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Safe Preparation and Purification of Sodium Tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBArF_{24}$): Reliable and Sensitive Analysis of Water in Solutions of Fluorinated Tetraarylborates

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Summary: A safe, convenient preparation of the reagent sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBArF_{24}$) has been devised by utilizing a magnesium−bromine exchange reaction in the absence of metallic magnesium. Purified material was then rigorously dried over P_2O_5 ($NaBArF_{24}$ with <500 ppm H_2O by mass) or recrystallized as a hydrate ($NaBArF_{24}\cdot(2.6 \pm 0.1)H_2O$). Accurate analysis of the water content of these samples by ^1H NMR was accomplished by using dimethylzirconocene ($Cp_2Zr(CH_3)_2$).

Introduction

Weakly coordinating anions[1] 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, $NaBArF_{24}$ (**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-bis(trifluoromethyl)phenyl]magnesium bromide, (2) quenching with $NaBF_4$ or $BF_3\cdot Et_2O$ 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 $NaBArF_{24}$, safety remains a major concern. The recent report by Leazer et al. confirms that while [3,5-bis(trifluoromethyl)phenyl]magnesium bromide is not a hazard by itself, explosive exothermic decomposition of (trifluoromethyl)aryl Grignard reagents occurs in the presence of *any excess magnesium metal*.[15] To date, every published procedure for the synthesis of $NaBArF_{24}$ 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 $NaBArF_{24}$ on a 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

By 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-bis(trifluoromethyl)benzene (**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 $NaBArF_{24}$ mixed etherate (**3**) (soluble in CH_2Cl_2) was dried in vacuo at 100 °C for approximately 10 h. 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 CH_2Cl_2* (ini-

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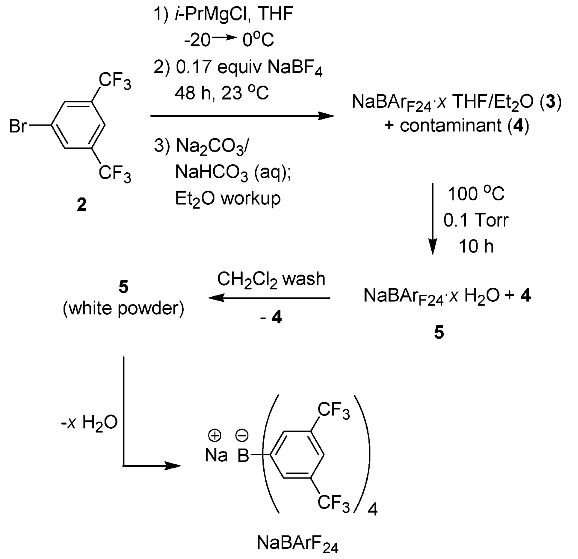
Scheme 1. Magnesium Metal Free Synthesis of $NaBArF_{24}$ (1)

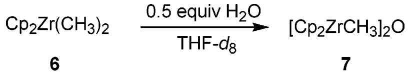


2

5

1

Table 1. $Cp_2Zr(CH_3)_2$ ^1H NMR Analysis of $NaBArF_{24}$ Hydration in THF-d_8



$$Cp_2Zr(CH_3)_2 \xrightarrow[\text{THF-}d_8]{0.5\text{ equiv }H_2O} [Cp_2ZrCH_3]_2O$$

6 **7**

sample	purification conditions	$Cp_2Zr(CH_3)_2$ anal.
1	recrystallized from C_6H_5F in air	$NaBArF_{24}\cdot(2.6 \pm 1)H_2O$
2	dried at 100 °C, 0.1 Torr, 48 h	$NaBArF_{24}\cdot(0.034 \pm 0.009)H_2O$
3	dried at 120 °C, 0.1 Torr, 18 h, over P_2O_5	$NaBArF_{24}\cdot(0.021 \pm 0.005)H_2O$

tially chilled to −30 °C) to remove the colored impurity **4** and furnish a white powder, as prescribed by Brookhart[7] 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 ^{11}B chemical shift distinct from $NaBArF_{24}$) arising from incomplete arylation. While the dichloromethane wash does remove a small portion of $NaBArF_{24}$ 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 $NaBArF_{24}$ is a hygroscopic salt, and the reported elemental analyses of hydrated samples had determined the presence of between 0.5 and 3 molar equiv of H_2O per mole of $NaBArF_{24}$.[10,12,18] The hydrate crystallizes from fluorobenzene, CH_2Cl_2,[14,19] or $CHCl_3$ [3] as large cubic, colorless crystals.[14,19] Drying this purified material had been previously accomplished by azeotropic removal of water with benzene[13] 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 P_2O_5 for 18 h.

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 $NaBArF_{24}$ samples. Using a known amount of dimethylzirconocene $[Cp_2Zr(CH_3)_2]$[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 equiv of water to produce $[Cp_2Zr(CH_3)]_2O$ (**7**).[21] The liberation of methane was complete within 1 h 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 $NaBArF_{24}$ 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 of $Cp_2Zr(CH_3)_2$ 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 of THF-d_8), the method could reliably detect 36 ± 9 ppm of H_2O 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 $NaBArF_{24}$ was 2.6 ± 0.1 mol equiv. This value was corroborated by elemental analysis, and it also correlated closely with the molecular formula ($NaBArF_{24}\cdot 2.5H_2O$) 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 mol equiv of water, an amount not reliably detectable using current elemental analysis methods. However, use of material dried in this way occasionally gave products that appeared to result from somewhat higher H_2O levels. The sample dried under vacuum over P_2O_5 was found to contain a smaller amount of water: 0.021 ± 0.005 mol equiv. The quantity of water present in the

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latter sample is less than 500 ppm by mass, and material dried in this way gave more reproducible results in water-sensitive reactions.

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 the 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 the activity of known catalysts and also may extend the use of $NaBArF_{24}$ to more water-sensitive, cationic transition-metal systems.

Experimental Section

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 and 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-bis(trifluoromethyl)benzene (**2**; 25 mL, 0.14 mol, 5.8 equiv) in THF (120 mL) chilled to −20 °C. After the reaction mixture was warmed from −20 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 N_2. The mixture then was stirred for 48 h at 23 °C (under N_2). (This long reaction time ensures high conversion to the tetraarylborate). The contents were then poured into a solution of Na_2CO_3 (44 g) and $NaHCO_3$ (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 Na_2SO_4. After filtration of the mixture and rotary evaporation of the filtrate, the crude $NaBArF_{24}{\cdot}x$THF/Et_2O (**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 P_2O_5 (0.1 Torr, 115 °C, 20 h) to yield pure, anhydrous $NaBArF_{24}$ (**1**) as a hygroscopic white powder (12.2 g, 57% yield). Mp: 330−335 °C dec. Anal. Calcd for $C_{32}H_{12}BF_{24}Na$: 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). $^{13}C\{^1H\}$ 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). ^{19}F NMR (376 MHz, acetone-d_6): δ −62.46 (s). ^{11}B NMR (160 MHz, acetone-d_6): δ −7.18 (s). The dichloromethane filtrate was concentrated to a tacky brown-yellow solid that contained both $NaBArF_{24}$ and the contaminant **4**: ^1H NMR (400 MHz, acetone-d_6) δ 7.98 (br s, 2 H), 7.56 (br s, 1 H); ^{19}F NMR (376 MHz, acetone-d_6) δ −62.12 (s); ^{11}B NMR (160 MHz, acetone-d_6) δ −2.26 (s). A sample of $NaBArF_{24}$ product was recrystallized from fluorobenzene in air on the benchtop to yield $NaBArF_{24}{\cdot}2.6H_2O$ as large, cubic colorless crystals: mp 300−302 °C dec. Anal. Calcd for $C_{32}H_{17.2}BF_{24}NaO_{2.6}$: C, 41.19; H, 1.86. Found: C, 41.39; H, 1.76. A powdered sample of $NaBArF_{24}{\cdot}2.6H_2O$ was dried in vacuo in the absence of desiccant (100 °C, 0.1 Torr, 48 h). Anal. Calcd for $C_{32}H_{12}BF_{24}Na$ ($NaBArF_{24}$): C, 43.37; H, 1.36; Found: C, 43.09; H, 1.16.

Typical Procedure for Analysis of H_2O Content by $Cp_2Zr(CH_3)_2$ 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−CH_3 of **6**). Next, the hydrated $NaBArF_{24}$ sample (6−20 mg) was added to the tube under an inert atmosphere, resulting in the immediate evolution of CH_4 (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, CH_4), −0.02 (s, Zr−CH_3 of **7**), −0.38 (s, 6H, Zr−CH_3 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 $BArF_{24}$, integrated against the internal standard, to determine the amount of water present in the original $NaBArF_{24}$ sample.

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