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Sodium Tetrakis[(3,5-trifluoromethyl)phenyl]borate (NaBArF₂₄): Safe Preparation, Standardized Purification, and Analysis of Hydration

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Abstract

A safe, convenient preparation of the reagent sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (NaBArF₂₄) has been devised by utilizing a magnesium-bromine exchange reaction in the absence of metallic magnesium. Purified material was then rigorously dried over P₂O₅ (NaBArF₂₄ with < 500 ppm H₂O by mass) or recrystallized as a hydrate (NaBArF₂₄·2.6 ± 0.1H₂O). Accurate analysis of the water content of these samples by ¹H NMR was accomplished by using dimethylzirconocene [Cp₂Zr(CH₃)₂].

Introduction

Weakly-coordinating anions¹ such as the fluorinated tetraarylborates^{2,3} have enabled the study of very reactive cationic transition metal complexes and their applications in polymerization,⁴ C-H bond activation,⁵ and Lewis acid catalysis.⁶ Sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate, NaBArF₂₄ (**1**), the most commonly used salt and precursor for other reagents,⁷⁻⁹ was first utilized by Kobayashi in 1981.¹⁰ The numerous synthetic protocols that have been developed since that initial report all employ three basic steps: 1) formation of (3,5-bistrifluoromethyl)phenylmagnesium bromide, 2) quenching with NaBF₄ or BF₃·Et₂O to form the borate, and 3) aqueous cation exchange.^{3,7,8,11-14} While moderate to good yields have been reported for the synthesis of NaBArF₂₄, safety remains a major concern. The recent report by Leazer et al. confirms that while (3,5-bistrifluoromethyl)phenylmagnesium bromide is not a hazard by itself, explosive exothermic decomposition of trifluoromethylaryl Grignard reagents occurs in the presence of *any excess magnesium metal*.¹⁵ To date, every published procedure for the synthesis of NaBArF₂₄ generates the arylmagnesium halide intermediate in the presence of magnesium turnings or dust, often in refluxing ethereal solvent.^{3,7,8,11-14} The hazards associated with these methods prompted us to develop a new, safe protocol for preparation of pure, anhydrous NaBArF₂₄ on multigram scale that, in place of magnesium metal, employs an alkyl Grignard reagent to effect metal-halogen exchange. Discrepancies in the reported appearance of the product as well as the varied procedures for its purification and drying inspired us to formulate a standardized protocol that would consistently provide material at a high level of purity.

Results and Discussion

Following the reported procedure for magnesium-halogen exchange,^{15,16} isopropylmagnesium chloride (conveniently purchased as a solution in THF)¹⁷ was added to a solution of 1-bromo-3,5-bistrifluoromethylbenzene (**2**) in THF at -20 °C (Scheme 1).

Vacuum-dried sodium tetrafluoroborate was then added to the newly formed aryl Grignard reagent. After aqueous workup and extraction with diethyl ether, the crude NaBArF₂₄ mixed etherate (**3**) (soluble in CH₂Cl₂) was dried in vacuo at 100 °C for approximately 10 hours. The crude product (**5**) then appeared as a yellowish/tan solid (as has been noted in several literature preparations and for the commercially-available material). It was critical that this crude material *be washed with CH₂Cl₂* (initially chilled to -30 °C) to remove the colored impurity **4** and furnish a white powder, as prescribed by Brookhart⁷ and Boudjouk.⁸ The identity of the contaminant **4** has not been previously addressed in the literature, but by NMR analysis, it appears to be a triarylborate species (with a ¹¹B chemical shift distinct from NaBArF₂₄) arising from incomplete arylation. While the dichloromethane wash does remove a small portion of NaBArF₂₄ from the crude mixture, the overall yield (55–70% over several runs) is still comparable to that reported for other syntheses and this procedure can be easily scaled for the safe production of larger amounts of pure material.

It has previously been noted that NaBArF₂₄ is a hygroscopic salt, and the reported elemental analyses of hydrated samples had determined the presence of between 0.5 and 3 molar equivalents of H₂O per mole of NaBArF₂₄.^{10,12,18} The hydrate crystallizes from fluorobenzene, CH₂Cl₂,^{14,19} or CHCl₃³ as large cubic, colorless crystals.^{14,19} Drying this purified material had been previously accomplished by azeotropic removal of water with benzene¹³ or heating under vacuum.^{7,8,12,19} After drying the product using reasonable conditions described in earlier preparations (0.1 Torr, 100 °C, 48 h), we found that adventitious water was sometimes still present in the material, causing unsuspected reactions to occur in certain experiments. Thus, a somewhat more rigorous, yet operationally simple drying protocol was successfully executed — heating the sample to 120 °C at 0.1 Torr over P₂O₅ for 18 hours.

Given the degree of error inherent in elemental analysis measurements, a more accurate method was required to quantify the small amounts of water present in the NaBArF₂₄ samples. Using a known amount of dimethylzirconocene [Cp₂Zr(CH₃)₂]²⁰ (**6**) as a kinetic, stoichiometric trap for water enabled accurate analysis of the samples by ¹H NMR spectroscopy (Table 1). Dimethylzirconocene is known to react rapidly with 0.5 equivalent of water to produce [Cp₂Zr(CH₃)₂]₂O (**7**)²¹. The liberation of methane was complete within 1 hour in THF-*d*₈, and the results were reproducible in multiple trials. The amount of water in the sample was then calculated from the increase in integration for the signals of **7** relative to the integrals of the aryl protons of the added NaBArF₂₄ against an internal standard of hexamethylbenzene. Measuring the decrease in integration of the signals for **6** proved to be a less reliable method because a large excess of dimethylzirconocene is employed relative to the small amount of water present in the samples.

A series of control experiments was performed to determine the error inherent in the detection of water using this ¹H NMR protocol. It was found that J. Young resealable NMR tubes furnished the best results due to the sensitivity Cp₂Zr(CH₃)₂ to both air and moisture. The concentration of the hexamethylbenzene internal standard was set at a level (approximately 30 μM) so that its integration would be comparable, within an order of magnitude, to the peaks of interest. At very low concentrations of water (0.5–1.0 μmol in 0.5 mL THF-*d*₈), the method could reliably detect 36 ± 9 ppm H₂O in THF-*d*₈. Higher concentrations of water could be detected with lower percent error, 180 ± 10 ppm, due to more precise integration of the correspondingly larger peaks of interest.

As shown in Table 1, the amount of water calculated in the recrystallized sample of NaBArF₂₄ was 2.6 ± 0.1 mole equivalents. This value was corroborated by elemental analysis, and it also correlated closely with the molecular formula (NaBArF₂₄·2.5H₂O) given in a footnote of the original 1981 Kobayashi communication.¹⁰ The material that was dried in the absence of additional desiccant still showed a residual 0.034 ± 0.009 mole equivalents of water,

an amount not reliably detectable using current elemental analysis methods. The sample dried under vacuum over P_2O_5 was found to contain a similar amount of water, 0.021 ± 0.005 mol equivalents. The quantity of water present in these dried $NaBArF_{24}$ samples is extremely small, less than 500 ppm by mass in the P_2O_5 -dried material.

In summary, a modified synthesis of $NaBArF_{24}$ has been devised that ensures the absence of metallic magnesium by utilizing the magnesium-bromine exchange reaction with commercially available isopropylmagnesium chloride in THF. Using the newly developed procedure, the crude material could then be rigorously purified and dried over a desiccant, consistently resulting in $NaBArF_{24}$ of identical appearance and composition. Analysis of water content at the parts per million level by use of dimethylzirconocene proved to be a valuable 1H NMR-based technique for the rapid quantification of the water present in small $NaBArF_{24}$ samples. Expanded application of this procedure to other salts of weakly-coordinating anions would be appropriate. The preparation and use of extremely pure, dry $NaBArF_{24}$ by this method may improve activity of known catalysts and also may extend the use of $NaBArF_{24}$ to more water-sensitive, cationic transition metal systems.

Experimental

General Procedures

Unless otherwise noted, reactions and manipulations were performed at 23 °C in an inert atmosphere (N_2) glovebox or using standard Schlenk and high-vacuum techniques. Glassware was dried for a minimum of 12 h at a temperature of 180 °C or greater. All NMR spectra were obtained using Bruker AV-400 or DRX-500 MHz spectrometers at 22 °C at the indicated frequency. Chemical shifts are reported in parts per million (δ), coupling constants are reported in Hertz (Hz), and integrations are reported as number of protons. 1H NMR spectra were recorded at 400 MHz and chemical shifts were referenced to the residual protons in the solvent. ^{13}C NMR spectra are proton decoupled and were recorded at 100 MHz; chemical shifts were referenced to the solvent. ^{19}F

NMR spectra were recorded at 376 MHz and chemical shifts are reported relative to external $CFCl_3$. ^{11}B NMR spectra were recorded at 160 MHz; chemical shifts were referenced to an external standard of $BF_3 \cdot Et_2O$. Melting point values were obtained in capillary tubes sealed under N_2 and are uncorrected. Elemental analyses were performed at the University of California, Berkeley, Microanalytical Facility on a Perkin-Elmer 2400 Series II CHNO/S analyzer.

Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran was passed through a column of activated alumina under N_2 and sparged with N_2 prior to use. Acetone- d_6 and THF- d_8 (Cambridge Isotope Laboratories) were dried using standard procedures [$CaSO_4(s)$ for acetone- d_6 ; sodium/benzophenone ketyl for THF- d_8] and vacuum-transferred prior to use. Dimethylzirconocene (stored at -35 °C) was prepared according to a standard procedure,²⁰ but it is also commercially available from Aldrich Chemical, Strem Chemical, and Acros Organics. Sodium tetrafluoroborate was dried under 0.1 Torr at 120 °C for 18 h.

Sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBArF_{24}$ (1))

A 2.0 M solution of *i*-PrMgCl in THF (80 mL, 0.16 mol, 6.6 equiv) was added by addition funnel over 45 min to a stirred solution of 1-bromo-3,5-bistrifluoromethylbenzene (**2**) (25 mL, 0.14 mol, 5.8 equiv) in THF (120 mL) chilled to -20 °C. After the reaction was allowed to warm from -20 °C to 0 °C over 1 h, $NaBF_4$ (2.68 g, 0.024 mol, 1.0 equiv) was quickly added

as a solid under a stream of N₂. The mixture then stirred for 48 h at 23 °C (under N₂). (This long reaction time ensures high conversion to the tetraarylborate). The contents were then poured into a solution of Na₂CO₃ (44 g) and NaHCO₃ (20 g) in water (600 mL) (all workup procedures are not air-sensitive). This mixture was stirred vigorously for 1 h and then extracted with diethyl ether (4 × 200 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After filtration of the mixture and rotary evaporation of the filtrate, the crude NaBArF₂₄·xTHF/Et₂O (**3**) was dried at 100 °C/0.1 Torr for 10 h to yield a tan/yellow solid. Dichloromethane, chilled to −30 °C, (3 × 20 mL) was used to wash all colored contaminant and filter it away from the product, a fine white powder. The product was then heated in vacuo over P₂O₅ (0.1 Torr, 115 °C, 20 h) to yield pure, anhydrous NaBArF₂₄ (**1**) as a hygroscopic white powder (12.2 g, 57 % yield). mp 330–335 °C (decomp). Anal. Calcd for C₃₂H₁₂BF₂₄Na: C, 43.37; H, 1.36; Found: C, 43.37; H, 1.27. ¹H NMR (400 MHz, acetone-*d*₆): δ 7.79 (br s, 8 H), 7.66 (br s, 4 H); ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 161.5 (q, ¹J_{B-C} = 50.0 Hz), 134.6 (s), 129.1 (q, ²J_{C-F} = 31.5 Hz), 124.5 Hz (q, ¹J_{C-F} = 270 Hz), 117.5 (s); ¹⁹F NMR (376 MHz, acetone-*d*₆) δ −62.46 (s); ¹¹B (160 MHz, acetone-*d*₆) δ −7.18 (s). The dichloromethane filtrate was concentrated to a tacky brown/yellow solid that contained both NaBArF₂₄ and a contaminant **4**: ¹H NMR (400 MHz, acetone-*d*₆): δ 7.98 (br s, 2 H), 7.56 (br s, 1 H); ¹⁹F NMR (376 MHz, acetone-*d*₆) δ −62.12 (s); ¹¹B (160 MHz, acetone-*d*₆) δ −2.26 (s). A sample of NaBArF₂₄ product was recrystallized from fluorobenzene in air on the benchtop to yield NaBArF₂₄·2.6H₂O as large, cubic colorless crystals: mp 300–302 °C (decomp); Anal. Calcd for C₃₂H_{17.2}BF₂₄NaO_{2.6}: C, 41.19; H, 1.86; Found: C, 41.39; H, 1.76. A powdered sample of NaBArF₂₄·2.5H₂O was dried in vacuo in the absence of desiccant (100 °C, 0.1 Torr, 48 h): Anal. Calcd for C₃₂H₁₂BF₂₄Na (NaBArF₂₄): C, 43.37; H, 1.36; Found: C, 43.09; H, 1.16.

Typical procedure for analysis of H₂O content by Cp₂Zr(CH₃)₂ NMR titration

Dimethylzirconocene (**6**) (20.7 mg, 82.3 μmol) and hexamethylbenzene (1.8 mg, 11 μmol) were dissolved in THF-*d*₈ (0.50 mL) in a J. Young NMR tube. A ¹H NMR single-pulse spectrum was recorded: ¹H NMR (400 MHz, THF-*d*₈): δ 6.13 (s, 10 H, Cp of **6**), 2.21 (s, internal std.), −0.38 (s, 6H, Zr-CH₃ of **6**). Next, the hydrated NaBArF₂₄ sample (6–20 mg) was added to the tube under an inert atmosphere, resulting in the immediate evolution of CH₄ (g). After 1 h, a second ¹H NMR single-pulse spectrum was obtained: ¹H NMR (400 MHz, THF-*d*₈): δ 7.81 (br s, BArF), 7.58 (br s, BArF), 6.13 (s, Cp of **6**), 5.97 (s, Cp of **7**), 2.22 (s, internal std.), 0.21 (s, CH₄), −0.02 (s, Zr-CH₃ of **7**), −0.38 (s, 6H, Zr-CH₃ of **6**). No further change in integration was evident after longer periods of time. The resulting increase in integration for the signals of **7** could then be compared to the peaks attributed to BArF₂₄, integrating against the internal standard, to determine the amount of water present in the original NaBArF₂₄ sample.

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Scheme 1.
Magnesium metal-free synthesis of NaBArF₂₄ (**1**).

Table 1

$\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ ^1H NMR-analysis of NaBArF_{24} hydration in $\text{THF-}d_8$.

$\text{Cp}_2\text{Zr}(\text{CH}_3)_2 \xrightarrow[\text{THF-}d_8]{0.5 \text{ equiv H}_2\text{O}} [\text{Cp}_2\text{ZrCH}_3]_2\text{O}$		
	6	7
sample	purification conditions	$\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ analysis
1	recrystallized from $\text{C}_6\text{H}_5\text{F}$ in air	$\text{NaBArF}_{24} \cdot 2.6 \pm 0.1\text{H}_2\text{O}$
2	dried at 100 °C, 0.1 Torr, 48 h	$\text{NaBArF}_{24} \cdot 0.034 \pm 0.009\text{H}_2\text{O}$
3	dried at 120 °C, 0.1 Torr, 18 h, over P_2O_5	$\text{NaBArF}_{24} \cdot 0.021 \pm 0.005\text{H}_2\text{O}$