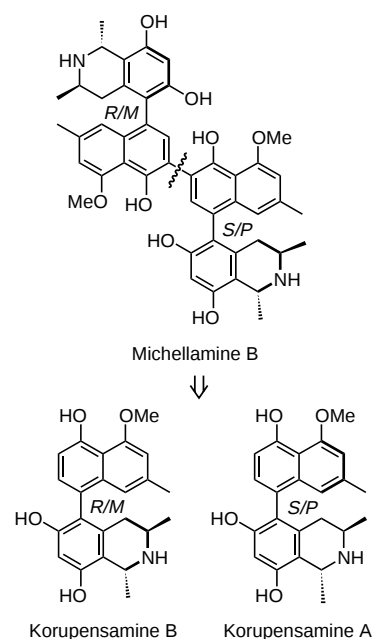


- [10] The workup was carried out chromatographically (SiO<sub>2</sub>, 40–60  $\mu$ ; dichloromethane/*tert*-butyl methyl ether 12/1). The mixture of the isomers of rotaxane **1** showed the expected mass spectrum: *m/z* 3148.6 [*M*+H]<sup>+</sup> (FAB, 9-nitroanthracene (9-NA)) *m/z* 3167.4 [*M*+Na]<sup>+</sup> (MALDI-TOF; calcd for C<sub>204</sub>H<sub>220</sub>N<sub>10</sub>O<sub>17</sub>S<sub>2</sub>: 3148.12). The compound has been characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. M.p. 278 °C; elemental analysis calcd for C<sub>204</sub>H<sub>220</sub>N<sub>10</sub>O<sub>17</sub>S<sub>2</sub>·3 CH<sub>2</sub>Cl<sub>2</sub>: C 73.06, H 6.69, N 4.12, S 1.88; found: C 72.98, H 6.77, N 4.13, S 2.31; the dichloromethane is detected by NMR spectroscopy.
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- [12] Each fraction was analyzed by mass spectroscopy (MALDI-TOF-MS). Every stereoisomer had the same mass peak. Conditions of the separation: Column Chiralpak AD (25 × 0.46 cm inner diameter), amylose tris[3,5-(dimethylphenyl)carbamate], eluent *n*-hexane/ethanol 81/19; flow rate 1.3 mL min<sup>-1</sup>; pressure 23 bar; detector UV (Millipore Waters, Lambda Max, Model 481, LC Spectrophotometer); sample 10 mg mL<sup>-1</sup> in chloroform/*n*-hexane (1/1).
- [13] Optical rotation: JASCO Polarimeter P-1020, cell 100 × 3.5 mm inner diameter (CHCl<sub>3</sub>); circular dichroism spectra: JASCO Spectropolarimeter J-720, cell 0.1 mm (trifluoroethanol).
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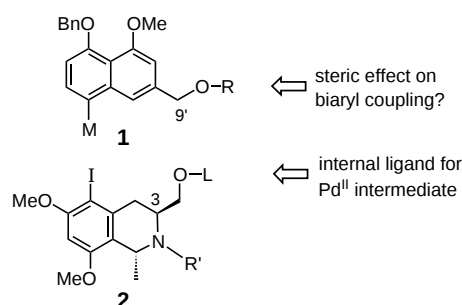
Scheme 1. Retrosynthesis of michellamine B to its components korupensamines A and B.

The guiding principles upon which our route was developed (Scheme 2) focus on the presence of a hydroxyl “handle” in each of the components. These were anticipated to afford considerable flexibility in fine-tuning the selectivity in the

## A Stereospecific, Intermolecular Biaryl-Coupling Approach to Korupensamine A En Route to the Michellamines\*\*

Bruce H. Lipshutz\* and John M. Keith

The michellamines make up a rather unusual group of highly active antiviral natural products, with michellamine B receiving most of the attention as a potent anti-HIV-1 and -2 agent.<sup>[1]</sup> The components of this alkaloid, korupensamines A and B, are related as diastereomers with respect to their axial chirality (Scheme 1).<sup>[2]</sup> All attempts to effect a *direct*, highly stereocontrolled biaryl coupling between the naphthyl and tetrahydroisoquinoline portions have thus far met with limited success,<sup>[3]</sup> which has encouraged a number of groups to devise clever, albeit indirect, alternatives.<sup>[4]</sup> We now describe a novel solution to this problem that allows for *exclusive* entry to the korupensamine A series through a Pd<sup>0</sup>-mediated intermolecular biaryl cross-coupling reaction.



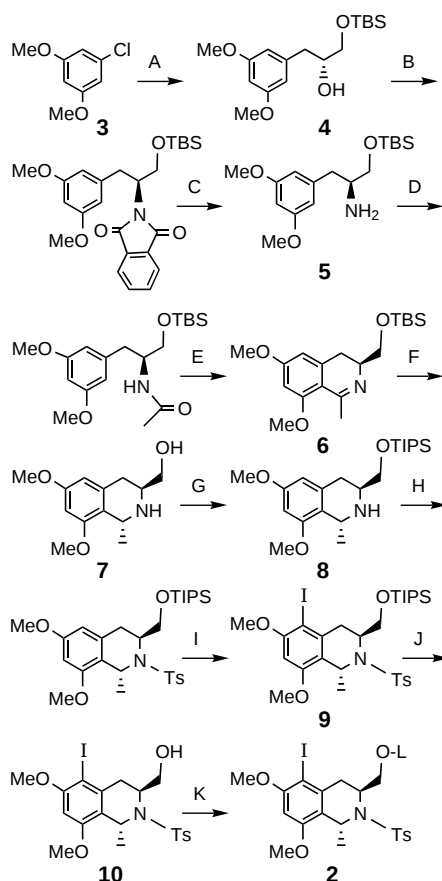
Scheme 2. Possible influence of substituents on the hydroxymethyl “handles”.

biaryl-forming step. Such a residue at C-9' in **1** might facilitate the introduction of a potentially influential steric component, while an OH function on the methyl group at C-3 in **2** would provide an opportunity for intramolecular chelation, thereby directing biaryl formation from one face of a transient polycyclic array.

Our route to nonracemic, protected hydroxymethylidiotetrahydroisoquinoline **9** began with aryl chloride **3** (Scheme 3).<sup>[5]</sup> A copper-catalyzed opening of commercially available (*S*)-TBS-glycidol (TBS = *tert*-butyldimethylsilyl) with the Grignard reagent derived from **3** leads to alcohol **4**, which is suitable for a Mitsunobu inversion<sup>[6]</sup> with phthalimide followed by hydrazinolysis to give nonracemic amine **5**. Acetamide formation sets the stage for a temperature-sensitive<sup>[7]</sup> Bischler–Napieralski cyclization to imine **6**. Careful reduction with a 1:7 mixture of Me<sub>3</sub>Al (in heptane) and

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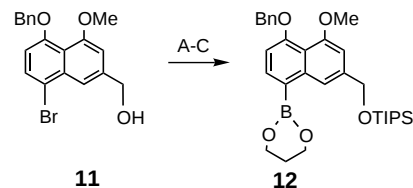
Scheme 3. A) 1) Mg, THF, BrCH<sub>2</sub>CH<sub>2</sub>Br  $\Delta$ , 10 h; 2) (*S*)-TBS-glycidol, 10% CuBr·SMe<sub>2</sub>, −20 °C, 4.5 h, 92%; B) phthalimide, PPh<sub>3</sub>, DEAD, THF, 0 °C to RT, 20 h, 88%; C) H<sub>2</sub>NNH<sub>2</sub>, EtOH,  $\Delta$ , 7 h, 89%; D) Ac<sub>2</sub>O, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, RT, overnight, 99%; E) POCl<sub>3</sub>, CH<sub>3</sub>CN, 2,4,6-collidine, 85 °C, 3 h, 97%; F) LAH, Me<sub>3</sub>Al, THF/hexanes, −78 °C to RT, overnight, 97% (3:1 *trans*:*cis*); G) NaH, TIPS-OTf, THF, −78 °C, 85%; H) TsCl, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, RT, 93%; I) PhI(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>, I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, −10 to 0 °C, 89%; J) TBAF, THF, RT, 2 h, 99%; K) NaH, THF, ClPPh<sub>2</sub>, 0 °C to RT, 21 h, then BH<sub>3</sub>·THF, RT, 40 min, 83%, or (2-diphenylphosphanyl)benzoic acid, DCC, CH<sub>2</sub>Cl<sub>2</sub>, RT, 14 h, 99%. DCC = dicyclohexylcarbodiimide; DEAD = diethyl azodicarboxylate; TBAF = tetrabutylammonium fluoride; Ts = *p*-H<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>.

lithiumaluminum hydride (LAH; solid)<sup>[8]</sup> gives **7** in a 3:1 ratio of *trans*:*cis* products<sup>[9]</sup> in excellent yield, albeit with concomitant loss of the TBS residue. To maximize the size of the L group in **2**, the triisopropylsilyl (TIPS) moiety was installed in **8** by conversion of **7** into its corresponding alkoxide followed by the low-temperature addition of TIPS-OTf (Tf = F<sub>3</sub>CSO<sub>2</sub>). *N*-Sulfonylation was accomplished without incident, and iodination<sup>[10]</sup> proceeds regiospecifically at −10 to 0 °C to give the coupling partner **9**.

The halonaphthol precursor to **1**, bromide **11**, was prepared, with minor modifications, according to Bringmann,<sup>[3a]</sup> thereby providing the hydroxymethyl “handle” required to test the effects of a bulky methyl group at this site. The nine-step sequence gave the desired derivative **11** in good overall yield (24%).

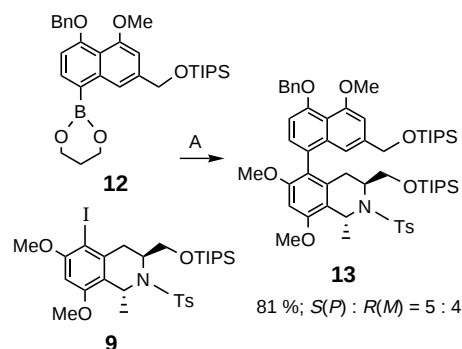
Numerous experiments designed to ascertain the most effective organometallic compound (M in **1**) for the intermolecular Pd<sup>0</sup>-catalyzed coupling led us to focus on Suzuki-based methodology, a conclusion also reached by Hoyer and Chen for this purpose.<sup>[11]</sup> However, it was essential in this case

to use a boronate (**12**; Scheme 4), rather than the precursor boronic acid, which has good hydrolytic stability due to the presence of the OTIPS residue in this molecule. Initial model couplings with a simple 1-naphthalene boronate, while



Scheme 4. A) TIPS-OTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, RT, 24 h, 82%; B) *n*BuLi, −78 °C, B(OiPr)<sub>3</sub>, RT, overnight, then NH<sub>4</sub>Cl, 81%; C) HO(CH<sub>2</sub>)<sub>3</sub>OH, PhCH<sub>3</sub>, RT, molecular sieves, 18 h, 98%.

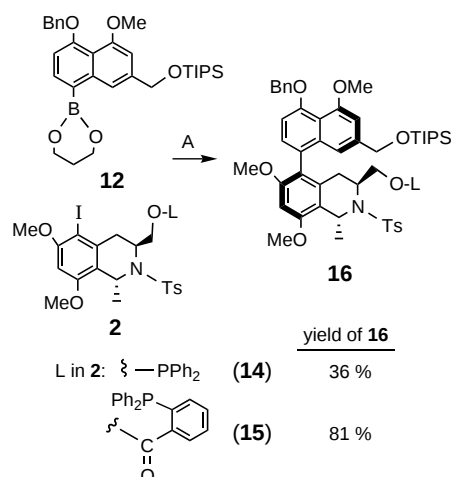
successful, did not translate to the “real” system, and revealed a critical need for 2,6-di-*tert*-butyl-4-methylphenol (BHT; 0.7 equiv)<sup>[12]</sup> in the reaction medium (DMF). The coupling of iodide **9** with **12** occurred efficiently under these modified conditions (81%; Scheme 5), but the 5:4 ratio of *S*(*P*):*R*(*M*) atropisomers obtained indicated that steric factors alone at each hydroxymethyl site in **1** and **2** (R = L = TIPS) are not sufficient for high diastereocontrol in the biaryl forming step.



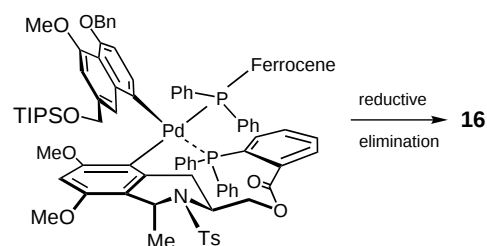
Scheme 5. A) cat. [Pd(PPh<sub>3</sub>)<sub>4</sub>], K<sub>3</sub>PO<sub>4</sub>, BHT, DMF, 96 °C.

The attachment of an internal chelating phosphane through the free hydroxyl group in **10** was far more rewarding.<sup>[13]</sup> After conversion of **10** into the diphenylphosphane derivative **14** (Scheme 6), its Pd<sup>0</sup>-mediated coupling with **12** afforded a modest (36%) yield of cross-coupling product; however, a *single diastereomer* was produced. A switch to the *ortho*-diphenylphosphanylbenzoic acid ester derivative **15**<sup>[14]</sup> was made because of the less than satisfactory level of efficiency and the tendency of **16** (L = PPh<sub>2</sub>) to autoxidize to the corresponding phosphane oxide upon workup. The coupling of ester **15** with **12**, which was found to be better catalyzed by [Pd(dppf)Cl<sub>2</sub>], also afforded a *single diastereomer*, now in 71% yield (dppf = 1,1'-bis(diphenylphosphanyl)ferrocenyl). Complete conversion into **16** could be accomplished by increasing the amount of catalyst and raising the temperature, thereby boosting the yield of the isolated product to 81%.

The sole formation of the *S*(*P*) atropisomer can be rationalized as viewed in Scheme 7. The PPh<sub>2</sub>-substituted benzoate residue is best accommodated with the phosphorus



Scheme 6. A) for **12** + **14**: 10 mol % [Pd(PPh<sub>3</sub>)<sub>4</sub>], K<sub>3</sub>PO<sub>4</sub>, BHT, DMF, 99 °C; for **12** + **15**: 20 mol % [Pd(dppf)Cl<sub>2</sub>], K<sub>3</sub>PO<sub>4</sub>, BHT, DMF, 117 °C.



Scheme 7. The stereochemical course of the reductive elimination.

atom ligated to the palladium atom from the bottom of the molecule relative to the plane of the tetrahydroisoquinoline moiety. Both the aryl ring of the ester, as well as the remaining two phenyl groups on phosphorus, combine to further block the back and underside. Since a dppf ligand occupies the fourth coordination site on the metal the bulky naphthylene moiety is forced to protrude forward over the aryl portion of the tetrahydroisoquinoline ring. Reductive elimination from this *cis* disposition about the palladium atom would give the observed isomer.

The assignment of the stereochemistry in **16** (L = *o*-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CO) as *S*(*P*), which is associated with the korupensamine A series, could be readily made on the basis of a comparison of its CD spectrum, as well as that of its hydrolysis product **16** (L = H; NaOH, MeOH, RT, 85 %), with those of korupensamines A and B reported by Bringmann.<sup>[1c, 2]</sup> Both derivatives of **16** (L = H, *o*-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CO) display an initial positive Cotton effect in the 230–240 nm region characteristic of korupensamine A, which is strongly indicative of the chirality of the biaryl group being responsible for the observed spectra.<sup>[15]</sup>

In summary, by virtue of a judiciously placed internal phosphane group that acts as a coordinating ligand for a Pd<sup>II</sup> intermediate formed during a Suzuki biaryl coupling, the incipient axial chirality resulting from an ensuing reductive elimination can be fully controlled; in this case it leads to the korupensamine A skeleton. With this discovery, a stereo-specific route to half of the michellamine B molecule is a reasonable expectation. Moreover, by altering the residue attached to the hydroxymethyl “handles” (as in **1** and **2**),

opportunities exist for directing the orientation of the two aryl units so as to encourage formation of the *R*(*M*) atropisomer associated with korupensamine B. These and related applications to tetrahydroisoquinoline-based biaryl alkaloids, as well as to other challenging naturally occurring biaryls (for example, vancomycin) are currently under study.

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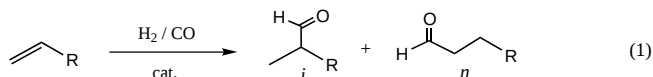
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- [15] From seminal work by Bringmann<sup>[14]</sup> it is appreciated that structural changes with such tetrahydroisoquinolines can alter the observed CD spectra, thereby leading to erroneous assignments. In the case of derivatives **16**, it is apparent that alterations at the C-3 methyl group do not impact, let alone overshadow, the significant bias imposed in each by the axially chiral, nonracemic, biaryl nuclei.

## Isomerization of Aldehydes Catalyzed by Rhodium(II) Olefin Complexes\*\*

Christian P. Lenges and Maurice Brookhart\*

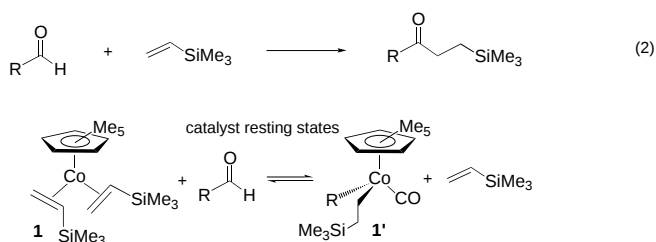
One of the earliest reported and most thoroughly investigated processes catalyzed by transition metals is the hydroformylation of olefins [Eq. (1)].<sup>[1–8]</sup> The oxidative addition of



H<sub>2</sub> to a transition metal center is combined with reversible olefin and CO insertion processes to yield an acyl hydride complex. The final step in this catalytic process is generally accepted as the irreversible reductive elimination of the acyl hydride to generate the aldehyde products.<sup>[9–11]</sup> In most applications the linear product is desired, although branched products are becoming increasingly important as indicated by recent efforts directed at the asymmetric hydroformylation of olefins.<sup>[7b, c]</sup> An ongoing effort in this area of research is dedicated to altering the linear:branched isomer ratio by varying the ligand and catalyst structure.

We have recently reported that [C<sub>5</sub>Me<sub>5</sub>Co(olefin)<sub>2</sub>] complexes can be used to carry out intermolecular hydroacylation reactions of bulky olefins such as vinyltrimethylsilane. The resting state of the catalyst was established as a mixture of the Co<sup>I</sup> bis-olefin complex and the Co<sup>III</sup> dialkyl carbonyl complex whose ratio is dependent on the substrate structures and concentrations [Eq. (2)].<sup>[12, 13]</sup>

When *n*-butyraldehyde was used as the substrate traces of isobutyraldehyde were evident near complete conversion of aldehyde, which indicated some reversibility prior to the reductive elimination of ketone.<sup>[12]</sup> Reductive elimination



with the second row rhodium analogues should exhibit higher energy barriers than the cobalt complexes; thus rhodium analogues may exhibit more extensive reversibility and have the potential to isomerize aldehydes prior to ketone formation.<sup>[14, 15]</sup> Indeed, we report here that rhodium(II) olefin complexes of the type [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>R)<sub>2</sub>] catalyze the interconversion of linear and branched aldehydes as well as transfer formylation reactions.<sup>[16]</sup>

Reduction of [(C<sub>5</sub>Me<sub>5</sub>RhCl<sub>2</sub>)<sub>2</sub>] with zinc in the presence of propene results in the formation of [C<sub>5</sub>Me<sub>5</sub>Rh(C<sub>2</sub>H<sub>3</sub>Me)<sub>2</sub>] (**2**), which was isolated as an analytically pure yellow solid.<sup>[17, 18]</sup> Characterization of **2** by NMR spectroscopy indicates a mixture of isomers. Recrystallization from acetone generates the single isomer **2a**, which was characterized by X-ray crystallographic analysis (Figure 1). When complex **2a** is dissolved in [D<sub>6</sub>]acetone a mixture of isomers **2a**, **2b**, and **2c**<sup>[19]</sup> is generated in minutes. These correspond to isomers generated by rotation around the Rh–olefin bond. Eventually a fourth isomer **2d** is observed, which is generated by olefin dissociation and rebinding (Scheme 1).

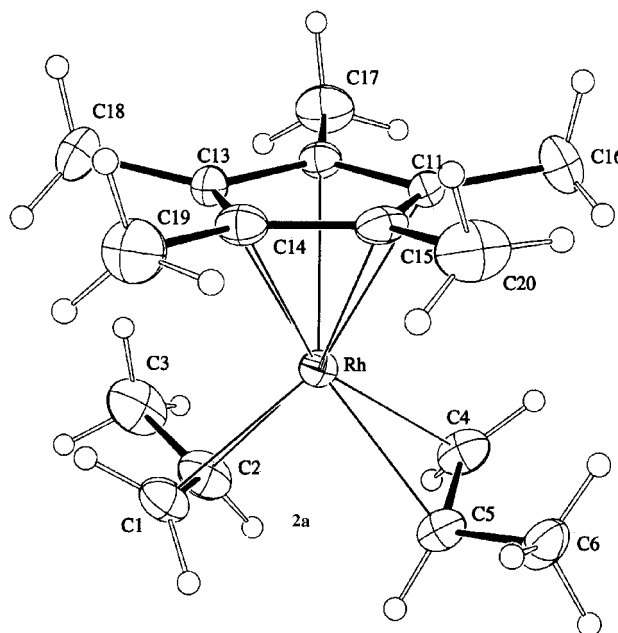


Figure 1. ORTEP diagram of complex **2a**; ellipsoids are drawn with 50% probability. Selected bond distances [Å] and angles [°]: Rh–C1 2.129(4), Rh–C2 2.129(5), Rh–C4 2.133(5), Rh–C5 2.134(4), C1–C2 1.404(6), C2–C3 1.493(7), C4–C5 1.416(6), C5–C6 1.517; C1–Rh–C2 38.51(18); C1–Rh–C4 108.61(19); C1–Rh–C5 87.38(18); C2–Rh–C4 85.15(20); C2–Rh–C5 87.00(20); C4–Rh–C5 38.77(16); C1–C2–C3 124.5(5); C4–C5–C6 120.4(4); C5–Rh–C1–C2 88.5(5); C4–Rh–C2–C1 128.4(6); C1–Rh–C4–C5 60.2(4); C2–Rh–C5–C4 86.0(5); C1–Rh–C2–C3 119.7(6); C2–Rh–C4–C5 91.2(5); C4–Rh–C5–C6 115.0(5); Rh–C1–C2–C3 110.1(7).

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