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Palladium-Catalyzed Selective Fluorination of o-Carboranes

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Supporting Information Placeholder

ABSTRACT: Palladium(II)-catalyzed direct selective fluorination reaction of carboranes using F^+ reagent has been developed, leading to a series of polyfluorocarboranes in high isolated yields. The mechanism involving electrophilic B–H activation, oxidation of Pd(II) by F^+ species and reductive elimination is proposed.

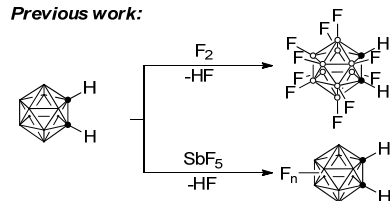
Functionalization of carboranes has received a growing interest owing to their applications in medicine as boron neutron capture therapy (BNCT) agents,¹ in supramolecular design as building blocks,² and in coordination/organometallic chemistry as ligands.³ Since the substitution of hydrogen for fluorine can significantly change both physical and chemical properties of compounds,⁴ it is anticipated that polyfluorinated carboranes would have great potential as key components of n-type organic semiconductors and donor-acceptor type of materials owing to their super electron-deficient nature,^{5a-d} of new BNCT agents due to enhanced biostability,⁴ and of weakly coordinating anions because of improved chemical inertness.^{5c} In general, there are two conventional synthetic methods leading to the cage boron substituted carboranes: electrophilic substitution at cage BH vertices by electrophiles⁶ and capitation reaction of nido- $C_2B_9H_{11}^{2-}$ with boron halides.⁷ Direct electrophilic halogenation is known to be an effective and convenient method for the preparation of cage boron chlorinated, brominated and iodinated carboranes.⁸ Selective mono-, di-, or polyhalogenation of carboranes can be achieved under appropriate conditions. In contrast, reaction of carborane with elemental fluorine is not selective, resulting in the formation of deca-B-fluorocarborane $C_2B_{10}H_2F_{10}$.⁹ Though nucleophilic substitution reaction of carboranyl diazonium,¹⁰ thallium¹¹ or iodonium¹² salts with F^- affords the corresponding mono-B-fluorocarboranes, the only reported selective fluorination of carboranes is to use SbF_5 as reagent. Such reactions must be performed in special perfluorinated hydrocarbon solvents under precisely controlled conditions in order to achieve the selectivity.¹³ Such reactions also involve the formation of HF, which largely limits the use of this method (Scheme 1).

Inspired by transition metal catalyzed direct fluorination of aryl C–H bonds,¹⁴ and the similarity in electrophilic substi-

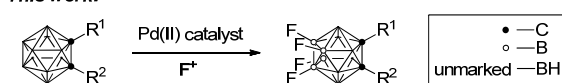
tution reaction between arenes and carboranes,^{5a,15} we initiated a research program to develop transition metal catalyzed direct fluorination of carboranes, and report herein a regioselective, efficient and safe method for the preparation of polyfluorocarboranes via Pd(II)-catalyzed B–H activation (Scheme 1).

Scheme 1. Fluorination of o-Carboranes

Previous work:

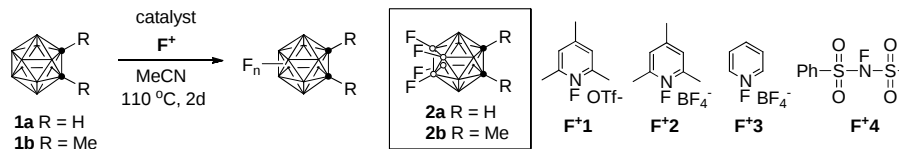


This work:



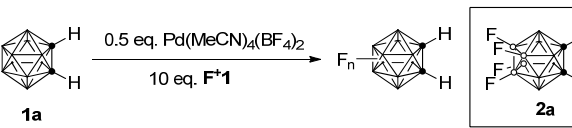
o-Carborane B–H activation by low-valent transition metals via oxidative addition has been known,^{16,17} which requires a directing group and has been a stoichiometric process.^{18,19} In view of the unique electronic structure of carboranes, we selected electrophilic transition metal species as catalysts and F^+ reagents as fluorination sources since the charge distribution of the cage²⁰ could make a selective fluorination feasible in the absence of a directing group. The screening results were summarized in Table 1.

Most of the Pd(II) complexes were catalytically active with $Pd(MeCN)_4(BF_4)_2$ giving 8,9,10,12-tetrafluorinated product **2a** in the best selectivity of 33% among mixtures of geometrical isomers of the tetrafluorinated species (Table 1, entries 4–8). In sharp contrast, nickel and platinum complexes such as $NiCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ were inactive (Table 1, entries 2 and 3). In the absence of a catalyst, no reaction was observed between **1a** and F^+ reagents (Table 1, entry 1). The yield and selectivity remained almost unchanged if the catalyst loading was increased from 0.5 to 1 equiv (0.5 equiv represents 12.5 mol% of catalyst loading per B–H conversion; Table 1, entry 9). The use of F^+2 led to a higher ratio of tetrafluorocarboranes as mixtures of geometrical isomers but the selectivity for **2a** had no obvious changes (Table 1, entry 10). F^+3 resulted in the formation of mixtures of geometrical isomers of pentafluorocarboranes as major products (Table 1, entry 11). On the

Table 1. Fluorination of *o*-Carboranes with F⁺ Reagents Catalyzed by Transition Metal Complexes^a


entry	1	catalyst	F ⁺	product (%) ^[b]				
				F ₁	F ₂	F ₃	F ₄ (2)	F ₅
1	1a or 1b	none	10 eq. F ⁺ 1				N.R.	
2	1a	0.5 eq. NiCl ₂ (PPh ₃) ₂	10 eq. F ⁺ 1				N.R.	
3	1a	0.5 eq. PtCl ₂ (PPh ₃) ₂	10 eq. F ⁺ 1				N.R.	
4	1a	0.5 eq. PdCl ₂ (PPh ₃) ₂	10 eq. F ⁺ 1				messy	
5	1a	0.5 eq. Pd(OAc) ₂	10 eq. F ⁺ 1	-	-	21	89(13)	-
6	1a	0.5 eq. Pd(TFA) ₂	10 eq. F ⁺ 1	12	60	27	1(1)	-
7	1a	0.5 eq. Pd(MeCN) ₄ (OTf) ₂	10 eq. F ⁺ 1	-	-	-	55(31)	45
8	1a	0.5 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 1	-	-	-	61(33)	39
9	1a	1 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 1	-	-	-	67(36)	33
10	1a	1 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 2	-	-	6	94(37)	-
11	1a	1 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 3	-	-	-	11(-)	89
12	1a	1 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 4	-	5	63	32(20)	-
13	1a	0.2 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 1	-	2	35	63(21)	-
14	1a	1 eq. Pd(MeCN) ₄ (BF ₄) ₂	5 eq. F ⁺ 1	-	27	50	23(6)	-
15	1b	0.5 eq. Pd(MeCN) ₄ (BF ₄) ₂	10 eq. F ⁺ 1	-	-	-	87(87)	10
16	1b	0.5 eq. Pd(MeCN) ₄ (BF ₄) ₂	5 eq. F ⁺ 1	-	-	-	86(86)	11

^aReactions were conducted at 0.02 mmol scale in 0.5 mL of CH₃CN at 110 °C for 2 d. ^bThe ratio and selectivity of 2 were determined by GC-MS. Noted that there were several geometrical isomers of tetrafluorinated species.

Table 2. Solvent and Additive Effects on Pd(II)-Catalyzed Fluorination of *o*-Carborane^a


entry	solvent	T (°C)	additive	product (%) ^b					
				F ₀	F ₁	F ₂	F ₃	F ₄ (2a)	F ₅
1	THF	110	-	48	46	-	-	-	-
2	toluene	110	-	87	13	-	-	-	-
3	PhCF ₃	110	-	100	-	-	-	-	-
4	MeCN	110	-	-	-	-	-	61(33)	39
5	MeCN	80	-	-	-	-	59	22(9)	19
6	MeCN	50	-	-	4	70	26	-	-
7	MeCN	110	2 eq. PPh ₃	-	-	-	26	73(19)	1
8	MeCN	110	2 eq. NEt ₃	66	34	-	-	-	-
9	MeCN	110	1 eq. BiPy	58	42	-	-	-	-

^aReactions were conducted at 0.02 mmol scale in 0.5 mL of solvents. ^bThe ratio and 2a selectivity were determined by GC-MS.

other hand, F⁺4 was the least reactive, giving a mixture of di-, tri- and tetrafluorinated carboranes. In view of efficiency, 2a

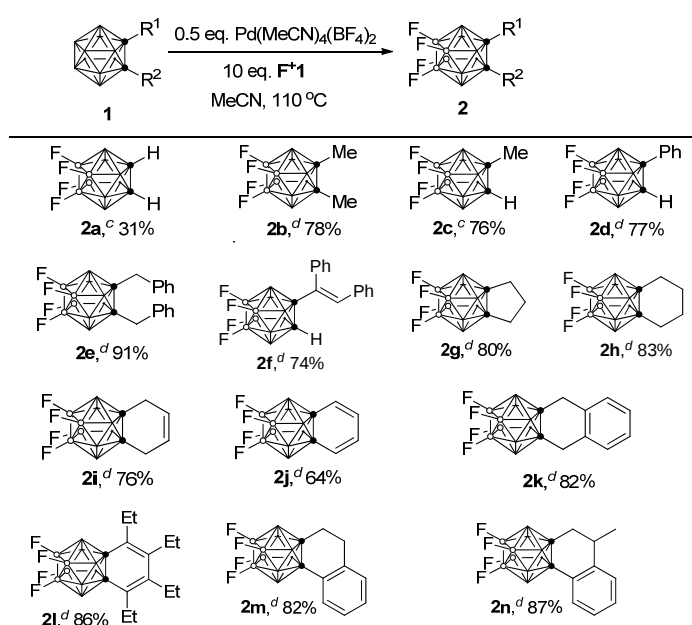
selectivity and easy separation of 2a, entry 8 (Table 1) was selected as the optimal reaction condition.

For 1,2-dimethyl-*o*-carborane **1b**, both the yields and selectivities were substantially increased. Compound **2b** was obtained as the only tetrafluorinated isomer. This result can be attributed to the increased charge gap among cage boron atoms imposed by the methyl groups on cage carbons (Table 1, entries 15–16).²¹

We then investigated the effects of solvents, temperatures and additives on this reaction. The results were compiled in Table 2. As Pd(MeCN)₄(BF₄)₂ catalyst was very poorly soluble in THF, toluene and trifluoromethylbenzene, the fluorination efficiency was very low (Table 2, entries 1–3). Temperatures below 110 °C resulted in the decreased amount of tetrafluorocarboranes (Table 2, entries 4–6). Addition of PPh₃ led to a big drop in both **2a** selectivity and pentafluorinated products, whereas NEt₃ and bipyridine (Bipy) significantly lowered the reactivity (Table 2, entries 7–9).

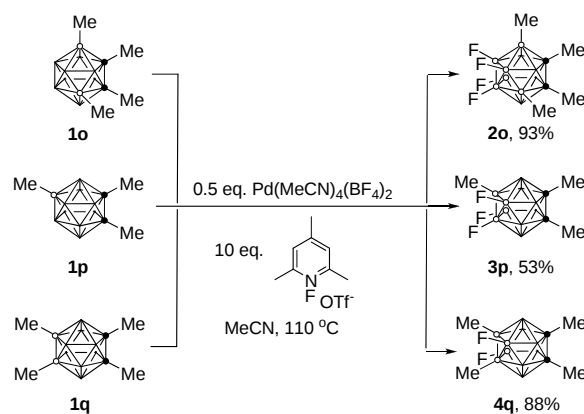
The reaction scope of this Pd(II)-catalyzed fluorination process was examined using various carboranes under optimal reaction conditions. The results were summarized in Table 3. Except that *o*-carborane **1a** offered the low isolated yield (31%) of the desired 8,9,10,12-tetrafluorocarborane **2a**, excellent regioselectivities were observed for mono- and di-*C*-substituted-*o*-carboranes, affording tetrafluorination products **2b–n** in very good isolated yields (64–91%). In addition, 1,2,4,7-tetramethyl-*o*-carborane **1o** gave 1,2,4,7-tetramethyl-8,9,10,12-tetrafluoro-*o*-carborane **2o** in 93% isolated yield. 1,2,12-Trimethyl-*o*-carborane **1p** and 1,2,9,12-tetramethyl-*o*-carborane **1q** produced the corresponding tri- and difluoro-*o*-carboranes [1,2,12-trimethyl-8,9,10-trifluoro-*o*-carborane (**3p**) and 1,2,9,12-tetramethyl-8,10-difluoro-*o*-carborane (**4q**)] in 53% and 88% isolated yields, respectively (Scheme 2). Phenyl and alkenyl groups were tolerated with this reaction condition. It was noteworthy that carboranes with Lewis-base functionalities, such as N, O or S containing

Table 3. Pd(II)-Catalyzed Regioselective Tetrafluorination of *o*-Carboranes^{a,b}



^aIsolated yields. ^bReactions were conducted at 0.2 mmol scale in 5 mL of CH₃CN at 110 °C. ^cHeated for 4 d. ^dHeated for 2 d.

Scheme 2. Fluorination of *B*-Methyl-*o*-carboranes



substituents, were not compatible with this reaction, producing mixtures of polyfluorocarboranes. On the other hand, under similar reaction conditions, 13- and 14-vertex carboranes²² gave the cage degradation products, finally leading to BF₃ as evidenced by ¹¹B NMR spectra.

Compounds **2–4** were fully characterized by ¹H, ¹³C, ¹¹B and ¹⁹F NMR spectroscopic data as well as high-resolution mass spectrometry. The molecular structures of **2b**, **g**, **k**, **l**, **m**, **3p** and **4q** were further confirmed by single-crystal X-ray analyses (see Figures S1–S7 in SI).

A palladium(II)-catalyzed fluorination process is proposed as the plausible mechanism. The electrophilic palladation of cage B–H is favored at the most nucleophilic site of *o*-carborane.²⁰ The strong oxidant F⁺ reagent can oxidatively add to the Pd(II) species to give a Pd(IV) complex,^{14,23} which undergoes reductive elimination to generate the B–F bond and reproduce the Pd(II). It is noted that the reductive elimination from a high-valent palladium fluoride species would be facilitated by a noncoordinating counterion BF₄[–] and weakly donating ligand CH₃CN.

In summary, a regioselective, efficient and safe palladium(II)-catalyzed direct fluorination of carboranes through B–H activation was developed, in which F⁺ species functioned as a fluorinating reagent as well as oxidant. This serves as a new methodology for the generation of a series of polyfluorocarboranes, which does not require special solvents and reaction vessels. This work also sets an example of catalytic electrophilic substitution of cage B–H bonds.

ASSOCIATED CONTENT

Supporting Information

Experimental details, complete characterization data, and X-ray crystallographic 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 interests.

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