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Nickel-catalyzed manipulation of tertiary phosphines *via* highly selective C–P bond cleavage†

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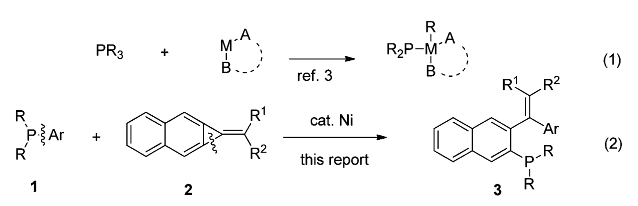
A catalytic cycle involving oxidative addition of nickel(0) with a carbon–carbon single bond in the three-membered ring of diarylmethylene-cyclopropa[*b*]naphthalenes, highly selective cleavage of the C–P bond, and migration of the aryl group of phosphine consequently provides a new type of bulky phosphine in excellent yields.

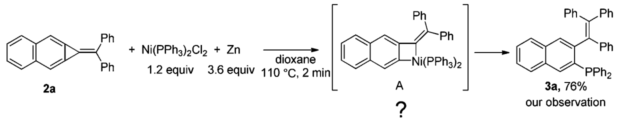
As a challenging topic, the cleavage of C–P bonds has attracted much attention in the past few decades.[1] Particularly, the C–P bond cleavage of tertiary phosphines has attracted much attention because many tertiary phosphines act as important ligands for transition metals and as versatile intermediates in organic synthesis.[2] Reports on C–P bond activation of tertiary phosphines with transition metals have been disclosed in the past years.[3] Most of these reports show C–P bond activation of tertiary phosphines with a stoichiometric amount of transition metal to provide stable metal compounds (Scheme 1, eqn (1)).[3a–f] However, very few examples of C–P activation of tertiary phosphines with a catalytic amount of transition metal have been reported. For example, Chan and coworkers have reported a catalytic user-friendly phosphination of aryltriflates and triarylphosphines providing a variety of substituted phosphines *via* C–P bond cleavage.[3g,h]



Scheme 1 C–P cleavage reactions reported previously and in this report.

In many transition-metal-catalyzed reactions, bulky phosphines show better reactivity than ordinary phosphines.[4] Thus, much attention has been focused on the synthesis of bulky phosphines in recent years. However, the methods are mostly limited to the reaction of a chlorophosphine with bulky organometallic reagents[5] and the transition-metal-catalyzed phosphination or phosphinylation of a bulky aryl halide.[6] We envisioned that selective cleavage of a C–P bond may provide a potential efficient synthesis of bulky phosphines. In this communication we wish to disclose an unprecedented nickel-catalyzed atom-economical and highly selective C–P bond cleavage of phosphines **1** coupled with a ring-opening reaction of diarylmethylenecyclopropa[*b*]-naphthalenes **2**,[7] leading to an efficient synthesis of a new type of bulky phosphine (Scheme 1, eqn (2)).

During our studies on the synthetic utility of diarylmethylenecyclopropa[*b*]naphthalenes **2**, we recently reported a highly regioselective Pd(0)-catalyzed [3+2] cycloaddition reaction of diarylmethylenecyclopropa[*b*]naphthalenes with alkenes, alkynes or arynes to produce 1(3)-alkylidene-2,3-dihydro-1*H*-cyclopenta[*b*]-naphthalene, 1-alkylidene-1*H*-cyclo-penta[*b*]naphthalene and 11-diarylmethylene-11*H*-benzo[*b*]fluorine derivatives, respectively.[8] We proposed a mechanism in which the reaction is initiated by the oxidative addition of a Pd(0) species to the three-membered ring of compound **2**. As a further exploration of the reaction mechanism, we recently tried to prepare the nickelacyclobutene **A**. We envisaged that the reaction of 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**2a**) with $Ni(PPh_3)_2$ generated *in situ* from $Ni(PPh_3)_2Cl_2$ and Zn would give **A** *via* oxidative addition. However, the expected nickelacyclobutene **A** was not isolated and a new product **3a** was obtained instead (Scheme 2). Through spectroscopic (^1H, ^{13}C, ^{31}P NMR, MS) and X-ray diffraction analysis,[9] we identified the structure of this new product, which is shown in Fig. S1 (ESI†). Obviously, the reaction showed an unexpected Ni-mediated ring-opening coupling of **2a**



Scheme 2 Our proposal and our observation.

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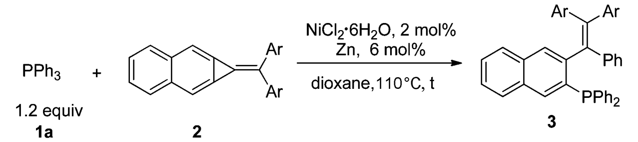
‡ Prof. Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping in completing all his projects with the help from Prof. Shengming Ma.

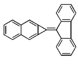
with the ligand, *i.e.*, triphenylphosphine, *via* a C–P bond cleavage reaction with a unique regioselectivity, serving as a direct and efficient synthesis of a new type of bulky tertiary phosphine.

We then focused our attention on realizing a catalytic reaction of triphenylphosphine (**1a**) with **2a** to produce **3a** using just a catalytic amount of $NiCl_2 \cdot 6H_2O$ and Zn. In a preliminary experiment, we observed that treatment of triphenylphosphine (**1a**) with 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**2a**) in the presence of $NiCl_2 \cdot 6H_2O$ (10 mol%) and Zn (30 mol%) in dioxane at 110 °C for 2 hours gave diphenyl[3-(1,2,2-triphenylvinyl)naphthalen-2-yl]phosphine (**3a**) in 96% yield (entry 2, Table S1, ESI†). When we reduced the amount of $NiCl_2 \cdot 6H_2O$ and Zn to 2 mol% and 6 mol%, respectively, the yield of **3a** was still maintained at 96%, although 10 hours were required (entries 3 and 4, Table S1, ESI†). To shorten the reaction time, the concentration was adjusted to 0.2 M and 0.4 M, with the best concentration being 0.2 M, which provided 96% of **3a** within 0.5 h (entries 5 and 6, Table S1, ESI†). Among the solvents examined, we found that dioxane was the best (entries 7–12, Table S1, ESI†). Therefore, a reaction in the presence of 2 mol% of $NiCl_2 \cdot 6H_2O$ and 6 mol% of Zn in dioxane at 110 °C at a concentration of 0.2 M was established as standard conditions to explore the reaction scope (entry 5, Table S1, ESI†). Here it should, of course, be noted that the reaction did not occur in the absence of the nickel catalyst (entry 1, Table S1, ESI†).

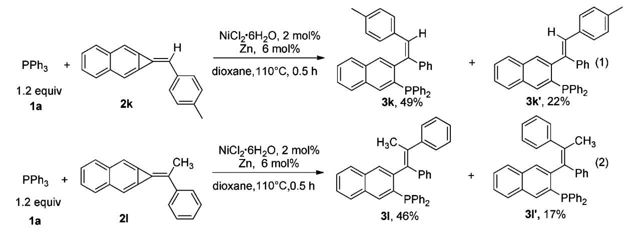
With the optimized conditions in hand, the scope of the reaction of **1a** with a variety of **2** was examined. The results summarized in Table 1 show that different products (**3**) could be obtained smoothly in high yields (entries 1–9, Table 1). (Diarylmethylene) cyclopropa[*b*]naphthalenes with *p*-tolyl (**2b**), *m*-tolyl (**2c**) and *o*-tolyl (**2d**) as the aryl groups gave their corresponding products in good yields in 1 hour, 3 hours and 48 hours, respectively (entries 2–4, Table 1). The prolonged reaction time for **3d** might result from the steric hindrance of the *ortho*-methyl groups. When (diarylmethylene) cyclopropa[*b*]naphthalenes bearing other electron-donating or electron-withdrawing aryl groups were employed, the reactions all gave the corresponding products **3** in good yields (entries 5–9, Table 1). The reaction of **2i** and **2j** needed longer times and were completed within 7 h and 18 h, respectively, because of the poor solublility of the substrates (entries 9 and 10, Table 1). The unsymmetrical substrate **2k**, upon reacting with **1a**, gave the desired compounds **3k** and **3k′** that were easily separated *via* chromatography on a silica gel and isolated in yields of 49% and 22% (eqn (1), Scheme 3). Similarly, the reaction of **1a** and **2l** produced **3l** and **3l′** in isolated yields of 46% and 17% (eqn (2), Scheme 3). The structures of **3k** and **3l** were confirmed by X-ray diffraction analysis (Fig. S1, ESI†).[9]

Table 1 Nickel-catalyzed ring-opening coupling of triphenylphosphine (**1a**) with diarylmethylenecyclopropa[*b*]naphthalenes (**2**)[a]



Entry	Ar	Time (h)	Isolated yield (%)
1	Ph (**2a**)	0.5	96 (**3a**)
2	4-MeC_6H_4 (**2b**)	1	96 (**3b**)
3	3-MeC_6H_4 (**2c**)	3	85 (**3c**)
4	2-MeC_6H_4 (**2d**)	48	86 (**3d**)
5	4-$MeOC_6H_4$ (**2e**)	0.5	98 (**3e**)
6	3,5-MeO-C_6H_3 (**2f**)	0.5	95 (**3f**)
7	4-FC_6H_4 (**2g**)	0.5	91 (**3g**)
8	4-ClC_6H_4 (**2h**)	1	98 (**3h**)
9	4-BrC_6H_4 (**2i**)	7	95 (**3i**)
10	(**2j**)	18	87 (**3j**)

[a] The reaction was conducted with 0.24 mmol of **1a**, 0.2 mmol of **2**, 0.004 mmol of $NiCl_2 \cdot 6H_2O$, 0.012 mmol of Zn and 1 mL of solvent at 110 °C.

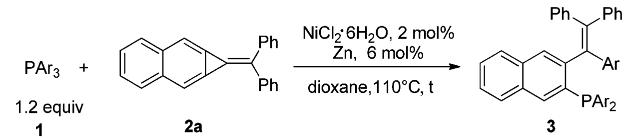


Scheme 3 Nickel-catalyzed ring-opening coupling of **1a** with **2k** and **2l**.

Next, we investigated the reaction of a variety of phosphines with substrate **2a** (Table 2). The reaction may be conducted with electron-donating, electron-withdrawing group-substituted aryl phosphines, tri(β-naphthyl)phosphine and tri(furan-2-yl)phosphine (Table 2). When Ar was the 2-methylphenyl group, no reaction was observed, which might result from the steric hindrance of the methyl group (entry 3, Table 2). The reaction gave a complex mixture when applying tri(*n*-butyl)phosphine **1k** (entry 10, Table 2). Noteworthily, when phosphines bearing only one phenyl, such as dibutyl(phenyl)phosphine (**1l**) and dicyclohexyl(phenyl)phosphine (**1m**), were used, the corresponding products **3u** and **3v** were obtained in 92% and 94%, respectively (eqn (1), Scheme 4), which showed that only the phenyl group migrated, exclusively.[5c,d,10] Furthermore, even triphenylarsine could react with **2a** to give its ring-opening coupling product **3w** in 95% yield in the presence of 10 mol% of $NiCl_2 \cdot 6H_2O$ and 30 mol% of Zn in 36 hours (eqn (2), Scheme 4).[11]

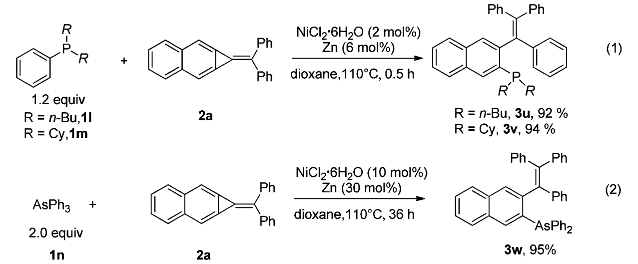
On the basis of the above observations, we propose a plausible mechanism for this reaction (Scheme 5). Firstly, the reduction reaction of $Ni(PPh_3)_2Cl_2$ with Zn affords $Ni^0(PPh_3)_2$. Subsequently, oxidative addition of $Ni^0(PPh_3)_2$ with the cyclopropane C–C bond of

Table 2 Nickel-catalyzed ring-opening coupling of phosphines (**1a**) with 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**2a**)[a]

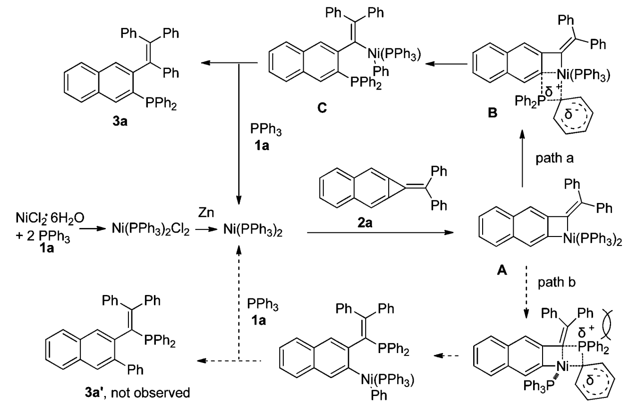


Entry	Ar	Time (h)	Isolated yield (%)
1	3-MeC_6H_4 (**1b**)	4	92 (**3m**)
2	4-MeC_6H_4 (**1c**)	4	98 (**3n**)
3	2-MeC_6H_4 (**1d**)	24	NR
4	4-$MeOC_6H_4$ (**1e**)	5	94 (**3o**)
5	4-FC_6H_4 (**1f**)	0.5	98 (**3p**)
6	4-ClC_6H_4 (**1g**)	1	95 (**3q**)
7	4-BrC_6H_4 (**1h**)	1	96 (**3r**)
8	2-Naphthyl (**1i**)	0.5	96 (**3s**)
9	2-Furayl (**1j**)	12	94 (**3t**)
10	*n*-Bu (**1k**)	24	Complex

[a] The reaction was conducted with 0.24 mmol of **1**, 0.2 mmol of **2a**, 0.004 mmol of $NiCl_2 \cdot 6H_2O$, 0.012 mmol of Zn and 1 mL of solvent at 110 °C.



Scheme 4 Nickel-catalyzed ring-opening coupling of **1l**, **1m** and **1n** with **2a**.



Scheme 5 Plausible mechanism of the nickel-catalyzed ring-opening coupling reaction.

2a generates a metallacyclobutane **A**.[7d] Then the phenyl ring migrates from phosphorus to nickel and the phosphorus migrates to the naphthyl ring to produce **C** *via* a four-membered transition structure **B** (path a).[3f] After that, intermediate **C** undergoes reductive elimination affording **3a** while accepting another equivalent of phosphine **1a** to regenerate the catalytically active Ni^0 catalyst. In principle, the formation of **3a′** *via* the intermediate **C′** is possible (path b). Interestingly, the formation of **3a′** was not observed, which is probably due to the steric hindrance in intermediate **B′**.

In conclusion, we have developed a nickel-catalyzed highly selective C–P bond cleavage of tertiary phosphines involving a ring-opening coupling reaction of diarylmethylenecyclopropa[*b*]naphthalenes to atom-economically provide differently substituted bulky phosphines in excellent yields. The reactions are applicable to a wide range of both phosphines and diarylmethylenecyclopropa[*b*]naphthalenes with different functionalities. Further studies on the scope, mechanism, and synthetic applications of this transformation are being carried out in our laboratory.

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