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Nickel-catalysed diversification of phosphine ligands by formal substitution at phosphorus†

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We report a diversification strategy that enables the direct substituent exchange of tertiary phosphines. Alkylated phosphonium salts, prepared by standard alkylation of phosphines, are selectively dearylated in a nickel-catalysed process to access alkylphosphine 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 derivatives of the parent ligand. The phosphine products of the reaction are converted *in situ* to air-stable borane adducts for isolation, and versatile derivatisation reactions of these adducts are demonstrated.

Introduction

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 centre. 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] or material sciences.[15,16] 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[17–20] or reactions of hydrophosphines such as the hydrophosphination of unsaturated systems,[21–23] cross-coupling with aryl halides,[24,25] or substitution reactions with electrophiles in the presence of base.[4,26] Combined, these methods allow access to a plethora of diverse phosphine architectures. However, they typically require multi-step procedures involving toxic or pyrophoric reagents and air-sensitive intermediates that are challenging to isolate. These drawbacks can make the preparation of phosphines arduous and restrict ligand optimisation campaigns to the evaluation of the limited collection of commercially available phosphines. However, if chemists only evaluate commercially available phosphines, they might fail to identify more active and selective catalysts. Therefore, new approaches towards the straightforward synthesis of phosphines and other phosphorus-containing compounds are in critical demand.[27–29]

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 endeavour for the rapid discovery and optimisation of new reactions. The direct access to ligand derivatives from a hit result also becomes increasingly important in light of recent advances in statistical and machine learning-based approaches that facilitate the *in silico* optimisation of ligand structures.[9,30,31] Most efforts directed at the modification of tertiary phosphines have focused on altering substituents, for instance by C–H functionalisation approaches.[32–34] 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).[35–37] As an alternative, Wang and co-workers reported that acyl phosphines can be used as surrogates for secondary phosphines in metal-catalysed alkylation and arylation reactions.[38–41] While these methods expand the toolbox of

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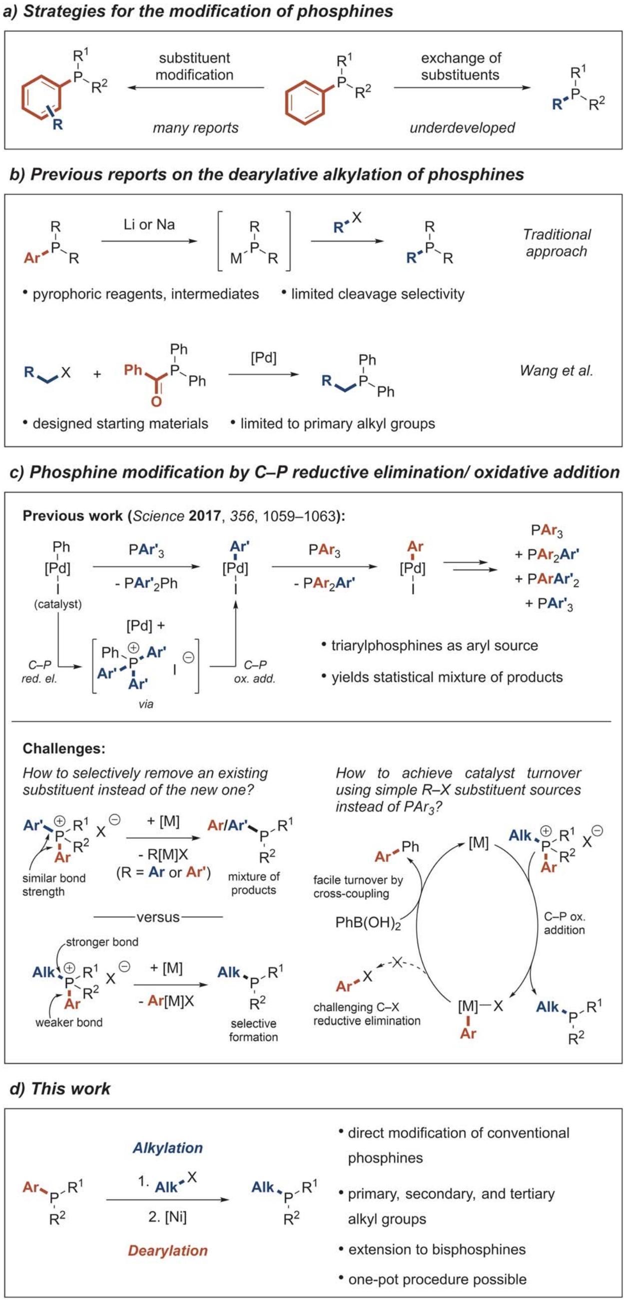


Scheme 1 Context of this work.

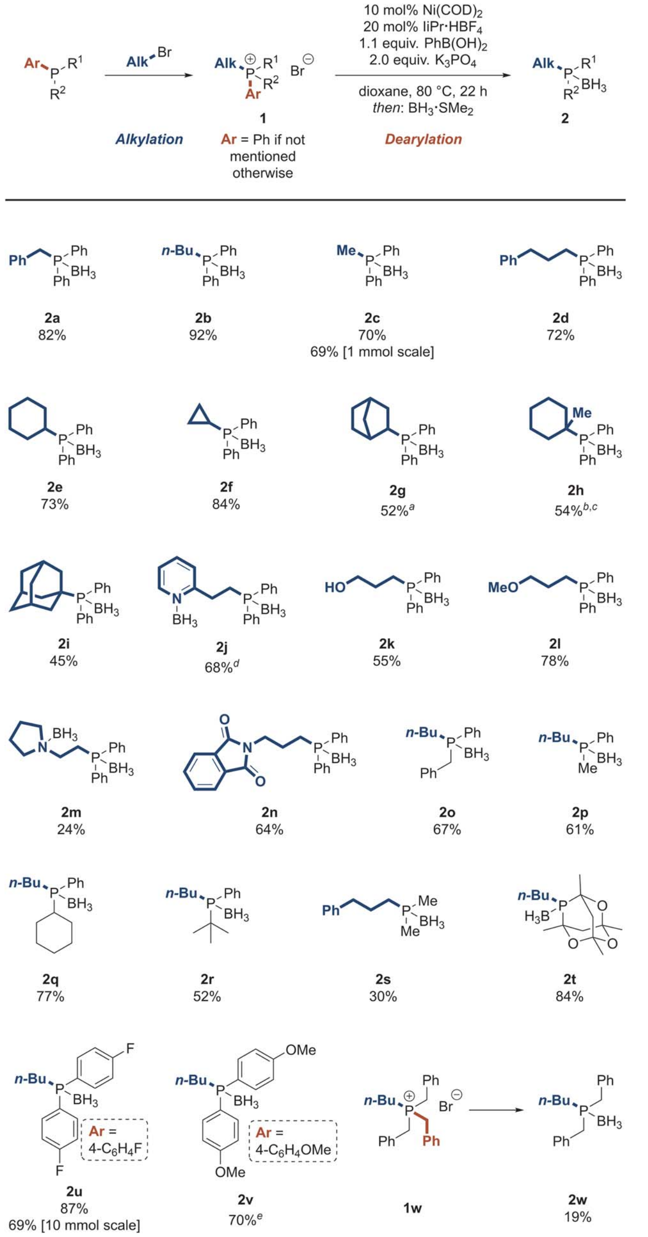
phosphine modification reactions, they suffer from poor cleavage selectivity or limited scope, respectively. A general and selective strategy to introduce alkyl substituents into tertiary phosphines has thus remained elusive.

Our group[42–44] and others[45–53] 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-catalysed process that scrambles aryl groups between two triarylphosphines (Scheme 1c top).[42] 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 centre. 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 unpractical 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.[54–56] 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.[47,50,57] 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 centre. Here, we report the realisation of this strategy as a versatile method that enables rapid diversification of commercial phosphines to access alkylphosphine ligand space (Scheme 1d).[58]

Results and discussion

After evaluation of a broad set of reaction conditions, we discovered that a combination of $Ni(COD)_2$ as pre-catalyst, the ligand precursor $IiPr\cdot HBF_4$ ($IiPr\cdot HBF_4$ = 1,3-di(iso-propyl) 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 ESI† for details).[47,50] 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 ESI† for details). Alternatively, the air-stable Ni(0) precatalysts developed by the groups of Cornella[59,60] and Engle[61] can be used instead of $Ni(COD)_2$ to set the reaction up on the benchtop with no decrease in yield (see ESI†). 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 ESI†) and then subjected to the dearylation reaction (Scheme 2). For ease of purification, the



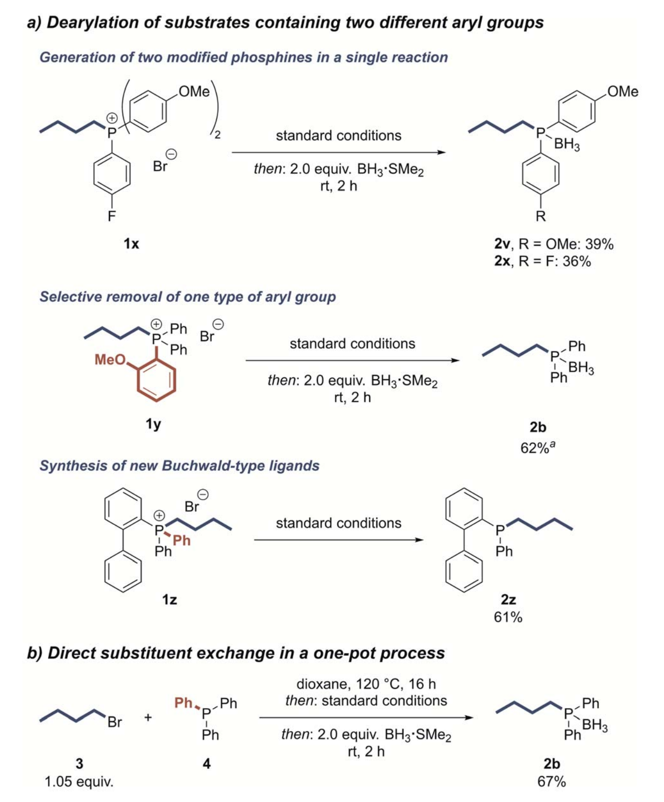
Scheme 2 Scope of monophosphines. Yields refer to isolated compounds for the dearylation process after derivatisation to the air-stable BH_3 adduct. [a]dr = 12 : 1. The starting material **1g** had a dr of 9 : 1. [b]From the iodide salt. [c]14 : 1 mixture with $Ph_3P·BH_3$. [d]From the chloride salt. [e]SIMes·HCl used instead of IiPr·HBF_4.

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*).[62,63]

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 as well as the *tert*-butyl and adamantyl groups are arguably the most widespread alkyl substituents in modern ligands. Our reaction not only tolerates the presence of these moieties (**2e**, **2i**, **2q–r**), but also allows to introduce other, 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 (**2j–2l**) 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 (**2m**, 24%). As an alternative, a phthalimide moiety, which can be used as a precursor for amines, was well tolerated (**2n**). 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 (**2o–r**). Trialkylphosphine **2s** was prepared in a lowered, but synthetically useful yield of 30%. In contrast, the caged trialkylphosphine **2t** 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 (**2u–2v**). Notably, the reaction can also be conducted on a large scale, as demonstrated by the preparation of two grams of **2u**. Besides the dearylation of phosphonium salts, the dealkylation is possible when the starting material does not contain an aryl group. Tetraalkylphosphonium salt **1w** was selectively debenzylated in 19% yield without additional optimisation.

We next investigated reactions of phosphonium salts containing two different aryl groups (Scheme 3a). The transformation of phosphonium salt **1x**, containing electron-



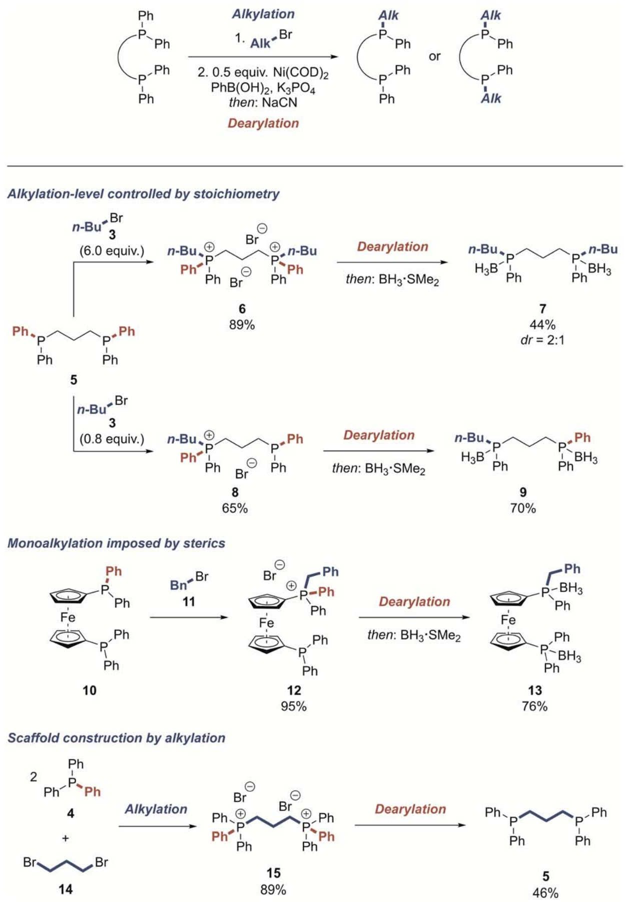
Scheme 3 Further applications. [a]8 : 1 mixture with 2-methoxybiphenyl.

donating and electron-withdrawing aryl groups, resulted in partial cleavage of both aryl groups to deliver the two alkylated phosphines **2v** and **2x** in useful yields in a single reaction. The products could be conveniently separated by column chromatography. In contrast, the 2-methoxyphenyl group was exclusively removed from phosphonium salt **1y**, 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 the air-stable JohnPhos derivative **2z** in good yield.

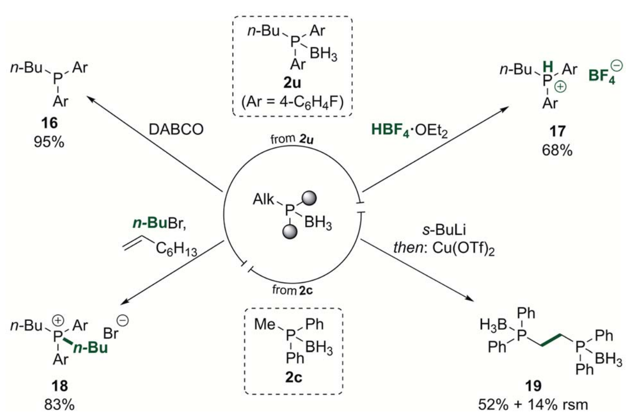
Results of further substrates that were tested in the reaction are summarized in Fig. S3.† Generally, substrates with high steric hindrance performed worse in the reaction than less sterically hindered substrates. Additionally, substrates with strongly coordinating moieties did not perform well or even led to cleavage of the alkyl group.

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-catalysed dearylation. Applying this protocol, we were able to prepare *n*-butyldiphenylphosphine from triphenylphosphine (**4**) in 67% yield after converting the product to its air-stable borane adduct **2b** (Scheme 3b). Notably, no intermediate workup or solvent change is required, making this process a direct substitution at the phosphorus centre and enabling rapid access to alkylated phosphine ligands.

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 ESI†). We thus tested a range of metal scavengers to de-coordinate the product from the nickel centre of this complex and found that sodium cyanide is highly active for this process.[64–67] 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 centres 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 unsymmetrical 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 unsymmetrical 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.



Scheme 4 Modification of bidentate ligands. See ESI† for detailed reaction conditions.



Scheme 5 Derivatisation of the phosphine borane products. DABCO = 1,4-diazabicyclo[2.2.2]octane. RSM = recovered starting material. See ESI† for detailed reaction conditions.

The phosphine borane adducts, as which the phosphine products were typically isolated, can be used in versatile derivatisation reactions (Scheme 5). The free phosphine **16** was accessed in nearly quantitative yield by treatment of the phosphine borane adduct **2u** with DABCO and a subsequent simple filtration through Celite.[68] Conversion to the HBF_4 salt **17** was achieved in good yield.[69,70] 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.[71]

Phosphonium salt **18** was accessed in 83% yield from the phosphine borane adduct **2u** by treating it with an alkyl halide in the presence of 1-octene.[72] The product phosphonium salt could then be used in the nickel-catalysed 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** was deprotonated in alpha-position to the phosphorus, and subsequent oxidative dimerisation yielded the bidentate product **19**, providing a means to extend the ligand diversification beyond the scope of the dearylation reaction.[73]

Conclusions

In conclusion, we demonstrated a general 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-catalysed 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 derivatisation methods, this methodology provides a rapid entry into alkylphosphine ligand space. We expect that this strategy will streamline ligand optimisation campaigns and enable the identification of new powerful ligands for use in catalysis.

Data availability

Full experimental and characterization data is available in the ESI.†

Author contributions

S. R. conceived the project. S. R. and S. U. L. performed the experimental studies. B. M. supervised the research. S. R. wrote the original draft of the manuscript which was edited by all authors.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding To Catalysis*, University Science Books, Sausalito, CA, USA, 2010.
2 A. L. Clevenger, R. M. Stolley, J. Aderibigbe and J. Louie, *Chem. Rev.*, 2020, **120**, 6124–6196.
3 *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, ed. P. C. J. Kamer and P. W. N. M. van Leeuwen, John Wiley & Sons, Ltd, Chichester, UK, 2012.
4 E. I. Musina, A. S. Balueva and A. A. Karasik, in *Organophosphorus Chemistry*, ed. L. J. Higham, D. W. Allen and J. C. Tebby, Royal Society of Chemistry, 2021, vol. 50, pp. 37–114.
5 R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461–1473.
6 R. J. Lundgren and M. Stradiotto, *Chem.–Eur. J.*, 2012, **18**, 9758–9769.
7 P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Acc. Chem. Res.*, 2001, **34**, 895–904.
8 A. Sarbajna, V. S. V. S. N. Swamy and V. H. Gessner, *Chem. Sci.*, 2021, **12**, 2016–2024.
9 K. Wu and A. G. Doyle, *Nat. Chem.*, 2017, **9**, 779–784.
10 L. Chen, P. Ren and B. P. Carrow, *J. Am. Chem. Soc.*, 2016, **138**, 6392–6395.
11 A. Zapf, A. Ehrentraut and M. Beller, *Angew. Chem., Int. Ed.*, 2000, **39**, 4153–4155.
12 H. Guo, Y. C. Fan, Z. Sun, Y. Wu and O. Kwon, *Chem. Rev.*, 2018, **118**, 10049–10293.
13 C. Xie, A. J. Smaligo, X.-R. Song and O. Kwon, *ACS Cent. Sci.*, 2021, **7**, 536–558.
14 D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441.
15 D. J. Young, S. W. Chien and T. S. A. Hor, *Dalton Trans.*, 2012, **41**, 12655.
16 Y. Ren and T. Baumgartner, *Dalton Trans.*, 2012, **41**, 7792.
17 Ł. Kapuśniak, P. N. Plessow, D. Trzybiński, K. Woźniak, P. Hofmann and P. I. Jolly, *Organometallics*, 2021, **40**, 693–701.
18 H.-C. Wu, J.-Q. Yu and J. B. Spencer, *Org. Lett.*, 2004, **6**, 4675–4678.
19 C. A. Busacca, R. Raju, N. Grinberg, N. Haddad, P. James-Jones, H. Lee, J. C. Lorenz, A. Saha and C. H. Senanayake, *J. Org. Chem.*, 2008, **73**, 1524–1531.
20 N. I. Rinehart, A. J. Kendall and D. R. Tyler, *Organometallics*, 2018, **37**, 182–190.
21 Y.-B. Li, H. Tian and L. Yin, *J. Am. Chem. Soc.*, 2020, **142**, 20098–20106.
22 M. M. I. Basiouny, D. A. Dollard and J. A. R. Schmidt, *ACS Catal.*, 2019, **9**, 7143–7153.
23 S. Pullarkat, *Synthesis*, 2015, **48**, 493–503.

24 M. Murata and S. L. Buchwald, *Tetrahedron*, 2004, **60**, 7397–7403.
25 J.-S. Zhang, T. Chen, J. Yang and L.-B. Han, *Chem. Commun.*, 2015, **51**, 7540–7542.
26 P. B. Arockiam, U. Lennert, C. Graf, R. Rothfelder, D. J. Scott, T. G. Fischer, K. Zeitler and R. Wolf, *Chem.–Eur. J.*, 2020, **26**, 16374–16382.
27 A. Mondal, N. O. Thiel, R. Dorel and B. L. Feringa, *Nat. Catal.*, 2022, **5**, 10–19.
28 H. Deng, M. Wang, Y. Liang, X. Chen, T. Wang, J. J. Wong, Y. Zhao, K. N. Houk and Z. Shi, *Chem*, 2022, **8**, 569–579.
29 T. Barber, S. P. Argent and L. T. Ball, *ACS Catal.*, 2020, **10**, 5454–5461.
30 T. Gensch, G. dos Passos Gomes, P. Friederich, E. Peters, T. Gaudin, R. Pollice, K. Jorner, A. Nigam, M. Lindner-D'Addario, M. S. Sigman and A. Aspuru-Guzik, *J. Am. Chem. Soc.*, 2022, **144**, 1205–1217.
31 S. Zhao, T. Gensch, B. Murray, Z. L. Niemeyer, M. S. Sigman and M. R. Biscoe, *Science*, 2018, **362**, 670–674.
32 X. Qiu, M. Wang, Y. Zhao and Z. Shi, *Angew. Chem., Int. Ed.*, 2017, **56**, 7233–7237.
33 J. Wen, B. Dong, J. Zhu, Y. Zhao and Z. Shi, *Angew. Chem., Int. Ed.*, 2020, **59**, 10909–10912.
34 M. R. Auth, K. A. McGarry and T. B. Clark, *Adv. Synth. Catal.*, 2021, **363**, 2354–2365.
35 A. M. Aguiar, J. Beisler and A. Mills, *J. Org. Chem.*, 1962, **27**, 1001–1005.
36 A. M. Aguiar, H. J. Greenberg and K. E. Rubenstein, *J. Org. Chem.*, 1963, **28**, 2091–2093.
37 J. Ye, J.-Q. Zhang, Y. Saga, S. Onozawa, S. Kobayashi, K. Sato, N. Fukaya and L.-B. Han, *Organometallics*, 2020, **39**, 2682–2694.
38 R. Yu, X. Chen and Z. Wang, *Tetrahedron Lett.*, 2016, **57**, 3404–3406.
39 J. Yang, H. Wu and Z. Wang, *J. Saudi Chem. Soc.*, 2018, **22**, 1–5.
40 M. Zhang, Z. Ma, H. Du and Z. Wang, *Tetrahedron Lett.*, 2020, **61**, 152125.
41 X. Chen, H. Wu, R. Yu, H. Zhu and Z. Wang, *J. Org. Chem.*, 2021, **86**, 8987–8996.
42 Z. Lian, B. N. Bhawal, P. Yu and B. Morandi, *Science*, 2017, **356**, 1059–1063.
43 Y. H. Lee and B. Morandi, *Nat. Chem.*, 2018, **10**, 1016–1022.
44 P. Boehm, T. Martini, Y. H. Lee, B. Cacherat and B. Morandi, *Angew. Chem., Int. Ed.*, 2021, **60**, 17211–17217.
45 F. Y. Kwong and K. S. Chan, *Chem. Commun.*, 2000, 1069–1070.
46 F. Y. Kwong and K. S. Chan, *Organometallics*, 2000, **19**, 2058–2060.
47 L. K. Hwang, Y. Na, J. Lee, Y. Do and S. Chang, *Angew. Chem., Int. Ed.*, 2005, **44**, 6166–6169.
48 K. Baba, Y. Masuya, N. Chatani and M. Tobisu, *Chem. Lett.*, 2017, **46**, 1296–1299.
49 H. Fujimoto, M. Kusano, T. Kodama and M. Tobisu, *Org. Lett.*, 2019, **21**, 4177–4181.
50 X. Zhang and A. McNally, *Angew. Chem., Int. Ed.*, 2017, **56**, 9833–9836.
51 X. Zhang and A. McNally, *ACS Catal.*, 2019, **9**, 4862–4866.
52 Y. Che, Y. Yue, L. Lin, B. Pei, X. Deng and C. Feng, *Angew. Chem., Int. Ed.*, 2020, **59**, 16414–16419.
53 H. Wang, M. Yang, Y. Wang, X. Man, X. Lu, Z. Mou, Y. Luo and H. Liang, *Org. Lett.*, 2021, **23**, 8183–8188.
54 S. A. Macgregor, *Chem. Soc. Rev.*, 2007, **36**, 67–76.
55 L. Wang, H. Chen and Z. Duan, *Chem.–Asian J.*, 2018, **13**, 2164–2173.
56 Y. H. Lee and B. Morandi, *Coord. Chem. Rev.*, 2019, **386**, 96–118.
57 M. Sakamoto, I. Shimizu and A. Yamamoto, *Chem. Lett.*, 1995, **24**, 1101–1102.
58 After this manuscript was deposited on a preprint server, a related work appeared: M. Lei, X. Chen, Y. Wang, L. Zhang, H. Zhu and Z. Wang, *Org. Lett.*, 2022, **24**, 2868–2872.
59 L. Nattmann, R. Saeb, N. Nöthling and J. Cornella, *Nat. Catal.*, 2020, **3**, 6–13.
60 L. Nattmann and J. Cornella, *Organometallics*, 2020, **39**, 3295–3300.
61 V. T. Tran, Z. Li, O. Apolinar, J. Derosa, M. V. Joannou, S. R. Wisniewski, M. D. Eastgate and K. M. Engle, *Angew. Chem., Int. Ed.*, 2020, **59**, 7409–7413.
62 J. M. Brunel, B. Faure and M. Maffei, *Coord. Chem. Rev.*, 1998, **178–180**, 665–698.
63 M. Ohff, J. Holz, M. Quirmbach and A. Börner, *Synthesis*, 1998, **1998**, 1391–1415.
64 T. A. DelDonno and W. Rosen, *J. Am. Chem. Soc.*, 1977, **99**, 8051–8052.
65 D. J. Brauer, F. Gol, S. Hietkamp, H. Peters, H. Sommer, O. Stelzer and W. S. Sheldrick, *Chem. Ber.*, 1986, **119**, 349–365.
66 C. D. Swor and D. R. Tyler, *Coord. Chem. Rev.*, 2011, **255**, 2860–2881.
67 B. P. Nell, C. D. Swor, E. A. Henle, L. N. Zakharov, N. I. Rinehart, A. Nathan and D. R. Tyler, *Dalton Trans.*, 2016, **45**, 8253–8264.
68 H. Brisset, Y. Gourdel, P. Pellon and M. Le Corre, *Tetrahedron Lett.*, 1993, **34**, 4523–4526.
69 L. McKinstry and T. Livinghouse, *Tetrahedron Lett.*, 1994, **35**, 9319–9322.
70 S. E. Denmark and N. S. Werner, *Org. Lett.*, 2011, **13**, 4596–4599.
71 M. R. Netherton and G. C. Fu, *Org. Lett.*, 2001, **3**, 4295–4298.
72 J. Uziel, N. Riegel, B. Aka, P. Figuière and S. Jugé, *Tetrahedron Lett.*, 1997, **38**, 3405–3408.
73 T. Imamoto, T. Kusumoto, N. Suzuki and K. Sato, *J. Am. Chem. Soc.*, 1985, **107**, 5301–5303.