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Non-directed C–H arylation of electron-deficient arenes by synergistic silver and Pd_3 cluster catalysis†

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Transition-metal clusters have attracted great attention in catalysis due to their unique reactivity and electronic properties, especially for novel substrate binding and activation modes at the bridging coordination sites of metal clusters. Although palladium complexes have demonstrated outstanding catalytic performance in various transformations, the catalytic behaviors of polynuclear palladium clusters in many important synthetic methodologies remain much less explored so far. Herein, we disclose the use of an atomically defined tri-nuclear palladium (Pd_3Cl) species as a catalyst precursor in Ag(I)-assisted direct C–H arylation with aryl iodides under mild conditions. This catalyst system leads to the formation of synthetically important biaryls in good yields with high site selectivities without the assistance of directing groups.

Introduction

While homogeneous catalysis with mononuclear transition metal complexes has dominated the field of catalytic organic synthesis over the past decades, there has been growing interest in metal cluster catalysis since such species provide a potential bridge from mononuclear metal complexes to nanoparticles (NPs) (Scheme 1a).[1–9] For example, small-sized clusters of palladium complexes have been used as models of a Pd metal surface and can also act as reservoirs to alternative catalytically active species.[10–18] Several species of tripalladium clusters have been isolated and characterized; however, to date the documented examples of catalysis using Pd_3 remain relatively limited (Scheme 1b).[19–23] In this context, Malacria and Maestri *et al.* observed highly promising activities with Pd trimers in cycloadditions and hydrogenations.[24–28] Another cluster, $[Pd_3(C_7H_7)_2]^{2+}$, was found to be an active catalytic species for the cycloisomerization reaction of 2-phenylethynylaniline by Liu *et al.*[29] Notably, a serious question in the area of cross-coupling reactions is the involvement of small Pd clusters as catalytically active species. For example, Wei and Zhu *et al.* used the Pd_3 cluster as an efficient catalyst for the Suzuki–Miyaura reaction in 2017 (Scheme 1c-i).[30,31] In addition, Schoenebeck and coworkers reported an elegant study using a Pd trimer for catalytically C–I selective cross-coupling of polyhalogenated arenes with Grignard reagents in 2019 (Scheme 1c-ii).[32] In 2019 and 2021, the Fairlamb group studied a Pd_3 cluster-catalyzed site-selective cross-coupling of halogenated heteroarenes with organoboron reagents, and the Pd_3 cluster could be generated *in situ* from a Pd(I) dimer species, which can enhance activity and selectivity in the cross-coupling of 2-bromo-pyridine or 2,4-dibromopyridine (Scheme 1c-iii).[33,34] Pérez-Ruiz and Leyva-Pérez *et al.* reported ligand-free, few-atom palladium cluster-catalyzed α-selective intramolecular Mizoroki–Heck coupling of iodoaryl cinnamates and intermolecular coupling of aryl iodides with styrenes (Scheme 1c-iv).[35] Due to the great potential of Pd clusters in C–C bond cross-coupling reactions, we aimed to investigate the catalytic behavior of polynuclear palladium clusters in the area of synthetically important C–H functionalization.

In recent years, C–H arylation has become a versatile tool for the construction of biaryl structures, which are common motifs in pharmaceuticals, agrochemicals, and organic materials.[36–40] Despite great advances achieved in this area, the intermolecular arylation of simple arenes, which do not

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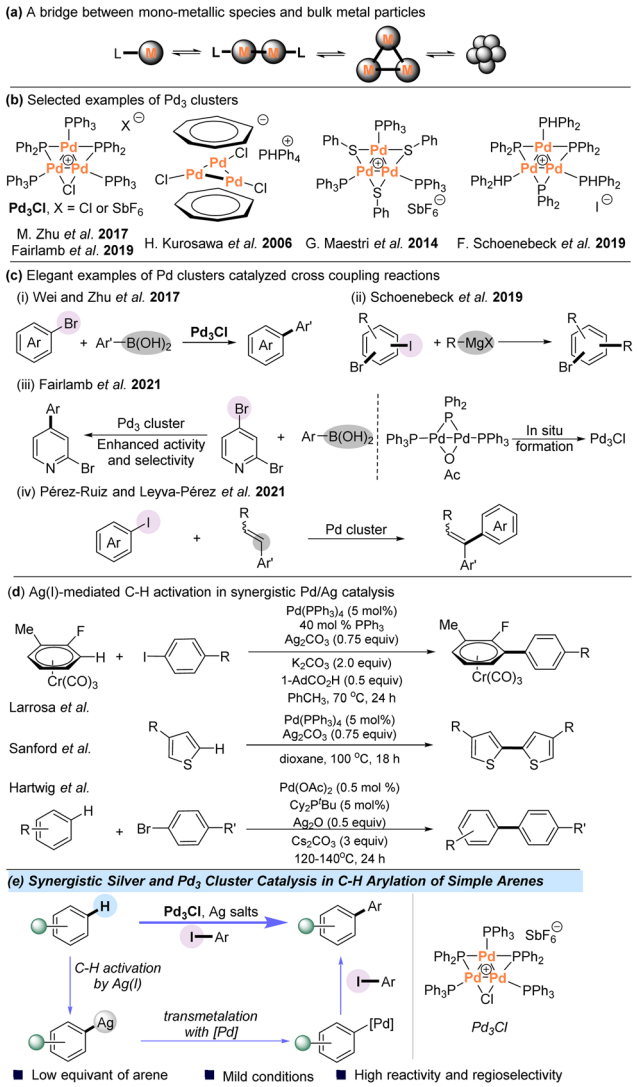


Scheme 1 Trinuclear cationic palladium clusters and strategies for the direct C–H arylation.

contain directing groups, remains a longstanding synthetic challenge.[41–55] Besides the powerful Pd-catalyzed C–H activation,[56–61] catalysis based on Pd/Ag cooperative bimetallic catalytic systems has been successfully developed for the C–H functionalization of simple arenes (Scheme 1d). Burés and Larrosa *et al.* disclosed that Ag(I) is actually responsible for the crucial C–H activation in the Pd/Ag-mediated C–H arylation system of electron-deficient arenes.[62–67] The Sanford group also reported the same role of Ag(I) in the homocoupling of thiophenes at 100 °C.[68] In addition, Hartwig *et al.* demonstrated AgOPiv-mediated C–H activation in selective allylation of aryl C–H bonds and direct arylation with aryl bromides.[69,70] In these pioneering discoveries, Ag(I) cleaves the aryl C–H bond and the palladium catalyst enables the formation of the coupling products. Combined with the great potency of the Pd_3 cluster in C–C bond cross-coupling reactions, we envisioned that Pd clusters might be utilized to achieve direct arylation of aryl C–H bonds with the assistance of Ag(I) under mild conditions.

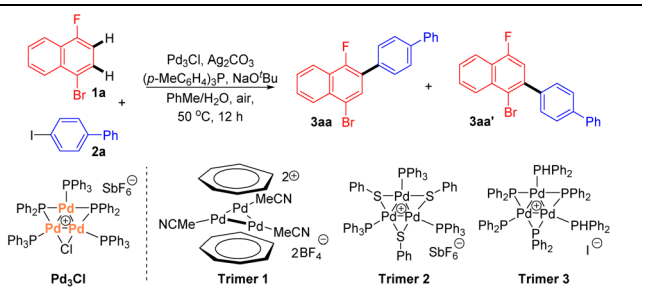
All-metal palladium clusters are intriguing cyclic molecules that could present delocalized metal–metal bonds[71–73] and the aromatic Pd–Pd bond of Pd_3^+ clusters can easily interact with Ag^+ ions.[74] Herein, we report the use of an atomically defined cationic $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+[SbF_6]^-$ (Pd_3Cl) cluster as a competent catalytic species for Ag(I)-assisted direct C–H arylation with aryl iodides, providing various biaryls in moderate to good yields (Scheme 1e). Mechanistic studies indicate that the phosphine-ligated silver complex is responsible for cleaving the C–H bond and the formation of Pd_3I is detected in the preliminary mechanistic studies. It seems that the Pd_3 core most likely remains intact throughout the reaction course.

Results and discussion

Reaction development and scope

Initially, we chose 1-bromo-4-fluoronaphthalene **1a** and aryl iodide **2a** as the substrates to commence our investigation using Pd_3Cl as the Pd catalyst. A careful survey revealed that cross-coupling product **3aa** was generated in a 70% isolated yield with 5.0 mol% Pd_3Cl as the catalyst in the presence of Ag_2CO_3, (p-MeC_6H_4)P and NaO^{t}Bu in the solvent (PhMe/H_2O). In this case, only monoarylation product **3aa** was observed. Notably, the reaction exhibited excellent regioselectivity (>20 : 1 **3aa** : **3aa′**) (Table 1, entry 1). The effects of several reaction

Table 1 Trinuclear cationic palladium clusters and strategies for the direct C–H arylation[a]

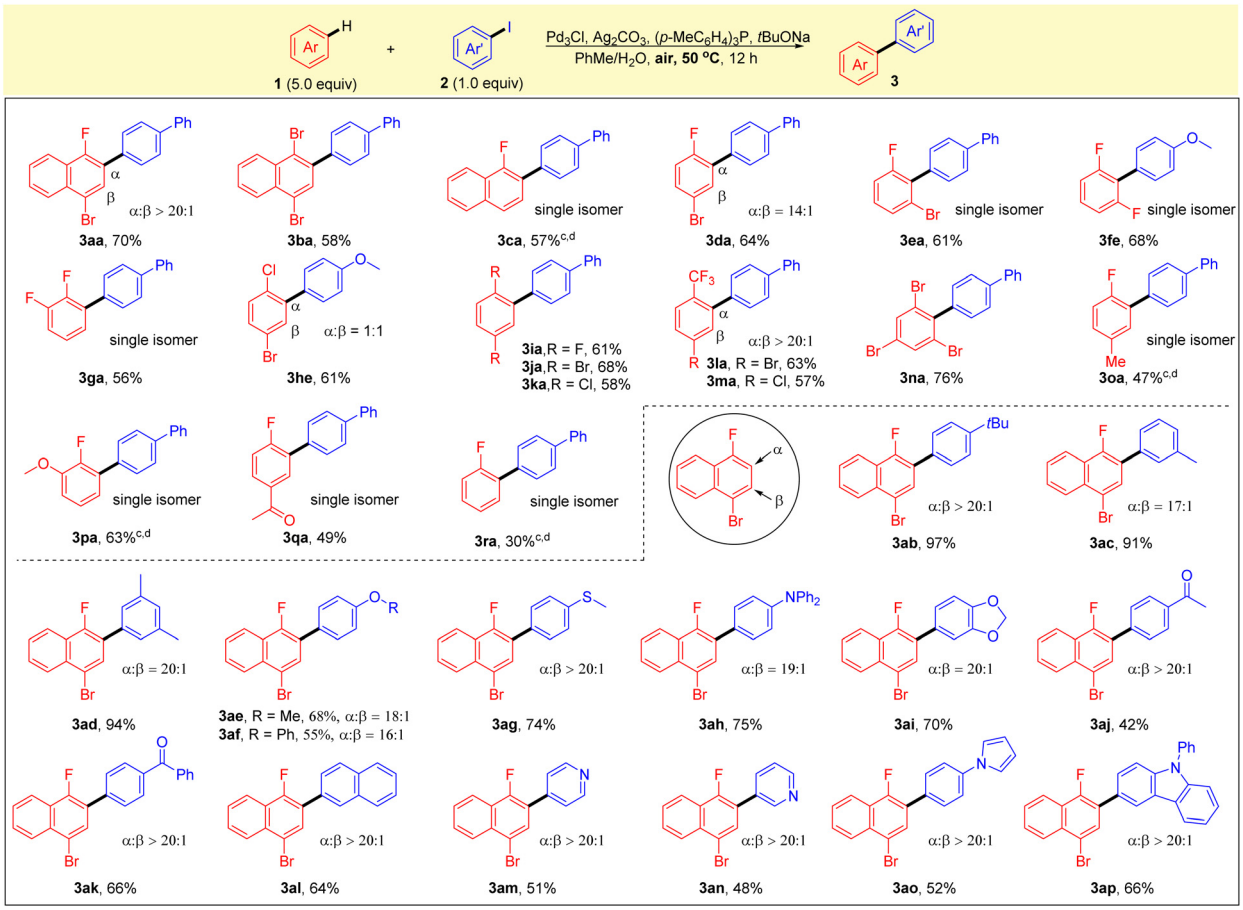


Entry	Deviation from standard conditions	Yield[b] (%)	Ratio[b] (**3aa**/**3aa′**)
1	None	71[c] (70)	>20 : 1
2	PPh_3	—	—
3	(p-$OMeC_6H_4$)$_3$P	Trace	—
4	(p-FC_6H_4)$_3$P	—	—
5	K_2CO_3	23	3 : 1
6	Other Ag sources: Ag_2O, AgOAc or AgF	Trace	—
7	TFA or HFIP as solvent	—	—
8	Trimer **1**	68	>20 : 1
9	Trimer **2**	62	>20 : 1
10	Trimer **3**	64	>20 : 1
11	Without [Pd] or [Ag]	Trace	—

[a] **1a** (1.0 mmol), **2a** (0.2 mmol), Ag_2CO_3 (0.4 mmol), ligand (0.8 mmol), NaO^{t}Bu (0.4 mmol) and Pd_3Cl catalyst (5 mol%) in PhMe/H_2O (0.5 mL/0.5 mL) at 50 °C for 12 h. [b] Determined by GC. [c] Isolated yield.

parameters on the catalysis are also shown in Table 1. The ligand for the Ag(I) salt was found to play an important role in the catalysis since under otherwise identical conditions, none of the reactions using PPh_3, $(p\text{-}OMeC_6H_4)_3P$ or $(p\text{-}FC_6H_4)_3P$ afforded the expected product **3aa** (entries 2–4 *vs.* 1). K_2CO_3 was used instead of NaO^{t}Bu and a much lower yield and regioselectivity were obtained in this case (entry 5). Other Ag salts, such as Ag_2O, AgF, or AgOAc, had no beneficial effect on forming the cross-coupling product **3aa** in comparison with the reaction using Ag_2CO_3 (entry 6). Changing the reaction solvent to trifluoroacetic acid (TFA) or hexafluoroisopropanol (HFIP) led to the complete inhibition of the catalysis (entry 7). These results suggested that a judicious choice of ligand, silver salt, and solvent is crucial for the reaction. Other palladium trimers **1–3** also showed activity in this reaction, giving slightly lower yields than that using Pd_3Cl (entries 8–10). Without the silver salt or palladium catalyst, product **3aa** was only detected in a trace amount (entry 11).

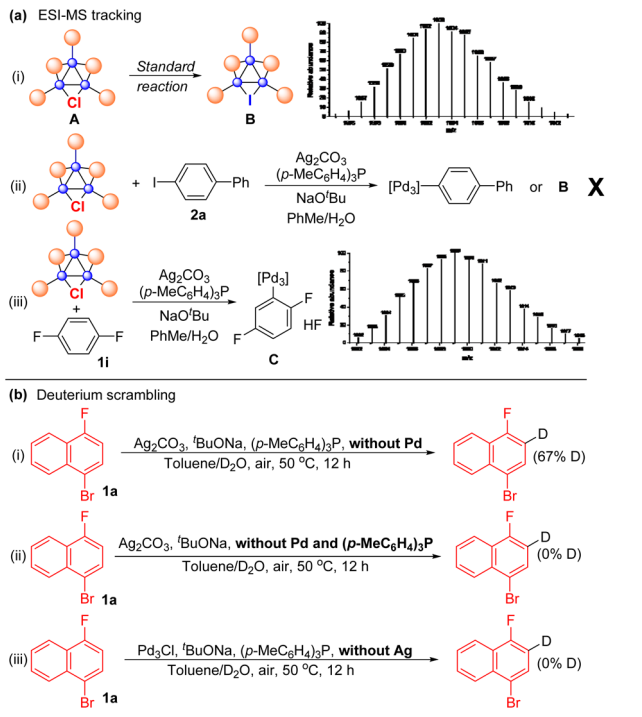
With the optimized reaction conditions in hand, the generality of this reaction was explored with various substituted arenes and aryl iodides. As shown in Scheme 2, a broad range of electron-deficient arenes was found to be compatible with the protocol, and the reactions gave the corresponding products in good yields and high selectivites. 1,4-Dibromonaphthalene **1b** and 1-fluoronaphthalene **1c** were found to be compatible with the current system, affording the corresponding single isomers in good yields (**3ba** and **3ca**). A reaction of 1-bromo-4-fluorobenzene **1d** with **2a** led to the formation of **3da** in high yield with good regioselectivity, and 1-bromo-3-fluorobenzene **1e** also worked well, giving the single isomer of **3ea** in 61% yield. The substrates of difluorobenzenes **1f**, **1g** and **1i** were all well tolerated, and high yields and selectivities were obtained. Simple arenes without a fluorine substituent, such as 1-bromo-4-chlorobenzene **1h**, also reacted smoothly under the optimal conditions to form biaryl **1he** in good yield with a mixture of two regioisomers. 1,4-Dibromobenzene **1j** and 1,4-dichlorobenzene **1k** were also tested and afforded the corresponding biaryls **3ja** and **3ka** in good yields. Notably, good yields (63% and 57%) and excellent selectivities (>20/1) were found for the reactions of substrates with trifluoromethyl groups (**1l** and **1m**). Sterically hindered arene 1,3,5-tribromobenzene **1n** also proceeded smoothly to afford the corresponding arylation product **3na** in 76% yield. It is noteworthy that the reaction using fluorobenzene or substi-



Scheme 2 Substrate scope. [a] Unless otherwise stated, reactions were performed with **1** (1.0 mmol, 5 equiv.), **2** (0.2 mmol), Ag_2CO_3 (0.4 mmol), $(p\text{-}MeC_6H_4)_3P$ (0.8 mmol), NaO^{t}Bu (0.4 mmol) and 5 mol% Pd_3Cl catalyst in $PhMe/H_2O$ (0.5 mL/0.5 mL) at 50 °C for 12 h. [b] Isolated yield. [c] Ph_2CyP was used instead of $(p\text{-}MeC_6H_4)_3P$. [d] Stirred at 80 °C.

tuted fluorobenzenes, such as 4-methyl, 2-methoxy and 4-acetyl, also gave the corresponding products with excellent selectivities, albeit in moderate to good yields (**3oa–3ra**). It was found that the standard reaction conditions in Table 1 (entry 1) were not applicable to the C–H arylation of electron-rich arenes. Next, aryl iodides **2** that underwent direct arylation with 1-bromo-4-fluoronaphthalene (**1a**) were tested. The alkyl-substituted aryl iodides worked well under optimal reaction conditions to provide the corresponding products in high yields with good selectivities (**3ab–ad**). Other substrates containing an electron-donating group (**2e–h**), such as methoxy, phenoxy, thiomethyl or diphenylamine, were converted smoothly to the corresponding products **3ae–3ah** with high selectivities. Substrates bearing reactive functionalities, such as ketone, pyridine, pyrrole or aniline moieties, were compatible with the reaction conditions, providing the corresponding biaryls (**3aj–3ap**) in moderate to high yields with excellent selectivities.

The protocols for Pd_3Cl-catalyzed direct C–H arylation have been established, but the exact nature of the active species is elusive. Several attempts were undertaken to shed light on the reaction mechanism (Scheme 3). ESI-MS was used to track the palladium cluster involved in the reaction of 1-bromo-4-fluoronaphthalene **1a** with aryl iodide **2a** performed under standard conditions. A signal with an *m*/*z* of 1603 was detected in this case, which might be attributed to $[Pd_3I(PPh_2)_2(PPh_3)_3]^+$ (Pd_3I, theoretical mass of 1602.99 Da) (Scheme 3a-i), indicating that the tripalladium core might be retained. However, we failed to isolate Pd_3I after the reaction.



Scheme 3 Preliminary mechanistic studies.

No signal corresponding to Pd_3Ar (Ar = biphenyl) or Pd_3I was detected in the mass spectrum for the reaction mixture of Pd_3Cl, Ag_2CO_3 and aryl iodide **2a**, probably suggesting that Pd_3Cl might not directly react with aryl iodide (Scheme 3a-ii). Notably, Pd_3Ar (Ar = 2,5-difluorophenyl) was detected by ESI-MS when Pd_3Cl was treated with 1,4-difluorobenzene **1i** under otherwise standard conditions in the absence of an aryl iodide, indicating that the tripalladium core was retained and the aryl Pd_3 species might be a key intermediate formed from Pd_3Cl and the arene under the assistance of the Ag(I) salt (Scheme 3a-iii). We failed to track the signal of the formed aryl Pd_3 species in the ^{31}P NMR or ^{1}H NMR analysis of the reaction mixture.[30,34] To further probe the C–H activation step, arene **1a** was treated with a mixture of toluene and D_2O under standard conditions in the absence of Pd_3Cl, affording 67% deuterated **1a** with deuterium incorporation (Scheme 3b-i). Other parallel experiments were also conducted, though deuterium scrambling was not observed under the conditions without Pd and the $(p\text{-MeC}_6H_4)_3P$ ligand or without Ag salts (Scheme 3b-ii and iii), indicating that the phosphine-ligated silver complex is responsible for cleaving the C–H bond in the direct arylation reaction.[61–70,75–81] Notably, ^{31}P-NMR analysis of the solution of Pd_3Cl and $(p\text{-MeC}_6H_4)_3P$ suggested that ligand exchange between $(p\text{-MeC}_6H_4)_3P$ and PPh_3 in the cluster occured.[82] In addition, the Pd_3Cl cluster mainly remained intact in the reaction mixture between Pd_3Cl and NaO^tBu by ^{31}P-NMR analysis (for details, see the ESI†), indicating that the base did not interact with Pd_3Cl directly. Kinetic isotope effect (KIE) studies *via* the parallel reactions of deuterated 1-bromo-4-fluoronaphthalene ***d*-1a** and nondeuterated **1a** were also conducted, respectively, giving the corresponding products with a primary k_H/k_D of 2.2, suggesting that the C–H bond cleavage is likely to be rate determining in the catalysis.[83] These available mechanistic data are consistent with those of synergistic Ag-mediated C–H activation and Pd_3 core-catalyzed arylation.[61–70,75–81] In this case, the initial C–H bond activation of arenes using a phosphine-ligated Ag(I) salt in the reaction can result in the formation of Ag(I)–aryl species, which would undergo transmetalation with Pd_3Cl. The oxidative addition and reductive elimination of Pd complexes and aryl iodides would deliver the product and regenerate the Pd_3I catalyst. However, due to the similar results in the reactions using other palladium trimers and mononuclear palladium sources, the mechanism of clusters acting as a reservoir to mononuclear Pd species or aggregation to nanoparticles as the catalytically active species is also possible.

Conclusions

In summary, we have developed an efficient method for direct C(sp^2)–H arylation with aryl iodides using a palladium trimer catalyst under the assistance of phosphine-ligated Ag(I). It should be highlighted that the current direct arylation of an aryl C–H bond proceeds smoothly under mild conditions which is highly appealing from the perspective of practical

applications. Mechanistic experiments suggested that catalytic intermediates feature an atomically defined cationic trinuclear Pd cluster core that may function throughout the cycle. The present study may pave the way to a broader application of the Pd_3 cluster in synthetic transformations.

Author contributions

J. Y. and X. W. directed the project; J. Y., X. K., M. Z. and X. W. designed the experiments; J. Bai and Y. G. performed all the SAESI-MS studies; J. Y. performed all the experiments and analyzed all the data; J. Y. and X. W. wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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