Supplementary information

Palladium(II)-Catalyzed Annulation of *N*-Methoxy Amides and Arynes: Computational Mechanistic Insights and Substituents Effects

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Contents

1 Gaussian Complete Reference

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2 Alternative C−H activation transition states

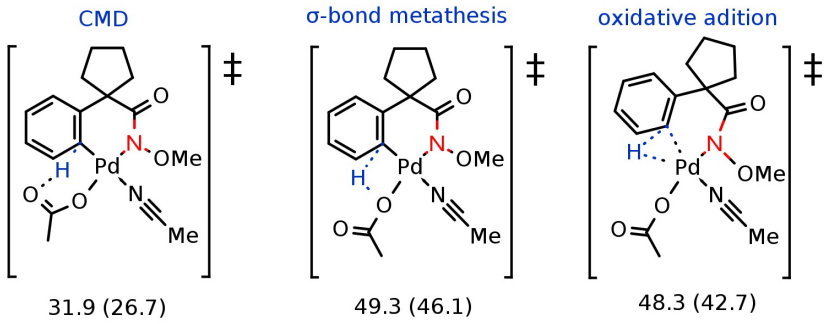

Figure S1: CMD, σ-bond metathesis, and oxidative addition transition states. Gibbs free energies (electronic energies) given in kcal.mol^{-1}.

3 AcCN x HOAc

Figure S2 depicts the Gibbs free for some intermediates with acetonitrile and acetic acid coordinate with the metal. In all cases acetontrile acts a better ligand than AcOH.

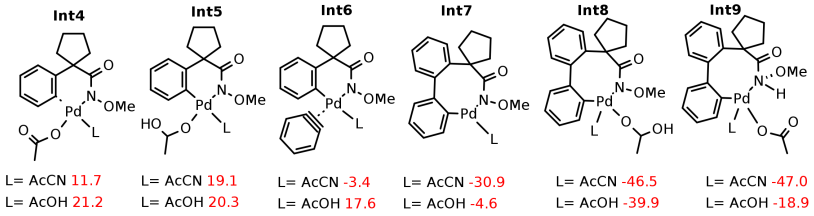

Figure S2: Comparision between AcOH and acetonitrile. Gibbs free energies given in kcal.mol^{-1}.

4 Substituent effect

Table S1: Tabular data of activation energies, reaction rates, Hammett constants, and NBO charges used to construct the Hammett and NBO plots.

R	$\Delta G^{\ddagger}$	$log k/k_0$	σ_p	q_{NBO}(PdL)	q_{NBO}(ArH)
H	31.9	0.00	0.00	0.22	0.21
p-NH_2	27.3	2.57	-0.66	0.15	0.32
p-OMe	27.2	2.61	-0.27	0.19	0.26
p-OH	29.1	1.58	-0.37	0.19	0.26
p-F	30.0	1.07	0.06	0.22	0.21
p-Cl	30.1	1.00	0.23	0.22	0.21
p-Br	30.4	0.84	0.23	0.22	0.21
p-Me	30.9	0.57	-0.17	0.21	0.23
p-CN	33.5	-0.90	0.66	0.26	0.13
p-NO_2	33.5	-0.44	0.78	0.26	0.13

Table S2: Wiberg bond indexes.

R	**Wiberg bond index (Pd-C)**	**Wiberg bond index (C-H)**
H	0.50	0.43
p-NH_2	0.57	0.39
p-OMe	0.54	0.42
p-OH	0.54	0.41
p-Me	0.52	0.43
p-F	0.51	0.43
p-Cl	0.50	0.43
p-Br	0.50	0.43
p-CN	0.48	0.44
p-NO_2	0.47	0.44