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Nickel-Catalyzed C–P Cross-Coupling by C–CN Bond Cleavage

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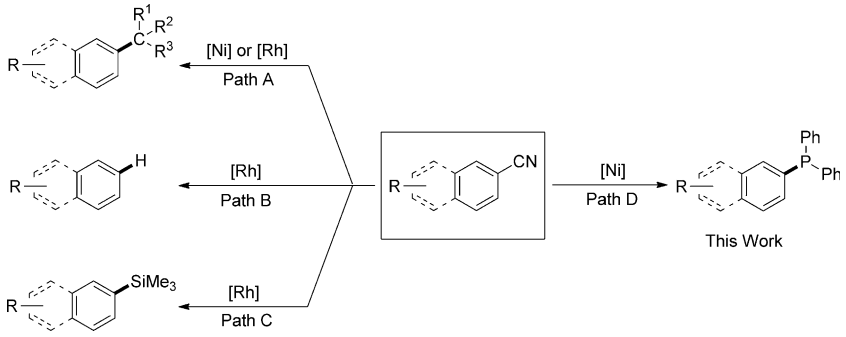
Selective C–C σ-bond activation (cleavage) by transition-metal complexes is one of the most challenging subjects in organometallic chemistry. This is due not only to its fundamental scientific interest, but also its potential utility in organic synthesis.[1] In general, this transformation depends heavily on either the release of ring strain or aromatization to provide the substantial driving force and thus lacks generality.[2] As an exception, C–CN σ-bond cleavage has gained significant attention due to the kinetically favorable interaction of metals with a cyano group through η^1- or η^2-coordination[3] and the resultant highly stable metal–CN bond as a thermodynamic driving force.[4] To date, C–CN cleavage has mainly focused on C–C bond formation by carbocyanation of alkynes and olefins,[5] cross-coupling with metal reagents (Scheme 1, Path A).[6] In addition, Chatani and co-workers



Scheme 1. Various C–X bond formations by C–CN cleavage.

respectively reported rhodium-catalyzed reductive decyanation (Scheme 1, Path B)[7] and silylation (Scheme 1, Path C);[8] however, examples of metal-mediated C–P bond formation has yet to be reported. Although a manifold of methods for the formation of C–P bonds has been established, generally only highly reactive aryl halides (such as I or Br) or triflates can be used as coupling partners or specific and expensive ligands are required to facilitate the high reactivities.[9] Inspired by these important studies of C–CN bond cleavage and our recent report of copper-catalyzed C–P coupling through decarboxylation,[10] we have explored the phosphination of aryl nitriles through C–CN bond activation. Here, we disclose the first example of Ni^{II}-catalyzed C–P coupling by C–CN bond cleavage for the synthesis of a variety of phosphorus ligands (Scheme 1, Path D). As a practical alternative, this methodology exhibits several very attractive features: 1) aryl nitriles are cheap, stable, and readily available in various structures; 2) the cyano group ensures the regioselectivity of the reaction; 3) namely the simple setup, mild conditions, and attractive scale-up possibilities.

In an initial study, we chose 2-cyanonaphthalene **1a** and Me_3SiPPh_2 as the model substrates to begin our investigation. Because monophosphorus or P, N bidentate ligands are key to many metal-catalyzed organic transformations, including many chiral reactions.[11] On the other hand, the pioneering reports of Bergman, Brookhart, and Chatani have shown that the silicon can assist in cleavage of the C–CN bond through a silyl–rhodium complex.[8,12] We started to test with various rhodium catalysts [{RhCl(cod)}$_2$], [Rh{$(C_6H_5)_3P$}$_3$]Cl, [Rh(cod)$_2$]BF_4, and [{Rh(OMe)(cod)}$_2$] in dioxane at 120 °C. Disappointingly, the results indicated that the rhodium catalysts were completely ineffective in this reaction. After further screening of catalysts we transferred to nickel catalysts, which are commonly used to activate C–CN bonds in different carbocyanation or cross-coupling reactions of aryl cyanides.[5,6] After extensive experimentation, we found that the use of [$NiCl_2(PPh_3)_2$] and [$NiCl_2(PCy_3)_2$] as a catalyst, *t*BuOK as the base and CuF_2 as the additive was critical for obtaining the desired aromatic diphenylphosphine in 91 and 95% yields, respectively (Table 1, entries 2 and 3). Encouraged by this result we chose the more stable and cheap [$NiCl_2(PPh_3)_2$] as the catalyst and evaluated a variety of bases and additives for their potential in this transformation. The results indicated that the base plays a crucial role in this reaction system; *t*BuONa and CH_3ONa were also promising, affording **2a** in 62 and 55% yields (Table 1, entries 4 and 6). Other bases such as K_3PO_4, Cs_2CO_3 were ineffective (Table 1, entries 5 and 7). A

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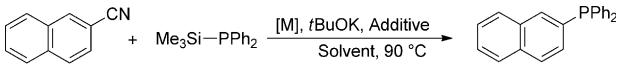
Table 1. C–CN cleavage under different conditions.[a]



1a 1b 2a

Entry	[M]	[mol %]	Base	[equiv]	Additives	[equiv]	Solvent	Yield [%][b]
1	$[Ni(cod)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	dioxane	N.R.
2	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	dioxane	91
3	$[NiCl_2(PCy_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	dioxane	95
4	$[NiCl_2(PPh_3)_2]$	10	*t*BuONa	2.0	CuF_2	2.0	dioxane	62
5	$[NiCl_2(PPh_3)_2]$	10	K_3PO_4	2.0	CuF_2	2.0	dioxane	N.R.
6	$[NiCl_2(PPh_3)_2]$	10	CH_3ONa	2.0	CuF_2	2.0	dioxane	55
7	$[NiCl_2(PPh_3)_2]$	10	Cs_2CO_3	2.0	CuF_2	2.0	dioxane	N.R.
8	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	toluene	51
9	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	DMF	33
10	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	THF	17
11	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CuF_2	2.0	NMP	15
12	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	NaF	2.0	dioxane	64
13	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	AgF	2.0	dioxane	29
14	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0	CsF	3.0	dioxane	73
15	$[NiCl_2(PPh_3)_2]$	10	*t*BuOK	2.0			Dioxane	92
16	$[NiCl_2(PPh_3)_2]$	10					dioxane	<5
17	$[NiCl_2(PPh_3)_2]$	5	*t*BuOK	2.0			dioxane	92
18	$[NiCl_2(PPh_3)_2]$	3	*t*BuOK	2.0			Dioxane	90
19	$[NiCl_2(PPh_3)_2]$	2	*t*BuOK	2.0			dioxane	70
20	$[NiCl_2(PPh_3)_2]$	3	*t*BuOK	1.5			dioxane	91
21	$[NiCl_2(PPh_3)_2]$	3	*t*BuOK	1.0			dioxane	63

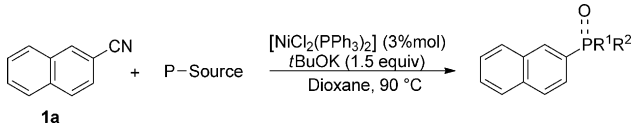
[a] All the reactions were carried out in the presence of **1a** (1.0 mmol) in of different solvents (5 mL) at 90°C. [b] Yield of isolated product. N.R. = no reaction.

screening of different fluoride salts showed that the choice is redundant. Based on prior knowledge, we believe that the fluoride anion can activate the C–Si bond by capturing the silyl group.[13] The solvent employed proved to be an important factor in the efficiency of the reaction. Among the solvents examined, dioxane was the best choice (Table 1, entry 8–11). Decreasing the amount of $[NiCl_2(PPh_3)_2]$ is worthwhile; a loading of only 3% catalyzed the reaction to afford **2a** in 90% yield without a distinct change in reactivity (Table 1, entry 18). The survey of *t*BuOK showed that 1.5 equivalents is the best choice and **2a** was obtained in 91% yield (Table 1, entry 20).

Under the optimized reaction conditions (Table 1, entry 20), various phosphate sources were surveyed using 2-cyanonaphthalene **1a** (Table 2). The $PhMeP–SiMe_3$ source worked well; the reaction proceeded smoothly and the corresponding phenylmethylphosphine product was obtained in 62% yield (Table 2, entries 1). In addition, Ph_2PK, Ph_2PH, MePhPOH, and Ph_2POH also worked well with moderate to high yields (Table 2, entries 5 and 8–10). On the other hand, all the phosphate chloride reagents tested were not effective in this reaction including diphenylphosphate acid.

We next examined the scope of different aromatic cyano compounds (Table 3). With naphthonitriles and benzonitriles (Table 3, entries **1a–1h**), the corresponding aromatic phosphine products were produced with moderate to good yields. Steric hindrance is very evident in these reactions: The use of 2-methylbenzonitrile (**1f**) and 2,4,6-trimethylbenzonitrile (**1g**) as substrates produced their desired products in 43% and trace yields. In addition, an electronic effect is also observed in this transformation. When the cyano group was introduced onto a pyridine ring, lower yields were obtained (47 and 40%, Table 3, entries **1j–1k**). Other electron-rich heterocyclic compounds such as 2-caynoindole, 2-phenylpyridine and caynobenzo[h]-quinoline worked very well in these reactions (Table 3, entries **1i** and **1l–1m**). For 2-tetrazolylbenzonitrile (**1n**), the corresponding product was obtained in 67% yield.

Table 2. C–P coupling with different phosphate sources.[a,b]



1a

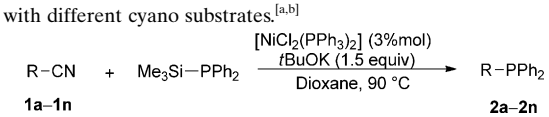
Entry	P Source	Yield [%][b]	Entry	P Source	Yield [%][b]
1	$Me_3Si–PMePh$	62	6	Ph_2PO_3OH	N.R.
2	Ph_2POCl	N.R.	7	MePhPOCl	N.R.
3	iPr_2PCl	N.R.	8	MePhPOH	67[c]
4	Ph_2PCl	N.R.	9	Ph_2PH	44
5	Ph_2PK	89	10	Ph_2POH	40

[a] All reactions were carried out under the optimal conditions reported in the text for 10 h. [b] Yields of isolated products. [c] Base is NaH.

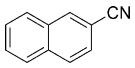
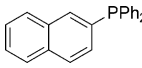
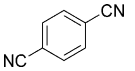
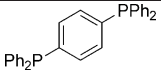
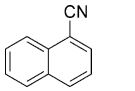
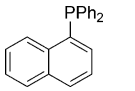
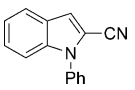
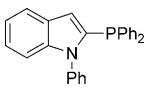
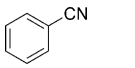
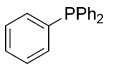
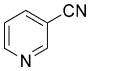
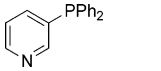
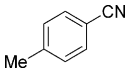
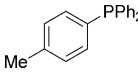
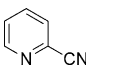
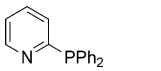
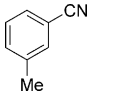
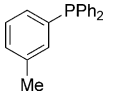
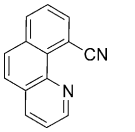
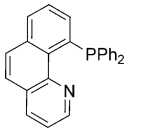
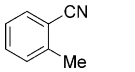
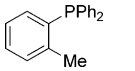
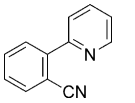
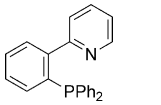
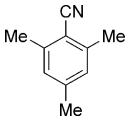
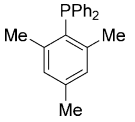
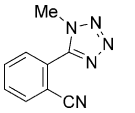
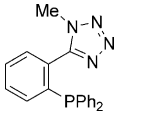
Chiral monophosphines have been demonstrated to be highly efficient ligands for transition-metal-catalyzed organic transformations, especially in reactions in which chelating bisphosphine ligands cannot be used.[14] Therefore, we aimed to extend this methodology to the synthesis of chiral monophosphorus ligands. With this in mind, we chose 2-cyanonaphthalene **1a** as a substrate to react with the chiral regents of (*S*)-phenylmethyl phosphine oxide under identical reaction conditions, but the racemic of **2aa** was obtained. Using chiral (*R*)-BINAP nickel dichloride as a catalyst proved to be effective and the chiral monophosphorus ligand (*R*)-**2aa** was afforded in 62% yield and the *ee* value can be preserved very well (Scheme 2). If the catalyst was changed to (*S*)-BINAP nickel dichloride, the reaction does not work. These results showed that the chiral matching is very crucial for the chiral transfer in this process (Scheme 2).

To the best of our knowledge, reactions involving nickel catalyzed C–P bond formation by C–CN bond cleavage have two typical pathways. One route is the same as the Pd-catalyzed phosphination of aryl halides[15] and the Ni^{II}-cata-

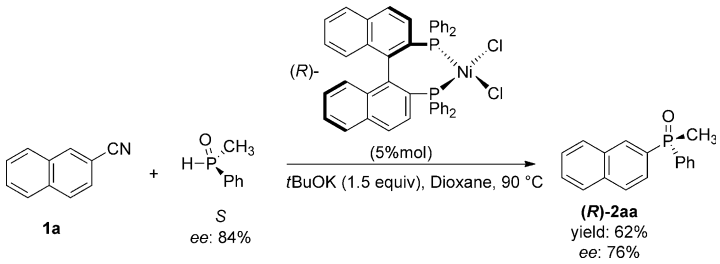
Table 3. C–P coupling with different cyano substrates.[a,b]



1a–1n 2a–2n

Entry	R–CN	Products	Yield [%][b]	Entry	R–CN	Products	Yield [%][b]
1a			91	**1h**			67
1b			77	**1i**			83
1c			99	**1j**			47
1d			80	**1k**			40
1e			66	**1l**			78
1f			43[c]	**1m**			81
1g			trace	**1n**			67

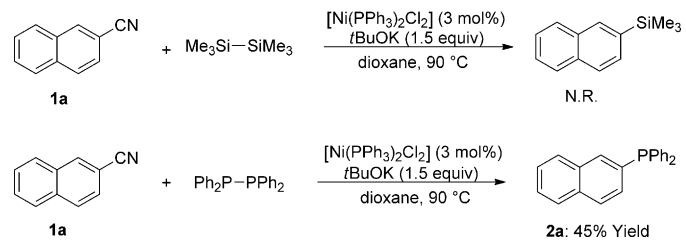
[a] All reactions were carried out under the optimal conditions reported in the text for 10 h. [b] Yields of isolated products. [c] Yield determined by ^{1}H NMR spectroscopy.



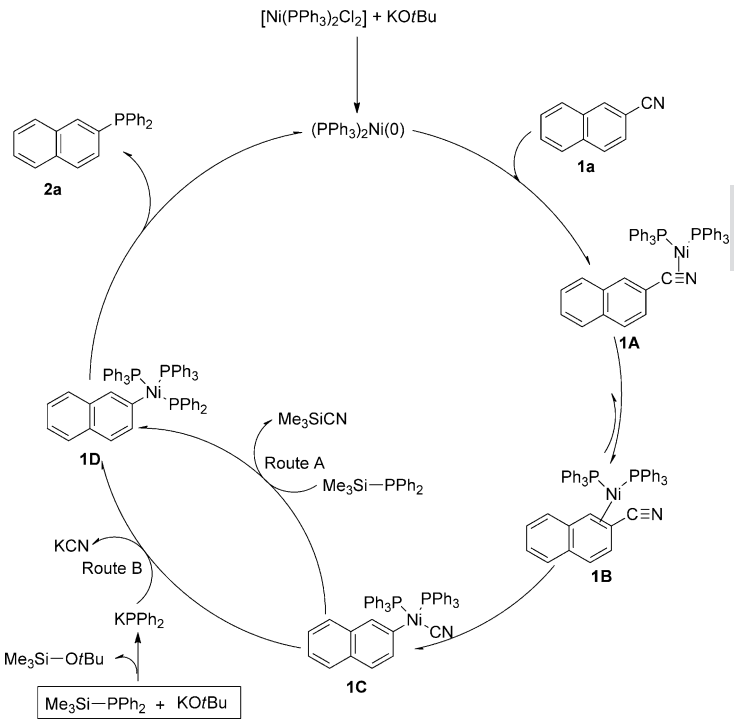
Scheme 2. Chiral phosphorus ligand synthesis by C–CN cleavage.

lyzed cross-coupling of aryl nitriles with aforementioned metal reagents. Firstly, the Ni^{II} is reduced to Ni^0 under the basic conditions, then the key step of oxidative addition occurred; the Ni^0 coordination with the cyano group. William and co-workers' studies shown that the η^2-arene complex with nickel coordinated to C=C double bond next to the cyano substituent is the crucial intermediate leading to oxidative addition in this transformation.[16] Another proposed mechanism involves a silicon-assisted catalytic cleavage of the C–CN bond.[8,17] Similar to the previous reports of rhodium-catalyzed silylation, it would involve the formation of a silylnickel species, coordination of the cyano group to form an η^2-iminoacyl nickel complex, and finally C–P bond formation followed by deinsertion of silyl isocyanide. To obtain more information about the mechanistic pathway and clarify the role of the silyl group in our transformation, two contrary reactions were carried out under identical reaction conditions. When Me_3SiPPh_2 was changed to hexamethyldisilane (Scheme 3, reaction 1), no reaction was observed. However, when Me_3SiPPh_2 was changed to tetraphenyldiphosphine (Scheme 3, reaction 2), the reaction proceeded smoothly and the desired product **2a** was obtained in 45% yield. Based on these results, we believe the mechanistic pathway involving silicon-assisted catalytic cleavage of the C–CN bond can be excluded.

On the basis of the observed experimental results, we believe that a plausible mechanistic pathway for the formation of the C–P bond by C–CN cleavage is outlined in Scheme 4. Similar to the Ni^{II}-catalyzed cross-coupling of aryl nitriles with Grignard regents and organozinc regents, $[NiCl_2(PPh_3)_2]$ is first reduced to Ni^0 under the basic conditions followed by Ni^0 coordination with the cyano group to produce an η^2-C, N nitrile adduct **1A** and make the cyano group less nucleophilic, which makes the migratory insertion step more favorable. Then, **1A** immediately converts into the η^2-arene complex **1B** with nickel coordinated to the C=C double bond next to the cyano substituent to form the oxidative addition intermediate **1C**. Following this, the ligand exchange has two possible routes: in route A (Scheme 4), Me_3SiPPh_2 directly participates in the ligand exchange and the cyano group is replaced by the diphenylphosphorus group to afford complex **1D** and Me_3SiCN simultaneously. Finally, the desired product is obtained by reductive elimination, re-



Scheme 3. The role of the silyl group investigation of C–P bond formation.



Scheme 4. Proposed mechanism of Ni-catalyzed C–P coupling by C–CN cleavage.

leasing the metal center to reinitiate the catalytic cycle. On the other hand, the Me_3SiPPh_2 could react with potassium *tert*-butoxide to form ionic $KPPh_2$ salt with a silyl *tert*-butoxy species (route B, Scheme 4), and then $KPPh_2$ undergoes ligand exchange with the nickel complex **1C** to afford complex **1D** equally. Although at this point no rigorous mechanistic studies have been conducted, this hypothesis does not affect the final results.

In summary, we have developed a highly efficient protocol for the preparation of various diphenylphosphoryl ligands through nickel-catalyzed C–CN bond cleavage. The availability of the substrates and the remarkable scope observed make this method attractive to synthetic chemists. Further applications of this approach to the synthesis of chiral ligands are ongoing in our laboratory.

Experimental Section

Representative procedure: (Table 3, entry 1a). An oven-dried 10 mL screw-capped vial was charged with $[NiCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol, 3 mol%), *t*BuOK (168 mg, 1.5 mmol, 1.5 equiv), and 2-naphthonitrile (153 mg, 1.0 mmol, 1.0 equiv) under a gentle stream of argon. After Me_3SiPPh_2 (516 mg, 2.0 mmol, 2.0 equiv) and 1, 4-dioxane (5 mL) were added to the vial by a syringe. The vessel was heated in an oil bath at 90 °C for 10 h followed by cooling. The contents were subjected to flash chromatography to give naphthalen-2-yldiphenylphosphine (91%) as a white solid. The purified material was dried under an oil-pump vacuum.

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