Supporting Information for 'Theoretical Study of Alternative Pathways for the Heck Reaction through Dipalladium and "Ligand-free" Palladium Intermediates'

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Standard state conversion[i]

To convert free energy from gas phase at 1 atm to solution phase at 1 M, we used the equation:

$$\Delta G^{o'} = \Delta G^{o} + RT\ln(\frac{Q^{o'}}{Q^{o}})$$

where Q is the reaction quotient, the ratio of concentrations that appear in the equilibrium constant. $\Delta G^{o'}$ and $Q^{o'}$ are defined for all species at 1 M and ΔG^{o} and Q^{o} are defined for all species at 1 atm. From ideal gas law, at 298.15 K and 1 atm the molar volume of a perfect gas is 22.47 L mol^{-1}. Assuming A, B, and C are ideal gases, their concentration at 1 atm are 1/22.47 M. For example: A + B → C, the reaction quotient Q is [C]/[A][B].

$$\Delta G^{o'} = \Delta G^{o} + RT\ln\left(\frac{\frac{1}{1\cdot 1}}{\frac{24.47\cdot 24.47}{24.47}}\right)$$

$$\Delta G^{o'} = \Delta G^{o} - RT\ln(24.47)$$

$$\Delta G^{o'} = \Delta G^{o} - 1.89 \quad \text{kcal/mol at 298.15 K}$$

[i] Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; 2nd ed.; Wiley 2004.

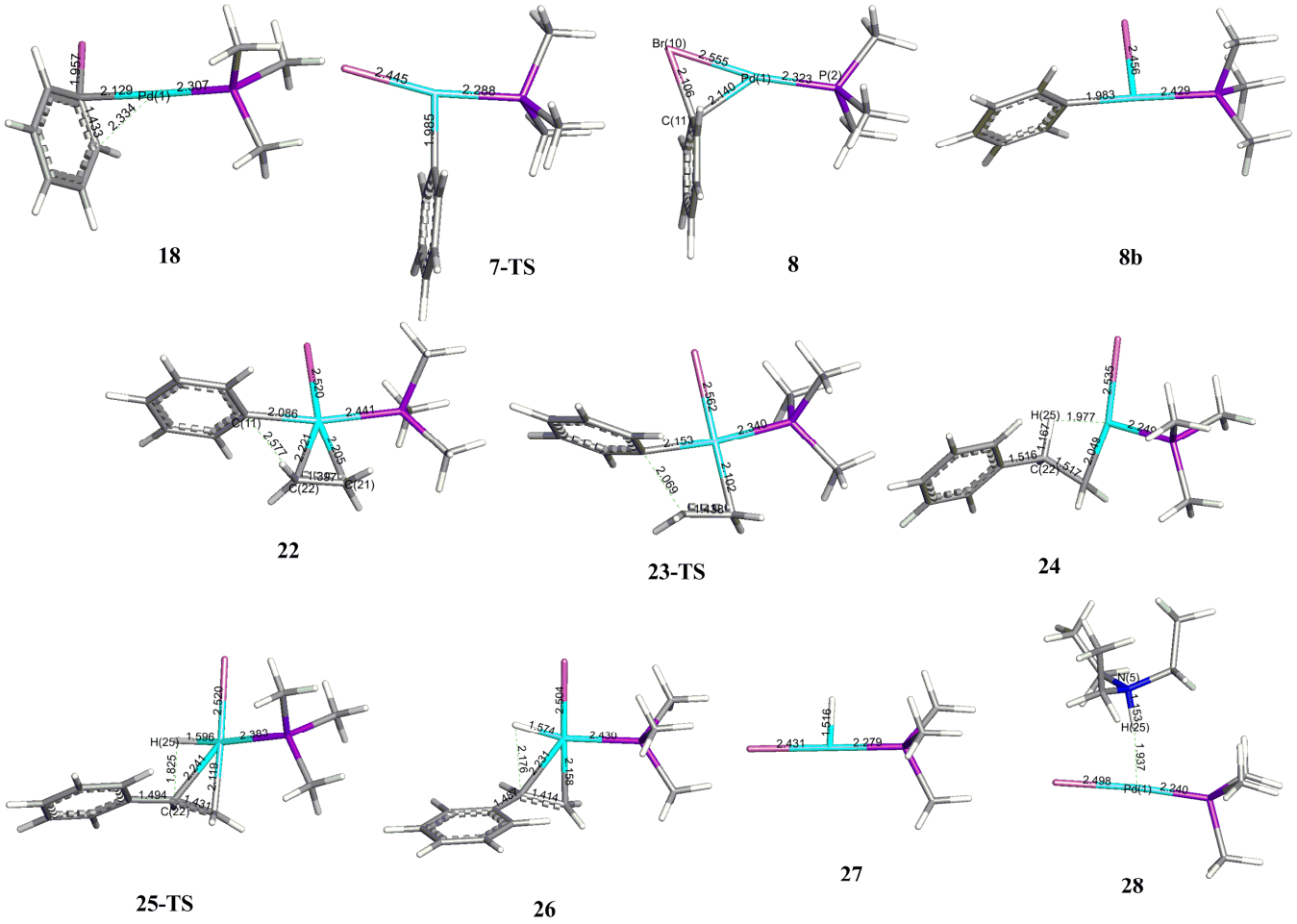

Figure S1. Molecular stuctures in the Heck reaction pathway involving mono-nuclear palladium complex with PMe_3 ligand. Calculated bond distances and angles are given in Å.

Table S1. Structure parameters involving **dipalladium**, $Pd_2(PR_3)_2$, in the oxidative addition step.

R	PMe_3					P^tBu_3				
Structure parameters (Å, °)	**6**	**44**	**45**	**46-TS**	**47**	**6**	**44**	**45**	**46-TS**	**47**
Pd(1)-P(1)	2.200	2.228				2.240	2.256			
Pd(1)-Pd(2)		2.652	2.660	2.690	2.626		2.648	2.777	2.843	2.674
Pd(2)-P(2)		2.250	2.329	2.319	2.342		2.262	2.385	2.395	2.458
Pd(2)-P(1)		2.870	2.325	2.329	2.340			2.389	2.384	2.413
Pd(1)-Br(10)				2.777	2.450				2.766	2.468
Pd(1)-C(11)			2.060	2.023	1.957			2.107	2.038	1.966
C(11)-Br(10)			1.986	2.095				1.981	2.121	3.354
Pd(1)-C(20)			2.201					2.176		
Pd(2)-Pd(1)-P(1)		71.5					116.8			
Pd(1)-Pd(2)-P(1)			82.3	87.0	92.4			91.0	92.1	92.0
Pd(1)-Pd(2)-P(2)		160.5	87.1	82.2	81.4		122.9	95.5	96.6	95.6
P(1)-Pd(2)-P(2)			169.4	169.1	172.6			173.3	171.3	168.6
C(11)-Pd(1)-Br(10)				48.7	99.1				49.6	97.6
C(11)-Pd(1)-Pd(2)			165.2	164.8	97.3			167.8	165.5	108.5
C(11)-Br(10)-Pd(1)-Pd(2)				179.0					171.9	
P(1)-Pd(2)-Pd(1)-C(11)			130.5	-17.1	-68.3			72.2	-58.2	-82.7
C(20)-C(11)-Pd(1)-Pd(2)					-44.2					-32.9

Table S2. Structure parameters involving **monopalladium** complexes, $Pd(PR_3)$, in the oxidative addition step.

R	P^tBu_3				PMe_3			
Structure parameters (Å, °)	**6**	**18**	**7-TS**	**8**	**6**	**18**	**7-TS**	**8**
Pd(1)-P(1)	2.240	2.359	2.394	2.367	2.200	2.307	2.323	2.288
Pd(1)-Br(10)			2.596	2.452			2.555	2.445
Pd(1)-C(11)		2.116	2.040	1.980		2.129	2.140	1.985
Pd(1)-C(20)		2.318				2.334		
C(11)-Br(10)		1.963	2.248	3.310		1.957	2.106	
C(11)-Pd(1)-Br(10)			56.5	96.0			52.4	105.0
P(1)-Pd(1)-Br(10)			132.4	163.7			169.9	167.9
C(11)-Pd(1)-P(1)		176.9	171.0	100.2		178.2		
C(11)-Br(10)-Pd(1)-P(1)			178.2				180.0	

Table S3. Structure parameters of **substrate-bound palladium** complexes in the oxidative addition step.

	free Pd			Pd(η^2-C_2H_4)					$PdBr^-$			
Structure parameters (Å, °)	**41**	**42-TS**	**43**	**32**	**33**	**34-TS**	**35**	**35b**	**60**	**61**	**62-TS**	**63**
Pd(1)-Br(12)									2.44	2.52	2.56	2.48
Pd(1)-Br(10)		2.720	2.392			2.531	2.427	2.453			2.86	2.48
Pd(1)-C(11)	2.069	2.015	1.930		2.102	1.993	1.988	2.006		2.03	1.98	1.95
Pd(1)-C(20)	2.190				2.549					2.16		
C(11)-Br(10)	1.970	2.094			1.951	2.479				2.02	2.17	
Pd(1)-C(21)				2.095	2.160	2.240	2.173	2.113				
Pd(1)-C(22)				2.095	2.162	2.199	2.173	2.153				
C(11)-C(22)												
C(21)-C(22)				1.421	1.402	1.393						
C(11)-Pd(1)-Br(10)		49.8	98.0			65.2	94.1	151.9			49.1	96.3
Br(12)-Pd(1)-Br(10)												167.3
C(21)-Pd(1)-C(11)						167.3						
C(22)-Pd(1)-C(11)						156.2						

Table S4. Structure parameters of **dipalladium, $Pd_2(PMe_3)_2$**, in the migratory insertion, β-H elimination, and catalyst recovery.

Structure parameters (Å, °)	**47**	**47b**	**52**	**53-TS**	**54**	**55-TS**	**56**	**57**	**58**
Pd(1)-Pd(2)	2.626	2.577	2.634	2.735	2.720	2.697	3.173	2.715	2.655
Pd(2)-P(2)	2.342	2.354	2.344	2.330	2.333	2.335	2.349	2.350	2.320
Pd(2)-P(1)	2.340	2.340	2.343	2.337	2.322	2.324	2.350	2.350	2.326
Pd(1)-Br(10)	2.450	2.522	2.586	2.499	2.449	2.494	2.488	2.431	2.466
Pd(1)-C(11)	1.957	1.975	2.049	2.112					
Pd(1)-C(21)			2.202	2.066	2.036	2.08	2.127		
Pd(1)-C(22)			2.208	2.295	2.346	2.215	2.179		
C(11)-C(22)			2.66	1.955	1.516				
C(21)-C(22)			1.399	1.453	1.497	1.45	1.414		
C(22)-H(25)					1.215	1.583			
Pd(1)-H(25)					1.824	1.612	1.686	1.583	1.798
Pd(2)-H(25)							1.683	1.867	
N(5)-H(25)									1.241
Pd(1)-Pd(2)-P(1)	92.4	87.5	91.7	92.6	87.6	88.2			
Pd(1)-Pd(2)-P(2)	81.4	85.8	91.7	92.8	90.7	89.8			
P(1)-Pd(2)-P(2)	172.6	170.6	167.8	165.0	174.3	174.4	174.8	170.3	162.9
C(11)-Pd(1)-Br(10)	99.1	159.2							
C(11)-Pd(1)-Pd(2)	97.3	91.8	81.1	91.0					
Pd(2)-Pd(1)-Br(10)		109.0	82.0	85.3	100.4	98.3	79.2	154.0	174.1
C(21)-Pd(1)-H(25)					69.8	84.4			
P(1)-Pd(2)-Pd(1)-C(11)	-68.3	-78.1	-97.0	-92.4					
C(20)-C(11)-Pd(1)-Pd(2)	-44.2	-40.6	-91.1						

Table S5. Structure parameters of **monopalladium** complexes in the migratory insertion, β-H transfer/olefin elimination, and catalyst recovery with **PMe_3 ligand**.

Structure parameters (Å, °)	**8**	**8b**	**22**	**23-TS**	**24**	**25-TS**	**26**	**27**	**28**
Pd(1)-P(1)	2.288	2.428	2.441	2.340	2.249	2.384	2.430	2.278	2.240
Pd(1)-Br(10)	2.445	2.456	2.520	2.562	2.534	2.519	2.504	2.432	2.498
Pd(1)-C(11)	1.985	1.984	2.086	2.154					
Pd(1)-C(21)			2.205	2.101	2.049	2.119	2.158		
Pd(1)-C(22)			2.221	2.306	2.439	2.241	2.232		
C(11)-C(22)			2.577	2.070	1.516				
C(21)-C(22)			1.397	1.438	1.517	1.432	1.415		
C(22)-H(25)					1.167	1.824	2.177		
Pd(1)-H(25)					1.977	1.595	1.574	1.516	1.937
N(5)-H(25)									1.154
C(11)-Pd(1)-Br(10)	105.0	86.5	82.2	87.8					
P(1)-Pd(1)-Br(10)	167.9	95.4	83.5	85.6	94.4	88.8	87.9	180.0	175.1
C(21)-Pd(1)-H(25)					66.3	91.5	102.9		

Table S6. Structure parameters of **ethylene-bound palladium** complexes in the migratory insertion, β-H transfer/olefin elimination, and catalyst recovery.

Structure parameters (Å, °)	**35**	**35b**	**36-TS**	**37**	**38-TS**	**39**	**40**	**59**
Pd(1)-Br(10)	2.427	2.453	2.432	2.397	2.411	2.418	2.371	2.425
Pd(1)-C(11)	1.988	2.006	2.061					
Pd(1)-C(21)	2.173	2.113	2.036	1.999	2.081	2.154		
Pd(1)-C(22)	2.173	2.153	2.226	2.335	2.240	2.171		
C(11)-C(22)			2.031	1.515				
C(21)-C(22)			1.454	1.502	1.435	1.410		
C(22)-H(25)				1.198	1.650			
Pd(1)-H(25)				1.828	1.556	1.518	1.509	1.855
N(5)-H(25)								1.188
C(11)-Pd(1)-Br(10)	94.1	151.9	162.1					
C(21)-Pd(1)-C(11)			96.0					
C(21)-Pd(1)-H(25)				69.9	83.9			
Br(10)-Pd(1)-H(25)				177.5	129.8	84.2	79.8	83.0
C(21)-Pd(1)-Br(10)				112.0	145.2			

Table S7. Structure parameters of **bromide-bound palladium** complexes in the migratory insertion, β-H transfer/olefin elimination, and catalyst recovery.

Structure parameters (Å, °)	**63**	**64**	**65-TS**	**66**	**67-TS**	**68**	**69**	**70**
Pd(1)-Br(12)	2.48	2.514	2.584	2.483	2.566	2.511	2.471	2.498
Pd(1)-Br(10)	2.48	2.627	2.537	2.503	2.558	2.672	2.471	2.487
Pd(1)-C(11)	1.95	2.021	2.135					
Pd(1)-C(21)		2.167	2.066	2.024	2.079	2.146		
Pd(1)-C(22)		2.167	2.306		2.192	2.201		
C(11)-C(22)			1.937	1.516				
C(21)-C(22)		1.403	1.452	1.534	1.448	1.413		
C(22)-H(25)					1.626			
Pd(1)-H(25)					1.592	1.549	1.502	1.566
N(5)-H(25)								1.677
C(11)-Pd(1)-Br(10)	96.4	178.3	177.0					
C(11)-Pd(1)-Br(12)	96.3	86.4	88.7					
Br(12)-Pd(1)-Br(10)	167.3	94.8	94.2	169.4	99.8	97.3		
C(21)-Pd(1)-H(25)					86.9			
Br(12)-Pd(1)-H(25)					82.4	77.8	90.4	89.8
Br(10)-Pd(1)-H(25)							90.7	90.6
C(21)-Pd(1)-Br(10)				95.2	90.9	86.3		
C(21)-Pd(1)-Br(12)				95.3	169.3	165.8		