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A terphenyl phosphine as a highly efficient ligand for palladium-catalysed amination of aryl halides with 1° anilines

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ABSTRACT

A terphenyl phosphine ligand (2,6-bis(2,4,6-triisopropylphenyl)phenyl-dicyclohexylphosphine, TXPhos) and its supported palladium complex [(TXPhos)(allyl)PdCl] have been developed and the catalyst system is highly efficient in amination of aryl halides with 1° anilines, especially effective for densely functionalized substrates including both partners possessing *ortho*-ester, acetyl, nitrile and nitro groups. With the TXPhos-supported catalyst system, many partner combinations have been unprecedentedly realized and the base scope has been even extended to KOAc, which is even the best choice in the amination of 2-nitrochlorobenzene.

1. Introduction

Aromatic amines are an important class of compounds related to pharmaceuticals, fine chemicals and novel materials with useful physical properties. The palladium-catalysed coupling reaction of aryl halides or pseudo-halides with nitrogen nucleophiles, called as Buchwald-Hartwig amination [1,2], has received much attention due to its milder reaction conditions and higher selectivity compared with the traditional Ullmann reaction and SNAr approaches. Owing to many groups' contributions mainly through innovation of supporting ligands and insight into the catalytic mechanism [3–11], significant advances have been achieved and have made this protocol an indispensable method for construction of C-N bonds in contemporary organic synthesis [12,13]. Several notable ligands exist for this transformation from bulky trialkylphosphines, N-heterocyclic carbenes and biaryl phosphines to chelating bidentate phosphine ligands, such as BINAP, XantPhos, dppf and Josiphos-type CyPF-*t*Bu. Nevertheless, significant limitations remain, and approximately 35% of the palladium-catalysed C-N couplings failed to deliver any desired products in the late-stage synthesis of drugs [14,15]. Therefore, the development of novel, efficient and general catalyst systems to address the remaining limitations is a dynamic and desirable area of research.

The structure of the supporting ligand defines the steric and electronic properties and coordination numbers of the palladium centre and is well recognized to influence every step of the catalytic cycle. Biaryl phosphines developed by Buchwald's group have been demonstrated to form highly active palladium catalysts for the Buchwald-Hartwig amination. The interaction between the phosphine-non-containing arene of the biaryl phosphine and the phosphine-ligated palladium centre is critical for the success of biaryl phosphine ligands. When the phosphine-ligated palladium centre was located above the phosphine-non-containing arene (Fig. 1a, the C-bound isomer), the biaryl effect occurred. However, the biaryl effect disappeared after the P-C bond was rotated by 180° and the O-bound isomer appeared. Buchwald et al. found that approximately 33% of the O-bound isomer formed with BrettPhos, and this unfavorable isomer can be entirely suppressed with EPhos synthesized through a relatively long route in low yield [16]. Indeed, the performance of the palladium catalyst supported by EPhos is much more enhanced compared with BrettPhos. To completely block such rotation of the phosphino group, Tang et al. synthesized a novel class of biaryl phosphines possessing a 2,3-dihydrobenzo[d][1,3]oxaphosphole framework to fix the rotation (Fig. 1b) [17]; the complexes with these supporting ligands resulted in very active palladium catalysts for Suzuki-Miyaura coupling of extremely hindered arylboronic acids with aryl bromides. However, a long synthetic route is needed to prepare such rotation-fixed biaryl phosphines. We envisioned that the rotation problem would not exist on a terphenyl phosphine (Fig. 1c) and that the steric hindrance around the phosphorus atom would be further increased by the two phosphine-non-containing arenes; consequently, new palladium catalysts created would be expected to exhibit higher activity than those with biaryl phosphines. Here, we disclose discoveries related to the palladium-catalysed aminations of aryl halides: a one-pot procedure to synthesize 2,6-bis(2,

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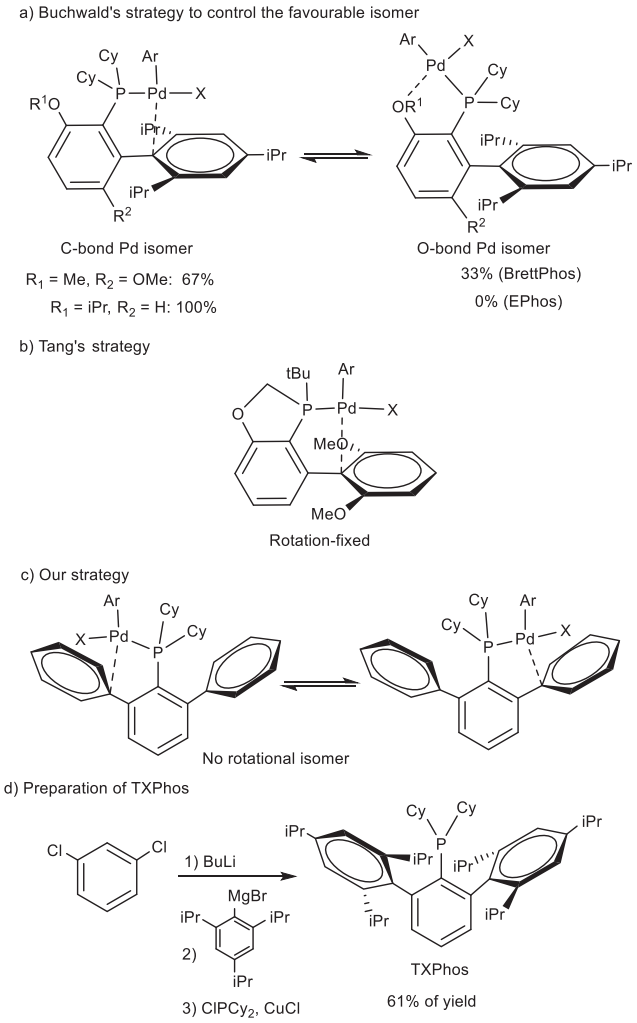


Fig. 1. Strategies to control the favourable isomer and preparation of TXPhos.

4,6-triisopropylphenyl)phenyl- dicyclohexylphosphine (TXPhos); a palladium catalyst system derived from TXPhos with higher catalytic activities compared to biaryl phosphine complexes; a substrate scope expanded unprecedentedly to include coupling partners that both contain *ortho*-ester, acetyl, nitrile and nitro groups; and, for the first time, the weak base KOAc demonstrated to be effective in these reactions.

2. Results and discussion

There are several reports on the synthesis and structure of terphenyl phosphines and their transition metal complexes [18], but Smith and co-workers used firstly a terphenyl phosphine palladium complex in Suzuki coupling reaction, and Kondoh et al. tested two Buchwald-Hartwig aminations with a terphenyl phosphine prepared by rhodium catalysed cyclization of triynes [19]. We prepared a series of terphenyl phosphines and their palladium complexes, and studied their performance on Buchwald-Hartwig amination reactions, and related works have been applied patents in 2018 [20] and were communicated in academic conferences in 2019 [21,22]. In 2020 Rama and co-authors have published several terphenyl phosphines covered by our patents and their performance in palladium-catalysed Buchwald-Hartwig aminations with NaO*t*Bu as base [23].

The terphenyl phosphine TXPhos was synthesized smoothly in a one-pot procedure from the inexpensive starting material 1,3-dichlorobenzene and purified by crystallization in 61% isolated yield (Fig. 1d). Interestingly, the ^{31}P NMR signal of TXPhos appearing at δ 9.6 is close to that of *t*BuXPhos (δ 21.4) comparably, containing a more bulky P*t*Bu$_2$ group, rather than that of XPhos with the same PCy$_2$ group (δ −11.5) [24,25]; this result may imply that the two phosphine-non-containing arenes in TXPhos further increase the steric hindrance around the phosphorus atom. The phosphine terphenyl TXPhos was found to be highly stable in the open air and can be stored as a solid at room temperature in the air for six months without observing any oxidation. The complex [(TXPhos)(allyl)PdCl] was prepared in an almost quantitative yield by mixing TXPhos with [(allyl)PdCl]$_2$ in THF for 1 h.

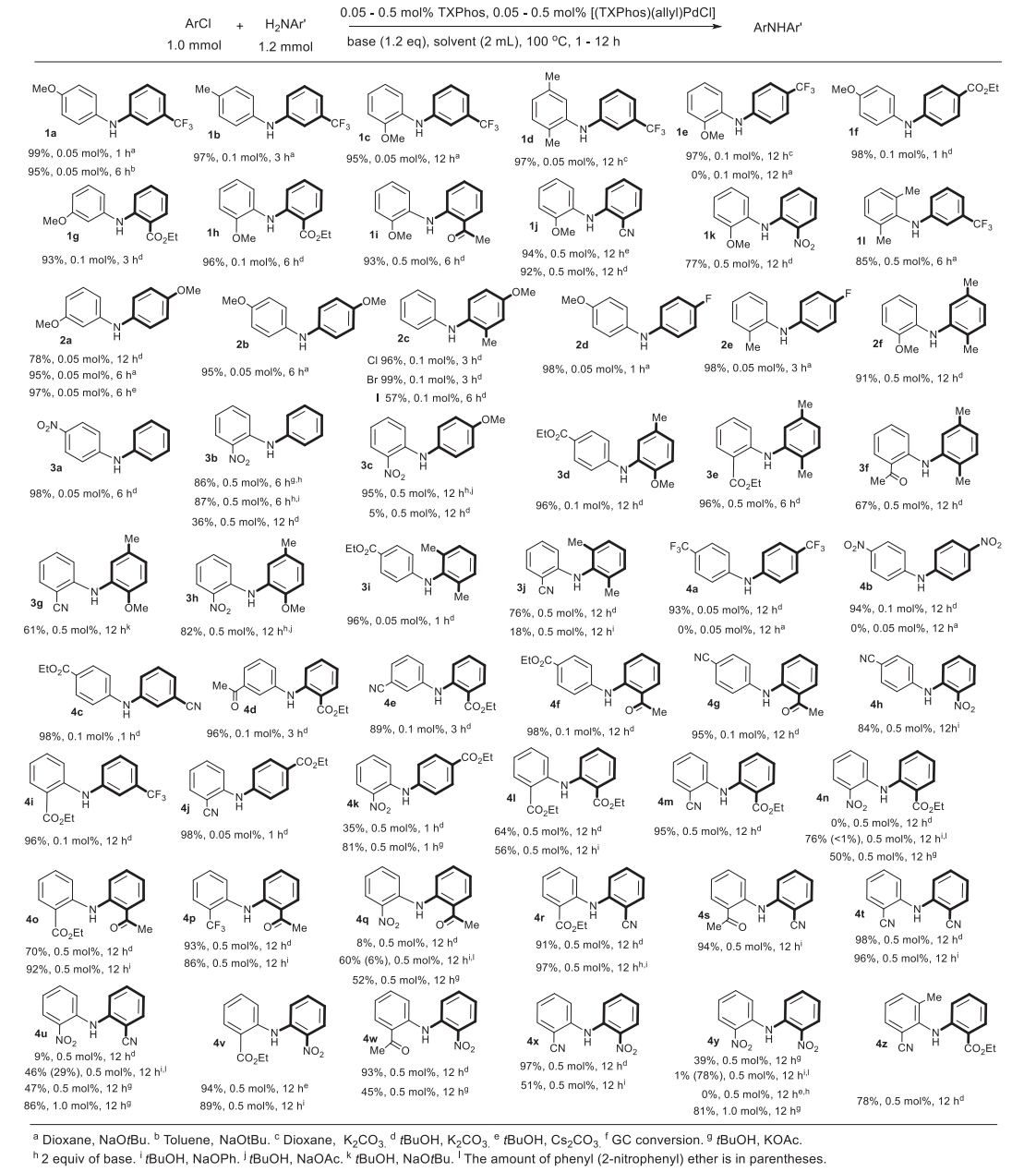
In the initial investigation into the performance of TXPhos as a supporting ligand for palladium catalysts, the amination of deactivated 4-chloroanisole with the electron-deficient 3-trifluoromethyl aniline, a difficult substrate due to low nucleophilicity, was examined using 0.1 mol% Pd with NaO*t*Bu as the base in toluene at 100 °C in the presence of 0.2 mol% TXPhos. Full conversion of 4-chloroanisole was observed with the catalyst systems generated by premixing corresponding [(allyl)PdCl]$_2$ and Pd(dba)$_2$ (dba = dibenzylideneacetone) with TXPhos for 1 h and 6 h, respectively, and only 32% conversion was shown by Pd(OAc)$_2$ (Table S1) because of inefficiency in forming the species [(TXPhos)Pd^0], as expected under the reaction conditions used. The preformed complex [(TXPhos)(allyl)PdCl] along with an additional equivalent of TXPhos can realize a clean transformation even at a loading as low as 0.05 mol% within 1 h in dioxane, and **1a** was isolated in 99% yield (Table 1) but with 83% conversion using the complex alone (Table S1). Since better results were obtained in the presence of an additional equivalent of TXPhos, the ratio 2:1 of P:Pd was then extended to the general reaction conditions in the following studies. The additional equivalents of the terphenyl TXPhos benefited to prolong the life of the catalyst, and the strategy has been employed conventionally with biaryl phosphines [26–29]. The reactions of chloroarenes containing one *ortho*-substituent with 3-trifluoromethyl aniline proceeded to completion within 12 h at 100 °C, and **1c** and **1d** were obtained in 95–97% yields. Notably, this is the first reported examples that when catalyst loading is down to 0.05 mol% the weak base K$_2$CO$_3$ is as good as NaO*t*Bu for palladium-catalysed C-N cross-coupling reactions [30].

Reaction conditions: chlorobenzene (1.0 mmol), aniline (1.2 mmol), base (1.2 mmol), solvent (2.0 mL), catalyst (0.5 mol% used in A, C and D, 0.1 mol% in B), reaction temperature 100 °C, 12 h. A for **1j**, B for **2a**, C for **3b**, and D for **4v**.

Surprisingly, NaO*t*Bu as the base could not promote any reactions of 4-trifluoromethyl aniline with 2-chloroanisole, but using K$_2$CO$_3$ afforded **1e** in 97% yield under the other-wise identical conditions. The colour of the 4-trifluoromethyl aniline solution turned dark black when mixed with NaO*t*Bu, implying the formation of 4-CF$_3$-PhNH$^-$ anions. The high concentration of the 4-CF$_3$-PhNH$^-$ anion might convert the [(TXPhos)(Ar)PdCl] species into an anionic [(TXPhos)(Ar)Pd(4-CF$_3$-PhNH)$_2$]$^-$ species, leading to a decrease in the activity of the catalyst [31].

Such an influential effect of base inspired us to survey different bases in several solvents for the reaction of 2-chloroanisole with 2-aminobenzonitrile, and the results are depicted in Fig. 2A. With 0.5 mol% loading of catalyst, bases Na$_2$CO$_3$, K$_2$CO$_3$, Cs$_2$CO$_3$, and K$_3$PO$_4$ in *t*BuOH or toluene were highly efficient in promoting the reaction to produce **1j**; however, Li$_2$CO$_3$ led to no conversion. Strong bases such as NaOMe, NaO*t*Bu, and LHMDS can promote complete consumption of the chloride, but the desired product was produced in 22–78% yield only, which might be ascribed to side reactions of nitrile groups with strong base. In addition, in

Table 1
The TXPhos/palladium-catalysed aminations of aryl chlorides with 1° anilines.



[a] Dioxane, NaO*t*Bu. [b] Toluene, NaOtBu. [c] Dioxane, K_2CO_3. [d] *t*BuOH, K_2CO_3. [e] *t*BuOH, Cs_2CO_3. [f] GC conversion. [g] *t*BuOH, KOAc.
[h] 2 equiv of base. [i] *t*BuOH, NaOPh. [j] *t*BuOH, NaOAc. [k] *t*BuOH, NaO*t*Bu. [l] The amount of phenyl (2-nitrophenyl) ether is in parentheses.

the case of NaOMe used as the base, 17% of reduced 2-chloroanisole was observed, implying that a β-H elimination reaction occurred from the species [(TXPhos)(Ar)Pd(OMe)]. Weak bases such as NaOAc, KOAc, and NaOPh were also found to be effective at producing **1j** in GC yields of 66–83%. To the best of our knowledge, such weak bases as NaOAc and KOAc have never been reported to be effective in palladium-catalysed C-N cross-coupling reactions before and should be greatly compatible with highly functionalized partners.

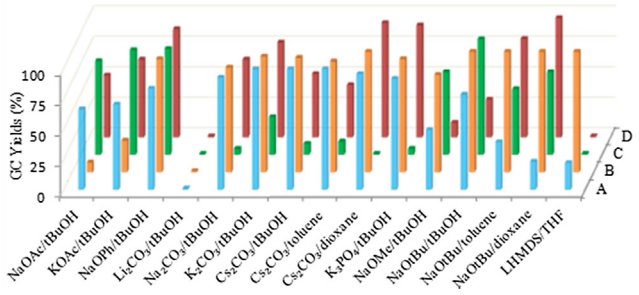


Fig. 2. Survey of bases and solvents for aminations of chlorobenzenes with primary anilines.

Ester, acetyl, nitrile, and nitro groups are common and important functional groups in fine chemicals, but the substrates containing such groups are challenging substrates in palladium-catalysed C-N cross-coupling reactions because of (1) their tolerance to reaction conditions, (2) their steric bulkiness, which hinders transmetallation, and (3) their possible coordination to the palladium centre inhibiting reductive elimination when the groups are in the ortho position [32,33]. Indeed, even using the easily activated XPhos palladacycle system, a 1 mol% loading of the catalyst was required for the arylation of ethyl 2-aminobenzoate with 3-chloroanisole at 110 °C to produce **1g** in 86% yield [21]. Promis-

ingly, **1g** was obtained in 93% yield using our catalyst only at even 0.1 mol% loading at 100 °C within 3 h. This result indicates that the terphenyl-type phosphine TXPhos is much better than the biaryl-type phosphine XPhos as a supporting ligand in palladium-catalysed C-N coupling reactions. Considering that the difference in structure between TXPhos and XPhos is only that TXPhos bears one additional 2,4,6-triisopropylphenyl group next to the PCy_2 unit compared to XPhos, this findings strongly support the feasibility of our hypotheses. The more challenging substrate combinations of 2-chloroanisole with ethyl 2-aminobenzoate, 2-aminoacetophenone, 2-aminobenzonitrile, and 2-nitroaniline were successfully coupled by 0.5 mol% of our catalyst in conjunction with K_2CO_3 as base in *t*BuOH, and **1h, 1i, 1j** and **1k** were isolated in 77–96% yields, of which the latter three cases have not been studied before.

For coupling both electron-rich partners, the palladium catalyst supported by TXPhos is highly effective. The survey of base and solvent revealed that a range of bases such as NaOPh, Na_2CO_3, K_2CO_3, Cs_2CO_3, K_3PO_4, NaOMe, NaO*t*Bu, and LHMDS in the solvents *t*BuOH, toluene, dioxane, and THF are suitable conditions for the coupling of 3-chloroanisole with 4-aminoanisole (Fig. 2B). The weak bases as NaOAc and KOAc in conjunction with our catalyst system promoted the reaction, despite its relatively low efficiency. With Cs_2CO_3 as the base, a catalyst loading of 0.05 mol% can make the reaction as efficient as that with NaO*t*Bu for **2a** in nearly quantitative yields (Table 1). Even using K_2CO_3 as the base, the electron-rich partners containing one or two *ortho*-substituents could be coupled by our catalyst at a loading of 0.1–0.5 mol% in excellent yields (**2c** and **2f**).

The coupling reaction of chloroarenes containing electron-withdrawing groups, recognized as a class of activated substrates, with electron-rich anilines is usually prone to proceed, but some complex situations can arise when these electron-withdrawing groups exist in the ortho position. Catalytic data for this type of substrate combination are listed in Table 1. With 0.05 mol% of the palladium/TXPhos system and 1.2 equivalents of K_2CO_3, the coupling product **3a**, an intermediate for an antioxidant used in rubber, could be produced from 4-chloronitrobenzene and aniline in 98% yield under much milder conditions compared to those used in industry. However, when replacing 4-chloronitrobenzene with 2-chloronitrobenzene as the substrate, even the loading of catalyst increased to 0.5 mol%, and only 31% of **3b** was produced when using K_2CO_3 as the base. Therefore, a survey of the base was carried out for this type of coupling reaction (Fig. 2C). Strong bases such as NaOMe, NaO*t*Bu, and LHMDS indeed promoted coupling, but a large quantity of side products were produced because of the intolerance of the nitro group to these strong bases. Na_2CO_3, Cs_2CO_3 and K_3PO_4 were even worse choices than K_2CO_3 as the base for the reaction. Surprisingly, the weak bases KOAc and NaOPh were the good choice for the reaction, and 86–87% of **3b** was isolated. The electron-rich substrates such as 4-methoxyaniline and 2-methoxy-4-methylaniline were amenable to coupling with 2-nitrochlorobenzene, and 95% and 82% of **3c** and **3h** were isolated using KOAc and NaOAc as the base, respectively. Notably, when using NaOPh as the base, no phenyl (2-nitrophenyl) ether was observed in the reaction mixtures using electron-neutral and electron-rich chloroarenes as substrates. Likewise, K_2CO_3 was not suitable for the two couplings.

With K_2CO_3 used as the base in *t*BuOH, the coupling of chloroarenes containing ester, acetyl, and nitrile functional groups, including in the ortho position, could be promoted with a range of anilines containing one or two *ortho*-methyl and *ortho*-methoxy substituents, and **3d, 3e, 3f, 3g, 3i**, and **3j** were obtained in good to excellent yields.

In a typical synthetic application for biologically active molecules, both the nucleophilic and electrophilic components may contain functional groups such as ester, acetyl, nitrile, and nitro, all of which are considered to be electron-withdrawing groups. However, very few catalyst systems can handle those coupling partners, especially when both of these coupling partners contain one of these substituents in the ortho position. In fact, BINAP and XantPhos have become the most frequently used ligands for these types of C-N coupling reactions [13]; that the bidentate ligands can prevent the coordination of these substituents on the substrates to the palladium centre should be the reason why they have evolved as supporting ligands [26,27]. However, 5–10 mol% of catalyst loading is usually necessitated even for bromoarene partners [34]; in fact, there are no reported examples of the coupling of both chloroarene and aniline bearing the abovementioned functional groups in the ortho position. A breakthrough in the aspect has been achieved along with the innovation of the terphenyl phosphine TXPhos. Catalytic data obtained from the TXPhos-based palladium catalyst system for the couplings of electron-deficient partners are listed in Table 1.

A survey of the base and solvent for the coupling of ethyl 2-chlorobenzoate with 2-nitroaniline to produce **4v** was carried out with 0.5 mol% of the palladium/TXPhos system, and the results are depicted in Fig. 2D. The base and solvent combinations NaOPh/*t*BuOH, Cs_2CO_3/*t*BuOH and K_2CO_3/*t*BuOH were found to be good conditions to realize a clean reaction and afford **4v** in 83–94% yields. The combinations NaO*t*Bu/dioxane and NaO*t*Bu/toluene also produced **4v** in 86–91% yields but with 4–7% of unidentified side products, and significant side products appeared in the combinations NaO*t*Bu/*t*BuOH, NaOMe/*t*BuOH and LHMDS/THF. Unexpectedly, the conditions K_3PO_4/ *t*BuOH also created large amounts of side products. For this coupling, the weak bases NaOAc and KOAc in *t*BuOH were effective as well, and **4v** was produced in appreciable yields of 64–68%.

While seeking drugs to treat malaria, the chemists in Merck reported the synthesis of an intermediate **4a** through the reaction of 4-trifluoromethyliodobenzene and 4-trifluoromethylaniline, and 10 mol% loading of a catalyst derived from XPhos was employed [35]. To our delight, at a lower temperature of 100 °C with 1.2 equivalents of K_2CO_3 in *t*BuOH, 0.05 mol% of our catalyst promoted the coupling of 4-trifluoromethylchlorobenzene to afford **4a** in 98% yield. Consistent with the finding during the preparation of **1e**, the employment of NaO*t*Bu as base did not produce any of the product **4a**.

When both the nucleophilic and electrophilic components containing an ester, acetyl, nitrile, or CF_3 functional group and only one was in the ortho position, using only 0.05–0.1 mol% of the TXPhos-based catalyst in conjunction with K_2CO_3 as base, **4c, 4d, 4e, 4f, 4g, 4i** and **4j** were produced in 89–98% isolated yields. Notably, the catalyst based on the easily activated palladacycle and the ligand BrettPhos, which is recognized as the most suitable biaryl phosphine for palladium-catalysed arylation of primary anilines, required a 1 mol% loading, 20 times that of our catalyst, to produce **4j** in 95% yield at the higher temperature of 110 °C [20]. These data demonstrate again that the design of TXPhos is very successful.

The TXPhos-based palladium catalyst at 0.5 mol% loading in conjunction with K_2CO_3, Cs_2CO_3, NaOPh or KOAc as base has unprecedentedly realized the coupling of ethyl 2-aminobenzoate, 2-acetylaniline, 2-aminobenzonitrile and even 2-nitroaniline with ethyl 2-chlorobenzoate, 2-acetylchloro-benzene, 2-chlorobenzonitrile and 2-trifluorochlorobenzene; **4m**, **4o**, **4p**, **4r**, **4s**, **4t**, **4v**, **4w** and **4x** were isolated in 91–98% yields, except for **4l**, which was isolated in 64% yield. The product **4z**, with three *ortho*-substituents, including an ester and a nitrile group, can be prepared with 0.5 mol% of our catalyst. The power of the TXPhos-based catalyst can be further highlighted by comparing it with the BINAP-based catalyst, the most commonly used catalyst system for highly functionalized partners: 5 mol% of the BINAP-based catalyst was loaded to couple ethyl 2-bromobenzoate with

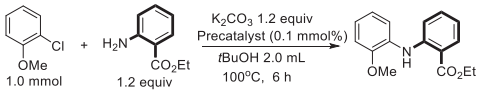
2-nitroaniline at 110 °C for 16 h [34], compared with 0.5 mol% of our catalyst for ethyl 2-chlorobenzoate as substrate at 100 °C for 12 h (**4v**).

The nitro group is a versatile and important functional group, but there are no reports on the coupling of 2-chloronitrobenzene with electron-poor anilines. With 0.5 mol% of our catalyst in conjunction with KOAc, NaOAc or NaOPh as the base in *t*BuOH, the coupling of 2-chloronitrobenzene with ethyl 4-aminobenzoate, ethyl 2-aminobenzoate, 2-acetylaniline, 2-aminobenzonitrile and even 2-nitroaniline afforded the corresponding **4k**, **4n**, **4q**, **4u** and **4y** in 39–81% yields. The bases K_2CO_3 and Cs_2CO_3 were inefficient in these cases with our catalyst system, consistent with the results found in the preparation of **3b** and **3c.** NaOPh was more efficient than KOAc for the anilines bearing moderate intensity electron-withdrawing groups such as ester (**4n**) and acetyl (**4q**), but was not suitable for those bearing strong electron-withdrawing groups such as nitrile (**4u**) and nitro groups (**4y**); the amounts of the side product (2-nitrophenyl)-phenylether increased significantly with the increasing electron withdrawing ability of the substituents on aniline, and it was even the sole product in the case of preparing **4y**. The base KOAc realized clean reactions for the preparation of the latter two products and was found to be the only base that effectively promotes the coupling of 2-chloronitrobenzene with 2-nitroaniline (**4y**). To our delight, the yield of **4y** increased from 39% to 81% when the catalyst loading was increased from 0.5% to 1.0 mol%. For comparison, the reaction of 4-chloronitrobenzene with 4-nitroaniline was carried out with 0.1 mol% of our catalyst in the presence of K_2CO_3, and **4b** was produced in 98% yield, further implying the deleterious effect of an ortho nitro group arising from its coordination to the palladium centre in combination with steric hindrance rather than its strong electron-withdrawing ability.

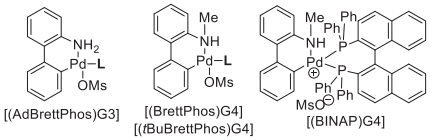
Through DFT and kinetic studies, Buchwald et al. [9] found that when the phosphine-ligated palladium was located above the phosphine-non-containing arene, the formation of κ^2-amidate complexes was inhibited and reductive elimination proceeded smoothly in the amination of aryl chlorides [27]. There are two phosphine-non-containing arenes next to PCy_2 on TXPhos, and the phosphine-ligated palladium centre always has one arene to locate above; thus, the biaryl phosphine effect can be guaranteed in terphenyl phosphines, and the prevention of coordination from the ortho substituent on the substrates to the palladium centre is always operative with TXPhos as the supporting ligand. This effect may be the reason why the TXPhos-based palladium catalyst is so powerful for coupling these substrates bearing substituents with coordination ability in the ortho position.

Further, 2-chloroanisole coupling with ethyl 2-aminobenzoate as a challenging model reaction [36] under the reaction conditions fluently used in literature [3] was conducted to compare TXPhos with the famous BrettPhos series ligands [37] and the most commonly used BINAP ligand in Buchwald-Hartwig amination reaction in a more direct fashion (Table 2) [13]. At 0.1 mol% loading of precatalyst, the conversion of 2-chloroanisole catalyzed by [(TXPhos)(allyl)PdCl] was as high as 99% (Table 2, entry 1), however, [(BrettPhos)(allyl)PdCl], [(BrettPhos)G4], [(*t*BuBrettPhos)G4], [(AdBrettPhos)G4] and [(BINAP)G4] only reached to 0–55% of conversions (Table 2, entries 2–6). It was reported that the full conversion of 2-chloroanisole coupled with ethyl 2-aminobenzoate can be realized at 0.25 mol% of $[(allyl)PdCl]_2$ combined with 0.6 mol% of BrettPhos in a packed-bed reactor at 100 °C [38]. This data combined with those above-filed demonstrates clearly that TXPhos is a highly efficient ligand for palladium-catalysed amination of aryl halides with 1° anilines.

Table 2
Comparison of precatalysts in Buchwald-Hartwig reactions of 2-chloroanisole.



Entry	Precatalyst (Pd 0.1 mol%)[a]	GC Conv (%)[b]
1	[(TXPhos)(allyl)PdCl]	99
2	[(BrettPhos)(allyl)PdCl]	54
3	[(BrettPhos)G4]	55
4	[(*t*BuBrettPhos)G4]	15
5	[(AdBrettPhos)G3]	18
6	[(BINAP)G4]	0



[a]Extra ligand added (0.001 mmol).
[b]GC conversion referenced to dodecane as an internal standard, average of two runs.

3. Conclusions

In summary, we have developed a highly efficient terphenyl phosphine TXPhos for palladium-catalyzed amination of aryl halides with 1° anilines. The palladium catalyst supported by TXPhos have shown higher activities for functionalized substrates, especially those containing *ortho*-esters, acetyls, nitriles and nitro groups, compared with those using biaryl phosphines and BINAP as supporting ligand, and many such substrate combinations have been realized. And the weak KOAc has been found as an effective base for the first time and even the best choice in the Buchwald-Hartwig amination of 2-chloronitrobenzene, an important and versatile starting material in pharmaceutical industry. Accessible in "one pot" and with great air-stability, TXPhos holds promise for practical applications in transition-metal-catalyzed cross-coupling reactions and relevant progress are ongoing within the group.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Two of the authors are inventors of a patent. J.-c. Shi, F. Zhou, Triaryl phosphine ligand, preparation method of triaryl phosphine ligand and purpose of triaryl phosphine ligand in catalytic coupling reaction, CN 110240616, 2018.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2021.08.017.

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