ORGANOMETALLICS

Article

16-Electron Nickel(0)-Olefin Complexes in Low-Temperature C(sp²)– C(sp³) Kumada Cross-Couplings

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ABSTRACT: Investigations into the mechanism of the low-temperature $C(sp^2)-C(sp^3)$ Kumada cross-coupling catalyzed by highly reduced nickel-olefin-lithium complexes revealed that 16-electron tris(olefin)nickel(0) complexes are competent catalysts for this transformation. A survey of various nickel(0)-olefin complexes identified Ni(nor)₃ as an active catalyst, with performance comparable to that of the previously described Ni-olefin-lithium precatalyst. We demonstrate that Ni(nor)₃, however, is unable to undergo oxidative addition to the corresponding $C(sp^2)$ -Br bond at low temperatures (<-40 °C), thus indicating that the canonical cross-coupling cycle is not operative under this condition. Instead, such binary nickel(0)-olefin complexes capitalize on the long-known Lewis acidity of the Ni(0) center when it is coordinated to olefins to accommodate the incoming charge from the Grignard reagent, forming a nickel(0)-alkylmagnesium complex. We demonstrate that this unique heterobimetallic complex is now primed for reactivity, thus cleaving the $C(sp^2)$ -Br bond and ultimately delivering the $C(sp^2)$ -C(sp³) bond in high yields.

■ INTRODUCTION

Catalytic methods employing nickel (Ni) as the main catalyst have been shown to be widely versatile for the formation of a plethora of C-C bonds of different hybridization nature, namely C(sp)-, $C(sp^2)$ -, and $C(sp^3)$ - and combinations thereof.¹ In addition to accessing different oxidation states by SET processes,² part of the success of Ni as a catalyst in such a variety of nucleophiles and electrophiles hinges on the successful tuning of ligands in order to prevent the deleterious β -hydride elimination.³ Within the vast realm of crosscouplings, of particular importance is the seminal reaction between Grignard reagents and (pseudo)halides, initially disclosed by Tamao and Kumada⁴ and Corriu⁵ independently in 1972. More specifically, this reaction is particularly effective when attempting the coupling of alkylmagnesium compounds $(C(sp^3)-MgX)$ and $C(sp^2)-X$ electrophiles (Figure 1A). Although various transition metals have been reported to catalyze this reaction,⁶⁻¹⁰ Ni still holds an important place as the catalyst of choice. Notably, the vast majority of the reported catalytic systems to forge such C-C bonds rely on the use of highly electron donating ligands: namely, phosphines, diamines, diimines and NHCs (Figure 1B).¹¹ It is generally accepted that the success of these ligands hinges on providing the metal center with an adequate electronic demand to aid in the oxidative addition and reductive elimination steps.^{3,12,13} In addition to taming the rates of oxidative



Figure 1. (A) Ni-catalyzed Kumada cross-couplings between a $C(sp^3)$ and $C(sp^2)$. (B, C) Qualitative comparison between electronically distinct situations. Adapted from ref 22.

Special Issue: Organometallic Solutions to Challenges in Cross-Coupling

Received: December 8, 2020



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addition and reductive elimination, the formation of L–Ni after reductive elimination prevents the metal center from decomposing and being eliminated from the system as Ni black.

Despite the wealth of literature involving the use of electrondonating ligands in Ni-catalyzed reactions, much less is known about an alternative electronic situation on the catalyst, where the metal center is highly reduced and the additional charge is stabilized through its ligands (Figure 1C). This situation is favored when certain π -accepting functionalities such as olefins are acting as ancillary ligands for the Ni center.¹⁴ Whereas σ electron-donating ligands favor oxidative addition, π -accepting ligands such as olefins offer opportunities for tuning other steps of the catalytic cycle.¹⁵ For example, seminal reports from Yamamoto demonstrated that electron-deficient olefins had a tremendous effect on the rate of reductive elimination from (diamine)Ni^{II}(alkyl)₂ complexes.¹⁶ Years later, Knochel developed Ni/styrene-catalyzed C(sp³)-C(sp³) cross-coupling reactions, where the styrenyl moiety was crucial for accelerating the reductive elimination step.¹⁷ Later, Rovis et al. reported the coupling of cyclic anhydrides (sp²-hybridized carbons) with $C(sp^3)$ organozinc reagents using solely $Ni(COD)_2$ as the catalyst.¹⁸ More recently, Doyle and Engle capitalized on the use of electron-deficient olefins (either in the substrate or as a ligand) to develop Ni-catalyzed aziridine ringopening Negishi couplings and diarylation of alkenes, respectively.¹⁹ In all these reports, olefins play a crucial role in tuning the reactivity and influencing the outcome of the Nicatalyzed C-C bond-forming event. However, the use of olefins as the sole ancillary ligand in Kumada cross-coupling reactions is still an underexplored area of research with few examples. Among many couplings using dienes,²⁰ Kambe et al. reported the coupling of alkylmagnesium compounds (C- (sp^3) -MgX) with alkyl halides $(C(sp^3)-X)$ catalyzed by Ni and derivatives of 1,3-butadienes as the sole ligands to forge $C(sp^3)-C(sp^3)$ bonds.^{21a,b} Interestingly, investigations on the mechanism suggested that butadiene was crucial for the intermediacy of a unique Ni(II)-allyl-dialkyl ate complex, which was structurally characterized by X-ray diffraction. However, despite these seminal reports, the use of simple olefins, and in particular, unactivated mono-olefins (1,2-dialkyl olefins) as ligands for Ni-catalyzed $C(sp^2)-C(sp^3)$ crosscouplings has yet to be explored and, more importantly, mechanistically understood.

Motivated by the potential catalytic properties of highly reduced Ni-olefin complexes, we have recently reported on the catalytic activity of Ni-Li-olefin complex 1 (Figure 2A),²² originally reported by Pörschke and Jonas.^{23,24} In the solid state, the structure of 1 consists of a distorted-trigonalbipyramidal geometry, with three olefin ligands occupying the base of the pyramid and two Li atoms in the vertices.²² The high electron density provided by the Li atoms is redistributed through the Ni and accommodated in the coordinated olefins through strong π -back-bonding. This effect is evidenced by the high degree of pyramidalization of the coordinated olefinic carbons and the heavily elongated C=C bonds (Figure 2B).²⁵ In addition to the interesting electronic and structural features, the reactivity of complex 1 is worthy of further comment. When complex 1 is used as a catalyst in the coupling of (hetero)aryl and vinyl (pseudo)halides $(C(sp^2)-X)$ with alkyl Grignard reagents ($C(sp^3)$ –MgX), high yields of product were obtained for a wide variety of substitution patterns (Figure



Figure 2. (A) Synthesis of 1. (B) Selected examples of the low-temperature Kumada coupling catalyzed by 1. (C) Scope. Adapted from ref 22.

2C). Some of the features of this C-C bond forming reaction include the following.

- the cryogenic temperatures employed permiting the presence of Grignard-sensitive functionalities such as esters and nitriles^{9a}
- (2) orthogonality with C(sp²)–OTs, sensitive to oxidative addition with Ni complexes bearing σ -donating ligands such as phosphine and NHCs^{1c}
- (3) the activation of C(sp²)-F bonds at -40 °C, which is usually restricted to the use of highly electron donating phosphines, phosphites, or NHC ligands²⁶
- (4) the coupling of primary, secondary, and even tertiary Grignard reagents bearing β -hydrogens, with no isomerized products being observed²⁷
- (5) the high activity of 1 at low temperatures (-65 to -20 °C), at which other catalysts failed to react [Ni(COD)₂ or NiCl₂(dppe)].^{4,9}

Despite these interesting features, a mechanistic understanding of the transformation has remained purely speculative and several questions remain unanswered. In this article, we report on our efforts toward a better understanding of the catalytic system, as well as the identification of the putative catalytic species involved.

RESULTS AND DISCUSSION

Oxidative Addition to the Vinyl Bromide. In our previous work,²² the idea of complex 1 operating in a canonical two-electron manifold (oxidative addition/transmetalation/ reductive elimination) was entertained (Figure 3A). Yet,



Figure 3. (A) Speculative mechanism in previous work, (B) Difference in reactivity between Ni-Li-olefin (1) and Ni(COD)₂. Data are extracted from ref 22.

such a hypothesis was discarded, as it would imply a formally Ni(-II)/Ni(0) redox cycle. As a result, a reductive elimination from a double negatively charged Ni(0) (*int-1*) complex would be necessary to regenerate the formal Ni(-II) catalyst. This process would require the placement of these additional electrons in a ligand-based orbital, which are quite high in energy and beyond reach for a C-C bond event. On the basis of reactivity studies, complex 1 has been described as a Ni(0) carrying two elemental Li(0) atoms rather than an oddly reduced Ni species.²⁸ Yet, the description of this catalyst as a Ni(0) complex poses a vital question: while complex 1 is extremely active at very low temperatures toward $C(sp^2)-C(sp^3)$ bond formation, its Li-free Ni(0) analogue (Ni-(COD)₂) fails to deliver 4 under the optimized conditions (MTBE at -65 °C, Figure 3B).

To investigate this difference in reactivity, we performed stoichiometric experiments where the reduction power of both 1 and Ni(COD)₂ was investigated. To this end, we separately reacted complex 1 and Ni(COD)₂ with styrenyl bromide (**5**) at -40 °C in THF- d_8 and monitored the reaction by ¹H NMR spectroscopy. In the case of Ni(COD)₂ no reaction was observed after 24 h and **5** was recovered unreacted (Scheme 1A). This indicates that Ni(COD)₂ is not able to cleave the $C(sp^2)$ -Br bond at such low temperatures. The poor solubility of Ni(COD)₂ under these conditions could also account for the lack of reactivity observed.

On the other hand, the reaction with 1 and 5 proceeded differently: styrene (6) and Ni(COD)₂ were obtained almost

Scheme 1. (A) Stoichiometric Experiments with $Ni(COD)_2$ and 1 and (B) 16-Electron Ni(0) Species as Putative Intermediate



in quantitative yields and in an \sim 1:1 ratio as judged by ¹H NMR (Scheme 1A).²⁹ This was accompanied by a detectable amount of aromatic polymerized material. The observation of polymeric material led us to postulate that, upon reduction of **5** by **1**, a fleeting vinyl radical (7) could be formed. Such reactivity has been previously observed by Blum, Jonas, and Krüger, who described **1** as a soluble "Li(0) carrier"; as a result it was noticed that **1** is capable of reducing naphthalene or anthracene through SET processes.²⁸ However, no examples were reported with aryl or vinyl halides.

The formation of 6 indicates the ability of 1 to reduce the vinyl bromide through the cleavage of the $C(sp^2)$ -Br bond. Yet, the formation of $Ni(COD)_2$ as the sole nickel-containing compound at -40 °C posed a fundamentally interesting controversy about the catalytically active species. Ni(COD), is generated when 1 reacts with 5 at -40 or -65 °C (Scheme 1A); however, $Ni(COD)_2$ is neither able to catalyze the reaction between alkyl Grignard reagents and vinyl bromides nor capable of activating the $C(sp^2)$ -Br bond of 5 at low temperatures (Figure 3 and Scheme 1A, top). To shed some light on this controversy, we hypothesized that, after the formation of 6, the Ni(0) species that remains in solution could be a fleeting 16-electron complex, with three olefins coordinated to Ni, prior to engaging in a bidentate chelation of the pending fourth olefin to form the 18-electron complex Ni(COD)₂ (Scheme 1B). 16-Electron complexes are known to be highly reactive, and we speculated that such an intermediate could potentially play a role in the low-temperature Kumada coupling under study.

Synthesis of 16-Electron Homoleptic Ni(0)-Olefin Complexes. To test this hypothesis, we then turned our attention to the synthesis of a variety of Ni(0)-tris(olefin) complexes and evaluated their catalytic activity. It is important to mention that the 16-electron Ni(0)-olefin complex proposed in this catalytic system would correspond to a Ni(0) coordinated to one COD in a bidentate fashion and monocoordinated to an additional COD (Scheme 2A). The synthesis of such a putative complex poses extreme difficulties, since the formation of the bis-coordinated 18-electron complex Scheme 2. (A) Hypothetical Fleeting Ni(0) Intermediate and (B) Synthesis of Homoleptic Tris(olefin)nickel(0) Complexes

A. Putative 16-electron Ni(0)-olefin complex with bidentate COD



 $Ni(COD)_2$ is favored when no competing pathways exist. In light of these potential issues, and to be as accurate as possible to the real catalytic system, we focused on synthetically accessible homoleptic analogues, bearing 1,2-dialkyl olefins as the sole ligands. Hence, we synthesized trans, trans, trans-(1,5,9cyclododecatriene)nickel(0) (t-Ni(CDT), 8),³¹ cis,cis,cis-(1,5,9-cyclododecatriene)nickel(0) (*c*-Ni(CDT), 9),³² and tris(bicyclo[2.2.1]hept-2-ene)nickel(0) (Ni(nor)₃, 10),³³ which have been previously synthesized and well characterized in the literature. With the exception of recently reported tris(stilbene)nickel(0) complexes,³⁴ 16-electron Ni(0)-olefin complexes are extremely sensitive to air (decomposition <1 s open air). Therefore, handling of these complexes should be carried out under rigorous exclusion of oxygen and, preferably, at low temperatures (<0 °C). Complex 8 was prepared in good yields according to the described procedure:³¹ reduction of $Ni(acac)_2$ with $Et_2(OEt)Al$ in the presence of t-CDT at low temperatures, followed by sublimation under ultrahigh vacuum (Scheme 2B).³¹ Complexes 9 and 10 were obtained as white crystalline solids after olefin exchange with 8.35,36

Catalytic Activity of 8-10. With complexes 8-10 in hand, we tested their catalytic activity in the cross-coupling of 5 and 3 at -60 °C in THF (Scheme 3A). In our previous work, we reported a 67% isolated yield for product 11 when 1 was used as the catalyst under these conditions.²² To our delight, the 16-electron t-Ni(CDT) (8) also exhibited certain catalytic activity (36%). The use of complex 9 resulted in lower yields in comparison to its isomer 8 (9%). The low yields of C-C bond formation suggest that despite the lability of CDT to exchange with other olefins, tethered ligand environments around the metal center are not beneficial for the reaction. Gratifyingly, when Ni(0) complex 10 bearing norbornene as a ligand was used instead, a remarkable 58% yield of product was obtained at -60 °C and 74% at -40 °C. The high catalytic performance of 10 in the low-temperature Kumada coupling supports the hypothesis that tris(olefin)nickel(0) complexes could certainly play a crucial role.

Influence of the Solvent. Due to the presence of the strong nucleophilic Grignard reagent, Ni-catalyzed Kumada cross-couplings are generally carried out in ethereal solvents

Scheme 3. (A) Comparison of the Catalytic Activity of Homoleptic Ni(0)-Olefin Complexes at Low Temperatures in THF and (B) Influence of the Solvent in the Ni(0)-Olefin-Catalyzed Kumada Cross-Coupling

A. Survey of different binary Ni(0)-olefin complexes as catalysts



(THF, Et₂O, or MTBE).¹² However, a strong dependence on the solvent has been demonstrated in certain contexts, resulting in a dramatic effect on the yield.³⁷ This phenomenon has been generally ascribed to the position of the Schlenk equilibrium, due to their different coordination abilities to Mg(II) (2 RMgX \rightleftharpoons R₂Mg + MgX₂).^{38,39} To address this possibility, we tested the reactivities of complexes 8 and 10 in the presence of both Et₂O and MTBE and compared them with the results obtained in THF (see Scheme 3A). As shown in Scheme 3B, complex 8 afforded similar yields of 11 (13% and 19%), in both MTBE and Et₂O, but the results were still far from the 36% yield obtained in THF. Finally, complex 10, which behaved extremely well in THF (58%), afforded lower yields of 11 in both Et_2O (39%) and MTBE (48%). Although complex 10 remains the most active catalyst, a clear trend in favor of THF as the superior solvent can be defined. These results combined suggest that the position of the Schlenk equilibrium of the alkyl Grignard reagent could play a crucial role in the reaction, thus influencing the formation of productive catalysis (vide infra).

Probing Oxidative Addition with Ni(nor)₃. Although the high reactivity exhibited by **10** clearly pointed toward 16electron Ni(0)-olefin complexes being competent catalysts, the fundamental steps by which the Ni produced the desired $C(sp^2)-C(sp^3)$ bond still remained an unsolved question. If the reaction follows the canonical steps postulated for a Ni(0)/ Ni(II) cross-coupling,^{1-4,11} the first step should involve the oxidative addition of **10** into the weak $C(sp^2)$ -Br bond of **5**. To explore this possibility, we reacted a 1:1 mixture of **10** and **5** in THF at -40 °C (Scheme 4).

However, vinyl bromide **5** and **10** were recovered unreacted after >6 h in solution at -40 °C. This observation suggests that the Ni center in complex **10** is not able to undergo oxidative addition via either two-electron or SET events. Hence, another pathway must be operative which involves a much more nucleophilic Ni, able to engage with the vinyl bromide and cleave the $C(sp^2)$ -Br bond. At this point, we considered the possibility that the Grignard reagent could play an important role in the very first steps of the reaction. Tris(ethylene)Ni(0)





complexes have been shown to behave as Lewis acids and generate Ni(0)-alkyl ate complexes when they are confronted with strong organometallic reagents (I, Figure 4A).⁴⁰ This



B. Proposed reaction between Ni(nor)₃ and organomagensium reagents



C. Proposed isolable heterobimetallic intermediate



Figure 4. (A) Acidity of tris(ethylene)nickel(0) enabling the addition of organometallic reagents with concomitant displacement of ethylene. (B) Postulated heterobimetallic intermediate from the reaction of Ni(nor)₃ and organomagnesium reagents. (C) General formula for the synthesis of stable and isolable heterobimetallic Ni(0)-dimethylmagnesium bearing ethylene as a ligand.

reactivity has been well-established during the discovery of the "nickel effect" and studied in detail by Kaschube, Pörschke, and Wilke, who also provided crystallographic evidence.⁴ Such Ni(0) complexes can accommodate the charge of strong incoming nucleophiles such as organolithium and organomagnesium compounds. According to the Dewar-Chatt-Duncanson model, these compounds are stabilized by the presence of olefin ligands, allowing partial delocalization of the charge at the Ni center into the C=C bond π^* orbital through π -back-donation. It was immediately apparent that all of these seminal studies on the Lewis acidity of Ni(olefin)₃ complexes could serve as an excellent platform to study our reactivity. Therefore, we attempted the reaction between alkylmagnesium halides and 10. However, the expected Ni-alkyl intermediates with the general structure of I could not be isolated when using olefins different from ethylene.²⁴ We speculated that, when 10 is used, the formation of a heterobimetallic adduct such as II would be imbalanced toward the starting materials (Figure 4B). Although this equilibrium could be productive in a

catalytic context, it became apparent that isolation of the Ni(0)-alkylmagnesium complex would be troublesome. This led us to consider the synthesis of III: analogous nickel(0)-alkylmagnesium complexes where the norbornene has been replaced by ethylene (Figure 4C).

Synthesis of a Heterobimetallic Ni(0)-Alkylmagnesium Adduct. We decided to prepare $[(CH_3)_2Mg(TMEDA)]$ (12), following the previous work by Kaschube, Pörschke, Wilke, and Westerhausen.^{41,42} In order to forge the Ni–C bond, complex 12 was reacted with Ni(C₂H₄)₃, which was prepared *in situ* by gently bubbling ethylene into a solution of 8 in Et₂O (Scheme 5). After the mixture was filtered through a

Scheme 5. Synthesis of a Heterobimetallic Nickel(0)-Alkylmagnesium Complex²⁴



cold frit (-20 °C), a yellow powder was isolated, which corresponds to complex **13**. Despite the presence of traces of *t*-CDT (<10%), the compound could be characterized by ¹H and ¹³C NMR. Although crystallographic data for **13** have been reported in the past,⁴¹ we decided to analyze this complex again with a more modern apparatus. Hence, recrystallization of **13** in Et₂O at -78 °C afforded yellow crystals suitable for X-ray diffraction (Figure 5).⁴³ As seen in the X-ray structure of **13** (Figure 5), Ni(1) is coordinated to two ethylene ligands and one of the CH₃ groups (C(11)) in a slightly distorted trigonal planar environment. The C=C distances of the coordinated ethylene units (C(9)-C(10) 1.389(2) Å and C(7)-C(8) 1.412(2) Å) are slightly longer than those in analogous nonionic Ni(0)-Me complexes, such as [(PMDTA)-



Figure 5. ORTEP drawing of compound 13. Hydrogen atoms are omitted for clarity. Color code: blue, Ni; pink, Mg; green, N; black, C. Selected bond lengths (Å) and angles (deg): C(7)-C(8) 1.412(2); C(9)-C(10) 1.389(2); Ni(1)-C(11) 2.0294(15); Mg(1)-C(11) 2.2786(16); Mg(1)-C(12) 2.179(7); Ni(1)-Mg(1) 2.5960(5); C(7)-Mg(1) 2.7151(15); Ni(1)-Mg(1)-C(11) 66.6(6); C(11)-Mg(1)-Ni(1) 48.67(4); Ni(1)-C(11)-Mg(1) 73.86(5).

 $Li(\mu-CH_3)Ni(C_2H_2)_2^{44}$ (C=C distances 1.389(8) and 1.404(7) Å) and $[Li(TMEDA)_2][MeCH_3(C_2H_2)_2]$, (C=C distances 1.36 and 1.38 Å).⁴⁵ At the same time, the C(11) attached to the Ni center is also shared in a μ -bridging fashion to Mg(1) (Ni(1)-C(11) 2.0294(15) Å and Mg(1)-C(11) 2.2786(16) Å).⁴⁶ The Ni(1)-C(11) distance is consistent with other CH₃-µ-bridges between two metals: namely, the 2.01 Å reported for the Ni–CH₃ distance in [(PMDTA)Li(μ - CH_3)Ni $(C_2H_2)_2$].⁴⁴ The Mg(1) atom is heavily interacting with the Ni(1) center, with a Ni(1)-Mg(1) distance of 2.5960(5) Å. Additionally, a close contact between the Mg center and one of the $C(sp^2)$ atoms from the ethylene units can also be observed (C(7)-Mg(1) 2.7151(15) Å). Finally, the Mg atom is engaged in coordination with TMEDA in a bidentate fashion. The electronic situation in the triangular Mg(1)-Ni(1)-C(11) could be best described as a cyclic three-center-two-electron bonding (3c-2e).⁴⁷ It is important to mention that the ORTEP drawing shown in Figure 5 is only 81% of the whole structure. The remaining 19% corresponds to an analogous ate complex where the methyl group (C12) has been replaced by a bromine atom (Br1).⁴³ This is explained by traces of a Br source in the synthesis of 12 present during the synthesis of 13. The observation of this brominated compound in the unit cell indicates that MeMgBr might also be able to form the heterometallic adduct.

The difference in reactivity observed when different ethereal solvents are used (THF > MTBE \approx Et₂O) suggests that a Schlenk equilibrium favoring the R₂Mg species over RMgX would be beneficial for the reaction.³⁹ Therefore, it is reasonable to believe that electron-rich organometallic compounds similar to 13 could be formed in our catalytic system, provided there is a favorable formation of R₂Mg. Such species would be provided with an adequate electron density to engage in the cleavage of the C(sp²)–Br bond of the vinyl bromide. To validate this hypothesis, we reacted complex 13 with 5 at low temperature (-40 °C). Despite the presence of TMEDA, the C(sp²)–C(sp³) formation product 14 was obtained in a 60% yield (Scheme 6). This result compares

Scheme 6. Stoichiometric Reaction between a Nickel(0)-Alkylmagnesium Complex and a Vinyl Bromide



well with the yield obtained using catalyst 1 (67%) and 10 (74%) in the catalytic reaction (*vide supra*). This reactivity confirms that a Ni(0)-alkylmagnesium complex bearing solely olefins as supporting ligands is capable of cleaving the $C(sp^2)-Br$ bond and subsequently forging the desired $C(sp^2)-C(sp^3)$ bond. This striking result strengthens the notion that nickel(0)-alkylmagnesium complexes can certainly be considered as putative intermediates in the low-temperature Niolefin-catalyzed Kumada cross-coupling.

Mechanistic Considerations. The results obtained in this study pose an interesting mechanistic scenario which differs from other pathways in Ni-catalyzed cross-coupling reactions. Usually, two-electron processes via Ni(0)/Ni(II) are invoked

when strongly electron donating ligands are used (phosphines, NHC).^{1b,2e,12} In these cases, the catalytic cycle is believed to operate as depicted in Scheme 7A. Initially, the highly nucleophilic complex Ni(0)-L (**IV**) would undergo oxidative addition into the weak $C(sp^2)$ –X bond to deliver the oxidative addition product **V**. Transmetalation between the electrophilic

Scheme 7. Comparison between (A) the Canonical Two-Electron Ni(0)-Catalyzed Kumada Coupling and (B) the Postulated Mechanistic Picture for the Tris(1,2dialkylolefin)nickel(0)-Catalyzed Low-Temperature Kumada $C(sp^2)-C(sp^3)$ Bond Formation"

A. Canonical two-electron Ni(0)/Ni(III)



B. Proposed mechanism

Unactivated 1,2-dialkyl olefin as ligand first step: organomagnesium-Ni(0) adduct formation



^{*a*}In the former, oxidative addition precedes transmetalation, whereas in the latter, heterobimetallic adduct formation precedes oxidative addition. Ethylene represents a 1,2-dialkyl olefin. metal in V and a strong organometallic nucleophile would afford intermediate VI, which would rapidly undergo reductive elimination to form the product and restore IV. From this general mechanistic picture, a crucial point can be concluded: *oxidative addition by the low-valent Ni species into the* $C(sp^2)-X$ *bond precedes transmetalation* and represents the initial fundamental step of the cycle. However, on the basis of all the collective experimental data provided in this report, tris(olefin)Ni(0) complexes are unable to cleave the $C(sp^2)-$ Br bond at the operating temperatures (<-40 °C). Hence, we believe that, in our Ni(0)-olefin-catalyzed Kumada crosscoupling, the first step of the catalytic cycle is not the oxidative addition, and the reaction proceeds through a slightly different mechanism.

On the basis of the long-known Lewis acidity of tris(olefin)-Ni(0) complexes demonstrated by Wilke, 40,41,44,45 we believe the first step of the cycle in our system involves the nucleophilic attack of the alkyl Grignard reagent on the Ni(0) (VII), affording the Ni(0)-alkyl complex (VIII).⁴⁸ This step would rely on the nucleophilicity of the organomagnesium reagent (R2Mg and/or RMgX) and, therefore, would be heavily influenced by the position of the Schlenk equilibrium (Scheme 3B). The observation of partially brominated 13 in the crystal structure does not rule out the possibility of adduct formation between the monorganomagnesium RMgX and tris(olefin)nickel(0) complex as a viable alternative.⁴³ With a strong nucleophile in place (VIII), oxidative addition into the $C(sp^2)$ -Br bond could occur with concomitant formation of the RMgX salt and intermediate IX. Reductive elimination would deliver the final product and restore the catalytically active species (VII). These postulated steps are consistent with the observation of 10 being inert toward oxidative addition into 5 (Scheme 4). They are also in good agreement with the otherwise high reactivity of the isolated complex 13 with 5 to forge the desired $C(sp^2)-C(sp^3)$ bond (Scheme 6). It is important to mention that evidence for an oxidative addition pathway that leads to compounds such as IX has not been gathered so far. Therefore, this last step remains purely speculative at present. This mechanistic picture for unactivated olefin-supported Ni(0) catalysts is reminiscent of the mechanism of the isoelectronic Cu(I)-catalyzed $C(sp^2)$ - $C(sp^3)$ cross-couplings,⁴⁹ where the addition of the Grignard to the Cu(I) salt is believed to be the initial step of the catalytic cycle, thus preceding the oxidative addition.

CONCLUSIONS

A mechanistic voyage into deciphering the active species in the low-temperature Kumada $C(sp^2)-C(sp^3)$ cross-coupling catalyzed by 1 led to the discovery of Ni(olefin)₃ complexes as being equally competent catalysts. Initial investigations revealed that complex 1 behaves as a precatalyst in this reaction and rapidly delivers highly active Ni(0) species. Stoichiometric experiments between 1 and vinyl bromide 5 revealed that 16-electron tris(olefin)Ni(0) complexes bearing 1,2-dialkyl substituents could be responsible for the catalytic activity observed at low temperatures. After a survey of structurally distinct complexes, $Ni(nor)_3$ (10) arose as an extremely active catalyst, affording up to a 74% yield of 11 containing a $C(sp^2)-C(sp^3)$ bond. Further experimentation pointed out the inability of tris(olefin)Ni(0) complexes to undergo oxidative addition into the vinylic $C(sp^2)$ -Br bond at low temperatures (-40 to -65 °C). This striking observation led us to re-evaluate a canonical mechanism and postulate an

alternative hypothesis, where oxidative addition between these two species is not the first step of the catalytic cycle. We demonstrated that an initial addition event between an organomagnesium reagent and a tris(olefin)Ni(0) complex could be considered as an important step in the cycle. Adducts between Grignards and Ni(0)-olefin complexes have been largely studied by Wilke and co-workers and are strongly influenced by the position of the Schlenk equilibrium. In our system, different ethereal solvents had a profound effect in the outcome of the reaction, where more nucleophilic solvents afforded higher yields. Further studies on the reactivity of nickelate complex 13 revealed that this complex engaged with 5 to produce yields of $C(sp^2)-C(sp^3)$ bond formation comparable to those reported in the catalytic reaction. All of these experimental facts combined led us to postulate that the low-temperature Ni(0)-olefin-catalyzed Kumada cross-coupling proceeds via a mechanism alternative to the traditionally postulated Ni(0)/Ni(II). In this scenario, an initial heterobimetallic adduct between Ni(0) and the organomagnesium occurs, which resembles the cross-couplings with isoelectronic Cu(I) catalysts. Whether such Ni(0)-alkyl intermediates forge the C-C bond through an oxidative addition pathway is currently under investigation. In any case, this change in fundamental steps might provide information for other similar catalytic systems and could lead to the design of olefin ligands for a Ni center en route to C-C cross-coupling reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00775.

Experimental procedures and analytical data (¹H and ¹³C NMR) for all new compounds (PDF)

Accession Codes

CCDC 2047047 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Funding

Financial support for this work was provided by Max-Planck-Gesellschaft, Max-Planck-Institut für Kohlenforschung, and Fonds der Chemischen Industrie.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. C. Weidenthaler for help in the XPS measurements and Dr. M. Leutzsch for support in the NMR analysis. We also thank Dr. R. Goddard for assistance in the X-ray diffraction, J. Busch for help in the synthesis of starting materials, and Prof. C. W. Lehmann for assistance with TEM-EDX. We also thank Prof. Dr. A. Fürstner for insightful discussions and generous support.

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