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Nickel Complexes of a Pincer Amidobis(amine) Ligand: Synthesis, Structure, and Activity in Stoichiometric and Catalytic C−C Bond-Forming Reactions of Alkyl Halides

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Abstract: The synthesis, properties, and reactivity of nickel(II) complexes of a newly developed pincer amidobis(amine) ligand ($^{Me}NN_2$) are described. Neutral or cationic complexes [($^{Me}NN_2$)NiX] (X = OTf (**6**), OC(O)CH_3 (**7**), CH_3CN (**8**), OMe (**9**)) were prepared by salt metathesis or chloride abstraction from the previously reported [($^{Me}NN_2$)NiCl] (**1**). The Lewis acidity of the {($^{Me}NN_2$)Ni} fragment was measured by the ^1H NMR chemical shift of the coordinated CH_3CN molecule in **8**. Electrochemical measurements on **1** and **8** indicate that the electron-donating properties of NN_2 are similar to those of the analogous amidobis(phosphine) (pnp) ligands. The solid-state structures of **6**–**8** were determined and compared to those of **1** and [($^{Me}NN_2$)NiEt] (**3**). In all complexes, the $^{Me}NN_2$ ligand coordinates to the Ni^{II} ion in a *mer* fashion, and the square-planar coordination sphere of the metal is completed by an additional donor. The coordination chemistry of $^{Me}NN_2$ thus resembles that of other three-dentate pincer ligands, for example, pnp and arylbis(amine) (ncn). Reactions of **2** with alkyl monohalides, dichlorides, and trichlorides were investigated. Selective C−C bond formation was observed in many cases. Based on these reactions, efficient Kumada–Corriu–Tamao coupling of unactivated alkyl halides and alkyl Grignard reagents with **1** as the precatalyst was developed. Good yields were obtained for the coupling of primary and secondary iodides and bromides. Double C–C coupling of CH_2Cl_2 with alkyl Grignard reagents by **1** was also realized. The scope and limitations of these transformations were studied. Evidence was found for a radical pathway in Ni-catalyzed C–C cross-coupling reactions, which involves Ni^{II} alkyl intermediates.

Keywords: C–C coupling · coordination modes · cross-coupling · nickel · pincer ligands

Introduction

Thanks to developments in Pd- and Ni-based catalysis, especially that of the Heck–Mizokori, Suzuki–Miyaura, Negishi, Kosugi–Migita–Stille, Hiyama, and Kumada–Corriu–Tamao types, metal-catalyzed C–C cross-coupling has become one of the most powerful tools in organic synthesis.[1,2] A prevailing mechanism for Pd^0- and Ni^0-catalyzed C–C coupling reactions involves first the oxidative addition of an organic electrophile to a low-valent metal center, then transmetalation of an organometallic nucleophile to the resulting X-M-C species, and finally C–C reductive elimination to give the desired products. Coupling of sp^3-, sp^2-, and sp-hybridized carbon atoms is now readily achieved by using a wide range of main-group organometallic nucleophiles and aryl, alkenyl, and even certain activated alkyl (e.g., allylic, benzylic, and α-halocarbonyl) electrophiles (C-X, X = Cl, Br, I, OTf, OMs, etc.; OTf = triflate, OMs = mesylate).[1,2] Unactivated alkyl halides, especially those with β-hydrogen atoms, are, however, challenging electrophiles for this type of transformation for the following reasons.[3,4] 1) Oxidative addition of alkyl halides is generally much slower than that of aryl and alkenyl halides. A recent DFT study of model reactions on Pd^0 suggested that this difference in reactivity is due to the availability of the Ar-X π^* orbitals for backbonding from Pd^0.[5] 2) If oxidative addition occurs, the resulting metal alkyl species can undergo unproductive β-H elimination, which is often both thermodynamically and kinetically favorable. Recent work by Knochel et al.,[6] Kambe et al.,[7,8] Fu et al.,[9–11] Vicic et al.,[12,13] Cárdenas et al.,[14] Van Koten et al.,[15] Cahiez et al.,[16] Nakamura et al.,[17] and Martin and

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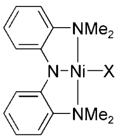
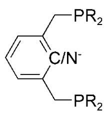
Fürstner[18] starts to address these challenges, and a number of efficient catalytic systems are found for the coupling of primary and secondary alkyl halides with alkyl nucleophiles. Many of these systems employ Ni salts or complexes as catalyst precursors.[6–8,10,12–14] Although the classical Ni^0/Ni^{II} catalytic cycles were proposed in some cases,[4] there are examples where two other mechanisms appear to be operational. Kambe and co-workers postulated a nonradical and formal Ni^{II}/Ni^{IV} mechanism for Ni-catalyzed Kumada–Corriu–Tamao coupling in the presence of 1,3-butadiene additives.[7,8] Vicic, Phillips, Cárdenas, and their co-workers reported experimental and theoretical support for a radical-initiated Ni^{I}/Ni^{III} catalytic cycle in Negishi alkyl–alkyl coupling catalyzed by Ni terpyridyl complexes.[12–14,19] The reaction pathways for Ni-catalyzed C–C coupling are therefore diverse. This can be advantageous as it may circumvent some of the limitations imposed by conventional Pd catalysis.

We recently synthesized a new pincer-type amidobis(amine) ligand ($^{Me}NN_2$) and its Ni^{II} complexes including hydrocarbyl species (**A**).[20] Herein, we describe the synthesis and structure of analogous Ni^{II} acetate, triflate, acetonitrile, and methoxide complexes. Our exploration of this ligand in coordination chemistry and catalysis is inspired by previous work on pincer ligands.[21–23] We notice particularly the broad applications of pincer phosphine ligands (**B** and **C**) in late-transition-metal-mediated small-molecule activation and homogeneous catalysis.[22–26] Pincer amine ligands are less exploited for similar applications. One might expect a mismatch between a soft late transition metal and the hard amine donors, yet the work by Van Koten and others demonstrated that stable pincer arylbis(amine) (ncn) complexes (**D**) of late transition metals could be made and showed promising activity in C–H activation, transfer hydrogenation, and C–C bond-forming reactions.[23,27,28] Our entry to Ni-mediated C–C coupling was provided by Ni^{II} alkyl complexes of the $^{Me}NN_2$ ligand. These compounds were thermally stable and the $[(^{Me}NN_2)NiEt]$ complex resisted β-H elimination. Preliminary study showed that the Ni^{II} methyl complex reacted with alkyl halides to give alkyl–alkyl coupled products in high yields according to Equation (1). Interestingly, reactions of Ni^{II} alkyl complexes with aryl halides, or Ni^{II} aryl complexes with alkyl/aryl halides, did not give the C–C coupled products. The metal-containing products of these reactions were $[(^{Me}NN_2)Ni]$ halides, which could be converted to a $[(^{Me}NN_2)Ni]$ alkyl compound by reaction with an alkyl Grignard reagent [Eq. (2)].[20] Thus, the principal components for a catalytic alkyl–alkyl coupling reaction between alkyl halides and Grignard nucleophiles are viable on this $[(^{Me}NN_2)Ni]$ platform. We now show that $[(^{Me}NN_2)NiCl]$ is indeed a precatalyst for Kumada–Corriu–Tamao coupling of unactivated alkyl halides, and present the scope and limitations of this catalysis.

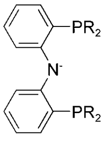


X = I, Br, Cl, Me, Et, Ph

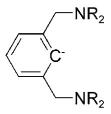
A



B



C



D

$$[(^{Me}NN_2)Ni\text{-}Me] + \text{alkyl-X} \longrightarrow [(^{Me}NN_2)Ni\text{-}X] + \text{Me-alkyl} \quad (1)$$

$$[(^{Me}NN_2)Ni\text{-}X] + \text{alkyl-MgCl} \longrightarrow [(^{Me}NN_2)Ni\text{-alkyl}] + MgClX \quad (2)$$

$$2\,[(^{Me}NN_2)Ni\text{-}R] + CH_2Cl_2 \longrightarrow 2\,[(^{Me}NN_2)Ni\text{-}Cl] + R_2CH_2 \quad (3)$$

$$3\,[(^{Me}NN_2)Ni\text{-}R] + CHCl_3 \longrightarrow 3\,[(^{Me}NN_2)Ni\text{-}Cl] + R_3CH \quad (4)$$

$$X = Cl, Br, I \qquad R = Me, Et$$

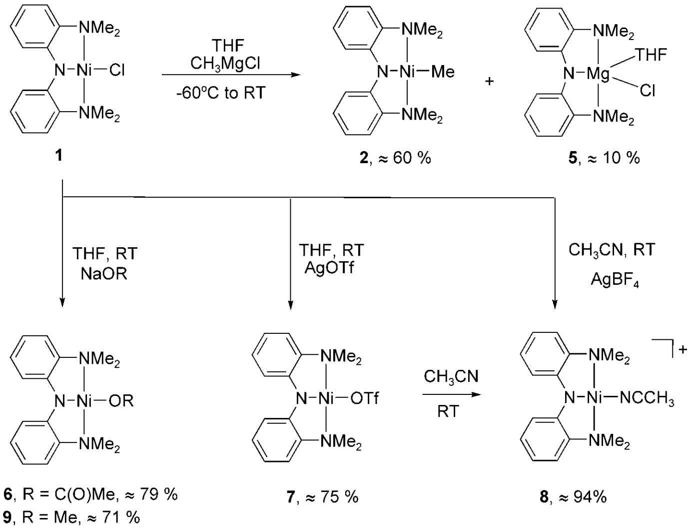
One unique feature of the $[(^{Me}NN_2)Ni]$ system is that the Ni^{II} alkyl complexes can react with CH_2Cl_2 and $CHCl_3$ to give doubly and triply coupled alkanes, respectively, in high selectivity [Eqs. (3) and (4)]. This led to our earlier communication on the first Kumada–Corriu–Tamao coupling of CH_2Cl_2 with *n*BuMgCl, which forms $n\text{Bu}CH_2n\text{Bu}$ as the main product.[20] Herein, we report our expansion of this study by employing other polychloroalkanes as electrophiles and additional Grignard reagents as nucleophiles for these intriguing transformations.

Results and Discussion

Synthesis and characterization of complexes: $[(^{Me}NN_2)NiCl]$ (**1**), $[(^{Me}NN_2)NiMe]$ (**2**), $[(^{Me}NN_2)NiEt]$ (**3**), and $[(^{Me}NN_2)NiPh]$ (**4**) were synthesized as reported earlier.[20] Reaction of **1** with CH_3MgCl often gave a small amount of an unknown compound (<10%) besides **2**. This compound is now identified as $[(^{Me}NN_2)MgCl(thf)]$ (**5**) by comparison of its NMR spectrum with that of an independently prepared sample, which was synthesized by reaction of ligand $H^{Me}NN_2$ with CH_3MgCl. Complex **5** is sparsely soluble in pentane, and by dissolution in pentane pure **2** with a negligible amount of **5** could be obtained.

We examined the thermal stability of nickel alkyl complexes **2** and **3**. Under an inert atmosphere and when dissolved in benzene, **2** does not undergo decomposition even when heated at 120°C for days. Similarly, **3** is stable up to 80°C; when heated at 100°C in benzene, it decomposed to form insoluble solids. The stability of **3** against β-H elimination at 80°C is noteworthy. Similar stability of Ni^{II} alkyl species was reported by Liang et al. on isoelectronic amidobis(phosphine) (pnp) complexes.[25]

Salt metathesis reactions of **1** produced the corresponding Ni^{II} acetate (**6**) and triflate (**7**) complexes (Scheme 1). Ab-



Scheme 1. Synthesis of new nickel(II) complexes of the $^{Me}NN_2$ ligand.

straction of the chloride ligand in **1** by $AgBF_4$ in CH_3CN gave the cationic CH_3CN complex with BF_4 as the counter anion (**8·BF$_4$**); alternatively, dissolution of **7** in CH_3CN gave the same cation with triflate as the counter anion (Scheme 1). The latter reaction suggests that the triflate ligand in **7** is labile. Reaction of **1** with NaOMe in THF led to the Ni^{II} methoxide complex **9**.

All $[(^{Me}NN_2)Ni^{II}]$ complexes have distinctive colors and their electronic absorption spectra are shown in Figure S1 in the Supporting Information. There is a significant difference between the hydrocarbyl complexes (**2**–**4**) and the other derivatives (**1** and **6**–**8**) in the visible spectra: the hydrocarbyl complexes do not absorb between 600 and 800 nm, whereas the spectra of the other compounds exhibit an absorption maximum with a molar absorption coefficient of 100–200 $L\,cm^{-1}\,mol^{-1}$.

The NMR spectra of **6**–**9** are consistent with the structural formation shown in Scheme 1. An effective C_{2v} symmetry was observed for the protons of the $^{Me}NN_2$ ligand, which suggests a fast rotation of the Ni–O bond in **6**, **7**, and **9**. The Lewis acidity of a metal center can be measured by how tightly it binds to a Lewis base, for example, crotonaldehyde or CH_3CN.[28,29] Previous studies employed CH_3CN to probe the Lewis acidity of group 10 metal pincer complexes. To better compare the Lewis acidity of $[(^{Me}NN_2)Ni^{II}]$ with them, we chose CH_3CN as well. The magnitude of the downfield shift for the methyl protons of the coordinated CH_3CN is proportional to the Lewis acidity of the complex. The ^1H NMR signal for CH_3CN in **8** was observed at 2.60 ppm in $CDCl_3$, 0.50 ppm higher than free CH_3CN. The $[(^{Me}NN_2)Ni^{II}]$ cation thus has a similar Lewis acidity to the $[(pnp)Ni^{II}]$ cation ($\delta(H) = 2.69$ ppm for CH_3CN),[26] but is more Lewis acidic than 2,6-bis(2-oxazolinyl)phenyl Ni^{II} and $[(pocop)Ni^{II}]$ complexes (pocop: diphosphinito; $\delta(H) = 2.4$ and 2.2 ppm for CH_3CN, respectively).[29,30]

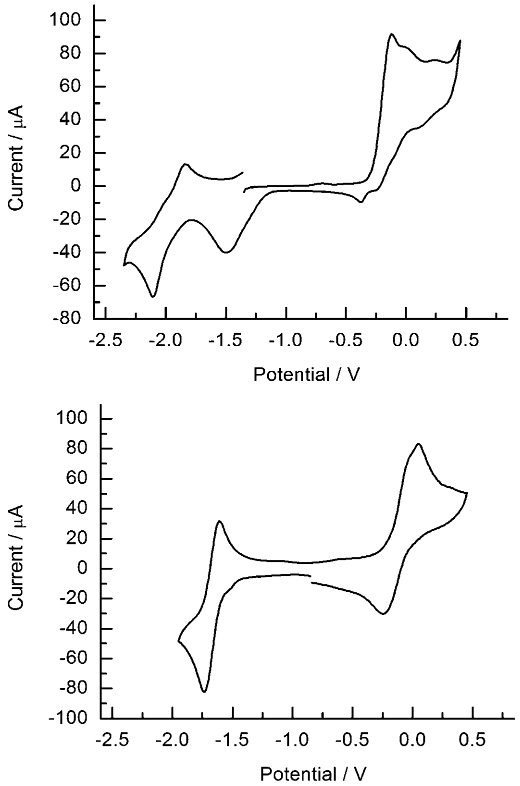


Figure 1. Cyclic voltammograms of complexes **1** (top; 2.1 mM) and **8** (bottom; 4 mM) recorded in CH_3CN solutions at scan rates of 100 (**1**) and 400 $mV\,s^{-1}$ (**8**); the potential is referenced to the ferrocene/ferrocenium couple.

The redox properties of **1**, **2**, **4**, and **8** were probed by cyclic voltammetry. Two reduction and one oxidation wave were observed for **1** in CH_3CN (Figure 1, top). The first reduction wave was irreversible ($E_{red} = -1.5$ V vs. ferrocene/ferrocenium (Fc/Fc^+), same below) and the second one ($E^{o'} = -1.94$ V) was quasi-reversible. The oxidation wave occurred at −0.12 V and its current height indicated that it could be a two-electron oxidation (assuming the reduction is one-electron). It is an irreversible oxidation even in the presence of excess halide ions. When the chloride ion in **1** was substituted by a CH_3CN molecule, the cyclic voltammogram changed dramatically. At scan rates higher than 400 $mV\,s^{-1}$, complex $[(^{Me}NN_2)Ni(CH_3CN)]BF_4$ (**8·BF$_4$**) could undergo one reversible reduction and one quasi-reversible oxidation at $E^{o'} = -1.67$ and −0.15 V, respectively (Figure 1, bottom). At lower scan rates, the reduction remained reversible whereas the oxidation became irreversible. The electron-donating property of the $^{Me}NN_2$ ligand could be estimated by the oxidation potential of its metal complex, for example, **1** and **8**. Thus, the $^{Me}NN_2$ ligand is as good an electron donor as the electron-rich amidobis(alkylphosphine) ligand, which gave rise to a [(pnp)NiCl] complex with $E^{o'} = -0.06$ V.[25] The cyclic voltammogram of the methyl and phenyl Ni complexes showed an irreversible oxidation at 0.13 and 0.27 V in THF, respectively (Figure S2 in the Supporting Information), which suggests an instability for a formal Ni^{III} alkyl or aryl species of the $^{Me}NN_2$ ligand.

Structure of complexes: The solid-state structures of complexes **6**–**8** were determined by X-ray crystallography (Figure 2). The key structural parameters for these complexes, together with those of **1** and **3**, are summarized in Table 1 and Table 2. The coordination geometry of Ni^{II} is approximately square-planar in all five complexes. The pincer NN$_2$ ligand binds to Ni in the expected *mer* fashion, and the fourth coordination site is occupied by an additional donor. The two phenyl rings deviate slightly from coplanar, with an angle of 22.22 (**1**), 21.66 (**3**), 25.49 (**6**), 7.51 (**7**), and 16.95° (**8**), respectively. The amide nitrogen atom is sp^2 hybridized, as the sums of the three bonds around it are all close to 360°. The Ni–N(amide) distance is about 1.83 Å in **1** and **6**–**8**, but increases to 1.89 Å in **3**. This is consistent with a high *trans* influence of alkyl ligands.[31] The Ni–N(amide) bonds are always about 0.1 Å shorter than the corresponding Ni–N(amine) bonds, which suggests some degree of π donation from the amide lone pair.

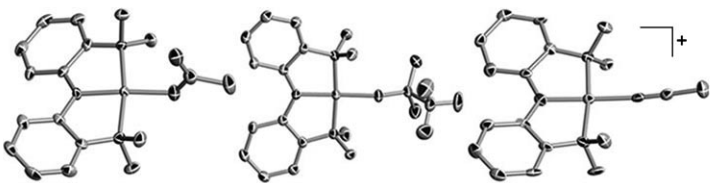


Figure 2. Crystal structures of complexes **6** (left), **7** (middle), and **8** (right). The thermal ellipsoids are displayed at 50 % probability.

Replacement of an anionic fourth ligand by a neutral donor (e.g., from **7** to **8**) causes no appreciable structural change in the {(^{Me}NN$_2$)Ni^{II}} fragment. The acetate ligand in **6** is coordinated in an η^1 fashion, a common coordination mode for mononuclear Ni^{II} acetate complexes.[32] The Ni–O distance is slightly shorter in **6** (1.890(3) Å) than in **7** (1.946(2) Å).

Table 1. Selected bond lengths for [(MeNN$_2$)Ni^{II}] complexes.[a]

Complex	Ni–N(amide)	Ni–N(amine)$_{av.}$	Ni–X[b]
[(^{Me}NN$_2$)NiCl] (**1**)[c]	1.835(2)	1.956(2)	2.2029(7)
[(^{Me}NN$_2$)NiEt] (**3**)	1.8907(18)	1.976(2)	1.959(2)
[(^{Me}NN$_2$)Ni(OC(O)CH$_3$)] (**6**)[c]	1.831(3)	1.957(3)	1.890(3)
[(^{Me}NN$_2$)Ni(OTf)] (**7**)	1.830(2)	1.9357(17)	1.946(2)
[(^{Me}NN$_2$)Ni(NCCH$_3$)]BF$_4$ (**8**·**BF$_4$**)[c]	1.825(5)	1.944(5)	1.875(6)

[a] Bond lengths are in Å; data for **1** and **3** are from ref. [20]. [b] X is the fourth ligand on Ni besides the tridentate NN$_2$ chelate. [c] Average of two independent molecules in the asymmetric unit.

Table 2. Selected bond angles for [(^{Me}NN$_2$)Ni^{II}] complexes.[a]

Complex	N(amine)-Ni-N-(amide)$_{av.}$	N(amine)-Ni-X$_{av.}$[b]	C-N(amide)-C	Ni-N(amide)-C$_{av.}$
[(^{Me}NN$_2$)NiCl] (**1**)[c]	86.26(8)	94.04(6)	127.2(2)	116.12(16)
[(^{Me}NN$_2$)NiEt] (**3**)	84.47(8)	95.51(10)	127.93(19)	113.93(17)
[(^{Me}NN$_2$)Ni(OC(O)CH$_3$)] (**6**)[c]	85.63(13)	93.27(18)	127.6(3)	116.1(2)
[(^{Me}NN$_2$)Ni(OTf)] (**7**)	87.33(5)	92.65(5)	128.8(3)	115.22(13)
[(^{Me}NN$_2$)Ni(NCCH$_3$)]BF$_4$ (**8**·**BF$_4$**)[c]	86.8(2)	93.3(2)	128.8(5)	115.5(4)

[a] Bond angles are in degrees; data for **1** and **3** are from ref. [20]. [b] X is the fourth ligand on Ni besides the tridentate NN$_2$ chelate. [c] Average of two independent molecules in the asymmetric unit.

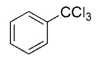
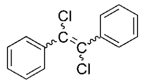
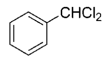
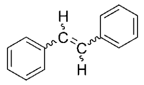
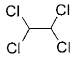
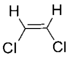
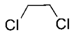
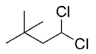
The overall structure of these [(^{Me}NN$_2$)Ni^{II}] complexes is similar to that of their counterparts supported by anionic ncn and pnp ligands. For the Ni^{II}Cl complexes, the Ni–Cl distances are comparable in **1**, [{N(SiMe$_2$CH$_2$PPh$_2$)$_2$}NiCl] (**10**, 2.1703(6) Å),[21] [{N(*o*-C$_6$H$_4$PPh$_2$)$_2$}NiCl] (**11**, 2.1636(11) Å),[25] and [{2,6-bis({dimethylamino}methyl)phenyl}NiCl] (**12**, 2.2388(5) Å).[33] The Ni–N(amine) distances in **1** and **12** are also close (1.9909(13) Å in the latter); however, the Ni–N(amide) bond in **1** is slightly shorter than in **10** and **11** (1.924(2) and 1.895(3) Å, respectively). For the Ni^{II} alkyl complexes, the Ni–C distance in **3** is nearly identical to that in [{N(*o*-C$_6$H$_4$PPh$_2$)$_2$}NiMe] (**13**, 1.967(11) Å) and [{N(*o*-C$_6$H$_4$PPh$_2$)$_2$}Ni(*n*Bu)] (**14**, 1.971(3) Å), whereas the Ni–N-(amide) distance is again shorter in **3** than in **13** and **14** (1.967(8) and 1.966(2) Å, respectively).[25]

Reactions of [(^{Me}NN$_2$)Ni^{II}Me] with alkyl halides: We reported previously that [(^{Me}NN$_2$)NiMe] (**2**) reacted with alkyl halides according to Equation (1). The rate of the reaction followed the orders: RI > RBr > RCl and benzyl > octyl > cyclohexyl. There was evidence for a radical process in these reactions.[20] We propose that **2** first reacts with an alkyl halide to undergo a one-electron oxidation, forming a transient alkyl radical, which quickly recombines with the metal to form a Ni bis(alkyl) complex. Reductive C–C elimination then gives a Ni^{II} halide complex and the C–C coupled product. Consistent with this radical-rebound mechanism, **2** does not react with trimethylsilyl triflate, an electrophile prone to S$_N$2 oxidative addition. Curiously, we find a large steric influence in the reaction rate even among primary alkyl halides. For instance, reaction with C$_2$H$_5$Cl takes place at room temperature, but reactions with *n*C$_3$H$_7$Cl and *n*C$_8$H$_{17}$Cl require a temperature of 60 and 100 °C, respectively. The origin of this difference is currently under investigation by DFT methods. It is noted that **2** reacts with *n*C$_2$H$_5$Cl at a rate that is comparable to that with CH$_2$Cl$_2$, thus indicating that *n*C$_2$H$_5$Cl is not an intermediate in the latter reaction, as no *n*C$_2$H$_5$Cl was detected during the reaction.

The reaction between **2** and aryl halides was much slower and did not afford the C–C coupled organic compounds. The phenyl complex [(^{Me}NN$_2$)NiPh] (**4**) did not react with either alkyl or aryl halides. It appears that only alkyl–alkyl coupling could be mediated by the [(^{Me}NN$_2$)Ni^{II}] system, in contrast to conventional Pd and Ni catalysis, in which the selectivity is higher for aryl–aryl coupling.[1]

Because [(^{Me}NN$_2$)MgCl(thf)] (**5**) is a byproduct in the synthesis of **2**, it is hard to completely prevent the contamination of a bulk sample of **2** by **5**. However, no reaction was found between **5** and alkyl halides, CH_2Cl_2, and $CHCl_3$, thus ruling out the involvement of **5** in Equations (1), (3), and (4). The reactions of **2** with CH_2Cl_2 and $CHCl_3$ [Eqs. (3) and (4)] are particularly interesting because they involve the cleavage of two and three C−Cl bonds to form new C−C bonds at the same carbon center. We examined the reactions of **2** with other alkyl dichlorides and polychlorides and the results are summarized in Table 3. Although [($^{Me}NN_2$)NiCl] (**1**) was formed as the only metal-containing product, no doubly or triply alkylated organic compounds were produced in these reactions. Instead, small amounts of radically coupled products can be identified. For instance, **2** reacted with benzotrichloride to give a 55% yield of 1,2-dichloro-1,2-diphenylethylene (entry 1, Table 3), derived presumably from reductive dehalogenation of the dimerization product, 1,1,2,2-tetrachloro-1,2-diphenylethylene. A similar reaction was reported earlier for sodium formate in the presence of Pd/C.[34] Similar radical dimerization and/or dehalogenation reactions are responsible for the production of other olefinic compounds (entries 2–4, Table 3). We were not able to identify any organic products for the reactions of **2** with other unactivated alkyl dichlorides (entries 5 and 6, Table 3). Thus, multiple C–C coupling is only efficient in the reactions of **2** with CH_2Cl_2 and $CHCl_3$.

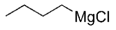
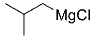
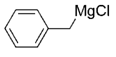
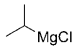
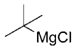
Table 3. Organic products identified in reactions of [($^{Me}NN_2$)NiMe] (**2**) with di- and polychloroalkanes.[a]

Entry	Substrate	Conditions	Product	Yield [%]
1		RT, 5 min		55
2		RT, 24 h		30
3		RT, 24 h		4
4		100 °C, 24 h	$CH_3CH_2CH_2Cl$ $CH_2{=}CH_2$	5 6
5		60 °C, 24 h	–	–
6	CH_3CHCl_2	RT, 24 h	–	–

[a] See Experimental Section for conditions.

Table 4. Catalytic coupling of octyl iodide with alkyl Grignard reagents.[a]

$$\text{octyl-I} + \text{alkyl-MgCl} \xrightarrow{\text{cat. } \mathbf{1}} \text{octyl–alkyl}$$

Entry	RMgCl	Yield [%][b]
1		65
2	CH_3MgCl	74
3		77
4		54
5		0
6		0

[a] 0.6 mmol (1.2 equiv) of RMgCl in THF (1–3 M) was added dropwise to a DMA (0.75 mL) solution of **1** (9 mol%) and octyl iodide (0.5 mmol) at −20 °C. The reaction time was 30 min. [b] GC yields relative to the organic halides.

Catalytic C–C coupling of alkyl monohalides: Based on Equations (1) and (2), a catalytic C–C coupling of alkyl halides and alkyl Grignard reagents with **1** as the precatalyst seems plausible. We examined whether **1** would be active for this Kumada–Corriu–Tamao type of coupling. Because the transmetalation of **1** with CH_3MgCl to give **2** has a higher yield when carried out at low temperature and because previous experiments showed that coupling of CH_2Cl_2 with *n*BuMgCl had the best yield at −20 °C, we decided to conduct the catalysis at the same temperature. Octyl iodide was chosen as the test substrate because it could react with **2** at room temperature and it contains β-hydrogen atoms. An initial screen showed that coupling of octyl iodide with CH_3MgCl and *n*BuMgCl with 9 mol% **1** in THF gave the desired product in 69 and 30% yield, respectively. Changing the solvent to dimethylacetamide (DMA) improved the yields, more for the β-H-containing *n*BuMgCl (65% yield, entry 1, Table 4) than for CH_3MgCl (74% yield, entry 2, Table 4). Therefore, DMA was chosen as the solvent for the rest of the catalysis runs. Bulkier primary Grignard reagent *i*BuMgCl could be coupled in good yield (entry 3, Table 4), whereas benzyl Grignard reagent gave a lower yield (54%, entry 4, Table 4). Coupling was ineffective for secondary and tertiary Grignard reagents (entries 5 and 6, Table 4).

The same protocol was then used for the coupling of other substrates. Primary and secondary alkyl iodides could be coupled to primary alkyl Grignard reagents in 70–80% yields (entries 1–3, 5, and 6, Table 5). An exception is the coupling of cyclohexyl iodide with CH_3MgCl, which gave only 39% yield (entry 7, Table 5). Benzyl Grignard reagent again gave lower coupling yields (entries 4 and 8, Table 5). Tertiary alkyl iodide could not be coupled (entry 9, Table 5).

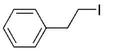
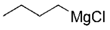
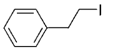
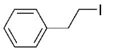
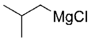
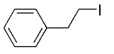
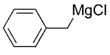
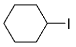
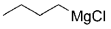
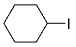
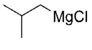
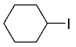
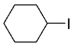
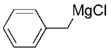
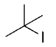
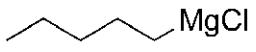
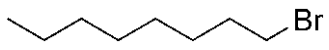
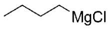
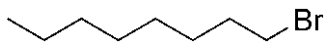
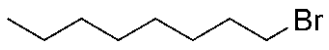
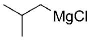
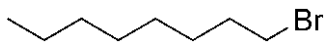
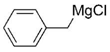
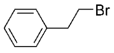
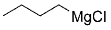
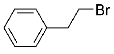
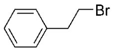
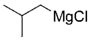
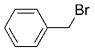
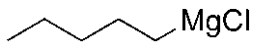
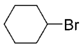
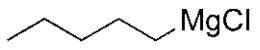
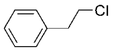
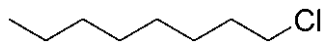
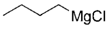
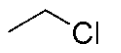
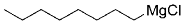
Primary alkyl bromide could also be used to give comparable yields (entries 10–16, Table 5). Coupling of benzyl bromide was sluggish due to the formation of the $PhCH_2CH_2Ph$ dimer (entry 17, Table 5). The yield also dropped when secondary alkyl bromide was used (entry 18, Table 5). Coupling of alkyl chlorides was ineffective (entries 19–21, Table 5).

Lowering the catalyst loading only slightly decreased the yields. For instance, with 3 mol% loading of **1**, coupling of $PhCH_2CH_2Br$ with CH_3MgCl gave $PhCH_2CH_2CH_3$ in 65% yield, and coupling of octyl bromide with *n*BuMgCl gave dodecane in 70% yield (entries 10 and 15, Table 5, see footnotes).

As alkyl–aryl or aryl–aryl coupling was not observed between Ni^{II} hydrocarbyl compounds and organic halides, no

Table 5. Catalytic coupling of alkyl halides with alkyl Grignard reagents.[a]

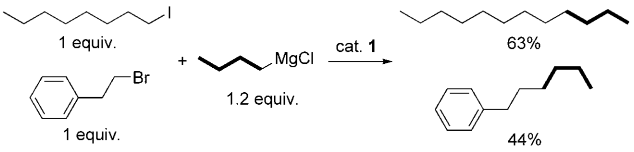
$$\text{alkyl}^1\text{-X} + \text{alkyl}^2\text{-MgCl} \xrightarrow{\text{cat. } \mathbf{1}} \text{alkyl}^1\text{–alkyl}^2$$

Entry	R^1-X	R^2MgCl	Yield [%][b]
1			70
2		CH_3MgCl	80
3			75
4			47
5			76
6			78
7		CH_3MgCl	39
8			10
9			0
10			75[c]
11		CH_3MgCl	80
12			58
13			23
14			88
15		CH_3MgCl	87[d]
16			78
17			32[e]
18			45
19		CH_3MgCl	4/25[f]
20			0
21			0

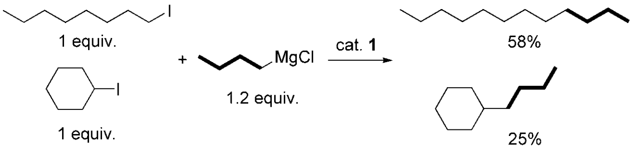
[a] 0.6 mmol (1.2 equiv) of RMgCl in THF (1–3 M) was added dropwise to a DMA (0.75 mL) solution of **1** (9 mol %) and organic halides (0.5 mmol) at −20 °C. The reaction time was 30 min. [b] GC yields relative to the organic halides. [c] 70 % yield when 3 mol % of **1** was used. [d] 65 % yield when 3 mol % of **1** was used. [e] $PhCH_2CH_2Ph$ was formed in 62 % yield. [f] 4 % yield at −20 °C, and 25 % yield at 60 °C.

attempts were made to test the activity of **1** in catalytic alkyl–aryl and aryl–aryl coupling.

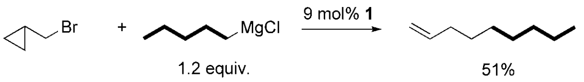
A few further observations are noteworthy. During the catalysis, the color of the reaction mixture resembles that of **2** and **3**. The electronic absorption spectrum of the solution mixture for the catalytic coupling of octyl bromide and CH_3MgCl under 9 mol % of **1** was similar to those of the $[(^{Me}NN_2)Ni]$ hydrocarbyls, but not the other $[(^{Me}NN_2)Ni]$ derivatives (Figure S3 in the Supporting Information). This suggests that the resting state of the catalyst is the nickel alkyl species. When an equal mixture of octyl iodide and $C_6H_5CH_2CH_2Br$ was coupled with *n*BuMgCl, the yields for $C_{12}H_{26}$ and $C_6H_5C_6H_{13}$ were 66 and 44 %, respectively [(Eq. (5)]. When an equal mixture of octyl iodide and cyclohexyl iodide was coupled with *n*BuMgCl, the yields for $C_{12}H_{26}$ and $C_6H_{11}C_4H_9$ were 58 and 25 %, respectively [(Eq. (6)]. Thus, alkyl iodides react faster than alkyl bromides, and primary halides react faster than secondary halides during the catalysis. This would be consistent with the turnover-determining step of the catalysis being the C–X activation of alkyl halides by the nickel alkyl intermediates. When bromomethylcyclopropane was coupled to $nC_5H_{11}MgCl$, 1-nonene was formed as the major product, thus giving further evidence for the intermediacy of an alkyl radical in the C–X activation step [(Eq. (7)]. Coupling of certain alkene-containing substrates gave mostly noncyclized products [(Eq. (8)]. This was probably due to a slower rate of cyclization for alkyl radicals derivatized from these substrates ($k \approx 10^5\,s^{-1}$) than for the ring opening of the cyclopropanyl methyl radical ($k \approx 10^7\,s^{-1}$), which competed with the cross-coupling reaction.[14] Similar observations were reported earlier by Cárdenas et al.[14]



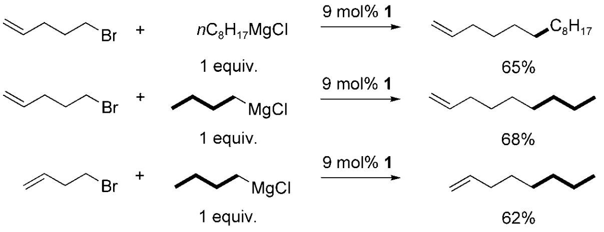
(5)



(6)



(7)



(8)

Concerning the mechanism of the catalysis, stoichiometric reactions of **1** and **2** suggest that the first step is the transmetalation of **1** by a Grignard reagent to form a Ni^{II} alkyl intermediate, which then reacts with an alkyl halide to form the C–C coupled product and **1** again, thereby reentering the catalyst cycle (Figure 3). Further support for this proposal comes from the fact that when 9 mol % of **2** was used as the precatalyst for the coupling of octyl iodide with CH_3MgCl, nonane was formed in 79 % yield, comparable to the result obtained with **1**. Although Ni has been widely used for Kumada–Corriu–Tamao coupling, this is the first time an isolable Ni^{II} alkyl intermediate has been shown to be a com-

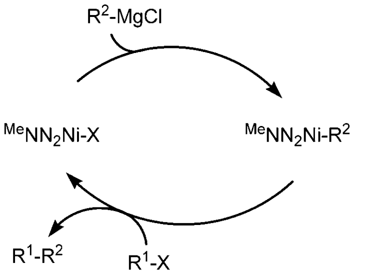


Figure 3. Proposed mechanism for alkyl–alkyl coupling catalyzed by **1**.

petent intermediate in the catalytic cycle. This is in contrast to the Ni terpyridyl system, in which a Ni^{II} alkyl compound was catalytically incompetent for the Negishi-type alkyl–alkyl coupling, but its one-electron reduced species was effective.[12] It is different from the systems developed by Fu and co-workers, for which a radical pathway was excluded.[11] The mechanism is also different from the classical C–C coupling mechanism by Pd^0, in which the activation of organic halides proceeds prior to transmetalation, rather than the reverse in the current system.

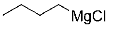
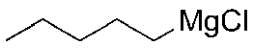
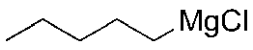
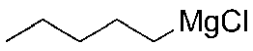
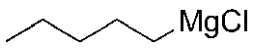
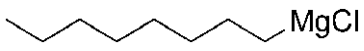
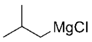
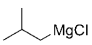
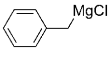
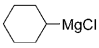
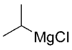
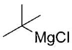
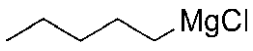
The scope and limitations of the catalysis are in line with this proposed mechanism. A low temperature (e.g., −20 °C) assures the efficiency of transmetalation and the stability of Ni alkyl intermediates, yet under such conditions only weaker alkyl−Br and alkyl−I bonds, but not alkyl−Cl bonds, can be activated. Therefore, no satisfactory cross-coupling of alkyl chlorides could be obtained. The tridentate ligand $^{Me}NN_2$ remains on the metal center throughout the catalytic cycle, including at the Ni^{II} alkyl stage. Such a four-coordinate square-planar Ni^{II} species is coordinatively rather saturated, and its subsequent reaction with alkyl halides would be sensitive to steric demands. This may lead to the inefficiency for the cross-coupling of bulky Grignard reagents and/or alkyl halides. The activation of organic halides goes through a single-electron transfer step, which can explain why aryl halides were not active. According to electrochemistry studies, Ni–Me is easier to oxidize than Ni–Ph (see above). This may explain why aryl Grignard reagents were not effective.

The mechanism in Figure 3 is quite similar to that proposed for the Ni-catalyzed cross-coupling of unactivated alkyl halides with alkyl Grignard reagents in the presence of 1,3-butadiene. Kambe et al. suggested that in the latter catalysis, the $NiCl_2$ precatalyst was first reduced to Ni^0 by a Grignard reagent, then reacted with 2 equivalents of 1,3-butadiene to give a bis-π-allyl Ni^{II} complex. The allyl species then reacted again with the Grignard reagent to form a nucleophilic Ni^{II} alkyl anion, which activated alkyl halides by oxidative addition to form a Ni^{IV} bis(alkyl) intermediate. Subsequent reductive elimination afforded the coupling product and completed the catalytic cycle.[7] Both systems involve first transmetalation by Grignard reagents to give a nucleophilic Ni^{II} alkyl intermediate, then activation of alkyl halides to give a formal Ni^{IV} bis(alkyl) species, and finally productive C–C reductive elimination. Whether this general reaction scheme operates for other Ni-catalyzed Kumada–Corriu–Tamao coupling reactions remains to be seen. There is, however, one major difference between the two systems: the activation of alkyl halide involves radical intermediates here but not in the Kambe system.[7]

Catalytic C–C coupling of alkyl polyhalides: It was shown earlier that **1** was a precatalyst for the double C–C coupling of CH_2Cl_2 with *n*BuMgCl at −20 °C (entry 1, Table 6).[20] A wide range of alkyl Grignard reagents were then examined for this reaction. Gratifyingly, other primary alkyl Grignard reagents worked. For example, coupling of CH_2Cl_2 with $nC_5H_{11}MgCl$ by using 3 mol % catalyst loading gave 68 % of nC_5H_{11}-CH_2-nC_5H_{11} (entry 2, Table 6). The yield could be increased to 81 % if 6 mol % of catalyst was used (entry 3, Table 6). $nC_5H_{11}MgCl$ in THF gave the best results; changing to $nC_5H_{11}MgBr$ in THF/ether lowered the yields (entries 4 and 5, Table 6). Coupling of CH_2Cl_2 with $nC_8H_{17}MgCl$ gave 69 % of nC_8H_{17}-CH_2-nC_8H_{17} (entry 6, Table 6). Bulkier alkyl Grignard reagents could be used but gave lower yields. For instance, *i*BuMgCl coupled with CH_2Cl_2 to give *i*Bu-CH_2-*i*Bu in 30 % yield with 4.5 mol % precatalyst (entry 7, Table 6). Increasing the precatalyst loading to 12 mol % improved the yield to 49 % (entry 8, Table 6). BenzylMgCl did not work, as it gave mainly the homocoupling product $C_6H_5CH_2CH_2C_6H_5$ (60 % yield, entry 9, Table 6). Coupling was not efficient with a secondary or tertiary Grignard reagent (entries 10–12, Table 6). When another soluble Ni^{II} complex, for example, [(dme)$NiCl_2$] (dme = dimethoxy-

Table 6. Double C–C coupling of CH_2Cl_2 with Grignard reagents.[a]

$$2\,RMgCl + CH_2Cl_2 \xrightarrow[\text{solvent}]{\text{cat. }\mathbf{1}} RCH_2R$$

Entry	RMgCl	Mol % of catalyst	*t* [h]	Yield [%][b]
1		6	0.1	59
2		3	0.3	68
3		6	0.3	81
4[c]		3	0.3	51
5[d]		3	0.3	23
6		3	0.3	69
7		4.5	0.3	30
8		12	0.3	49
9		3	0.3	0
10		9	0.5	6
11		3	0.3	0
12		3	0.3	0
13		0[e]	0.5	4

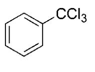
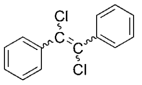
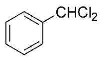
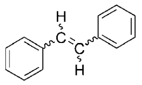
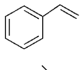
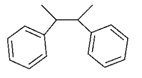
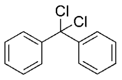
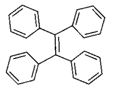
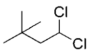
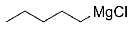
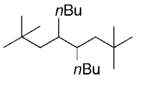
[a] 0.8 mmol of RMgCl (1–2 M solution in THF) as the limiting reagent; RMgCl was added dropwise to a CH_2Cl_2 (1.5 mL, 25 equiv) solution of **1**. [b] GC yields relative to the Grignard reagents. [c] $C_5H_{11}MgBr$ in THF was used. [d] $C_5H_{11}MgBr$ in ether was used. [e] 3 mol % [(dme)$NiCl_2$] was used as the precatalyst.

ethane), was used as the precatalyst, only a trace amount of the doubly coupled product was formed (entry 13, Table 6), thus confirming the unique activity of **1** for this catalysis. The overall results suggest that the double C–C coupling between CH_2Cl_2 and a primary alkyl Grignard reagent catalyzed by **1** is general and rapid. The yields are remarkably high considering the fact that these alkyl Grignard reagents contain β-hydrogen atoms. The ability of $[(^{Me}NN_2)Ni]$ alkyl species to resist β-hydrogen elimination is likely a key factor for this high efficiency. The catalysis does not tolerate well the steric bulkiness of the Grignard reagents, as bulkier primary Grignard reagents give lower yields, and secondary and tertiary Grignard reagents cannot be coupled.

Although its detailed mechanism warrants further studies, based on stoichiometric reactions, the double coupling catalysis is proposed to proceed through similar sequences as in the Kumada–Corriu–Tamao coupling: transmetalation of **1** by a Grignard reagent gives a Ni^{II} alkyl species, which reacts with CH_2Cl_2 to give the coupling product and regenerate **1**.

Catalytic coupling experiments were also carried out on other dichloroalkanes with 3 mol% of **1** as the precatalyst. No doubly C–C coupled products were formed, even with CH_3CHCl_2. This is consistent with the results from stoichiometric reactions of **2** and dichloroalkanes (Table 3). In some cases, the organic products could be identified. For instance, coupling of benzotrichloride with CH_3MgCl gave 1,2-dichloro-1,2-diphenylethylene in 25% yield (entry 1, Table 7), and coupling of benzodichloride with CH_3MgCl gave stilbene, styrene, and $[Ph(CH_3)CH]_2$ in 8, 16, and 22% yields, respectively (entry 2, Table 7). Coupling of 1,1-dichloro-3,3-dimethylbutane with *n*BuMgCl (R^1L_2) gave BuR^1R^1Bu in 42% yield (entry 3, Table 7),[20] and coupling of Ph_2CCl_2 with MeMgCl gave $Ph_2C{=}CPh_2$ in 70% yield (entry 4, Table 7). A radical dimerization process is likely to be operational in these reactions.

Table 7. Catalytic coupling of alkyl polyhalides.[a]

Entry	RCl_x	R′MgCl	Product	Yield [%][b]
1		CH_3MgCl		25
2		CH_3MgCl		8
				16
				22
3		CH_3MgCl		70
4[c]				40

[a] 0.4 mmol of RMgCl (1–2 M solution in THF) was added dropwise to a THF (1.5 mL) solution of polyhalides (1 equiv with respect to the number of C−Cl bonds) and **1** (3 mol%). [b] GC and/or NMR yields relative to the organic polyhalides. [c] Reported in ref. [20].

Conclusion

We have described the synthesis, characterization, structure, and reactivity of a series of Ni^{II} compounds of the newly developed pincer amidobis(amine) ligand $^{Me}NN_2$. The coordination chemistry of $^{Me}NN_2$ on Ni^{II} is comparable to that of the analogous pincer amidobis(phosphine) (pnp) and arylbis(amine) (ncn) ligands, whereas its electron-donating ability is similar to that of alkyl pnp. The Lewis acidity of the $[(^{Me}NN_2)Ni]$ cation is comparable to that of its isoelectronic [(pnp)Ni] complex. A significant difference in the electronic properties of the two classes of pincer ligands (NN_2 versus pnp) is, however, expected. Replacing phosphine with amine donors makes the ligand “harder” and more suitable for stabilizing higher-oxidation-state metal ions. This might be the origin for the enhanced activity of $[(^{Me}NN_2)Ni]$ alkyl complexes towards alkyl halides relative to the [(pnp)Ni] alkyl complexes.[25] A Ni bis(alkyl) species with a formal oxidation state of +III or +IV is the presumed intermediate in such a reaction. Furthermore, compared to pnp complexes, intramolecular metal-to-ligand π backbonding is diminished in NN_2 complexes. Therefore, NN_2 complexes might be more active in π-bond activation chemistry, which we plan to explore in the near future.

The $[(^{Me}NN_2)NiMe]$ (**2**) complex reacted cleanly with alkyl halides, CH_2Cl_2, and $CHCl_3$ to give C–C coupled products in high yields. The reactions of **2** with other di- and polychloroalkanes were also probed but a different reactivity pattern was observed. Based on stoichiometric reactions of **2** and $[(^{Me}NN_2)NiCl]$ (**1**), catalytic Kumada–Corriu–Tamao coupling of unactivated alkyl halides and alkyl Grignard reagents was achieved by using as **1** the precatalyst. Good yields were obtained for this challenging type of cross-coupling that suffered from the inertness of alkyl halides and the decomposition of catalytic intermediates via facile β-H elimination. The catalysis was rapid and primary and secondary iodides and bromides were tolerated. Although Ni-catalyzed alkyl–alkyl coupling has been reported by a number of groups, complex **1** is one of the very few isolated and well-characterized (pre)catalysts known. Complex **2** is the first isolable Ni^{II} alkyl species that has been shown to be catalytically competitive. The resting state of the catalysis is the Ni alkyl species. Transmetalation occurred before the activation of organic halides in the catalytic cycle. The mechanism of this catalysis is therefore unique. This underscores the viability of several distinctive reaction pathways for Ni-catalyzed C–C coupling reactions, which can be beneficial in terms of substrate scope and selectivity.

The double C–C coupling between CH_2Cl_2 and Grignard reagents catalyzed by **1** has been further investigated. Long-chain primary alkyl Grignard reagents could be successfully coupled in 60–80% yields; bulkier primary alkyl Grignard reagents could also be used but with lower yields. Extension to secondary and tertiary alkyl Grignard reagents was not successful, probably for steric reasons. Coupling of other di- and polychloroalkanes with Grignard reagents was attempted, and in several cases radical dimerization products were produced.

Future work in this area includes kinetic and computational studies on the mechanism of the reactions between **2** and alkyl monohalides, CH_2Cl_2, and $CHCl_3$, and the application of ligand $^{Me}NN_2$ in other metal-catalyzed bond-forming reactions.

Experimental Section

Chemicals and reagents: All manipulations were carried out under an inert $N_2(g)$ atmosphere with standard Schlenk or glove box techniques. Solvents were purified with a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves. All other reagents were purchased from commercial sources and were degassed by standard freeze–pump–thaw procedures prior to use. Ligand $H^{Me}NN_2$ and complexes $[(^{Me}NN_2)NiCl]$ (**1**), $[(^{Me}NN_2)NiMe]$ (**2**), $[(^{Me}NN_2)NiEt]$ (**3**), and $[(^{Me}NN_2)NiPh]$ (**4**) were prepared as described previously.[20,35]

Physical methods: The ^1H and ^{13}C NMR spectra were recorded at 293 K on a Bruker Avance 400 spectrometer. ^1H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si ($\delta=0$ ppm). The $^{13}C\{^1H\}$ chemical shifts are reported in ppm relative to the carbon resonance of $[D_6]DMSO$ ($\delta=39.52$ ppm), CD_3CN ($\delta=118.26$ ppm), or C_6D_6 ($\delta=128.02$ ppm). GC–MS measurements were conducted on a Perkin–Elmer Clarus 600 chromatograph equipped with a Clarus 600T mass spectrometer. GC measurements were conducted on a Perkin–Elmer Clarus 400 chromatograph with a flame ionization detector. UV/Vis measurements were carried out with a Varian Cary 50 Bio spectrophotometer controlled by Cary WinUV software. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL. X-ray diffraction studies were carried out in the EPFL Crystallographic Facility. Data collections were performed at 140(2) K on a four-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire charge-coupled device. Data were reduced by CrysAlis PRO.[36] The absorption correction was applied by using a semiempirical method.[37] The SHELXTL program was used for structure solution, refinement, and geometrical calculation.[38] Cyclic voltammetric measurements were recorded in a glove box by an IviumStat electrochemical analyzer that was connected to a glassy carbon working electrode (surface area $=0.07\ cm^2$), a platinum wire auxiliary electrode, and an $Ag/AgNO_3$ (0.01 M) reference electrode filled with acetonitrile and $[nBu_4][PF_6]$ (0.1 M). All potentials were referenced to Fc/Fc^+ as internal standard. The temperature of reactions below room temperature was regulated by a Julabo FT-902 chiller.

Synthetic methods

*$[(^{Me}NN_2)MgCl(thf)]$ (**5**)*: A 3.0 M solution of CH_3MgCl in THF (0.26 mL, 0.78 mmol) was added to a solution of $H^{Me}NN_2$ (200 mg, 0.78 mmol) in THF (5 mL) under stirring. After 1 h, the solvent was evaporated and the solid residue was dissolved in a minimum quantity of benzene and filtered. Pentane was added to the filtrate and a precipitate was formed. The precipitate was collected, washed with pentane, and dried under vacuum (204 mg, 83 %).

^1H NMR (400.13 MHz, C_6D_6): $\delta=7.84$ (dd, $J=8.2$, 1.0 Hz, 2H), 7.12 (td, $J=7.2$, 1.7 Hz, 2H), 7.00 (dd, $J=7.9$, 1.4 Hz, 2H), 6.64 (td, $J=7.9$, 1.4 Hz, 2H), 3.54 (b, 4H; THF), 2.55 (s, 12H), 1.31 ppm (b, 4H; THF); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta=147.1$ (C^{arom}), 142.2 (C^{arom}), 127.1 ($C^{arom}H$), 119.9 ($C^{arom}H$), 114.9 ($C^{arom}H$), 113.9 ($C^{arom}H$), 68.3 ($CH_2CH_2O^{THF}$), 45.8 ($N(CH_3)_2$), 25.2 ppm ($CH_2CH_2O^{THF}$).

*$[(^{Me}NN_2)Ni(OAc)]$ (**6**)*: $[(^{Me}NN_2)NiCl]$ (**1**; 50 mg, 0.14 mmol) was dissolved in THF (5 mL) and 10 mol excess of NaOAc (118 mg, 1.40 mmol) was added. This mixture was vigorously stirred for 6 h and the resulting precipitate was isolated by filtration. A 10 mol excess of NaOAc (118 mg, 1.40 mmol) was added again and the mixture was stirred for another 6 h. The precipitate was isolated by filtration and the filtrate was evaporated. The green solid residue was washed with a mixture of pentane and benzene (5:1, 3×2 mL), and dried under vacuum (42 mg, 79 %). Single crystals suitable for X-ray crystallography were obtained by cooling a toluene/pentane solution (1:4) of **6** at −35 °C.

^1H NMR (400.13 MHz, C_6D_6): $\delta=7.30$ (d, $J=8.4$ Hz, 2H), 6.95 (t, $J=8.1$ Hz, 2H), 6.48 (dd, $J=7.7$, 1.0 Hz, 2H), 6.32 (t, $J=7.7$ Hz, 2H), 2.64 (s, 12H; $N(CH_3)_2$), 2.04 ppm (s, 3H; $COCH_3$); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta=175.3$ ($COCH_3$), 146.6 (C^{arom}), 145.8 (C^{arom}), 127.7 ($C^{arom}H$), 119.6 ($C^{arom}H$), 116.0 ($C^{arom}H$), 115.3 ($C^{arom}H$), 49.3 ($N(CH_3)_2$), 24.6 ppm ($COCH_3$); elemental analysis calcd (%) for $C_{18}H_{23}N_3NiO_2$: C 58.10, H 6.23, N 11.29; found: C 57.44, H 6.22, N 11.37.

*$[(^{Me}NN_2)Ni(OTf)]$ (**7**)*: A solution of AgOTf (73 mg, 0.39 mmol) in THF (2 mL) was added to a solution of **1** (100 mg, 0.39 mmol) in THF (3 mL). The resulting solution was stirred for 30 min and then the white precipitate of AgCl was isolated by filtration. The filtrate was evaporated and the brown solid residue was washed with pentane (3 mL) and dried under vacuum (99 mg, 75 %). Single crystals suitable for X-ray crystallography were obtained by diffusion of pentane into a benzene solution of **7**.

^1H NMR (400.13 MHz, $[D_6]DMSO$): $\delta=7.27$ (dd, $J=8.2$, 1.4 Hz, 2H), 7.13 (dd, $J=8.2$, 1.7 Hz, 2H), 6.98 (td, $J=7.5$, 1.4 Hz, 2H), 6.84 (m, 2H), 2.60 ppm (s, 12H); ^{13}C NMR (100.62 MHz, $[D_6]DMSO$): $\delta=143.4$, 137.3, 128.8, 124.1 ($C^{arom}H$), 120.5 ($C^{arom}H$), 120.0 ($C^{arom}H$), 115.4 ($C^{arom}H$), 44.1 ppm ($N(CH_3)_2$); elemental analysis calcd (%) for $C_{17}H_{20}N_3NiSO_3F_3$: C 44.18, H 4.36, N, 9.09; found: C 44.76, H 4.44, N 9.14.

*$[(^{Me}NN_2)Ni(CH_3CN)]BF_4$ (**8**)*: A solution of $AgBF_4$ (56 mg, 0.39 mmol) in CH_3CN (2 mL) was added to a solution of **1** (100 mg, 0.39 mmol) in CH_3CN (3 mL). The resulting green solution was stirred for 30 min and then the white precipitate of AgCl was isolated by filtration. The filtrate was evaporated and the green solid was washed with benzene (2 mL) and pentane (3 mL), and dried under vacuum (119 mg, 94 %). Single crystals suitable for X-ray crystallography were obtained by cooling a CH_3CN/ether (1:4) solution of **8** at −35 °C.

^1H NMR (400.13 MHz, CD_3CN): $\delta=7.32$ (dd, J$=7.8$, 1.0 Hz, 2H), 7.24 (m, 4H), 6.49 (m, 2H), 3.54 ppm (s, 12H); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta=7.40$ (dd, $J=8.2$, 1.0 Hz, 2H), 7.05 (m, 4H), 6.59 (td, $J=8.2$, 1.0 Hz, 2H), 2.98 (s, 12H; $N(CH_3)_2$), 2.60 ppm (br, 3H; CH_3CN); ^{13}C NMR (100.62 MHz, CD_3CN): $\delta=145.7$ (C^{arom}), 142.6 (C^{arom}), 129.5 ($C^{arom}H$), 121.4 ($C^{arom}H$), 119.3 ($C^{arom}H$), 118.8 ($C^{arom}H$), 50.4 ppm ($N(CH_3)_2$); elemental analysis calcd (%) for $C_{18}H_{23}N_4NiBF_4$: C 49.03, H 5.26, N 12.71; found: C 48.97, H 5.34, N 12.26.

*$[(^{Me}NN_2)Ni(OMe)]$ (**9**)*: Compound **1** (150 mg, 0.43 mmol) was dissolved in THF (2 mL) and a solution of NaOMe (23 mg, 0.43 mmol) in THF (1 mL) was added. The mixture was stirred for 1 h and the solvent was evaporated. The solid residue was dissolved in benzene and the resulting solution was filtered to remove NaCl. The filtrate was evaporated to give **9** as the crude product. It was recrystallized from toluene/pentane (3:1, 2 mL) at −35 °C (105 mg, 71 %).

^1H NMR (400.13 MHz, C_6D_6): $\delta=7.39$ (dd, $J=8.5$, 1.4 Hz, 2H), 6.95 (td, $J=7.2$, 1.4 Hz, 2H), 6.59 (dd, $J=7.9$, 1.4 Hz, 2H), 6.40 (td, $J=7.2$, 1.4 Hz, 2H), 3.35 (s, 3H; OCH_3), 2.53 ppm (s, 12H; $N(CH_3)_2$); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta=147.9$ (C^{arom}), 147.5 (C^{arom}), 128.0 ($C^{arom}H$), 119.8 ($C^{arom}H$), 114.9 ($C^{arom}H$), 114.1 ($C^{arom}H$), 53.8 (OCH_3), 49.0 ppm ($N(CH_3)_2$); elemental analysis calcd (%) for $C_{17}H_{23}N_3NiO$: C 59.34, H 6.74, N 12.21; found: C 59.26, H 6.62, N 11.82.

*Reaction of $[(^{Me}NN_2)NiMe]$ (**2**) with alkyl monohalides*: In a typical experiment, **2** (0.015 mmol) was loaded into an NMR tube along with C_6D_6 (0.6 mL). Alkyl halide (0.15 mmol, 10 equiv or 0.015 mmol, 1 equiv) was added to this solution and the reaction was periodically monitored by ^1H NMR spectroscopy. If the reaction did not occur at room temperature, the solution was heated at 60 or 100 °C. The identification and quantification of products were achieved by ^1H NMR spectroscopy. The results are summarized in Table S1 in the Supporting Information. Yields are referred to the formation of Ni^{II} halides. For example, reaction of **2** with 10 equivalents of CH_3CH_2Cl in benzene took place at room temperature and finished within 18 h to give **1** (near quantitative) and propane (35% remained in solution). Heating a benzene solution of **2** in the presence of 10 equivalents of propyl chloride at 60 °C for 18 h gave 33% conversion; at 100 °C the reaction finished in 4 h and produced **1** (near quantitative) and *n*-butane (30% remained in solution). The yields of the propane and butane were determined by NMR integration references to **1**. ^1H NMR (in C_6D_6): propane (0.82, 1.25 ppm), butane (0.85, 1.25 ppm).

Reaction of [($^{Me}NN_2$)NiMe] (**2**) *with alkyl polyhalides*: Same as the reaction with alkyl monohalides. The identification of organic products was made by GC–MS or NMR spectroscopy, and quantification was made by GC, with decane or dodecane as an internal standard. See the Supporting Information for GC–MS, NMR, and GC data.

Typical procedure for the synthesis of R-R′ from R′-X and RMgCl: A vial was charged with a certain amount of **1**, R′-X, and DMA (0.75 mL). After the solution reached the desired temperature, a solution of RMgCl in THF was added dropwise under vigorous stirring. The reaction was allowed to proceed for a certain period of time, and then the solution was warmed or cooled to room temperature. A mixture of distilled water (15 mL), hydrochloric acid (25%, 1 mL), and dodecane (internal standard, 60 μL, 0.265 mmol) or decane (internal standard, 60 μL, 0.422 mmol) was added to the reaction mixture. The resulting solution was extracted with diethyl ether (3×10 mL) and the organic phase was separated, dried over $MgSO_4$, and filtered. The loading of the catalyst and the reaction time are shown in Table 4 and Table 5. The organic products were identified by GC–MS, and the yields were determined by GC with decane or dodecane as the internal standard. See the Supporting Information for GC–MS, NMR, and GC data.

Typical procedure for the synthesis of RCH_2R from CH_2Cl_2 and RMgCl: A vial was charged with a certain amount of **1** and CH_2Cl_2 (1.5 mL). After the solution reached the desired temperature, a solution of RMgCl was added dropwise under vigorous stirring. The reaction was allowed to proceed for a certain period of time, and then the solution was warmed to room temperature. A mixture of distilled water (15 mL), hydrochloric acid (25%, 1 mL), and dodecane (internal standard, 60 μL, 0.265 mmol) was added to the reaction mixture. The resulting solution was extracted with diethyl ether (3×10 mL) and the organic phase was separated, dried over $MgSO_4$, and filtered. The loading of the catalyst and the reaction time are shown in Table 6. The organic products were identified by GC–MS. The yield of RCH_2R was determined by GC with decane or dodecane as the internal standard. See the Supporting Information for GC–MS, NMR, and GC data.

Crystallographic details for [($^{Me}NN_2$)Ni(OAc)] (6): A total of 30213 reflections ($-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-39 \leq l \leq 39$) were collected at T=140(2) K in the range of 2.76 to 26.37° of which 6862 were unique (R_{int}=0.0349); $Mo_{K\alpha}$ radiation (λ=0.71073 Å). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.615 and −0.487 eA^{-3}, respectively. The absorption coefficient was 1.166 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F)$=0.0441, $wR(F^2)$=0.1046, and GOF=1.049 ($I>2\sigma(I)$). $C_{18}H_{23}N_3NiO_2$; M_w=522.58; space group $P2_12_12_1$; orthorhombic; a=8.3469(2), b=12.7857(4), c=31.5964(9) Å; V=3372.00(16) $Å^3$; Z=8; ρ_{calcd}=1.466 $Mg\,m^{-3}$.

Crystallographic details for [($^{Me}NN_2$)NiOTf] (7): A total of 16903 reflections ($-8 \leq h \leq 8$, $-17 \leq k \leq 17$, $-24 \leq l \leq 23$) were collected at T=140(2) K in the range of 2.80 to 26.37° of which 2107 were unique (R_{int}=0.0529); $Mo_{K\alpha}$ radiation (λ=0.71073 Å). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.340 and −0.388 eA^{-3}, respectively. The absorption coefficient was 1.129 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F)$=0.0344, $wR(F^2)$=0.0597, and GOF=1.076 ($I>2\sigma(I)$). $C_{17}H_{20}F_3N_3O_3SNi$; M_w=462.13; space group $Pnma$; orthorhombic; a=7.0081(3), b=14.5619(6), c=19.5131(9) Å; V=1991.34(15) $Å^3$; Z=4; ρ_{calcd}=1.541 $Mg\,m^{-3}$.

Crystallographic details for [($^{Me}NN_2$)Ni(NCCH$_3$)]BF$_4$ (8·BF$_4$): A total of 31050 reflections ($-22 \leq h \leq 21$, $-7 \leq k \leq 7$, $-47 \leq l \leq 47$) were collected at T=140(2) K in the range of 2.80 to 26.37° of which 7783 were unique (R_{int}=0.0467); $Mo_{K\alpha}$ radiation (λ=0.71073 Å). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.353 and −1.632 eA^{-3}, respectively. The absorption coefficient was 1.041 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F)$=0.0613, $wR(F^2)$=0.1108, and GOF=1.268 ($I>2\sigma(I)$). $C_{18}H_{23}BF_4N_4Ni$; M_w=440.92; space group $Pca2_1$; orthorhombic; a=17.8380(7), b=5.7806(2), c=37.8747(12) Å; V=3905.4(2) $Å^3$; Z=8; ρ_{calcd}=1.500 $Mg\,m^{-3}$.

CCDC 704456 (**7**), 704457 (**6**), and 704458 (**8·BF$_4$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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