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# Cyclization of Bisphosphines to Phosphacycles via the Cleavage of Two Carbon−Phosphorus Bonds by Nickel Catalysis

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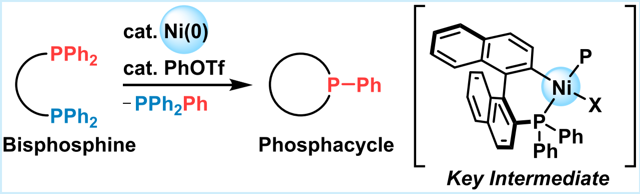
*Supporting Information*

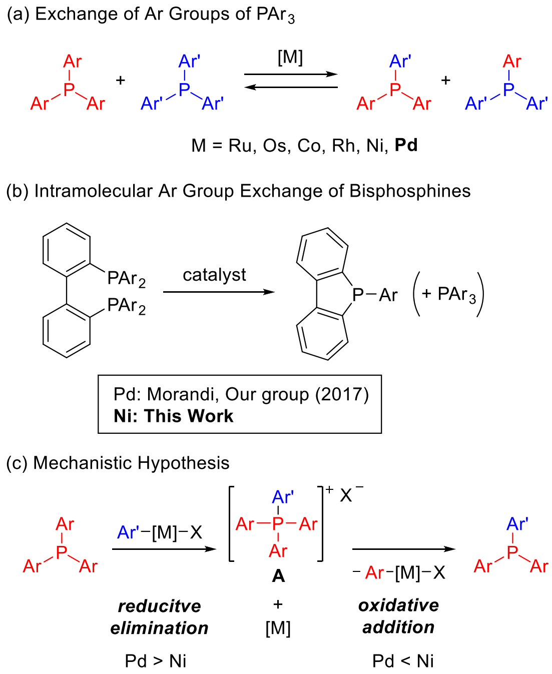
**ABSTRACT:** The nickel-catalyzed cyclization of bisphosphine derivatives to form various phosphacycles is reported. The reaction proceeds via the cleavage of two carbon−phosphorus bonds of the bisphosphine. Unlike the previously reported palladium catalysts, the use of nickel as a catalyst allows for the cyclization that requires C(alkyl)−P bond cleavage. A phospha-nickelacycle intermediate was successfully isolated and characterized by X-ray crystallography.



Tertiary phosphines are the essential components of transition metal catalysts in regulating the reactivity and selectivity of the catalytic reactions. In phosphine-ligated metal-catalyzed processes, carbon−phosphorus (C−P) bond cleavage is frequently encountered as an undesired side reaction.[1] For example, in palladium-catalyzed cross-coupling reactions of aryl halides, the aryl group of a triarylphosphine ligand has been known to be incorporated to the product in place of the aryl group of the aryl halide substrate.[2] Such an undesired reaction proceeds via a C−P bond exchange pathway (Scheme 1a), which can be mediated by several metal species with palladium being most active.[3] Although this intermolecular aryl group exchange has limited synthetic utility due to the reversibility of the reaction,[4] Morandi et al.[5] and our group[6] independently reported an intramolecular variant, which enables the palladium-catalyzed selective synthesis of dibenzophosphole derivatives from readily available bisphosphines (Scheme 1b). We report herein that this intramolecular C−P bond exchange reaction can be catalyzed by nickel. Nickel complexes are much less active in mediating C−P bond exchange reactions,[3b] and there are no general catalytic reactions[7] involving the cleavage of C−P bonds of tertiary phosphines, except for one isolated example using highly strained methylenecyclopropa[*b*]naphthalenes.[8] The C−P bond exchange reaction is mediated most efficiently by ArPdX species, through reductive elimination to form phosphonium salt **A** and Pd(0), followed by oxidative addition of a C−P bond of **A**[9] to provide an exchanged product (Scheme 1c, M = Pd). It is generally accepted that nickel can mediate the oxidative addition process more efficiently than palladium, whereas reductive elimination by nickel would require a higher barrier than palladium.[10] Therefore, nickel would be expected to exhibit a complementary reactivity to palladium in some of the elementary steps of the catalytic cycle, thus potentially allowing for a transformation that would be unique to nickel.

We initially investigated the nickel-catalyzed cyclization of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, **1a**) using $Ni(cod)_2$ as a nickel(0) catalyst (Table 1). To our delight, the desired phosphole was formed in 8% without the need for any additives (entry 1). Because phosphole derivatives are sensitive to oxygen, the product was quantified as the air-stable phosphole oxide **2a** after an oxidative workup with $H_2O_2$. Inspired by the seminal work by Morandi et al.,[5] in which added PhI serves as a cocatalyst to facilitate the

**Scheme 1. Metal-Mediated C−P Bond Exchange and Its Application to the Catalytic Synthesis of Phospholes**



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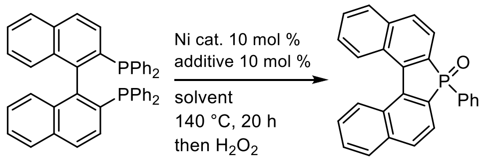
### Table 1. Nickel-Catalyzed Cyclization of 1a to 2a[a]



**1a** **2a**

| entry | catalyst | additive | solvent | NMR yield of **2a**/% |
|---|---|---|---|---|
| 1 | Ni(cod)$_2$ | none | toluene | 8 |
| 2 | Ni(cod)$_2$ | PhI | toluene | 19 |
| 3 | Ni(cod)$_2$ | PhBr | toluene | 23 |
| 4 | Ni(cod)$_2$ | PhOTf | toluene | 79 |
| 5 | Ni(cod)$_2$ | PhOTf | 1,4-dioxane | 61 |
| 6 | Ni(cod)$_2$ | PhOTf | DMF | 99 (84)[b] |
| 7 | Ni(OAc)$_2$ | PhOTf | toluene | trace |
| 8 | Ni(OTf)$_2$ | PhOTf | toluene | trace |

[a] Reaction conditions: **1a** (0.20 mmol), Ni cat. (0.020 mmol), and additive (0.020 mmol) in solvent (1.0 mL) at 140 °C for 20 h. The NMR yield was determined using 1,1,2,2,-tetrachloroethane as an internal standard. [b] Isolated yield.

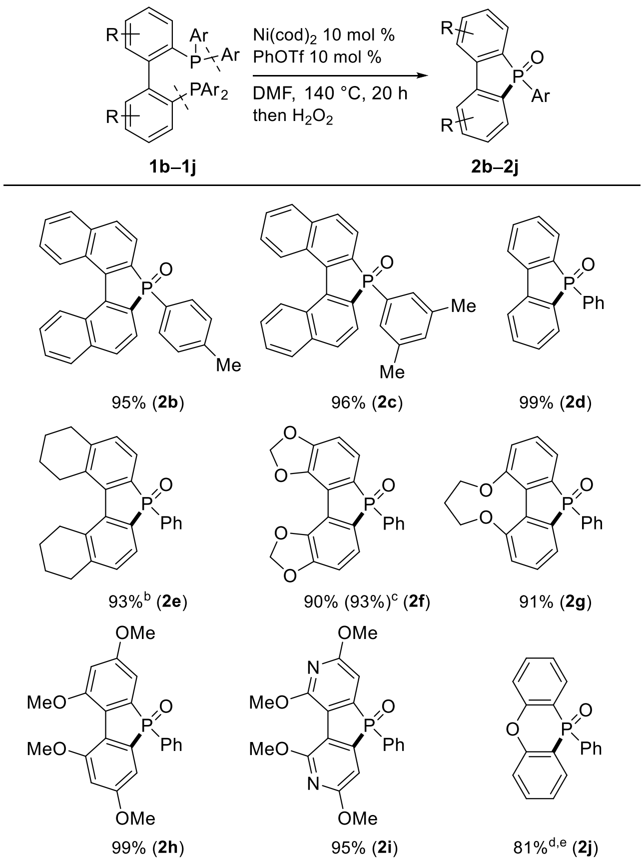
formation of a phosphonium salt, a key intermediate, we examined a nickel catalyst in conjunction with an aryl halide. The addition of a catalytic amount of PhI (entry 2) and PhBr (entry 3) increased the yield of **2a** to ca. 20%. We were then able to increase the yield to 79% when PhOTf was used as a cocatalyst (entry 4). The use of DMF (entry 6) allowed the reaction to proceed quantitatively to give **2a** in 84% isolated yield, along with a stoichiometric amount of triphenylphosphine oxide, thus confirming the fate of the cleaved phosphorus residue. The use of Ni(OAc)$_2$ (entry 7) and Ni(OTf)$_2$ (entry 8) as nickel(II) catalysts failed to promote the reaction.

The scope of this nickel-catalyzed cyclization reaction was examined using a series of commercially available bisphosphine derivatives (Scheme 2). The scope of the substituent on the phosphorus atom was initially examined. Aryl groups, such as *p*-tolyl (**1b**) and 3,5-xylyl (**1c**), were found to participate in this cyclization to provide the corresponding phosphole derivatives **2b** and **2c** in excellent yields. The cyclization reaction is not limited to a binaphthyl-based skeleton, but a simpler biphenyl system, including **1d**−**1h**, also participated successfully in the reaction. Although these bisphosphines have a diverse range of bite angles,[11] which could potentially affect the efficiency of the reaction, all provided the corresponding phospholes **2d**−**2h** in >90% yields. It was also possible to synthesize heterocyclic (**2i**) and six-membered (**2j**) phosphacycles using the corresponding bisphosphines **1i** and **1j** under these nickel-catalyzed conditions.

Apart from the earth-abundant nature, the use of nickel in place of palladium provides an opportunity to realize some unique transformations. Since oxidative addition occurs more readily in the presence of nickel than palladium,[10] a nickel catalyst shows superior reactivity to a palladium catalyst in cyclization reactions of electron-rich substrates (Scheme 3). For example, a bulky and electron-rich bisphosphine **1k** (DTBM-SEGPHOS) can be cyclized more efficiently using a nickel-catalyzed method (method A) than the previously reported palladium-catalyzed methods (methods B and C) to form the elaborate phosphole **2k**. Another example involves the cleavage of more challenging C(sp$^3$)−P bonds. The cyclization of an alkylene linked bisphosphine such as 1,4-bis(diphenylphosphino)butane (**1l**, DPPB) failed to proceed under palladium-catalyzed conditions.[6,12] However, to our delight, when the Ni(cod)$_2$/PhOTf was used, **1l** underwent cyclization to form the aliphatic phosphacycle **2l** in 50% yield. The combination of Pd$_2$(dba)$_3$/PhOTf was also studied, but cyclization of **1l** did not proceed. The phosphacyle **2l** can be used as a framework of the phosphine organocatalyst of catalytic Appel,[13] Staudinger,[14] Wittig[15] and Mitsunobu[16] reactions. Although conventional synthetic methods of **2l** involve the use of reactive phosphorus reagents, this nickel-catalyzed method gives **2l** from commercially available and stable bisphosphine derivatives. It should be noted that selectivity between C(sp$^2$)−P and C(sp$^3$)−P bonds of the phosphonium salt intermediates would not be expected to significantly affect the product selectivity, since the reverse selectivity simply results in the reverse reaction to form the previous intermediate and the compound would still participate in the productive catalytic cycle.

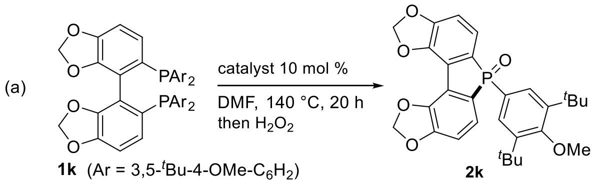
The reaction is presumably initiated by the oxidative addition of PhOTf to Ni(0) to form a Ni(OTf)Ph(bisphosphine), which then serves as a catalytically active species. To confirm this possibility, NiCl(2-Np)(PCy$_3$)$_2$ (2-Np = 2-naphthalenyl)[17] was synthesized as a model of Ni(OTf)Ph(bisphosphine), and its catalytic activity was examined (Scheme 4a). The BINAP **1a** provided the corresponding

### Scheme 2. Reaction Scope[a]

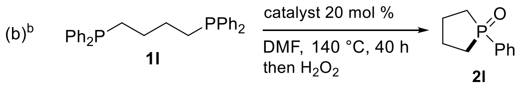


[a] Reaction conditions: bisphosphine (0.20 mmol), Ni(cod)$_2$ (0.020 mmol), PhOTf (0.020 mmol) in DMF (1.0 mL) for 20 h at 140 °C. Yields of isolated products are given. [b] 0.10 mmol scale. [c] Run on a 3.0 mmol scale using a NiCl(2-Np)(PCy$_3$)$_2$ catalyst. 1.05 g of **2f** was obtained. [d] Run using 0.040 mmol of Ni(cod)$_2$ and PhOTf. [e] Isolated as a mixture of triphenylphosphine oxides (1:1).

### Scheme 3. Comparison with Palladium Catalyst[a]



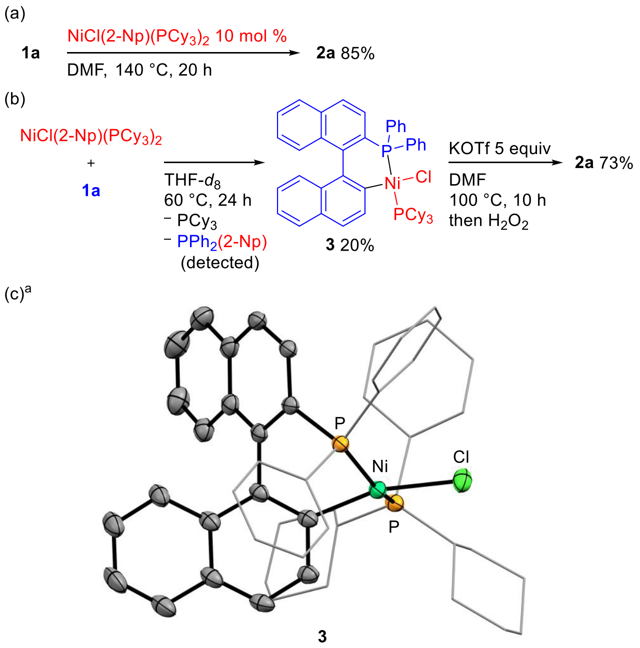
| method | catalyst | yield |
|---|---|---|
| A | $Ni(cod)_2$/PhOTf | 76% |
| B[6] | $[(allyl)PdCl]_2$ | 23% |
| C[5] | $Pd_2(dba)_3$/PhI | 12% |



| method | catalyst | yield |
|---|---|---|
| A | $Ni(cod)_2$/PhOTf | 50% |
| B[6] | $[(allyl)PdCl]_2$ | 0% |
| C[5] | $Pd_2(dba)_3$/PhI | 0% |

[a] Reaction conditions: method A, $Ni(cod)_2$/PhOTf; method B,[6] $[(allyl)PdCl]_2$; method C,[5] $Pd_2(dba)_3$/PhI. Isolated yield. [b] Isolated as a mixture with triphenylphosphine oxide after second reduction/oxidation (see the SI for details).

### Scheme 4. Mechanistic Studies



[a] Molecular structure of the nickelacycle **3** with thermal ellipsoids at 50% probability (except for the phenyl and cyclohexyl groups) and all the hydrogen atoms are omitted for clarity.

phosphole **2a** in 85% yield, even in the absence of PhOTf. Stoichiometric experiments were performed to gain additional insights into the reaction mechanism (Scheme 4b). When $NiCl(2\text{-}Np)(PCy_3)_2$ was reacted with 1.0 equiv of BINAP **1a** at 60 °C in THF-$d_8$, $^{31}P$ NMR signals corresponding to two mutually *trans* phosphine resonances (doublets at 16.6 and 22.8 ppm with $J_{PP}$ = 318 Hz) were observed (Figure S2). Single-crystal X-ray diffraction of the crystallized material revealed that the six-membered phospha-nickelacycle complex **3** was formed via the cleavage of a C−P bond of **1a** (Scheme 4c). Hartwig et al.[18] reported on a similar phospha-nickelacycle by the reaction of a BINAP-ligated Ni(0) complex with an electron-rich aryl chloride. During the course of the formation of the phospha-nickelacycle **3**, the 2-naphthyldiphenylphosphine $[PPh_2(2\text{-}Np)]$, the cleaved phosphorus residue, was also observed by FAB-MS. In addition, a BINAP-ligated Ni(I) complex **4**, which is formed by the bimolecular reductive elimination of 2,2′-binaphthalene from the BINAP-ligated Ni(II) complex, was also formed (Figure S3). The phospha-nickelacycle **3** could be used to catalyze the cyclization of **1a** to form **2a** in 98% yield, even in the absence of PhOTf, whereas the Ni(I) complex **4** showed no catalytic activity. Heating the phospha-nickelacycle **3** in DMF at 100 °C for 10 h afforded **2a** in 73% yield. In this process, the addition of KOTf accelerated the formation of **2a** by approximately 2-fold (Figure S4), probably by decreasing the electron density of the nickel center through exchanging the ligand from Cl to OTf.[19] These results indicate that reductive elimination to form the cyclic phosphonium salt[20] is the turnover limiting step of this reaction, and the role of a PhOTf cocatalyst is best rationalized to facilitate this C−P bond forming reductive elimination.

In conclusion, we report on the nickel-catalyzed cyclization of bisphosphines to diverse phosphacycles via the cleavage of two C−P bonds. The method features nickel-catalyzed C−P bond cleavage, which allows for the transformation of bulky and C($sp^3$)−P bonds. Detailed studies related to the mechanism of this reaction revealed that the phospha-nickelacycle **3** is a key intermediate. The formation of the C−P cleavage complex **3**, even at 60 °C, indicates that precautions are needed when evaluating nickel-catalyzed reactions using BINAP-related bisphosphine ligands, since undesired ligand decomposition via C−P bond cleavage may be involved. Applications of this method to the synthesis of other heterocycle through carbon−heteroatom bond cleavage are currently being investigated in our laboratory.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01355.

Experimental details and characterization data (PDF)

### Accession Codes

CCDC 1907794 and 1907915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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