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Synthesis of Quinoline-Based NNN-Pincer Nickel(II) Complexes: A Robust and Improved Catalyst System for C−H Bond Alkylation of Azoles with Alkyl Halides

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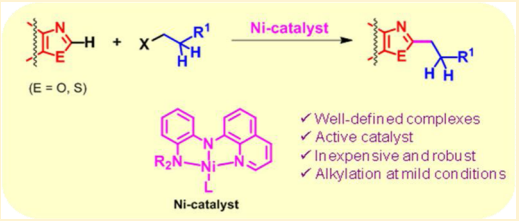
Supporting Information

ABSTRACT: The quinoline-based pincer nickel(II) complexes $\kappa^N,\kappa^N,\kappa^N$-{$R_2N$-$C_6H_4$-($\mu$-N)-$C_9H_6N$}NiX (($^{R2}NNN^Q$)NiCl: R = Me, **2a**; R = Et, **2b**) were synthesized by the reaction of the ligand precursors ($^{R2}NNN^Q$)H (R = Me, **1a**; R = Et, **1b**) with (DME)$NiCl_2$ in the presence of Et_3N. Similarly, the pincer nickel(II) derivatives ($^{R2}NNN^Q$)NiX (R = Me, X = Br, **3a**; R = Et, X = Br, **3b**; R = Me, X = OAc, **4a**) were obtained by treatment of the ligands ($^{R2}NNN^Q$)H with the nickel precursor $(THF)_2NiBr_2$ or $Ni(OAc)_2$. All of these complexes were characterized by ^1H and ^{13}C NMR spectroscopy as well as by elemental analysis. Further, the molecular structures of **2a** and **3a**,**b** were elucidated by X-ray crystallography. Complex **2a** is found to be an efficient catalyst for the direct C−H bond alkylation of substituted benzothiazoles and oxazoles with various unactivated alkyl halides containing β-hydrogens under mild reaction conditions. The catalyst **2a** is very robust and was recycled and reused five times for the alkylation reaction without a decrease in its catalytic activity. Preliminary studies reveal that the catalyst **2a** acts as an active catalyst and the alkylation reaction appears to operate via a radical pathway.



INTRODUCTION

Pincer-ligated transition-metal complexes have been extensively pursued as catalysts for various chemical transformations, mostly due to their exceptional stability and unusual chemical reactivity.[1] Among the various pincer−metal complexes, noble metals such as palladium, rhodium, iridium, and ruthenium are very often employed and explored as catalysts in many challenging chemical reactions.[2] From an economical prospective, the use of a pincer system with an earth-abundant metal in these catalytic processes would be highly desirable. Toward this endeavor, pincer-ligated catalysts based on inexpensive first-row transition metals,[3] particularly pincer nickel complexes, have successfully been applied to the traditional C−C and C−S cross-couplings,[4] C═C bond functionalization,[5] hydrosilylation of aldehydes and ketones,[6] hydroamination of nitriles,[7] and CO_2 reduction reaction.[8] In contrast, the use of pincer nickel complexes as catalysts for the relatively challenging C−H bond functionalization[9−11] has rarely been investigated.[12]

In particular, the C−H bond alkylation of azoles with unactivated alkyl halides containing β-hydrogen is a promising yet challenging reaction, due to the undesired β-elimination from these electrophiles.[10b,13] Noble-metal palladium precursors with added ligands,[14] as well as earth-abundant nickel[14b,15] and copper[16] precursors, are known to catalyze the alkylation of azoles with alkyl halides.[17] Though, the reported nickel- and copper-catalyzed method is significant from an economic prospective; it uses an in situ generated catalyst, needs a high reaction temperature, and/or shows poor activity for the sulfur-containing thiazoles. Hu et al. reported a well-defined pincer nickel complex, ($^{Me}NN_2$)NiCl, that shows excellent catalytic activity for the direct C−H bond alkylation of oxazoles and thiazoles with unactivated alkyl halides (Figure 1).[12] However,

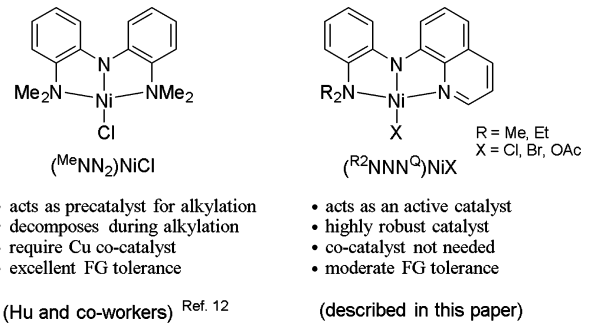


Figure 1. Pincer nickel complexes for the C−H bond alkylation of azoles.

this catalyst system requires an additional copper cocatalyst for achieving good yields of the desired alkylated products. In addition, ($^{Me}NN_2$)NiCl acts as a precatalyst and decomposes to nanoparticles during the catalysis, which might hamper a mechanistic investigation involving this catalyst. Within our research program directed toward the development of pincer-based metal catalysts for C−H bond functionalization[18] and

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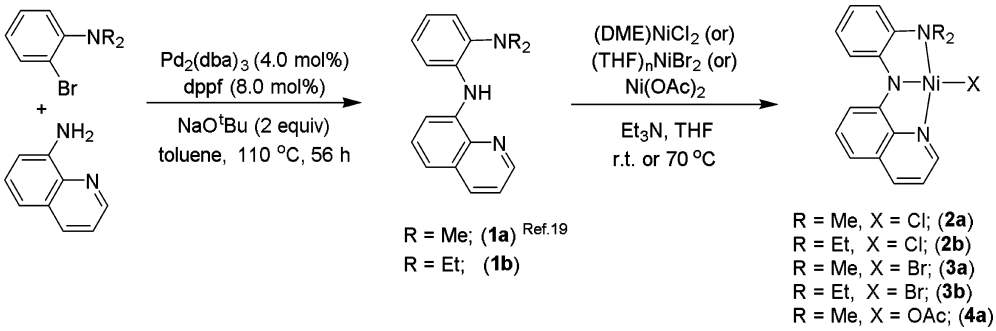
Scheme 1. Synthesis of (^{R2}NNN^{Q})H Ligand Precursors and (^{R2}NNN^{Q})NiX Complexes



inspired by the excellent catalytic behavior of (^{Me}NN$_2$)NiCl, developed by the Hu group, herein we report the synthesis of a sterically less demanding and electronically distinct quinolinyl-based nickel pincer system, (^{R2}NNN^{Q})NiCl, and its catalytic activity for the C−H bond alkylation of oxazoles and thiazoles with unactivated alkyl halides (Figure 1). The present catalyst system (^{R2}NNN^{Q})NiCl is highly robust, does not need a cocatalyst, and acts as an active catalyst; in addition, the reactions were efficiently carried out at 100−120 °C. Preliminary studies have been carried out to establish the status of the catalyst and the pathway of the alkylation reaction.

RESULTS AND DISCUSSION

Synthesis and Characterization of ^{R2}NNN^{Q} Nickel Complexes. The tridentate proligand precursors R$_2$N-C$_6$H$_4$-N(H)-8-quinolinyl ((^{R2}NNN^{Q})H: R = Me, **1a**;[19] R = Et, **1b**) were prepared in one step by the palladium-catalyzed amination reaction of 2-bromo-*N*,*N*-dialkylaniline with 8-aminoquinoline in moderate yields (Scheme 1). These compounds were readily isolated by column chromatography. Compound **1a** was initially obtained as a viscous liquid and solidified at room temperature in 3−4 days. The ^{1}H and ^{13}C NMR data of **1a** are in good agreement with those reported in the literature for the same compound.[19] Compound **1b** was obtained as an orange solid, which was fully characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by HRMS and elemental analysis.

The metalation reaction of the proligand (^{Me2}NNN^{Q})H (**1a**) with (DME)NiCl$_2$ in the presence of Et$_3$N in THF at 70 °C produced the amido pincer complex (^{Me2}NNN^{Q})NiCl (**2a**) in good yield, whereas the treatment of **1a** with (THF)$_2$NiBr$_2$ and Ni(OAc)$_2$ in the presence of Et$_3$N at room temperature afforded (^{Me2}NNN^{Q})NiBr (**3a**) and (^{Me2}NNN^{Q})Ni(OAc) (**4a**), respectively (Scheme 1). In ^{1}H NMR spectra of complexes **2a**−**4a**, the disappearance of the N−H signal corresponding to **1a** suggests covalent bonding between the central nitrogen and the nickel center. Further, the −NMe$_2$ protons in these complexes resonate as a singlet in the range 2.96−3.20 ppm, which were significantly deshielded in comparison to those observed for the same protons in ligand **1a** (δ 2.75 ppm). The C−H proton ortho to the quinolinyl N atom resonates differently from that in the free ligand **1a**. All of these observations clearly suggest the tridentate amido pincer coordination of the ligand **1a** to the Ni center in complexes **2a**−**4a**. For complex **4a**, analysis of the ^{1}H and ^{13}C NMR spectra of the −OCOCH$_3$ group is consistent with the terminal bonding of −OCOCH$_3$.[20] Notably, in particular, the −NMe$_2$ protons are deshielded and the C−H proton ortho to the quinolinyl N atom is shielded in the Ni complexes in comparison to those observed in the free ligand. Interestingly, Peters and co-workers have shown the bidentate coordination of amido ligand **1a** with a Pt precursor under similar conditions, with the dimethylamino (−NMe$_2$) group being unbound.[19] However, we have observed the tridentate amido pincer coordination of the ligand **1a** with different nickel precursors, which could be due to the small binding pocket of **1a** that is able to accommodate the small Ni ion rather than the large Pt ion in a tridentate fashion.

The pincer complexes (^{Et2}NNN^{Q})NiCl (**2b**) and (^{Et2}NNN^{Q})NiBr (**3b**) were synthesized in excellent yields by the reaction of (^{Et2}NNN^{Q})H (**1b**) with (DME)NiCl$_2$ and (THF)$_2$NiBr$_2$, respectively, in the presence of Et$_3$N in THF at 70 °C. These pincer nickel complexes were obtained as purple solids, and they are highly air and moisture stable. In the ^{1}H NMR spectra of complexes **2b** and **3b**, the −CH$_2$ protons of the −NEt$_2$ group displayed two sets of multiplets, one in the shielded region (δ_H ∼2.55−2.43 ppm) and other in the deshielded region (δ_H ∼3.62−3.46 ppm), against one quartet for the four protons in **1b** (δ_H 3.05 ppm), which could be due to the diastereotopic −CH$_2$ protons generated upon the coordination of the −NEt$_2$ group to the nickel center. All these complexes were further characterized by ^{13}C NMR spectroscopy, elemental analysis, and HRMS techniques. The molecular structures of **2a** and **3a**,**b** were determined by single-crystal diffraction studies.

The ORTEP diagrams of complexes **2a** and **3a**,**b** are shown in Figures 2−4. Selected bond lengths and bond angles are given in Table 1. For these three complexes, the geometry around the nickel is slightly distorted from the expected square planar. The Ni−N1$_{amido}$ bond lengths are in the range 1.842(2)−1.845(±2) Å, which are comparable with the similar bond length in (^{Me}NN$_2$)NiCl (1.835(2) Å).[21] Similarly, the

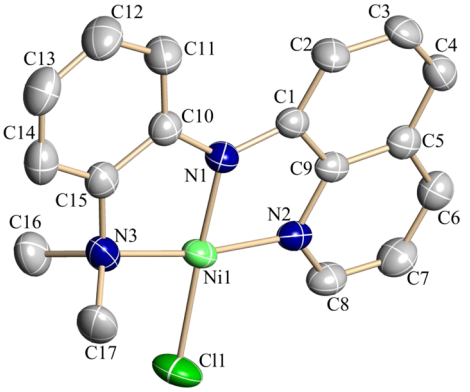


Figure 2. Thermal ellipsoid plot of (^{Me2}NNN^{Q})NiCl (**2a**). All hydrogen atoms are omitted for clarity.

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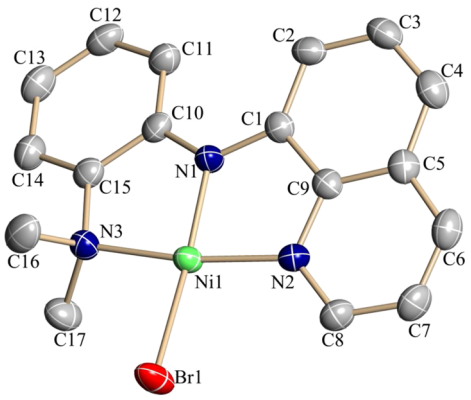

Figure 3. Thermal ellipsoid plot of (^{Me2}NNN^{Q})NiBr (**3a**). All hydrogen atoms are omitted for clarity.

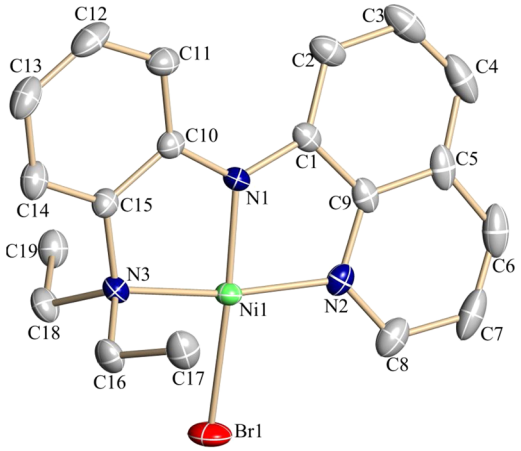

Figure 4. Thermal ellipsoid plot of (^{Et2}NNN^{Q})NiBr (**3b**). All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a and 3a,b

	2a	3a	3b
Ni(1)−N(1)	1.8441(18)	1.842(2)	1.8447(18)
Ni(1)−N(2)	1.8990(18)	1.902(2)	1.9073(19)
Ni(1)−N(3)	1.9545(19)	1.962(2)	1.9678(18)
Ni(1)−Cl(1)	2.1850(8)		
Ni(1)−Br(1)		2.3471(4)	2.3349(4)
N(1)−Ni(1)−N(2)	84.77(8)	84.59(9)	84.83(8)
N(1)−Ni(1)−N(3)	86.32(8)	85.41(10)	85.91(8)
N(2)−Ni(1)−N(3)	170.77(8)	169.57(9)	170.57(8)
N(1)−Ni(1)−Cl(1)	177.21(6)		
C(1)−N(1)−C(10)	128.09(18)	127.8(2)	128.04(19)
C(1)−N(1)−Ni(1)	115.89(14)	115.45(18)	115.32(15)
C(10)−N(1)−Ni(1)	116.02(14)	116.49(18)	116.59(14)
N(1)−Ni(1)−Br(1)		171.60(8)	173.20(6)

Ni−N3$_{amine}$ bond lengths (1.954(±2)−1.967(±2) Å) are comparable with the Ni−NMe$_2$ bond length (1.959 Å) in the complex (^{Me}NN$_2$)NiCl. However, the Ni−N2$_{quinolinyl}$ bond lengths (1.899(±2)−1.907(±2) Å) in complexes **2a** and **3a,b** are slightly shorter than the Ni−N3$_{amine}$ bond lengths (1.954(±2)−1.967(±2) Å), which suggest that the quinoline nitrogen strongly binds to the nickel center than the −NMe$_2$ or −NEt$_2$ nitrogen. This further emphasizes the greater rigidity of the current ligand binding to nickel in comparison to that in the complex (^{Me}NN$_2$)NiCl. The Ni−Cl bond length (2.185 Å) in complex **2a** is slightly shorter than that observed in the complex (^{Me}NN$_2$)NiCl (Ni−Cl = 2.203 Å), which could be due to the less steric and more planar structure of former than of the latter. The N2−Ni−N3 (170.77(8)°) and N1−Ni−Cl (177.21(6)°) bond angles in complex **2a** are significantly greater than the similar bond angles in the complex (^{Me}NN$_2$)NiCl (N2−Ni−N3 = 169.73(8)°, N1−Ni−Cl = 174.75(7)°), which is consistent with the more planar geometry of Ni in complex **2a** in comparison to that in (^{Me}NN$_2$)NiCl. The comparison of bond lengths and bond angles of the complex **2a** with those of (^{Me}NN$_2$)NiCl suggests that complex **2a** has a more planar and rigid structure than the latter species, which might provide extra stability to complex **2a** during catalysis.

Catalytic Activity of (^{R2}NNN^{Q})NiX Complexes for Alkylation of Azoles. The newly developed quinolinyl-based pincer nickel complexes (^{R2}NNN^{Q})NiX (**2a**−**4a**) were screened and optimized for the direct C−H bond alkylation of benzothiazole using nonactivated alkyl halides (Table 2). Initially, the nickel complex **2a** was employed and the reaction parameters were optimized for the alkylation of benzothiazole (**5a**) with 1-iodooctane (**6a**) as electrophile. After a thorough investigation of the various experimental parameters, we found that the coupled product 2-*n*-octylbenzothiazole (**7aa**) could be obtained in 91% yield by employing 5 mol % of catalyst **2a**, in the presence of LiO^{t}Bu in 1,4-dioxane at 100 °C (Table 2, entry 7). Mild inorganic bases such as Li_2CO_3, Na_2CO_3, K_2CO_3, LiOAc, and KOAc were found to be ineffective (entries 1−5), whereas the employment of K_3PO_4 gave 35% of coupled product **7aa** (entry 6). In addition to the alkylation reaction in 1,4-dioxane, the reaction in other solvents such as 1,2-dimethoxyethane (DME), THF, and toluene is also competent (entries 8−10). The nickel complexes **3a** and **4a** are slightly less efficient, whereas complexes **2b** and **3b** are very poor for the alkylation reaction in comparison with the catalyst **2a** (entries 13−16). Notably, the dimethyl derivatives **2a**−**4a** were more active in comparison to the diethyl derivatives **2b** and **3b**, which might be due to the decreased sterics around the Ni center in dimethyl derivatives in comparison to the latter species. Catalytic coupling of benzothiazole with 1-iodooctane also occurs at 80 °C to produce the desired product in 78% yield (entry 17). The alkylation reaction occurs smoothly even with a catalyst loading of 2 mol % of **2a**, giving the coupled product **7aa** in 78% yield (entry 18). More challenging alkyl electrophiles, such as 1-bromooctane and 1-chlorooctane, were also coupled with benzothiazole in good yields, by employing NaI and by performing the reactions at 120 °C (entries 19 and 20). The presence of a nickel catalyst under the standard conditions is necessary; without it, alkylation did not occur (entry 21).

Having the optimized reaction conditions in hand, we explored the scope of the alkylation of various azoles. As shown in Table 3, an array of alkyl bromides and alkyl iodides containing *β*-hydrogen can be coupled with the benzothiazole to yield the desired alkylated products. Alkyl bromides with different chain lengths are coupled in good yields (Table 3, entries 1−8). Various important functional groups such as halide, ether, alkene, and heteroarene are well tolerated under the alkylation conditions. Substrates containing alkene and carbazole moieties coupled in moderate to good yields (entries 12 and 13). The substituted benzothiazoles reacted with 1-iodooctane to produce the desired alkylated products in

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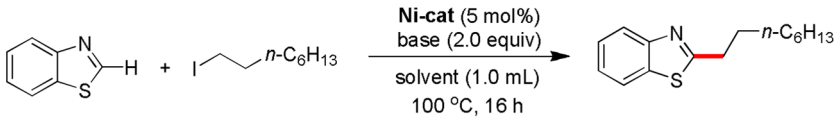
Table 2. Optimization of Catalytic Conditions for the Nickel-Catalyzed Alkylation of Benzothiazole[a]



(5a) (6a) (7aa)

entry	Ni cat.	base	solvent	yield (%)[b]
1	**2a**	Na_2CO_3	1,4-dioxane	
2	**2a**	K_2CO_3	1,4-dioxane	trace
3	**2a**	KOAc	1,4-dioxane	
4	**2a**	Li_2CO_3	1,4-dioxane	
5	**2a**	LiOAc	1,4-dioxane	trace
6	**2a**	K_3PO_4	1,4-dioxane	35
7	**2a**	**LiO^{t}Bu**	**1,4-dioxane**	**95 (91)**
8	**2a**	LiO^{t}Bu	DME	82 (80)
9	**2a**	LiO^{t}Bu	THF	74
10	**2a**	LiO^{t}Bu	toluene	78 (77)
11	**2a**	LiO^{t}Bu	diglyme	trace
12	**2a**	LiO^{t}Bu	DMF	trace
13	**3a**	LiO^{t}Bu	1,4-dioxane	74
14	**4a**	LiO^{t}Bu	1,4-dioxane	84
15	**2b**	LiO^{t}Bu	1,4-dioxane	33
16	**3b**	LiO^{t}Bu	1,4-dioxane	35
17[c]	**2a**	LiO^{t}Bu	1,4-dioxane	78
18[d]	**2a**	LiO^{t}Bu	1,4-dioxane	78
19[e]	**2a**	**LiO^{t}Bu**	**1,4-dioxane**	**85 (81)**
20[f]	**2a**	LiO^{t}Bu	1,4-dioxane	64
21		LiO^{t}Bu	1,4-dioxane	

[a]Conditions unless specified otherwise: benzothiazole (0.068 g, 0.503 mmol), 1-iodooctane (0.180 g, 0.750 mmol), base (1.0 mmol), solvent (1.0 mL). [b]GC yield (isolated yields are given in parentheses). [c]At 80 °C for 16 h. [d]2 mol % of catalyst **2a**. [e]Employing 1-bromooctane (0.145 g, 0.75 mmol) and NaI (0.112 g, 0.75 mmol) at 120 °C. [f]Employing 1-chlorooctane (0.112 g, 0.75 mmol) and NaI (0.112 g, 0.75 mmol) at 120 °C.

excellent yields (entries 14−16). In addition to benzothiazole, 5-arylated oxazoles were alkylated in good yields, whereas the naphthalenyl- and pyridinyl-substituted oxazoles were moderately coupled with 1-bromooctane. Notably, all of these alkylation reactions proceeded with the nickel catalyst **2a** and without the use of an external cocatalyst, which makes this catalyst distinct from the existing well-defined nickel catalyst (^{Me}NN$_2$)NiCl.[12] Furthermore, the reactions were performed at temperatures as low as 100−120 °C to achieve the alkylated products of benzothiazoles in excellent yields. Though undefined and precatalyst systems are known for the alkylation of relatively activated oxazole substrates, they show very poor activity for the alkylation of sulfur-containing benzothiazole derivatives[14b,15] and/or need a Cu cocatalyst.[12] However, the catalyst **2a** performed uniquely for the alkylation of a variety of benzothiazoles and azoles under rather mild reaction conditions. In addition, this catalyst system acts as an active catalyst and was found to be highly robust for the alkylation reaction (discussed below).

Considering the well-defined nature of catalyst **2a** and its excellent catalytic activity for the alkylation of azoles under mild reaction conditions, we performed a preliminary mechanistic investigation for the **2a**-catalyzed alkylation of azoles with alkyl halides. Hu and co-workers have reported that the well-defined pincer complex (^{Me}NN$_2$)NiCl decomposes to heterogeneous nanoparticles, which in turn act as a catalyst for the alkylation of azoles. In view of that, initially, we examined the status of the well-defined, newly developed catalyst **2a** during the alkylation reaction of benzothiazole with 1-iodooctane. The standard alkylation reaction of benzothiazole with 1-iodooctane in the presence of 200 equiv and 600 equiv (with respect to **2a**) of mercury (Hg) afforded the desired alkylated product **7aa** in 88% and 85% yields, respectively, against the 91% yield in the absence of mercury (Scheme 2a). This indicates the mercury has no significant effect on the **2a**-catalyzed alkylation reaction; hence, this ruled out the possibility of nickel nanoparticles or colloids being the active catalyst during catalysis. In addition, a filtration experiment was conducted to support this finding (Scheme 2b). Hence, a catalytic reaction mixture of benzothiazole with 1-iodooctane was heated at 100 °C for 1 h, and the reaction mixture was then filtered into a new reaction vessel. The reaction was continued further after adding fresh LiO^{t}Bu to the filtrate, wherein the yield of the product **7aa** obtained was 85%. This further supports the probability of a catalytically active insoluble nanoparticle being unlikely during the alkylation reaction. Again, the GC analysis of a standard alkylation reaction, which was performed employing 25 mol % of the catalyst **2a**, does not show the formation of free ligand **1a**, which suggests that the dissociation of ligand from complex **2a** and generation of soluble Ni particles during the alkylation reaction is less likely.

Further, the progress of the alkylation reaction was monitored by gas chromatography (GC) analysis at regular intervals of time (see section 2 in the Supporting Information for details). The reaction profile of the benzothiazole alkylation catalyzed by **2a** over a period of 3 h is shown in Figure 5. As shown, the alkylated product **7aa** formed steadily and an induction period for the reaction is absent. This again confirms the direct involvement of the catalyst **2a** during the alkylation

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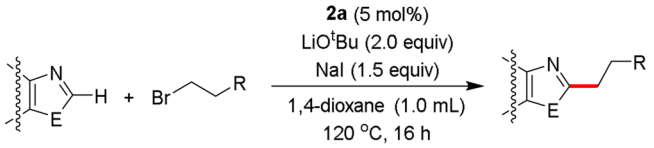
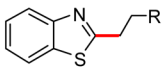
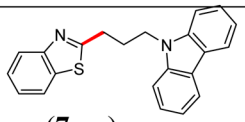
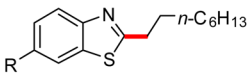
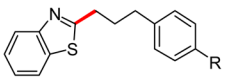
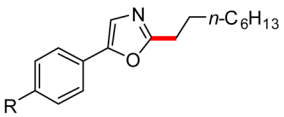
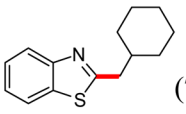
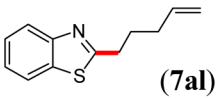
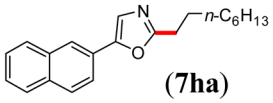
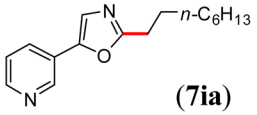
Table 3. Scope for the 2a-Catalyzed Alkylation of Azoles with Alkyl Halides[a]



Entry	Product	Yield (%)[b]	Entry	Product	Yield (%)[b]
					
1	R = n-C_6H_{13} (**7aa**)	81 (91[c])	13	(**7am**)	82
2	R = n-C_4H_9 (**7ab**)	71			
3	R = n-C_8H_{17} (**7ac**)	80 (73[d])			
4	R = n-$C_{10}H_{21}$ (**7ad**)	88 (87[c])			
5	R = n-$C_{11}H_{23}$ (**7ae**)	84	14	R = Me (**7ba**)	82[c]
6	R = n-$C_{12}H_{25}$ (**7af**)	81	15	R = OEt (**7ca**)	82[c]
7	R = n-$C_{14}H_{29}$ (**7ag**)	81	16	R = F (**7da**)	83[c]
8	R = n-$C_{16}H_{33}$ (**7ah**)	88			
					
9	R = H (**7ai**)	65 (58[d])	17	R = OMe (**7ea**)	60
10	R = OMe (**7aj**)	76	18	R = Cl (**7fa**)	70
11	 (**7ak**)	46	19	R = CF_3 (**7ga**)	70
12	 (**7al**)	40	20	 (**7ha**)	43
			21	 (**7ia**)	40

[a]Conditions unless specified otherwise: compound **5** (0.5 mmol), compound **6** (0.75 mmol), LiO^{t}Bu (0.081 g, 1.0 mmol), NaI (0.112 g, 0.75 mmol), 1,4-dioxane (1.0 mL), 120 °C, 16 h. [b]Isolated yield. [c]Employing alkyl iodide (NaI was not used). [d]Employing alkyl chloride (NaI was used).

reaction and rules out the generation of a new catalytically active species.

To probe the probability of a free radical pathway, the **2a**-catalyzed alkylation of benzothiazole with 1-iodooctane was performed in the presence of 1.5 equiv of TEMPO, a free radical inhibitor (Scheme 2a). In this reaction, the alkylation reaction completely shut down and formation of the coupled product was not observed. This suggests the probable involvement of a radical intermediate during the **2a**-catalyzed alkylation reaction.

On the basis of our preliminary mechanistic studies and literature precedent for the alkylation reaction,[14b,15,22,23] we assume that the catalysis starts with the reaction of (^{Me2}NNN^{Q})NiCl (**2a**) with benzothiazole in the presence of LiO^{t}Bu to produce the Ni(II) intermediate (^{Me2}NNN^{Q})Ni(benzothiazolyl) (**8**) (Figure 6). This species might trigger the formation of an alkyl radical via single-electron transfer, followed by radical rebound to form a Ni(IV) species, (^{Me2}NNN^{Q})Ni(benzothiazolyl)(alkyl)X (**9**). The reductive elimination would deliver the desired alkylated product and regenerate the catalytically active species. The electron-rich pincer ligand moiety is assumed to stabilize the Ni species in a higher oxidation state. Though the possibility of a Ni(IV) species is assumed by the reaction of alkyl electrophiles, a

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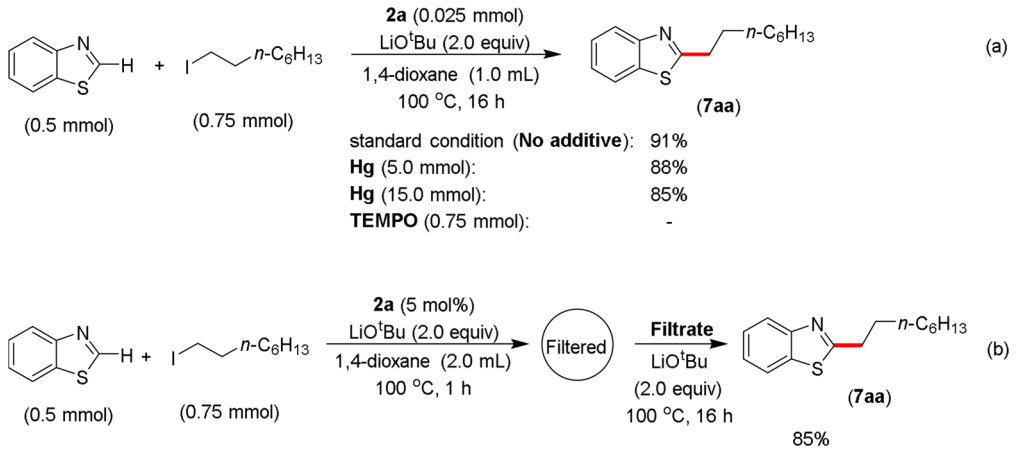
Scheme 2. Alkylation Reaction under Controlled Conditions



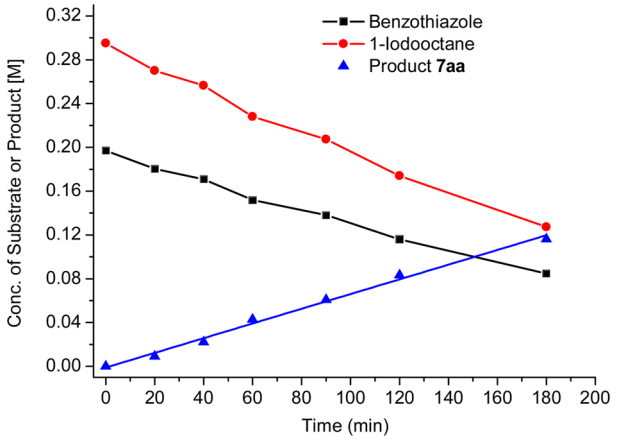


Figure 5. Reaction profile for the **2a**-catalyzed alkylation of benzothiazole (**5a**) with 1-iodooctane (**6a**).

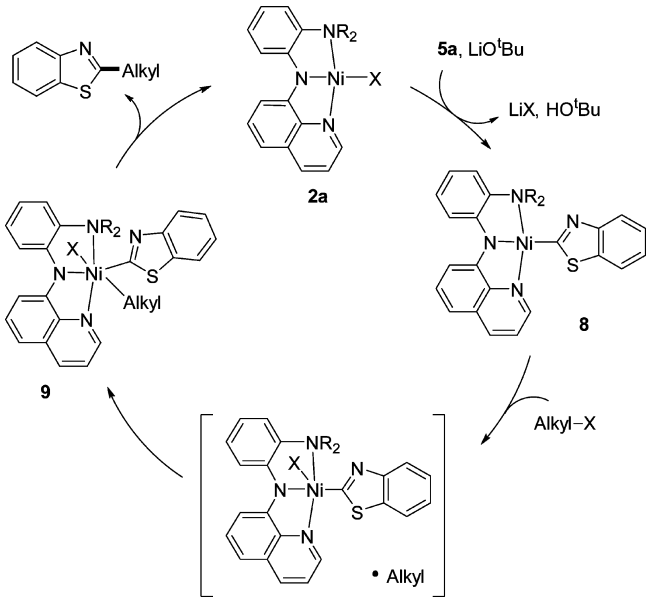


Figure 6. Proposed mechanism for **2a**-catalyzed alkylation reactions.

probable Ni(I)/Ni(III) mechanism cannot be ruled out at this moment. The detailed mechanistic pathway for this **2a**-catalyzed alkylation reaction, through kinetic studies, controlled reactivity studies, and isolation and reactivity of the intermediate species, is currently under investigation.

The robustness and stability of the catalyst **2a** was examined by conducting recycling experiments. As the alkylation reaction is inhibited by both the substrate (benzothiazole) and product **7aa**,[24] we performed a recycling experiment by distilling out the product and other volatiles after each catalytic cycle (Figure 7). Hence, after the catalytic reaction of benzothiazole with 1-iodooctane under the standard conditions, the yield of the product **7aa** obtained was 92% in the first cycle. The product and other volatiles were distilled out under vacuum at 110 °C. In the same reaction vessel were placed fresh benzothiazole, 1-iodooctane, LiO^{t}Bu, and 1,4-dioxane and the reaction mixture was heated at 100 °C for the second cycle, wherein the coupled product **7aa** was analyzed to be 90%. Similarly, in the third, fourth, and fifth cycles, the yields of product **7aa** obtained were 89%, 91%, and 85%, respectively. This chain of experiments clearly suggests that the catalyst **2a** is very robust and active for a long period of time and that the catalyst can be recycled and reused several times. This is a very significant aspect of this catalyst, considering the importance of the alkylation of azoles.

CONCLUSION

In summary, the inexpensive and novel pincer nickel complexes (^{R2}NNN^{Q})NiX were synthesized and fully characterized by various spectroscopic techniques. These complexes were demonstrated for the direct C−H bond alkylation of important benzothiazoles and azoles with unactivated alkyl halides containing β-hydrogen atoms. In particular, the complex (^{Me2}NNN^{Q})NiCl (**2a**) shows excellent activity for the alkylation reaction under mild reaction conditions, without the use of an additional cocatalyst. Catalyst **2a** is very robust and could be recycled and reused several times for the alkylation reaction without a decrease in its catalytic activity. In the course of alkylation reactions, catalyst **2a** tolerates numerous functional groups such as halide, ether, alkene, heteroarene, etc. A preliminary study reveals that complex **2a** acts as an active catalyst during the alkylation and the reaction follows a free radical pathway. We are currently investigating the detailed mechanistic pathway for the **2a**-catalyzed alkylation reaction, which will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Considerations. All manipulations were conducted under an argon atmosphere either in a glovebox or using

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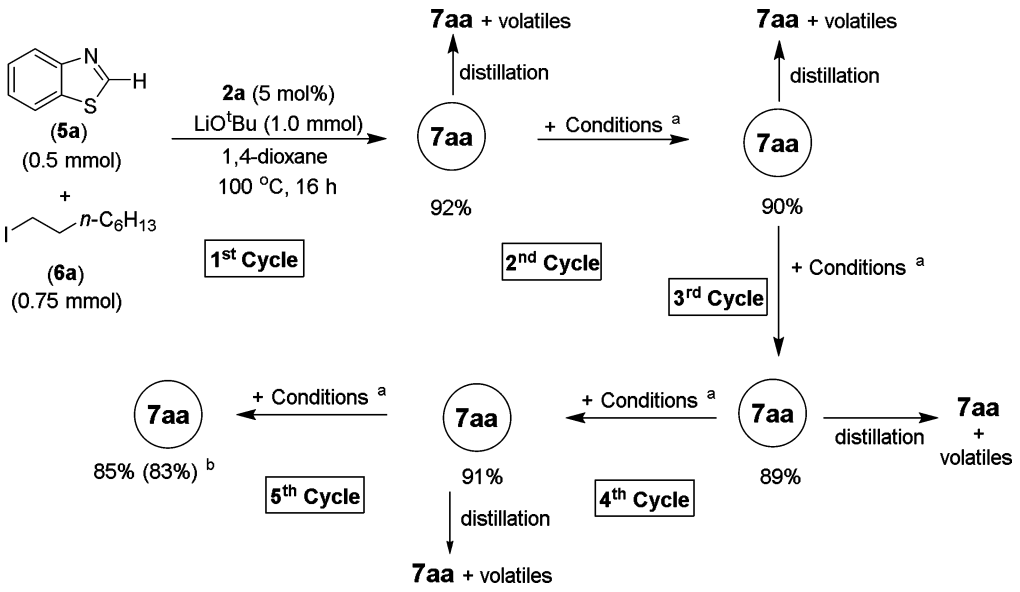

Figure 7. Catalyst recycling experiment. The yield refers to the GC yield using *n*-dodecane as internal standard; slight variations in yields might be due to experimental error. Legend: (a) conditions, **5a** (0.5 mmol), **6a** (0.75 mmol), LiO^{t}Bu (1.0 mmol), 1,4-dioxane (1.0 mL), 100 °C, 16 h; (b) isolated yield in parentheses.

standard Schlenk techniques in predried glassware. The catalytic reactions were performed in flame-dried reaction vessels with a Teflon screw cap. Solvents were dried over Na/benzophenone or CaH_2 and distilled prior to use. Liquid reagents were flushed with argon prior to use. The compounds 2-bromo-*N*,*N*-dimethylaniline,[25] 2-bromo-*N*,*N*-diethylaniline,[26] (^{Me2}NNN^{Q})H,[19] (THF)$_2$NiBr$_2$,[5b] substituted benzothiazoles,[27] and 5-arylazoles[28] were synthesized according to previously described procedures. All other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR. TLC used silica gel 60 F_{254}, with detection under UV light at 254 nm. In chromatography, separations were carried out on Spectrochem silica gel (0.120−0.250 mm, 100−200 mesh). High-resolution mass spectroscopy (HRMS) was carried out on a Thermo Scientific Q-Exactive, Accela 1250 pump. Melting points were determined on a Büchi 540 capillary melting point apparatus; values are uncorrected. NMR (^{1}H and ^{13}C) spectra were recorded at 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C, DEPT (distortionless enhancement by polarization transfer)), and 377 MHz (^{19}F) on Bruker AV 400 and AV 500 spectrometers in $CDCl_3$ solutions, if not otherwise specified; chemical shifts (δ) are given in ppm. The ^{1}H and ^{13}C NMR spectra are referenced to residual solvent signals ($CDCl_3$: δ(H) 7.26 ppm, δ(C) 77.2 ppm).

Synthesis of (^{Et2}NNN^{Q})H (1b). A Schlenk flask was charged with $Pd_2(dba)_3$ (0.208 g, 0.227 mmol) and 1,1′-bis(diphenylphosphino)-ferocene (DPPF; 0.253 g, 0.456 mmol), and toluene (30 mL) was added to this mixture under an argon atmosphere. The resulting suspension was stirred at room temperature for 10 min. To the resulting catalyst solution were added 8-aminoquinoline (0.82 g, 5.69 mmol), *N*,*N*-diethyl-2-bromoaniline (1.30 g, 5.70 mmol), and NaO^{t}Bu (0.66 g, 6.87 mmol). The reaction mixture was then refluxed for 3 days. At ambient temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with distilled water (30 mL × 3) and dried over Na_2SO_4. The volatiles were then evaporated under vacuum, and the crude mixture was purified by column chromatography on silica gel (*n*-hexane/EtOAc 40/1) to obtain an orange solid. Yield: 0.91 g, 55%. Mp: 89−91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.27 (br s, NH), 8.86 (d, $^3J_{H-H}$ = 3.9 Hz, 1H, Ar-H), 8.12 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, Ar-H), 7.72 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.66 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 7.46−7.41 (m, 2H, Ar-H), 7.23−7.20 (m, 2H, Ar-H), 7.15 (vt, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 6.97 (vt, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar-H), 3.05 (q, $^3J_{H-H}$ = 7.0 Hz, 4H, CH_2), 1.09 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (CH), 141.2 (C_q), 140.1 (C_q), 139.6 (C_q), 139.1 (C_q), 136.0 (CH), 129.1 (C_q), 127.4 (CH), 124.2 (CH), 123.0 (CH), 121.6 (CH), 120.6 (CH), 116.5 (CH), 116.4 (CH), 107.8 (CH), 47.9 (2C, CH_2), 13.0 (2C, CH_3). HRMS (ESI): *m*/*z* calcd for $C_{19}H_{21}N_3$ + H^+ [M + H]$^+$ 292.1808, found 292.1812. Anal. Calcd for $C_{19}H_{21}N_3$: C, 78.32; H, 7.26; N, 14.42. Found: C, 79.05; H, 6.58; N, 13.59.

Synthesis of (^{Me2}NNN^{Q})H (1a). This compound was synthesized following the literature procedure[19] similarly to the synthesis of (^{Et2}NNN^{Q})H. Yield: 0.98 g, 50%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (dd, $^3J_{H-H}$ = 4.3, $^4J_{H-H}$ = 1.6 Hz, 1H, Ar-H), 8.72 (br s, NH), 8.12 (dd, $^3J_{H-H}$ = 8.3, $^4J_{H-H}$ = 1.6 Hz, 1H, Ar-H), 7.67 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.6 Hz, 1H, Ar-H), 7.58 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 7.47−7.39 (m, 2H, Ar-H), 7.24−6.95 (m, 4H, Ar-H), 2.75 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7 (CH), 145.1 (C_q), 140.0 (C_q), 139.3 (C_q), 136.2 (CH), 136.0 (C_q), 129.1 (C_q), 127.4 (CH), 123.3 (CH), 121.6 (2C, CH), 119.4 (CH), 117.8 (CH), 116.4 (CH), 107.8 (CH), 44.0 (2C, CH_3). HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}N_3$ + H^+ [M + H]$^+$ 264.1495, found 264.1498.

Synthesis of (^{Me2}NNN^{Q})NiCl (2a). A solution of (^{Me2}NNN^{Q})H (**1a**; 0.50 g, 1.899 mmol) in THF (15 mL) was added to a suspension of (DME)$NiCl_2$ (0.50 g, 2.276 mmol) in THF (10 mL) using a cannula. After the reaction mixture was stirred for 15 min, Et_3N (0.53 mL, 3.803 mmol) was added and the resulting reaction mixture was refluxed for 5 h under an argon atmosphere (N.B.: completion of the reaction was confirmed by TLC monitoring of the reaction mixture). At ambient temperature, the reaction mixture was filtered through a cannula and the filtrate was concentrated to 5 mL. To the concentrated solution was added *n*-hexane to precipitate the product **2a** in analytically pure form. Compound **2a** was further recrystallized from an *n*-hexane solution by slow evaporation to obtain X-ray-quality single crystals. Yield: 0.56 g, 83%. Mp: 150−152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (d, $^3J_{H-H}$ = 4.9 Hz, 1H, Ar-H), 8.08 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, Ar-H), 7.54 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, Ar-H), 7.41 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.34 (vt, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.20 (dd, $^3J_{H-H}$ = 8.1, $^3J_{H-H}$ = 5.2 Hz, 1H, Ar-H), 7.13−7.08 (m, 2H, Ar-H), 6.87 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 6.61 (vt, $^3J_{H-H}$ = 7.5 Hz, 1H, Ar-H), 3.05 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6 (CH), 148.1 (C_q), 147.4 (C_q), 147.2 (C_q), 147.1 (C_q), 138.6 (CH), 129.8 (C_q), 129.4 (CH), 128.7 (CH), 121.0 (CH), 120.5 (CH), 117.3 (CH), 115.0 (CH), 113.0 (CH), 110.6 (CH), 51.8 (2C, CH_3). HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}ClN_3Ni$ − Cl^+ [M − Cl]$^+$ 320.0692, found

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320.0689. Anal. Calcd for $C_{17}H_{16}ClN_3Ni$: C, 57.28; H, 4.52; N, 11.79. Found: C, 57.22; H, 4.25; N, 11.69.

Synthesis of (^{Et2}NNN^{Q})NiCl (2b). This compound was synthesized following a procedure similar to the synthesis of **2a**, employing (^{Et2}NNN^{Q})H (**1b**; 0.50 g, 1.716 mmol), (DME)$NiCl_2$ (0.452 g, 2.057 mmol), and Et_3N (0.48 mL, 3.444 mmol) in THF (20 mL). Yield: 0.58 g, 88%. Mp: 195−198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (dd, $^3J_{H-H}$ = 5.2, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 8.10 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 1.5 Hz, 1H, Ar-H), 7.53 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 0.9 Hz, 1H, Ar-H), 7.40 (dd, $^3J_{H-H}$ = 7.3, $^4J_{H-H}$ = 0.6 Hz, 1H, Ar-H), 7.33 (vt, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.23 (dd, $^3J_{H-H}$ = 8.2, $^3J_{H-H}$ = 5.2 Hz, 1H, Ar-H), 7.13 (td, $^3J_{H-H}$ = 7.8, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 6.98 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 6.86 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 6.64 (td, $^3J_{H-H}$ = 7.4, $^4J_{H-H}$ = 0.9 Hz, 1H, Ar-H), 3.50−3.43 (m, 2H, CH_2), 2.47−2.40 (m, 2H, CH_2), 2.20 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8 (C_q), 150.2 (CH), 148.2 (C_q), 147.2 (C_q), 141.7 (C_q), 138.4 (CH), 129.8 (C_q), 129.3 (CH), 128.5 (CH), 120.9 (CH), 120.3 (CH), 117.5 (CH), 114.7 (CH), 112.5 (CH), 110.4 (CH), 57.9 (2C, CH_2), 13.3 (2C, CH_3). Anal. Calcd for $C_{19}H_{20}ClN_3Ni$: C, 59.35; H, 5.24; N, 10.93. Found: C, 59.38; H, 4.92; N, 10.38.

Synthesis of (^{Me2}NNN^{Q})NiBr (3a). A solution of (^{Me2}NNN^{Q})H (**1a**; 0.35 g, 1.329 mmol) in THF (10 mL) was added dropwise to a suspension of $(THF)_2NiBr_2$ (0.53 g, 1.461 mmol) in THF (20 mL), and Et_3N (0.37 mL, 2.655 mmol) was added to this mixture. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a cannula, and the filtrate was evaporated to dryness under vacuum. The resultant crude product was washed several times with *n*-hexane to give compound **3a** as an orange solid. Compound **3a** was recrystallized from *n*-hexane solution by slow evaporation to obtain X-ray-quality single crystals. Yield: 0.304 g, 57%. Mp: 147−150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (br s, 1H, Ar-H), 8.05 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 7.55 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 7.40 (d, $^3J_{H-H}$ = 6.6 Hz, 1H, Ar-H), 7.34 (vt, $^3J_{H-H}$ = 7.6 Hz, 1H, Ar-H), 7.19 (br s, 1H, Ar-H), 7.12−7.06 (m, 2H, Ar-H), 6.86 (d, $^3J_{H-H}$ = 7.3 Hz, 1H, Ar-H), 6.60 (vt, $^3J_{H-H}$ = 6.8 Hz, 1H, Ar-H), 3.20 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2 (CH), 147.7 (C_q), 146.9 (C_q), 146.8 (C_q), 146.7 (C_q), 138.6 (CH), 129.8 (C_q), 129.3 (CH), 128.6 (CH), 121.6 (CH), 120.6 (CH), 117.4 (CH), 115.2 (CH), 113.2 (CH), 110.9 (CH), 52.8 (2C, CH_3). HRMS (ESI): *m*/*z* calcd for $C_{17}H_{16}BrN_3Ni - Br^+$ $[M - Br]^+$ 320.0692, found 320.0688. Anal. Calcd for $C_{17}H_{16}BrN_3Ni$: C, 50.93; H, 4.02; N, 10.48. Found: C, 49.42; H, 4.15; N, 10.29.

Synthesis of (^{Et2}NNN^{Q})NiBr (3b). This compound was synthesized following a procedure similar to the synthesis of **2a**, employing (^{Et2}NNN^{Q})H (0.10 g, 0.343 mmol), $(THF)_2NiBr_2$ (0.137 g, 0.377 mmol), and Et_3N (0.096 mL, 0.686 mmol) in THF (20 mL). Yield: 0.124 g, 84%. Mp: 188−191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, $^3J_{H-H}$ = 5.4, $^4J_{H-H}$ = 1.5 Hz, 1H, Ar-H), 8.09 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 1.5 Hz, 1H, Ar-H), 7.57 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 1.0 Hz, 1H, Ar-H), 7.45 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.0 Hz, 1H, Ar-H), 7.33 (vt, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.20 (dd, $^3J_{H-H}$ = 8.3, $^3J_{H-H}$ = 5.4 Hz, 1H, Ar-H), 7.13 (td, $^3J_{H-H}$ = 7.7, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 6.97 (dd, $^3J_{H-H}$ = 7.9, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 6.86 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, Ar-H), 6.65 (td, $^3J_{H-H}$ = 8.1, $^4J_{H-H}$ = 1.2 Hz, 1H, Ar-H), 3.66−3.57 (m, 2H, CH_2), 2.57−2.49 (m, 2H, CH_2), 2.19 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1 (CH), 150.9 (C_q), 148.4 (C_q), 147.2 (C_q), 141.6 (C_q), 138.5 (CH), 129.9 (C_q), 129.3 (CH), 128.6 (CH), 121.3 (CH), 120.5 (CH), 117.7 (CH), 114.7 (CH), 112.7 (CH), 110.4 (CH), 58.9 (2C, CH_2), 13.5 (2C, CH_3). Anal. Calcd for $C_{19}H_{20}BrN_3Ni$: C, 53.20; H, 4.70; N, 9.80. Found: C, 52.65; H, 4.38; N, 9.54.

Synthesis of (^{Me2}NNN^{Q})Ni(OAc) (4a). A solution of (^{Me2}NNN^{Q})H (**1a**; 0.40 g, 1.519 mmol) in THF (20 mL) was added dropwise to a mixture of $Ni(OAc)_2$ (0.295 g, 1.671 mmol) and Et_3N (0.42 mL, 3.013 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature for 24 h under an argon atmosphere. The reaction mixture was then filtered through a cannula, and the filtrate was concentrated under vacuum. To the concentrated solution was added *n*-hexane to precipitate the product, which was then washed several times with *n*-hexane to obtain a pure product of **4a**. Yield: 0.39 g, 68%. Mp: 218−220 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.51 (br s, 1H, Ar-H), 7.43 (d, $^3J_{H-H}$ = 7.9 Hz, 1H, Ar-H), 7.34−7.28 (m, 2H, Ar-H), 7.23 (br s, 1H, Ar-H), 7.10−7.08 (m, 2H, Ar-H), 6.83 (d, $^3J_{H-H}$ = 6.7 Hz, 1H, Ar-H), 6.59 (vt, $^3J_{H-H}$ = 7.1 Hz, 1H, Ar-H), 2.96 (s, 6H, CH_3), 2.09 (s, 3H, $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1 (CO), 147.9 (C_q), 147.4 (CH), 147.2 (C_q), 147.0 (C_q), 146.7 (C_q), 138.5 (CH), 129.9 (C_q), 129.5 (CH), 128.8 (CH), 121.1 (CH), 120.1 (CH), 116.9 (CH), 115.2 (CH), 112.5 (CH), 111.0 (CH), 50.5 (2C, CH_3), 24.9 ($COCH_3$). HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}N_3O_2Ni - OC(O)CH_3^+$ $[M - OC(O)CH_3]^+$ 320.0692, found 320.0692. Anal. Calcd for $C_{19}H_{19}N_3O_2Ni$: C, 60.04; H, 5.04; N, 11.06. Found: C, 60.25; H, 4.52; N, 10.36.

Representative Procedure for Alkylation of Azoles: Synthesis of 2-*n*-Octylbenzo[*d*]thiazole (7aa). In a flame-dried screw-cap tube equipped with a magnetic stir bar were introduced catalyst **2a** (0.009 g, 0.025 mmol), LiO^tBu (0.081 g, 1.012 mmol), benzothiazole (**5a**; 0.068 g, 0.503 mmol), and 1-iodooctane (**6a**; 0.180 g, 0.750 mmol) inside the glovebox. To the above reaction mixture was added 1,4-dioxane (1.0 mL) under an argon atmosphere, and the resultant reaction mixture was stirred at 100 °C in a preheated oil bath for 16 h. At ambient temperature, the reaction mixture was quenched with distilled water (5 mL) and neutralized with 2 N HCl (0.5 mL). The crude product was then extracted with ethyl acetate (15 mL × 3) and the combined organic extract was washed with distilled water (15 mL × 3). The organic extract was dried over Na_2SO_4, and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 100/1) to yield the compound **7aa** as a yellow liquid.

Note: when alkyl bromides and alkyl chlorides were employed as coupling partners, NaI (1.5 equiv, i.e. same amount as for alkyl bromide or alkyl chloride) was added to the reaction mixture and the reactions were carried out at 120 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00201.

Detailed experimental procedures, analytical data for the compounds, and ^{1}H and ^{13}C NMR spectra of pincer precursors, nickel complexes, and alkylated compounds (PDF)

Crystallographic data for **2a** (CCDC-1457902) (CIF)

Crystallographic data for **3a** (CCDC-1457903) (CIF)

Crystallographic data for **3b** (CCDC-1457904) (CIF)

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Notes

The authors declare no competing financial interest.

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