Synthesis and Characterization of Amido Pincer Complexes of Lithium and Nickel and Catalysis of the Nickel Complexes in the Kumada Cross-Coupling

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Reaction of *N*-benzylidene-2-(diphenylphosphino)benzenamine (**2**) with Ph_2PLi yielded [Li{N{CH(Ph)-PPh_2}C_6H_4(PPh_2)-2}] (**3**), and that with $Ph_2PCH_2Li\cdot$TMEDA generated [Li{N{CH(Ph)-CH_2PPh_2}C_6H_4(PPh_2)-2}] (**4**). Treatment of **3** with (DME)$NiCl_2$ gave [Ni(Cl){N{CH(Ph)PPh_2}C_6H_4-(PPh_2)-2}] (**5**). Reaction of **4** with $(Et_3P)_2NiCl_2$ afforded [Ni(Cl){N{CH(Ph)CH_2PPh_2}C_6H_4(PPh_2)-2}] (**6**). *N*-(2-(Diphenylphosphino)benzylidene)-2-(diphenylphosphino)benzenamine reacted with LiMe to give [Li{N{CH(Me)C_6H_4-(PPh_2)-2}{C_6H_4(PPh_2)-2}}] (**8**), which reacted with $(Et_3P)_2NiCl_2$ to produce [Ni(Cl){N{CH(Me)C_6H_4-(PPh_2)-2}{C_6H_4(PPh_2)-2}}] (**9**). **2** was converted to iminophosphoranes 2-{ArN=P(Ph_2)}C_6H_4N=CHPh (Ar = *p*-MeC_6H_4, **10a**; Ar = 2,6-$Pr^i_2C_6H_3$, **10b**) by reaction with *p*-$MeC_6H_4N_3$ and 2,6-$Pr^i_2C_6H_3N_3$, respectively. **10a** reacted with Ph_2PLi and then (DME)$NiCl_2$ to form [Ni(Cl){N{CH(Ph)PPh_2}C_6H_4[P(Ph_2)=NC_6H_4Me-4}-2}] (**11**). The respective reaction of **10a** and **10b** with $Ph_2PCH_2Li\cdot$TMEDA afforded [Li{N{CH(Ph)CH_2PPh_2}C_6H_4{P(Ph_2)=NAr}-2}] (Ar = *p*-MeC_6H_4, **12a**; Ar = 2,6-$Pr^i_2C_6H_3$, **12b**). Treatment of **12a** and **12b**, respectively, with (DME)$NiCl_2$ yielded corresponding nickel complexes [Ni(Cl){N{CH(Ph)CH_2PPh_2}C_6H_4{P(Ph_2)=NAr}-2}] (Ar = *p*-MeC_6H_4, **13a**; Ar = 2,6-$Pr^i_2C_6H_3$, **13b**). Compounds **10a** and **10b** and the lithium complexes **3**, **4**, **8**, **12a**, and **12b** were characterized by elemental analyses and NMR spectroscopy. The diamagnetic nickel complexes **6**, **9**, **13a**, and **13b** were characterized by elemental analyses, NMR spectroscopy, and mass spectra. The paramagnetic nickel complexes **5** and **11** were characterized by elemental analyses and mass spectra. The structures of compounds **2**, **6**, and **13a** were further characterized by single-crystal X-ray diffraction techniques. Catalysis of the nickel complexes in the Kumada cross-coupling was investigated. Complexes **5**, **6**, **11**, and **13a** exhibited high catalytic activity, while complexes **9** and **13b** showed relatively low catalytic activity.

Introduction

The search for appropriate ligands for effectively controlling the stability and reactivity of metal complexes has been an important topic of coordination and organometallic chemistry. As a result, a range of new ligands have become available. Recently amido pincer ligands have attracted considerable attention.[1−3] These ligands can stabilize main group and transition metal ions. Some of the complexes with this type of ligand displayed interesting reactivity, catalytic activity, or photoluminescent properties.[2−4] For example, the dinuclear copper complex of [Bu^i-PNP]$^-$, [Cu{Bu^i-PNP}]$_2$, has been found to be an exceptionally efficient luminophore that exhibits both an exceptionally high quantum yield and a long lifetime;[4] a rhodium complex of a bulky diarylamino-based PNP pincer ligand is an efficient catalyst for the dimerization of terminal alkynes and highly selective for the *trans*-enyne product.[3c] Amido pincer complexes of group 10 metals are also able to catalyze C−C cross-coupling such as Heck, Kumada, Suzuki, and Negishi reactions.[3h−n] On the other hand, the Kumada reaction, the first transition-metal-catalyzed cross-coupling reaction, discovered in 1972,[5] continues to attract considerable attention. Because boronic acids and other organometallic reagents used in C−C coupling reactions are usually derived from Grignard reagents,[6] the Kumada reaction offers a more direct approach to the desired products when the substrates tolerate the background reactivity of a Grignard reagent.[7] Some new catalytic systems have been developed in recent years to improve the activity of catalysts and extend the scope of substrates.[7,8] Recently we synthesized a new series of amido pincer complexes of nickel (Chart 1) and proved that they could efficiently catalyze the Kumada reaction.[9] We hope to further probe the structural effects on catalytic activity such as steric

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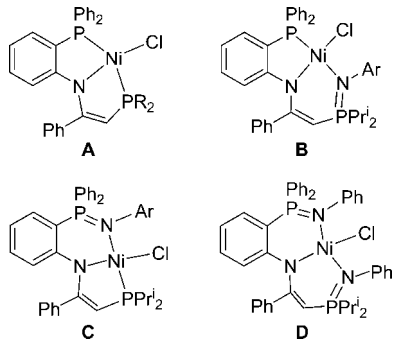
Chart 1

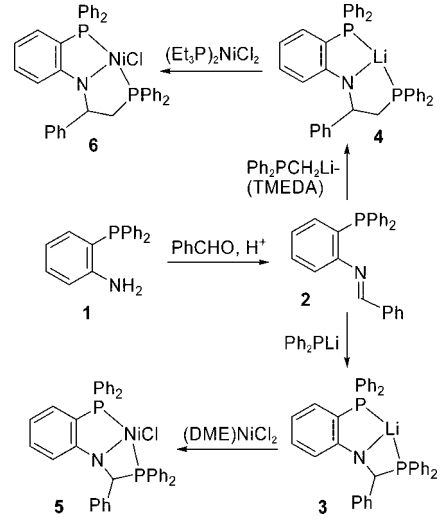


effects, chelate ring size, and ligand rigidity. Therefore we designed several related ligands, prepared their nickel complexes, and investigated the catalysis of the nickel complexes in the Kumada reaction. Herein we report the results.

Results and Discussion

Synthesis and Characterization of Compounds 2−13b. Synthesis of compounds **2**−**6** is summarized in Scheme 1. Compound **2** was prepared by a modified literature procedure.[10] Thus, a mixture of **1**, PhCHO, activated 4 Å molecular sieves, toluene, and three drops of HCOOH was stirred at room temperature for 12 h to afford compound **2** in good yield. This procedure required much less solvent and gave higher product yield compared with the previous procedure. Reaction of **2** with 1 equiv of Ph_2PLi gave the corresponding lithium complex **3**, while reaction with 1 equiv of $Ph_2PCH_2Li \cdot TMEDA$ generated complex **4**. Treatment of **3** with $(DME)NiCl_2$ afforded the nickel complex **5**. Reaction of **4** with $(Et_3P)_2NiCl_2$ produced the nickel complex **6**. Compound **2** is known and was characterized by ^1H NMR spectroscopy and single-crystal X-ray diffraction. Its ORTEP drawing is presented in Figure 1, along with selected bond lengths and angles. In the molecule, the phenyl group on the imine carbon atom is *trans* to the phenylene group on the nitrogen atom. C(18)N(1)C(19)C(20) atoms are coplanar, but the plane is not coplanar with the phenylene ring. The N(1)−C(19) distance of 1.274(3) Å is indicative of a C−N double bond. Complex **3** is a white solid, and complex **4** is yellow solid. Both of them are soluble in THF and ether and slightly soluble in hexane. They were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. The spectral and analytical results showed no coordinated solvent molecules or TMEDA in the complexes. However, recrystallization of **4** from THF gave a THF adduct. The ^1H NMR spectrum of **3** displayed a CH signal at δ 5.35 ppm as a doublet and corresponding phenyl and phenylene signals. The ^{31}P NMR spectrum gave two signals at δ −26.25 and 4.29 ppm, respectively. The ^1H NMR spectrum of **4**·THF exhibited THF, CH, CH_2, and aryl signals. Complex **5** is paramagnetic. This may be caused by the existence of a small chelate ring, which compels the central nickel atom to deviate from square-planar geometry. Complex **5** was characterized by elemental analysis and mass spectra. An electro-spray mass spectrum gave a $[M - Cl]^+$ fragment, and HR-MS gave a $[M - Cl - Ph_2P]^+$ fragment. Attempts to grow single crystals of complex **5** for X-ray diffraction analysis were unsuccessful. The solution of complex **5** in toluene was set aside for two months to form traces of crystals. An X-ray diffraction study proved it to be complex **5′**. Complex **5′** may be formed through oxidation of **5** due to leakage of air after storing for a long period. Complex **5′** is monomeric in the solid state and crystallizes with two molecules in the unit cell. An ORTEP structural drawing of a single molecule is shown in Figure 2, along with selected bond

Scheme 1



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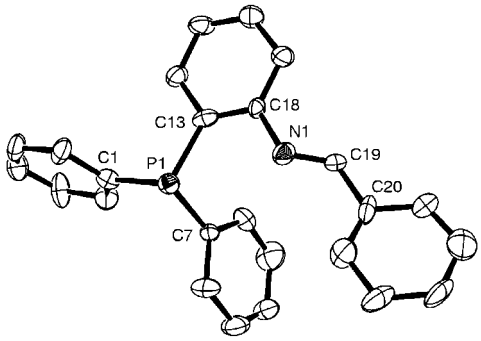
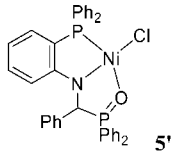


Figure 1. ORTEP drawing of **2** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): N(1)−C(18) 1.428(2), N(1)−C(19) 1.274(3),C(19)−C(20)1.479(3),P(1)−C(13)1.850(2),C(18)−N(1)−C(19) 117.11(19), N(1)−C(19)−C(20) 119.7(2).



5'

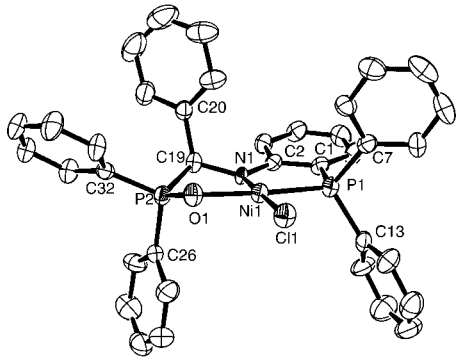


Figure 2. ORTEP drawing of **5′** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ni(1)−N(1) 1.893(5), Ni(1)−O(1) 1.925(4), Ni(1)−P(1) 2.1234(18), Ni(1)−Cl(1) 2.184(2), O(1)−P(2) 1.521(4), N(1)−Ni(1)−O(1) 89.9(2), N(1)−Ni(1)−P(1) 87.11(17), O(1)−Ni(1)−P(1) 176.10(16), N(1)−Ni(1)−Cl(1) 177.92(18), O(1)−Ni(1)−Cl(1) 92.00(15), P(1)−Ni(1)−Cl(1) 91.01(8).

lengths and angles. In the molecule the central nickel atom has a distorted square-planar geometry. Both O(1)−Ni(1)−P(1) [176.10(16)°] and N(1)−Ni(1)−Cl(1) [177.92(18)°] are approximately linear. The Ni−P distance of 2.1234(18) Å is a little shorter than those in [R-PNP]NiR[1] (R = Ph, R[1] = Me, Et, Bu[n], Bu[i], *n*-hexyl, CH_2SiMe_3, Ph; R = Pr[i], R[1] = Me, Et, Bu[n]; R = Cy, R[1] = Me, Et, Bu[n]) [from 2.154(2) to 2.1966(9) Å].[3k] The Ni−N distance of 1.893(5) Å is close to that of [Ph-PNP]NiCl [1.895(3) Å], but shorter than those in [Ni(Cl){N[C(Ph)-CHP(Pr[i])$_2$=NAr]C_6H_4P(Ph)$_2$-2}] and [Ni(Cl){N[C(Ph)CH-P(Pr[i])$_2$]C_6H_4[P(Ph)$_2$=NAr]-2}] (Ar = 2,6-Pr[i]$_2C_6H_3$) [1.955(3) and 1.9386 Å, respectively].[9]

Complex **6** is green and very soluble in CH_2Cl_2 and soluble in ether. It gave satisfactory elemental analysis. The HR-MS displayed a molecular ion signal, and the fragmental mass matches the calculated value very well. Complex **6** is diamagnetic, and the ^{1}H, ^{13}C, and ^{31}P NMR spectral data are consistent with its structure. The structure of **6** was also further characterized by single-crystal X-ray diffraction. The ORTEP drawing is presented in Figure 3, along with selected bond lengths and angles. The skeletal structure of complex **6** is similar to that of complex **5′**, having a distorted square-planar coordination

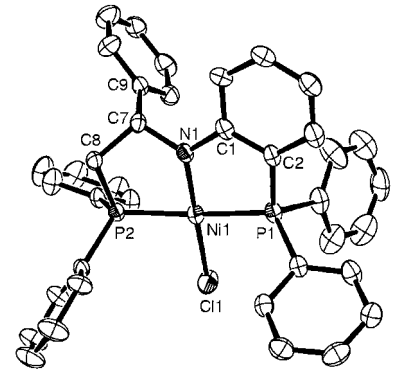
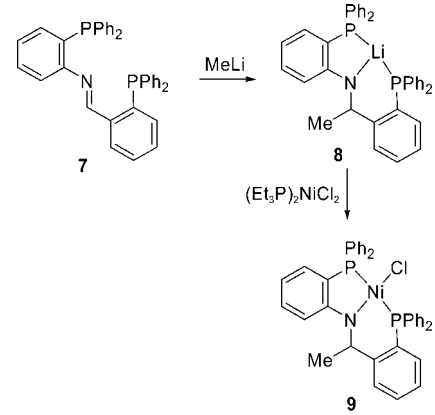


Figure 3. ORTEP drawing of **6** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ni(1)−N(1) 1.878(5), Ni(1)−Cl(1) 2.170(2), Ni(1)−P(1) 2.1729(19), Ni(1)−P(2) 2.1796(18), N(1)−C(1) 1.390(7),N(1)−C(7) 1.464(7),C(7)−C(8) 1.520(7),N(1)−Ni(1)−Cl(1) 179.49(16), N(1)−Ni(1)−P(1) 86.54(16), Cl(1)−Ni(1)−P(1) 93.26(8), N(1)−Ni(1)−P(2)86.72(17),Cl(1)−Ni(1)−P(2)93.52(7),P(1)−Ni(1)−P(2) 171.65(8), C(1)−N(1)−C(7) 116.8(5), C(1)−N(1)−Ni(1) 120.9(4), C(7)−N(1)−Ni(1) 121.6(4), N(1)−C(7)−C(8) 107.7(5).

Scheme 2. Synthesis of Complexes 8 and 9

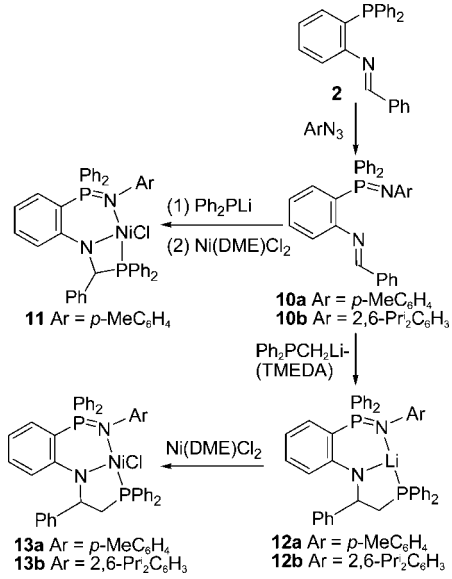


geometry. N(1)−Ni(1)−Cl(1) is linear [179.49(16)°], while P(1)−Ni(1)−P(2) is slightly bent [171.65(8)°]. The N(1)−Ni(1)−P(1) angle [86.54(16)°] is almost the same as that of N(1)−Ni(1)−P(2) [86.72(17)°], and both of them are narrower than those of Cl(1)−Ni(1)−P(1) and Cl(1)−Ni(1)−P(2) [93.26(8)° and 93.52(7)°, respectively]. The Ni(1)−N(1) distance of 1.878(5) Å is a little shorter than that of **5′**. The Ni−P distances [2.1729(19) and 2.1796(18) Å, respectively] are longer than that in **5′**, but within the normal range for P,N,P-chelate nickel complexes.[3k,9]

Synthesis of complexes **8** and **9** is summarized in Scheme 2. Complex **8** was prepared by reaction of **7** with LiMe in THF. Reaction of **8** with $(Et_3P)_2NiCl_2$ afforded nickel complex **9** in good yield. Complex **8** is a yellow solid and very soluble in THF and soluble in Et_2O. It gave a satisfactory elemental analytical result. The ^{31}P NMR spectrum exhibited two signals at δ −23.60 and −22.24 ppm, respectively. The ^{1}H and ^{13}C NMR spectral data were also consistent with its structure. Complex **9** is a brown powder and slightly soluble in THF and toluene. It gave a satisfactory elemental analysis and ^{1}H NMR, ^{31}P NMR, and HR-MS spectral data.

Synthesis of compounds **10a**−**13b** is summarized in Scheme 3. Both **10a** and **10b** were prepared by reaction of **2** with the corresponding aryl azide in CH_2Cl_2 at room temperature. Treatment of **10a** with Ph_2PLi and then (DME)$NiCl_2$ gave nickel complex **11**. Reaction of **10a** and **10b** with Ph_2PCH_2Li·TMEDA afforded lithium complexes **12a** and **12b**, respectively.

Scheme 3. Synthesis of Compounds 10a−13b



Treatment of **12a** and **12b**, respectively, with $(DME)NiCl_2$ produced the corresponding nickel complexes **13a** and **13b**. Both **12a** and **12b** are air-sensitive yellow solids. Complex **12a** was washed with Et_2O to form the diethyl ether adduct **12a**·Et_2O. Complex **12b** was recrystallized from Et_2O to form **12b**·$1.5Et_2O$. Complex **13a** is a green solid and was recrystallized from Et_2O to form **13a**·$0.5Et_2O$. Complex **13b** is a red solid. It was recrystallized from toluene to give **13b**·$PhCH_3$. Each of compounds **10a**−**13b** gave satisfactory elemental analyses. Compounds **10a**, **10b**, **12a**, and **12b** were charzcterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Complex **11** is paramagnetic and was characterized by an electro-spray mass spectrum, which gave a $[M - Cl]^+$ fragment at *m*/*z* 713. Both complexes **13a** and **13b** are diamagnetic and were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and HR-MS, which exhibited molecular ion signals. The structure of complex **13a** was additionally characterized by single-crystal X-ray diffraction. The ORTEP drawing is presented in Figure 4, along with selected bond lengths and angles. In the molecule of **13a** the central nickel atom has a distorted square-planar geometry. The N(1)−Ni(1)−Cl(1) angle of 171.39(13)° is close to that in

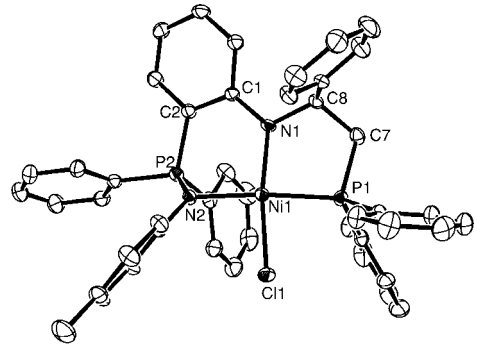


Figure 4. ORTEP drawing of **13a** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ni(1)−N(1) 1.923(4), Ni(1)−N(2) 1.949(4), Ni(1)−P(1) 2.1160(15), Ni(1)−Cl(1) 2.1812(14), C(7)−C(8) 1.515(7), P(1)−C(7) 1.805(5), N(2)−P(2) 1.591(4), N(1)−Ni(1)−N(2) 96.54(17), N(1)−Ni(1)−P(1) 87.20(12), N(2)−Ni(1)−P(1) 173.75(13), N(1)−Ni(1)−Cl(1) 171.39(13), N(2)−Ni(1)−Cl(1) 91.75(12), P(1)−Ni(1)−Cl(1) 84.34(6), P(2)−N(2)−Ni(1) 106.82(19), C(7)−P(1)−Ni(1) 102.70(17), C(1)−N(1)−Ni(1) 127.6(3), C(8)−N(1)−Ni(1) 115.9(3).

Table 1. Evaluation of Complexes 5, 6, 9, 11, 13a, and 13b in the Cross-Coupling Reactions of *p*-MeC_6H_4MgBr with *p*-$MeOC_6H_4I$[a]

entry	complex (mol %)	yield (%)[b]
1	**5** (0.005)	98
2	**6** (0.01)	89
3	**9** (0.01)	43
4	**11** 0.005)	97
5	**13a** (0.005)	96
6	**13b** (0.01)	48

[a] Reaction conditions: 1.0 equiv of *p*-$MeOC_6H_4I$, 1.3 equiv of Grignard reagent, 2.5 mL of toluene, rt, 12 h. [b] Isolated yields.

Table 2. Catalytic Coupling of *p*-MeC_6H_4MgBr with *p*-RC_6H_4Cl by Complexes 5−13b[a]

entry	R	complex (mol %)	yield (%)[b]
1	H	**5** (2)	79
2	MeO	**5** (2)	56
3	MeO	**5** (4)	75
4	H	**6** (2)	95
5	MeO	**6** (2)	79
6	MeO	**6** (4)	94
7	H	**9** (2)	3
8	H	**11** (2)	93
9	MeO	**11** (2)	81
10	MeO	**11** (4)	98
11	H	**13a** (2)	94
12	MeO	**13a** (2)	70
13	MeO	**13a** (4)	97
14	H	**13b** (2)	9

[a] Reaction conditions: 1.0 equiv of aryl chloride, 1.3 equiv of Grignard reagent, 2.5 mL of THF, rt, 36 h. [b] Isolated yields.

$[Ni(Cl)\{N[C(Ph)CHP(Pr^i)_2]C_6H_4[P(Ph)_2{=}NAr]\text{-}2\}]$ (Ar = 2,6-$Pr^i_2C_6H_3$) [172.39(5)°],[9] but smaller than that in complex **6**. The N(2)−Ni(1)−P(1) angle of 173.75(13)° is a little smaller than that of $[Ni(Cl)\{N[C(Ph)CHP(Pr^i)_2]C_6H_4[P(Ph)_2{=}NAr]\text{-}2\}]$ (Ar = 2,6-$Pr^i_2C_6H_3$) [176.29(5)°], the latter being closer to a line. The C(7)−N(1)−Ni(1)−P(1) atoms are approximately coplanar, the torsion angle being 1.4°, while the C(8) atom is out of the plane. The Ni(1)−N(1) distance of 1.923(4) Å is longer than those in complex **6**, [Pr^i-PNP]NiCl [1.9030(17) Å] and [Ph-PNP]NiCl [1.895(3) Å],[3k] and shorter than that found in $[Ni(Cl)\{N[C(Ph)CHP(Pr^i)_2]C_6H_4[P(Ph)_2{=}NAr]\text{-}2\}]$ (Ar = 2,6-$Pr^i_2C_6H_3$) [1.9386(17) Å].[9] The distance of the nickel atom to the iminophosphorano-nitrogen atom [Ni(1)−N(2), 1.949(4) Å] is longer than that to the formally negatively charged nitrogen atom [Ni(1)−N(1), 1.923(4) Å]. Each of the phosphorus atoms exhibits distorted tetrahedral geometry, and the N(2)−P(2) distance of 1.591(4) Å is indicative of a P−N double bond.[11]

Catalysis of the Nickel Complexes in the Kumada Cross-Coupling Reactions. We first evaluated the catalysis of the nickel complexes in the cross-coupling reaction between *p*-MeC_6H_4MgBr and *p*-$MeOC_6H_4I$. The results are listed in Table 1. From the table, it can be found that complexes **5**, **11**, and **13a** were highly active, 0.005 mol % of complexes being able to catalyze the reaction to completion. Complexes **9** and **13b** displayed relatively low catalytic activity. Complex **6** showed lower catalytic activity than complexes **5**, **11**, and **13a**, but higher activity than complexes **9** and **13b**. Then we tested the catalysis of the nickel complexes in the cross-coupling reaction of *p*-MeC_6H_4MgBr with aryl chlorides. The reactions were carried out in THF at room temperature, and the results are listed in Table 2. Complexes **6**, **11**, and **13a** exhibited high catalytic activity. Two mol % of catalysts can drive the reaction of *p*-MeC_6H_4MgBr with PhCl to completion. If deactivated aryl

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chloride, *p*-$MeOC_6H_4Cl$, was employed as electrophilic substrate, 4 mol % of catalysts was necessary to complete the reactions (entries 6, 10, and 13, Table 2). Complex **5** showed lower activity than **6**, **11**, and **13** (entries 1−3, Table 1), 4 mol % of catalyst leading to 75% of cross-coupling product in the reaction of *p*-MeC_6H_4MgBr with *p*-$MeOC_6H_4Cl$ under the same conditions mentioned above. Compared with complexes **5** and **6**, complex **9** exhibited much lower catalytic activity. Thus, in the P,N,P-chelate nickel complexes, the complex with two fused five-membered rings showed higher catalytic activity, while the complex with five- and six-membered chelate rings displayed lower catalytic activity. It seems that the larger chelate ring in complex **9** leads to its low activity. The N,N,P-chelate complexes **11** and **13a** displayed similar catalytic activity to complex **6** and better than complex **5**. Complex **13b** showed very low catalytic activity. This is attributed to steric effects of the ligand. A similar result was observed in the catalytic systems we previously reported.[9] It is also noticed that complex **13a** has similar catalytic activity to complex **C** (Ar = *o*-MeC_6H_4), while complex **6** is a little more active than complex **A** (R = Ph), which showed relatively low catalytic activity in the reaction of *p*-MeC_6H_4MgBr with *p*-$MeOC_6H_4Cl$.[9]

Summary

We have synthesized and characterized a series of lithium and nickel complexes supported by unsymmetrical amido pincer ligands. Single-crystal X-ray diffraction results showed that the central metal atoms of complexes **5′**, **6**, and **13a** have distorted square-planar geometries. The diamagnetic **9** and **13b** are expected to have similar coordination geometries. However, the central nickel atoms of paramagnetic **5** and **11** may markedly deviate from square-planar geometries. Complexes **5**, **6**, **11**, and **13a** can efficiently catalyze cross-coupling reactions of *p*-MeC_6H_4MgBr with aryl halides, including unactivated and deactivated aryl chlorides, while **9** and **13b** exhibited low catalytic activity. The approximate activity order in catalytic cross-coupling of *p*-MeC_6H_4MgBr with aryl chlorides is **6** ≅ **11** ≥ **13a** > **5** > **13b** > **9**.

Experimental Section

General Procedures. All air- or moisture-sensitive manipulations were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane, THF, and diethyl ether), or CaH_2 (CH_2Cl_2) and degassed prior to use. $LiBu^n$ and LiMe were purchased from Acros Organics and used as received. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories, Inc., and C_6D_6 was degassed and stored over Na/K alloy (C_6D_6) or 4 Å molecular sieves ($CDCl_3$). ArN_3,[12] PEt_3,[13] $Ph_2PCH_2Li\cdot TMEDA$,[14] *p*-MeC_6H_4MgBr,[15] $(DME)NiCl_2$,[16] $(Et_3P)_2NiCl_2$,[17] 2-(diphenylphosphino)benzenamine[18] and *N*-(2-(diphenylphosphino)benzylidene)-2-(diphenylphosphino)benzenamine[19] were prepared according to the reported methods. All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances. MS data were recorded on an Agilent6890/Micromass GCT-MS spectrometer (EI) or Thermo Finnigan LCQ Advantage Max ion trap mass spectrometer (ESI). Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China.

Synthesis of Compounds 2−6 and 8−13b. 2-$Ph_2PC_6H_4N$=CHPh (2). In a three-necked flask was added activated 4 Å molecular sieves (30 g), toluene (40 mL), 2-(diphenylphosphino)benzenamine (13.85 g, 0.05 mol), and PhCHO (10.6 g, 0.1 mol). Then three drops of HCOOH was added. The mixture was stirred at room temperature for 12 h and then filtered. The molecular sieves were washed with toluene (3 × 20 mL). The combined organic layers were washed with water and then dried over Na_2SO_4. Na_2SO_4 was removed by filtration, and volatiles were removed from the filtrate by rotary evaporation. MeOH was added to the residue to form a yellowish solid (14.5 g, 79.4%), mp 108−110 °C. ^1H NMR ($CDCl_3$): δ 6.82−6.86 (m, 1H, Ar), 7.00−7.04 (m, 1H, Ar), 7.12 (t, *J* = 7.4 Hz, 1H, Ar), 7.24−7.39 (m, 14H, Ar), 7.63−7.67 (m, 2H, Ar), 8.13 (s, 1H, CH).

[Li{N{CH(Ph)PPh_2}C_6H_4(PPh_2)-2}] (3). Compound **2** (0.913 g, 2.5 mmol) was dissolved in THF (10 mL) and cooled to about −80 °C. To the solution was added a THF solution of Ph_2PLi [prepared in situ from Ph_2PH (0.465 g, 2.5 mmol) and $LiBu^n$ (1 mL, 2.5 M solution in hexane, 2.5 mmol) in THF (6 mL)] with stirring. The mixture was warmed to room temperature and stirred for 12 h. Solvents were removed in vacuo, and the residue was dissolved in Et_2O and then filtered. The filtrate was concentrated in vacuo and kept at 0 °C overnight to afford a white solid of **3** (1.25 g, 89.8%), mp 136−138 °C. Anal. Calcd for $C_{37}H_{30}NP_2Li$: C, 79.71; H, 5.42; N, 2.51. Found: C, 79.38; H, 5.63; N, 2.61. ^1H NMR (C_6D_6): δ 5.35 (d, *J* = 7 Hz, 1H, CH), 5.88−5.95 (m, 1H, Ar), 6.52 (t, *J* = 7.1 Hz, 1H, Ar), 6.62−6.67 (m, 1H, Ar), 6.90−7.05 (m, 19H, Ar), 7.23−7.40 (m, 7H, Ar). ^{13}C NMR (C_6D_6): δ 65.9, 112.0, 118.3, 120.3, 127.0 (d, *J* = 2.6 Hz), 127.9, 128.5, 128.6, 128.71, 128.74, 128.8, 128.83, 128.86, 128.9, 129.0, 129.3, 131.1, 133.7, 134.0, 134.1, 134.2, 134.3, 134.5, 134.5, 134.8, 135.0, 136.0, 136.1, 136.3, 136.4, 140.6, 140.8, 150.2 (d, *J* = 4.3 Hz), 150.5 (d, *J* = 4.2 Hz). ^{31}P NMR (C_6D_6): δ −26.25, 4.29.

[Li{N{CH(Ph)CH_2PPh_2}C_6H_4(PPh_2)-2}] (4). Compound **2** (0.913 g, 2.5 mmol) was dissolved in THF (10 mL) and cooled to about −80 °C. To the solution was added a solution of $Ph_2PCH_2Li\cdot$TMEDA (0.805 g, 2.5 mmol) in THF (6 mL) with stirring. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed in vacuo, and the residue was dissolved in Et_2O and then filtered. The filtrate was concentrated in vacuo and kept at 0 °C overnight to give a yellow solid of **4** (1.32 g, 92.4%), mp 158−160 °C. Anal. Calcd for $C_{38}H_{32}NP_2Li$: C, 79.85; H, 5.64; N, 2.45. Found: C, 79.49; H, 5.93; N, 2.75. An NMR spectral analytical sample was recrystallized from THF and gave an adduct of THF (**4**·THF). ^1H NMR (C_6D_6): δ 1.21−1.26 (m, THF), 2.40−2.46 (m, 1H, CH_2), 2.80−2.86 (m, 1H, CH_2), 3.42−3.47 (m, THF), 4.49 (dd, *J* = 6.4 Hz, 1H, CH), 6.24−6.32 (m, 2H, Ar), 6.93 (t, *J* = 6.9 Hz, 1H, Ar), 7.01−7.03 (m, 4H, Ar), 7.06−7.21 (m, 12H, Ar), 7.33−7.37 (m, 4H, Ar), 7.49 (t, *J* = 6.9 Hz, 2H, Ar), 7.57 (t, *J* = 6.7 Hz, 2H, Ar), 7.70 (t, *J* = 7.5 Hz, 2H, Ar). ^{13}C NMR (C_6D_6): δ 25.5, 39.9, 60.4 (d, *J* = 11.8 Hz), 68.4, 109.2, 111.7, 126.1, 128.0, 128.47, 128.53, 128.6, 128.9, 132.0, 133.3,

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133.4, 133.55, 133.63, 134.1, 134.2, 134.4, 134.5, 134.6, 138.2 (d, J = 3.3 Hz), 138.5, 139.7 (d, J = 9.4 Hz), 150.5 (d, J = 3.4 Hz), 163.8, 164.0. ^{31}P NMR (C_6D_6): δ −26.98, −16.11.

[Ni(Cl){N{CH(Ph)PPh$_2$}C$_6$H$_4$(PPh$_2$)-2}] (5). To a solution of (DME)$NiCl_2$ (0.274 g, 1.25 mmol) in THF (10 mL) was added a solution of **3** (0.696 g, 1.25 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to afford a brown solid identified as **5**·0.5CH_2Cl_2 (0.66 g, 77%), mp 155−157 °C. Anal. Calcd for $C_{37}H_{30}NP_2NiCl$·0.5CH_2Cl_2: C, 65.54; H, 4.55; N, 2.04. Found: C, 65.57; H, 4.87; N, 2.32. HR-MS (EI): m/z 423.0663 [M − Cl − 2Ph − P]$^+$, calcd 423.0687. ESI-MS: m/z 608 [M − Cl]$^+$.

[Ni(Cl){N{CH(Ph)CH$_2$PPh$_2$}C$_6$H$_4$(PPh$_2$)-2}] (6). To a solution of $(Et_3P)_2NiCl_2$ (0.458 g, 1.25 mmol) in THF (10 mL) was added a solution of **4** (0.714 g, 1.25 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to form green crystals of **6** (0.658 g, 80%), mp 195−197 °C. Anal. Calcd for $C_{38}H_{32}NP_2NiCl$: C, 69.28; H, 4.90; N, 2.13. Found: C, 69.42; H, 4.77; N, 2.17. ^{1}H NMR ($CDCl_3$): δ 2.72−2.90 (m, 2H, CH2), 4.81 (dd, J = 6.7, 38.2 Hz, CH), 6.13 (dd, J = 5.7, 8.4 Hz, 1H, Ar), 6.20 (t, J = 6.9 Hz, 1H, Ar), 6.76−6.82 (m, 1H, Ar), 6.87−6.90 (m, 3H, Ar), 6.98−7.06 (m, 3H, Ar), 7.14−7.20 (m, 1H, Ar), 7.28−7.31 (m, 4H, Ar), 7.37−7.44 (m, 9H, Ar), 7.66−7.70 (m, 2H, Ar), 7.79−7.85 (m, 2H, Ar), 7.89−7.95 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 40.6 (d, J = 23 Hz), 64.1−64.2 (m), 113.9 (d, J = 6.6 Hz), 114.7, 114.9, 117.2, 117.8, 125.5, 126.7, 126.8, 128.2, 128.23, 128.3, 128.4, 128.7 (d, J = 1.1 Hz), 128.74, 128.8 (d, J = 1.5 Hz), 128.9, 129.2, 130.2 (d, J = 2.5 Hz), 130.5 (d, J = 2.6 Hz), 130.6 (d, J = 2.5 Hz), 130.7 (d, J = 2.6 Hz), 132.9, 133.1, 133.2 (d, J = 1.8 Hz), 133.5 (d, J = 1.4 Hz), 133.7 (d, J = 1.4 Hz), 133.8, 133.9 (d, J = 1.6 Hz), 134.0 (d, J = 1.6 Hz), 138.0, 143.5 (d, J = 2.4 Hz), 166.1 (d, J = 4.2 Hz), 166.5 (d, J = 4.4 Hz). ^{31}P NMR ($CDCl_3$): δ 19.95 (d, J = 335.8 Hz), 28.71 (dm, J = 330.7 Hz). HR-MS (EI): m/z 657.1044 [M]$^+$, calcd 657.1052.

[Li{N{CH(Me)C$_6$H$_4$(PPh$_2$)-2}{C$_6$H$_4$(PPh$_2$)-2}}] (8). To a stirred solution of **7** (0.25 g, 0.455 mmol) in THF (8 mL) was added dropwise LiMe (0.29 mL, a 1.6 M solution in Et_2O, 0.464 mmol) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was washed with hexane and then dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to yield a yellow solid of **8** (0.22 g, 84.6%), mp 177−179 °C. Anal. Calcd for $C_{38}H_{32}NP_2Li$: C, 79.85; H, 5.64; N, 2.45. Found: C, 79.55; H, 5.69; N, 2.49. ^{1}H NMR (C_6D_6): δ 1.28 (d, J = 6.3 Hz, 3H, CH_3), 5.54 (t, J = 6 Hz, 1H, Ar), 5.73 (q, J = 6.3 Hz, 1H, CH), 6.64 (t, J = 7.5 Hz, 1H, Ar), 6.72−6.76 (m, 1H, Ar), 6.97 (t, J = 6.6 Hz, 1H, Ar), 6.99−7.27 (m, 16H, Ar), 7.38−7.45 (m, 3H, Ar), 7.51−7.61 (m, 5H, Ar). ^{13}C NMR (C_6D_6): δ 24.6, 51.1, 112.6 (d, J = 2.4 Hz), 112.7 (d, J = 2.3 Hz), 117.76 (d, J = 3.7 Hz), 118.9, 119.1, 125.6 (d, J = 5.6 Hz), 127.4, 127.9, 128.2, 128.8, 128.85, 128.9, 128.94, 128.99, 129.04, 130.2, 131.2, 134.0 (d, J = 5.5 Hz), 134.2, 134.3 (d, J = 2.4 Hz), 134.38, 134.41, 134.6, 134.7, 134.9, 135.2 (d, J = 6.8 Hz), 136.4 (d, J = 2 Hz), 136.5 (d, J = 2.2 Hz), 137.1, 137.2 (d, J = 2.6 Hz), 137.3, 150.2, 150.5, 150.6, 150.9. ^{31}P NMR (C_6D_6): δ −23.60, −22.24.

[Ni(Cl){N{CH(Me)C$_6$H$_4$(PPh$_2$)-2}{C$_6$H$_4$(PPh$_2$)-2}}] (9). To a solution of $(Et_3P)_2NiCl_2$ (0.457 g, 1.25 mmol) in THF (10 mL) was added a solution of **8** (0.714 g, 1.25 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Red-brown precipitates were formed. The mixture was filtered and the solid was washed with THF to give complex **9** (0.67 g, 81.4%), mp 263−264 °C. Anal. Calcd for $C_{38}H_{32}NP_2NiCl$: C, 69.28; H, 4.90; N, 2.13. Found: C, 68.99; H, 4.77; N, 2.11. ^{1}H NMR ($CDCl_3$): δ 1.75 (d, J = 6.6 Hz, 3H, CH_3), 4.03 (q, J = 6.9 Hz, 1H, CH), 6.21 (t, J = 7.2 Hz, 1H, Ar), 6.53−6.58 (m, 1H, Ar), 7.01 (t, J = 8.1 Hz, 2H, Ar), 7.22−7.49 (m, 16H, Ar), 7.72−7.82 (m, 8H, Ar). ^{31}P NMR ($CDCl_3$): δ −17.30 (d, J = 363.7 Hz), 20.66 (d, J = 362.1 Hz). HR-MS (EI): m/z 657.1060 [M]$^+$, calcd 657.1052.

2-{*p*-MeC$_6$H$_4$N=P(Ph$_2$)}C$_6$H$_4$N=CHPh (10a). To a stirred solution of **2** (1.83 g, 5.01 mmol) in CH_2Cl_2 (15 mL) was added dropwise *p*-$MeC_6H_4N_3$ (0.82 g, 6.15 mmol). The mixture was stirred at room temperature for 2 h. Solvent was removed in vacuo, and the residue was washed with hexane to afford a yellow powder (2.2 g, 93.3%), mp 128−130 °C. Anal. Calcd for $C_{32}H_{27}N_2P$: C, 81.68; H, 5.78; N, 5.95. Found: C, 81.60; H, 5.75; N, 5.99. ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H, CH_3), 6.56 (d, J = 7.8 Hz, 2H, Ar), 6.71 (d, J = 8.1 Hz, 2H, Ar), 6.94 (dd, J = 4.5, 7.2 Hz, 1H, Ar), 7.18−7.21 (m, 2H, Ar), 7.25−7.34 (m, 10H, Ar), 7.53−7.58 (m, 1H, Ar), 7.80 (s, 1H, CH), 7.85−7.97 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$): δ 20.6, 118.7 (d, J = 7.5 Hz), 123.4 (d, J = 16.6 Hz), 123.9, 125.1, 125.7 (d, J = 11.2 Hz), 126.0, 128.1, 128.3 (d, J = 3.3 Hz), 129.1, 129.2, 131.0 (d, J = 2.9 Hz), 131.4, 131.5, 132.6 (d, J = 9.8 Hz), 132.8, 133.4 (d, J = 2.4 Hz), 135.1 (d, J = 8.3 Hz), 135.9, 149.0 (d, J = 2.6 Hz), 154.4 (d, J = 5 Hz), 160.2. ^{31}P NMR ($CDCl_3$): δ −0.09.

2-{2,6-Pr$^i_2$C$_6$H$_3$N=P(Ph$_2$)}C$_6$H$_4$N=CHPh (10b). Compound **10b** was prepared according to a similar procedure to that of **10a**. To a stirred solution of **2** (0.516 g, 1.41 mmol) in CH_2Cl_2 (10 mL) was added dropwise 2,6-$Pr^i_2C_6H_3N_3$ (0.31 g, 1.52 mmol). The mixture was stirred at room temperature for 12 h. Solvent was removed in vacuo. The oily residue was dissolved in Et_2O and then filtered. The filtrate was concentrated to produce yellow crystals (0.55 g, 72%), mp 135−137 °C. Anal. Calcd for $C_{37}H_{37}N_2P$: C, 82.19; H, 6.90; N, 5.18. Found: C, 82.01; H, 6.83; N, 5.26. ^{1}H NMR ($CDCl_3$): δ 0.67 (d, J = 6.8 Hz, 12H, CH_3), 2.97−3.11 (m, 2H, Pr^i), 6.59−6.65 (m, 1H, Ar), 6.75 (d, J = 6.9 Hz, 2H, Ar), 6.78−6.83 (m, 1H, Ar), 7.10−7.31 (m, 12H, Ar), 7.47 (t, J = 7.5 Hz, 1H, Ar), 7.53−7.59 (m, 4H, Ar), 7.67 (s, 1H, CH), 7.87−7.94 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 23.5, 28.6, 118.5 (d, J = 2.9 Hz), 118.7 (d, J = 8.1 Hz), 120.1, 122.5, 125.5, 125.6, 127.9 (d, J = 12.3 Hz), 128.3, 129.3, 130.5 (d, J = 2.8 Hz), 131.4, 132.2 (d, J = 9.7 Hz), 133.1, 133.2, 134.6, 134.7, 136.0, 142.6 (d, J = 6.7 Hz), 145.1, 159.7. ^{31}P NMR ($CDCl_3$): δ −11.93.

[Ni(Cl){N{CH(Ph)PPh$_2$}C$_6$H$_4${P(Ph$_2$)=NC$_6$H$_4$Me-4}-2}] (11). Compound **10a** (0.49 g, 1.04 mmol) was dissolved in THF (5 mL) and cooled to about −80 °C. To the solution was added a THF solution of Ph_2PLi [prepared in situ from Ph_2PH (0.195 g, 1.05 mmol) and $LiBu^n$ (0.42 mL, 2.5 M solution in hexane, 1.05 mmol) in THF (5 mL)] with stirring. The mixture was warmed to room temperature and stirred for 12 h. The formed solution was added to a stirred solution of (DME)$NiCl_2$ (0.231 g, 1.05 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to afford a brown solid. The solid was washed with toluene to give a brown powder of **11**·$PhCH_3$ (0.73 g, 85.2%), mp 111−113 °C. Anal. Calcd for $C_{44}H_{37}N_2P_2NiCl$·$PhCH_3$: C, 72.75; H, 5.39; N, 3.33. Found: C, 72.66; H, 5.62; N, 3.25. ESI-MS: m/z 713 [M − Cl]$^+$.

[Li{N{CH(Ph)CH$_2$PPh$_2$}C$_6$H$_4${P(Ph$_2$)=NC$_6$H$_4$Me-4}-2}] (12a). Compound **10a** (0.289 g, 0.61 mmol) was dissolved in THF (5 mL) and cooled to about −80 °C. To the solution was added a solution of Ph_2PCH_2Li·TMEDA (0.198 g, 0.61 mmol) in THF (5 mL) with stirring. The mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed in vacuo, and the residue was washed successively with hexane and Et_2O to give a yellow powder of **12a**·Et_2O (0.365 g, 79.1%), mp 186−188 °C. Anal. Calcd for $C_{45}H_{39}N_2P_2Li$·Et_2O: C, 78.36; H, 6.58; N, 3.73.

Table 3. Details of the X-ray Structure Determinations of Complexes 2, 5′, 6, and 13a

	2	**5′**·0.5C_7H_8	**6**·0.5CH_2Cl_2	**13a**·C_7H_8
formula	$C_{25}H_{20}NP$	$C_{81}H_{68}Cl_2N_2Ni_2O_2P_4$	$C_{38.5}H_{33}Cl_2N\ NiP_2$	$C_{52}H_{47}ClN_2NiP_2$
fw	365.39	1413.57	701.21	856.02
temp, K	294(2)	298(2)	298(2)	298(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*1*c*1	$P2_1$	$P2_1/c$	$P2_1/c$
a, Å	15.108(3)	15.922(2)	14.647(2)	15.2015(15)
b, Å	13.258(3)	9.7547(16)	17.098(3)	18.635(2)
c, Å	20.346(4)	23.679(3)	15.666(3)	16.855(2)
β, deg	98.395(3)	107.689(2)	115.807(2)	113.301(2)
V, Å^3	4031.6(15)	3503.8(8)	3532.1(9)	4385.3(9)
Z	8	2	4	4
D_{calcd}, g cm^{-3}	1.204	1.340	1.319	1.297
F(000)	1536	1468	1452	1792
μ, mm^{-1}	0.145	0.754	0.819	0.614
θ range for data collecn, deg	1.54 to 25.00	1.34 to 25.01	1.87 to 25.00	1.46 to 25.01
no. of reflns collected	30 031	17 717	17 296	17 873
no. of indep reflns (R_{int})	11 604 (R_{int} = 0.0401)	11 859 (R_{int} = 0.0572)	6140 (R_{int} = 0.0905)	7701 (R_{int} = 0.0769)
no. of data/ restraints/params	11 604/26/974	11 859/1/838	6140/86/415	7701/120/523
goodness of fit on F^2	1.041	0.816	1.002	1.061
final *R* indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0566	R_1 = 0.0561	R_1 = 0.0620	R_1 = 0.0673
	wR_2 = 0.1321	wR_2 = 0.0619	wR_2 = 0.1019	wR_2 = 0.1177
R indices (all data)	R_1 = 0.1092	R_1 = 0.1313	R_1 = 0.1607	R_1 = 0.1387
	wR_2 = 0.1658	wR_2 = 0.0748	wR_2 = 0.1173	wR_2 = 0.1430
largest diff peak and hole, e Å^{-3}	0.211 and −0.195	0.632 and −0.366	0.590 and −0.412	0.752 and −0.457

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Found: C, 78.49; H, 6.63; N, 3.46. ^{1}H NMR (C_6D_6): δ 1.16 (t, J = 6.9 Hz, 6H, Et_2O), 2.25 (s, 3H, CH_3), 2.34 (t, J = 11.7 Hz, 1H, CH_2), 2.55−2.69 (m, 1H, CH_2), 3.36 (q, J = 6.9 Hz, 4H, Et_2O), 4.64−4.74 (m, 1H, CH), 6.16 (b, 1H, Ar), 6.39 (t, J = 6.9 Hz, 1H, Ar), 6.79−6.80 (m, 1H, Ar), 6.99−7.29 (m, 22H, Ar), 7.40 (s, 2H, Ar), 7.53−7.59 (m, 2H, Ar), 7.93−8.06 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ 15.4, 20.7, 43.4, 60.4 (d, J = 8.8 Hz), 65.8, 107.2 (d, J = 15.9 Hz), 115.2 (d, J = 8.9 Hz), 123.1 (d, J = 18.2 Hz), 125.9, 127.2, 127.9, 128.2, 128.5, 128.6, 128.7, 128.8 (d, J = 3.2 Hz), 128.85, 128.9, 129.0, 130.0, 133.1, 133.3, 133.4, 133.6, 133.7, 133.8, 134.1, 134.2, 149.6, 149.8. ^{31}P NMR (C_6D_6): δ −23.14, 14.44.

[Li{N{CH(Ph)CH_2PPh_2}C_6H_4{P(Ph_2)=N$C_6H_3Pr^i_2$-2,6}-2}] (12b). Compound **10b** (1.206 g, 2.23 mmol) was dissolved in THF (10 mL) and cooled to about −80 °C. To the solution was added a solution of Ph_2PCH_2Li·TMEDA (0.73 g, 2.26 mmol) in THF (10 mL) with stirring. The mixture was stirred at room temperature for 1 h and then at 60 °C overnight. Volatiles were removed in vacuo, and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to afford a yellow solid of **12b**·1.5Et_2O (1.25 g, 65.3%), mp 189−191 °C. Anal. Calcd for $C_{50}H_{49}N_2P_2Li$·1.5Et_2O: C, 78.37; H, 7.52; N, 3.27. Found: C, 78.66; H, 7.33; N, 3.40. ^{1}H NMR (C_6D_6): δ 0.73 (d, J = 6.6 Hz, 3H, Pr^i), 1.24 (t, J = 6 Hz, 9H, Et_2O), 1.36 (d, J = 5.7 Hz, 3H, Pr^i), 1.38 (d, J = 5.7 Hz, 3H, Pr^i), 1.57 (d, J = 6.6 Hz, 3H, Pr^i), 2.31−2.38 (m, 2H, CH_2), 3.47 (q, J = 6 Hz, 9H, Et_2O), 3.58−3.68 (m, 1H, Pr^i), 4.22−4.32 (m, 1H, Pr^i), 4.62−4.70 (m, 1H, CH), 6.22−6.28 (m, 1H, Ar), 6.63 (t, J = 6.9 Hz, 1H, Ar), 6.80 (d, J = 6.9 Hz, 2H, Ar), 6.96−7.36 (m, 22H, Ar), 7.49 (t, J = 7.5 Hz, 2H, Ar), 7.57 (t, J = 8.7 Hz, 2H, Ar), 8.01−8.07 (m, 2H, Ar). ^{13}C NMR (C_6D_6): δ 14.4, 15.6, 23.1, 23.9, 24.3, 24.6, 29.1, 29.3, 32.0, 65.9, 120.3, 123.1, 123.6, 126.8, 128.4, 128.5, 128.6, 128.7, 129.1, 129.6, 130.6, 131.1, 131.4, 132.1, 132.3, 132.5, 132.6, 132.8, 132.9, 133.0, 133.1, 135.0, 135.2, 142.6, 143.0, 143.1. ^{31}P NMR (C_6D_6): δ −26.07, 12.65.

[Ni(Cl){N{CH(Ph)CH_2PPh_2}C_6H_4{P(Ph_2)=NC_6H_4Me-4}-2}] (13a). To a solution of (DME)$NiCl_2$ (0.118 g, 0.537 mmol) in THF (5 mL) was added a solution of **12a**·OEt_2 (0.401 g, 0.534 mmol) in THF (5 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was washed with hexane and then dissolved in CH_2Cl_2. The solution was filtered and the filtrate was distilled to dryness. The residual solid was dissolved in Et_2O and then concentrated to give green crystals of **13a**·0.5Et_2O (0.323 g, 74.5%), mp 142−144 °C. Anal. Calcd for $C_{45}H_{39}N_2P_2NiCl$·0.5Et_2O: C, 70.48; H, 5.54; N, 3.50. Found: C, 70.23; H, 5.45; N, 3.31. ^{1}H NMR ($CDCl_3$): δ 1.13−1.27 (m, 3H, Et_2O), 2.28 (s, 3H, CH_3), 2.30 (b, 2H, CH_2), 3.41−3.54 (m, 2H, Et_2O), 4.70 (b, 1H, CH), 6.08−6.22 (m, 1H, Ar), 6.33−6.47 (m, 1H, Ar), 6.63−6.87 (m, 3H, Ar), 7.00−7.30 (m, 16H, Ar), 7.40−7.60 (m, 7H, Ar), 7.64−7.82 (m, 3H, Ar), 8.16−8.30 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 15.4, 20.9, 38.8, 59.0, 66.0, 106.9, 127.4, 127.9, 128.1, 128.4, 128.6, 128.8, 129.0, 129.9, 130.1, 133.0, 133.4, 134.2, 134.5, 134.8, 147.8. ^{31}P NMR ($CDCl_3$): δ −27.65, 24.87. HR-MS (EI): *m*/*z* 762.1628 [M]$^+$, calcd 762.1631.

[Ni(Cl){N{CH(Ph)CH_2PPh_2}C_6H_4{P(Ph_2)=N$C_6H_3Pr^i_2$-2,6}-2}] (13b). To a solution of (DME)$NiCl_2$ (0.286 g, 1.3 mmol) in THF (5 mL) was added a solution of **12b**·1.5OEt_2 (1.115 g, 1.3 mmol) in THF (10 mL) at about −80 °C. The mixture was stirred at room temperature for 1 h and at 60 °C overnight. Volatiles were removed in vacuo, and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was distilled to dryness. The residual solid was dissolved in toluene and then concentrated to give a red solid of **13b**·$PhCH_3$ (0.884 g, 73.4%), mp 117−119 °C. Anal. Calcd for $C_{50}H_{49}N_2P_2NiCl$·C_7H_8: C, 73.92; H, 6.20; N, 3.02. Found: C, 73.94; H, 6.43; N, 3.39. The sample for NMR spectral analyses was crystallized from Et_2O. ^{1}H NMR ($CDCl_3$): δ 0.82 (d, J = 5.1 Hz, 6H, Pr^i), 0.86 (d, J = 5.1 Hz, 6H, Pr^i), 1.21 (t, J = 5.1 Hz, Et_2O), 2.11 (dd, J = 7.2, 9.9 Hz, 1H, CH_2), 2.29 (dd, J = 3.3, 9.9 Hz, 1H, CH_2), 3.33−3.43 (m, 2H, Pr^i), 3.48 (t, J = 5.1 Hz, Et_2O), 4.17−4.25 (m, 1H, CH), 6.24 (dd, J = 3.9, 6 Hz, 1H, Ar), 6.45 (dt, J = 1.5, 5.1 Hz, 1H, Ar), 6.76−6.87 (m, 4H, Ar), 6.95 (d, J = 5.4 Hz, 2H, Ar), 7.02−7.20 (m, 9H, Ar), 7.24−7.32 (m, 5H, Ar), 7.35−7.48 (m, 5H, Ar), 7.52−7.57 (m, 3H, Ar), 7.70 (dd, J = 6, 9 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.8, 23.8, 24.0, 28.7, 31.7, 38.4 (d, J = 14.6 Hz), 55.5, 55.7, 112.5 (d, J = 7.9 Hz), 115.3, 115.5, 115.8, 117.1, 119.3 (d, J = 2.7 Hz), 122.9, 126.9, 127.2, 128.26, 128.3, 128.34, 128.4, 128.5, 128.6, 128.7, 128.9, 131.3, 132.4, 132.5, 132.7, 132.9, 133.0, 133.2, 133.5, 142.8 (d, J = 7.3 Hz), 150.3 (d, J = 4.5 Hz). ^{31}P NMR ($CDCl_3$): δ −28.77, −5.30. HR-MS (EI): *m*/*z* 832.2414 [M]$^+$, calcd 832.2412.

X-ray Crystallography. Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected

on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97[20] and refined against F^2 by full-matrix least-squares using SHELXL-97.[21] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 3.

General Procedures for the Kumada Reaction. A Schlenk tube was charged with **11** (15 mg, 0.02 mmol), THF (1.2 mL), and chlorobenzene (0.1126 g, 1 mmol) to form a homogeneous solution. To the stirred solution was added dropwise a solution of *p*-MeC_6H_4MgBr in THF (1.3 mmol, ca. 1 M in THF) at room temperature. Stirring was continued at room temperature for 36 h. The reaction was ceased by addition of water (5 mL). The mixture was extracted with Et_2O (3 × 5 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. The Na_2SO_4 was removed by filtration and washed with Et_2O. The resulting Et_2O solution was concentrated by rotary evaporation, and the residue was purified by column chromatography on silica gel (hexane) to afford *p*-MeC_6H_4Ph (0.157 g, 93.3%) as colorless crystals.

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Supporting Information Available: X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **2**, **5′**, **6**, and **13a** may be obtained free of charge via the Internet at http://pubs.acs.org.

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