Asymmetric Synthesis

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Me-bipam for Enantioselective Ruthenium(II)-Catalyzed Arylation of Aldehydes with Arylboronic Acids**

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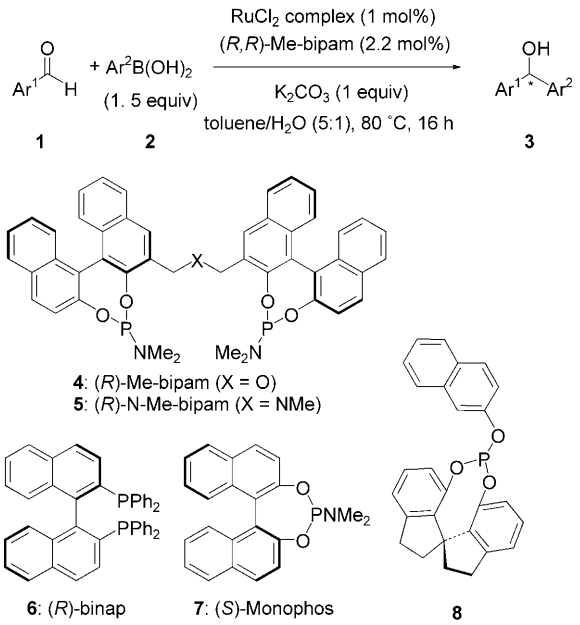
The arylation of carbonyl compounds with organolithium,[1] organomagnesium,[2] and organozinc[3,4] reagents is the traditional way in which to access diarylmethanols, but there has been recent interest in the transition-metal-catalyzed arylation using nonmetallic boron[5] and silicon[6] compounds; such compounds are stable in air and water, are compatible with a broad range of functional groups, and have potential applications in asymmetric synthesis. The basis of the chemistry involved can be found in early contributions by Oi, Inoue, and co-worker[7a] for rhodium-catalyzed arylation of ketones and aldehydes with arylstannanes. This discovery was then followed by additions of B and Si compounds with rhodium,[5,6] palladium,[8] and nickel[9] catalysts. Such an insertion of the C–O double bond into a late transition metal–carbon bond is rare compared to that of C–C double bonds, but it was recently established by the stoichiometric reaction of arylrhodium(I) complexes with aldehydes.[10] Because of the importance of a chiral diarylmethanol fragment for the syntheses of biologically and pharmaceutically active compounds, there have been many attempts at arylation of aldehydes with arylboronic acids and chiral rhodium catalysts.[11] However, the protocol is limited mainly becasue of the inefficiency of traditional bis(phosphine)s designed on the basis of C_2 symmetry.[12] Among them, the rhodium(I)/spiromonophosphite (**8**) complex developed by Zhou and co-workers was the most promising catalyst, achieving 62–87% *ee* for representative aromatic aldehydes.[13]

We have developed new bidentate chiral phosphoramidites (Me-bipam, *N*-Me-bipam), derived from linked binol (binol = 1,1′-binaphthalene-2,2′-diol) units, for the enantioselective 1,4-addition of arylboronic acids to enones,[14] arylation of aldimines,[15] and hydrogenation of α-dehydroamino esters.[16] Herein, we report the arylation of aromatic aldehydes with arylboronic acids catalyzed by a chiral ruthenium complex, generated in situ from [{$RuCl_2$(*p*-cymene)}$_2$] and Me-bipam (Scheme 1). Since the corresponding rhodium(I) complexes were inefficient, the use of ruthenium(II) as the central metal was critical for achieving high enantioselectivities. Although it is the first successful use of a ruthenium catalyst for arylation of carbonyl compounds, the transmetalation of arylboronic acids to $RuCl_2$ complexes has been reported by Brown and co-workers[17] in the oxidative Heck reaction of acrylates, and by Shintani and Hayashi[18] in 1,4-addition reactions to enones.



Scheme 1. Enantioselective arylation of aldehydes. binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.

Several solvents were screened for the reactions involving a [{$RuCl_2$(*p*-cymene)}$_2$]/2 Me-bipam catalyst and KOH. The highest efficiency with regard to the reaction was observed in toluene and 1,2-dichloroethane for the arylation of 4-chlorobenzaldehyde with $PhB(OH)_2$ (1.5 equiv) at 80 °C (Table 1, entries 1 and 2), which is in contrast to observing no reaction in donating solvents such as dimethoxyethane, dioxane, tetrahydrofuran, and *N*,*N*-dimethylacetamide. The reaction required the presence of one equivalent of a base, as has been reported in most metal-catalyzed reactions of organoboronic acids which involve transmetalation to transition-metal halides in a catalytic cycle.[5] There were no differences in the yields and selectivities observed when either KOH or K_3PO_4 or K_2CO_3 were used (Table 1, entries 1–4); amine bases were less efficient (Table 1, entry 10). The choice in appropriate precursors was critical for high yields (Table 1, entries 4–9). [{$RuCl_2$(*p*-cymene)}$_2$], [RuCl(*p*-cymene)]PF_6, and [{$RuCl_2$(nbd)}$_n$] all resulted in better product yields compared with those obtainec with [$RuCl_3(H_2O)_n$],

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[**] bipam = bidentate phosphoramidite.

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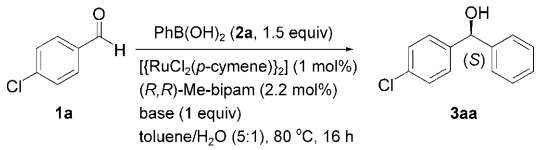
Table 1: Reaction conditions.[a]



Entry	Ru precursor	Base	Yield [%]	*ee* [%][b]
1	$[\{RuCl_2(p\text{-cymene})\}_2]$	KOH	89	94 (*S*)
2[c]	$[\{RuCl_2(p\text{-cymene})\}_2]$	KOH	94	96 (*S*)
3	$[\{RuCl_2(p\text{-cymene})\}_2]$	K_3PO_4	91	95 (*S*)
4	$[\{RuCl_2(p\text{-cymene})\}_2]$	K_2CO_3	95	96 (*S*)
5[d]	$[RuCl(p\text{-cymene})(MeCN)_2]PF_6$	K_2CO_3	91	97 (*S*)
6	$[RuCl_3(H_2O)_n]$	K_2CO_3	62	95 (*S*)
7	$[\{Cp^*RuCl_2\}_2]$	K_2CO_3	31	77 (*S*)
8	$[\{RuCl_2(cod)\}_n]$	K_2CO_3	51	94 (*S*)
9	$[\{RuCl_2(nbd)\}_n]$	K_2CO_3	75	94 (*S*)
10	$[\{RuCl_2(p\text{-cymene})\}_2]$	NEt_3	51	92 (*S*)
11[e]	$[[\{RuCl_2(p\text{-cymene})\}_2]$	K_2CO_3	8	13 (*R*)
12[f]	$[\{RuCl_2(p\text{-cymene})\}_2]$	K_2CO_3	32	49 (*R*)
13[g]	$[\{RuCl_2(p\text{-cymene})\}_2]$	K_2CO_3	94	93 (*S*)

[a] Reaction conditions: 4-chlorobenzaldehyde (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), base (0.5 mmol), $RuCl_2$ precursor (1 mol%), and (*R*,*R*)-Me-bipam (1.1 equiv to Ru) in toluene/H_2O (5:1, 2.5 mL) was stirred at 80°C for 16 h. [b] The letter within the parentheses indicates the absolute configuration of the chiral center within the product. [c] $ClCH_2CH_2Cl$/H_2O (5:1) was used as the solvent. [d] Run at 50°C. [e] (*R*)-binap was used instead of (*R*,*R*)-Me-bipam. [f] (*S*)-Monophos was used. [g] (*R*,*R*)-*N*-Me-bipam was used. cod = 1,5-cyclooctadiene, nbd = norbornadiene.

Table 2: Arylation of aldehydes (see Scheme 1).[a]

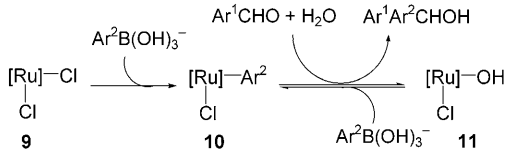
Entry	Ar^1	Ar^2	Yield [%]	*ee* [%]
1	$4\text{-}ClC_6H_4$ (**1a**)	Ph (**2a**)	95 (**3aa**)	96 (*S*)
2	$4\text{-}ClC_6H_4$ (**1a**)	$4\text{-}MeOC_6H_4$ (**2b**)	84 (**3ab**)	92 (*S*)
3	$4\text{-}ClC_6H_4$ (**1a**)	$3\text{-}MeOC_6H_4$ (**2c**)	88 (**3ac**)	84 (*S*)
4	$4\text{-}BrC_6H_4$ (**1b**)	Ph (**2a**)	83 (**3ba**)	96 (*S*)
5	$4\text{-}CF_3C_6H_4$ (**1c**)	Ph (**2a**)	89 (**3ca**)	92 (*S*)
6	$4\text{-}NO_2C_6H_4$ (**1d**)	Ph (**2a**)	93 (**3da**)	92 (*S*)
7	$4\text{-}NO_2C_6H_4$ (**1d**)	$4\text{-}ClC_6H_4$ (**2d**)	95 (**3dd**)	99 (+)
8	$4\text{-}NO_2C_6H_4$ (**1d**)	$3\text{-F-}4\text{-}BrC_6H_4$ (**2e**)	69 (**3de**)	86 (+)
9	$4\text{-}MeC_6H_4$ (**1e**)	Ph (**2a**)	87 (**3ea**)	94 (*S*)
10	$4\text{-}MeOC_6H_4$ (**1f**)	Ph (**2a**)	85 (**3fa**)	92 (*S*)
11	$3\text{-}ClC_6H_4$ (**1g**)	Ph (**2a**)	95 (**3ga**)	96 (*S*)
12	$3\text{-}ClC_6H_4$ (**1g**)	$4\text{-}MeOC_6H_4$ (**2b**)	99 (**3gb**)	91 (+)
13	$2\text{-}ClC_6H_4$ (**1h**)	Ph (**2a**)	97 (**3ha**)	93 (*S*)
14	$2\text{-}ClC_6H_4$ (**1h**)	$4\text{-}MeOC_6H_4$ (**2b**)	95 (**3hb**)	91 (+)
15	$3\text{-}MeOC_6H_4$ (**1i**)	Ph (**2a**)	91 (**3ia**)	94 (*S*)
16	$2\text{-}MeOC_6H_4$ (**1j**)	Ph (**2a**)	94 (**3ja**)	95 (*S*)
17	$2,4\text{-}Cl_2C_6H_3$ (**1k**)	Ph (**2a**)	96 (**3ka**)	93 (*S*)
18	$2\text{-MeO-}5\text{-}BrC_6H_3$ (**1l**)	Ph (**2a**)	93 (**3la**)	97 (*S*)
19	2-naphthyl (**1m**)	Ph (**2a**)	79 (**3ma**)	94 (*S*)
20[c]	1-naphthyl (**1n**)	Ph (**2a**)	70 (**3na**)	98 (*S*)
21[d]	$3,4\text{-}(CH_2O_2)C_6H_3$ (**1o**)	Ph (**2a**)	62 (**3oa**)	90 (+)
22[c]	2-thienyl (**1p**)	Ph (**2a**)	78 (**3pa**)	92 (*S*)
23	2-furyl (**1q**)	Ph (**2a**)	92 (**3qa**)	82 (*S*)
24	6-MeO-3-pyridyl (**1r**)	Ph (**2a**)	95 (**3ra**)	96 (−)

[a] Reaction conditions: A mixture of aldehyde (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), K_2CO_3 (0.5 mmol), $[\{RuCl_2(p\text{-cymene})\}_2]$ (1 mol%), and (*R*,*R*)-Me-bipam (2.2 mol%) in toluene (2.5 mL) and H_2O (0.5 mL) was stirred at 80°C for 16 h. [b] The letter or sign within the parentheses indicates the absolute configuration of the chiral center or the optical rotation, respectively, of the product. [c] $ClCH_2CH_2Cl$ and KOH were used instead of toluene and K_2CO_3. [d] 3,4-Methylenedioxyphenyl.

$[\{Cp^*RuCl_2\}_2]$, and $[\{RuCl_2(cod)\}_n]$, but their effect on the enantioselectivities was not significant. The results suggest that π ligands have an effect on the rate of complex formation between the ruthenium and the bis(phosphine), but they are not involved in the active intermediate for the arylation of aldehydes. Among chiral ligands screened, Me-bipam and *N*-Me-bipam achieved a 96% *ee* and 93% *ee*, respectively (Table 1, entries 4 and 13), whereas analogous C_2-symmetric binap (**6**; Table 1, entry 11) and monodentate phosphoramidite, (*S*)-Monophos (**7**; Table 1, entry 12), resulted in lower selectivities.

$[RuCl_2(p\text{-cymene})]$/Me-bipam (2 mol%) catalyzed the addition of arylboronic acids to representative aromatic aldehydes in high yields in the presence of one equivalent of K_2CO_3 at 80°C in toluene/H_2O (5:1) (Table 2). Enantioselectivities exceeding 90% *ee* were easily achieved when using most combinations of aromatic rings on either the aldehyde or boronic acid, having either electron-donating or electron-withdrawing substituents at the *para*, *meta*, and *ortho* positions. Thus, the performance of Ru/Me-bipam is much better than that of other catalysts previously reported for the arylation of aldehydes. However, this catalyst may prefer unsubstituted arylboronic acids since the reaction of substituted boronic acids resulted in selectivities that were a few percent lower than those obtained with phenylboronic acid (Table 2, entries 2, 3, 8, 12, and 14). It was also interesting that the reaction tolerates heteroatoms such as those in thienyl and furyl rings, and even nitrogen atoms as in pyridyl rings (Table 2, entries 22–24). Most reactions took place smoothly in toluene/H_2O (5:1), but 1,2-dichloroethane/H_2O (5:1) was a better solvent for the slow addition of the boronic acid to 1-naphthyl and thienyl carbaldehyde (Table 2, entries 20 and 22). 1-Naphthyl carbaldehyde resulted in 55% yield when toluene was used as the solvent, and the yield was increased to 70% with 98% *ee* when 1,2-dichloroethane was used as the solvent.

The reaction may proceed by transmetalation between **9** and $Ar^2B(OH)_3^-$ to yield the arylruthenium(II) intermediate [Ru](Ar^2)Cl (**10**), which is analogous to a Ph–Cl exchange between either Ph_2Hg and $[Ru(CO)_2(PMe_2Ph)_2(Cl)_2]$[19] or $PhB(OH)_2$ and $[Ru(p\text{-cymene})(PPh_3)Cl_2]$ (Scheme 2).[17] Insertion of the C–O double bond into the C–Ru bond, giving [Ru]($OCHAr^1Ar^2$)Cl, can then undergo hydrolysis. This process is not known for ruthenium complexes, but related arylrhodium(I) complexes in water produce diarylmethanols without an accompanying β-hydride elimination to give $Ar^1Ar^2C{=}O$ compounds.[10,20] Finally, [Ru](OH)Cl (**11**)[21] thus produced reacts with $Ar^2B(OH)_3^-$ to regenerate [Ru](Ar^2)Cl (**10**). (*R*,*R*)-Me-bipam afforded compounds (*S*)-**3**



Scheme 2. Proposed reaction mechanism.

(Table 2) through a facial selection similar to that of rhodium(I)-catalyzed arylation of *N*-sulfonyl arylaldimines.[15] However, the asymmetric environment of ruthenium(II)/Me-bipam complex is different from a *cis*-ligated square-planar rhodium complex. To elucidate the enantioselection in the mechanism, the characterization of the catalyst and the intermediate **10** are in progress .

Experimental Section

General procedure for arylation of aldehydes with arylboronic acids (Table 1): A flask was charged with $[\{RuCl_2(p\text{-cymene})\}_2]$ (0.005 mmol, 1 mol%) and (*R*,*R*)-Me-bipam (0.011 mmol, 2.2 mol%) under a nitrogen atmosphere. Toluene (2.5 mL) was added to the flask and the mixture was then stirred at room temperature for 30 min to prepare the catalyst. Phenylboronic acid (0.75 mmol), 4-chlorobenzaldehyde (0.5 mmol), K_2CO_3 (0.5 mmol), and H_2O (0.5 mL) were then added to this catalyst solution. Thre reaction mixture was stirred at 80 °C for 16 h, at which time the crude reaction mixture was extracted using ethyl acetate, washed with saturated NH_4Cl and brine, and dried over $MgSO_4$. Chromatography of the crude reaction mixture on silica gel with hexane/ethyl acetate (10:1 to 5:1) gave **3aa** in 95% yield. $[\alpha]_D^{22} = +18.1\ deg\,cm^3\,g^{-1}\,dm^{-1}$ ($c = 3.7\times10^{-3}\ g\,cm^{-3}$, $CHCl_3$); 96% *ee* (Chiralcel AD-H, hexane/2-propanol = 9:1, flow = 0.5 mL min^{-1}, wavelength = 230 nm, t_R = 17.6 and 19.3 min); ^{1}H NMR ($CDCl_3$): δ = 7.35–7.25 (m, 9H), 5.81 (d, J = 3.2 Hz, 1H), 2.26 ppm (d, J = 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 143.5, 142.3, 133.4, 128.8, 128.7, 128.0, 126.6, 75.7 ppm; HRMS (EI) *m*/*z* calcd for $C_{13}H_{11}ClO_2$ (M^+): 218.0498, found: 218.0504.

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