Halogen-Substituted Mesoionic-Carbene/Palladium Complexes for Catalytic Arylation of Aldehydes

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Abstract: Various halogenated mesoionic-carbene-coordinated palladium complexes (denoted as TAPs and e-TAPs) were prepared using triazolylidene precursors that were synthesized in only two steps via a click reaction. Among the prepared complexes, Br-e-TAP showed optimal catalytic activity for the arylation of aldehydes with arylboronic compounds. Additionally, the Br-e-TAP catalyst assisted in synthesizing a wide range of functionalized diarylmethanols and arylmethanols in 29%–95% yields with loadings of 0.2–0.6 mol% Pd.

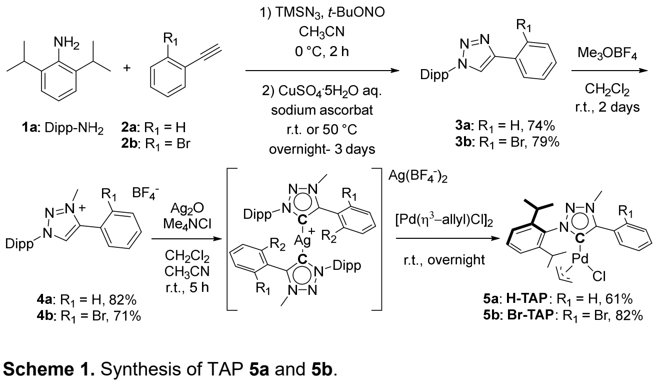
Introduction

N-heterocyclic carbenes (NHCs) have strong donor properties towards metals and are extensively used as ligands in metal-catalysed reactions.[1,2] In particularly, mesoionic carbenes (MICs) have higher donor capacities than those of conventional Arduengo-type NHCs based on the 2-imidazolylidene scaffold; consequently, MICs have attracted attention as promising ligands for transition-metal catalysis.[2] MICs, 1,2,3-triazolylidenes are particularly attractive as ligands because of the ease of synthesis of their precursors—triazolinium salts—which are obtained via the [2 + 3] cycloaddition of alkynes and azides to produce the corresponding 1,2,3-triazoles, which then undergo selective alkylation at the N3 position. Indeed, triazolylidenes are more efficient than Arduengo-type NHCs in palladium-catalyzed cross-coupling reactions, such as the Suzuki–Miyaura coupling, Mizoroki–Heck reaction, and Hiyama coupling.[3]

Recently, transition-metal-catalyzed addition reactions involving carbonyl compounds using aryl boron compounds as nucleophiles have drawn attention for the synthesis of highly functionalized alcohols because of their superiority to the Grignard reaction in terms of functional group tolerance.[4–9] Strong σ-donating ligands, such as tertiary phosphines and NHCs, are effective for this type of addition reaction, and the use of NHCs with greater donating attributes in Rh-[5,6] and Pd-assisted[7,8] catalysis tends to reduce catalyst loading. However, their catalysts are limited to Arduengo-type NHCs, and the catalytic activity is expected to be improved using the more donor-oriented MICs. The combination of [PdCl(η^3-allyl)]$_2$ and bromo-substituted 1,3-diaryl-imidazoline carbene precursors was previously demonstrated by our group to catalyze the addition reaction of arylboronic acids to aldehydes; replacing these Arduengo-type NHCs with MICs would be assumed to improve the catalytic efficiency.[7f] Therefore, the synthesis of (η^3-allyl)palladium complexes coordinated with halogen-substituted 1,4-diaryl-1,2,3-triazolylidene and their catalytic activity for arylation of aldehydes using arylboron compounds were investigated in this study.

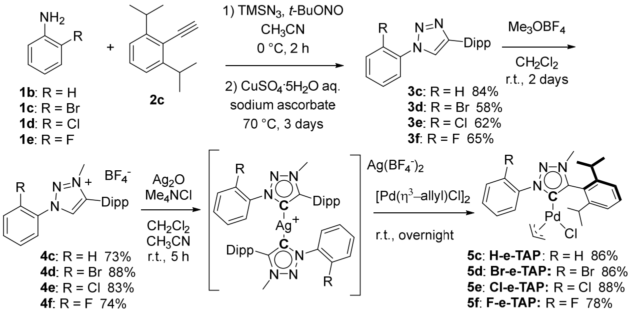
Results and Discussion

(η^3-Allyl)palladium chloride complexes coordinated with 1-(2,6-diisopropylphenyl)-4-aryl-1,2,3-triazolylidene (TAPs) were readily obtained in good yields from commercially available 2,6-diisopropylphenylaniline (**1a**: Dipp-NH$_2$) and arylalkynes (**2a**/**b**) according to the literature procedure in five steps (Scheme 1).[3j]



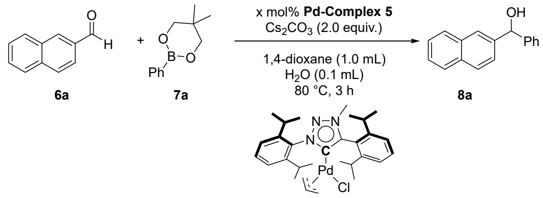
Scheme 1. Synthesis of TAP **5a** and **5b**.

First, 1,4-diaryl-1,2,3-triazoles (**3a**/**3b**) were obtained via Cu-catalyzed azide–alkyne cycloaddition (CuAAC)[10] and then subjected to methylation with trimethyloxonium tetrafluoroborate to yield triazolium salts. The salts (**4a**/**4b**) were reacted with Ag_2O to form triazolylidene silver complexes, which were then reacted with $[PdCl(\eta^3\text{-allyl})]_2$ to produce the TAPs **5a** and **5b**, respectively. Similar to the specimens above, aryl groups at N1 and C4 positions of 1,4-diaryl-1,2,3-triazolylidene were exchanged TAPs, referred to as e-TAPs (**5c**–**f**) were prepared from 2-ethynyl-1,3-diisopropylbenzene (**2c**)[3h] and corresponding anilines (**1b**–**e**) (Scheme 2).



Scheme 2. Synthesis of e-TAP **5c–f**.

Table 1. Pd complexes **5a-d** catalyzed addition[a]



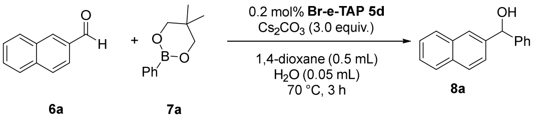
5g: **(allyl)(TPr)PdCl**

Entry	Pd Complex	x	Yield[b]
1	H-TAP **5a**	1.0	6
2	Br-TAP **5b**	1.0	29
3	H-e-TAP **5c**	1.0	9
4	Br-e-TAP **5d**	1.0	91
5[c]	Br-e-TAP **5d**	1.0	52
6	Br-e-TAP **5d**	0.2	86
7[d]	Br-e-TAP **5d**	0.2	95
8[d]	Cl-e-TAP **5e**	0.2	89
9[d]	F-e-TAP **5f**	0.2	46
10[d]	(allyl)(TPr)PdCl **5g**	0.2	trace

[a] Reaction conditions: **6a** (0.5 mmol), **7a** (1.0 mmol), Pd complex (**5**), and Cs_2CO_3 (1.0 mmol) were reacted in 1,4-dioxane (1.0 mL) and H_2O (0.1 mL) at 80 °C for 3 h. [b] Isolated yields. [c] Phenylboronic acid was used instead of phenyl boronate **6a**, and the reaction was carried out for 18 h. [d] The reactions were carried out using 1,4-dioxane (0.5 mL), H_2O (0.05 mL), and Cs_2CO_3 (1.5 mmol) at 70 °C.

In Table 1, we summarized Pd complexes (**5**) catalyzed addition of phenyl boronate (**7a**) to 2-naphthaldehyde (**6a**). H-TAP (**5a**) and H-e-TAP (**5c**) showed low catalytic activity in this reaction (Entries 1 and 3). This type of addition is generally promoted by five-membered cyclometalated palladium(II) complexes.[7,8a] Therefore, these results are due to the rapid reduction of allyl palladium(II) complexes to palladium(0) species under the conditions, generating few cyclometalated palladium complexes via intramolecular C–H bond cleavage orthopalladation. Br-TAP (**5b**) showed moderate catalytic activity, whereas the Br-e-TAP (**5d**) specimens with loadings of less than 0.2 mol% promoted the reaction (Entries 2, 4, and 6, respectively). These results suggest that catalytically active five-membered cyclometalated palladium complexes were efficiently formed via the oxidative addition of the C-Br bond to palladium (0) species. The use of phenylboronic acid instead of **7a** did not provide adequate results for the addition of **6a** (Entry 5). However, the yield was improved to 95% by increasing the reaction solution concentration and the amount of Cs_2CO_3 used (entry 7). The activity of (**5e**; Entry 8) was similar to that of **5d** and superior to that of F-e-TAP (**5f**; Entry 9). (Allyl)(TPr)PdCl (**5g**),[3j] which structurally could not produce a five-membered cyclometalated palladium complex, showed no catalytic activity in this reaction (entry 10).

Table 2. The optimization of reaction condition of Br-e-TAP **5d**-catalyzed phenylation of 2-Naphthaldehyde **7a**[a]



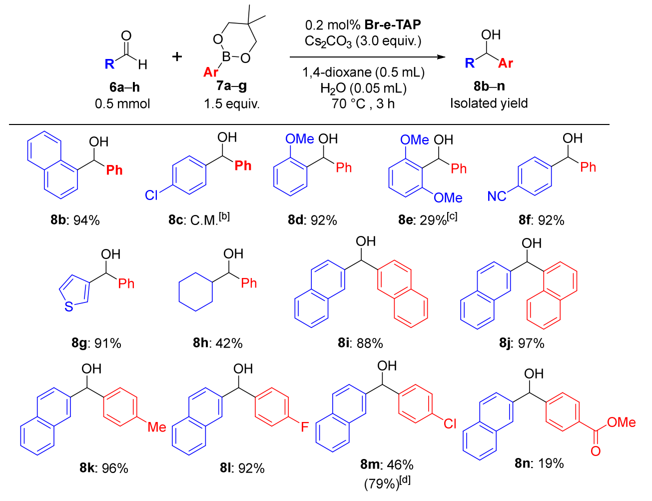
Entry	Base	Solvent	Yield (%)[b]
1	K_2CO_3	1,4-Dioxane	84
2	Na_2CO_3	1,4-Dioxane	61
3	CsF	1,4-Dioxane	80
4	KF	1,4-Dioxane	62
5	K_3PO_4	1,4-Dioxane	93
6	NEt_3	1,4-Dioxane	7[c]
7	Cs_2CO_3	THF	94
8	Cs_2CO_3	2-Methyl-THF	93
9	Cs_2CO_3	Toluene	87
10	Cs_2CO_3	2-Propanol	65
11	Cs_2CO_3	CH_3CN	16
12	Cs_2CO_3	DMSO	trace[c]

[a] Reaction conditions: **6a** (0.5 mmol), **7a** (0.75 mmol), Br-e-TAP (**5d**), and base (1.5 mmol) were reacted in solvent (0.5 mL) and H_2O (0.05 mL) at 70 °C for 3 h. [b] Isolated yields. [c] Determined by 1H NMR with triphenylmethane as an internal standard.

The experiments conducted to optimize reaction conditions for the Br-e-TAP (**5d**)-catalyzed phenylation of **6a** are summarized in Table 2. K_3PO_4 was as effective as Cs_2CO_3, whereas other carbonates (K_2CO_3 and Na_2CO_3) and fluoride salts (CsF and KF) were moderately effective for this reaction (Entries 1–5). Triethylamine was significantly less effective than the inorganic bases (Entry 6). Moreover, the reaction proceeded smoothly when the solvent was changed from 1,4-dioxane to tetrahydrofuran (THF) or 2-methyltetrahydrofuran (2-Me-THF); however, the yield declined slightly in toluene—a nonpolar solvent (Entries 7–9). Highly polar solvents—2-propanol, acetonitrile, and dimethyl sulfoxide (DMSO)—were unsuitable for this reaction as they led to significantly low yields (Entries 10–12).

The substrate scope of aldehydes and aryl boronates was subsequently examined under the optimized conditions (Table 3). 1-Naphthaldehyde (**6b**), which has a sterically crowded structure compared to that of **6a**, reacted as smoothly as **6a** did with **7a** to yield the corresponding alcohol **8b** in 94% yield. The reaction with 4-chlorobenzaldehyde (**6c**) produced a complex mixture, and the desired alcohol **8c** could not be isolated because the chlorine atom on the aromatic ring caused Suzuki–Miyaura coupling. Sterically bulky 2-methoxybenzaldehyde (**6d**), which has a methoxy group at the ortho-position, was converted to **8d** in 92% yield. However, the sterically bulkier 2,6-dimethoxybenzaldehyde (**6e**) afforded **8e** in low yield despite heating to 120 °C. Arylaldehydes bearing electron-withdrawing groups or sulfur atoms—4-formylbenzonitrile (**6f**) and thiophene-3-carbaldehyde (**6g**)—afforded the corresponding alcohols **8f** and **8g** in 92% and 91% yields, respectively. However, the aliphatic aldehyde cyclohexanecarbaldehyde (**6h**) produced **8h** in 42% yield under the employed reaction conditions. 2-Naphthyl, 1-naphthyl, 4-methylphenyl, and 4-fluorophenyl boronates (**7b**–**e**) were as reactive as **7a** and reacted with **6a** to yield the corresponding alcohols **8i**–**l** in 88%–97% yields. Moreover, 4-Chlorophenyl boronate (**7f**) produced little Suzuki-Miyaura coupling under the conditions, giving the desired alcohol **8m** in 79% yield under 0.4 mol% catalyst loading. However, 4-Methoxycarbonylphenyl boronate (**7g**), which has a strong electron-withdrawing group, produced **8n** in low yield.

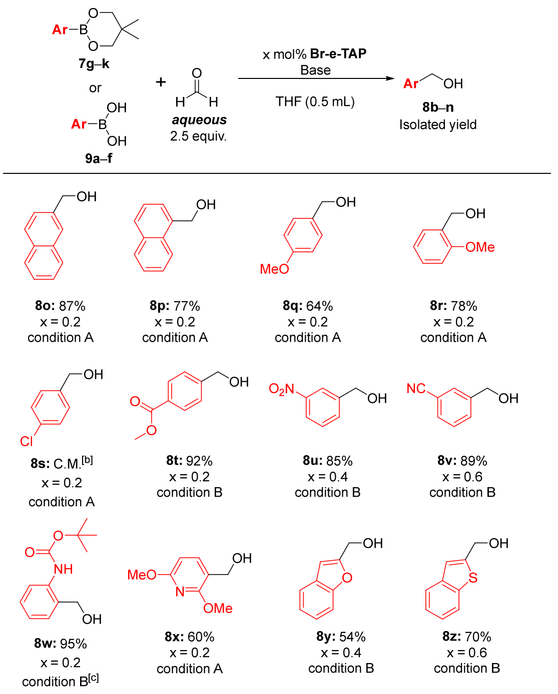
Table 3. Scope and limitations of Br-e-TAP (**5d**)-catalyzed arylation of aryl boronates to aldehydes[a]



[a] Reaction conditions: **6** (0.5 mmol), **7** (0.75 mmol), Br-e-TAP (**5d**), and Cs_2CO_3 (1.5 mmol) were reacted in 1,4-dioxane (0.5 mL) and H_2O (0.05 mL) at 70 °C for 3 h. [b] Complex mixture. [c] This reaction was carried out at 120 °C. [d] 0.4 mol% Br-e-TAP (**5d**) was used.

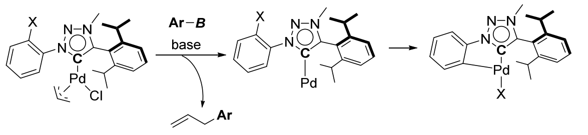
The scope of Br-e-TAP (**5d**)-catalyzed arylation of aqueous formaldehyde using various (hetero)arylboronic acids and boronates is summarized in Table 4. THF was considerably more effective than 1,4-dioxane as the solvent for the arylation of formaldehyde, and optimal results were obtained using Cs_2CO_3 for arylboronic acids (Condition A) and CsF for aryl boronates (Condition B). Arylboronic acids containing electron-neutral and electron-donating groups, such as naphthyl and methoxyphenyl groups, afforded the corresponding alcohols **8o**–**r** in 64%–87% yields. However, 4-chlorophenylboronic acid was unsuitable for the arylation of formaldehyde because Suzuki–Miyaura coupling occurred competitively under the employed reaction conditions. Aryl boronates with electron-withdrawing groups, such as methoxycarbonyl, nitro, and nitrile groups, and sterically hindered (tert-butoxycarbonyl)amino groups produced **8t**–**w** in 85%–95% yields. Additionally, **5d**-catalyzed heteroarylation afforded **8x**–**z** in moderate yields.

Table 4. Br-e-TAP (**5d**)-catalyzed arylation of aqueous formaldehyde with arylboronic acids and aryl boronates[a]



[a] Reaction conditions A: an aqueous formaldehyde solution (37 wt%, 1.25 mmol), **9** (0.50 mmol), Br-e-TAP (**5d**), and Cs_2CO_3 (1.0 mmol) were reacted in THF (0.5 mL) at 50 °C for 3 h. Reaction conditions B: an aqueous formaldehyde solution (37 wt%, 1.25 mmol), **7** (0.50 mmol), Br-e-TAP **5d** and CsF (1.0 mmol) were reacted in THF (0.5 mL) at 70 °C for 3 h. [b] Complex mixture. [c] Pinacol boronate was used instead of neopentylglycol boronate.

Overall, these results indicate that the MIC-coordinated cyclometalated palladium complexes (**5**), which were generated via oxidative addition between the 2-halophenyl group on the side chain of the MIC and zero-valent palladium, functioned as the catalytically active species (Scheme 3). NHC-coordinated allyl palladium complexes readily undergo reductive elimination under Suzuki–Miyaura coupling conditions to yield zero-valent palladium complexes.[11] Intramolecular oxidative addition affords a five-membered cyclometalated palladium complex, which initiates the catalytic cycle for the addition reaction of the arylboron compound to the aldehyde. Because the oxidative addition of the C-F bond is less likely to occur, F-e-TAP (**5f**) did not show good catalytic activity. Additionally, because of the generation of zero-valent palladium species in the reaction system, intermolecular oxidative addition also presumably occurred, making this catalytic system ineffective for converting halogen-containing substrates.



Scheme 3. Proposed the generation of catalytic active species.

Conclusion

A new series of MIC-coordinated (η^3-allyl)palladium chloride complexes (denoted TAP/e-TAP) that bore an ortho-halogenated aryl group at the N1 or C1 position of 1,4-diaryl 1,2,3-triazolylidene was developed in this study. The halogenated e-TAPs exhibited superior catalytic activity for the arylation of aldehydes with arylboron compounds. These complexes have a potential advantage in terms of the easier preparation of the MIC precursor (triazolium salts) than that of Arduengo-type NHC precursors (unsymmetric 1,3-diaryl imidazolinium salts). The synthesis and catalytic activity of MIC-coordinated five-membered cyclometalated palladium complexes are being further analyzed in our laboratory.

Experimental Section

General Procedure for Br-e-TAP (5d)-Catalyzed Arylation of Aldehydes: Br-e-TAP (**5d**) (1.0–2.0 μmol), aldehyde (**6**) (0.5 mmol), (hetero)aryl boronate (**7**) (0.75 mmol) and, Cs_2CO_3 (1.5 mmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon, and this sequence was repeated five times. Then 1,4-dioxane (0.5 mL) and H_2O (0.05 mL) ware added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 70–120 °C. After the reaction mixture was stirred for 3 h and cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane/ethyl acetate eluent.

General Procedure for Br-e-TAP (5d)-Catalyzed Arylation of Formaldehyde: Br-e-TAP (**5d**) (1.0–3.0 μmol), (hetero)aryl boronate (**7**) or (hetero)aryl boronic acid (**9**) (0.50 mmol) and, Cs_2CO_3 or CsF (1.0 mmol) were charged in a 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon, and this sequence was repeated five times. Then THF (0.5 mL) and 37 wt% formaldehyde in H_2O (102 mg, 1.25 mmol) were added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The test tube was placed into an oil bath preheated at 50–70 °C. After the reaction mixture was stirred for 3 h and cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane/ethyl acetate eluent.

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Keywords: palladium • mesoionic carbenes • arylation • arylboron compounds • aldehydes

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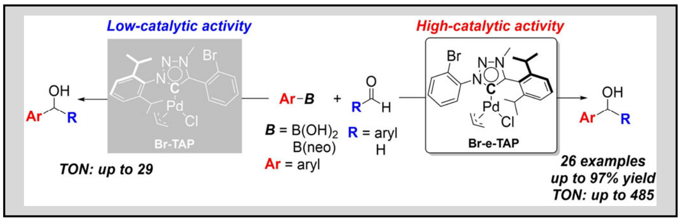

The halogenated mesoionic-carbene-coordinated palladium complexes (TAPs/e-TAPs) were synthesized and acted as the catalyst for the arylation of aldehydes using arylboron compounds. Among them, 1-(bromophenyl)-1,2,3-triazolidene (η^3-allyl)palladium chloride (Br-e-TAP) promoted the arylation most efficiently.

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