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Functionalization of the Aryl Moiety in the Pincer Complex $(NCN)Ni^{III}Br_2$: Insights on Ni^{III}-Promoted Carbon−Heteroatom Coupling

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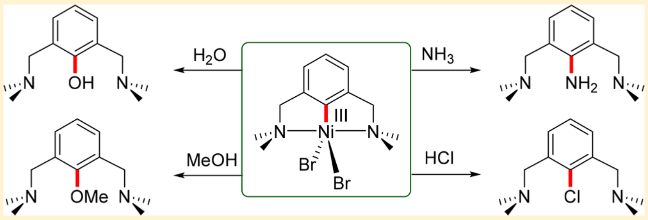
Supporting Information

ABSTRACT: This report describes the C−O, C−N, and C−halogen functionalization of the Ni^{III}−Ar moiety stabilized within a pincer framework that serves as a model system for studying C−heteroatom coupling reactions promoted by high-valent Ni compounds. Treating van Koten's pincer complex $(NCN)Ni^{III}Br_2$ under a nitrogen atmosphere with water, 1° or 2° alcohols, 1° amines, HCl, or HBr results in heterofunctionalization at the *ipso*-C of the pincer ligand's aryl moiety. The yields of these heterofunctionalizations are generally <50%, which has been attributed to the occurrence of a comproportionation reaction between the trivalent precursor and a Ni^{I} species arising from the reductive elimination step in the functionalization process. Other side-reactions include a C−OH coupling with residual water and C−H coupling (net protonation) that is prevalent with mineral acids, some alcohols, and aqueous NH_3. Kinetic measurements have established that the reaction with MeOH is first-order with respect to $[(NCN)Ni^{III}Br_2]$, and a kinetic isotope effect of 0.47 has been obtained for functionalization with CH_3OH/CD_3OD. These and other observations have allowed us to propose two different mechanistic postulates for the involvement of trivalent intermediates in the functionalization reactions under discussion. Tetravalent species such as $[(NCN)Ni^{IV}Br_2]^+$ can be generated *in situ* under strongly oxidative conditions and they do promote C−Br coupling, but such species play no role in the C−heteroatom coupling reactions under nonoxidative conditions.



INTRODUCTION

The past few decades have witnessed a steady rise in the number of reports on new catalytic methodologies for the coupling/functionalization of both activated C−X and "inert" C−H bonds. A more recent trend is the move to develop catalytic protocols based on abundant 3d metals. From a mechanistic viewpoint, 3d metals boast reactivity features that are often distinct from those of their 4d and 5d counterparts, including the prevalence of single-electron redox processes and involvement of odd-electron intermediates in key steps of the catalytic cycle. These considerations warrant further mechanistic investigations of 3d metal-catalyzed coupling processes so that the new insights thus gained may pave the way to more efficient and sustainable synthetic methodologies.

Classical 3d metal-catalyzed coupling reactions that exemplify the above-alluded reactivity features include Ni-catalyzed C−C coupling methodologies such as Kumada−Corriu, Suzuki, and Negishi coupling reactions, many of which are thought to proceed through Ni^{III} intermediates.[1] The analogous Ni-promoted C−heteroatom coupling reactions have been studied less extensively, but these too are believed to involve high-valent species.[2] In this context, Hillhouse was among the first to demonstrate that C−N and C−O coupling reactions proceed via Ni^{III} species (Scheme 1).[3]

Hillhouse's findings inspired a number of research groups to investigate the fundamental reactivities of high-valent Ni complexes and test their potential in stoichiometric and catalytic C−heteroatom coupling reactions. Notable examples of these investigations include systematic studies reported by Mirica[4] and Sanford[5] on C−N, C−O, and C−halogen coupling reactions using authenticated Ni^{III} and Ni^{IV} model compounds (Chart 1).[6] In this context, a very recent report by the groups of Canty and Sanford[7] has demonstrated that Ni^{IV} species appear to be more reactive than their Pd^{IV} homologues toward C−C and C−heteroatom bond formation.[8]

Other important milestones in the area of Ni^{III}-catalyzed C−heteroatom coupling include reports by the groups of MacMillan and Molander, which have shown that photolytically generated, cationic Ni^{III} intermediates catalyze the coupling of alcohols and thiols with aryl halides.[9] These and other recent developments in the organometallic chemistry of high-valent Ni complexes[10] are certain to further invigorate research efforts in this field with the ultimate objective of supplanting Pd in C−heteroatom coupling reactions.

Our group's studies of Ni^{III} complexes evolved from a long-standing interest in organonickel chemistry,[11] but it was van Koten's seminal reports on pincer-backboned trivalent Ni complexes $(NCN)Ni^{III}X_2$ (NCN = κ^N, κ^C, κ^N-1,3(CH_2NMe_2)-C_6H_3; X = Br, I, NO_3, NO_2)[12] that prompted us to investigate the chemistry of this family of complexes. To complement the rigid *m*-phenylene backbone of these complexes and their peripheral

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Scheme 1. Literature Precedents on Aerobic-Oxidation-Induced C−X Bond Formation

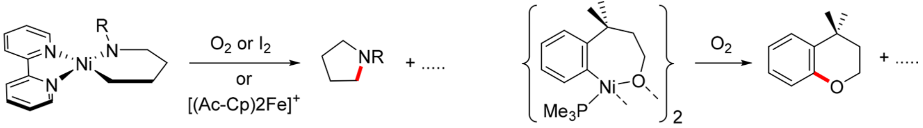
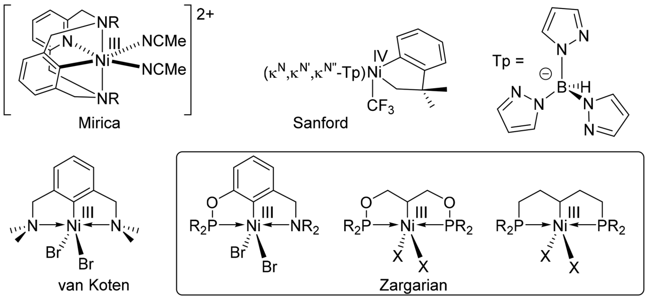
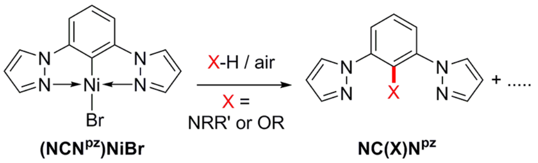


Chart 1. Examples of Authenticated Ni^{III} and Ni^{IV} Complexes Relevant to C−Heteroatom Coupling Reactions



hard donor moieties, we prepared a number of PCP- and POCOP-variants based on less rigid nonaromatic backbones and featuring soft donor moieties, as well as new complexes featuring the hybrid POCN-type ligands (Chart 1).[13] However, these trivalent complexes did not show promising reactivity in C−heteroatom coupling, promoting only Kharasch-type additions of CCl_4 to olefins.[13b]

Next, we focused on nickel complexes featuring NCN^{pz}-type ligands, close analogues of van Koten's NCN platform featuring pyrazole donor moieties. We showed that $(NCN^{pz})Ni^{II}Br$ reacts with water, alcohols, and amines under mild oxidative conditions of ambient air to promote C−O and C−N coupling with the aryl moiety of the ligand:[14]



(1)

This ligand functionalization reaction was reminiscent of the above-cited work by Hillhouse's group,[3] with the important difference that in the latter case both C- and O/N-based ligands were preassembled on the Ni^{II} center (unimolecular coupling), whereas $(NCN^{pz})Ni^{II}Br$ reacts with external substrates (bimolecular coupling).

As was the case in Hillhouse's system, the trivalent intermediates generated from oxidation of our $(NCN^{pz})Ni^{II}Br$ complexes could not be isolated and authenticated. This shortcoming prompted us to launch follow-up studies using different ligand platforms that might give access to sufficiently stable trivalent intermediates capable of serving as suitable models for probing the mechanism of the C−heteroatom coupling reactions. Screening tests showed that van Koten's original NCN ligand platform was a suitable candidate for these purposes, which was an intriguing finding since Canty and van Koten had shown in 2004 that the Pt^{IV} complex $(NCN)Pt(O_2CPh)_3$ was stable to C−O bond formation involving the aryl moiety of the NCN ligand.[15] This led us to systematically investigate the reactivities of van Koten's compound in heterofunctionalization of the Ni−Ar moiety.

The present report describes the reactivities of $(NCN)Ni^{III}Br_2$ with water, alcohols, and amines to promote C−O and C−N coupling reactions under inert atmosphere. Significantly, this trivalent precursor also reacts with strong mineral acids HBr and HCl to give halogen-functionalization of the NCN ligand, a counterintuitive reactivity likely arising from the electrophilic character of the Ni−C bond in this high-valent compound. The results reported herein serve to illustrate the stark contrast between the reactivities of various trivalent organonickel species generated *in situ* from $(NCN)Ni^{III}Br_2$ relative to their divalent counterparts and the $(NCN)Pt^{IV}$ complex alluded to above.[15]

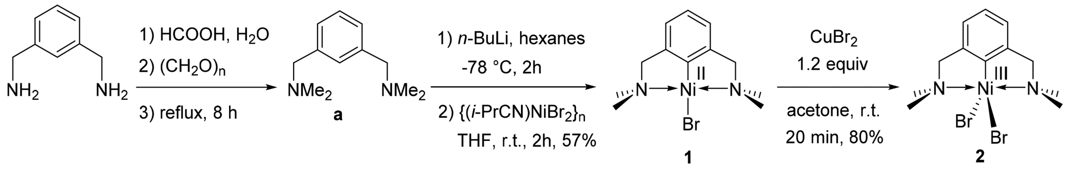
RESULTS AND DISCUSSION

Synthesis of $(NCN)Ni^{II}Br$, 1, and $(NCN)Ni^{III}Br_2$, 2. van Koten's group has reported different methods for the preparation of the divalent pincer complexes $(NCN)Ni^{II}X$[16] and has used them as convenient precursors to the thermally stable trivalent species $(NCN)Ni^{III}X_2$.[12] For instance, the divalent complex $(Me_3Si\text{-}NCN)NiCl$ bearing a *p*-trimethylsilyl substituent on the central phenylene ring has been prepared by treating the lithium salt of the proligand with the Ni^{II} precursor $(PEt_3)_2NiCl_2$.[17] We used a revised version of this protocol (Scheme 2) to prepare complex $(NCN)Ni^{II}Br$, **1**, which was then oxidized by $CuBr_2$ to give the target trivalent complex $(NCN)Ni^{III}Br_2$, **2**.[12]

Anaerobic Reactions of 2 with Water, Alcohols, and Amines. Screening studies showed that trivalent complex **2** reacts with protic substrates XH under anaerobic conditions to give C−O and C−N functionalization of the NCN ligand (Scheme 3, Table 1).

Inspection of the results listed in Table 1 indicates that the success of the functionalization reactions depends on the nature of XH, C−O coupling being fairly sluggish with water or alcohols compared to C−N coupling with amines. For instance, stirring **2** in water at r.t. gave a 53% yield of NC(OH)N over 3 days, whereas the analogous reactions with MeOH and *i*-$PrNH_2$ gave, respectively, a 23% yield of NC(OMe)N over 7 h versus a 31% yield of NC(*i*-PrNH)N in only 2 h (entries 1, 3, and 5). The latter reaction also generated 9% of NC(OH)N, presumably due to a competitive side-reaction with residual water (*vide infra*).

Scheme 2. Syntheses of Complexes 1 and 2



Scheme 3. Functionalization of (NCN)$Ni^{III}Br_2$, 2, with Water, Alcohols, and Amines

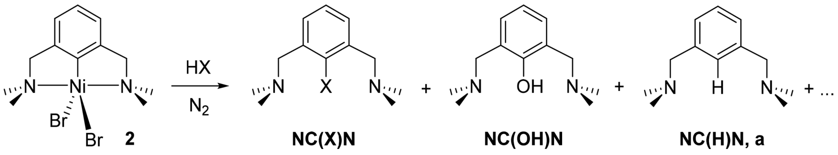


Table 1. Functionalization of the NCN Ligand in 2[a]

			yield		
entry	substrate HX	conditions	NC(X)N	NC(OH)N	a
1	H_2O	r.t., 3 days		53%	
2		70 °C, 24 h		36%	21%
3	MeOH	r.t., 7 h	23%		
4		65 °C, 7 h	33%	5%	
5	i-PrNH_2	r.t., 2 h	31%	9%	
6	EtOH	70 °C, 24 h	27%		8%
7	CF_3CH_2OH	70 °C, 12 h	24%		8%[b]
8	i-PrOH	70 °C, 12 h	37%		15%
9	t-BuOH	70 °C, 24 h		22%	
10	i-Pr_2NH	r.t., 15 min		32%	
11	NH_3 (28% in H_2O)	r.t., 2 h	24%	15%	15%
12	$MeNH_2$ (33% in EtOH)	r.t., 5 min	31%[c]	4%	
13	Me_2NH (40% in H_2O)	r.t., 15 min		11%	
14	$H_2NCH_2CH_2OH$	r.t., 1 h	24%[c]		13%

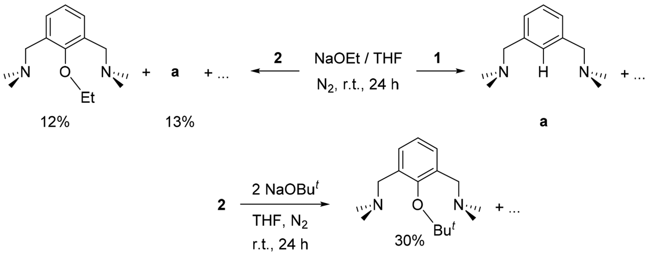
[a] See Supporting Information for experimental and operational details and for additional comments on yields. [b] This reaction also generated 8% of the C−Br coupling product NC(Br)N. [c] This is the yield for the C−N coupling product.

The much slower rates of C−O coupling with water and MeOH prompted us to test the impact of heating on these functionalization reactions. For the reaction of **2** with MeOH, heating did improve the yield of the desired NC(OMe)N from 23% at r.t. to 33% at 65 °C (entry 4), but the higher temperature also gave 5% NC(OH)N. For the reaction of **2** with water, however, heating to 70 °C led to a lower yield of NC(OH)N and generated significant quantities of proligand **a** (entry 2). The latter side-product is believed to be due to protonolysis of *in situ* generated (NCN)Ni^{II}Br (*vide infra*). It should be noted, however, that proligand **a** was also generated in the reactions with EtOH, CF_3CH_2OH, and *i*-PrOH (entries 6−8).

On the basis of the observations reported by Mirica's group on Ni^{III} promoted ligand functionalizations,[18] we suspected that a different side-reaction is responsible for the formation of proligand **a** in the reactions with alcohols. Our suspicions were confirmed by these observations: The anaerobic reaction of divalent complex **1** with NaOEt gave proligand **a** as the only product, whereas the analogous reaction with trivalent **2** gave both **a** and NC(OEt)N (Scheme 4).

The above observations confirmed that C−OEt coupling requires a trivalent precursor, whereas the net protonolysis giving proligand **a** arises from a divalent species. We suspect that the latter side reaction originates from (NCN)Ni^{II}−OEt, a divalent ethoxy intermediate generated *in situ* during the C−OEt functionalization reaction. *β*-H Elimination from the Ni^{II}−OEt moiety would give a thermally unstable hydride species that would, in turn, give **a** via reductive elimination. Consistent with this assertion, the direct reaction of **2** with the *β*-H free salt NaO(*t*-Bu) gave only NC(OBu^t)N, none of proligand **a** or NC(OH)N is detected.

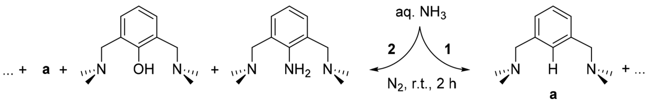
Scheme 4. Reactions of 1 and 2 with NaOR



In contrast to the success of the C−O(*t*-Bu) coupling from the reaction with NaO(*t*-Bu), the analogous reaction of **2** with *t*-BuOH gave only NC(OH)N (entry 9). A similar result was observed with *i*-Pr_2NH (entry 10), which implied that sterics can hinder the functionalization reaction, presumably because of the weak nucleophilicity of these bulky substrates. Comparing the results of these two reactions to those with *t*-BuOH and water allows two other conclusions. First, the observation that NC(OH)N is generated in the reaction with *t*-BuOH but not NaO(*t*-Bu) supports the above-mentioned proposal that the formation of the C−OH coupling side-product with various alcohols and amines is due to residual moisture. Second, C−OH coupling is clearly much more facile with the residual moisture in *i*-Pr_2NH versus the reaction of **2** with pure water (32% over 15 min vs 53% over 3 days) or with the residual moisture in *t*-BuOH (22% over 24 h at 70 °C).

The acceleration of C−OH coupling with water in the presence of amines was also noted when we treated **2** with deoxygenated NH_4OH (28% aqueous ammonia): Running this reaction at ambient temperature over 2 h gave NC(NH_2)N as the major product (ca. 24%) as well as 15% each of NC(OH)N and proligand **a** (entry 11). The formation of significant quantities of **a** in this case implies that NH_4^+ can protonate the *in situ* generated divalent species fairly readily, an assertion which was supported by the observation that treating divalent species **1** with aqueous ammonia (under anaerobic conditions) gave **a** as the only tractable product (Scheme 5).

Scheme 5. Reactions of 1 and 2 with Aqueous NH_3



Three other C−N versus C−O functionalization tests were conducted, as follows. Functionalization of **2** with a 30% EtOH solution of $MeNH_2$ turned out to be even faster than the analogous reaction with aqueous ammonia, requiring only 5 min to give NC(NMeH)N as the major product in addition to a minor amount of NC(OH)N (31 and 4%, respectively; entry 12 in Table 1). It is significant that no C−OEt functionalization was detected in this reaction even though it was conducted in EtOH as solvent; evidently, C−X functionalization follows the order MeNH > OH > OEt. The functionalization with a 40% aqueous solution of the more sterically demanding Me_2NH was also quite fast but gave only NC(OH)N (entry 13), presumably because of the greater steric bulk of this substrate. Finally, the reaction of **2** with ethanolamine, a substrate that features a primary amine and a primary alcohol in the same molecule, gave the C−$NHCH_2CH_2OH$ coupling product (24%) as well as **a** (13%) but not the C−$OCH_2CH_2NH_2$ coupling product (entry 14).

C−Halogen Functionalization of NCN in (NCN)$Ni^{III}Br_2$, 2. Having established that a preformed trivalent complex such as **2** can react under inert atmosphere with the protic substrates water, alcohols, and primary amines to promote C−N and C−O coupling, we wondered whether the analogous C−halogen coupling might also be possible with hydrohalides. To be sure, there are precedents for Ni^{III}-promoted C−halide coupling: Sanford's group has reported that trivalent intermediates generated *in situ* by oxidation of the divalent precursors L_2Ni^{II}(Ar)(halide) or $L_2Ni^{II}(Ar)_2$ promote C−C and C−halide bond formation reactions,[19] whereas Mirica's group has shown that the authenticated trivalent species $[L_4Ni(Ar)Br]^+$ promotes reductive elimination of Ar−Br.[4b] Moreover, the detection of minor amounts of the C−Br coupling product NC(Br)N in the reaction of **2** with trifluoroethanol at 70 °C (Table 1, entry 7) hinted that such reactivity is feasible and encouraged us to explore this idea.

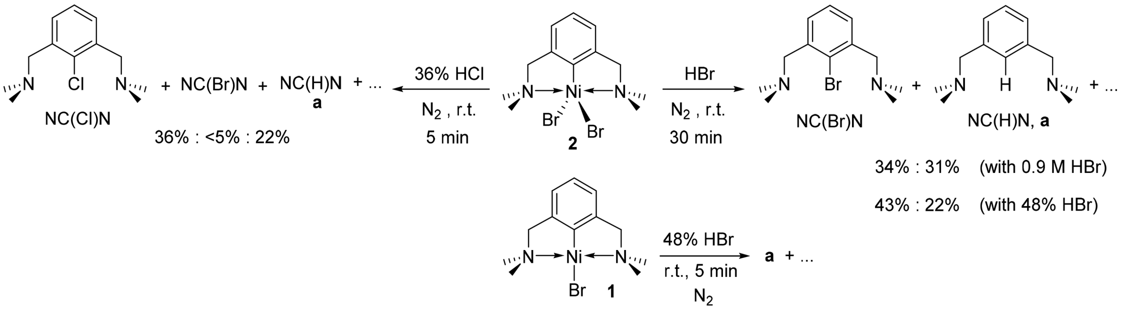
Treating **2** with hydrohalides confirmed that C−halide coupling is feasible and fairly efficient, but protonation (C−H coupling) is a major side-reaction. For instance, treating trivalent complex **2** with 0.9 M HBr at r.t. over 30 min gave nearly equal yields of the desired C−Br coupling product (34%) and proligand **a** (31%), in addition to traces of unidentified degradation products (Scheme 6).[20] To probe the importance of acid concentration for this reaction, we repeated the reaction with 48% HBr, which gave a higher yield of the C−Br at the expense of **a** (43:22 vs 34:31). The reaction with 36% HCl was even faster, requiring only 5 min to give a mixture of the halo-functionalized products NC(Cl)N (36%) and NC(Br)N (<5%), as well as proligand **a** (22%).

The observed Brønsted acid triggered C−halide coupling reactivity of **2** is in stark contrast to the protonolysis of the Ni-aryl moiety in divalent complex **1** (Scheme 6): The latter reaction results in an immediate bleaching of the mixture and generates only proligand **a**, which was obtained in near quantitative yields after basic extraction. It is worth emphasizing here that no C−X coupling product is detected from the reaction of **1** with HCl, HBr, or other acids. Thus, we conclude that the reactivity of $(NCN)Ni^{(n+1)}Br_n$ with hydrohalides depends on the oxidation state of the Ni center: Divalent complex **1** ($n = 1$) leads to protonolysis of the Ni^{II}-aryl moiety exclusively, whereas both halogenation and protonolysis occur with trivalent species **2** ($n = 2$). A similar case of such dual reactivity has been reported by Roddick for the reactions of *trans*-$\{PMe(C_2F_5)_2\}_2Pt(X)Me$ with different HX: HOTf leads to elimination of Me−H, i.e., protonolysis), whereas the more oxidizing acid $HOSO_2F$ generates Me-OSO_2F, i.e., C−X coupling presumably via a Pt^{IV}−Me intermediate (Scheme 7).[21]

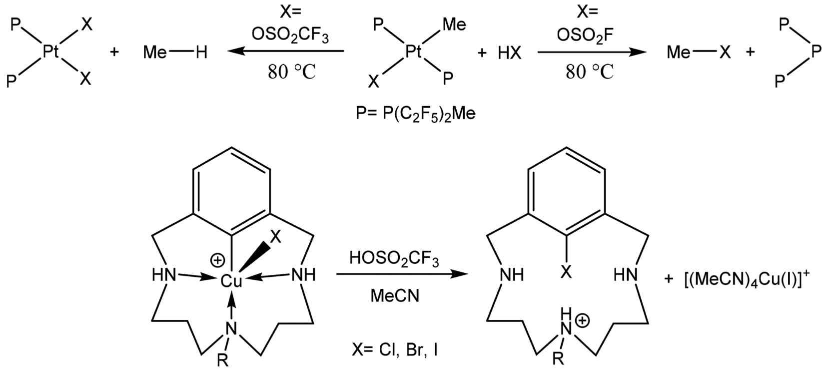
Ar−halide coupling observed with **2** is also reminiscent of the analogous reactivity reported for the Cu^{III} complex shown in Scheme 7.[22] Protonation of the tertiary amine ligand moiety in this compound compromises its thermal stability and leads to C−halide bond formation. That the observed reactivity does not involve the weakly coordinating conjugate base triflate implies that the functionalization reaction proceeds via reductive elimination. To determine if a similar scenario governs the Ni^{III} system under discussion, we treated **2** with aqueous HBF_4, which led to C−Br coupling (ca. 40%) as well as protonolysis (ca. 26% of **a**; Scheme 8). We infer from this observation that C−X functionalization in this system is an inner-sphere event that favors Ni-bound anions such as chloride and bromide over unbound anions and nucleophiles such as H_2O that cannot be deprotonated under low pH conditions. Interestingly, C−Br coupling in **2** can also take place, albeit to a small extent, under nonacidic conditions and in the presence of aqueous Br^- (Scheme 8). In contrast, no C−Br coupling takes place when **2** is treated with 20 equiv of Bu_4NBr in MeCN, showing that an aqueous medium is essential for this reactivity and suggesting that C−OH coupling likely precedes C−Br coupling.

Insights on the C−X Bond Forming Step. The results presented in the preceding sections have established that trivalent species **2** reacts with HX and leads to C−O, C−N,

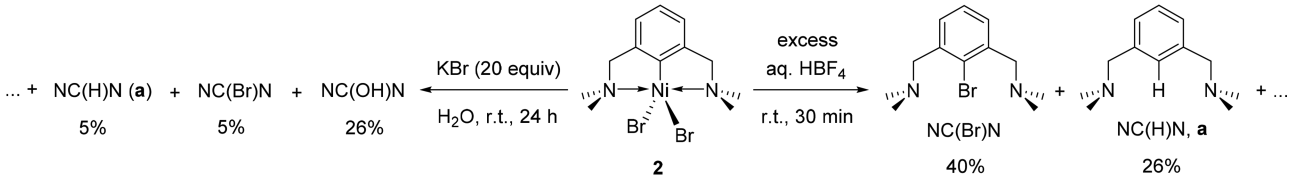
Scheme 6. Reactivity of 2 with HBr and HCl



Scheme 7. Literature Precedents for C−X Bond Formation Triggered by Reaction with Brønsted Acids HX



Scheme 8. Reaction of 2 with HBF_4 or H_2O/KBr

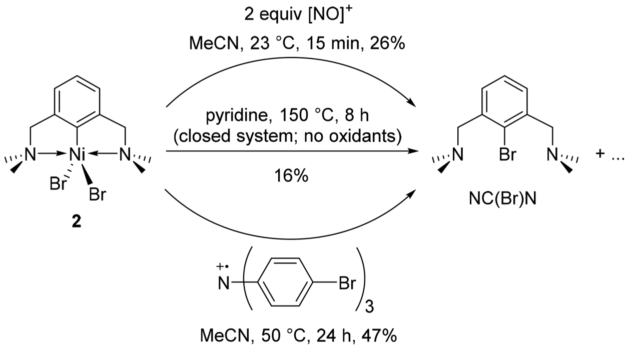


and C−halogen functionalization of the central aryl moiety of the NCN ligand, giving NC(X)N; in contrast, no functionalization takes place in the analogous reactions with divalent complex **1**. On the basis of these observations, it would seem reasonable to assume *a priori* that the heterofunctionalization reactions under discussion must involve Ni^{III} intermediates, as opposed to Ni^{IV} species, because (a) these functionalizations proceed in the absence of added oxidants and (b) the oxidation potential of **2** is relatively high ($E°'$ for $Ni^{IV/III}$ is 0.69 V vs $Fc^{+1/0}$ in MeCN; see Figure S41). These considerations notwithstanding, we felt compelled to question whether the observed functionalizations of **2** might in fact involve *in situ* generated tetravalent intermediates, because strong evidence has been presented in recent literature in support of the viability of Ni^{IV} intermediates in C−C and C−X bond forming reactions (*vide infra*). For instance, we wondered if tetravalent species might be generated by disproportionation of **2**; this scenario seemed feasible in principle, because the requisite conversion of 2 equiv of **2** into a Ni^{II} and a Ni^{IV} species in such a mechanism would also explain the generally <50% yields observed. The following experiments were, therefore, undertaken to probe this question.

First, we made kinetic measurements to determine the order of [**2**] in the C−OMe coupling reaction with MeOH. Thus, UV−vis spectroscopy was used to monitor the time profile of a reaction between **2** and a large excess of MeOH (7000−8000 equiv). These measurements showed a first order decay for [**2**], indicating a pseudo-first-order reaction with respect to Ni^{III}; this finding argues against the involvement of a bimolecular disproportionation reaction in the formation of NC(OMe)N from **2** and MeOH.

Next, we probed the question of whether oxidative conditions might facilitate functionalization of **2**, regardless of whether or not tetravalent species might be accessible in standard conditions of functionalization. For this purpose, we selected to examine the bromo-functionalization of **2**, because this reaction does not occur in the absence of external sources of bromide or under nonoxidative conditions. Indeed, Sanford's group has shown that the thermal reaction of **2** under inert atmosphere is very sluggish, requiring heating to 150° or higher temperatures (Scheme 9).[23]

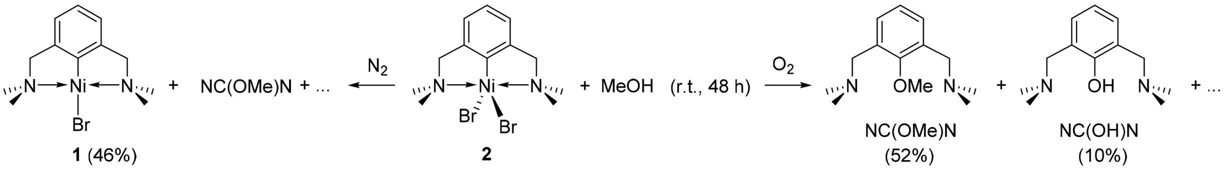
Scheme 9. Thermolytic and Oxidative Decomposition of 2



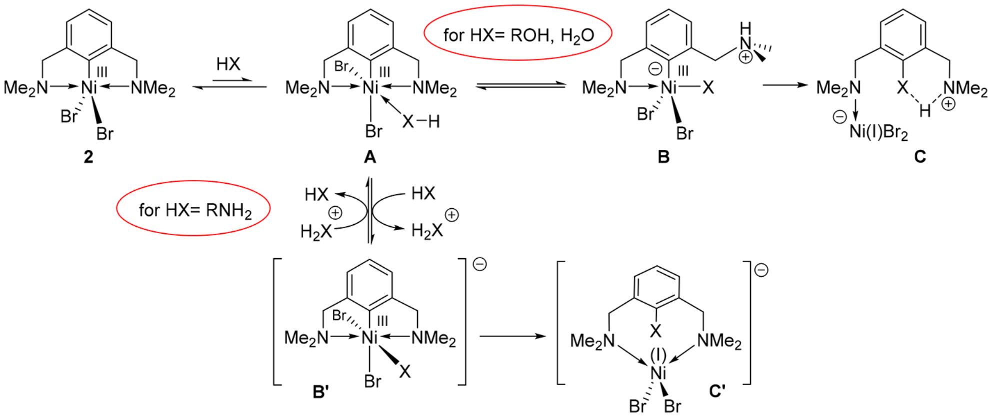
As oxidants, we tested NO^+ and the triarylaminium radical cation $[N(4\text{-}Br{-}C_6H_4)_3]^+$ (magic blue), both of which possess formal potentials $E°'$ that are comparable to that of **2**: 0.87 and 0.67 V, respectively, versus 0.69 V for **2**.[24] We were intrigued to find that C−Br coupling was fairly facile in the presence of NO^+: Stirring an acetonitrile solution of **2** with $NOBF_4$ at ambient temperature gave 26% of NC(Br)N in 15 min. The analogous C−Br functionalization also proceeded with the aminium radical cation, but heating to 50 °C was required in this case (47% yield over 24 h). It should be noted that these reactions did not generate any of the usual side-products NC(OH)N or NC(H)N.

The more facile C−Br bond formation under oxidative conditions relative to the results of Sanford's thermal reaction demonstrates that **2** is less stable under oxidative conditions. We propose that the oxidation-induced C−Br coupling reactions shown in Scheme 9 proceeds by an inner-sphere reductive elimination from a transient tetravalent intermediate akin to $[\mathbf{2}]^+$. As mentioned earlier, there are some literature precedents for the involvement of tetravalent intermediates in Ni-promoted C−X and C−C bond formation reactions. For instance, Mirica's group has shown that both C−O[4a] and C−C[6a,b] reductive eliminations take place in authenticated Ni^{III} species, but some of their observations indicate that these reactions proceed more readily and with higher yields under oxidative conditions, implicating *in*

Scheme 10. Aerobic and Non-Aerobic Reaction of 2 with MeOH



Scheme 11. Proposed Mechanism for the Functionalization of 2 with Amines, Alcohols, or Water



situ generated Ni^{IV} species in these C–O and C–C bond forming.

The competence of Ni^{IV} precursors in C–C bond formation has also been demonstrated clearly by Sanford's group.[5a] Particularly relevant to this discussion are the reports by the groups of Sanford and Canty that compare ease of C–C and C–X coupling with tri- and tetravalent precursors. They showed, for instance, that *in situ* oxidation of the trivalent compound $(Tp)Ni(Ph)(CF_3)$ (Tp = tris(pyrazolyl)borate) facilitates reductive elimination of $Ph-CF_3$, presumably through a tetravalent intermediate.[5b] These authors have also proposed C–X bond formation promoted by Ni^{IV} species proceeds via nucleophilic attack of an unbound X^- on the Ni^{IV}–C bond of an octahedral species (an outer-sphere S_N2 mechanism) as opposed to a reductive elimination (an inner-sphere mechanism).[7,25]

To further examine the impact of oxidative conditions on the functionalization of **2** with protic reagents, we probed in more detail the reaction with MeOH. First, we noted that conducting the reaction of **2** in MeOH in air gave the highest yield of C–OMe coupling product obtained in this study: 52% of NC(OMe)N was obtained over 2d, in addition to 10% of the C–OH coupling product NC(OH)N, i.e., a 62% combined C–O functionalization yield (Scheme 10). It should be recalled that aerobic oxidation of **2** is not feasible, which rules out the involvement of tetravalent species here. As a second test, we conducted the reaction of **2** with MeOH at room temperature and under N_2, which gave significant quantities (~46%) of divalent complex **1** (Scheme 10); by comparison, no trace of **1** was observed in the analogous aerobic reaction.

The above results can be reconciled with the postulate that the reductive elimination step that gives the product of C–OMe coupling also generates Ni^{I} intermediates that undergo a comproportionation reaction with **2** (or other trivalent species present in the reaction mixture) to give **1**. This would, of course, consume 1 equiv of the trivalent precursor, thereby limiting the maximum functionalization yield to 50%. Such an unproductive side-reaction can be circumvented when an alternative pathway is available for the oxidation of the *in situ* generated monovalent species, for instance when the reaction is conducted in air; this would explain the enhanced yield of the C–OMe coupling product in air.[26]

Mechanistic Proposals for C–Heteroatom Functionalization of the Aryl Moiety in 2. Putting together the observations described in the preceding sections has allowed us to envisage a mechanistic scenario for the observed ligand functionalization reactions of **2** with the protic substrates HX. A simplified version of this mechanism for the reactions with amines, alcohols, or water is illustrated in Scheme 11 and explained below; a different sequence of steps will be invoked for the analogous functionalization with hydrohalides (*vide infra*).

The functionalization reactions would begin by substrate coordination to the electrophilic Ni^{III} center in precursor **2**, converting this penta-coordinate, 17-electron precursor to octahedral, 19-electron species **A**. This should be an uphill process on both electronic and steric grounds,[27] and the resulting equilibrium should have a very small K_{eq}, which is consistent with the observed requirement for a very large excess of the weakly nucleophilic or sterically hindered XH (*vide supra*).

Coordination of XH to the trivalent center in **A** would activate the X–H bond and facilitate the crucial H^+-transfer step. In the case of reactions with the weakly basic substrates water and alcohols, deprotonation would be assured by the NMe_2 moiety of the pincer arm to give **B**, whereas in the case of reactions with primary amines the H^+-transfer might be assisted by additional molecules of substrate instead of the pincer arm, giving **B′**. Such acceleration of the H^+-transfer step would also explain the above-noted facile C–OH coupling in the presence of *i*-Pr_2NH, NH_3, and Me_2NH (entries 10, 11, and 13 in Table 1). Also consistent with this assertion, addition of NEt_3 to aqueous or MeOH solutions of **2** accelerated the formation of the C–O coupling products. For instance, whereas reaction of pure water gives little or no functionalization over 2–3 h, the presence of just 1 equiv of NEt_3 led to a 24% yield of NC(OH)N in 1 h, implying that expediting the H^+-transfer step greatly influences the overall functionalization rate.

To confirm the impact of the H$^+$-transfer step on the functionalization rate, we measured the kinetics of the reaction of **2** with CH_3OH and CD_3OD as follows. UV−vis spectra were recorded for 0.81×10^{-3} M solutions of **2** in CH_3OH or CD_3OD, at r.t. and under pseudo-first-order conditions (substrate: Ni^{III} ratio >1:500). Monitoring the disappearance of the absorption band at 553 nm allowed us to extract the observed rate constants for the functionalization reaction (Figure 1). Observation of nonunity isotope effects indicated that the H$^+$-transfer step has a significant influence on reaction rates, likely occurring before the rate-determining step. Running these experiments in triplicate yielded an inverse $k_{obs}(H)/k_{obs}(D)$ value of 0.47, which implied that we are dealing with an equilibrium isotope effect (EIE). In other words, the H$^+$-transfer step(s) must take place over one or more equilibria that lead to the final and rate determining C−X bond formation step.

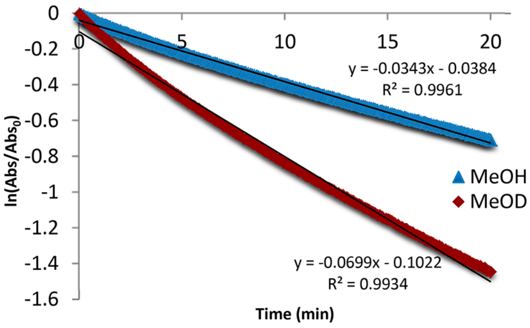


Figure 1. Kinetic profile for the functionalization of a 0.81 mM solution of **2** in MeOH/MeOD. The slope corresponds to the observed rate constant.

Continuing our discussion of the mechanistic proposal shown in Scheme 11, generation of a Ni-X moiety in species **B** and **B′** by deprotonation of the coordinated substrate HX sets the stage for a reductive elimination that gives the C−X functionalized product and generates an anionic Ni^I species. These products likely remain bound to each other in the form of species **C** and **C′**. These monovalent adducts would then undergo a net comproportionation reaction with trivalent precursor **2** (or related trivalent species generated during the course of the reaction). Such comproportionation can be viewed as the transfer of a Br radical from the trivalent species to its monovalent partner, generating divalent NCN complex **1** and a second divalent adduct of the functionalized product. This unproductive consumption of a trivalent species would explain the generally low (<50%) functionalization yields observed throughout this work, and this proposal is consistent with the observation that functionalization with MeOH is higher-yielding under aerobic conditions.

The above mechanistic scheme needs to be modified slightly to account for the much more facile and rapid functionalization reactions observed with the mineral acids HCl and HBr. We propose that these reactions begin with a direct protonation of one or both of the chelating amine moieties,[28] followed by coordination of one or two halide atoms at the liberated coordination sites around the trivalent Ni center, as shown in Scheme 12. The loss of chelation would render the Ni−aryl moiety much more susceptible to reductive elimination. It is also noteworthy that monovalent species generated *in situ* after the halogen-functionalization step would be readily oxidized, either as above (comproportionation with **2**) or in direct reaction with the mineral acids HX.

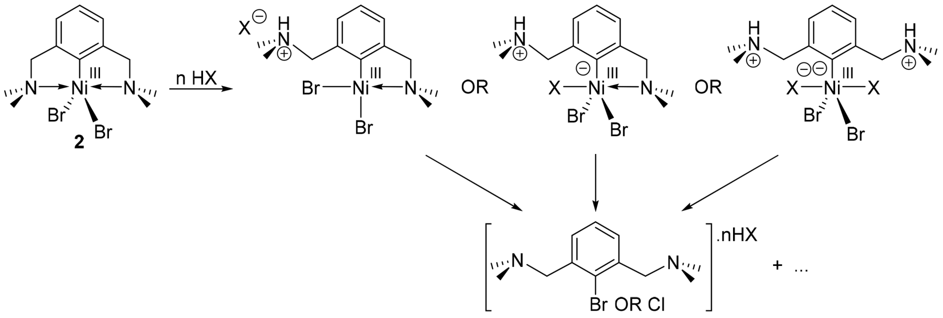
The mechanistic scenarios shown in Schemes 11 and 12 do not depict the side-reactions responsible for the commonly observed side-product NC(H)N, **a**. As stated earlier, we believe that the formation of proligand **a** in the reaction with EtOH arises from a *β*-H elimination from the Ni^{II}−OEt intermediate, while its formation in other cases (reaction of **2** with H_2O, NH_4OH, HCl, HBr, and KBr/H_2O) likely occurs by protonation of the *in situ* generated divalent species (NCN)Ni^{II}Br.

■ SUMMARY AND CONCLUDING REMARKS

The results discussed in this report show that the reaction of water, aliphatic alcohols, and primary aliphatic amines with $(NCN)NiBr_2$, **2**, leads to the direct heterofunctionalization of the Ni^{III}-bound aryl moiety in this authenticated trivalent pincer complex. The main findings of this study are in line with those of recent reports by the groups of Mirica and Sanford on C−C and C−heteroatom coupling reactions involving thermally stable Ni^{III} complexes and support our proposal that *in situ* generated trivalent species are involved in the analogous heterofunctionalization of the pyrazole-based pincer complex (NCN^{pz})NiBr[14] for which thermally stable trivalent derivatives have proven to be hitherto inaccessible. Moreover, halo-functionalization of **2** is observed upon treatment with Brönsted acids HX, as well as with strong oxidants NO$^+$ or aminium radical cations, but the latter reactions are thought to involve tetravalent intermediates.

That the observed C−X coupling reactions are generally low-yielding is believed to be due primarily to the unproductive consumption of the trivalent precursor in a comproportionation reaction with monovalent species generated *in situ* via the C−X reductive elimination step. This comproportionation side-reaction leads to the divalent species (NCN)NiBr, which is eventually converted to a tetravalent hydride derivative that in turn gives the proteo form of the pincer ligand via C−H reductive elimination. Another common side-product arises from C−OH

Scheme 12. Proposed Mechanism for the C−Halogen Functionalization of 2 with HBr or HCl



coupling due to reaction of the trivalent precursor with substrate residual moisture.

From a mechanistic viewpoint, the results discussed in this report have established the importance of the following factors for C−X functionalization rates. Destabilization of the pincer complex **2** due to Brönsted acid-induced protonation/dechelation of one or both of the chelating $\mathrm{NMe_2}$ donor moieties results in rapid C−Br and C−Cl coupling reactions (on the order of minutes). Functionalization is also fast (2 h or less) with primary amines, because the greater nucleophilicity of these substrates favors their coordination to the $\mathrm{Ni^{III}}$ center, while their basicity facilitates the crucial $\mathrm{H^+}$-transfer step that generates the requisite $\mathrm{Ni^{III}}$−NRH moiety. The importance of these factors is evident in (a) the sluggish reactivity of sterically hindered amines and alcohols and (b) the much faster C−O functionalization rates in the presence of amines.

An important mechanistic issue that remains to be established unequivocally is whether C−X bond formation proceeds via an inner-sphere reductive elimination or an outer-sphere $\mathrm{S_N}$Ar-type nucleophilic attack on the aryl moiety of the trivalent species. Sanford and Canty have presented evidence in favor of outer-sphere mechanisms dominating the heterofunctionalization reactions promoted by coordinatively saturated $\mathrm{Ni^{III}}$ compounds.[5a,7] In the reaction of nonacidic substrates HX with coordinatively unsaturated complex **2**, we believe that the nucleophilic attack is more likely to occur on the $\mathrm{Ni^{III}}$ center (i.e., coordination), followed by $\mathrm{H^+}$-transfer to generate the requisite $\mathrm{Ni^{III}}$−X and finally Ar−X reductive elimination. In the case of reaction with Brönsted acids, the functionalization appears to favor the more strongly coordinating conjugate base, thus also favoring the inner-sphere reductive elimination scenario. The successful functionalization of the aryl moiety in **2** following treatment with the weak nucleophile *t*-BuO$^-$ also argues against an outer-sphere nucleophilic attack in this system. Nevertheless, future investigations will seek to shed more light on this question.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00103.

Experimental and operational details for the syntheses of complexes **1** and **2**, functionalization reactions and characterization of various products, and kinetic studies (PDF)

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Notes

The authors declare no competing financial interest.

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Relevance to electrophilic aromatic nitration. *Acc. Chem. Res.* **1992**, *25* (1), 39−47. The redox potential for **2**, i.e., the Ni$^{IV/III}$ redox couple, was measured as described in the Supporting Information. All $E^{\circ\prime}$ values cited in the text are measured in acetonitrile and have been referenced against the ferrocenium/ferrocence couple (at 0.40 V in acetonitrile against SCE)..

(25) Another interesting finding reported by Sanford and Canty is the much greater propensity of cationic versus charge-neutral Ni^{IV} species to undergo C−C reductive elimination.[7]

(26) Cyclic voltammetry measurements conducted on **2** showed that aerobic oxidation of this species is not likely (E_{ox}(Ni^{IV}/Ni^{III}) = +1.2 V. Thus, we can dismiss the possibility of generating tetravalent intermediates under aerobic conditions.

(27) It should be noted here that the solid state structure of **2** (ref 12) shows that the Ni center is out of the equatorial plane while the two NMe_2 moieties are pushed away from the apical Br presumably due to the greater steric demand of the latter.

(28) Note that protonation of the Ni^{III} center in **2** is not possible, as this would imply the improbable formation of a pentavalent species.