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Regiodivergent metal-catalyzed B(4)- and C(1)-selenylation of *o*-carboranes†

Kyungsup Lee, ‡[a] Jordan L. Harper,‡[b] Tae Hyeon Kim,[a] Hee Chan Noh,[a] Dongwook Kim, [cd] Paul Ha-Yeon Cheong*[b] and Phil Ho Lee *[a]

Regiodivergent transition metal-catalyzed B(4)- and C(1)-selenylation reactions of *o*-carboranes have been demonstrated. Namely, Ru(II)-catalysis selectively generated B(4)-selenylated *o*-carboranes from the reaction of *o*-carborane acids with arylselenyl bromides with the release of carbon dioxide. In contrast, Pd(II) catalysis provided exclusively C(1)-selenylated *o*-carboranes from the decarboxylative reaction of *o*-carborane acids with diaryl diselenides. In contrast to previous milestones in this area, these reactions demonstrate broad substrate scope with excellent yields. Combination of these methods leads to the formation of B(4)–C(1)-diselenylated *o*-carboranes. DFT studies revealed the mechanism of the Ru-process, with initial selenylation of the carborane cluster discovered to be essential for an energetically reasonable decarboxylation. This results in selenylation on the B(4) position prior to the decarboxylation event at C(1). This contrasted with the Pd-process in which the ready decarboxylation at C(1) leads to selenylation at C(1).

Introduction

Carboranes, icosahedral boron-carbon molecular clusters,[1] have recently found a variety of applications ranging from versatile building blocks in the construction of boron neutron capture therapy agents[2] and ligands in organometallic/coordination chemistry[3] to the design of supramolecular materials.[4] Accordingly, the selective introduction of functional groups onto the boron and carbon vertexes of carboranes through B–H and C–H functionalization has received considerable attention.[5] Of late, a large number of transition metal-catalyzed functionalization reactions of *o*-carboranes have been reported, allowing for the introduction of a wide range of functional groups onto the boron and carbon vertexes.[6]

Organoselenium compounds occupy a significant place in organic synthesis due to their latent bioactivities.[7] In particular, aryl selenide scaffolds are frequently found in drug candidates displaying a wide range of biological activities[8] and have versatile applications in materials science.[9] As a result, the development of synthetic methods for the generation of aryl selenides, as well as methods for their introduction as functional groups, has attracted tremendous research interest.

In our continuing efforts to develop synthetic methodology for the regioselective B–H functionalization of *o*-carboranes,[10] we envisioned site selective syntheses of *o*-carboranes bearing organoselenyl groups through transition metal-catalyzed, regioselective B–Se and C–Se bond formations. To date, a limited number of methods for the synthesis of such compounds have been reported (Scheme 1): (a) C(1)-selenylation through the reaction of *o*-carboranes with *n*-BuLi followed by the addition of Se and HCl,[11] (b) C(1,2)-diselenylation through the treatment of dilithio-*o*-carboranes obtained from *o*-carboranes and *n*-BuLi with diphenyl diselenide,[12] (c) B(9,12)-diselenylation through the reaction of *o*-carboranes with $(SeCl)_2$ in the presence of $AlCl_3$ (3.0 equiv.),[13] and (d) B(4,5)-diselenylation through a traceless, bidentate directing group-guided Cu-mediated reaction of *o*-carboranes with diphenyl diselenide.[14] These methods have several disadvantages such as harsh reaction conditions including overly basic reaction conditions, excessive use of $AlCl_3$ (3.0 equiv.) and $Cu(OTf)_2$ (1.0 equiv.)/*t*-BuOLi (4.0 equiv.), as well as limited substrate scope, often restricted to only a single example. Although tremendous progress has been made in the areas of boron cluster and organoselenium chemistries, control of selectivity between B- and C-arylselenyl functionalization in *o*-carboranes remains a significant challenge. Furthermore, direct selenylation of an inert B–H bond is especially challenging due to the strong coordinating properties of organoselenium compounds.[15] Herein, we demonstrate regiodivergent B(4)- and C(1)-selenylation of *o*-carboranes through the use of Ru(II) and Pd(II) catalysts respectively (e and f). Moreover, these methods may also be combined to achieve selective B(4)- and C(1)-diselenyation (g).

[a]*Department of Chemistry, Kangwon National University, Chuncheon 24341, Republic of Korea. E-mail: phlee@kangwon.ac.kr*

[b]*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA. E-mail: cheongh@oregonstate.edu*

[c]*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea*

[d]*Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea*

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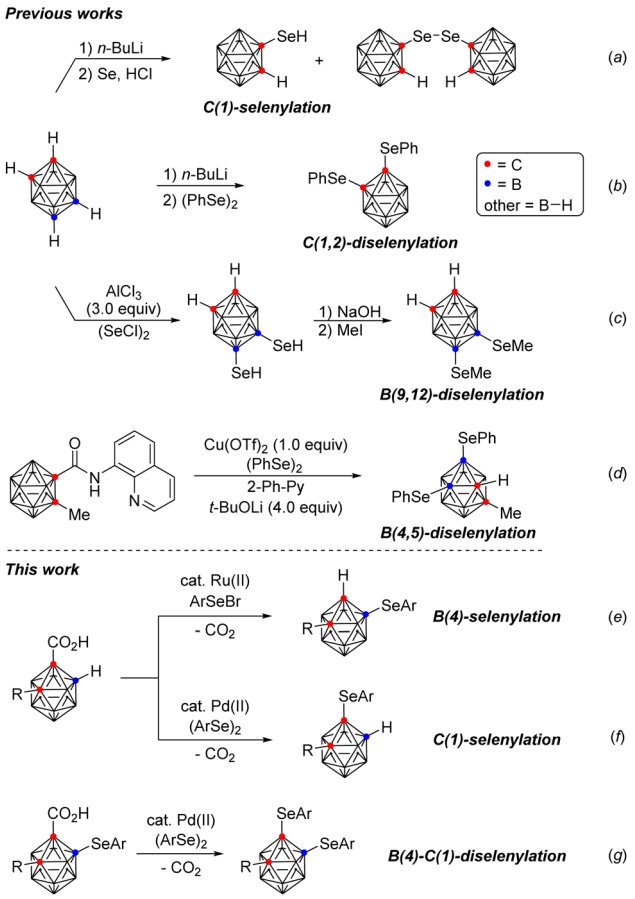
‡ These authors contributed equally to this work.



Scheme 1 Regioselective selenylation of *o*-carboranes.

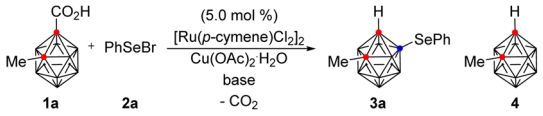
Results and discussion

First, we investigated the reaction of 2-methyl *o*-carborane acid (**1a**) with phenylselenyl bromide (**2a**) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv.), and K_2CO_3 (1.5 equiv.) at 70 °C for 12 h in a V-vial (Table 1). Dichloroethane (DCE) gave the desired B(4)-selenylated *o*-carborane (**3a**) in 13% yield (entry 1). Encouraged by this result, a variety of solvents were examined. Tetrahydrofuran (THF) and methanol disappointingly gave decarboxylated *o*-carborane **4** (entries 2 and 3). However, hexafluoroisopropanol (HFIP) and trifluoroethanol (TFE) selectively provided **3a** in 50% and 83% yields respectively (entries 4 and 5). Next, a number of bases, including K_2HPO_4, KOAc, and CsOAc, were examined in TFE (entries 5–8) and CsOAc was the choice of base, providing **3a** in 85% yield (entry 8). When the reaction temperature was reduced to 50 °C, the yield of **3a** dropped to 20% (entry 9), and when the temperature was raised to 90 °C, decarboxylation of **1a** occurred, reducing the yield of **3a** to 67% (entry 10). The best results were obtained using 1.5 equivalents of **2a** at 70 °C and **3a** was thus obtained in 91% isolated yield (entry 11).

To demonstrate the efficiency and scope of these decarboxylative B(4)-selenylation reactions, we applied this catalytic system to a variety of aryl selenyl bromides **2** in the reaction with **1** (Table 2). When **1a** was reacted with 2-methylphenyl and 4-methylphenyl organoselenyl bromides, the desired products **3b** and **3c** were obtained in 93% and 98% yields, respectively. The structure of **3c** was unambiguously confirmed by X-ray crystallography (see the ESI†). The location and identity of the substituents on the aryl ring of the selenyl bromide affect the reaction efficiency. For example, the use of 2-methoxyphenylselenyl bromide provided **3d** in 83% yield, while the use of 4-methoxylphenylselenyl bromide afforded **3e** in 51% yield. Additionally, when 3-bromophenylselenyl bromide gave the corresponding product **3j** in 16% yield, the reaction conditions were modified; gratifyingly, the use of hexafluoroisopropanol (HFIP) instead of TFE increased the yield of **3j** to 70%. Other aryl selenyl bromides bearing halo substituents on the phenyl ring were also well tolerated under the modified reaction conditions, giving the corresponding arylselenylated *o*-carboranes **3f–3k** in moderate to good yields, varying from 51% to 72%. On the other hand, *n*-pentylselenyl bromide was less reactive, and the reaction with **1a** in TFE produced **3l** in 35% yield. Nevertheless, to demonstrate the applicability of the present method to larger scale processes, 6.0 mmol of **1a** (1.21 g) was treated with **2a** (1.5 equiv.) under the optimum reaction conditions, giving **3a** in 97% yield.

Stimulated by these results, a wide range of alkyl- and aryl-substituted *o*-carboranes **1** were examined with *p*-tolylselenyl bromide (**2c**). When *n*-butyl-, benzyl-, and cyclohexyl-substituted *o*-carboranes were reacted with **2c** under the optimized reaction conditions, the corresponding selenylated products **3m**, **3n**, and **3o**, were obtained in excellent yields, ranging from 91% to 98%. In addition, *tert*-butyl-substituted *o*-carboranes gave the desired product (**3p**) in 74% yield, despite the possibility of steric interference. Phenyl-substituted *o*-

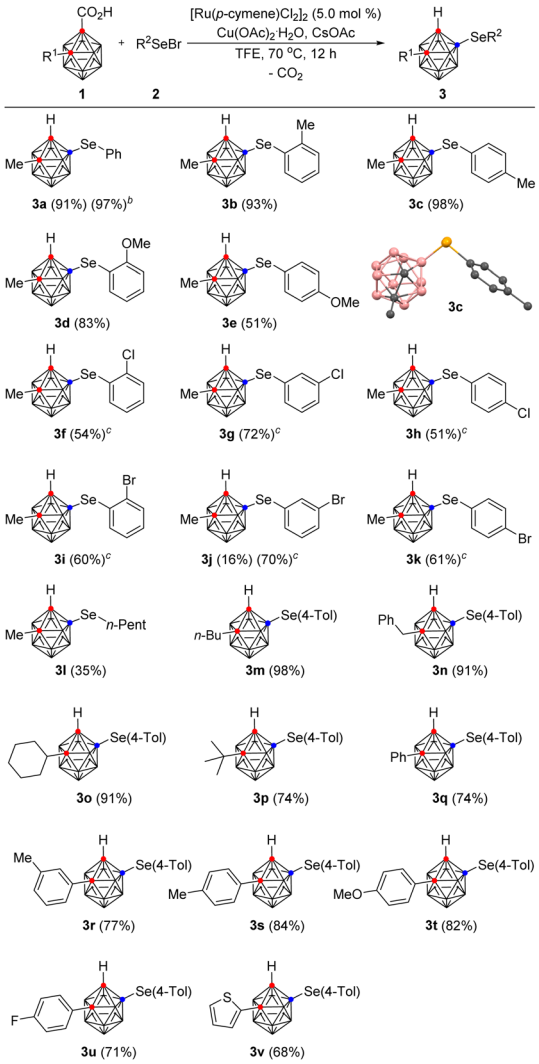
Table 1 Reaction optimization[a]



Entry	Base	Solvent	Temp. (°C)	Yield[b] (%)
1	K_2CO_3	DCE	70	13
2	K_2CO_3	THF	70	97[c]
3	K_2CO_3	MeOH	70	82[c]
4	K_2CO_3	HFIP	70	50
5	K_2CO_3	TFE	70	83
6	K_2HPO_4	TFE	70	58
7	KOAc	TFE	70	61
8	CsOAc	TFE	70	85
9	CsOAc	TFE	50	20
10	CsOAc	TFE	90	67
11[e]	CsOAc	TFE	70	93(91)[d]
12[f]	CsOAc	TFE	70	78

[a] Reactions were carried out with **1a** (0.1 mmol, 1.0 equiv.) and **2a** (2.0 equiv.) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv.), and base (1.5 equiv.) in solvent (1.0 mL) for 12 h in a V-vial. [b] NMR yield using CH_2Br_2 as an internal standard. [c] NMR yield of decarboxylated *o*-carborane (**4**) of **1a**. [d] Isolated yield. [e] **2a** (1.5 equiv.) was used. [f] **2a** (1.2 equiv.) was used.

Table 2 Scope of organoselenyl bromides and *o*-carboranes in B(4)-selenylation[a]



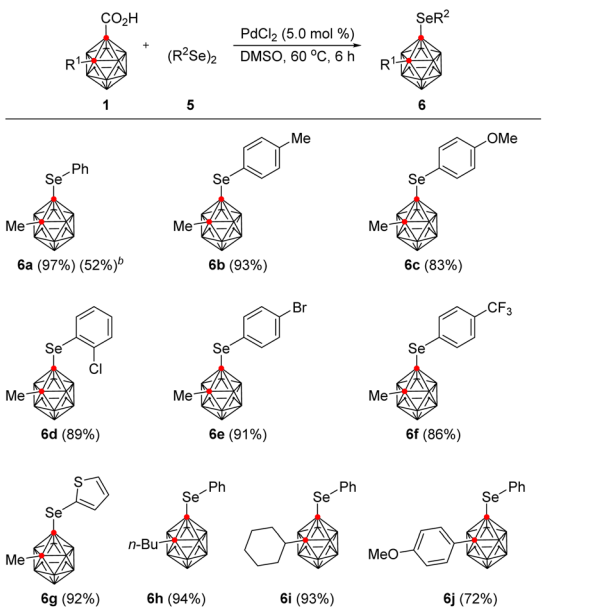
[a] Reaction conditions: **1** (0.10 mmol, 1.0 equiv.) reacted with **2** (1.5 equiv.) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%), $Cu(OAc)_2.H_2O$ (2.0 equiv.), and CsOAc (1.5 equiv.) in TFE (1.0 mL) at 70 °C for 12 h in a V-vial. [b] Reaction scale is 6.0 mmol of **1a**. [c] HFIP was used as a solvent.

carboranes were also smoothly converted to the selenylated product (**3q**) in 74% yield. Electronic modification of the substituents on the aryl ring of **1** did not largely influence the efficiency of the B(4)-selenylation. For example, *o*-carboranes bearing 3- and 4-methyl-, 4-methoxy-, and 4-fluoro-substituted phenyl groups are all amenable to the reaction conditions, providing the desired products (**3r–3u**) in good yields, varying from 71% to 84%. Thiophen-2-yl-substituted *o*-carboranes are also compatible, giving **3v** in 68% yield.

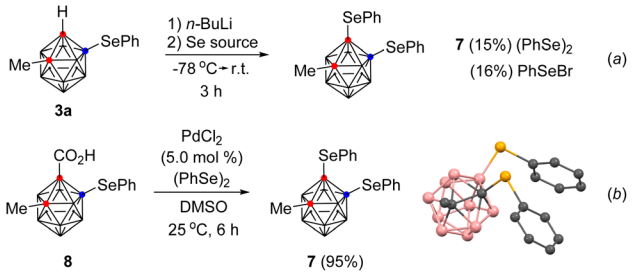
In addition to B(4)-selenylation, we also sought to install selenium substituents at other positions on the *o*-carborane. We thus envisioned that other transition metal catalysts would exhibit selectivity in contrast to that displayed by Ru. Accordingly, a variety of transition metal catalysts and selenylating agents were examined (see the ESI†). To our delight, the reaction of **1a** with diphenyl diselenide and $PdCl_2$ (5.0 mol%) in DMSO at 60 °C for 6 h provided C(1)-selenylated *o*-carborane **6a** regioselectively in 97% yield with the release of carbon dioxide. Phenylselenyl bromide gave an inferior result (52%) compared to diphenyl diselenide. To demonstrate the efficiency and scope of this method, we applied the Pd-catalytic system to a wide range of 2-substituted *o*-carborane acids and diaryl diselenides (Table 3). The presence of various substituents on the aryl rings of the diphenyl diselenides had little effect on either the reaction rate or the product yield. Electron-donating groups such as methyl and methoxy, as well as electron-withdrawing groups such as chloride, bromide, and trifluoromethyl all afforded the corresponding C(1)-selenylated *o*-carboranes in high yields, ranging from 83% to 93%. Di(thiophen-2-yl) diselenide also smoothly underwent C(1)-selenylation to produce **6g** in 92% yield. *o*-Carborane acids bearing *n*-butyl, cyclohexyl, and 4-methoxyphenyl groups on the C(2)-position are also amenable to C(1)-selenylation, affording the desired products (**6h–6j**) in good to excellent yields, varying from 72% to 94%.

The versatility of the current method was demonstrated in the synthesis of B(4)–C(1)-diselenyl *o*-carborane **7**. When an *o*-carboranyl anion was generated *in situ* from **3a** and *n*-butyl lithium and then treated with diphenyl diselenide or phenylselenyl bromide, the B(4)–C(1)-diselenyl *o*-carborane was obtained in low yield (Scheme 2, (a)). In contrast, the Pd-catalyzed

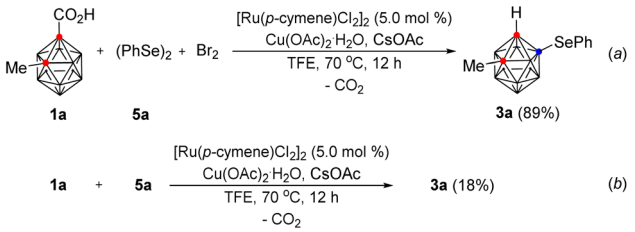
Table 3 Scope of *o*-carboranes and diaryl diselenides in C(1)-selenylation[a]



[a] Reaction conditions: **1** (0.10 mmol, 1.0 equiv.) reacted with **5** (1.2 equiv.) in the presence of $PdCl_2$ (5.0 mol%) in DMSO (0.5 mL, 0.20 M) at 60 °C for 6 h in a test tube. [b] PhSeBr (2.0 equiv.) was used instead of diphenyl diselenide.



Scheme 2 Comparison to efficiency of B(4)–C(1)-diselenylation.



Scheme 3 B(4)-Selenylation reaction using diphenyl diselenide and bromine.

decarboxylative C(1)-selenylation method provided the desired product (**7**) in 95% yield from B(4)-phenylselenyl *o*-carborane acid (**8**) (b). These results indicate that the Pd-catalyzed decarboxylative C(1)-selenylation is higher yielding than the previous approach under mild reaction conditions. A plausible reaction mechanism for Pd-catalyzed decarboxylative C(1)-selenylation is described in the ESI.†

Because **1a** was smoothly reacted with phenylselenyl bromide in the presence of Ru(II) to give **3a**, we attempted to perform the same selenylation reaction with phenylselenyl bromide generated *in situ* from diphenyl diselenide and bromine in one-pot. This reaction gave **3a** in 89% yield (Scheme 3, (a)). However, the reaction of **1a** with diphenyl diselenide under the optimum reaction conditions and in the absence of bromine gave **3a** in 18% yield (b).

To gain further insight into the more unusual Ru(II)-catalyzed process, we turned to DFT. All structures were optimized at the PBE[16]/6-31G*[17] level of theory with the LANL2DZ[18] effective core potential for Ru, Cs, Br, and Se, in the gas phase, with the D3BJ[19] empirical dispersion model (Fig. 1). Solvation single point energy refinements were performed with the SMD[20] implicit solvation model for 2,2,2-trifluoroethanol (TFE) at the PBE-D3BJ/def2-QZVP[21] level of theory. CsOAc was also assumed to convert 2-methyl *o*-carborane acid **1a** into the analogous cesium salt. Furthermore, since it has previously been demonstrated that monometallic systems based on Ru(II),[22] Rh(I),[23] and Pd(II)[24] effectively catalyze decarboxylations in the absence of Cu or Ag salts, we assumed that $Cu(OAc)_2$ acts solely as a halogen abstractor to generate the active Ru(II) catalyst.

Extensive exploration of the initial coordination complexes revealed that the Ru(II) catalyst readily undergoes ligand exchange, losing the *p*-cymene ligand in favor of coordination with the cesium carboxylate salt of *o*-carborane **1a**, phenylselenyl bromide **2a**, and 2 equivalents of acetate to give complex **I**.

An agostic interaction between the B(4)–H bond of the *o*-carborane and Ru ostensibly facilitates deprotonation by a carboxylate (B–H functionalization **TS II**), leading to the Ru–carborane complex **III**. Deprotonation at B(4) is preferred over deprotonation at B(3) – the position adjacent to both the carboxyl and methyl group – by 1.7 kcal mol^{-1}.

The nascent nucleophilic B–Ru bond then attacks the backside of the phenylselenyl bromide (**TS IV**), displacing bromide to the Ru catalyst, and leading to the irreversible formation of selenylated carborane complex **V**.

The decarboxylation of this complex (**TS VI**), which is the rate determining step, has an energy barrier of 30.6 kcal mol^{-1}, and leads to the formation of the decarboxylated selenylated carborane–Ru complex **VII**. To our considerable surprise, we discovered that the direct protonolysis to form the product–catalyst complex **XI** is energetically disfavored compared to a stepwise process involving the formation (**TS VIII**) and reductive elimination (**TS X**) of Ru(IV) hydride carborane complex **IX** (**TS VIII′** $\Delta G^{\ddagger} = 14.3$ kcal mol^{-1} *vs.* **TS X** $\Delta G^{\ddagger} = 6.6$ kcal mol^{-1}, see the ESI†).

We also investigated the possibility of decarboxylation occurring prior to *o*-carborane deprotonation. Extensive exploration of the ligand sphere of **TS VI** reveals that three interactions are key to achieving a reasonable barrier (see the ESI†): (i) B–H agostic interaction; (ii) Ru···Se coordination; and (iii) a Ru–Br bond. The barrier to decarboxylation of **I** is 53.9 kcal mol^{-1}. We hypothesize that this enormous barrier hinges on the fact that the *o*-carborane has not yet been selenylated. Following selenylation of the cluster, the selenium ostensibly functions as a directing group. Thus, the selenium brings the Ru sufficiently close to the cluster that a B–H agostic interaction can form, and such that the Ru is more proximal to the C–C bond that must be broken in the decarboxylation TS. Indeed, in the decarboxylation TS of **I**, there is no agostic interaction and Ru is more distal to the decarboxylation event.

The B(4) regioselectivity over B(3) occurs naturally because of steric interactions with the carborane C(2)-substituent. The regioselectivity of selenylation for B(4) over C(1) in the Ru-catalyzed process is entirely governed by the need for Ru–selenium coordination for a reasonable decarboxylation barrier. In the absence of initial selenylation, and thus the absence of the directing Se interaction, the decarboxylation barrier is extraordinarily high ($\Delta G^{\ddagger} > 53.9$ kcal mol^{-1}, see the ESI† for examples). This necessitates the selenylation of B(4) prior to the C(1)-decarboxylation event, which would naturally preclude selenylation on C(1). This is distinctly different from the Pd-process where the decarboxylation is noticeably facile, making the C(1) selenylation process preferable.

Overall, the turnover barrier is 30.6 kcal mol^{-1} (**TS VI**) and the exothermicity is −15.6 kcal mol^{-1} (**XI**). Catalyst transfer from the product to another equivalent of the starting material (**XI** to **I**) is another −15.6 kcal mol^{-1}, indicating that there is no product inhibition.

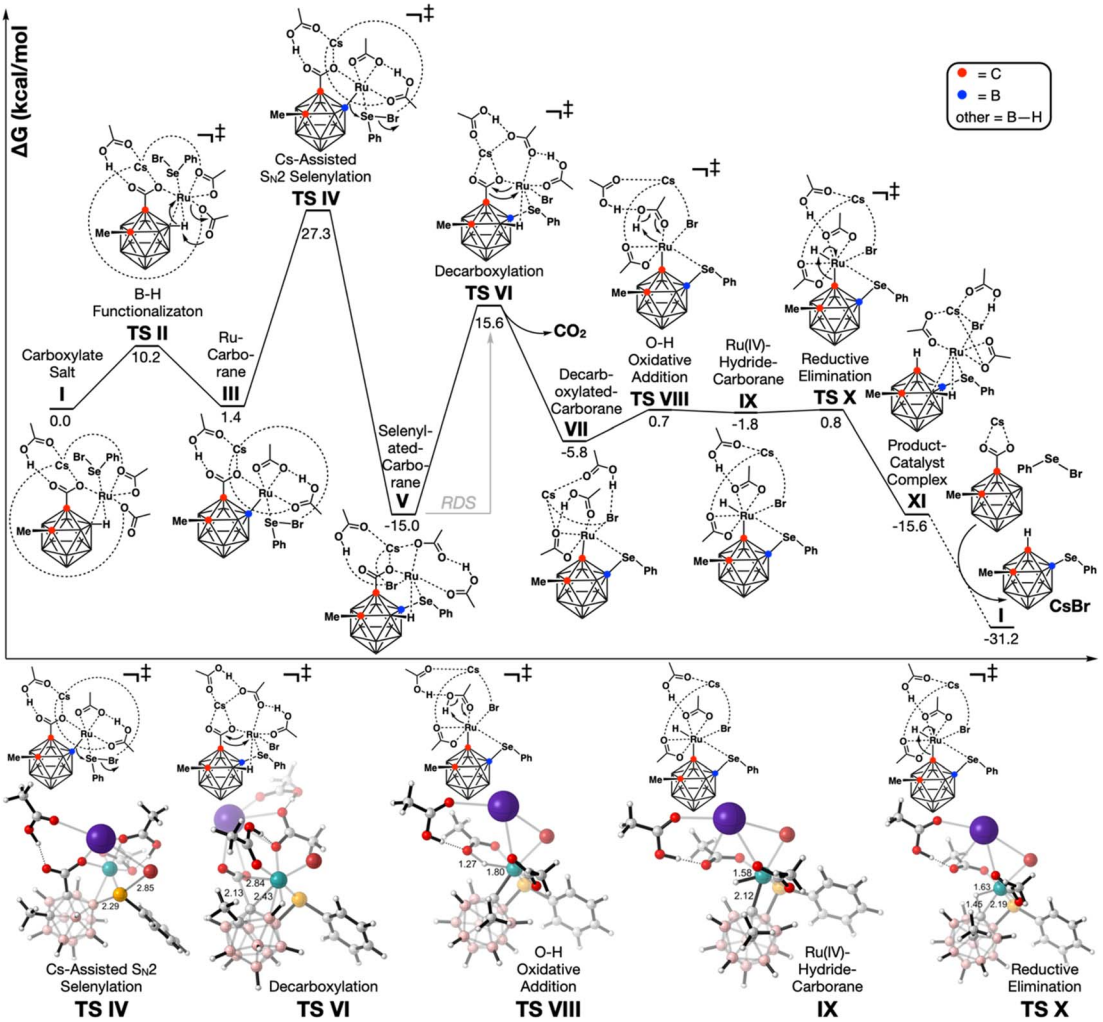


Fig. 1 Computed reaction coordinate diagram for the Ru(II)-catalyzed decarboxylative B(4)-selenylation of *o*-carboranes. Several ligand rearrangement steps have been omitted; non-covalent interactions have been drawn as accurately as possible, while attempting to maintain clarity.

Conclusions

In summary, we have developed regiodivergent metal-catalyzed B(4)- and C(1)-selenylation reactions applicable to a wide range of *o*-carboranes. Ru(II)-catalysis selectively generated B(4)-selenylated *o*-carboranes from *o*-carborane acids and arylselenyl bromides, with the release of carbon dioxide. In contrast, Pd(II) catalysis exclusively formed C(1)-selenylated *o*-carboranes from the decarboxylative reaction of *o*-carborane acids with diaryl diselenides. The regioselectivity is controlled by the transition metal catalyst. Unlike previous milestones in this area, both transformations show broad substrate scope and high yield. These selenylation reactions are thus a highly efficient way to selectively introduce an organoselenium functionality onto the B(4)- and C(1)-positions of *o*-carboranes.

Data availability

All of the related experimental and computational data are provided in the ESI.† Crystallographic data for compound **3c** and **7** have been deposited in the Cambridge Crystallographic Data Centre under accession number CCDC 1950362 and CCDC 2055987.

Author contributions

K. L., T. H. K., and H. C. N. performed the experimental work, which was directed by P. H. L. J. L. H. conducted the computational studies, which were directed by P. H.-Y. C. D. K. performed the X-ray crystal structure analysis. The manuscript was written by P. H. L. and P. H.-Y. C. with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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