Unravelling the Mechanism of Nickel Mediated Cross-Electrophile- Electrophile Coupling Between Katritzky Salts and Acid Chlorides

Ramadevi Pilli,[a] Bincy Chindan,[a] and Ramesh Rasappan*[a]

Dedicated to Professor Oliver Reiser on the occasion of his 60th birthday

Modern nickel-mediated cross-electrophile coupling reactions devoid of organometallic nucleophiles have garnered a great deal of interest due to their ability to enhance functional group compatibility. Despite the recent advances in the field, various mechanistic pathways, such as radical chain and sequential oxidative addition, in addition to finding the active nickel species and reductant, render the reaction complex. Although the reduction of Ni(II) complexes by heterogeneous Mn could produce either Ni(I) or Ni(0) species, the latter is more generally proposed as an active species. Likewise, Ni(I) mediated reduction of pyridinium salts is commonly invoked to generate the transient alkyl radicals. In stark contrast, we present a comprehensive mechanistic examination and experimental evidence for the intermediacy of Ni(I) species, a synergistic reduction of pyridinium salts by Ni(I) and Mn. Using a combination of kinetic analysis, control experiments, and spectroscopic methods, the rate-limiting reductive alkylation and resting state Ni(II) species have been identified.

Introduction

Nickel-mediated cross-electrophile coupling reactions have garnered a considerable deal of interest since the technique eliminates the need for a highly reactive nucleophilic coupling partner (Scheme 1a).[1] Due to nickel's stagnant β-hydride elimination, $C(sp^3)$ coupling partners are also well-suited for use in nickel catalysis. The group of Weix,[2] Gosmini[3] and Gong[4] have made significant strides in the recent years. An in-depth understanding of the mechanistic process could help chemists build innovative and efficient catalytic systems for analogous cross-coupling reactions; however, the range of oxidation states nickel can adopt[5] and the plethora of mechanistic pathways impede the investigation. Due to the involvement of two different electrophiles, cross-electrophile coupling reactions are known to work via two distinct mechanisms: the radical chain mechanism and sequential reduction (Scheme 1b). While the majority of the literature, including Reisman,[6] Nevado,[5l,7] Diao,[8] Shu[9] and Oestreich[10] reported sequential double oxidative addition, two independent works from the groups of Weix[11] and Gong[12] proposed radical chain mechanism. Hegedus et al. reported the pioneering work on nickel-mediated radical chain reaction at the beginning of 1975.[13] Additionally, the active nickel species generated by the reduction of Ni(II) with Mn could be either Ni(I) or Ni(0) species (Scheme 1c).
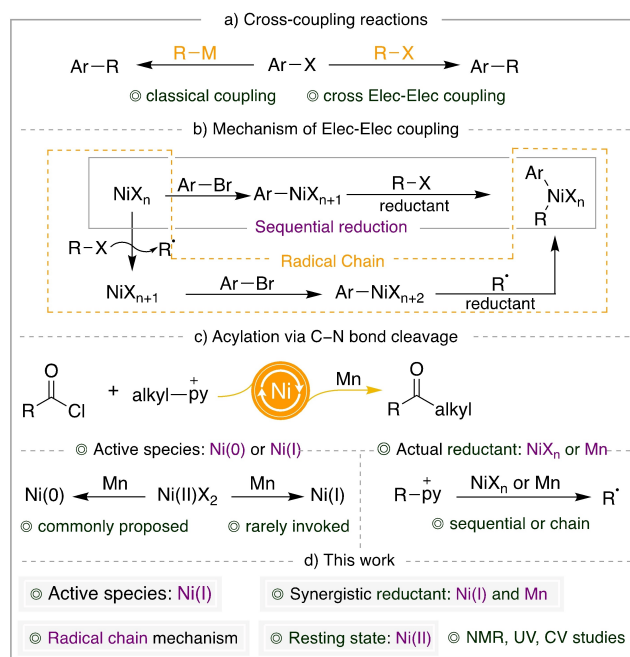
Scheme 1. Cross-electrophile coupling.

A vast majority of published research postulate the formation of Ni(0) species upon the reduction of Ni(II) complex by Mn,[9a,c,11,14] a theory based on the high reduction potential of Mn. Our group has recently developed a cross-electrophile coupling of pyridinium salts and acid chlorides by cleaving the C–N bond (Scheme 1c).[15] Despite the fact that a feasible mechanistic route involving both mechanisms was proposed, intriguingly, no distinction could be made between the radical and stepwise pathways (Scheme 1b). In addition, the active

[a] R. Pilli, B. Chindan, Dr. R. Rasappan
School of Chemistry,
Indian Institute of Science Education and Research Thiruvananthapuram
Thiruvananthapuram, Kerala, India
E-mail: rr@iisertvm.ac.in
http://rameshrasappan.com

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nickel species produced by the reduction of Ni(II) with Mn was unknown (Scheme 1a). Likewise, the actual reductant during the formation of alkyl radical from pyridinium salt is an intriguing topic, as nickel and manganese are supported as an actual reductant (Scheme 1c). Once more, contradictory findings are reported in the literature.[14c,f,16] Thus, a systematic study is required on distinguishing the radical chain reaction from sequential reduction, identify the active nickel species and the actual reductant. As part of our ongoing study on nickel-mediated cross-coupling reactions[15,17] and mechanistic investigations,[17b] we present here our experimental and spectroscopy-based mechanistic studies, including NMR, UV, and CV. Our finding reveals the active Ni(I) species, a radical chain mechanism, a synergistic reduction of pyridinium salts by
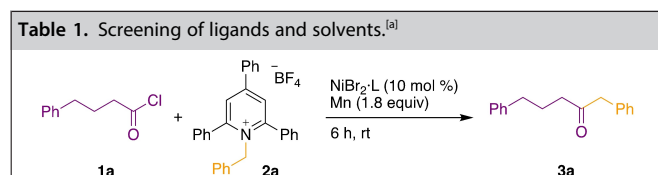
Ni(I) and Mn, the rate-limiting reductive alkylation and the resting state Ni(II) species.

Results and Discussion

Prior to the mechanistic investigations, we carried out cross-electrophile coupling of Katritzky salt **2a** and acid chloride **1a** by varying ligands and solvents since the stability of the intermediate complex can be influenced by the ligands (Table 1). The selection of ligands was not arbitrary; rather, it was guided by the stability of subsequent complexes and their compatibility with a variety of spectroscopic techniques. Under the optimal condition previously reported,[15] we obtained ketone **3a** in excellent yield (entry 1, Table 1). The reaction was equally efficient when ligand bipyridine was replaced by 1,10-phenanthroline (entry 2); however, the reaction offered moderate yield when phen* (2,9-di-sec-butyl-1,10-phenanthroline) was employed (entry 3). As shown in entries 4 and 5, change in solvent had a substantial effect on the reaction, with DMA alone producing moderate to poor yields.
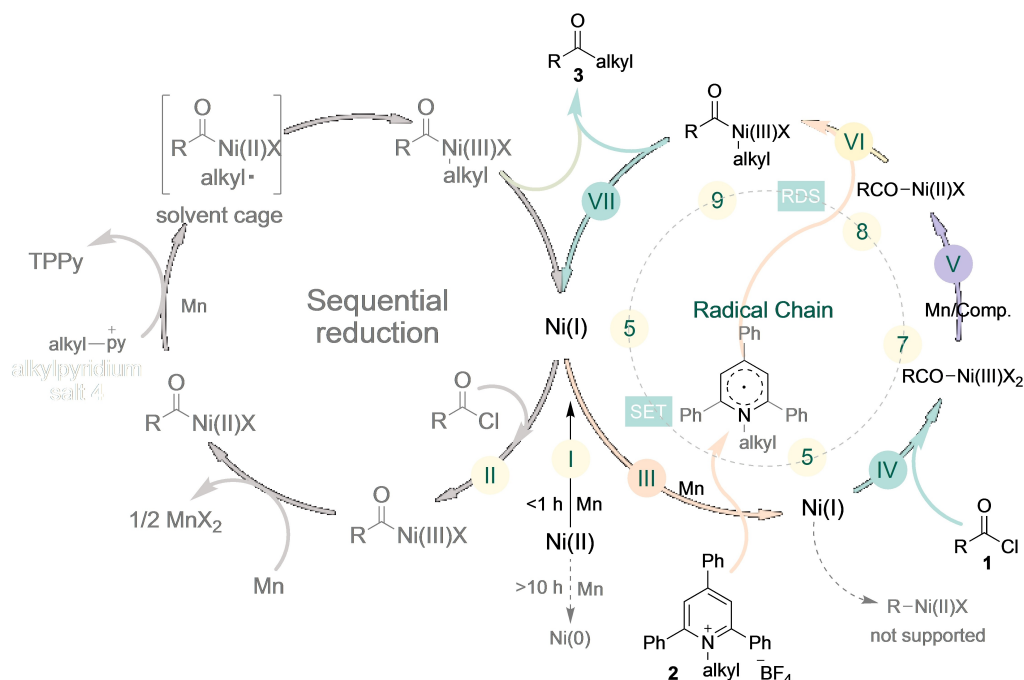
Identifying the active nickel species: At the outset of our mechanistic studies, experiments were designed to identify the actual nickel species which is formed during the reduction of Ni(II) complex **6b** by Mn (step I, Figure 1). As mentioned earlier, a wealth of literature data supports the formation of Ni(0) species upon the reduction of Ni(II) complex by Mn,[9,11,14,18] which is consistent with the high reduction potential of Mn. An exception to this tendency was recently reported by Schoenebeck et al. based on DFT calculations in which a Ni(I)-dimer complex was postulated when Ni(II)-NHC complex was reacted

Table 1. Screening of ligands and solvents.[a]

Entry	Ni(II) source	Solvent	3a [%][b]
1	Ni(II)Br$_2$·bpy **6a**	ACN+DMA (19:1)	93
2	Ni(II)Br$_2$·phen **6b**	ACN+DMA (19:1)	94
3	Ni(II)Br$_2$·phen* **6c**	ACN+DMA (19:1)	54
4	Ni(II)Br$_2$·phen **6b**	DMA	58
5	Ni(II)Br$_2$·phen* **6c**	DMA	21

[a] Reaction conditions: 0.295 mmol of **2a**, 0.59 mmol of **1a**, 0.0295 mmol of [Ni], 0.531 mmol of Mn, 0.1 M solvents. [b] determined by GC. bpy = bipyridine, phen = 1,10-phenanthroline, phen* = 2,9-di-sec-butyl-1,10-phenanthroline.

Figure 1. Mechanistic proposal.

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with Mn.[5i] The group of Lautens proposed an indirect Ni(I)-Ni(III) catalytic cycle since Ni(0) failed to catalyze the reaction.[19] In addition, the instability of in-situ generated Ni(0) species makes their identification difficult. The reduction potentials of Ni(II)Br$_2$·phen complex **6b**, MnBr$_2$ and pyridinium salt **2a** were determined by cyclic voltammetry, and the results are presented in Table 2. According to the aforementioned literature and the reduction potentials listed in Table 1, Mn with higher reduction potential (−2.00 V) could produce Ni(0) when combined with Ni(II) complex.

Ni(II)Br$_2$·phen* **6c** was treated with either Mn or Zn in an effort to gather additional insight, and the mother liquor from these reaction mixtures were subjected to UV analysis. Strikingly, both Mn and Zn exhibited similar UV absorption (Figure 2a). It is anticipated that Zn will produce Ni(I)-complex due to its lesser propensity for reduction.[8] In addition, cyclic voltammogram of the mixture resulting from the reaction of Ni(II)Br$_2$·phen **6b** and Mn exhibited Ni(I)→Ni(0) and Ni(0)→Ni(−1) cathodic peaks, confirming the presence of Ni(I) species (see SI-13). This outcome was unanticipated, as the literature on Mn mediated reduction of Ni(II) complex,[9,11,14,18] unanimously support the formation of Ni(0) species.

Further attempts to crystallize Ni(I)·phen complex **5b** were unsuccessful; this may be due to the instability of Ni(I)·phen complex **5b**. It is known in the literature[20] that a bulkier substitution on N- or P-based ligands can substantially improve the stability of Ni(I) complex. Fortunately, we were able to

isolate and obtain crystal structure for the Ni(I)·phen* complex **5c** (SI-10).[8] Although, our results support the formation of Ni(I) complex, the formation of minuscule quantity of Ni(0) complex and its participation in catalysis cannot be ruled out without additional studies.

Our initial attempts to determine the formation of Ni(0) complex using UV spectroscopy were notoriously difficult due to inconsistent results, which can be related to the poor solubility or instability of Ni(0) species. Fortunately, cyclic voltammetry allowed us to monitor the formation of Ni(I) and Ni(0) species when Ni(II)Br$_2$·phen **6b** and Mn were combined. The reaction was probed for twenty hours, and the results are plotted in Figure 2b. (see SI-15) It is apparent from Figure 2b that the formation of Ni(0) requires considerably longer time (> 10 h); however, under the optimal condition (Table 1, entry 1), the product **3a** formation reaches saturation in less than an hour (Figure 7a). These data contradict that Ni(0) species **4** is an active catalyst and indicate that Ni(I) complex is the actual catalyst (Figure 2). Having identified the active Ni(I) species **5**, we set out to find the actual catalytic cycle. As mentioned earlier, both sequential double oxidative addition (Figure 1) and radical chain reaction mechanism (Figure 1) are known in the literature. The generated Ni(I) species **5** can either undergo oxidative addition with acid chloride **1** (step II, Figure 1) or reduce pyridinium salt **2** to yield the corresponding alkyl radical **10** (step III, Figure 1). Notably, Weix et al. reported that the two electron oxidative addition of Ni(0) with PhI is 4.7 times faster than the one electron reduction of Csp^3−I to produce alkyl radical, hence suggesting sequential double oxidative addition.[11] The group of Nevado[5i] and Diao[8] also reported similar findings based on theoretical calculations. We carried out the standard reaction with stoichiometric Ni(II)Br$_2$·phen **6b** and monitored the reaction for the consumption of both acid chloride **1a** and pyridinium salt **2a**. While **2a** consumed more rapidly with in-situ generated Ni(I)Br·phen **5b**, a gradual consumption of **1a** was observed in conjunction with the gradual formation of ketone **3a** (Figure 3a). This result supports the reduction of pyridinium salt **2a** in-prior to the oxidative addition.

Although, we confirmed the reduction of pyridinium salt **2a** occurs in the initial stage, the reductant might be either Ni(I) or Mn (Step III, Figure 1). From Table 2, it is apparent that the pyridinium salt **2a** can be reduced by either in-situ generated

Table 2. Cyclic voltammetry studies. [a]

Entry	Complex/Compound	Cathodic peaks	E_p
1	Ni(II)Br$_2$·phen **6b**	Ni(II) to Ni(I)	−1.08 V vs. SCE
		Ni(I) to Ni(0)	−1.25 V vs. SCE
		Ni(0) to Ni(−1)	−1.90 V vs. SCE
2	Ni(I)·phen **5b**	Ni(I) to Ni(0)	−1.20 V vs. SCE
		Ni(0) to Ni(−1)	−1.85 V vs. SCE
3	MnBr$_2$		−2.00 V vs. SCE
4[b]	ZnBr$_2$		−1.02 V vs. SCE[8]
5	Pyridinium salt **2a**		−0.9 V vs. SCE
6	Pyridinium salt **2c**		−0.9 V vs. SCE

[a] In DMA at 25 °C, NBu$_4$PF$_6$ as electrolyte, Fc$^+$/Fc as internal reference, [b] $E_{p/2}$.
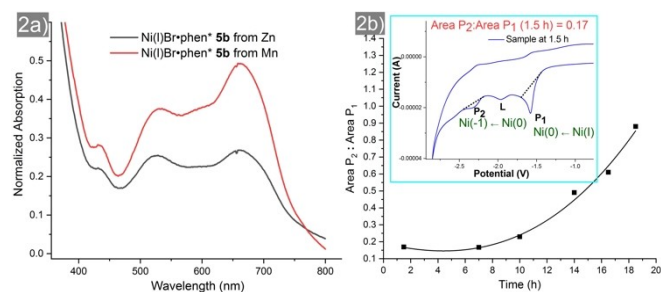
Figure 2.
[a] Reduction of Ni(II)Br$_2$·phen* with Zn/Mn [b] Plot of Time vs. Area P$_2$:Area P$_1$. [Inset] CV of the reaction crude resulting from the reduction of Ni(II)Br$_2$·phen with Mn at 1.5 h, L is free ligand (see SI-14 for the CV of samples at different time intervals).
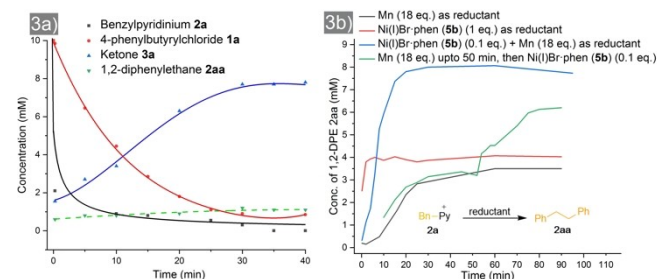
Figure 3. [a] Reaction profile for the consumption of **1a** and **2a** with stoichiometric **6b** and Mn. Conditions: **1a** (0.301 mmol), **6b** (1 eq.), **2a** (1 eq.) and Mn (18 eq.) [b] Dimerization of pyridinium salt **2a**.

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Ni(I) complex **5b** (−1.25 V) or Mn (−2.00 V). Although Mn has higher reduction potential than Ni(I) complex **5b**, it is important to note that the Ni(I) complex **5b** forms a homogeneous mixture in the reaction media, whereas Mn is heterogeneous, which may result in a less effective transfer of electrons. Rueping et al. reported, based on DFT calculations, that Ni(I) complex reduces the pyridinium salt.[14c] A similar finding is also reported by Watson[16a] and Li[14f] co-workers. Recently, Martin and co-workers studied[16b] the consumption of cyclohexyl pyridinium salt in presence of TEMPO and revealed poor conversion (< 5%) when pyridinium salt was treated with either Ni(0)- or Ni(I)-complex, whereas Mn offered the TEMPO adduct, confirming that Mn is an actual reductant.

Experiments were designed to probe the consumption of pyridinium salt **2a**. The dimerization of **2a** in the presence of either the in-situ prepared Ni(I) complex **5b** (1 eq.) or Mn (18 eq.) was monitored by periodical collection of aliquots from the reaction. Figure 3b demonstrates that Ni(I) complex **5b** accelerated the dimerization of pyridinium salt **2a** than Mn. Surprisingly, the combination of both Ni(I) complex **5b** (1 eq.) and Mn (18 eq.) was superior to Ni(I) complex **5b** or Mn alone. This result is in stark contrast to that of Martin and co-workers, who identified that Mn is the actual reductant. Notably, they employed an unactivated cyclohexyl pyridinium salt in conjunction with TEMPO under reflux conditions. Likewise, we have also subjected the cyclohexyl pyridinium salt **2c** to the TEMPO trap experiments and the outcomes are described in Table 3. To our surprise, we discovered that the combination of Ni(I) complex **5b** (1 eq.) and Mn (18 eq.) yielded the TEMPO adduct, although neither Mn nor Ni(I) alone can induce the formation of TEMPO adduct at room temperature (repeated twice). While Mn alone can promote the formation of TEMPO adduct **12** at 70°C, the optimal condition does not require heating (Table 1). These findings demonstrate that both Ni(I) complex **5** and Mn reduce pyridinium salts in a synergistic manner. Formation of bimetallic complex between nickel and manganese cannot be excluded. It is worth to note that an accelerated dimerization of **2a** was observed in the absence of acid chloride **1a** (Figure 3b), whereas no dimerization was observed under the standard condition in the presence of **1a** (Table 1, entry 1), demonstrat-

ing a faster oxidative addition of acid chloride to Ni(I) than the radical dimerization.

Upon the reduction of pyridinium salt **2**, an alkyl radical **10** is generated via C—N bond cleavage (step III, Figure 1), in conjunction with the formation of Ni(II) species **6**, which is then reduced to Ni(I) species **5** (step III, Figure 1). The intermediate species **5** could undergo oxidative addition with acid chloride **1** to generate the intermediate RCONi(III)X₂ complex **7** (step IV in Figure 1), which is again reduced to generate RCONi(II)X complex **8** (step V, Figure 1). Experiments were devised to examine the viability of Ni(II) intermediate **8** during the course of reaction. Initially, we carried out UV analysis, while Ni-(II)Br₂·phen* **6c** gave an absorption peak at 517 nm, Ni(0)·phen* (847 nm, 655 nm, 548 nm and 460 nm-shoulder)[21] (SI-12) and Ni(I)·phen* **5c** (634 nm, 523 nm-shoulder and 426 nm) exhibited multiple absorption peaks as described in the literature (Figure 2a).[8] The in-situ generated RCONi(II)X·phen* **8ac** from the reaction of Ni(0)·phen* **4c** and acid chloride **1a** displayed a strong absorption at 500 nm (Figure 4b); a similar absorption was seen when Ni(I)·phen* **5c** was reacted with acid chloride **1a** in the presence of Mn (Figure 4c). These results are consistent with the formation of transient RCONi(II)X·phen* species **8ac** in the reaction media. The UV spectrum of the mixture from the reaction of Ni(I)·phen* **5c** and **1a** (stirred for < 1 min. without Mn) exhibited a broad absorption band with λ_{max} at 733 nm, 655 nm-shoulder, and 441 nm (Figure 4d); however, to our surprise, the same reaction mixture gave an absorption peak at 500 nm after being stirred for 10 min. at rt, which is an RCONi(II)X·phen* complex **8ac** rather than RCONi(III)X₂·phen* complex **7ac** (Figure 4d).

To gain further insights, we sought to utilize ¹⁹F NMR spectroscopy. The reaction of Ni(0)dtbpy **4d** and 4-fluorobenzoyl chloride **1b** generated ArCONi(II)X **8bd**, which exhibited a resonance peak at −109.3 ppm[22] (Figure 5a). As expected, the standard reaction mixture with acid chloride **1b** likewise gave the same peak (associated with Ni(II) species), confirming that the resting state of the catalyst is ArCONi(II)X **8bd** (Figure 5b). This also supports the radical chain mechanism is operative. Unexpectedly, the same peak appeared when the in-situ-generated Ni(I)·dtbpy* **5d** reacted with acid chloride **1b** in the absence of Mn (Figure 5c), and a similar result was obtained in UV analysis. We believe that the generated ArCONi(III)X₂ complex **7bd** comproportionates with a second equivalent of Ni(I) species **5d** to produce Ni(II) complex **8bd** (Figure 5c). The
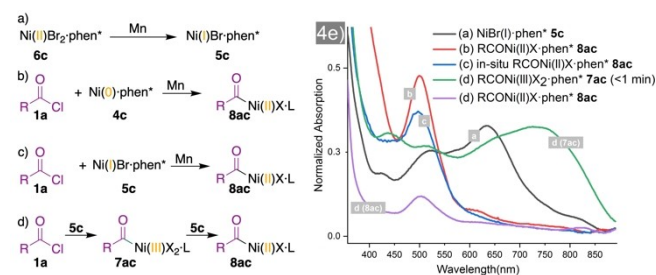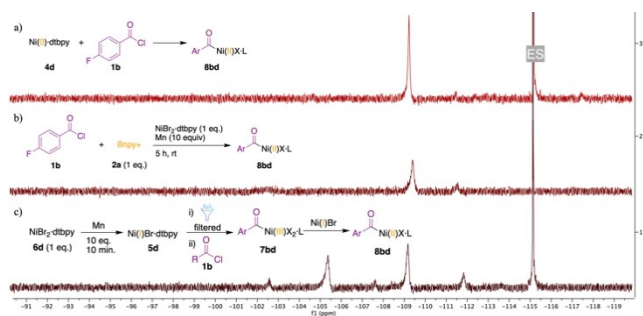
Table 3. TEMPO trap experiments. [a]

entry	reductant	temp.	12 (%)[b]	TPPy (%)[b]
1[c]	Ni(I) **5b** (1 eq.)	rt	ND	ND
2[c]	Mn (18 eq.)	rt	6	< 5
3	Ni(I) **5b** + Mn	rt	51	79
4[d]	Ni(I) **5b** (1 eq.)	70°C	< 5	35
5[d]	Mn (18 eq.)	70°C	58	> 99

[a] 0.0758 mmol of **2c**, 1.37 mmol of Mn, 0.0758 mmol of Ni(I), 0.05 M DMA, [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard, [c] average of two repeated reactions, **5b** (10 mol%) and Mn (18 eq.), [d] 24 h.

Figure 4. UV spectra(a-d) corresponding to the respective reaction crudes.

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Figure 5. ^{19}F NMR studies corresponding to the respective reaction crudes from schemes [a-c]. ES: 1-chloro-4-fluorobenzene as external reference.

comproportionation of nickel species is known in the literature.[22–23] Recently, the group of Doyle demonstrated the comproportionation of Ni(III) and Ni(I) complexes to generate Ni(II) species, which occurred due to the unstable nature of Ni(III) species and can be prevented with a suitable stabilizing ligand.[23f] In this context, the Nocera laboratory has recently demonstrated the comproportionation of Ni(I) and Ni(III) species that led to the formation of inactive Ni(II) species.[23e] While attempting to crystallize an analogous $^{t}BuCONi(III)X_2 \cdot phen^*$ complex **7cc**, generated from the reaction of Ni(I)·phen* **5c** and pivaloyl chloride **1c**, we obtained a Ni cluster **13** (Figure 6a), an off-cycle species produced with trace of moisture.[24–25] A further reduction of ArCONi(II)X **8bd** to ArCONi(I) has been ruled out, as the peak at -109.3 ppm persisted after re-treatment of complex **8bd** with Mn (SI-17). Of note was that the rapid reduction of Ni(II) to Ni(I) by Mn and the subsequent faster oxidative addition with acid chloride indicate that neither Ni(II) **6d** nor Ni(I) **5d** would exist for long enough, and the ^{19}F NMR study confirmed Ni(II) intermediate **8bd** is the resting state.

Using cyclic voltammetry, the oxidative addition of Ni(I) complex with acid chloride **1a** (step IV, Figure 1) was investigated. Ni(II)Br₂·phen **6b** exhibited three quasi reversible reduction peaks (Ni(II)→Ni(I), Ni(I)→Ni(0) and Ni(0)→Ni-ate; see Figure 6b). With the addition of 0.2 eq. of acid chloride **1a** to the same cell and performing one redox cycle, an increase in the current of the first reduction [Ni(II)→Ni(I)] had occurred with a slight cathodic shift (See SI-15). The disappearance of the
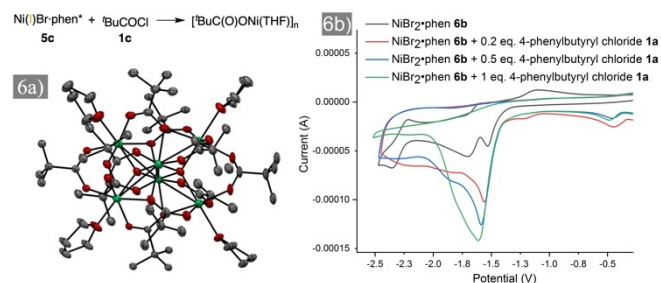
second and third reduction peaks, as well as the re-oxidation peaks can be attributed to the consumption of Ni(I) by chemical reaction with acid chloride **1a**. Similar results were obtained with increased equivalents of **1a** (0.5 or 1 eq.). These results demonstrate the intermediate Ni(I) complex **5b** undergoes oxidative addition with acid chloride **1a** (step IV, Figure 1).

The RCONi(II)X·L complex **8** could combine with the alkyl radical **10** present in the medium (step VII, Figure 1), resulting in the formation of R′(RCO)Ni(III)X·L complex **9**. To acquire additional insights, control experiments (Scheme 2) were designed, and the RCONi(II)X·phen complex **8ab** devoid of Mn was prepared from Ni(II)Br₂·phen **6b**, as depicted in Scheme 2b. As illustrated in Scheme 2a, the Ni(I) complex **5b** devoid of Mn was treated with stoichiometric pyridinium salt **2a** to generate transient benzylic radical **10**. As expected, when the intermediate Ni(II) complex **8ab** devoid of Mn was treated with the transitory benzylic radical **10** (Scheme 2d), we obtained 40% of the ketone **3a**. Pleasingly, similar results were obtained when the complex **8ab** was treated with pyridinium salt **2a** in the presence of Mn (Scheme 2e). In contrast, traces of product **3a** was observed when the mother liquor from the mixture of pyridinium salt **2a** and Mn (Scheme 2c) was treated with complex **8ab** as illustrated in Scheme 2f. These results may validate the oxidative alkylation of benzylic radical **10** to RCONi(II)X·phen* **8ab** to produce the intermediate complex **9** (step VI, Figure 1) and reaffirm that nickel is the actual reductant required to generate benzylic radical **10** from pyridinium salt **2a**.

Figure 7 depicts the reaction profile for the standard reaction at 0 °C. We have also performed same excess studies to verify the catalyst decomposition during reaction. Our experimental results indicate that the catalyst remains stable during the earliest stages of the reaction (See SI-5). Kinetic studies revealed first order behavior with respect to catalyst **6a**, acid chloride **1a** and pyridinium salt **2a**. These results imply that the rate determining step may be the oxidative alkylation (step VI, Figure 1) of alkyl radical **10** to the intermediate complex **8**, consistent with Ni(II) intermediate **8** being the catalyst's resting-state. Finally, reductive elimination of **9** delivers the product **3a** and reiterates the active nickel species as illustrated in Figure 1.
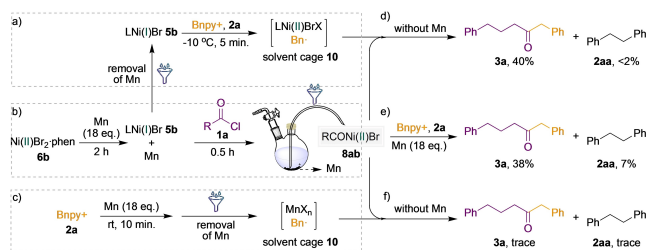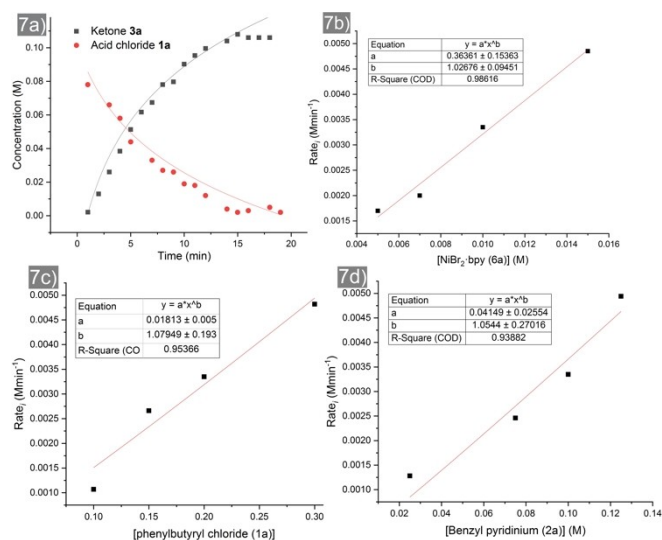

Figure 6. [a] X-ray crystal structure of decomposed nickel **13** at 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. [b] CVs of Ni(II)Br₂·phen **6b** and mixture of the same with varying amount of 4-phenylbutyryl chloride **1a**.

Scheme 2. Control experiments.

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Figure 7. [a] Time course plot for the consumption of **1a** and formation of **3a**. [0.4 mmol of **2a**, 0.8 mmol of **1a**, 0.04 mmol of NiBr$_2$·bpy **6a**, 0.72 mmol of Mn, 0.1 M ACN + DMA (19:1) at 0 °C] [b] Plot of rate$_i$ vs. [Ni(II)Br$_2$·bpy (**6a**)]. [c] Plot of rate$_i$ vs. [phenylbutyryl chloride (**1a**)]. [d] Plot of rate$_i$ vs. [benzyl pyridinium salt (**2a**)].

Conclusion

In summary, our experimental results demonstrated that the active catalyst being Ni(I) species rather than the typically proposed Ni(0) species. We also demonstrated that the reduction of Ni(II) by Mn for prolonged time can result in the generation of Ni(0). We identified a synergistic reduction of pyridinium salts by the combination Ni(I) species and Mn. Collectively, ^{19}F NMR, UV and CV studies, control experiments and kinetic data revealed the rate limiting reductive alkylation, Ni(II) species being the resting-state of the catalyst and the radical chain mechanism. We anticipate that our in-depth mechanistic study will aid in the comprehension of cross-electrophile coupling reactions.

Experimental Section

Procedure for screening ligands/solvents:

A flame dried Schlenk tube, equipped with a magnetic stir bar, was charged with appropriate pre-complex NiBr$_2$·L **6** (0.023 mmol, 5 mol%) and 2.7 mg of Mn (0.414 mmol, 1.8 eq.) from glove box. Under Schlenk conditions, ACN (2.2 mL) and DMA (0.12 mL) (Table 1, entries 1–3) or DMA (2.3 mL) (Table 1, entry 4–5) [0.1 M] were added followed by the addition of 84 mg of 4-phenylbutyryl chloride **1a** (0.46 mmol, 2 eq.), 112 mg of 1-benzyl-2,4,6-triphenyl-pyridin-1-ium tetrafluoroborate **2a** (0.23 mmol). The reactions were run for about 6 h. Decane was added as internal standard and the yields were calculated w.r.t. decane using GC.

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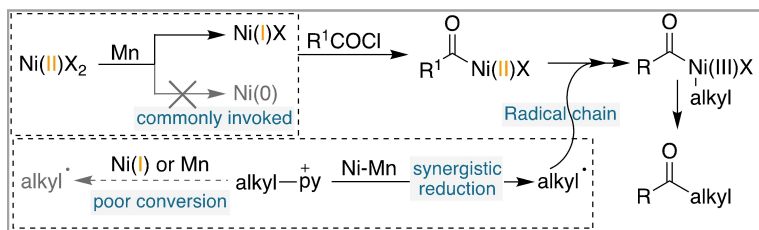
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RESEARCH ARTICLE

Experimental evidence for the intermediacy of Ni(I) species rather than the typically proposed Ni(0) species. Synergistic reduction of pyridinium salts by the combination Ni(I) species and Mn. Radical chain mechanism is operative.

R. Pilli, B. Chindan, Dr. R. Rasappan*

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Unravelling the Mechanism of Nickel Mediated Cross-Electrophile- Electrophile Coupling Between Katritzky Salts and Acid Chlorides

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Bincy Chindan
Dr. Ramesh Rasappan http://orcid.org/0000-0002-3209-3315
Ramadevi Pilli