

Cite this: *Dalton Trans.*, 2017, **46**, 7672Received 15th May 2017,
Accepted 19th May 2017

DOI: 10.1039/c7dt01760j

rsc.li/dalton

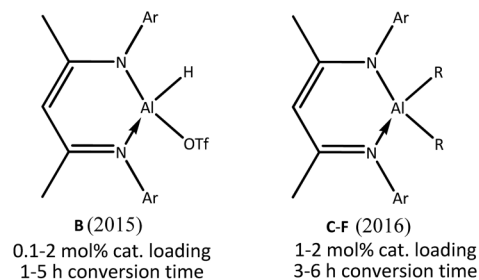
A cationic aluminium complex: an efficient mononuclear main-group catalyst for the cyanosilylation of carbonyl compounds†

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A structurally characterized cationic aluminium complex [(AT)Al(DMAP)]⁺[OTf]⁻ (**3**) stabilized through a relatively nonbulky aminotroponate (AT) ligand is reported (DMAP = 4-(dimethylamino)pyridine). This compound was found to work as an excellent mononuclear main-group catalyst of the cyanosilylation of a variety of aldehydes and ketones. Loadings of 1 to 2 mol% of this catalyst consumed these substrates in just 5 to 30 min at room temperature.

In recent years, catalysis using compounds with main-group elements abundant on earth has been attracting attention due to their benign environmental nature, low cost, and so forth.^{1,2} In this regard, organoaluminium compounds have also been actively studied as catalysts for various organic transformations.³ Hydroboration of alkynes⁴ 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 compounds¹² have been achieved using various aluminium compounds. With respect to cyanosilylation of carbonyl compounds, [LAlH(OTf)] **B** is the best mononuclear main-group catalyst known to date,¹³ and the catalyzed reaction takes 1–5 h to complete with 0.1–2 mol% catalyst loadings (Chart 1). The catalysts (LAl[(μ-S)(*m*-pyrimidine)(CH₂)₂]₂ **C**, LAl[(μ-O)(*o*-C₆H₄)CN(C₅NH₄)]₂ **D**, LAlH[(μ-O)(*o*-C₄H₄)CN(2,6-ⁱPr₂C₆H₃)] **E** and LAl[(μ-NH)(*o*-C₈SH₈)(COOC₂H₅)₂ **F** (L = HC{C(Me)N(Ar)}₂, Ar = 2,6-(ⁱ-Pr)₂C₆H₃; Tf = SO₂CF₃)) take 3–6 h with 1–2 mol% catalyst loadings to afford the corresponding cyanohydrin trimethylsilyl ethers (Chart 1).¹⁴ Germanium(II) cyanide [*t*-Bu₂(ATI)GeCN] **H** (ATI = aminotroponate

Previous work



Current work

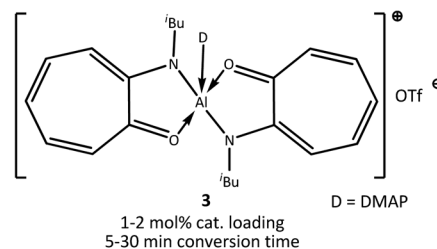


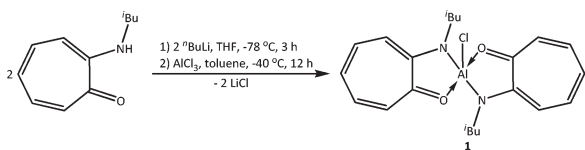
Chart 1 Aluminium catalysts for the cyanosilylation of carbonyl compounds.

nimate ligand) works as a catalyst (1 mol%), and has been shown to cyanosilylate a few aliphatic aldehydes within 45–135 minutes.¹⁵ To further improve the efficiency of cyanosilylations of carbonyl compounds using main-group catalysts, we set out 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 aim was attractive, it was a challenge as relatively nonbulky ligands may not sufficiently stabilize 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 using its nitrogen and oxygen atoms to bind the metal. After successfully isolating compound **3**, we here demonstrated

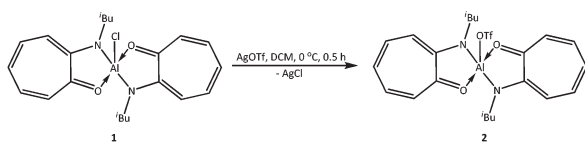
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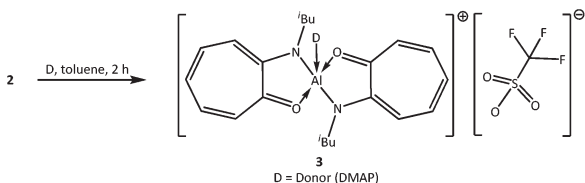
† Electronic supplementary information (ESI) available: Experimental section, general procedure for the cyanosilylation, NMR data of cyanosilylated products, and details of X-ray structural analysis. CCDC 1531062 and 1531063. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt01760j



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



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



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

it to be the most efficient mononuclear main-group catalyst of the cyanosilylation of carbonyl compounds. Using 1–2 mol% of compound **3**, a variety of aldehydes and ketones were observed to be cyanosilylated in 5–30 min at room temperature (Chart 1). The cationic aluminium compound **3** was isolated according to the following three-step synthetic route. *In situ* lithiation of 2-*i*-butylaminotroponone using one equivalent of *t*-BuLi, followed by the addition of 0.5 equivalent of AlCl₃ afforded aminotroponate-stabilized aluminium(III) monochloride **1** as a yellow solid in 73% yield (Scheme 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). Compounds **1–3** were found to be soluble in common organic solvents such as benzene, toluene, diethyl ether, tetrahydrofuran, dichloromethane, and chloroform, and to be stable at room temperature under an inert atmosphere of dry nitrogen or argon.

Compounds **1–3** were characterized in solution by carrying out NMR spectroscopic studies. According to the ¹H NMR spectrum of compound **1**, the methyl, methine, and methylene protons of the iso-butyl substituents resonated 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 resonated as two triplets (6.77 ppm and 7.13 ppm) and a multiplet (7.22–7.36 ppm). In compound **2**, iso-butyl protons resonated as a doublet (0.91 ppm), a multiplet (2.00–2.09 ppm), and a doublet (3.64 ppm). Its seven-

membered ring protons appeared as a triplet (6.92 ppm) and two multiplets (7.18–7.48 ppm). Compound **3** showed three broad singlet resonances (0.84, 1.95 and 3.54 ppm) for its methyl, methine, and methylene protons, respectively. The methyl protons of the 4-(dimethylamino)pyridine donor attached to the aluminium atom were seen as a singlet at 3.10 ppm. Its seven-membered ring and pyridyl protons resonated between 6.60 and 7.98 ppm. In the ¹³C NMR spectra of compounds **1**, **2**, and **3**, ten, twelve, and fifteen signals were observed, respectively. In the ¹⁹F 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 carrying out single crystal X-ray diffraction studies. (See ESI† for details.) They crystallized in the orthorhombic and triclinic space groups *Pnna* and *P1*, respectively. In compound **1**, the geometry around the aluminium atom was observed to be square pyramidal [$\tau = 0.007$; $\tau = 1$ (trigonal bipyramidal), $\tau = 0$ (square pyramidal)]¹⁶ with two nitrogen atoms, two oxygen atoms, and a chlorine atom (Fig. S1; see ESI†). In compound **3**, triflate was completely separated from the aluminium atom with a smallest cation–anion distance of 5.426 Å between Al(1) and O(4) (Fig. 1). The length of the Al(1)–N(3)_{DMAP} bond and average length of the Al–O bonds in compound **3** were measured to be 1.963(4) and 1.830(3) Å, respectively (Fig. 1). The average length of the Al–N_{ligand} bonds (1.915(4) Å) in compound **3** was found to be slightly less than that in compound **1** (1.940(2) Å), with this difference attributed to the cationic nature of the aluminium atom in compound **3**.

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, at room temperature, a quantitative conversion of benzaldehyde to the corres-

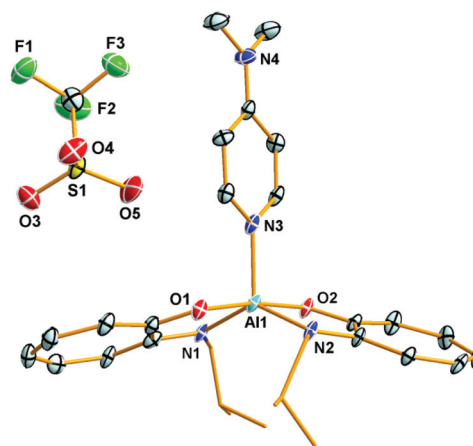


Fig. 1 Molecular structure of compound **3**. All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Al1–O1 1.826(3), Al1–O2 1.834(3), Al1–N1 1.907(4), Al1–N2 1.923(3), Al1–N3 1.963(4); O1–Al1–N1 83.44(2), O1–Al1–N3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

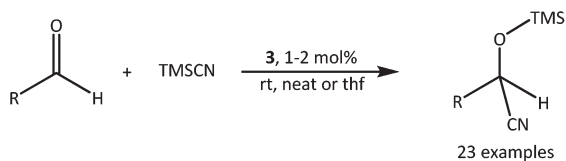
Table 1 Cyanosilylation of benzaldehyde using TMSCN with compound 2 or 3 as the catalyst

Entry	Catalyst	Catalyst (mol%)	Reaction 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 determined using ^1H NMR spectroscopy.

ponding cyanohydrin trimethylsilylether ($\text{PhCH}(\text{CN})\text{OSiMe}_3$) occurred within 10 min (entry 1, Table 1), according to a ^1H NMR spectroscopic analysis. The same reaction took 60 minutes when the catalyst was changed from the cationic aluminium compound 3 to the neutral aluminium compound 2 (entry 2, Table 1). This result revealed the efficiency of the cationic aluminium compound 3. When the loading of catalyst 3 was reduced to 0.5 mol%, a duration of 25 min was required for the reaction between benzaldehyde and TMSCN to complete (entry 3, Table 1). Note that no reaction occurred without the catalysts under otherwise identical reaction conditions (entry 4, Table 1).

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-thiophenecarbaldehyde 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 those of the aliphatic aldehydes. Thus, they were 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.**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), for entry 8: TMSCN (2.2 mmol), room temperature. Yields were determined using ^1H NMR spectroscopy.

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, cycloheptanone, and 1,4-cyclohexanedione (Table 2, entries 5–8). Under the same catalyst loading of 2 mol%, longer reaction times (of 25 to 30 min) were required for the aromatic ketones (Table 2, entries 9–12) than for the aromatic aldehydes.

The higher catalytic efficiency of cationic aluminium compound **3** in the cyanosilylation reactions of carbonyl compounds than the most efficient aluminium catalyst **B** known to date may have been due to the higher Lewis acidity/charge on the aluminium atom than that in compound **B**. To prove this, natural bond order (NBO) analysis was performed on the cationic part of compound **3**, and the NPA charge on the Al atom (2.03e) was determined to be 0.22e higher than that (1.81e) for compound **B**.

In summary, a cationic aluminium(III) complex **3** stabilized by a semi-bulky aminotroponate ligand is reported. To the best of our knowledge, the measured catalytic activities of **3** for the cyanosilylations of aldehydes and ketones using TMSCN were superior to those of the available mononuclear main-group catalysts. This result may have been due to the high Lewis acidity/positive charge on the aluminium atom, and less bulky nature of the ligands that stabilize it. Mechanistic studies to determine exactly how compound **3** functions as a catalyst are currently in progress in our laboratory.

M. K. S. and S. S. B. thank the Indian Institute of Technology Delhi (IITD), New Delhi, India and the University Grants Commission (UGC), New Delhi, India, for research fellowships, respectively. S. N. thanks the SERB, Department of Science and Technology (DST), New Delhi, India, for funding (SB/S1/IC-46/2013) and DST-FIST for establishing single-crystal X-ray diffraction and HRMS facilities in the Department of Chemistry, IIT Delhi.

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