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LETTER

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Catalyst Control of Site Selectivity in the $Pd^{II/IV}$-Catalyzed Direct Arylation of Naphthalene

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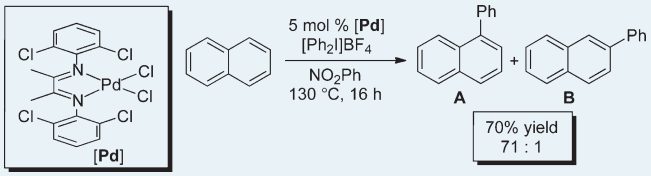
Supporting Information

ABSTRACT: This letter describes a new method for the highly site- and chemoselective Pd-catalyzed direct arylation of naphthalene. Tuning the structure of the diimine-ligated Pd catalyst results in formation of the α-arylated product in high yield and >50:1 selectivity. This is, to our knowledge, the first systematic evaluation of catalyst control in the C−H arylation of an unactivated aromatic substrate. Preliminary studies implicate an unusual mechanism involving sequential naphthalene π-coordination/metalation at Pd^{IV}.



KEYWORDS: C−H functionalization, catalyst control, regioselective functionalization, naphthalene, palladium

Aryl−aryl bonds are ubiquitous in organic molecules, including pharmaceuticals, agrochemicals, and natural products.[1] Although these linkages are most commonly formed via the cross-coupling of two prefunctionalized arenes,[1] there has been tremendous recent progress in the development of metal-catalyzed C−H arylation reactions.[2−5] In these systems, the aryl−aryl bond is formed by directly merging an arene or heteroarene with an aryl halide, aryl organometallic (e.g., $ArB(OH)_2$, $ArSnBu_3$, $ArSiX_3$), or aryl iodonium salt.

A major challenge in the field of direct arylation is achieving site-selective C−H functionalization. The three most common strategies are to use (1) arene substrates that contain directing groups,[6−9] (2) arene substrates bearing intramolecular coupling partners,[10,11] or (3) heteroarene substrates with highly activated C−H bonds (e.g., indoles, pyrroles).[12−16] All three approaches have provided powerful methods for the selective assembly of complex molecules. However, the requirement for substrate-based control over selectivity inherently restricts the scope of these transformations.

In contrast, the site-selective direct arylation of unactivated aromatics remains extremely rare.[17−20] Naphthalene has proven to be a particularly challenging substrate for this type of reaction, and previously reported methods have provided either low yields[21] or only modest (<3.5:1) preference for the alpha isomer (Table 1).[22−24] Catalyst-based control (i.e., using steric and electronic modification of ancillary ligands at the metal to dictate the preferred site of C−H arylation) would be a powerful approach for modulating the selectivity of such transformations. Although catalyst control of selectivity and reactivity is common in other areas of Pd catalysis,[25−30] C−H functionalization reactions often work best with simple Pd salts such as $Pd(OAc)_2$ and $PdCl_2$ (for example, Table 1; entries 1, 2, and 4), which do not contain readily tunable ligands.

This communication reports the first systematic examination of catalyst-controlled selectivity in the Pd-catalyzed arylation of an unactivated arene.[31−35] We demonstrate that modular diimine-ligated Pd catalysts can be tuned to enhance both the reaction yield and site selectivity of naphthalene phenylation with $[Ph_2I]BF_4$. Preliminary investigations implicate a mechanism in which naphthalene π-coordination and subsequent metalation occur at a high oxidation state Pd center.

Table 1. Metal-Catalyzed Direct Arylation of Naphthalene

entry	Ar−X	catalyst/oxidant	yield, %	α/β
1[23]	p-$NO_2C_6H_4I$	$Pd(OAc)_2$/none	88	3.3:1
2[24]	$PhSnCl_3$	$PdCl_2/CuCl_2$	40	3.4:1
3[22]	PhBr	Cp_2Ni-KO^{t}Bu-BEt_3	70	2.3:1
4[21]	PhH	$Pd(OAc)_2$/TFA/$K_2S_2O_8$	32	>20:1

Our initial investigations focused on the Pd-catalyzed C−H phenylation of naphthalene with Ph_2IBF_4. $Pd(OAc)_2$ was the first catalyst examined, since it has been used for other C−H functionalization reactions with $[Ar_2I]^+$ reagents.[24,36−41] We were pleased to find that phenylated products **A** and **B** were formed in a variety of different solvents. Under the optimal conditions (NO_2Ph at 130 °C for 16 h), $Pd(OAc)_2$ provided 24% yield and 5:1 selectivity for isomer **A** (Table 2, entry 1). This selectivity is comparable to that observed in many other naphthalene arylation reactions (Table 1, entries 1−3).[22−24] A survey of Pd salts (Table 2, entries 2−4) revealed that the X-type ligand has a significant influence on selectivity, with $PdCl_2$ providing the best results (**A**/**B** = 13:1, entry 2).

We next examined naphthalene phenylation with $PdCl_2$ complexes of 1,4-bisphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene ($^{Ph}DAB^{Me}$), di-*tert*-butyl bipyridine (dtbpy), and 1,10-phenanthroline

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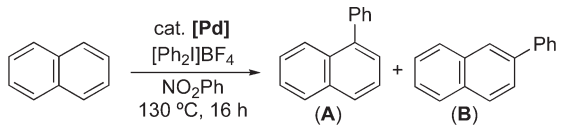
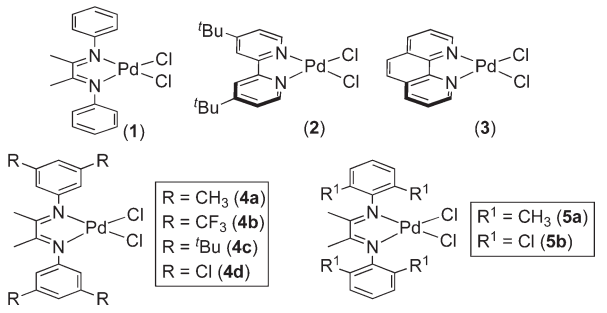
Table 2. Catalyst and Solvent Effects in the Phenylation of Naphthalene with $[Ph_2I]BF_4$[a]



entry	catalyst	yield, %	A/B
1	$Pd(OAc)_2$	24	5:1
2	$PdCl_2$	22	13:1
3	$PdBr_2$	21	8:1
4	PdI_2	12	8:1

[a] Conditions: Pd catalyst (3.68 μmol, 5 mol %), naphthalene (47.1 mg, 0.368 mmol, 5 equiv), Ph_2IBF_4 (27.1 mg, 0.0735 mmol, 1 equiv) in NO_2Ph (0.75 mL) at 130 °C for 16 h. Yield and selectivity determined by GC/MS.

Table 3. Substituted Diimine Pd^{II} Catalysts for the Phenylation of Naphthalene with $[Ph_2I]BF_4$[a]



entry	catalyst	yield, %	A/B
1	**1**	54	9:1
2	**2**	22	78:1
3	**3**	12	10:1
4	**4a**	47	9:1
5	**4b**	50	10:1
6	**4c**	32	18:1
7	**4d**	42	22:1
8	**5a**	43	27:1
9	**5b**	70	71:1

[a] Conditions: Pd catalyst (3.68 μmol, 5 mol %), naphthalene (47.1 mg, 0.368 mmol, 5 equiv), Ph_2IBF_4 (27.1 mg, 0.0735 mmol, 1 equiv) in NO_2Ph (0.75 mL) at 130 °C for 16 h. Yield and selectivity determined by GC/MS.

(phen) (**1**−**3**). These ligands were selected because they are all known to support Pd^{II} and/or Pt^{II} complexes that promote arene C−H activation.[42−44] We were gratified that distinct changes in both reactivity and selectivity were observed as a function of catalyst structure. For example, complex **1** afforded double the yield of $PdCl_2$ (Table 3, entry 1), whereas **2** provided dramatically enhanced selectivity for isomer **A** (**A**/**B** = 78:1, entry 2). *These results clearly demonstrate the potential for catalyst control in Pd-catalyzed C−H arylation.*

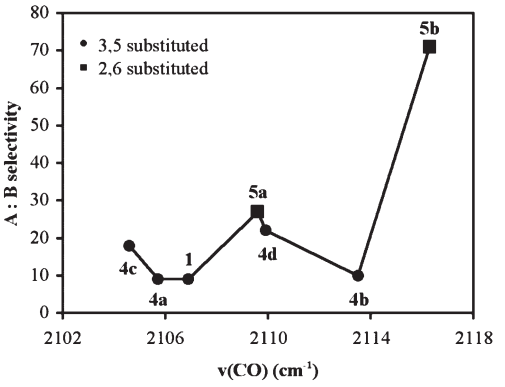


Figure 1. **A**/**B** ratio versus diimine electronics (as measured by ν_{CO} for (diimine)$Pt(CH_3)(CO)^+$). ●, 3,5-substituted diimines; ■, 2,6-substituted diimines.

Complex **1** is an attractive starting point for systematically evaluating ligand effects because electronically and sterically diverse diimine analogues are readily available.[45] A series of bis(aryl)diimine$PdCl_2$ complexes containing various R and R^1 substituents (**4a**−**d**; **5a**, **b**) were prepared, and substitution at both R and R^1 had a significant influence on selectivity and yield (Table 3). The 2,6-Cl diimine complex **5b** was particularly effective for this transformation (entry 9), providing the highest yield (70%) and **A**/**B** selectivity (71:1) of the series.[46−48] Notably, the **5b**-catalyzed reaction was also very clean and afforded <5% yield of diarylated naphthalene, biphenyl, or binaphthyl side products.

To obtain more quantitative information about the influence of ligand structure on selectivity, we examined the **A**/**B** ratio as a function of the electronic character of the diimine [as measured by ν_{CO} for (diimine)$Pt(CH_3)(CO)^+$].[49] As shown in Figure 1, there was no clear relationship between ν_{CO} and the **A**/**B** ratio, even when potential steric contributions were eliminated (3,5-substituted derivatives, Figure 1, ●). These data suggest that the observed ligand effects are not predominantly electronic in nature. In addition, the poor correlation between ligand electronic properties and selectivity/yield suggests against a Lewis acid catalyzed mechanism, since the Lewis acidity of the Pd center is expected to track closely with the electron withdrawing ability of the ligand.[50]

We also probed the chemoselectivity of **5b**-catalyzed C−H arylation. A 1:1 mixture of naphthalene and other electron-rich and -deficient arenes was subjected to the standard conditions in the presence of 0.2 equiv of $[Ph_2I]BF_4$. In all cases, the reaction was remarkably selective for naphthalene, with (**A** + **B**)/**C** ratios ranging from >600:1 (trifluorotoluene, benzene) to 12:1 (veratrole) (Table 4).[51] Chemoselectivity did not track well with nucleophilicity (N);[52,53] substrates that are much more nucleophilic than naphthalene (1,3-dimethoxybenzene, anisole) were significantly less reactive in this competition experiment. These results indicate that the chemoselectivity-determining step does not proceed via a classical electrophilic aromatic substitution pathway.[54]

The kinetic isotope effect (KIE) was determined by comparing the initial rate of naphthalene phenylation to that of naphthalene-d_8. This study showed a KIE of 1.0 ± 0.1, suggesting that C−H bond cleavage is not involved in the rate-determining step of the catalytic cycle. A competition experiment between naphthalene and naphthalene-d_8 afforded a competition k_H/k_D

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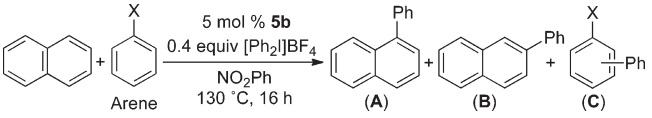
Table 4. Chemoselectivity of C−H Phenylation Catalyzed by 5b[a]



entry	arene	N[52]	total yield, %	(A + B)/C
1	1,3-dimethoxybenzene	2.4	39	43:1
2	veratrole	na	52	12:1
3	anisole	−1.6	63	210:1
4	*o*-xylene	−3.7	60	597:1
5	naphthalene	−3.8	70	
6	*p*-xylene	−4.2	60	>600:1
7	benzene[b]	−6.3	27	>600:1
8	trifluorotoluene	−10.3	55	>600:1

[a] Conditions: catalyst **5b** (2.0 mg, 3.68 μmol, 5 mol %), naphthalene (23.6 mg, 0.184 mmol, 2.5 equiv), arene (0.184 mmol, 2.5 equiv), Ph_2IBF_4 (27.1 mg, 0.0735 mmol, 1 equiv) in NO_2Ph (0.75 mL) for 16 h at 130 °C. Yield and selectivity determined by GC/MS. [b] Using *p*-tol_2IBF_4.

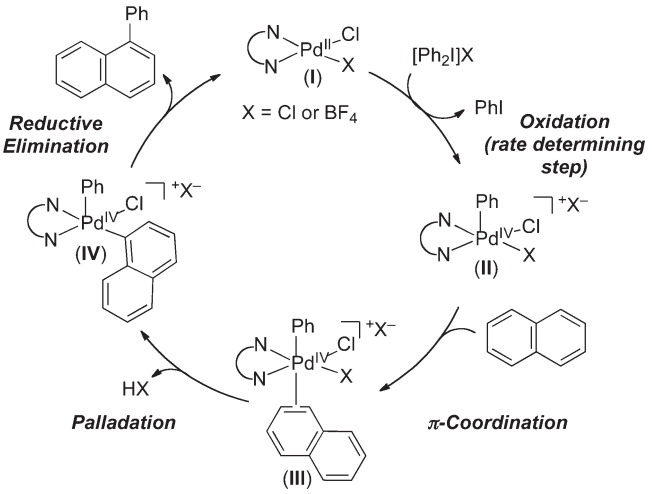
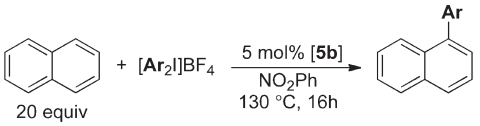


Figure 2. Proposed mechanism for C−H phenylation of naphthalene with Ph_2IBF_4.

of 1.07 ± 0.03. This value is significantly smaller than is typical for Pd-catalyzed C−H arylation reactions that involve palladation at Pd^{II} centers (general range = 1.8−5.5).[55−57] However, the observed value is similar to that reported for the Pd-catalyzed carboamination of alkenes with benzene (competition k_H/k_D = 1.1). Michael and co-workers proposed that this small isotope effect resulted from π-coordination of benzene to a Pd^{IV} intermediate prior to C−H bond-breaking.[58]

Finally, we established the kinetic order of C−H arylation in both Ph_2IBF_4 and naphthalene. As shown in Figure S7 of the Supporting Information, this transformation is 0 order with respect to naphthalene, which provides further evidence against rate determining C−H bond cleavage. In contrast, a first-order dependence on Ph_2IBF_4 was observed (Figure S6 of the Supporting Information), indicating that the arylating reagent is involved in the turnover-limiting step of the catalytic cycle.

Table 5. Oxidant Scope for Arylation of Naphthalene with Catalyst 5b[a]



entry	Ar	yield,[b] %
1	C_6H_5	72
2	*p*-$CH_3C_6H_4$	68
3	*p*-BrC_6H_4	65
4	*p*-$CF_3C_6H_4$	62
5	*m*-$NO_2C_6H_4$	71
6	*o*-$CH_3C_6H_4$	trace[c]
7	*p*-$MeOC_6H_4$	nr

[a] Conditions: catalyst **5b** (19.3−24.5 μmol, 5 mol %), naphthalene (7.7−9.8 mmol, 20 equiv), $[Ar_2I]BF_4$ (0.39−0.49 mmol, 1 equiv) in NO_2Ph (98 mM in oxidant) for 16 h at 130 °C. [b] Isolated yields. [c] Detected by GC/MS.

Collectively, these observations are consistent with the $Pd^{II/IV}$ mechanism shown in Figure 2. This pathway involves (i) rate-determining oxidation of Pd^{II} catalyst **I** with Ph_2IBF_4 to form Pd^{IV} intermediate **II**,[59] (ii) π-coordination of naphthalene to Pd^{IV} to generate **III**, (iii) palladation to produce **IV**, and (iv) C−C bond-forming reductive elimination to release the product. We propose that π-coordination to Pd^{IV} is the chemoselectivity-determining step. This is consistent with the competition KIE (1.07 ± 0.03), which is very similar to that seen by Michael for an analogous mechanism.[58] In addition, this provides a compelling explanation for the unusually high chemoselectivity because naphthalene is well-known to form more stable metal π-complexes than benzene derivatives.[60]

Preliminary stoichiometric studies provide further support for the mechanism in Figure 2. For example, no reaction was observed between catalyst **5b** and naphthalene when these two reagents were stirred at 130 °C in NO_2Ph.[61] In addition, the stoichiometric reaction between **5b** and Ph_2IBF_4 in the absence of naphthalene resulted in complete consumption of oxidant and concomitant formation of 1 equiv of PhCl and 1 equiv of PhI. This is consistent with the generation of Pd^{IV} intermediate **II** that undergoes C−Cl bond-forming reductive elimination in the absence of naphthalene.[62]

On the basis of this mechanism, we hypothesized that electron deficient diaryliodonium oxidants would be particularly effective, since they should accelerate the rate-determining oxidation step. Indeed, Ar_2IBF_4 reagents containing electron-deficient and neutral aryl groups provided high yield and selectivity (Table 5, entries 1−5). In contrast, arylating agents containing electron-rich aryl groups, such as *p*-methoxyphenyl (Table 5, entry 7) and ortho-substituted aryl groups (Table 5, entry 6), performed poorly in this reaction. Again, these results are all consistent with the proposed mechanism.

In conclusion, we have developed the first high-yielding site- and chemoselective process for the C−H arylation of naphthalene. Preliminary mechanistic data is consistent with a $Pd^{II/IV}$ catalytic cycle involving naphthalene π-coordination and subsequent palladation. This work adds to a small but growing body of literature implicating C−H activation at high oxidation state Pd

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centers in catalysis.[24,58,63,64] It also suggests, for the first time, that both reactivity and selectivity in Pd^{IV}-mediated C−H arylation can be tuned through modification of supporting ligand structure. We are currently applying a similar strategy to develop catalyst-controlled direct arylation reactions of diverse unactivated C−H substrates.

■ ASSOCIATED CONTENT

Supporting Information. Complete experimental details, catalyst characterization, and kinetic data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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