



Note

A straightforward preparation of acetonitrile ligated silver perfluoroalkoxy aluminate $[\text{Ag}(\text{NCCH}_3)_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

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ABSTRACT

Acetonitrile ligated silver perfluoroalkoxy aluminate can be applied as versatile anion transfer reagent for several complexes with weakly coordinating counter anions. Its synthesis, however, is not as inexpensive and easy as it would be desirable. Accordingly, a new and straightforward synthesis for this useful compound, avoiding the use of expensive AgF and an ultrasonic bath has been developed, affording 90% yield.

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1. Introduction

The importance of weakly coordinating anions (WCAs) in chemistry is well established [1–4]. Particularly in applied chemistry WCAs have proven to be useful, e.g. for the synthesis of ionic liquids [5], in lithium battery technology [6], and especially in transition metal polymerization catalysts [7–11]. Consequently, many efforts have been dedicated to the syntheses of new and easily accessible WCAs during the past decade.

A recent development in WCA synthesis is the preparation of aluminates with poly- (and per-) fluorinated alkoxy ligands of composition OR_F , e.g. in $\text{Al}(\text{OR}_F)_4^-$ ($R_F = \text{C}(\text{H})(\text{CF}_3)_2$ (**1a**), $\text{C}(\text{CH}_3)(\text{CF}_3)_2$, (**1b**), $\text{C}(\text{CF}_3)_3$ (**1c**), and $\text{C}(\text{Ph})(\text{CF}_3)_2$) (**1d**) [12,13]. Compared to the more commonly used $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and related borates, these aluminates have the main advantage of being safely and easily accessible on a large scale and are also easy modified. Although only known since quite recently, these aluminates have found use in quite different areas such as Lewis acidic catalysts for various organic transformations, e.g. Diels–Alder reactions and as salt metathesis reagents, to introduce the counter ion [14], foreshadowing their promising future.

The synthesis and characterization of silver polyfluoro alkoxy aluminates **1a–1c** was reported in 2001 [12], making it possible to introduce the associated WCAs through silver metathesis, which

is in many cases an excellent strategy. However, the procedure requires comparatively expensive AgF (ca. 20 Euro/g) as reactant and relatively long reaction times (≥ 12 h at 40 °C). Even more importantly, without promoting the reaction in a strong ultrasound bath, there is no hope for success.

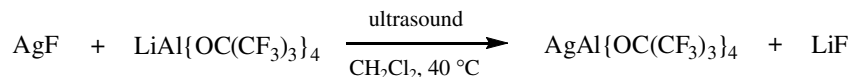
In this communication, a much simpler and more cost efficient procedure to synthesize tetrahedral coordinated $[\text{Ag}(\text{NCCH}_3)_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ is reported, avoiding the use of AgF and the application of an ultrasound bath.

2. Results and discussion

The reported procedure (Scheme 1) was first repeated with a normal ultrasound bath (BANDELIN RK 1028 35 kHz) and extended reaction time (24 h), however only trace amounts of a dark-brown, oily solid were obtained. Then the temperature was raised to 70 °C with acetonitrile as solvent, hoping to compensate for the weak ultrasound. However, no detectable product was found. It was concluded that the application of strong ultrasound, which should have a frequency >50 kHz, is unavoidable [15]. Since such equipment is not available in our laboratories, we were tempted to search for an alternative procedure, which should avoid using (and purchasing) such a strong ultrasound bath.

A distinguished property of the counter anion $\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^-$ drew our attention: extraordinary stability in water [12]. Indeed, this water resistance of certain WCAs has been utilized already in synthesizing the potassium salt of pentafluorophenyl borate

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Scheme 1. Original procedure to synthesize $\text{AgAl}\{\text{OC}(\text{CF}_3)_3\}_4$.



Scheme 2. Synthesis of $\text{AgAl}\{\text{OC}(\text{CF}_3)_3\}_4$ via $\text{KAl}\{\text{OC}(\text{CF}_3)_3\}_4$ as intermediate.

Table 1
Comparison of the two procedures for synthesizing $\text{AgAl}\{\text{OC}(\text{CF}_3)_3\}_4$

Procedure	Instrument needed	Reagent	Time (h)	Temperature	Yield (%)
[12]	Ultrasound bath 1000–5000 Euro	AgF 20 Euro/g	12–24	40 °C	95
This work	None	AgNO ₃ / KCl	6	RT	90

from its lithium salt, affording excellent yields [16]. Previous experiences have proven that it is indeed very convenient to prepare the silver salt of pentafluorophenyl borate from its potassium salt [17]. Considering these observations, a new procedure (Scheme 2) was designed.

This new procedure affords an overall yield of ca. 90% at room temperature. The intermediate $\text{KAl}\{\text{OC}(\text{CF}_3)_3\}_4$ is simply obtained by adding a saturated aqueous KCl solution into a diethyl ether solution of its lithium salt. The silver salt is subsequently obtained by a salt metathesis reaction. The silver salt $[\text{Ag}(\text{NCCH}_3)_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ can be further purified by re-crystallization from *n*-hexane/dichloromethane. However, the crude product is already pure enough to give satisfactory characterization data. Other solvents than diethyl ether as reaction media were found not to produce equally good results. Dichloromethane, for example, is not polar enough to dissolve the Li and K salt of the anion, while acetonitrile dissolves certain amounts of the by-products LiCl and KNO_3 , rendering the product separation more difficult.

Table 1 shows the advantages of the new procedure compared to the original one. Besides avoiding the use of a strong ultrasound, the reaction time and temperature are also significantly reduced. More importantly, compared to AgF (harmful) and LiF (toxic), AgNO_3 and LiCl are much more environmental friendly. The product yield, however, is only insignificantly lower. Nevertheless, it has to be noted that this procedure is not suitable for water sensitive aluminates, such as **1a** and **1b**.

3. Conclusions

A new procedure to prepare $[\text{Ag}(\text{NCCH}_3)_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ has been developed. Significant improvements with respect to efficiency, cost, and environmental friendliness have been achieved, compared to the previous procedure. The easy access to the potassium and silver salt of the weakly coordinating anion $\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^-$ makes the application of the counter anion more convenient. Moreover, recent reports [17,18] have shown several examples, in which different organic reactions were catalyzed by silver compounds incorporating WCAs with high to excellent yields. Further efforts with respect to investigating the catalytic potential of the silver salt, introducing the counter anion into other systems by metathesis reactions, and extending the procedure to other water stable poly/per-fluorinated aluminates, are currently undertaken in our laboratories.

4. Experimental

All preparations and manipulations were carried out under argon atmosphere using standard Schlenk techniques and all solvents were dried by standard procedures.

^1H NMR and ^{13}C NMR measurements were performed on a JEOL 400 MHz spectrometer. ^{19}F NMR and ^{27}Al NMR measurements were performed on a Bruker AVANCE-DPX-400 MHz spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using KBr pellets as matrix. Elemental analyses were carried out at the Mikroanalytisches Labor of the TU München.

4.1. $\text{KAl}\{\text{OC}(\text{CF}_3)_3\}_4$

In a 100 ml flask, a saturated aqueous KCl solution (15 ml) was added dropwise to a diethyl ether solution (15 ml) of $\text{LiAl}\{\text{OC}(\text{CF}_3)_3\}_4$ (2.435 g, 2.5 mol) [12]. The mixture was then stirred vigorously for 2 h at room temperature. The solvents were dried by rotary evaporator at 40 °C, affording a large amount of a white solid, which was extracted by diethyl ether (15 ml × 3). The resulting solution was washed by saturated aqueous KCl solution (10 ml) and brought to dryness, affording the crude product as white solid, which was re-dissolved in dry diethyl ether (15 ml), filtered, dried and further exposed to high vacuum (1×10^{-3} mbar, 40 °C) for 2 h to remove the coordinated solvent. The product was obtained as white powder (2.415 g, 2.4 mmol), yield: 96%. Elemental Anal. Calc. (%) for $\text{C}_{16}\text{AlF}_{36}\text{KO}_4$ (1006.19): C, 19.08. Found: C, 19.59.

4.2. $[\text{Ag}(\text{NCCH}_3)_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

A dry acetonitrile (10 ml) solution of AgNO_3 (0.408 g, 2.4 mmol) was added to a dry acetonitrile (10 ml) solution of $\text{KAl}\{\text{OC}(\text{CF}_3)_3\}_4$ (2.415 g, 2.4 mmol) in a predried Schlenk in the darkness. The reaction mixture was kept stirring for 15 min. 20 ml of dry diethyl ether was added. Then the volatiles were removed *in vacuo*, affording the product as white solid, which was re-dissolved in dry dichloromethane (10 ml). Filtration and removal of the volatile in darkness afforded the product as white powder (2.780 g, 2.24 mmol), yield: 93%. Elemental Anal. Calc. (%) for $\text{C}_{24}\text{H}_{12}\text{AgAlF}_{36}\text{N}_4\text{O}_4$ (1239.17): C, 23.26; H, 0.98; N, 4.52. Found: C, 23.48; H, 0.93; N, 4.47; ^1H NMR (400 MHz, CD_2Cl_2 , 25 °C, δ (ppm)): 2.01 (CH_3 , s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 °C, δ (ppm)): 1.8 (CH_3 , s, 4C), 81.0 (C–O, m, 4C), 117.0 (CN, s, 4C), 118.95 (CH_3 , q, 12C); ^{27}Al NMR (104.3 MHz, CD_2Cl_2 , 25 °C, δ (ppm)): 29.33 (s); ^{19}F NMR (376.5 MHz, CD_2Cl_2 , 25 °C, δ (ppm)) –79.91 (s); selected IR (KBr, cm^{-1}): ν (CN), 2270, 2304.

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