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RESEARCH ARTICLE

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Ligand-Enabled Nickel-Catalyzed Redox-Relay Migratory Hydroarylation of Alkenes with Arylborons

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Dedicated to the 70th anniversary of Shanghai Institute of Organic Chemistry

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Abstract: A redox-relay migratory hydroarylation of isomeric mixtures of olefins with arylboronic acids catalyzed by nickel complexes bearing diamine ligands is described. A range of structurally diverse 1,1-diarylalkanes, including those containing a 1,1-diarylated quaternary carbon, were obtained in excellent yields and with high regioselectivity. Preliminary experimental evidence supports the proposed non-dissociated chainwalking of aryl-nickel(II)-hydride species along the alkyl chain of alkenes before selective reductive elimination at a benzylic position. A catalyst loading as low as 0.5 mol% proved in large-scale synthesis to be sufficient while retaining high reactivity, highlighting the practical value of this transformation.

Introduction

Selective introduction of a functional group onto an inert sp^3 carbon is of considerable synthetic utility and will allow access to structures with a more concise synthetic route or from more readily available starting materials.[1] To distinguish between multiple, yet similar, inert sp^3 C–H bonds, a pre-installed polar directing group nearby is necessary in most reported processes and this limits their generality and applicability. Given the abundance and easy accessibility of alkene feedstock, remote functionalization through alkene isomerization and sequential selective cross-coupling has recently emerged as an attractive alternative in which a non-polar C=C double bond in an arbitrary position is used as a traceless directing group and the distant C–H bond is selectively functionalized.[2-6] Previously, starting from isomeric olefins and a wide variety of electrophilic coupling partners, nickel[7] catalyzed reductive remote hydrofunctionalization[6c-e,g-i,l,m,o-u,x,z] has been developed *via* proposed nickel hydride intermediates[8,9] (Figure 1a). Despite robust investigation, these methods are generally limited by the need of a stoichiometric amount of extra reductant.

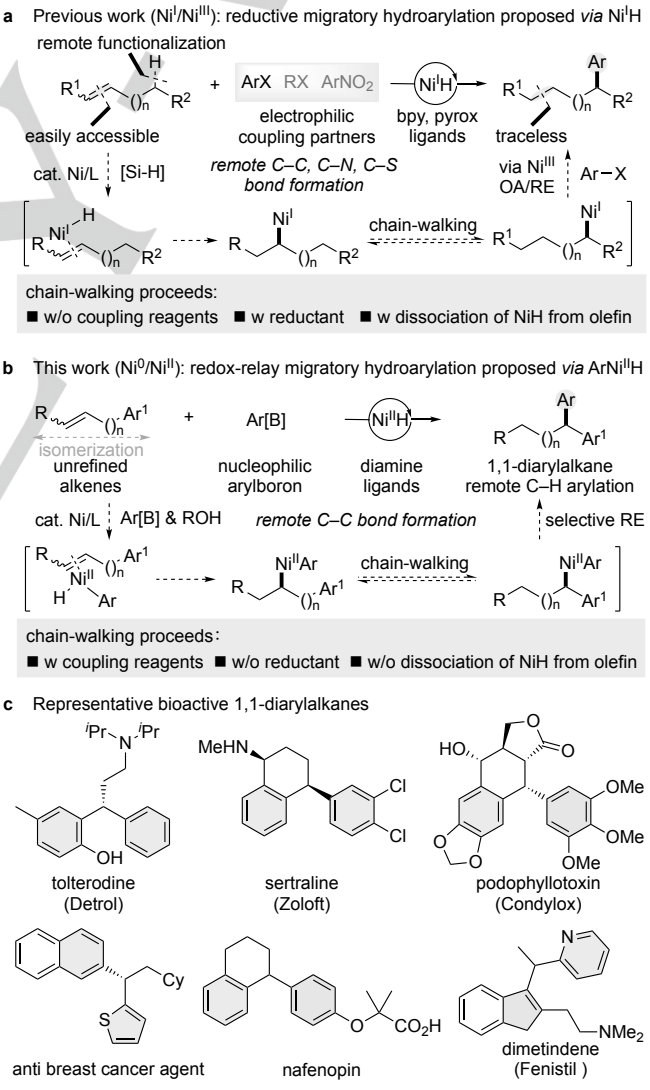


Figure 1. Design plan: redox-relay migratory hydroarylation *via* the aryl-nickel(II)-hydride generated *in situ*.

Distinct from the previously reported nickel-catalyzed reductive remote hydroarylation systems,[6e,h,s,z] two precedents of redox-neutral olefin remote hydroarylation have been reported by Lee[6a] and by Hartwig[6b]. However, the scope of the arylation is limited to only trifluoromethylarenes or heteroarenes with low pK_a values. To address these shortcomings, we speculated that oxidative addition of a ligated nickel(0) with alcohol[10c-f] followed by a transmetalation with commercial available arylboronic acids would provide rapid access to a broad range of aryl-nickel(II)-hydride species, which could also serve as a platform for remote hydroarylation of alkenes (Figure 1b). Specifically, if the aryl-nickel(II)-hydride generated *in situ* is active enough to insert into an isomer or mixture of isomers of the olefin substrate and promote a fast and reversible chain-walking process along the hydrocarbon chain prior to a selective reductive elimination, then a convergent and regioselective migratory arylation instead of hydroarylation at the *ipso* position[10,11] would be achieved. Ideally, depending on the choice of the ligand, selective reductive elimination at the benzylic position would provide a complementary approach to the synthesis of a wide variety of 1,1-diarylalkanes as important pharmacophores[12] (Figure 1c). Unlike our previously proposed reductive nickel(I)-hydride catalyst system,[6e,h,s] this proposed aryl-nickel(II)-hydride process suggests that: (1) no extra reductant is required, (2) chain-walking happens with the participation of the coupling partners to form the active catalyst, aryl-nickel(II)-hydride, (3) chain-walking proceeds efficiently with no dissociation of the aryl-nickel(II)-hydride catalyst from the alkenes.

A detailed description of our proposed pathway is outlined in Figure 2. Initially, the nickel(0) species (**I**) is formed from a Ni(II) precursor with a catalytic amount of arylboronic acid. It then undergoes a reversible oxidative addition with the alcohol to generate a nickel(II) hydride adduct (**II**), followed by transmetalation with arylboronic acid (**2**) to form the active aryl-nickel(II)-hydride species (**III**) which inserts into the alkene (**1a**) to generate an alkyl-nickel-aryl intermediate (**IV**). This readily undergoes fast and reversible β-hydride elimination to afford the isomeric complex (**V**). A series of isomeric alkyl-nickel(II)-aryl species (**IV**, **VI**, **VII**, **….**) is then accessed through a series of rapid and reversible iterative β-hydride elimination/migratory reinsertions. In particular, if selective reductive elimination of benzyl-nickel(II)-aryl intermediate (**VII**) is favorable relative to other alkyl-nickel(II)-aryl isomers, the benzylic arylation product could be obtained with high regioselectivity, along with a nickel(0) species (**I**) thus closing the catalytic cycle. There are three major challenges to such a mechanistically unique process. First, the aryl-nickel(II)-hydride species must be sufficiently *stable* to avoid the undesired irreversible reductive elimination producing an arene. Second, the aryl-nickel(II)-hydride species must be sufficiently *reactive* to promote a fast and reversible chain-walking process. Third, the reductive elimination of the alkyl-nickel(II)-aryl intermediate must be highly *selective*, a less reactive alkyl-nickel(II)-aryl species would be converted by chain-walking into a more reactive alkyl-nickel(II)-aryl intermediate.

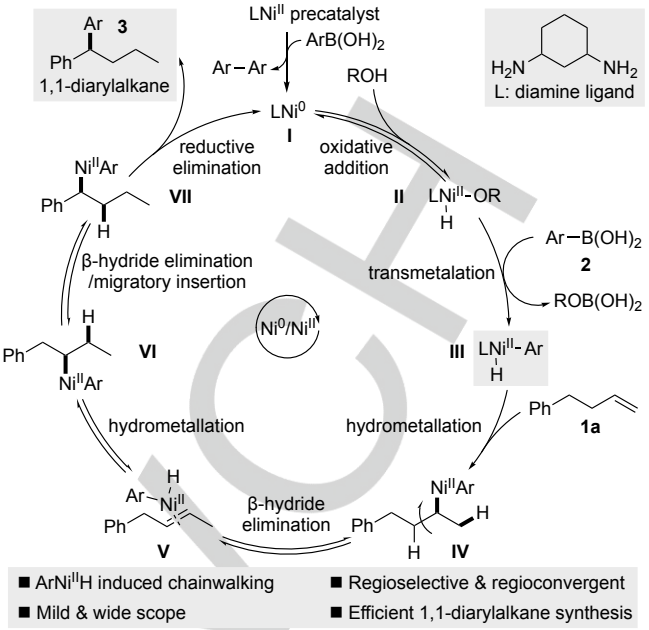
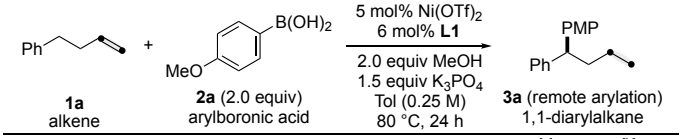


Figure 2. Envisioned catalytic cycle.

Results and Discussion

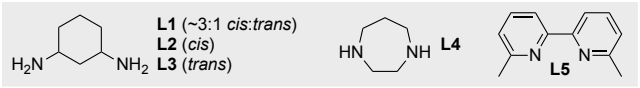
Based on this hypothesis, we first examined the proposed remote hydroarylation with 4-phenyl-1-butene (**1a**) and (4-methoxyphenyl)boronic acid (**2a**). After systematic manipulation of the reaction parameters and ligand evaluation, the desired migratory arylation product (**3a**) was isolated in good yield (84%) as a single isomer using a combination of bench-stable $Ni(OTf)_2$ as a precatalyst, methanol as a hydride source, and a simple diamine (**L1**) as a ligand[13] (Table 1, entry 1). $Ni(cod)_2$ was originally explored as a nickel source (entry 2), but the air-stable nickel(II) precatalysts were also effective. Notably, the ligand **L1** used is a *cis*- and *trans*- mixture (~3:1 *cis*:*trans*), in which the *cis*-isomer (**L2**) reacted effectively (entry 3) but the pure *trans*-isomer (**L3**) led to a significantly lower yield and selectivity (entry 4). Since a mixture (**L1**) is much cheaper than pure *cis*-isomer (**L2**), it was chosen for subsequent investigations. Another diamine ligand (**L4**) could also facilitate the migratory arylation, although only a moderate yield was obtained (entry 5). The electron-rich phosphine ligand P^tBu_3 or the 6,6'-dimethyl-2,2'-bipyridine ligand (**L5**), which were previously used in reductive NiH catalyst system[6e,h,s,z], gave no reaction. As expected, control experiments revealed that the alcohol is crucial. Poor conversion was observed in the absence of methanol (entry 7); and ethanol was less effective (entry 8). Use of other solvents such as THF led to only a moderate yield (entry 9). However, methanol was shown to be an unsuitable solvent (entry 10). Inferior results were obtained when replacing CsF as base (entry 11) or using 1.5 equiv of the arylboronic acid (entry 12) or conducting the reaction at 70 °C (entry 13).

Table 1: Variation of reaction parameters.



1a alkene | **2a** (2.0 equiv) arylboronic acid | **3a** (remote arylation) 1,1-diarylalkane

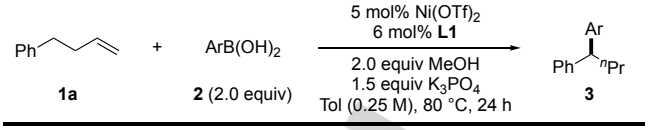
Entry	Variation from standard conditions	Yield [%][a]	rr[b]
1	none	99 (84)	>99:1
2	$Ni(cod)_2$ instead of $Ni(OTf)_2$	91	>99:1
3	**L2** instead of **L1**	99	>99:1
4	**L3** instead of **L1**	71	89:11
5	**L4** instead of **L1**	57	>99:1
6	P^tBu_3 or **L5** instead of **L1**	NR	–
7	no MeOH	8	>99:1
8	EtOH instead of MeOH	83	>99:1
9	THF instead of Tol	76	>99:1
10	MeOH as solvent	NR	–
11	CsF instead of K_3PO_4	77	>99:1
12	1.5 equiv **2a**	78	>99:1
13	70 °C	85	>99:1



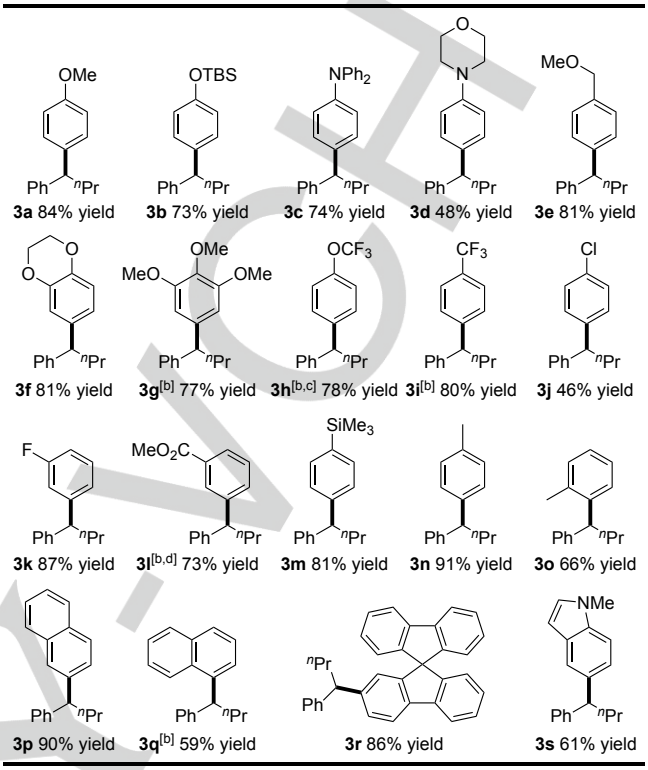
[a] Yields determined by GC using *n*-dodecane as the internal standard, the yield in parentheses is the isolated yield. [b] Regioselectivities (rr) determined by GC and GCMS analysis. Tol = toluene; THF = tetrahydrofuran; PMP = 4-methoxyphenyl.

With the optimal conditions in hand, we sought to define the scope of the arylboronic acid partner (Table 2). A wide range of arylboronic acids including both electron-rich (**2a**–**2e**) and electron-deficient (**2f**–**2l**) arylboronic acids, are accommodated well. A variety of functional groups are also readily accommodated, including ethers (**2a**, **2b**, and **2d**–**2h**), amines (**2c**, **2d**), a trifluoromethyl group (**2i**), an aryl chloride (**2j**), an aryl fluoride (**2k**), an ester (**2l**), a silane (**2m**), and alkyl groups (**2n**, **2o**). Notably, *ortho*-substituted arylboronic acids (**2o**, **2q**) could also be coupled in good yields while the corresponding *ortho*-substituted aryl halides could not be coupled using our previous reductive chain-walking protocols[6e,h]. Moreover, heterocycles such as indole (**2s**) are also competent coupling partners.

Table 2: Scope of arylboronic acid coupling partner.[a]



1a | **2** (2.0 equiv) | **3**



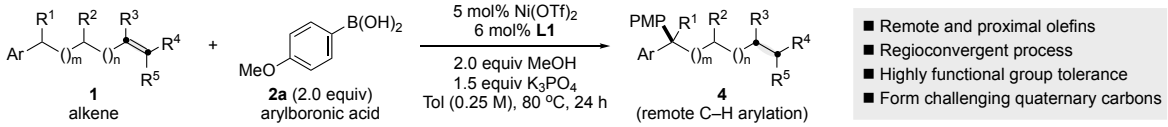
[a] Yield under each product refers to isolated yield of purified product (0.5 mmol scale, average of two runs), >99:1 regioisomeric ratio (rr) unless otherwise noted. [b] 6.0 equiv MeOH used. [c] **L4** used. [d] 1.0 equiv K_3PO_4 used.

The scope of the alkenes was also explored (Table 3). As shown in Table 3a, an array of terminal aliphatic alkenes with a variety of substituents on the remote aromatic ring, including both electron-withdrawing (**1c**–**1g**) and electron-donating (**1h**–**1k**) substituents underwent migratory hydroarylation smoothly. Moreover, a series of heterocycles frequently found in the medicinally active agents in place of the aryl group, including furan (**1l**), benzofuran (**1m**), and indole (**1n**, **1o**), were shown to be viable substrates. The reaction is insensitive to the length of the chain between the C=C bond and the remote aryl group, regardless of the starting position of the C=C bond (**1a**, **1p**–**1r**). Notably, an alkene (**1s**) with an internal branching, e.g. a tertiary sp^3 carbon between the C=C double bond and the remote aryl group, along the alkyl chain was also a suitable substrate. Moreover, 1,1-disubstituted alkenes (**1t**, **1u**) could also be employed. In a more striking example, a 1,1-disubstituted alkene (**1v**) containing a pre-existing tertiary carbon at the benzylic position can also undergo migratory hydroarylation to produce a product with a challenging quaternary carbon at the benzylic position.

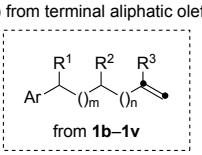
Unactivated aliphatic internal alkenes are also competent substrates, regardless of the *E*/*Z* configuration or the starting position of the C=C bond (Table 3b, **1w**–**1a'**) and even a trisubstituted internal alkene could also be well-tolerated (**1a'**). To get better yields, CsF is used as base in most cases. Additionally, the current transformation could also be applied to

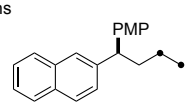
styrenes themselves, to producing the desired 1,1-diarylalkanes exclusively (Table 3c). Both *E* (**1b'**) and *Z* (**1c'**) styrenes, as well as styrenes with a variety of substituents on the remote aryl ring (**1f'**, **1g'**) are suitable substrates. Remarkably, with α-alkyl substituted styrenes (**1d'**–**1g'**), benzylic arylation exclusively producing the challenging products bearing a quaternary carbon were still preferred in all cases.

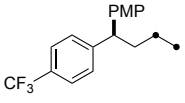
Table 3: Scope of alkene coupling component.[a]

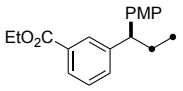


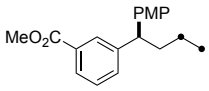
a) from terminal aliphatic olefins

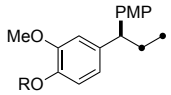


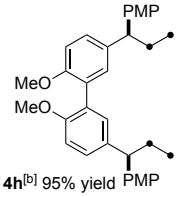

4b 69% yield

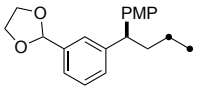

4c 56% yield

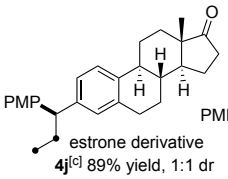

4d 76% yield

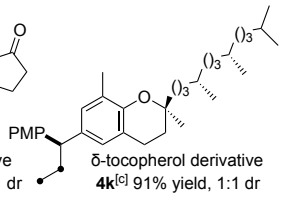

4e 61% yield

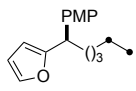

4f R=TBS, 93% yield
4g R=Bn, 94% yield

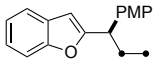

4h[b] 95% yield

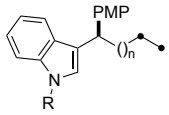

4i 43% yield

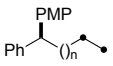

estrone derivative
4j[c] 89% yield, 1:1 dr

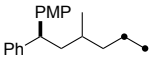

δ-tocopherol derivative
4k[c] 91% yield, 1:1 dr

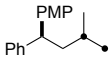

4l 45% yield

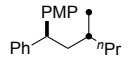

4m 60% yield

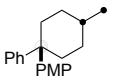

4n R=Bn, n=2, 83% yield
4o R=Boc, n=0, 74% yield


4p n=3, 87% yield
4q n=6, 74% yield
4r[d] n=10, 68% yield


4s[c,d] 68% yield, 2:1 dr

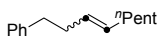

4t 62% yield

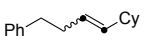

4u[c,d] 56% yield, 2:1 dr

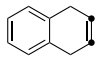

>20:1 dr
4v 48% yield, 95:5 rr

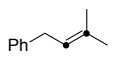
b) from unactivated internal olefins

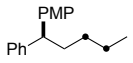

1w

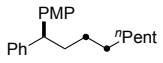

1x

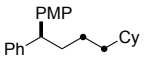

1y

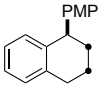

1z

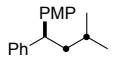

1a'


4w[e] 65% yield


4x[e] 47% yield

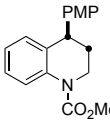

4y[e] 43% yield


4z 98% yield

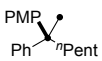

4a'[e] 45% yield

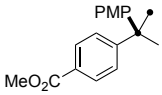
c) from styrenes

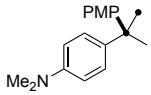

4b' 87% yield


4c' 69% yield


4d' 99% yield


4e' 79% yield


4f' 57% yield


4g' 79% yield

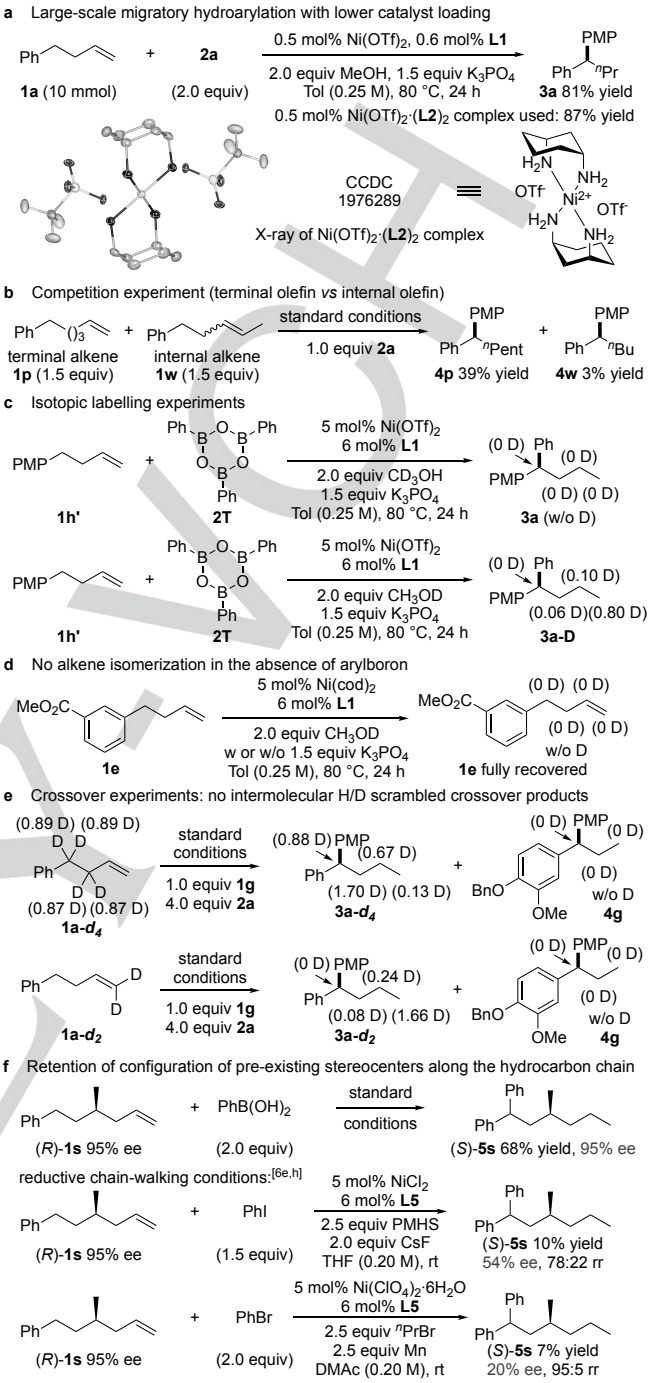
[a] Yield under each product refers to isolated yield of purified product (0.5 mmol scale, average of two runs), >99:1 regioisomeric ratio (rr) unless otherwise noted. [b] 0.25 mmol **1h** used. [c] Diastereomeric ratio (dr) determined by crude ^{1}H NMR analysis. [d] 2.5 equiv **2a** used. [e] 2.5 equiv **2a**, 2.0 equiv CsF, and 4.0 equiv MeOH used.

The practical value of this transformation was further highlighted by large-scale synthesis using lower catalyst loading (Scheme 1a). When conducting the reaction on the 10 mmol scale, it could proceed to completion with only 0.5 mol% catalyst. By treating $Ni(OTf)_2$ and **L1** in methanol, a dark yellow air-stable solid $Ni(OTf)_2$·(**L2**)$_2$ was obtained.[14] Accordingly, with 0.5 mol% loading of this stable precatalyst, the standard reaction on 10 mmol-scale also proceeds well. Further experiments were conducted to assess the reactivity of different olefins. As shown in Scheme 1b, competition experiments indicate that terminal alkenes are more reactive than internal alkenes.

As suggested in the initial mechanistic proposal, a stoichiometric amount of alcohol could provide the alcohol O−H group as a hydride source. To verify this hypothesis, isotopic labeling experiments of an alkene (**1h'**) and arylboroxine **(2T**) were carried out using CD_3OH or CH_3OD, respectively (Scheme 1c). No deuterium incorporation was observed in **3a** when CD_3OH was used. However, deuterium incorporation in **3a-D** was observed when CH_3OD was used. These results indicate that the nickel-hydride intermediate was initially generated from the O−H group of the alcohol instead of the C−H bond of the methanol.

To gain more insight into the chain-walking process, the alkene (**1e**) was subjected to the reaction conditions in the absence of arylboronic acid but using more reactive $Ni(cod)_2$ instead of pre-catalyst $Ni(OTf)_2$ and CH_3OD instead of CH_3OH.

After 24 hours, with or without base, the alkene **1e** was fully recovered without any observation of isomerization or H/D exchange (Scheme 1d). These results are consistent with a mechanism in which chain-walking happens only with the participation of the cross-coupling partner through an aryl-nickel(II)-hydride. Further experiments were conducted to assess whether the nickel-hydride catalyst disengages during the chain-walking process. Two crossover experiments using a 1:1 mixture of deuterium-labeled olefin and undeuterated olefin were carried out. Unlike in our previous proposed Ni(I)H catalyst system,[6e,h,s] no H/D scrambled crossover products were obtained (Scheme 1e). This observation indicates that as the nickel-hydride catalyst proceeds through the iterative β-hydride elimination/migratory insertion, no dissociation of the catalyst from the olefin substrate occurs throughout the relay process. To support the chain-walking proposal further, alkene (*R*)-**1s** containing a pre-existing stereogenic center in the alkyl chain was evaluated (Scheme 1f). Preservation of the chiral integrity was observed in this case which is also consistent with the non-dissociated chain-walking mechanism, in contrast to the partial racemization of this stereocenter under our previous reductive chain-walking conditions[6e,h].



Scheme 1. Large-scale and mechanistic experiments.

Conclusion

In conclusion, we have developed a highly efficient and robust nickel-catalyzed redox-relay migratory hydroarylation reaction from two readily available chemicals, olefins and arylboronic acids. An array of structurally diverse 1,1-diarylalkanes, including some containing a 1,1-diarylated quaternary carbon, were obtained with excellent regio- and chemoselectivity, from a reaction with high functional group tolerance. The practical value of this transformation is highlighted by the large-scale synthesis with low catalyst loading.

Finally, mechanistic experiments are consistent with the generation of an aryl-nickel(II)-hydride which participates in a non-dissociated chain-walking before selective reductive elimination at a benzylic position to produce the final product. The development of an asymmetric version of this transformation is currently in progress.

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Keywords: C–H activation • cross-coupling • isomerization • nickel • regioselectivity

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[13] Currently, the exact role of the bidentate N-based ligand is still under investigation.

[14] CCDC 1976289 ($Ni(OTf)_2{\cdot}(\mathbf{L2})_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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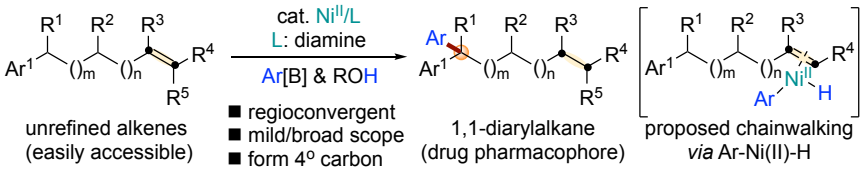
Entry for the Table of Contents



A highly efficient and selective nickel-catalyzed redox-relay migratory hydroarylation process was reported. This mild process was proposed to proceed through non-dissociated chain-walking of aryl-nickel(II)-hydride along the hydrocarbon chain of alkene.

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