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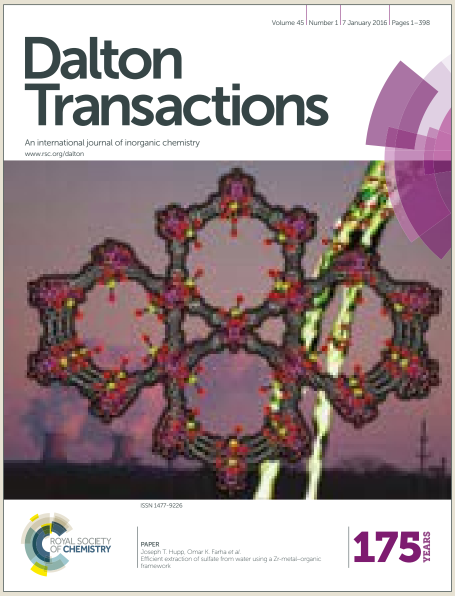

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COMMUNICATION

A Cationic Aluminium Complex: An Efficient Mononuclear Main-Group Catalyst for the Cyanosilylation of Carbonyl Compounds

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Abstract: A structurally characterized cationic aluminium complex $[(AT)Al(DMAP)]^+[OTf]^-$ (3) stabilized through less bulky aminotroponate (AT) ligand is reported (DMAP = 4-(dimethylamino)pyridine). It works as an excellent mononuclear main-group catalyst (1 to 2 mol%) for the cyanosilylation of a variety of aldehydes and ketones by consuming just 5 to 30 min at room temperature.

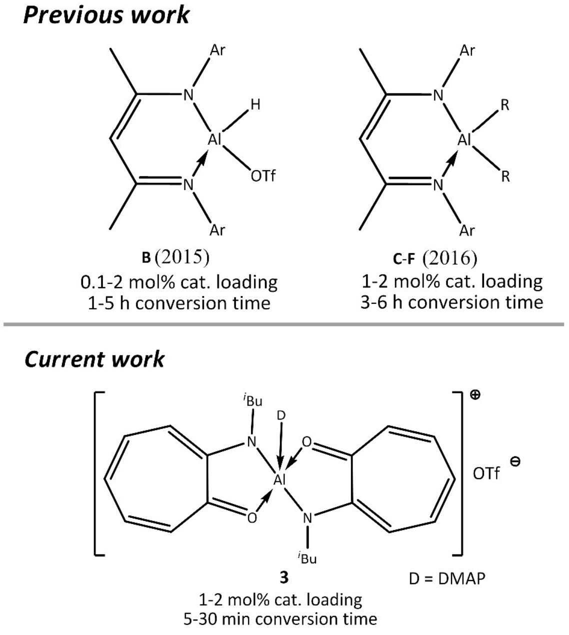

Chart 1. Aluminium catalysts for the cyanosilylation of carbonyl compounds

In recent years, catalysis using compounds with earth-abundant main-group elements is attracting the attention due to their benign environmental nature, low cost, and so forth.[1-2] In this regard, organoaluminium compounds are also studied actively as catalysts for various organic transformations.[3] Hydroboration of alkynes[4] and carbonyl compounds;[5-7] dehydrocoupling of boranes with amines, thiols, and phenols;[4] hydrosilylation of olefins,[8] carbonyl compounds,[9-10] and imines;[9] ethylene polymerization;[11] and cyanosilylation of carbonyl compounds[12] were achieved using various aluminium compounds. With respect to cyanosilylation of carbonyl compounds, [LAlH(OTf)] **B** is the best mononuclear main-group catalyst known till now,[13] and it takes 1-5 h with 0.1-2 mol% catalyst loadings. Catalysts $(LAl[(\mu\text{-S})(m\text{-pyrimidine})(CH_2)_2]_2$ **C**, $LAl[(\mu\text{-O})(o\text{-}C_6H_4)CN(C_5NH_4)]_2$ **D**, $LAlH[(\mu\text{-O})(o\text{-}C_4H_4)CN(2,6\text{-}{}^iPr_2C_6H_3)]$ **E** and $LAl[(\mu\text{-NH})(o\text{-}C_8SH_8)(COOC_2H_5)]_2$ **F** (L = $HC\{C(Me)N(Ar)\}_2$, Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$; Tf = SO_2CF_3) take 3-6 h with 1-2 mol% catalyst loadings to afford corresponding cyanohydrin trimethylsilyethers.[14] Germanium(II) cyanide [t-Bu_2(ATI)GeCN] **H** (ATI = aminotroponiminato ligand) works as a catalyst (1 mol%), and cyanosilylates a few aliphatic aldehydes within 45-135 minutes.[15] To further improve the efficiency of cyanosilylation reactions of carbonyl compounds using main-group catalysts, we planned to employ a cationic aluminium catalyst stabilized by a less bulky ligand to facilitate the facile binding of substrates to the cationic aluminium atom. Though this vision is attractive, it is a challenge as the less bulky ligands may not offer enough stability to the cationic aluminium atom. Nevertheless, we were able to synthesize such a cationic aluminium compound $[(AT)Al(DMAP)]^+[OTf]^-$ (**3**) through the stabilization offered by a semi-bulky aminotroponate (AT) ligand that binds through nitrogen and oxygen atoms. With this successful isolation, here we demonstrate compound **3** as the most efficient mononuclear main-group catalyst for the cyanosilylation of carbonyl compounds. Using 1-2 mol% of compound **3**, a variety of aldehydes and ketones are cyanosilylated in 5-30 min at room temperature.

The cationic aluminium compound **3** was isolated according to the following three-step synthetic route. *In-situ* lithiation of 2-^{i}butylaminotropone using one equivalent of ^{n}BuLi, followed by

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† Electronic Supplementary Information (ESI) available: [including experimental section, general Procedure for the cyanosilylation, NMR data of cyanosilylated products, and details of X-ray structural analysis]. See DOI: 10.1039/x0xx00000x

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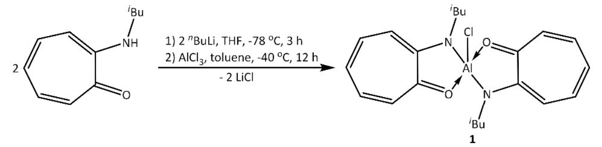
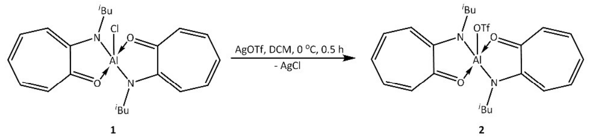
the addition of 0.5 equivalent of $AlCl_3$ afforded aminotroponate stabilized aluminium(III) monochloride **1** as a yellow solid in 73% yield (Scheme 1).



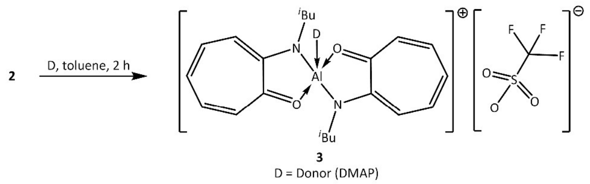
Scheme 1. Synthesis of aminotroponatealuminium chloride **1**

An equimolar reaction of compound **1** with AgOTf in dichloromethane at 0 °C gave aluminium triflate **2** in 97% yield as a brown solid (Scheme 2). Addition of 4-(dimethylamino)pyridine to a toluene solution of compound **2** at room temperature afforded the cationic aluminium(III) complex **3** in a quantitative yield as a yellow solid (Scheme 3).



Scheme 2. Synthesis of aminotroponatealuminium triflate **2**

Compounds **1**-**3** are soluble in common organic solvents such as benzene, toluene, diethyl ether, tetrahydrofuran, dichloromethane, and chloroform. Compounds **1**-**3** are stable at room temperature under an inert atmosphere of dry nitrogen or argon.



Scheme 3. Synthesis of cationic aluminium complex **3**

Compounds **1-3** are characterized in solution by NMR spectroscopic studies. In the ^{1}H NMR spectrum of compound **1**, the methyl, methine, and methylene protons of the *iso*-butyl substituents resonate as a broad singlet (0.96 ppm), a multiplet (2.15-2.24 ppm), and a broad singlet (3.65 ppm), respectively. Its seven-membered ring protons resonate as two triplets (6.77 ppm and 7.13 ppm) and a multiplet (7.22-7.36 ppm). In compound **2**, *iso*-butyl protons resonate as a doublet (0.91 ppm), a multiplet (2.00-2.09 ppm), and a doublet (3.64 ppm). Its seven membered ring protons appear as a triplet (6.92 ppm) and two multiplets (7.18-7.48 ppm). Compound **3** shows three broad singlet resonances (0.84, 1.95 and 3.54 ppm) for its methyl, methine, and methylene protons, respectively. The methyl protons of 4-(dimethylamino)pyridine donor attached to the aluminum atom were seen as a singlet at 3.10 ppm. Its seven-membered ring and pyridyl protons resonate between 6.60 to 7.98 ppm. In the ^{13}C NMR spectra of compounds **1**, **2**, and **3**, ten, twelve, and fifteen signals were observed, respectively. In the ^{19}F NMR spectra of compounds **2** and **3**, singlet resonances at -77.95 and -78.04 ppm were seen, respectively.

Structures of compounds **1** and **3** were characterized by single crystal X-ray diffraction studies (See the Supporting Information for details); they crystallized in the orthorhombic and triclinic space groups *Pnna* and $P\overline{1}$, respectively. In compound **1**, the geometry around aluminium atom is square pyramidal [$\tau = 0.007$; $\tau = 1$ (trigonal bipyramidal), $\tau = 0$ (square pyramidal)]^{16} with two nitrogen, two oxygen, and a chlorine atoms (Figure S1; see SI). In compound **3**, triflate is completely separated from the aluminium atom with a closest cation-anion distance of 5.426 Å between Al(1)-O(4). The lengths of Al(1)-N(3)$_{DMAP}$ and average Al-O bonds are 1.963(4) and 1.830(3) Å, respectively. The average Al-N$_{ligand}$ bond (1.915(4) Å) is slightly shorter than that in compound **1** (1.940(2) Å). This is due to the cationic nature of aluminium atom in compound **3**.

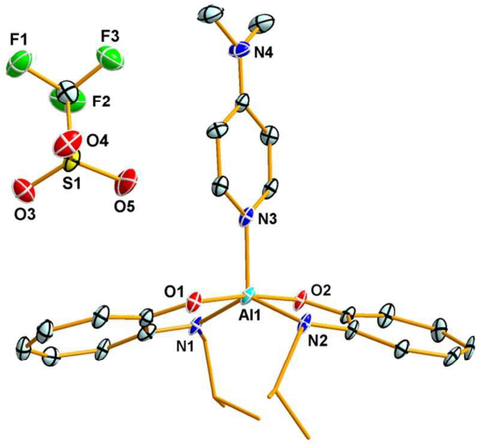


Figure 1. Molecular structure of compound **3**. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Al1-O1 1.826(3), Al1-O2 1.834(3), Al1-N1 1.907(4), Al1-N2 1.923(3), Al1-N3 1.963(4); O1-Al1-N1 83.44(2), O1-Al1-N3 94.70(1), O2-Al1-N1 93.56(1), O1-Al1-O2 171.68(2). Data collection temperature: 100 K.

With the successful synthesis and characterization of compound **3**, a reaction of benzaldehyde with a slight excess of trimethylsilylcyanide (TMSCN) and 1 mol% of catalyst **3** in neat conditions was tried. Interestingly, quantitative conversion of benzaldehyde to the corresponding cyanohydrin trimethylsilylether ($PhCH(CN)OSiMe_3$) occurred within 10 min at room temperature (time was monitored by ^{1}H NMR spectroscopic analysis) (entry 1, Table 1). The same reaction took 60 minutes when the catalyst was changed from cationic aluminium compound **3** to neutral aluminium compound **2** (entry 2, Table 1). This shows the efficiency of the cationic aluminium catalyst **3**. When the catalyst loading was reduced to 0.5 mol% in the compound **3** catalyzed reaction between benzaldehyde and TMSCN, 25 min was required for complete conversion (entry 3, Table 1); Further, no reactions were observed without the catalysts under the same reaction conditions (entry 4, Table 1).

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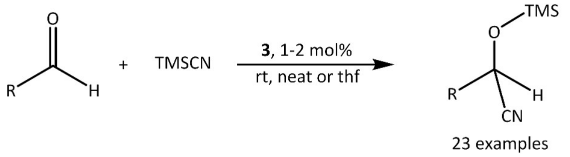
Table 1. Cyanosilylation of benzaldehyde using TMSCN with compounds **2** and **3** as catalyst.

Entry	Catalyst	Catalyst (mol%)	Time	Yield (%)
1	**3**	1	10 min	99
2	**2**	1	60 min	99
3	**3**	0.5	25 min	99
4	**2/3**	0	12 h	0

Conditions: benzaldehyde (1 mmol), TMSCN (1.2 mmol), room temperature. Yields were obtained by ^{1}H NMR spectroscopy.

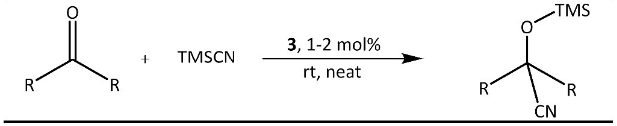
In view of these data, further catalytic reactions were performed using compound **3** with at least 1 mol% loadings, and various aliphatic/aromatic aldehydes/ketones were converted to the corresponding cyanohydrin trimethylsilylethers in excellent yields at room temperature (Scheme 4, Table S2, and Table 2). The reaction of aliphatic aldehydes *iso*-butyraldehyde, *iso*-valeraldehyde, propionaldehyde, *n*-butyraldehyde, heptaldehyde, and 2-phenyl propionaldehyde with a slight excess of TMSCN in the presence of catalyst **3** (1 mol%) took only 5 min at ambient temperature to give the corresponding cyanosilylated products in quantitative yields (Table S2, entries 1-6, respectively). Heterocyclic aldehydes, furfural and 3-thiophenecarboaldehyde produced the corresponding cyanohydrin trimethylsilylether (99% yield) in 10 min with 1 mol% of compound **3** (Table S2, entries 7 and 8, respectively). Aromatic aldehydes with different electron withdrawing and electron donating substituents required higher catalyst loadings to have reaction times closer to aliphatic aldehydes. Thus, they are converted to corresponding cyanohydrin trimethylsilylethers (93-99% yields) in 10-20 min with 2 mol% of catalyst **3** (Table S2, entries 10-22). With 1 mol% of catalyst **3**, ferrocene carboxaldehyde took 25 min to produce the desired cyanosilylated product in 99% yield (Table S2, entry 23).

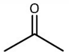
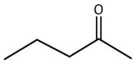
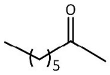
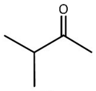
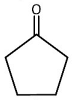
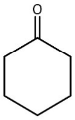
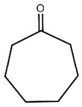
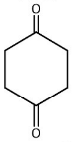
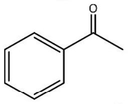
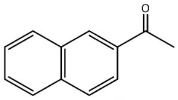
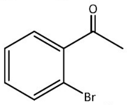
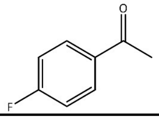


Scheme 4. Cyanosilylation of aldehydes catalyzed by **3**

Similarly, reactions of ketones with TMSCN were investigated using catalyst **3**. Like aliphatic aldehydes, aliphatic ketones, acetone, 2-pentanone, 2-octanone, and methylisopropylketone gave corresponding cyanosilylated products quantitatively in 5 minutes with 1 mol% of catalyst **3** (Table 2, entries 1-4). This trend was also seen with cyclic ketones, cyclopentanone, cyclohexanone, and cycloheptanone (Table 2, entries 5-8). Unlike aromatic aldehydes, aromatic ketones took relatively more reaction times (25 to 30 min) under the same catalyst loading of 2 mol% (Table 2, entries 9-12).

Table 2. Cyanosilylation of ketones catalyzed by compound **3**.



Entry	Substrate	Catalyst (mol%)	Time (min)	Yield (%)
1		1	5	99
2		1	5	99
3		1	5	99
4		1	5	99
5		1	5	99
6		1	5	99
7		1	5	99
8		2	15	98
9		2	30	95
10		2	30	98
11		2	30	97
12		2	25	97

Conditions: ketones (1 mmol), TMSCN (1.2 mmol), room temperature. Yields were obtained by ^{1}H NMR spectroscopy.

The higher catalytic efficiency of cationic aluminium compound **3** in the cyanosilylation reactions of carbonyl compounds than the most efficient aluminium catalyst **B** known till date may be due to the higher Lewis acidity/charge on the aluminium atom than that in compound **B**. To prove

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this, Natural Bond Order (NBO) analysis was performed on the cationic part of compound **3**, and found that the NPA charge on Al atom (2.03 e) is 0.22 e higher than that in compound **B** (1.81 e).

In summary, a cationic aluminium(III) complex **3** stabilized by a semi-bulky aminotroponate ligand is reported. To the best of our knowledge, its catalytic activity in the cyanosilylation reactions of aldehydes and ketones using TMSCN is the best among the available mononuclear main-group catalysts. This may be due to the high Lewis acidity/positive charge on the aluminium atom, and less bulky nature of ligands that stabilize it. Further, mechanistic studies to find out how compound **3** exactly functions as a catalyst are currently under progress in our laboratory.

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Main-group Catalysis: A cationic aluminium complex supported by a semi-bulky aminotroponate ligand is synthesized. It functions as an excellent catalyst for the cyanosilylation of carbonyl compounds using trimethylsilyl cyanide (TMSCN).