetylene, stilebene, and azobenene, with PdP(*t*-Bu)$_3$, respectively.

4. Appendix.

4-1. Optimized geometries.

The geometries were given by ball and bond type model (atom color: silver = carbon, white = hydrogen, dark yellow = phosphine, blue = nitrogen, dark blue = palladium).

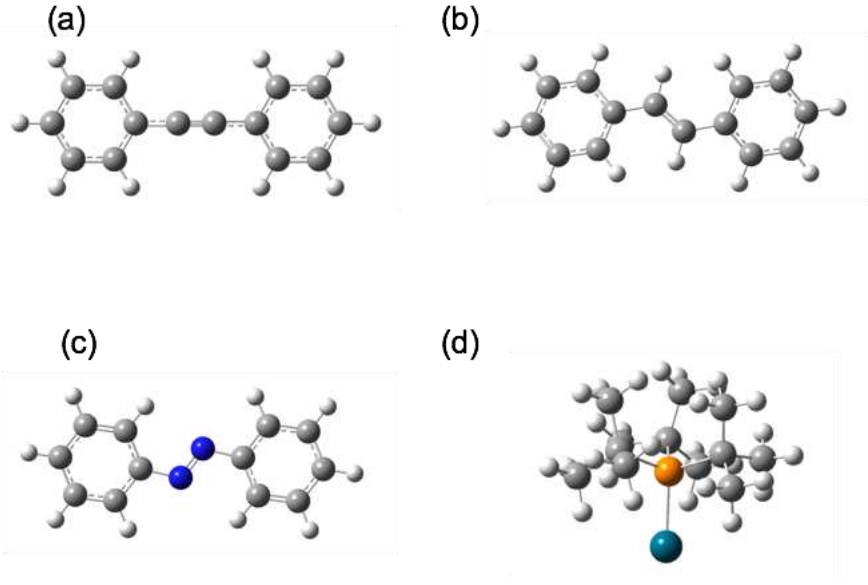

Figure S4. Optimized geometries of (a) diphenylacetylene, (b) stilbene, (c) azobenzene and (d) PdP(*t*-Bu)$_3$.

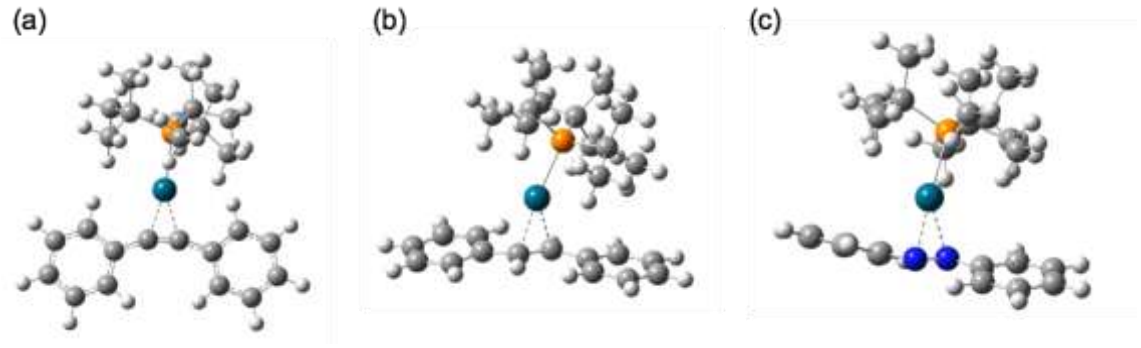

Figure S5. Optimized geometries of (a) diphenylacetylene + PdP(*t*-Bu)$_3$, (b) stilbene + PdP(*t*-Bu)$_3$, (c) azobenzene + PdP(*t*-Bu)$_3$.

4-2. Cartesian Coordinates (in Å) and Energies

Diphenylacetylene

Energy (RM06) = -539.0319174 A.U.
Free Energy = -538.879245 A.U.

C	4.12914900	1.20477900	0.00001900
C	4.82711900	0.00001800	0.00000400
C	4.12918200	-1.20475500	-0.00001200
C	2.74200700	1.20887100	0.00001200
H	4.67120600	2.14887700	0.00003300
H	5.91553100	0.00003200	0.00000600
H	4.67126100	-2.14884100	-0.00002300
H	2.18860900	2.14621900	0.00002300
C	2.74203700	-1.20888700	-0.00001400
H	2.18867600	-2.14625700	-0.00002500
C	0.60708200	-0.00000300	-0.00000800
C	-0.60708300	-0.00001600	-0.00000200
C	2.03028500	-0.00002300	-0.00000600
C	-2.03028500	-0.00002000	-0.00000300
C	-2.74200600	1.20887000	-0.00001500
C	-2.74203800	-1.20888800	0.00001300
C	-4.12915000	1.20477800	-0.00001200
H	-2.18861200	2.14622200	-0.00002800
C	-4.12918100	-1.20475600	0.00001700
H	-2.18867100	-2.14625500	0.00002500
C	-4.82711800	0.00002000	0.00000300
H	-4.67120600	2.14887800	-0.00002200
H	-4.67126300	-2.14884000	0.00003100
H	-5.91553100	0.00003200	0.00000600

Stilbene

Energy (RM06) = -540.2737427 A.U.
Free Energy = -540.097701 A.U.

C	3.84399300	1.27790100	0.20541200
C	4.70909200	0.20819800	-0.01637900
C	4.18588500	-1.06414300	-0.21853700
C	2.47213300	1.07940300	0.22095100
H	4.24573600	2.27584700	0.37404400
H	5.78591300	0.36687100	-0.02507800
H	4.85160700	-1.90874600	-0.38850800
H	1.81280600	1.92427400	0.41565400
C	2.81148400	-1.26123800	-0.20289000
H	2.40258600	-2.25979400	-0.36180900
C	1.92689100	-0.19530800	0.00851900
C	-1.92687800	0.19526000	0.00845700
C	-2.81143000	1.26123100	-0.20290200
C	-2.47218700	-1.07943000	0.22088600
C	-4.18584500	1.06420400	-0.21850100
H	-2.40249200	2.25977200	-0.36181000
C	-3.84405100	-1.27786200	0.20539700
H	-1.81289800	-1.92434000	0.41555100
C	-4.70910900	-0.20810800	-0.01634800
H	-4.85152100	1.90885000	-0.38843600
H	-4.24583800	-2.27579000	0.37402600
H	-5.78593700	-0.36673500	-0.02501800
C	-0.49142800	0.45773600	0.00428700
H	-0.22338400	1.51737500	-0.02271400
C	0.49144400	-0.45785400	0.00439400
H	0.22345400	-1.51751100	-0.02238100

Azobenzene

Energy (RM06) = -572.3270587 A.U.
Free Energy = -572.175508 A.U.

C	3.65011800	-1.29760600	0.09540900
C	4.51270100	-0.20281900	0.01674600
C	3.99807600	1.08608000	-0.07572400
C	2.27816000	-1.11005700	0.08081400
H	4.05866100	-2.30399600	0.17132700
H	5.59013000	-0.35862400	0.03017500
H	4.66908200	1.94093000	-0.13536400
H	1.58638400	-1.94644100	0.14210600
C	2.62281600	1.28033300	-0.08671800
H	2.18381100	2.27417300	-0.15504400
C	1.75964300	0.18643500	-0.01183900
C	-1.75964300	-0.18643500	-0.01183900
C	-2.62281600	-1.28033300	-0.08671700
C	-2.27816000	1.11005700	0.08081400
C	-3.99807600	-1.08608000	-0.07572400
H	-2.18381200	-2.27417300	-0.15504400
C	-3.65011800	1.29760600	0.09540900
H	-1.58638400	1.94644100	0.14210600
C	-4.51270100	0.20281900	0.01674600
H	-4.66908200	-1.94093000	-0.13536400
H	-4.05866100	2.30399600	0.17132700
H	-5.59013000	0.35862400	0.03017500
N	-0.38009900	-0.49916900	-0.02361900
N	0.38009900	0.49916900	-0.02361900

PdP(*t*-Bu)$_3$

Energy (RM06) = -942.3884287 A.U.
Free Energy = -942.063505 A.U.

Pd	2.12229800	-0.00079200	0.00488000
P	-0.15243500	-0.00043200	0.00006900
C	-0.83942300	1.65858000	-0.70495000
C	-0.84795400	-0.22037200	1.78527000
C	-0.84004800	-1.43780000	-1.08500900
C	0.01670200	-1.52701400	-2.35523000
H	1.08115200	-1.63583700	-2.10284300

H	-0.29579200	-2.41256000	-2.93092000
H	-0.08330700	-0.65832300	-3.01210300
C	-0.62526800	-2.76629400	-0.35491600
H	-0.83188600	-3.58855800	-1.05694100
H	0.41201100	-2.87856600	-0.01005400
H	-1.29786700	-2.90124500	0.49965300
C	-2.31356300	-1.33956500	-1.48614500
H	-2.58891200	-2.24272500	-2.05357600
H	-2.98887000	-1.28116700	-0.62387000
H	-2.51870200	-0.48175300	-2.13815600
C	-0.61458200	1.69083200	-2.21901800
H	-1.27707100	1.01365700	-2.76987100
H	-0.82443700	2.70891300	-2.58131900
H	0.42690200	1.45568700	-2.47877800
C	-2.31500500	1.95126000	-0.42790700
H	-2.59322000	2.89001200	-0.93250000
H	-2.98565900	1.17030800	-0.80563400
H	-2.52515700	2.09188100	0.63937500
C	0.01067500	2.80576000	-0.14167400
H	1.07742600	2.64034400	-0.34866000
H	-0.29625600	3.74482700	-0.62891800
H	-0.10107500	2.94650400	0.93693500
C	0.00013300	-1.28250700	2.49816500
H	-0.30653900	-1.33050500	3.55489700
H	-0.11397700	-2.28695100	2.07935200
H	1.06749700	-1.02130600	2.45833200
C	-2.32449200	-0.60463800	1.89513800
H	-2.60546000	-0.63689600	2.95977700
H	-2.99153800	0.11554700	1.40587700
H	-2.53464500	-1.59843300	1.48192500
C	-0.62769400	1.07624200	2.57039500
H	-1.28861800	1.89086800	2.25253400
H	-0.84610500	0.88271300	3.63172900
H	0.41404900	1.41956100	2.50352200

Diphenylacetylene+PdP(*t*-Bu)$_3$

Energy (RM06) = -1481.452457 A.U.

Free Energy = -1480.952329 A.U.

C	3.05033700	-4.14973300	-0.45439300
C	4.37986700	-4.22864000	-0.04777100
C	5.05347400	-3.07332900	0.34185800
C	2.39373100	-2.92659800	-0.46918000
H	2.51997000	-5.04948300	-0.76246700
H	4.89141800	-5.18963800	-0.03499100
H	6.09360300	-3.12799700	0.65947100
H	1.35503200	-2.84931200	-0.79140000
Pd	0.30825000	-0.11090000	-0.06388500
P	-2.05545000	-0.14505600	0.03754600
C	-2.87327700	0.61746500	-1.53077300
C	-2.66743700	0.84086800	1.57444900
C	-2.66038400	-1.96493600	0.20390300
C	4.40337800	-1.84770800	0.32728000
H	4.92460700	-0.94097800	0.63201700
C	2.41318400	-0.47783500	-0.08812200
C	2.25404700	0.76593700	-0.09171800
C	3.06219100	-1.75797300	-0.07821300
C	2.53584700	2.17322300	-0.08391100
C	1.59944900	3.11303600	-0.53735100
C	3.78044500	2.62608500	0.38179600
C	1.90230400	4.46739400	-0.52897000
H	0.63646400	2.75021900	-0.89781300
C	4.07526800	3.98184900	0.39231200
H	4.50785100	1.89818000	0.73921800
C	3.13871900	4.90708600	-0.06293300
H	1.16833200	5.18643400	-0.88971900
H	5.04317100	4.32067900	0.75861100
H	3.37337200	5.97019100	-0.05486600
C	-2.49992500	-2.67738800	-1.14272700
H	-1.48740400	-2.55581300	-1.55329000
H	-2.66712400	-3.75438100	-0.98820300
H	-3.22509400	-2.34858200	-1.89602600
C	-1.71313000	-2.69148000	1.16959700
H	-1.97550800	-3.76114600	1.18407600
H	-0.66519500	-2.59920200	0.84843600
H	-1.77433100	-2.32753300	2.19837300
C	-4.10108500	-2.15406700	0.68024900
H	-4.83217000	-1.66640400	0.02441700
H	-4.33642600	-3.23016700	0.68858800
H	-4.26313800	-1.78708400	1.70088800
C	-2.07504700	0.14577900	-2.75411200
H	-2.16014600	-0.92711300	-2.94641800
H	-2.45373900	0.66798500	-3.64672800
H	-1.00712300	0.38176100	-2.64279800
C	-2.70139200	2.13931100	-1.50004500
H	-1.65161800	2.42532100	-1.34431000
H	-3.01071100	2.54472900	-2.47550600
H	-3.31622100	2.63347600	-0.73957200
C	-4.35414700	0.30166700	-1.74034100
H	-4.70923800	0.82978100	-2.63943300
H	-4.53763400	-0.76642900	-1.90719600
H	-4.98253700	0.62857100	-0.90262400
C	-1.81820600	2.11555100	1.67649400
H	-1.98763900	2.82419600	0.86106800
H	-2.06911400	2.63447400	2.61510000
H	-0.74545500	1.87327800	1.69476100
C	-4.14995900	1.21390300	1.59244800
H	-4.37691300	1.73071700	2.53833200
H	-4.42469400	1.90054500	0.78275900
H	-4.80887000	0.33833400	1.53561100
C	-2.35516100	0.04514000	2.84614500
H	-2.54181300	0.69460900	3.71498700
H	-2.98919600	-0.84017600	2.96944400
H	-1.30106800	-0.26245100	2.88688000

Stilbene+PdP(*t*-Bu)$_3$

Energy (RM06) = -1482.696483 A.U.

Free Energy = -1482.169735 A.U.

C	-0.12818700	4.43017800	-1.19570500
C	0.46097500	5.05295700	-0.09558200
C	0.24770300	4.53127400	1.17623500
C	-0.91067200	3.29713400	-1.03026400
H	0.02373700	4.83517300	-2.19546900
H	1.07454700	5.94180700	-0.23108200
H	0.69376200	5.01089300	2.04649000
H	-1.35121100	2.81703400	-1.90425800
Pd	-0.60237600	-0.11157100	-0.25336300
P	1.61852800	-0.84769100	-0.02243900
C	1.96133300	-2.44110500	-1.04460300
C	2.02059500	-1.22137400	1.82187800
C	2.81034700	0.53680600	-0.63389900
C	-0.53328200	3.39354100	1.34190800
H	-0.68951500	2.98117700	2.34026400
C	-1.11848100	2.74566400	0.24419400
C	-3.58633700	-0.26013400	-0.16143000
C	-4.40536300	-0.73386800	-1.19569600
C	-3.73791600	-0.83531000	1.11099400
C	-5.34183100	-1.73595500	-0.97333300
H	-4.29800700	-0.29929300	-2.19062500
C	-4.67523900	-1.83284800	1.33358500
H	-3.10227700	-0.50478500	1.93280500
C	-5.48385700	-2.29071400	0.29397500
H	-5.96591700	-2.08237500	-1.79597600
H	-4.77465800	-2.26290400	2.32945100
H	-6.21726400	-3.07514100	0.47261700
C	-2.61289500	0.79773000	-0.45913700
H	-2.65044300	1.16646800	-1.48871100
C	-1.89140400	1.52017200	0.48265100
H	-2.06025600	1.30484100	1.54233800
C	2.00444800	-2.08607300	-2.53453900
H	2.00052200	-3.02094900	-3.11559500
H	1.12392200	-1.50398900	-2.84126200
H	2.90713900	-1.53553400	-2.82262600
C	0.74872400	-3.37015500	-0.88387900
H	-0.18502300	-2.85945000	-1.16102900
H	0.87596700	-4.23527300	-1.55334400
H	0.62401500	-3.75952000	0.13012000
C	3.23510300	-3.21081500	-0.69438400
H	3.21480200	-3.62100900	0.32251600
H	3.33746700	-4.06575200	-1.38135800
H	4.14099800	-2.60056300	-0.79614700
C	2.22948300	1.12716600	-1.92662500
H	2.82959500	2.00549300	-2.21289600
H	2.24710100	0.43284700	-2.77045200
H	1.19204500	1.46010100	-1.77924300
C	2.80922600	1.69254100	0.37353800
H	3.34200800	2.54385200	-0.07818500
H	1.79196600	2.04081800	0.60658700
H	3.33057600	1.45181800	1.30751900
C	4.25705000	0.11102100	-0.88424200
H	4.34923100	-0.60659400	-1.70836100
H	4.84809300	0.99696500	-1.16521200
H	4.72941300	-0.32822000	0.00230900
C	3.50344800	-1.30791600	2.18806300
H	4.02367800	-0.34976600	2.06686700
H	3.59337300	-1.58574400	3.25021100
H	4.04386900	-2.06631300	1.60708100
C	1.34128500	-2.53261300	2.22905500
H	1.80929700	-3.42029300	1.78817300
H	1.41905300	-2.64045200	3.32184600
H	0.27229500	-2.53180300	1.97304300
C	1.35398900	-0.13805200	2.68231300
H	1.49086600	-0.39718900	3.74416100
H	1.77236300	0.86127600	2.53271200
H	0.27479600	-0.08552800	2.47556500

Azobenzene++PdP(*t*-Bu)$_3$

Energy (RM06) = -1514.741601 A.U.

Free Energy = -1514.239188 A.U.

C	3.53002300	-3.30228900	-1.17302700
C	3.27504500	-4.21652200	-0.15070800
C	2.80315000	-3.76254900	1.07884500
C	3.30449700	-1.94632600	-0.98327300
H	3.91358600	-3.65366500	-2.13023400
H	3.45509700	-5.27837900	-0.31029600
H	2.61447200	-4.46887700	1.88593300
H	3.49696100	-1.22478600	-1.77363900
Pd	0.48928400	0.24260600	-0.42071200
P	-1.74259300	-0.21758200	-0.00708800
C	-2.07614700	-0.30058400	1.88515300
C	-2.30202100	-1.87591800	-0.79688700
C	-2.78497800	1.21398800	-0.75623200
C	2.58119200	-2.40722000	1.28021900
H	2.21545700	-2.02252600	2.23238100
C	2.81117500	-1.49346000	0.24658600
C	2.42491100	2.03196200	-0.13180300
C	2.18839900	2.89681300	-1.20848600
C	2.44169800	2.53465100	1.17625000
C	1.93863800	4.24378600	-0.97862200
H	2.19503900	2.47936800	-2.21521100
C	2.19540000	3.88211400	1.39318100
H	2.63941400	1.85059100	1.99804000
C	1.93719000	4.73963200	0.32264300
H	1.74820900	4.91011600	-1.81834700
H	2.20740300	4.27342500	2.40959800
H	1.74665400	5.79604400	0.50468700
N	2.59461200	0.66370000	-0.46861900

N	2.53913600	-0.13630700	0.55547800
C	-2.57661600	2.47111100	0.09429100
H	-1.50797300	2.69454200	0.23637300
H	-3.02642300	3.32718800	-0.43147800
H	-3.05850400	2.41036200	1.07655400
C	-2.19342300	1.55426400	-2.13262900
H	-2.68681300	2.46163600	-2.51521200
H	-1.11469700	1.76448500	-2.05747700
H	-2.33218200	0.76882200	-2.88099200
C	-4.28517300	0.96025200	-0.90309800
H	-4.76546700	1.86727400	-1.30313300
H	-4.50965200	0.14641900	-1.60406000
H	-4.77211800	0.73038300	0.05239600
C	-1.22326200	0.77774500	2.56983000
H	-1.49489100	1.80131500	2.29582200
H	-1.35178700	0.68504300	3.65992300
H	-0.15764200	0.64101300	2.33590700
C	-3.53634200	-0.14197300	2.31167400
H	-3.60662700	-0.27069700	3.40338100
H	-3.93863700	0.85316900	2.08350700
H	-4.19575800	-0.88973100	1.85294700
C	-1.55029700	-1.63202600	2.42999700
H	-0.50766700	-1.80974300	2.13148700
H	-1.57642600	-1.59040500	3.52962800
H	-2.15407400	-2.49561200	2.12930600
C	-2.37819700	-1.70274900	-2.31649100
H	-2.51307400	-2.69464600	-2.77414400
H	-3.22660300	-1.08661000	-2.63619000
H	-1.45235800	-1.27564700	-2.72633500
C	-3.64133200	-2.43236800	-0.31273900
H	-3.87848200	-3.34554800	-0.88112100
H	-3.62932000	-2.71297000	0.74731100
H	-4.46875800	-1.72873800	-0.46779700
C	-1.19510800	-2.91342500	-0.55465100
H	-1.07087600	-3.18760900	0.49663400
H	-1.44855100	-3.83321800	-1.10472200
H	-0.22191000	-2.55314500	-0.92048700

References

S1. Gaussian 09, Revision A.02, 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 Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT (2009).

S2. Zhao, Y.; Truhlar, D. Theor. Chem. Acc. 2008, 120 (1−3), 215−241.

S3. Fuentealba, P., Preuss, H., Stoll, H. & Szentpaly, L. V. Chem. Phys. Lett. 89, 418–422 (1982).

S4. Szentpaly, L. V., Fuentealba, P., Preuss, H. & Stoll, H. Chem. Phys. Lett. 93, 555–559 (1982).