Synthesis and Reactivity of Fluorinated Triaryl Aluminum Complexes

Darren M. C. Ould, Jamie L. Carden, Rowan Page, and Rebecca L. Melen*

ABSTRACT: The addition of the Grignard 3,4,5-ArF\(_2\)MgBr to aluminum(III) chloride in ether generates the novel triarylanal Al(3,4,5-ArF\(_3\))-OEt\(_2\). Attempts to synthesize this alane via transmetalation from the parent borane with trimethylaluminum gave a dimeric structure with bridging methyl groups, a product of partial transmetalation. On the other hand, the novel alane Al(2,3,4-ArF\(_3\)) \(_2\) was synthesized from the parent borane and trimethylaluminum. Interestingly, the solid-state structure of Al(2,3,4-ArF\(_3\)) \(_2\) shows an extended chain structure resulting from neighboring Al···F contacts. Al(3,4,5-ArF\(_3\))-OEt\(_2\) was then found to be an effective catalyst for the hydroboration of carbonyls, imines, and alkynes with pinacolborane.

INTRODUCTION

Since the ground-breaking discovery of frustrated Lewis pairs (FLPs) in 2006\(^1\), the use of triarylboranes to aid organic transformations has rapidly grown in the past 20 years.\(^2,3\) Interestingly though, the use of the heavier aluminum analogues has received notably less attention. Pohlmann and Brinckmann successfully prepared tris(pentafluorophenyl)-alane [Al(C\(_6\)F\(_5\))\(_3\)] as the Et\(_2\)O adduct in 1965,\(^4\) but no further reports were made until the analogous THF adduct was generated in 1995.\(^5\) Since these reports there have been disputes in the literature regarding the Lewis acidity of Al(C\(_6\)F\(_5\))\(_3\) and whether it is a stronger Lewis acid than B(C\(_6\)F\(_5\))\(_3\), with claims by Lee et al. and Stahl et al. that the latter is the much stronger Lewis acid.\(^6,7\) On the other hand, a number of experimental and computational observations contradict this view and support Al(C\(_6\)F\(_5\))\(_3\) being the stronger Lewis acid.\(^8\)\(^−\)\(^10\) A possible explanation for the disagreement in the Lewis acidity of Al(C\(_6\)F\(_5\))\(_3\) is its tendency to form strong adducts with Lewis bases, which in turn quenches its reactivity. In fact, it was not until 2016 that the unsolvated structure of Al(C\(_6\)F\(_5\))\(_3\) was reported by Chen et al., who achieved this by transmetalation from B(C\(_6\)F\(_5\))\(_3\) with AlEt\(_3\) in hexane.\(^11\)

Since its first isolation as a THF adduct, Al(C\(_6\)F\(_5\))\(_3\) has been used in optimizations toward sequential retro-ene arylation and [3,3]-sigmatropic rearrangement/nucleophilic arylation reactions.\(^12,16\) Additionally, Al(4-ArF\(_3\))\(_3\) has been used in optimizations toward sequential retro-ene arylation and [3,3]-sigmatropic rearrangement/nucleophilic arylation reactions.\(^18,19\)

Grignard C\(_6\)F\(_5\)MgBr in ether led to an explosion, as did heating a solution of AlEt\(_3\) with B(C\(_6\)F\(_5\))\(_3\) to 70 °C.\(^4\) Chen proposed that the thermal and shock sensitive nature of unsolvated Al(C\(_6\)F\(_5\))\(_3\) derives from the ability of the compound to readily decompose to form strong Al···F bonds and explosive tetrafluorobenzene. This was observed in the solid-state structure of the compound which exists as a dimer [Al(C\(_6\)F\(_5\))\(_3\)]\(_2\) that displayed close intermolecular Al···F interactions between the aluminum center of one molecule and an ortho-fluorine atom of a second molecule.\(^11\)

Literature reports of fluorinated triarylanalates with alternate fluorine substitution patterns to Al(C\(_6\)F\(_5\))\(_3\) are surprisingly sparse (Figure 1). One example includes the use of Al(2,3,5,6-ArF\(_4\))\(_3\) for FLP assisted H\(_2\) and olefin activation.\(^17\) Additionally, Al(4-ArF\(_3\))\(_3\) has been used in optimizations toward sequential retro-ene arylation and [3,3]-sigmatropic rearrangement/nucleophilic arylation reactions.\(^18,19\)

Given our group’s recent interest in the borane B(3,4,5-ArF\(_3\))\(_2\),\(^20−22\) we were inspired to synthesize its aluminum analogue, in part due to the absence of ortho-positioned fluorine atoms. We propose that the alane counterpart would possess similar Lewis acidity as Al(C\(_6\)F\(_5\))\(_3\), but devoid of ortho-fluorine atoms, it may offer more stability.

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Herein, we report the synthesis of several new alanes bearing fluorinated aryl rings and explore their structural properties. In addition, we explore their reactivity as a catalyst for the reduction of carbonyls, imines, and alkynes with the terminal reductant pinacolborane (HBpin).

**RESULTS AND DISCUSSION**

Early attempts to synthesize unsolvated tris(3,4,5-trifluorophenyl)alane, Al(3,4,5-Ar F)₃, procedurally mirrored that of the previously reported unsolvated tris(perfluorophenyl)alane, Al(C₆F₅)₃, by Chen.¹¹ Trimethylaluminum (1 M in hexane) was added to B(3,4,5-Ar F)₃ (1) in hexane and left undisturbed for 2 days at room temperature. After this time crystals suitable for single-crystal X-ray diffraction had formed. The ¹H NMR spectrum of these crystals showed the expected aromatic signal at δ = 6.87 ppm, but more significantly, an upfield singlet resonance at δ = −0.39 ppm was also present, with an integral ratio of 6:2 compared to the aromatic signal. Unexpectedly, structural refinement of the single-crystal data revealed that an aluminum dimer with bridging methyl groups and only one aryl group had formed (2), as opposed to the expected Al(3,4,5-Ar F)₃ triarylalane (Scheme 1). Given the equivalence of the terminal and bridging methyl groups in the compound, variable temperature ¹H NMR studies were performed. At −80 °C, the signals were found to resolve; however, results were inconclusive due to the reduced solubility of the species (see the Supporting Information).

The formation of 2 can be rationalized as a partial transmetalation reaction in which only one of the aryl groups from the starting borane has transferred, leaving two methyl groups from the trimethylaluminum still bonded. Repeating this transmetalation reaction at 40 °C still failed to give complete transfer of all three aryl groups to the aluminum center. Recent work by Stammler et al. on the bonding of Al₂Me₆ suggests that the bridging CH₃ groups are assignable to two highly ionic 2e,3c bonds with tetra-coordinate aluminum atoms.²³ Similar dimeric species containing 2e,3c bonds have

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**Scheme 1. Synthesis of μ₂-Dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane] from Partial Transmetallation**
been recorded from incomplete transmetalation of B(C_{6}F_{5})_{3} with AlMe_{3}.^{24}

![Figure 2](https://dx.doi.org/10.1021/acs.inorgchem.0c01076)

*Figure 2. Solid-state structure of μ-dimethyl-bis[(3,4,5-trifluorophenyl)methyl-alane]. H atoms are omitted for clarity, and thermal ellipsoids are drawn at 50% probability.*

Inspection of the solid-state structure of dimer 2 (Figure 2), which crystallizes in the triclinic space group $\mathbf{P}$ with half a molecule in the asymmetric unit, revealed an Al(1)···Al(1') distance of 2.599(2) Å. The bridging Al(1)···C(1) bond was measured at 2.096(3) Å, which is appreciably longer than the terminal Al(1)···C(2) bond (1.940(5) Å). Interestingly, the Al(1)···C(1') bridging bond length is longer than that of Al(1)···C(1), measuring 2.134(3) Å and showing asymmetry in the dimer.

Measuring the bond angles around the aluminum center shows a C(2)···Al(1)···C(3) bond angle of 116.7(2)$^\circ$, which is approximately 7$^\circ$ lower than what is seen in AlMe_{3}. However, the C(1)···Al(1)···C(3) bond angle measures 106.5(1)$^\circ$, which is comparable to that seen in Al_{3}Me_{6}.^{23}

Although the transmetalation reaction did not give the desired 3,4,5-ArF$^5$ derived triarylalane, use of the novel B(2,3,4-ArF)$^3$, triarylborane (3, Figure 3, top) under the same conditions gave the expected unsolvated Al(2,3,4-ArF)$^3$ alone (4) (Scheme 2) from the transmetalation reaction. Initially 4 was characterized using single-crystal X-ray diffraction, where it crystallizes in the orthorhombic $\mathbf{P}b\mathbf{a}$ space group, with one molecule present in the asymmetric unit (Figure 3, bottom). 4 could also be isolated as the THF adduct. The solid-state configuration revealed the expected triarylalane structure, with the three 2,3,4-fluorinated aryl groups coordinated to the aluminum center. The geometry of Al(2,3,4-ArF)$^3$ is similar to that of the parent borane, in that it is near trigonal planar, with C···Al···C bond angles measuring 115.0(2)$^\circ$, 121.5(2)$^\circ$, and 115.9(2)$^\circ$.

Analysis of the unit cell of 4 shows short Al···F contacts, where the ortho-fluorine from one aryl group interacts with the aluminum center on a neighboring triarylalane. This donation from the ortho-fluorine creates a long chain arrangement in the packing structure of 4, where this bridging ortho-fluoride interaction is repeated (Figure 4). This Al···F interaction is strong, as seen by the Al···F distance of 2.034(3) Å. As a consequence of this specific chain formation, π-stacking between two of the aryl groups in neighboring alanes (one from each triarylalane) is permitted, with the two aryl plane distances measuring 3.401(5) Å. The long chain arrangement of 4 is different to that seen in the unsolvated Al(C_{6}F_{5})_{3}, where Chen reports a dimeric packing structure of the alane through ortho-fluorine atoms.^{12}

Due to difficulties in the synthesis of Al(3,4,5-ArF)$^3$ by transmetalation, a Grignard method was instead adopted from 1-bromo-3,4,5-trifluorobenzene and aluminum trichloride in ether solvent (Scheme 3). Upon workup, the $^1$H NMR spectrum in C_{6}D_{6} showed the expected aryl proton signal at $\delta = 6.99$ ppm, but in addition it also showed stoichiometric ether present, with signals appearing at $\delta = 3.00$ ppm and $\delta = 0.28$ ppm. The latter is much more upfield compared to free uncoordinated ether. The $^{19}$F NMR spectrum shows the expected two signals in a 2:1 ratio at $\delta = -153.5$ ppm and $\delta = -160.7$ ppm, respectively.

The solid-state structure of triarylalane 5 was obtained, and structural refinement found that it crystallizes in the triclinic $\mathbf{P}$ space group with one molecule in the asymmetric unit. The solid-state structure also showed that the triarylalane exists as an etherate adduct, Al(3,4,5-ArF)$^3$,OEt_{2} (5) (Figure 5), as was suggested from the $^1$H NMR spectrum. The coordination of ether means that unlike in 4, 5 adopts a near tetrahedral geometry, with O···Al···C bond angles of 104.1(2)$^\circ$, 104.5(2)$^\circ$, and 107.1(2)$^\circ$.

Density functional theory (DFT) was then employed to better understand the structural properties possessed by these triarylalanes. Initially, geometry optimization and vibrational frequency calculations on the unsolvated structures were
undertaken using the theory M06-2X/cc-pVDZ. Natural bond orbital (NBO) analysis showed a significantly greater buildup of positive charge at the aluminum center than at the boron center in the analogous triarylboranes, which led us to believe these triarylalanes would show enhanced Lewis acidic behavior (see the Supporting Information). To quantify this, fluoride ion affinity (FIA) calculations were performed (Table 1).

As the fluoride ion is relatively small and highly basic, it will interact with most Lewis acids. At this level of theory, the well-known strong Lewis acid B(C₆F₅)₃ had a FIA of 459 kJ mol⁻¹, similar to that previously reported. Proceeding with this, the triarylalanes Al(3,4,5-ArF)₃ and Al(2,3,4-ArF)₃ were found to have a FIA of 511 and 501 kJ mol⁻¹, respectively, whereas their triarylborane counterparts B(3,4,5-ArF)₃ and B(2,3,4-ArF)₃ produced values of 427 and 404 kJ mol⁻¹ accordingly. What is interesting about these values is that the triarylalanes appear to be approximately 15% more Lewis acidic than their triarylborane counterparts.

With Al(3,4,5-ArF)₃·OEt₂ (5) in hand, its reactivity was probed by using it in the first reported example of triarylalane-assisted hydroboration reduction catalysis. For the optimization conditions, the hydroboration of acetophenone with HBpin was performed (Table 2). Initial use of 5 mol % catalytic loading at room temperature proved kinetically slow, as did increasing the catalytic loading to 10 mol % 5. However,
use of 10 mol % 5 at 70 °C gave quantitative conversion to the boronate ester in 6 h. Switching the solvent from CDCl₃ to benzene-d₆ gave no deleterious effect, but moving from 1.2 equiv to stoichiometric HBpin did. Testing alternative borane sources found that neither 9-BBN nor HBcat were reactive toward the hydroboration of acetophenone.

Proceeding with the optimum conditions of 10 mol % precatalyst 5, 1.2 equiv of HBpin, and 70 °C in CDCl₃, the substrate scope was expanded to determine the versatility and suitability of 5 as a catalyst for hydroboration reduction (Scheme 4).

First, aldehydes were readily reduced within 2 h and obtained as alcohols in high isolated yields up to 97% (6a–d), with little discrepancy in tolerance between electron-withdrawing, electron-donating, and bulky substrates. Likewise, ketones and aldimines were readily reduced, with smooth conversion to the product and excellent isolated yields upon hydrolysis workup (7a–d, 8a–d). We then investigated the reduction of C–C multiple bonds. Preliminary studies with the olefins styrene, alpha-methylstyrene, 4-chlorostyrene, and 4-(trifluoromethyl)styrene were promising, showing good conversions (>90%) in 24–48 h. Finally, terminal alkynes were also hydroborated efficiently into their corresponding boronate esters (9a–d), with bulky, along with electron-withdrawing and electron-donating, substituents being tolerated. The internal alkynes diphenylacetylene and 1-phenyl-1-propyne showed no conversion under these conditions. Note boronate esters 9a–d were stable even under basic conditions.

Table 2. Optimization of Hydroboration Catalysis

| entry | catalyst loading (mol %) | T (°C) | borane source (equiv) | yield | time (h) |
|-------|--------------------------|--------|-----------------------|-------|----------|
| 1     | 0                        | 25     | HBpin (1.2)           | <5%   | 24       |
| 2     | 5                        | 25     | HBpin (1.2)           | <5%   | 24       |
| 3     | 10                       | 25     | HBpin (1.2)           | <5%   | 24       |
| 4     | 0                        | 70     | HBpin (1.2)           | <5%   | 24       |
| 5     | 5                        | 70     | HBpin (1.2)           | 68%   | 24       |
| 6     | 10                       | 70     | HBpin (1.2)           | >95%  | 6        |
| 7     | 10                       | 70     | HBpin (1.2)           | >95%  | 6        |
| 8     | 10                       | 70     | HBpin (1.0)           | 85%   | 24       |
| 9     | 10                       | 70     | HBcat (1.2)           | <5%   | 24       |
| 10    | 10                       | 70     | 9-BBN (1.2)           | <5%   | 24       |

*Acetophenone (0.2 mmol, 24 mg). *Conversion determined by ¹H NMR spectroscopy with internal mesitylene standard (0.1 mmol, 14 mL). *Benzene-d₆ solvent instead of CDCl₃.

Scheme 4. Hydroboration of Aldehydes, Ketones, Aldimines, and Alkynes with HBpin using 5

**Time taken to reach quantitative conversion by ¹H NMR spectroscopy. Isolated yields in parentheses.**
**EXPERIMENTAL SECTION**

General Experimental. Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using standard Schlenk and glovebox techniques. With the exception of THF, Et2O, and deuterated solvents, all solvents used were dried by passing them through an alumina column incorporated into an MB SPS-800 solvent purification system, degassed, and finally stored in an ampule fitted with a Teflon valve under a dinitrogen atmosphere. THF was dried over molten potassium for 3 days and distilled over argon, whereas Et2O was dried over sodium wire and benzophenone before being distilled over argon. Deuterated solvents were dried over calcium hydride, distilled, freeze–pump–thaw degassed, and stored over 3 Å molecular sieves in a glovebox. Starting materials were purchased from commercial suppliers and used as received. 1H, 13C{1H}, 19F, and 11B NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) and are referenced to CDCl3 (7.26/77.16 ppm) or C6D6 (−6.8 ppm). Elemental analysis was performed by Dr. Nigel Howard of the University of Cambridge, and the closure of our house elemental analysis (EA) facilities, and the description of signals includes s = strong, m = medium, w = weak, sh = shoulder, and br = broad. Mass spectra were measured by the School of Chemistry in Cardiff University on a Waters LCT Premier/XE or a Waters GCT Premier mass spectrometer. The description of signals includes s = strong, m = medium, w = weak, sh = shoulder, and br = broad. Mass spectra were measured by the School of Chemistry in Cardiff University on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Elemental analysis was performed by Dr. Nigel Howard at Cambridge University.

Note 1: Caution! The aluminum compounds prepared in this manuscript are potentially shock and thermally sensitive due to the potential formation of benzene intermediates. Appropriate care should be taken.

Note 2: Due to the potential for benzene formation, lack of in-house elemental analysis (EA) facilities, and the closure of our laboratory as well as the external EA facilities due to the COVID-19 pandemic, elemental analysis of some of the compounds was not performed.

**General Procedure 1.** The triarylboranes were synthesized in a procedure adapted from Lancaster28 whereby magnesium turnings (1.0 equiv), BF3·OEt2 (0.8 mL, 6.7 mmol, 0.33 equiv), and BF3·OEt2 (0.8 mL, 6.7 mmol, 0.33 equiv). Yield: 0.38 g, 0.93 mmol, 14%. 1H NMR (400 MHz, CD2Cl2, 295 K) δ/ppm: 6.43–6.38 (m, 6H, Ar–H). 13C{1H} NMR (126 MHz, CD2Cl2, 295 K) δ/ppm: 151.5–150.6 (m, 3C, Ar), 154.2–153.5 (m, 3C, Ar), 141.3–140.3 (m, 3C, Ar), 139.1–138.8 (m, 3C, Ar), 132.3 (ddd, JFC = 12.9 Hz, JFC = 3.7 Hz, 3C), 122.8 (dd, JF = 16.7 Hz, JFC = 3.1 Hz, 3C). 19F{1H} NMR (126 MHz, CD2Cl2, 295 K) δ/ppm: 62.6 (s), 19F{1H} NMR (376 MHz, CD2Cl2, 295 K) δ/ppm: −121.6 (dd, JF = 20.9 Hz, JFC = 12.4 Hz, 3F), −126.0 (dd, JF = 20.9 Hz, JFC = 12.4 Hz, 3F), −160.8 (t, JFC = 20.9 Hz, 3F) HRMS (ES+) [M]+ [C18H6BF9]+: calcd 404.0410; found 404.0419.

**General Procedure 2.** The parent borane (1.0 equiv) was suspended in hexane (3 mL). To this, trimethylaluminum (1.0 equiv) was added dropwise and the reaction was left undisturbed for 4 days. During this time, crystals of the alane were developed. The solvent level was reduced by removal in vacuo and placed in the freezer at −40 °C to ensure all the product had crystallized out. The hexane solvent was removed via pipet, and the crystals were briefly dried in vacuo to give the product.

**Synthesis of 1,2-Dimethyl-bis[3,4,5-trifluorophenyl]methyl-alane (1). Caution! This compound is potentially shock and thermally sensitive; appropriate care should be taken.**

1,2-Dimethyl-bis[3,4,5-trifluorophenyl]methyl-alane was synthesized in accordance with general procedure 2, using tris(3,4,5-trifluorophenyl)borane (210 mg, 0.51 mmol, 1.0 equiv) and trimethylaluminum (0.25 mL, 0.51 mmol, 1.0 equiv, 2.0 M solution in hexanes). Yield: 158 mg, 0.42 mmol, 83%. Mp: 105–110 °C. 1H NMR (500 MHz, CD2Cl2, 295 K) δ/ppm: 6.87 (ov dd, JFH = 8.5 Hz, 3H, Ar–H), −0.39 (s, 12H, CH2). 13C{1H} NMR (126 MHz, CD2Cl2, 295 K) δ/ppm: 151.5 (ddd, JFC = 256 Hz, JFC = 12.3 Hz, JFC = 1.6 Hz, 4C, mC), 141.4 (dt, JFC = 254 Hz, JFC = 12.3 Hz, 2C, pC), 138.5 (2C, C–C), 121.9 (1.16 Hz, JFC = 3.0 Hz, 6C, cC), −79.7 (4C, CH3). 11B NMR (376 MHz, CD2Cl2, 295 K) δ/ppm: −133.3 (dd, JF = 19.8 Hz, JFB = 5.8 Hz, 4F, mF) −158.2 (s, 2F, pF). IR νmax (cm−1): 1516 (m), 1387 (m), 1302 (mH), 1198 (w), 1088 (m), 1030 (m), 878 (m), 849 (m), 654 (br, m), 579 (br, m). Note: approximately 8% impurity was observed in the 19F NMR spectrum due to the parent borane and other unidentified partially transmetalated species.

**Synthesis of Tris(2,3,4-trifluorophenyl)borane (2).**

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1H NMR (500 MHz, CD2Cl2, 295 K) δ/ppm: 7.29–7.16 (m, 6H, Ar–H). 13C{1H} NMR (126 MHz, CD2Cl2, 295 K) δ/ppm: 152.3–150.2 (m, 6C, Ar), 144.2–141.9 (m, 3C, Ar), 136.4 (3C, C–B), 122.8–121.2 (m, 6C, Ar). 19F{1H} NMR (160 MHz, CD2Cl2, 295 K) δ/ppm: 64.5 (s). 19F NMR (471 MHz, CD2Cl2, 295 K) δ/ppm: −133.3 (dd, JFC = 20.0 Hz, JFC = 7.2 Hz, 6F, mF) −158.2 (tt, JFC = 20.0 Hz, JFC = 6.8 Hz, 3F, pF). EA calc for C18H6BF3C: C, 53.51; H, 1.50; N, 0.00. Found: C, 53.27; H, 1.41; N, 0.00.

**Synthesis of Tris(2,3,4-trifluorophenyl)borane (3).**

Tris(2,3,4-trifluorophenyl)borane was synthesized according to general procedure 1, using trimethylaluminum (0.37 mL, 0.74 mmol, 1.0 equiv) and 1,2-dibromoethane was added if the Grignard reaction was slow to initiate. After it stirred at ambient temperature for 1 h, the mixture was transferred via filter cannula to a stirred solution of BF3·OEt2 (0.33 equiv) in toluene (30 mL). The diethyl ether solvent was removed in vacuo, and the resulting toluene solution was heated to reflux for 3 h. After this time the reaction was allowed to stir for 16 h at ambient temperature, after which the solvent was removed in vacuo. The resulting solid was subjected to a 2-fold sublimation (120 °C, 1 x 10−3 mbar), whereupon the pure borane was collected as a white crystalline solid.

**Characterization of Tris(2,3,4-trifluorophenyl)borane-THF (4-THF).**

1H NMR (400 MHz, CD2Cl2, 295 K) δ/ppm: 7.10–7.00 (m, 3H, Ar–H). 6.99–6.88 (m, 3H, Ar–H), 4.39 (s, 6H, THF), 2.64–2.13 (m, 6H, THF). 13C{1H} NMR (101 MHz, CD2Cl2, 295 K) δ/ppm: 156.5 (ddd, JFC = 236.2 Hz, JFC = 2.9 Hz, 3C, cC), 152.2 (ddd, JFC = 249.5 Hz, JFC = 10.0 Hz, 3C, pC), 139.4 (dd, JFC = 253.9 Hz, JFC = 22.3 Hz, 3C, mC–F), 132.5–132.2 (m, 3C, cC–H), 126.2 (d, JFC = 5.15 Hz, 3C, iC), 113.4 (d, JFC = 15.5 Hz, 3C, mC–H), 74.0 (s, 4C, THF), 25.7 (s, 4C, C-...
Due to the potential for benzyne formation, the product was not a white powder (1.58 g, 3.2 mmol, 48%). Crystals suitable for single-crystal X-ray diffraction were obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**CONCLUSIONS**

In conclusion, we have reported the synthesis of Al(3,4,5-ArF)_3·Et,O, which was prepared from the corresponding Grignard solution. Attempts to synthesize the triarylalane from transmetalation resulted in the formation of the bridging dimer μ₂-Al(3,4,5-ArF)_2Me_2. On the other hand, the synthesis of the novel triarylalane Al(2,3,4-ArF)_3 was found to form an extended chain structure via Al–F strong contacts. Lastly, Al(3,4,5-ArF)_3·Et,O was found to be an efficient catalyst for hydride reduction, with wide tolerance toward carbonyls, imines, and alkynes. Further studies are underway in our laboratory to explore the full potential of these triarylalanes in catalysis.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01076.

Catalysis information, NMR spectra, XRD data, and DFT calculations (PDF)

Accession Codes

CCDC 1996144—1996147 and 2022498 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

Information about the data that underpins the results presented in this article, including how to access them, can be found in the Cardiff University data catalogue at http://doi.org/10.17035/d.2020.0114501208.

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