consistent with all the experimental evidence. We expect the same-strength isotope effect if the 2D crystals are combined with other proton conductors based on oxides (13, 25–28), and the separation factor should be even larger for proton-conducting media with stronger hydrogen bonds; for example, in fluorides (28).

The above explanation allows for several observations about proton transport through 2D crystals. First, it partially explains the disagreement between the experiment (5) and theory (5, 8–10) in the absolute value of E_H for graphene: Zero-point oscillations reduce the activation barrier by ≈0.2 eV compared to theoretical values. We speculate that the remaining differences [<20% in the case of (8)] may be accounted for by considering other effects of the surrounding media (for example, two-body processes involving a distortion of the electron clouds by protons residing at the Nafion-graphene interface). Second, the experiments confirm that hydrogen chemisorption to 2D crystals is not the limiting step in the transfer process because, otherwise, the isotope effect would be different for hBN and graphene. Third, the described sieving mechanism implies α ≈30 for tritium-hydrogen separation. Fourth, it is quite remarkable that zero-point oscillations, a purely quantum effect, can still dominate room-temperature transport properties of particles 4000 times heavier than electrons.

The observed large α compares favorably with sieving efficiencies of the existing methods for hydrogen isotope separation (15–20). The high proton conductivity exhibited by graphene and boron nitride monolayers, comparable to that of commercial Nafion films (5, 22), makes them potentially interesting for such applications. In this respect, the increasing availability of graphene grown by chemical vapor deposition (CVD) (29, 30) provides a realistic prospect of scaling up the described devices from micrometer sizes to those required for industrial uses. Indeed, although micromechanical cleavage allows 2D membranes of highest quality, the approach is not scalable. As a proof of concept, we repeated the mass spectrometry measurements using centimeter-sized membranes made from CVD graphene and achieved the same α ≈ 10 (fig. S7). Notably, this shows that macroscopic cracks and pinholes present in CVD graphene do not affect the efficiency, because hydrons are electrochemically pumped only through the graphene areas that are electrically contacted (22). Furthermore, we estimate the energy costs associated with this isotope separation method as ≈0.3 kWh per kilogram of feed water (22), appreciably lower than costs of the existing enrichment processes (15, 16). All this comes on top of the fundamentally simple and robust sieving mechanism, potentially straightforward setups, and the need for only water at the input without the use of chemical compounds (16).

REFERENCES AND NOTES

1. J. S. Bunch et al., Nano Lett. **8**, 2458–2462 (2008).
2. S. P. Koenig, L. Wang, J. Pellegrino, J. S. Bunch, Nat. Nanotechnol. **7**, 728–732 (2012).
3. O. Leenaerts, B. Partoens, F. M. Peeters, Appl. Phys. Lett. **93**, 193107 (2008).
4. V. Berry, Carbon **62**, 1–10 (2013).
5. S. Hu et al., Nature **516**, 227–230 (2014).
6. L. Britnell et al., Nano Lett. **12**, 1707–1710 (2012).
7. L. Tsetseris, S. T. Pantelides, Carbon **67**, 58–63 (2014).
8. W. L. Wang, E. Kaxiras, New J. Phys. **12**, 125012 (2010).
9. M. Miao, M. B. Nardelli, Q. Wang, Y. Liu, Phys. Chem. Chem. Phys. **15**, 16132–16137 (2013).
10. J. L. Achtyl et al., Nat. Commun. **6**, 6539 (2015).
11. K. B. Wiberg, Chem. Rev. **55**, 713–743 (1955).
12. B. E. Conway, Proc. R. Soc. A Math. Phys. Eng. Sci. **256,** 128–144 (1960).
13. K. D. Kreuer, A. Fuchs, J. Maier, Solid State Ion. **77**, 157–162 (1995).
14. A. Paris et al., Adv. Funct. Mater. **23**, 1628–1635 (2013).
15. H. K. Rae, Ed., Separation of Hydrogen Isotopes (ACS Symposium Series, Washington, DC, 1978).
16. A. I. Miller, Can. Nucl. Soc. Bull. **22**, 1–14 (2001).
17. J. J. M. Beenakker, V. D. Borman, S. Y. Krylov, Chem. Phys. Lett. **232**, 379–382 (1995).
18. X. Zhao, S. Villar-Rodil, A. J. Fletcher, K. M. Thomas, J. Phys. Chem. B **110**, 9947–9955 (2006).
19. B. E. Conway, Proc. R. Soc. London Ser. A **247**, 400–419 (1958).
20. J. H. Rolston, J. Den Hartog, J. P. Butler, J. Phys. Chem. **80**, 1064–1067 (1976).
21. J. B. Marling, I. P. Herman, S. J. Thomas, J. Chem. Phys. **72**, 5603–5634 (1980).
22. See supplementary materials on Science Online.
23. K. A. Mauritz, R. B. Moore, Chem. Rev. **104**, 4535–4586 (2004).
24. K. W. Feindel, S. H. Bergens, R. E. Wasylishen, J. Power Sources **173**, 86–95 (2007).
25. T. Hibino, K. Mizutani, H. Iwahara, J. Electrochem. Soc. **140**, 2588 (1993).
26. K. D. Kreuer, Chem. Mater. **8**, 610–641 (1996).
27. D. Marx, M. E. Tuckerman, J. Hutter, M. Parrinello, Nature **397**, 601–604 (1999).
28. D. Marx, ChemPhysChem **7**, 1848–1870 (2006).
29. A. Reina et al., Nano Lett. **9**, 30–35 (2009).
30. K. S. Kim et al., Nature **457**, 706–710 (2009).

ORGANIC CHEMISTRY

Catalytic conjunctive cross-coupling enabled by metal-induced metallate rearrangement

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Transition metal catalysis plays a central role in contemporary organic synthesis. Considering the tremendously broad array of transition metal–catalyzed transformations, it is remarkable that the underlying elementary reaction steps are relatively few in number. Here, we describe an alternative to the organometallic transmetallation step that is common in many metal-catalyzed reactions, such as Suzuki-Miyaura coupling. Specifically, we demonstrate that vinyl boronic ester ate complexes, prepared by combining organoboronates and organolithium reagents, engage in palladium-induced metallate rearrangement wherein 1,2-migration of an alkyl or aryl group from boron to the vinyl α-carbon occurs concomitantly with C−Pd σ-bond formation. This elementary reaction enables a powerful cross-coupling reaction in which a chiral Pd catalyst merges three simple starting materials—an organolithium, an organoboronic ester, and an organotriflate—into chiral organoboronic esters with high enantioselectivity.

Organoboronic acids and their derivatives are widely available and broadly useful starting materials for organic synthesis (1). In addition to being environmentally benign and generally inexpensive, these reagents exhibit a near-ideal balance of stability and reactivity. Although chemically and configurationally stable, organoboronic esters engage in a broad array of carbon-carbon and carbon-heteroatom bond-forming processes upon activa-tion. The most commonly practiced such reaction is the transition metal–catalyzed Suzuki-Miyaura cross-coupling reaction between organic electrophiles and organoboron compounds (2). In broad strokes, the mechanism of the Suzuki-Miyaura reaction involves a sequence of (i) oxidative addition between a metal catalyst and the electrophile, (ii) transmetallation with the organoboron reagent, and (iii) reductive elimination of the C-C bonded product (3). Here, we used an alternative pathway to the organoboron transmetallation step. The overall putative catalytic cycle enables a class of organoboron cross-coupling that we term "conjunctive cross-coupling" (Fig. 1A) because it merges

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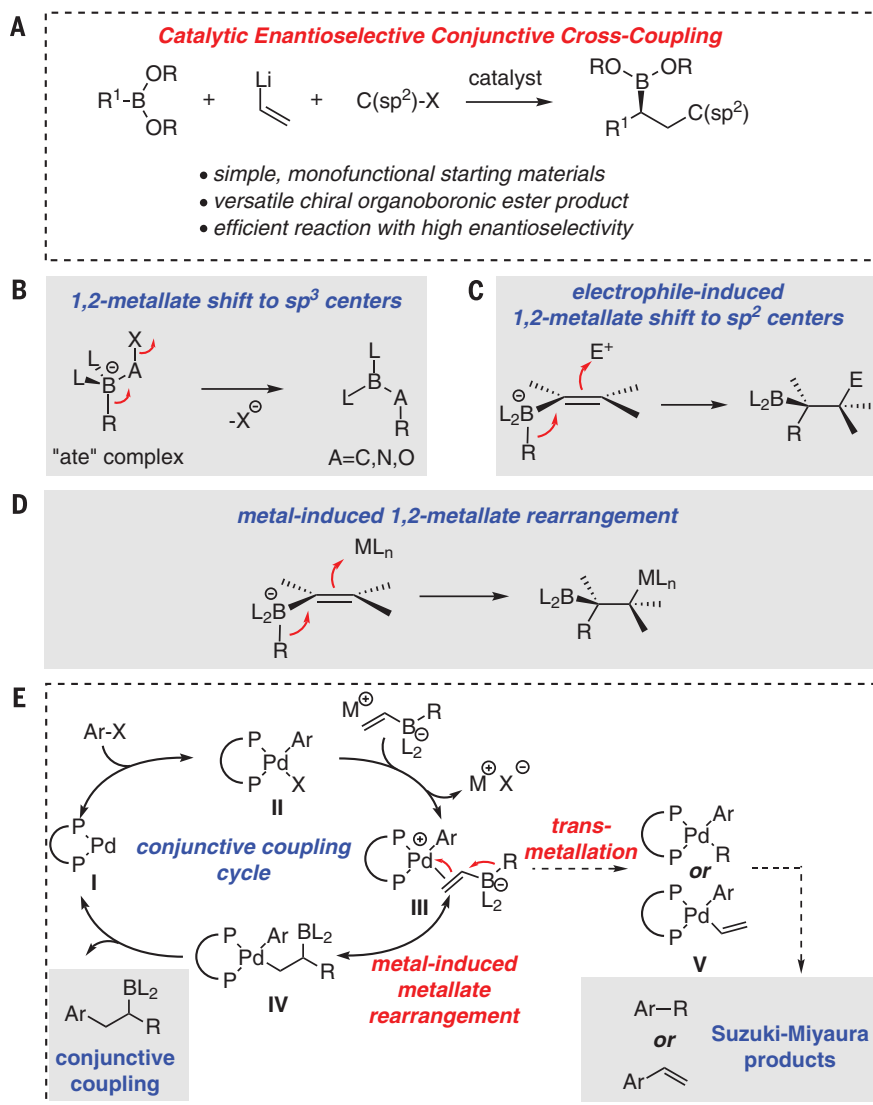*Corresponding author. E-mail: morken@bc.edu

Fig. 1. Metal-induced metallate shift as a strategy for catalytic reaction design. (**A**) The catalytic conjunctive cross-coupling process. (**B**) Common metallate shift to saturated carbon centers requires a leaving group. L, ligand. (**C**) Metallate shift to unsaturated carbons is often activated by addition of an external electrophile. M, metal; E, electrophile. (**D**) A metallate shift promoted by a metal complex can serve as an alternative to a transmetallation process. (**E**) Proposed catalytic cycle for conjunctive cross-coupling. Ar, aryl group.

two nucleophilic reagents into one during the course of the reaction. Overall, the conjunctive cross-coupling constructs chiral products by merging three simple starting materials: an organolithium reagent, an organoboronic ester, and an organic electrophile. The reaction, which adds to recent catalytic alkene carboboration reactions (*4*, *5*), establishes two new carbon-carbon bonds and forms a stereogenic center bearing a useful organoboronic ester with high enantioselectivity.

Organoboronic esters are known to participate in a wide range of reactions that occur by stereospecific 1,2-metallate rearrangements (*6*, *7*). The preponderance of these reactions occur with a four-coordinate anionic boron-centered "ate" complex (Fig. 1B) that rearranges by a 1,2-carbon shift from boron to an adjacent sp^3-hybridized electrophilic center (designated "A") bearing an attached leaving group (X). The stereoelectronic requirements of the metallate shift dictate an anti-periplanar arrangement of the migrating carbon atom (R) and the leaving group such that the overall process is stereoretentive at R but stereoinvertive at A (*8*).

These processes are common (*9*) for transformations where the "A" group is a carbon, nitrogen, or oxygen atom and less common but still established for sulfur and phosphorus (*10*, *11*). Because of the stereospecific nature of the above-described processes, stereoselectivity in metallate shifts is generally subject to substrate control (*12*), although Jadhav and Man reported an example with selectivity dictated by a chiral catalyst (*13*). Metallate rearrangement from boron to sp (*14*) and sp^2 (*15*) hybridized carbons often require the addition of an external electrophilic activator (Fig. 1C), and generally the 1,2-metallate shift is followed by elimination to reestablish unsaturation (*16*). In this context, we considered that in place of stoichiometric electrophilic activating agents, π-acidic late transition metals might similarly promote the 1,2-metallate shift of alkenyl boronates (Fig. 1D) and that the resulting chiral organometallic intermediate might be used in subsequent bond-forming processes.

In one embodiment of catalysis based on metal-induced 1,2-metallate rearrangements, we considered that an electrophilic palladium complex (**II**, Fig. 1E), generated by oxidative addition of **I** with an organic electrophile, might induce 1,2-migration in a vinyl boronate-derived ate complex (**III→IV**) and establish a new C–C bond and a boron-substituted stereogenic center. Subsequent reductive elimination (**IV→I**) would serve to establish a second C–C bond, release the product, and concomitantly furnish a reduced Pd complex that might continue a catalytic cycle. The net reaction, in this cycle, is aligned with important work from Murakami, who studied reactions of alkynyl boron ate complexes (*17*). Although π-acidic late transition metal complexes are well known to activate alkenes for nucleophilic attack, nucleopalladation with Pd(II) complexes generated by oxidative addition reactions are less common (*18*, *19*). For the envisioned process to be successful, several key questions emerged: Would the Pd(II) aryl complexes be sufficiently π-acidic to facilitate metallate rearrangement (**III→IV**)? Would common direct transmetallation (**III→V**) dominate the reaction and furnish Suzuki-Miyaura products?

Fig. 2. Scope of the catalytic conjunctive cross-coupling reaction starting from vinyl boronic esters. Yields represent isolated yield of purified material and are an average of two experiments. The absolute configuration was determined by anomalous dispersion x-ray and by chromatographic comparison to known compounds. *VinylB(neo) was replaced with vinylB(pin); †reaction conducted at 80°C. er was determined by chiral supercritical fluid chromatography. OAc, acetate; Me, methyl group; Ph, phenyl group; OTf, trifluoromethanesulfonate; OTBS, tert-butyldimethylsiloxy.
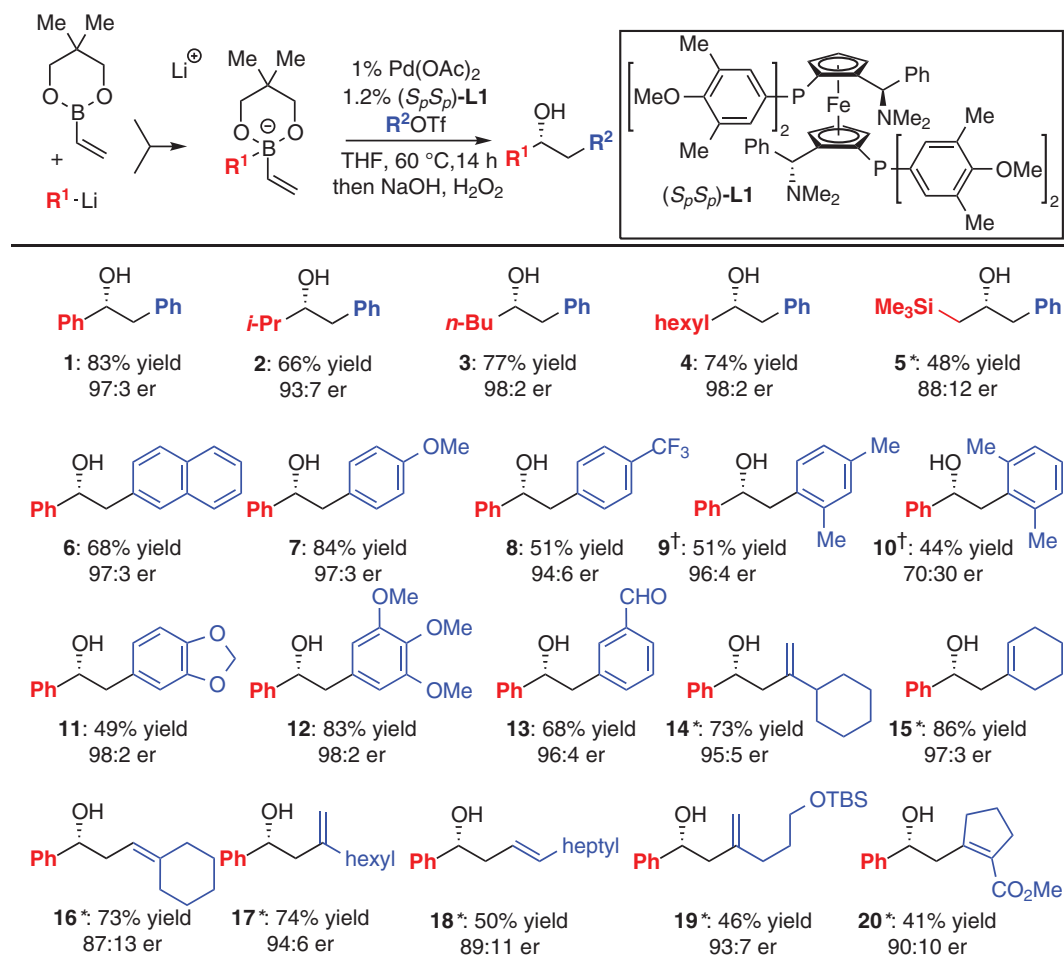
Could facial selectivity in olefin binding render the migration (**III**→**IV**) enantioselective? Last, would β-hydrogen elimination in intermediates such as **IV** compete with reductive elimination?

To begin our studies of the conjunctive cross-coupling reaction, we selected phenyl triflate as the electrophile, anticipating that the outer-sphere triflate anion would leave open a coordination site on Pd for alkene binding (Fig. 1E, **III**). In an effort to minimize steric penalties that might inhibit metallate shift, we opted for an unsubstituted vinyl group in construction of the boron ate complex. Similarly, on the basis of recent studies from Mayr and Aggarwal (20, 21), we selected a neo-pentylglycolato ligand for boron because the ate complexes derived from this ligand (versus others readily available) were determined to be the most nucleophilic. Last, in an effort to favor reductive elimination relative to β-hydrogen elimination in putative intermediate **IV**, we selected ligands with large bite angles for the palladium complex. Initial experiments with achiral bidentate ferrocenyl 1,1′-diphosphines were promising and suggested that the conjunctive cross-coupling could indeed operate. A survey of a number of chiral diphosphine structures revealed that Josiphos (22) and MandyPhos (Solvias AG, Kaiseraugst, Switzerland) (23) are particularly effective ligand classes, with the MandyPhos ligand **L1** providing an outstanding level of enantio-

selectivity and very good catalyst efficiency in the reaction.

In optimizing the reaction conditions, we found tetrahydrofuran (THF) to be the most effective solvent. Therefore, when the migratory R group was appended to boron by addition of hydrocarbon solutions of organolithium reagents to the neopentyl glycol–derived vinyl boronic ester vinylB(neo) (Fig. 2), the resulting ate complexes were evaporated to dryness and redissolved in THF before reaction. The efficiency of the reaction was also greatly diminished by chloride, bromide, or iodide ions, an obstacle easily overcome by the continued use of aryl and alkenyl triflates as the electrophile. For coupling of alkenyl triflate electrophiles, the reaction selectivity was markedly enhanced with boron ate complexes derived from pinacolato ligands in place of the neo-pentylglycol derivative [e.g., product **15** is formed in 53% yield and 82:18 enantiomeric ratio (er) when using the neo-pentylglycol ligand], whereas for aryl triflates, the neo-pentylglycol ligand furnished higher selectivity [**1** formed in 94% yield, 93:7 er using B(pin) group]. With these features optimized, the scope of the conjunctive coupling was explored with an array of ate complexes and electrophiles. During these experiments, it was most convenient to oxidize the product organoboronic ester to the derived alcohol by treatment with NaOH and H₂O₂; how-

ever, isolation of the organoboron product itself is also possible (the organoboron precursor to alcohol **1** was isolated in 76% yield by silica gel chromatography). As shown in Fig. 2, both aryl and alkyl groups proved competent migrating elements in conjunctive coupling reactions. In cases where the yield of product is low, analysis of the reaction mixture before oxidation showed that by-products generally consist of recovered organoboronic ester (likely generated during workup by protonolysis of one carbon ligand from the ate complex) and direct Suzuki-Miyaura products. Primary and secondary alkyl groups migrate, as do functionalized alkyl appendages [e.g., (trimethylsilyl)methyl]. Conjunctive couplings were also effective for both electron-rich and electron-poor electrophiles. Moderately encumbered electrophiles, such as ortho-substituted arenes, can engage in the reaction, although the more highly substituted 2,6-dimethylphenyl derivative suffered from lower selectivity. With respect to preparation of chiral hydrocarbon frameworks, a range of substituted alkenyl triflates participate, and the configuration of the product alkene directly reflects that of the precursor electrophile.

The ate complex could be generated either by addition of an organolithium reagent to vinylB(neo) (Fig. 2) or by addition of vinyllithium to organoboronic esters (Fig. 3). Considering the broad
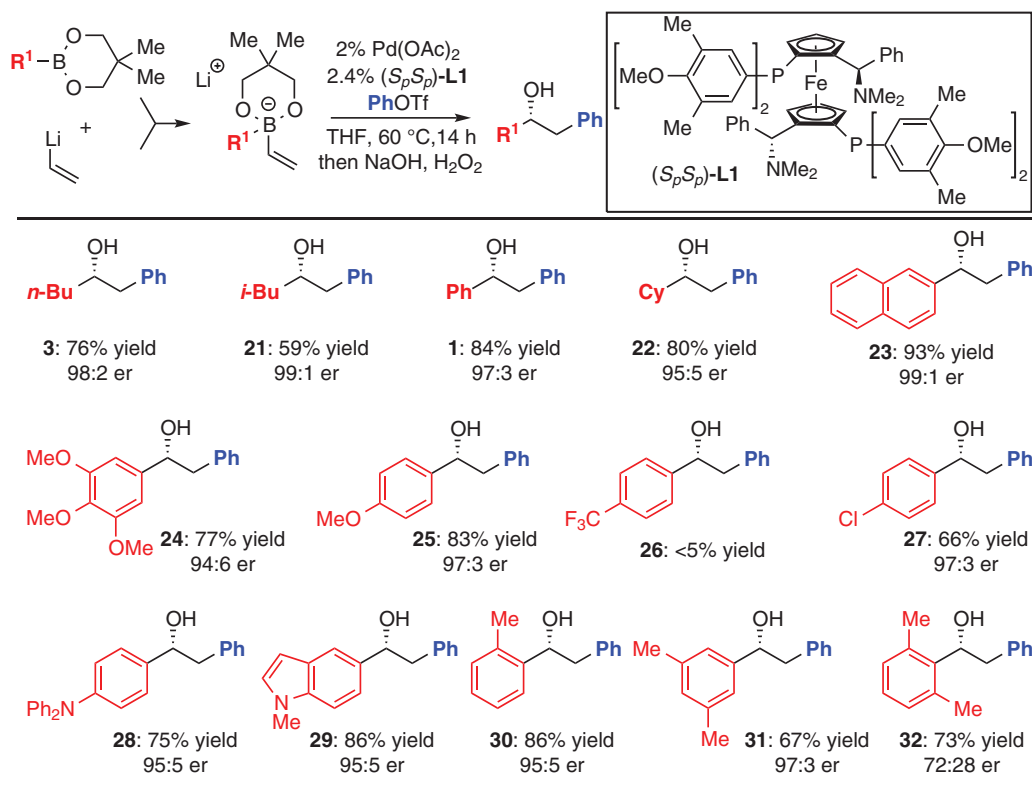
Fig. 3. Scope of the catalytic conjunctive cross-coupling reaction starting from alkyl or aryl boronic esters. Yields represent isolated yield of purified material and are an average of two experiments. Cy, cyclohexyl group.

3: 76% yield
98:2 er

21: 59% yield
99:1 er

1: 84% yield
97:3 er

22: 80% yield
95:5 er

23: 93% yield
99:1 er

24: 77% yield
94:6 er

25: 83% yield
97:3 er

26: <5% yield

27: 66% yield
97:3 er

28: 75% yield
95:5 er

29: 86% yield
95:5 er

30: 86% yield
95:5 er

31: 67% yield
97:3 er

32: 73% yield
72:28 er

array of organoboronic esters that are already available for use in common cross-coupling processes, the latter strategy is particularly enabling. In this context, we found that the presence of lithium halide salts, even at 1 to 2 mole percent (mol %) loading, markedly erodes conjunctive coupling efficiency. Thus, to perform the reaction with highest efficiency with 2 mol % catalyst loading, it is critical that halide-free vinyllithium be used. To prepare this reagent, we developed a procedure that involved lithium-halogen exchange with *n*-BuLi (Bu, butyl group) in hexane, followed by low-temperature recrystallization of pure vinyllithium. When these precautions are taken, conducting the reaction as in Fig. 3 allowed the scope of the migrating group to be surveyed more completely and revealed that, although reactions requiring migration of very electron-deficient groups are still a challenge, electron-neutral and electron-rich arenes can engage in the migration, as can those that are more highly substituted (i.e., 2,6-disubstituted arenes). We also found that, with 5 mol % catalyst loading, vinyllithium prepared as above but without recrystallization was effective (e.g., **3** formed in 69% yield, 98:2 er) and that vinyllithium prepared by lithium-tin exchange (*24*) could be used directly (2 mol % catalyst, **1** formed in 83% yield, 97:3 er).

To probe the utility of conjunctive cross-coupling to practical organic synthesis, we were attracted to the natural product (–)-combretastatin (*25*), a member of a family of cytotoxic stilbene-derived natural products that bind β-tubulin (Fig. 4A). Although many synthetic methods have facilitated the construction of combretastatins (*26*),
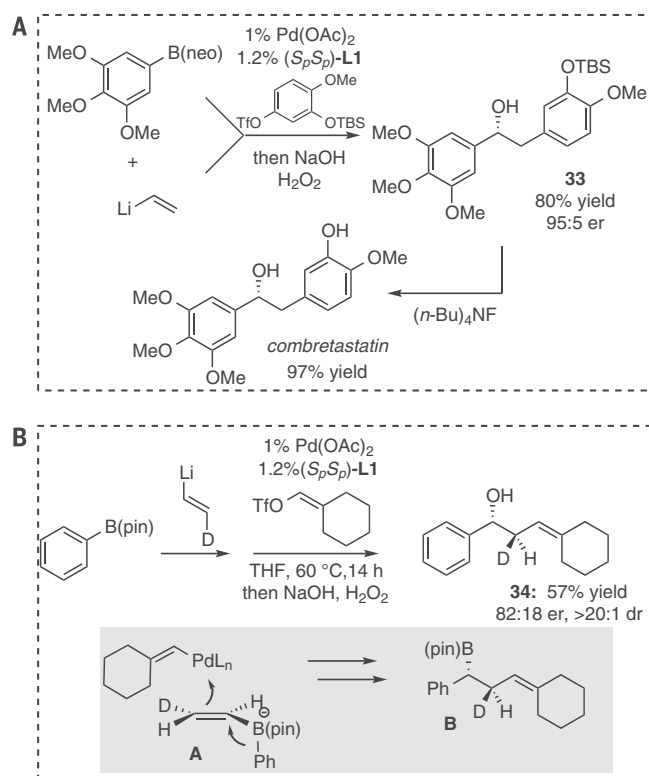
alternative processes may engage different starting materials and thereby provide access to distinct analogs. In the case of conjunctive cross-coupling, the requisite boronic ester and electrophile are

readily available and, as depicted in Fig. 4A, are readily converted to the coupled product in an efficient and highly selective fashion. Removal of the silicon protecting group furnished the target

Fig. 4. Synthesis and mechanistic studies. (**A**) Synthesis of combretastatin by conjunctive cross-coupling. (**B**) The stereochemical course of metal-induced metallate rearrangement. dr, diastereomeric ratio.

A

33
80% yield
95:5 er

combretastatin
97% yield

B

34: 57% yield
82:18 er, >20:1 dr

structure, spectra of which were fully consistent with the natural isolate.

The mechanism of the conjunctive coupling reaction is the subject of ongoing investigations, although the substrate scope (Figs. 2 and 3) gives clues about the process. The observation that electron-deficient arenes are less prone to migration is consistent with the mechanistic hypothesis put forward in Fig. 1E. According to this hypothesis, formation of **IV** would likely be stereochemistry determining, and, in line with this prediction, the selectivity of the reaction depends not only on the ligand framework but also on the organoboronic ester ligand (pinacol versus *neo*-pentylglycol), the migrating group, and the electrophile. In addition to these observations, one preliminary experiment sheds important light on the nature of the metal-induced metallate rearrangement that appears to underlie the conjunctive coupling process. As depicted in Fig. 4B, when the reacting ate complex was constructed from stereochemically defined deuterium-labeled vinyllithium (27) and phenylB(pin), the (1R,2R) stereoisomer of the conjunctive coupling product was formed in >20:1 diastereoselection (82:18 er). Although other interpretations are possible, should the mechanism be in line with that proposed in Fig. 1E and reductive elimination occur with retention of configuration at carbon (a reasonable assumption), the observed stereochemical outcome in Fig. 4B is consistent with anti-migration of the arene group to a Pd-olefin complex (Fig. 1D). Such an outcome is reminiscent of nucleometallation reactions that do not involve preassociation of the migrating group and the metal center (28).

We anticipate that many other transition metal–catalyzed reactions might also be reengineered to incorporate metal-induced metallate rearrangements, thereby providing distinct strategies for catalytic enantioselective synthesis.

REFERENCES AND NOTES

1. D. G. Hall, Ed., *Boronic Acids* (Wiley-VHC, Weinheim, Germany, 2011).
2. N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **20**, 3437–3440 (1979).
3. N. Miyaura, A. Suzuki, *Chem. Rev.* **95**, 2457–2483 (1995).
4. T. Jia et al., *J. Am. Chem. Soc.* **137**, 13760–13763 (2015).
5. W. Su et al., *Angew. Chem. Int. Ed.* **54**, 12957–12961 (2015).
6. E.-I. Negishi, *Org. React.* **33**, 1–246 (1985).
7. V. K. Aggarwal, G. Y. Fang, X. Ginesta, D. M. Howells, M. Zaja, *Pure Appl. Chem.* **78**, 215–229 (2006).
8. M. M. Midland, A. R. Zolopa, R. L. Halterman, *J. Am. Chem. Soc.* **101**, 248–249 (1979).
9. A. Suzuki, *Top. Curr. Chem.* **112**, 67–115 (1983).
10. P. M. Draper, T. H. Chan, D. N. Harpp, *Tetrahedron Lett.* **11**, 1687–1688 (1970).
11. S. P. Thomas, R. M. French, V. Jheengut, V. K. Aggarwal, *Chem. Rec.* **9**, 24–39 (2009).
12. D. Leonori, V. K. Aggarwal, *Top. Organomet. Chem.* **49**, 271–295 (2015).
13. P. K. Jadhav, H.-W. Man, *J. Am. Chem. Soc.* **119**, 846–847 (1997).
14. A. Suzuki et al., *J. Am. Chem. Soc.* **95**, 3080–3081 (1973).
15. For lead references, see (29).
16. G. Zweifel, H. Arzoumanian, C. C. Whitney, *J. Am. Chem. Soc.* **89**, 3652–3653 (1967).
17. N. Ishida, Y. Shimamoto, M. Murakami, *Org. Lett.* **11**, 5434–5437 (2009).
18. J. S. Nakhla, J. W. Kampf, J. P. Wolfe, *J. Am. Chem. Soc.* **128**, 2893–2901 (2006).
19. D. Bruyère, D. Bouyssi, G. Balme, *Tetrahedron* **60**, 4007–4011 (2004).
20. G. Berionni, A. I. Leonov, P. Mayer, A. R. Ofial, H. Mayr, *Angew. Chem. Int. Ed.* **54**, 2780–2783 (2015).
21. K. Feeney, G. Berionni, H. Mayr, V. K. Aggarwal, *Org. Lett.* **17**, 2614–2617 (2015).
22. A. Togni et al., *J. Am. Chem. Soc.* **116**, 4062–4066 (1994).
23. J. J. Almena Perea, M. Lotz, P. Knochel, *Tetrahedron Asymmetry* **10**, 375–384 (1999).
24. D. Seyferth, M. A. Weiner, *J. Am. Chem. Soc.* **83**, 3583–3586 (1961).
25. G. R. Pettit, G. M. Cragg, D. L. Herald, J. M. Schmidt, P. Lohavanijaya, *Can. J. Chem.* **60**, 1374–1376 (1982).
26. R. Singh, H. Kaur, *Synthesis* **2009**, 2471–2491 (2009).
27. R. P. Hughes, H. A. Trujillo, J. W. Egan Jr., A. L. Rheingold, *J. Am. Chem. Soc.* **122**, 2261–2271 (2000).
28. R. I. McDonald, G. Liu, S. S. Stahl, *Chem. Rev.* **111**, 2981–3019 (2011).
29. A. Bottoni, M. Lombardo, A. Neri, C. Trombini, *J. Org. Chem.* **68**, 3397–3405 (2003).

MICROBIAL ENGINEERING

Self-photosensitization of nonphotosynthetic bacteria for solar-to-chemical production

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Improving natural photosynthesis can enable the sustainable production of chemicals. However, neither purely artificial nor purely biological approaches seem poised to realize the potential of solar-to-chemical synthesis. We developed a hybrid approach, whereby we combined the highly efficient light harvesting of inorganic semiconductors with the high specificity, low cost, and self-replication and -repair of biocatalysts. We induced the self-photosensitization of a nonphotosynthetic bacterium, *Moorella thermoacetica*, with cadmium sulfide nanoparticles, enabling the photosynthesis of acetic acid from carbon dioxide. Biologically precipitated cadmium sulfide nanoparticles served as the light harvester to sustain cellular metabolism. This self-augmented biological system selectively produced acetic acid continuously over several days of light-dark cycles at relatively high quantum yields, demonstrating a self-replicating route toward solar-to-chemical carbon dioxide reduction.

The necessity of improving the natural mechanisms of solar energy capture for sustainable chemical production (1) has motivated the development of photoelectrochemical devices based on inorganic solid-state materials (2). Although solid-state semiconductor light absorbers often exceed biological light harvesting in efficiency (3), the transduction of photoexcited electrons into chemical bonds (particularly toward multicarbon compounds from CO_2) remains challenging with abiotic catalysts (4, 5). Such catalysts struggle to compete with the high-specificity, low-cost material requirements and the self-replicating, self-repairing properties of biological CO_2 fixation (6). Thus, a viable solution must combine the best of both worlds: the light-harvesting capabilities of semiconductors with the catalytic power of biology.

Several inorganic-biological hybrid systems have been devised: semiconductor nanoparticles with hydrogenases to produce biohydrogen (7), long wavelength–absorbing nanomaterials to improve the photosynthetic efficiency of plants (8), and whole cells with photoelectrodes for CO_2 fixation (9, 10). Whole-cell microorganisms are favored to facilitate the multistep process of CO_2 fixation and can self-replicate and self-repair (11). Furthermore, bacteria termed "electrotrophs" can undergo direct electron transfer from an electrode (12). However, traditional chemical synthesis of the semiconductor component often requires high-purity reagents, high temperatures, and complex microfabrication techniques. Additionally, the integration of such foreign materials with biotic systems is nontrivial (13). Many reports have shown that some microorganisms induce the precipitation of nanoparticles (14), producing an inherently biocompatible nanomaterial under mild conditions.

Although photosynthetic organisms can precipitate semiconductor nanoparticles, their metabolic pathways are arguably less desirable than those of their nonphotosynthetic counterparts. Although gene modification of phototrophs has

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