JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 10 Oct 2018

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A Highly Reduced Ni-Li-Olefin Complex for Catalytic Kumada–Corriu Cross-Couplings

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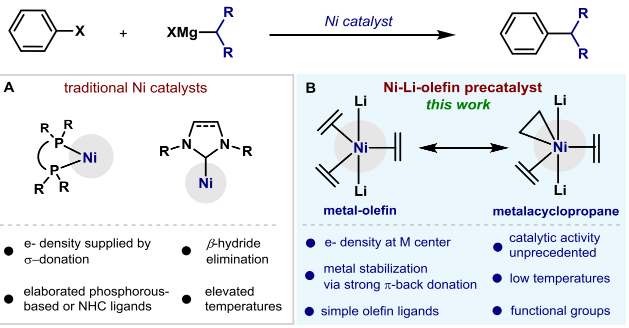
Supporting Information Placeholder

ABSTRACT: The catalytic activity of a highly reduced Ni catalyst in the context of a Kumada–Corriu cross-coupling has been studied. This nickel complex is characterized by its high electron-density, stabilized by simple olefin ligands in combination with two Li ions. Landmark reactivity has been found with this precatalyst which operates at cryogenic temperatures, thus allowing the presence of sensitive functionalities. Structural elucidation of oxidative addition intermediates and their reactivity suggest highly reduced species being operative in the C–C bond forming event.

In 1972 two seminal reports from Kumada and Corriu demonstrated the ability of Ni salts to catalyze the formation of C(sp^2)–C(sp^2) bonds.[1] Since then, the field of Ni-catalyzed cross-coupling has grown exponentially finding applications across the chemical sciences.[2] In this sense, the ability of Ni catalysts to efficiently maneuver across different oxidation states (Ni(0), Ni(I), Ni(II), Ni(III) or Ni(IV) species) has proved efficient and versatile, thus providing extremely powerful synthetic methodologies.[2] While other transition metals have been shown to efficiently catalyze Kumada-Corriu cross-couplings,[3-7] nickel salts have reign sovereign due to their efficiency with a variety of electrophiles and nucleophiles. In particular, nickel salts have been widely employed in challenging transformations such as the coupling of C(sp^2) and C(sp^3) with alkyl groups bearing β-hydrogen atoms, due to their ability to suppress the commonly observed β-hydride elimination/isomerization byproducts.[8] In the particular case of alkyl nucleophiles with C(sp^2) electrophiles, the catalytic systems are traditionally based on a nickel metal supported by highly electron-donating ligands such as phosphines or NHCs which serve a double purpose: (i) stabilization of the metal center and (ii) donation of electron density into the Ni thereby increasing its nucleophilicity (Scheme 1A). In spite of comprehensive literature reports in this area, fundamental investigations on the catalytic activity of *complexes with nickel in an extremely low-valent oxidation state* remain elusive. Herein we disclose the unprecedented catalytic activity of a well-defined low-valent Ni precatalyst capable of forging C–C bonds at temperatures as low as –65 ºC (Scheme 1B). In contrast to the traditional catalyst designs, this catalytic system features a highly electron-rich Ni center stabilized by simple olefin ligands, which outperforms its parent Ni(0) precatalyst at low temperatures and tolerates the presence of functional groups in a Kumada coupling.[9]

We began our investigations by synthesizing complex **1**, from the parent Ni(0) source Ni(COD)$_2$ (Figure 1). This complex was obtained by reduction with lithium sand in THF at 0 ºC, as described by Jonas and Pörschke.[10] After filtration and crystallization with Et$_2$O, compound **1** was isolated as a bright orange complex. As depicted in the ORTEP in Figure 2, complex **1** has *three of the four olefins* in the ancillary ligands coordinated to the Ni, thus rendering an 18 electron complex configuration. In solution however, the ^{1}H NMR signals of the olefins in **1** indicate a coalescence event when increasing the temperature, thus suggesting a fluxional behavior of the four olefinic ligands at this temperature.[10c,11] In the solid state, two Li atoms are bonded to the central Ni, but severely shifted from the central axis (**1**: Li1–Ni1–Li2 133.75(6) deg);[12] The coordination of two molecules of THF and the average Ni–Li distance of 2.42 Å, suggest a metal-metal bond.[13] Importantly, complex **1** exhibits a significant elongation of the three coordinated double bonds in the 1,5-cyclooctadiene moiety (C1–C2 1.4635(12), C5–C6 1.4198(12), C9–C10 1.4735(12) Å) compared to its Ni(0) congener Ni(COD)$_2$ (1.391(2) Å)[14] or the free COD (1.34(3) Å)[15]. The extreme elongation of the bound olefins and the large rehybridization of the C(sp^2) atoms suggest a high electron density at the Ni center which is in turn stabilized by a significant back-donation to the empty π^* orbitals of the double bonds.[11] This experimental observations are in agreement with the Dewar-Chatt-Duncanson model, in which the olefins can be described by the continuum from metallacyclopropane to olefin (metal-olefin complex *vs* metallacyclopropane).

Scheme 1. Ligand features in Ni-catalyzed aryl-alkyl Kumada cross-couplings.



With complex **1** in hand, we turned our attention to examining its catalytic activity in the Kumada–Corriu coupling. We subjected complex **1** to a mixture of (*E*)-1-(2-bromovinyl)-4-methoxybenzene (**2**) and hexMgBr (**3**) in MTBE. To our delight, 5 mol% of **1** effectively catalyzed the formation of coupling product **4** in 76% yield at –65 ºC (Scheme 2). On the other hand, when Ni(COD)$_2$ was utilized instead, only traces of product were observed. The addition of various lithium salts to the system did not lead to conversion and starting material was recovered unreacted. When the traditional NiCl$_2$(dppe) was used instead, low yields of **4** were obtained. This highlights the high activity of **1** when compared to highly nucleophilic phosphine-supported Ni(0) species. Control experiments revealed no Mg-halogen exchange between **2** and **3**.[16] The intriguing reactivity posed by **1** led us to explore the generality of this transformation to other organic halides. As shown in Table 1, the electronics on the ring had minimal influence on the reaction outcome, as exemplified by **5**. Interestingly, no isomerization to the more stable *E*-isomer was observed when *Z*-styrenyl was used instead (**6**), thus suggesting a non-radical mechanism (*vide infra*). Non-conjugated vinyl bromides and 1,1-disubstituted vinyl bromide could also smoothly couple to deliver **7** and **8** respectively. Vinyl triflates posed no problem and could be readily activated (**9**). The presence of a sulfonate group prone to oxidative addition under Ni catalysis was well accommodated affording 61% of **10**. Heterocyclic motifs bearing chlorides and bromides, such as thiophene, isoquinoline and quinoline, also performed well under the reaction conditions (**11-13**). Pleasingly, a moderate but relevant yield was obtained when 2-fluoroquinoline was utilized. This result is of special importance since C(sp^2)–F activation is traditionally restricted to the realm of nickel catalysts bearing electron donating ligands.[17]

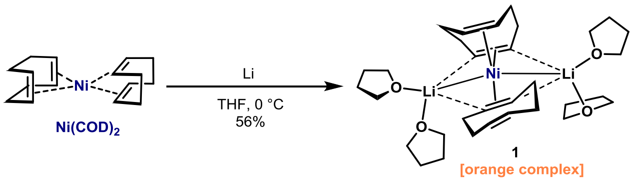


Figure 1. Synthesis of complex **1**.

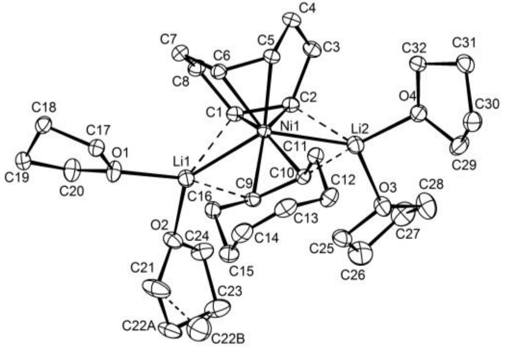
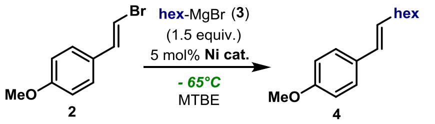


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Li1–Ni1 2.4171(17), Li2–Ni1 2.4184(17), C1–C2 1.4635(12), C5–C6 1.4198(12), C9–C10 1.4735(12), C13–C14 1.3311(17), C10–Li2 2.2978(19), Li1–Ni1–Li2 133.75(6).

Scheme 2. Catalytic activity of **1**.

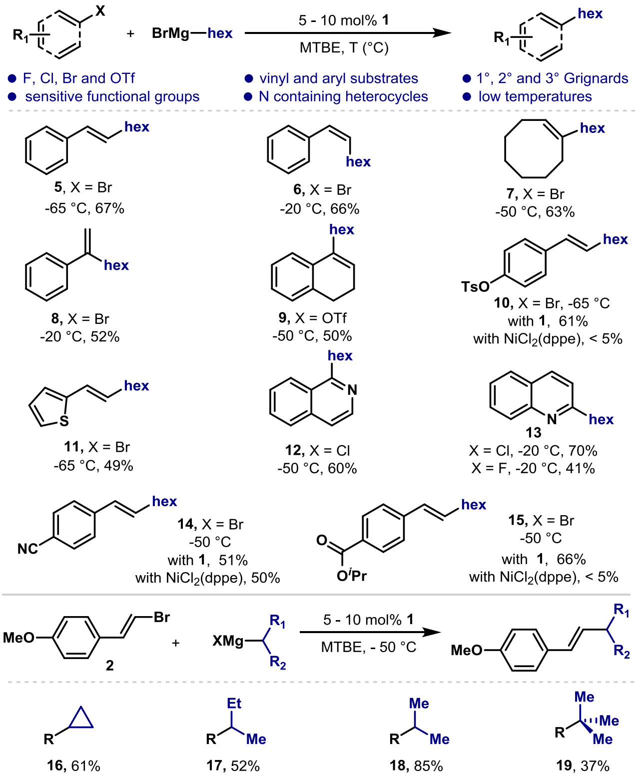


Ni cat.	Yield **4**[a]
1	76%[b]
Ni(COD)$_2$	<5%
Ni(COD)$_2$ + LiOTf	<5%
Ni(COD)$_2$ + LiCl	<5%
Ni(COD)$_2$ + LiBr	6%
NiCl$_2$(dppe)[c]	30%[b]

[a] Yields determined by GC-FID. [b] Isolated yield. [c] 10 mol% NiCl$_2$(dppe) was used instead.

We speculated that the ability of **1** to perform well at such low temperatures would enable compatibility with sensitive functionalities. It is well established that ester or nitrile groups react immediately with alkyl Grignards at low temperatures; however, when substrates bearing nitrile (**14**) and ester (**15**) were subjected to the reaction conditions, satisfactory yields of coupling were obtained. This distinctive reactivity highlights the possibility of adapting functional groups in Ni-catalyzed Kumada couplings without observable side reactions at the electrophilic site.[18] For these sensitive substrates, the reactivity of **1** was compared with NiCl$_2$(dppe). Although comparable yields were obtained for compound **14**, no conversion was obtained towards **10** and **15**. Importantly, in all the aforementioned examples no isomerized by-products from the alkyl Grignard were observed. Hence, we speculated that β-hydride elimination/isomerization events could be suppressed with **1**. Indeed, when secondary Grignard reagents such as ^{i}PrMgCl and ^{s}BuMgCl were subjected to the reaction conditions, good to excellent yields of the coupling product were observed without isomerization of the alkyl chain (**17** and **18**). Gratifyingly, a tertiary nucleophile such as ^{t}BuMgCl proved amenable in the reaction; despite the low yield, **19** was obtained without isomerization.[19]

Table 1. Scope of the Kumada coupling catalyzed by **1**.[a]



5, X = Br
-65 °C, 67%

6, X = Br
-20 °C, 66%

7, X = Br
-50 °C, 63%

8, X = Br
-20 °C, 52%

9, X = OTf
-50 °C, 50%

10, X = Br, -65 °C
with **1**, 61%
with NiCl$_2$(dppe), < 5%

11, X = Br
-65 °C, 49%

12, X = Cl
-50 °C, 60%

13
X = Cl, -20 °C, 70%
X = F, -20 °C, 41%

14, X = Br
-50 °C
with **1**, 51%
with NiCl$_2$(dppe), 50%

15, X = Br
-50 °C
with **1**, 66%
with NiCl$_2$(dppe), < 5%

16, 61%

17, 52%

18, 85%

19, 37%

[a] Yields of isolated pure material. Reaction conditions: **1** (5 – 10 mol%), aryl halide (1 equiv.), alkyl Grignard (1.5 equiv.), 0.1 M MTBE at the indicated temperatures.

At this point, we questioned the stability of such Ni precatalyst and we investigated the homogeneity of the system. Yet, the addition of an excess of Hg(0) to the reaction with **1** did not affect the kinetic profile.[20,21] Moreover, the use of freshly prepared Ni nanoparticles did not lead to any catalytic activity at –65 °C, suggesting a homogeneous catalytic process.[20c,21] The interesting reactivity observed for **1** led us to consider a possible oxidative addition to the organic halide electrophile (Figure 3A, top). Indeed, when **1** was reacted with 1 equiv. of bromostyrene, a change in color was observed and a highly air- and temperature-sensitive intermediate was obtained. Although speculative in structure, we attributed this intermediate to nickelate compound **20** based on its reactivity in solution. When 2 equiv. of hexMgBr (**3**) were added to a solution of **20**, a gratifying 32% of **5** was obtained. Moreover, when this intermediate was quenched with H_2O, styrene and COD were the only products observed by GC-FID in 1:2 ratio respectively. These results point out to the existence of rather polarized C–M bond in **20**, formed upon C–Br cleavage. In order to gather additional evidence of the oxidative addition to **1**, an alternative route was devised to provide a more stable nickelate intermediate. For this reason, we turned to the organometallic addition of PhLi to Ni(0); this would result in a compound analogous to the postulated oxidative addition species (Figure 3B, bottom). A mixture of Ni(CDT) ((*trans*,*trans*,*trans*-1,5,9-cyclododecatriene)nickel(0)) and PhLi (solid) were reacted under ethylene atmosphere in a mixture of Et_2O and TMEDA.[22] A yellow solid precipitated which was characterized by NMR spectroscopy as the Ni(0) complex **21**. Following numerous attempts in Et_2O, an extremely sensitive crystal could be isolated and identified by X-ray spectroscopy as compound **22** (Figure 4). The structure of **22** supports the characterization of **21**. This result also underscores the solvent-dependent ionic character of Ni(0)-ate complexes, and their ability to form stable Ni–Li bonds. Albeit different from **20** in ligands, complex **21** provided an well-defined platform to study the reactivity of a putative oxidative addition of Ar–X to a formal Ni(–II). The solid state structure of complex **22** features a Ni attached to a phenyl ring, with two slightly elongated ethylene ligands acting as π-acceptors. Judging by the elongation of the olefins, C7–C8 1.411(2) and C9–C10 1.397(2), the Ni center partially relocates its electron density onto the ethylene ligands. The Li in the solid state is faintly bridging both the *ipso* and *ortho* carbon on the Ph ring and the Ni center. Simultaneously, the Li is also coordinated to a carbon from the ethylene moiety.

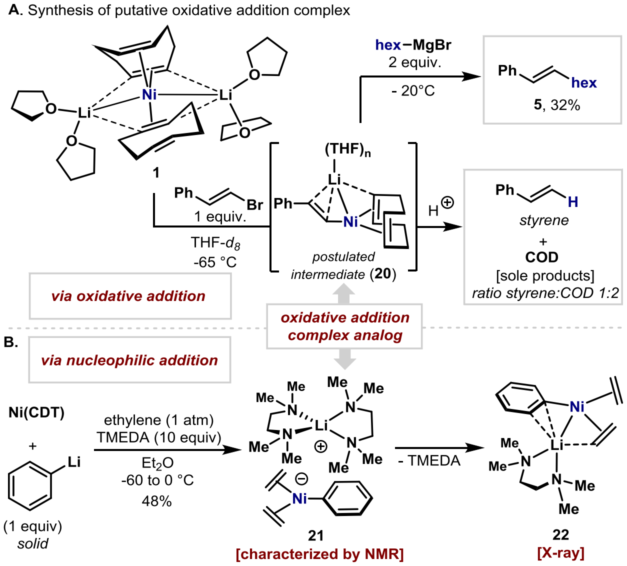


Figure 3. (**A**) Reaction of **1** with bromostyrene (**B**) Synthesis of nickelate complexes **21** and **22**. CDT: *trans,trans,trans*-1,5,9-cyclododecatriene.

With complex **21** in hand, we explored its reactivity with organometallic reagents in direct comparison to the equivalent catalytic reaction with Ph–Br. When Ph–Br was reacted with hexMgBr (**3**), 18% yield of the cross-coupling product was obtained (Scheme 3A). It is important to point out that during our scope studies, reaction of **1** with unactivated aryl bromides proved sluggish and the presence of highly coordinating TMEDA was detrimental to the reactivity.[23] Nevertheless, the stoichiometric reaction of complex **21** with hexMgBr (**3**) delivered a 10% yield of the direct C–C bond product, which compares well with the 18% yield obtained under catalytic conditions.[23] Similarly, the lower reactivity is attributed to the effect of TMEDA, which renders the Ni(0)–Ph intermediate less electrophilic and hence, less able to accept more negative charge from the nucleophile. The Ni(0) center would be more electrophilic if THF, a weaker coordinating ligand, was the ligand at the Li atom. Based on this hypothesis, we turned our attention to the use of stronger organometallic nucleophiles, such as organolithium reagents. When MeLi (**24**) was tested under catalytic conditions, 87% yield of cross-coupling product was obtained. Notably, when MeLi (**24**) is reacted with complex **21**, 47% yield of C–C bond formation was observed. Although still preliminary, these results highlight the *possibility of forging* $C(sp^2)$-$C(sp^3)$ *bonds from a Ni(0) complex with an organometallic reagent*.[24] The mechanism of such transformation is unknown at the present stage. However, previous observations by Pörschke on the acidity of Ni(0) complexes revealed the ability of tris-olefin Ni(0) complexes to accommodate two organolithium reagents resulting in dilithiated adducts of Ni(0).[10,25] Importantly, these adducts were shown to undergo reductive elimination to afford the C–C bond product. In line with these observations, we believe that such a C–C forming event from putative intermediate **II** and **III** could proceed via a similar mechanism, delivering the C–C bond product upon reductive elimination of intermediate **IV** (Scheme 3B).

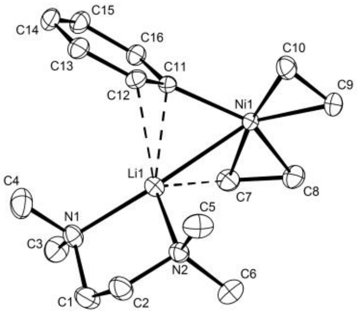
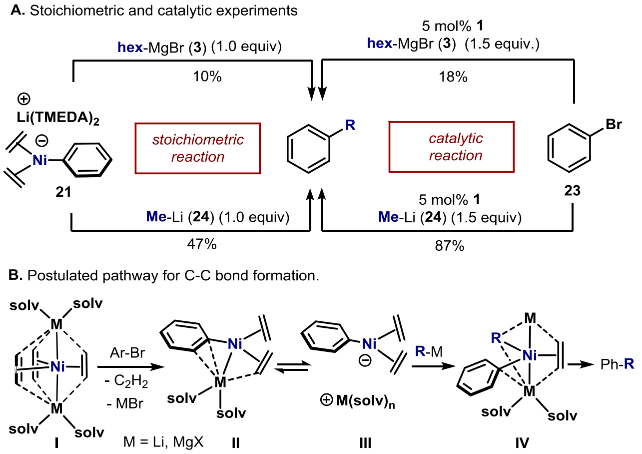


Figure 4. Molecular structure of complex $[(C_2H_4)_2NiPh]Li(TMEDA)$ (**22**). Selected bond distances (Å) and angles (deg): C7–C8 1.411(2), C9–C10 1.397(2), Ni1–C11 1.9634(12), Ni1–Li1 2.500(2), Li1–C11 2.197(3), Li1–C7 2.419(3), Li1–C12 2.607(3); C11–Ni1–C7 99.14(5), C11–Ni1–Li1 57.46(7).

Scheme 3. Mechanistic investigations.



In summary, this work has established the viability of highly reduced Ni-Li-olefin complexes as competent precatalysts in Kumada-Corriu cross-couplings between a series of aryl and vinyl halides with alkyl Grignard reagents. The coupling proceeds at extremely low temperatures, allowing the presence of sensitive functional groups with Grignard reagents. The catalytic system features a unique electronically congested Ni center stabilized by olefin ligands. Stoichiometric experiments reveal a potential scenario in which C–C bonds can be forged from a nickelate Ni(0)–Ph complex and an organometallic reagent. Further investigations to fully elucidate the operative mechanism as well as other synthetic applications are currently under investigation.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and analytical data (^{1}H and ^{13}C NMR, HRMS) for all new compounds. This material is available free of charge *via* the internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Financial support for this work was provided by Max-Planck-Gesellschaft and Max-Planck-Institut für Kohlenforschung. We thank Ms. J. Busch for synthesis of starting materials. We also thank Prof. Dr. A. Fürstner, Prof. Dr. T. Ritter and Prof. Dr. K. R. Pörschke for insightful discussions and generous support. We thank Mr. A. Schlüter for TEM images.

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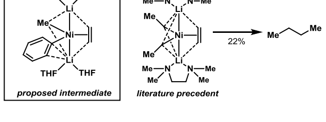

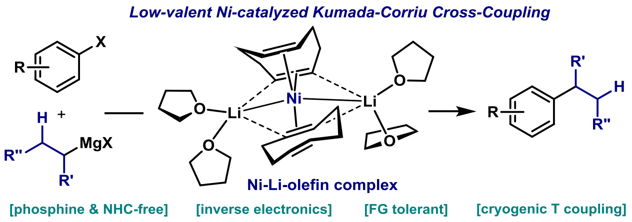
Low-valent Ni-catalyzed Kumada-Corriu Cross-Coupling
R
X
H
+
R''
MgX
R'
O
Li
O
Ni
Li
O
O
Ni-Li-olefin complex
R
R'
H
R''
[phosphine & NHC-free]
[inverse electronics]
[FG tolerant]
[cryogenic T coupling]