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C–Br Activation of Aryl Bromides at Ni⁰(NHC)₂: Stoichiometric Reactions, Catalytic Application in Suzuki–Miyaura Cross-Coupling, and Catalyst Degradation

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Supporting Information

ABSTRACT: Complex $[Ni_2({}^{i}Pr_2Im)_4(COD)]$ (1) $({}^{i}Pr_2Im = 1,3-$ diisopropylimidazolin-2-ylidene) is a very efficient catalyst for the Suzuki–Miyaura cross-coupling reaction of 4-bromotoluene with phenylboronic acid and also mediates the Ullmann-type homocross-coupling reaction of bromobenzene with a moderate



efficiency. Stoichiometric reactions of complex 1 with aryl bromides (ArBr) at room temperature lead to mixtures of aryl bromo complexes of the type *trans*-[Ni(ⁱPr₂Im)₂(Br)(Ar)] and the bis(bromo) complex *trans*-[Ni(ⁱPr₂Im)₂(Br)₂] **2**. The complexes *trans*-[Ni(ⁱPr₂Im)₂(Br)(Ar)] (for Ar = Ph **3**, 4-MeC₆H₄ **4**, 4-Me(O)CC₆H₄ **5**, 4-MeOC₆H₄ **6**, 4-MeSC₆H₄ **7**, 4-Me₂NC₆H₄ **8**, 2-C₅NH₄ **9**) can be selectively synthesized by working at low temperatures and using a high dilution of the starting materials. A major deactivation pathway for *trans*-[Ni(ⁱPr₂Im)₂(Br)(Ar)] was identified in the presence of aryl bromides. This deactivation process includes (i) the formation of *trans*-[Ni(ⁱPr₂Im)₂(Br)(Ar)] was identified in the presence of aryl bromides. This deactivation of an imidazolium salt of the type $2[^{i}Pr_{2}Im-Ar]^{+}[NiBr_{4}]^{2-}$ from *trans*-[Ni(ⁱPr₂Im)₂(Br)(Ar)] (**2**) and ArBr and (ii) the formation of an imidazolium salt of the type $2[^{i}Pr_{2}Im-Ar]^{+}[NiBr_{4}]^{2-}$ from *trans*-[Ni(ⁱPr₂Im)₂(Br)₂] (**2**) and ArBr. The reactions of complex **2** with a series of aryl halides at higher temperatures lead to the decomposition of the bis(carbene) nickel moiety with formation of the imidazolium salts $2[^{i}Pr_{2}Im-Ar]^{+}[NiBr_{2}X_{2}]^{2-}$ (for X = I, Ar = Ph **10** and X = Br, Ar = Ph **11**, 4-MeC₆H₄ **12**, 4-FC₆H₄ **13**, 4-OSi(CH₃)₃-C₆H₄ **14**) in high yields.

INTRODUCTION

Transition metal mediated cross-coupling reactions are among the most powerful tools in the area of catalytic C–C bond formation.¹ We² and others³⁻⁶ have shown that NHCstabilized nickel complexes are efficient catalysts for Kumada-Corriu and Suzuki-Miyaura cross-coupling reactions of aryl fluorides and aryl chlorides. In earlier studies, we have shown that dinuclear $[Ni_2(^iPr_2Im)_4(COD)]$ (1) $(^iPr_2Im = 1,3$ diisopropylimidazolin-2-ylidene), which acts as a source for the electron-rich {Ni(ⁱPr₂Im)₂} complex fragment in stoichiometric and catalytic reactions,^{2,7} readily activates Ar-F and Ar-Cl bonds and catalyzes Suzuki-Miyaura cross-coupling reactions of perfluorinated arenes and unactivated aryl chlorides with aryl boronic acids. In stoichiometric reactions we have demonstrated that oxidative addition of poly- and perfluorinated arenes $(Ar_F - F)$ affords four-coordinated square-planar nickel-(II) complexes of the type trans- $[Ni({}^{i}Pr_{2}Im)_{2}(F)(Ar_{F})]$. Oxidative addition reactions of different aryl chlorides to complex 1 revealed high selectivity for a broad range of substrates, ranging from activated to deactivated aryl chlorides to give complexes of the type trans- $[Ni(^{i}Pr_{2}Im)_{2}(Cl)(Ar)]$. In the case of alkyl and aryl bromides and iodides, Cavell et al. reported the synthesis of the complexes trans-[Ni- $(Me_2ImMe_2)_2(Br)(2-MeC_6H_4)$] and trans-[Ni- $(Me_2ImMe_2)_2(I)(Me)$] $(Me_2ImMe_2 = 1,3,4,5$ -tetramethylimidazolin-2-ylidene) from the oxidative addition of the corresponding organic halides to the in situ generated ${Ni(Me_2ImMe_2)_2}$ fragment prepared from the reaction of $[Ni(COD)_2]$ with 2 equivalents of the ligand.^{4a}

Matsubara and co-workers^{6a} reported recently the synthesis of a three-coordinated, T-shaped nickel(I) chloride complex, $[Ni^{I}(Dip_{2}Im)_{2}(Cl)]$ (Dip_{2}Im = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene), stabilized by two bulky NHC ligands from the reaction of $[Ni(Dip_2Im)_2]$ with aryl chlorides. This complex was isolated in a yield of 34% and has been characterized using crystal structure determination and proton NMR spectroscopy. Matsubara et al. demonstrated that this nickel(I) complex catalyzes Kumada-Corriu cross-coupling reactions of aryl bromides with phenyl magnesium chloride, and a Ni(I)/Ni(III) cycle was proposed for this reaction. Similarly, Louie et al. reported the synthesis and structural characterization of the paramagnetic T-shaped complexes $[Ni^{I}(Mes_{2}Im)_{2}(X)]$ (X = Cl, Br, I; Mes_{2}Im = 1,3-bis(2,4,6trimethylphenyl)imidazolin-2-ylidene).^{6b} These complexes have also been prepared from the reaction of $[Ni(Mes_2Im)_2]$ with aryl halides Ar-X, and the potential products trans- $[Ni^{II}(Mes_2Im)_2(X)(Ar)]$, which would arise from oxidative addition, have not been observed. These Ni^I complexes have been employed as efficient catalysts in Kumada-Corriu and Suzuki-Miyaura cross-coupling reactions. Most interestingly, reinvestigating Cavell's system, these authors found complexes of the type trans- $[Ni(Me_2ImMe_2)_2(Br)(Ar)]$ (Ar = 4- $MeOC_6H_4$, 4- MeC_6H_4 , 4- $CF_3C_6H_4$) to be unstable, even in the solid state under an N₂ atmosphere.

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All these results suggest that the generally accepted mechanism for the cross-coupling reactions via oxidative addition, transmetalation, and reductive elimination may not be applicable to all NHC/Ni-based systems. At least the steric demand of the NHC and presumably also its donor strength and the nature of the substrate Ar–X have an influence on the catalytic pathway. This implies the question of the formation of the (expected) nickel(II) aryl halide complexes *trans*[Ni^{II}(R₂Im)₂(X)(Ar)] or the (rather unexpected) Ni^I aryl halide complexes [Ni^{I1}(R₂Im)₂(Ar)]/[Ni^{I1}(R₂Im)₂(X)] obtained from the reaction of a {Ni(R₂Im)₂} source and Ar–X. In continuation of our earlier work on C_{ar}–F and C_{ar}–Cl bond activation we report here the reactivity of 1 with respect to aryl bromides and aryl iodides as well as on deactivation pathways of Ni-catalyzed cross-coupling reactions.

RESULTS AND DISCUSSIONS

Stoichiometric C_{ar}-Br Activation. Although complex 1 readily reacts with poly- and perfluorinated arenes $(Ar_F - F)$ with formation of products of an oxidative addition,² no transformation was observed in stoichiometric reactions with fluorobenzene, even under elevated temperatures or photolytic conditions. Similarly to previously reported deactivation reactions for NHC complexes of group 10 metals,⁸ the reaction of complex 1 with iodobenzene resulted in the formation of elemental nickel. Chlorobenzene^{2e} and bromobenzene react with compound 1 with formation of the corresponding aryl halide complex. The room-temperature reactions of $[Ni_2(Pr_2Im)_4(COD)]$ (1) with stoichiometric amounts of different arvl bromides Ar-Br result in the formation of a mixture of diamagnetic products. These mixtures include the Ni^{II} aryl bromide complex *trans*- $[Ni(Pr_2Im)_2(Br)(Ar)]$, the Ni^{II} bis(bromide) complex trans- $[Ni(Pr_2Im)_2(Br)_2]$ (2), and another species, presumably the Ni^{II} bis(aryl) complex $[Ni(^{i}Pr_{2}Im)_{2}(Ar)_{2}]$, in various amounts. Depending on the nature of the aryl bromide and on the conditions employed, the amount on the secondary reaction products $[Ni(^{i}Pr_{2}Im)_{2}(Br)_{2}]$ and $[Ni({}^{i}Pr_{2}Im)_{2}(Ar)_{2}]$ can increase to more than 50%. Although radical intermediates cannot be ruled out, we did not observe any Ni^I intermediates in these reactions.

The selective synthesis of the complexes *trans*-[Ni-(${}^{i}Pr_{2}Im)_{2}(Br)(Ar)$] (Ar = Ph 3, 4-MeC₆H₄ 4, 4-Me(O)CC₆H₄ 5, 4-MeOC₆H₄ 6, 4-MeSC₆H₄ 7, 4-Me₂NC₆H₄ 8, 2-C₅NH₄ 9) (see Scheme 1) can be achieved by performing the reaction at

Scheme 1. Synthesis of the Activation Products of Aryl Bromides of the Type *trans*- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)(Ar)]$ for Ar = Ph 3, 4-MeC₆H₄ 4, 4-Me(O)CC₆H₄ 5, 4-MeOC₆H₄ 6, 4-MeSC₆H₄ 7, 4-Me₂NC₆H₄ 8, and 2-C₅NH₄ 9



low temperature $(-78 \, ^{\circ}\text{C})$ and in high dilution of the reactants. The complexes 3-9 were isolated in more than 80% yield, but small amounts (<5%) of the bis(bromo) complex *trans*- $[\text{Ni}(^{1}\text{Pr}_{2}\text{Im})_{2}(\text{Br})_{2}]$ (2) were observed occasionally in the crude reaction mixture. In contrast to the observations made by Louie et al. for the 1,3,4,5-tetramethylimidazolin-2-ylidene-

ligated complexes trans-[Ni(Me₂ImMe₂)₂(Br)(Ar)] (Ar = 4- $MeOC_6H_4$, 4-MeC₆H₄, 4-CF₃C₆H₄), we have found that the isolated compounds 3-9 are stable in solution and in the solid state for several months under an inert atmosphere. Once formed, the complexes *trans*- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(Ar)]$ seem to be very robust towards decomposition. Thus, heating a sample of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(C_{6}H_{5})]$ (3) in deuterobenzene for several days to 80 °C does not lead to decomposition or to ligand scrambling (vide infra). However, heating a sample of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(C_{6}H_{5})]$ (3) in the presence of additional phenyl bromide in deuterobenzene leads among other products (vide infra) to minor amounts of trans-[Ni- $({}^{i}Pr_{2}Im)_{2}(Br)_{2}$ (2) and biphenyl (detected by GC-MS). This finding may allow the assumption that the formation of the side products observed for the reaction of 1 and Ar-Br at room temperature originates from the reaction of the aryl bromide complexes with additional aryl bromide.

The compounds 3-9 were characterized by elemental analysis, EI-MS, IR and multinuclear NMR spectroscopy. The results of the CHN analyses are in a good agreement with the proposal of the reaction product as given in Scheme 1. The ¹H and ${}^{13}C{}^{1}H$ NMR spectra of the products 3–9 clearly reveal a trans-configuration of the NHC ligands in solution, and the integrations of the NHC and aryl ligand protons confirm the formation of *trans*- $[Ni(Pr_2Im)_2(Br)(Ar)]$. The compounds display inequivalent methyl groups of the NHCs' isopropyl substituents, represented by two distinct sets of resonances in the ¹H and ¹³C $\{^{1}H\}$ NMR spectra. The spectra reveal sets of equivalent methine resonances of the isopropyl groups and equivalent backbone and carbene carbon resonances. A summary of the ¹H NMR and ¹³C{¹H} NMR resonances of the NHC ligands in the complexes 3-9 is given in Tables 1 and 2.

Table 1. ¹H NMR Chemical Shifts (C_6D_6) of the NHC Ligands in Compounds 3–9

compound	d, 12 H, CH ₃	d, 12 H, CH ₃	s, 4 H, CHCH	sept, 4 H, ⁱ Pr- CH
3	1.18	1.56	6.22	6.55
4	1.20	1.57	6.23	6.58
5	1.16	1.54	6.19	6.47
6	1.19	1.56	6.25	6.55
7	1.18	1.56	6.23	6.51
8	1.22	1.58	6.27	6.58
9	1.28	1.63	6.23	6.81

The reactions of differently substituted aryl bromides, ranging from electron-rich to electron-poor substrates, show a high chemoselectivity toward C_{ar} -Br activation. The reaction of **1** with 4-bromoacetophenone affords the complex *trans*-

Table 2. ¹³C NMR Chemical Shifts (C_6D_6) of the NHC Ligands in Compounds 3–9

compound	CH_3	CH_3	ⁱ Pr-CH	CHCH	NCN
3	22.9	23.9	52.0	115.9	184.0
4	22.9	24.0	52.0	115.8	184.4
5	22.9	23.9	52.1	116.1	182.7
6	22.9	23.9	52.0	115.9	184.5
7	22.9	23.9	52.0	116.0	183.6
8	22.9	24.0	52.0	115.8	185.1
9	23.2	23.9	51.8	115.8	183.8

 $[Ni({}^{i}Pr_{2}Im)_{2}(Br)(4-Me(O)CC_{6}H_{4})]$ (5) in a high yield and does not lead to a likely C=O *side-on* coordinated nickel ketone complex. The IR spectrum of compound 5 clearly reveals the CO stretch at 1660 cm⁻¹, and the ${}^{13}C\{{}^{1}H\}$ NMR spectrum shows a resonance for the carbonyl carbon atom at 196.7 ppm. Furthermore, we have previously shown that complex 1 reacts with thioethers delivering C_{ar}-S bond activation products,^{7d} but the reaction of 1 with 4-MeSC₆H₄-Br leads exclusively to the oxidative addition of the C–Br bond. Single crystals of *trans*-[Ni(${}^{i}Pr_{2}Im)_{2}(Br)(4-Me_{2}NC_{6}H_{4})]$ (8) have been obtained from a saturated benzene solution at room temperature. The result of the X-ray diffraction analysis (see Figure 1) clearly confirms the formation of a reaction product



Figure 1. ORTEP diagram of the molecular structure of *trans*. [Ni($^{1}Pr_{2}Im$)₂(Br)(4-Me₂NC₆H₄)] (8) in the solid state (ellipsoids set at the 50% probability level). The hydrogen atoms have been omitted for clarity. Bond lengths (Å) and angles (deg): Ni–C1 1.909(2), Ni–C11 1.907(2), Ni–C21 1.910(2), Ni–Br 2.4064(6), C21–Ni–C1 90.0(4), C21–Ni–C11 89.4(4), C1–Ni–C11 177.7(4), C21–Ni–Br 174.7(3), C1–Ni–Br 90.0(3), C11–Ni–Br 90.8(3).

of C–Br oxidative addition to give the square-planar, fourcoordinate nickel(II) complex *trans*- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(4-Me_{2}NC_{6}H_{4})]$ (8). The distances and angles observed are unexceptional.

Catalytic Car-Br Activation: Suzuki-Miyaura Cross-Coupling and Reductive Homocoupling. We reported earlier that complex 1 is an efficient catalyst for Suzuki-Miyaura cross-coupling reactions of aryl chlorides with phenylboronic acid.^{2e} Variation of the reaction conditions such as catalyst loading, temperature, and kind and stoichiometric amount of the additive led to quantitative conversion of chlorobenzene and 4-chlorotoluene to the corresponding biaryl in the cross-coupling reaction with phenylboronic acid. The optimized catalytic reactions were performed in the presence of 3.0 equivalents of KO^tBu in boiling toluene with a catalyst loading of 2.4 mol % for 16 h. Catalyst 1 shows under the same conditions a significantly higher catalytic efficiency using aryl bromides. Quantitative conversion of 4-bromotoluene to 4-methylbiphenyl was observed with a catalyst loading of 0.61 mol % (see Scheme 2). Minor amounts of 4,4'-dimethyl-1,1'-biphenyl (1.1% with respect to 4-methylbiphenyl) and biphenyl (4.3% with respect to 4-methylbiphenyl) were detected due to homocoupling of the aryl bromide and the boronic acid, respectively.

Different NHC-, phosphine-, and amine-ligated nickel complexes have been reported as active catalysts for the Suzuki–Miyaura cross-coupling reactions of aryl bromides so far,⁹ and the substrates tested ranged from activated to deactivated aryl bromides. It is unfeasible to compare catalyst activities in cross-coupling reactions between different studies,

Scheme 2. Catalytic C–Br Activation: (i) $[Ni_2({}^iPr_2Im)_4(COD)]$ (1)-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of 4-Bromotoluene with Phenylboronic Acid^{*a*}; (ii) $[Ni_2({}^iPr_2Im)_4(COD)]$ (1)-Catalyzed Reductive Homocoupling Reaction of Bromobenzene^{*b*}



^{*a*}Reaction conditions for quantitative conversion of the aryl bromide: 0.61 mol % catalyst 1, 1.1 equiv of phenyboronic acid, 16 h in boiling toluene, 3.0 equiv of KO'Bu. ^{*b*}Reaction conditions: 0.80 mol % catalyst 1, 1.6 equiv of zinc, 16 h, 125 °C, ^{*n*}Bu₄NBr, 46% yield.

since the temperatures, additives, solvents, and most importantly the substrates used vary. However, it might be stated that complex 1 reveals a significantly higher catalytic efficiency in this type of transformation compared to other reported nickel-based catalysts. Leadbeater et al. obtained 80% yield of the cross-coupling product in the reaction of 4bromotoluene with phenylboronic acid in the presence of 3.0 mol % trans-[Ni(NEt₃)₂(Cl)₂] and 3.0 equivalents of Na₃PO₄ in dioxane at 95 °C.^{9a} Furthermore they demonstrated in this report that the analogue 2,2'-bipyridine complex [Ni(bipy)-(Cl)₂] is less active. In another publication, the Leadbeater group studied cross-coupling reactions of aryl bromides catalyzed by in situ generated phosphine-ligated nickel complexes $[Ni(dppf)(Cl)_2]$ (with dppf = 1,10-bis-(diphenylphosphino)ferrocene) and $[Ni{P(OMe)_3}_2(Cl)_2]^{.9b}$ Perec et al. applied phosphine complexes of the type $[Ni(L)_2(Cl)_2]$ in the presence of additional ligand L (with $(L)_2 = (PPh_3)_2$ and dppe = 1,2-bis(diphenylphosphino)ethane) in cross-coupling reactions of electron-rich and electron-poor aryl bromides with phenylboronic acid.9d The dppe-chelated complex revealed a higher activity. A reaction of methyl-4bromobenzoate (activated substrate) with 1.2 equivalents of phenylboronic acid and 3.0 equivalents of K₃PO₄ at a catalyst loading of 1.0 mol % $[Ni(dppe)(Cl)_2]$ and the addition of 1.0 mol % dppe led to the formation of 88% of the cross-coupling product after heating the reaction for 14 h to 80 °C in toluene. Lee and co-workers used nickel(II) complexes of bidentate NHC/phoshine ligands as catalysts for cross-coupling reactions of aryl bromides and chlorides with phenylboronic acid.^{9e} The catalytic coupling of bromobenzene with 1.3 equivalents of phenylboronic acid in the presence of 2.6 equivalents of base (K_3PO_4) and 3.0 mol % of the complex led to the formation of 95% biphenyl after heating the reaction mixture for 12 h in toluene to 80 °C. Full conversion of the aryl bromide was achieved under the same conditions with the addition of 6 mol % PPh₃. Similarly, Chen et al. observed a poor catalytic activity of nickel(II) complexes of the type $[Ni(L)](PF_6)_2$ with L = bis(N-pyridylimidazol)methane and bis(Npicolylbenzimidazol)methane. Using this catalyst for the reaction of 4-bromotoluene with 1.2 equivalents of phenylboronic acid (2.4 equiv of K₃PO₄·3H₂O, 3.0 mol % catalyst, 80 °C, 10 h), the yield of cross-coupling product was raised from 21% up to 100% upon addition of 6.0 mol % PPh₃.

Complex $[Ni_2(Pr_2Im)_4(COD)]$ (1) also catalyzes the reductive homocoupling reaction of bromobenzene in the

presence of zinc metal (see Scheme 2). First attempts to use **1** as a catalyst in boiling toluene as a solvent and potassium *tert*butoxide or cesium carbonate as a base were not successful, since the reaction in the presence of 3.0 equivalents of the corresponding base, 1.6 equivalents of zinc powder, and 1.2 mol % **1** led to the formation of biphenyl in only 9% and 18% yield, respectively (see Experimental Section, Table 3). A higher

Table 3. Isolated Yields of Biphenyl from the Reductive Homocoupling Reactions of Bromobenzene a

	base	yield (%)		mol % 1	yield (%)
1^b	Et ₃ N	9	3 ^c	0.8	46
2^{b}	Cs_2CO_3	18	4 ^c	2.5	54
			5 ^c	7.5	73

"Variation of reaction conditions (base, catalyst loading). The reaction time was 16 h and 1.6 equiv of zinc was used. b 3.0 equiv of base, refluxing toluene, 1.2 mol % catalyst. c 2.2 equiv of NBu₄Br, 125 °C.

catalytic activity was observed for the reactions performed in the ionic liquid tetra-*n*-butylammonium bromide at 125 $^{\circ}$ C. With a lower catalyst loading of 0.8 mol % the homocoupling product was formed in a higher yield of 46%. An increase in catalyst loading up to 7.5 mol % led to a rise of the yield up to 73% under the same conditions.

Deactivation Pathways. NHCs are currently widely employed as strong donor ligands for the synthesis of metal complexes and in catalysis. It is generally accepted that these ligands should in principle provide stable catalyst systems, and in some cases NHC complexes have been used at very high temperatures. One of the major problems using NHCs as ligands in catalysis is that—despite strong transition metal— NHC binding—NHCs are susceptible to loss by reductive elimination reaction from the metal center, leading to deactivation of the catalyst. The reductive elimination of imidazolium salts represents a major catalyst deactivation pathway of NHC complexes.^{8,11} In contrast to transition metal phosphine complexes, these reactions are generally irreversible for transition metal NHC complexes.

During our work on catalytic cross-coupling reactions using **1** as a catalyst, we became aware of two major decomposition products that arise from reactions of **1** with organic halides, especially in the absence of coupling reagents. One of the products is the dihalide complex *trans*- $[Ni(Pr_2Im)_2(X)_2]$, and the other the imidazolium salt $2[Pr_2Im-C_6H_5]^+[NiX_4]^{2-}$ (see Scheme 3). As mentioned above, heating a sample of *trans*- $[Ni(Pr_2Im)_2(Br)(C_6H_5)]$ (**3**) in deuterobenzene for several days to 80 °C does not lead to decomposition or ligand scrambling. Thus, we speculated on the formation of

Scheme 3. Catalyst Deactivation Reactions: (i) Formation of Aryl Imidazolium Salts; (ii) Quaternization of Tertiary Phosphines as Reported by Horner et al. for M = Ni, Co, Zn; X = Br, Cl



deactivation products from the complexes trans-[Ni- $({}^{i}Pr_{2}Im)_{2}(Br)(Ar)$ in the presence of Ar–X. Heating a sample of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(C_{6}H_{5})]$ (3) with 8 equivalents of phenyl bromide in deuterobenzene for 16 h leads to the formation of $2[{}^{i}Pr_{2}Im-C_{6}H_{5}]^{+}[NiBr_{4}]^{2-}$ (11) in high yields and to minor amounts of *trans*- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ (2). Biphenyl was detected from this mixture via GC-MS analysis. The formation of 11 was also observed in an almost quantitative yield starting from 1 and an excess of phenyl bromide at higher temperatures. In principle, similar reactions (quarternization of phosphines) have been known for phosphine systems for a very long time. Over 50 years ago, Horner et al. reported the reaction of tertiary phosphines with aryl halides to afford quaternary phosphonium salts in the presence of 3d transition metal halides,¹² and also identified some intermediates (A, B, and C in Scheme 3).

Similar reactions of NHC ligands have been observed in the case of group 8 metals by Cavell et al. at $[Pd(Me_2ImMe_2)_2]$.⁸ If iodobenzene is used as a coupling substrate, 2-phenyl-1,3,4,5-tetramethylimidazolium iodide salt was isolated, which was formed by reductive elimination from $[Pd(Me_2ImMe_2)_2(I)-(C_6H_5)]$. Similarly, in the case of nickel, 1,2,3,4,5-pentamethylimidazolium ion formation was observed from the reaction of " $[Ni(Me_2ImMe_2)_2]$ " with MeI, even when the reaction and workup were performed at temperatures as low as -50 °C.

The formation of imidazolium salts of the type $2[NHC-Ar]^+[NiX_4]^{2-}$ seems to be the final product of the deactivation using **1** as a catalyst. Since the major deactivation path identified includes (i) formation of *trans*- $[Ni(^iPr_2Im)_2(Br)_2]$ from *trans*- $[Ni(^iPr_2Im)_2(Br)(Ar)]$ and ArBr and (ii) formation of $2[^iPr_2Im-Ar]^+[NiX_2Br_2]^{2-}$ from *trans*- $[Ni(^iPr_2Im)_2(Br)_2]$ and ArBr, we examined the reaction of the Ni(II) complex *trans*- $[Ni(^iPr_2Im)_2(Br)_2]$ (**2**)¹³ with an excess of different aryl halides Ar–X (see Scheme 4). Whereas fluorobenzene and

Scheme 4. Reactions of *trans*- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ (2) with Aryl Halides (for X = I, R = H 10 and for X = Br, R = H 11, R = CH₂ 12, R = F 13, R = OSi(CH₂)₂ 14)



chlorobenzene are unreactive, the reactions of bromobenzene, iodobenzene, and some bromo benzene derivates with **2** lead to the formation of ionic compounds of the type $2[{}^{i}Pr_{2}Im-Ar]^{+}[NiBr_{2}X_{2}]^{2-}$ (for X = I, R = H **10** and for X = Br, R = H **11**, R = CH₃ **12**, R = F **13**, R = OSi(CH₃)₃ **14**). However, the reaction conditions to drive the stoichiometric reaction to completeness are rather vigorous. In order to obtain good yields of the resulting blue- to green-colored products, the starting materials needed to be stirred for several days at high temperatures (>100 °C) in toluene. A stoichiometric use of the starting material does not lead to full conversion under these conditions, and in all cases some *trans*-[Ni(${}^{i}Pr_{2}Im$)₂(Br)₂] (**2**) remains in the red-colored solution. The imidazolium salts show the characteristic color of the particular anionic nickel component [NiBr₂I₂]²⁻ (green) and [NiBr₄]²⁻ (blue).¹⁴ All

isolated imidazolium salts have been characterized by elemental analysis and IR and NMR spectroscopy. The ¹H and ¹³C{¹H} NMR spectra of these compounds show in addition to the signals for the aryl substituent a resonance for the isopropyl methyl group, for the isopropyl methine group, and for the backbone unit, indicating their NMR spectroscopic equivalence. The resonances of the aryl-binding imdiazolium carbon atoms were detected in a close range between 144.0 (13) and 144.9 ppm (14), a region typically observed for an aryl-substituted imidazolium salt of the type $[R_2Im-Ar]^{+.15}$

The formation of the imidazolium salts was confirmed by X-ray crystallography. Single crystals of $2[{}^{i}Pr_{2}Im-C_{6}H_{5}]^{+}[NiBr_{4}]^{2-}$ (11) have been obtained from a saturated acetone solution at room temperature. The molecular structure of the imidazolium cation is shown in Figure 2. The bond distances and angles



Figure 2. ORTEP diagram of the molecular structure of the imidazolium cation $[{}^{1}\text{Pr}_2\text{Im-C}_6\text{H}_5]^+$ of **11** in the solid state (ellipsoids set at the 50% probability level). The hydrogen atoms have been omitted for clarity. Bond lengths (Å) and angles (deg): C1–N1 1.329(12), C1–N2 1.339(10), C1–C10 1.483(12); N1–C1–N2 108.6(8), N1–C1–C10 126.0(8), N2–C1–C10 125.3(8), C1–C10–C11 119.5(8), C1–C10–C15 119.7(8), C11–C10–C15 120.7(9).

observed are as expected, and the dihedral angle (between the planes N2–N1–C1 and C10–C11–C15) along the C–C bond between the imidazolium ring and the phenyl ring of 96.7(5)° is close to perpendicular. For the reaction of aryl bromides with *trans*-[Ni(ⁱPr₂Im)₂(Br)₂] (**2**) we assume a stepwise deactivation via intermediates of the type [ⁱPr₂Im-Ar]⁺[Ni(ⁱPr₂Im)Br₃]⁻.

CONCLUSION

In summary, we have shown that the compound $[Ni_2(^iPr_2Im)_4(COD)]$ (1) is an excellent catalyst for the Suzuki-Miyaura cross-coupling of aryl bromides with phenyl boronic acid. Its activity is higher than reported for other nickel-based catalysts. Recent reports in the literature describe the formation of Ni(I) radicals of the type $[Ni^{I}(NHC)_{2}(X)]$ in reactions of [Ni(NHC)₂] with aryl halides if sterically demanding NHCs are employed. In contrast to these findings we have demonstrated that stoichiometric reactions of 1 with a variety of aryl bromides lead to oxidative addition and the formation of stable, four-coordinated, diamagnetic nickel(II) aryl bromide complexes of the type trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)-$ (Ar)]. Furthermore, we present some insights into NHC catalyst deactivation. On the basis of observations in stoichiometric reactions we revealed a deactivation pathway of $\{Ni(NHC)_2\}$ by reactions with any bromides at elevated temperatures. This catalyst degradation might be responsible for the relatively poor activity of 1 as a catalyst for the reductive homocoupling of bromobenzene to biphenyl. The process involves the reaction of the aryl bromo complexes trans $[Ni({}^{i}Pr_{2}Im)_{2}(Br)(Ar)]$ with aryl bromide to give the bis-(bromo) complex *trans*- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ (2), followed by formation of an aryl-imidazolium salt of the type $[{}^{i}Pr_{2}Im Ar]^{+}[NiBr_{4}]^{2-}$.

EXPERIMENTAL SECTION

General Considerations. All reactions and subsequent manipulations involving organometallic reagents were performed under a nitrogen or argon atmosphere using standard Schlenk techniques as reported previously.¹⁶ Elemental analyses were performed in the microanalytical laboratory of the Inorganic Chemistry Department of the University of Würzburg. The EI mass spectra were recorded with a Varian MAT 3830 (70 eV). NMR spectra were recorded with Bruker Avance 400 and Avance 500 spectrometers at 296 K in C₆D₆ or acetone- d_6 . NMR spectroscopic data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (1H, 13C, 29Si) and tri(chloro)fluoromethane (¹⁹F) as external standard. Coupling constants are quoted in hertz (Hz). The 13 C NMR spectra are broadband proton-decoupled and internally referenced to the naturalabundance carbon resonances (¹³C: C_6D_6 128.02 ppm and acetone- d_6 29.87 ppm). The assignments of the ¹³C{¹H} NMR resonances are supported by DEPT 135 NMR experiments. The ¹H NMR spectra are referenced internally to residual protio-solvent resonances (1H: C_6D_5H 7.15 ppm and acetone- d_5 2.05 ppm). Infrared spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer or with a Nicolet 380 FT-IR from solid samples using attenuated total reflectance (ATR) or as KBr pellets. All IR data are quoted in wavenumbers (cm⁻¹). GC-MS samples of the cross-coupling reactions were diluted with diethyl ether, and their analyses were performed using a Varian 320-MS (70 eV) equipped with a Varian 450-GC. Compound $1^{2a,7a}$ and trans- $[Ni(Pr_2Im)_2(Br)_2]$ (2)¹³ were prepared according to literature procedures; all other compounds have been obtained from commercial sources and were used without further purification.

Synthesis. General Method for the Synthesis of the Complexes trans- $[Ni(Pr_2Im)_2(Br)(Ar)]$. $[Ni_2(^{i}Pr_2Im)_4(COD)]$ (1) was suspended in *n*-hexane, and the mixture was cooled to -78 °C using a dry-ice/ isopropyl-alcohol bath. The corresponding aryl bromide was dissolved in *n*-hexane and added dropwise to the mixture. The reaction mixture was allowed to reach room temperature overnight, and all volatiles were removed *in vacuo*. The residue was suspended in *n*-hexane, and the product was filtered off, washed with *n*-hexane, and dried *in vacuo*.

Synthesis of trans-[Ni(ⁱPr₂Im)₂(Br)(Ph)], 3. A 336 mg amount of $[Ni_2(Pr_2Im)_4(COD)]$ (1) (0.40 mmol) was suspendend in 120 mL of *n*-hexane, and 85 μ L of phenyl bromide (0.80 mmol) in 50 mL of *n*hexane was added. Workup: 20 mL n-hexane for suspending and 10 mL of n-hexane for washing. Yield: 383 mg (92%) of a brownishyellow solid. Anal. Calcd (found) for C₂₄H₃₇BrN₄Ni [520.17 g/mol]: C 55.42 (55.90), H 7.17 (7.13), 10.77 (10.86). EI-MS m/z (%): 520 (1.4) $[M]^+$, 443 (16.5) $[Ni({}^{i}Pr_2Im)_2(Br)]^+$, 439 (3.7) [Ni- $({}^{1}Pr_{2}Im)_{2}(Ph)]^{+}$. ${}^{1}H$ NMR (500 MHz, C₆D₆, 23 °C): δ /ppm 1.18 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH_{3}$), 1.56 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH_{3}$) CH₃), 6.22 (s, 4 H, CHCH), 6.55 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH$), 6.77 (m, 1 H, aryl-H_p), 7.64 (m, 2 H, aryl-H_{tert}), 7.55 (m, 2 H, aryl- H_{tert}). ¹³C{¹H} NMR (100 MHz, C₆D₆, 23 °C): δ /ppm 22.9 (^{*i*}Pr-CH₃), 23.9 (^{*i*}Pr-CH₃), 52.0 (^{*i*}Pr-CH), 115.9 (NCCN), 121.1 (aryl-C_n), 126.0 (aryl-C_{tert}), 138.2 (aryl-C_{tert}), 158.3 (aryl-C_i), 184.0 (NCN). IR $(ATR, [cm^{-1}]): 673 (w), 704 (s, Ph-\delta_{CH,oop}), 734 (m, Ph-\delta_{CH,oop}), 755$ (vw), 799 (vw), 831 (vw), 881 (vw), 998 (vw), 1018 (vw), 1028 (vw), 1053 (vw), 1080 (vw), 1133 (w), 1177 (vs), 1215 (s, NHC-γ_{CH}), 1247 (w), 1302 (w), 1371 (m), 1394 (m), 1412 (m), 1425 (m), 1445 (w), 1465 (w), 1513 (vw), 1530 (vw), 1562 (w), 1630 (w), 1659 (m), 2876 (vw, ν_{CH}), 2934 (vw, ν_{CH}), 2974 (w, ν_{CH}), 3083 (vw, $\nu_{=CH}$). trans- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ (2). If the same reaction is performed at room temperature in a reduced volume of solvent (hexane, thf, diethyl ether, benzene, or toluene), a mixture of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(Ph)]$ (3), trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)_{2}]$ (2), and a third NHC-Ni-containing component, presumably trans-[Ni('Pr₂Im)₂(Ph)₂], can be isolated. The exact amount of each product formed in the mixture varies

strongly and leads to mixtures containing up to 50% of compound 2. Single crystals of compound 2 were obtained by storing a saturated toluene solution of the reaction mixture obtained from the reaction of 1 with PhBr at room temperature at -30 °C. X-ray analysis of these crystals led to an identical structure to that reported in the literature.⁵⁷ Anal. Calcd (found) for C18H32Br2N4Ni [522.97 g/mol]: C 41.49 (41.34), H 6.52 (6.17), 10.24 (10.71). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ /ppm 1.51 (d, 24 H, ${}^{3}J_{HH} = 6.8$ Hz, 'Pr-CH₃), 6.28 (s, 4 H, CHCH), 6.93 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH$). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ/ppm 23.1 (ⁱPr-CH₃), 52.4 (ⁱPr-CH), 116.6 (NCCN). Due to the low solubility of the compound in benzene, the resonance of the carbene carbon atom was not detected in benzene, but in acetone- d_6 . ¹H NMR (500 MHz, acetone- d_6 , 23 °C): δ /ppm 1.65 (d, 24 H, ${}^{3}J_{HH}$ = 6.8 Hz, ${}^{i}Pr-CH_{3}$), 6.73 (sept, 4 H, ${}^{3}J_{HH}$ = 6.8 Hz, ⁱPr-CH), 7.15 (s, 4 H, CHCH). ¹³C{¹H} NMR (125 MHz, acetone-d₆, 23 °C): δ/ppm 24.1 (ⁱPr-CH₃), 53.9 (ⁱPr-CH), 119.0 (NCCN), 170.4 (NCN). IR (ATR, [cm⁻¹]): 709 (m), 735 (w), 833 (vw), 1005 (vw), 1032 (vw), 1135 (w), 1176 (w), 1213 (vs, NHC-γ_{CH}), 1309 (w), 1340 (vw), 1370 (m), 1393 (m), 1416 (m), 1429 (s), 1431 (s), 1448 (w), 1457 (w), 1465 (w), 1472 (w), 1476 (vw), 2875 (w, $\nu_{\rm CH}$), 2931 (w, $\nu_{\rm CH}$), 2972 (m, $\nu_{\rm CH}$), 3093 (vw, $\nu_{=\rm CH}$), 3122 (w, $\nu_{=\rm CH}$), 3142 (vw), 3154 (vw).

Synthesis of trans-[Ni(Pr₂Im)₂(Br)(4-MeC₆H₄)], 4. A 336 mg sample of [Ni₂(ⁱPr₂Im)₄(COD)] (1) (0.40 mmol) was suspendend in 100 mL of n-hexane, and 100 µL of 4-bromotoluene (0.80 mmol) in 75 mL of n-hexane was added. Workup: 20 mL n-hexane for suspending and 10 mL of *n*-hexane for washing. Yield: 364 mg (83%) of a yellow solid. Anal. Calcd (found) for C25H39BrN4Ni [534.20 g/mol]: C 56.21 (56.27), H 7.36 (7.31), 10.49 (10.51). EI-MS m/z (%): 443 (5.5) $[Ni({}^{i}Pr_{2}Im)_{2}(Br)]^{+}$, 243 (100.0) $[Ni(CH_{2}CHHIm)(C_{6}H_{4}Me)]^{+}$, 233 (18.3) $[Ni(CH_2CHHIm)(Br)]^+$. ¹H NMR (400 MHz, C₆D₆, 23 °C): δ /ppm 1.20 (d, 12 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH₃), 1.57 (d, 12 H, ³J_{HH} = 6.8 Hz, ⁱPr-CH₃), 2.10 (s, 3 H, aryl-CH₃), 6.23 (s, 4 H, CHCH), 6.58 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH$), 6.78 (m, 2 H, aryl-H), 7.44 (d, 2 H, aryl-H). ¹³C{¹H} NMR (125 MHz, C₆D₆, 23 °C): δ/ppm 20.9 (aryl-CH₃), 22.9 (ⁱPr-CH₃), 24.0 (ⁱPr-CH₃), 52.0 (ⁱPr-CH), 115.8 (NCCN), 127.2 (aryl- C_{tert}), 129.4 (aryl- C_{quart}), 137.9 (aryl- C_{tert}), 152.6 (aryl- C_{quart}), 184.4 (NCN). IR (ATR, [cm⁻¹]): 609 (w), 675 (s), 688 (vs), 708 (s), 735 (w), 791 (m, Ph- $\delta_{CH,oop}$), 816 (w), 831 (w), 881 (w), 930 (vw), 1013 (w), 1028 (w), 1045 (w), 1082 (w), 1114 (w), 1133 (m), 1185 (w), 1215 (vs, NHC-γ_{CH}), 1262 (vw), 1301 (w), 1369 (m), 1391 (m), 1406 (m), 1425 (m), 1466 (w), 1478 (w), 1561 (vw), 1615 (vw), 1663 (vw), 2870 (vw, ν_{CH}), 2933 (w, ν_{CH}), 2968 (w, ν_{CH}).

Synthesis of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(4-Me(O)CC_{6}H_{4})]$, 5. A 336 mg portion of $[Ni_2(^{i}Pr_2Im)_4(COD)]$ (1) (0.40 mmol) was suspendend in 100 mL of "hexane. A 160 mg sample of 4-bromoacetophenone (0.80 mmol) in 35 mL of n-hexane was added. Workup: 20 mL n-hexane for suspending and 10 mL of *n*-hexane for washing. Yield: 405 mg (90%) of a yellow solid. Anal. Calcd (found) for C₂₆H₃₉BrN₄NiO [562.21 g/ mol]: C 55.54 (55.21), H 6.99 (7.03), 9.97 (9.98). EI-MS m/z (%): 520 (3.0) $[Ni({}^{i}Pr_{2}Im)_{2}(Br)(C_{6}H_{5})^{+}, 443 (23.3) [Ni({}^{i}Pr_{2}Im)_{2}(Br)]^{+},$ 271 (100.0) [Ni(CH₂CHHIm)(CH₃(O)CC₆H₄)]⁺, 233 (24.2) [Ni- $(CH_2CHHIm)(Br)]^+$. ¹H NMR (400 MHz, C₆D₆, 23 °C): δ /ppm 1.16 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH_{3}$), 1.54 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ⁱPr-CH₃), 2.12 (s, 3 H, C(O)CH₃), 6.19 (s, 4 H, CHCH), 6.47 (sept, 4 H, ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}$, ${}^{1}\text{Pr-CH}$), 7.56 (m, 2 H, aryl- H_{m}), 7.74 (d, 2 H, aryl- H_{o}). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (125 MHz, C₆D₆, 23 °C): δ /ppm 22.9 (${}^{1}\text{Pr-CH}_{3}$), 23.9 (ⁱPr-CH₃), 25.8 (C(O)CH₃), 52.1 (ⁱPr-CH), 116.1 (NCCN), 124.9 (aryl- C_{tert}), 131.7 (aryl- C_{quart}), 137.5 (aryl- C_{tert}), 174.4 (aryl- C_{quart}), 182.7 (NCN), 196.7 ($\dot{C}(O)CH_3$). IR (ATR, $[cm^{-1}]$): 631 (vw), 645 (vw), 676 (w), 689 (m), 702 (vs), 733 (w), 809 (m, Ph- $\delta_{\rm CH,oop}$), 839 (vw), 881 (vw), 951 (w), 1009 (w), 1027 (w), 1039 (w), 1078 (w), 1134 (w), 1181 (m), 1215 (vs, NHC- γ_{CH}), 1274 (s), 1301 (w), 1357 (m), 1370 (m), 1391 (w), 1408 (m), 1425 (m), 1467 (vw), 1534 (w), 1567 (vs), 1660 (vs, $\nu_{\rm CO})$, 2874 (vw, $\nu_{\rm CH})$, 2933 (vw, $\nu_{\rm CH})$, 2971 (w, $\nu_{\rm CH}$), 3086 (vw, $\nu_{=\rm CH}$), 3116 (vw, $\nu_{=\rm CH}$).

Synthesis of trans- $[Ni(^{h}Pr_{2}Im)_{2}(Br)(4-MeOC_{6}H_{4})]$, **6**. A 336 mg amount of $[Ni_{2}(^{h}Pr_{2}Im)_{4}(COD)]$ (1) (0.40 mmol) was suspendend in 100 mL of *n*-hexane, and 100 μ L of 4-bromoanisole (0.80 mmol) in 75 mL of *n*-hexane was added. Workup: 20 mL *n*-hexane for suspending

and 10 mL of n-hexane for washing. Yield: 357 mg (81%) of a light brown solid. Anal. Calcd (found) for C25H39BrN4NiO [550.20 g/ mol]: C 54.57 (54.41), H 7.14 (7.18), 10.18 (10.13). EI-MS m/z (%): 550 (3.8) $[M]^+$, 259 (3.3) $[Ni(CH_2CHHIm)(C_6H_4OMe)]^+$. ¹H NMR (400 MHz, C_6D_6 , 23 °C): δ /ppm 1.19 (d, 12 H, ${}^3J_{HH}$ = 6.8 Hz, 'Pr-CH₃), 1.56 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH_{3}$), 3.33 (s, 3 H, OCH₃), 6.25 (s, 4 H, CHCH), 6.55 (sept, 4 H, ${}^{3}J_{HH}$ = 6.8 Hz, ⁱPr-CH), 6.66 (m, 2 H, aryl-H), 7.26 (m, 2 H, aryl-H). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 23 °C): δ/ppm 22.9 (ⁱPr-CH₃), 23.9 (ⁱPr-CH₃), 52.0 (ⁱPr-CH), 54.4 (OCH₃), 112.7 (aryl-C_{tert}), 115.9 (NCCN), 138.2 (aryl-C_{tert}), 143.6 (aryl- C_{quart}), 155.9 (aryl- C_{quart}), 184.5 (NCN). IR (ATR, [cm⁻¹]): 630 (s), 675 (s), 691 (vs), 704 (vs), 732 (m), 811 (m, Ph- $\delta_{\rm CH,oop}$), 846 (m), 880 (m), 926 (w), 1005 (m), 1025 (m), 1080 (w), 1132 (m), 1174 (m), 1216 (vs, NHC-γ_{CH}), 1258 (w), 1300 (m), 1369 (s), 1391 (s), 1405 (s), 1424 (s), 1465 (m), 1518 (w), 1595 (w), 1660 (vw), 2870 (vw, $\nu_{\rm CH}$), 2932 (w, $\nu_{\rm CH}$), 2969 (w, $\nu_{\rm CH}$), 3135 (vw, $\nu_{=CH}$).

Synthesis of trans- $[Ni(^{\dagger}Pr_{2}Im)_{2}(Br)(4-MeSC_{6}H_{4})]$, 7. A 168 mg sample of [Ni₂(ⁱPr₂Im)₄(COD)] (1) (0.20 mmol) was suspendend in 50 mL of *n*-hexane, and 85 mg of 4-bromothioanisol ($0.4\overline{2}$ mmol) in 20 mL of n-hexane was added. Workup: 10 mL n-hexane for suspending and 10 mL of *n*-hexane for washing. Yield: 171 mg (76%) of a light brown solid. Anal. Calcd (found) for $C_{25}H_{39}BrN_4NiS$ [566.26 g/mol]: C 53.03 (53.43), H 6.94 (7.07), 9.89 (9.68). EI-MS m/z (%): 443 (14.1) [Ni(ⁱPr₂Im)₂(Br)]⁺, 275 (82.2) [Ni- $(CH_2CHHIm)(C_6H_5-S-CH_3)]^+$, 233 (12.7) $[Ni(CH_2CHHIm)(Br)]^+$. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ /ppm 1.18 (d, 12 H, $^{3}J_{HH} = 6.8$ Hz, ^{*i*}Pr-CH₃), 1.56 (d, 12 H, ³ $J_{\rm HH}$ = 6.8 Hz, ^{*i*}Pr-CH₃), 2.04 (s, 3 H,SCH₃), 6.23 (s, 4 H, CHCH), 6.51 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr$ -CH), 7.01 (d, 2 H, ${}^{3}J_{HH} = 8.1$ Hz, aryl- H_{p}), 7.46 (d, 2 H, ${}^{3}J_{HH} = 8.1$ Hz, aryl- H_{o}). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ /ppm 17.2 (SCH₃), 22.9 (ⁱPr-CH₃), 23.9 (ⁱPr-CH₃), 52.0 (ⁱPr-CH), 116.0 (NCCN), 126.7 (aryl- C_{quart}), 129.3 (aryl- C_{tert}), 138.5 (aryl- C_{tert}), 155.6 (aryl-C_{quart}), 183.6 (NCN). IR (ATR, [cm⁻¹]): 455 (w), 466 (w), 511 (vw), 579 (w), 698 (vs), 799 (m, Ph- $\delta_{CH,oop}$), 880 (w), 1027 (m), 1096 (m), 1132 (w), 1173 (w), 1217 (vs, NHC- γ_{CH}), 1262 (w), 1300 (w), 1370 (m), 1391 (w), 1407 (m), 1424 (m), 1467 (w), 1562 (vw), 2871 (vw), 2932 (w, ν_{CH}), 2969 (w, ν_{CH}), 3059 (vw, $\nu_{=CH}$).

Synthesis of trans-[Ni(ⁱPr₂Im)₂(Br)(4-Me₂NC₆H₄)], 8. A 336 mg portion of [Ni₂(ⁱPr₂Im)₄(COD)] (1) (0.40 mmol) was suspendend in 100 mL of n-hexane, and 161 mg of 4-bromo-N,N-dimethylaniline (0.42 mmol) in 20 mL of n-hexane was added. Workup: 20 mL nhexane for suspending and 10 mL of n-hexane for washing. Yield: 388 mg (86%) of a light brown solid. Single crystals suitable for X-ray diffraction were obtained from recrystallization in benzene. Anal. Calcd (found) for C₂₆H₄₂BrN₅Ni [563.24 g/mol]: C 55.44 (55.08), H 7.52 (7.51), 12.43 (12.34). EI-MS m/z (%): 443 (2.7) $[Ni(Pr_2Im)_2(Br)]^+$, 362 (33.5) $[Ni({}^{i}Pr_{2}Im)_{2}]^{+}$, 272 (11.1) $[Ni(CH_{2}CHHIm)_{-}]^{+}$ $(C_6H_4NMe_2)]^+$, 233 (9.3) $[Ni(CH_2CHHIm)(Br)]^+$. ¹H NMR (500 MHz, C₆D₆, 23 °C): δ /ppm 1.22 (d, 12 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{i}Pr-CH_{3}$), 1.58 (d, 12 H, ${}^{3}J_{HH}$ = 6.8 Hz, ${}^{i}Pr-CH_{3}$), 2.52 (s, 6 H, NCH₃), 6.27 (s, 4 H, CHCH), 6.52 (m, 2 H, aryl- H_m), 6.58 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{1}Pr-CH$), 7.19 (d, 2 H, aryl- H_o). ${}^{13}C{}^{1}H$ NMR (125 MHz, C_6D_6 , 23 °C): δ/ppm 22.9 (ⁱPr-CH₃), 24.0 (ⁱPr-CH₃), 41.2 (NCH₃), 52.0 (ⁱPr-CH), 113.4 (aryl-C_{tert}), 115.8 (NCCN), 138.5 (aryl-C_{tert}), 139.2 (aryl- C_{quart}), 146.8 (aryl- C_{quart}), 185.1 (NCN). IR (ATR, [cm⁻¹]): 630 (w), $675 \text{ (m)}, 697 \text{ (vs)}, 729 \text{ (w)}, 746 \text{ (w)}, 794 \text{ (s, Ph-}\delta_{CH,oop}), 816 \text{ (w)}, 827$ (w), 880 (vw), 941 (w), 1001 (w), 1028 (w), 1054 (w), 1080 (w), 1116 (w), 1133 (m), 1158 (w), 1172 (m), 1218 (vs, NHC- γ_{CH}), 1302 (m), 1326 (w), 1369 (m), 1388 (m), 1406 (m), 1425 (w), 1460 (m), 1484 (vw), 1538 (vw), 1580 (vw), 1612 (w), 2785 (vw), 2784 (vw), 2870 (vw, $\nu_{\rm CH})$, 2932 (vw, $\nu_{\rm CH})$, 2967 (w, $\nu_{\rm CH})$, 3059 (vw, $\nu_{=\rm CH})$, 3094 (vw, $\nu_{=CH}$), 3156 (vw).

Synthesis of trans- $[Ni(^{1}Pr_{2}Im)_{2}(Br)(2-C_{5}NH_{4})]$, **9**. A 336 mg amount of $[Ni_{2}(^{1}Pr_{2}Im)_{4}(COD)]$ **1** (0.40 mmol) was suspendend in 100 mL of *n*-hexane, and 77 μ L of 4-bromopyridine (0.80 mmol) in 75 mL of *n*-hexane was added. Workup: 20 mL *n*-hexane for suspending and 10 mL of *n*-hexane for washing. Yield: 363 mg (87%) of a light brown solid. Anal. Calcd (found) for C₂₃H₃₆BrN₅Ni [521.16 g/mol]: C 53.01 (52.74), H 6.96 (6.96), 13.44 (12.99). EI-MS m/z (%): 521 (1.3)

 $[M]^+$, 520 (6.6) $[Ni(^{i}Pr_{2}Im)_{2}(Br)(2-C_{5}NH_{3})]^+$, 443 (10.7) [Ni- $({}^{P}Pr_{2}Im)_{2}Br)]^{+}$, 233 (57.2) $[Ni(CH_{2}CHHIm)(Br)]^{+}$, 230 (28.0) $[Ni(CH_2CHHIm)(C_5NH_4)]^+$. ¹H NMR (400 MHz, C₆D₆, 23 °C): δ /ppm 1.28 (d, 12 H, ${}^{3}J_{HH}$ = 6.8 Hz, i Pr-CH₃), 1.63 (d, 12 H, ${}^{3}J_{HH}$ = 6.8 Hz, ⁱPr-CH₃), 6.20 (m, 1 H, aryl-H), 6.23 (s, 4 H, CHCH), 6.62 (m, 1 H, aryl-H), 6.81 (sept, 4 H, ${}^{3}J_{HH} = 6.8$ Hz, ${}^{1}Pr-CH_{3}$), 7.56 (m, 2 H, aryl-H), 8.43 (m, 1 H, aryl-H). ${}^{13}C{}^{1}H$ NMR (100 MHz, $C_{6}D_{6}$, 23 °C): δ/ppm 23.2 (ⁱPr-CH₃), 23.9 (ⁱPr-CH₃), 51.8 (ⁱPr-CH), 115.2 (aryl-C_{tert}), 115.8 (NCCN), 129.4 (aryl-C_{tert}), 132.5 (aryl-C_{tert}), 147.6 (aryl-C_{tert}), 183.8 (NCN), 192.2 (aryl-C_{quart}). IR (ATR, [cm⁻¹]): 673 (m), 695 (vs), 741 (w), 759 (m), 798 (vw), 818 (vw), 931 (vw), 972 (vw), 1001 (vw), 1027 (w), 1041 (vw), 1081 (w), 1107 (vw), 1133 (w), 1175 (vw), 1213 (vs, NHC- γ_{CH}), 1254 (vw), 1271 (vw), 1305 (w), 1324 (vw), 1370 (m), 1395 (m), 1407 (m), 1423 (m), 1436 (m), 1465 (w), 1515 (vw), 1538 (w), 1562 (w), 1605 (vw), 1663 (w), 1980 (vw), 2163 (vw), 2872 (vw, $\nu_{\rm CH}$), 2935 (vw, $\nu_{\rm CH}$), 2971 (w, $\nu_{\rm CH}$), 3057 (vw, $\nu_{=CH}$), 3127 (vw, $\nu_{=CH}$).

Cross-Coupling Reaction of 4-Bromotoluene with Phenylboronic Acid. A 656 mg sample of phenylboronic acid (5.37 mmol, 1.1 equiv), 1.64 g of KOtBu (14.64 mmol, 3.0 eqiuv), and 25 mg of $[Ni_2(Pr_2Im)_4(COD)]$ (29.8 µmol, 0.61 mol %) (1) were suspended in 10 mL of toluene. After adding 600 μ L (4.88 mmol, 1.0 equiv) of 4bromotoluene the reaction mixture was refluxed for 16 h. After cooling the mixture to room temperature the mixture was analyzed by GC-MS and ¹H NMR spectroscopy. 4-Methyl-1,1'-biphenyl: EI-MS m/z (%): 168 (100) [M]⁺.

General Procedure of the Reductive Homocoupling Reactions. In Toluene. A 500 μ L amount of bromobenzene (4.78 mmol) was added to a suspension of 48 mg of $[Ni_2(Pr_2Im)_4(COD)]$ (1) (57.1 μ mol, 1.20 mol %), 500 mg of zinc (7.64 mmol, 1.6 equiv), and the corresponding base in 10 mL of toluene. The reaction mixture was refluxed for 16 h. After cooling the mixture to room temperature all volatiles were removed in vacuo. Afterward the residue was dissolved in 60 mL of hexane, and 50 mL of half-concentrated aqueous potassium hydroxide solution was added. The organic layer was separated and the organic phase was extracted three times with 50 mL of halfconcentrated aqueous potassium hydroxide solution. The combined aqueous phases were extracted five times with 50 mL of hexane and three times with 50 mL of dichloromethane. All organic phases were combined, dried over sodium sulfate, and filtered. All volatiles were removed in vacuo. For the low yield conversions the product was chromatographically purified over silica gel with hexane as solvent. Yields are given in Table 3.

In Tetra-n-butylammonium Bromide. A 5.00 g portion of tetra-nbutylammonium bromide (15.51 mmol) was dried in vacuo at 100 °C for 5 h. After cooling the ionic liquid to room temperature the salt was added to the corresponding amount of $[Ni_2(Pr_2Im)_4(COD)]$ (1) and 500 mg of zinc (7.64 mmol, 1.6 equiv). After adding 500 μ L of bromobenzene (4.78 mmol) the mixture was heated to 125 °C for 16 h. After cooling the reaction mixture to room temperature all volatiles were removed in vacuo, and the residue was solved in 50 mL of water. The water was extracted eight times with 50 mL of diethyl ether. The combined organic layers were dried over sodium sulfate and filtered. The diethyl ether was removed in vacuo. Yields are given in Table 1. Anal. Calcd (found) for C₁₂H₁₀ [154.21 g/mol]: C 93.46 (93.28), H 6.54 (6.40). EI-MS m/z (%): 154 (100) [M]⁺. ¹H NMR (400 MHz, acetone-*d*₆, 23 °C): δ/ppm 7.31 (m, 2 H, aryl-*H*_p), 7.46 (m, 4 H, aryl- $\begin{array}{l} H_{\text{tert}}, 7.65 \text{ (m, 4 H, aryl-<math>H_{\text{tert}}). ^{13}\text{C}^{1}\text{H} \text{ NMR (100 MHz, acetone-}d_{6}, \\ 23 ^{\circ}\text{C}): \delta/\text{ppm 128.7 (aryl-}C_{\text{p}}), 128.7 (aryl-C_{\text{tert}}), 130.7 (aryl-C_{\text{tert}}), \\ 142.9 (aryl-C_{\text{i}}). \text{ IR (ATR, [cm^{-1}]): 693 (vs), 725 (vs), 834 (vw), 903 \\ \end{array}$ (w), 1006 (w), 1041 (vw), 1091 (vw), 1112 (vw), 1170 (w), 1182 (vw), 1308 (vw), 1345 (w), 1385 (vw), 1429 (m), 1477 (m), 1516 (vw), 1570 (vw), 1597 (vw), 1650 (vw), 1691 (vw), 1748 (vw), 1797 (vw), 1878 (vw), 1952 (vw), 3034 (w), 3062 (vw), 3089 (vw), 3111 $(\mathbf{v}\mathbf{w})$.

Reaction of 3 with an Excess of Bromobenzene at Higher **Temperatures.** Method A: 81.7 μ L (775 μ mol, 8 equiv) of bromobenzene was added to a suspension of 50 mg (96.9 μ mol) of trans- $[Ni(^{i}Pr_{2}Im)_{2}(Br)(C_{6}H_{5})]$ (3) in 5 mL of toluene. The colorless mixture was stirred for 16 h at 100 °C. All volatiles were removed in

vacuo to afford 88 mg (94.5 μ mol, 98%) of $2[^{i}Pr_{2}Im-C_{6}H_{5}]^{+}[NiBr_{4}]^{2-}$ (11) (see below) as a blue solid.

Method B: 632 µL (6.00 mmol, 50 equiv) of bromobenzene was added to a suspension of 100 mg (120 μ mol) of $[Ni_2(^iPr_2Im)_4(COD)]$ (1) in 5 mL of toluene. The mixture was stirred for 16 h at 100 °C. All volatiles were removed in vacuo to afford 111 mg (119 µmol, 99%) of $2[^{i}Pr_{2}Im-C_{6}H_{5}]^{+}[NiBr_{4}]^{2-}$ (11) (see below) as a blue solid.

In both cases biphenyl could be detected in the GC-MS of the reaction mixture.

Synthesis of $2[{}^{i}Pr_{2}Im-C_{6}H_{5}]^{+}[NiBr_{2}I_{2}]^{2-}$, **10**. A 112 μ L (1.00 mmol) amount of iodobenzene was added to a suspension of 260 mg (0.50 mmol) of trans- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ in 15 mL of toluene. The red mixture was stirred for 70 h at 120 °C. A brown precipitate that formed during this time was filtered off from the solution while hot. The product was washed with 5 mL of toluene and was dried in vacuo to give 250 mg (0.23 mmol, 46%) of a brown solid. Anal. Calcd (found) for C₃₀H₄₂Br₂I₂N₄Ni [930.99 g/mol]: C 38.70 (38.88), H 4.55 (4.88), N 6.02 (5.98). ¹H NMR (400 MHz, acetone- d_6): δ /ppm 1.62 (d, 12 H, ${}^{3}J_{HH} = 6.5$ Hz, ${}^{i}Pr-CH_{3}$), 4.54 (sept, 2 H, ${}^{3}J_{HH} = 6.5$ Hz, ⁱPr-CH), 7.86 (m, 3 H, aryl- $H_{\rm m}$ + aryl- $H_{\rm p}$), 7.97 (d, 2 H, ³ $J_{\rm HH}$ = 6.8 Hz, aryl- $H_{\rm o}$), 8.21 (s, 2 H, NCHCHN). ¹³C{¹H} NMR (100 MHz, acetone-d₆): δ /ppm 25.5 (ⁱPr-CH₃), 53.1 (ⁱPr-CH), 121.9 (NCCN), 123.6 (aryl- C_i), 131.8 (aryl- C_{tert}), 133.1 (aryl- C_{tert}), 134.4 (aryl- C_p), 144.7 (NCN). IR (ATR, $[cm^{-1}]$): 707 (s), 733 (s), 775 (s), 1080 (w), 1114 (vw), 1139 (w), 1185 (w), 1215 (vs, NHC-γ_{CH}), 1377 (w), 1399 (vw), 1419 (vw), 1443 (s), 1453 (m), 1461 (m), 1485 (vs), 1488 (m), 1572 (w), 1605 (vw), 2879 (vw, $\nu_{\rm CH}$), 2935 (w, $\nu_{\rm CH}$), 2981 (s, $\nu_{\rm CH}$), 3075 (m, $\nu_{=CH}$), 3112 (m, $\nu_{=CH}$).

Synthesis of $2[Pr_2 Im - C_6 H_5]^+ [NiBr_4]^2 -$, **11**. A 105 μ L (1.00 mmol) sample of bromobenzene was added to a suspension of 260 mg (0.50 mmol) of trans-[Ni(ⁱPr₂Im)₂(Br)₂] in 15 mL of toluene. The red mixture was stirred for 70 h at 120 °C. A blue precipitate that formed during this time was filtered off from the solution while hot. The product was washed with 10 mL of toluene and was dried in vacuo to give 340 mg (0.41 mmol, 81%) of a blue solid. Anal. Calcd (found) for C₃₀H₄₂Br₄N₄Ni [836.99 g/mol]: C 43.05 (42.25), H 5.06 (5.33), N 6.69 (6.48). ¹H NMR (400 MHz, acetone- d_6): δ /ppm 1.62 (d, 12 H, ${}^{3}J_{HH} = 6.6 \text{ Hz}, {}^{i}\text{Pr-CH}_{3}$, 4.58 (sept, 2 H, ${}^{3}J_{HH} = 6.5 \text{ Hz}, {}^{i}\text{Pr-CH}$), 7.84 (m, 3 H, aryl- $H_{\rm m}$ + aryl- $H_{\rm p}$), 7.96 (d, 2 H, ${}^{3}J_{\rm HH} = 6.8 \text{ Hz}, \text{aryl-}H_{\rm o}$), 8.11 (s, 2 H, NCHCHN). ¹³C{¹H} NMR (100 MHz, acetone- d_6): δ/ppm 26.5 (ⁱPr-CH₃), 53.3 (ⁱPr-CH), 121.6 (NCCN), 123.9 (aryl-C_i) 132.0 (aryl-C_{tert}), 133.3 (aryl-C_{tert}), 134.5 (aryl-C_p), 144.8 (NCN). IR (ATR, [cm⁻¹]): 712 (s), 733 (s), 776 (vs), 1011 (vw), 1081 (vw), 1115 (vw), 1140 (w), 1181 (w), 1213 (vs, NHC-γ_{CH}), 1295 (vw), 1377 (w), 1399 (vw), 1419 (vw), 1445 (m), 1462 (m), 1466 (m), 1485 (s), 1488 (m), 1572 (w), 1606 (vw), 1640 (vw), 2936 (w, $\nu_{\rm CH})$, 2984 (s, $\nu_{\rm CH})$, 3110 $(s, \nu_{=CH}).$

Synthesis of $2[^{i}Pr_{2}Im-C_{6}H_{4}-CH_{3}]^{+}[NiBr_{4}]^{2-}$, **12**. 121 µL (1.00 mmol) 4-Bromotoluene were added to a suspension of 260 mg (0.50 mmol) trans- $[Ni({}^{i}Pr_{2}Im)_{2}(Br)_{2}]$ in 15 mL toluene. The red mixture was stirred for 90 h at 100 °C. A blue precipitate which formed during this time was filtered off from the solution while hot. The product was washed with 25 mL toluene and was dried in vacuo to give 200 mg (0.23 mmol, 46%) of a light blue solid. Anal. Calcd (found) for C₃₂H₄₆Br₄N₄Ni [865.04 g/mol]: C 44.43 (44.44), H 5.36 (5.42), N 6.48 (6.49). ¹H NMR (400 MHz, acetone- d_6): δ /ppm =1.63 (d, 12 H, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{i}Pr-CH_{3}$), 2.54 (s, 3 H, CH₃), 4.60 (sept, 2 H, ${}^{3}J_{HH} = 6.6$ Hz, ${}^{i}Pr-CH$), 7.67 (d, 2 H, ${}^{3}J_{HH} = 7.6$ Hz, aryl- H_{m}), 7.83 (d, 2 H, ${}^{3}J_{HH} = 7.9$ Hz, aryl- H_{o}), 8.16 (s, 2 H, NCHCHN). ${}^{13}C{}^{1}H$ NMR (100 MHz, acetone-d₆): δ /ppm =22.6 (CH₃), 27.5 (ⁱPr-CH₃), 52.5 (ⁱPr-CH), 120.1 (aryl-C_i), 122.0 (NCCN), 132.3 (aryl-C_{tert}), 133.2 (aryl- C_{tert}), 144.2 (aryl- C_p), 144.4 (NCN). IR (ATR, [cm⁻¹]): 725 (m), 764 (vw), 819 (s), 831 (s), 1007 (vw), 1082 (w), 1093 (vw), 1133 (w), 1185 (m), 1207 (vs, NHC- γ_{CH}), 1221 (m), 1319 (vw), 1380 (m), 1394 (vw), 1411 (w), 1419(w), 1437 (w), 1463 (m), 1469 (m), 1475 (m), 1479 (s), 1488 (m), 1526 (vw), 1539 (vw), 1574 (vw), 1615 (w), 1618 (w), 2879 (w, $\nu_{\rm CH}$), 2978 (s, $\nu_{\rm CH}$), 3026 (m, $\nu_{=CH}$), 3061 (m, $\nu_{=CH}$), 3113 (m, $\nu_{=CH}$), 3172 (w). Synthesis of 2['Pr₂Im-C₆H₄-F]⁺[NiBr₄]²⁻, **13**. A 109 µL (1.00 mmol)

portion of 4-bromofluorobenzene was added to a suspension of 260

mg (0.50 mmol) of *trans*- $[Ni(^{i}Pr_{2}Im)_{2}(Br)_{2}]$ in 15 mL of toluene. The red mixture was stirred for 70 h at 120 °C. A blue precipitate that formed during this time was filtered off from the solution while hot. The product was washed with 5 mL of toluene and was dried in vacuo to give 300 mg (0.34 mmol, 68%) of a blue solid. Anal. Calcd (found) for C₃₀H₄₀Br₄F₂N₄Ni [872.97 g/mol]: C 41.28 (40.74), H 4.62 (4.69), N 6.42 (6.27). ¹H NMR (400 MHz, acetone- d_6): δ /ppm 1.66 (d, 12 H, ${}^{3}J_{HH} = 6.6$ Hz, ${}^{i}Pr-CH_{3}$), 4.57 (sept, 2 H, ${}^{3}J_{HH} = 6.5$ Hz, ${}^{i}Pr-CH$), 7.58 (t, 2 H, ${}^{3}J_{HH}$ = 8.3 Hz, aryl- H_{m}), 8.16 (m, 4 H, NCHCHN + aryl- H_0). ¹³C{¹H} NMR (100 MHz, acetone- d_6): δ /ppm 27.4 (ⁱPr-CH₃), 53.4 (ⁱPr-CH), 119.4 (aryl- C_i), 119.6 (aryl- C_m), 122.1 (NCCN), 135.5 (aryl- C_o), 144.0 (NCN), 165.5 (aryl- C_p). ¹⁹F NMR (376 MHz, acetone- d_6): δ /ppm -107.9 (s, F). IR (ATR, [cm⁻¹]): 740 (m), 789 (w), 844 (s), 1081 (vw), 1137 (vw), 1163 (w), 1182 (w), 1217 (vs, NHC- γ_{CH}), 1242 (w), 1378 (w), 1414 (vw), 1437 (vw), 1462 (s), 1484 (s), 1526 (m), 1613 (m), 2984 (m, $\nu_{\rm CH}$), 3104 (s, $\nu_{=\rm CH}$), 3121 (s, $\nu_{=CH}$).

Synthesis of $2[{}^{P}P_{2}Im-C_{6}H_{4}-OSi(CH_{3})_{3}]^{+}[NiBr_{4}]^{2-}$, 14. A 266 μ L (1.00 mmol) amount of 4-(trimethylsilyloxy)bromobenzene was added to a suspension of 260 mg (0.50 mmol) of trans- $[Ni(Pr_2Im)_2(Br)_2]$ in 15 mL of toluene. The red mixture was stirred for 70 h at 120 °C. A blue precipitate that formed during this time was filtered off from the solution while hot. The product was washed with 10 mL of toluene and was dried in vacuo to give 400 mg (0.40 mmol, 79%) of a blue solid. Anal. Calcd (found) for C₃₆H₅₈Br₄N₄NiO₂Si₂ [1013.35 g/mol]: C 42.67 (42.31), H 5.77 (5.67), N 5.53 (5.55). ¹H NMR (400 MHz, acetone- d_6): δ /ppm 0.36 (s, 9 H, Si-CH₃), 1.61 (d, 12 H, ${}^{3}J_{HH} = 6.7$ Hz, ${}^{i}Pr-CH_{3}$), 4.57 (sept, 2 H, ${}^{3}J_{HH} = 6.6$ Hz, ${}^{i}Pr-CH$), 7.26 (d, 2 H, ${}^{3}J_{HH} = 8.3$ Hz, aryl-H_m), 7.86 (d, 2 H, ${}^{3}J_{HH} = 8.5$ Hz, aryl-H_o), 8.15 (s, 2 H, NCHCHN). ${}^{13}C{}^{1}H$ NMR (100 MHz, acetone-d₆): δ/ppm 1.7 (Si-CH₃), 27.9 (CH₃), 53.1 (ⁱPr-CH), 116.3 (aryl- C_i), 121.8 (NCCN), 123.5 (aryl- C_m), 135.2 (aryl- C_o), 144.9 (NCN), 160.6 (aryl- C_p). ²⁹Si NMR (79 MHz, acetone- d_6): δ /ppm 21.7 (m, Si). IR (ATR, [cm⁻¹]): 738 (w), 766 (w), 823 (m), 844 (vs), 910 (s), 1077 (vw), 1106 (w), 1136 (w), 1179 (m), 1211 (s, NHC- $\gamma_{\rm CH}$), 1253 (s), 1280 (vs), 1375 (w), 1394 (vw), 1419 (w), 1437 (w), 1462 (m) 1469 (s), 1475 (m), 1519 (w), 1524 (m), 1526 (m), 1608 (s), 2983 (w, ν_{CH}), 3105 (w, $\nu_{=CH}$), 3151 (vw), 3322 (m).

Crystallography. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS II image plate diffractometer (Mo K α , 200 K). The structures were solved by direct methods and refined with the SHELXTL software package.¹⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations. Extinction corrections were applied as required. Crystal Data for $[8 \cdot 2(C_6H_6)]$: $C_{26}H_{42}BrN_5Ni$, $M_r = 719.48$, orangecolored block, $0.21 \times 0.19 \times 0.15$ mm, monoclinic, space group $P2_1/c$, a = 19.215(4) Å, b = 9.0535(18) Å, c = 23.233(5) Å, $\beta = 108.52(3)^{\circ}$, V = 3832.4(13) Å³, Z = 4, ρ_{calcd} = 1.247 g·cm⁻³, μ = 1.580 mm⁻¹, F(000)= 1520, T = 200(2) K, all data: R_1 = 0.0647 and wR_2 = 0.1169, I > $2\sigma(I)$: $R_1 = 0.0492$ and $wR_2 = 0.1104$, Goof 1.091, 9130 independent reflections $[2\theta \le 61.7^\circ]$ and 416 parameters, 0 restraints. Crystal Data for 11: $C_{30}H_{42}Br_4N_4N_i$, $M_r = 836.97$, blue block $0.25 \times 0.20 \times 0.14$ mm, monoclinic, space group $P2_1/c$, a = 21.236(4) Å, b = 20.872(4) Å, c = 16.673(3) Å, $\beta = 106.39(3)^{\circ}$, V = 7090(2) Å³, Z = 8, $\rho_{calcd} = 1.568$ $g \cdot cm^{-3}$, $\mu = 5.080 \text{ mm}^{-1}$, F(000) = 3344, T = 200(2) K, all data: $R_1 =$ 0.1020 and $wR_2 = 0.2370$, $I > 2\sigma(I)$: $R_1 = 0.0816$ and $wR_2 = 0.2208$, Goof 1.068, 1415 independent reflections $[2\theta \leq 53.4^{\circ}]$ and 719 parameters, 0 restraints.

ASSOCIATED CONTENT

S Supporting Information

X-ray crystal data in CIF format. 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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DEDICATION

Dedicated to Professor David Milstein on the occasion of his 65th birthday.

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