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Novel and efficient Ni-mediated pinacol coupling of carbonyl compounds

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Abstract—It was firstly found that the Rieke Ni generated in situ was able to promote the pinacol coupling of various carbonyls efficiently. Based on this information, another catalytically effective, cheaper and more convenient $NiCl_2$(Cat.)/Mg/TMSCl system was designed and developed further successfully. The interesting single-electron transfer (SET) mechanisms for the coupling reactions were proposed. Additionally, the DL/*meso* diastereoselectivity and some additive effects were also explained in terms of the proposed mechanisms.

1. Introduction

One of the significant structure units in nature is the pinacols, which have wide occurrence in many biologically active molecules, such as Taxol,[1a] (−)-grayanotoxin III[1b] and so on. Recently, pinacols have been also used as the chiral ligands, auxiliaries[2] as well as versatile synthetic intermediates.[3] Generally, the pinacol units could be constructed through several approaches.[4] Among them, the particularly important and most widely used is the coupling of carbonyl compounds, which can be induced photochemically[5] and electrochemically,[6] or by use of various metals or their salts.[7] For the latter, the currently used metals included Sm, Ti and so on, however some limitations are still present. For example, some systems (e.g., $TiCl_4$/Li(Hg)[7r]) were only able to give low yield of corresponding pinacol products because of their strong reducing abilities; some metal coupling agents (e.g., Nb,[7l] Yb,[7n] Bi,[7p] U[7q]) were too expensive due to their rare deposits; and the experimental conditions in some systems (e.g., Na[7a]) were too rigorous to operate conveniently. In particular, the reported low-valent Ni coupling agents,[8] $Ni(COD)_2$ and $NiCl_2$/Li/Arene(Cat.), either was only limited to an intramolecular pinacol coupling or merely gave the pinacols as minor by-product. In general, these couplings mentioned above were only applicable to a relatively narrow scope of substrates.[9] Therefore, it is still of major importance to develop a mild, extensive and effective pinacol coupling sequence. In our efforts to this subject, we discovered two interesting pinacol coupling protocols for carbonyls, which were promoted by Ni generated in situ through the reaction of stoichiometric or catalytic amount of $NiCl_2$ with Li or Mg/TMSCl, respectively. Although increasing number of applications with organonickel agents have been reported in organic synthesis,[8c,10] to our knowledge, the two Ni-mediated coupling systems we developed have not been reported before. The major valuable features of both two coupling systems involved the broader application scope of substrates, the more convenient experiment operation and the low-cost of the Ni-mediated coupling reagents. Herein, we would like to report our results on the two systems.

2. Results and discussions

The Rieke Ni we examined was simply prepared by stirring a mixture of $NiCl_2$ (1.0 equiv.), Li (small cuts, 2.1 equiv.) and the naphthalene (0.3 equiv.) in THF under Ar at room temperature for 1 h.[11] The pinacol coupling was performed with various substrates and the Rieke Ni generated in situ following a general procedure (see Section 4.3). The results were listed in Table 1, from which we can see that the Rieke Ni-mediated pinacol coupling was effective, in good to excellent yields as well as with the preferential DL-diastereoselectivity, to a wide range of substrates including aromatic aldehydes (entries 1–7), aliphatic aldehydes (entries 10 and 11), aromatic ketones (entries 12–14) and aliphatic ketone (entry 15). It was notable that the Rieke Ni system exhibited the tolerance for some heteroatomic substituents (entries 3, 5 and 6) on substituted benzaldehydes.[11b] In addition the property and position of the substituents (entries 2–6) showed no significant effect on this coupling. However, when the substrate bears $-NO_2$ or −OH group (entries 8 and 9), no expected pinacol products,

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Keywords: Pinacol; Coupling; Carbonyl compounds.

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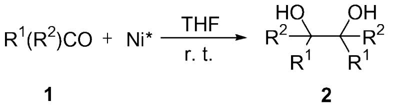
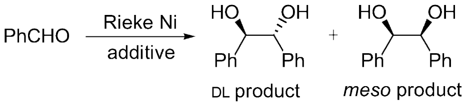
Table 1. Rieke Ni-mediated pinacol coupling reaction



Entry	Substrate	R^1	R^2	Product[a]	Yield (%)	DL/*meso*[b]
1	**1a**	Ph	H	**2a**	82	67:33
2	**1b**	2-MeC_6H_4	H	**2b**	92	74:26
3	**1c**	2-ClC_6H_4	H	**2c**	76	59:41
4	**1d**	3-MeC_6H_4	H	**2d**	94	73:27
5	**1e**	3-$MeOC_6H_4$	H	**2e**	88	72:28
6	**1f**	4-$(Me_2N)C_6H_4$	H	**2f**	76	73:27
7	**1g**	1-Naphthyl	H	**2g**	72	74:26
8	**1h**	4-$NO_2C_6H_4$	H	[c]	72	
9	**1i**	3-MeO,4-HOC_6H_4	H	[c]	54	
10	**1j**	*n*-C_3H_7	H	**2j**	66	65:35
11	**1k**	Cyclohexyl	H	**2k**	62	75:25
12	**1l**	Ph	Me	**2l**	96	79:21
13	**1m**	Ph	*n*-Bu	**2m**	99	73:27
14	**1n**	Ph	Ph	**2n**	70	
15	**1o**	$PhCH_2CH_2$	Me	**2o**	64	79:21

[a] All analytical data of the diols are identical with those literature reported.
[b] Measured by ^1H NMR spectroscopy.
[c] Only the reduction product $R^1(R^2)CHOH$ was obtained.

Table 2. Additive effects on the Rieke Ni-mediated pinacol coupling reaction



Entry	Additive	Ratio[a]	Yield (%)	DL/*meso*[b]
1	TMEDA	2	40	73:27
2	HMPA	2	45	78:22
3	$ZnCl_2$	0.2	86	76:24
4	$AlCl_3$	0.2	80	74:26
5	$TiCl_4$	0.2	85	73:27
6	H_2O	0.1[c]	73[d]	
7	18-crown-6	2	86[d]	
8	1,3-Dinitrobenzene	2	92[d]	

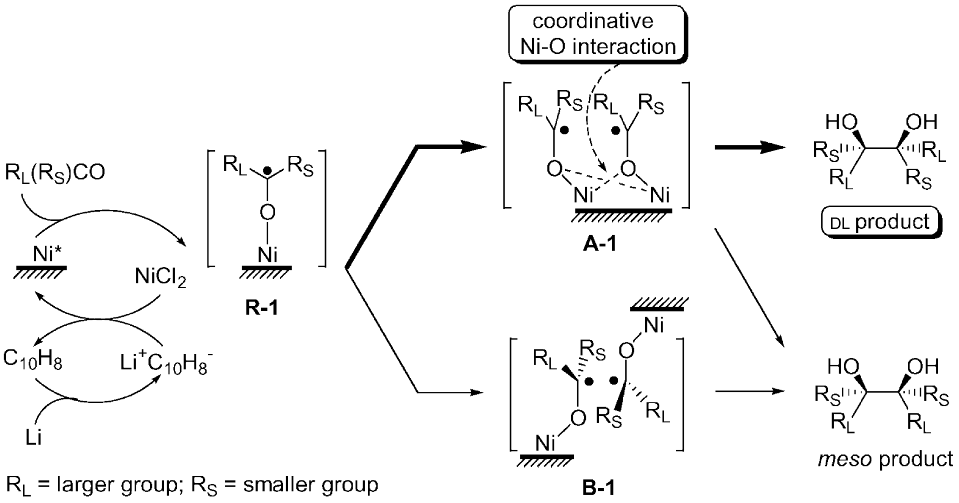
[a] The mole ratio between the additive and PhCHO **1a**.
[b] Measured by ^1H NMR spectroscopy.
[c] The volume ratio between H_2O and THF.
[d] The main products of entries 6–8 are $PhCH_2OH$.

but only simple reduction product $R^1(R^2)CHOH$ was formed.

To further examine the property of Rieke Ni-mediated pinacol coupling and also investigate the reaction mechanism, some additives, e.g. Lewis acid or base, or those with the –OH, $-NO_2$ or ether group were chosen to probe this reaction using PhCHO **1a** as a model substrate following a general procedure (see Section 4.4). From the results listed in Table 2, we found that when Lewis base (2.0 equiv.) was added in this reaction (entries 1 and 2), an improved distereoselectivity (DL/*meso*≈3/1) was observed in comparison with that of the corresponding entry 1 (DL/*meso*≈2/1) in Table 1 despite of their lower yields. Furthermore, when catalytic amount of Lewis acid was added (entries 3–5), both DL-selectivity (DL/*meso*≈3/1) and yield were improved. These results demonstrated that both Lewis acid and base were in favour of the DL-selectivity in this Rieke Ni-mediated coupling. However, if H_2O, 18-crown-6, or 1,3-dinitrobenzene was used as an additive (entries 6–8), only the simple reduction product $PhCH_2OH$ was given without the formation of desired pinacol product.

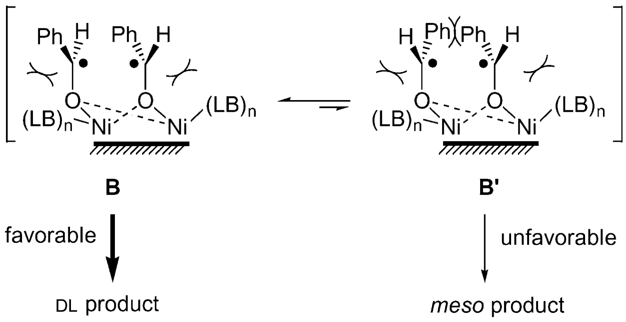
Based on the above experimental results together with corresponding literatures,[12] a plausible single-electron transfer (SET) mechanism was proposed as indicated in Scheme 1. The initial radical **R-1** was generated via a SET process between Rieke Ni and $R_L(R_S)CO$. Next two possible key coupling species **A-1** and **B-1** led to the formation of corresponding DL- and *meso*-products. Owing to the high oxyphilic ability and the high coordination number of the low-valent Ni, the formation of **A-1** with the coordinative Ni–O interaction was favoured than **B-1** without such interaction. Furthermore, two bulky R_L groups in **A-1** tended to display a favourable anticlinal conformation which resulted in the formation of DL-product, than the synperiplanar one which yielded the *meso*-product. Consequently, the Rieke Ni-mediated coupling could exhibit the more preferential DL-selectivity.

On the basis of the proposed reaction mechanism, some additives (entries 6–8 of Table 2) and substrates behavior (entries 8 and 9 of Table 1) in the coupling reaction could be

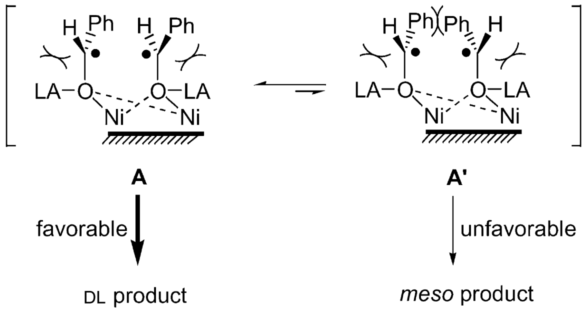


Scheme 1. Proposed mechanisms for Rieke Ni-promoted coupling pinacol reaction.

understood. Because the −OH, $-NO_2$ or ether group presented in the additives or substrates readily quench the radical **R**-**1**, the coupling process through **A**-**1** and **B**-**1** was inhibited to give the simple reduction product. Moreover, some properties of the coupling reaction in the presence of Lewis acid or base additives could be explained with the favourable **A**-**1**. Firstly, the improvement of the DL-selectivity caused by Lewis base (LB) additives (entries 1 and 2 of Table 2) could be understood from **B** and **B′** resulting from their coordination with the low-valent Ni (as shown in Scheme 2). Due to the steric encumbrance imposed by the coordinating LB additives on the nickel center, the rotation of C−O single bond in **B**, leading to the formation of more hindered **B′**, was restricted to some extent, so to improve DL-selectivity. Similarly, the additive effect of Lewis acid (LA) (entries 3–5 of Table 2) could also be explained in terms of the proposed Scheme 3. Because their coordination with the oxygen gave a more sterically crowded environment, the formation of **A** was favourable than that of **A′** and consequently improved DL-selectivity.



Scheme 2. The effect of Lewis base in Rieke Ni system.

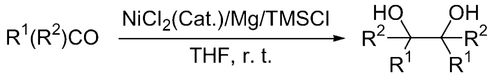


Scheme 3. The effect of Lewis acid in Rieke Ni system.

Encouraged by the above information that the Ni generated in situ can efficiently induce the pinacol coupling of carbonyl compounds via an interesting SET process, and also on considering that few reports on the Ni-mediated catalytic pinacol coupling were documented, we subsequently designed and developed another novel effective catalytical system, the $NiCl_2$(Cat.)/Mg/TMSCl, which has not been mentioned before to our knowledge.[13] Although a Mg/TMSCl system reported previously did not work at all for such kind of coupling,[7j] our experimental results below demonstrated the $NiCl_2$(Cat.)/Mg/TMSCl system we developed was effective to couple of aldehydes and ketone to the pinacol. The major values of this system involved the catalytic effectiveness, the use of cheap Mg metal and the convenient operation.

The preparation of $NiCl_2$(Cat.)/Mg/TMSCl system and the catalytic coupling experiment were performed in the following procedure: the catalytic amount of $NiCl_2$ (0.05 equiv.) was first mixed with Mg (2.0 equiv.) in THF to give a suspension, to which a solution of $R^1(R^2)CO$ (1.0 equiv.) and TMSCl (2.0 equiv.) was then added dropwise. The pinacol coupling took place readily (see Section 4.5). The results were tabulated in Table 3, which indicated that this catalytic system was effective, to a broad range of substrates including aromatic aldehydes (entries 1–9), aliphatic aldehyde (entry 10) and aromatic ketone (entry 11) to give pinacols in moderate to good yields. Further inspection of Table 3 showed some more important information. For example, in comparison with the corresponding Rieke Ni-mediated couplings in Table 1, the *meso*-selectivity for some substrates, such as **1e**, **1f**, **1j** and **1l**, was improved in different degree. In particularly, substrate **1f** (entry 8) gave exclusively the *meso*-product, which is of particular importance in organic synthesis.[14] It was also important that an intermolecular cross-pinacol coupling[15] was successfully conducted to produce the cross-coupling product **2al** in 52% yield (entry 12).

Table 3. $NiCl_2$(Cat.)/Mg/TMSCl-mediated pinacol coupling reaction

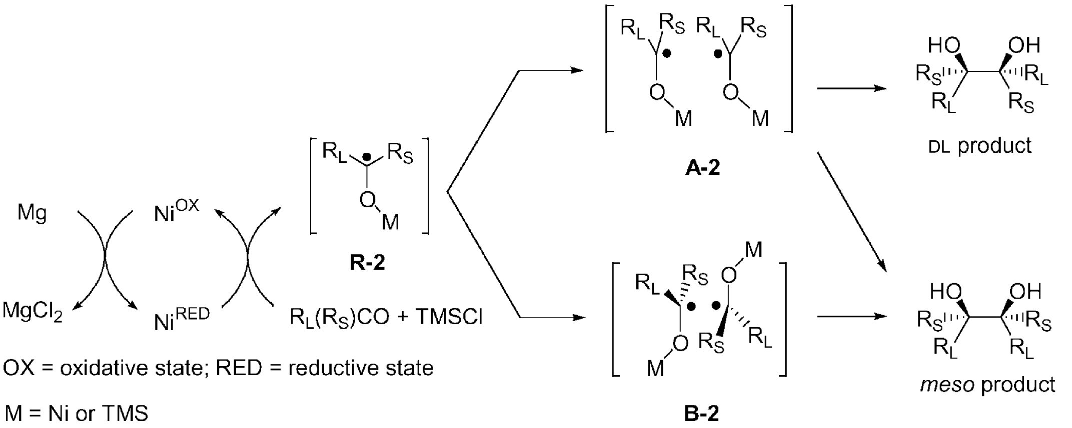


1 **2**

Entry	Substrate	R^1	R^2	Product[a]	Yield (%)	DL/*meso*[b]
1	**1a**	Ph	H	**2a**	70	78:22
2	**1p**	$2-BrC_6H_4$	H	**2p**	72	53:48
3	**1q**	$2-MeOC_6H_4$	H	**2q**	72	64:36
4	**1r**	$3-ClC_6H_4$	H	**2r**	77	57:43
5	**1e**	$3-MeOC_6H_4$	H	**2e**	79	52:48
6	**1s**	$4-ClC_6H_4$	H	**2s**	77	45:55
7	**1t**	$4-MeOC_6H_4$	H	**2t**	71	55:45
8	**1f**	$4-(Me)_2NC_6H_4$	H	**2f**	67	1:99
9	**1u**	2-Furyl	H	**2u**	66	69:31
10	**1j**	$n-C_3H_7$	H	**2j**	61	59:41
11	**1l**	Ph	Me	**2l**	51	50:50
12	**1a+1l**[c]			**2al**	52[d]	50:50

[a] The analytical data of the diols are all identical with those previously reported.
[b] Measured by ^1H NMR spectroscopy.
[c] Zn was co-reductant.
[d] A cross-pinacol coupling product **2al** (left R^2=right R^2=Ph, left R^1=Me, right R^1=H) was isolated, together with the minor diol **2a** (40%).

The Ni-catalyzed mechanism in this pinacol coupling was proposed in Scheme 4 on the basis of the above results and the related literatures.[13] The initial step would involve the reduction of oxidative state Ni (Ni^{OX}) by Mg to generate the active reductive state Ni (Ni^{RED}), which subsequently coordinated with the carbonyl of substrate $R_L(R_S)CO$ to form a radical **R-2** (M=Ni). Next two different coupling ways may be involved. If the Ni−O bond in the initially formed **R-2** (M=Ni) was cleaved by TMSCl before the pinacol coupling, the formation of **B-2** (M=TMS) would be favourable than that of **A-2** (M=TMS) because of the less hindrance in **B-2** (M=TMS) with the antiperiplanar conformation, and the subsequent coupling reaction would result in the formation of more *meso*-product. The other way



Scheme 4. Proposed mechanism for Ni-catalyzed pinacol coupling reaction.

may be that the initially formed **R-2** (M=Ni) directly underwent a pinacol coupling through **A-2** (M=Ni) and **B-2** (M=Ni), after which the Ni^{OX} was replaced by TMS for the next catalytic cycle This was just like the Rieke Ni system as shown in Scheme 1 resulted in the formation of more DL-product. In this catalytic system, we may determine the reaction type was the former, the latter or the combination of the two, according to the DL/*meso* selectivity which was highly dependent upon the substrate structure.

3. Conclusions

In conclusion, we have developed two novel and effective Ni-mediated pinacol coupling systems which were applicable to a broad substrate scope. Particularly we believe the optimized $NiCl_2$(Cat.)/Mg/TMSCl system would bring much application in practical organic synthesis. The further investigation is ongoing in our group.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of argon. THF was dried and freshly distilled over sodium/benzophenone before use. All reagents were commercial and used without further purification. All reactions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. The silica gel (200–300 meshes) for column chromatography was from the Qingdao Marine Chemical Factory in China, and the distillation range of petroleum is 60–90 °C. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on the Avance DRX-200 instruments, and spectral data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of ESI technique.

Spectroscopic data for these pinacol coupling adducts has been reported previously.[16]

4.2. General procedure for the preparation of Rieke Ni

In a typical process, Li (small cuts, 2.1 equiv.), naphthalene (0.3 equiv.) and anhydrous $NiCl_2$ (1.0 equiv.) were stirred in freshly distilled THF for 1–3 h at room temperature under argon atmosphere, then a black slurry was obtained and ready for use.

4.3. General procedure A: the Rieke Ni-mediated pinacol coupling

To a slurry of Rieke Ni (1.0 equiv.) prepared in situ was added the substrate **1** (0.5 equiv.) at room temperature under Ar. The reaction mixture was stirred and monitored by TLC until the substrate was consumed completely. Then the reaction was quenched with an aqueous solution (3 M) of $Na_2S_2O_3$ followed by the addition of CH_2Cl_2. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with the brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and column chromatography of the crude pinacol product on silica gel (petroleum/ethyl acetate 4/1→2/1) afforded the desired diol **2**.

4.4. General procedure B: the Rieke Ni-mediated pinacol coupling with the additives

To a stirred suspension of Rieke Ni (1.0 equiv.) and the additive (0.1 or 1.0 equiv.) in freshly distilled THF was added PhCHO (0.5 equiv.) at room temperature under Ar. The reaction mixture was further stirred efficiently. When TLC analysis indicated the PhCHO was consumed completely, the reaction was quenched. The following workup was similar to that of the general procedure A.

4.5. General procedure C: the $NiCl_2$(Cat.)/Mg/TMSCl-mediated pinacol coupling

A mixture of $NiCl_2$ (0.05 equiv.) and activated Mg powder (2.0 equiv.) in freshly distilled THF was stirred for 10 min at room temperature under Ar. Then a solution of substrate **1** (1.0 equiv.) and TMSCl (2.0 equiv.) was added dropwise to the above suspension, and the reaction mixture was stirred efficiently. After the substrate consumed by the check of TLC, Et_2O and an aqueous solution (1.5 M) of HCl were added to the resulting mixture. The organic layer was separated followed by the extraction of the aqueous layer with Et_2O. The combined organic extracts were washed with saturated $NaHCO_3$ solution and brine, and dried over anhydrous Na_2SO_4. After removing the solvent the residue was purified by the column chromatography on silica gel (petroleum/ethyl acetate 4/1→2/1) to furnish the expected diol **2**.

Acknowledgements

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