

a cobalt(III) ion.<sup>14</sup> In fact the difference in the Co-N distances of the central and external metal ions, 0.115 Å, corresponds well to the difference in octahedral covalent radii of cobalt(II) and cobalt(III).<sup>15</sup>

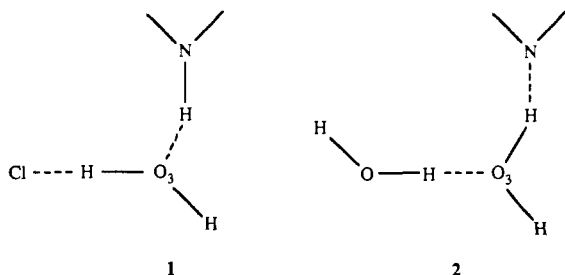
We formulate the cation therefore as  $[\text{Co}_3(\text{dat})_4(\text{datH})_2(\text{H}_2\text{O})_6]^{3+}$  and postulate that four guanazoles are deprotonated to guanazolate. This result is in line with the observed distance between nitrogen and terminal cobalt ion, which is slightly shorter than that observed in cobalt-triazole complexes.<sup>16</sup> A further confirmation comes from the electronic spectra, which show the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$  transition of octahedral cobalt(II) at  $10\,000\text{ cm}^{-1}$ . In analogous cobalt(II) complexes with protonated triazoles the corresponding band is observed<sup>17</sup> at  $8500\text{ cm}^{-1}$  ca. The spectra show also a shoulder at ca.  $17\,000\text{ cm}^{-1}$  and a maximum at  $21\,000\text{ cm}^{-1}$ . The latter may be due to the  ${}^4\text{F} \rightarrow {}^4\text{P}$  transitions of cobalt(II) and to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$  transitions of cobalt(III).

The distortion from ideal octahedral geometry of the coordination polyhedra solely involved the bond angles, whose deviations from ideal values are the same around the terminal and the central metal atoms (maximum of  $4.1^\circ$ ).

The cobalt atoms are displaced from the mean planes through the triazole rings by 0.014 and 0.006 Å.

The Co(III)-Co(II) distance within the trimeric molecule is 3.653 (3) Å, lower than the 3.7121 (16)<sup>18</sup> and 3.828 (9)<sup>16</sup> Å found in the case of Co(II)-Co(II). The triazole rings are found to be planar within experimental error. Bond distances and angles of the ring compare well with those found by other authors.<sup>6,8</sup> The dihedral angles between the ring planes are  $60.0^\circ$ .

Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur among the water molecules, the  $\text{NH}_2$  and  $\text{NH}$  groups of the 2,5-diamino-triazole molecules, and the chloride ions. The results of the refinement of the disordered chlorides and water molecules appear to indicate that ca. 46% of chlorine and ca. 54% of water oxygen is present in the compound. This means that, with chlorine ions present (as in **1**), the water



molecule O(3) is oriented such that one proton hydrogen bonds to the  $\text{Cl}^-$  ion, while the protonated ligand hydrogen bonds to O(3). In contrast, when a water molecule O(2) replaces the  $\text{Cl}^-$  ion, the O(3) water molecule reorients so that hydrogen bonding depicted in **2** occurs; e.g., the O(2) water molecule hydrogen bonds to O(3), while the O(3) water molecule now hydrogen bonds to the deprotonated N atom on the ligand.

**Magnetic Properties.** The magnetic properties of  $[\text{Co}_3(\text{dat})_4(\text{datH})_2(\text{H}_2\text{O})_6]\text{Cl}_3 \cdot 9\text{H}_2\text{O}$  agree with the formulation  $\text{Co}^{\text{II}}_2\text{Co}^{\text{III}}$ . In fact the room-temperature effective magnetic moment,  $\mu_B = 7.15$ , agrees well with the presence of two uncoupled high-spin octahedral cobalt(II) ions each with  $\mu_{\text{eff}} = 5.1\ \mu_B$ , while it would be too small for three cobalt(II) ions, each with  $\mu_{\text{eff}} = 5.1\ \mu_B$ . In fact the range of  $\mu_{\text{eff}}$  values for octahedral cobalt(II) ions is 4.8–5.4  $\mu_B$ . Further the temperature independence of  $\chi T$  down to ca. 100 K rules out any possibility of relevant antifer-

romagnetic interaction which might in principle reduce the room-temperature effective magnetic moment. The observed decrease of  $\chi T$  at lower temperature can be attributed to the thermal depopulation of the excited Kramers's doublets originated by spin-orbit and low-symmetry splitting of  ${}^4\text{T}_{1g}$  of the two cobalt(II) ions. Below 20 K  $\mu_{\text{eff}}$  stabilizes to 5  $\mu_B$ , which agrees with two uncoupled effective  $S = 1/2$  spins with  $g = 4.1$ .

The polycrystalline powder EPR spectra recorded at 4.2 K are axial, with  $g_{\parallel} = 8.8$  and  $g_{\perp} = 1.5$ . These values compare well with those observed in octahedral high-spin cobalt(II)<sup>19</sup> and show that the two ions are substantially uncoupled. Further, the fact that only one set of signals is observed rules out the presence of a third cobalt(II) ion.

**Conclusion.** In conclusion,  $[\text{Co}_3(\text{dat})_4(\text{datH})_2(\text{H}_2\text{O})_6]\text{Cl}_3 \cdot 9\text{H}_2\text{O}$  is the first example of mixed-valence trinuclear cobalt derivative with 1,2,4-triazoles. All the evidence is that the valences are effectively trapped. The analysis of the magnetic data provided evidence that the coupling between the external cobalt(II) ions is indeed very weak, thus solving a long debated problem<sup>20</sup> in the analysis of the magnetic properties of trinuclear cobalt(II) complexes.

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**Registry No.**  $[\text{Co}_3(\text{dat})_4(\text{datH})_2(\text{H}_2\text{O})_6]\text{Cl}_3 \cdot 9\text{H}_2\text{O}$ , 136822-82-7.

**Supplementary Material Available:** Tables SMI-SMVI, listing bond distances and bond angles, intensity data collection details, thermal parameters, positional and thermal parameters for hydrogen atoms, bond distances and angles involving hydrogen atoms and hydrogen-bonding interactions, and selected least-squares planes (6 pages); Table SF, listing calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.

(19) Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Struct. Bonding* **1982**, *52*, 38.

(20) Vreugdenhil, W.; Haasnoot, J. G.; Schoondergang, M. F. J.; Reedijk, J. *Inorg. Chim. Acta* **1987**, *130*, 235 and references quoted therein.

Contribution from the Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow, USSR, and Department of Chemistry, Moscow State University, Moscow, USSR

### Reactions of Aryl(*B*-carboranyl)iodonium Cations with the Fluoride Anion. Synthesis of Icosahedral *o*-Carboran-9-yl, *m*-Carboran-9-yl, and *p*-Carboran-2-yl Fluorides

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#### Introduction

Hundreds of different icosahedral *closo*-carborane(12) derivatives containing boron-element bonds (element = halogen, nitrogen, carbon, oxygen, sulfur, main-group and transition metals, etc.) have been synthesized over the last 25–30 years.<sup>1</sup> Direct electrophilic chlorination, bromination, and iodination is known to be an effective and convenient method for the preparation of boron halogenated *o*-, *m*-, and *p*-carboranes.<sup>2</sup> Similarly, selective

(14) Engelfriet, D. W.; Den Brinker, W.; Verschoor, G. C.; Gorter, S. *Acta Crystallogr.* **1979**, *B35*, 2922.

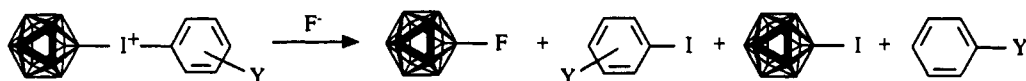
(15) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(16) Groeneveld, L. R.; Le Febre, R. A.; De Graaff, R. A. G.; Haasnoot, J. G.; Vos, G.; Reedijk, J. *Inorg. Chim. Acta* **1985**, *102*, 69.

(17) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.

(18) Wen, T.; Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 4190.

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‡ Moscow State University.

**Table I.** Reactions of Aryl(*B*-carboranyl)iodonium Tetrafluoroborates with the Fluoride Anion

entry	iodonium salt	carborane nucleus isomer/substituent position	Y	reacn conditions <sup>a</sup>	temp, °C	time, h	yield, % (GLC)			
							C <sub>2</sub> B <sub>10</sub> H <sub>11</sub> F	ArI	C <sub>2</sub> B <sub>10</sub> H <sub>11</sub> I	ArH
1	1	ortho/9	H	A	25	0.1	90–95 <sup>b</sup>	90	2–5	5
2	2	meta/9	H	A	25	0.5	85	90	5	7
3	2	meta/9	H	B	40	6	89 <sup>b</sup>	90	2	2
4	2	meta/9	H	C	56	1	75	92	7	5
5	3	meta/9	4-CH <sub>3</sub> O	C	56	1.25	80	85	15	13
6	4	meta/9	4-F	C	56	1.25	83	82	2	9
7	5	meta/9	3-NO <sub>2</sub>	C	56	2	86	73	7	4
8	6	meta/9	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	C	56	2.5	78	75	16	14
9	7	para/2	H	B	25	0.5	99	95	traces	<0.5
10	7	para/2	H	D	25	0.6	99.5 <sup>b</sup>	99	c	<0.5

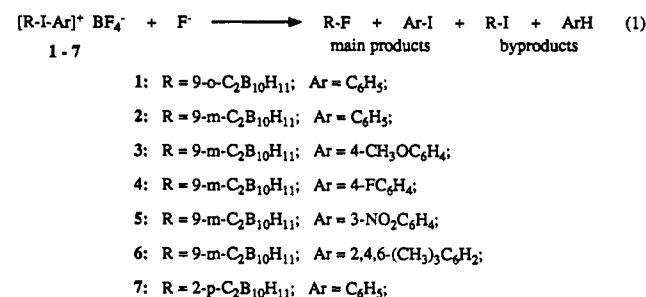
<sup>a</sup>A: anhydrous KF–18-crown-6 ether–dry CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>, 25 °C. B: NaHF<sub>2</sub>–CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O, 40 °C. C: NaF–CHCl<sub>3</sub>–H<sub>2</sub>O, 56 °C. D: NaF–CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O, 25 °C. <sup>b</sup>Isolated yield. <sup>c</sup>2-Iodo-*p*-carborane was not found among the reaction products.

mono-, di-, or polyhalogenation of carboranes can be achieved under appropriate conditions. In contrast, reactions of *o*-, *m*-, and *p*-carboranes with elemental fluorine are not selective at all, leading instead to deca-*B*-fluorocarboranes, C<sub>2</sub>H<sub>2</sub>B<sub>10</sub>F<sub>10</sub>, as the only products.<sup>3</sup> Therefore, an interaction between *closo*-carboranes (12) and F<sub>2</sub> cannot be used for the synthesis of monofluorinated products. Although development of simple and effective procedures for selective introduction of fluorine to a carborane icosahedron seems to be a challenging problem, only a very few methods for the preparation of monofluorocarboranes are known. For instance, the reaction of the unstable *o*-carboran-3-yl diazonium cation with liquid HF afforded 3-fluoro-*o*-carborane,<sup>4</sup> while the action of the boron trifluoride etherate complex on *o*- and *m*-carboran-9-ylthallium bis(trifluoroacetates) was shown to produce the corresponding 9-fluorocarboranes in moderate yield (no more than 40%).<sup>5</sup> Very recently, Lebedev et al.<sup>6</sup> described fluorination of *o*- and *m*-carboranes with SbF<sub>5</sub>, leading to 9-fluoro-*o*-carborane and 9-fluoro-*m*-carborane in 42% and 75% isolated yields, respectively.

A few years ago, two of us briefly reported the synthesis of *o*-carboran-9-yl, *m*-carboran-9-yl, and *p*-carboran-2-yl fluorides by reactions of the corresponding phenyl(*B*-carboranyl)iodonium ions with F<sup>−</sup> under phase-transfer or biphasic conditions.<sup>7</sup> The synthesis of fluorocarboranes (94–100% yields) via stable and readily available carboranyl iodonium compounds<sup>7</sup> possesses some practical advantages. These reactions are also interesting from a theoretical point of view, as they represent the first example of nucleophilic substitution of a halogen attached to an icosahedral carborane boron by the fluoride anion. In contrast to *closo*-2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> derivatives,<sup>8</sup> icosahedral carboranyl halides undergo nucleophilic substitution neither by F<sup>−</sup> nor by other nucleophiles.<sup>1</sup> In the present paper, we wish to report a detailed investigation of nucleophilic substitution in different aryl(*B*-carboranyl)iodonium cations by the fluoride anion.

## Results and Discussion

Aryl(*B*-carboranyl)iodonium tetrafluoroborates 1–7 react with the fluoride anion to give the corresponding carboranyl fluoride and iodoarene as the main products, together with some small amounts of the corresponding arene and iodo-carborane (eq 1; Table I).



All the reaction mixtures were investigated by GLC and by GC–MS, because arenes and their monofluoro derivatives usually have similar boiling points and chromatographic parameters. No reaction was found to produce even traces of fluoroarenes, although it is known that the interaction of diphenyliodonium tetrafluoroborate with the fluoride ion leads to fluorobenzene and iodobenzene in high yields.<sup>9</sup> Therefore, nucleophilic substitution in all the cations of 1–7 by the fluoride ion is *regiospecific*.

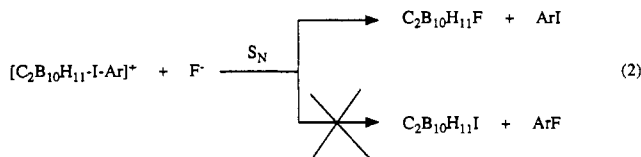
The reaction of the iodonium salt 1 with F<sup>−</sup> requires anhydrous conditions. Strong electron-withdrawing properties of the phenyliodonium group<sup>10</sup> make the *o*-carborane nucleus in 1 very susceptible to degradation from weak bases,<sup>1</sup> including water.<sup>11</sup> However, 9-fluoro-*o*-carborane can be synthesized in high yield (up to 90–95%) with the use of anhydrous KF and 18-crown-6 ether in dry chloroform (see Table I). Water–chloroform (or –dichloromethane) biphasic systems have been found suitable for the reactions of the salts 2–7 with NaF or NaHF<sub>2</sub>. The highest yield of 9-fluoro-*m*-carborane (89%) was obtained when NaHF<sub>2</sub> was used as the source of the fluoride ion. Introduction of different substituents to the aromatic ring of 2 (cations of 3–6) did not cause dramatic changes in the yields of 9-fluoro-*m*-carborane (Table I, entries 4–8). Reactions of 7 (entries 9 and 10) afforded 2-fluoro-*p*-carborane in almost quantitative yield, regardless of the fluoride ion source (NaF or NaHF<sub>2</sub>). *B*-Carboranyl fluorides

- (1) Grushin, V. V.; Bregadze, V. I.; Kalinin, V. N. *J. Organomet. Chem. Libr.* **1988**, 20, 1.
- (2) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970; see also references cited therein.
- (3) Kongpricha, S.; Schroeder, H. *Inorg. Chem.* **1969**, 8, 2449.
- (4) (a) Zakharkin, L. I.; Kalinin, V. N.; Kvasov, B. A.; Fedin, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2415. (b) Zakharkin, L. I.; Kalinin, V. N.; Gedymin, V. V. *J. Organomet. Chem.* **1969**, 16, 371.
- (5) Bregadze, V. I.; Usyatinsky, A. Ya.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2836.
- (6) Lebedev, V. N.; Balagurova, E. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Zakharkin, L. I. *J. Organomet. Chem.* **1990**, 385, 307.
- (7) (a) Grushin, V. V.; Shcherbina, T. M.; Tolstaya, T. P. *J. Organomet. Chem.* **1985**, 292, 105. (b) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 2165; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1983**, 32, 1957.
- (8) (a) Ng, B.; Onak, T. *J. Fluorine Chem.* **1985**, 27, 119. (b) Ng, B.; Onak, T.; Fuller, K. *Inorg. Chem.* **1985**, 24, 4371.

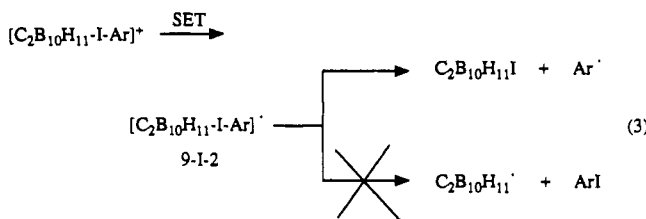
- (9) (a) van der Puy, M. *J. Fluorine Chem.* **1982**, 21, 385. (b) Grushin, V. V.; Kantor, M. M.; Tolstaya, T. P.; Shcherbina, T. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 2332; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1984**, 33, 2130.
- (10) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P.; Galakhov, M. V.; Bakhmutov, V. I. *Metallurg. Khim.* **1989**, 2, 727.
- (11) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 2633; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1982**, 31, 2329.

isolated in 89–99% yields appeared to be identical with authentic samples prepared by independent methods<sup>5,6</sup> (<sup>19</sup>F and <sup>11</sup>B NMR spectra,<sup>6,12</sup> melting points, GLC parameters).

The formation of arenes and iodocarboranes in nearly every reaction of the iodonium salts 1–7 with F<sup>−</sup> indicates that a competition between nucleophilic substitution and a one-electron reduction of the starting iodonium cation takes place under described conditions.<sup>1</sup> Similar competition has already been observed in reactions of 2 with KCN<sup>7a</sup> and NaNO<sub>2</sub>.<sup>13</sup> The nucleophilic substitution by the fluoride ion in 1–7 is regiospecific (it occurs only at a carborane boron; see eq 2), as are all other S<sub>N</sub>-type reactions of phenyl(*B*-carboranyl)iodonium cations.<sup>1,7,10,11,13,14</sup>

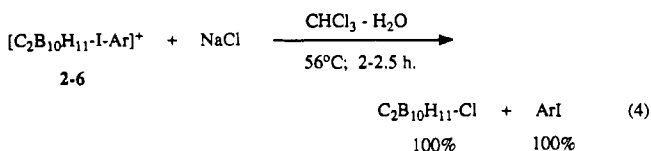


Probably, the mechanism for the nucleophilic substitution in 1–7 is similar to that described in ref 1. The fluoride ion attacks the onium iodine to give a tricoordinated iodine(III) complex which then undergoes synchronous reductive elimination of the fluoro-carborane. Only ipso substitution has been observed. At the same time, a one-electron reduction of the iodonium ion occurs independently of the S<sub>N</sub>-type reaction. This single-electron-transfer (SET) process leads to a labile 9-I-2 intermediate which regio-



specifically decomposes to the corresponding aryl radical and iodocarborane<sup>1,10</sup> (eq 3). A hydrogen abstraction from the solvent by the aryl radicals formed results in the formation of arenes.

Thus, the fluoride anion *formally* plays the role of a one-electron donor toward the iodonium cations in 1–7. This behavior of F<sup>−</sup> is quite unusual, especially if taking into account that neither Cl<sup>−</sup> nor Br<sup>−</sup> caused a one-electron reduction of the cations of 1 and 2 under similar conditions.<sup>7a</sup> As we showed in the present work, reactions of 2–6 with NaCl under biphasic conditions produce 9-chloro-*m*-carborane and the corresponding iodoarenes in quantitative yields (eq 4). Not even traces of 9-iodo-*m*-carborane and arenes were found among the reaction products.



Since a *direct* SET from F<sup>−</sup> seems unlikely, some other mechanisms for the fluoride anion mediated one-electron reduction of the cations of 1–7 should be considered. Hydrogen fluoride is a weak acid ( $K = 3.53 \times 10^{-4}$  at 25 °C).<sup>15</sup> Due to this, sodium fluoride (in contrast to NaCl and NaBr) is partially hydrolyzed in aqueous solution to produce hydroxide anions. The latter has been shown to react with 2 via a radical pathway, producing

benzene and 9-iodo-*m*-carborane as the major products.<sup>7a</sup> Indeed, reaction of 2 with almost neutral NaHF<sub>2</sub> instead of basic NaF (see Table I, entries 3 and 4) in a CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O biphasic system produces a noticeably higher yield of 9-fluoro-*m*-carborane and lower yields of benzene and 9-iodo-*m*-carborane. Therefore, the OH<sup>−</sup> produced in the hydrolysis of NaF could (at least in part) be responsible for the radical reaction of the cations of 2–7. The ability of the hydroxide ion to work as a one-electron donor in many reactions,<sup>16</sup> including reactions with different aromatic halonium ions,<sup>17</sup> is well-documented. On the other hand, reactions of 1 and 2 with anhydrous KF in dry CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub> in the presence of 18-crown-6 ether (Tables I, entries 1 and 2) were also found to give some small amounts of benzene and iodocarborane along with the main products. This shows that there must be another mechanism for the fluoride ion mediated one-electron reduction of the aryl(*B*-carboranyl)iodonium cations.

Very recently, the fluoride ion was shown to be capable of degrading *o*- and *m*-carboranes(12) into 7,8- and 7,9-dicarba-*nido*-undecaborate anions, respectively.<sup>18,19</sup> In contrast to F<sup>−</sup>, other halide anions (Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>) do not react with carboranes.<sup>18</sup> We have already proposed that a weakly solvated fluoride anion can cause the degradation of a carborane icosahedron bearing strong electron-withdrawing halonium groups.<sup>20</sup> The *nido*-carboranes formed could reduce aryl(*B*-carboranyl)iodonium cations into the corresponding 9-I-2 radicals which give iodocarborane and phenyl radicals upon decomposition (eq 3). In order to examine this proposal, 2 was allowed to react with trimethylammonium 7,9-dicarba-*nido*-undecaborate. Benzene and 9-iodo-*m*-carborane (50–60% yields) were found among other products. The *p*-carborane icosahedron is much more resistant toward degradation under the action of bases than the ortho and meta isomers.<sup>21</sup> That is probably why only traces of iodocarborane and benzene formed in the reactions of *p*-carboranyl iodonium salt 7 with F<sup>−</sup>.

The optimum conditions for the preparation of *B*-carboranyl fluorides should be summarized. 9-Fluoro-*o*-carborane can be synthesized by the reaction of 1 with KF in dry chloroform in the presence of 18-crown-6 ether. The best method to synthesize 9-fluoro-*m*-carborane is the reaction between 2 and NaHF<sub>2</sub> in a CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O biphasic system. The reaction of 7 with NaF in a CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O system leads to 2-fluoro-*p*-carborane in almost 100% yield. The corresponding iodocarboranes formed as by-products of these reactions in 0–5% yields can be easily removed with one recrystallization.

### Experimental Section

<sup>11</sup>B and <sup>19</sup>F NMR spectra were recorded on a Bruker WP-200 SY spectrometer. GLC measurements were performed with a Biokrom-1 instrument equipped with a 50 m × 0.22 mm XE-60 capillary column. GC–MS analyses were carried out with a Finnigan Ion Trap-700 instrument. Chloroform and methylene chloride were distilled from P<sub>2</sub>O<sub>5</sub> prior to use in the experiments with anhydrous KF. 18-Crown-6 ether (Sigma) was dried over sodium and distilled under reduced pressure. Potassium fluoride was dried under vacuum at 200 °C and then stored under argon. All other chemicals were used as received. Iodonium salts 1,<sup>22</sup> 2,<sup>22</sup> 3–6,<sup>23</sup> and 7<sup>b</sup> and trimethylammonium 7,9-dicarba-*nido*-unde-

- (12) Antonovich, V. A. Unpublished results.  
 (13) Demkina, I. I.; Grushin, V. V.; Vanchikov, A. N.; Tolstaya, T. P.; Orlinkov, A. V. *Zh. Obshch. Khim.* **1987**, *57*, 1341; *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 1199.  
 (14) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N.; Vanchikov, A. N. *Dokl. Akad. Nauk SSSR* **1982**, *264*, 868; *Dokl. Chem. (Engl. Transl.)* **1982**, *264*, 163.  
 (15) *CRC Handbook of Chemistry and Physics*, 68th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1987.

- (16) Sawyer, D. T.; Roberts, J. L. *Acc. Chem. Res.* **1988**, *21*, 469.  
 (17) (a) Sandin, R. B.; Brown, R. K. *J. Am. Chem. Soc.* **1947**, *69*, 2253. (b) Caserio, M. C.; Glusker, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 336. (c) Tolstaya, T. P.; Demkina, I. I.; Grushin, V. V.; Vanchikov, A. N. *Zh. Org. Khim.* **1989**, *25*, 2569; *J. Org. Chem. USSR (Engl. Transl.)* **1989**, *25*, 2305.  
 (18) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812.  
 (19) Varadrajana, A.; Gomez, F.; Hawthorne, M. F. Unpublished results, cited in ref 18.  
 (20) (a) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P. *Inorg. Chem.* **1991**, *30*, 1760. (b) Demkina, I. I. Ph.D. Thesis, Department of Chemistry, Moscow State University, Moscow, 1987.  
 (21) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862.  
 (22) Grushin, V. V.; Tolstaya, T. P.; Lisichkina, I. N. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 99; *Dokl. Chem. (Engl. Transl.)* **1981**, *261*, 456.  
 (23) Demkina, I. I.; Vanchikov, A. N.; Grushin, V. V.; Tolstaya, T. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 940; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1985**, *34*, 858.

borate<sup>21</sup> were prepared as described in the literature.

**9-Fluoro-*o*-carborane.** The iodonium salt **1** (1.50 g; 3.5 mmol) was added portionwise to a stirred mixture of KF (1.0 g; 17.2 mmol), 18-crown-6 ether (1.34 g; 5.1 mmol), and dry chloroform (10 mL). The exothermic reaction was complete within 1–5 min. The liquid phase was analyzed by GLC and then evaporated, and the residue was chromatographed on alumina (benzene–hexane, 1:3) to give 0.52 g (93%) of 9-fluoro-*o*-carborane, mp 287–288 °C (from benzene–hexane; sealed tube). The compound was found to be identical with an authentic sample.<sup>5,6</sup>

**9-Fluoro-*m*-carborane.** A mixture of **2** (0.70 g; 1.62 mmol), NaHF<sub>2</sub> (0.30 g; 4.84 mmol), water (7 mL), and dichloromethane (7 mL) was vigorously stirred under reflux for 6 h. Internal standard (chlorobenzene) was added, and the organic layer was analyzed by GLC and GC–MS. The organic phase was evaporated, and the residue was chromatographed on silica gel (40–100 mesh; hexane) to give 9-fluoro-*m*-carborane (0.23 g; 89%), mp 267–268 °C (hexane; sealed tube). The compound was found to be identical with an authentic sample.<sup>5,6</sup>

**2-Fluoro-*p*-carborane.** A mixture of **7** (0.7 g; 1.6 mmol), NaF (0.2 g; 4.8 mmol), water (4 mL), and dichloromethane (5 mL) was vigorously stirred at 25 °C for 35 min. The organic phase was separated off, filtered through a short alumina plug, and evaporated. The residue (a mixture of iodobenzene and 2-fluoro-*p*-carborane) was dissolved in dry CCl<sub>4</sub> (5 mL), and the solution was saturated with Cl<sub>2</sub> at 5 °C and then evaporated, to give the mixture of iodobenzene dichloride and the fluoro-carborane. The latter was extracted with pentane [the yield of PhICl<sub>2</sub> left was 0.31 g (70%)], and the pentane solution was filtered through an alumina plug and evaporated to dryness. Vacuum sublimation of the residual solid gave 0.26 g (99.5%) of analytically pure 2-fluoro-*p*-carborane, mp 256 °C (sealed tube). Anal. Calcd for C<sub>2</sub>H<sub>11</sub>B<sub>10</sub>F: F, 11.71. Found: F, 11.74.

**Reactions of 2–6 with NaF.** A mixture of aryl(*m*-carboran-9-yl)-iodonium tetrafluoroborate (0.62 mmol), NaF (0.08 g; 1.9 mmol), water (2 mL), and chloroform (2 mL) was vigorously stirred under reflux for 2.5 h. Internal standard (chlorobenzene) was added, and the organic phase was analyzed by GLC and GC–MS.

**Reactions of 3–6 with NaCl.** A mixture of aryl(*m*-carboran-9-yl)-iodonium tetrafluoroborate (0.24 mmol), NaCl (0.04 g; 1.9 mmol), water (1 mL), and chloroform (1 mL) was vigorously stirred under reflux for 2.5 h. Internal standard (iodobenzene) was added, and the organic layer was analyzed by GLC.

**Reaction of 2 with Trimethylammonium 7,9-Dicarba-*nido*-undecaborate.** A solution of **2** (0.84 g; 1.94 mmol) and trimethylammonium dicarba-*nido*-undecaborate (0.44 g; 2.11 mmol) in acetone (8 mL) was refluxed for 4 h. The resulting solution was analyzed by GLC and then evaporated to dryness. The residue was chromatographed on silica gel (40–100 mesh; hexane) to give 0.26 g (50%) of 9-iodo-*m*-carborane, mp 110–112 °C (hexane; see ref 2).

**Registry No.** **1**, 81353-28-8; **2**, 81353-33-5; **3**, 99506-45-3; **4**, 99506-39-5; **5**, 99506-41-9; **6**, 99506-43-1; **7**, 88242-78-8; 9-*o*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 73050-36-9; 9-*m*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 73050-37-0; 2-*p*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>F, 22762-43-2; 9-*m*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>I, 17157-02-7.

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### Carbon–Carbon Double-Bond Formation in the Intermolecular Acetonitrile Reductive Coupling Promoted by a Mononuclear Titanium(II) Compound. Preparation and Characterization of Two Titanium(IV) Imido Derivatives

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#### Introduction

Reactions forming carbon–carbon bonds are among the most fundamental organic chemical transformations mediated by

early-transition-metal complexes. Today, reductive couplings and insertion reactions are successfully used with a considerable number of transition metals, to form C–C bonds through either catalytic or stoichiometric reactions.<sup>1</sup> While the insertion reactions are the most versatile chemical pathway for polymerization processes,<sup>1a,2</sup> reductive couplings are target of continuous studies for regio- and stereoselective metal-promoted organic syntheses.<sup>3</sup> Group 4 transition metals seem to be especially versatile for this second class of reactions,<sup>1a,4</sup> reductive couplings being documented for the large majority of unsaturated organic compounds (dienes,<sup>5</sup> olefins,<sup>6</sup> acetylenes,<sup>7</sup> isocyanides,<sup>8</sup> nitriles,<sup>9</sup> and carbon monoxide<sup>10</sup>). We were especially interested in defining the chemical reactivity of (TMEDA)<sub>2</sub>TiCl<sub>2</sub> (TMEDA = *N,N,N',N'*-tetramethylethylenediamine),<sup>11</sup> which is one of the rare examples of low-valent titanium complexes.<sup>12,13</sup> In this paper we describe the reaction

- (1) (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982. (b) Wilkinson, G. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, 1987.
- (2) See, for example: (a) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (b) Boor, J. *Ziegler-Natta Catalysts and Polymerization*, Academic Press: New York, 1979. (c) Fisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. G.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (d) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479. (e) Watson, P. J. *Am. Chem. Soc.* **1982**, *104*, 337. (f) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (g) Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1647. (h) Jordan, R. F.; LaPointe, R. E.; Chandrasekhar, S. B.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (i) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902.
- (3) See for example: (a) Erker, G.; Dorf, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 777. (b) Tikkanen, W. R.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 1646. (c) Heck, R. F. *Organotransition Metal Chemistry*; Academic Press: New York, 1974. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. L.; Finke, R. J. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Bird, C. *Transition Metal Intermediates in Organic Synthesis*; Academic Press: New York, 1967. (f) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (g) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (h) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (i) Durfee, L. D.; McMullen, A. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 1463. (j) Walsh, P. J.; Hollander, F. J.; Bergman, B. G. *J. Am. Chem. Soc.* **1990**, *112*, 894. (k) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600. (l) Fryzuk, M. D.; Haddad, T. S.; Retting, S. J. *Organometallics* **1988**, *7*, 1224.
- (4) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -hafnium Compounds*; Ellis Horwood Ltd.: Chichester, England, 1986.
- (5) (a) Yasuda, H.; Kajihara, K.; Nagasuna, K.; Mashima, K.; Nakamura, A. *Chem. Lett.* **1981**, 719. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 915. (c) Yasuda, H.; Okamoto, T.; Yamamoto, H.; Nakamura, A. *Shokubai* **1986**, *97*. (d) Brauer, D. J.; Kruger, C. *Organometallics* **1982**, *1*, 207.
- (6) (a) Cohen, S. A.; Auburn, P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (b) Demersman, B.; Coupance, P. L.; Dixneuf, P. U. *J. Organomet. Chem.* **1985**, *297*, C35. (c) Wielstra, Y.; Gambarotta, S.; Chiang, M. Y. *Organometallics* **1988**, *7*, 1866. (d) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15. (e) Pez, G. J. *Chem. Soc., Chem. Commun.* **1977**, 560.
- (7) (a) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (c) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717. (d) Famili, A.; Faron, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435. (e) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, *8*, 2696.
- (8) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1988**, *110*, 1319.
- (9) (a) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1985**, *5*, 443. (b) De Boer, E. J. M. *J. Organomet. Chem.* **1978**, *153*, 53.
- (10) (a) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *103*, 146. (b) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (c) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (d) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.
- (11) Edema, J. J. H.; Duchateau, R.; Gambarotta, S.; Hynes, R.; Gabe, E. *Inorg. Chem.* **1991**, *30*, 154.

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