

Nickel-Catalyzed Diversification of Phosphine Ligands by Formal Substitution at Phosphorus

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Abstract: We report a general diversification strategy for phosphines that enables the rapid discovery of new ligands. Alkylated phosphonium salts, prepared by standard alkylation of phosphines, are selectively dearylated in a nickel-catalyzed process to access alkylated phosphine products via a formal substitution at the phosphorus center. The reaction can be used to introduce a wide range of alkyl substituents into both mono- and bisphosphines. We also show that the alkylation and dearylation steps can be conducted in a one-pot sequence, enabling accelerated access to underexplored ligand space. The phosphine products of the reaction are converted *in situ* to air-stable borane adducts for isolation, and versatile derivatization reactions of these adducts are demonstrated.

Many of the recent advances in transition metal catalysis have been driven by the design of bespoke ancillary ligands that modulate the catalyst's reactivity in an unprecedented fashion.^[1] Despite the emergence of a large variety of ligand classes, phosphines remain the ligands of choice for many applications.^[2,3] A significant benefit of phosphines is that the ligand's electronic and steric properties can be tuned with precision by varying the substituents on the phosphorus center. Taking advantage of a versatile toolbox of synthetic methods to access phosphines,^[4] many powerful phosphine ligand architectures have been developed.^[5–11] Phosphines have also been employed in numerous other applications such as organocatalysis,^[12,13] frustrated Lewis pair catalysis,^[14,15] or material sciences.^[16,17] It can be expected that the continued design of phosphines will lead to even more active ligands, opening further avenues for the application of this intriguing class of compounds.

Traditionally, phosphine ligands are prepared by *de novo* synthetic approaches such as nucleophilic substitution reactions of halophosphine substrates with organometallic reagents.^[4] Alternative strategies include the reduction of phosphine oxides^[18–21] or reactions of hydrophosphines such as the hydrophosphination of unsaturated systems,^[22–24] cross-coupling with aryl halides,^[25,26] or substitution reactions with electrophiles in the presence of base.^[4,27] Combined, these methods allow access to a plethora of diverse phosphine architectures. However, they typically require multi-step procedures involving highly toxic or pyrophoric reagents and air-sensitive intermediates. These drawbacks make the preparation of phosphines arduous and ultimately often limit ligand optimization campaigns to the evaluation of commercially available phosphines. The chemical space of these phosphines is however strongly restricted in many regards. For instance, the diversity of commercially available alkylated phosphines is significantly more limited than that of their

arylated counterparts. If chemists only evaluate commercially available phosphines, they might fail to identify more active and selective catalysts. Therefore, more user-friendly approaches towards the synthesis of phosphines are in critical demand.

A strategy to address this problem is the direct modification of tertiary phosphines (Scheme 1a). In this approach, substituents of phosphines are either altered or exchanged entirely, hence bypassing the need to handle toxic primary and secondary phosphines or even PH_3 . It is also an efficient way to quickly generate libraries of ligands, which is a central endeavor for the rapid discovery and optimization of new reactions. Most efforts in this area have focused on altering substituents, for instance by C–H functionalization approaches.^[28–30] Reactions that entirely replace one of the substituents of a phosphine remain rare although they would arguably be the most versatile tools to modify a wide range of phosphines. Such a strategy would be particularly useful to access underexplored alkylated phosphines. Approaches towards this goal are however limited and mainly rely on the formation and subsequent reaction of metal phosphides by engaging phosphines with highly reactive alkali metals (Scheme 1b).^[31–33] As an alternative, Wang and co-workers reported that acyl phosphines can be used as surrogates for secondary phosphines in metal-catalyzed alkylation and arylation reactions.^[34–37] While these methods expand the toolbox of phosphine modification reactions, they suffer from poor cleavage selectivity or limited scope, respectively. A general and selective strategy to introduce alkyl substituents into tertiary phosphines has thus remained elusive.

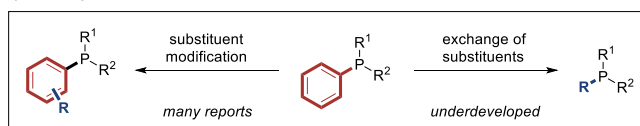
Our group^[38–40] and others^[41–49] have used the ability of transition metals to oxidatively add into P–C bonds of phosphonium salts for catalytic reactions. In the context of phosphine modification, we have reported a palladium-catalyzed process that scrambles aryl groups between two triarylphosphines (Scheme 1c top).^[38] The *in situ* formed phenylpalladium iodide catalyst undergoes C–P reductive elimination with a phosphine and subsequent C–P oxidative addition into another C–P bond of the formed phosphonium salt, leading to an exchange of the aryl group on the metal center. Reaction with another phosphine results in further exchange of aryl groups between the different phosphine starting materials. While this process enables the formation of a large variety of triarylphosphines, it is not synthetically useful as the scrambled triarylphosphines are formed as a statistical mixture. Furthermore, the use of triarylphosphines as the source of the transferred aryl group is impractical as separation of the desired product from the by-products becomes very demanding. To improve this process,

we identified two key challenges that needed to be addressed. First, selective cleavage of one C–P bond over another in the intermediate phosphonium salt would be necessary to obtain a single product. Second, the use of simple R–X compounds instead of PAr_3 as source of the introduced phosphine substituent would be more versatile and simplify purification.

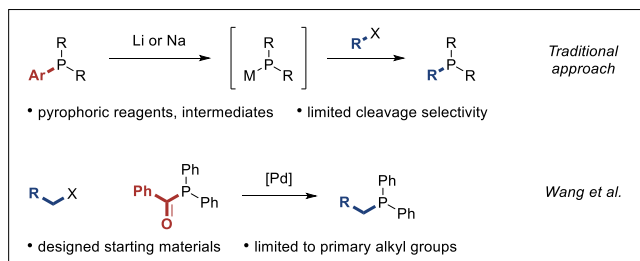
Although the oxidative addition of transition metals into P–C(aryl) bonds is well established, only few examples are known in which a P–C(alkyl) bond of a phosphonium salt is cleaved.^[50–52] We hypothesized that this contrast in reactivity could provide a convenient entry to alkylated phosphines. A metal catalyst could undergo selective oxidative addition into a P–C(aryl) bond of an alkylarylphosphonium salt, retaining the alkyl group, to form the desired alkylphosphine (Scheme 1c bottom). The resulting metal aryl complex could then be engaged in a standard cross-coupling manifold to enable catalyst turnover and to avoid a challenging C–X reductive elimination.^[43,46,53] As the phosphonium salt starting material could be prepared by routine alkylation of a ubiquitous arylphosphine, the overall process would represent a formal substitution of aryl for alkyl groups at the phosphorus center. Here, we report the realization of this strategy as a versatile method that enables rapid diversification of commercial phosphines to access underexplored ligand space (Scheme 1d).

After evaluation of a broad set of reaction conditions, we discovered that a combination of $\text{Ni}(\text{COD})_2$ as pre-catalyst, the ligand precursor $\text{liPr}\cdot\text{HBF}_4$ ($\text{liPr}\cdot\text{HBF}_4 = 1,3\text{-di}(\text{iso-propyl})\text{imidazolium tetrafluoroborate}$), and potassium phosphate as base enabled the desired dearylation of a model phosphonium salt in high yield by trapping the cleaved aryl group in a Suzuki-type coupling with phenylboronic acid (see SI for details).^[43,46] The resulting biphenyl by-product from the Suzuki coupling can be easily separated from the desired product. For convenience, the reactions were typically set up in an argon-filled glovebox. Of note, a benchtop setup also provided the products in only slightly lower yield (see SI for details). Alternatively, the air-stable $\text{Ni}(0)$ precatalysts developed by the groups of Cornella^[54,55] and Engle^[56] can be used instead of $\text{Ni}(\text{COD})_2$ to set the reaction up on the benchtop with no decrease in yield (see SI). With these results in hand, we investigated the scope of the reaction. Phosphonium salts containing different alkyl groups were prepared by alkylation of phosphines in good to high yields using standard methods^[4] (see SI) and then subjected to the dearylation reaction (Scheme 2). For ease of purification, the phosphine products were typically isolated after *in situ* conversion to the borane adducts. These adducts are air-stable, can be conveniently purified by column chromatography, and are easily deprotected (*vide infra*).^[57,58]

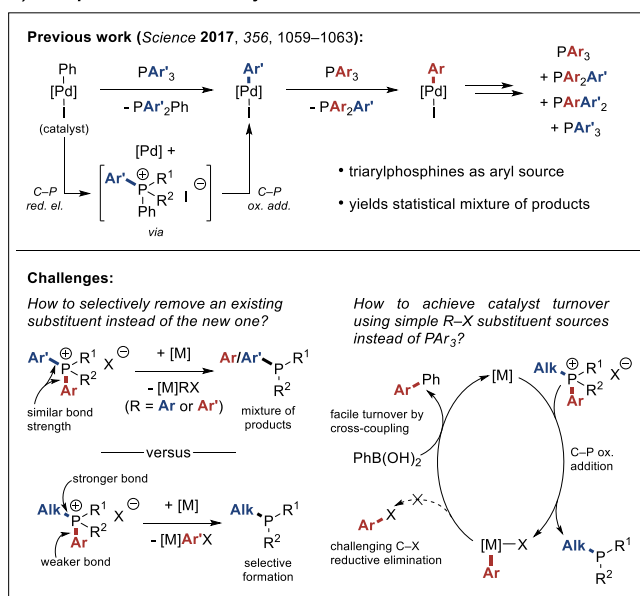
a) Strategies for the modification of phosphines



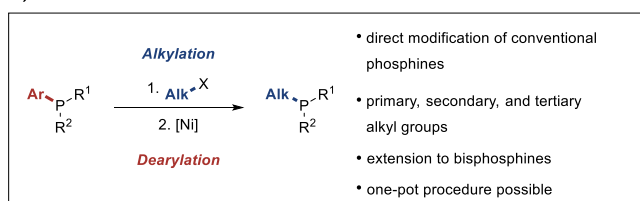
b) Previous reports on the dearylative alkylation of phosphines



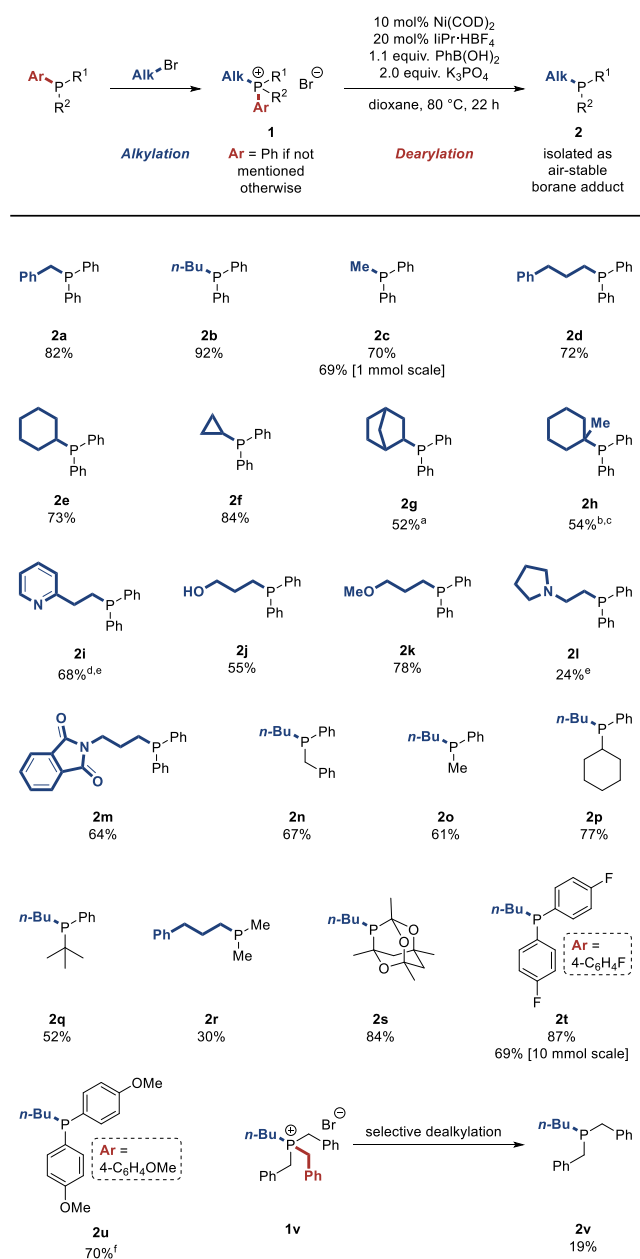
c) Phosphine modification by C–P reductive elimination/ oxidative addition



d) This work



Scheme 1. Context of this work.



Scheme 2. Scope of monophosphines. Yields refer to isolated compounds for the dearylation process after derivatization to the air-stable BH₃ adduct. a: Both the product and the starting material are a 9:1 mixture of diastereomers. b: From the iodide salt. c: 14:1 mixture with Ph₃P-BH₃. d: From the chloride salt. e: Isolated as bis-borane adduct. f: SIMes-HCl as ligand precursor.

Phosphines containing both activated and unactivated primary alkyl groups were prepared in high yield by our dearylation strategy (**2a–d**). A cyclohexyl group was incorporated in 73% yield (**2e**). This moiety and the *tert*-butyl group are arguably the most widespread alkyl substituents in modern ligands. Our reaction not only tolerates the presence of these moieties (**2e**, **2p–q**), but also allows to introduce less prevalent cyclic secondary alkyl groups (**2f–g**) or tertiary alkyl groups (**2h**). Alkyl groups containing coordinating moieties like pyridyl, primary alcohol, and ether groups were incorporated in good yield (**2i–2k**) and provide opportunities to use the reaction to prepare chelating ligands with two different coordinating atoms. A low, but synthetically useful yield was observed for a substrate containing

a tertiary amine (**2l**, 24%). As an alternative, a phthalimide moiety, which can be used as a precursor for amines, was well tolerated (**2m**). The reaction can also be used to synthesize phosphines containing more than one alkyl group. Dialkylphosphonium salts with differing steric demand afforded the desired product in good yield (**2n–q**). Trialkylphosphine **2r** was prepared in a lowered, but synthetically useful yield of 30%. In contrast, the caged trialkylphosphine **2s** was obtained in high yield (84%).

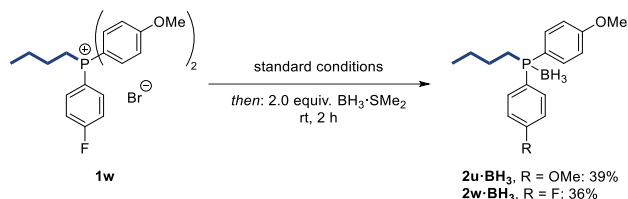
Besides the introduced alkyl group, the nature of the removed aryl group can also be varied. Electron-rich and electron-poor aryl groups can be cleaved in the reaction in high yield (**2t–2u**). Notably, the reaction can also be conducted on a large scale, as demonstrated by the preparation of two grams of **2t**. Besides the dearylation of phosphonium salts, the dealylation is possible when the starting material does not contain an aryl group. Tetraalkylphosphonium salt **1v** was selectively debenzylated in 19% yield without additional optimization.

We next investigated reactions of phosphonium salts containing two different aryl groups (Scheme 3a). The transformation of phosphonium salt **1w**, containing electron-donating and electron-withdrawing aryl groups, resulted in partial cleavage of both aryl groups to deliver the two alkylated phosphines **2u** and **2w** in useful yields in a single reaction. The products could be conveniently separated by column chromatography after *in situ* conversion to the respective phosphine borane adducts. In contrast, the 2-methoxyphenyl group was exclusively removed from phosphonium salt **1x**, indicating a directing effect of the *ortho*-methoxy moiety. The reaction can also be used to modify Buchwald-type ligands, as demonstrated by the synthesis of JohnPhos derivative **2y** in good yield.

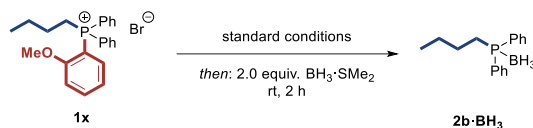
To further increase the utility of our strategy, we developed a one-pot protocol in which the phosphonium salt is first formed by the alkylation of a phosphine and then directly treated with the reagents for the nickel-catalyzed dearylation. Applying this protocol, we were able to prepare *n*-butyldiphenylphosphine (**2b**) from triphenylphosphine (**4**) in 67% yield after converting the product to its air-stable borane adduct (**2b-BH₃**) (Scheme 3b). Notably, no intermediate workup or solvent change is required, making this process a direct substitution at the phosphorus center and enabling rapid access to alkylated phosphine ligands.

a) Dearylation of substrates containing two different aryl groups

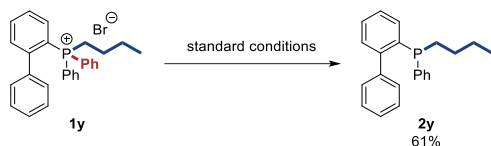
Generation of two modified phosphines in a single reaction



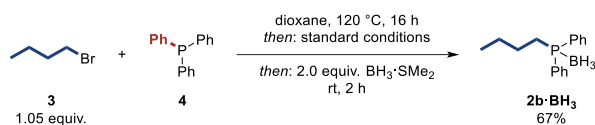
Selective removal of one type of aryl group



Synthesis of new Buchwald-type ligands



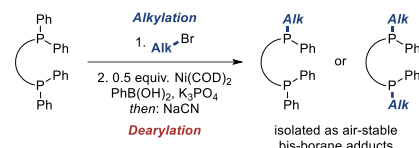
b) Direct substituent exchange in a one-pot process



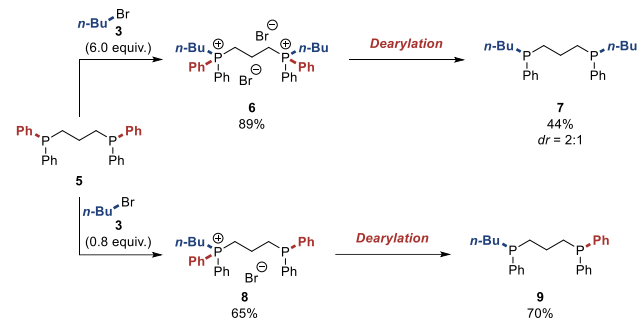
Scheme 3. Further applications. a: 8:1 mixture with 2-methoxybiphenyl.

Due to the high importance of bidentate ligands in catalysis,² we attempted the synthesis of bisphosphines by the twofold dearylation of a bisphosphonium salt. However, no product was detected. Mechanistic experiments showed that the desired dearylation occurred, but the bidentate phosphine product **L** deactivated the catalyst by irreversibly coordinating to it in a NiL_2 complex (see SI). We thus tested a range of metal scavengers to de-coordinate the product from the nickel center of this complex and found that sodium cyanide is highly active for this process.^[59–62] This insight enabled us to develop a strategy for the dearylative alkylation of bisphosphines. After an alkylation step, the nickel complexes NiL_2 of the desired dearylated ligand products were formed by a stoichiometric Suzuki reaction of the bisphosphonium salt and then directly exposed to sodium cyanide to afford the free bidentate phosphines. Notably, the protocol offers the possibility to modify the starting ligand selectively on both phosphorus centers or just one. 1,3-Bis(diphenylphosphino)propane (DPPP) (**5**) could be mono- or dialkylated in good yield, respectively, by simply changing the stoichiometry of the alkylation step (Scheme 4). The dearylation of the resulting phosphonium salts **6** and **8** proceeded smoothly to yield the symmetrically modified ligand **7** in 44% yield and the unsymmetric ligand **9** in 70% yield, respectively. Other privileged ligand scaffolds such as 1,1'-bis(diphenylphosphino)-ferrocene (DPPF) (**10**) can also be altered using this process. Alkylation of **10** selectively yielded the monophosphonium salt **12** potentially because of the hindered nature of the second phosphino moiety after the first alkylation. The dearylation of **12** occurred in good yield to furnish the unsymmetric DPPF-type ligand **13** that would be difficult to prepare by traditional means. The reaction can not only be used to modify bidentate ligands but also to construct them. DPPP (**5**) could be prepared in 46% yield

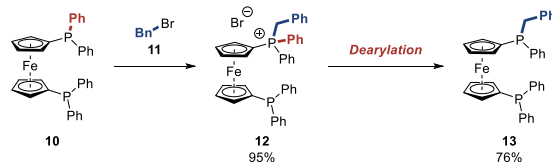
by the reaction of triphenylphosphine (**4**) with the alkyl dihalide **14** and subsequent two-fold dearylation.



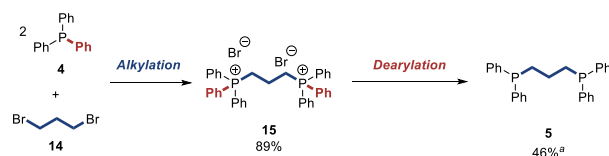
Alkylation-level controlled by stoichiometry



Monoalkylation imposed by sterics



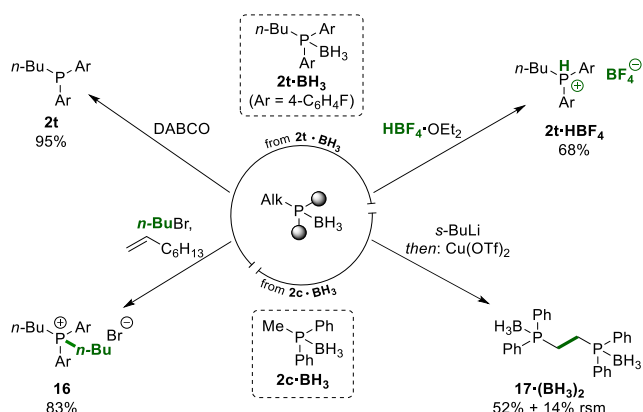
Scaffold construction by alkylation



Scheme 4. Modification of bidentate ligands. See SI for detailed reaction conditions. a: Isolated without borane protection.

The phosphine borane adducts, as which the phosphine products were typically isolated, can be used in versatile derivatization reactions (Scheme 5). The free phosphine **2t** was accessed in nearly quantitative yield by treatment of the phosphine borane adduct **2t**· BH_3 with DABCO and a subsequent simple filtration through Celite.^[63] Conversion to the HBF_4 salt **2t**· HBF_4 was achieved in good yield.^[64,65] Such salts are air-stable and can be used directly as ligand precursors in catalysis by releasing the free phosphine *in situ* after treatment with a base.^[66]

Phosphonium salt **16** was accessed in 83% yield from the phosphine borane adduct **2t**· BH_3 by treating it with an alkyl halide in the presence of 1-octene.^[67] The product phosphonium salt could then be used in the nickel-catalyzed dearylation reaction again, allowing to quickly introduce multiple alkyl groups in a phosphine in a programmed fashion. As an additional way to modify the products, the alkyl group in the phosphine borane adduct **2c**· BH_3 was deprotonated in α -position to the phosphorus, and subsequent oxidative dimerization yielded the bidentate product **17**·(BH_3)₂, providing a means to extend the ligand diversification beyond the scope of the dearylation reaction.^[68]



Scheme 5. Derivatization of the phosphine borane products. DABCO = 1,4-diazabicyclo[2.2.2]octane. rsm = recovered starting material. See SI for detailed reaction conditions.

In conclusion, we demonstrated a general and user-friendly strategy for the modification of phosphine ligands. The reaction enables the substitution of aryl groups in phosphines for alkyl groups in a protocol relying on the straightforward alkylation of a phosphine and a subsequent nickel-catalyzed dearylation reaction. Besides the broad scope of the dearylation method, we demonstrate that the overall process can also be directly conducted as a one-pot protocol. Together with the development of a related strategy for the modification of bidentate ligands and versatile product derivatization methods, this methodology provides a rapid entry into underexplored ligand space. We expect that this strategy will streamline ligand optimization campaigns and enable the identification of new powerful ligands for use in catalysis.

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Keywords: Ligand modification • Nickel • Phosphine • Diversification • Catalysis

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