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Chiral phenoxyimino-amido aluminum complexes for the asymmetric cyanation of aldehydes†

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The reactivity of triethylaluminum towards salicylaldimine sulfonamides was probed, affording well-defined complexes through consecutive protonolysis of two Al–C bonds by the proligand. These complexes, when combined with an achiral anilinic *N*-oxide, catalyze the asymmetric addition of trimethylsilylcyanide to a wide range of aldehydes, with good activity and enantioselectivity (up to 91% ee). Insertion of the benzaldehyde substrate into the Al–N amido bond was observed, bringing elements for discussion around the nature of the actual active species.

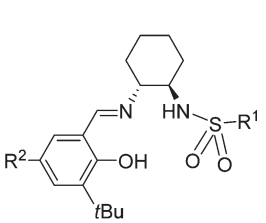
Introduction

The addition of a cyanide source to a carbonyl compound in order to form enantiomerically pure cyanohydrins is one of the most popular carbon–carbon bond forming reactions in organic synthesis.[1] Optically active cyanohydrins and their derivatives are important intermediates for the preparation of a variety of valuable classes of chiral compounds. Due to their importance, much effort has been devoted to the design and development of efficient chiral catalysts,[2] a significant class composed of chiral metal species. Among them, chiral salen complexes are the most widely studied, thanks to the versatility and ease of tuning of the salen framework.[3]

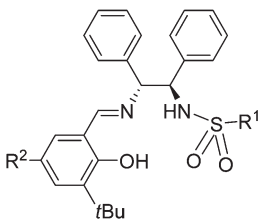
Furthermore, the concept of bifunctional catalysis has been successfully applied to asymmetric reactions. It consists, for example, of catalytic systems composed of Lewis acid/Lewis base moieties able to simultaneously activate both an electrophile and a nucleophile, respectively.[4] The efficiency of this dual activation, *i.e.* a metal-based Lewis acid/Lewis base, relies on enhanced reactivity and higher control of the transition structure with respect to the catalyst pair. Indeed, this dual activation concept has been successfully applied to the asymmetric cyanosilylation of carbonyl derivatives.[5] Kim[6] and Zhou[7] demonstrated that salen–Al complexes were able to mediate this reaction efficiently, provided that a phosphine oxide co-catalyst was used.

Inspired by the successful use of cyanosilylation (pre)-catalysts bearing C_1 chiral inducers as reported by Oguni (phenoxyimine ligands)[8] and Choi (*N*-sulfonyl derivatives of aminoalcohols),[9] we have recently reported the successful application of salicylaldimine sulfonamides[10] (that can be viewed as chiral C_1-symmetric hemisalen ligands, **1a–j**, Fig. 1) as efficient chiral inducers in asymmetric cyanation of aldehydes.[11]

These proligands react with $AlEt_2Cl$ to afford chiral phenoxyimine Al(III) complexes featuring a sulfonamide moiety, that is, with a free NH functionality. Depending on the reaction stoichiometry, one can introduce one or two of these ligands in the aluminum coordination sphere (see Fig. 2). The corresponding complexes **2a–j** and **3a–j**, respectively of C_1 or C_2 symmetry, efficiently catalyze asymmetric addition of



1a: R^1= *p*-tolyl, R^2= *t*Bu
1b: R^1= *p*-tolyl, R^2= NO_2
1c: R^1= 1-naphtyl, R^2= *t*Bu
1d: R^1= 2-naphtyl, R^2= *t*Bu
1e: R^1= *o*-$NO_2C_6H_4$, R^2= *t*Bu
1f: R^1= *m*-$NO_2C_6H_4$, R^2= *t*Bu
1g: R^1= *p*-$NO_2C_6H_4$, R^2= *t*Bu
1h: R^1= *m*-$NO_2C_6H_4$, R^2= NO_2
1i: R^1= (*R*)-camphoryl, R^2= *t*Bu
1j: R^1= (*S*)-camphoryl, R^2= *t*Bu



1k: R^1= *p*-tolyl, R^2= *t*Bu
1l: R^1= *p*-tolyl, R^2= NO_2
1m: R^1= *m*-$NO_2C_6H_4$, R^2= NO_2

Fig. 1 Phenoxyimino-sulfonamide proligands used in the present study.

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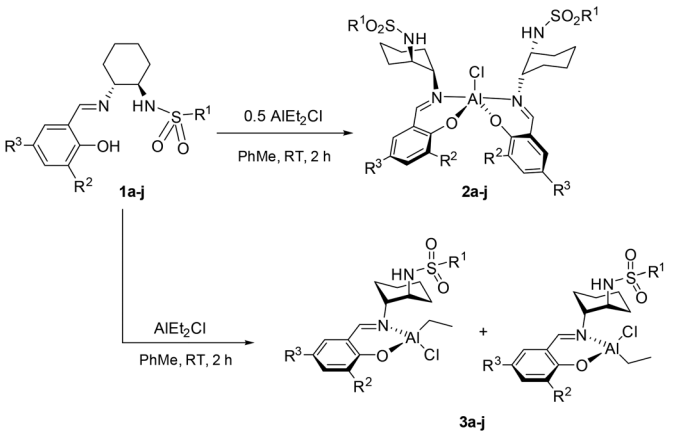

Fig. 2 Reactivity of ligands **1a–j** toward $AlEt_2Cl$.

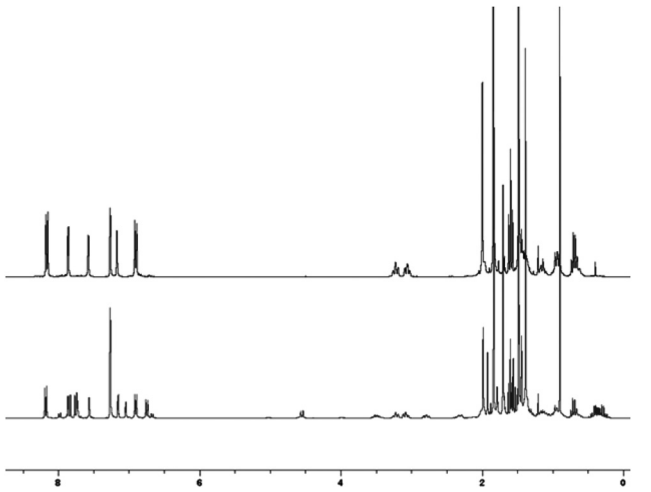

Fig. 3 ^1H NMR monitoring of the reaction between $AlEt_3$ and **1a** (1 : 1 molar ratio, C_6D_6, 300 MHz, 297 K): after 2 hours of reaction at room temperature (bottom) and after 24 hours of heating at 40 °C (top).

trimethylsilylcyanide to a broad range of aldehydes with high yields and good to excellent enantioselectivities (up to 97% ee) in the presence of a Lewis base as a co-catalyst. From these elements, as variation of the chiral ligand's structure leads to significant progress of the catalytic performances, an attractive option for further improvement of the system is the variation of the non-chiral ancillary ligands, which can easily be probed by switching the aluminum precursor. We present, in this contribution, the reactivity of the phenoxyimine sulfonamides toward triethylaluminum along with the reactivity of the resulting chiral complexes in enantioselective silylcyanation of aldehydes.

Results and discussion

Chiral aluminum complex synthesis

We have demonstrated in the preceding communication that ligands **1a–j** reacted at room temperature to afford complexes **2a–j** and **3a–j**, which bear chloro aluminum and ethyl chloro aluminum moieties, respectively, along with sulfonamide N–H functionalities as mixtures of two isomers. Here, the reactivity of readily available triethylaluminum toward proligand **1a** was probed to explore the synthesis of the related chiral Lewis acid. Thus, the reaction of an equimolar ratio of triethylaluminum and proligand **1a** in C_6D_6 at room temperature afforded within minutes a mixture of complexes, as shown by ^1H NMR (Fig. 3). Reaction of aluminum-ethyl groups was evidenced by the presence of the ethane signal at 0.80 ppm.[12] No trace of the phenolic proton (13.0 ppm for **1a**) was observed, indicating a fast reaction with the aluminum alkyl. Furthermore, the chiral ligand was exhibiting a doublet at 4.70 ppm ($^2J_{H-H}$ = 6.3 Hz) attributed to the sulfonamide NH proton, and two sets of multiplets in the 3.5–2.5 ppm range characteristic of cyclohexyl CH–N protons. Heating this reaction mixture at 40 °C for 24 hours led to simplification of the ^1H NMR spectrum, as a single set of chiral ligand's signals was observed, consistent with the presence of a single C_1-symmetric species in solution. Most particularly, the N–H signal was no longer observed in the final complex. Given the ^1H NMR characteristic of the **4a–j** complexes described below, one can postulate that the intermediate compound was the bis-ethyl derivative **5a** (Fig. 4), which afforded the mono-ethyl complex **4a** after reaction of the N–H with an aluminum ethyl fragment. Such phenoxyimine bis-alkyl aluminum species have been described by several authors, and were successfully used, mostly in polymerization catalysis.[13]

Next, on a preparative scale, reaction of an equimolar amount of **1a** and $AlEt_3$ in toluene at 40 °C for 24 hours afforded the corresponding Al(III) complex **4a** as a pale yellow solid in 89% isolated yield. This complex was characterized by ^1H and ^{13}C NMR, infrared spectroscopy, and elemental analysis. In the ^1H NMR spectrum, the AlEt group was evidenced by signals at 0.7 (multiplet, Al–CH_2) and 1.6 ppm (triplet, CH_3), while the coordinated phenoxyimino ligand gave rise most particularly to two multiplets at 3.1 and 3.2 ppm (CH–N), and two singlets accounting for the *t*-butyl protons (1.5 and 1.8 ppm). In the ^{13}C NMR spectrum, the coordinated imine carbon resonates at 164.0 ppm and the phenolic C–O at 161.2 ppm. The

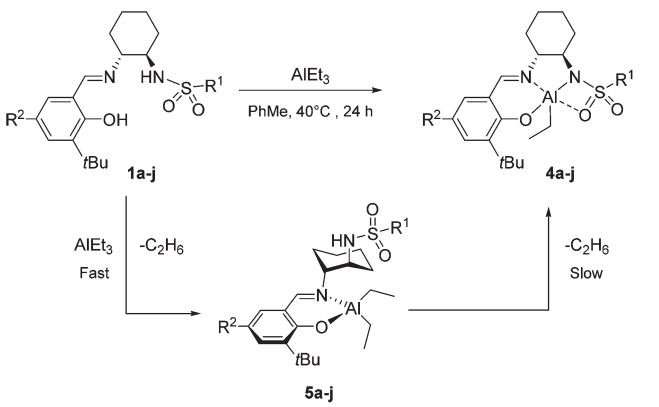

Fig. 4 Preparation of Al(III) complexes.

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infrared spectrum displays a ν(C=N) band at 1628 cm^{-1} and confirms the absence of NH functionality. Despite repeated efforts, we did not succeed in isolating single crystals suitable for X-ray diffraction studies. However, based on the related work from Wu *et al.*, the geometry around the aluminum center is most probably a distorted square pyramid with the ethyl group at the axial position, the nitrogen and oxygen atoms occupying the basal positions.[14] The analogous complex **4h**, which was also synthesized on a preparative scale and isolated in 82% yield, features similar spectroscopic characteristics.

As we intended to screen the efficiency of the series of proligands **1a–f** in combination with triethylaluminum in asymmetric silylcyanation of aldehydes, we studied the *in situ* preparation of the corresponding chiral aluminum ethyl derivatives by NMR monitoring. As was observed in the case of **1a**, these reactions proceeded cleanly to quantitative formation of the expected species, after 24 hours of heating at 40 °C. Selected ^{1}H and ^{13}C NMR data for a range of complexes generated from different proligands are presented in Table 1.

In order to extend the scope of these aluminum-based catalysts, we attempted to convert the previously reported complex **3a**, as a mixture of two isomers, into the corresponding phenoxyimino-amido chloro aluminum derivative using the same procedure as for the synthesis of **4a** (prolonged heating in toluene). Unfortunately, the reaction proved to be non-selective, affording a mixture of complexes. Most particularly, in the ^{1}H NMR spectrum, the CH–N region comprises three main sets of signals, corresponding to unreacted **3a** (10%), complex **2a** (that bears two chiral ligands, 45%) and the expected amido complex (45%). Assignment of the latter was based on the 3.3 and 3.15 ppm signals that are close to those of the amido ethyl complex **4a**. Further attempts did not allow isolating the desired amido aluminum complex in pure form.

Catalytic studies

The catalytic performances of **4a** were first probed in benzaldehyde silylcyanation. As reported in our preliminary communication on the related phenoxyimino complexes **2a–j** and **3a–j**,[11] the presence of a co-catalyst exerted an important influence on the stereoselectivity outcome of the reaction. The results summarised in Table 2 show that here, in the absence of a Lewis base as a co-catalyst, no asymmetric induction could be achieved at all. Use of *N*,*N*-dimethylaniline *N*-oxide (DMNO) as a co-catalyst afforded promising results under optimized experimental conditions, *i.e.* 2 mol% **4a**, 1.5 mol% DMNO, 0.66 M of benzaldehyde in CH_2Cl_2, −20 °C, and 1.5 eq. of TMSCN. Very interestingly, similar results were obtained for isolated and *in situ*-prepared catalytic systems, where the organoaluminum species was reacted with the proligand at 40 °C for 24 hours. This is relevant to mention, as it was demonstrated that the chemistry of the related salen based catalytic systems, which were generated *in situ*, was indeed complex, leading to unexpected species.[15] In the present case, this validates a catalytic approach implying the use of a proligand without the need to isolate its complex.

As shown in Table 3, under the optimal conditions, this highly efficient catalytic system converted a wide range of aromatic aldehydes with moderate to good asymmetric induction. Indeed, in the presence of 2 mol% of **4a** and 1.5 mol% of DMNO, benzaldehyde was converted into *O*-silyl mandelonitrile in 15% yield in 2 hours at −20 °C with 80% ee (*R* isomer, entry 1). 18 hours were required to reach full substrate conversion. No change in the amplitude of enantioselectivity was observed over the course of the reaction. The presence of an electron donating group on the substrate induced the formation of the silylated cyanohydrins with good levels of enantioselectivity (Table 3, entries 2–4; 70–90% ee) while an electron withdrawing moiety on the substrate

Table 1 Selected ^{1}H and ^{13}C NMR data for some complexes **4** (C_6D_6, 297 K)

	^{1}H NMR			^{13}C NMR		
Complex	CHN=	CHNS	N=CH	CHN=	CHNS	N=CH
4a	3.1	3.2	7.9	66.0	60.2	164.0
4b	3.0	3.2	7.7	67.5	61.2	165.1
4c	3.0	3.1	8.1	67.1	60.8	163.8
4h[a]	3.0	3.2	8.2	71.5	57.8	173.5

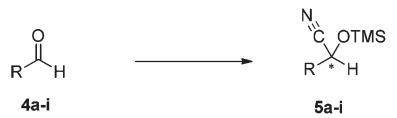
[a] CD_2Cl_2, 297 K.

Table 2 Influence of the co-catalyst on benzaldehyde silylcyanation[a]

Entry	Co-catalyst (mol%)	Time to full conversion[b] (h)	Conv. at 2 hours[b] (%)	ee[b] (%)	Config.
1	—	>24	<5	0	—
2	DMNO (1.5)	18	15	80	*R*
3	Ph_3PO (10)	>24	5	16	*R*
4	Ph_2HPO (10)	>24	5	11	*R*

[a] **1a** : $AlEt_3$ (1 : 1; 2 mol%), −20 °C, TMSCN (1.5 eq.), [PhCHO] = 0.66 M. [b] From GC analysis on Chirasil DEX CB.

Table 3 Enantioselective cyanosilylation of aldehydes catalyzed by complex **4a**[a]



4a-i **5a-i**

Entry	R	Time to full conversion[b] [h]	Conv. at 2 hours[b] [%]	ee[b] [%]	Config.
1	Ph	18	15	80	*R*
2	*o*-MeC_6H_4	18	15	90	*R*
3	*p*-MeC_6H_4	22	12	77	*R*
4	*o*-$OMeC_6H_4$	>24	10	70	*R*
5	*p*-ClC_6H_4	>24	10	68	*S*
6	*p*-$CF_3C_6H_4$	22	12	72	*S*
7	2-C_5H_4N	2	100	0	—
8	3-C_5H_4N	4	65	0	—
9	C_6H_{13}	2	99	25	*S*

[a] **4a** (2 mol%), DMNO (1.5 mol%), −20 °C, TMSCN (1.5 eq.), [substrate] = 0.66 M in CH_2Cl_2. [b] From GC analysis on Chirasil DEX CB.

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induced the formation of the silylated cyanohydrins with only moderate selectivities (Table 3, entries 5 and 6; 68–72% ee) and with opposite configuration. The change in the major isomer configuration indicates that electronic effects play an important role in the enantiodiscriminating step of the reaction. Heteroaromatic aldehydes are more efficiently converted, but without asymmetric induction (Table 3, entries 7 and 8). Most noteworthy, in the case of *ortho*-pyridylcarboxaldehyde, a fast reaction rate was observed, most probably due to preferential substrate binding onto the Al center *via* pyridine coordination. However, this obviously generated a transition state that does not lead to any significant chirality transfer from the chiral catalyst. In the case of cyclohexanecarboxaldehyde, fast conversion was observed, with poor enantioselectivity transfer (Table 3, entry 9).

The stereoelectronic properties of the ligand framework were then tuned (Table 4). Substituents at the R^2 position affected strongly the activity of the corresponding catalyst but had little effect on the ee values. For example, introduction of the electron withdrawing nitro group at that position allows for higher activity and slightly higher enantioselectivity (Table 4, entry 2 *vs.* 1). Indeed, in the case of benzaldehyde as a substrate, the use of a catalyst based on a ligand containing a salicylaldehyde residue bearing a nitro group as the R^2 substituent and a *p*-tolyl sulfonamide on the cyclohexyl moiety led to the formation of a silylated product with 60% conversion after 2 hours (*vs.* 15% with *t*-Bu as the R^2 group) and an enantioselectivity up to 84% (*vs.* 80% with *t*-Bu as the R^2 group). This contrasts with the observation of Belokon and coworkers,[3] who reported a decrease of selectivity upon introduction of NO_2 in R^2 position. Concerning the sulfonamide moiety, several combinations were used and the framework derived from *m*-nosyl (*m*-NO_2-$C_6H_4SO_2$) proved to be the most effective. Thus, the catalyst derived from ligand **1h**, containing a *m*-nosyl group and a salicylaldehyde bearing a nitro group in R^2 position, exhibited the best catalytic performances (Table 4, entry 8). In this case, benzaldehyde was converted into the corresponding silyl cyano ether with a total conversion in 2 hours and selectivity up to 91% ee. About camphoryl sulfonyl derivatives (Table 4, entries 9 and 10), activity and selectivity were highly dependent on the camphoryl enantiomer linked to the (*R*,*R*) diaminocyclohexyl ligand framework. Thus, the Al complex bearing the (*R*)-camphoryl substituted ligand was particularly unreactive and non-selective while the use of the (*S*)-camphoryl substituted moiety led to up to 58% of enantiomeric excess. This probably results from quite different stereoelectronic environments of the aluminum center while applying camphoryl modified ligands. Consequently, the catalyst performances are somehow inhibited in the case of both cyclohexyldiamine and camphoryl configuration combinations, one exhibiting nonetheless a match situation even if significantly less active (Table 4, entry 10).

After having probed the effect of sulfonamide moieties and of the salicylaldehyde substituents, the impact of the chiral backbone on catalytic performances was studied (Table 5). Indeed, systems based on ligands derived from (*R*,*R*)-1,2-diphenylethylenediamine exhibited lesser performances. In all cases, a decrease in both activity and selectivity was observed (Table 3, entries 1–3). However, trends similar to cyclohexanediamine-based systems were obtained: a nitro group in R^2 position in the salicylaldehyde moiety and a *m*-nosyl group as a sulfonamide substituent are both beneficial in terms of selectivity. However, the role of the sulfonamide substituent is subtle: the *m*-nosyl group affords the opposite major enantiomer as compared to its *p*-tolyl analogue. This was not observed in the case of the more rigid systems involving proligand **1a–j**. Here, the flexibility on the ethylenediamine backbone affects the structure of the catalytic intermediate responsible for the enantiodiscriminating step, which translates into markedly different selectivity.

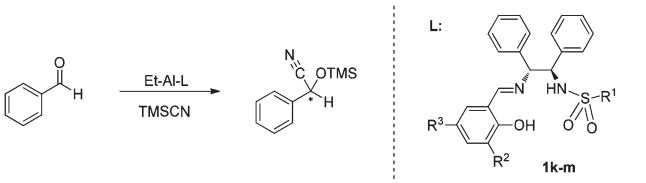
Our catalytic results compare well to those obtained with salen-based systems, such as the one developed by Kim[6] and by Zhou.[7] These require 1 mol% of catalyst loading but also a significant amount of a co-catalyst (10 mol%) to convert aldehydes with good activity and ee values (up to 92% ee, in

Table 4 Influence of the ligand structure on benzaldehyde silylcyanation[a]

Entry	L	Time to full conversion[b] [h]	Conv. at 2 hours[b] [%]	ee[b] [%]
1	**1a**	18	15	80
2	**1b**	2	60	84
3	**1c**	14	20	54
4	**1d**	>24	10	55
5	**1e**	16	18	70
6	**1f**	12	30	83
7	**1g**	14	20	68
8	**1h**	2	100	91
9	**1i**	18	15	0
10	**1j**	>24	9	58

[a] (**1a–j**) : $AlEt_3$ (1 : 1; 2 mol%), *N*-oxide (1.5 mol%), −20 °C, TMSCN (1.5 eq.), [benzaldehyde] = 0.66 M in CH_2Cl_2. [b] From GC analysis on Chirasil DEX CB; the major isomer is of *R* configuration.

Table 5 Influence of the ligand's backbone on benzaldehyde silylcyanation[a]



Entry	L	Time to full conversion[b] (h)	Conv. at 2 hours[b] (%)	ee[b] (%)	Config.
1	**1k**	9	15	65	*S*
2	**1l**	21	60	73	*S*
3	**1m**	32	20	85	*R*

[a] (**1k–m**) : $AlEt_3$ (1 : 1; 2 mol%), *N*-oxide (1.5 mol%), −20 °C, TMSCN (1.5 eq.), [benzaldehyde] = 0.66 M in CH_2Cl_2. [b] GC analysis on Chirasil DEX CB.

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12–16 h). The catalysts developed here with an aluminum center accommodating a tridentate hemisalen moiety with a *N*-sulfonamido group proved to be easily tunable and thus allowed fast optimization to achieve very good catalytic performances for a broad range of aldehydes. However, the sulfonamide moiety does not, most probably, act as an efficient intramolecular co-catalyst (Lewis base) as the cyanation of benzaldehyde was very sluggish with no asymmetric induction without an external assistance (Table 1, entry 1). Indeed, our system requires the use of an external base to enforce high levels of stereoselection.

Attempts were made to provide further understanding of the complex catalytic system described above. On the one hand, addition of benzaldehyde (1 equivalent) to complex **4a** induced immediate change of the solution's color from pale to deep yellow. However, this did not lead to any significant change on the ^{1}H NMR spectrum. On the other hand, addition of DMNO (1 equivalent) significantly perturbed the spectrum: featureless signals are observed, among which one can distinguish signals due to the coordinated DMNO methyl groups (3.8 and 4.0 ppm, to be compared to 3.6 ppm for free DMNO). This may be expected from coordination of this base on the chiral Lewis acidic Al center, generating diastereotopic methyl groups. However, further understanding is still out of reach. Further, reaction of **4a** with TMSCN and benzaldehyde in benzene afforded colorless crystals, which proved to be of poor quality but amenable to X-ray diffraction study. If refining the structure was not possible due to significant thermal agitation in the crystal even at low temperature, the coordination scheme of the compound could be assessed and presented a most peculiar structural pattern (Fig. 5). The species consisted of a dinuclear assembly of C_2 symmetry, bearing a chiral ligand on each metal center, two bridging benzaldehydes, and no ethyl group. Aluminum is thus pentacoordinated. Aluminum being at the (III) oxidation state, this implies a dicationic structure, the nature of expected anions not being determined due to poor crystal quality. The chiral ligand resulted from the insertion of a benzaldehyde into the Al–N sigma bond, generating a *O*-coordinated hemiaminal group. The chiral ligand in this case is of the (O,N,O) type compared to the (O,N,N) phenoxyimino-amido entity initially present on the aluminum moiety. This type of reactivity was previously reported by Mimoun and Floriani, in the course of their studies on ketone reduction mediated by zinc-based systems.[16] The implication of this observation for the catalytic systems described above will require further specific studies, but this emphasizes the peculiarity of the herein described (pre)catalysts.

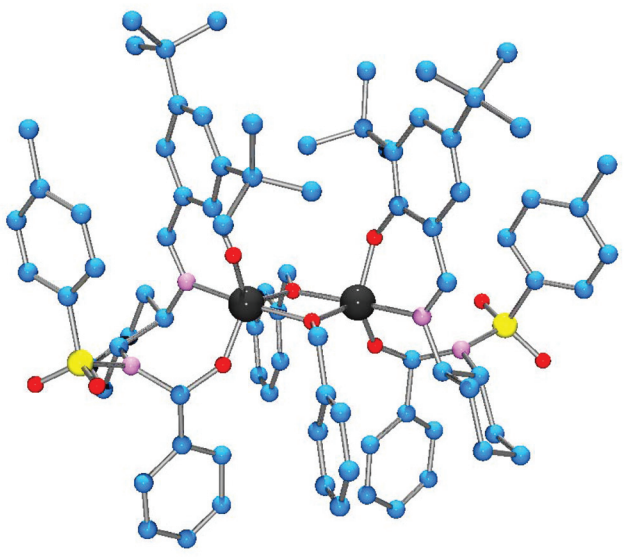

Fig. 5 Ball and stick representation of the molecular connectivity of the species resulting from the reaction of **4a**, $SiMe_3CN$ and PhCHO (black: aluminum; red: oxygen; pink: nitrogen; blue: carbon; yellow: sulfur; hydrogen atoms not depicted).

Conclusions

In summary, we have described here how modification of the aluminum precursor affects the coordination chemistry of phenoxyimine sulfonamide ligands. In contrast with the related $AlEt_2Cl$ chemistry, $AlEt_3$ affords chiral amido species that proved to be efficient catalysts for aldehyde silylcyanation in combination with an external Lewis base. Some elements indicate that the amido functionality may not be innocent and could play a role in the modification of the chiral aluminum coordination sphere.

Experimental

Materials and methods

All the experiments (except proligands synthesis) have been carried out under an inert atmosphere using conventional Schlenk techniques or in an argon-filled glove-box. All reagents and solvents were of commercial grade and purified prior to use when necessary. ^{1}H and ^{13}C NMR were acquired on a Bruker AC300 instrument. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ = 7.26 ppm and δ = 77.1 ppm ($CDCl_3$) for ^{1}H and ^{13}C, respectively. Enantiomeric excesses were determined with a Shimadzu instrument (Chirasil-DEX CB, 25 m × 0.25 mm column). Absolute configurations were determined by comparing the known order of elution of the two enantiomers or the sign of optical rotation with literature data.[17] Infrared spectra were recorded on a Nicolet 6700 FTIR. Elemental analyses were conducted using a VarioMIRO Superuser automatic analyser in the UCCS, or in London Metropolitan University Services. All substrates, TMSCN, substituted salicylaldehydes and (1*R*,2*R*)-diamines were purchased from Acros, Aldrich, and Fluka, and were used without further purification. DMNO was synthesized according to the procedure described in the literature.[18] Solvents and substrates were purified by conventional methods. CAUTION: $SiMe_3CN$ is a highly toxic chemical and should be handled with care using appropriate precautions.

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Preparation of ligands 1a–m. To a solution of the selected aminosulfonamide (1 mmol) in dichloromethane (5 ml), a mixture of the selected salicylaldehyde derivative (1 mmol) in dichloromethane (3 ml) was added at room temperature. The mixture was stirred overnight. $MgSO_4$ was then added; the mixture was filtered and evaporated to dryness. After crystallization in ethanol, yellow crystals were obtained. Proligands **1a–j** were described in a previous communication.[11]

1l: Yield = 96%. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 14.54 (s, 1H, O*H*), 8.25 (s, 1H, C*H*═N), 8.24 (d, ^3J = 2.7 Hz, 1H, H_{ArOH}), 7.95 (d, ^4J = 2.7 Hz, 1H, H_{ArOH}), 7.45 (d, ^3J = 8.2 Hz, 2H, $H_{p\text{-Tol}}$), 7.20–7.05 (m, 10H, H_{Ar}), 7.02 (d, ^3J = 8.2 Hz, 2H, $H_{p\text{-Tol}}$), 5.51 (d, ^3J = 7.5 Hz, 1H, NH), 4.81 (dd, ^3J = 7.5 Hz, ^3J = 6.6 Hz, 1H, CH–N), 4.53 (d, ^3J = 6.6 Hz, 1H, C*H*–NH), 2.29 (s, 3H, CH_3), 1.43 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 166.4 (CH═N), 166.0 (C–OH), 143.1, 139.3, 139.0, 137.4, 137.0, 136.8, 129.3, 128.6, 128.2, 127.8, 127.6, 127.4, 126.8, 126.3, 125.3, 117.2, 107.5 (C_{Ar}), 78.1 (CH–N), 63.4 (CH–NH), 35.3, 29.0, 21.4. IR (KBr): ν = 3283 (νN–H), 3062 (νC_{sp^2}–H), 3032 (νC_{sp^2}–H), 2957 (νO–H), 1626 (νC═N), 1320, 1290, 1160, 1059 cm^{-1}. Anal. calculated for $C_{32}H_{33}N_3O_5S$ (571.69 g mol^{-1}): C 67.23; H 5.82; N 7.35; S 5.61; found C 67.38; H 5.87; N 7.47; S 5.29.

1m: Yield = 93%. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 14.54 (s, 1H, O*H*), 8.27 (s, 1H, CH═N), 8.20 (d, ^3J = 2.4 Hz, 1H, $H_{m\text{-Nosyl}}$), 8.01 (s, 1H, $H_{m\text{-Nosyl}}$), 7.95 (d, ^3J = 8.4 Hz, 1H, $H_{m\text{-Nosyl}}$), 7.43 (t, ^3J = 7.7 Hz, 1H, $H_{m\text{-Nosyl}}$), 7.22–7.05 (m, 11H, H_{Ar}), 6.91 (s, 1H, H_{ArOH}), 5.72 (d, ^3J = 7.5 Hz, 1H, NH), 4.93 (t, ^3J = 6.9 Hz, 1H, CH–N═C), 4.66 (d, ^3J = 6.6 Hz, 1H, C*H*–$NHSO_2$), 1.43 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 166.9 (CH═N), 165.9 (C–OH), 147.7, 142.0, 139.5, 139.2, 137.2, 136.2, 132.2, 129.9, 128.8, 128.4, 128.3, 128.2, 127.4, 127.3, 126.6, 126.4, 125.6, 122.3, 117.2 (C_{Ar}), 77.9 (CH–N), 63.6 (CH–NH), 35.3, 28.9. IR (KBr): ν = 3301 (νN–H), 3063 (νC_{sp^2}–H), 3033 (νC_{sp^2}–H), 2962 (νO–H), 1622 (νC═N), 1354, 1290, 1166, 1051 cm^{-1}. Anal. calculated for $C_{31}H_{30}N_4O_7S$ (602.66 g mol^{-1}): C 61.78; H 5.02; N 9.30; S 5.32; found C 61.50; H 5.12; N 9.30; S 4.80.

Complex 4a. To a stirred solution of (*R*,*R*)-**1a** (0.485 g, 1 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of triethylaluminum (0.114 g, 1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for another 24 hours at 40 °C. After removal of the solvent, the crude product was recrystallized from dry toluene (5 mL) to afford complex **4a** as a yellow solid. Yield = 89%. ^{1}H NMR (C_6D_6, 300 MHz, δ ppm): 8.19 (d, ^3J = 7.9 Hz, 2H, H *p*-Tol), 7.87 (d, ^3J = 2.0 Hz, 1H, H ArO), 7.55 (s, 1H, CH═N), 7.16 (d, ^3J = 2.0 Hz, 1H, H ArO), 6.90 (d, ^3J = 7.9 Hz, 2H, H *p*-Tol), 3.29–3.16 (m, 1H, CH–N═C), 3.15–3.02 (m, 1H, CH–NSO_2), 1.98 (s, 3H, CH_3), 1.84 (s, 9H, *t*-Bu), 1.61 (m, 3H, CH_2–CH_3, 1.49 (s, 9H, *t*-Bu), 1.24–0.82 (m, 8H, CH_2), 0.73 (m, 2H, CH_3–CH_2–Al). ^{13}C NMR (C_6D_6, 75 MHz, δ ppm): 164.0 (CH═N), 161.2 (C–O–Al), 142.7 (C_q Ar), 141.6 (C_q Ar), 139.9 (C_q Ar), 139.0 (C_q Ar), 130.5 (CH Ar), 129.6 (CH *p*-Tol), 127.7 (CH Ar), 127.2 (CH *p*-Tol), 119.5 (C_q Ar), 66.0 (*C*H–N═C), 60.2 (CH–NSO_2), 35.9 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 32.9 (CH_2CH–N), 31.6 (C(CH_3)$_3$), 29.8 (C(CH_3)$_3$), 25.8 (CH_2CH–N), 24.0 (CH_2), 23.8 (CH_2), 21.1 (Ar–CH_3), 10.2 (CH_3–CH_2–Al), 0.3 (broad, CH_3–CH_2–Al). IR (KBr, cm^{-1}): ν = 2985 (ν(sp^3-CH)), 1628 ($\nu_{C=N}$). Anal. calculated for $C_{30}H_{43}AlN_2O_3S$ (538.72 g mol^{-1}): C 66.88; H 8.05; N 5.20; found C 66.32; H 7.96; N 5.17.

Complex 4h. To a stirred solution of **1h** (0.558 g, 1 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of triethylaluminum (0.114 g, 1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for 24 hours at 40 °C. After removal of the solvent, the orange crude product was recrystallized from dry pentane (50 mL) to afford complex **4h** as an orange solid. Yield = 82%. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ ppm): 8.47 (t, ^4J = 1.9 Hz, 1H, H *m*-Nosyl), 8.19 (s, 1H, CH═N), 8.16–7.90 (m, 5H, H ArO and *m*-Nosyl), 7.45–7.32 (m, 1H, H *m*-Nosyl), 3.18 (m, 2 H, CH–N), 2.98 (m, 2H, CH–NSO_2), 1.31 (s, 9H, *t*-Bu), 1.82–1.18 (m, 8H, CH_2), 0.67 (t, 3H, ^3J = 6.3 Hz, CH_3–CH_2), 0.35 (m, 2H, CH_2–CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ ppm): 173.5 (CH═N), 160.5 (C–OAl), 147.9 (C–NO_2), 143.0 (C_q Ar), 137.4 (C_q Ar), 137.3 (C_q Ar), 132.9 (CH Ar), 129.6 (CH Ar), 126.3 (CH Ar), 125.2 (CH Ar), 121.9 (CH Ar), 121.5 (CH Ar), 117.2 (C_q Ar), 71.5 (C–N═C), 57.8 (CH–NSO_2), 35.1 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 33.9 (CH_2CH–N), 31.2 (CH_2CH–N), 29.4 (C(CH_3)$_3$), 29.1 (C(CH_3)$_3$), 23.7 (CH_2), 23.2 (CH_2), 8.1 (CH_3–CH_2–Al), 0.7 (broad, CH_3–CH_2–Al).

General procedure for catalyzed asymmetric cyanosilylation of aldehydes in the presence of synthesized aluminium complexes. A mixture of the selected aluminium complex (0.02 mmol), benzaldehyde (0.1 ml, 1 mmol), and dry dichloromethane (1.5 mL) was stirred for 0.5 h at room temperature under a nitrogen atmosphere. To the mixture was added *N*,*N*-dimethylaniline *N*-oxide (0.015 mmol) and the resulting medium was stirred for another 0.5 h at the same temperature. Then, the mixture was stirred at −20 °C and then trimethylsilylcyanide (0.2 ml, 1.5 mmol) was added with a syringe. After stirring for 2–24 h at this temperature, the crude reaction mixture was concentrated under reduced pressure and purified through silica gel column chromatography (200–300 mesh, gradient of petroleum ether–ethyl acetate) to yield the silylated cyanohydrin which was used for further chiral GC analysis.

General procedure for catalyzed asymmetric cyanosilylation of aldehydes in the presence of *in situ* generated catalysts. A mixture of selected ligand **1** (0.02 mmol) and $AlEt_3$ (0.02 mmol) in dry dichloromethane (1 ml) was stirred overnight at 40 °C. Then, benzaldehyde (0.1 ml, 1 mmol) was added and stirred for 0.5 h at room temperature under a nitrogen atmosphere. To the mixture was added *N*,*N*-dimethylaniline *N*-oxide (0.015 mmol) and the resulting mixture was stirred for another 0.5 h at the same temperature. Then, the mixture was stirred at −20 °C and trimethylsilylcyanide (0.2 ml, 1.5 mmol) was added with a syringe. After stirring for 2–24 h at this temperature, the mixture was concentrated under reduced pressure and purified through silica gel column chromatography (200–300 mesh, gradient of petroleum ether–ethyl acetate) to yield the silylated cyanohydrin which was used for further chiral GC analysis.

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