Hypervalent Compounds

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Diaryliodoniums by Rhodium(III)-Catalyzed C–H Activation: Mild Synthesis and Diversified Functionalizations**

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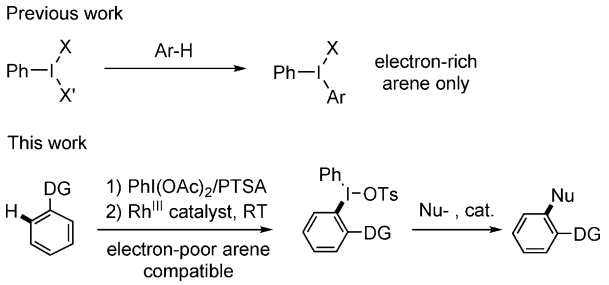
Abstract: *Diaryliodonium salts play an increasingly important role as an aryl source. Reported is the first synthesis of diaryliodoniums by rhodium(III)-catalyzed C–H hyperiodination of electron-poor arenes under chelation assistance. This C–I coupling reaction occurred at room temperature with high regio-selectivity and functional-group compatibility. Subsequent diversified nucleophilic functionalization of a diaryliodonium allowed facile construction of C–C, C–N, C–O, C–S, C–P and C–Br bonds, and in all cases the initial functionalization occurred at the arene containing the chelating-group.*

Hypervalent iodine compounds are versatile electrophiles with the appealing combination of high reactivity, stability, selectivity, and environmental friendliness.[1] Diaryliodonium salts are particularly useful,[2] and they are typically accessed by transmetalation between a boron reagent and a simple iodine(III) source,[3] or by electrophilic functionalization of an electron-rich arene (Scheme 1).[4] The latter method is appealing because no prior functionalization of the arene is necessary. However, the restriction to electron-rich arenes may significantly limit the applications.

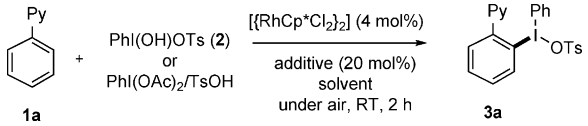
It has been well demonstrated that unactivated arenes can be readily functionalized by metal-catalyzed C–H activation.[5] In particular, [Cp*Rh^{III}]-catalyzed C–H activation reactions have shown very broad substrate scope in the mild and selective functionalization of arenes.[6] This broad substrate scope is in part ascribable to the high polarity and reactivity of the Rh^{III}–aryl bond, in which the aryl ligand functions as a relatively strong nucleophilic aryl source and can be regenerated.[7] We reasoned that rhodium-catalyzed C–H activation of electron-poor arenes may be extended to the synthesis of unsymmetrical diaryliodonium salts. Indeed, we[8] and others[9] recently demonstrated that arene C–H activation and hypervalent iodines could be successfully combined by using a [Cp*Rh^{III}] catalyst, although in all cases the iodine(III) reagents delivered no iodine to the product. We now report a rhodium(III)-catalyzed C–H activation strategy for the mild hyperiodination of electron-poor arenes. Significantly, these diaryliodonium products can be selectively and conveniently functionalized by a large array of nucleophiles.

We embarked on our studies with the optimization of the reaction conditions for the coupling between 2-phenylpyridine (**1a**) and Koser's reagent (**2**) catalyzed by [{RhCp*Cl$_2$}$_2$] (4 mol%) (Table 1). When using $AgSbF_6$ as an additive in CH_2Cl_2, no *ortho* phenylation product was detected. Instead, the hyperiodination product **3a** was isolated in 32% yield (entry 1). The yield of **3a** was doubled when the solvent was



Scheme 1. Synthesis of diaryliodonium salts. PTSA = *para*-toluene sulfonic acid.

Table 1: Optimization studies.



1a **3a**

Entry	Iodine(III)	Additive	Solvent	Yield [%][a]
1[b]	PhI(OH)OTs	$AgSbF_6$	CH_2Cl_2	32
2[b]	PhI(OH)OTs	$AgSbF_6$	acetone	65
3[b]	PhI(OH)OTs	CuO	acetone	64
4[b]	PhI(OH)OTs	CuO	TFE	35
5[b]	PhI(OH)OTs	$Cu(OAc)_2$	acetone	48
6[b]	PhI(OH)OTs	Ag_2O	acetone	24
7[c]	$PhI(OAc)_2$/PTSA	$AgSbF_6$	acetone	70
8[c]	$PhI(OAc)_2$/PTSA	–	acetone	58
9[c]	$PhI(OAc)_2$/PTSA	CuO	acetone	74
10[d]	$PhI(OAc)_2$/PTSA	CuO	acetone	85
11[c]	PhI=O/PTSA	–	acetone	< 5

[a] Yield of product isolated after column chromatography. [b] Reaction conditions: **1a** (0.2 mmol), iodine(III) (0.4 mmol), additive (0.04 mmol), [{RhCp*Cl$_2$}$_2$] (0.008 mmol), solvent (2 mL), 2 h, RT under air. [c] Reaction conditions: $PhI(OAc)_2$ (0.3 mmol), *p*-TsOH·H_2O (0.3 mmol), acetone (2 mL), 1 h. Then **1a** (0.2 mmol), additive (0.04 mmol), and [{RhCp*Cl$_2$}$_2$] (0.008 mmol) were then added and were stirred under air for 2 h. [d] $PhI(OAc)_2$ (0.36 mmol) was used. Cp* = C_5Me_5, TFE = 2,2,2-trifluoroethanol, Ts = 4-toluenesulfonyl.

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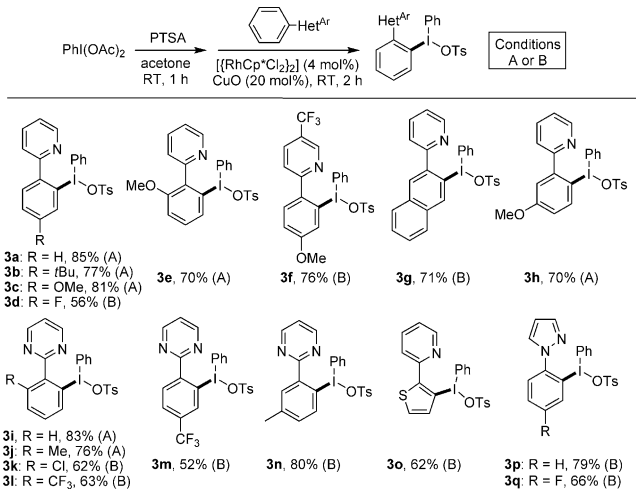
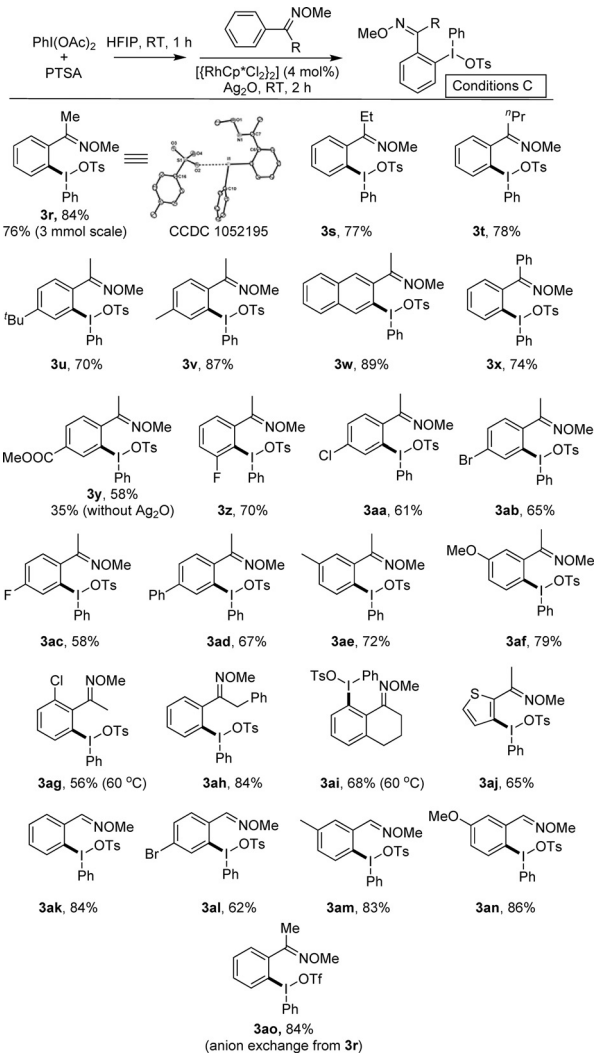
switched to acetone (entry 2). Further optimization using a combination of $PhI(OAc)_2$ (PIDA) and PTSA, which afforded HOAc and **2** in situ, improved the yield (entries 7 and 9). Finally, **3a** was isolated in 85% yield when the amount of PIDA was increased to 1.8 equivalents with CuO being an additive (Conditions A; entry 10). Control experiments verified that no product was detected when the rhodium catalyst was omitted.

The scope of the coupling system was next explored under the optimized reaction Conditions A (Scheme 2). Simple or 2-



Scheme 2. Hyperiodination assisted by heterocycles. [a] Conditions A: PIDA (0.36 mmol) and PTSA (0.3 mmol) were stirred in acetone (2 mL) under air for 1 h. Arene (0.2 mmol), $[\{Cp^*RhCl_2\}_2]$ (0.008 mmol), and CuO (0.04 mmol) were added and was stirred for another 2 h. Conditions B: PIDA (0.4 mmol) and PTSA (0.4 mmol) were stirred in acetone (2 mL) under air for 1 h. Arene (0.2 mmol), $[\{Cp^*RhCl_2\}_2]$ (0.008 mmol), CuO (0.04 mmol), PIDA (1.5 equiv), 2 h. [b] Yield of isolated products.



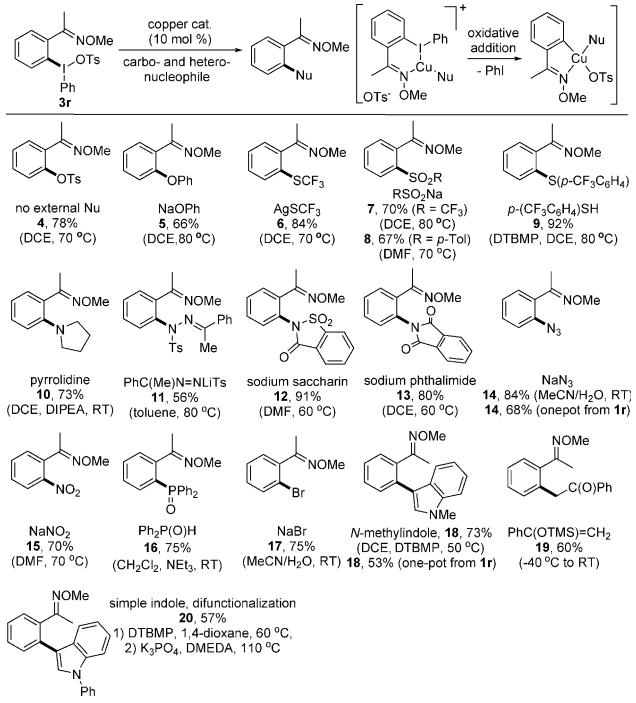
Scheme 3. Hyperiodination of oxime ethers. [a] Conditions C: PIDA (0.4 mmol) and PTSA (0.4 mmol) were stirred in HFIP (2 mL) under air for 1 h. Oxime (0.2 mmol), $[\{Cp^*RhCl_2\}_2]$ (0.008 mmol), Ag_2O (0.04 mmol), and PIDA (0.3 mmol) were added, followed by stirring for 2 h. [b] Yield of the isolated product. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

phenylpyridines substituted with electron-donating groups (EDGs) underwent smooth coupling and the iodoniums **3a–g** were isolated in good to high yields. However, introduction of an electron-withdrawing group (EWG) onto either the phenyl or the heterocyclic ring retarded the reaction. Fortunately, introducing a second batch of PIDA improved the catalytic efficiency (Conditions B). Under these two reaction conditions, EDG, EWG, and halogen substituents at different positions were fully tolerated, and the directing group (DG) was extended to include pyrimidine and pyrazole rings. The coupling of arenes bearing a *meta* substituent occurred at the less hindered C–H bond (**3g**, **3h**, and **3n**), thus suggesting that the site selectivity is dictated by steric effects. In addition, the arene is not limited to a benzene ring, and 2-pyridylthiophene proved to be a viable substrate (**3o**).

Extension of the arene substrate to oxime ethers met with failure under both reaction Conditions A and B. It turned out that the choice of solvent is crucial. Switching to HFIP as a solvent and Ag_2O (20 mol%) as an additive significantly improved the efficiency of hyperiodination of the oxime ether **1r** (Scheme 3), and the diaryliodonium **3r** was isolated in 84% yield, and was additionally characterized by X-ray crystallography (CCDC 1052195).[10] The HFIP is a polar solvent which activated the iodonium(III) reagent.[11] While the Ag_2O additive is unnecessary for oximes bearing an EDG (**3r–w**), it significantly improved the yield for those with an EWG or a halogen substituent. Under the globally optimized reaction Conditions C, a broad spectrum of halogenated, electron-rich, and electron-poor oxime ethers is fully tolerated. The iminyl substituent can be smoothly extended to other alkyl (**3s**, **3t**, and **3ai**) and aryl (**3x**) groups. Significantly, oxime ethers of benzaldehyde are equally competent, although they are generally much less efficient in C–H activation.[12] The mild reaction conditions and high polarity of the HFIP solvent may contribute to the applicability of such substrates. In all cases, high site selectivity and good to high yields (56–89%) were obtained, and for *meta*-substituted arene substrates the C–H functionalization occurred at the less hindered site except for the product **3z**, which bears

a *meta*-F substituent. In addition, the high-yielding synthesis of **3r** at a scale of 3 mmol using a reduced catalyst loading (2 mol%) can also be achieved.

The rich chemistry of diaryliodonium as an arylating reagent has been increasingly explored and it provides a stepping stone for functionalized arenes, as in the seminal work by the groups of Gaunt and Sanford.[13] By taking full advantage of the electrophilicity of the diaryliodonium salt **3r**, we next explored its synthetic applications (Scheme 4). In

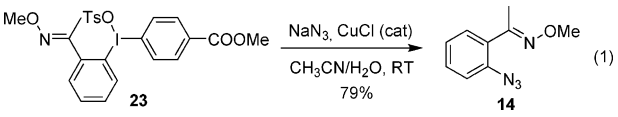


Scheme 4. Copper-catalyzed diverse nucleophilic functionalizations. See the Supporting Information for details. DCE = 1,2-dichloroethane, DMEDA = *N*,*N*′-dimethylethylenediamine, DMF = *N*,*N*-dimethylformamide, DIPEA = *N*,*N*-diisopropylethylamine, DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine, TMS = trimethylsilyl.

the absence of any external nucleophile, $Cu(OTf)_2$-catalyzed reductive coupling afforded the tosylation product **4** in good yield. Phenoxylation using NaOPh produced the ether **5** in 66% yield. C–S coupling as in trifluoromethylthiolation, sulfonylation, and arylthiolation (**6**–**9**) has been readily achieved using the corresponding $AgSCF_3$, sodium sulfinates, and mercaptan. Of note, the reaction of the Langlois reagent is sulfonyl-retentive, thus indicating that a radical pathway is not operational.[14] Analogously, smooth amination, amidation, imidation, azidation, and nitration afforded the C–N coupled[15] products (**10**–**15**) in good to high yield starting from the corresponding secondary amine or sodium salts. The mild hetero-functionalization can be further extended to bromination using NaBr (**17**) and to phosphorylation (**16**) using diphenylphosphine oxide.

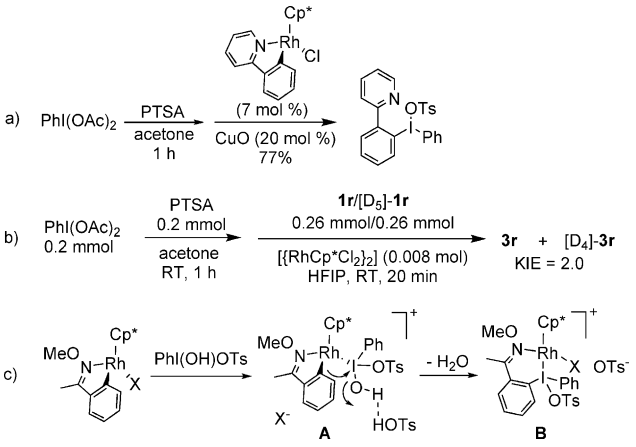
Carbofunctionalization of the iodonium salt **3r** also proved successful (Scheme 4). $Cu(OTf)_2$-catalyzed attack of *N*-methylindole afforded the 3-arylated indole **18** in the presence of 1,6-di-*tert*-butyl-4-methylpyridine (DTBMP).[16] α-Trimethylsiloxystyrene even reacted (−40 °C to RT) to afford the phenacylation product **19** in 60% yield. By following a procedure recently reported by Modha and Greaney,[17] copper(I)-catalyzed one-pot coupling with a simple indole led to selective and sequential difunctionalization at the 1- and 3-positions (**20**), in which both aryl groups of the iodonium salt have been utilized. In all cases, only the DG-bearing arene ring was initially functionalized. Notably, one-pot functionalization of acetophenone *O*-methyl oxime (**1r**) with *N*-methylindole and with NaN_3 afforded **18** and **14**, respectively, albeit in somewhat lower yield. Besides copper catalysis, palladium-catalyzed Sonogashira and Suzuki couplings of **3r** have also been achieved (products **21** and **22**; see the Supporting Information).[18]

Our functionalization reactions are complementary to those known using unsymmetrical diaryliodoniums, in which an aryl group (such as mesityl) is typically sterically deactivated.[19] To further probe the origin of the biased aryl groups, we performed the azidation of the iodonium salt **23** (synthesized following reaction Conditions C). The fact that only the azide **14** was detected [79% yield; Eq. (1)] indicated that the



two aryl groups in **23** were differentiated, likely by the ligating effect of the oxime DG. We propose that chelation-assisted C–I oxidative addition to copper(I) affords a copper(III) species, C–C reductive elimination of which furnishes the final functionalization product (Scheme 4 and see the Supporting Information).[15d,20]

Preliminary mechanistic studies have been performed to briefly explore the mechanism. To probe the relevancy of C–H activation, a cyclometalated [Cp*Rh^{III}Cl] complex (7 mol%) was prepared and was designated as a catalyst for the C–H functionalization of 2-phenylpyridine under otherwise identical reaction conditions, from which **3a** was isolated in a yield of 77% (Scheme 5a). This result suggests that C–H



Scheme 5. Mechanistic considerations.

activation is likely involved. To further probe the C–H activation process, the kinetic isotope effect (KIE) of hyperiodination of the oxime **1r** has been measured (Scheme 5b). An intermolecular competition using an equimolar amount of **1r** and [D_5]-**1r** at low conversion gave a KIE value of 2.0, thus indicating that C–H cleavage might be involved in the rate-limiting step.[21]

A plausible mechanism[22] for this C–I coupling may involve coordination of PhI(OH)OTs to give the rhodium(III) intermediate **A**, followed by nucleophilic 1,2-migration of the aryl group to the iodine with concomitant displacement of the OH leaving group which is activated by TsOH and/or HFIP to afford the rhodium(III) intermediate **B** (Scheme 5c).[7c,8a,12c] Dissociation of the coupled product furnishes a [Cp*Rh^{III}] intermediate which allows the turnover of the catalytic cycle. The CuO and Ag_2O additives possibly activate the hypervalent iodine reagent and the catalyst by removal of the Cl ligand. We noted the difference of reaction patterns in our previous azidation system with $PhI(N_3)OTs$ being a likely intermediate,[8a] where the azide ligand is soft and readily undergoes umpolung upon coordination to iodine(III), thus giving higher reactivity. In the current system the OH group in PhI(OH)OTs is a hard ligand, and the Rh–Ar bond reacts preferentially with the iodine atom.

In summary, we have achieved the first synthesis of diaryl iodonium salts by rhodium-catalyzed C–H hyperiodination of electron-poor arenes. Nitrogen chelators such as pyridine, pyrimidine, pyrazole, and oxime proved to be viable directing groups. Subsequent diverse nucleophilic functionalization of the iodonium product provided a stepping stone to access a broad spectrum of carbo- and hetero-functionalized arenes under copper catalysis. In all cases the initial functionalization occurred at the DG-containing arene. The functionalization can be one-pot starting from the arene. Streamlining of C–hyperiodination and nucleophilic functionalization overcame some limitations of the C–H functionalization of arenes because tedious individual optimization of the conditions of metal catalyzed C–H activation and C–E (E = C, O, N, S, P, Br) coupling is no longer necessary. The mild hyperiodination conditions and the rich chemistry of hypervalent iodine make this method attractive, and future work will be directed to detailed mechanistic studies and extension of the arenes.

Keywords: arenes · C–H activation · copper · hypervalent compounds · rhodium

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[22] The alternative mechanism of oxidative addition of PhI(OH)OTs to the Rh^{III} to give a Rh^{V} species is also possible.

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