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Synthesis and Reactivities of New NCN-Type Pincer Complexes of Nickel

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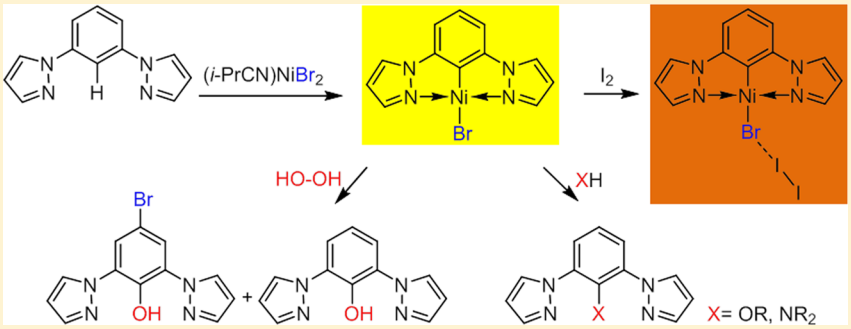
Supporting Information



ABSTRACT: This report describes the preparation, characterization, and reactivities of a new family of Ni(II) complexes based on the pincer-type ligands R-NCN^{pz} ($\kappa^N,\kappa^C,\kappa^{N'}$-1,3-bis(pyrazole),5-R-$C_6H_2$; R = H, OMe). Ullman coupling of pyrazole with 1,3-diiodobenzene or 1,3-dibromo-5-methoxybenzene gave the compounds R-NC(H)N^{pz}, which were refluxed in xylene with (*i*-PrCN)NiBr$_2$ and NEt$_3$ to give the complexes (NCN^{pz})NiBr (**1**) and (MeO-NCN^{pz})NiBr (**2**) via C−H nickelation. The aryloxide derivative (NCN^{pz})Ni(OAr) (**3**; Ar = 2,6-*t*-Bu$_2$-4-Me-OC$_6$H$_2$) was prepared by treating the bromo precursor **1** with NaOAr, whereas the analogous reaction with NaOEt gave instead the protonated or ethoxy-functionalized ligand NC(H)N^{pz} (major) and NC(OEt)N^{pz} (minor). The new complexes **1**−**3** were fully characterized, including solid-state structures. Attempted oxidation of these complexes failed to give the target trivalent derivatives, leading instead to intractable, deeply colored Ni-containing solids, various ligand-derived side products, or an unusual I$_2$ adduct. For example, treatment of **1** or **2** with *N*-bromosuccinimide gave sparingly soluble dark solids that appear to be paramagnetic, whereas **3** reacted with Br$_2$ to give short-lived dark intermediates that decomposed over seconds to give ArOH. Reaction of the bromo complexes with aqueous H_2O_2 (30%) gave the functionalized ligands Br-NC(OH)N^{pz} and NC(OH)N^{pz} (from **1**) or MeO-NC(OH)N^{pz} (from **2**), whereas **1** reacted with I$_2$ to generate (NCN^{pz})NiBr·I$_2$, an iodine adduct displaying weak Br−I interactions. Heating **1** in EtOH in air generated NC(OEt)N^{pz}. This ligand derivatization could be extended to other alcohols (MeOH, *i*-PrOH, CF_3CH_2OH) and amines (morpholine, cyclohexylamine, aniline). Possible mechanistic scenarios for the observed oxidative, Ni-promoted C_{ipso}−X bond formation reactions are discussed in the context of relevant literature precedents.

INTRODUCTION

Transition-metal complexes featuring NCN-type pincer ligands have proven to be highly versatile in diverse applications, including catalysis and materials.[1] NCN ligands have also played a prominent role in the context of organonickel chemistry. For instance, a variety of mononuclear, divalent species (NCN)NiX and [(NCN)NiL]$^+$ are known to promote Heck type cross-coupling[2] and Michael additions,[3] whereas polynuclear dendrimers composed of (NCN)Ni structural units have displayed important materials properties.[4] Another important characteristic of NCN ligands is their capacity to stabilize trivalent nickel species that catalyze atom transfer radical additions and polymerizations.[5] Isolable and stable complexes such as (NCN)NiX$_2$, featuring Ni^{III}−C bonds, are valuable models for difficult to isolate trivalent species that play important roles in hydrocarbon oxidation,[6] in various coupling reactions,[7] and in many bioinorganic and enzymatic reactions, including the C−H activation step involved in the anaerobic oxidation of methane by methanotrophic archaea.[8]

van Koten's group introduced the (NCN)Ni^{II} and (NCN)-Ni^{III} families of complexes in the early 1980s,[9] and most of the major developments in this area, including the elaboration of synthetic routes for the preparation of a large variety of these complexes, have been driven by this group. The two main synthetic strategies employed for this purpose involve (a) oxidative addition of halogenated NCN ligands, NC(X)N (X = Br, I), to zerovalent nickel precursors and (b) transmetalation of a lithiated ligand, NC(Li)N, first to Au(I) and then to Ni(II).[9b,10] While these synthetic routes generally lead to good yields of the target (NCN)NiX complexes, they involve manipulation of air- and moisture-sensitive reagents (e.g.,

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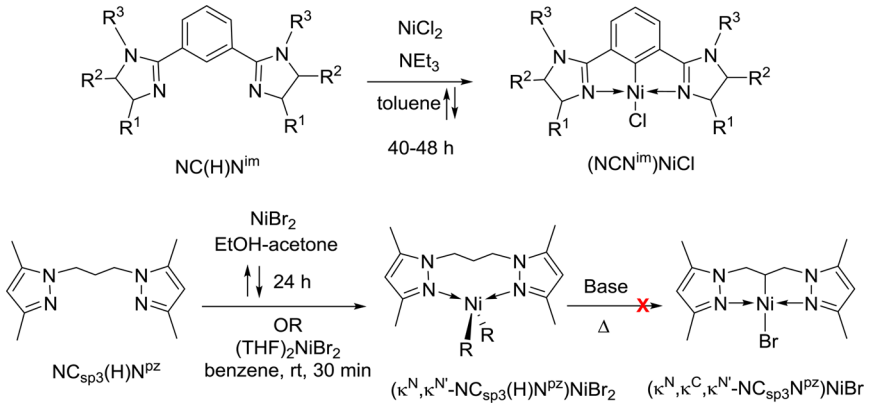
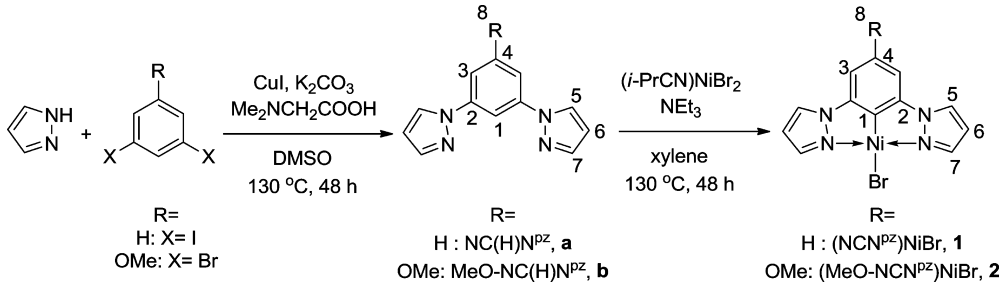
Scheme 1. Reactivities of NC(H)N^{im}- and NC(H)N^{pz}-Type Ligands with Ni(II) Salts



Scheme 2. Synthetic Routes to Ligands a and b and Complexes 1 and 2



RLi, Ni(COD)$_2$) and require the use of elaborate (halogenated) preligands and relatively expensive gold precursors. In contrast, a number of pincer-Ni compounds can be prepared more conveniently through direct C−H nickelation of the ligand by simple Ni(II) salts (e.g., PCP,[11] POCOP,[12] POCN,[13] PIMCOP[14]). Given many of the unique characteristics of NCN-Ni systems, it would be desirable to develop simple synthetic routes to this family of complexes involving a direct C−H nickelation strategy. Just such an approach appeared in 2011: the group of Gong and Song reported that 1,3-phenylene-based NC(H)N ligands featuring imidazole donor moieties react directly with $NiCl_2$ to give (NCN^{im})NiCl (Scheme 1), the first NCN-type complex of nickel prepared by C−H nickelation.[15]

Our longstanding interest in organonickel chemistry[16] and pincer-type Ni complexes,[17] as well as the great promise of NCN ligands for developing the chemistry of Ni(III) complexes, inspired us to explore the efficient synthesis of new families of NCN-Ni complexes via C−H nickelation. An initial effort in this direction was unsuccessful: 1,3-bis(3,5-dimethylpyrazolyl)propane reacted with $NiBr_2$ (EtOH/acetone, reflux, 24 h) or $(THF)_2NiBr_2$ (benzene or toluene, room temperature, 30 min) to give the blue tetrahedral complex ($\kappa^N,\kappa^{N'}$-NC$_{sp3}$(H)N^{pz})NiBr$_2$, which could not be induced to undergo the required C−H nickelation to yield the target pincer compound ($\kappa^N,\kappa^C,\kappa^{N'}$-NC$_{sp3}$N^{pz})NiBr (Scheme 1).[18] This finding prompted us to modify our approach in two respects. First, we focused on examining the reactivities of NCN^{pz} ligands based on a 1,3-phenylene backbone, which is usually more prone to undergo the requisite C−H nickelation. Second, we selected the starting materials $(MeCN)_nNiBr_2$[19] and (*i*-PrCN)NiBr$_2$,[20] which have proven to be effective Ni precursors for C−H nickelation of a variety of pincer ligands.

The present report describes the preparation of (R-NCN^{pz})NiBr (R = H (**1**), MeO (**2**)) via direct C−H nickelation. Spectroscopic and solid-state characterization of **1**, **2**, and the aryloxide derivative (NCN^{pz})Ni(OAr) (Ar = 2,6-*t*-Bu$_2$, 4-Me-C$_6$H$_2$; **3**) has allowed us to compare the main structural features of these complexes to those of previously reported NCN-Ni complexes. Attempts to oxidize these new complexes did not lead to the target Ni(III) derivatives, revealing instead unexpected and uncommon reactivities that allow functionalization of NCN^{pz} ligands by fairly facile C−O and C−N bond formation reactions, as described below.

RESULTS AND DISCUSSION

The synthetic methodology used for the preparation of the 1,3-bis(pyrazolyl)arene ligands **a** and **b** and their nickelation is shown in Scheme 2. Ligand **a** is a known substance that can be prepared using a Cu-catalyzed Ulmann coupling of pyrazole with dihalobenzenes.[21] A modified version of this coupling methodology allowed the preparation of the new ligand 1,3-bis(pyrazolyl)-5-methoxybenzene (**b**) from 1,3-dibromo-5-methoxybenzene, which was, in turn, obtained from methylation of commercially available 3,5-dibromophenol using MeI and K_2CO_3. Treating **a** or **b** with (*i*-PrCN)NiBr$_2$[20] in refluxing xylene over 2 days gave the target complexes **1** or **2** in 50% and 24% yields, respectively (Scheme 2). Both complexes are stable in air and are quite robust thermally: **1** can be heated to 250 °C without decomposition, and **2** starts decomposing at ∼190 °C.

The ^{1}H NMR spectrum of **a** matches reported data,[21] and **b** displayed the expected ^{1}H resonances, namely three doublets and two triplets for the aromatic protons, plus a singlet for OC*H*$_3$. The ^{1}H NMR spectra of **1** and **2** display four resonances for the eight aromatic protons that are pairwise equivalent, thanks to the C_2 axis bisecting these structures and overlapping C4, C1, Ni, and Br atoms; they also display a triplet

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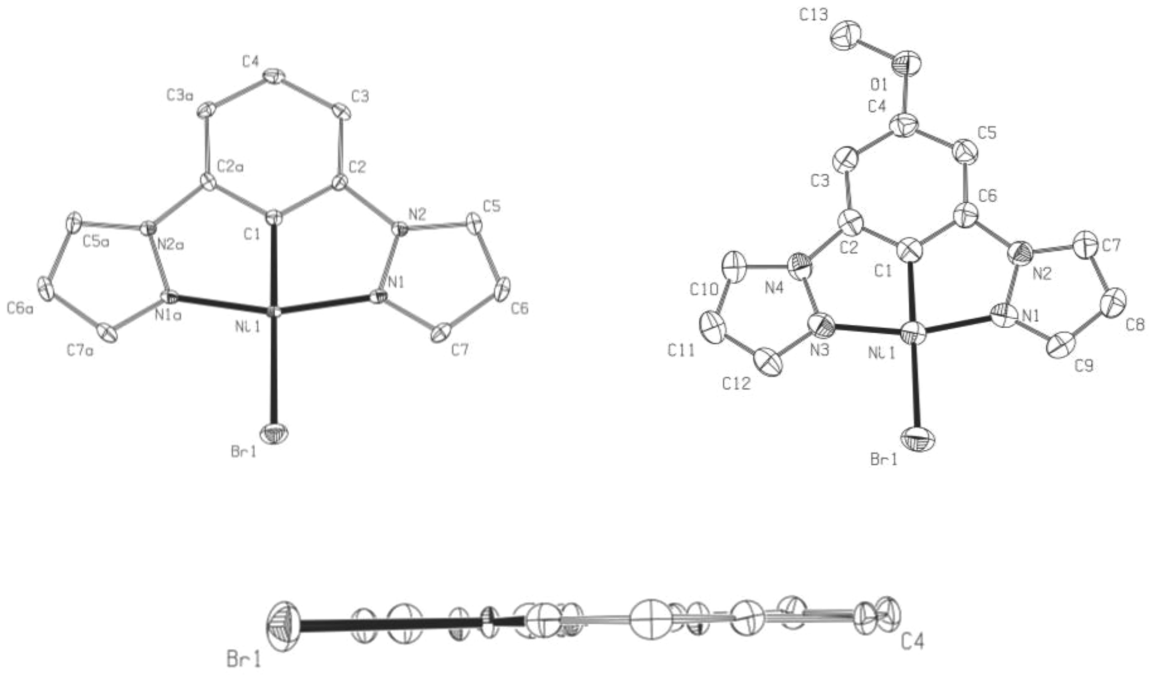
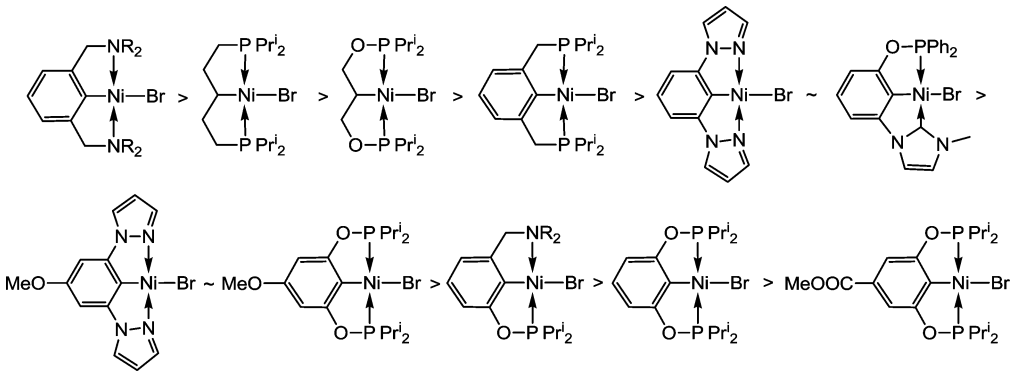


Figure 1. Molecular structures of **1** (full view, top left; side view, bottom) and **2** (top right; only one of the two molecules present in the asymmetric unit is shown). Thermal ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows. **1**: Ni1−Br1 = 2.3680(9); Ni−N1 = 1.908(3); Ni−C1 = 1.825(5); C1−Ni1−Br1 = 180.000(1); N1a−Ni1−N1 = 162.07(17). **2**: Ni1−Br1 = 2.3846(7); Ni1−N1 = 1.902(3); Ni1−N3 = 1.898(3); Ni1−C1 = 1.822(4); N3−Ni1−N1 = 162.00(13); C1−Ni1−Br1 = 177.05(11).

Chart 1. Relative Ease of Oxidation for (ECE)NiBr Complexes



for H4 in **1** and a singlet for OCH_3 in **2**. The following features of these spectra most readily confirmed the nickelation of **a** and **b**. First, the spectra of **1** and **2** did not show a signal due to H2, the proton ortho to both pyrazole moieties. Second, the signal for H7 shifted downfield by ca. 0.10 ppm in **1** and 0.15 ppm in **2**, whereas the remaining protons in both complexes shifted upfield, by about 0.7 ppm for H3 and 0.06−0.1 ppm for all others. Lastly, multiplicities of the methoxy and pyrazole protons remained unchanged, but H4 changed from a multiplet to a triplet and H3 changed from a multiplet to a doublet in **1** and from a doublet to a singlet in **2**. The $^{13}C\{^1H\}$ NMR spectra of the complexes displayed eight singlets, five for the pairwise-equivalent carbon nuclei off the C_2 axis and three for *ipso*-C, *p*-C, and OCH_3.

Single crystals suitable for X-ray analysis were obtained by slow recrystallization of **1** and **2** from warm THF; Figure 1 shows the solid-state structures of these complexes, and Table S1 (in the Supporting Information) gives the crystal data and details of data collection. The Ni center in both compounds adopts a square-planar geometry, and the solid-state structures are virtually flat, as can be inferred from the near-coplanarity (angle <1°) of the two fused five-membered nickelacycles defining the (NCN)Ni moiety. The smaller than ideal N−Ni−N angles of 162° observed in **1** and **2** are due to the small bite angle of the NCN ligand, a phenomenon observed in other NCN-Ni systems, including van Koten's phebox- or imine-based (NCN)NiBr systems.[22] The Ni−Br bond distances in the latter complexes are somewhat shorter relative to those of **1** and **2** (2.36 and 2.34 Å vs 2.37 and 2.38 Å, respectively), whereas less consistent differences were noted in the Ni−C and Ni−N bond distances of these complexes (Ni−C, 1.83 and 1.82 Å vs 1.85 and 1.82 Å, respectively; Ni−N, 1.91 and 1.90 Å vs 1.94 and 1.91 Å, respectively).[22]

Cyclic Voltammetry Measurements and Chemical Oxidation Attempts on Complexes 1 and 2. As mentioned earlier, some of the main characteristics of the tertiary amine

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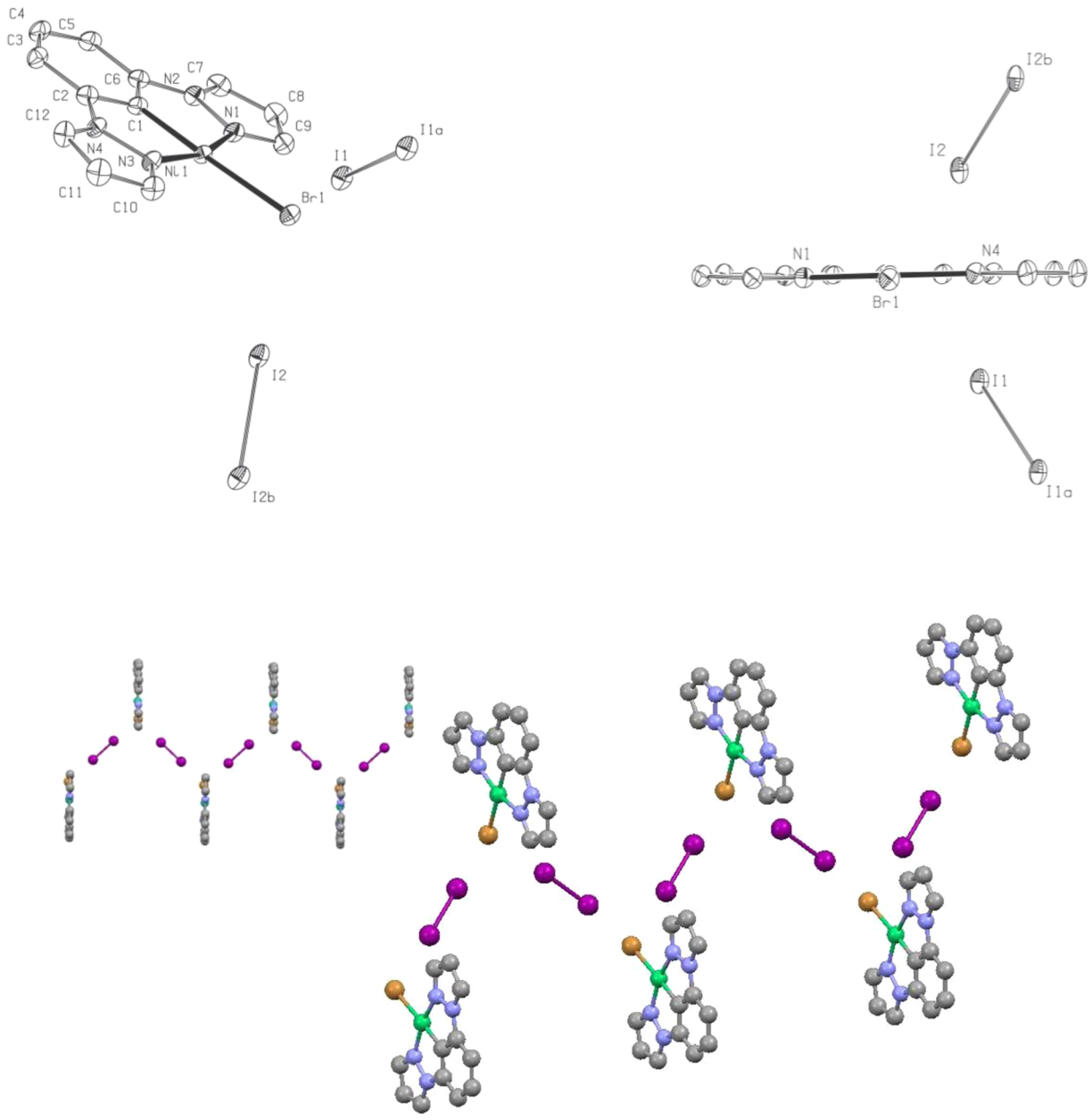

Figure 2. Molecular structure of **1**·I_2 (side view, left; plane view, right; one-dimensional polymer, bottom). Thermal ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1−Br1= 2.3744(5); Ni−N1 = 1.905(3); Ni−N3= 1.901(3); Ni−C1 = 1.827(3); I1−I1a = 2.7233(4); I2−I2b = 2.7322(4); Br1−I1 = 3.2406(4); Br1−I2 = 3.2110(6); C1−Ni1−Br1 = 178.23(10); N1−Ni1−N3 = 163.11(12); Ni1−Br1−I1 = 115.60; Ni1−Br1−I2 = 114.21; Br1−I1−I1a = 177.12; Br1−I2−I2a = 169.64; I1−Br1−I2 = 92.36.

based (NCN^{NR2})NiX complexes pioneered by van Koten were their highly electron-rich character and strong tendency to form stable trivalent derivatives. With the new NCN^{pz} complexes **1** and **2** in hand, we have investigated their redox properties and tested their reactivity toward chemical oxidants, as described below.

Cyclic voltammetry measurements (Figure S22 in the Supporting Information) showed that the redox profiles of **1** and **2** are quite different from those of their tertiary amine based counterparts: **1** showed a quasi-reversible Ni^{II}/Ni^{III} redox couple at 452 mV, whereas **2** showed an irreversible oxidation at a higher potential (E_{ox} = 545 mV).[23] Both of these values are much higher than the $E^{\circ}_{1/2}$ value for van Koten's (NCN^{NMe2})-NiBr,[24] which can be rationalized by the poorer electron donating character of the pyrazole moieties in our complexes. Comparing these oxidation potentials to the corresponding values measured for closely related ECE-Ni pincer complexes[14,17,25,26] allows us to arrange these compounds in terms of their ease of oxidation, summarized in Chart 1.

It is noteworthy that the methoxy-substituted system in **2** appears to be *less* susceptible to oxidation relative to **1**; this is in contrast to our previous observation that (*p*-MeO-POCOP)-NiBr is *more* susceptible (by ca. 190 mV) to undergo a Ni^{II}/Ni^{III} oxidation relative to its unsubstituted analogue, whereas (*p*-MeOOC-POCOP)NiBr is *less* susceptible (by ca. 130 mV).[26] We speculate that the observed higher oxidation potential of **2** relative to **1** may be due to a less efficient conjugation in this molecule brought about by the slight planar

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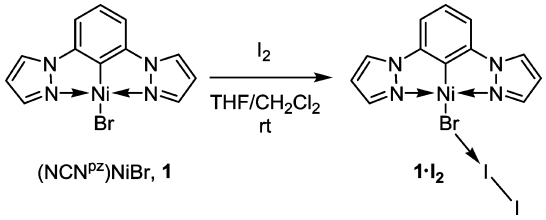
distortion that is presumably caused by the methoxy substituent (Figure 1).

Even though the new (R-NCN^{pz})NiBr complexes **1** and **2** appeared to be less electron rich than most (ECE)NiX systems that are known to give isolable trivalent species (e.g., (NCN^{NR2})NiX, (PC$_{sp3}$P)NiBr, and (POC$_{sp3}$OP)NiBr), we were encouraged that they appeared to be more electron rich than the related (POCN)NiBr compounds, which are known to stabilize trivalent species.[13] Therefore, we proceeded to test the capacity of R-NCN^{pz} ligands to stabilize trivalent compounds by treating **1** and **2** with oxidants that had proven effective for generation of trivalent Ni species from some of the pincer-type Ni(II) complexes studied by our group (e.g., Br_2, *N*-bromosuccinimide (NBS), or $CuBr_2$).[12b,13a,25,27] In all cases, we observed the same color changes as noted previously during the oxidation attempts on other (ECE)NiX systems: the reaction mixture turned dark immediately and a deeply colored solid precipitated out of the solution.

These sparingly soluble compounds appeared to be very similar to the trivalent species previously isolated by our group.[12b,13a,25,27,28] For instance, dissolving the solids in question in pyridine or acetonitrile gave deep purple samples that proved NMR silent, consistent with the anticipated paramagnetism of the trivalent derivatives; these solutions also displayed UV−vis spectral patterns similar to those of fully characterized octahedral (NCN^{NMe2})NiBr$_2$(L).[9c] A crude sample obtained from the attempted oxidation of **2** with NBS registered a magnetic susceptibility of 2.96, which is much higher than the value anticipated for a single unpaired electron. The observation of higher than expected magnetic moment for the paramagnetic samples obtained by oxidation of complex **1** can be rationalized by invoking a scenario in which these samples exist in both low- and high-spin states with one and three unpaired electrons, respectively, which would result in an intermediate value for the magnetic moment corresponding to the bulk sample. Unfortunately, all attempts to obtain analytically pure samples and grow crystals suitable for X-ray analysis were unsuccessful, circumventing an unambiguous identification of these products.

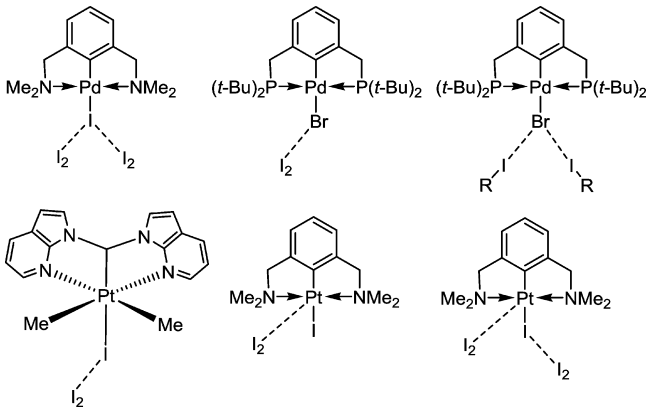
Reactivity of 1 with I_2. An unexpected result was obtained when we treated complex **1** with iodine in anticipation of oxidizing the Ni center (eq 1). Addition of 1 equiv of I_2 to a THF solution of **1** generated a deep orange mixture from which an orange-brown solid precipitated over 20 min. In contrast to the dark solids obtained from the oxidation attempts noted above, the orange-brown solid obtained from the I_2 reaction was soluble in CD_2Cl_2 and $CDCl_3$ and displayed well-resolved NMR spectra, attesting to its diamagnetic character. Curiously, the ^{1}H NMR spectrum of this orange solid was virtually identical with the spectral pattern of the starting material, yet the sample was still orange-brown (as opposed to yellow for **1**). Fortunately, recrystallization (from CH_2Cl_2) gave single crystals that allowed us to identify this product as the iodine adduct **1·I$_2$** shown in Figure 2.



(1)

In its solid state, each **1·I$_2$** exhibits Br−I interactions with half of two I_2 molecules, thus creating a one-dimensional zigzag chain parrallel to the *c* axis. Interlocking of four of these chains results in π stacking of the (NCN^{pz})NiBr units parallel to the *c* axis with a 3.3 Å distance. Although most structural features of the (NCN^{pz})NiBr unit are largely unperturbed in the solid-state structure of **1·I$_2$**, close inspection of some parameters reveals slight but meaningful differences in comparison to those of **1**. For instance, **1·I$_2$** displays a somewhat longer Ni−Br bond distance and a very slightly larger N1−Ni−N3 bite angle relative to **1** (2.3744(5) vs 2.3680(9) Å; ca. 163 vs 162°), as well as a slightly longer I−I bond distance relative to that of free I_2 (average 2.727(4) vs 2.715(6) Å).[29] These observations are consistent with the partial transfer of electron density from Br to I_2. Similar observations are often encountered in transitionn-metal halides engaged in noncovalent-type halogen bonds.[30,31] Although there are many examples of such transition-metal−halogen−halogen interactions in the literature,[32] to our knowledge **1·I$_2$** is only the second complex to display Ni−X−halogen bonding.[33] On the other hand, halogen−halogen interactions have been observed in the closely related PCP-Pd and NCN-M complexes (M = Pd, Pt) shown in Chart 2.

Chart 2. Other Pincer Complexes Featuring Halogen Bonding



A very close analogue of **1·I$_2$** is the complex (NCN)PdI·I_2 reported by van Koten.[34] The solid-state structure of this compound shows two iodine molecules interacting with the Pd−I moiety and forming nearly linear outer Pd−I−I−I angles (172−176°) and virtually perpendicular inner I_2−(PdI)−I_2 angles. In this compound, the I−I distance for the I_2 molecules is ca. 2.760(1) Å, and the average PdI−I_2 distance is 3.280 Å, which is nearly 17% shorter than the sum of van der Waals (vdW) radii for two iodide atoms (3.96 Å).

Wendt et al. have also reported X−I interactions between (PCP)PdX (X = Cl, Br, I) and one iodine or two electron-poor hydrocarbyl iodides.[35] These authors have argued that the strong trans influence of the central aryl moiety in these compounds elevates the energy of the halide lone pairs, thus promoting their noncovalent interactions with I_2 or RI. The Br−I_2 distance in (PCP)**PdBr·I$_2$** is nearly 24% shorter than the sum of vdW radii for Br and I atoms (3.83 Å);[35] by comparison, we observe ∼16% compression in **1·I$_2$**.

Of the Pt complexes shown in Chart 2, (NCN^{BAM})**Pt(Me)$_2$I·I$_2$** (BAM = bis(7-azaindol-1-yl)methyl) shows I−I_2 interactions similar to those in the cases discussed above,[36] whereas in (NCN^{NMe2})**PtI·I$_2$** the noncovalent interaction is between the

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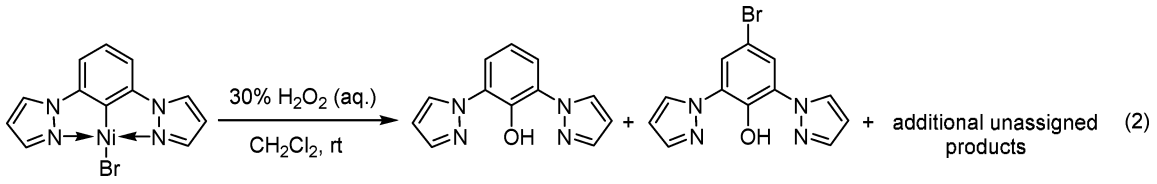

Pt-based HOMO and I_2.[37] Finally, both types of interactions, PtI–I_2 and Pt–I_2, are observed in (NCN)PtI(I_2)$_2$.[38] These latter compounds have been proposed by van Koten et al. as models for the initial stage of dihalide oxidative addition to Pt(II).

Reactivities of 1 and 2 with Hydrogen Peroxide. Following the unsuccessful oxidation attempts described above, we sought a different chemical oxidant for the preparation of trivalent derivatives. The absence in **1** and **2** of donor moieties such as phosphines and phosphinites that are susceptible to oxidation opens up the possibility of using a stronger oxidant such as hydrogen peroxide for the purpose of generating trivalent species. Thus, as a final attempt to oxidize our (R-NCN^{pz})NiBr complexes, we tested their reactivities with this oxidant, as described below.

Addition of an excess of H_2O_2 (30% solution in water) to a CH_2Cl_2 solution of **1** brought about an immediate color change from yellow to deep purple. The intense color of the reaction reaction mixture turned gradually to pale orange (ca. 12 h at room temperature), indicating that the in situ generated product has limited thermal stability. All attempts at arresting this deep purple species before it decomposed proved unsuccessful, giving intractable dark solids that have remained unidentified. Thus, we turned our attention to isolating and identifying the product(s) of decomposition in the hopes of finding clues to the nature of the oxidation process. For this purpose, the pale orange final reaction mixture of an oxidation reaction using H_2O_2 was further diluted with water and extracted with CH_2Cl_2, followed by column chromatography of the organic layer on silica. This workup procedure afforded two products arising from the oxidative degradation of **1**, namely NC(OH)N^{pz} (32%) and Br-NC(OH)N^{pz} (7%), as shown in eq 2. Control experiments confirmed that the Ni center plays a crucial role in this reaction: none of the latter species was detected when NC(H)N^{pz} (**a**) was treated with H_2O_2 or NBS in the absence of **1**.

The functionalized derivatives of ligand **a** have been characterized by NMR and MS analyses (electrospray ionization source). The ^{1}H NMR of NC(OH)N^{pz} is consistent with its C_{2v} symmetry and displays a triplet and a doublet for the mutually coupled protons of the central ring ($^3J_{HH}$ = 8 Hz), whereas the ^{1}H NMR of Br-NC(OH)N^{pz} displays only a singlet for the symmetry-related protons of the central ring. Perhaps the most interesting feature in these spectra is the downfield signal due to the acidic O*H* proton, at 12.32 ppm for NCN^{pz}-OH and 12.43 ppm for Br-NC(OH)N^{pz}. Isolation of a suitable single crystal for the latter substance has allowed us to examine its solid-state structure by X-ray diffraction studies. The molecular structure thus elucidated (Figure 3) shows the O–H–N interaction responsible for the downfield NMR signals; the observed O–H, N–H, and N–O distances are 0.827, 1.78, and 2.54 Å, respectively. It is also interesting to note that one of the pyrazole moieties has rotated 180°, placing the imine nitrogen away from the OH moiety.

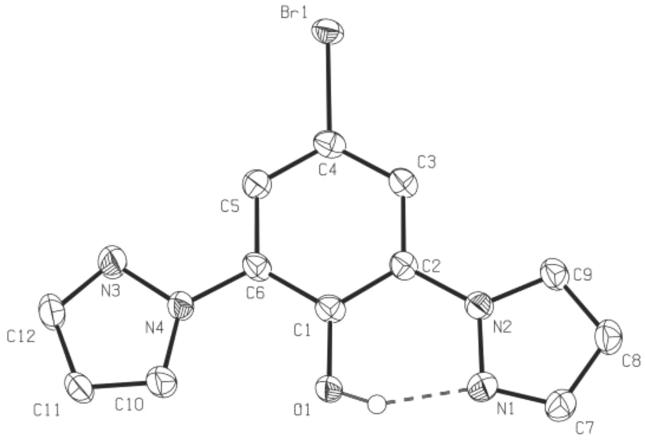

Figure 3. Molecular structure of Br-NCN^{pz}-OH. Thermal ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. See the Supporting Information for the CIF file giving complete structural parameters and Table S2 for selected bond distances.

Complex **2** reacted in a similar manner to give the hydroxylated product, MeO-NC(OH)N^{pz}, but no bromination product was observed. It is worth noting that the yellow to deep purple color change observed for **1** was not detected in the reaction of **2**, suggesting that this phenomenon is related to bromination of the *p*-C–H moiety; the latter presumably involves aromatic intermediates featuring unpaired electrons. Two tests were conducted to probe the nature of this reaction. First, we repeated the treatment of **1** with H_2O_2 in the presence of 1.2 equiv of TEMPO; this experiment yielded only NC(OH)N^{pz}, implying that free radicals are likely involved in the formation of Br-NC(OH)N^{pz}. Second, it was established that neither of the above functionalization products was observed when a THF mixture of **1** and NaOH was refluxed for 18 h; the only tractable product of this experiment was the protonated ligand NC(H)N^{pz}. We conclude that an in situ generated Ni–OH derivative is insufficient for this functionalization reaction, the oxidizing character of H_2O_2 being an essential requirement.

The oxidatively induced functionalization of the NCN^{pz} ligand in **1** noted above, i.e., hydroxylation at the ipso position and bromination at the para position, are reminiscent of analogous reactivities reported in the literature. For instance, Hillhouse has demonstrated that $L_2Ni^{II}(R)(X)$ (X = OR′, NR′$_2$) can be induced to undergo reductive elimination of R-X in the presence of external oxidants that can generate reactive Ni(III) intermediates, including O_2, I_2, and $(AcCp)_2Fe^+$.[39] A very recent report has also shown that a pincerlike complex of Ni(II) can promote bromination of aromatic substrates in the

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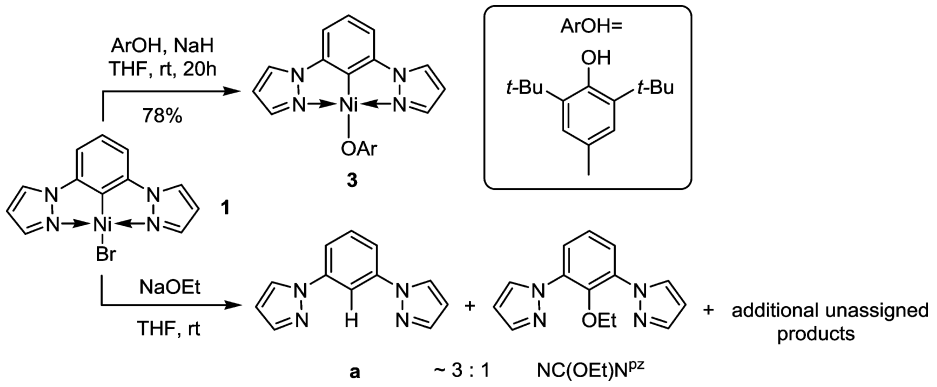
Scheme 3. Reactivities of 1 with $[OR]^-$



presence of strong oxidants such as $PhI(OAc)_2$ and $(C_6F_5)I(OCOCF_3)_2$.[40]

On the other hand, van Koten's group has reported a number of studies documenting the CuX_2-induced (X = Cl, Br) para chlorination and para bromination of NCN ligands in the trivalent pincer complexes $[(NCN)Ru(tpy)]^{2+}$ (NCN = 2,6-bis[(dimethylamino)methyl]phenyl, 2,6-bis(2-pyridyl)phenyl; tpy = 2,2′:6′,2″-terpyridine).[41] Mechanistic probes of these halogenations have established that a first-order oxidation of the divalent Ru center precedes the halogenation. Moreover, depending on reaction conditions, the oxidized species can undergo a C−C bond formation that leads to a dimerization of the trivalent complex.[42] Similar reactivities, including dimerization, have been observed with the PCP analogue of these complexes.[43,44] These observations imply that the spin density in the paramagnetic species $[(pincer)Ru(tpy)]^{2+}$ generated by the one-electron oxidation of the pincer complexes is partially localized on the para position of the phenylene ligand. We speculate that a similar phenomenon is at play in our NCN^{pz}-Ni systems, which can explain the observed bromination reaction, the irreversible electrochemical oxidation, and also the unstable products of chemical oxidation.

Preparation of (NCN)Ni(OR) and Oxidation Attempts. Previous studies have shown that the nature of X ligands in pincer-type complexes (EXE)NiX has a dramatic influence on the oxidation potential of these species. For instance, the oxidation half-cell potential values, E_O, are much larger for (POCN)NiBr than for their amido derivatives,[45] and the same trend has been observed with $(POC_{sp3}OP)NiX$ (OR < Br) and (PCP)NiX (X = NH_2, OH, CN).[46] In light of the generally greater thermal stability of Ni-OR derivatives, we elected to prepare $(NCN^{pz})Ni(OR)$ and attempt their oxidation, as shown in Scheme 3 and described below.

Complex **1** reacted very differently with different sources of OR^- (Scheme 3): treatment with the in situ deprotonated BHT (butylated hydroxytoluene, 2,6-$(t\text{-Bu})_2$-4-Me-C_6H_2OH) gave the anticipated simple Ni-OAr derivative **3**, whereas NaOEt gave instead the protio ligand **a** as the major product, as well as the ethoxide-functionalized compound $NC(OEt)N^{pz}$. Although no intermediate species was detected during the latter reactions, we speculate that the observed side products are derived from decomposition of the unstable intermediate $(NCN^{pz})Ni(OEt)$. For instance, β-H elimination of the latter would give acetaldehyde and (NCN)Ni(H), the latter giving **a** by reductive elimination.[47] On the other hand, direct reductive elimination from $(NCN^{pz})Ni(OEt)$ would generate the ethoxy-functionalized product $NC(OEt)N^{pz}$ by C−O bond formation.[48,49] The analogous reaction with KO(*t*-Bu) did allow the observation of a more persistent intermediate, but the detected species decomposed to intractable materials before it could be identified with confidence.

That the reactions observed above with alkoxide salts are, in fact, even more complex than they appear was revealed by the following observations. First, when the reaction with NaOEt was conducted under rigorously oxygen-free conditions, we obtained ligand **a** only, the ethoxy-functionalized product not being detected at all; the analogous reaction with KO(*t*-Bu) led to a complex mixture from which no tractable compound could be isolated or identified. Second, simply refluxing an ethanol solution of **1** in air (without any base or source of ethoxide) led to exclusive formation of the C−O coupling product, $NC(OEt)N^{pz}$; the same reactivity was observed with complex **2**. Although these observations do not provide a clear mechanistic picture for this reactivity, they have encouraged us to seek a novel methodology for functionalization of the pyrazole-based NCN ligands under study; the results of these studies are presented in the next section.

The aryloxide derivative **3** was isolated as a bright orange powder that proved to be much more soluble in standard solvents relative to its precursor **1**. This new derivative was found to be highly stable at higher temperatures, decomposition of solid-state samples starting above 220 °C. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** were in accordance with the proposed structure of this complex. For instance, we observed five aromatic signals each integrating for two protons, indicating the pairwise equivalence of the symmetry-related NCN^{pz} and BHT aryl protons. In addition, the signal due to the *p*-H on the central aryl moiety of NCN^{pz} is a triplet, and there is only one signal for the 18 equivalent protons of the *t*-Bu moieties, implying a low energy barrier for the rotation of BHT about the Ni−O and C−O axes. Finally, conversion of the bromo precursor to the BHT derivative caused upfield shifts for all NCN^{pz} protons by 0.5−1.28 ppm.

The solid-state structure of **3** was confirmed by X-ray diffraction studies conducted on single crystals obtained from recrystallization using Et_2O at room temperature (Figure 4). The geometry around the Ni center in this complex is distorted square planar (N−Ni−N = 163°), and most structural parameters are similar to the corresponding values in **1** and **2**. The BHT ring is nearly perpendicular to the coordination plane (88°). The Ni−O distance in **3** is similar to the corresponding distance in $(POC_{sp3}OP)Ni(OMes)$ (ca. 1.88 Å vs 1.89 Å; Mes = 2,4,6-$(Me)_3C_6H_2$).[50]

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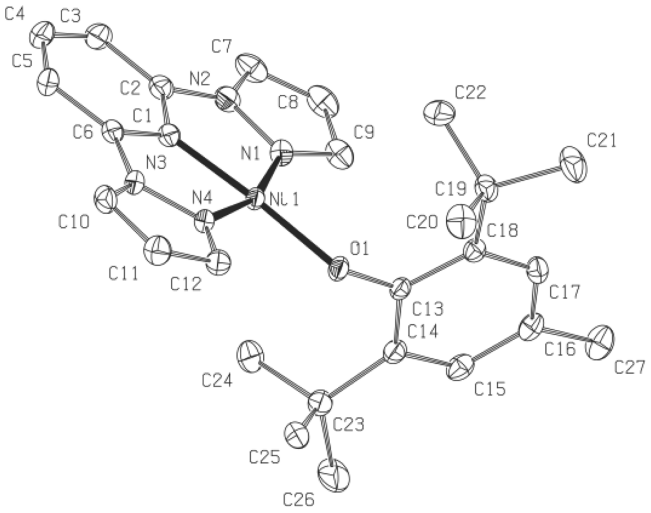
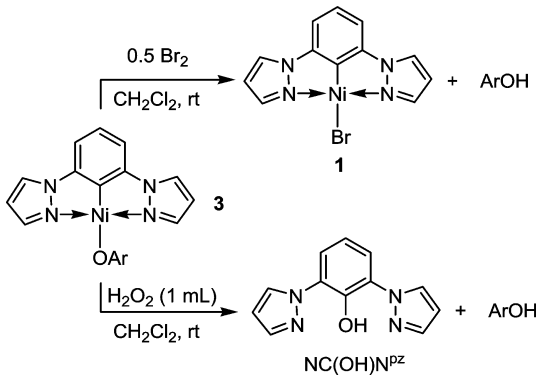


Figure 4. Molecular view of **3**: only one of the three molecules in the unit cell is shown here. Thermal ellipsoids are shown at the 50% probability level, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1−O1 = 1.8827(14); Ni1−N4 = 1.8990(17); Ni1−N1 = 1.9143(17); Ni1−C1 = 1.822(2); N1−Ni1−N14 = 162.64(7); C1−Ni1−O1 = 173.37(8); Ni1−O1−C13 = 129.68(12).

Cyclic voltammetry measurements carried out on **3** (Figure S22 in the Supporting Information) confirmed the much lower oxidation potential of this aryloxide derivative relative to its bromo precursor (−73 vs 452 mV); indeed, **3** undergoes a one-electron irreversible oxidation at a potential lower than that of ferrocene. Observation of such a facile electrochemical oxidation seemed to bode well for the prospects of preparing trivalent derivatives by chemical oxidation, but treatment of **3** with Br_2, I_2, or H_2O_2 failed to yield the target products. For instance, reaction with 0.5 equiv of Br_2 led to generation of **1** and free BHT, whereas the reaction with excess H_2O_2 gave the hydroxylated ligand, NC(OH)N^{pz}, and protonated BHT (Scheme 4). Evidently, the lower oxidation potential

Scheme 4. Attempted Oxidation of 3



engendered by the presence of the aryloxide moiety does not translate into a stable and isolable trivalent derivative, implying an inherent aspect of NCN^{pz} ligands that renders such pentacoordinate, 17-electron derivatives inaccessible.

Functionalization of NCN^{pz} via Alcoholysis and Aminolysis of 1. As mentioned earlier, **1** and **2** react with EtOH to yield ethoxide-functionalized derivatives of the NCN^{pz} and MeO-NCN^{pz} ligands, respectively. These observations inspired us to explore the scope of this unusual reaction, as described below (eq 3 in Table 1); the preliminary studies undertaken to date were conducted with complex **1** only.

Refluxing **1** with 99% EtOH for 24 h *while exposing the mixture to ambient air* led to the formation of NC(OEt)N^{pz} in ca. 77% yield, whereas using 95% EtOH gave the same yield but the ethoxylation reaction proceeded much more quickly (Table 1, entry 1). The analogous reactions with MeOH and *i*-PrOH were more sluggish, but in the presence of added water (5% by volume) we obtained 65 and 70% yields, respectively (entries 2 and 3). Small and variable quantities of the protonated ligand **a** were also detected in the reactions with MeOH. Interestingly, alcohols featuring more acidic O−H moieties resulted in either no reaction at all (PhOH and $PhCH_2OH$) or a much lower yield (CF_3CH_2OH, entry 4); for the latter reaction, addition of 5% water had no impact on the yield or reaction time.

To our delight, the functionalization could be extended to amines to give C−N bond formation products, albeit in generally lower yields. For instance, the secondary amine morpholine gave 41% yield (Table 1, entry 5) and the primary amines cyclohexylamine and aniline gave 10% and 32% yields, respectively (entries 5 and 6), whereas *p*-fluorobenzylamine and ethanolamine did not react at all. As was the case with the alcoholysis reaction using CF_3CH_2OH, addition of water had no impact on the aminolysis of **1**.

The C−O and C−N bond formation reactions observed with complex **1** are somewhat analogous to a recently reported Pd-catalyzed amination of alkenes in the presence of O_2,[51] and even more so to the stoichiometric intra- or intermolecular C−N bond formation involving a dicationic Cu(III) species featuring a tetradentate macrocyclic ligand.[52] Heating the latter in the absence of a "nucleophilic" substrate leads to the intramolecularly *N*-functionalized ligand arising via an apparent trans C−N reductive elimination reaction between the aryl and the tertiary amine moieties present in the coordination sphere of the Cu center (Scheme 5). The product of intermolecular *N*-functionalization is obtained at room temperature in the presence of weakly nucleophilic amide-type substrates possessing a fairly acidic N−H bond (pK_a < 17; e.g., pyridone, phthalimide, sulfanamide, etc.), whereas less acidic substrates give a mixture of the two products. Evidently, the intermolecular C−N bond formation reactions promoted by this Cu(III) system require acidic substrates, in contrast to the reactivity of complex **1** toward alcohols or amines.

As stated earlier, the alcoholysis and aminolysis reactions promoted by (NCN^{pz})NiBr (Table 1) appear to require aerobic conditions: conducting these reactions using degassed substrates and under a nitrogen purge gave protonated ligand and only traces of the functionalized products. It occurred to us that other mild oxidants might also promote this reaction, and to test this idea we treated the iodine adduct **1**·I_2 with MeOD in an NMR tube; the sample was kept at room temperature and under a nitrogen atmosphere. ^{1}H NMR analysis confirmed the complete conversion to NC(OMe)N^{pz} over 5 min, implying a dramatic acceleration of the methanolysis reaction, which otherwise requires refluxing over several hours under aerobic conditions.

■ CONCLUSION

This study has led to the elaboration of a convenient, C−H nickelation-based synthetic route for the preparation of the first members of a new family of pyrazole-based NCN complexes. Access to complexes **1** and **2** has allowed us to evaluate their

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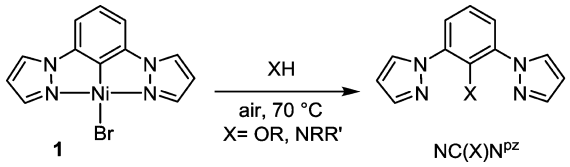
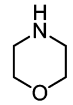
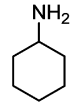
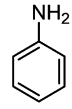
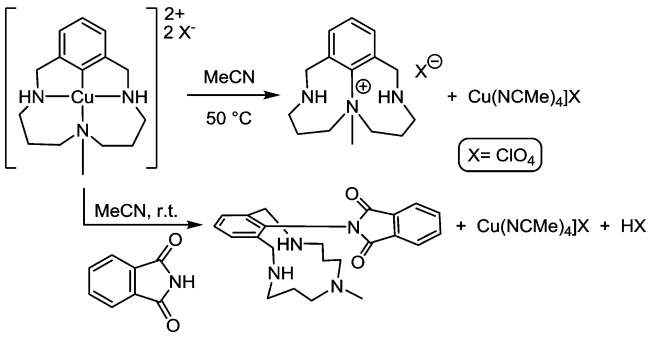
Table 1. Functionalization of NCN^{pz}[a]



Entry	XH	Time (h)	%Yield of $NC(X)N^{pz}$ GC/MS (isolated)
1	EtOH (95%)	2	77 (68)
2	MeOH (95%)	18	65 (48)
3	*i*-PrOH (95%)	18	70 (68)
4	CF_3CH_2OH	24	15
5		4	41 (29)
6		24	10
7		24	32

[a]Reaction conditions: complex **1** (0.072 mmol), XH (10 mL), and 1-bromo-3,5-dimethoxybenzene (internal standard) were stirred at 70 °C for the required time. In all cases, yields were determined by GC/MS using a previously prepared calibration curve based on $NC(OEt)N^{pz}$. In some cases, the product was isolated following a standard chromatographic workup.

Scheme 5. Cu(III)-Promoted C−N Bond Formation



oxidation potentials and assess their propensity toward oxidation of the nickel center. The results presented in this report do not bode well for the prospects of isolating stable high-valent species based on pyrazole donor moieties; on the other hand, the chemical oxidation attempts undertaken in the course of this work have revealed potentially useful C−O and C−N bond formation reactions that facilitate oxidative, Ni-promoted alcoholysis and aminolysis of 1,3-bis(pyrazolyl)-benzene. Although the scope of these reactions remains rather narrow so far, and even though they require stoichiometric quantities of Ni(II), we are hopeful that with a better understanding of the complex pathways involved in these reactions it might be possible to elaborate more efficient, practical, and catalytic methodologies for functionalizing a wide range of these aromatic substrates. Future studies will be designed to attain these objectives.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise indicated, all manipulations were carried out using standard Schlenk and glovebox techniques under a dry nitrogen atmosphere. Where necessary, the solvents were dried to water contents of less than 10 ppm (determined using a Mettler-Toledo C20 coulometric Karl Fischer titrator) by passage through activated aluminum oxide columns (MBraun SPS) and storage over 4 Å molecular sieves. The following starting materials were purchased from commercial sources and used without further purification: 1,3-diiodobenzene, 3,5-dibromophenol, pyrazole, methyl iodide, CuI, *N*,*N*-dimethylglycine, Ni powder, Br_2, I_2, *i*-PrCN, 2,6-*t*-

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Bu_2-4-Me-C_6H_2OH (BHT), *t*-BuOK, *N*-bromosuccinimide, and morpholine (Aldrich); NEt_3 and H_2O_2 (Acros); *c*-$C_6H_{11}NH_2$ (American Chemicals). $NiBr_2$(NCiPr) was synthesized according to a literature procedure.[20]

The NMR spectra were recorded on the following spectrometers: Bruker AV400rg (^1H at 400 MHz) and Bruker ARX400 (^1H at 400 MHz and $^{13}C\{^1H\}$ at 100.56 MHz). Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (^1H and ^{13}C: 7.26 and 77.16 ppm for $CDCl_3$; 7.16 and 128.06 ppm for C_6D_6). Coupling constants are reported in Hz. The elemental analyses were performed by the Laboratoire d'Analyze Élémentaire, Département de chimie, Université de Montréal.

(5-Methoxy-1,3-phenylene)bis(1*H*-pyrazole) (b). A dried Schlenk flask was charged with 3,5-dibromo-1-methoxybenzene (1.13 g, 4.25 mmol), pyrazole (0.868 g, 12.8 mmol), K_2CO_3 (3.52 g, 25.5 mmol), CuI (0.032 mg, 0.170 mmol), and *N*,*N*-dimethylglycine (0.029 g, 0.286 mmol). The system was purged three times with N_2, and 15 mL of DMSO was added. This mixture was then heated at 130 °C for 96 h and then cooled to room temperature. Water (30 mL) and ethyl acetate (30 mL) were then added to the final mixture, and the resulting mixture was partitioned. The organic layer was extracted with ethyl acetate (3 × 15 mL) and washed with brine. The ethyl acetate fractions were combined and evaporated next, and the residue was purified by column chromatography (silica gel; eluent 20/80 to 40/60 mixtures of ethyl acetate and hexanes). Evaporation of the combined fractions gave the final product as an off-white solid (0.171 g, 46%). ^1H NMR ($CDCl_3$, 400 MHz), δ 7.99 (2H, d, J_{HH} = 2.5, H5), 7.74 (2H, d, J_{HH} = 1.6, H7), 7.64 (1H, t, J_{HH} = 1.9, H1), 7.22 (2H, d, J_{HH} = 1.9, H3), 6.49 (2H, t, J_{HH} = 1.9, H6), 3.93 (3H, s, H8). ^{13}C NMR ($CDCl_3$): δ 161.42 (1C, s, C4), 142.01 (2C, s, C2), 141.47 (2C, s, C7), 127.19 (2C, s, C5), 108.13 (2C, s, C6), 102.98 (2C, s, C3), 102.23 (1C, s, C1), 56.02 (1C, s, C8). MS: *m*/*z* 240; the mass spectrum is shown in the Supporting Information (Figure S23).

{$\kappa^N,\kappa^C,\kappa^{N'}$-2,6-(pyrazole)$_2$-$C_6H_3$}NiBr (1). An oven-dried Schlenk was taken inside the glovebox and charged with $NiBr_2$(NC(*i*-Pr)) (1.64 g, 5.71 mmol), ligand **a** (1.00 g, 4.76 mmol), and NEt_3 (0.927 mL, 0.673 g, 6.67 mmol). The reaction vessel was then taken out of the glovebox and 10 mL of *m*-xylene added against a flow of N_2. The resulting mixture was refluxed for 36 h, cooled to room temperature, and evaporated under reduced pressure. The resulting solid residue was stirred with distilled water (3 × 20 mL, in air) and filtered on a Buchner funnel, the solid residue being washed consecutively with 3 × 20 mL each of cold MeOH and hexanes. The yellow powder thus obtained was then extracted with THF, concentrated under reduced pressure, and allowed to crystallize to give the target complex as orange crystals (0.720 g, 44%). ^1H NMR ($CDCl_3$): δ 7.95 (2H, d, J_{HH} = 2.2, H5), 7.85 (2H, d, J_{HH} = 2.7, H7), 7.18 (1H, t, J_{HH} = 7.8, H4), 6.85 (2H, d, J_{HH} = 7.8, H3), 6.35 (2H, t, J_{HH} = 2.4, H6). ^{13}C NMR (DMSO-d_6): δ 144.07 (2C, s, C5), 142.74 (2C, s, C2), 137.34 (1C, s, C1), 128.58 (2C, d, C7), 126.87 (1C, s, C4), 108.66 (2C, s, C6), 108.57 (2C, s, C3). Anal. Calcd for $C_{12}H_9BrN_4Ni$ (347.82): C, 41.44; N, 16.11; H, 2.61. Found: C, 41.41; N, 16.16; H, 2.53.

{$\kappa^N,\kappa^C,\kappa^{N'}$-2,6-bis(pyrazole),4-MeO-C_6H_2}NiBr (2). The above procedure was followed using $NiBr_2$(NC(*i*-Pr)) (1.06 g, 3.68 mmol), ligand **b** (0.632 g, 2.63 mmol), and NEt_3 (0.513 mL, 0.373 g, 3.69 mmol) in xylene (10 mL). The target complex **2** was obtained as orange crystals (0.235 mg, 24%). ^1H NMR ($CDCl_3$): δ 7.89 (2H, d, J_{HH} = 2.0, H5), 7.81 (2H, d, J_{HH} = 2.7, H7), 6.46 (2H, s, H3), 6.34 (2H, t, J_{HH} = 2.4, H6), 3.87 (3H, s, H8). ^{13}C NMR ($CDCl_3$): δ 159.82 (1C, s, C4), 144.50 (2C, s, C5), 142.68 (2C, s, C2), 127.92 (1C, s, C1), 125.59 (2C, s, C7), 107.85 (2C, s, C6), 94.76 (2C, s, C3), 56.19 (1C, s, C8). Anal. Calcd for $C_{12}H_9BrN_4Ni$ (377.85): C, 41.32; N, 14.83; H, 2.93. Found: C, 41.23; N, 14.78; H, 2.86.

{$\kappa^N,\kappa^C,\kappa^{N'}$-2,6-(pyrazole)$_2$-$C_6H_3$}NiBr·$I_2$, (1·$I_2$). A CH_2Cl_2 solution of I_2 (0.073 g, 0.288 mmol, in 10 mL) was added dropwise to a THF solution of **1** (0.100 g, 0.288 mmol, in 30 mL). The mixture turned immediately from yellow to deep orange, and an orange powder precipitated after 20 min. The final mixture was filtered after an additional 2 h of stirring to give the crude product as an orange solid (57 mg, 33%). Recrystallization from warm CH_2Cl_2 gave orange crystals after standing overnight. Gradual, spontaneous sublimation of iodine circumvented an accurate elemental analysis of this compound. The ^1H NMR and UV−vis spectra of this adduct were virtually identical with the corresponding spectra of **1** (see Figures S1 and S31 in the Supporting Information).

{$\kappa^N,\kappa^C,\kappa^{N'}$-2,6-(pyrazole)$_2$-$C_6H_3$}Ni(BHT) (3). A dry Schlenk flask purged with N_2 was charged with **1** (0.200 g, 0.575 mmol), BHT (0.127 g, 0,575 mmol), and THF (30 mL). NaH (0.022 g, 0.96 mmol) was then added slowly to this mixture against a flow of N_2. The final mixture was stirred at room temperature for 20 h. The resulting orange solution was evaporated under vacuum and the yellow residue extracted with dry Et_2O (5 × 10 mL). Evaporation to dryness gave a bright orange powder (0.280 g, 78% yield). ^1H NMR (C_6D_6): δ 7.39 (2H, s, H10), 6.88 (2H, d, J_{HH} = 2.1, H5), 6.67 (1H, t, J_{HH} = 7.8, H4), 6.57 (2H, d, J_{HH} = 2.4, H7), 6.05 (2H, d, J_{HH} = 7.8, H3), 5.47 (2H, t, J_{HH} = 2.4, H6), 2.63 (3H, s, H12), 2.19 (18H, s, H14). ^{13}C NMR (C_6D_6): δ 167.6 (1C, s, C8), 143.97 (2C, s, C2), 141.18 (2C, s, C5), 140.64 (2C, s, C9), 139.88 (1C, s, C1), 126.30 (2C, s, C10), 124.77 (1C, s, C4), 124.36 (2C, s, C7), 121.82 (1C, s, C11), 107.23 (2C, s, C6), 106.91 (2C, s, C3), 36.22 (2C, s, C13), 32.37 (6C, s, C14), 22.09 (1C, s, C12). Anal. Calcd for $C_{27}H_{32}N_4NiO$ (487.26): C, 66.55; N, 11.50; H, 6.62. Found: C, 66.16; N, 11.30; H, 6.58.

4-Bromo-2,6-bis(1*H*-pyrazol-1-yl)phenol and 2,6-Bis(1*H*-pyrazol-1-yl)phenol. A Schlenk flask was charged with **1** (0,050 g, 0,144 mmol), CH_2Cl_2 (30 mL), and H_2O_2 (1 mL of 30% solution in water, 9.79 mmol), and the mixture was stirred for 18 h. The initially yellow mixture changed to deep purple over 20 min, but this color faded gradually such that the final mixture was yellowish. Addition of H_2O (20 mL) followed by extraction with CH_2Cl_2 (3 × 20 mL) and evaporation of the combined organic layers gave an oily residue which was purified by column chromatography (silica; eluent $CHCl_3$). Evaporation of the first and second fractions gave the minor and major components of the product mixture, respectively, as white powders (6 mg, 7%; 22 mg, 32%).

Characterization Data for 4-Bromo-2,6-bis(1H-pyrazol-1-yl)-phenol. ^1H NMR ($CDCl_3$): δ 12.43 (1H, s, H8), 8.21 (2H, d, J_{HH} = 2.4 H5), 7.75 (2H, d, H7), 7.71 (2H, s, H3), 6.52 (2H, t, J_{HH} = 2.1, H6).^{13}C NMR ($CDCl_3$): δ 140.91 (1C, s, C1), 140.10 (2C, s, C7), 129.75 (2C, s, C5), 129.09 (2C, s, C2), 121.84 (2C, s, C3), 111.05 (1C, s, C4), 107.37 (2C, s, C6). LRMS: expected mass (M + H^+) 305.0, 307.0; found (M + H^+) 305.1, 307.1.

Characterization Data for 2,6-Bis(1H-pyrazol-1-yl)phenol. ^1H NMR ($CDCl_3$): δ 12.32 (1H, s, H8), 8.20 (2H, d, J_{HH} = 2.3 H5), 7.75 (2H, s, H7), 7.55 (2H, d, J_{HH} = 8.1, H3), 7.01 (1H, t, J_{HH} = 8.1, H4), 6.51 (2H, t, J_{HH} = 2.0, H6). ^{13}C NMR ($CDCl_3$): δ 142.07 (1C, s, C1), 139.72 (2C, s, C7), 129.62 (2C, s, C5), 128.38 (2C, s, C2), 119.47 (2C, s, C3), 119.42 (1C, s, C4), 106.91 (2C, s, C6). LRMS: expected mass (M + H^+) 227.1, found (M + H^+) 227.2.

(2-Methoxy-1,3-phenylene)bis(1*H*-pyrazole). A round-bottom flask was charged with **1** (0.040 g, 0.116 mmol), MeOH (30 mL), and distilled water (1.5 mL), and the mixture was stirred at reflux for 24 h. The resulting pale yellow mixture was cooled to room temperature and evaporated. The residue was extracted with diethyl ether (3 × 20 mL) and evaporated, and the solid mixture was purified by column chromatography (silica; eluent 20/80 ethyl acetate/hexane) to give both the protonated ligand and the functionalized ligand (13 mg, 48% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (2H, d, J_{HH} = 2.4, H5), 7.75 (2H, d, J_{HH} = 1.6, H7), 7.69 (2H, d, J_{HH} = 8.0, H3), 7.32 (1H, t, J_{HH} = 8.0, H4), 6.49 (2H, t, J_{HH} = 2.0, H6), 3.28 (3H, s, H8). ^{13}C NMR ($CDCl_3$): δ 144.85 (1C, s, C1), 140.98 (2C, s, C7), 134.97 (2C, s, C2), 131.28 (2C, s, C5), 125.09 (1C, s, C4), 124.18 (2C, s, C3), 107.40 (2C, s, C6), 60.94 (1C, s, C8). GC/MS: *m*/*z* 240.

(2-Ethoxy-1,3-phenylene)bis(1*H*-pyrazole). A round-bottom flask was charged with **1** (0.150 g, 0.431 mmol) and 95% EtOH (40 mL), and the mixture was stirred for 5 h at reflux. The resulting pale yellow solution was cooled to room temperature and then evaporated. The solid residue was then purified by column chromatography on silica with acetone as eluent. The combined fractions were evaporated to give the desired product as an oil (47 mg, 68% yield). ^1H NMR

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($CDCl_3$): δ 8.13 (2H, d, J_{HH} = 2.4, H5), 7.75 (2H, d, J_{HH} = 1.6, H7), 7.69 (2H, d, J_{HH} = 8.1, H3), 7.32 (1H, t, J_{HH} = 8.1, H4), 6.49 (2H, t, J_{HH} = 2.1, H6), 3.39 (2H, q, H8), 0.96 (3H, t, H9). ^{13}C NMR ($CDCl_3$): δ 143.81 (1C, s, C1), 140.93 (2C, s, C5), 135.41 (2C, s, C2), 131.39 (2C, s, C7), 125.06 (1C, s, C4), 124.16 (2C, s, C3), 107.17 (2C, s, C6), 70.00 (1C, s, C8), 15.05 (1C, s, C9). GC/MS: *m*/*z* 254.

1,1′-(2-Isopropoxy-1,3-phenylene)bis(1*H*-pyrazole). The procedure used above was repeated with 0.040 g (0.115 mmol) of **1** in *i*-PrOH to give the target product as an oil (22 mg, 70% yield). ^{1}H NMR ($CDCl_3$): δ 8.11 (2H, d, J_{HH} = 2.4, H5), 7.74 (2H, d, J_{HH} = 1.5, H7), 7.67 (2H, d, J_{HH} = 8.1, H3), 7.32 (1H, t, J_{HH} = 8.1, H4), 6.48 (2H, t, J_{HH} = 2.1, H6), 3.38 (1H, sept, J_{HH} = 6.1, H8), 0.82 (6H, d, J_{HH} = 6.1, H9). ^{13}C NMR ($CDCl_3$): δ 142.6 (1C, s, C1), 140.88 (2C, s, C7), 136.0 (2C, s, C2), 125.0 (2C, s, C5), 124.97 (1C, s, C4), 124.28 (2C, s, C3), 106.9 (2C, s, C6), 29.86 (1C, s, C8), 21.58 (2C, s, C9). GC/MS: *m*/*z* 268.

4-(2,6-Bis(1*H*-pyrazol-1-yl)phenyl)morpholine. The procedure used above for the preparation of 1,1′-(2-ethoxy-1,3-phenylene)bis-(1*H*-pyrazole) was repeated with **1** (34 mg, 0.098 mmol) and morpholine (20 mL) to give an off-white solid after evaporation (8 mg, 29%). ^{1}H NMR ($CDCl_3$): δ 7.75 (2H, d, J_{HH} = 1.8, H5), 7.73 (2H, d, J_{HH} = 1.8, H7), 7.41 (2H, d, J_{HH} = 7.8, H3), 7.24 (1H, t, J_{HH} = 7.5, H4), 6.47 (2H, t, J_{HH} = 1.9, H6), 3.38 (4H, t, J_{HH} = 4.6, H8), 2.51 (4H, t, J_{HH} = 4.6, H9). ^{13}C NMR ($CDCl_3$): δ 142.7 (1C, s, C1), 140.81 (2C, s, C7), 138.2 (2C, s, C2), 131.80 (2C, s, C5), 129.0 (1C, s, C4), 124.34 (2C, s, C3), 106.83 (2C, s, C6), 67.13 (2C, s, C8), 50.06 (2C, s, C9). GC/MS: *m*/*z* 295.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving NMR, UV−vis, and GC/MS spectra, cyclic voltammetry traces, tables of crystal data and collection/refinement parameters, procedures for data collection and structure resolution, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org. Complete details of the X-ray analyses reported herein have also been deposited at The Cambridge Crystallographic Data Centre (CCDC 1027168 (**1**), 1027169 (**2**), 1027126 (**1**·I_2), 1027124 (**3**), 1027125 (Br-NC(OH)N^{pz})). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. (fax +44 1223 336033).

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For a historical review of NCN-type pincer complexes see: Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(2) Mitsudo, K.; Imura, T.; Yamaguchi, T.; Tanaka, H. *Tetrahedron Lett.* **2008**, *49*, 7287.

(3) Fossey, J. S.; Richards, C. J. *J. Organomet. Chem.* **2004**, *689*, 3056.

(4) (a) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (b) Gossage, R. A.; Jastrzebski, T. B. H.; van Ameijde, J.; Mulders, S. J. E.; Brouwer, A. J.; Liskamp, R. M. J.; van Koten, G. *Tetrahedron Lett.* **1999**, *40*, 1413. (c) Kleij, A. W.; Gossage, R. A.; Klein Gebbink, R. J. M.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 12112. (d) Pathmamanoharan, C.; Wijkens, P.; Grove, D. M.; Philipse, A. P. *Langmuir* **1996**, *12*, 4372. (e) van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, *6*, 1675.

(5) (a) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985. (b) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169. (c) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G. *J. Organomet. Chem.* **1989**, *372*, C1. (d) van de Kuil, L. A.; Veldhuizen, Y. S. J.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 267. (e) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.

(6) Yoon, H.; Wagler, T. R.; O'Connor, K. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4568.

(7) (a) Madhira, V. N.; Ren, P.; Vechorkin, O.; Hu, X.; Vicic, D. A. *Dalton Trans.* **2012**, *41*, 7915. (b) Zhang, C.-P.; Wang, H.; Klein, A.; Biewer, C.; Stirnat, K.; Yamaguchi, Y.; Xu, L.; Gomez-Benitez, V.; Vicic, D. A. *J. Am. Chem. Soc.* **2013**, *135*, 8141. (c) Zheng, B.; Tang, F.; Luo, J.; Schultz, J. W.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2014**, *136*, 6499.

(8) (a) Cammack, R. *Adv. Inorg. Chem.* **1988**, *32*, 297. (b) *Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988. (c) Halcrow, M. A.; Christou, G. *Chem. Rev.* **1994**, *94*, 2421. (d) Ermler, U.; Grabarse, W.; Shima, S.; Goubeaud, M.; Thauer, R. K. *Science* **1997**, *278*, 1457. (e) Evans, D. J. *Coord. Chem. Rev.* **2005**, *249*, 1582. (f) Yang, N.; Reiher, M.; Wang, M.; Harmer, J.; Duin, E. C. *J. Am. Chem. Soc.* **2007**, *129*, 11028. (g) Dey, M.; Telser, J.; Kunz, R. C.; Lees, N. S.; Ragsdale, S. W.; Hoffman, B. M. *J. Am. Chem. Soc.* **2007**, *129*, 11030. (h) Ragsdale, S. W. *J. Biol. Chem.* **2009**, *284*, 18571. (i) Scheller, S.; Goenrich, M.; Mayr, S.; Thauer, R. K.; Jaun, B. *Angew. Chem., Int. Ed.* **2010**, *49*, 8112. (j) Scheller, S.; Goenrich, M.; Boecher, R.; Thauer, R. K.; Jaun, B. *Nature* **2010**, *465*, 606.

(9) (a) Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R. *Organometallics* **1984**, *3*, 1003. (c) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A. A. H.; Terheijden, J. *Organometallics* **1986**, *5*, 322.

(10) (a) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; Van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 11822. (b) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. *Organometallics* **2002**, *21*, 4556.

(11) (a) Moutlon, C. J.; Shaw, B. L. *Dalton Trans.* **1976**, 1020. (b) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6. (c) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52. (d) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195. (e) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (f) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 4015. (g) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D. *Can. J. Chem.* **2005**, *83*, 634. (h) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Inorg. Chem.* **2009**, *48*, 3177.

(12) (a) Gómez-Benítez, V.; Baldovino-Pantaleón, O.; Herrera-Álvarez, C.; Toscano, R. A.; Morales-Morales, D. *Tetrahedron Lett.* **2006**, *47*, 5059. (b) Pandarus, V.; Zargarian, D. *Chem. Commun.* **2007**, 978. (c) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582. (d) Zhang, J.; Medley, C. M.; Krause, J. A.; Guan, H. *Organometallics* **2010**, *29*, 6393. (e) Lefèvre, X.; Durieux, G.; Lesturgez, S.; Zargarian, D. *J. Mol. Catal. A* **2010**, *335*, 1. (f) Salah,

DOI: 10.1021/om5010176
Organometallics 2015, 34, 133−145

A.; Offenstein, C.; Zargarian, D. *Organometallics* **2011**, *30*, 5352. (g) Hao, J.; Vabre, B.; Mougang-Soumé, B.; Zargarian, D. *Chem. Eur. J.* **2014**, *20*, 12544.
(13) (a) Spasyuk, D. M.; Zargarian, D.; van der Est, A. *Organometallics* **2009**, *28*, 6531. (b) Zhang, B.-S.; Wang, W.; Shao, D.-D.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Organometallics* **2010**, *29*, 2579. (c) Yang, M.-J.; Liu, Y.-J.; Gong, J.-F.; Song, M.-P. *Organometallics* **2011**, *30*, 3793. (d) Sanford, J.; Dent, C.; Masuda, J.; Xia, A. *Polyhedron* **2011**, *30*, 1091.
(14) Vabre, B.; Canac, Y.; Duhayon, C.; Chauvin, R.; Zargarian, D. *Chem. Commun.* **2012**, *48*, 10446.
(15) Shao, D.-D.; Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Dalton Trans.* **2011**, *40*, 9012.
(16) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*−*234*, 157.
(17) Zargarian, D.; Castonguay, A.; Spasyuk, D. M.; van Koten, G.; Milstein, D. *Top. Organomet. Chem.* **2013**, *40*, 131−174.
(18) Pandarus, V.; Castonguay, A.; Zargarian, D. *Dalton Trans.* **2008**, 4756.
(19) (a) Castonguay, A.; Spasyuk, D. M.; Madern, N.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2009**, *28*, 2134. (b) Lefèvre, X.; Spasyuk, D. M.; Zargarian, D. *J. Organomet. Chem.* **2011**, *696*, 864. (c) Salah, A.; Zargarian, D. *Dalton Trans.* **2011**, *40*, 8977.
(20) (a) Vabre, B.; Lambert, M. L.; Petit, A.; Ess, D. H.; Zargarian, D. *Organometallics* **2012**, *31*, 6041. (b) Vabre, B.; Lindeperg, F.; Zargarian, D. *Green Chem.* **2013**, *15*, 3188. (c) Vabre, B.; Petiot, P.; Declercq, R.; Zargarian, D. *Organometallics* **2014**, *33*, 5173.
(21) Develay, S.; Blackburn, O.; Thompson, A. L.; Williams, J. A. G. *Inorg. Chem.* **2008**, *47*, 11129.
(22) Stol, M.; Snelders, D. J. M.; Godbole, M. D.; Havenith, R. W. A.; Haddleton, D.; Clarkson, G.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2007**, *26*, 3985.
(23) All potentials are referenced to the Fe^{2+}/Fe^{3+} redox couple for ferrocene measured under identical conditions.
(24) According to van Koten the E°_{ox} value for $(NCN^{NMe2})NiBr$ is 240 mV and the E°_{red} value for $(NCN^{NMe2})NiBr_2$ is 50 mV, both values being measured in acetone and referenced to Ag/AgCl. Under these conditions, the $E^{\circ}_{1/2}$ potential for Fc/Fc^{+} is given as 630 mV, which means that $(NCN^{NMe2})NiBr$ is much more susceptible to oxidation relative to $(R\text{-}NCN^{pz})NiBr$ (by nearly 1 V). See: Grove, D. M.; van Koten, G.; Mul, P.; Zoet, R.; van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27*, 2466.
(25) Pandarus, V.; Zargarian, D. *Organometallics* **2007**, *26*, 4321−4334.
(26) Vabre, B.; Spasyuk, D. M.; Zargarian, D. *Organometallics* **2012**, *31*, 8561.
(27) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2008**, *27*, 5723.
(28) Spasyuk, D. M.; Gorelsky, S. I.; van der Est, A.; Zargarian, D. *Inorg. Chem.* **2011**, *50*, 2661.
(29) van Bolhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90.
(30) Halogen bonds are a subset of so-called "σ-hole" bonds consisting of highly directional, electrostatically driven interactions between a region of positive electrostatic potential (e.g., σ^* orbital of I_2) and a negative site (e.g., lone pair of a charge-neutral Lewis base or anion). For a discussion of the theoretical underpinnings of halogen bonds see: (a) Politzer, P.; Murray, J. S.; Clark, T. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7748. (b) Politzer, P.; Murray, J. S.; Clark, T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178.
(31) Some halogen bonds are considered to be comparable in energy to H bonds and have been used for the elaboration of supramolecular assemblies. For a selection of reports on this topic, see: (a) Zordan, F.; Brammer, L.; Sherwood, P. *J. Am. Chem. Soc.* **2005**, *127*, 5979. (b) Metrangolo, P.; Resnati, G. *Science* **2008**, *321*, 918. (c) Rissanen, K. *CrystEngComm* **2008**, *10*, 1107.
(32) (a) Le Bras, J.; Amouri, H.; Vaissermann, J. *Inorg. Chem.* **1998**, *37*, 5056. (b) Tebbe, K.-F.; Grafe-Kavoosian, A.; Freckmann, B. Z.; Naturforsch, B. *Chem. Sci.* **1996**, *51*, 999. (c) Ambrosetti, R.; Baratta, W.; Dell'Amico, D. B.; Calderazzo, F.; Marchetti, F. *Gazz. Chim. Ital.* **1990**, *120*, 511. (d) Wieczorrek, C. *Acta Crystallogr., Sect. C* **2000**, *C56*, 1085. (e) Masuhara, N.; Nakashima, S.; Yamada, K. *Chem. Lett.* **2005**, *34*, 1352. (f) Belicchi, M. F.; Fava, G. G.; Pelizzi, C. *Acta Crystallogr., Sect. B* **1981**, *B37*, 924. (g) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chem.* **1983**, *22*, 2362. (h) Chaviara, A. T.; Tsipis, A. C.; Cox, P. J.; Bolos, C. A. *Eur. J. Inorg. Chem.* **2005**, 3491.
(33) For the only other Ni complex displaying Ni−I−I interactions see: Blanchard, S.; Neese, F.; Bothe, E.; Bill, E.; Wehermuller, T.; Wieghardt, K. *Inorg. Chem.* **2005**, *44*, 3636.
(34) Mills, A. M.; van Beek, J. A. M.; van Koten, G.; Spek, A. L. *Acta Crystallogr., Sect. C* **2002**, *C58*, m304.
(35) Johnson, M. T.; Džolić, Z.; Cetina, M.; Wendt, O. F.; Öhrström, L.; Rissanen, K. *Cryst. Growth Des.* **2012**, *12*, 362.
(36) Zhao, S.-B.; Wang, R.-Y.; Wang, S. *Organometallics* **2009**, *28*, 2572.
(37) Van Beek, J. A. M.; Van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010.
(38) Gossage, R. A.; Ryabov, A. D.; Spek, A. L.; Stufkens, D. J.; van Beek, J. A. M.; van Eldik, R.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 2488.
(39) (a) Koo, K.; Hillhouse, G. L. *Organometallics* **1996**, *15*, 2669. (b) Koo, K.; Hillhouse, G. L. *Organometallics* **1995**, *14*, 4421. (c) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 8135. (d) Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890.
(40) Bhattacharya, M.; Cluff, D. B.; Das, S. *Inorg. Chim. Acta* **2014**, *423*, 238. It is worth noting that the mechanistic evidence presented in this report does not support the involvement of free radicals in the bromination reactions under discussion. For instance, the presence of TEMPO does not hinder substrate bromination, in contrast to what is observed in our system.
(41) Wadman, S. H.; Havenith, R. W. A.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *J. Am. Chem. Soc.* **2010**, *132*, 1914.
(42) (a) Sutter, J.-P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; van Koten, g. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1282. (b) Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647.
(43) Gagliardo, M.; Amijs, C. H. M.; Lutz, M.; Spek, A. L.; Havenith, R. W. A.; Hartl, F.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2007**, *46*, 11133.
(44) Similar cases of (electrophilic) substitution (halogenation and nitration) at the para position with respect to a metalated aromatic carbon have also been observed with non-pincer complexes: (a) Coudret, C.; Fraysse, S.; Launay, J.-P. *Chem. Commun.* **1998**, 663. (b) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1999**, *18*, 2813. (c) Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2000**, *598*, 262. (d) Arm, K. J.; Williams, J. A. G. *Chem. Commun.* **2005**, 230. (e) Ghosh, R.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 11317.
(45) Spasyuk, D. M.; Zargarian, D. *Inorg. Chem.* **2010**, *49*, 6203.
(46) Schmeier, T. J.; Nova, A.; Hazari, N.; Maseras, F. *Chem. Eur. J.* **2012**, *18*, 6915.
(47) Although it might be conceptually difficult to envisage such a reductive elimination reaction given the mutually trans relationship between the hydride and the central aryl moiety of NCN, it should be noted that such a reaction has been observed previously with $(PC_{sp3}P)NiH$, a putative intermediate arising from β-H elimination from $(PC_{sp3}P)Ni(n\text{-}Bu)$: Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. On the other hand, the closely related complex $(POC_{sp3}\text{-}OP)NiEt$ is stable to decomposition.[25]
(48) Reductive elimination to form C−O bonds is generally thought to be less facile in comparison to the analogous reactions forming C−H or C−C bonds, but there are a few precedents for this reactivity with Ni[39] and many more with high-valent species such as Ir(III), Pd(III), Pd(IV), and Pt(IV): (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (b) Rosini, G. P.; Wang, K.; Patel, B.; Goldman, A. S. *Inorg. Chim. Acta* **1998**, *270*, 537. (c) Williams, B. S.;

DOI: 10.1021/om5010176
Organometallics 2015, 34, 133−145

Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (d) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576. (e) Yamashita, M.; Vicario, J. V. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347. (f) Canty, A. J.; Denney, M. C.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 1122. (g) Canty, A. J.; Denney, M. C.; van Koten, G.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 5432. (h) Khusnutdinova, J. R.; Zavalij, P. Y.; Vedernikov, A. N. *Organometallics* **2007**, *26*, 3466. (i) Pawlikowski, A. V.; Getty, A. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 10382. (j) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974. (k) Powers, D. C.; Benitez, D.; Tkatchouk, E.; Goddard, W.A., III; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 14092. (l) Marquard, S. L.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 7119. (m) Hayashi, Y.; Wada, S.; Yamashita, M.; Nozaki, K. *Organometallics* **2012**, *31*, 1073. (n) Peng, H.; Yuan, Z.; Wang, H.-Y.; Guo, Y.-L.; Liu, G. *Chem. Sci.* **2013**, *4*, 3172. (o) Camasso, N. M.; Pérez-Temprano, M. H.; Sanford, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 12771.

(49) For mini-reviews on the topic of C−heteroatom reductive elimination reactions see: (a) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936. (b) Vedernikov, A. N. *Chem. Commun.* **2009**, 4781.

(50) Hao, J.; Mougang-Soumé, B.; Vabre, B.; Zargarian, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 3218.

(51) Ji, X.; Huang, H.; Wu, W.; Li, X.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 11155.

(52) Huffman, L. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 9196.

DOI: 10.1021/om5010176
Organometallics 2015, 34, 133−145