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A Highly Diastereoselective Synthesis of Deep Molecular Baskets

Lei Zhiquan,[a] Michael J. Gunther,[a] Vageesha W. Liyana Gunawardana,[a] Radoslav Z. Pavlović,[a] Han Xie,[a] Xingrong Zhu,[a] Mason Keenan,[a] Alex Riggs[a] and Jovica D. Badjić*[a]

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We describe a preparative method for directing Mizoroki-Heck cyclotrimerization of enantioenriched bromonorbornenes into molecular baskets having increasingly deeper and extendable aromatic cavities. Such diastereoselective cyclotrimerizations of the bromo-olefinic substrates resulted from prevalent β migratory insertions without the formation of palladacycle intermediate(s). The facile access to multigram quantity of a new series of basket-like hosts clears the way for creating novel supramolecular materials for storage, sequestration and catalysis.

Recently, we described a practical synthetic method for obtaining cup-shaped $\mathbf{1}_{syn}$ (Figure 1A) carrying six ester groups at its rim.[1] The key step was comprised of Cu(I) assisted[2] cyclotrimerization (i.e. Stille coupling) of enantioenriched bromo(trimethylstannyl)alkene (–)–**3** with diastereoselectivity equally favouring the formation of both *syn* and *anti* diastereomers of **1** (Figure 1A).[3] While exploring avenues for improving the reaction's poor diastereoselectivity, we identified potential areas to reduce the number of steps, waste and labour.[4] Based on literature precedents[5] and the remarkable versatility of the Mizoroki-Heck reaction,[6] we decided to probe and optimize the cyclotrimerization of enantioenriched (–)–**2** using palladium as a catalyst (Figure 1A). That is to say, if (–)–**2** could be directed to couple in head-to-tail fashion (Figure 1A), with (a) β migratory insertion dominating product-determining steps[5e, 7] (Scheme 1A) and (b) the suppression of concerted metalation-deprotonation[5e, 8] (CMD) in Scheme 1B, there should follow the exclusive formation of $\mathbf{1}_{syn}$. Moreover, by skipping the tedious stannylation (or iodination)[9] of (–)–**2** (Figure 1A) we shall improve the accessibility to $\mathbf{1}_{syn}$ and concurrently avoid the production of tin waste.[1] Importantly, cavitand $\mathbf{1}_{syn}$ with six esters at its rim can be converted into molecular baskets of type **4** (Figure 1B).[9] Such hosts possess a semi-rigid[10] and nonpolar cavity conjugated to three polar functional groups that are complementary to: nerve agents,[11] pesticides,[12] components of natural gas,[13] haloalkanes,[14]

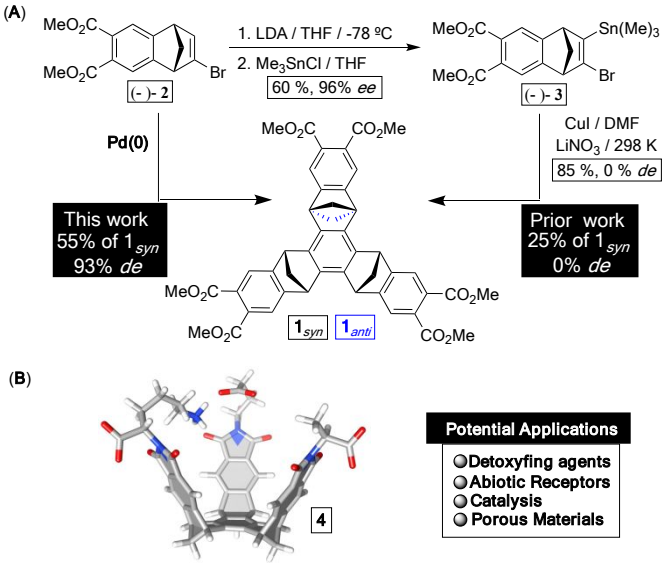

Figure 1. (A) The CuI promoted cyclotrimerization of (–)–**3** (96% *ee*) gives $\mathbf{1}_{syn}$ in a low yield. We studied Mizoroki-Heck cyclotrimerizations of three enantioenriched substrates of type (–)–**2**. (B) Hosts of type **4** can be used for a variety of applications.

ammonium bolaamphiphiles,[15] fullerenes,[16] anticancer agents[17] and drugs.[18] With three photoresponsive phthalimide chromophores[19] being part of the cage, C_3 symmetric baskets of type **4** were also demonstrated to undergo α–decarboxylation[20] of the amino-acid appendages followed by the assembly of amphiphilic products into spherical nanoparticles capable of trapping[21] or releasing[22] guests. At last, with advances in the field of organic frameworks[23] as well as shape-persistent organic cages,[24] one can foresee the potential utility of C_3 symmetric $\mathbf{1}_{syn}$ for creating porous materials capable of storing and/or sequestering targeted molecules (Figure 1B).[25] For facilitating and expanding the additional studies of baskets, we hereby delineate effective stereoselective syntheses of $\mathbf{1}_{syn}$ (Figure 1A) as well as its congeners possessing deeper cavities.

We decided to begin with the large-scale preparation of enantioenriched (–)–**2**, using accessible and cheap (*L*)–dimenthyl fumarate (MEF) and cyclopentadiene (CPD, Figure 2).[1] Thus, roughly 20 grams of (–)–**2** (99% *ee*) could, in our hands, be obtained in 10 days. When (–)–**2** was subjected to cyclotrimerization using the Heck conditions reported by

[a] *Department of Chemistry & Biochemistry, The Ohio State University 100 West 18th Avenue, 43210 Columbus, Ohio USA. E-mail: badjic.1@osu.edu*

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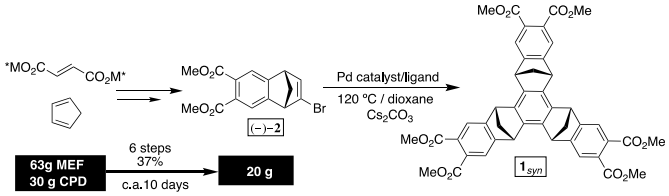
DeLucchi and co-workers ($Pd(OAc)_2/PPh_3/Et_3N/n$–Bu_4NBr/DMF),[5c] we noted the predominant formation of $\mathbf{1}_{syn}$ in 16% yield (78% *de*, Table S1). Surprisingly, after the same procedure was run without PPh_3 ligand, the yield of desired $\mathbf{1}_{syn}$ jumped to 30% (88% *de*, Table S1)! Evidently, the "ligandless" Pd(0)[26] was quite effective in promoting the cyclotrimerization



	Ligand	Catalyst	Θ (°)	DMAP	$\mathbf{1}_{syn}$ (%)	$\mathbf{1}_{anti}$ (%)	*de* (%)	$\mathbf{1}_{syn/anti}$ (%)
a	Ph_2OP–PPh_2 (DPPPO; 33 mM)[1]	$Pd(OAc)_2$	141	2.2	25	3	79	28
b	Ph_2OP–PPh_2 (DPPPO, 0.1 M)[1]	$PdCl_2$	141	1.1	39	1	95	40
c	DMPHEN	$PdCl_2$		1.1	55	2	93	57
d	Ph_2OP–PPh_2 (DPPPO, 0.1 M)[1]	$PdCl_2$	141		1	2	33	3
e	—[2]	$PdCl_2$	141	1.1	36	1	95	37
f	DMPHEN	$PdCl_2$			1	1	0	2

[1]DPPP was used, with DPPPO formed in situ (Table S6, entry 1 and 5). [2]Toluene was used as a solvent

Figure 2. Enantioenriched (–)–**2** (99% *ee*) can be prepared on large scale from cyclopentadiene (CPD) and (*L*)–dimenthyl fumarate (MEF); CPD, fumaric acid and *L*-menthol are <$100 per kg. We probed cyclotrimerization of (–)–**2** (33 mM a; 0.1 M b-f) using 5 mol % of palladium catalyst, 1.1 molar equivalents of Cs_2CO_3, 5 mol % of ligand at 120 ºC in dioxane (except e, toluene). All of the reported yields were obtained from ^{1}H NMR spectroscopy. The Tolman cone angle Θ of DPPPO was estimated using cone angles for PPh_3 and n-Bu_3P ($\Theta=2/3\Sigma(\Theta_i/2)$). For additional experimental details, see Tables S3-S13. Red and blue arrows (circles) denote reactions with (beginning) and without (end) DMAP.

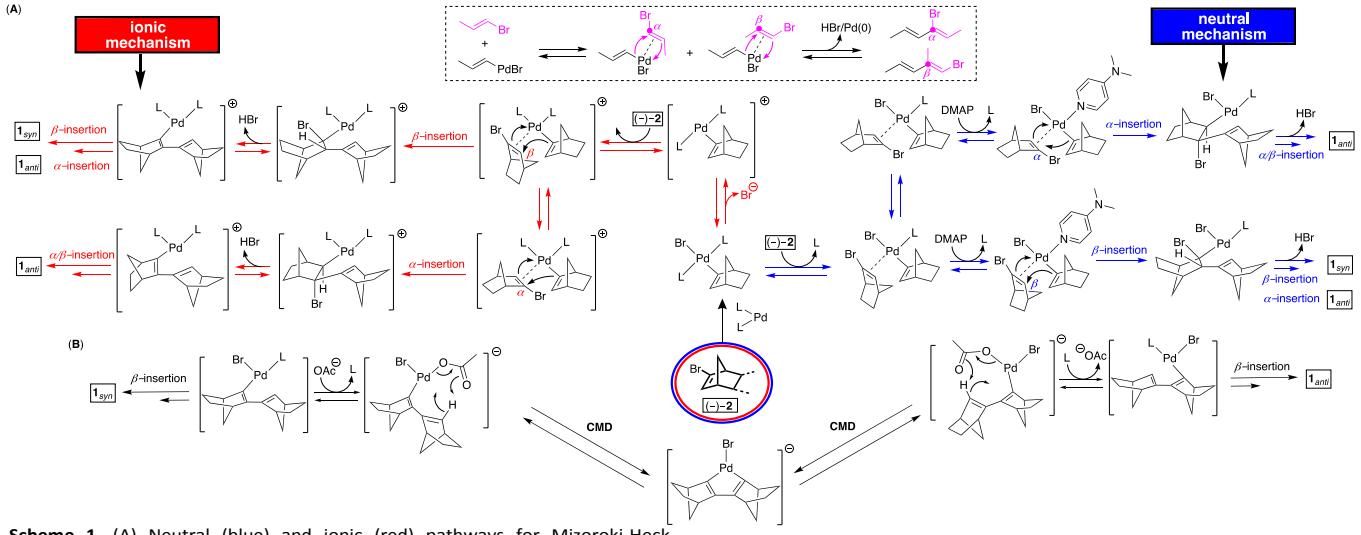
of (–)–**2**. The olefinic substrates (Scheme 1A) might in the absence of PPh_3 possess more room to undergo faster coordination and migratory insertions[6] around the palladium.[5e] In addition to steric reasons, the migratory insertion should be electronically facilitated for "ligandless" Pd in which there is no strongly σ donating phosphine *trans* to the newly forming Pd–C bond holding the vinyl group. On the other hand, following the Heck conditions optimized by Sakurai and co-workers ($Pd(OAc)_2/PPh_3/Et_3N/n$–Bu_4NOAc/dioxane),[5b] iodonorbornene (–)–**5** (Table S2) did not give any of the desired cyclotrimers with the reaction being slow and likely producing oligomers after a prolonged time.

In light of the existing methods failing to give desired results, we proceeded to investigate different conditions for self-coupling of (–)–**2**.[27] In order to facilitate the oxidative addition of less reactive chloro arenes in Heck reactions, Fu and co-workers employed electron-rich $(t\text{-Bu})_3P$ in dioxane.[28] In the context of our results above, we maintained that bulky $(t\text{-Bu})_3P$, having the cone angle (Θ) of 182º,[29] could perhaps inhibit the placement and/or proper positioning of (–)–**2** in the first coordination sphere of the palladium in spite of having a favourable electronic influence on the oxidative addition. Indeed, in the presence of $Pd_2(dba)_3$ with $(t\text{-Bu})_3P$ we found that (–)–**2** would give only 6% of $\mathbf{1}_{syn/anti}$ cyclotrimers (33% *de*, Table S3, entries 1/2). Following, we chose to probe the effectiveness of smaller PPh_3 (Θ = 145º) with $Pd(OAc)_2$.[5c] The yield of desired $\mathbf{1}_{syn}$ increased to 13% (44% *de*, Table S3, entry 3). Importantly, using DPPPO (Θ = 141º, Table S3, entry 4) or similarly sized 2–$PyPPh_2$ (Θ = 145º, Table S3, entry 5) led to the formation of $\mathbf{1}_{syn}$ in 12 and 16% yields, respectively.[30] A modest improvement with 2–$PyPPh_2$ caught our attention and prompted us to elucidate the utility of pyridine-type ligands in the transformation.[31] Accordingly, we decided to test 4-(dimethylamino)pyridine (DMAP)[6] as this molecule is planar, smaller than phosphines and a less effective σ donor for assisting migratory insertions. By using 2.2 molar equivalents of DMAP, we found that both the reaction's total yield (28%, Figure 2a) and diastereoselectivity (79% *de*) considerably improved. Further optimizations of the concentration of (–)–**2** (Table S4), the quantity of DMAP (Table S5) or DPPPO (Table S6), the nature of phosphine ligand(s) (Tables S7/S9) and the source of palladium (Table S8) allowed us to identify the best coupling conditions in which a combination of $PdCl_2$/DPPPO/DMAP gave $\mathbf{1}_{syn}$ in 39% yield and 95% *de* (Figure 2b).

In line with such improved synthesis of $\mathbf{1}_{syn}$ (Figure 2b),[1] we found that bidentate and nitrogen based neocuproine (DMPHEN, Figure 2c)[32] would promote the formation of $\mathbf{1}_{syn}$ in 55% yield and 93% *de*! Note that several other nitrogen-based ligands were also effective in directing the transformation (Table S10).[33]

Using DPPPO and DMPHEN, the best performing phosphines, we examined the effect of changing the solvent (Tables S11-S12), the base and other additives (Table S13) on the catalytic transformation. In brief, less polar THF, dioxane and toluene showed comparable results while in more polar DMF the reaction gave unidentified products. With regard to the base, Cs_2CO_3 worked best. The addition of bromide anions (n-Bu_4NBr, Table S13) inhibited the transformation, while scavenging these anions with silver (Ag_2CO_3, Table S13) gave $\mathbf{1}_{syn/anti}$ in 43% yield, although with diastereoselectivity being reduced to 81% *de* (when compared to Figure 2b).

Our results could be viewed using neutral and ionic mechanistic alternatives proposed by W. Cabri and co-workers (Scheme 1A)[7] along with the formation of intermediate palladacycles discussed by Sakurai and co-workers (Scheme 1B).[5e] In essence, neutral RPdX and ionic RPd^+ intermediates formed in the oxidative addition undergo α or β migratory insertions (inset in Scheme 1A) with Pd–C bond formation preceding the transfer of carbon-based fragment;[6] this is the reason that the reaction can cautiously be viewed as an electrophilic addition of palladium with a development of partial positive charge at the adjacent carbon. Importantly, α/β migratory insertions are product-determining steps controlling the formation of two potential products. However, predicting their outcome is a challenging task, being a function of both electronic and steric parameters.[6-7] The conventional wisdom, though, is that the neutral pathway favours β insertions for any olefin (with EWGs or EDGs) while the ionic one promotes α-insertions for electron-rich olefins (with EDGs).[7] Since vinyl bromides could be classified as borderline electron-rich, one



Scheme 1. (A) Neutral (blue) and ionic (red) pathways for Mizoroki-Heck cyclotrimerization of electron deficient (–)–**2** occurring via α and β migratory insertions to give $\mathbf{1}_{syn/anti}$; (inset) mechanistic scheme shows a fictional Heck reaction with migratory insertions constituting product-determining steps. (B) Acetate mediated formation of achiral palladacycle intermediate via CMD mechanism.

could, depending on the mechanism, expect a tendency toward both migrations (inset, Scheme 1A). Since in the case of bromonorbornene (–)–**2** we found that $\mathbf{1}_{syn}$ prevailed (*de*>0, Figure 2),[5e] we concluded that the β channel dominated the transformation (Scheme 1A). Furthermore, the formation of palladacycle(s) via CMD mechanism[8] (Scheme 1B) could, in the presence of acetates ($Pd(OAc)_2$, Figure 2a), have participated to increase the production of $\mathbf{1}_{anti}$[5e] in comparison to $PdCl_2$ acting as the catalyst (Figure 2b).

With DPPPO as the ligand (Figure 2a-b),[34] the conversions likely proceeded via neutral pathway (right, Scheme 1A) with consecutive β migratory insertions of (–)–**2** dominating the process:[6] in spite of high regioselectivity supporting such neutral pathway,[7] the reaction was highly favoured in less polar solvents (Tables S11-S12) in which neutral, but not charged, intermediates ought to have a greater stability. The removal of bromides with silver,[35] as expected, switched the mechanism to ionic (left, Scheme 1A), which led to a greater degree of α–insertions and, as noted in Table S13, the greater production of $\mathbf{1}_{anti}$. On the other hand, the addition of bromide anions in the form of TBAB (Table S13) must have suppressed the coordination of bromonorbornene (–)–**2** to stop the catalytic transformation and permit to the insertion of propylene (Figure S2).[36] Apropos the postulated neutral pathway, the results also suggested that DMAP (Figure 2d) was more essential to the catalysis than DPPPO (Figure 2e). Accordingly, we hypothesize that this ligand substituted the phosphine at the palladium center (Scheme 1A): it is a weaker σ–donating group than the phosphine and thus able to assist the catalysis by facilitating the development of a trans and σ–donating Pd–C bond in the square-planar complex. With DMAP being smaller and planar while DPPPO is larger and cone-like, one could presume that the pyridine ligand caused a smaller van-der Waals strain in this coordination environment.[6] And finally, DMAP suppressed the coordination of acetate (Figure 2a vs Table S3), thereby shutting off the CMD pathway (Scheme 1B) and reducing the production of $\mathbf{1}_{anti}$.[5e] Indeed, with no acetate in the system, the formation of $\mathbf{1}_{anti}$ slowed down resulting in greater diastereoselection (Figure S13, entries 1/8).

In the case of bidentate DMPHEN, we suspect that the mechanism could be of the neutral type as well (right, Scheme 1A).[6] The logic behind our hypothesis is threefold. First, in this environment bromide is a poor leaving group.[7, 32] Second, the presence of DMAP is essential for the catalysis (Figure 2c/f), suggesting its role as a ligand displacing DMPHEN to facilitate the migratory insertion (Scheme 1A). Third, the reaction's stereoselectivity is almost identical for DMPHEN (Figure 2c, 93% *de*) and DPPPO (Figure 2b, 95% *de*).[7]

With two consecutive β–insertions, three molecules of (–)–**2** would combine into a hexatriene. This organometallic species is poised to undergo a disrotatory 6π electrocyclization and thus set the Pd(II) and the neighbouring hydrogen for *syn*-stereospecific β–hydride elimination.

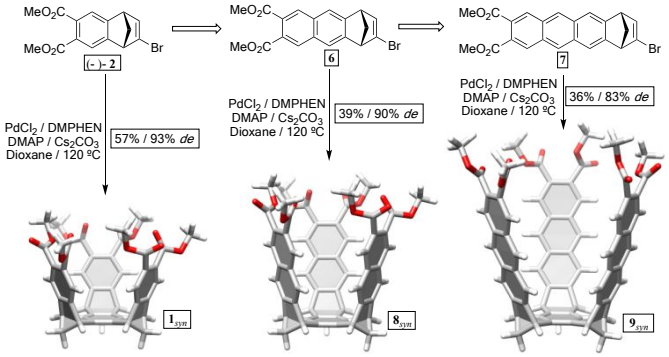


Figure 3. Synthesis of basket $\mathbf{1}_{syn}$, deeper cavity baskets $\mathbf{8}_{syn}$ and $\mathbf{9}_{syn}$ from enantioenriched (–)–**2**, **6** and **7**, respectively. The reported total yields and diastereoselectivities were obtained from ^{1}H NMR spectroscopic measurements.

Using the optimized conditions (Figure 3), we converted 2 grams of (–)–**2** into 0.75 grams of $\mathbf{1}_{syn}$. Importantly, the ^{1}H NMR spectrum of the reaction upon its completion (Figure S3) showed the clean formation of $\mathbf{1}_{syn}$ with, perhaps, oligomers as side products having their resonances broaden into the baseline (Figure S4). Indeed, the ESI analysis (Figure S5) suggested the presence of linear tetramers to octamers of **2** therefore

disclosing the nature of competitive pathways occurring in the formation of $\mathbf{1}_{syn/anti}$.

In order to obtain deeper cavity baskets $\mathbf{8}_{syn}$ and $\mathbf{9}_{syn}$ (Figure 3), we iteratively extended the benzene ring in (–)–(**2**) into naphthalene in **6** and then anthracene in **7**.[37] Following, the Mizoroki-Heck cyclotrimerization of enantioenriched **6** and **7** showed a high diastereoselectivity (Figure 3) to give deeper cavitands $\mathbf{8}_{syn}$ and $\mathbf{9}_{syn}$ in 36–39% yields. More spacious and flexible baskets $\mathbf{8}_{syn}$ and $\mathbf{9}_{syn}$ should possess useful photochemical characteristics[38] for applications in the areas of chemosensors and catalysis as induced-fit hosts.

In summary, we have presented a novel protocol for completing the Mizoroki-Heck self-coupling of enantioenriched and accessible[5e] bromonorbornenes into three variously sized molecular baskets. Remarkably, the cyclotrimerizations of aromatic bromonorbornenes are now tuned to exclusively follow β–migratory insertions, without a participation of palladacycles, providing a more facile access to larger quantities of molecular baskets possessing functionalized and extended aromatics. The stage is set for using these C_3 symmetric hosts toward obtaining novel supramolecular materials.[24, 39]

Acknowledgement

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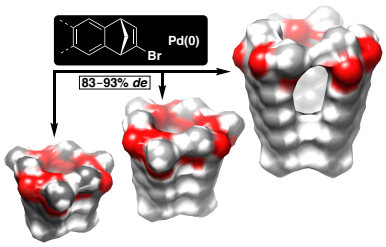

A novel synthetic method for obtaining multigram quantities of uniquely functionalized and deep molecular baskets is now available, clearing the way toward useful supramolecular materials.