Analysis of the Concerted Metallation-Deprotonation Mechanism in Palladium-Catalyzed Direct Arylation Across a Broad Range of Aromatic Substrates

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Supporting Information

COMPUTATIONAL DETAILS:

Density Functional Theory (DFT) calculations have been performed using the *Gaussian 03* program.[1] In all calculations, the spin-restricted method was employed. Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation (XC) functional[2, 3] with the mixed basis set (DZVP[4] on Pd and TZVP[5] on all other atoms). The Pd catalyst was modeled with the PMe_3 ligand and the acetate base (Figure S1). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force gradients (OPT=CalcAll) were used to determine the nature of the stationary points. Intrinsic reaction coordinate (IRC)[6, 7] calculations were used to confirm the reaction pathways through the CMD transition states (TSs) for all reactants. Free energies of species were evaluated at 298K and 1 atm.

Orbital populations and compositions were calculated using Mulliken population analysis (MPA)[8] using the *AOMix* program.[9] The analysis of the orbital compositions of the CMD transition states in terms of orbitals of the fragment molecules (Table S1) was

performed using the *AOMix-CDA* program.[10, 11] Mayer bond orders[12] were calculated using the *AOMix-L* program.[11] Atomic charges were evaluated by using the natural population analysis (NPA).[13]

Figure S1. The optimized structure of the Pd^{II} catalyst for the CMD step.

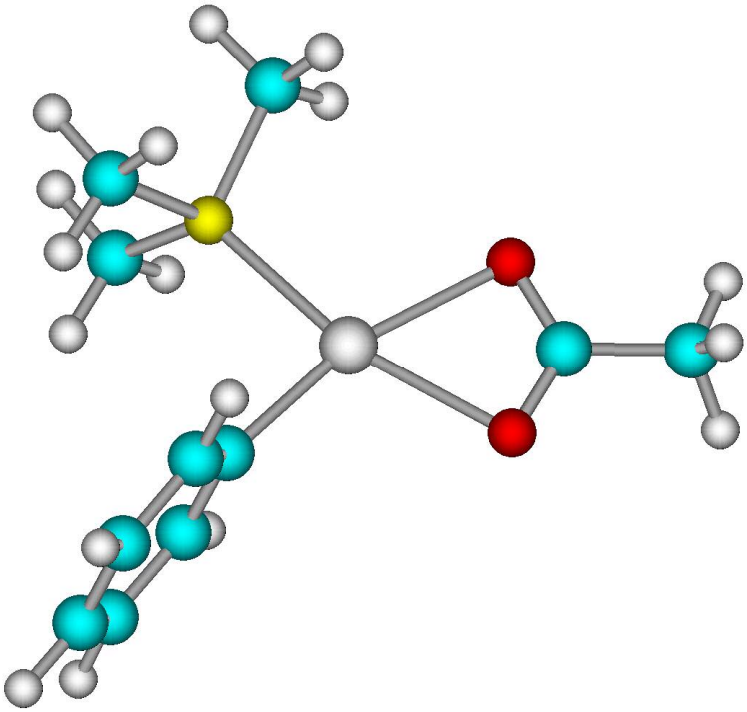

Table S1. Changes[a] in fragment orbital populations (%) at the formation of the CMD transition state from its fragments (the Pd(Ph)(PMe_3)Ac and ArH).

	Pd(Ph)(PMe_3)(Ac)		ArH	
Species[b]	OMOs	UMOs	OMOs	UMOs
1	HOMO 13.6%	LUMO 14.5%	HOMO 3.5% HOMO-2 6.0% HOMO-5 3.7%	LUMO 11.5% LUMO+1 2.6% LUMO+3 3.3%
2	HOMO 13.9%	LUMO 16.2%	HOMO 4.3% HOMO-4 3.1% HOMO-10 3.0%	LUMO 8.4% LUMO+1 7.2%
3	HOMO 13.8%	LUMO 15.0%	HOMO-2 7.9% HOMO-4 6.1%	LUMO 11.5% LUMO+2 5.3%
4	HOMO 13.8%	LUMO 18.2%	HOMO 11.2%	LUMO 11.7% LUMO+1 5.2%
5	HOMO 14.1%	LUMO 20.6%	HOMO 14.8%	LUMO 13.4% LUMO+1 4.6%
6	HOMO 14.9%	LUMO 22.0%	HOMO 14.9% HOMO-2 5.0%	LUMO 15.7% LUMO+1 2.7%
7	HOMO 15.1%	LUMO 23.2%	HOMO 17.7% HOMO-6 5.1%	LUMO 5.7% LUMO+1 10.2% LUMO+2 3.6%
8	HOMO 16.0%	LUMO 26.2%	HOMO 15.4% HOMO-1 3.2% HOMO-2 3.8% HOMO-4 3.8%	LUMO 14.3% LUMO+1 4.0% LUMO+2 3.0%
9	HOMO 16.5%	LUMO 27.0%	HOMO 16.1% HOMO-1 2.5% HOMO-2 4.7% HOMO-4 3.4%	LUMO 15.8% LUMO+1 3.7% LUMO+2 2.6%
10	HOMO 15.0%	LUMO 21.7%	HOMO 12.3% HOMO-1 2.5% HOMO-4 2.2% HOMO-7 4.2%	LUMO 13.5% LUMO+3 4.2%
11	HOMO 13.1%	LUMO 13.0%	HOMO-1 8.6% HOMO-4 3.9%	LUMO 11.3% LUMO+3 4.7%
12	HOMO 14.4%	LUMO 22.0%	HOMO 15.2% HOMO-2 4.6% HOMO-5 2.3%	LUMO 13.6% LUMO+2 3.6%
13	HOMO 13.8%	LUMO 19.2%	HOMO 3.4% HOMO-1 8.1% HOMO-3 2.4%	LUMO 11.7% LUMO+2 4.9%
14	HOMO 13.7%	LUMO 16.9%	HOMO 3.4% HOMO-1 6.8% HOMO-7 3.7%	LUMO 10.2% LUMO+2 5.8%

a) fragment molecular orbitals (OMO = occupied molecular orbital of a fragment, UMO = the unoccupied molecular orbital of a fragment) with a significant change (> 2%) in

electron population are listed. B) Numbering of species corresponds to Table 1 in the manuscript.

EXPERIMENTAL

General Methods:

All starting materials and reagents were purchased from Aldrich and used without further purification. All reactions were performed in air-dried or oven-dried glassware. Microwave heating was performed using a *CEM* Discover Microwave (specific reaction conditions are described below). Analysis of crude reaction mixtures were done on an Agilent 6890 Network GC System with an Agilent 5973 Network Mass Selective Detector. Reactions were purified with silica gel by flash chromatography. ^{1}H, ^{13}C, and DEPTQ-135 spectra were recorded in $CDCl_3$ solutions on a Bruker AVANCE 400 MHz spectrometer at ambient temperature and chemical shifts are reported relative to tetramethylsilane (TMS). Fourier-transform infra-red (FTIR) spectra were obtained as thin films on sodium chloride plates. High resolution mass spectra were obtained with a Kratos Concept IIH mass spectrometer. Melting points were recorded using a Gallenkamp Melting Point Apparatus and are reported uncorrected.

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