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Exhaustive Chlorination of $[B_{12}H_{12}]^{2-}$ without Chlorine Gas and the Use of $[B_{12}Cl_{12}]^{2-}$ as a Supporting Anion in Catalytic Hydrodefluorination of Aliphatic C−F Bonds

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S *Supporting Information*

ABSTRACT: The fully chlorinated *closo*-dodecaborate salt $Cs_2[B_{12}Cl_{12}]$ was prepared in high yield from $Cs_2[B_{12}H_{12}]$ and SO_2Cl_2 in acetonitrile at refluxing temperature. $[Ph_3C]_2[B_{12}Cl_{12}]$ was obtained by simple metathesis reactions. Catalytic hydrodefluorination of benzotrifluoride sp^3 C−F bonds was accomplished using $[Ph_3C]_2[B_{12}Cl_{12}]$ as a precatalyst and Et_3SiH as a stoichiometric reagent. Full consumption of the sp^3 C−F bonds in *p*-$FC_6H_4CF_3$ and $C_6F_5CF_3$ with a turnover number up to 2000 was achieved.

Weakly coordinating anions (WCAs) are an important concept in chemistry because they allow the use and study of highly reactive cations in condensed phases.[1−3] Over the last 2 decades, halogenated carborane anions $[HCB_{11}X_{11}]^-$ (X = H, Me, Hal) have been demonstrated to be an especially advantageous WCA class owing to their low basicity and nucleophilicity combined with a matchless stability and propensity for crystallization (Figure 1).[4,5] However, the arduousness inherent in the syntheses of both the parent $[HCB_{11}H_{11}]^-$ and its halogenated derivatives, and the consequently high cost, has so far prevented truly widespread use of halogenated carboranes. In contrast, their isoelectronic brethren, halogenated *closo*-dodecaborates $[B_{12}X_{12}]^{2-}$ (X = Hal), are derived from the much more easily accessible parent $[B_{12}H_{12}]^{2-}$ dianion,[6,7] especially in view of Knapp et al.'s recent report of a single-step, multigram synthesis from $NaBH_4$.[8] Fluorination of $[B_{12}H_{12}]^{2-}$ with F_2 was thoroughly examined recently by Strauss et al.[9] The 2− charge on $[B_{12}X_{12}]^{2-}$ makes them an unconventional choice for WCAs, and perhaps that is why they have rarely been considered for WCA applications despite having been known for decades.[9−11]

Our interest in WCAs stems from our studies on the use of highly electrophilic main-group cation species for C−F bond activation, where resistance of the anion to extreme levels of Brønsted and Lewis acidity is key.[12−14] Halogenated carborane anions performed very well, but the concerns over their cost and lengthy syntheses remained. Hence, we were heartened to learn from the work of Knapp et al.[8,15−17] and of Reed et al.[18] that $[B_{12}Cl_{12}]^{2-}$ can be a WCA comparable to the halogenated carboranes, albeit engendering considerably lower solubility. Isolation of the highly reactive $Me_2B_{12}Cl_{12}$, $[Et_3Si]_2[B_{12}Cl_{12}]$, and $H_2[B_{12}Cl_{12}]$ demonstrated the robustness of $[B_{12}Cl_{12}]^{2-}$, while similar $\nu(CH_2)$ frequencies in the $C_6H_7^+$ (protonated benzene) and ν(NH) in the R_3NH^+ salts of $[B_{12}Cl_{12}]^{2-}$ and $[HCB_{11}X_{11}]^-$ argued for comparably low basicity.[15−18] In this Communication, we present a new, simple, and chlorine gas-free method of synthesis of *closo*-dodecachlorododecaborate $[B_{12}Cl_{12}]^{2-}$ from $[B_{12}H_{12}]^{2-}$, as well as experiments demonstrating the competence of $[B_{12}Cl_{12}]^{2-}$ as a robust WCA in catalytic hydrodefluorination (HDF) of sp^3 C−F bonds (Scheme 1).

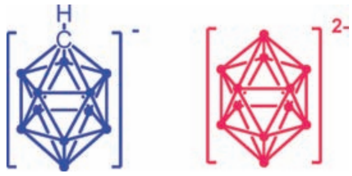

Figure 1. Representation of the monocarba-*closo*-dodecaborate(−) $[HCB_{11}H_{11}]^-$ anion (left) and *closo*-dodecaborate $[B_{12}H_{12}]^{2-}$ dianion (right). Dots at vertices represent boron atoms; each vertex is capped with a hydrogen atom.

Scheme 1. New Synthesis of the Perchlorinated Dodecaborate $[B_{12}Cl_{12}]^{2-}$

$$Cs_2[B_{12}H_{12}] \xrightarrow[\text{reflux/8-24 h}]{SO_2Cl_2\,/\,MeCN} Cs_2[B_{12}Cl_{12}]$$

Syntheses of polychlorinated dodecaborates have previously relied on the use of Cl_2 as the chlorinating agent. $[B_{12}H_6Cl_6]^{2-}$ was synthesized by the reaction of $[H_3O]_2[B_{12}H_{12}]$ with chlorine in water at 0 °C.[19] Selectivity in the partial chlorination of $[B_{12}H_{12}]^{2-}$ has been analyzed computationally.[20] Muetterties et al. first reported the synthesis of $[B_{12}Cl_{12}]^{2-}$ in 1964 by reacting $[B_{12}H_{12}]^{2-}$ with excess Cl_2 in an autoclave.[11] Knapp et al. reported an improved method in 2009 that avoided the high-pressure autoclave by passing chlorine gas through an aqueous solution of $Na_2B_{12}H_{12}$ at 100 °C for 40 h.[8] In the wake of our recent report[21] on the chlorination of a monocarba-*closo*-dodecaborate anion $[HCB_{11}H_{11}]^-$ with $SbCl_5$ or SO_2Cl_2, we set out to explore the potential utility of SO_2Cl_2 as the chlorination reagent in the synthesis of $[B_{12}Cl_{12}]^{2-}$. Compared to chlorine gas, SO_2Cl_2 is inexpensive, less hazardous to handle in the laboratory under standard safety precautions, and more amenable to use on different reaction scales.

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The direct reaction of 100 mg of $Cs_2[B_{12}H_{12}]$ with refluxing neat SO_2Cl_2 for 24 h only led to a mixture of various partially chlorinated $[B_{12}H_{12-x}Cl_x]^{2-}$, based on ^{11}B NMR evidence (Figure 2). The incomplete chlorination of $Cs_2[B_{12}H_{12}]$ by neat SO_2Cl_2 is likely due to the low solubility of $Cs_2[B_{12}H_{12-x}Cl_x]$ in neat SO_2Cl_2 because a white suspension was observed throughout the reaction. Converting $Cs_2[B_{12}H_{12}]$ to $(Et_3NH)_2[B_{12}H_{12}]$ did not drastically improve the solubility in SO_2Cl_2, and the reaction with $[Et_3NH]_2[B_{12}H_{12}]$ in neat SO_2Cl_2 did not lead to complete chlorination either. We noted that acetonitrile, in which $Cs_2[B_{12}H_{12}]$ is more soluble, was successfully used as a solvent for the fluorination of $K_2[B_{12}H_{12}]$ with F_2.[9] Refluxing $Cs_2[B_{12}H_{12}]$ in a 1:1 mixture of SO_2Cl_2 and acetonitrile for 24 h led to complete conversion to $Cs_2[B_{12}Cl_{12}]$ (Figure 2), which was isolated upon recrystallization from water.[22] We were able to obtain 75−82% yield of $Cs_2[B_{12}Cl_{12}]$ starting with 0.1, 1, or 10 g of $Cs_2[B_{12}H_{12}]$, and it was characterized by ^1H and ^{11}B NMR, IR spectroscopy, and elemental analysis.[23]

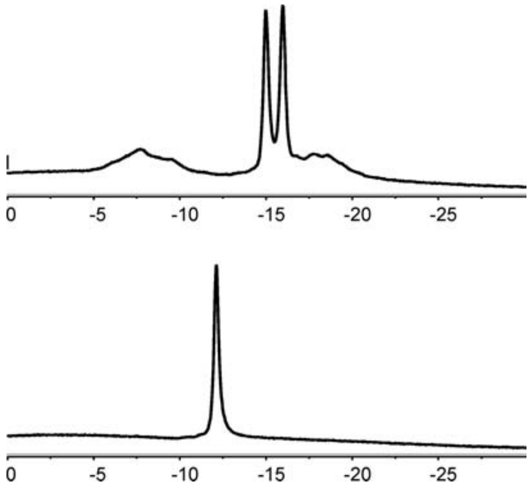
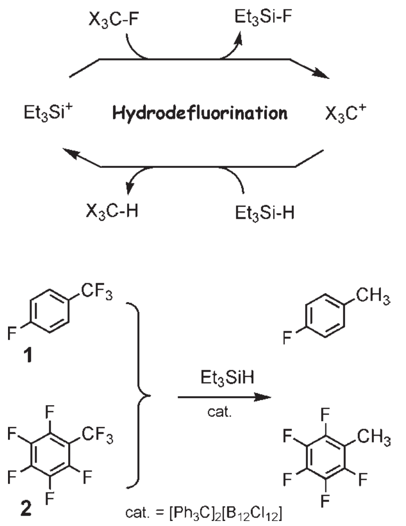


Figure 2. Top: ^{11}B NMR spectrum for the reaction of $Cs_2[B_{12}H_{12}]$ with refluxing SO_2Cl_2 for 24 h. Bottom: ^{11}B NMR spectrum for the reaction of $Cs_2[B_{12}H_{12}]$ with refluxing SO_2Cl_2 and acetonitrile for 8 h. The *x*-axis scale is in ppm.

Scheme 2. Proposed Mechanism of HDF and the Reactions with Benzotrifluorides under Study in This Work



Following our original publication on the chlorination of $Cs[HCB_{11}H_{11}]$ with SO_2Cl_2, we discovered that it was remarkably sensitive to the origin of the reagents and only worked well with select and unpurified reagents.[20] This may indicate that some unknown impurities perform a catalytic role in that reaction, but at present, we do not completely understand the origin of the observed effects. In order to rule out the possibility that the chlorination of $[B_{12}H_{12}]^{2-}$ might also be catalyzed by some impurities in the starting materials, the chlorination of $Cs_2[B_{12}H_{12}]$ was performed with recrystallized $Cs_2[B_{12}H_{12}]$, distilled acetonitrile, and distilled SO_2Cl_2 and also with protection[24] from light. All of these variations led to complete conversion to the $[B_{12}Cl_{12}]^{2-}$ product after 24 h at refluxing temperature.[22]

Using literature cation-exchange procedures,[8,17,18] we obtained $[Ph_3C]_2[B_{12}Cl_{12}]$. We have previously used trityl salts of $[B(C_6F_5)_4]^-$ and of halogenated carboranes as precatalysts for the HDF of aliphatic C−F bonds with Et_3SiH.[12] The proposed HDF mechanism and the reactions under study in this work are outlined in Scheme 2. The trityl salts are convenient to store and are readily converted to triethylsilylium by reaction with excess triethylsilane in the reaction mixture.

The results of the HDF reactions are summarized in Table 1. In all reactions, *o*-dichlorobenzene was used as the solvent. Et_3SiF and Et_2SiF_2[25] were observed as the Si−F products. Along with the Ar−CH_3 HDF products, Friedel−Crafts products from the attack on the aromatic rings of the solvent (or substrate and product) were also observed by ^{19}F NMR, as with other catalysts.[12] The HDF reactions of p-$FC_6H_4CF_3$ worked well using $[Ph_3C]_2[B_{12}Cl_{12}]$ as the precatalyst at 22 °C, with full consumption of the sp^3 C−F bonds, no conversion of the sp^2 C−F bond, and a turnover number (TON)[26] of ca. 2000. To further evaluate the competence of $[B_{12}Cl_{12}]^{2-}$, we performed HDF reactions with the more challenging substrate $C_6F_5CF_3$ (Table 1). At 22 °C, the reaction is fairly slow, with consumption of only 6% of the C−F bonds in 24 h. However, the HDF reaction accelerated dramatically at elevated temperature. Complete

Table 1. HDF Results (Ar−CF_3 → Ar−CH_3)

no.	substrate	T (°C)	time (h)	catalyst mol %[a]	Si−F convn %[b]	C−F convn %[b]	TON[c]
1	**1**	22	0.5	0.049	87	>97	2040
2	**2**	22	24	0.053	1	6	110
3	**2**	50	24	0.052	82	96	1850
4	**2**	80	1	0.052	90	>97	1920

[a] $[Ph_3C]_2[B_{12}Cl_{12}]$ was used as a catalyst in these reactions. Catalyst loading was calculated based on the moles of $[B_{12}Cl_{12}]^{2-}$ versus the moles of C−F bonds. [b] Conversion was based on the disappearance of C−F bonds or the appearance of Si−F bonds by ^{19}F NMR. [c] TON was calculated as the number of C−F bonds converted per each unit of $[Ph_3C]_2B_{12}Cl_{12}$.

or near-complete consumption of all sp^3 C−F bonds with a TON of ca. 2000 was achieved within 24 h at 50 °C and within 1 h at 80 °C. The poor reactivity at room temperature may largely reflect the much lower solubility of $[Ph_3C]_2[B_{12}Cl_{12}]$ compared with the carborane analogues. Nonetheless, these results illustrate that $[B_{12}Cl_{12}]^{2-}$ can be used as a WCA in HDF catalysis, which sustains thousands of turnovers, similarly to the results that we reported with halogenated carboranes as supporting anions.[12]

In summary, we report a new, straightforward, chlorine gas-free method for synthesis of the valuable $[B_{12}Cl_{12}]^{2-}$ dianion. It is also shown that $[B_{12}Cl_{12}]^{2-}$ can be used as a WCA for C−F bond activation mediated by electrophilic silylium species. The $[B_{12}Cl_{12}]^{2-}$-based catalysis showed longevity to comparable to that of carborane-based catalysis in the HDF reactions.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full synthetic procedures, spectroscopic methods, and HDF reaction details. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066–2090.

(2) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.

(3) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025–1027.

(4) (a) Reed, C. A. *Acc. Chem. Res.* **2010**, *43*, 121–128. (b) Reed, C. A. *Chem. Commun.* **2005**, *48*, 1669. (c) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133–139.

(5) Körbe, S.; Schreiber, P. J.; Michl, J. *Chem. Rev.* **2006**, *106*, 5028–5249.

(6) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3885–3886.

(7) Ellis, I. A.; Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1963**, *85*, 3885.

(8) (a) Geis, V.; Guttsche, K.; Knapp, C.; Scherer, H.; Uzun, R. *Dalton Trans.* **2009**, 2687–2694.

(9) Peryshkov, D. V.; Popov, A. A.; Strauss, S. H. *J. Am. Chem. Soc.* **2009**, *131*, 18393−18403 and references cited therein.

(10) Pitochelli, A. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 3228–3229.

(11) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 159–167.

(12) (a) Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852–2853. (b) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188–1190. (c) Gu, W.; Haneline, M. R.; Douvris, C.; Ozerov, O. V. *J. Am. Chem. Soc.* **2009**, *131*, 11203–11212. (d) Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2010**, *132*, 4946–4953.

(13) (a) Panisch, R.; Bolte, M.; Mueller, T. *J. Am. Chem. Soc.* **2006**, *128*, 9676–9682. (b) Klahn, M.; Fischer, C.; Spannenberg, A.; Rosenthal, U.; Krossing, I. *Tetrahedron Lett.* **2007**, *48*, 8900–8903.

(14) Douvris, C.; Stoyanov, E. S.; Tham, F. S.; Reed, C. A. *Chem. Commun.* **2007**, 1145–1147.

(15) Derendorf, J.; Keβler, M.; Knapp, C.; Rühle, M.; Schulz, C. *Dalton Trans.* **2010**, *39*, 8671–8678.

(16) Bolli, C.; Derendorf, J.; Keβler, M.; Knapp, C.; Scherer, H.; Schulz, C.; Warneke, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 3536–3538.

(17) Kessler, M.; Knapp, C.; Sagawe, V.; Scherer, H.; Uzun, R. *Inorg. Chem.* **2010**, *49*, 5223–5230.

(18) Avelar, A.; Tham, F. S.; Reed, C. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3491–3493.

(19) Sivaev, I. B.; Bregadze, V. I.; Sjöberg, S. *Collect. Czech. Chem. Commun.* **2002**, *67*, 679–727.

(20) Lepšík, M.; Srnec, M.; Hnyk, D.; Grüner, B.; Plešek, J.; Havlas, Z.; Rulíšek, L. *Collect. Czech. Chem. Commun.* **2009**, *74*, 1–27.

(21) Gu, W.; McCulloch, B. J.; Reibenspies, J. H.; Ozerov, O. V. *Chem. Commun.* **2010**, *45*, 2820−2822. An Addition/Correction is now available at http://www.rsc.org/suppdata/CC/c0/c001555e/addition.htm.

(22) Synthetic details for $Cs_2[B_{12}Cl_{12}]$. **1 g scale**: To a suspension of $Cs_2[B_{12}H_{12}]$ (1.00 g, 2.45 mmol) in acetonitrile (30 mL) in a Schlenk flask was slowly added SO_2Cl_2 (30 mL, 370 mmol). The mixture soon became a clear solution and was heated to reflux for 8 h. The removal of all volatiles gave a white solid, which was treated with 0.2 mL of a 10% NaOH aqueous solution and then recrystallized from hot water with 1.5 g of CsCl (8.9 mmol) to give $Cs_2[B_{12}Cl_{12}]$. Yield: 1.64 g (82%). **10 g scale**: To a suspension of $Cs_2[B_{12}H_{12}]$ (9.98 g, 24.3 mmol) in acetonitrile (300 mL) in a three-necked flask was slowly added SO_2Cl_2 (300 mL, 3.71 mol). The mixture soon became a clear solution and was heated to reflux. After 8 h, an aliquot was taken from the reaction mixture. The removal of all volatiles gave a white solid, which was redissolved in CD_3CN for ^{11}B NMR study, which showed that conversion was only ca. 95% complete. After 24 h, all volatiles were removed under vacuum to give a white solid, which was redissolved in CD_3CN for ^{11}B NMR study. The resulting white powder was recrystallized from hot water to give $Cs_2[B_{12}Cl_{12}]$. Yield: 16.03 g (81%). ^{11}B NMR (128 MHz, CD_3CN): δ −13.0 (s). (See a full description and data in the Supporting Information).

(23) In some reactions, complete conversion was accomplished in 8 h, but a 24 h reaction time is recommended for reproducibility.

(24) "Light" here means regular fluorescent laboratory lighting. The reaction apparatus was wrapped in aluminum foil for protection from light. We cannot help but wonder whether the observed effect of such protection is indeed due to protection from light or instead to perturbation of the thermal gradients within the reaction apparatus.

(25) Et_2SiF_2 presumably forms via redistribution of the substituents on silicon under Lewis acid catalysis.

(26) We calculate TON based on the amount of the $[B_{12}Cl_{12}]^{2-}$ counterion. It is not clear whether both cations associated with it can be catalytically engaged simultaneously at all times. If they are, then our TON values should be divided by 2.