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Chiral Organomagnesiates as Dual Reagents for Bromine–Magnesium Exchange of 2-Bromopyridine and Access to Chiral α-Substituted 2-Pyridylcarbinols

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New chiral ligand containing butyl and dibutylmagnesiates have been prepared from a range of ligands and their reactivity studied. The reagents were generally efficient in promoting the clean bromine–magnesium exchange of 2-bromopyridine at room temperature and the subsequent reaction with aldehydes to afford α-substituted 2-pyridylcarbinols in good yields. (*R*,*R*)-TADDOLate proved to be the best ligand, leading to acceptable to good enantioselectivities. To the best of our knowledge this is the first example of an organomagnesiate-induced halogen–metal exchange followed by an enantioselective addition.

Introduction

The asymmetric addition of achiral alkylmetals to carbonyl derivatives is a powerful methodology to access chiral alcohols, an important class of compounds. It has been investigated extensively during the two past decades.[1] The principle is to coordinate the metal to a chiral ligand and thus create an intermediate able to next induce facial selection during approach to the aldehyde or ketone. Several alkylmetals have been used for this purpose, the most popular being diorganozinc,[2] alkyllithium,[3] lithium amides,[4] and Grignard reagents.[5]

The use of dilithium dialkylmagnesiates, obtained by reaction of Grignard reagents with lithium BINOLate, has been reported by Noyori to give high enantioselectivities in the alkylation of prochiral electrophiles.[6] The interest in such an approach is to have a well-arranged bimetallic reagent with saturated metal coordination sites avoiding side aggregation and subsequent loss of chirality. An additional benefit effect is a potential cooperative effect of lithium and magnesium in the activation of both the nucleophile and electrophile.

2-Pyridylcarbinols are important compounds as such or as precursors of chiral ligands for asymmetric synthesis and kinetic resolution.[7] Thus, their preparation in enantiomerically pure form is a critical issue to develop their synthetic usefulness. The most efficient syntheses of non-racemic pyridyl alcohols involve enantioselective reduction of the corresponding pyridyl ketones.[8] Several diastereoselective approaches have been also developed, the first being reported by Chelucci who trapped 2-pyridyllithium intermediates with naturally occurring optically active ketones.[9] There is, however, a lack of straightforward methods to access chiral pyridyl alcohols from a pyridine derivative and a prochiral carbonyl electrophile.

Some of us have reported the use of the chiral superbase BuLi–LiPM* [LiPM* = lithium (*S*)-(–)-*N*-methyl-2-pyrrolidine methoxide][10] promotes a chemo- and regioselective deprotonation of pyridine derivatives at C-2 and a notable enantioselection upon reaction with aldehydes. We have shown recently that BuLi–LiPM* was coordinated to the pyridine nitrogen atom as a tetrameric aggregate.[11] This could be a source of configurational instability by possible side aggregation and, furthermore, could be responsible for the moderate enantioselectivities obtained.

Iida and Mase have reported the magnesiation of bromopyridines and aromatic halides by using a substoichiometric amount of nBu$_3$MgLi in apolar solvents.[12] At the same time, Oshima described the stoichiometric use of nBu-Me$_2$MgLi[13] to avoid the presence of an excess amount of reactive butyl ligands and side reactions such as reduction or alkylation of electrophilic reagents in the trapping step. Thus, the inclusion of ligands into organomagnesiates[14] could be a promising alternative for several reasons: (i) only the expected reactive species should be transferred; (ii) the ate complex benefits in terms of stability and gentle reaction conditions should be maintained; (iii) tuning of the reactivity and access to asymmetric synthesis by using appropriate ligands should be possible.

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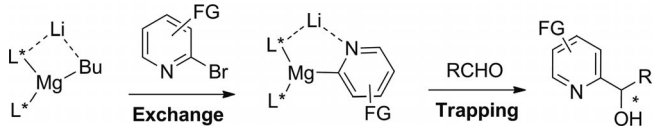
Examination of the literature revealed that the ability of chiral ligand containing organomagnesiates to achieve bromine–magnesium exchange of bromopyridines as well as the reactivity of the formed organometallics toward carbonyl electrophiles still remain unexplored.

Herein we report the preparation of organomagnesiates containing chiral ligands, their reactivity in bromine–magnesium exchange, and the subsequent asymmetric pyridyl transfer from the formed pyridylorganometallics to aldehydes (Scheme 1).

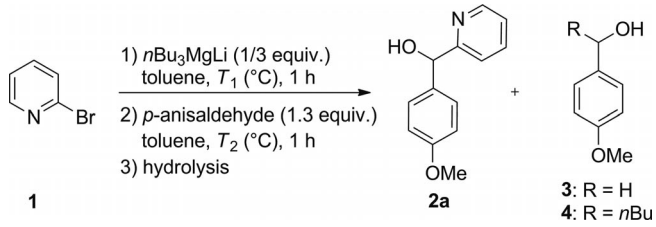


Scheme 1. The exchange–trapping sequence for the synthesis of chiral pyridylcarbinols from chiral ligand containing magnesiates.

Results and Discussion

Ida and Mase[12] have shown that the reaction between 2,6-dibromopyridine and nBu$_3$MgLi and subsequent formylation had to be performed at –5 °C in toluene as the main solvent (THF is present in low amounts from the preparation of the magnesiate). Consequently, we initially selected these experimental conditions to examine the reactivity of nBu$_3$MgLi towards 2-bromopyridine and the subsequent trapping by *p*-anisaldehyde (Table 1). nBu$_3$MgLi was prepared by mixing nBuLi (2 equiv.) with nBuMgCl (1 equiv.). The halogen–metal exchange of 2-bromopyridine by using the formed nBu$_3$MgLi (1/3 equiv.) was found to be quantitative after 1 h. We observed that the trapping step had to be performed at –60 °C (then r.t.) instead of –5 °C to prevent the formation of reduction and alkylation products **3** and **4** and to afford pyridylcarbinol **2a** with complete conversion (Table 1, Entry 3).

Table 1. Optimization of the exchange of 2-bromopyridine by using nBu$_3$MgLi followed by trapping with *p*-anisaldehyde.

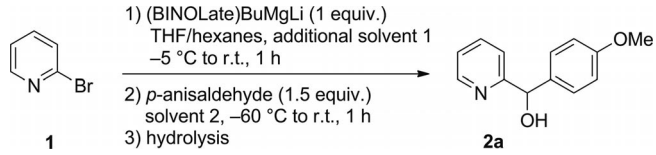


Entry	T_1 [°C]	T_2 [°C]	**2a** [%][a]	**3** and **4** [%][a]
1[b,c]	–5	–5	79	16
2[d]	–5 to r.t.	–5 to r.t.	63	37
3[b]	–5	–60 to r.t.	>98	–

[a] Determined by ^{1}H NMR integration, bromine–magnesium exchange was quantitative. [b] nBu$_3$MgLi magnesiate was prepared at –5 °C in toluene. [c] 5% (^{1}H NMR integration) of *p*-anisaldehyde was recovered. [d] nBu$_3$MgLi was prepared at –5 °C with subsequent warming to r.t. in toluene.

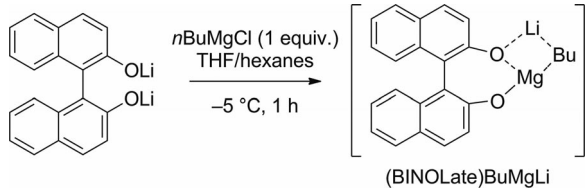
Having in hand the appropriate experimental conditions for performing the bromine–magnesium exchange using by homoleptic butyl magnesiate, nBu$_3$MgLi, we then examined the reactivity of heteroleptic magnesiates in this reaction. From the works of Noyori and co-workers on the asymmetric alkylation of carbonyl derivatives,[6] BINOL was first chosen as a ligand, and the less-expensive racemic form was used for reactivity experiments (Table 2). *rac*-BINOL was first deprotonated with nBuLi (2 equiv.) in THF and the formed BINOLate was treated with nBuMgCl (1 equiv.) to afford putative (BINOLate)BuMgLi (Scheme 2). 2-Bromopyridine (**1**) was then treated with a stoichiometric amount of generated (BINOLate)BuMgLi magnesiate, and the mixture quenched with *p*-anisaldehyde (Table 2).

Table 2. Optimization of the exchange of 2-bromopyridine by using (BINOLate)BuMgLi followed by trapping with *p*-anisaldehyde.



Entry	Solvent 1, conc.	Solvent 2, conc.	**2a** [%][c]
1[d]	PhMe, 0.10 M[a]	PhMe, 0.31 M[b]	>98 (71)
2[e]	PhMe, 0.21 M[a]	PhMe, 0.63 M[b]	>98 (76)
3[e]	–	–	>98 (75)
4[e,f]	–	–	80[g]

[a] Concentration of a solution of **1** in toluene. [b] Concentration of a solution of *p*-anisaldehyde in toluene. [c] Conversion determined by ^{1}H NMR spectroscopy. Isolated yield in brackets. [d] Magnesiate concentration in THF was 0.07 M. [e] Magnesiate concentration in THF was 0.14 M. [f] 1 equiv. of *p*-anisaldehyde was used. [g] Reduction product **3** was also formed.



Scheme 2. Preparation of putative (BINOLate)BuMgLi.

As shown, whatever the conditions, (BINOLate)BuMgLi promoted the exchange reaction, leading to expected alcohol **2a** as the main product. In a separate experiment, we checked that, in contrast with *i*PrMgCl,[15] nBuMgCl was unable to promote the exchange of 2-bromopyridine, strongly supporting the formation of the magnesiate by contact with BINOLate. The (BINOLate)BuMgLi reagent was found to be efficient in exchanging the bromine of 2-bromopyridine at room temperature, and the corresponding pyridine organometallic was readily trapped by *p*-anisaldehyde under experimental conditions similar to those used with nBu$_3$MgLi (Table 2, Entry 1). This result supports the hypothesis of the generation of the (BINOLate)BuMgLi species in the medium under the experimental conditions used. A clean reaction was consequently obtained, leading to pyridylcarbinol **2a** in 71% isolated yield. A higher con-

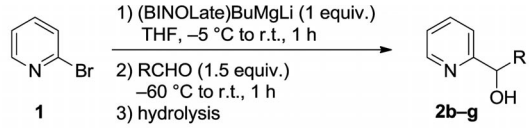
centration of the reaction medium was not deleterious and also gave **2a** in 76% yield (Table 2, Entry 2). Interestingly, we have shown that the reaction could be conducted with the same efficiency by using exclusively THF as solvent (Table 2, Entry 3), whereas toluene was reported to be necessary to ensure the stability of the metalated pyridines after reaction with Bu_3MgLi.[12] Finally, a 50% excess of aldehyde was required to avoid a reduction process; indeed, the use of 1 equiv. instead of 1.5 equiv. of *p*-anisaldehyde induced a decrease in the conversion into **2a** in favor of the formation of the reduction product (Table 2, Entry 4).

The scope of the exchange–trapping sequence on 2-bromopyridine (**1**) was investigated by using variously substituted aldehydes (Table 3). As shown, aromatic and aliphatic aldehydes reacted efficiently, giving expected alcohols **2b**–**g** in good to high yields. Electron-donating as well as electron-withdrawing substituents at the *para* position of the benzaldehydes gave similar yields (Table 3, Entries 1 and 2); alcohol **2c** bearing a CF_3 group was obtained in 83% yield (Table 3, Entry 2). The introduction of a methoxy or methyl group *ortho* to the carbonyl group did not affect the reactivity, also giving a high yield of 84 and 81%, respectively (Table 3, Entries 3 and 4); a similar result was obtained with bulky 1-naphthaldehyde (Table 3, Entry 5). Trimethylacetaldehyde reacted efficiently, and the corresponding alcohol **2g** was isolated in acceptable yield despite a marked trend for it to undergo sublimation (Table 3, Entry 6).

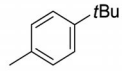
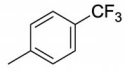
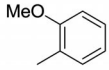
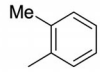
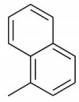
After having demonstrated the efficiency of the exchange–trapping sequence by using *rac*-BINOLate as a model ligand, we turned to the asymmetric version of the reaction (Table 4). Various parameters (solvent, type of magnesiate, and trapping temperature) and several ligands based on the BINOLate and TADDOLate[16] skeletons were screened (Figure 1). TADDOL analogues **T1** and **T2** were prepared from *trans*-dimethyl tartrate acetonide and the appropriate Grignard reagents.[17,18] Monobutyl magnesiate LBuMgLi and putative dibutyl magnesiate LBu_2MgLi_2 were prepared according to Scheme 3 (L = chiral ligand). Two routes were investigated to generate the LBu_2MgLi_2 species.

After deprotonation of the diol with *n*BuLi (2 equiv.), the resulting alkoxide was treated according to two different

Table 3. Pyridyl alcohols synthesis with the use of (BINOLate)-BuMgLi.

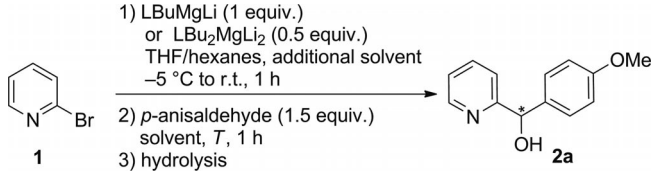


1 **2b–g**

Entry	R	Product, Yield [%][a,b]
1		**2b**, 71
2		**2c**, 83
3		**2d**, 84
4		**2e**, 81
5		**2f**, 85
6		**2g**, 58[c,d]

[a] The conversion, determined by ^1H NMR spectroscopy, was >98% except when mentioned. [b] Isolated yield after column chromatography. [c] 2 h trapping step. [d] Partial sublimation of **2j** occurred upon workup.

Table 4. Screening of chiral diols in the exchange–trapping sequence with magnesiates.[a]



1 **2a**

Entry	Ligand	Magnesiate	Solvent, *T* [°C]	**2a** [%][b]	*er*[c]
1	(*R*)-BINOL	LBuMgLi	PhMe, 60 to r.t.	74	50:50
2	(*S*)-BINOL	LBuMgLi	PhMe, 60 to r.t.	88	50:50
3	(*R*,*R*)-TADDOL	LBuMgLi	PhMe, 60 to r.t.	59	61:39
4	(*R*,*R*)-TADDOL	LBuMgLi	–60	56	63:37
5	(*R*,*R*)-TADDOL	LBu_2MgLi_2[d]	–60	64	73:27
6	(*R*,*R*)-TADDOL	LBu_2MgLi_2[e]	–60	68	70:30
7	**T1**	LBu_2MgLi_2[d]	–60	64	66:34
8	**T2**	LBu_2MgLi_2[d]	–60	56	50:50
9	(*R*)-BINOL	LBu_2MgLi_2[d]	–60	68	54:46
10	(*R*)-BIPHEN H2	LBu_2MgLi_2[d]	–60	79	28:72
11	(*R*)-BIPHEN H2	LBu_2MgLi_2[d]	–100	54	17:83
12	(*R*,*R*)-TADDOL	LBu_2MgLi_2[d]	–100	28	88:12

[a] The bromine–metal exchange was complete. [b] Yields determined by GC. [c] Determined by chiral GC. [d] Prepared according to Route A (see Scheme 3). [e] Prepared according to Route B (see Scheme 3).

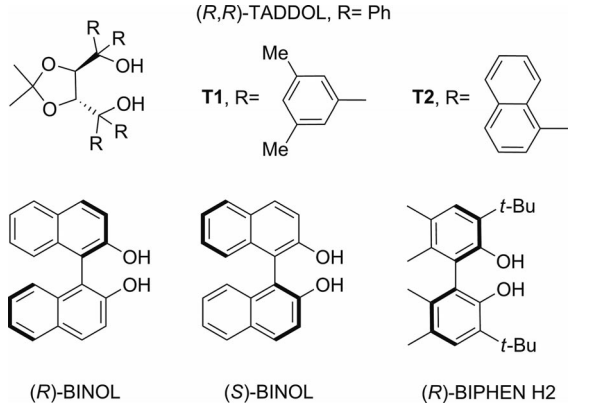
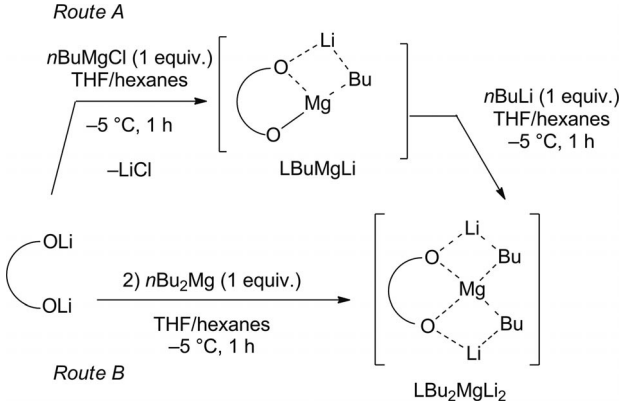


Figure 1. Chiral diols used for screening experiments.



Scheme 3. Preparation of the LBuMgLi and LBu_2MgLi_2 reagents from chiral diols.

procedures: either 1 equiv. of *n*BuMgCl and *n*BuLi, respectively, were added successively (Route A), or nBu_2Mg (1 equiv.) was added (Route B).

The formed magnesiate (0.5 equiv.) was then treated with **1** and the medium subsequently quenched by the aldehyde. LBuMgLi reagents prepared from (*R*)- or (*S*)-BINOLate and (*R*,*R*)-TADDOLate led to alcohol **2a** in 59–88% yield after complete bromine–metal exchange (Table 4, Entries 1–3). Whereas BINOLate ligands afforded racemic products, (*R*,*R*)-TADDOLate induced a promising level of enantioselectivity. Hence, a 61:39 enantiomeric ratio was determined by chiral GC (Table 4, Entry 3). When the trapping step temperature was maintained at –60 °C and toluene was removed in both exchange and trapping steps (Table 4, Entry 4), little effect was observed on the reactivity and the enantioselectivity (63:37 *er*). As no benefit was noted in the enantioselectivity, toluene was discarded for the rest of the study. Much better enantiocontrol was obtained by using the LBu_2MgLi_2 magnesiate, as a 73:27 *er* was measured (Table 4, Entry 5). Pyridylcarbinol **2a** was obtained in 64% yield in this case.

Route A was chosen to investigate the effect of TADDOL analogues **T1** and **T2**. The methyl groups on the phenyl groups in **T1** were found to cause only a small loss of enantioselectivity compared with (*R*,*R*)-TADDOL (Table 4, Entry 7). In contrast, the naphthyl group in **T2**, while allowing **2a** to be prepared in acceptable yield, led to a racemic product (Table 4, Entry 8).[19] (*R*)-BINOL was also compared under the same conditions, leading to poor enantioselectivity (54:46) but good yield (Table 4, Entry 9). Another axially chiral diol, BIPHEN H2, gave **2a** in 79% yield and 28:72 *er* (Table 4, Entry 10). Interestingly the opposite enantiomer was obtained in this case. Finally, we were pleased to obtain a substantial improvement by performing the trapping step at –100 °C, leading to a good 17:83 *er* with BIPHEN H2 (Table 4, Entry 11) and 88:12 *er* with (*R*,*R*)-TADDOL (Table 4, Entry 12).

Conclusions

In summary, we have shown that two alkyl chains of trialkylmagnesiates could be replaced by a bidentate ligand with maintained efficiency in the bromine–magnesium exchange of 2-bromopyridine. BINOLate-containing butylmagnesiate has been prepared and promoted the bromine–magnesium exchange of 2-bromopyridine at room temperature. The formed hetaryl magnesiate was found to be reactive toward various aldehydes, leading to the corresponding pyridylcarbinols in good to high yields. The same reaction was performed by using optically pure chiral diols and revealed that the dibutyl magnesiates built from (*R*,*R*)-TADDOL or (*R*)-BIPHEN H2 were the best ligands for the asymmetric addition of the pyridyl organometallics, leading to 88:12 and 17:83 enantiomeric ratios, respectively. In contrast, (*R*)- or (*S*)-BINOL led to racemic pyridylcarbinols. This study reveals that the chiral ligand used in the process is able to induce asymmetry, indicating its coordination to the metal center of the putative ate species. To the best of our knowledge, this is the first example of an organomagnesiate-induced asymmetric exchange–addition sequence. A detailed study of this promising strategy for the straightforward synthesis of enantioenriched chiral α-substituted pyridylcarbinols is in progress and will be published in due course.

Experimental Section

General Procedure for Br–Mg Exchange Reaction by Using [(*rac*)-BINOLate]BuMgLi and Synthesis of Pyridylcarbinols 2a–g: In a Schlenk tube flushed with argon, *rac*-BINOL (0.3 g, 1.05 mmol, 1 equiv.) was dissolved in anhydrous THF (7.5 mL). *n*BuLi (1.6 M in hexanes, 1.31 mL, 2.1 mmol, 2 equiv.) was slowly added at –5 °C. After stirring at this temperature for 1 h, *n*BuMgCl (2 M in THF, 0.52 mL, 1.05 mmol, 1 equiv.) was added at –5 °C, and the resulting solution was stirred for an additional 1 h at the same temperature. 2-Bromopyridine (158 mg, 1 mmol, 1 equiv.) was then added at –5 °C. The mixture was warmed to room temperature and stirred for 1 h. The reaction was monitored by TLC (cyclohexane/ethyl acetate, 8:2.5). The medium was then cooled to –60 °C and the electrophile (1.5 equiv.) was added. The mixture was warmed to room temperature and stirred for a given time. The reaction was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with ethyl acetate and acidified (pH 3–4) by using 0.4 M HCl. The aqueous solution was then extracted with

ethyl acetate (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography, leading to products **2a**–**g**.

Procedure for Br–Mg Exchange Reaction by Using [(*R*,*R*)-TADDOLate]Bu_2MgLi_2 and Synthesis of Enantioenriched Pyridylcarbinols (Method A, see Table 4). In a Schlenk tube flushed with argon, (*R*,*R*)-TADDOL (0.3 g, 0.64 mmol,1 equiv.) was dissolved in anhydrous THF (*c* = 0.14 M). *n*BuLi (1.5 M in hexanes, 2 equiv.) was slowly added at –5 °C. After stirring at this temperature for 1 h, *n*BuMgCl (2 M in THF, 1 equiv.) was added at –5 °C, and the resulting solution was stirred for an additional 1 h at the same temperature. *n*BuLi (1.5 M in hexanes, 1 equiv.) was finally added at –5 °C and the mixture was stirred for 1 h at –5 °C. 2-Bromopyridine (2 equiv.) was then added at –5 °C. The mixture was warmed to room temperature and stirred for 1 h. The reaction was monitored by TLC (cyclohexane/ethyl acetate, 8:2.5). The medium was then cooled to –100 °C and the aldehyde (3 equiv.) was added. The mixture was left at –100 °C and stirred for 1 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with ethyl acetate and acidified (pH 3–4) by using 0.4 M HCl. The aqueous solution was then extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and then analyzed by GC to determine yields and enantiomeric ratios of the desired product.

Supporting Information (see footnote on the first page of this article): General methods, characterization data for **2a**–**g**, ^1H and ^{13}C spectra of **2a**–**g**, and ^{19}F spectrum of **2c**.

Acknowledgments

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