Mechanistic Features of Boron−Iodine Bond Activation of B−Iodocarboranes

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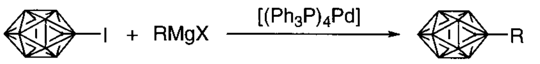
Oxidative addition of the B−I bond of 9-iodo-*m*-carborane to $[(Ph_3P)_nPd]$ ($n = 3, 4$) is reversible, the equilibrium being shifted to the Pd(0) and the iodocarborane. In the presence of $[(Ph_3P)_4Pd]$ and $[Bu_4N]Br$ in THF, 9-iodo-*m*-carborane undergoes halide exchange to produce 9-bromo-*m*-carborane. Coordinatively unsaturated Pd(0) and hydrido Pd(II) species generated upon thermal decomposition of $[(Ph_3P)_2Pd(Ph)(O_2CH)]$ and $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ reduce 9-iodo-*m*-carborane to *m*-carborane with 100% selectivity. The thermal decomposition of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ in the presence of excess 9-iodo-*m*-carborane and PhI (1:1) results in the formation of *m*-carborane (3%) and $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ (97%), whose structure was confirmed by single-crystal X-ray diffraction. X-ray analysis of 9-iodo-*m*-carborane and *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate shows that in the iodonium salt the B−I bond is longer by ca. 0.03 Å than in the iodocarborane. In contrast, the C−I bond distances in carboran-9-yl(phenyl)iodonium tetrafluoroborate (2.111(2) Å) and in iodobenzene (2.098(4) Å) are only marginally different. The elongation of the B−I bond, not the C−I bond, likely contributes to (i) the enhanced reactivity of B−carboranyl(phenyl)-iodonium cations toward nucleophiles and (ii) the remarkably high selectivity of these S_N reactions that occur exclusively at the boron atom. A new crystallographic form of 9,10-diiodo-*m*-carborane is reported.

Introduction

Functional derivatives of icosahedral *closo*-carboranes $C_2B_{10}H_{12}$ have received much attention due to their use in synthesis and potential applications in medicine.[1] While in most instances more easily accessible C-functionalized carboranes are reported, considerable progress has also been made in the chemistry of B-substituted derivatives of *o*-, *m*-, and *p*-carboranes.[2] Readily available via direct electrophilic iodination, B−carboranyl iodides have become key starting materials for the preparation of various carborane derivatives containing a boron-element bond. To solve the problem of the notoriously poor reactivity of the B−I bond of iodocarboranes toward nucleophiles,[2,3] two distinct strategies for B−I activation have been developed. One of the two employs the Pd-catalyzed cross-coupling reactions[4] (e.g., the Kumada-type coupling; eq 1) similar to the catalytic methods widely employed in the chemistry of haloarenes.[5]



(1)

Alternatively, the B−I bond is activated by converting a B−carboranyl iodide to the corresponding carboranyl-

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[†] Contribution No. 8128.

(1) For selected recent reviews, see: (a) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, *99*, 3421. (b) Lesnikowski, Z. J.; Shi, J.; Schinazi, R. F. *J. Organomet. Chem.* **1999**, *581*, 156. (c) Hawthorne, M. F. *Mol. Med. Today* **1998**, *4*, 174. (d) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515. (e) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267. (f) Godovikov, N. N.; Balema, V. P.; Rys, E. G. *Usp. Khim.* **1997**, *66*, 1125. (g) Hawthorne, M. F.; Yang, X.; Zheng, Z. *Pure Appl. Chem.* **1994**, *66*, 245. (h) Vinogradova, S. V.; Valetskii, P. M.; Kabachii, Yu. A. *Usp. Khim.* **1995**, *64*, 390. (i) Jones, M., Jr. *Adv. Carbene Chem.* **1994**, *1*, 161. (j) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950. (k) Sivaev, I. B.; Solntsev, K. A.; Kuznetsov, N. T. *Koord. Khim.* **1993**, *19*, 194. (l) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.

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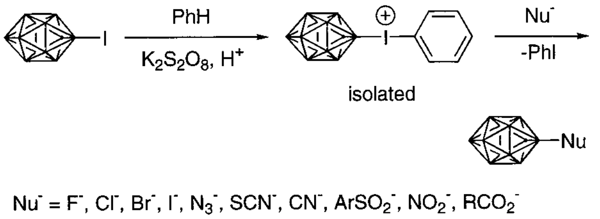
(phenyl)iodonium salt, which undergoes highly selective nucleophilic substitution at the boron atom under mild conditions (eq 2).[6]



(2)

Given the importance of B−iodocaboranes in synthesis, it is surprising that there have been no literature reports describing mechanistic studies of B−I activation with Pd(0) complexes (eq 1). Furthermore, structural aspects of B−I activation via iodonium ion intermediates (eq 2) have received insufficient attention. In this paper, we report unexpected results of our studies of reactivity of 9-iodo-*m*-carborane toward Pd(0) complexes and precise X-ray structures of 9-iodo-*m*-carborane and *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate. A new crystallographic form of 9,10-diiodo-*m*-carborane is also reported.

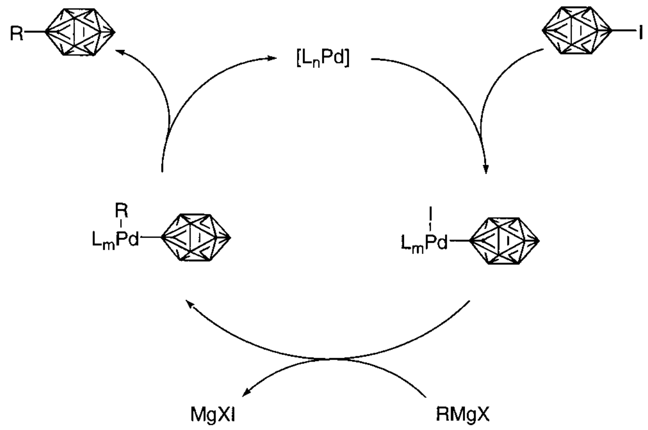
Results and Discussion

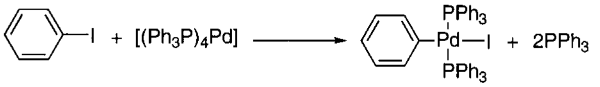
Derivatives of more stable *m*-carborane (1,7-dicarba-*closo*-dodecaborane) were selected for our studies to avoid the nucleophile-induced degradation reaction of the carborane framework.[7]

Reactions of 9-Iodo-*m*-carborane with $[(Ph_3P)_4M]$ (M = Pd, Pt). Oxidative addition of the B−I bond of iodocarboranes to a zerovalent Pd species is believed to be the first key step of the catalytic cycle that produces the desired carborane derivative (Scheme 1).[4f,n−p] Since B−iodocarboranes and iodobenzene are closely related in terms of stability and reactivity,[2] one would expect oxidative addition reactions of iodocarboranes to Pd(0) to exhibit mechanistic features similar to those involving iodobenzene. This, however, did not appear to be the case.

Iodobenzene reacts readily and irreversibly with $[(Ph_3P)_4Pd]$ to give $[(Ph_3P)_2Pd(Ph)I]$ in quantitative yield within seconds at room temperature (eq 3).[8] Yellow solutions of $[(Ph_3P)_4Pd]$ in benzene, toluene, or THF exhibit a broad ^{31}P NMR singlet at ca. 17 ppm due to ligand exchange processes.[9] When PhI is added to these solutions, the broad resonance at 17 ppm from $[(Ph_3P)_4Pd]$ disappears, while two new sharp singlet resonances of equal intensity emerge at 22.3 and −5.5 ppm from $[(Ph_3P)_2Pd(Ph)I]$ and Ph_3P, respectively (eq 3). As the reaction rapidly occurs, the originally yellow solution decolorizes due to the quantitative formation of the two colorless products.

Scheme 1





(3)

In sharp contrast, when 9-iodo-*m*-carborane (10 molar equiv) was added to $[(Ph_3P)_4Pd]$ in toluene-d_8 at 25 °C, the yellow solution did not decolorize, and no visible sign of any reaction was observed after the solution was kept at room temperature for 12 h. The ^{31}P NMR spectra of the sample before and after the addition of the iodocarborane were indistinguishable, containing only one broad ($\Delta\nu_{1/2} = 90$ Hz) resonance at ca. 16 ppm from $[(Ph_3P)_4Pd]$.[9] Heating the solution for 3 h at 70 °C, a temperature commonly used to run some Pd-catalyzed cross-coupling reactions of iodocarboranes, led to a marginally noticeable darkening. The signal from $[(Ph_3P)_4Pd]$ shifted upfield by ca. 1.5 ppm, while retaining its line shape, and a very weak sharp singlet resonance at 12.4 ppm appeared (ca. 2% of the intensity of the main signal) due to formation of $[(Ph_3P)_2PdI_2]$. Addition of PhI (2 molar equiv per Pd) resulted in instant consumption of the Pd(0), *as if there were no iodocarborane present*. The spectral pattern changed immediately, with the broad resonance disappearing and two singlets (1:1) appearing at 22.3 and −5.5 ppm from $[(Ph_3P)_2Pd(Ph)I]$ and Ph_3P, respectively. The weak resonance at 12.4 ppm from $[(Ph_3P)_2PdI_2]$ remained unchanged. GC−MS analysis of the mixture revealed the presence of the unreacted 9-iodo-*m*-carborane and trace amounts of *m*-carborane. As no deuterium incorporation from the solvent (toluene-d_8) into the *m*-carborane product took place (MS), the source of hydrogen for the B−I bond reduction was probably the Ph_3P ligands. In a similarly designed experiment, no reaction was observed between $[(Ph_3P)_4Pd]$ and 9-iodo-*m*-carborane in THF at room temperature. The unreacted Pd(0) complex was isolated in the form of $[(Ph_3P)_3Pd]$ in 73% yield (see the Experimental Section).

In the hope to obtain an isolable B−carboranyl platinum complex,[10] $[(Ph_3P)_4Pt]$ and a 7-fold excess of

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(5) See, for example: Tsuji, J. *Palladium Reagents and Catalysis: Innovations in Organic Synthesis*; Wiley: Chichester, 1995.

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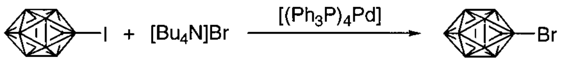
9-iodo-*m*-carborane were reacted in toluene-d_8. However, no sign of any reaction was observed (^{31}P NMR) at room temperature, nor after this mixture was kept at 100 °C for 2.5 h.

The lack of NMR-observable reactivity of 9-iodo-*m*-carborane toward $[(Ph_3P)_4M]$ (M = Pd, Pt) was surprising because the conditions used for these experiments were comparable to those commonly employed for the cross-coupling reactions of B−iodocarboranes, which do occur in the presence of Pd catalysts but not in their absence.[4]

Reactions of 9-Iodo-*m*-carborane with $[(Ph_3P)_4Pd]$ in the Presence of $[Bu_4N]X$ (X = I, Br). Convincing evidence for B−I activation with Pd(0) was obtained by reacting 9-iodo-*m*-carborane with $[(Ph_3P)_4Pd]$ in the presence of $[Bu_4N]Br$.

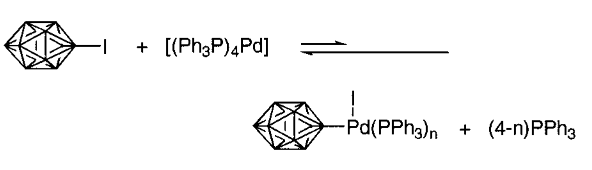
Halide anions are known[11,12] to promote oxidative addition reactions of Pd(0) complexes due to the formation of electron-rich anionic phosphine palladium halides. Keeping that in mind, we reacted 9-iodo-*m*-carborane, $[(Ph_3P)_4Pd]$, and $[Bu_4N]I$ in a 10:1:1 molar ratio in THF. After 3 days at ambient temperature and then 3 h at 60 °C no ^{31}P NMR spectral evidence for any reaction was observed, except for the formation of trace amounts of $[(Ph_3P)_2PdI_2]$ and *m*-carborane (GC−MS). Both these products were also formed in comparable quantities when the reaction was conducted in the absence of the tetrabutylammonium salt in THF or toluene (see above).

A similar ^{31}P NMR spectral pattern was observed when an excess of $[Bu_4N]Br$ was used instead of $[Bu_4N]I$. However, GC−MS analysis of the reaction solution revealed the formation of 9-bromo-*m*-carborane. After 12 h at 30 °C and then 2 h at 55 °C, the ratio of 9-bromo-*m*-carborane to 9-iodo-*m*-carborane was measured at 1:7 and 1:5, respectively. Therefore, $[(Ph_3P)_4Pd]$ does cleave the B−I bond of iodocarboranes and is capable of promoting the halogen exchange reaction under mild conditions (eq 4). This result suggests that B−iodocarboranes may undergo Pd-*catalyzed* nucleophilic displacement reactions with anionic nucleophiles (e.g., Br^-, Cl^-, F^-, N_3^-, CN^-, SCN^-, etc.).



(4)

Reactions of 9-Iodo-*m*-carborane with $[(Ph_3P)_2Pd(Ph)(O_2CH)]$ and $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$. From the above data it is clear that the reaction between $[(Ph_3P)_4Pd]$ and 9-iodo-*m*-carborane is reversible, the equilibrium (eq 5) being shifted to the left.

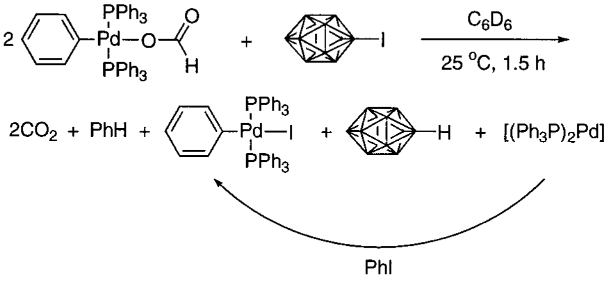


(5)

In an attempt to shift equilibrium 5 to the right, toward a carboranyl Pd(II) complex, and thus increase the probability of its isolation, we decided to react 9-iodo-*m*-carborane with low-ligated and more reactive $[(Ph_3P)_nPd]$ (n = 1 or 2). It has been established that the actual reactive triphenylphosphine Pd(0) species which oxidatively adds the C−I bond of iodoarenes is dicoordinate 14-e $[(Ph_3P)_2Pd]$, which is present in solutions of $[(Ph_3P)_4Pd]$ or $[(Ph_3P)_3Pd]$ in very low concentrations.[12,13]

We chose to generate $[(Ph_3P)_2Pd]$ and $[(Ph_3P)Pd]$ via the thermal decomposition of phenyl palladium formato complexes, $[(Ph_3P)_2Pd(Ph)(O_2CH)]$ and $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$, respectively.[14,15] Both reactions were carried out in standard 5 mm NMR tubes, and the products were analyzed by NMR spectroscopy and then by GC−MS (see the Experimental Section for details).

When $[(Ph_3P)_2Pd(Ph)(O_2CH)]$ was decomposed in the presence of a 3-fold excess of 9-iodo-*m*-carborane in benzene-d_6, B−I activation did rapidly occur under very mild conditions (1.5 h at 25 °C). However, instead of an observable/isolable σ-B−carboranyl Pd complex, this smooth and highly selective reaction resulted in the formation of *m*-carborane (GC−MS), along with $[(Ph_3P)_2Pd(Ph)(I)]$ and $[(Ph_3P)_2Pd]$ in a 1:1:1 ratio (eq 6). The former of the two complexes was reliably identified in situ by its ^{31}P, ^{13}C, and ^{1}H NMR spectral characteristics.[8,16−18] The highly unstable $[(Ph_3P)_2Pd]$ exhibited a broadened singlet resonance at 21.7 ppm (^{31}P NMR),[19] which rapidly disappeared upon addition of PhI to the sample, due to the formation of $[(Ph_3P)_2Pd(Ph)(I)]$. At that point, the ^{31}P NMR spectrum contained only one sharp signal at 22.3 ppm from $[(Ph_3P)_2Pd(Ph)(I)]$.[20]



(6)

The thermal decomposition of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ to generate "$[(Ph_3P)Pd]$" is known[14] to require a higher temperature (50−65 °C). When this formato Pd dimer was decomposed in the presence of 9-iodo-*m*-carborane (3.3 equiv per Pd) in benzene-d_6 (40 min at 55 °C), again no formation of an NMR observable

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(10) (a) It has been claimed[10b] that *m*-carboran-9-ylmercury chloride reacts with $[(Ph_3P)_3Pt]$ in benzene at 20 °C to produce stable $[(Ph_3P)_2Pt(C_2B_{10}H_{11})Cl]$, which has been characterized by elemental analysis (C, H, Cl, and P) and a melting point. Neither yield nor spectroscopic/structural data have been reported for the isolated material. (b) Zakharkin, L. I.; Pisareva, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 252.

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(14) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.

(15) (a) An alternative way to generate "$[(Ph_3P)Pd]$" is the reaction between $[(Ph_3P)_2PdCl_2]$ and alkali.[15b] As the latter may cause the degradation reaction of the carborane skeleton,[7] we did not use this method. (b) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.

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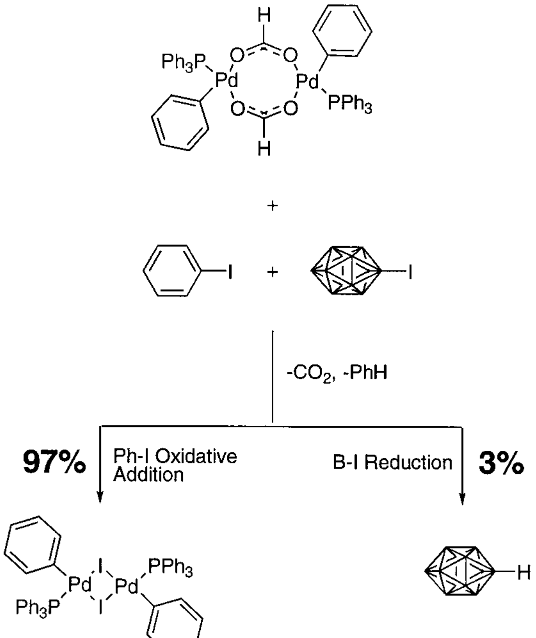
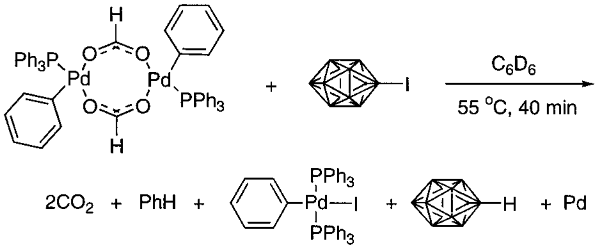
Scheme 2



carboranyl palladium complex took place, but $[(Ph_3P)_2Pd(Ph)I]$, *m*-carborane, and Pd metal formed instead. The stoichiometry of this markedly selective reaction is shown in eq 7. Like in the previous experiment, the σ-phenyl complex $[(Ph_3P)_2Pd(Ph)I]$ that formed in >98% selectivity[21] was unambiguously identified by its ^1H, ^{13}C, and ^{31}P NMR parameters, whereas *m*-carborane was found by GC–MS analysis of the reaction mixture after the NMR runs.



(7)

To compare reactivities of 9-iodo-*m*-carborane and iodobenzene toward Pd(0), the formato dimer $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ was decomposed in a benzene-d_6 solution containing excess quantities of 9-iodo-*m*-carborane and iodobenzene in a 1:1 molar ratio. A highly selective reaction was observed, leading almost exclusively to $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ and small amounts (<3%) of *m*-carborane (Scheme 2).

No incorporation of deuterium in the *m*-carborane molecule was observed (MS) for reactions 6 and 7. Therefore, the intermediate formation of free carboranyl radicals via homolytic cleavage of the Pd–B bond can be ruled out. A mechanism proposed for reactions 6 and 7 likely involves the intermediate formation of B–carboranyl palladium hydrides, which are expected[22] to undergo facile and irreversible reductive elimination of carborane (e.g., Scheme 3). The B–carboranyl hydrido palladium complexes likely form due to I/H and/or σ-phenyl/σ-carboranyl exchange, similar to the previously studied Me/Ph exchange.[23] A mechanism involving oxidative addition of the B–I bond to a palladium(II) hydrido intermediate to produce a Pd(IV) carboranyl hydrido species is unlikely. Had this happened, $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ would have been produced as a result of the decomposition of the dinuclear formato complex. It is to be emphasized that $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ forms quantitatively when $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ is decomposed in the presence of iodobenzene.[14]

The experiments with the formato complexes demonstrate that the B–I bond of 9-iodo-*m*-carborane is easily cleaved by Pd(0) species bearing only one or two Ph_3P ligands. However, like the B–I activation with $[(Ph_3P)_4Pd]$ (eq 5), these reactions are also reversible, with the equilibria being shifted toward the Pd(0) species. It is particularly remarkable that even when $[(Ph_3P)_2Pd]$ and 9-iodo-*m*-carborane were both present in solution in high concentrations, no formation of a carboranyl Pd complex was detected by ^{31}P NMR.

Oxidative Addition to Pd(0): Iodobenzene vs 9-Iodo-*m*-carborane. As seen from the above, while often exhibiting very similar reactivity,[2] PhI and the iodocarborane behave differently when reacted with the zerovalent palladium species, $[(Ph_3P)_nPd]$. Two major distinctions merit emphasis.

1. While oxidative addition of iodoarenes to Ph_3P complexes of zerovalent Pd is virtually irreversible (eq 3), 9-iodo-*m*-carborane appears to react with $[(Ph_3P)_nPd]$ reversibly. The equilibrium between the product, a B–carboranyl Pd(II) complex, and the Pd(0) is shifted to the latter (eq 5).

2. Complexes of the type $[(Ph_3P)_2Pd(Ar)I]$ undergo C–P rather than C–I reductive elimination. As a result, the thermal decomposition reactions of σ-aryl phosphine complexes of palladium lead to the formation of arylphosphonium salts. Both stoichiometric[24,25] and catalytic[25,26] reactions of this type have been reported. In contrast, B–carboranyl iodo Pd complexes readily undergo reductive elimination of the iodocarborane but not $[9\text{-}m\text{-}C_2B_{10}H_{11}PPh_3]^+$. The latter is known to be a stable

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[20] Small amounts (<10%) of Ph_3P (^{31}P NMR: $\delta = -5.5$ ppm) and Pd metal were also present due to expected[14] disproportionation of the unstable $[(Ph_3P)_2Pd]$ to $[(Ph_3P)_3Pd]$ and Pd during and after the formation of the dicoordinate complex before the addition of PhI. Being in fast ligand exchange, $[(Ph_3P)_2Pd]$ and small amounts of $[(Ph_3P)_3Pd]$ exhibited one broadened singlet at 21.7 ppm (see above). It is remarkable that in the presence of 9-iodo-*m*-carborane the disproportionation of $[(Ph_3P)_2Pd]$ appeared to be noticeably slower than usual,[14] perhaps due to stabilization via $Pd\cdots I\text{–}B_{10}C_2H_{11}$ coordination. For a review of complexes of the type R–X–M (X = halogen), see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89. See also: Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831, and references therein.

[21] In addition, ca. 1% of $[(Ph_3P)_2PdI_2]$ (^{31}P NMR: $\delta = 12.6$ ppm) also formed. There was one more weak (ca. 0.5%) ^{31}P NMR signal observed ($\delta = 21.6$ ppm), which was not identified.

[22] Grushin, V. V. *Chem. Rev.* **1996**, *96*, 2011.

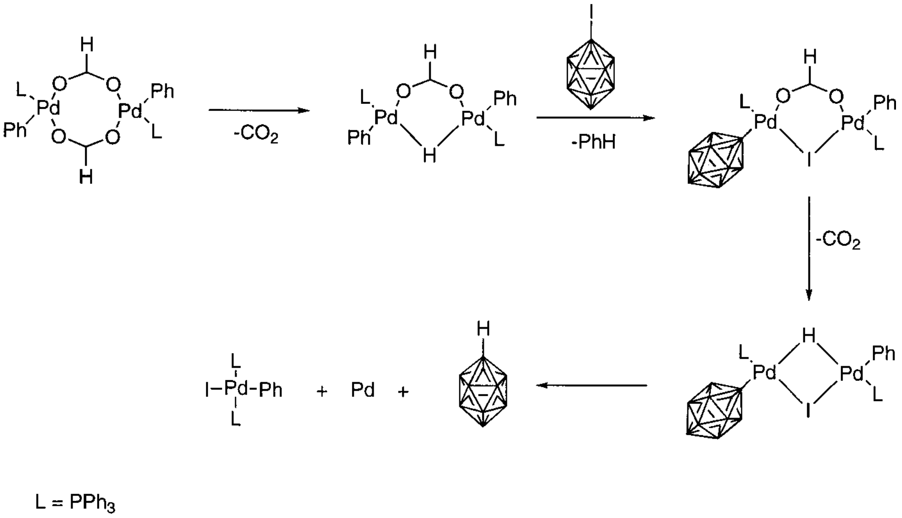
[23] Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180.

[24] (a) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1101. (b) Vicente, J.; Arcas, A.; Bautista, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *New J. Chem.* **1996**, *20*, 345. (c) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (d) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441. (e) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066. (f) Grushin, V. V. *Organometallics* **2000**, *19*, 1888.

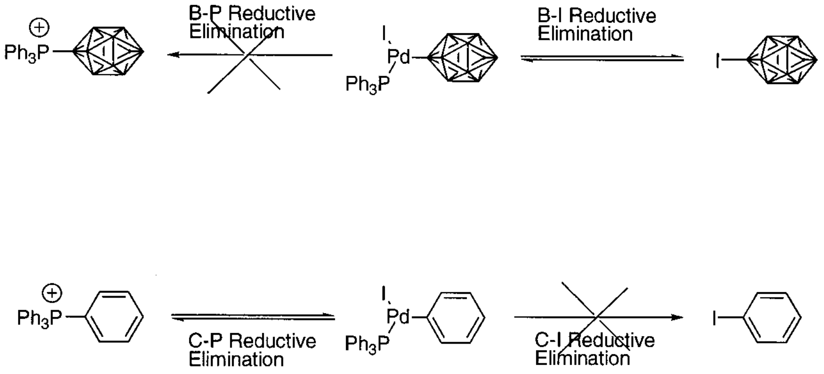
[25] Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

[26] Migita, T.; Nagai, T.; Kiuchi, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2869.

Scheme 3



Scheme 4



species forming isolable salts.[27] Moreover, our attempts to extend the Pd-catalyzed arylation of Ph_3P with ArI[26] to the synthesis of $[9\text{-}m\text{-}C_2B_{10}H_{11}PPh_3]^+I^-$ from 9-iodo-*m*-carborane and triphenylphosphine failed. Not even traces of carboranyl phosphonium salts were detected.[28] Scheme 4 illustrates the difference in trends for reductive elimination from σ-phenyl and σ-B−carboranyl Pd iodo complexes.

The exact structure of B−carboranyl palladium iodo complexes, the products of the B−I oxidative addition to $[(Ph_3P)_nPd]$, remains unknown. It is conceivable that due to the large effective steric bulk of the σ-carboranyl ligand, this complex may be *cis*-$[(Ph_3P)_2Pd(I)(C_2B_{10}H_{11})]$[29] or a dimer containing one phosphine per metal, e.g., $[(Ph_3P)_2Pd_2(\mu\text{-}I)_2(C_2B_{10}H_{11})_2]$, which may exist in equilibrium with mononuclear $[(Ph_3P)Pd(I)(C_2B_{10}H_{11})]$.[30] The B−I reductive elimination is likely to be governed by the three-center synchronous mechanism,[31] rather than the two-step mechanism[32] that would involve metal−iodine bond ionization, followed by nucleophilic attack of the I^- on the *ipso*-boron atom. The empty σ-(B−Pd)* antibonding orbital of the carboranyl Pd complex (LUMO) is "hidden" inside the polyhedron and therefore inaccessible for interaction with the HOMO of a nucleophile.

The results of our studies may account for the poor yields of the Suzuki-type coupling of B−iodocarboranes with phenylboronic acid.[4s] Because oxidative addition of the B−I bond to Pd(0) is reversible and thermodynamically disfavored (see above), solutions of $[(Ph_3P)_n\text{-}Pd]$ and a iodocarborane contain σ-B−carboranylpalladium species in a low concentration. Both RLi and RMgX are reactive enough to efficiently trap (carboranyl)Pd(I) intermediates present in low concentrations, converting them to (carboranyl)Pd(R), which then reductively eliminate the product, carboranyl−R. Arylbo-

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(27) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N.; Grishin, Yu. K.; Shcherbina, T. M.; Kampel, V. Ts.; Bregadze, V. I.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 472.

(28) (a) No carboranylphosphonium salt formation was observed when 9-iodo-*m*-carborane and Ph_3P in the presence of $Pd(OAc)_2$ were heated in xylenes at 130 °C for 30 h, i.e., under reaction conditions certainly suitable for the formation of tetraarylphosphonium salts from Ph_3P and ArI.[26] It has been shown[4p] that in certain cases CuI can promote the Pd-catalyzed cross-coupling reactions of B−iodocarboranes and RMgX. However, when the reaction between 9-iodo-*m*-carborane and Ph_3P was conducted in THF in the presence of both $Pd(OAc)_2$ (7%) and CuI (35%), no carboranylphosphonium salt formed after 15 h at 65 °C. (b) The formation of a B−P bond has recently been reported in the reaction of a C−monophosphino-*nido*-carborane with $[(Ph_3P)_2\text{-}PdCl_2]$: Vinas, C.; Nunez, R.; Texidor, F.; Sillanpaa, R.; Kivekas, R. *Organometallics* **1999**, *18*, 4712.

(29) Oxidative addition of ArI to Pd(0) triphenylphosphine complexes produces *cis*-$[(Ph_3P)_2Pd(I)Ar]$, which isomerize to the trans-isomer rapidly and quantitatively. See: Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954.

(30) Palladium complexes containing a σ-B−carboranyl ligand have been reported. See, for example: Kalinin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Metalloorg. Khim.* **1989**, *2*, 54. Ryabov, A. D.; Eliseev, A. V.; Sergeenko, E. S.; Usatov, A. V.; Zakharkin, L. I.; Kalinin, V. N. *Polyhedron* **1989**, *8*, 1485. See also: Corcoran, E. W., Jr.; Sneddon, L. G. *Mol. Struct. Energ.* **1988**, *5*, 71.

(31) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852.

(32) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

Table 1. Selected Crystallographic Data for $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$, $[9\text{-}m\text{-}C_2B_{10}H_{11}IPh]^+BF_4^-$, $9\text{-}m\text{-}C_2B_{10}H_{11}I$, and $9,10\text{-}m\text{-}C_2B_{10}H_{10}I_2$

	$[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$	$[9\text{-}m\text{-}C_2B_{10}H_{11}IPh]^+BF_4^-$	$9\text{-}m\text{-}C_2B_{10}H_{11}I$	$9,10\text{-}m\text{-}C_2B_{10}H_{10}I_2$
empirical formula	$C_{48}H_{40}I_2P_2Pd_2$	$C_8H_{16}B_{11}F_4I$	$C_2H_{11}B_{10}I$	$C_2H_{10}B_{10}I_2$
fw	1155.40	434.03	270.11	396.00
cryst size, mm	0.40 × 0.43 × 0.44	0.24 × 0.30 × 0.40	0.09 × 0.14 × 0.19	0.14 × 0.18 × 0.23
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pnma$ (No. 62)
temp, K	173	173	173	173
a, Å	14.388(1)	7.072(1)	11.430(1)	13.843(1)
b, Å	9.189(1)	20.564(1)	7.013(1)	12.827(1)
c, Å	17.362(1)	11.952(1)	13.288(1)	7.000(1)
β, deg	109.11(1)	99.71(1)	105.34(1)	
volume, Å^3	2169.0	1713.3	1027.2	1242.9
Z	4	4	4	4
calcd density, g·cm^{-1}	1.753	1.682	1.746	2.116
μ(Mo), cm^{-1}	23.31	18.72	30.16	49.55
diffractometer	Bruker SMART 1K CCD	Bruker SMART 1K CCD	Bruker SMART 1K CCD	Bruker SMART 1 K CCD
2θ range, deg	3.0−66.3	4.0−56.6	3.7−56.6	5.9−56.6
abs corr	SADABS	SADABS	SADABS	SADABS
no. of reflns collected	60971	19836	6249	13450
no. of unique reflns used in refinement ($I > 3\sigma(I)$)	6662	3282	1946	1270
no. of params refined	244	281	162	70
data-to-param ratio	27.27	11.66	11.99	18.01
R_1, %	1.8	1.7	1.8	1.5
R_w, %	2.1	1.9	2.0	1.7
error of fit	0.85	0.82	0.83	0.70

ronic acids (Suzuki) and organotin compounds (Stille) are much less nucleophilic. In many instances it is transmetalaition that is the rate-determining step of the Suzuki and Stille coupling reactions.[33] As a result, ligand exchange to produce (carboranyl)Pd(Ar) from (carboranyl)Pd(I) and $ArB(OH)_2$ is too slow to compete with side processes. The latter may involve, for example, ortho-palladation of coordinated PPh_3 to give a carboranyl Pd hydride which produces carborane upon B−H reductive elimination.

X-ray Structure of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$. The thermal decomposition of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}O_2CH)_2]$ in the presence of iodobenzene and 9-iodo-*m*-carborane furnished $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ as the main product (see Scheme 2 and text above). As the reaction occurred, the iodo dimer product precipitated slowly to form X-ray quality crystals. We took this opportunity to determine an X-ray structure of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$, whose poor solubility and limited thermal stability[24a] obstruct crystal growth by conventional methods.

Selected crystallographic data for $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ are presented in Table 1. The molecule sits on a crystallographic center of symmetry with the asymmetric unit containing one-half of the dimer in anti configuration (Figure 1). Coordination bond distances and angles for $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ are presented in Table 2, along with similar parameters previously determined for $[(Ph_3P)_2Pd(Ph)I]$[18] and $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$.[15b] As seen from Table 2, $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ displays almost ideal square-planar geometry around Pd, as expected. The Pd−I bonds distances are different, the one trans to the carbon (2.7185(3) Å) being noticeably longer than the Pd−I bond trans to the phosphine ligand (2.6645(4) Å). Therefore, the σ-Ph ligand exerts stronger trans-influence than PPh_3. A similar trend has been observed previously for the X-ray structure of $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$,[15b] except that the even longer Pd−I bond trans to the benzoyl ligand (2.766(1) Å) points to PhCO being a stronger trans-influencing ligand than Ph. All coordination bond angles found in $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ and $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$ are similar.

For all three complexes the Pd−C bond distances are only marginally different, obviously due to the same trans-influence of bridging iodine trans to the organic ligand. The Pd−P bond distance in $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ (2.265(1) Å) is slightly shorter than in $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$ (2.285(2) Å) and considerably shorter than in $[(Ph_3P)_2Pd(Ph)I]$ (2.338(1) and 2.342(1) Å), as expected from the well-established order of trans-influence $R_3P >$ halogen.

X-ray Structures of *m*-Carboran-9-yl(phenyl)iodonium Tetrafluoroborate, 9-Iodo-*m*-carborane, and 9,10-Diiodo-*m*-carborane. As mentioned above, unlike B−iodocarboranes, B−carboranyl(phenyl)iodonium cations exhibit remarkably high reactivity toward nucleophiles, undergoing nucleophilic displacement reactions selectively at the boron atom (eq 2).[6] The mechanism of these reactions and similar reactions of diaryliodonium salts involves nucleophilic attack on the iodonium center, followed by reductive elimination of the product from the resulting 10-I-3 intermediate (Scheme 5).[6a,b,34] The reductive elimination is symmetry-forbidden from the ground-state T-shape tricoordinate iodine(III) complex but allowed from its Y-shape conformer which mediates the cis−trans isomerization (or pseudorotation if the two lone electron pairs on the iodine are viewed as substituents, so-called “phantom-ligands”). Of the two substituents, the bulkier one (carboranyl) reductively eliminates from the tricoordinate complex probably because (i) the required obtuse Nu−I−B angle is more easily attained than Nu−I−C and (ii) elimination of the cumbersome carboranyl ligand results in a larger decrease in steric strain.[35]

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[33] Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. Farina, V.; Kapadia, S.; Krishnan, B.; Chenjie, W.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905. Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73. Louie, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11598.

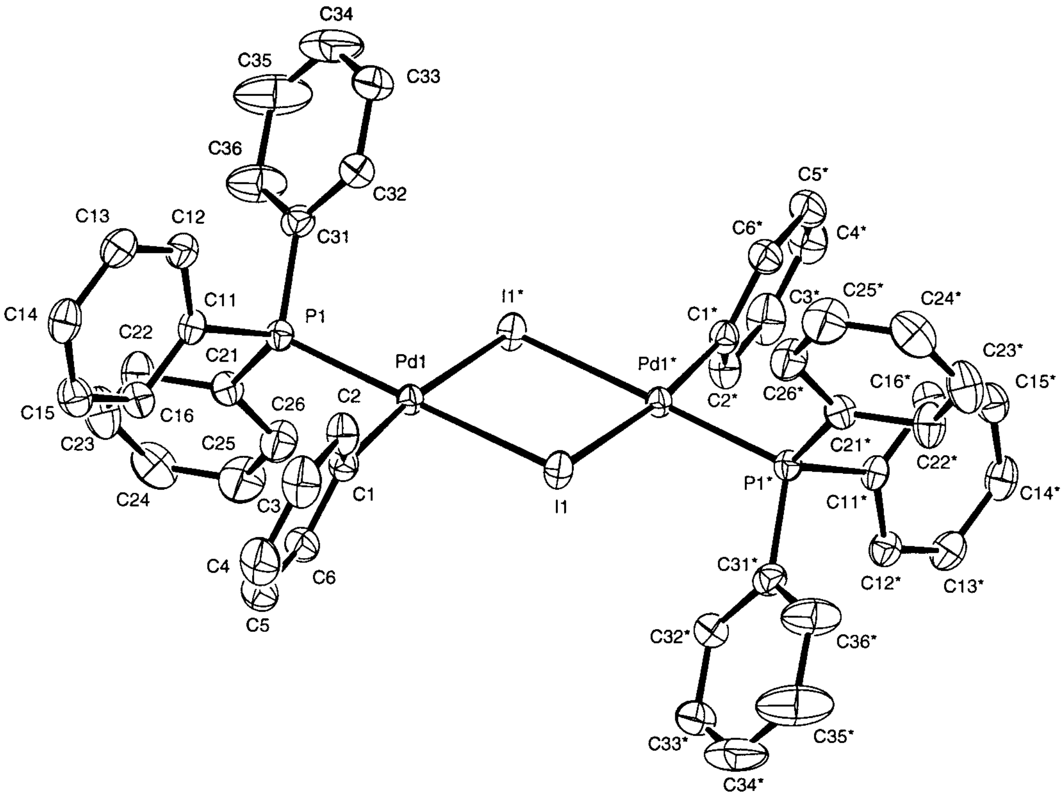

Figure 1. Molecular structure of *anti*-$[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 2. Selected Geometry Parameters for Complexes *trans*-$[(Ph_3P)_2Pd(Ph)_2(\mu\text{-}I)_2]$, *trans*-$[(Ph_3P)_2Pd(Ph)(I)]$,[18] and $[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$[15b]

	$[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$	$[(Ph_3P)_2Pd(Ph)(I)]$[18]	$[(Ph_3P)_2Pd_2(PhCO)_2(\mu\text{-}I)_2]$[15b]
	Interatomic Distances, Å		
Pd−I (trans to P)	2.6645(4)		2.6862(12)
Pd−I (trans to C)	2.7185(3)	2.7011(8)	2.7658(11)
Pd−C	1.993(1)	2.029(4)	1.986(7)
Pd−P	2.265(1)	2.338(1); 2.342(1)	2.285(2)
	Bond Angles, deg		
Pd−I−Pd	92.68(1)		92.25(3)
I−Pd−I	87.32(1)		87.75(3)
I−Pd−P	97.41(1)	90.87(3); 95.24(3)	97.06(6)
I−Pd−P	173.55(3)		174.62(5)
I−Pd−C	172.47(5)	171.4(1)	172.9(2)
I−Pd−C	87.62(4)		87.1(2)
P−Pd−C	88.08(4)	88.0(1); 86.1(1)	88.2(2)

To gain further insight into the exceptional selectivity of S_N reactions of B−carboranyl(phenyl)iodonium salts, we obtained and compared precise X-ray structures of *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate (Figure 2) and 9-iodo-*m*-carborane (Figure 3).[36] Crystallographic data obtained from these studies are collected in Table 1.

In the structure of the iodonium salt (Figure 2), the cation and anion are separated. As seen from the shortest intermolecular I−F (BF_4^-) distances found (2.854(1) and 3.112(1) Å), no strong bonding contacts between the anion and cation take place in the solid state. The B−I−C bond angle of 96.72(7)° slightly deviates from the expected[35b] ideal value of 90°, possibly due to the steric bulk of the carboranyl ligand. The strong electron-withdrawing effect of the iodonium atom[40] (for $9\text{-}m\text{-}C_2H_2B_{10}H_9I^+$, $\sigma_I = +1.39$; $\sigma_R = 0$ in

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(34) Grushin, V. V. *Chem. Soc. Rev.* **2000**, *29*, 315.

(35) (a) Likewise, diaryliodonium cations $[Ar-I-Ar']^+$ containing two aromatic substituents of different steric bulk arylate nucleophiles selectively with the bulkier of the two aryls.[6a,b,35b] This phenomenon is commonly observed when one of the aryls bears ortho substituent(s), whereas the other one does not. The selective binding of a nucleophile to the ortho-substituted aryl is called "ortho-effect". (b) For reviews, see: Koser, G. F. In *The Chemistry of Functional Groups, Suppl. D*; Patai, S., Rappoport, Z., Eds.; Wiley Interscience: Chichester, 1983; p 1173. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, 1992.

(36) Limited information has been accrued on molecular and crystal structures of monosubstituted B−iodocarboranes and B−carboranyl iodonium salts. In addition to the very early crystallographic studies of 9-iodo-*o*-carborane[37] and 9-iodo-*m*-carborane,[38] molecular and crystal structures of only few such compounds, namely, 2-iodo-*p*-carborane[4o] and *o*-carboran-9-yl(phenyl)iodonium iodide,[39] have been published. Hawthorne and co-workers[4o,p] have also reported X-ray structures of a series of di- and polyiodinated carboranes.

(37) Andrianov, V. G.; Stanko, V. I.; Struchkov, Yu. T.; Klimova, A. I. *Zh. Strukt. Khim.* **1967**, *8*, 707.

(38) Andrianov, V. G.; Stanko, V. I.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1967**, *8*, 558.

(39) Ionov, V. M.; Subbotin, M. Yu.; Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N.; Aslanov, L. A. *Zh. Strukt. Khim.* **1983**, *24*, 139.

(40) (a) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P.; Galakhov, M. V.; Bakhmutov, V. I. *Metalloorg. Khim.* **1989**, *2*, 727. (b) Mironova, A. A.; Maletina, I. I.; Iksanova, S. V.; Orda, V. V.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1989**, *25*, 306.

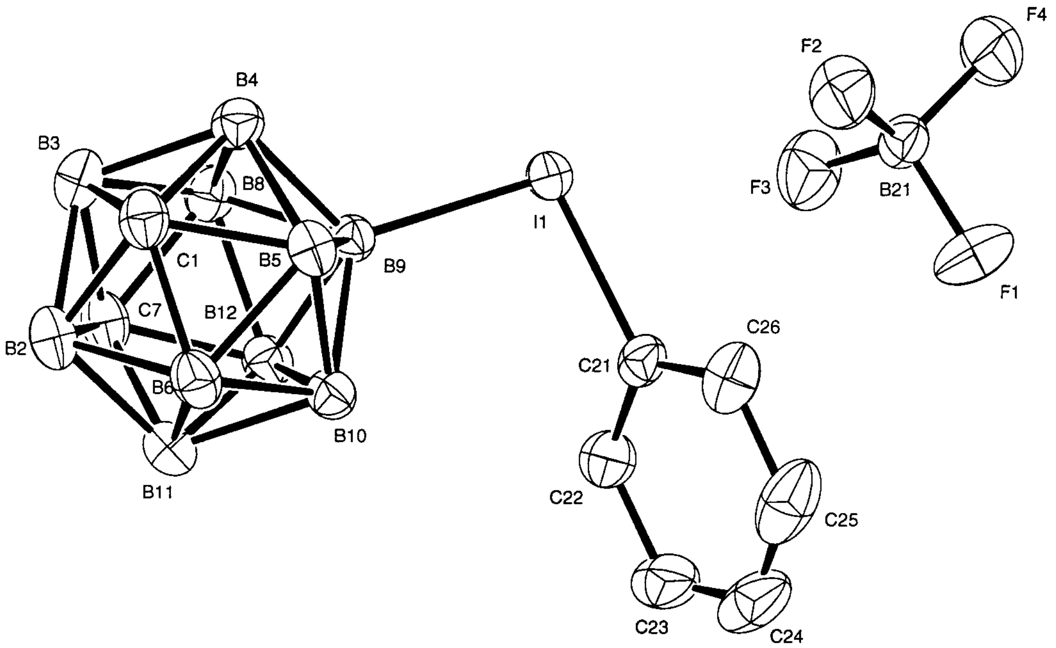
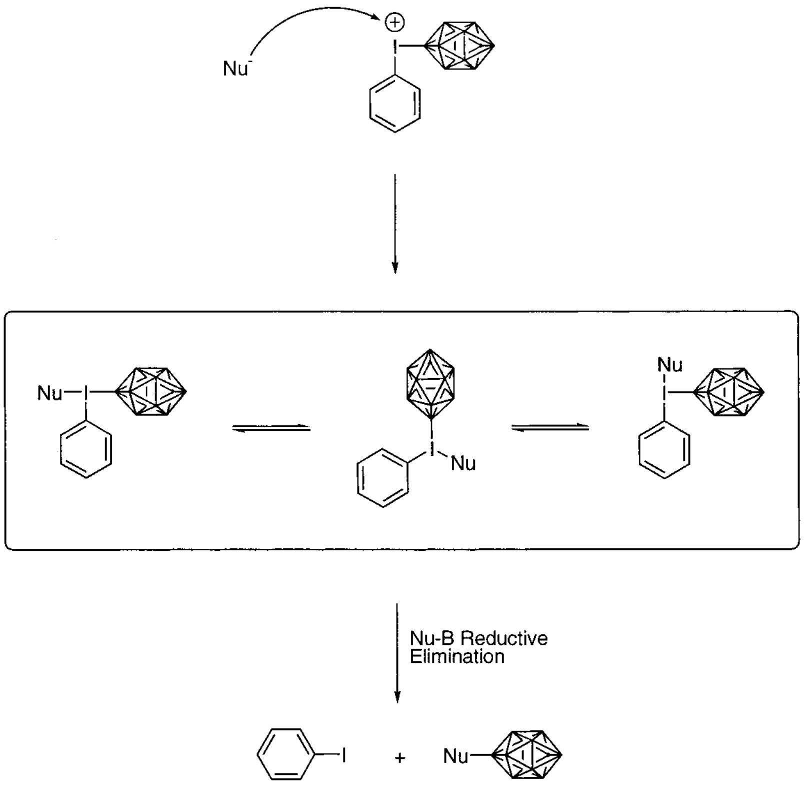


Figure 2. Molecular structure of *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Scheme 5



chloroform)[40a] is manifested[41] by the uncommonly large C−C−C ipso angle of 123.2(2)°. In substituted benzenes, the C−C−C ipso angle is an accurate structural measure of electronic effects of the substituent.[41] The C−C−C ipso angle is larger than 120° for electron-withdrawing groups and smaller than 120° for electron-donating substituents. For comparison, in the X-ray structure of nitrobenzene[42] the C−C−C ipso angle (122.7(1)°) is less obtuse than in the carboranyl(phenyl)iodonium salt (Figure 2), indicating that the carboranyliodonio substituent is a stronger electron acceptor than a nitro group. The strong electron-accepting effect of the phenyliodonio group ($\sigma_I = +1.35$; $\sigma_R = 0$ in

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[41] Domenicano, A. In *Accurate Molecular Structures: Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press: New York, 1992; p 437, and references therein. Domenicano, A.; Vaciago, A.; Coulsen, C. A. *Acta Crystallogr. B* **1975**, *31*, 1630. Schultz, G.; Hargittai, I.; Seip, R. *Z. Naturforsch. A* **1981**, *36*, 669, and references therein.

[42] Boese, R.; Blaser, D.; Nussbaumer, M.; Krygowski, T. M. *Struct. Chem.* **1992**, *3*, 363.

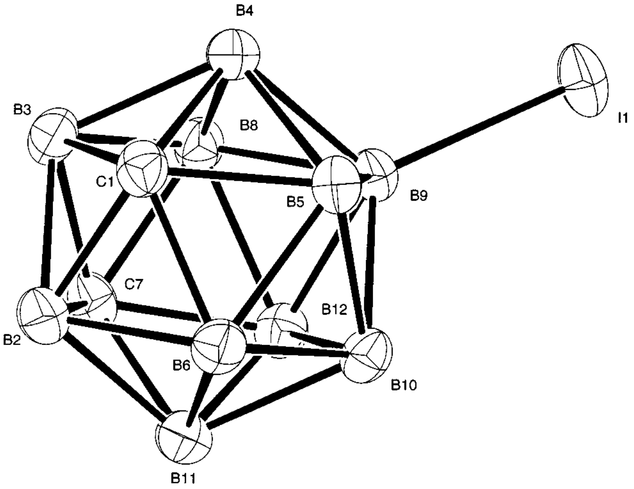

Figure 3. Molecular structure of 9-iodo-*m*-carborane with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

chloroform)[40a] is manifested by the sum of B−B−B bond angles at the substituted boron in the *m*-carboran-9-yl-(phenyl)iodonium salt (304.6°), which is noticeably larger than that measured for the structure of 9-iodo-*m*-carborane (301.0°).

Of special interest was to compare the B−I and C−I bond distances in the *m*-carboran-9-yl(phenyl)iodonium salt with the corresponding parameters of 9-iodo-*m*-carborane (Figure 3) and iodobenzene. While the difference between the C−I bond distance in the iodonium cation (2.111(2) Å) and iodobenzene (2.098(4) Å)[43] is marginal, the B−I bond distance in the iodonium salt (2.214(2) Å) is noticeably elongated, as compared to the value determined for 9-iodo-*m*-carborane (2.180(2) Å). The same trend was previously observed for the structure of *o*-carboran-9-yl(phenyl)iodonium iodide, for two independent molecules of which the B−I and C−I bond distances were measured at 2.261(9); 2.234(9) Å and 2.111(8); 2.104(8) Å, respectively.[39] Importantly, the B−I bond elongation is observed for both the *ionic* structure of *m*-carboran-9-yl(phenyl)iodonium tetrafuloroborate and *covalent* *o*-carboran-9-yl(phenyl)iodonium iodide, in which the iodide is coordinated to the iodonium center. Therefore, the B−I bond appears to be weakened before and after nucleophilic attack on the central iodine, whereas the C−I bond remains insignificantly activated, if at all, in both the ionic and covalent structures. This factor likely contributes to the selectivity of S_N reactions of the B−carboranyl(phenyl)iodonium salts, which all occur exclusively with B−I rather than C−I bond cleavage.

We also wish to mention an X-ray structure of 9,10-diiodo-*m*-carborane (Table 1, Figure 4), which is different from the structure of the same compound recently reported by Hawthorne and co-workers.[4p] We grew crystals of 9,10-diiodo-*m*-carborane from dichloromethane/heptane, whereas Hawthorne et al.[4p] obtained crystals of this diiodo derivative from pure dichloromethane. The space group determined in this work ($Pnma$) and previously ($P2_1c$)[4p] indicated polymorphism for 9,10-diiodo-*m*-carborane. Despite the different packing, molecular structures, i.e., bond distances and angles measured for the two crystallographic forms, appear very similar (see ref 4p and the Supporting Information).

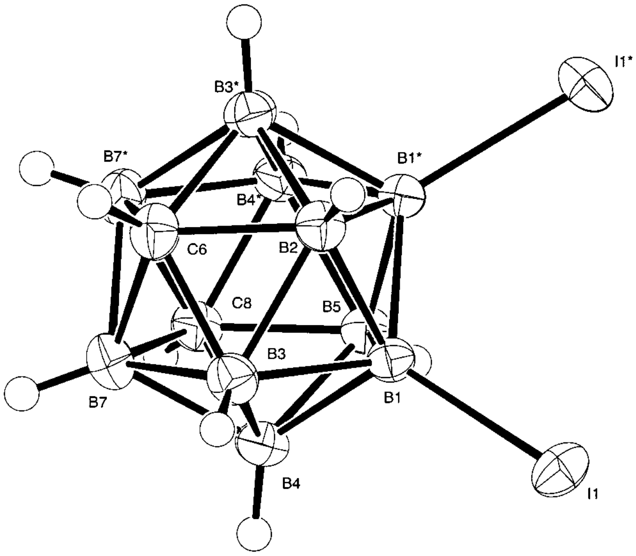

Figure 4. Molecular structure of 9,10-diiodo-*m*-carborane with thermal ellipsoids drawn at the 50% probability level.

Experimental Section

9-Iodo-*m*-carborane and 9,10-diiodo-*m*-carborane were prepared by the iodination of *m*-carborane (Aldrich) with I_2/HIO_3 in AcOH in the presence of H_2SO_4.[44] *m*-Carboran-9-yl(phenyl)iodonium tetrafluoroborate was synthesized by the oxidative condensation of 9-iodo-*m*-carborane with benzene in a $K_2S_2O_8/Ac_2O/H_2SO_4$ mixture, followed by anion metathesis with aqueous HBF_4.[45] The phenylpalladium formato complexes were prepared as described in the literature.[14] GC−MS and NMR spectroscopy were used for purity control of commercially unavailable reagents prepared and used in this work. All other chemicals were purchased from Aldrich, Strem, and Lancaster chemical companies. Reactions involving zerovalent complexes of Pd and Pt were carried out in a glovebox. Deuterated solvents were dried using standard procedures and stored over freshly calcined molecular sieves (4 Å) in the glovebox. NMR spectra were obtained with a Bruker Avance DPX 300 spectrometer. GC−MS analysis was carried out with a Hewlett-Packard 6890 Series instrument.

1. Reactions of 9-Iodo-*m*-carborane with $[(Ph_3P)_4M]$ (M = Pd, Pt). (a) To a yellow solution of $[(Ph_3P)_4Pd]$ (6.0 mg; 0.005 mmol) in toluene-d_8 (0.65 mL) was added 9-iodo-*m*-carborane (15.0 mg; 0.055 mmol). The iodocarborane easily dissolved without any noticeable change in color. The solution was placed in a standard 5 mm NMR tube, which was sealed with a rubber septum. The ^{31}P NMR spectra of this sample (**A**) recorded immediately and 12 h after the preparation were identical, exhibiting only one broad ($\Delta\nu_{1/2}$ = ca. 90 Hz) resonance at ca. 16 ppm. Indistinguishable ^{31}P NMR spectral patterns were observed for a control

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(43) The gas-phase structure of iodobenzene was determined by conjoint analysis of electron diffraction intensities and microwave rotational constants: Brunvoll, J.; Samdal, S.; Thomassen, H.; Vilkov, L. V.; Volden, H. V. *Acta Chem. Scand.* **1990**, *44*, 23.

(44) Stanko, V. I.; Brattsev, V. A.; Vostrikova, T. N.; Danilova, G. N. *Zh. Obshch. Khim.* **1968**, *38*, 1348.

(45) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 99; *Dokl. Chem. (Engl. Transl.)* **1981**, *261*, 456.

sample (**B**) prepared similarly, but without 9-iodo-*m*-carborane. Heating sample **A** for 3 h at 70 °C (oil bath) resulted in a slight darkening and an upfield shift of the broad ^{31}P NMR signal by ca. 1.5 ppm. Also, a very weak sharp singlet resonance at 12.4 ppm appeared (ca. 2% of the intensity of the main signal) which was assigned to $[(Ph_3P)_2PdI_2]$ (authentic sample). Addition of PhI (1 μL; ca. 2 equiv per Pd) to sample **A** resulted in instant decoloration and concomitant change in the spectral pattern. The broad resonance disappeared and two singlets (1:1) appeared at 22.3 ppm ($[(Ph_3P)_2Pd(Ph)I]$) and −5.5 ppm (Ph_3P). The weak resonance at 12.4 ppm from $[(Ph_3P)_2PdI_2]$ remained unchanged. GC−MS analysis indicated the presence of unreacted 9-iodo-*m*-carborane and trace amounts of *m*-carborane. No deuterium incorporation into the *m*-carborane product was observed (MS).

(b) To a yellow solution of $[(Ph_3P)_4Pd]$ (115 mg; 0.10 mmol) in THF (8 mL) was added 9-iodo-*m*-carborane (52 mg; 0.19 mmol), which quickly dissolved upon gentle shacking. No visible color changes occurred upon mixing, nor after 2 h at room temperature. After hexane (10 mL) was added and the mixture was kept overnight at −20 °C, the precipitated solid (light yellow plates) was collected, washed with hexanes, and dried under vacuum to yield 65 mg (73%) of $[(Ph_3P)_3Pd]$. The stoichiometry of the product was established by reacting it with PhI. Before the reaction, the ^{31}P NMR spectrum of the yellow solid in benzene-d_6 displayed only one broad resonance at ca. 17 ppm. The solution rapidly decolorized upon treatment with PhI, and the ^{31}P NMR spectrum of the resulting solution exhibited two resonances, at 22.3 ppm from $[(Ph_3P)_2Pd(Ph)I]$ and −5.5 ppm from Ph_3P. Integration of the signals (2:1) allowed for unambiguous determination of the stoichiometry of the complex, i.e., $[(Ph_3P)_3Pd]$ rather than $[(Ph_3P)_4Pd]$.

(c) A solution of $[(Ph_3P)_4Pt]$ (13 mg; 0.01 mmol) and 9-iodo-*m*-carborane (20 mg; 0.07 mmol) in toluene-d_8 was analyzed by ^{31}P NMR immediately after preparation and then after 2.5 h at 100 °C (oil bath). No sign of reaction was observed.

2. Reactions of 9-Iodo-*m*-carborane with $[(Ph_3P)_4Pd]$ in the Presence of Bu_4NX (X = I, Br). (a) Experiment 1a was repeated with a sample prepared with $[(Ph_3P)_4Pd]$ (6 mg; 0.005 mmol), 9-iodo-*m*-carborane (15 mg; 0.055 mmol), and tetrabutylammonium iodide (20 mg; 0.054 mmol) in THF (0.8 mL). The ^{31}P NMR spectral patterns observed were identical with those described in experiment 1a.

(b) A mixture of $[(Ph_3P)_4Pd]$ (10 mg; 0.009 mmol), 9-iodo-*m*-carborane (35 mg; 0.13 mmol), and tetrabutylammonium bromide (250 mg; 0.78 mmol) in THF (4 mL) was stirred at 30 °C overnight. The ^{31}P NMR spectrum of the solution exhibited a broad singlet at 16 ppm from $[(Ph_3P)_4Pd]$ and no other resonances. One-half of the solution was evaporated and extracted with 2 mL of heptane. GC−MS analysis of the heptane extract after filtration through a short silica plug revealed the presence of only 9-iodo-*m*-carborane ($m/z = 270$) and 9-bromo-*m*-carborane ($m/z = 223$) in a 7:1 ratio. After the remaining half of the reaction mixture was kept at 55 °C (oil bath) for 2 h and then analyzed as described above the ratio of 9-iodo-*m*-carborane to 9-bromo-*m*-carborane was determined at 5:1.

3. Reaction of 9-Iodo-*m*-carborane with $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OOCH)_2]$. In a glovebox, a solution of 9-iodo-*m*-carborane (34 mg; 0.13 mmol) and freshly prepared $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OOCH)_2]$ (18 mg; 0.02 mmol) in benzene-d_6 (0.8 mL) was placed in a 5 mm NMR tube and sealed with a rubber septum. The ^{31}P NMR spectrum of this sample exhibited one sharp singlet at 30.0 ppm from the formato complex.[14] In the ^1H NMR spectrum, aromatic and HCOO (8.3 ppm) signals from the formato complex[14] and broad resonances (1.0−4.0 ppm) from the iodocarborane were observed. Heating the sample at 55 °C (oil bath) for 40 min resulted in full conversion of the formato complex and precipitation of Pd metal. The ^{31}P NMR spectrum of the thermolyzed sample contained one sharp singlet at 22.5 ppm, which was assigned to $[(Ph_3P)_2Pd(Ph)I]$. The assignment was confirmed by obtaining ^1H and ^{13}C NMR spectra for the sample, which were identical with those described in the literature for $[(Ph_3P)_2Pd(Ph)I]$.[18,24f] GC−MS analysis after evaporation, extraction with heptane, and filtration through silica indicated the formation of *m*-carborane. No incorporation of deuterium was detected by comparison of the mass spectrum of the product with that from an authentic sample of *m*-carborane.

4. Reaction of 9-Iodo-*m*-carborane with $[(Ph_3P)_2Pd(Ph)(OOCH)]$. In a glovebox, a solution of 9-iodo-*m*-carborane (35 mg; 0.13 mmol) and $[(Ph_3P)_2Pd(Ph)(OOCH)]$ (0.04 mmol) generated in situ[14] from $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OOCH)_2]$ (19 mg; 0.02 mmol) and Ph_3P (10.5 mg; 0.04 mmol) in benzene-d_6 (0.8 mL) was prepared in a 5 mm NMR tube and sealed with a rubber septum. In accord with the literature data,[14] the decomposition of the formato complex started immediately and was complete after 1 h at room temperature. The ^{31}P NMR spectrum of the decomposed sample exhibited a sharp singlet at 22.5 ppm from $[(Ph_3P)_2Pd(Ph)I]$ and a broad resonance at 21.7 ppm from $[(Ph_3P)_2Pd]$.[19] The latter resonance disappeared, while the former grew in intensity upon addition of PhI. The formation of $[(Ph_3P)_2Pd(Ph)I]$ was confirmed by ^1H and ^{13}C NMR spectral data (see above). GC−MS analysis was carried out as described in the previous experiment, to reveal the presence of nondeuterated *m*-carborane.

5. Decomposition of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OOCH)_2]$ in the Presence of 9-Iodo-*m*-carborane and Iodobenzene. A solution of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OOCH)_2]$ (14 mg; 0.014 mmol), 9-iodo-*m*-carborane (27 mg; 0.1 mmol), and iodobenzene (20.5 mg; 0.1 mmol) in benzene-d_6 in a 5 mm NMR tube was kept at 65 °C (oil bath) for 3 h. The ^{31}P NMR spectrum indicated full conversion of the formato complex to $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ (27.7 ppm).[15b,24f] Due to its poor solubility, the iodo Pd dimer precipitated almost completely from the reaction mixture in the form of well-shaped dark red-orange crystals. These were separated, washed with hexane (ca. 1 mL), and dried under vacuum. The yield was 15.8 mg (97%). A crystal from this crop was selected for X-ray analysis. The combined mother liquor and hexane washings were filtered through a short silica plug and analyzed by GC−MS. The formation of *m*-carborane (ca. 3%) was detected.

6. Attempted Preparation of $[Ph_3P(C_2B_{10}H_{11})]I$ from 9-Iodo-*m*-carborane and Ph_3P in the Presence of a Pd Catalyst. A previously reported[26] method for the Pd-catalyzed arylation of triarylphosphines with aryl iodides was used. A solution of 9-iodo-*m*-carborane (110 mg; 0.41 mmol), Ph_3P (135 mg; 0.52 mmol), and $Pd(OAc)_2$ (5 mg; 0.02 mmol) in xylenes (1.5 mL) was heated under nitrogen at 130 °C (oil bath) for 2 days. The dark reaction mixture was evaporated, extracted with CD_2Cl_2, and analyzed by ^{31}P NMR. No formation of the phosphonium cation, $[Ph_3PC_2B_{10}H_{11}]^+$,[27] was detected. Similarly, when the reaction was repeated in the presence of CuI (35 mol %) in THF at 65 °C for 3 days, no formation of $[Ph_3PC_2B_{10}H_{11}]I$ was observed.

7. Single-Crystal X-ray Diffraction Studies. X-ray quality crystals of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ were obtained directly from the reaction mixture, as described in experiment 5. Crystals of *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate, 9-iodo-*m*-carborane, and 9,10-diiodo-*m*-carborane were grown from dichloromethane/ether, hexane, and dichloromethane/heptane, correspondingly. A Bruker SMART 1K CCD diffractometer (Mo Kα radiation) was used for X-ray analysis at −100 °C of all four compounds. In all cases, SADABS correction was applied. The structures were solved by direct methods and refined by full-matrix least-squares on *F*. All non-hydrogen atoms were refined anisotropically. For *m*-carboran-9-yl(phenyl)iodonium tetrafluoroborate and 9-iodo-*m*-carborane all hydrogens refined reasonably and were left in the final refinement. Because for $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ and 9,10-diiodo-*m*-carborane the refinement of a few of the hydrogen atoms gave unrealistic bond distances (0.79 and 1.07 Å, respectively), all of the hydrogen atoms were idealized close to their previously refined positions. The refinement converged to the *R* values listed in Table 1. Full details of the crystallographic studies are presented in the Supporting Information.

Supporting Information Available: Full details of the X-ray crystallographic studies of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}I)_2]$, $[9\text{-}m\text{-}C_2B_{10}H_{11}IPh]^+BF_4^-$, $9\text{-}m\text{-}C_2B_{10}H_{11}I$, and $9,10\text{-}m\text{-}C_2B_{10}H_{10}I_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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