Simple Synthesis of CpNi(NHC)Cl Complexes (Cp = Cyclopentadienyl; NHC = N-Heterocyclic Carbene)

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The reaction of saturated and unsaturated imidazolium salts with nickelocene in refluxing THF results in the formation of NHC complexes of general formula CpNi(NHC)Cl (NHC = SIMes (**2**), IPr (**3**), SIPr (**4**)). This protonation of Cp_2Ni was also tested using phosphonium salts, and the reaction of nickelocene with triethylphosphonium chloride leads to CpNi(PEt_3)Cl (**5**). All compounds were characterized by NMR and X-ray crystallography. The catalytic activity of the NHC compounds was tested in aryl amination (Buchwald−Hartwig reaction) and in aryl halide dehalogenation reactions.

Introduction

N-heterocyclic carbenes (NHCs) have become a very important class of ligand in organometallic chemistry.[1] Oftentimes compared to tertiary phosphines because of similarities in bonding and transition-metal (TM) catalyst activity, the NHCs possess properties that render them more desirable for a number of catalytic applications.[2] A minor hurdle hindering a more widespread use of NHCs as ligands is the need to generate them from their respective imidazolium salt, thus either requiring an additional isolation step or, alternatively, forming them in situ. The most common method of affixing a NHC onto a metal center is synthesizing the free carbene by action of a base on the imidazolium salts and subsequently reacting the NHC with a metal complex.[3] A method gaining popularity in recent reports is the transmetalation of the NHC from a silver complex that can be synthesized by reacting Ag_2O with the azolium chloride.[4] This transmetalation has been especially useful with NHCs that are difficult to isolate or that are somewhat unstable as a free carbene. Both of these current methods require an additional step, increasing the cost and generating waste.

We have recently taken advantage of a Ni system ((NHC)Ni(CO)$_x$; $x = 2, 3$) to quantify the steric and electronic parameters characterizing a number of NHCs.[5] Recent reports of Ni−NHC complexes capable of mediating organic transformations have drawn attention to this low-cost organometallic system. Louie and coworkers have shown that a Ni−NHC system successfully facilitated the cycloaddition of alkynes with either isocyanates or carbon dioxide at a higher rate than when Ni−tertiary phosphine systems were employed.[6] Fort has had success with Ni-catalyzed aryl amination and transfer hydrogenation using NHCs as ancillary ligands.[7,8] Mori has recently reported on the stereoselective synthesis of (*Z*)-allylsilanes from dienes and aldehydes mediated by a Ni/NHC system,[9] and a similar system involving alkynes[10] has been used by Montgomery. A most recent report by Jamison uses an IPr/Ni(0) system to effect the enantioselective and regioselective coupling of allenes, aldehydes, and silanes.[11] While this paper was in preparation, very recent work from the Snieckus group came to our attention where CpNi(IMes)Cl (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was used as precatalyst in a cross-coupling of aryl Grignards with sulfamates.[12] Since a general synthetic route has not yet been demonstrated leading to these CpNi(NHC)Cl catalysts, we felt that in this context a simple route to a large number of compounds in this family would be a welcome contribution.

The first transition-metal−NHC complexes were not formed by the use of a free carbene, as they were

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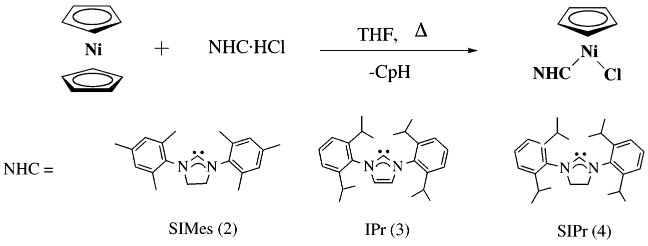
Scheme 1. Synthetic Route to CpNi(NHC)Cl Complexes



considered unstable at the time. Öfele[13] and Wanzlick[14] both use the direct addition of imidazolium salts to metal precursors. Since Arduengo[15] showed the feasibility of generating a stable free carbene, the use of direct addition of the azolium salt to a transition metal has seen limited use. The reaction of an imidazolium salt and $Pd(OAc)_2$ has been shown to form Pd−NHC complexes,[16] and there have been a few reports of Ni−NHC complexes made in this fashion.[17] One report describes the use of $Ni(indenyl)_2$ and an alkyl-substituted imidazolium salt, but the generality of the approach was not expanded upon.[17c] There has only been one example reported so far that makes use of a simple assembly protocol involving IMes·HCl and Cp_2Ni leading to CpNi(IMes)Cl (**1**) in one pot.[17a] Since recent publications have focused on catalytically active Ni−NHC complexes (see above), a facile synthetic method of preparation leading to such complexes seemed desirable. We therefore undertook a detailed study probing the generality of the one-pot synthetic approach from nickelocene.

Results and Discussion

The saturated NHC complexes do exhibit enhanced reactivity in certain instances.[18] For this reason, it was of interest to test whether SIMes·HCl could be reacted directly with nickelocene. Interestingly, this appears to be a fairly straightforward reaction, as a solution of nickelocene and the saturated imidazolium chloride upon being refluxed in THF gave the desired product. Reaction completion is apparent by a change of color from dark green to red. This protocol also proved valid for the more sterically encumbered IPr and its saturated congener, SIPr (see Scheme 1). The isolated products are all stable in solution as well as being air-stable in the solid state. Complexes CpNi(SIMes)Cl (**2**; SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene), CpNi(IPr)Cl (**3**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), and CpNi(SIPr)Cl (**4**; SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) were synthesized as shown in Scheme 1. Initial support for the proposed structure was derived from both ^{1}H and ^{13}C NMR, which showed one carbene ligand and one η^5-bonded cyclopentadienyl ligand. The NMR spectroscopy was also consistent with the reported data for the IMes derivative.[17a] Elemental analysis confirmed the expected product composition.

Attempts to synthesize in a similar manner the I^{t}Bu, ICy, and IAd nickel complexes failed. All three bear alkyl substituents (*tert*-butyl, cyclohexyl, and adamantyl, respectively) directly on the imidazolium nitrogens, rendering the C−H imidazolium bond stronger and possibly more difficult to activate.

Exchanging the counterion from Cl to BF_4 or PF_6 leads to no reaction of either aryl- or alkylimidazolium salts and recovery of nickelocene. We believe that the strong Ni−Cl bond formed in the reaction with imidazolium chlorides must act as a significant thermodynamic driving force leading to product.

We also wondered if the protocol could be extended to trialkylphosphine complexes using a phosphonium salt as the phosphine source. $CpNi(PR_3)Cl$ (PR_3 = tertiary phosphine) complexes have been known for quite some time.[19] The preferred synthetic route to these complexes involved a disproportionation reaction where a mixture of nickelocene and $Ni(PR_3)_2Cl_2$ is refluxed until an equilibrium is reached. Yields are generally very low, and workup is not always straightforward. The handling of trialkylphosphines is also a possible complication, as these are extremely air-sensitive compounds. In attempting this one-pot synthesis with phosphonium salts[20] of trialkylphosphines, we targeted a solution that would address these two shortcomings.

Our first attempts involved the bulky [P^{t}Bu$_3$]HCl. The reaction with nickelocene and the salt did not lead to formation of the desired product. In light of the very bulky nature of P^{t}Bu$_3$ and of the small size of Ni, we reasoned that steric congestion might be at the origin of this failure. Use of a less sterically demanding but electronically equivalent tertiary phosphine, triethylphosphine (PEt_3), was then tested. The synthesis requires the quaternization of the phosphine, but this is easily achieved, since the air-sensitive triethylphosphine can be straightforwardly treated with an anhydrous HCl solution in dioxane to yield the air-stable phosphonium salt. A solution of nickelocene and triethylphosphonium chloride was stirred at room temperature until the characteristic green to red color change occurred after 2 h. This procedure afforded a moderate yield (32%) of $CpNi(PEt)_3Cl$ (**5**) (eq 1). The identity of **5** was confirmed

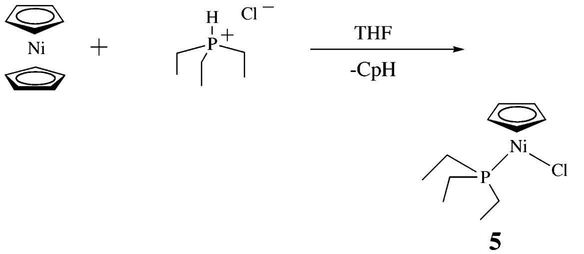


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Figure 1. Ball and stick structures of CpNi(SIMes)Cl (**2**) (left) and CpNi(IPr)Cl (**3**) (right). Most hydrogen atoms have been omitted for clarity.

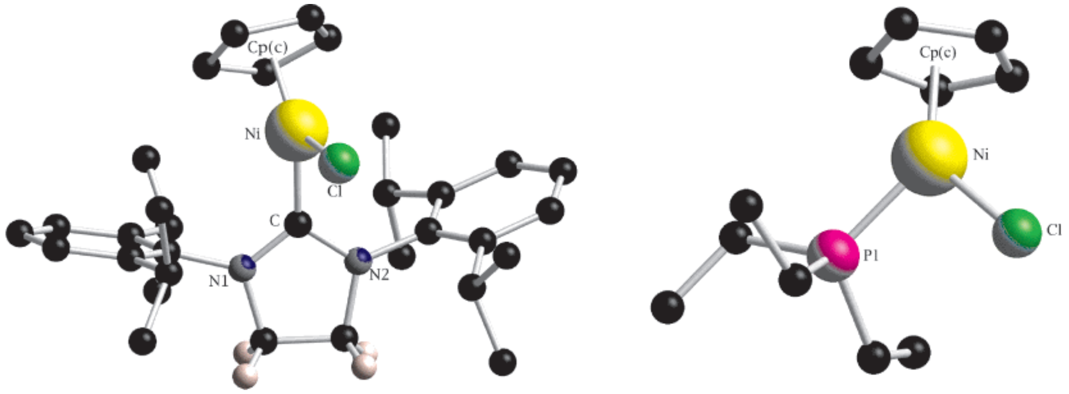

Figure 2. Ball and stick structures of CpNi(SIPr)Cl (**4**) (left) and CpNi(PEt_3)Cl (**5**) (right). Most hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for CpNi(SIMes)Cl (2), CpNi(IPr)Cl (3), CpNi(SIPr)Cl (4), CpNi(PEt_3)Cl (5), and CpNi(IMes)Cl (1)

	2[a]	**3**	**4**	**5**	**1**[b]
Ni−L[c]	1.85(2), 1.89(2)	1.8748(11)	1.8752(16)	2.1505(3)	1.917(9)
Ni−Cl	2.199(5), 2.183(6)	2.1876(3)	2.1795(5)	2.1871(3)	2.185(2)
Ni−Cp(c)	1.77(6), 1.76(7)	1.80(2)	1.768(8)	1.753(8)	1.760(7)
L−Ni−Cp(c)	133.5(8), 134.4(8)	134.8(8)	137.5(3)	136.2(3)	132.4(2)
Cl−Ni−Cp(c)	127.4(8), 127.1(9)	131.0(8)	130.4(3)	131.3(2)	129.2(2)
L−Ni−Cl	98.1(6), 99.4(6)	93.86(3)	92.06(5)	92.386(11)	98.2(2)

[a] Two independent molecules are present in the asymmetric unit. [b] Values taken from ref 17a. [c] L = SIMes, IPr, SIPr, PEt_3.

by comparison with the previously reported literature spectroscopic data.[19] To the best of our knowledge, this is the first report of the isolation of a metal−phosphine complex through the use of a phosphonium salt. This method may well be general for a variety of phosphine ligands and is especially applicable to systems containing larger metal centers, where steric crowding about the metal coordination sphere is not a concern.

To unequivocally determine the identity of **2**−**5**, single crystals were obtained from slow cooling of a warm saturated toluene solution of the respective compounds. The molecular structures of the complexes of type CpNi(L)Cl (L = SIMes (**2**), IPr (**3**), SIPr (**4**), PEt_3 (**5**)) are shown as ball-and-stick diagrams in Figure 1 (**2** and **3**) and Figure 2 (**4** and **5**), and relevant bond lengths and angles are provided in Table 1. In the case of **2**, poor-quality crystals yielded a higher *R* value than for complexes **3**−**5**. Nevertheless, the skeletal arrangement is correct, with the asymmetric unit comprising of two independent molecules with their bond distances and angles lying close to those obtained for **3** and **4**. In all cases the coordination geometry can be described as trigonal planar (sum of bond angles using the Cp ring centroid ~360.0°) comprised of a η^5-Cp ligand, a carbene (or phosphine in the case of **5**), and a chloride ion. For complexes **2**−**4**, the Ni−carbene bond lengths lie in the range 1.85−1.89 Å and are similar to those reported for $[Ni(Cp)(NHC)_2]^+$ (1.883(2) Å; NHC = tetramethylimidazol-2-ylidene)[21] and $(Cp)_2Ni(NHC)$ (1.885(4) Å; NHC = 1,3-bis(2,6-dimethyl-4-bromophenylimidazol-2-ylidene)[21] but are somewhat shorter than that reported for **1** (1.917(9) Å).[17a] The complexes containing the saturated NHC ligands (compounds **2** and **4**) show slightly shorter bond distances than their corresponding unsaturated analogues (Table 1); however, these differences are not significant. The Ni−Cl distances are similar to those of **1** (2.185(2) Å). As also observed for **1**,[17a] the aryl substituents on the NHC ligand are

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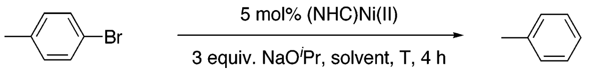
Table 2. Dehalogenation of *p*-Bromotoluene with CpNi(NHC)Cl Complexes as Precatalysts



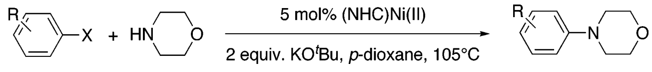
solvent, T (°C)	conversion^a (%) CpNi-(IPr)Cl	CpNi-(SIPr)Cl	CpNi-(IMes)Cl	CpNi-(SIMes)Cl
THF, 65	24	29	40	37
p-dioxane, 105	30	31	40	23

^{a} Conversions were determined by GC and are averages of two runs.

twisted (by 34.7(8) and 33.34(70)° for **2**, 37.91(5)° for **3**, and 31.12(0.08)° for **4**), resulting in a favorable steric arrangement with the metal center. In addition the two sp^3 carbons in the SIMes and SIPr complexes show torsion angles lower than the known value for free SIMes (13.4°), suggesting that some restriction in rotation is present (1.6(2)° for **2** and 6.8(3)° for **4**). For complex **5**, the nickel−phosphorus (2.1505(3) Å) and nickel−chloride (2.1871(3) Å) distances lie within the ranges reported for other three-coordinate nickel complexes.[22−25]

Catalytic Activity. The reactivity of these (NHC)Ni(II) complexes was tested in aryl dehalogenation and aryl amination reactions. Dehalogenation of aryl halides is an important reaction in organic chemistry as well as in the design of environmentally benign industrial processes, due to the high toxicity of these types of compounds.[26] Metal-catalyzed hydrogenation,[27] Grignard reagents,[28] and the use of Raney Ni−Al alloy under basic conditions[29] are some of the most widely studied methods of dehalogenation. Fort et al.[30] recently reported on the reduction of aryl halides catalyzed by nickel(II)/imidazolium chloride in the presence of a β-hydrogen-containing alkoxide. Conditions similar to those reported by Fort were tested with our CpNi(NHC)Cl complexes. The results of these catalytic tests are presented in Table 2. Moderate toluene formation was observed by GC after 4 h of reaction when bromotoluene was subjected to these conditions. No further conversion was observed after longer reaction times. The yields are similar for all nickel complexes, but the fastest reaction rates were observed with CpNi(IMes)Cl (**1**): 36% conversion after 1 h in THF at 65 °C. With CpNi(IPr)Cl (**3**), for example, only 14% of the dehalogenated product was obtained under the same conditions. Similar results were observed under reflux in both THF and dioxane, despite the difference in reaction temperature. These results are somewhat puzzling, but the activation step in this transformation may require reduction of Ni(II) to Ni(0) prior to oxidatively adding the aryl halide. The ease with which this reduction is accomplished (or lack thereof) may be at the origin of the poor catalytic performance in dehalogenation using this system.

Table 3. Aryl Amination Catalyzed with CpNi(NHC)Cl Complexes as Precatalysts



entry	R	X	time (h)	yield^a (%) CpNi-(IMes)Cl	CpNi-(SIMes)Cl	CpNi-(IPr)Cl	CpNi-(SIPr)Cl
1	*p*-Me	Cl	20	20^b	20^b	45^b	48^b
2	*p*-CN	Cl	7	32^b	34^b	75	82
3	*p*-Me	Br	7	98	92	90	98
4	*o*-Me	Br	20	49	50	76	80

^{a} Isolated yields. ^{b} Conversion determined by ^{1}H NMR of the crude product.

Carbon−nitrogen bond-forming reactions have been most widely studied with palladium complexes bearing sterically demanding ligands such as phosphines[31] and N-heterocyclic carbenes.[32] Much less attention has been paid to nickel-catalyzed aryl amination, even though it is an attractive alternative to the more costly palladium derivatives. Different nickel-based catalysts have shown their utility for this transformation: Ni(COD)$_2$ (COD = cyclooctadiene) associated with 1,1′-(bis(diphenylphosphino)ferrocene (DPPF) or 1,10-phenanthroline,[33] heterogeneous Ni(0)/C−DPPF,[34] and Ni(0)−2,2′-bipyridine.[35] Fort et al.[36] developed the amination of aryl chlorides based on a nickel/N-heterocyclic carbene system. The Ni(II)/SIPr·HCl precatalyst in the presence of NaO^{t}Bu was found to be efficient in the arylation of secondary cyclic or acyclic amines and anilines.

To achieve aryl amination reactions, we first tested the conditions reported by Fort. Unfortunately, no conversion was observed by GC. Some optimization studies were then carried out and revealed that 2 equiv of KO^{t}Bu in dioxane at 105 °C provided the best catalytic system. Under these conditions, *p*-chlorobenzonitrile and *p*-bromotoluene yielded the corresponding coupling products with morpholine in good yields (Table 3). Lower conversions were observed using *o*-bromotoluene. It is noteworthy that no difference in reactivity was observed between nickel complexes in the coupling of morpholine and *p*-bromotoluene, but more challenging aryl halides showed that CpNi(IPr)Cl (**3**) and CpNi-

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(SIPr)Cl (**4**) were the best catalyst precursors for this transformation. Studies aimed at exploiting this system in related catalytic transformations are ongoing.

Conclusions. We have prepared a series of catalytically active NHC–nickel compounds directly from a relatively inexpensive and readily available metal precursor and imidazolium salts. We were also able to synthesize a trialkylphosphine nickel complex through the use of an air-stable salt of an otherwise pyrophoric material. We plan to expand on the use of stable starting materials in the development of catalytically active compounds.

Experimental Section

General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon or in MBraun gloveboxes containing dry argon and less than 1 ppm of oxygen. Solvents were distilled from appropriate drying agents or were passed through an alumina column in an MBraun solvent purification system prior to use. Other anhydrous solvents were purchased from Aldrich and degassed prior to use by purging with dry argon and were kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. Aryl halides and morpholine were used as received. Flash column chromatography was performed on silica gel 60 (320–400 mesh). NMR spectra were collected on a 400 MHz Varian Gemini spectrometer. Elemental analyses were performed by Robertson Microlit Labs.

CpNi(SIMes)Cl (2). A solution of nickelocene (2.0 g, 10.6 mmol) in tetrahydrofuran (100 mL) was added to 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride (3.77 g, 11.0 mmol). The mixture was refluxed overnight. During the first 1 h of reflux, the color of the solution changed from dark green to dark red. The solvent was removed under vacuum, and the resulting red residue was extracted with hot (100 °C) toluene (100 mL). The solution was filtered and reduced in volume to 25 mL. When the solution stood for 12 h at ambient temperature, large red crystals of the product formed. These were collected by filtration and washed with pentane (25 mL), leading to the isolation of 4.3 g (87%) of the title compound. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.39 (s, 18H, CH_3); 3.90 (s, 4H, $NCH_2{-}CH_2N$); 4.54 (s, 5H, C_5H_5); 7.07 (s, 4H, *m-H*). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 201.04 (s, N–C–N), 138.51 (s, SIMes *C*), 137.11 (s, SIMes *C*), 129.70 (s, SIMes-*C*), 92.70 (s, C_5H_5), 51.21 (s, NCH_2CH_2N), 21.36 (s, SIMes CH_3), 18.74 (s, SIMes CH_3). Anal. Calcd for $C_{26}H_{31}N_2ClNi$: C, 67.06; H, 6.71; N, 6.02, Cl, 7.61. Found: C, 67.25; H, 6.67; N, 5.98; Cl, 7.87.

CpNi(IPr)Cl (3). A solution of nickelocene (2.0 g, 10.6 mmol) in tetrahydrofuran (100 mL) was added to 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (4.68 g, 11.0 mmol). The mixture was refluxed for 2.5 h. During the first 30 min of reflux, the color of the solution changed from dark green to bright red. The solvent was removed under vacuum, and the resulting red residue was extracted with hot (100 °C) toluene (100 mL). The solution was filtered and reduced in volume to 25 mL. When the solution stood for 12 h at ambient temperature, large red crystals of the product formed. These were collected by filtration and washed with pentane (25 mL), leading to 4.1 g (71% yield) of the title compound. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 1.10 (d, 12H, CH_3); 1.44 (d, 12H, CH_3); 2.84 (m, 4H, $CH(CH_3)_2$); 4.51 (s, 5H, C_5H_5); 7.11 (s, 2H, NC*H*); 7.22 (d, 4H, *m-H*); 7.58 (t, 2H, *p-H*). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 169.31 (s, N–*C*–N), 146.37 (s, IPr *C*), 136.71 (s, IPr *C*), 130.13 (s, IPr *C*), 125.51 (s, IPr *C*), 123.95 (s, NCH=CHN), 92.02 (s, C_5H_5), 28.61 (s, IPr *C*H), 26.11 (s, IPr CH_3), 22.50 (s, IPr CH_3). Anal. Calcd for $C_{32}H_{41}N_2ClNi$: C, 70.16; H, 7.54; N, 5.11; Cl, 6.47. Found: C, 69.99; H, 7.48; N, 4.99; Cl, 6.54.

CpNi(SIPr)Cl (4). A solution of nickelocene (2.0 g, 10.6 mmol) in tetrahydrofuran (100 mL) was added to 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride (4.69 g, 11.0 mmol). The mixture was refluxed overnight. During the first 1 h of reflux, the color of the solution changed from dark green to dark red. The solvent was removed under vacuum, and the resulting red residue was extracted with hot (100 °C) toluene (100 mL). The solution was filtered and reduced in volume to 25 mL. When the solution stood for 12 h at ambient temperature, large red crystals of the product formed. These were collected by filtration and washed with pentane (25 mL), leading to 4.7 g (81% yield) of the title compound. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 1.23 (d, 12H, CH_3); 1.47 (s, 12H, CH_3); 3.31 (m, 4H, $CH(CH_3)_2$); 3.99 (s, 4H, CH_2CH_2); 4.48 (s, 5H, C_5H_5); 7.35 (d, 4H, *m-H*); 7.49 (t, 2H, *p-H*). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 203.18 (s, N–C–N), 147.74 (s, SIPr *C*), 137.52 (s, SIPr *C*), 129.49 (s, SIPr *C*), 124.58 (s, SIPr *C*), 92.70 (s, C_5H_5), 53.57 (s, NCH_2CH_2N), 28.79 (s, SIPr *C*H), 26.89 (s, SIPr CH_3), 23.52 (s, SIPr CH_3). Anal. Calcd for $C_{32}H_{43}N_2ClNi$: C, 69.90; H, 7.88; N, 5.09; Cl, 6.45. Found: C, 69.85; H, 8.09; N, 5.07; Cl, 6.72.

CpNi(PEt$_3$)Cl (5). A solution of nickelocene (0.2 g, 1.06 mmol) in tetrahydrofuran (20 mL) was added to triethylphosphonium chloride (0.18 g, 1.16 mmol). The mixture was stirred at room temperature overnight. During the first 2 h, the color of the solution changed from dark green to dark red. The solvent was removed under vacuum, and the resulting residue was extracted with dry pentane. The solution was filtered, and the solvent was removed by vacuum to yield a red powder in 32% yield (178 mg). ^{1}H NMR (C_6D_6, 400 MHz, δ): 0.89 (m, 9H, CH_3); 1.13 (m, 6H, CH_2); 5.04 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ): 92.37 (s, C_5H_5); 16.92 (d, CH_2); 8.50 (s, CH_3). ^{31}P NMR (C_6D_6, 161.9 MHz, δ): 30.17 (s, 1P, PEt_3).

General Procedure for Dehalogenation of *p*-Bromotoluene. In an oven-dried vial fitted with a septum screw cap, NaH (60 mg, 1.5 mmol, 3 equiv), CpNi(NHC)Cl (0.025 mmol, 5 mol %), and 1 mL of THF were loaded inside a glovebox. Outside of the glovebox, the mixture was heated to 65 °C and *i*-PrOH (0.155 mL, 3 equiv) was added. After 1 h of further heating, *p*-bromotoluene was added and the reaction was monitored by GC.

General Procedure for Arylation of Morpholine. In an oven-dried vial fitted with a septum screw cap, KO^{t}Bu (0.112 g, 1 mmol, 2 equiv), CpNi(NHC)Cl (0.025 mmol, 5 mol %), and 1 mL of *p*-dioxane were loaded inside a dry glovebox. Outside of the glovebox, the mixture was heated to 105 °C and morpholine (65 μL, 1.5 equiv.) was added. After 30 min of further heating, the aryl halide (0.5 mmol) was added and the reaction was monitored by GC. After consumption of the starting halide or no further conversion, the reaction mixture was cooled to room temperature and adsorbed onto silica gel. The crude reaction mixture was purified by silica gel chromatography. All compounds described in Table 2 are known in the literature and were characterized by comparing their ^{1}H and ^{13}C NMR spectra to the previously reported data: *N*-(4-methylphenyl)morpholine (Table 2, entries 1 and 3),[37] *N*-(4-cyanophenyl)morpholine (Table 2, entry 2),[38] and *N*-(2-methylphenyl)morpholine (Table 2, entry 4).[39]

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Supporting Information Available: X-ray crystallographic information for **2**–**5** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org. Alternatively, the files CCDC 266059–266062 (compounds **2**–**5**) contain the supplementary crystallographic data for this paper. These data can be downloaded free of charge via www.ccdc.cam.ac.uk/conts/retrieving.hmtl (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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