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Regio- and Stereoselective Diarylation of 1,3-Dienes via Ni/Cr Cocatalysis

Wei-Song Zhang, Ding-Wei Ji, Ying Li, Xiang-Xin Zhang, Chao-Yang Zhao, Yan-Cheng Hu, and Qing-An Chen*

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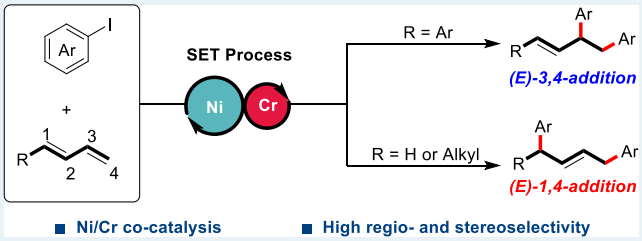
ABSTRACT: Through the formation of the thermodynamically favored Cr(III)−O bond, the Nozaki−Hiyama−Kishi reaction has been widely applied in the functionalization of carbonyl compounds with the help of Ni catalysis. Herein, a divergent regio- and stereoselective diarylation of dienes has been developed under Ni/Cr cocatalysis without the inherent driving force for the formation of polar metal alkoxides. Preliminary experimental studies have been conducted to elucidate the key roles of Ni, Cr, and redox-active bis(imino)pyridine (PDI) ligands. The proposed mechanism suggests that the newly formed C−C bond of this diarylation was created by organonickel species instead of organochromium species.



KEYWORDS: *nickel, chromium, co-catalysis, diarylation, 1,3-dienes, regioselectivity*

Since its discovery, the Nozaki−Hiyama−Kishi (NHK) reaction has been recognized as one of the most powerful synthetic tools for the construction of new carbon−carbon bonds and widely applied in the total synthesis of natural products.[1] With regard to the mechanism, the first step is the reduction of Ni(II) to Ni(0), which undergoes oxidative addition with organic halides. The subsequent transmetallation between organonickel species with Cr(III) generates a vital organochromium(III) nucleophile, which is then easily captured by the carbonyl compounds. Thermodynamically, the driving force of the classic NHK reaction is the formation of a strong Cr(III)−O bond or other metal alkoxides (Scheme 1A).[2]

Alkenes are also important building blocks in organic synthesis. However, without the formation of thermodynamically favored metal−oxygen bonds, alkenes are not amenable to the NHK reaction, and the scope is limited to aldehydes and ketones. Moreover, although the NHK reaction has shown its strong power for C−C bond formation, only a single bond was constructed once in the most established cases. Forging multiple C−C bonds simultaneously, for example, diarylation of alkenes, still remains underexplored. Inspired by recent precedents on the Ni-catalyzed functionalization of alkenes,[3] we wondered the possibility that reforms the role of the nickel catalyst in a traditional NHK reaction and makes it suitable for the catalytic diarylation of alkenes. Given that Cr(II) is a good one-electron donor, we envisioned that this proposal could be realized through a single electron-transfer (SET) process between Cr and Ni species with the help of a ligand. Moreover, the formation of the C−C bond was created by organonickel species instead of organochromium species (Scheme 1B).

The catalytic functionalization of 1,3-dienes is one of the most powerful strategies to build up molecular complexity.[4−6] Compared with that of mono alkenes, the arylation of dienes brings extra challenges in selective control owing to the existence of an additional C═C bond.[7] Although diarylation of aryl dienes has been reported by Sigman et al., stoichiometric organotin reagents and noble palladium catalysts were required in their work.[8] Therefore, it is of great interest to develop the selective arylation of dienes with simple organic halides under the catalysis of earth-abundant metals.[9−11] Herein, we developed a regio- and stereoselective diarylation of 1,3-dienes through Ni/Cr co-catalysis with the help of redox-active bis(imino)pyridine (PDI) ligands (Scheme 1C).

4-Iodoanisole **1a** and diene **2a** were chosen as model substrates to test the feasibility of 3,4-diarylation (Table 1). We first employed the known catalytic systems to promote diarylations. However, the desired product **3aa** could not be obtained from **1a** and **2a** (entries 1 and 2). In view of the fact that Cr(II) is a versatile one-electron donor, $NiCl_2/CrCl_2$ catalysis was further attempted. A small amount of diarylated product **3aa** (8% yield) was indeed detected when using PPh_3 as a ligand and Mn as a reductant, accompanied by the Heck (**4**) and hydroarylated (**5**, **6**, and **7**) products (entry 3). No improvement on the reactivity and ratio of *E*/*Z* was observed

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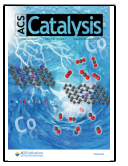

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Scheme 1. Transition-Metal-Catalyzed Arylations of 1,3-Dienes

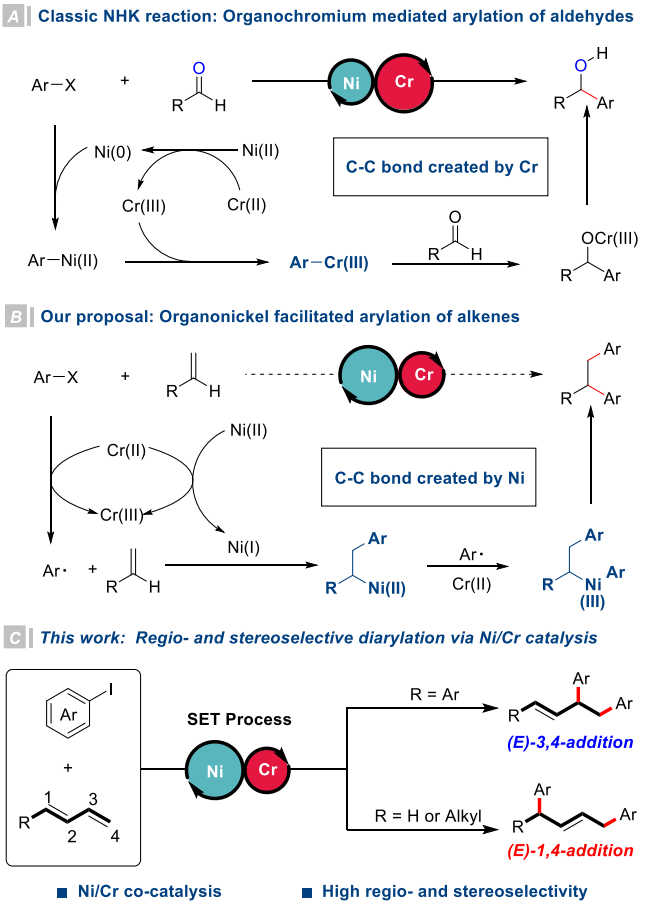
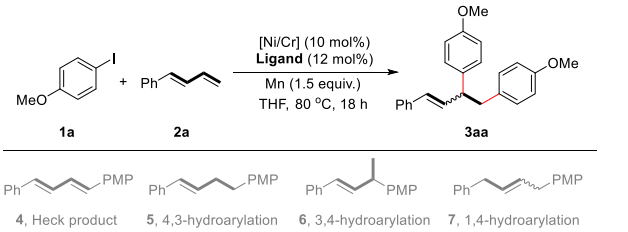
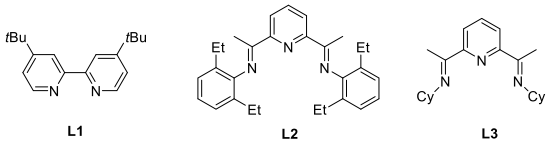


Table 1. Optimization of Reaction Conditions[a]



Entry	Established catalytic systems for diarylations	3aa (%)
1	*Refs. 8* [Pd] (See Table S1 entries 1-2 for details)	N.D.
2	*Refs. 11* [Ni] (See Table S1 entries 4-7 for details)	N.D.

Entry	Catalyst	Ligand	3aa (%)	*E*/*Z*	4 (%)	5+6+7 (%)
3	$NiCl_2/CrCl_2$	PPh_3[b]	8	12:1	3	2
4	$NiCl_2/CrCl_2$	PCy_3[b]	7	3:1	3	4
5	$NiCl_2/CrCl_2$	dppe	--	--	--	--
6	$NiCl_2/CrCl_2$	**L1**	23	>20:1	3	4
7	$NiCl_2/CrCl_2$	**L2**	52	>20:1	5	6
8	**$NiCl_2/CrCl_2$**	**L3**	**84**[c]	**>20:1**	**5**	**6**
9	$NiBr_2/CrCl_2$	**L3**	72	>20:1	6	7
10	$Ni(DME)Cl_2/CrCl_2$	**L3**	78	>20:1	5	7
11[d]	$NiCl_2/CrCl_2$	**L3**	15	>20:1	6	2
12[e]	$NiCl_2/CrCl_2$	**L3**	16	>20:1	3	1
13	$CrCl_2$	**L3**	trace	--	--	--
14	$NiCl_2$	**L3**	--	--	--	--



[a]Condition: **1a** (0.22 mmol), **2a** (0.10 mmol), [Ni/Cr] (10 mol %), ligand (12 mol %), Mn (1.5 equiv), THF (0.50 mL), 80 °C, 18 h. Yield and ratio of *E*/*Z* were determined by GC-FID analysis with mesitylene as the internal standard. [b]Ligand (24 mol %). [c]Isolated yield. [d]DMA instead of THF. [e]MeCN instead of THF.

with either mono- or bisphosphine ligands (entries 4 and 5). With the help of bipyridine ligand **L1**, the yield of product **3aa** was enhanced to 23%, and the ratio of *E*/*Z* increased from 12:1 to >20:1 (entry 6). Notably, tridentate bis(imino)pyridine (PDI) ligands **L2** and **L3** could further improve the efficiency, and the latter gave a higher yield of **3aa** (entries 7 and 8). Other nickel precursors such as $NiBr_2$ and $Ni(DME)Cl_2$ displayed a negative impact (entries 9 and 10). The solvents DMA and MeCN suppressed the reaction (entries 11 and 12). Control experiments confirmed that both nickel and chromium were indispensable for this reaction (entries 13 and 14).

With the optimized conditions in hand, we subsequently explored the scope of substrates toward 3,4-diarylation. As illustrated in Table 2, iodobenzenes bearing either electron-donating or electron-withdrawing substituents at the 4-position of the phenyl ring all reacted with diene **2a** in good reactivities and excellent regio- and stereoselectivities (**3aa**−**3ja**). Substrates possessing groups at the 3- or 2-position of iodobenzenes were also well applicable, giving products **3ka**−**3ma** in 64−88% yields. 1-Iodonaphthalene was also a suitable substrate for the current transformation (**3na**). Besides, synthetically versatile functional groups such as −F (**3ea**), −Cl (**3fa**), −CN (**3ga**), and $-CO_2Me$ (**3ha**) could be well tolerated in these cases. It is worth noting that this diarylation could even proceed in a 4 mmol scale with high efficiency (80% yield for **3ba**).

Then, we continued to investigate the scope of 1,3-dienes in coupling with 4-iodoanisole under Ni/Cr catalysis (Table 3). Generally, the reaction exhibited no obvious loss in both reactivities and selectivities when electron-rich or electron-deficient dienes were subjected (**3ab**-**3ak**), although **L2** as the ligand is a better choice for electron-rich dienes in terms of reactivity (**3ae** and **3af**). Good yields and selectivities could also be achieved even when ortho-substituted 1-aryl-1,3-dienes were employed, regardless of their steric hindrance (**3al** and **3am**). In addition, substrates with naphthyl and furyl rings showed good reactivities as well, producing the products in 70−78% yields (**3an** and **3ao**).

1,3-Butadiene is an important bulk chemical feedstock that could be produced from both petroleum and biomass with an annual production scale of over 10 million tons. Therefore, it is highly appealing to realize divergent diarylation of 1,3-butadiene. The difunctionalization of 1,3-butadiene usually suffers from the regio- and stereoselectivity issues. Indeed, poor selectivities (**9aa**/**10aa** 3:1, *E*/*Z* 1:1) were observed in the initial investigation of the diarylation between 1,3-butadiene **8a** and 4-iodoanisole **1a** (Table 4, entry 1). To further improve the reaction performance, reaction parameters, including ligands, additives, and solvents, were carefully evaluated (Tables 4 and S3). Pleasingly, an enhanced selectivity (*E*/*Z* = 12/1, *rr* = 12/1) with a decent yield could be obtained when the reaction

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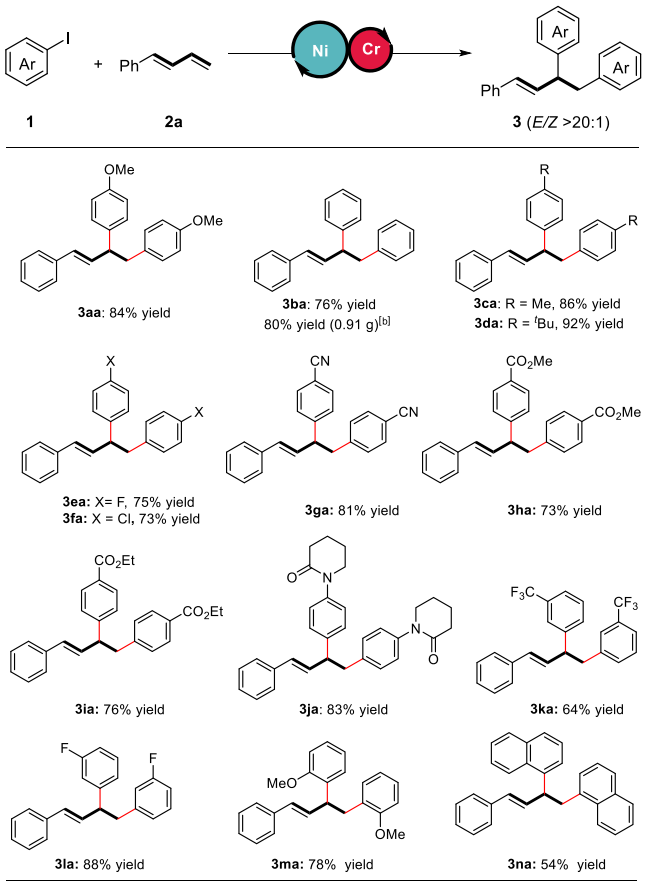
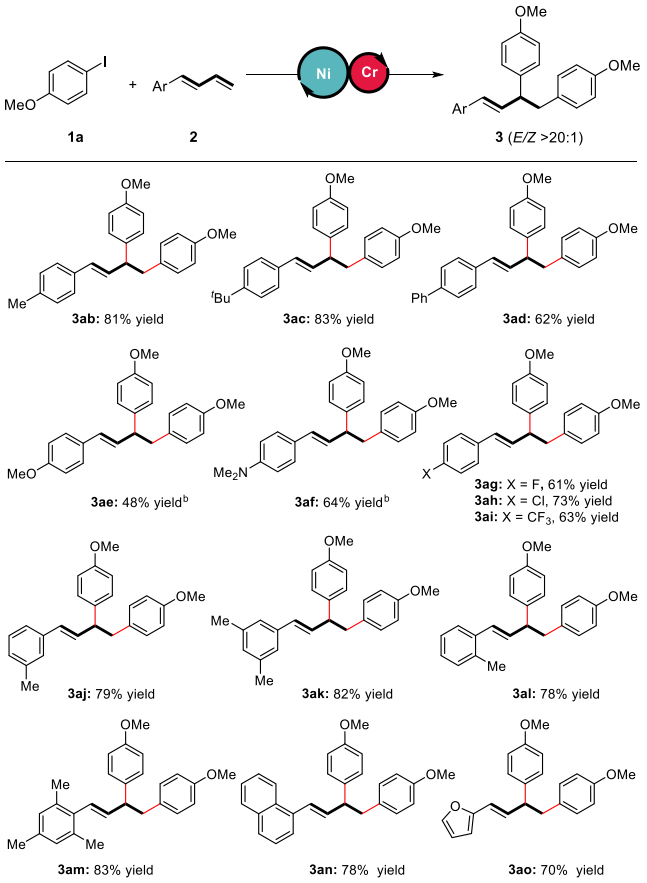
Table 2. Scope of Aryl Iodides for 3,4-Diarylation[a]



[a]Conditions: **1** (0.22 mmol), **2** (0.10 mmol), $NiCl_2$ (10 mol %), $CrCl_2$ (10 mol %), **L3** (12 mol %), Mn (1.5 equiv), THF (0.50 mL). Isolated yields were given. [b]**1a** (9.0 mmol) and **2a** (4.0 mmol).

Table 3. Scopes of Dienes for 3,4-Diarylation[a]



[a]Conditions: **1** (0.22 mmol), **2** (0.10 mmol), $NiCl_2$ (10 mol %), $CrCl_2$ (10 mol %), **L3** (12 mol %), Mn (1.5 equiv), THF (0.50 mL). Isolated yields were given. [b]**L2** was used instead of **L3**.

was conducted in MeCN with a catalytic amount of $(PhO)_2PO_2H$ as an additive and **L2** as the ligand (entry 9).

Subsequently, we examined the substrate generality of the 1,4-diarylation of 1,3-butadiene with iodobenzenes (Table 5). Subjecting unsubstituted iodobenzene to the standard conditions furnished the 1,4-diarylation product (**9ba**) in 59% yield with 18:1 *E*/*Z* and >20:1 *rr* (**9ba**/**10ba**). Alkyl and alkoxy on the phenyl ring, regardless of their positions, were all well tolerated and generated desirable products in 54−69% yields and good selectivities (**9aa**, **9ca**, **9da**, **9ha**, and **9ia**). It is noteworthy that halides, such as F, Cl, and Br, on the para-position of iodobenzenes, all remained intact under this process (**9ea**−**9ga**). Moreover, alkyl-substituted dienes at different positions such as cyclohexadiene (**9ab**), isoprene (**9ac**), and benzyl or phenylethyl dienes (**9ad** and **9ae**) showed moderate to good reactivities.

To demonstrate the synthetic utility of the diarylation products, programmable and concise synthesis of polyarylated functional molecules were performed from compounds **3ac** (81% yield from **1a** and **2c**, Scheme 2). Through an oxidative cyclization, polyaryl thiophene **11** which is a potential pesticide could be afforded from inorganic sulfurating reagents K_2S and **3ac** in 86% yield.[12] On the other hand, employing alkyne as a coupling partner for intermolecular C−H activation, polyarylated naphthalene **12** was constructed in a 61% yield with the help of the allylic C═C bond as a directing group.[13]

Detailed studies were carried out to shed light on the mechanistic insights. When submitting a *E*/*Z* mixture of diene isomers (**2a**/**2a'** = 1/1) to the 3,4-diarylation conditions, product **3aa** was obtained in a 77% yield with *E*/*Z* > 20/1 (Scheme 3a). This strong stereoconvergent effect implies the existence of a fast isomerization from *cis*-alkene to *trans*-alkene. Besides, a radical clock experiment between **1a** and **13** under this Ni/Cr co-catalysis successfully gave the ring-opening diarylation product **14** in 31% yield (Scheme 3b), which indicated the possibility of a SET process. Moreover, in the absence of Mn powder, 28% yield of **3aa** could still be produced with a stoichiometric amount of $CrCl_2$. This reveals that Mn probably served as a reductant for the regeneration of the $CrCl_2$ cocatalyst from Cr(III) species (Scheme 3c). Besides, the control experiments showed that $CrCl_2$ was indispensable for the generation of aryl radicals (Scheme 3d).

To further probe the active nickel species during this diarylation, electron paramagnetic resonance (EPR) investigations were carried out (Scheme 4). No EPR signals were observed for the mixture of $NiCl_2$ and **L3** with a molar ratio of 1:1.2 (Scheme 4a-1). The replacing of $NiCl_2$ with $CrCl_2$ showed a singlet resonance with a *g* value of 1.98 (Scheme 4a-2). This characteristic signal matched with that of Cr species (Scheme 4b).[14] Then, upon the addition of $NiCl_2$ to the mixture of $CrCl_2$/**L3**, a new singlet resonance appeared with a *g* value of 2.16 (Scheme 4a-3), which is consistent with the value reported for Ni(I) species.[15] Moreover, EPR spectra in 77 K was

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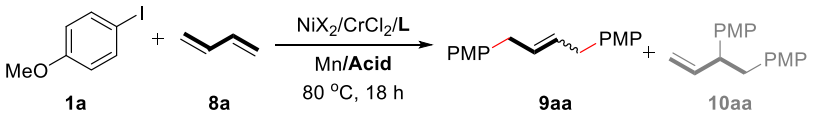
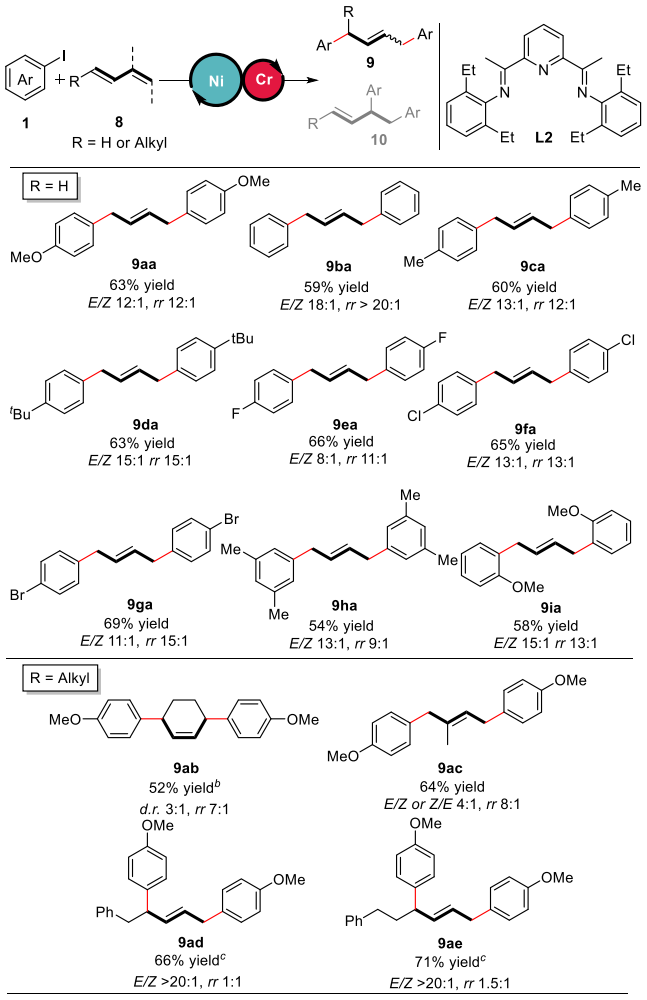
Table 4. Optimization of 1,4-Diarylation for Butadiene[a]



entry	ligand	acid	solvent	yield (%)	*E*/*Z* of **9aa**	**9aa**/**10aa**
1	**L3**		THF	66	1:1	3:1
2	**L2**		THF	65	4:1	5:1
3	**L2**		MeCN	13	12:1	9:1
4[b]	**L2**		MeCN	40	16:1	11:1
5[b]	**L2**	TFA	MeCN	70	12:1	10:1
6[b]	**L2**	CSA	MeCN	42	12:1	7:1
7[b]	**L2**	$AdCO_2H$	MeCN	46	12:1	10:1
8[b]	**L2**	$(PhO)_2PO_2H$	MeCN	83	12:1	10:1
9	**L2**	$(PhO)_2PO_2H$	MeCN	78[c] (63[d])	16:1 (12:1)	11:1 (12:1)

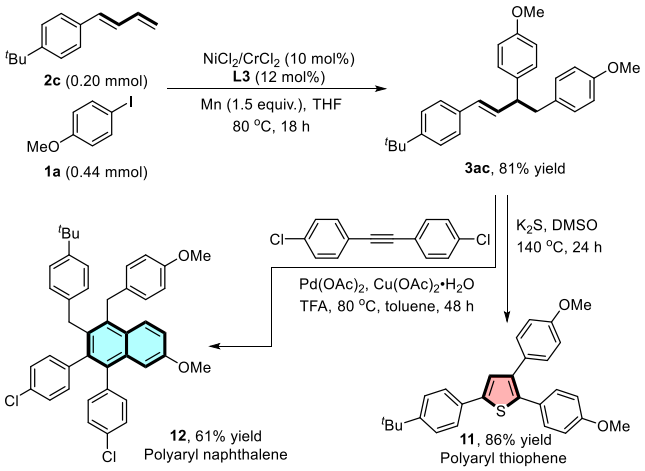
[a]Conditions: **1a** (0.20 mmol), **8a** (0.60 mmol), $NiBr_2$ (0.02 mmol), ligand (0.025 mmol), $CrCl_2$ (0.02 mmol), acid (0.04 mmol), Mn (0.40 mmol), solvent (0.40 mL), 80 °C, 18 h. The yield and selectivity were determined by GC-FID or ^1H NMR analysis with mesitylene as the internal standard. [b]$CrCl_2$ (0.04 mmol). [c]$NiCl_2$ was used in place of $NiBr_2$. [d]**1a** (0.40 mmol), **8a** (1.0 mmol), $NiCl_2$ (0.04 mmol), **L2** (0.048 mmol), $(PhO)_2PO_2H$ (0.03 mmol), $CrCl_2$ (0.08 mmol), Mn (0.60 mmol), MeCN (1.0 mL). Isolated yield was given.

Table 5. Substrate Scope Toward 1,4-Diarylation[a]



[a]Conditions: **1** (0.40 mmol), **8** (1.0 mmol), $NiCl_2$ (0.04 mmol), **L2** (0.048 mmol), $(PhO)_2PO_2H$ (0.03 mol), $CrCl_2$ (0.08 mmol), Mn (0.60 mmol), MeCN (1.0 mL), 80 °C, 18 h. Isolated yields of mixture (**9** and **10**) were given in all cases. Selectivities were determined by ^1H NMR analysis (*rr* is the ratio of **9**/**10**). [b]**1a** (0.44 mmol), **8** (0.20 mmol). [c]**1a** (0.22 mmol), **8** (0.10 mmol), $NiCl_2$ (0.02 mmol), **L2** (0.024 mmol), $(PhO)_2PO_2H$ (0.02 mmol), $CrCl_2$ (0.04 mmol), Mn (0.30 mmol), MeCN (0.50 mL).

Scheme 2. Transformations of Diarylation Products



conducted to further confirm the formation of Ni(I) species (see the Supporting Information for details). Thanks to PDI ligand's dual role as a strong σ-donor and a π-acceptor, these paramagnetic intermediates are stable enough to be detected.[11h,16] It is notable that there was no obvious signal when Mn was used instead of $CrCl_2$ (Scheme 4a-4). These EPR results suggest that $CrCl_2$ is indispensable for the generation of Ni(I) species (Scheme 4b).

Kinetic studies and interchange conversions were conducted to figure out the diarylation process (Scheme 5a). With the increase of the reaction time, the yield of **3aa** increased slowly and no other transitional products were detected during this period. Interchange conversion experiments also confirmed that Heck product **4** could not be converted into diarylated product **3aa** or **17** under standard conditions (Scheme 5b). Therefore, a stepwise process, which goes through reduplicated aryl-Ni insertions to achieve diarylation, is probably not involved.

On the basis of the above observations and previous work, a plausible mechanism for the selective diarylation via Ni/Cr co-catalysis is shown in Scheme 6.[17,18] A single-electron transfer (SET) between iodobenzene **1** and $Cr^{II}X_2$ produces Cr^{III} species and aryl radical **A**, which subsequently undergoes the radical addition with diene **2** or **8** to yield a new radical species **C**. Meanwhile, a reduction of $Ni^{II}X_2$ by $CrCl_2$ gives active Ni(I)

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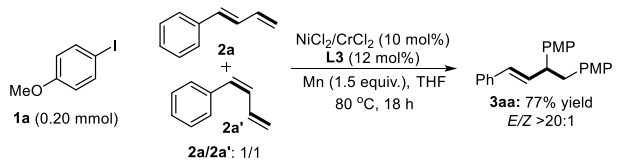
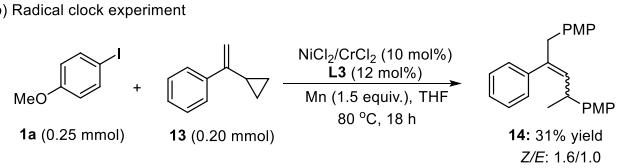
Scheme 3. Mechanistic Studies for the Diarylation Reaction

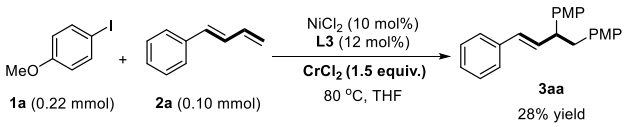
a) Stereoconvergent diarylation of dienes



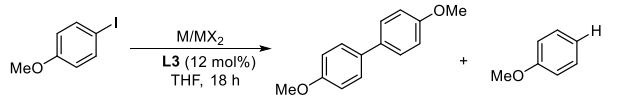
b) Radical clock experiment



c) Stochiometric amount of $CrCl_2$ (**without Mn powder**)



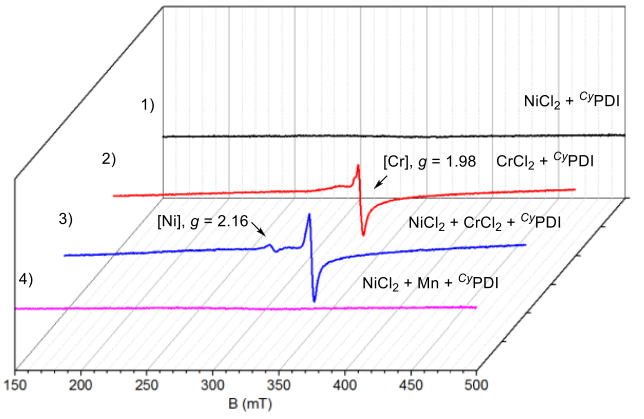
d) The control experiments for the generation of aryl radical



Entry	$NiCl_2$ (mmol)	$CrCl_2$ (mmol)	Mn (mmol)	15	16
1	0.01	0.10	--	34%	8%
2	0.01	--	0.10	0%	0%
3	--	0.01	0.10	11%	33%

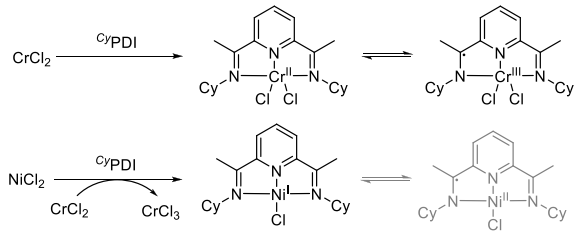
Scheme 4. EPR Spectra and Analysis

a) EPR spectra



EPR spectra in 292 K. 1) $NiCl_2$/^{cy}PDI (1.0:1.2) in THF; 2) $CrCl_2$/^{cy}PDI (1.0:1.2) in THF; 3) $NiCl_2$/$CrCl_2$/^{cy}PDI (1.0:2.0:1.2) in THF; 4) $NiCl_2$/Mn/^{cy}PDI (1.0:2.0:1.2) in THF

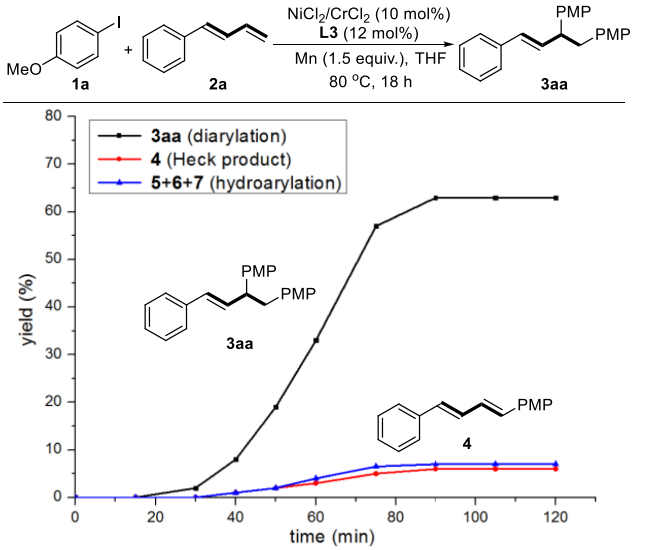
b) The formation of paramagnetic Ni and Cr species for diarylation



species **B** in situ in the presence of the PDI ligand.[19] Two regioisomers of the allyl-Ni^{II} intermediate (**D** and **D′**) could be expected via the combination of Ni(I) species **B** with allylic radical **C**. The steric hindrance between the PDI ligand and the allylic moiety will determine which isomers (**D** and **D′**) are favored in this coordinatively saturated (18-electron) complex. The presence of substitution on the C1 position of diene **1** favors a direct SET transfer between **B** and **C** to deliver allylic Ni(II) **D**. However, a S_N2'-type SET transfer becomes a dominant pathway for the combination between **B** and **C**.

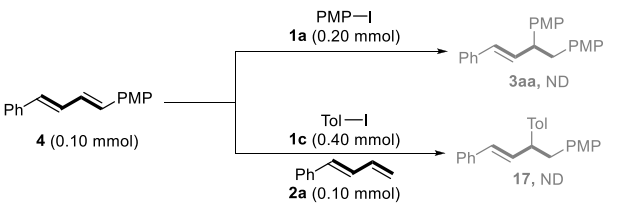
Scheme 5. Kinetic Studies and Interchange Conversion

a) Kinetic studies on Ni/Cr-catalyzed diarylation of diene



Condition: **1a** (0.22 mmol), **2a** (0.10 mmol), $NiCl_2$ (10 mol%), $CrCl_2$ (10 mol%), **L3** (12 mol%), Mn (1.5 equiv.), THF (1.5 mL), *n*-dodecane (0.5 equiv.), 80 °C.

b) Interchange conversion experiment



Condition: $NiCl_2$/$CrCl_2$ (10 mol%), **L3** (12 mol%), Mn (1.5 equiv.), THF, 80 °C, 18 h

Scheme 4 EPR spectra in 292 K. 1) $NiCl_2$/^{cy}PDI (1.0:1.2) in THF; 2) $CrCl_2$/^{cy}PDI (1.0:1.2) in THF; 3) $NiCl_2$/$CrCl_2$/^{cy}PDI (1.0:2.0:1.2) in THF; 4) $NiCl_2$/Mn/^{cy}PDI (1.0:2.0:1.2) in THF

In the catalytic cycle for the formation of diarylation product **3**, the reduction of allyl-Ni^{II} **D** by $Cr^{II}X_2$ furnishes allyl-Ni^{I} species **E** with coordinative unsaturation (17-electron). Therefore, a classic two-electron oxidative addition between **E** and aryl iodide **1** is not possible to be involved. However, a SET transfer from **E** and aryl iodide **1** could facilitate the formation of allyl-Ni^{III} species through a radical rebound mechanism. The presence of CrX_3 or MnX_2 could help the halogen abstraction during the generation of allyl-Ni^{III} species **F** through the formation of a weakly coordinating counteranion (MX^{Θ}_{n+1}). A final reductive elimination from allyl-Ni^{III} species **F** leads to 3,4-diarylation product **3** and regenerates Ni(I) catalyst **B** for the next catalytic cycle. Notably, Cr^{III} species can be reduced by Mn powder to realize the recirculation of $Cr^{II}X_2$. 1,4-Diarylation product **9** is generated through the left cycle (**D′**-**E′**-**F′**-**B**). Another pathway which proceeded through Ni^0 species cannot be ruled out (see Scheme S1 in the Supporting Information for details).

In summary, a selective diarylation of 1,3-dienes with aryl iodides has been developed under Ni/Cr co-catalysis. With the help of the redox-active PDI ligand, 3,4- and 1,4- diarylation of 1,3-dienes could be demonstrated in high regio- and

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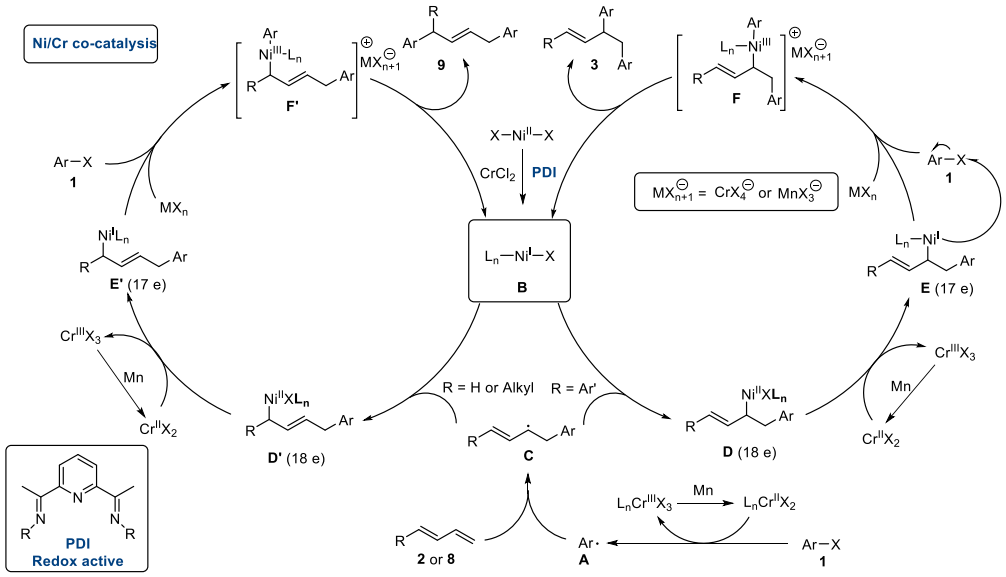
Scheme 6. Proposed Mechanism for Diarylation via Ni/Cr Catalysis



stereoselectivity, respectively. Preliminary mechanistic studies showed that $CrCl_2$ served as a necessary single-electron reductant for the formation of active Ni species and aryl radicals for diarylation. Further studies and application of this divergent arylation of dienes are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c05441.

Experimental procedures, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Qing-An Chen − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China;* orcid.org/0000-0002-9129-2656; Email: qachen@dicp.ac.cn

Authors

Wei-Song Zhang − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

Ding-Wei Ji − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China*

Ying Li − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

Xiang-Xin Zhang − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China;* orcid.org/0000-0003-0897-5577

Chao-Yang Zhao − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

Yan-Cheng Hu − *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China;* orcid.org/0000-0002-8731-4445

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.1c05441

Notes

The authors declare no competing financial interest.

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