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Efficient Nickel-catalyzed Phosphinylation of C-S Bonds Forming C-P Bonds

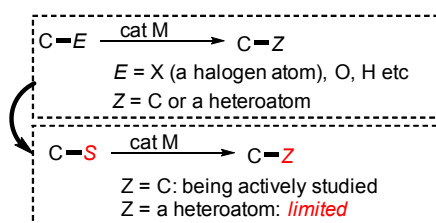
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Accepted 00th January 20xxJia Yang,^a Jing Xiao,^a Tieqiao Chen,^{*a} Shuang-Feng Yin,^{*a} and Li-Biao Han,^{*b}

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The first nickel-catalyzed phosphinylation of C-S bonds forming C-P bonds is developed. This transformation can proceed readily with the simple Ni(cod)₂ at a loading down to 0.1 mol% at 10 mmol scale. A variety of aryl sulfur compounds, i.e. sulfides, sulfoxides and sulfones all coupled with P(O)-H compounds to produce the corresponding organophosphorus compounds in high yields, which provides an efficient new method for C-P bonds construction.

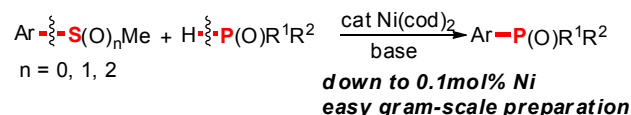
The transition metal-catalyzed transformation of a C-E bond to a different C-Z bond is a fundamental process in organic synthesis (Scheme 1). Halogen compounds have been most frequently used in this process. Recently, transformations of C-O bonds and C-H bonds are also attracting great attention.^{1,2}



Scheme 1. Transition metal-catalyzed transformation of a C-E bond to a different C-Z bond.

Sulphur is an abundant and naturally occurring element. Organosulfur compounds are widely present in nature products as well as in petroleum. Therefore, sulfur compounds could serve as a cheap chemical feedstock in the above mentioned transformation because of their ready accessibility. However, such a metal-catalyzed C-S transformation has met

with only a limited success (Scheme 1).^{3,4} Partly because of the poisoning property of a sulfur compound to the metal catalyst, the TON is usually low and a relatively large amount of the catalyst is required in order to get a good yield. Takei and Wenkert reported the NiCl₂(PPh₃)₂-catalyzed coupling of organosulfides with Grignard reagents generating new C-C bonds.⁵ Later, a palladium-catalyzed version was developed and organozincs could also be used as the coupling counterpart.⁶ On the other hand, transformation of a C-S bond to a C-heteroatom bond was limited.⁷ Yorimitsu and Murakami reported a novel palladium-catalyzed amination of arylsulfides with anilines.⁷ However, the reaction requires both a special Pd-N-heterocyclic carbene catalyst (2.5 mol%) and over-stoichiometric amount of a very strong base KHMDS (a weaker base such as KOH and KOBu-t was not effective).



Scheme 2. The first efficient Ni-catalyzed C-S bond transformation generating organophosphorus compounds.

Herein, we communicate an efficient nickel-catalyzed transformation of C-S bonds to C-P bonds (Scheme 2). Thus, in the presence of a tiny amount of a simple Ni catalyst, a variety of organosulfur compounds can be efficiently transformed to the corresponding highly valuable organophosphorus compounds in high yields. No phosphine or other ligands are required for the reaction since a simple Ni(cod)₂ or even NiCl₂ is enough. In addition, this reaction can take place efficiently with a catalytic loading down to 0.1 mol%, and a gram-scale preparation of the phosphorus compounds is easily conducted. The present reaction represents a rare example of highly efficient catalytic C-S bond transformations where a large amount of catalysts is usually required.^{3,8}

As shown in Table 1, a mixture of thioanisole **1a** (0.4 mmol), diphenylphosphine oxide (0.4 mmol) and *t*-BuONa (0.6 mmol) in dioxane (1.0 mL) was heated at 100 °C overnight. The reaction mixture was analyzed by GC chromatography. As

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COMMUNICATION

Journal Name

expected, in the absence of metal catalyst, the coupling product could not be detected at all (run 1). Palladium or rhodium catalysts selected were not effective (runs 2 and 3).

Table 1. Nickel-catalyzed phosphinylation of thioanisole **1a** with diphenylphosphine oxide **2a**^a

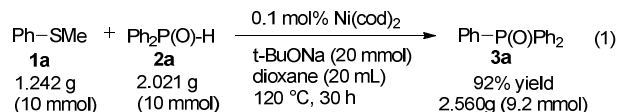
Ph-SMe + Ph ₂ P(O)-H		cat Ni(cod) ₂ base, solvent		Ph-P(O)Ph ₂
1a	2a			3a
Run	Cat M	Base	Solvent	Yield ^b
1	-	<i>t</i> -BuONa	dioxane	n.d.
2 ^c	Pd ₂ (dba) ₃	<i>t</i> -BuONa	dioxane	trace
3 ^c	(Rh(OAc) ₂) ₂	<i>t</i> -BuONa	dioxane	n.d.
4 ^c	Rh(PPh ₃) ₂ (CO)Cl	<i>t</i> -BuONa	dioxane	trace
5	Ni(cod) ₂ /dppp	<i>t</i> -BuONa	dioxane	88%
6	Ni(cod) ₂	<i>t</i> -BuONa	dioxane	82%
7	NiCl ₂	<i>t</i> -BuONa	dioxane	65%
8	Ni(cod) ₂	<i>t</i> -BuOK	dioxane	73%
9	Ni(cod) ₂	Cs ₂ CO ₃	dioxane	trace
10	Ni(cod) ₂	K ₂ CO ₃	dioxane	trace
11	Ni(cod) ₂	Et ₃ N	dioxane	trace
12	Ni(cod) ₂	<i>t</i> -BuONa	hexane	84%
13	Ni(cod) ₂	<i>t</i> -BuONa	DMF	63%
14 ^c	Ni(cod) ₂	<i>t</i> -BuONa	dioxane	91%
15 ^d	Ni(cod) ₂	<i>t</i> -BuONa	dioxane	94%
16 ^e	Ni(cod) ₂	<i>t</i> -BuONa	dioxane	88%
17 ^f	Ni(cod) ₂	<i>t</i> -BuONa	dioxane	7%

^a Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), 5 mol% metal catalyst, a base (0.6 mmol), solvent (1.0 mL), 100 °C, 18 h. ^b GC yield using tridecane as an internal standard. ^c 2.5 mol% metal catalyst (based on metal). ^d 1.25 mol% metal catalyst (based on metal). ^e 0.5 mol% metal catalyst (based on metal). ^f 80 °C.

By adding Ni(cod)₂ (5 mol%) and a phosphine ligand dppp (Ph₂P(CH₂)₃PPh₂, 5 mol%), the coupling reaction took place readily to give the coupling product **3a** in 88% yield (run 5). Surprisingly, it was soon realized that, unlike other Ni-mediated C-S bond transformations, a phosphine ligand was not necessary for the current coupling reaction. Thus, in the absence of dppp, by simply adding Ni(cod)₂ alone to the mixture, the coupling product **3a** was obtained in 82% yield (run 6). More surprisingly, even a common nickel salt, NiCl₂ could catalyze this coupling well to give **3a** in 65% yield (run 7). As to the base, *t*-BuOK was also effective (run 8), however, Cs₂CO₃, K₂CO₃ and Et₃N (runs 9–11) only gave a trace amount of the coupling product. As to the solvent, the reaction also took place in hexane and DMF (runs 12 and 13). Remarkably, the reaction was operable at a lower loading of the nickel catalyst. Thus, 91% yield of **3a** was produced with 2.5 mol% Ni(cod)₂ (run 14), and 94% yield of **3a** was produced with 1.25 mol% Ni(cod)₂ (run 15). When the catalyst loading was further decreased to 0.5 mol%, 88% yield of **3a** was obtained (run 16).⁹ However, the reaction only progressed sluggishly at 80 °C and gave 7% yield of **3a** (run 17).

With the above optimization results in hands, a gram-scale reaction was conducted (eqn 1). Thus, an equivalent of

PhSMe (10 mmol) and Ph₂P(O)H (10 mmol) in dioxane (20 mL) in the presence of *t*-BuONa (15 mmol) and Ni(cod)₂ (0.01 mmol) was heated at 120 °C for 30 h. The mixture was extracted with CH₂Cl₂. The crude product after removing the volatiles under a reduced pressure was passed through a short SiO₂ column using EtOAc as an eluent to give spectroscopically pure **3a** in 92% yield.



This nickel-catalyzed C-S/P(O)-H cross coupling was a rather general reaction. As shown in Table 2, various aryl methyl sulfides coupled with P(O)-H compounds to produce the corresponding products **3** in high yields. Thus, sulfides with electron-donating groups like methyl and methoxyl groups on benzene ring gave the expected coupling products in good yields (runs 2–4). 61% yield of **3e** was obtained from (4-phenyl)phenyl methyl sulfide **1e** (run 5). The substrate with an electron-withdrawing CF₃ group also coupled with diphenylphosphine oxide under the current conditions (run 6). Notably, a dicyclic and heterocyclic phosphine oxides were also efficiently produced via this nickel-catalyzed C-S/P(O)-H cross coupling (runs 7–9). Diphenyl sulfide was also applicable as a good substrate which coupled readily with diphenylphosphine oxide to produce **3a** in 94% yield (run 10). It was noted that both aromatic and aliphatic secondary phosphine oxides were applicable to this reaction. In addition to diphenylphosphine oxide, di(4-methylphenyl)phosphine oxide and *n*-Bu₂P(O)H both coupled with thioanisole readily under similar reaction conditions (runs 11 and 12). However, diisopropyl phosphonate did not give the corresponding product under the optimized reaction conditions (run 13).

This nickel-catalyzed phosphinylation also took place efficiently with sulfones. High yields of **3** were obtained from a variety of methyl aryl sulfones. Thus, methyl phenyl sulfones including those with methyl and methoxy groups on the benzene ring all gave the corresponding products in high yields (runs 14–16). The double bond and thiophenyl groups were tolerated under the reaction conditions (runs 18 and 19). Interestingly, the substrate **1n** bearing an electron-withdrawing CN group could couple with diphenylphosphine oxides in the absence of nickel catalyst to give the corresponding **3m** in 97% yield (run 17). Similarly, substrate bearing a pyrimidinyl group also gave the corresponding product in 72% yield without addition of Ni(cod)₂ (run 20). Aliphatic secondary phosphine oxides like *n*-Bu₂P(O)H and Cy₂P(O)H also served well under similar reaction conditions (runs 21 and 23); whereas the catalyst was necessary when *t*-BuPhP(O)H was loaded (run 22). Notably, H-phosphonate diisopropyl phosphite was also applicable to this reaction and could react with electron-deficient **1n** to produce the corresponding **3s** in 62% yield in the absence of the catalyst (run 24).

Ethyl phenyl sulfone **1r** and diphenyl sulfone **1s** also were phosphorylated efficiently with diphenylphosphine oxide,

affording **3a** in 97% and 98% yields, respectively (runs 25 and 26). Finally, a sulfoxide **1t** could also be used as the substrate

Table 2. Ni-catalyzed P-C bond formation via C-S bond cleavage^a

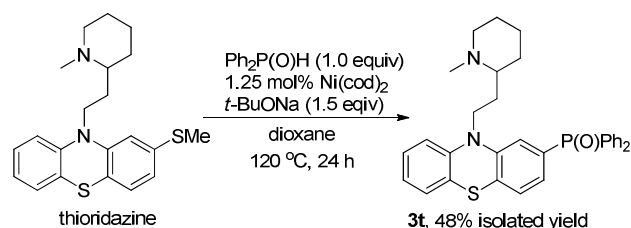
Run	Substrate 1	Substrate 2	Product 3 (isolated yield)
	1	2	3
1	1a , R = 4-H	Ph ₂ P(O)H	3a , R = 4-H, 91%
2	1b , R = 4-Me	Ph ₂ P(O)H	3b , R = 4-Me, 98%
3	1c , R = 4-MeO	Ph ₂ P(O)H	3c , R = 4-MeO, 65%
4	1d , R = 3-MeO	Ph ₂ P(O)H	3d , R = 3-MeO, 81%
5	1e , R = 4-Ph	Ph ₂ P(O)H	3e , R = 4-Ph, 61%
6	1f , R = 4-CF ₃	Ph ₂ P(O)H	3f , R = 4-CF ₃ , 30%
7	1g	Ph ₂ P(O)H	3g , 90%
8	1h	Ph ₂ P(O)H	3h , 70%
9	1i	Ph ₂ P(O)H	3i , 95%
10	1j	Ph ₂ P(O)H	3a , 94%
11	1a	(4-MeC ₆ H ₄) ₂ P(O)H	3j , [P] = (4-MePh) ₂ P(O), 84%
12 ^b		<i>n</i> -Bu ₂ P(O)H	3k , [P] = <i>n</i> -Bu ₂ P(O), 56%
13		(<i>i</i> -PrO) ₂ P(O)H	3l , [P] = (<i>i</i> -PrO) ₂ P, n.d.
14	1k , R = 4-H	Ph ₂ P(O)H	3a , R = 4-H, 91%
15	1l , R = 4-Me	Ph ₂ P(O)H	3b , R = 4-Me, 98%
16 ^c	1m , R = 4-MeO	Ph ₂ P(O)H	3c , R = 4-MeO, 81%
17 ^d	1n , R = 4-CN	Ph ₂ P(O)H	3m , R = 4-CN, 97%
18	1o	Ph ₂ P(O)H	3n , 53%
19 ^d	1p	Ph ₂ P(O)H	3o , 57%
20	1q	Ph ₂ P(O)H	3p , 72%
21 ^d	1k	<i>n</i> -Bu ₂ P(O)H	3k , [P] = <i>n</i> -Bu ₂ P(O), 96%
22 ^c		<i>t</i> -BuPhP(O)H	3q , [P] = <i>t</i> -BuPhP(O), 51%
23 ^{d,e}		Cy ₂ P(O)H	3r , [P] = Cy ₂ P(O), 63%
24 ^{d,f}	1n	(<i>i</i> -PrO) ₂ P(O)H	3s , [P] = (<i>i</i> -PrO) ₂ P, 62%
25	1r , R = Et	Ph ₂ P(O)H	3a , 97%
26	1s , R = Ph	Ph ₂ P(O)H	3a , 98%
27 ^c	1t	Ph ₂ P(O)H	3a , 38%

^a Reaction conditions: **1** (0.4 mmol), **2** (0.4 mmol), 1.25 mol% Ni(COD)₂, 0.6 mmol *t*-BuONa, dioxane (1.0 mL), 100 °C, 18 h; runs 14–24, 26–28: 1.1 equiv **1** was used.

^b *t*-BuOK was used, 110 °C, 24 h. ^c 120 °C. ^d In the absence of catalyst. ^e *t*-BuOK, 120 °C. ^f 2 equiv **2**, 2 equiv Cs₂CO₃, 110 °C, 24 h.

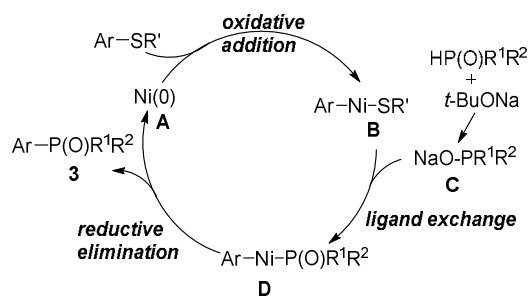
which reacted with diphenylphosphine oxide to give **3a** in 38% yield under similar reaction conditions (run 27).

It should be noted the novelty of the present catalytic reaction as a new method for C-P bond formation is also clear compared with similar known coupling reactions.^{10,11} For example, although a C-P bond can be constructed by metal-mediated couplings of P(O)H compounds with organic halides (Hirao's coupling)¹⁰ and phenoxide derivatives,^{11e} most of these reactions require a phosphine ligand and a relatively large amount of the catalyst. The recently reported nickel-mediated coupling of phenoxide derivatives typically used 10 mol% nickel catalyst and the currently expensive phosphine ligand Cy₂PCH₂CH₂PCy₂.^{11e}



Scheme 3. Modification of thioridazine via nickel-catalyzed C-S/P(O)-H cross coupling

As an application of the current method, this new cross coupling reaction can be used to modify a complex molecule. For example, thioridazine was an antipsychotic drug used in the treatment of schizophrenia and psychosis. By employing our new method, a phosphoryl group could be readily introduced to the structure of the medicine. Thus, by heating a mixture of thioridazine with Ph₂P(O)H under similar reaction conditions, **3t** was obtained in 48% yield via the cleavage of Ar-SMe bond, showing the potential of the current method for the modification of a complex molecule (Scheme 3).



Scheme 4. Proposed mechanism for the nickel-catalyzed phosphinylation of C-S bonds forming C-P bonds.

The mechanism is not fully understood. We propose a plausible catalytic cycle for the nickel-catalyzed C-S/P(O)-H cross coupling as shown in Scheme 4. Ni(0) complex **A** firstly oxidatively adds to C-S bond,¹² generating species **B**, followed by ligand exchange with P-ONa compounds **C** generated from the reaction of P(O)-H compounds with a base^{13,14} to give the intermediate **D**. Reductive elimination of **D** to afford the coupling product **3** and regenerate Ni(0) complex **A**.¹⁵ However, for sulfones, there would be another reaction path via nucleophilic substitution, because

COMMUNICATION

Journal Name

some reactions could also take place in the absence of nickel catalyst.

In summary, we have developed an efficient nickel-catalyzed P-C bond-forming reaction via C-S/P-H cross coupling. A simple Ni(cod)₂ at a loading down to 0.1 mol% enables the reaction to take place smoothly at 10 mmol scale. Sulfides, sulfoxides and sulfones all can couple with P-H compounds to produce the corresponding organophosphorus compounds in moderate to high yields, providing an efficient method to construct P-C bonds. Further mechanistic studies are in progress in our laboratory.

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Notes and references

- (a) M. Tobisu and N. Chatani, *Acc. Chem. Res.*, 2015, **48**, 1717; (b) T. Chen and L.-B. Han, *Angew. Chem. Int. Ed.*, 2015, **54**, 8600; (c) J. Cornella, C. Zarate and R. Martin, *Chem. Soc. Rev.*, 2014, **43**, 8081; (d) S. Z. Tasker, E. A. Standley and T. F. Jamison, *Nature*, 2014, **509**, 299; (e) M. Tobisu and N. Chatani, *Top. Organomet. Chem.*, 2013, **44**, 35; (f) J. Yamaguchi, K. Muto and K. Itami, *Eur. J. Org. Chem.*, 2013, 19; (g) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg and V. Percec, *Chem. Rev.*, 2011, **111**, 1346; (h) D.-G. Yu, B.-J. Li and Z.-J. Shi, *Acc. Chem. Res.*, 2010, **43**, 1486.
- (a) A. F. M. Noisier and M. A. Brimble, *Chem. Rev.*, 2014, **114**, 8775; (b) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 74; (c) R. Waterman, *Chem. Soc. Rev.*, 2013, **42**, 5629; (d) J. Wencel-Delord and F. Glorius, *Nat. Chem.*, 2013, **5**, 369; (e) G. Rouquet and N. Chatani, *Angew. Chem. Int. Ed.*, 2013, **52**, 11726; (f) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; (g) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (h) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780; (i) C.-J. Li, *Acc. Chem. Rev.*, 2009, **42**, 335.
- Recent reviews on metal-catalyzed C-S transformation: (a) F. Pan and Z.-J. Shi, *ACS Catal.*, 2014, **4**, 280; (b) L. Wang, W. He and Z. Yu, *Chem. Soc. Rev.*, 2013, **42**, 599; (c) S. G. Modha, V. P. Mehta and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2013, **42**, 5042; (d) H. Prokopcová and C. O. Kappe, *Angew. Chem. Int. Ed.*, 2009, **48**, 2276; (e) S. R. Dubbaka and P. Vogel, *Angew. Chem. Int. Ed.*, 2005, **44**, 7674.
- Selected examples on metal-catalyzed C-S transformation: (a) S. Otsuka, H. Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2015, **21**, 14703; (b) Z.-J. Quan, Y. Lv, F.-Q. Jing, X.-D. Jia, C.-D. Huo and X.-C. Wang, *Adv. Synth. Catal.*, 2014, **356**, 325; (c) S. E. Denmark and A. J. Cresswell, *J. Org. Chem.*, 2013, **78**, 12593; (d) J. Luis, G. Ruano, J. Alemán and C. G. Paredes, *Org. Lett.*, 2006, **8**, 2683; (e) K. Itami, M. Mineno, N. Muraoka and J.-I. Yoshida, *J. Am. Chem. Soc.*, 2004, **126**, 11778; (f) K. Murakami, H. Yorimitsu and A. Osuka, *Angew. Chem. Int. Ed.*, 2014, **53**, 7510; (g) K. Gao, H. Yorimitsu and A. Osuka, *Angew. Chem. Int. Ed.*, 2016, **55**, 4573.
- (a) H. Okamura, Y. Mitsuhiro, M. Miura and H. Takei, *Chem. Lett.*, 1978, 517; (b) H. Okamura, Y. Mitsuhiro, M. Miura and H. Takei, *Tetrahedron Lett.*, 1979, **20**, 43; (c) E. Wenkert, T. W. Ferreira and E. L. Michelotti, *J. Chem. Soc. Chem. Commun.*, 1979, 637; (d) E. Wenkert, M. E. Shepard and A. T. McPhail, *J. Chem. Soc. Chem. Commun.*, 1986, 1390; (e) E. Wenkert and D. Chianelli, *J. Chem. Soc. Chem. Commun.*, 1991, 627; (f) E. Wenkert, J. B. Fernandes, E. L. Michelotti, C. S. Swinnell, *Synthesis*, 1983, 701; (g) E. Wenkert, E. L. Michelotti and C. S. Swinnell, *J. Am. Chem. Soc.*, 1979, **101**, 2246.
- (a) S. Zhang, D. Marshall and L. S. Liebeskind, *J. Org. Chem.*, 1999, **64**, 2796; (b) J. Srogl, W. Liu, D. Marshall and L. S. Liebeskind, *J. Am. Chem. Soc.*, 1999, **121**, 9449.
- (a) T. Sugahara, K. Murakami, H. Yorimitsu and A. Osuka, *Angew. Chem. Int. Ed.*, 2014, **53**, 9329; (b) K. Gao, H. Yorimitsu and A. Osuka, *Eur. J. Org. Chem.*, 2015, 2678; A palladium-catalyzed desulfurative cross-coupling reaction of sodium aryl sulfinates with H-phosphonates was reported, see: (c) T. Miao and L. Wang, *Adv. Syn. Catal.*, 2014, **356**, 967.
- (a) F. Zhu and Z.-X. Wang, *Org. Lett.*, 2015, **17**, 1601; (b) N. Barbero and R. Martin, *Org. Lett.*, 2012, **14**, 796; (c) J. Begouin, M. Rivard and C. Gosmini, *Chem. Commun.*, 2010, **46**, 5972; (d) J. Liu and M. J. Robins, *Org. Lett.*, 2005, **7**, 1149.
- During the reaction, a by-product methyldiphenyl phosphine oxide via cleavage of S-Me bond was detected. It was found that the yield of by-product as well as the reaction rate decreased with decreasing the loading of catalyst. Elevating the temperature or lengthening the reaction time could improve the yield of product with a lower loading of catalyst.
- (a) T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Tetrahedron Lett.*, 1980, **21**, 3595; (b) T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56; (c) M. Tobisu, T. Shimasaki and N. Chatani, *Chem. Lett.*, 2009, **38**, 710.
- (a) I. Wauters, W. Debrouwer, C. V. Stevens and Beilstein *J. Org. Chem.*, 2014, **10**, 1064; (b) C. S. Demmer, N. Krogsgaard-Larsen and L. Bunch, *Chem. Rev.*, 2011, **111**, 7981; (c) A. L. Schwan, *Chem. Soc. Rev.*, 2004, **33**, 218; (d) F. M. J. Tappe, V. T. Trepohl and M. Oestreich, *Synthesis*, 2010, 3037; (e) J. Yang, T. Chen and L.-B. Han, *J. Am. Chem. Soc.*, 2015, **137**, 1782; (f) J.-S. Zhang, T. Chen, J. Yang and L.-B. Han, *Chem. Commun.*, 2015, **51**, 7540; (g) C.-G. Feng, M. Ye, K.-J. Xiao, S. Li and J.-Q. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 9322; (h) Y.-L. Zhao, G.-J. Wu and F.-S. Han, *Chem. Commun.*, 2012, **48**, 5868; (i) T. Fu, H. Qiao, Z. Peng, G. Hu, X. Wu, Y. Gao and Y. Zhao, *Org. Biomol. Chem.*, 2014, **12**, 2895; (j) R. Zhuang, J. Xu, Z. Cai, G. Tang, M. Fang and Y. Zhao, *Org. Lett.*, 2011, **13**, 2110; (k) M. Andaloussi, J. Lindh, J. Sävmarker, P.J.R. Sjöberg and M. Larhed, *Chem.-Eur. J.*, 2009, **15**, 13069.
- (a) M. R. Grochowski, T. Li, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.*, 2010, **132**, 12412; (b) T. Schaub, M. Backes and U. Radius, *Chem. Commun.*, 2007, 2037; (c) M. J. Sgro and D. W. Stephan, *Organometallics*, 2012, **31**, 1584; (d) E. Wenkert, M. E. Shepard and A. McPhail, *J. Chem. Soc., Chem. Commun.*, 1986, 1390.
- As indicated from ³¹P NMR spectroscopies, P-ONa compound **C** (δ 89 ppm) was generated after mixing the Ph₂P(O)-H compounds and *t*-BuONa in dioxane (See SI). Similar transformations have been reported, see (a) K. Issleib, B. Walther and E. Fluck, *Z. Chem.*, 1968, **8**, 67; (b) J. Zhang, C. M. Medley, J. A. Krause and H. Guan, *Organometallics*, 2010, **29**, 6393; (c) L.-B. Han, C. Zhang, H. Yazawa and S. Shimada, *J. Am. Chem. Soc.*, 2004, **126**, 5080; (d) N. P. N. Wellala and H. Guan, *Org. Biomol. Chem.*, 2015, **13**, 10802; (e) S. I. Pascu, K. S. Coleman, A. R. Cowley, M. L. H. Green and N. H. Rees, *New. J. Chem.*, 2005, **29**, 385.
- (a) L.-C. Liang, C.-W. Li, P.-Y. Lee, C.-H. Chang and H. M. Lee, *Dalton Trans.*, 2011, **40**, 9004; (b) S. Ge, R. A. Green and J. F. Hartwig, *J. Am. Chem. Soc.*, 2014, **136**, 1617; (c) D. Martin, D. Moraleda, T. Achard, L. Giordano and G. Buono, *Chem. Eur. J.*, 2011, **17**, 12729.
- P(O)-H compounds and the in-situ P-ONa compounds can be ligated to nickel; however, a heterogeneous process could not be excluded out. For a review on P(O)-H compounds acting as ligands in cross coupling, see: T. M. Shaikh, C.-M. Weng, F.-E Hong, *Coordin. Chem. Rev.*, 2012, **256**, 771-803.