

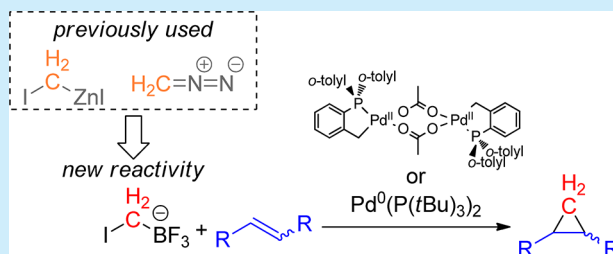
A Palladium-Catalyzed Methylenation of Olefins Using Halomethylboronate Reagents

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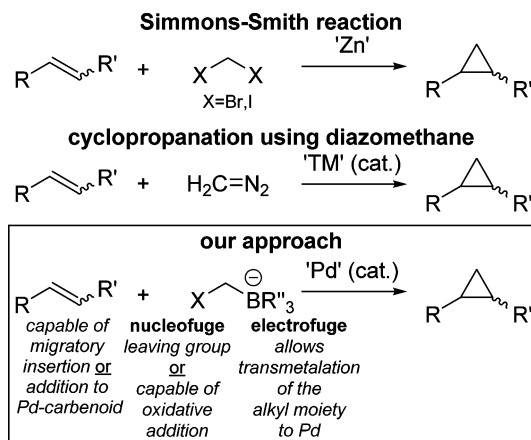
S Supporting Information

ABSTRACT: Methylenation of electron-rich olefins is a highly challenging reaction, for which we have developed a new methodology exploiting Pd-catalysis and halomethylboronate reagents, the latter replacing diazomethane and zinc carbenoids as methylene donors. Optimization of the reaction for norbornene and extension to several other olefins are reported, with reasonable-to-excellent yields of cyclopropanes in combination with β -H elimination products. Several mechanisms are plausible for this methylenation reaction.



Methylenation of electron-rich olefins, other than styrene and styrene analogs, is one of the most challenging cyclopropanation reactions^{1,2} (Scheme 1). Despite the

Scheme 1. Approaches for the Methylenation of Electron-Rich Olefins



generation of Zn-waste in an at least stoichiometric ratio to products and problems associated with scale-up, the Simmons–Smith reaction^{3,4} is the method of choice for this transformation in industry. An alternative for small scale methylenations is the transition metal (TM) catalyzed decomposition of diazomethane,⁵ although safety issues have largely prevented large-scale applications; *in situ* preparation of this reagent has been suggested.⁶ An alternative, scalable, safe method for the methylenation of olefins is accordingly highly desirable.

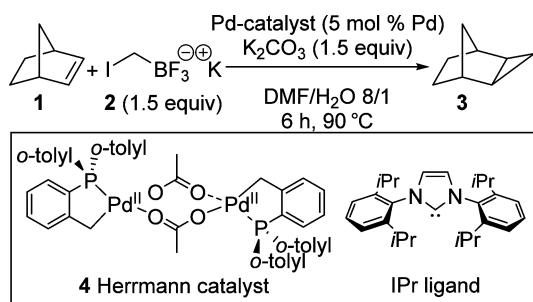
In addition to the synthesis of cyclopropanes using diazo reagents,^{1,7} Pd-catalysis has also been employed to prepare several substituted cyclopropanes using other reagents.^{8–10} However, these transformations allegedly proceed via (oxa)- π -

allyl Pd^{II} ,⁸ vinyl Pd^{II} ,⁹ or alkynyl Pd^{II} ¹⁰ intermediates, which would exclude the corresponding methylenation reactions *a priori*. For the Pd-catalyzed introduction of methylene synthons, other than diazomethane,⁵ only a single example using a high Pd-catalyst loading (~ 3 turnovers) has been reported.¹¹ All alkenylations mentioned here^{8–11} are limited to norbornenes and other strained bicyclic substrates.

We anticipated that the use of halomethylboronate reagents in combination with a Pd-catalyst would allow us to replace diazomethane/zinc carbenoids altogether. We envision several possible mechanisms for this transformation (*vide infra*). In this methylenation all functionalities featured in substrate and reagent would have a specific role (Scheme 1): (1) the alkylboron functionality would be capable of transferring its alkyl moiety to a Pd^{II} -intermediate via either an inter-¹² or intramolecular transmetalation; (2) the halide (X) could act as leaving group, allowing the formation of a Pd-methylene carbenoid intermediate,¹³ or the alkyl-X bond could oxidatively add¹⁴ to a Pd^0 -catalyst; (3) the olefin could either perform a migratory insertion¹⁵ (inner sphere mechanism¹⁶) or react with a Pd-methylene carbenoid intermediate (outer sphere mechanism¹³). In this paper, we report the methylenation of several electron-rich olefins using Pd^0 , as well as, Pd^{II} -catalysts, and we propose several possible mechanisms for this transformation.

Initially, we chose to study the methylenation of norbornene, **1**, using several Pd-catalysts (Table 1). Substrate **1** was chosen for the strong metal coordinating properties of its double bond, and because the only *syn* β -H available after migratory insertion of a Pd-catalyst cannot eliminate due to Bredt's rule. Commercially available iodomethyltrifluoroborate, **2**, was selected as a methylenation reagent for the leaving group properties of the iodide/the reactivity of the C–I bond for oxidative addition.¹⁴ A combination of base and H_2O was used

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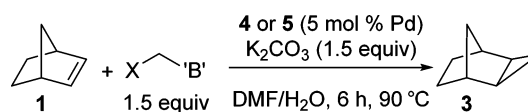
Table 1. Screening of Catalysts for the Methylenation of Norbornene^a

no.	catalyst	yield ^b	remaining 1 ^b
1	none	0%	80%
2	Pd ⁰ (PPh ₃) ₄	6%	71%
3 ^c	Pd ⁰ (dba) ₂ + IPr	2%	81%
4	Pd ⁰ (IPr) ₂	37%	45%
5	Pd ⁰ (P(<i>t</i> Bu) ₃) ₂ (5)	85%	15%
6	Pd ^{II} -Herrmann (4)	98%	0%
7	Pd ^{II} IPrCl ₂ -dimer (6)	88%	4%

^aConditions: scale 0.117 mmol of **1**, 0.06 M concentration of **1**.
^bStandardized GC yield and recovery of **1**. ^cPd⁰(dba)₂ (5 mol %) and IPr ligand (6 mol %) were used.

for the *in situ* activation¹⁷ of the trifluoroborate for transmetalation. Without a Pd-catalyst the reaction of **1**, **2**, base, and DMF/H₂O gave no cyclopropane (entry 1). Traces of the cyclopropane *exo*-tricyclo[3.2.1.0-2,4]octane (**3**) were observed when 5 mol % Pd⁰(PPh₃)₄ or a combination of 5 mol % Pd⁰ source and 6 mol % 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) ligand were used as the catalyst (entries 2 and 3). The use of the preformed¹⁸ Pd⁰(IPr)₂ catalyst gave an encouraging 37% yield of **3** (entry 4). Finally, a good 85% yield (GC) of **3** as a single diastereomer was obtained when the bulky tris(*tert*-butyl)phosphine ligand¹¹ in Pd⁰ catalyst **5** was used (entry 5). Interestingly, the use of two Pd^{II} catalysts, Herrmann catalyst **4**¹⁹ and the Pd^{II}IPrCl₂-dimer **6**,²⁰ also gave efficient methylenation (entries 6 and 7), affording **3** in 98% and 88% yield respectively.

Since in all of the reactions in Table 1 extensive formation of Pd-black was observed, omission of base and/or water, as well as the use of alternative halomethylboronate reagents, was studied using either the Pd^{II}-Herrmann catalyst **4** or Pd⁰(P(*t*Bu)₃)₂ **5** (Table 2; see also Tables SI1–SI4). Compared to the combined use of K₂CO₃, H₂O, and either catalyst **4** (entry 1) or **5** (entry 2), when either H₂O (entry 3 and 4) or base (entries 5 and 6) was omitted a much lower yield of the cyclopropane **3** was obtained. Interestingly, omission of both H₂O and K₂CO₃ led to the formation of only 1% of **3** when catalyst **4** was used (entry 7); however, the use of catalyst **5** gave cyclopropane **3** in a good 87% yield (entry 8). In both cases only traces of Pd-black were formed using these conditions. Also the preactivation of ICH₂BF₃K (**2**) in the presence of K₂CO₃ and H₂O for 30 min at 90 °C, before substrate **1** and either catalyst were added to the reaction mixture, were tested. When catalyst **4** was used product **3** was obtained in a substantial lower 37% yield (entry 9), while the use of catalyst **5** gave a slightly lower yield of **3** (entry 10). Apparently, when catalyst **4** or **5** is used there is an optimum between the rate of *in situ* activation of the trifluoroborate reagent **2** and the (hydroxide/fluoride mediated) decomposition of catalyst **4** or **5**. The use of another nucleofuge,

Table 2. Optimization of Norbornene Methylenation Using the Herrmann (**4**) and Pd⁰(P(*t*Bu)₃)₂ (**5**) Catalysts^a

no.	cat.	XCH ₂ 'B'	base	DMF/H ₂ O	yield ^b	rem. 1 ^b
1	4	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	8/1	98%	0%
2	5	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	8/1	85%	15%
3	4	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	DMF only	25%	56%
4	5	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	DMF only	47%	42%
5	4	ICH ₂ BF ₃ K (2)	none	8/1	24%	54%
6	5	ICH ₂ BF ₃ K (2)	none	8/1	35%	52%
7	4	ICH ₂ BF ₃ K (2)	none	DMF only	1%	73%
8	5	ICH ₂ BF ₃ K (2)	none	DMF only	87%	7%
9 ^c	4	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	8/1	38%	37%
10 ^c	5	ICH ₂ BF ₃ K (2)	K ₂ CO ₃	8/1	66%	17%
11	5	BrCH ₂ BF ₃ K	none	DMF only	7%	73%
12	5	ICH ₂ B(OR) ₂ ^d	CsF ^e	DMF only	70%	16%
13	5	ICH ₂ B(OR) ₂ ^d	K ₂ CO ₃ + CsF ^e	8/1	92%	8%

^aConditions: scale 0.117 mmol of **1**, 0.06 M concentration of **1**.
^bStandardized GC-yield and recovery of **1**. ^cBefore addition of **1** and the catalyst the B-reagent was preactivated at 90 °C for 30 min. ^d2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used. ^e3.0 equiv of CsF were used.

bromide, gave some cyclopropane **3** when catalyst **5**, but no base and water, was used (entry 11). Finally, when 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used as the B-reagent, in the presence of appropriate reagents for activation, being either CsF (entry 12) or both K₂CO₃/H₂O and CsF (entry 13), product **3** was obtained in respectively 70% and 92% yield (see also Table SI4).

After further optimization of the reaction conditions (see Tables SI5, SI9, and SI10) the methylenation of several other electron-rich olefins was found to be feasible (Table 3; see also Tables SI6–SI8). Using the Herrmann catalyst **4**, *cis* bicyclo[6.1.0]nonane, **8a**, was obtained in a reasonable yield from the aliphatic cyclic olefin cyclooctene (**7a**, entry 1). Concomitant formation of the exocyclic olefin methylenecyclooctane, **9a**, was observed as well; presumably the latter product is formed via a β-H elimination²¹ from one of the Pd^{II}-intermediates (*vide infra*). Furthermore, Pd-black was formed. When either the terminal acyclic olefin 4-phenyl-1-butene, **7b**, or styrene, **7c**, was used as the substrate, a mixture of β-H elimination products (**9b** or **9c**) and cyclopropane (**8b** or **8c**) were obtained in a lower yield (entries 2 and 3).

The formation of the cyclopropane products from the methylenation of several classes of olefins indicates that a wide variety of olefins can be used as substrates using our method, although further optimization of the catalyst and/or reaction conditions is required to obtain higher turnover numbers (less/slower formation of Pd-black) and better selectivities for the cyclopropanation products vs β-H elimination products. Our experimental results do not yet give straightforward guidelines for the improvement of the catalyst and/or conditions; this is illustrated by the methylenation of **1** using either Pd⁰- or Pd^{II}-

Table 3. Methylenation of Several Electron-Rich Olefins Using Herrmann Catalyst 4^a

$\text{R} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{R} \text{ (7)} + \text{I} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{BF}_3^{\ominus} \text{K}^{\oplus} \xrightarrow[\text{DMA/MeOH 8/1, 90 }^{\circ}\text{C, 24 h}]{\text{4 (5 mol \% Pd), 10 (7.5\%), 2 and K}_2\text{CO}_3 \text{ (both 1.1 equiv)}} \text{R} \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{R} \text{ (8)} + \beta\text{-H elim. product(s) (9)} \quad \boxed{\text{P(o-tolyl)}_3 \text{ 10}}$				
no.	substrate	cyclopropane ^b	β -H elimination product(s) ^b	remaining 7 ^b
1		31 %	7 %	58 %
2		16 %	21 %	43 %
3		22 %	22 % ^c	39 %

^aConditions: for scale see Tables SI6–SI8, 0.06 M concentration of 7. ^bStandardized GC yield and recovery of 7. ^cA mixture of several olefins was obtained; see Table SI8 for details.

catalysts and, when specific catalysts are employed, the necessity for the use of H₂O and base and/or CsF for efficient cyclopropanation.

Methylenations using Pd-catalysts can proceed via a variety of mechanisms, which may be enumerated and classified by the heuristic diagram in Figure 1. These mechanisms can be

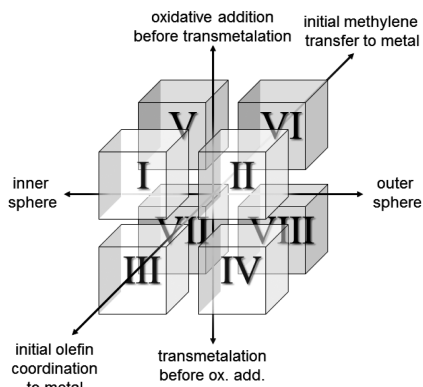
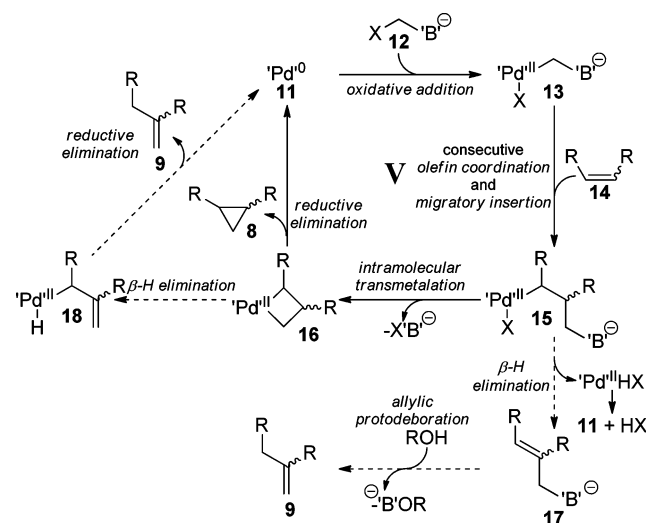


Figure 1. Classification of mechanisms for cyclopropanation.

classified according to (1) whether there is an initial olefin coordination or an initial methylene transfer, (2) whether transmetalation (Pd^{II}-catalyst) proceeds before oxidative addition (Pd⁰-catalyst) or *vice versa*, and (3) whether the reaction proceeds via an inner- or outer-sphere mechanism. For the developed methylenation method several mechanisms (see Scheme SI1) are consistent with the results presented here, although mechanism V (Scheme 2) presently appears most likely. This “diverted Heck” mechanism would feature initial oxidative addition¹⁴ of 12, coordination of olefin 14, migratory insertion,¹⁵ intramolecular transmetalation²² to give palladocyclobutane 16,²³ and finally a reductive elimination to give cyclopropane 8. It is important to note that several pathways exist to access Pd⁰-mechanisms from Pd^{II}-catalysts.^{24,25} The multiplicity of possible mechanisms makes their analysis complicated; it is even feasible that several mechanisms would be operative simultaneously.

Side reactions from two intermediates present in the possible methylenation mechanism V could be the cause for the formation of the β -H elimination products 9 (Scheme 2). From intermediate 15 a β -H elimination would give 17, and

Scheme 2. Hypothetical Mechanism V and the Formation of β -H Elimination Products 9

consecutive allylic protodeboration²⁶ of 17 would then give the exocyclic double bond. Alternatively, consecutive β -H elimination and reductive elimination could give 9 from palladocyclobutane 16.

In conclusion, taking advantage of versatile Pd catalysis, we have developed a new method for the methylenation of electron-rich olefins. In our method halomethylboronate reagents replace diazomethane and zinc carbenoids. Norbornene is the preferred substrate for this reaction, although other olefins also exhibit the desired reactivity. Mechanistically, several viable pathways are available. The complicated dependence of cyclopropanation yield on various experimental parameters, and the diversity of possible mechanisms, suggests that a mechanistic study may present the best option for gaining a broader substrate scope and higher turnover numbers.

■ ASSOCIATED CONTENT

Supporting Information

Mechanistic proposals, further screening tables, experimental details, and GC, GC-MS, and NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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