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Mono- and Dinuclear Pincer Nickel Catalyzed Activation and Transformation of C−Cl, C−N, and C−O Bonds

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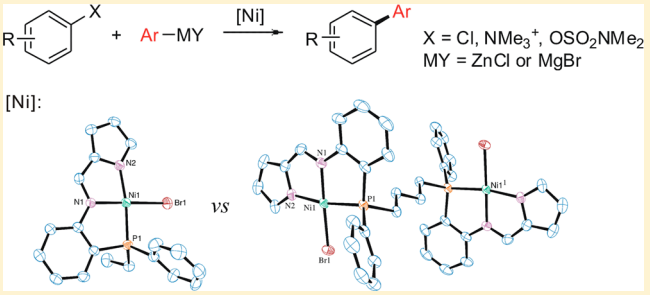
Supporting Information

ABSTRACT: Condensation of 2-$NH_2C_6H_4P(Et)Ph$ (**2**) with pyrrole-2-carboxaldehyde generated 2-$(C_4H_4N$-2′-CH═N)-$C_6H_4P(Et)Ph$ (**3**). Treatment of **3** with NaH and followed by $(DME)NiX_2$ (X = Cl, Br) afforded mononuclear pincer nickel complexes [Ni{2-$(C_4H_3N$-2′-CH═N)$C_6H_4P(Et)Ph$}-X] (**4a**, X = Cl; **4b**, X = Br). Reaction of [2-$NH_2C_6H_4P$-$(Ph)]_2(CH_2)_n$ (**5a**, n = 3; **5b**, n = 4) with pyrrole-2-carboxaldehyde or 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde formed [2-$(C_4H_4N$-2′-CH═N)$C_6H_4P(Ph)]_2(CH_2)_n$ (**6a**, n = 3; **6b**, n = 4) and [2-(5′-*t*BuC_4H_3N-2′-CH═N)C_6H_4P-$(Ph)]_2(CH_2)_4$ (**6c**). Respective treatment of **6a−c** with NaH followed by $(DME)NiX_2$ (X = Cl, Br) gave the dinuclear nickel complexes [Ni{2-(5′-RC_4H_2N-2′-CH═N)$C_6H_4P(Ph)$}-$X]_2(CH_2)_n$ (**7a**, R = H, X = Cl, n = 3; **7b**, R = H, X = Cl, n = 4; **7c**, R = H, X = Br, n = 4; **7d**, R = *t*Bu, X = Cl, n = 4). Catalysis of the complexes for the activation and transformation of C−Cl, C−N, and C−O bonds was evaluated. Complex **7c** exhibited excellent catalytic activity in the cross-coupling of aryl chlorides or aryltrimethylammonium iodides with arylzinc reagents as well as of aryl sulfamates with aryl Grignard reagents. The dinuclear nickel complexes **7b−d** showed higher catalytic activity than the mononuclear complexes in each type of reaction.



INTRODUCTION

Transition-metal-catalyzed cross-coupling reactions are powerful tools for construction of C−C bonds in organic systhesis.[1] Nucleophiles used in the cross-couplings include Grignard reagents and organozinc, -boron, -silicon, and -tin reagents.[1,2] Electrophiles are principally organic halides, especially bromides and iodides at the earlier stage.[1−3] Organic chlorides as the inert electrophiles have received intense attention over the past 15 years because of their lower cost and the wider diversity of available compounds in comparison with bromides and iodides.[4] Some effective catalysts, including palladium, nickel, copper, iron, and cobalt catalysts, have been developed for the C−Cl bond activation.[2f,5] Representative examples include Buchwald biarylphosphine/Pd catalysts,[5b] sterically demanding trialkylphosphine/Pd catalysts,[5c,d] N-heterocyclic carbene/Pd catalysts,[5e−g] pincer nickel catalysts,[5i,j] butadiene/Ni catalysts,[5k−m] N-heterocyclic carbene/Fe and $Co(acac)_3$ catalysts, etc.[5q−s] In recent years aromatic amines have gained increasing attention as electrophiles through C−N bond activation. However, the C−N bonds in an aromatic amine are very inert. Hence, aromatic amines were usually transformed to ammonium salts or diazonium salts to weaken the C−N bonds before catalytic cleavage.[6,7] For example, Wenkert and Reeves respectively reported nickel- or palladium-catalyzed reactions of aryltrimethylammonium salts with Grignard reagents.[6f,i] MacMillan et al. reported the Suzuki coupling of aryltrimethylammonium triflates using $Ni(cod)_2$/IMes as the catalyst.[6g] Our group carried out the reaction of aryltrimethylammonium salts with organozinc reagents using $Ni(PCy_3)_2Cl_2$ or amido pincer nickels as the catalysts.[6b,c,e] Phenolic derivatives are other types of versatile electrophiles. Aryl triflates and sulfonates were most widely investigated in the phenol-derived electrophiles.[8] Less common phenol-based electrophiles such as esters, carbonates, carbamates, sulfamates, phenolate, and ethers were also developed in the past few years.[8−10] Among them, sulfamates are attractive due to their ease of preparation, significant stability under various reaction conditions, and the potential to direct the installation of other functional groups onto an aromatic ring by C−H activation or ortho metalation prior to cross-coupling.[10d,j] The reported catalytic reactions using sulfamates as electrophilic partners include Suzuki couplings,[10b−i] Kumada couplings,[10j−l] amination reactions,[10m−p] and C−H bond functionalizations.[10q,r] Nickel, palladium, iron, and cobalt complexes were demonstrated to catalyze these transformations.[10c−p] For example, $FeCl_2$/SIMes catalyzes cross-coupling of aryl sulfamates and primary or secondary alkyl Grignard reagents.[10l] Ni(Cl)(Cp)-IMes catalyzes cross-coupling of aryl sulfamates and aryl Grignard reagents.[10j]

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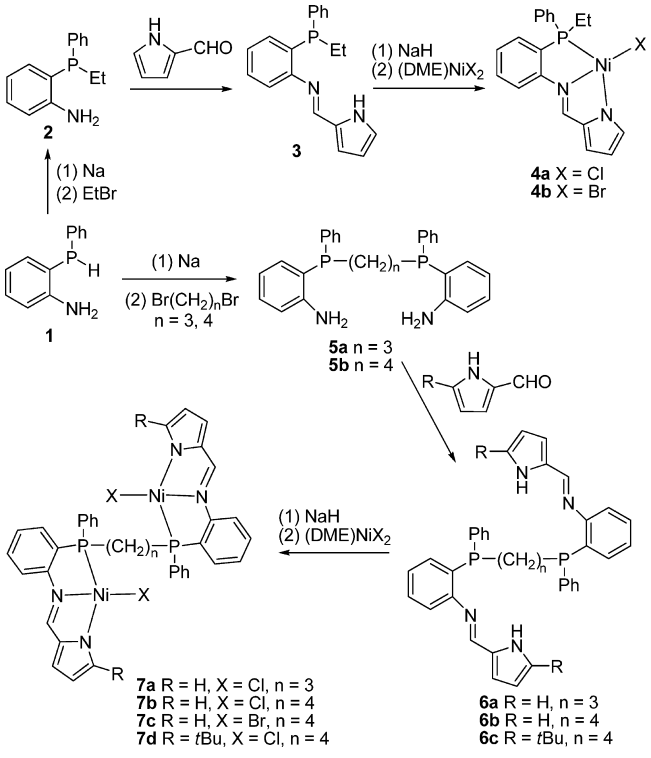
We intended to develop highly effective and widely applicable catalyst systems for the activation and transformation of C−Cl, C−N, and C−O bonds. The use of bimetallic catalysts was considered as an efficient way to achieve this aim. Bimetallic catalysts have attracted considerable attention in recent years due to the existence of cooperative catalytic effects.[11−14] The bimetallic cooperativity can improve the activities and/or selectivities of the catalysts, make reaction conditions milder, and lead to making the reaction more efficient. A range of reactions such as ethylene polymerization,[12] ring-opening polymerization of cyclic esters,[13] C−C couplings,[14] and asymmetric transformations[11b,15] have been carried out using bimetallic catalysts, and the cooperative effect was observed in the reactions. On the basis of the achievements of bimetallic catalysis indicated above and the studies of pincer nickel catalysts by us and other groups,[5j,6a−c,16] we designed and synthesized bimetallic nickel complexes supported by P,N,N-pincer ligands. These bimetallic complexes were proven to effectively catalyze the activation of aryl C−Cl, C−N, and C−O bonds. For the purpose of comparison, two related monounclear complexes of nickel were also synthesized and evaluated for the catalysis. Herein we report the results.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mono- and Dinuclear P,N,N-Pincer Nickel Complexes. The synthesis of the ligand precursors and mono- and dinuclear nickel complexes is summarized in Scheme 1. Compound **1** is known and was prepared according to the reported method.[17] The reaction of **1** with sodium metal and then EtBr yielded 2-$NH_2C_6H_4P(Et)Ph$ (**2**). Condensation of **2** with pyrrole-2-carboxaldehyde afforded the corresponding pyrrolylimine 2-$(C_4H_4N\text{-}2'\text{-}CH{=}N)C_6H_4P(Et)Ph$ (**3**). Treatment of **3** with sodium hydride and then $Ni(DME)X_2$ (X = Cl, Br) generated the nickel complexes $[Ni\{2\text{-}(C_4H_3N\text{-}2'\text{-}CH{=}N)C_6H_4P(Et)\text{-}Ph\}X]$ (**4a**, X = Cl; **4b**, X = Br). Similar treatment of **1** with sodium followed by 0.5 equiv of 1,3-dibromopropane or 1,4-dibromobutane gave $[2\text{-}NH_2C_6H_4P(Ph)]_2(CH_2)_n$ (**5a**, n = 3; **5b**, n = 4). Reaction of **5a**,**b** with 2 equiv of pyrrole-2-carboxaldehyde or 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde produced the diimines $[2\text{-}(5'\text{-}RC_4H_3N\text{-}2'\text{-}CH{=}N)C_6H_4P\text{-}(Ph)]_2(CH_2)_n$ (**6a**, R = H, n = 3; **6b**, R = H, n = 4; **6c**, R = *t*Bu, n = 4). Deprotonation of **6a**−**c** with sodium hydride followed by treatment of the deprotonated species with $Ni(DME)X_2$ (X = Cl, Br) afforded the dinuclear nickel complexes $[Ni\{2\text{-}(5'\text{-}RC_4H_3N\text{-}2'\text{-}CH{=}N)C_6H_4P(Ph)\}\text{-}X]_2(CH_2)_n$ (**7a**, R = H, X = Cl, n = 3; **7b**, R = H, X = Cl, n = 4; **7c**, R = H, X = Br, n = 4; **7d**, R = *t*Bu, X = Cl, n = 4). **5a**,**b** are both known compounds, and they were characterized by ^1H, ^{13}C, and ^{31}P NMR spectra.[18] Compounds **2**, **3**, and **6a**−**c** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. It is noteworthy that the respective NMR spectra of **6a**,**b** gave two sets of signals. For example, the ^{31}P NMR spectra of **6a** showed two signals at δ −23.89 and −27.58, respectively. The ^{31}P NMR signals of **6b** appeared at δ −21.41 and −22.53, respectively. This is ascribed to the presence of cis and trans isomers of the imines. On the basis of their ^1H and ^{31}P NMR spectra, the ratios of the isomers are about 2:1 for **6a** and 1.1:1 for **6b**. Compound **6c** showed only one set of NMR signals. Its ^{31}P NMR signal appeared at δ −24.64. This is ascribed to the steric hindrance of *t*Bu groups, which leads to the existence of only trans imines in the molecule. Complexes **4a**,**b** and **7a**−**d** are diamagnetic crystalline solids and were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, HR-MS, and elemental analyses. The NMR spectra of each of the complexes displayed one set of signals, with no isomers being observed. For example, the ^{31}P NMR spectrum of each complex showed only one signal. The ^1H and ^{13}C NMR spectra of the complexes also matched their respective structures. The HR-MS of **4a**,**b** gave molecular ion signals, whereas the HR-MS of **7a**−**d** gave $[M - X]^+$ fragment signals.

Scheme 1. Synthesis of Mono- and Dinuclear P,N,N-Pincer Nickel Complexes



The structures of complexes **4b** and **7c** were further confirmed by single-crystal X-ray diffraction analyses. The ORTEP drawing of complex **4b** is presented in Figure 1, along with selected bond lengths and angles. In the molecule the central nickel atom is coordinated by P1, N1, N2, and Br atoms, having a distorted-square-planar geometry. The N1−Ni1−Br1 atoms (bond angle 178.65(10)°) is approximately linear. The P1−Ni1−N2 atoms (bond angle 170.86(12)°) are also near linear. The N1−Ni1−P1 and N1−Ni1−N2 angles (87.05(10) and 83.88(14)°, respectively) are both slightly smaller than a right angle. The Ni1−N1 distance of 1.898(3) Å is slightly shorter than that of Ni1−N2 (1.906(3) Å), and both are close to those in pincer nickel complexes $[Ni(Cl)\{N(2\text{-}Ph_2PC_6H_4)_2\}]$ (1.895(3) Å)[19] and $[Ni(Cl)\{N\{CH(Ph)P\text{-}(Ph_2){=}O\}C_6H_4(PPh_2)\text{-}2\}]$ (1.893(5) Å).[16h] The Ni−P distance of 2.1402(11) Å is within the normal range in the pincer nickel complexes.[16h,i,19]

The ORTEP drawing of complex **7c** is presented in Figure 2, along with selected bond lengths and angles. The molecule is centrosymmetric. Each nickel atom has a distorted-square-planar geometry, and the two pincer nickel units are bridged by a 1,4-butylene group attached to the P atoms. The distance between Ni1 and Ni1i is 8.5129 Å. In each pincer nickel unit the coordination environment of the central nickel atom is very

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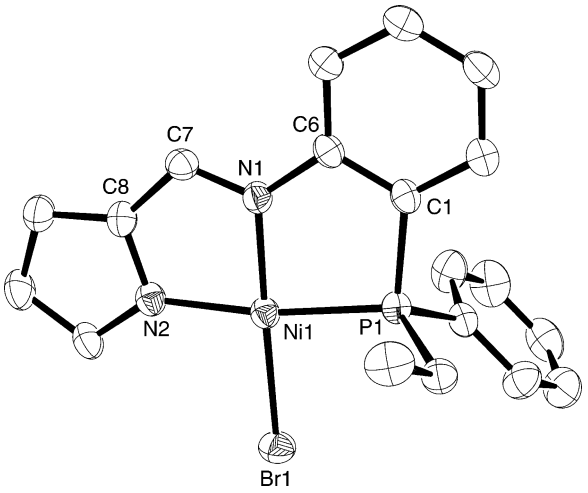

Figure 1. ORTEP drawing (30% probability) of complex **4b**. Selected bond lengths (Å) and angles (deg): Ni1−P1 2.1402(11), Ni1−N1 1.898(3), Ni1−N2 1.906(3), Ni1−Br1 2.2866(7), N1−C7 1.318(5); P1−Ni1−N1 87.05(10), N1−Ni1−N2 83.88(14), N2−Ni1−Br1 97.32(11), P1−Ni1−Br1 91.75(4), P1−Ni1−N2 170.86(12), N1−Ni1−Br1 178.65(10).

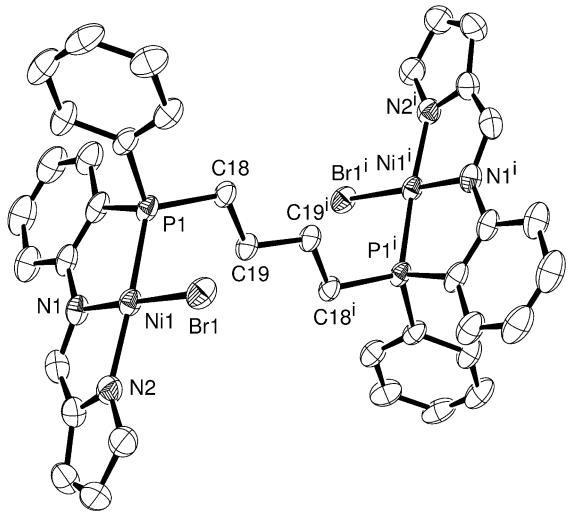

Figure 2. ORTEP drawing (30% probability) of complex **7c**. Selected bond lengths (Å) and angles (deg): Ni1−N1 1.899(3), Ni1−N2 1.896(3), Ni1−P1 2.1399(11), Ni1−Br1 2.2956(7); N1−Ni1−P1 86.57(11), N1−Ni1−N2 83.85(15), P1−Ni1−Br1 93.00(4), N2−Ni1−Br1 96.46(11), P1−Ni1−N2 169.87(12), N1−Ni1−Br1 177.91(9).

similar to that in **4b**. The Ni1−N1 distance of 1.899(3) Å is almost same as that of Ni1−N2 (1.896(3) Å), and both are close to the corresponding values in **4b**. The Ni−P distance of 2.1399(11) Å is also very close to that in **4b** (2.1402(11) Å), whereas the Ni−Br distance of 2.2956(7) Å is slightly longer than that in **4b** (2.2866(7) Å).

Catalysis of Complexes 4a,b and 7a−d. *(1). Catalytic Coupling of Aryl Chlorides with Arylzinc Chlorides.* The reaction conditions were screened through the reaction of *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4ZnCl using **7c** as the catalyst. A 1/1 mixture of THF and NMP has been reported to be a suitable solvent for a range of Negishi couplings. We also chose this solvent for the preliminary condition screening. When 0.25 mol % of complex **7c** was loaded, it showed relatively low catalytic efficiency at 20, 65, and 90 °C, respectively. However, the above reactions also showed that higher temperature was beneficial to improving the product yields (Table 1, entries 1−3). The reaction was markedly improved when the catalyst loading was increased to 0.5 mol % and the reaction time was lengthened to 24 h, an almost quantitative yield being achieved (Table 1, entries 4 and 5). Solvents were also screened for the **7c**-catalyzed reaction, including NMP, THF, DMA, 1/2 and 2/1 mixtures of THF and NMP, and a 1/1 mixture of THF and DMA. All of these solvents were proven to be less effective than the 1/1 mixture of THF and NMP (Table 1, entries 6−11).

Table 1. Optimization of Reaction Conditions and Evaluation of Catalytic Activity of Complexes 4a,b and 7a−d in the Cross-Coupling of *p*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4ZnCl[a]

entry	complex (amt (mol %))	solvent	*T* (°C)	time (h)	yield (%)[b]
1	**7c** (0.25)	THF/NMP (1/1)	20	12	10
2	**7c** (0.25)	THF/NMP (1/1)	65	12	65
3	**7c** (0.25)	THF/NMP (1/1)	90	12	68
4	**7c** (0.5)	THF/NMP (1/1)	90	12	86
5	**7c** (0.5)	THF/NMP (1/1)	90	24	96
6	**7c** (0.5)	THF/NMP (2/1)	90	24	31
7	**7c** (0.5)	THF/NMP (1/2)	90	24	62
8	**7c** (0.5)	NMP	90	24	40
9	**7c** (0.5)	THF	90	24	34
10	**7c** (0.5)	DMA	90	24	67
11	**7c** (0.5)	THF/DMA (1/1)	90	24	30
12	**7a** (0.5)	THF/NMP (1/1)	90	24	79
13	**7b** (0.5)	THF/NMP (1/1)	90	24	85
14	**7d** (0.5)	THF/NMP (1/1)	90	24	88
15	**4a** (1.0)	THF/NMP (1/1)	90	24	66
16	**4b** (1.0)	THF/NMP (1/1)	90	24	76

[a]Unless otherwise stated, *p*-MeC_6H_4ZnCl was prepared from *p*-MeC_6H_4MgBr and $ZnCl_2$ in the presence of 2 equiv of LiCl; 0.5 mmol of *p*-$MeOC_6H_4Cl$, and 0.75 mmol of *p*-MeC_6H_4ZnCl. [b]Isolated yield.

We then examined the catalysis of other complexes using the optimized conditions. Complexes **7a**,**b**,**d** were effective for the cross-coupling reaction (Table 1, entries 12−14). However, their activity is lower than that of **7c** and the activity order is approximately **7c** > **7d** > **7b** > **7a**. It seems that a longer linker between the two pincer nickel units is beneficial to the catalytic activity. A pincer nickel bromide also displayed catalytic activity higher than that of its chloride partner (**7a** vs **7b**) for unclear reasons. The *t*Bu group on the pyrrolyl ring seems to affect the activity to a lesser extent (**7b** vs **7d**). Mononuclear complexes **4a**,**b** were also evaluated using the same reaction as above at 90 °C with 1 mol % of complex loadings. Both of them showed activity lower than that of any of the complexes **7a−d**. The bromide **4b** was also more active than chloride **4a** (Table 1, entries 15 and 16).

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In the reactions mentioned above, the zinc reagent *p*-MeC_6H_4ZnCl was prepared from the corresponding Grignard reagent and $ZnCl_2$ in the presence of 2 equiv of LiCl. The zinc reagent prepared from Grignard reagent and $ZnCl_2$ in the absence of LiCl resulted in a slightly lower product yield (Table 2). Deactivated, unactivated, and activated electrophilic substrates gave consistent results. The low reactivity of the zinc reagent prepared from a Grignard reagent and $ZnCl_2$ might be due to aggregation of the arylzinc reagent with the coproduct $MgCl_2$. The role of LiCl additive might be to break the aggregation.[20]

Table 2. LiCl effect in 7c-Catalyzed Cross-Coupling Reaction of Aryl Chlorides with ArZnCl[a]

$$Ar^1\text{-Cl} + Ar^2\text{-ZnCl} \xrightarrow[\text{THF/NMP} = 1/1,\ 90^\circ\text{C}]{\mathbf{7c}\ (0.5\ \text{mol}\ \%)} Ar^1\text{-}Ar^2$$

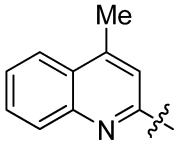
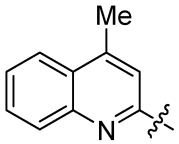
entry	Ar^1	Ar^2	time (h)	yield (%)[b]
1[c]	C_6H_5	*p*-$MeOC_6H_4$	24	94
2[d]	C_6H_5	*p*-$MeOC_6H_4$	24	16
3[c]	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	12	86
4[d]	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	12	82
5[c]	*p*-$CF_3C_6H_4$	*p*-MeC_6H_4	12	93
6[d]	*p*-$CF_3C_6H_4$	*p*-MeC_6H_4	12	68

[a]The reactions were performed with 0.5 mmol of aryl chlorides and 0.75 mmol of arylzinc chlorides according to the conditions indicated by the above equation. [b]Isolated yield. [c]Arylzinc chlorides were prepared from the corresponding Grignard reagents and $ZnCl_2$ in the presence of 2 equiv of LiCl. [d]Arylzinc chlorides were prepared from the corresponding Grignard reagents and $ZnCl_2$ without LiCl additive.

The substrate scope was examnied using complex **7c** under the optimized conditions. Unactivated and deactivated aryl chlorides, including PhCl, *p*-MeC_6H_4Cl, *p*-$MeOC_6H_4Cl$, and *o*-$MeOC_6H_4Cl$, were proven to couple smoothly with *p*-MeC_6H_4ZnCl, *o*-MeC_6H_4ZnCl, *p*-$MeOC_6H_4ZnCl$, and *p*-$Me_2NC_6H_4ZnCl$ in the presence of 0.5 mol % of **7c** (Table 3, entries 1−7). *p*-$Me_2NC_6H_4ZnCl$ showed higher reactivity than the others. Its reaction with *p*-MeC_6H_4Cl can be carried out at lower temperature and less loading of **7c** (Table 3, entries 4 and 5). *o*-MeC_6H_4ZnCl was less reactive than the para-substituted phenylzinc reagents due to steric hindrance. Reaction of *o*-$MeOC_6H_4Cl$ with *p*-MeC_6H_4ZnCl gave a good result on catalysis with 0.5 mol % of **7c**, but the yield was lower than that of *p*-$MeOC_6H_4Cl$ under the same conditions (Table 1, entry 5 and Table 3, entry 7). Electron-poor aryl or heteroaryl chlorides, including *p*-$Et_2NC(O)C_6H_4Cl$, *p*-PhC(O)C_6H_4Cl, *p*-EtOC(O)C_6H_4Cl, *p*-$CF_3C_6H_4Cl$, 2-chloropyridine, and 2-chloro-4-methylquinoline, exhibited good reactivity. Their reaction with electron-rich arylzinc reagents often required less catalyst loading or lower reaction temperature and gave excellent product yields (Table 3, entries 8−25). However, *p*-NCC_6H_4Cl as an electron-poor electrophile showed relatively low reactivity in comparison with those mentioned above. Its reaction required much higher catalyst loading to achieve good product yield (Table 3, entries 26 and 27). This is ascribed to the coordination of the nitrile group with the catalyst species, which decreases the catalytic activity of the active catalyst.[21] *p*-$CF_3C_6H_4ZnCl$ displayed relatively low reactivity due to its electron-poor properties. It led to good reaction results only when electron-poor aryl chlorides such as *p*-$Et_2NC(O)C_6H_4Cl$, *p*-PhC(O)C_6H_4Cl, and *p*-EtOC(O)C_6H_4Cl were employed

Table 3. Reaction of Aryl Chlorides with ArZnCl Catalyzed by 7c or 4b[a]

$$Ar^1\text{-Cl} + Ar^2\text{-ZnCl} \xrightarrow[\text{THF/NMP}\ (1/1),\ 90\ ^\circ\text{C},\ 12\ \text{or}\ 24\ \text{h}]{\mathbf{7c}\ (0.5\ \text{mol}\ \%)\ \text{or}\ \mathbf{4b}\ (1\ \text{mol}\ \%)} Ar^1\text{-}Ar^2$$

Entry	Ar^1	Ar^2	Time (h)	Yield (%)[b] **7c**	**4b**
1	Ph	*p*-$MeOC_6H_4$	24	94	64
2	Ph	*p*-$Me_2NC_6H_4$	12	96	82
3	*p*-MeC_6H_4	*p*-$MeOC_6H_4$	24	84	72
4	*p*-MeC_6H_4	*p*-$Me_2NC_6H_4$	12	99	99
5[c,d]	*p*-MeC_6H_4	*p*-$Me_2NC_6H_4$	12	93	61
6	*p*-$MeOC_6H_4$	*o*-MeC_6H_4	24	78	55
7	*o*-$MeOC_6H_4$	*p*-MeC_6H_4	24	87	79
8[d]	*p*-$Et_2NOCC_6H_4$	*p*-MeC_6H_4	12	99	99
9[c,d]	*p*-$Et_2NOCC_6H_4$	*p*-MeC_6H_4	12	98	90
10	*p*-$Et_2NOCC_6H_4$	*o*-MeC_6H_4	12	99	90
11	*p*-$Et_2NOCC_6H_4$	*p*-$MeOC_6H_4$	12	89	81
12[c,d]	*p*-PhC(O)C_6H_4	*p*-MeC_6H_4	12	99	79
13	*p*-$EtOOCC_6H_4$	*p*-MeC_6H_4	12	99	99
14[c,d]	*p*-$EtOOCC_6H_4$	*p*-MeC_6H_4	12	99	92
15	*p*-$EtOOCC_6H_4$	*o*-MeC_6H_4	12	99	93
16	*p*-$EtOOCC_6H_4$	*p*-$MeOC_6H_4$	12	99	99
17	*p*-$EtOOCC_6H_4$	*p*-$MeOC_6H_4$	12	99	89
18	*p*-$CF_3C_6H_4$	*p*-MeC_6H_4	12	99	61
19	*p*-$CF_3C_6H_4$	*p*-$MeOC_6H_4$	12	93	72
20	*p*-$CF_3C_6H_4$	*p*-$Me_2NC_6H_4$	12	99	99
21[c,d]	*p*-$CF_3C_6H_4$	*p*-$Me_2NC_6H_4$	12	99	86
22	2-Py	*p*-MeC_6H_4	12	99	81
23	2-Py	*p*-$MeOC_6H_4$	12	96	86
24		*p*-MeC_6H_4	12	99	99
25[c,f]		*p*-MeC_6H_4	12	99	58
26	*p*-NCC_6H_4	*p*-MeC_6H_4	12	78	45
27[e]	*p*-NCC_6H_4	*p*-MeC_6H_4	24	94	79
28	*p*-PhC(O)C_6H_4	*p*-$CF_3C_6H_4$	12	82	61
29	*p*-$Et_2NOCC_6H_4$	*p*-$CF_3C_6H_4$	12	81	64
30	*p*-$EtOOCC_6H_4$	*p*-$CF_3C_6H_4$	12	89	81

[a]Unless otherwise stated, reactions were performed with 0.5 mmol of aryl chlorides and 0.75 mmol of arylzinc chlorides according to the conditions indicated by the above equation; arylzinc chlorides were prepared from the corresponding Grignard reagents and $ZnCl_2$ in the presence of 2 equiv of LiCl. [b]Isolated yield. [c]The bath temperature was 40 °C. [d]0.25 mol % of **7c** or 0.5 mol % of **4b** was employed. [e]1 mol % of **7c** or 2 mol % of **4b** was employed. [f]0.125 mol % of **7c** or 0.25 mol % of **4b** was employed.

(Table 3, entries 28−30). As seen above, functional groups, including OMe, NMe_2, CF_3, C(O)OEt, $C(O)NEt_2$, PhC(O), CN, and heteroaryl groups, are well tolerated. For comparison the catalysis of complex **4b** was tested in each reaction (Table 3). Under comparable conditions **4b** exhibited lower activity than **7c**. This may be due to the existence of cooperative effects in a bimetallic system.

(2). Catalytic Coupling of Aryltrimethylammonium Salts with Arylzinc Chlorides. Complex **7c** was chosen as the catalyst for the condition screening using the reaction of $PhNMe_3^+I^-$ with *p*-$MeOC_6H_4ZnCl$ in a 1/1 mixture of THF and NMP with 0.5 mol % of catalyst loading. The reaction temperature

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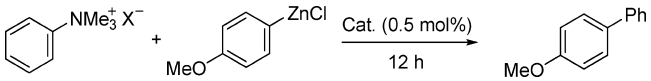
remarkably affected the product yields. When the temperature changed from 25 to 65 °C the yields changed from 70 to 99% (Table 4, entries 1−3). A series of solvents were screened, including 1/2 and 2/1 mixtures of THF and NMP, THF, NMP, toluene, DMA, DMF, a 1/1 mixture of THF and DMA, and a 1/1 mixture of THF and DMF. The results showed that all of the solvents were less effective than the 1/1 mixture of THF and NMP, although a 1/1 mixture of THF and DMA also led to good results (Table 4, entries 4−12). The zinc reagent *p*-$MeOC_6H_4ZnCl$ used in the above reactions was prepared from *p*-$MeOC_6H_4MgBr$ and $ZnCl_2$ in the presence of 2 equiv of LiCl. When the LiCl additive was absent, the reaction resulted in a much lower yield (Table 4, entry 13). The reason may be same as that indicated in Catalytic Coupling of Aryl Chlorides with Arylzinc Chlorides. The counterion effect was also investigated with Br^-, Cl^-, OTf^-, and BF_4^-, respectively, as a counterion in a 1/1 mixture of THF and NMP at 65 °C. The tetrafluoroborate and triflate salts exhibited the lowest reactivity. The bromide salt showed higher reactivity than the chloride salt, the reaction of the former giving 94% product yield and that of the latter giving 87% yield. However, both of them were less reactive than the iodide salt (Table 4, entries 14−17). In addition, KI additive was found to improve the reaction of $PhNMe_3^+Cl^-$ and $PhNMe_3^+OTf^-$ with *p*-$MeOC_6H_4ZnCl$. The former gave a 90% yield of 4-methoxy-1,1′-biphenyl, and the latter led to the product in 93% yield (Table 4, entries 18 and 19). The counterion effect may result from interaction of the central metal with the anions during the catalytic cycle. The iodide anion may provide better stabilization to the central nickel atom or ion through coordination. The weakly coordinating anion OTf^- and noncoordinating anion BF_4^- do not provide better stabilization or provide less stabilizing actions.[22]

Table 4. Optimization of Reaction Conditions and Evaluation of Catalytic Activity of Complexes 4a,b and 7a−d in the Cross-Coupling Reactions of $PhNMe_3^+X^-$ with *p*-$MeOC_6H_4ZnCl$[a]



entry	complex	X	solvent	*T* (°C)	yield (%)[b]
1	**7c**	I	THF/NMP (1/1)	25	70
2	**7c**	I	THF/NMP (1/1)	45	83
3	**7c**	I	THF/NMP (1/1)	65	99
4	**7c**	I	THF/NMP (1/2)	65	69
5	**7c**	I	THF/NMP (2/1)	65	64
6	**7c**	I	THF	65	69
7	**7c**	I	NMP	65	66
8	**7c**	I	toluene	65	–
9	**7c**	I	DMA	65	86
10	**7c**	I	DMF	65	76
11	**7c**	I	THF/DMA (1/1)	65	93
12	**7c**	I	THF/DMF (1/1)	65	75
13[c]	**7c**	I	THF/NMP (1/1)	65	11
14	**7c**	OTf	THF/NMP (1/1)	65	76
15	**7c**	BF_4	THF/NMP (1/1)	65	77
16	**7c**	Br	THF/NMP (1/1)	65	94
17	**7c**	Cl	THF/NMP (1/1)	65	87
18[d]	**7c**	Cl	THF/NMP (1/1)	65	90
19[d]	**7c**	OTf	THF/NMP (1/1)	65	93
20	**7a**	I	THF/NMP (1/1)	65	79
21	**7b**	I	THF/NMP (1/1)	65	88
22	**7d**	I	THF/NMP (1/1)	65	96
23[e]	**4a**	I	THF/NMP (1/1)	65	74
24[e]	**4b**	I	THF/NMP (1/1)	65	78

[a]Unless otherwise stated, reactions were carried out according to the conditions indicated by the above equation using 0.5 mmol of phenyltrimethylammonium salts and 0.75 mmol of *p*-$MeOC_6H_4ZnCl$; *p*-$MeOC_6H_4ZnCl$ was prepared from *p*-$MeOC_6H_4MgBr$ and $ZnCl_2$ in the presence of 2 equiv of LiCl. [b]Isolated yield. [c]*p*-$MeOC_6H_4ZnCl$ was prepared from *p*-$MeOC_6H_4MgBr$ and $ZnCl_2$. [d]1 equiv of KI additive was employed. [e]1 mol % of catalyst was used.

The catalysis of complexes **7a,b,d** and **4a,b** was evaluated at 65 °C in a 1/1 mixture of THF and NMP with 0.5 mol % (for **7a,b,d**) or 1 mol % (for **4a,b**) catalyst loadings (Table 4, entries 20−24). Complex **7d** was proven to have activity close to that of **7c**. Complex **7b** is more active than **7a**. The activity of complex **4b** is higher than that of **4a** and is close to that of **7a**. The activity order is **7c** ≥ **7d** > **7b** > **7a** ≅ **4b** > **4a**. This activity order is approximately consistent with that for catalyzing coupling of aryl chlorides with arylzinc reagents and shows that the dinuclear complexes with 1,4-butylene as a linker are more active than the complex with a 1,3-propylene linker or the mononuclear complexes. In addition, a bulkier ligand seems to be beneficial to the catalysis in this coupling (**7b** vs **7d**).

The substrate scope was examined using complex **7c**. We noticed that a 0.25 mol % amount of **7c** can drive most coupling reactions to completion under the optimized temperature and solvent conditions. For an electron-rich arylzinc reagent such as *p*-$Me_2NC_6H_4ZnCl$ or activated electrophile such as *p*-$EtOC(O)C_6H_4NMe_3^+I^-$ 0.125 mol % of **7c** is able to drive the reaction to completion (Table 5, entries 3, 10, 13, and 16). Unactivated and deactivated aryltrimethylammonium salts can effectively react with para-substituted phenylzinc chlorides (Table 5, entries 1−5). However, the reaction of *o*-MeC_6H_4ZnCl with *p*-$MeOC_6H_4NMe_3^+I^-$ gave a relatively low product yield (Table 5, entry 7). Increasing catalyst loadings can improve the reaction to a lesser extent. For example, 0.5 mol % of **7c** led to 81% yield of the cross-coupling product. This results from the hindering effect of the *o*-methyl group in *o*-MeC_6H_4ZnCl. The *o*-methyl group in *o*-$MeC_6H_4NMe_3^+I^-$ seems to affect the reactions to a lesser extent. The reaction of *o*-$MeC_6H_4NMe_3^+I^-$ with *p*-$MeOC_6H_4ZnCl$ or *p*-$Me_2NC_6H_4ZnCl$ gave excellent yields (Table 5, entries 8 and 10). The reaction of activated aryltrimethylammonium salts such as *p*-$PhC(O)C_6H_4NMe_3^+I^-$, *p*-$EtOC(O)C_6H_4NMe_3^+I^-$, and *p*-$CF_3C_6H_4NMe_3^+I^-$ with electron-rich and electron-poor arylzinc reagents (even *o*-MeC_6H_4ZnCl) gave excellent yields (Table 5, entries 11−21). Reaction of *p*-$CF_3C_6H_4ZnCl$ with deactivated *p*-$MeOC_6H_4NMe_3^+I^-$ afforded th cross-coupling product in low yield. The reaction cannot be further improved by increasing catalyst loadings. The reaction of 2-pyridyltrimethylammonium iodide with either *p*-$MeC_6H_4NMe_3^+I^-$ or *p*-$MeOC_6H_4NMe_3^+I^-$ gave moderate yields. However, the reactions were markedly improved by increasing the amount of **7c** to 0.5 mol %, affording the corresponding products in 99% and 91% yields, respectively (Table 5, entries 23−26). In all the reactions the C_{Ar}−N bonds of the aryltrimethylammonium salts are selectively activated, although the C_{Ar}−N bonds are stronger than the C_{Me}−N bonds.[23] A series of functional groups, including OMe, NMe_2, CF_3, C(O)OEt, PhC(O), and pyridyl groups, are tolerated.

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Table 5. Reaction of Aryltrimethylammonium Iodides with ArZnCl Catalyzed by 7c or 4b[a]

$$Ar^1\text{-}NMe_3^+I^- + Ar^2\text{-}ZnCl \xrightarrow[\text{THF/NMP (1/1)}]{\text{7c (0.25 mol \%) or 4b (0.5 mol \%)}} Ar^1\text{-}Ar^2$$

65 °C, 12 h

			yield (%)[b]	
entry	Ar^1	Ar^2	**7c**	**4b**
1	Ph	*p*-$MeOC_6H_4$	98	72
2	Ph	*p*-$Me_2NC_6H_4$	99	99
3[c]	Ph	*p*-$Me_2NC_6H_4$	99	91
4	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	96	69
5	*m*-$MeOC_6H_4$	*p*-MeC_6H_4	98	93
6	*m*-$MeOC_6H_4$	*p*-$Me_2NC_6H_4$	99	91
7	*p*-$MeOC_6H_4$	*o*-MeC_6H_4	78	59
8	*o*-MeC_6H_4	*p*-$MeOC_6H_4$	87	85
9	*o*-MeC_6H_4	*p*-$Me_2NC_6H_4$	99	99
10[c]	*o*-MeC_6H_4	*p*-$Me_2NC_6H_4$	99	92
11	*p*-$PhC(O)C_6H_4$	*p*-MeC_6H_4	99	80
12	*p*-$EtOOCC_6H_4$	*p*-MeC_6H_4	99	99
13[c]	*p*-$EtOOCC_6H_4$	*p*-MeC_6H_4	97	84
14	*p*-$EtOOCC_6H_4$	*o*-MeC_6H_4	99	92
15	*p*-$EtOOCC_6H_4$	*p*-$MeOC_6H_4$	99	99
16[c]	*p*-$EtOOCC_6H_4$	*p*-$MeOC_6H_4$	96	90
17	*p*-$CF_3C_6H_4$	*p*-MeC_6H_4	99	85
18	*p*-$CF_3C_6H_4$	*p*-$MeOC_6H_4$	96	82
19	*p*-$PhC(O)C_6H_4$	*p*-$CF_3C_6H_4$	83	61
20[d]	*p*-$PhC(O)C_6H_4$	*p*-$CF_3C_6H_4$	98	86
21	*p*-$EtOOCC_6H_4$	*p*-$CF_3C_6H_4$	97	88
22	*p*-$MeOC_6H_4$	*p*-$CF_3C_6H_4$	56	28
23	2-Py	*p*-MeC_6H_4	76	53
24[d]	2-Py	*p*-MeC_6H_4	99	71
25	2-Py	*p*-$MeOC_6H_4$	70	70
26[d]	2-Py	*p*-$MeOC_6H_4$	91	75

[a]Unless otherwise stated, reactions were carried out according to the conditions indicated by the above equation using 0.5 mmol of aryltrimethylammonium iodides and 0.75 mmol of arylzinc chlorides; arylzinc chlorides were prepared from the corresponding arylmagnesium bromides and $ZnCl_2$ in the presence of 2 equiv of LiCl. [b]Isolated yield. [c]0.125 mol % of **7c** or 0.25 mol % of **4b** was employed. [d]0.5 mol % of **7c** or 1 mol % of **4b** was employed.

For comparison, the catalysis of complex **4b** was tested for each reaction (Table 5). Complex **4b** showed good catalytic activity in quite a few reactions tested but exhibited lower activity than complex **7c** in almost every case under comparable conditions.

Several nickel-catalyzed cross-coupling reactions of aryltrimethylammonium salts and arylzinc reagents have been reported.[6b,c,e] The dinuclear complex **7c** exhibited the highest activity in comparison with the reported complexes. For example, the $Ni(PCy_3)_2Cl_2$-catalyzed reaction of *p*-$MeOC_6H_4NMe_3^+I^-$ with *p*-MeC_6H_4ZnCl required 2 mol % catalyst loading and 90 °C reaction temperature.[6e] The same reaction catalyzed by the pincer nickel complex [Ni(Cl){N(2-$Ph_2PC_6H_4$)(C(Ph)=NC_6H_4Me-4′)}] required 1 mol % catalyst loading and 85 °C reaction temperature.[6b] However, the reaction catalyzed by **7c** proceeded under milder conditions (65 °C), required a lower catalyst amount (0.25 mol % **7c**), and gave a higher product yield (96%).

(3). Catalytic Coupling of Aryl Sulfamates with Aryl Grignard Reagents. $PhOSO_2NMe_2$ and *p*-$MeOC_6H_4MgBr$ were used as reactants and **7c** was used as the catalyst for the screening of reaction conditions. The reaction gave a low yield when it was performed in THF at room temperature for 12 h with 0.5 mol % catalyst loading. The product yield was markedly increased when the reaction time was prolonged to 24 h and the reaction temperature was raised to 35 °C (Table 6, entries 1−3). The reaction was further improved when the catalyst loading was increased to 0.75 mol %, 88% yield being achieved (Table 6, entry 4). Other solvents, including Et_2O, dioxane, and toluene, were also examined, and they were proven to be less effective than THF (Table 6, entries 5−7).

Table 6. Optimization of Reaction Conditions and Evaluation of Catalytic Activity of Complexes 4a,b and 7a−d in the Cross-Coupling Reactions of $PhOSO_2NMe_2$ with *p*-$MeOC_6H_4MgBr$[a]

entry	complex (amt (mol %))	solvent	*T* (°C)	yield (%)[b]
1[c]	**7c** (0.5)	THF	25	8
2[c]	**7c** (0.5)	THF	35	27
3	**7c** (0.5)	THF	35	69
4	**7c** (0.75)	THF	35	88
5	**7c** (0.75)	Et_2O	35	38
6	**7c** (0.75)	dioxane	35	34
7	**7c** (0.75)	toluene	35	78
8	**7a** (0.75)	THF	35	69
9	**7b** (0.75)	THF	35	82
10	**7d** (0.75)	THF	35	87
11	**4a** (1.5)	THF	35	65
12	**4b** (1.5)	THF	35	71

[a]Unless otherwise stated, the reactions were run for 24 h using 0.5 mmol of $PhOSO_2NMe_2$ and 0.75 mmol of *p*-$MeOC_6H_4MgBr$. [b]Isolated yield. [c]Reaction time was 12 h.

Complexes **7a,b,d** and **4a,b** were tested under the optimized conditions. Complex **7d** showed almost the same activity as **7c**, and they are more active than **7b** and **7a**. The activity of complex **4b** is close to that of **7a** and higher than that of **4a**. The activity order is **7c** ≅ **7d** > **7b** > **7a** ≅ **4b** > **4a** (Table 6, entries 8−12). The results are consistent with those seen in Catalytic Coupling of Aryl Chlorides with Arylzinc Chlorides and Catalytic Coupling of Aryltrimethylammonium Salts with Arylzinc Chlorides. Thus, the dinuclear complexes with a 1,4-butylene linker are more active than the complexes with a 1,3-propylene linker. The dinuclear complexes also exhibited higher activity than the mononuclear complexes under comparable conditions (**7b** vs **4a** and **7c** vs **4b**).

Complexes **7c,d** exhibited almost the same activity on the basis of the above evaluation. We chose **7c** as the catalyst to examine the substrate scope under the optimized conditions. $PhOSO_2NMe_2$ also reacted smoothly with *p*-$Me_2NC_6H_4MgBr$ in the presence of **7c**, giving *p*-$Me_2NC_6H_4Ph$ in 96% yield (Table 7, entry 1). The deactivated aryl sulfamate *p*-$MeOC_6H_4OSO_2NMe_2$ reacted with *p*-MeC_6H_4MgBr to afford 4-methoxy-4′-methylbiphenyl in 90% yield. No C−OMe bond activation was observed. The reaction of *p*-$Me_2NC_6H_4MgBr$ with *p*-$MeOC_6H_4OSO_2NMe_2$ gave an unusually low yield in comparison with *p*-MeC_6H_4MgBr for unclear reasons. Increasing the catalyst loading to 1 mol % resulted in a 99% yield of the desired product (Table 7, entries 2−4). The reaction of *o*-MeC_6H_4MgBr with *p*-$MeOC_6H_4OSO_2NMe_2$ gave a yield much lower than that of *p*-MeC_6H_4MgBr (72% vs 90%). This is ascribed to the steric hindrance of *o*-MeC_6H_4MgBr (Table 7,

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Table 7. Reaction of Aryl Sulfamates with Aryl Grignard Reagents Catalyzed by 7c or 4b[a]

$$Ar^1\text{-}OSO_2NMe_2 + Ar^2\text{-}MgBr \xrightarrow[\text{THF, 35 °C, 24 h}]{\textbf{7c}\ (0.75\ \text{mol \%})\ \text{or}\ \textbf{4b}\ (1.5\ \text{mol \%})} Ar^1\text{-}Ar^2$$

			yield (%)[b]	
entry	Ar^1	Ar^2	**7c**	**4b**
1	Ph	*p*-$Me_2NC_6H_4$	96	83
2	*p*-$MeOC_6H_4$	*p*-MeC_6H_4	90	83
3	*p*-$MeOC_6H_4$	*p*-$Me_2NC_6H_4$	78	46
4[c]	*p*-$MeOC_6H_4$	*p*-$Me_2NC_6H_4$	99	91
5	*p*-$MeOC_6H_4$	*o*-MeC_6H_4	72	43
6	*o*-MeC_6H_4	*p*-$MeOC_6H_4$	81	62
7	*o*-MeC_6H_4	*p*-$Me_2NC_6H_4$	93	89
8	2-naphthyl	*p*-$MeOC_6H_4$	99	93
9	2-naphthyl	*p*-$Me_2NC_6H_4$	99	92
10[d]	*p*-$EtOOCC_6H_4$	*p*-MeC_6H_4	97	89
11[d]	*p*-$EtOOCC_6H_4$	*o*-MeC_6H_4	99	80
12[d]	*p*-$EtOOCC_6H_4$	*p*-$MeOC_6H_4$	99	78
13	*p*-$CF_3C_6H_4$	*p*-MeC_6H_4	86	72
14	*p*-$CF_3C_6H_4$	*p*-$MeOC_6H_4$	78	56
15[c]	*p*-$CF_3C_6H_4$	*p*-$MeOC_6H_4$	83	61
16	*p*-$CF_3C_6H_4$	*p*-$Me_2NC_6H_4$	89	83
17	2-Py	*p*-MeC_6H_4	99	90
18	2-Py	*p*-$MeOC_6H_4$	92	56

[a]Unless otherwise stated, reactions were performed with 0.5 mmol of aryl sulfamates and 0.75 mmol of arylmagnesium bromides according to the conditions indicated by the above equation. [b]Isolated yield. [c]1 mol % of **7c** or 2 mol % of **4b** was employed. [d]LiCl (2 equiv) was added.

entry 5). Greater catalyst loadings did not further improve the product yield. The reaction between *o*-$MeC_6H_4OSO_2NMe_2$ and *p*-$MeOC_6H_4MgBr$ suffered the same situation, affording only 81% product yield. However, *p*-$Me_2NC_6H_4MgBr$ behaved better in the reaction with *o*-$MeC_6H_4OSO_2NMe_2$, the cross-coupling product being isolated in 93% yield (Table 7, entries 6 and 7). 2-Naphthyl sulfamate is also a slightly sterically hindered electrophile. However, it showed reactivity higher than that of *o*-$MeC_6H_4OSO_2NMe_2$. Its reaction with either *p*-$MeOC_6H_4MgBr$ or *p*-$Me_2NC_6H_4MgBr$ gave the corresponding products quantitatively (Table 7, entries 8 and 9). *p*-$EtOC(O)C_6H_4OSO_2NMe_2$ can react with a Grignard reagent in the presence of 2 equiv of LiCl. In the absence of LiCl, partial addition products were observed. As an electron-poor electrophile, it showed high reactivity, as expected. It reacted smoothly with *p*-MeC_6H_4MgBr, *p*-$MeOC_6H_4MgBr$, and even *o*-MeC_6H_4MgBr in the presence of 0.75 mol % of **7c**, giving the desired products in 97%−99% yields (Table 7, entries 10−12). *p*-$CF_3C_6H_4OSO_2NMe_2$ also reacted with *p*-MeC_6H_4MgBr, *p*-$MeOC_6H_4MgBr$, and *p*-$Me_2NC_6H_4MgBr$, respectively, in good to excellent yields. However, it displayed lower reactivity in comparison with *p*-$EtOC(O)C_6H_4OSO_2NMe_2$ (Table 7, entries 13−16). 2-Pyridyl sulfamate is a good electrophile in the reaction with *p*-MeC_6H_4MgBr or *p*-$MeOC_6H_4MgBr$ in the presence of 0.75 mol % of **7c**, an excellent product yield being achieved in each reaction (Table 7, entries 17 and 18). For comparison, each reaction given in Table 7 was also carried out in the presence of **4b**. **4b** exhibited good catalytic activity, but it was lower than that of **7c**.

The nickel-catalyzed Kumada-type coupling of sulfamates is very rare. Macklin and Snieckus reported that Ni(Cl)(Cp)IMes can catalyze the reaction of aryl sulfamates with aryl Grignard reagents.[10j] Complex **7c** exhibited better catalytic results than Ni(Cl)(Cp)IMes. For example, the Ni(Cl)(Cp)IMes-catalyzed reaction of *p*-$MeOC_6H_4OSO_2NMe_2$ with PhMgBr at 40 °C with 1 mol % catalyst loading gives the cross-coupling product in 47% yield. However, the **7c**-catalyzed reaction of *p*-$MeOC_6H_4OSO_2NMe_2$ with *p*-MeC_6H_4MgBr at 35 °C and 0.75 mol % catalyst loading leads to 90% yield of cross-coupling product.

The catalysts we present above show similar activity order for each type of reaction, including the activation and transformation of aryl C−Cl, C−N, and C−O bonds. The bimetallic complexes with $(CH_2)_4$ linkers are more active than that with a $(CH_2)_3$ linker and are superior to the monometallic systems. This is ascribed to bimetallic cooperative activation of the electrophilic substrate, as shown in Figure 3 (structure **B**). In

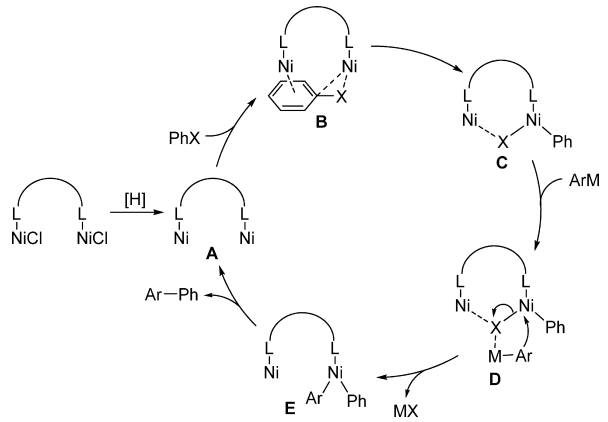

Figure 3. Possible catalytic cycle for the cross-couplings using the bimetallic catalyst.

structure **B** the aromatic ring of the electrophilic substrate coordinates to one of the nickel atoms of the active bimetallic species and the coordination promotes the oxidative addition of the C−X bond at another nickel atom through changing the electron distribution of the substrate. The length of the spacer between the two pincer nickel units affects the efficiency of bimetallic cooperation. This is supported by the experimental fact that the bimetallic systems with $(CH_2)_4$ linkers (**7b−d**) are more active than that with a $(CH_2)_3$ linker (**7a**) because an appropriate separation between the two metal centers is important for the cooperativity.[11c] In fact, the activity of **7a** is only slightly higher than that of mononuclear complex **4a** in the tested catalytic reactions. On the basis of the above analysis, a possible catalytic cycle using **7b−d** is proposed (Figure 3). Thus, the dinuclear Ni(II) complex is converted to the catalytically active nickel complex **A** at first through reduction by an arylmagnesium or -zinc reagent. The reaction of **A** with PhX results in complex **B**, which further transforms into the oxidative addition species **C**. Reaction of **C** with the arylmagnesium or -zinc reagent ArM forms **E** via **D**. Reductive elimination of Ar-Ph from **E** regenerates the active catalyst **A**. In previous studies of pincer nickel catalyzed cross-couplings, Ni(I)/Ni(III) intermediates were suggested in most cases.[5i,j,16a,l,k] We also observed an obvious inhibitory action of the free radical inhibitor 1,1-diphenylethylene to the reaction of *p*-ClC_6H_4OMe with *p*-MeC_6H_4ZnCl catalyzed by **7c**. However, on the basis of current experimental results, we cannot

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determine the oxidation states of the nickels in the catalytic cycle.

CONCLUSION

We have synthesized and characterized mono- and dinuclear P,N,N-pincer nickel complexes. These complexes were shown to be active catalysts for the cross-couplings of aryl chlorides or aryltrimethylammonium salts with arylzinc reagents, as well as of aryl sulfamates with aryl Grignard reagents. The reactions covered a broad scope of substrates, including electron-rich and -poor electrophiles and nucleophiles. A range of functional groups were tolerated in the Negishi-type reactions. Hence, these complexes are widely applicable catalysts for cross-couplings. The dinuclear complexes with 1,4-butylene linkers are more active than the complex with a 1,3-propylene linker. Complex **7c** displayed the highest activity in each type of coupling reaction, and **7d** exhibited comparable activity for the activation and transformation of aryl C−N and C−O bonds. Dinuclear complexes displayed catalytic activity higher than that of the mononuclear complexes under comparable conditions (**7b** vs **4a** and **7c** vs **4b**). This is ascribed to cooperative effects in a bimetallic system.

EXPERIMENTAL SECTION

All air- or moisture-sensitive manipulations were performed under nitrogen using standard Schlenk techniques. Toluene and dioxane were distilled under nitrogen over sodium, THF and diethyl ether were distilled under nitrogen over sodium/benzophenone;, CH_2Cl_2 was distilled under nitrogen over calcium hydride, and NMP, DMF, and DMA were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. $CDCl_3$ and DMSO-d_6 were purchased from Cambridge Isotope Laboratories and stored over activated molecular sieves. (DME)-$NiCl_2$,[24] (DME)$NiBr_2$,[24] 2-(phenylphosphino)aniline (**1**),[17] 2,2′-(propane-1,3-diylbis(phenylphosphinediyl))dianiline (**5a**), 2,2′-(butane-1,4-diylbis(phenylphosphinediyl))dianiline (**5b**),[18] Grignard reagents,[25] and aryl sulfamates[10e] were prepared according to the reported methods. Aryltrimethylammonium salts were obtained either by purchasing from commercial vendors or by preparation according to the procedures we used previously.[6e] NMR spectra were recorded on a Bruker av300 or Bruker avance III 400 spectrometer at ambient temperature. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was performed using an Elementar Vario EL Cube instrument. The mass spectrometry analysis was performed on a Bruker Autoflex Speed MALDI TOF mass spectrometer.

Synthesis of 2-$NH_2C_6H_4$P(Et)Ph (2). Sodium (0.46 g, 20 mmol) was added to a solution of (2-aminophenyl)phenylphosphine (4.02 g, 20 mmol) in THF (60 mL), and the resulting clear red solution was stirred overnight at room temperature. The reaction mixture was cooled to about −80 °C, and a solution of ethyl bromide (2.18 g, 20 mmol) in THF (50 mL) was added dropwise with stirring. The reaction mixture was warmed to ambient temperature and stirred for a further 48 h. An aqueous solution of ammonium chloride (20% w/w, 3 mL) was added, and the solvents were removed under reduced pressure. Water (45 mL) and dichloromethane (30 mL) were added to the residue. The organic layer was separated, and the water phase was extracted with dichloromethane (2 × 30 mL). The combined organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude product was distilled under reduced pressure to give a colorless liquid (1.97 g, 43%), bp 92 °C/0.1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (dt, J = 7.6, 17.6 Hz, 3H, CH_3), 1.96−2.12 (m, 2H, CH_2), 4.18 (b, 2H, NH_2), 6.63−6.67 (m, 1H, Ar), 6.76 (dt, J = 1.2, 7.6 Hz, 1H, Ar), 7.11−7.22 (m, 2H, Ar), 7.25−7.33 (m, 3H, Ar), 7.35−7.41 (m, 2H, Ar). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 10.2, 19.4, 115.5 (d, J = 2.7 Hz), 118.8 (d, J = 2.4 Hz), 119.8 (d, J = 10.3 Hz), 128.4, 128.5 (d, J = 14.2 Hz), 130.4 (s), 132.2 (d, J = 17.2 Hz), 132.7 (d, J = 3.1 Hz), 138.2 (d, J = 10.4 Hz), 150.5 (d, J = 18.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −29.75. Anal. Calcd for $C_{14}H_{16}NP$: C, 73.35; H, 7.03; N, 6.11. Found: C, 73.41; H, 7.00; N, 6.06.

Synthesis of 2-(C_4H_4N-2′-CH═N)C_6H_4P(Et)Ph (3). A mixture of pyrrole-2-carboxaldehyde (0.43 g, 4.5 mmol), **2** (0.92 g, 4 mmol), activated 4 Å molecular sieves (10 g), and toluene (60 mL) was heated at 90 °C for 26 h with stirring. The mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure, and the residue was recrystallized from ethanol to give yellow crystals of **3** (0.95 g, 78%), mp 104−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (dt, J = 7.6, 16.8 Hz, 3H, CH_3), 1.92−2.02 (m, 1H, CH_2), 2.04−2.14 (m, 1H,CH_2), 6.24−6.27 (m, 1H, Ar), 6.52−6.57 (m, 1H, Ar), 6.92 (s, 1H, Ar), 6.94−6.98 (m, 1H, Ar), 7.17 (t, J = 7.4 Hz, 1H, Ar), 7.22−7.30 (m, 4H, Ar), 7.33 (dt, J = 1.2, 7.6 Hz, 1H, Ar), 7.38−7.47 (m, 2H, Ar), 7.99 (s, 1H, CH═N), 9.14 (b, 1H, NH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 10.5 (d, J = 17.3 Hz), 19.6 (d, J = 10.1 Hz), 110.4, 116.0, 117.5 (d, J = 1.8 Hz), 122.9, 125.4 (d, J = 1.3 Hz), 128.3 (d, J = 7.2 Hz), 128.5, 129.6, 131.1 (d, J = 3 Hz), 131.2, 133.3 (d, J = 19.3 Hz), 133.6 (d, J = 13.7 Hz), 138.8 (d, J = 12.3 Hz), 148.6, 154.3 (d, J = 15.4 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −19.76. Anal. Calcd for $C_{19}H_{19}N_2P$: C, 74.49; H, 6.25; N, 9.14. Found: C, 74.27; H, 6.21; N, 9.15.

Synthesis of [Ni{2-(C_4H_3N-2′-CH═N)C_6H_4P(Et)Ph}Cl] (4a). A solution of compound **3** (0.67 g, 2.2 mmol) in THF (10 mL) was added dropwise to a suspension of NaH (0.1 g, 60% dispersion in mineral oil, 2.5 mmol) in THF (5 mL) at 0 °C with stirring. The resultant mixture was stirred for 6 h at room temperature. This solution was then transferred into a suspension of (DME)$NiCl_2$ (0.55 g, 2.5 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed in vacuo. The residue was dissolved in CH_2Cl_2 and the solution filtered by the use of a cannula fitted with filter paper. The filtrate was concentrated to give red crystals of complex **4a** (0.67 g, 76%), mp 178−180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (dt, J = 7.6, 20.8 Hz, 3H, CH_3), 1.98−2.12 (m, 1H, CH_2), 2.54−2.66 (m, 1H, CH_2), 6.29−6.34 (m, 1H, Ar), 6.95 (d, J = 3.9 Hz, 1H, Ar), 7.16 (t, J = 7 Hz, 1H, Ar), 7.20 (s, 1H, Ar), 7.35 (t, J = 8.0 Hz, 1H, Ar), 7.39−7.52 (m, 5H, Ar), 7.68−7.78 (m, 2H, Ar), 7.80 (d, J = 2.4 Hz, 1H, *CH*═N). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.9, 18.6 (d, J = 32.1 Hz), 114.6 (d, J = 10.3 Hz), 116.0 (d, J = 3.9 Hz), 122.4 (d, J = 1.3 Hz), 124.4, 124.9, 125.7 (d, J = 6.5 Hz), 129.2 (d, J = 10.6 Hz), 129.7, 131.1 (d, J = 2.9 Hz), 131.9 (d, J = 9.4 Hz), 132.3 (d, J = 1.4 Hz), 133.4 (d, J = 1.9 Hz), 141.5 (d, J = 1.4 Hz), 142.4, 150.0 (d, J = 2.1 Hz), 154.4 (d, J = 20.3 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 31.32. MS: m/z 398.0568 $[M]^+$; calcd for $C_{19}H_{18}ClN_2NiP$ 398.0250. Anal. Calcd for $C_{19}H_{18}ClN_2NiP$: C, 57.13; H, 4.54; N, 7.01. Found: C, 57.48; H, 4.67; N, 6.88.

Synthesis of [Ni{2-(C_4H_3N-2′-CH═N)C_6H_4P(Et)Ph}Br] (4b). Complex **4b** was synthesized using the same procedure as for **4a**. Thus, compound **3** (0.674 g, 2.2 mmol) was treated with NaH (0.1 g, 60%, 2.5 mmol) and the resulting sodium salt was further treated with (DME)$NiBr_2$ (0.772 g, 2.5 mmol) to generate a dark red crystalline solid of complex **4b** (0.83 g, 85%), mp 186−188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (dt, J = 7.6, 21.2 Hz, 3H, CH_3), 2.07−2.21 (m, 1H, CH_2), 2.63−2.76 (m, 1H, CH_2), 6.31 (s, 1H, Ar), 6.97 (d, J = 3.2 Hz, 1H, Ar), 7.15 (t, J = 6 Hz, 1H, Ar), 7.31 (t, J = 8 Hz, 1H, Ar), 7.35 (s, 1H, Ar), 7.38−7.53 (m, 5H, Ar), 7.66−7.79 (m, 2H, Ar), 7.89 (d, J = 1.6 Hz, 1H, *CH*═N). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 8.9, 19.2 (d, J = 33.8 Hz), 114.5 (d, J = 10.2 Hz), 116.3 (d, J = 3.7 Hz), 122.5 (d, J = 1.1 Hz), 125.3, 125.7, 125.9 (d, J = 6.5 Hz), 129.1 (d, J = 10.5 Hz), 129.8, 130.3, 131.1 (d, J = 3 Hz), 132.1 (d, J = 9.2 Hz), 132.3 (d, J = 1.2 Hz), 133.4 (d, J = 1.8 Hz), 142.7, 149.9 (d, J = 1.8 Hz), 154.1 (d, J = 20.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 35.46. MS: m/z 441.9783 $[M]^+$; calcd for $C_{19}H_{18}BrN_2NiP$ 441.9744. Anal. Calcd for $C_{19}H_{18}BrN_2NiP$: C, 51.41; H, 4.09; N, 6.31. Found: C, 51.77; H, 4.08; N, 6.36.

Synthesis of [2-(C_4H_4N-2′-CH═N)C_6H_4P(Ph)]$_2$(CH_2)$_3$ (6a). A mixture of pyrrole-2-carboxaldehyde (0.82 g, 8.7 mmol), compound **5a**

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(1.77 g, 4 mmol), 4 Å molecular sieves (15 g), and toluene (60 mL) was heated at 90 °C for 26 h with stirring. The mixture was cooled to room temperature and then filtered. The filtrate was concentrated under reduced pressure. The residue was recrystallized from ethanol to afford pale yellow crystals of **6a** (1.26 g, 53%), mp 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (b, 0.6H, CH_2), 1.63 (b, 1.4H, CH_2), 2.22 (b, 2H, CH_2), 2.60−2.80 (m, 2H, CH_2), 6.17 (b, 2H, Ar), 6.59 (d, J = 25.7 Hz, 4H), 6.78 (b, 0.6H, Ar), 6.88 (b, 1.4H, Ar), 6.96−7.13 (m, 4H, Ar), 7.23−7.37 (m, 8H, Ar), 7.38−7.52 (m, 4H, Ar), 8.15 (s, 1.4 H, CH═N), 8.18 (s, 0.6H, CH═N), 10.57 (b, 1.4H, NH), 11.42 (b, 0.6H, NH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 21.8 (t, J = 13.6 Hz), 25.5 (t, J = 12.5 Hz), 27.0 (t, J = 12.1 Hz), 110.1, 110.3, 117.4, 117.6, 117.8, 124.06, 124.12, 125.5, 128.6 (d, J = 7.4 Hz), 128.9, 129.0, 129.4, 129.5, 130.8, 130.9, 131.9, 132.1, 133.9, 134.1, 134.4 (d, J = 21 Hz), 135.1 (d, J = 15.4 Hz), 136.1 (d, J = 12.5 Hz), 150.0, 154.0 (d, J = 16.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −23.89, −27.58. Anal. Calcd for $C_{37}H_{34}N_4P_2$·0.8EtOH: C, 73.18; H, 6.17; N, 8.84. Found: C, 73.25; H, 6.10; N, 8.84.

Synthesis of [2-(C_4H_4N-2′-CH═N)C_6H_4P(Ph)]$_2$(CH_2)$_4$ (6b). Compound **6b** was synthesized using the same procedure as for **6a**. Thus, the reaction of pyrrole-2-carboxaldehyde (0.82 g, 8.7 mmol) with **5b** (1.82 g, 4 mmol) in toluene (60 mL) in the presence of 4 Å molecular sieves (15 g) afforded, after similar workup, pale yellow crystals of compound **6b** (2.10 g, 86%), mp 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30−1.46 (m, 1H, CH_2), 1.47−1.68 (m, 3H, CH_2), 1.90−2.02 (m, 1H, CH_2), 2.14−2.26 (m, 1H, CH_2), 2.27−2.38 (m, 1H, CH_2), 2.63−2.75 (m, 1H, CH_2), 6.11−6.18 (m, 2H, Ar), 6.23 (b, 1H, Ar), 6.48 (b, 1H, Ar), 6.54 (b, 1H, Ar), 6.62 (b, 1H, Ar), 6.84 (dd, J = 4.4, 7.2 Hz, 1H, Ar), 6.91−6.99 (m, 2H, Ar), 7.07 (t, J = 7.2 Hz, 1H, Ar), 7.12−7.18 (m, 2H, Ar), 7.27−7.38 (m, 8H, Ar), 7.46−7.58 (m, 4H, Ar), 7.93 (s, 1H, CH═N), 8.12 (s, 1H, CH═N), 10.13 (b, 1H, NH), 10.49 (b, 1H, NH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 23.9 (d, J = 11.8 Hz), 24.7 (d, J = 10.2 Hz), 25.7 (t, J = 15.0 Hz), 26.4 (t, J = 14.3 Hz), 110.2 (d, J = 4.1 Hz), 117.1, 117.5, 118.4, 124.0, 124.4, 125.3 (d, J = 3.3 Hz), 125.5, 128.3 (d, J = 7.3 Hz), 128.6, 128.7, 129.2 (d, J = 8.8 Hz), 129.7, 130.7 (d, J = 12.1 Hz), 131.6 (d, J = 2.0 Hz), 132.4 (d, J = 9.3 Hz), 133.7 (d, J = 15.6 Hz), 133.8 (d, J = 19.8 Hz), 134.5, 134.6, 134.7, 136.3 (d, J = 11.6 Hz), 137.7 (d, J = 12.1 Hz), 150.0, 150.4, 154.7 (d, J = 16.6 Hz), 155.0 (d, J = 13.3 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −21.41, −22.53. Anal. Calcd for $C_{38}H_{36}N_4P_2$: C, 74.74; H, 5.94; N, 9.17. Found: C, 74.58; H, 6.01; N, 8.95.

Synthesis of [2-(5′-*t*BuC_4H_3N-2′-CH═N)C_6H_4P(Ph)]$_2$(CH_2)$_4$ (6c). Compound **6c** was synthesized using the same procedure as for **6a**. Thus, the reaction of 5-*tert*-butyl-1*H*-pyrrole-2-carbaldehyde (1.31 g, 8.7 mmol) with compound **5b** (1.82 g, 4 mmol) in toluene (60 mL) in the presence of 4 Å molecular sieves (15 g) afforded, after similar workup, a pale yellow crystalline solid of **6c** (1.18 g, 41%), mp 50−52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 18H, CH_3), 1.41−1.53 (m, 2H, CH_2), 1.54−1.67 (m, 2H, CH_2), 1.83−1.93 (m, 2H, CH_2), 1.96−2.07 (m, 2H, CH_2), 5.97 (d, J = 3.7 Hz, 2H, Ar), 6.41 (d, J = 3.7 Hz, 2H, Ar), 6.92 (dd, J = 3.5, 7.4 Hz, 2H, Ar), 7.13 (t, J = 7.6 Hz, 2H, Ar), 7.18−7.25 (m, 8H, Ar), 7.30 (dt, J = 1.2, 7.6 Hz, 2H, Ar), 7.33−7.40 (m, 4H, Ar), 7.86 (s, 2H, CH═N), 9.26 (b, 2H, NH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 26.8 (d, J = 11.2 Hz), 27.9 (m), 30.4 (s), 31.9 (s), 105.6 (s), 117.0 (s), 117.6 (s), 125.1 (s), 128.3 (dd, J = 11.1, 7.2 Hz), 129.6 (s), 129.9 (s), 130.8 (s), 133.3 (t, J = 18.3 Hz), 139.2 (d, J = 12.2 Hz), 148.1 (s), 148.6 (s), 154.6 (d, J = 15.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −24.64. Anal. Calcd for $C_{46}H_{52}N_4P_2$·1.3EtOH: C, 74.57; H, 7.70; N, 7.16. Found: C, 74.28; H, 7.72; N, 7.50.

Synthesis of [Ni{2-(C_4H_3N-2′-CH═N)C_6H_4P(Ph)}Cl]$_2$(CH_2)$_3$ (7a). A solution of **6a** (0.60 g, 1 mmol) in THF (10 mL) was added dropwise to a suspension of NaH (0.092 g, 60% dispersion in mineral oil, 2.3 mmol) in THF (5 mL) at 0 °C with stirring. The mixture was further stirred at room temperature for 6 h. The resulting solution was then transferred into a suspension of (DME)$NiCl_2$ (0.51 g, 2.3 mmol) in THF (10 mL) at about −80 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed in vacuo. The residue was dissolved in CH_2Cl_2 and filtered by the use of a cannula fitted with filter paper. The filtrate was concentrated to give red crystals of **7a** (0.41 g, 47%), mp 198−200 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (b, 2H, CH_2), 2.71−2.85 (m, 2H, CH_2), 3.66 (b, 2H, CH_2), 5.75 (s, CH_2Cl_2), 6.30 (d, J = 2.4 Hz, 2H, Ar), 6.98−7.02 (m, 6H, Ar), 7.26 (d, J = 6.8 Hz, 2H, Ar), 7.40−7.47 (m, 6H, Ar), 7.55 (t, J = 7.2 Hz, 2H, Ar), 7.75 (d, J = 8.4 Hz, 2H, Ar), 7.92 (d, J = 6.8 Hz, 4H, Ar), 8.45 (s, 2H, CH═N). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 19.0, 24.7, 114.9, 115.6, 122.0, 126.3, 129.1, 131.5 (d, J = 19.3 Hz), 132.0, 133.3, 139.2, 142.3, 153.1, 153.7. ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ 28.04. MS: m/z 744.9958 [M − Cl]$^+$; calcd for $C_{37}H_{32}ClN_4Ni_2P_2$ 745.0498. Anal. Calcd for $C_{37}H_{32}Cl_2N_4Ni_2P_2$·0.15$CH_2Cl_2$: C, 56.08; H, 4.09; N, 7.04. Found: C, 56.09; H, 4.14; N, 6.91. **7a** cocrystallizes with CH_2Cl_2, and the CH_2Cl_2 molecules can be partially removed under vacuum. The CH_2Cl_2 signal can be observed in its ^{1}H NMR spectrum (δ 5.75).

Synthesis of [Ni{2-(C_4H_3N-2′-CH═N)C_6H_4P(Ph)}Cl]$_2$(CH_2)$_4$ (7b). Complex **7b** was synthesized using the same procedure as for **7a**. Thus, the sodium salt prepared from **6b** (0.61 g, 1 mmol) and NaH (0.092 g, 60% dispersion in mineral oil, 2.3 mmol) was treated with (DME)$NiCl_2$ (0.51 g, 2.3 mmol) afforded, after workup, a red crystalline solid of complex **7b** (0.54 g, 67%), mp 238−240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05−2.25 (m, 4H, CH_2), 2.38−2.54 (m, 2H, CH_2), 2.55−2.68 (m, 2H, CH_2), 5.30 (s, CH_2Cl_2), 6.30−6.36 (m, 2H, Ar), 6.93 (d, J = 3.9 Hz, 2H, Ar), 7.05 (t, J = 7.4 Hz, 2H, Ar), 7.14 (s, 2H, Ar), 7.17−7.21 (m, 2H, Ar), 7.31−7.50 (m, 10H, Ar), 7.60 (d, J = 2.7 Hz, 2H, Ar), 7.70−7.82 (m, 4H, Ar + CH═N). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 23.9, 24.2, 25.8 (dd, J = 1.6, 13.9 Hz), 53.6 (CH_2Cl_2), 114.8 (d, J = 10.4 Hz), 115.7 (d, J = 3.9 Hz), 122.1, 124.3, 124.7, 126.1 (d, J = 6.5 Hz), 129.2 (d, J = 10.7 Hz), 129.7 (s), 131.2 (d, J = 2.8 Hz), 131.9 (d, J = 9.6 Hz), 132.5, 133.4, 141.1, 142.4, 150.2, 153.8 (d, J = 9.6 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 27.61. MS: m/z 760.9639 [M − Cl]$^+$; calcd for $C_{38}H_{34}ClN_4Ni_2P_2$ 761.0609. Anal. Calcd for $C_{38}H_{34}Cl_2N_4Ni_2P_2$: C, 57.27; H, 4.30; N, 7.03. Found: C, 57.24; H, 4.12; N, 7.02. **7b** cocrystallizes with CH_2Cl_2 (indicated by the NMR spectra), and the CH_2Cl_2 molecules can be removed by pumping the sample for a long time.

Synthesis of [Ni{2-(C_4H_3N-2′-CH═N)C_6H_4P(Ph)}Br]$_2$(CH_2)$_4$ (7c). Complex **7c** was synthesized using the same procedure as for **7a**. Thus, the sodium salt prepared from **6b** (0.61 g, 1 mmol) and NaH (0.092 g, 60% dispersion in mineral oil, 2.3 mmol) was treated with (DME)$NiBr_2$ (0.71 g, 2.3 mmol) to afford dark red crystals of complex **7c** (0.75 g, 85%), mp 244−246 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00−2.16 (m, 2H, CH_2), 2.17−2.34 (m, 2H, CH_2), 2.36−2.56 (m, 2H, CH_2), 2.66−2.82 (m, 2H, CH_2), 6.32 (b, 2H, Ar), 6.95 (d, J = 3.2 Hz, 2H, Ar), 7.07 (t, J = 3.2 Hz, 2H, Ar), 7.16 (dd, J = 3.6, 8.0 Hz, 2H, Ar), 7.26 (s, 2H, Ar), 7.29−7.50 (m, 10H, Ar), 7.63 (d, J = 1.6 Hz, 2H, Ar), 7.68−7.78 (m, 4H, Ar + CH═N). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 24.5, 24.8, 25.7 (dd, J = 2.2, 13.7 Hz), 114.9 (d, J = 10.3 Hz), 115.9 (d, J = 3.6 Hz), 122.1, 125.1, 125.5, 126.2 (d, J = 6.5 Hz), 129.1 (d, J = 10.7 Hz), 131.2 (d, J = 2.8 Hz), 132.0 (d, J = 9.5 Hz), 132.4, 133.4, 142.1, 142.7, 150.2 (d, J = 1.6 Hz), 153.5 (d, J = 20.4 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 31.57. MS: m/z 805.0887 [M − Br]$^+$; calcd for $C_{38}H_{34}BrN_4Ni_2P_2$ 805.0129. Anal. Calcd for $C_{38}H_{34}Br_2N_4Ni_2P_2$: C, 51.52; H, 3.87; N, 6.32. Found: C, 51.23; H, 3.95; N, 6.31.

Synthesis of [Ni{2-(5′-*t*BuC_4H_2N-2′-CH═N)C_6H_4P(Ph)}-Cl]$_2$(CH_2)$_4$ (7d). Complex **7d** was synthesized using the same procedure as for **7a**. Thus, the sodium salt prepared from **6c** (0.72 g, 1 mmol) and NaH (0.092 g, 60% dispersion in mineral oil, 2.3 mmol) was treated with (DME)$NiCl_2$ (0.51 g, 2.3 mmol) to form, after similar workup, a red crystalline solid of complex **7d** (0.39 g, 43%), mp 160−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 18H, CH_3), 1.90−2.04 (m, 2H, CH_2), 2.05−2.21 (m, 2H, CH_2), 2.48−2.64 (m, 2H, CH_2), 2.81−2.92 (m, 2H, CH_2), 5.30 (s, CH_2Cl_2), 6.31 (dd, J = 2.0, 4.0 Hz, 2H, Ar), 6.86 (d, J = 4.0 Hz, 2H, Ar), 6.93 (t, J = 7.2 Hz, 2H, Ar), 7.17−7.20 (m, 2H, Ar), 7.24−7.32 (m, 4H, Ar), 7.40 (dt, J = 2.0, 7.6 Hz, 4H, Ar), 7.46−7.52 (m, 4H, Ar), 7.72−7.77 (m, 4H, Ar + CH═N). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 24.4, 24.7, 25.5 (d, J = 15.3 Hz), 31.1, 34.0, 114.0 (d, J = 10.8 Hz), 115.3 (d, J = 4.4 Hz), 123.7, 124.2, 124.6, 125.0 (d, J = 6.4 Hz), 129.1 (d, J = 10.9 Hz),

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129.9, 130.4, 131.1 (d, J = 2.9 Hz), 131.9 (d, J = 2.2 Hz), 132.0 (d, J = 10.1 Hz), 133.5 (d, J = 1.5 Hz), 143.3 (d, J = 1.7 Hz), 148.0, 154.3 (d, J = 20.9 Hz), 170.8 (d, J = 4.4 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 22.15. MS: m/z 873.1777 $[M - Cl]^+$; calcd for $C_{46}H_{50}ClN_4Ni_2P_2$ 873.1861. Anal. Calcd for $C_{46}H_{50}Cl_2N_4Ni_2P_2 \cdot 0.1CH_2Cl_2$: C, 60.34; H, 5.51; N, 6.11. Found: C, 60.34 H, 5.51 N, 6.11%. **7d** cocrystallizes with CH_2Cl_2, and the CH_2Cl_2 molecules can be partially removed under vacuum. The CH_2Cl_2 signal can be observed in its ^1H NMR spectrum (δ 5.30).

X-ray Crystallography. Single crystals of complexes **4b** and **7c** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on an Oxford Diffraction Gemini S Ultra diffractometer with mirror-monochromated Cu Kα radiation (λ = 1.54184 Å). The structures were solved by direct methods using SHELXS-97[26] and refined against F^2 by full-matrix least squares using SHELXL-97 (for **4b**) or SHELXL-2013 (for **7c**).[27] Hydrogen atoms were placed in calculated positions. Due to large thermal vibration and disorder of the CH_2Cl_2 molecules in **7c** crystals, ISOR restraints were applied to the U_{ij} values of the carbon and chlorine atoms. Crystal data and experimental details of the structure determinations are given in Table S-1 (Supporting Information).

General Procedure for the Negishi Cross-Coupling of Aryl Chlorides. A thick-walled Schlenk tube was charged with aryl chloride (0.5 mmol), NMP (1.5 mL), and complex **4b** (0.005 mmol) or **7c** (0.0025 mmol). To the stirred mixture was added ArZnCl solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) by syringe. The reaction mixture was stirred at 90 °C (bath temprature and the Schlenk tube was sealed) for 12 h. Water (10 mL) and several drops of acetic acid were successively added. The mixture was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

General Procedure for Reaction of ArZnCl with Aryltrimethylammonium Iodides. A Schlenk tube was charged with aryltrimethylammonium iodide (0.5 mmol), complex **4b** (0.0025 mmol) or **7c** (0.00125 mmol), and NMP (1.5 mL). To the stirred mixture was added ArZnCl solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) by syringe. The reaction mixture was stirred at 65 °C (bath temperature) for 12 h and then cooled to room temperature. Water (10 mL) and several drops of acetic acid were successively added. The resulting mixture was extracted with Et_2O (3 × 10 mL). The extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on sillca gel.

General Procedure for Reaction of ArMgBr with Aryl Sulfamates. A Schlenk tube was charged with aryl sulfamate (0.5 mmol), THF (1.5 mL), and complex **4b** (0.0075 mmol) or **7c** (0.00375 mmol). To the stirred mixture was added ArMgBr solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) slowly by syringe. The mixture was stirred at 35 °C for 24 h. Water (10 mL) and several drops of acetic acid were successively added. The mixture was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving characterization data for all compounds prepared in this paper and X-ray crystallographic data for complexes **4b** and **7c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) *Cross-Coupling Reactions: A Practical Guide*; Miyaura, N., Ed.; Springer: Berlin, 2002. (b) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004.

(2) (a) Miller, J. A.; Farrell, R. P. *Tetrahedron Lett.* **1998**, *39*, 6441. (b) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263. (c) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (d) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (e) Wolf, C.; Xu, H. *J. Org. Chem.* **2008**, *73*, 162. (f) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417.

(3) (a) Yang, L.-M.; Huang, L.-F.; Luh, T.-Y. *Org. Lett.* **2004**, *6*, 1461. (b) Shi, M.; Liu, L.-P.; Jie, T. *J. Org. Chem.* **2005**, *70*, 10420. (c) Wang, Z.-X.; Chai, Z.-Y. *Eur. J. Inorg. Chem.* **2007**, 4492. (d) Martin, R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3844. (e) Zhang, Y.; Song, G.; Ma, G.; Zhao, J.; Pan, C.; Li, X. *Organometallics* **2009**, *28*, 3233. (f) Jothibasu, R.; Huang, K.-W.; Huynh, H. V. *Organometallics* **2010**, *29*, 3746. (g) Ackermann, L.; Potukuchi, H.; Kapdi, A.; Schulzke, C. *Chem. Eur. J.* **2010**, *16*, 3300.

(4) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 2002. (b) Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719. (c) Burukin, A. S.; Vasilév, A. A.; Chizhov, A. O.; Zlotin, S. G. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 970. (d) Ackermann, L.; Born, R.; Spatz, J. H.; Althammer, A.; Gschrei, C. J. *Pure Appl. Chem.* **2006**, *78*, 209.

(5) (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (b) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461. (c) Fleckenstein, C. A.; Plenio, H. *Chem. Soc. Rev.* **2010**, *39*, 694. (d) Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555. (e) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Aldrichimica Acta* **2006**, *39*, 97. (f) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151. (g) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 3314. (h) Zhang, J.; Bellomo, A.; Trongsiriwat, N.; Jia, T.; Carroll, P. J.; Dreher, S. D.; Tudge, M. T.; Yin, H.; Robinson, J. R.; Schelter, E. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 6276. (i) Phapale, V. B.; Cárdenas, D. J. *Chem. Soc. Rev.* **2009**, *38*, 1598. (j) Wang, Z.-X.; Liu, N. *Eur. J. Inorg. Chem.* **2012**, 901. (k) Terao, J.; Watanabe, H.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2002**, *124*, 4222. (l) Terao, J.; Todo, H.; Watanabe, H.; Ikumi, A.; Kambe, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 6180. (m) Terao, J.; Nii, S.; Chowdhury, F. A.; Nakamura, A.; Kambe, N. *Adv. Synth. Catal.* **2004**, *346*, 905. (n) *Copper-mediated cross-coupling reactions*, Evano, G., Blanchard, N., Eds.; Wiley: Hoboken, NJ, 2014. (o) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (p) Li, J.; Li, X.; Wang, L.; Hu, Q.; Sun, H. *Dalton Trans.* **2014**, *43*, 6660. (q) Gosmini, C.; Bégouin, J.-M.; Moncomble, A. *Chem. Commun.* **2008**, 3221. (r) Hatakeyama, T.; Nakamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 9844. (s) Ghorai, S. K.; Jin, M.; Hatakeyama, T.; Nakamura, M. *Org. Lett.* **2012**, *14*, 1066. (t) Hatakeyama, T.; Hashimoto, S.; Ishizuka, K.; Nakamura, M. *J. Am. Chem. Soc.* **2009**, *131*, 11949. (u) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217. (v) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500.

(6) (a) Zhang, X.-Q.; Wang, Z.-X. *Org. Biomol. Chem.* **2014**, *12*, 1448. (b) Zhang, X.-Q.; Wang, Z.-X. *J. Org. Chem.* **2012**, *77*, 3658. (c) Zhang, Q.; Zhang, X.-Q.; Wang, Z.-X. *Dalton Trans.* **2012**, *41*, 10453. (d) Guo, W.-J.; Wang, Z.-X. *Tetrahedron* **2013**, *69*, 9580. (e) Xie, L.-G.; Wang, Z.-X. *Angew. Chem., Int. Ed.* **2011**, *50*, 4901. (f) Reeves, J. T.; Fandrick, D. R.; Tan, Z.; Song, J. J.; Lee, H.; Yee, N.

K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 4388. (g) Blakey, S. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 6046. (h) Buszek, K. R.; Brown, N. *Org. Lett.* **2007**, *9*, 707. (i) Wenkert, E.; Han, A.-L.; Jenny, C.-J. *J. Chem. Soc., Chem. Commun.* **1988**, 975.

(7) (a) Roglans, A.; Pla-Quintana, A.; Moreno-Mañas, M. *Chem. Rev.* **2006**, *106*, 4622. (b) Bonin, H.; Fouquet, E.; Felpinb, F.-X. *Adv. Synth. Catal.* **2011**, *353*, 3063. (c) Werner, E. W.; Sigman, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 9692. (d) Fabrizi, G.; Goggiamani, A.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4067. (e) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Persiani, D. *Org. Lett.* **2008**, *10*, 1597. (f) Cheng, K.; Wang, C.; Ding, Y.; Song, Q.; Qi, C.; Zhang, X.-M. *J. Org. Chem.* **2011**, *76*, 9261. (g) Mo, F.; Jiang, Y.; Qiu, D.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1846. (h) Wu, X.-F.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11142. (i) Callonnec, F. L.; Fouquet, E.; Felpin, F.-X. *Org. Lett.* **2011**, *13*, 2646. (j) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Commun.* **2011**, *47*, 7959.

(8) (a) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev.* **2011**, *111*, 1346. (b) Li, B.-J.; Yu, D.-G.; Sun, C.-L.; Shi, Z.-J. *Chem. Eur. J.* **2011**, *17*, 1728.

(9) (a) Quasdorf, K. W.; Tian, X.; Garg, N. K. *J. Am. Chem. Soc.* **2008**, *130*, 14422. (b) Guan, B.-T.; Wang, Y.; Li, B.-J.; Yu, D.-G.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 14468. (c) Antoft-Finch, A.; Blackburn, T.; Snieckus, V. *J. Am. Chem. Soc.* **2009**, *131*, 17750. (d) Chen, H.; Huang, Z.; Hu, X.; Tang, G.; Xu, P.; Zhao, Y.; Cheng, C.-H. *J. Org. Chem.* **2011**, *76*, 2338. (e) Zhao, F.; Zhang, Y.-F.; Wen, J.; Yu, D.-G.; Wei, J.-B.; Xi, Z.; Shi, Z.-J. *Org. Lett.* **2013**, *15*, 3230. (f) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486.

(10) (a) Mesganaw, T.; Garg, N. K. *Org. Process Res. Dev.* **2013**, *17*, 29. (b) Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270. (c) Chen, G.-J.; Han, F.-S. *Eur. J. Org. Chem.* **2012**, 3575. (d) Quasdorf, K. W.; Riener, M.; Petrova, K. V.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748. (e) Quasdorf, K. W.; Antoft-Finch, A.; Liu, P.; Silberstein, A. L.; Komaromi, A.; Blackburn, T.; Ramgren, S. D.; Houk, K. N.; Snieckus, V.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 6352. (f) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. *J. Org. Chem.* **2011**, *76*, 1507. (g) Leowanawat, P.; Zhang, N.; Percec, V. *J. Org. Chem.* **2012**, *77*, 1018. (h) Leowanawat, P.; Zhang, N.; Safi, M.; Hoffman, D. J.; Fryberger, M. C.; George, A.; Percec, V. *J. Org. Chem.* **2012**, *77*, 2885. (i) Zhang, N.; Hoffman, D. J.; Gutsche, N.; Gupta, J.; Percec, V. *J. Org. Chem.* **2012**, *77*, 5956. (j) Macklin, T. K.; Snieckus, V. *Org. Lett.* **2005**, *7*, 2519. (k) Gøgsig, T. M.; Lindhardt, A. T.; Skrydstrup, T. *Org. Lett.* **2009**, *11*, 4886. (l) Silberstein, A. L.; Ramgren, S. D.; Garg, N. K. *Org. Lett.* **2012**, *14*, 3796. (m) Ramgren, S. D.; Silberstein, A. L.; Yang, Y.; Garg, N. K. *Angew. Chem., Int. Ed.* **2011**, *50*, 2171. (n) Ackermann, L.; Sandmann, R.; Song, W. *Org. Lett.* **2011**, *13*, 1784. (o) Hie, L.; Ramgren, S. D.; Mesganaw, T.; Garg, N. K. *Org. Lett.* **2012**, *14*, 4182. (p) Park, N. H.; Teverovskiy, G.; Buchwald, S. L. *Org. Lett.* **2014**, *16*, 220. (q) Song, W.; Ackermann, L. *Angew. Chem., Int. Ed.* **2012**, *51*, 8251. (r) Ackermann, L.; Barfüsser, S.; Pospech, J. *Org. Lett.* **2010**, *12*, 724. (s) Xu, L.; Li, B.-J.; Wu, Z.-H.; Lu, X.-Y.; Guan, B.-T.; Wang, B.-Q.; Zhao, K.-Q.; Shi, Z.-J. *Org. Lett.* **2010**, *12*, 884. (t) Cívicos, J. F.; Gholinejad, M.; Alonso, D. A.; Nájera, C. *Chem. Lett.* **2011**, *40*, 907. (u) Li, B.-J.; Li, Y.-Z.; Lu, X.-Y.; Liu, J.; Guan, B.-T.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 10124.

(11) (a) Bratko, I.; Gómez, M. *Dalton Trans.* **2013**, *42*, 10664. (b) Park, J.; Hong, S. *Chem. Soc. Rev.* **2012**, *41*, 6931. (c) van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985. (d) Powers, D. C.; Ritter, T. *Acc. Chem. Res.* **2012**, *45*, 840. (e) van der Vlugt, J. I. *Eur. J. Inorg. Chem.* **2012**, 363.

(12) (a) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450. (b) Rodriguez, B.; Delferro, M.; Marks, T. J. *Organometallics* **2014**, *33*, 831. (c) Rodriguez, B.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2013**, *135*, 17651. (d) Weberski, M. P., Jr.; Chen, C.; Delferro, M.; Marks, T. J. *Chem. Eur. J.* **2012**, *18*, 10715. (e) Rodriguez, B.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 4971. (f) Radlauer, M. R.; Buckley, A. K.; Henling, L. M.; Agapie, T. *J. Am. Chem. Soc.* **2013**, *135*, 3784. (g) Radlauer, M. R.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 1478. (h) Radlauer, M. R.; Day, M. W.; Agapie, T. *Organometallics* **2012**, *31*, 2231.

(13) (a) Allan, L. E. N.; Bélanger, J. A.; Callagan, L. M.; Cameron, D. J. A.; Decken, A.; Shaver, M. P. *J. Organomet. Chem.* **2012**, *706*−*707*, 106. (b) Sun, S.; Nie, K.; Tan, Y.; Zhao, B.; Zhang, Y.; Shen, Q.; Yao, Y. *Dalton Trans.* **2013**, *42*, 2870. (c) Thibault, M.-H.; Fontaine, F.-G. *Dalton Trans.* **2010**, *39*, 5688. (d) Lian, B.; Thomas, C. M.; Casagrande, O. L., Jr.; Lehmann, C. W.; Roisnel, T.; Carpentier, J.-F. *Inorg. Chem.* **2007**, *46*, 328. (e) Arbaoui, A.; Redshaw, C.; Hughes, D. L. *Chem. Commun.* **2008**, 4717.

(14) (a) Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. *Chem. Eur. J.* **2012**, *18*, 1864. (b) Xi, Z.; Zhou, Y.; Chen, W. *J. Org. Chem.* **2008**, *73*, 8497. (c) Guisado-Barrios, G.; Hiller, J.; Peris, E. *Chem.*−*Eur. J.* **2013**, *19*, 10405. (d) Yoshikai, N.; Matsuda, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 9590. (e) Prabhu, R. N.; Ramesh, R. *Tetrahedron Lett.* **2012**, *53*, 5961. (f) Yang, J.; Li, P.; Zhang, Y.; Wang, L. *Dalton Trans.* **2014**, *43*, 7166. (g) Xue, F.; Zhao, J.; Hor, T. S. A. *Dalton Trans.* **2013**, *42*, 5150.

(15) (a) Matsunaga, S.; Shibasaki, M. *Chem. Commun.* **2014**, *50*, 1044. (b) Hellmuth, T.; Rieckhoff, S.; Weiss, M.; Dorst, K.; Frey, W.; Peters, R. *ACS Catal.* **2014**, *4*, 1850. (c) Wu, B.; Gallucci, J. C.; Parquette, J. R.; RajanBabu, T. V. *Chem. Sci.* **2014**, *5*, 1102. (d) Ford, D. D.; Nielsen, L. P. C.; Zuend, S. J.; Musgrave, C. B.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2013**, *135*, 15595. (e) Wang, J.; Liu, D.; Liu, Y.; Zhang, W. *Org. Biomol. Chem.* **2013**, *11*, 3855.

(16) (a) Wang, L.; Wang, Z.-X. *Org. Lett.* **2007**, *9*, 4335. (b) Zhang, C.; Wang, Z.-X. *Organometallics* **2009**, *28*, 6507. (c) Liu, N.; Wang, L.; Wang, Z.-X. *Chem. Commun.* **2011**, *47*, 1598. (d) Wu, D.; Wang, Z.-X. *Org. Biomol. Chem.* **2014**, *12*, 6414. (e) Zhang, X.-Q.; Wang, Z.-X. *Synlett* **2013**, *24*, 2081. (f) Guo, W.-J.; Wang, Z.-X. *J. Org. Chem.* **2013**, *78*, 1054. (g) Liu, N.; Wang, Z.-X. *J. Org. Chem.* **2011**, *76*, 10031. (h) Sun, K.; Wang, L.; Wang, Z.-X. *Organometallics* **2008**, *27*, 5649. (i) Wang, Z.-X.; Wang, L. *Chem. Commun.* **2007**, 2423. (j) Liang, L.-C.; Lee, W.-Y.; Hung, Y.-T.; Hsiao, Y.-C.; Cheng, L.-C.; Chen, W.-C. *Dalton Trans.* **2012**, *41*, 1381. (k) Hu, X. *Chem. Sci.* **2011**, *2*, 1867. (l) Hu, X. *Chimia* **2010**, *64*, 231. (m) Gu, S.; Chen, W. *Organometallics* **2009**, *28*, 909. (n) Anderson, T. J.; Jones, G. D.; Vicic, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 8100. (o) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 2756.

(17) Bennett, J.; Doyle, R. J.; Salem, G.; Willis, A. C. *Dalton Trans.* **2006**, 4614.

(18) Bennett, J.; Rae, A. D.; Salem, G.; Ward, N. C.; Waring, P.; Wells, K.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2002**, 234.

(19) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399.

(20) (a) Shirakawa, E.; Tamakuni, F.; Kusano, E.; Uchiyama, N.; Konagaya, W.; Watabe, R.; Hayashi, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 521. (b) Jin, L.; Liu, C.; Liu, J.; Hu, F.; Lan, Y.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B.; Lei, A. *J. Am. Chem. Soc.* **2009**, *131*, 16656.

(21) Gavryushin, A.; Kofink, C.; Manolikakes, G.; Knochel, P. *Tetrahedron* **2006**, *62*, 7521.

(22) Zapf, A.; Beller, M. *Chem. Eur. J.* **2001**, *7*, 2908.

(23) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

(24) Ward, L. G. L. *Inorg. Synth.* **1971**, *13*, 154.

(25) Elson, L. F.; McKillop, A.; Taylor, E. C. *Org. Synth.* **1976**, *55*, 48.

(26) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467.

(27) Sheldrick, G. M. *SHELXL97, Programs for structure refinement*; Universität Göttingen, Göttingen, Germany, 1997.