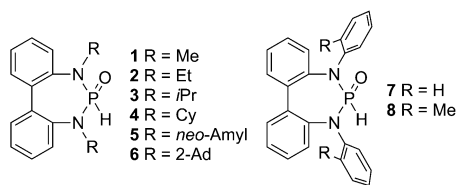


Biphenyl-Based Diaminophosphine Oxides as Air-Stable Preligands for the Nickel-Catalyzed Kumada–Tamao–Corriu Coupling of Deactivated Aryl Chlorides, Fluorides, and Tosylates

Zhong Jin,^{*,[a]} Yan-Jing Li,^[a] Yong-Qiang Ma,^[b] Ling-Ling Qiu,^[a] and Jian-Xin Fang^{*,[a]}

Transition-metal-catalyzed cross-coupling reactions^[1] of aryl halides or pseudo-halides with organometallic reagents, such as Grignard reagents, organozinc compounds, boronic acids, organostannanes, and organosiloxanes, are powerful tools for the synthesis of the biaryl motif, which is prevalent in natural products, pharmaceuticals, chiral ligands, liquid crystals, and macromolecular polymers. Over the last decade, transition-metal-catalyzed cross-coupling with aryl chlorides^[2] has been elegantly achieved by using well-designed ligands, such as bulky electron-rich tertiary phosphines,^[3] N-heterocyclic carbenes (NHCs),^[4] secondary phosphine oxides (SPOs),^[5] and so on. Relative to the C–Cl bonds, the C–F bonds are more stable and thus inert. To date, only a few protocols are known for cross-coupling with electronically deactivated aryl fluorides.^[6,7] Despite the rather expensive cost, using aryl fluorides as coupling partners contributes to the fundamental conception of the reactivity of the very stable bonds and is, therefore, of great importance in organometallic chemistry. Herein, we report a new class of readily accessible, air-stable SPOs derived from 1,1'-biphenyl-2,2'-diamine (Scheme 1), which show high reactivity in the nickel-catalyzed cross-coupling of electronically deactivated aryl chlorides and fluorides at room tem-



Scheme 1. Structures of secondary phosphine oxides (SPOs).

[a] Prof. Dr. Z. Jin, Y.-J. Li, L.-L. Qiu, Prof. J.-X. Fang
State Key Laboratory and Institute of Elemento-organic Chemistry
Nankai University
Tianjin 300071 (P.R. China)
E-mail: zjin@nankai.edu.cn
fjx@nankai.edu.cn

[b] Prof. Dr. Y.-Q. Ma
Department of Applied Chemistry
China Agricultural University
Beijing 100193 (P.R. China)

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perature. Recently, great progress in transition-metal-mediated cross-coupling reactions using the commonly unreactive aryl/alkenyl sulfonylates,^[8a,d] carbamates,^[9] carboxylates,^[10] phenolates,^[11] and so on, as the coupling substrates has been made. The present SPO ligands are also found to be very effective on activation of the unreactive C–O bonds in the aryl tosylates.^[12]

The reactivity of the complexes generated in situ from these diaminophosphine oxides in the nickel-catalyzed Kumada cross-coupling reaction significantly relates to the substituted manner on the heteroatom adjacent to phosphorus atom (Table 1). With diaminophosphine oxides **1**, **2**, and **3** as a preligand, although conversion ratios of aryl chloride were obviously improved relative to a control experiment (entry 1, Table 1), up to 15% of the homocoupling products 4,4'-dimethoxybiphenyl were observed except the desired cross-coupling products (entries 2–4, Table 1). On the contrary, when the sterically congested diaminophosphine

Table 1. Nickel-catalyzed Kumada coupling of 4-chloroanisole and PhMgBr.^[a]

Entry	SPO ligand	[Ni]	Solvent	Conv. [%] ^[b]
1	–	Ni(acac) ₂	THF	44 (21) ^[c]
2	1	Ni(acac) ₂	THF	55 (28)
3	2	Ni(acac) ₂	THF	54 (26)
4	3	Ni(acac) ₂	THF	67 (49)
5	4	Ni(acac) ₂	THF	93 (77)
6	5	Ni(acac) ₂	THF	90 (64)
7	6	Ni(acac) ₂	THF	100 (91)
8	7	Ni(acac) ₂	THF	88 (75)
9	8	Ni(acac) ₂	THF	91 (84)
10	6	Ni(acac) ₂	Et ₂ O	39 (20) ^[d]
11	6	Ni(acac) ₂	THF/Et ₂ O (2:1, v/v)	98 (89) ^[d]
12	6	Ni(acac) ₂	THF/DME (2:1, v/v)	57 (33)
13	6	NiCl ₂ ·6H ₂ O	THF	100 (90) ^[e]
14	6	NiCl ₂	THF	98 (87)
15	6	Ni(OAc) ₂ ·4H ₂ O	THF	92 (79) ^[e]
16	6	NiCO ₃ ·H ₂ O	THF	21 (–) ^[e,f]
17	6	Ni(acac) ₂	THF	98 (89) ^[g]

[a] Reaction conditions: 4-chloroanisole (1 mmol), PhMgBr (1.5 mmol, 1.0 mol L⁻¹ in THF), [Ni] (3 mol %), SPO ligand (3 mol %), solvent volume (3 mL), 20 h, RT (ca. 25 °C). [b] GC analysis data with *n*-dodecane as an internal standard, isolated product yields are reported in the parentheses. [c] Without diaminophosphine oxide. [d] PhMgBr in Et₂O (1.5 mol L⁻¹) was used. [e] PhMgBr (2.0 mmol) in THF was used. [f] No coupling products were isolated. [g] 6 mol % **6** was used.

oxides **4**, **5**, and **6** were used (entries 5–7, Table 1), the homocoupling side reactions were greatly suppressed. Amongst them, preligand **6** gave rise to an almost quantitative conversion and no homocoupling products were identified (entry 7, Table 1). In addition, *N,N'*-diaryl substituted diaminophosphine oxides **7** and **8** were also found to be effective ligands in the catalytic procedure (entries 8 and 9, Table 1). The effects of solvent on the coupling reactions were rather important; tetrahydrofuran proved to be the choice of solvent, whereas ethyl ether and 1,2-dimethoxyethane (DME) caused an incomplete conversion (entries 10–12, Table 1). Further investigation revealed that the forms of the nickel salts were less pronounced, and hexahydrate and anhydrous nickel(II) chlorides afforded an equal catalytic performance to that of Ni(acac)₂ (entries 13 and 14, Table 1), whereas the low reactivity of NiCO₃·H₂O might

result from its insolubility in THF (entry 16, Table 1). Notably, a 2:1 ratio of **6**/Ni did not provide an obviously better conversion (entry 17, Table 1), which suggested a highly active monophosphine-coordinated nickel species was probably dominant in the catalytic process.^[13]

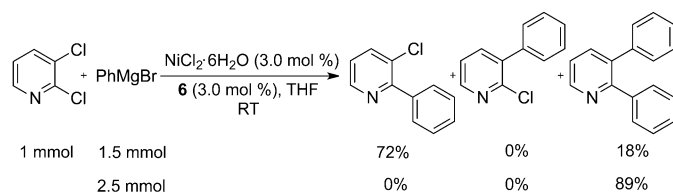
A variety of electron-rich aryl chlorides and heteroaryl chlorides were capable of coupling with Grignard reagents at ambient temperature (entries 1–13, Table 2). Except for aryl chlorides, electronically deactivated aryl fluorides could be also coupled at room temperature using the present catalytic protocol (entries 14–20, Table 2). For polychloro- and polyfluoroarenes, polysubstituted benzenes were obtained in excellent yields by using an excess of a Grignard reagent (entries 10, 11, 18, and 20, Table 2). 3-Fluorobiphenyl was selectively produced from 1,3-difluorobenzene by using the stoichiometrical PhMgBr (entry 19, Table 2). It is noteworthy

Table 2. Nickel-catalyzed cross-coupling of aryl chlorides or fluorides with ArMgBr.^[a]

$\begin{array}{c} \text{Ar-X} \\ \text{or} \\ (\text{het})\text{Ar-X} \end{array} + \text{Ar}'\text{-MgBr} \xrightarrow[\text{RT, 20 h}]{\text{NiCl}_2 \cdot 6\text{H}_2\text{O}/\mathbf{6}, \text{THF}} \begin{array}{c} \text{Ar-Ar}' \\ \text{or} \\ (\text{het})\text{Ar-Ar}' \end{array}$							
Entry	ArCl/ArF	Product	Yield [%] ^[b]	Entry	ArCl/ArF	Product	Yield [%] ^[b]
1			91	11			88 ^[c]
2			89	12			86 ^[d]
3			85	13			83 ^[d]
4			92	14			87
5			87	15			89
6			93	16			88
7			94	17			85
8			84	18			92 ^[c]
9			85	19			76 ^[c]
10			97 ^[c]	20			90 ^[c]

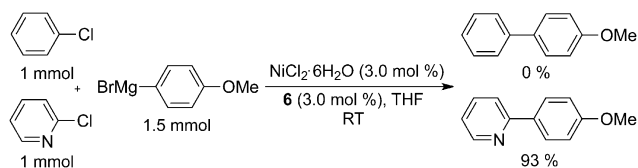
[a] Reaction conditions: ArCl or ArF (1 mmol), Grignard reagent (1.5 mmol in THF), NiCl₂·6H₂O (3 mol %), SPO ligand **6** (3 mol %), THF (3 mL), RT, 20 h. Reaction time not optimized. [b] Isolated product yield on the average of two runs. [c] Grignard reagent (2.5 mmol) was used. [d] Ni(acac)₂ (3 mol %) was used. [e] *m*-Terphenyl (15%) was isolated.

thy that the 2- and 3-chloro in the pyridine ring exhibited obviously different reactivity and the coupling preferred to take place regioselectively at the 2-position of pyridine ring (Scheme 2). Furthermore, relative to chlorobenzene, 2-chloro-



Scheme 2. Regioselective cross-coupling of 2,3-dichloropyridine with PhMgBr.

pyridine is more reactive. Thereby, 2-chloropyridine could be chemoselectively coupled with 4-methoxyphenyl magnesium bromide in the presence of chlorobenzene (Scheme 3). Syntheses of sterically hindered *ortho*-substituted biaryls continue to constitute a significant challenge in transition-metal-catalyzed cross-coupling reactions.^[14] The present catalytic protocol was found very effective in the formation of di- and tri-*ortho*-substituted biaryls (entries 8, 9, 12, and 13, Table 2). However, due to the considerable strong repulsion, the coupling to the most challenging tetra-*ortho*-substituted biaryls was less efficient.



Scheme 3. Chemoselective cross-coupling of 2-chloropyridine and chlorobenzene.

The nickel catalyst derived from diaminophosphine oxide **6** also proved applicable to electronically deactivated aryl tosylates (Table 3, entries 1–10). For aryl triflates, coupling reactions could be performed even at ambient temperature or lower. The versatile catalytic potential of the Ni/**6** complex makes it a powerful tool for synthesis of unsymmetric *o*-, *m*- and *p*-terphenyls, which are often exploited in the design of organic electroluminescent (OEL) devices^[15] and liquid crystalline materials^[16] (Scheme 4).

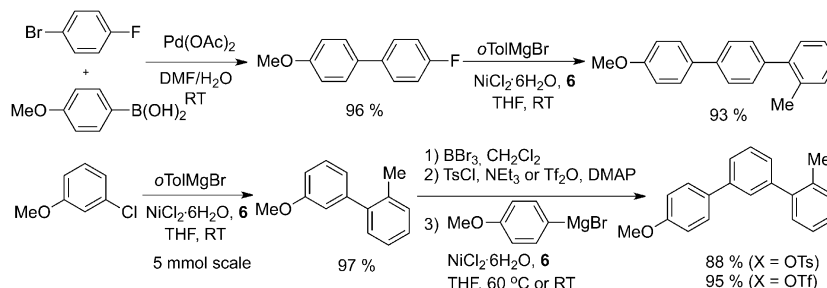
Analysis of the ¹H NMR spectra of compounds **1–6** suggests that two unequivalent *N*-alkyl substituents exist in solution, probably resulting from the chiral center on the phosphorus atom and two rigid *N*-alkyl groups. The diamino-

Table 3. Nickel-catalyzed cross-coupling of aryl tosylates with ArMgBr.^[a]

Entry	ArOTs	Product	Yield [%] ^[b]
1			89 (96) ^[c]
2			91
3			85
4			88 (94) ^[c]
5			90 (98) ^[c]
6			87
7			90
8			86
9			85
10			84 (92) ^[c]

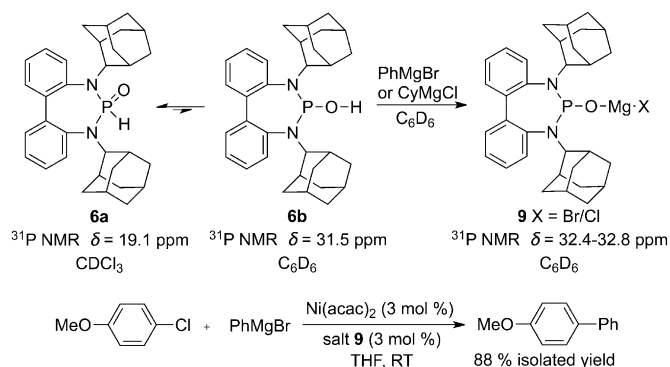
[a] Reaction conditions: aryl tosylate (1 mmol), Grignard reagent (1.5 mmol in THF), NiCl₂·6H₂O (3 mol%), ligand **6** (3 mol%), THF (3 mL), 60 °C, 20 h. For the corresponding aryl triflates, reactions were performed at ambient temperature (ca. 25 °C). Reaction time not optimized. [b] Isolated product yield on the average of two runs. [c] Yield with the corresponding triflate.

phine oxide **6** had different ³¹P chemical shifts in CDCl₃ (δ = 19.1 ppm) and C₆D₆ (δ = 31.5 ppm), which were probably related to two tautomers. The P–O–Mg halide salt **9** derived from diaminophosphine oxide **6** and Grignard reagents, which were probably actual ligand, showed high catalytic activity in the nickel-mediated cross-coupling of aryl



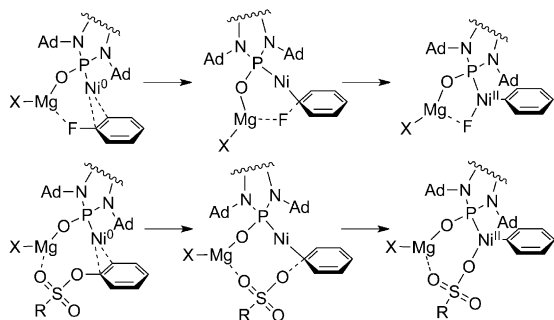
Scheme 4. Combined cross-coupling strategies for synthesis of unsymmetric *m*- and *p*-terphenyls.

chloride (Scheme 5). As a consequence, a cooperative Ni/Mg bimetallic action mode^[6a,17] was suggested for explanation of the easy activation of the C–F and C–O bonds by



Scheme 5. Nickel-catalyzed cross-coupling using the P–O–Mg salt as ligand.

the present diaminophosphine oxide system (Scheme 6). The two bulky adamantyl groups in **6** were not only beneficial to the reductive elimination step in the catalytic cycle, but also accelerated the ligand-exchange process from the coupling product to the haloarene as the first irreversible step in the nickel-catalyzed cross-coupling reactions,^[18] which greatly improve the turnover efficiency.



Scheme 6. Cooperative action modes of oxidative addition toward the C–F and C–O bonds.

In summary, we have developed a new class of air-stable diaminophosphine oxides from the commercially available 1,1'-biphenyl-2,2'-diamine. The nickel complex of the sterically encumbered diaminophosphine oxide **6** exhibited superior reactivity in the cross-coupling of electronically deactivated aryl chlorides, fluorides, and tosylates with Grignard reagents. As far as we know, the catalytic system that is simultaneously effective for the activation of the C–Cl, C–F, and C–O bonds is rare.^[19] The present catalytic protocol also provides convenient access to sterically crowded di- and tri-*ortho*-substituted biaryls as well as unsymmetric *o*-, *m*- and *p*-terphenyls. Further applications of this type of air-stable diaminophosphine oxides for catalysis, as well as development of the corresponding chiral 1,1'-binaphthyl-2,2'-

diamine (BINAM)-derived diaminophosphine oxides for asymmetric cross-coupling,^[20] are currently under investigation.

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Keywords: aryl fluoride • aryl tosylate • cross-coupling • diaminophosphine oxide • nickel

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