Neutral and cationic enantiopure group 13 iminophosphonamide complexes†

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Synthesis and reactivity of enantiopure iminophosphonamide ligand $L\cdot H$ ($L = \left[\text{Ph}_2\text{P}(\text{N}(\text{R})(\text{CH})(\text{CH}_2)\text{Ph})_3\right]^{-}$ with group 13 metal compounds has been investigated. The reaction of $L\cdot H$ with $\text{LiAlH}_4$ afforded the aluminium monohydride complex $[L_2\text{AlH}]$. The monochloride complexes $[L_2\text{MCl}]$ ($M = \text{Al, Ga}$) were accessed by reacting corresponding $\text{MCl}_3$ ($M = \text{Al, Ga}$) with $L\cdot \text{Li}$. Furthermore, the tetracoordinated aluminium cation $[L_2\text{Al}]^+\text{[GaCl}_4]^{-}$ and gallium cation $[L_2\text{Ga}]^+\text{[AlCl}_4]^{-}$ were obtained by chloride abstraction from $[L_2\text{MCl}]$ ($M = \text{Al, Ga}$), respectively. The title complexes represent the first examples of enantiopure group 13 metal complexes coordinated by chiral iminophosphonamides. All complexes have been characterized by single crystal X-ray diffraction, multinuclear NMR, EA and IR studies.

Introduction

Over the past decades, electron rich chelating mono anionic amido ligands have widely been used in coordination chemistry to stabilize metal complexes. The isoelectronic analogy of nitrogen-based species with their oxygen counterpart is the guiding principle for the preparation of these $N$-donor ligands. Amidinate anions of the general formula $[\text{RC}(\text{NR})_2]^{-}$ and iminophosphonamide anions of the general formula $[\text{R}_2\text{P}(\text{NR})_2]^{-}$ can be considered as the nitrogen analogue of the carboxylate and phosphate anions, respectively. To date, ligand design is an important aspect in coordination chemistry to fine-tune specific structural and reactivity properties in metal complexes. In this regard, $\text{NXN}$ ligand scaffolds are very attractive due to the possibility of different substituents for $R$ and many variants for $X$ such as $\text{CR}$ (amidinate), $\text{BR}$ (boraamidinate), $\text{C(NR)}_2$ (guanidinates), $\text{N}$ (triazenide), $\text{SR}$ (sulfinamidinate), and $\text{PR}_2$ (iminophosphonamide).

The coordination chemistry with the achiral version of $\text{NXN}$ ligand systems is very well explored. However, chemistry dealing with the chiral analogues of $\text{NXN}$ ligand systems is scarce. In 2011, our group has described the synthesis of chiral amidinate ($\text{NCN}$) and subsequently synthesized corresponding alkaline earth metal and lanthanide complexes, which were active catalysts for hydroamination, hydrophosphination reactions and ring opening polymerization of racemic lactide. In comparison to amidinate, iminophosphonamide ligands show different structural features such as $X-N$ bond lengths and $\text{NXN}$ bite angles. In addition, the iminophosphonamide ligand system features an active nucleus for fluorination reactions and ring opening polymerization of racemic lactide. In comparison to amidinate, iminophosphonamide ligands show different structural features such as $X-N$ bond lengths and $\text{NXN}$ bite angles. In addition, the iminophosphonamide ligand system features an active nucleus for fluorination reactions and ring opening polymerization of racemic lactide. In comparison to amidinate, iminophosphonamide ligands show different structural features such as $X-N$ bond lengths and $\text{NXN}$ bite angles. In addition, the iminophosphonamide ligand system features an active nucleus for fluorination reactions and ring opening polymerization of racemic lactide. In comparison to amidinate, iminophosphonamide ligands show different structural features such as $X-N$ bond lengths and $\text{NXN}$ bite angles. In addition, the iminophosphonamide ligand system features an active nucleus for fluorination reactions and ring opening polymerization of racemic lactide. In comparison to amidinate, iminophosphonamide ligands show different structural features such as $X-N$ bond lengths and $\text{NXN}$ bite angles. In addition, the iminophosphonamide ligand system features an active nucleus for fluorination reactions and ring opening polymerization of racemic lactide.
Herein, we report the synthesis and characterization of chiral group 13 (Al and Ga) complexes utilising the recently reported chiral iminophosphonamide ligand (L).

Results and discussion

Reacting LiAlH₄ with L-H in a molar ratio of 1:2, resulted in the formation of complex [L₂AlH] (1) in 65% yield (Scheme 1). The ¹H NMR spectrum of complex 1 shows a doublet corresponding to Ph(CH)CH₃ protons at δ 1.90 ppm with a coupling constant of JHH = 6.45 Hz. However, the corresponding Ph(CH)CH₃ resonances for the ligand (L-H) are observed at δ 1.66 and 1.13 ppm due to proton (NH) exchange (tautomerization). The Ph(CH)CH₃ protons of complex 1 appear as a broad signal at δ 4.99 ppm (Δνᵥ₁ = 55 Hz) without fine resolution. A resonance for the Al–H could not be observed possibly due to quadrupole relaxation of ²⁷Al nuclei. In the IR spectrum of complex 1, a peak at 1693 cm⁻¹ was assigned for the vibrational stretching of the Al–H bond (Fig. S18, ESIF). However, this value is not in the literature reported range of 1780–1853 cm⁻¹ for related Al–H valence modes. This unusual red shift in the Al–H frequency for complex 1 could be due to stronger donor ability of ligand L.

To further confirm the existence of the Al–H bond, the L₂AlD (1D) isotopomer of complex 1 was synthesized by reacting LiAlD₄ with L-H in the appropriate stoichiometric ratio. Complex 1D showed exactly the same ¹H NMR as shown for complex 1H. Moreover, in the IR spectrum of 1D no peak was observed at 1693 cm⁻¹ (Fig. S20 and S21, ESIF). Theoretical study suggests that the Al-D stretching frequency should appear at 1198 cm⁻¹ due to isotopic shift. However, this region of IR spectrum is obstructed due to C-N stretch. Therefore, to confirm further theoretical calculations of these complexes were conducted. According to a theoretical calculation, the experimental spectra fit nicely with the calculated ones for both complexes 1H and 1D (see ESIF). Another method to differentiate between Al–H (D) bonding in 1H and 1D is provided by the investigation of the two usually very intense Al–H (D) deformation modes in the IR spectrum. They are found at 636 and 606 cm⁻¹ (1H) as well as close to 482 cm⁻¹ (1D). A second Al-D deformation mode is presumably overlapped by the signals of the AlN₄ framework at 537 and 508 cm⁻¹ (both 1H and 1D). These findings are also confirmed by the DFT calculation.

The ³¹P ²H NMR spectrum of complex 1 shows a single resonance at δ 33.6 ppm, which is downfield shifted compared to L-H (δ 2.7 ppm). Absence of N–H stretch in the IR of complex 1 further indicates the deprotonation of the ligand by LiAlH₄.

Single crystals suitable for X-ray analysis were obtained from a saturated solution of complex 1 in diethyl ether. Complex 1 crystallises in an orthorhombic chiral space group P2₁2₁2 with half of the molecule in the asymmetric unit cell. The aluminium centre in complex 1 is pentacoordinated and form a distorted trigonal bipyramidal (tbp) polyhedron (Fig. 1). The hydride atom could be found and refined in the difference Fourier map.

Two nitrogen atoms (N2 and N2') of the iminophosphonamide ligand and the hydride form the equatorial plane, the sum of bond angles involving Al in this plane is 360°. The remaining two nitrogen atoms of the ligand backbone (N1 and N1') occupy the axial positions with a N1–Al–N1' bond angle of 165.03(9)°, which is significantly wider than the equatorial N2–Al–N2' bond angle (121.99(11)°).

The Al–N1 bond length of 2.040(2) Å is longer than 1.932(2) Å of Al–N2 equatorial bond length. Deviation in the bond angles from the ideal tbp geometry is clearly arising from the chelating effect of the bidentate ligand (N1–P1–N2 96.46(9)°). The N2–Al–N1 angle (74.93(7)°) in complex 1 is almost similar to the N–Al–N bite angle reported in [[(Ph₂P)(ṄSiMe₃)₂]₂AlH] (75.66(5)°).

Using our previously reported ligand lithium salt (L-Li), and subsequent reaction with MCl₃ (M = Al, Ga) resulted in a facile elimination of LiCl and formation of [L₂MCl] (M = Al (2), Ga (3); Scheme 2). Both complexes 2 and 3 were fully characterized by multinuclear NMR, IR, elemental analysis as well as single crystal X-ray diffraction studies. Complexes 2 and 3 are stable in the solid state at room temperature for several months under an inert atmosphere and are soluble in organic solvents such as thf, Et₂O and toluene while they are insoluble in n-hexane.
In the $^1$H NMR spectra of 2 and 3, the Ph(CH)CH$_3$ protons of the ligand backbone show broad resonances at $\delta$ 5.17 ($\Delta$ $^3$J$_{HH}$ = 140 Hz) (2) and 5.10 ppm ($\Delta$ $^3$J$_{HH}$ = 40 Hz) (3). A broad resonance at $\delta$ 1.89 ($\Delta$ $^3$J$_{HH}$ = 40 Hz) ppm could be observed for Ph(CH)CH$_3$ protons of 2 whereas, same resonance for complex 3 showed a doublet at $\delta$ 1.90 ppm with $^3$J$_{HH}$ = 6.52 Hz. 

To investigate the dynamic behaviour of these complexes (2 and 3) a VT (variable temperature) $^1$H NMR of complex 2 in thf-$d_8$ was recorded in the temperature range of 283–173 K with 10 K decrease in each spectrum (Fig. S6$^\dagger$). The broad resonance for Ph(CH)CH$_3$ at room temperature in the area of 4.3–5.3 ppm splits into two different signals at low temperature with integral ratio of 1:1. While cooling down from 253 to 243 K the doublet at $\delta$ 1.59 ppm ($^3$J$_{HH}$ = 6.58 Hz) of Ph(CH)CH$_3$ splits into two different signals.

At 203 K one signal could be detected as a doublet at $\delta$ 1.47 ppm ($^3$J$_{HH}$ = 6.40 Hz) whereas the other one is merged with the solvent peak at $\delta$ 1.73 ppm. Furthermore, the $^{31}$P($^1$H) NMR signals for 2 and 3 show downfield shift as compared to L-Li ($\delta$ 35.6 (2) and 36.5 (3)] vs. 29.7 ppm (L-Li)). The solid-state structures of complexes 2 and 3 show that both are isostructural and crystallizes in orthorhombic chiral space group $P2_12_12$ with half of the molecule in the asymmetric unit cell. Likewise, complex 1, complexes 2 and 3 adopt distorted trigonal bipyramidal geometry with the central metal atoms surrounded by one chlorine atom and four nitrogen atoms of the ligand backbone (Fig. 2 and 3). Since complex 2 and 3 are isostructural, only complex 2 is discussed in detail here. The average P–N bond length in complex 2 is 1.6195(3) Å, which is in the range of previously reported single and double P–N bonds.$^{48}$

The Al–Cl bond length in complex 2 (Al–Cl 2.174(2) Å) is within the range (2.141(2)–2.202(6) Å) of related bis-amidinate aluminium monochloride complexes reported before.$^{49–52}$ The N1–P1–N2 bond angle of 96.2(2)$^\circ$ in complex 2 is slightly narrower than 96.46(9)$^\circ$ as seen in case of complex 1, however wider than 93.90(6)$^\circ$ as reported for [Ph$_3$P(N(SiMe$_3$)$_2$)AlH]$^{39}$ in complex 2, the two individual four membered N$_2$PAl plane are twisted to each other with a dihedral angle of 49.92$^\circ$.

Fig. 3 Molecular structure of complex 3 in the solid state. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Ga–N1 1.950(6), Ga–N2 2.087(5), Ga–Cl 2.240(2), P1–N1 1.617(6), P1–N2 1.625(7), N1–Ga–Cl 116.2(2), N2–Ga–Cl 96.8(8), N2–Ga–N2' 166.2(3), N1–Ga–N1' 127.7(3), N1–Ga–N2 73.4(2), N1–Ga–N2' 100.4(2), N1–P1–N2 96.4(3).

Attempted synthesis of mono and trisubstituted complexes failed, possibly the ligand is not bulky enough to stabilize the monosubstituted product and may be trisubstituted products suffers from steric crowding of the ligand. These results suggest that disubstituted product is thermodynamically more stable.

In order to access cationic analogues of complexes 2 and 3, GaCl$_3$ and AlCl$_3$ were used as halide abstracting agents. The stoichiometric reaction of complex 2 with GaCl$_3$ and 3 with AlCl$_3$ in thf resulted in the formation of the expected products [L$_2$Al][GaCl$_4$]$^-$ (4) and [L$_2$Ga][AlCl$_4$]$^-$ (5), respectively (Scheme 3). By using GaCl$_3$ for the chloride abstraction of the aluminium complex 2 and AlCl$_3$ for the same reaction of the gallium complex 3, we show that ligand scrambling does not
take place. Complexes 4 and 5 are sparingly soluble in n-hexane and toluene. The symmetric nature of the ligands around the metal centre in both 4 and 5 could be seen by appearance of a single set of signals for Ph(CH)CH3 and Ph(CH)CH2 protons in the corresponding 1H NMR spectrum. In accordance, the 31P{1H} NMR spectrum shows singlets at δ 43.3 ppm for complex 4, and at δ 48.6 ppm for complex 5. Further, upon heating the NMR samples of complexes 4 and 5 (in CDCl3) at 50 °C for 16 h, no changes were observed in the 1H and 31P{1H} NMR, suggesting that the cationic complexes (4 and 5) are stable under these conditions. Both complexes 4 and 5 crystallizes in a chiral trigonal space group P3121 with two halves of the cationic part and one anionic [MCl3]− (M = Ga (4) and Al (5)) part in the asymmetric unit cell. The central metal atoms in both cationic and anionic parts of [L2Al][GaCl4]− 4 and [L2Ga][AlCl4]− 5 adopt distorted tetrahedral geometry (Fig. 4 and 5). The central metal atom forms two N2PM planes with NPN ligand backbones, which are twisted with the dihedral angle of 89.97(1)° (4) and 87.53(2)° (5). The average M–N bond distance 1.864(4) Å (M = Al, 4) is smaller than 1.931(6) Å (M = Ga, 5). Obviously, the larger M–N bond distance in case of complex 5 is due to the larger ionic radii of gallium compared to aluminium.

Similarly, in case of the counter anion [MCl3]− the average M–Cl (M = Ga(4), Al(5)) bond distance 2.161(2) Å for complex 4 is larger compared to 2.123(4) Å for complex 5 and are in the expected range of literature reports.3,54

Complexes (1, 4 and 5) could be considered as a catalytically active species. Therefore, to check the catalytic activity of these complexes, an initial test reaction was conducted in the racemic lactide polymerization, however none of these complexes showed any catalytic activity. Further, in contrast to our previously reported alkali metal complexes of the ligand, observing these complexes (1–5) under UV light at room we did not observe any luminescence behavior of these complexes.

Conclusions

In conclusion, we have reacted the enantiopure ligand L-H (L = [Ph2P[N(R)CH(CH3)Ph]2]) and L-Li with group 13 metal compounds such as LiAlH4 and MCl3 (M = Al, Ga), respectively, to afford corresponding enantiopure monohydride (1) and monochloride complexes (2 and 3). Further the cationic complexes (4 and 5) were accessed by halide abstraction of complexes (2 and 3) using MCl3 (M = Al, Ga). To the best of our knowledge such enantiopure group 13 complexes based on chiral iminophosphonamide are not reported yet. All the complexes have been characterised thoroughly including their solid-state structure.

Experimental section

All manipulations of air-sensitive materials were performed under the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10−3 Torr) line, or in an argon-filled MBraun glove box. Hydrocarbon solvents (toluene, Et2O, n-pentane, n-heptane) were dried by using an MBraun solvent purification system (SPS-800), degassed and stored under vacuum over lithium aluminium hydride (LiAlH4). n-Hexane was pre-dried over CaCl2 before decantation and distillation from potassium and storage over 4 Å molecular sieves. Tetrahydrofuran was distilled under nitrogen from potassium benzophenonate before storage over lithium aluminium hydride (LiAlH4). NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance III 400 MHz. Elemental analyses were carried out with a Vario Micro Cube (Elementar Analysensysteme GmbH). IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLATGS detector, a diamond ATR (attenuated total reflection) unit, and a nitrogen flushed chamber In terms of their intensity, the signals were classified into the categories vs =
very strong, s = strong, m = medium, w = weak and vw = very weak. [L-H]²³ was prepared according to literature procedure.

**Synthesis of [L₂AlH] (1)**

LiAlH₄ was used in the following synthesis was purified by extracting with diethyl ether followed by filtration and removal of the solvent from the filtrate under vacuum to obtain LiAlH₄ as white powder.

To the mixture of Li-H (425 mg, 1.0 mmol, 2.00 eq.) and LiAlH₄ (19 mg, 0.5 mmol, 1.00 eq.) 40 mL of diethyl ether was added at room temperature. The reaction mixture was stirred overnight. After filtration and storing the concentrated filtrate at -30 °C for 2 days afforded colourless crystals suitable for X-ray analysis. The mother liquor was decanted-off and the crystals were washed with n-pentane (5 mL) and dried under vacuum.

**Yield (based on crystals):** 285 mg (65%).

**Elemental analysis**

Calcd (%) for [C₅₆H₅₆N₄P₂AlGaCl₄] (1085.54): C 61.96, H 5.20, N 5.16; found: C 62.69, H 5.25, N 5.08.

**Synthesis of [L₂AlCl] (2)**

To the mixture of Li-Li (1.00 g, 2.32 mmol, 2.00 eq.) and AlCl₃ (155 mg, 1.16 mmol, 1.00 eq.), 10 mL of thf was added at room temperature. The reaction mixture was stirred 2 days at -30 °C for 2 days a

**Yield (based on crystals):** 650 mg (59%).

**Elemental analysis**

Calcd (%) for [C₅₆H₅₆N₄P₂AlGaCl₄] (952.21): C 70.64, H 5.93, N 5.88; found: C 70.74, H 6.57, N 5.58.

**Synthesis of [L₂AlCl]²⁻ (4)**

To the mixture of 2 (150 mg, 0.33 mmol, 1.00 eq.) and GaCl₃ (29 mg, 0.33 mmol, 1.00 eq.), 10 mL of thf was added at room temperature. All the volatiles were removed in vacuo after stirring for 2 hours to obtain white powder. Single crystals suitable for X-ray structure analysis were grown from concentrated benzene solution at room temperature.

**Yield (based on crystals):** 98 mg (55%).

**Elemental analysis**

Calcd (%) for [C₅₆H₅₆N₄P₂AlGaCl₄] (1085.54): C 61.96, H 5.20, N 5.16; found: C 62.69, H 5.25, N 5.08.
(w), 974 (vw), 883 (w), 857 (vs), 766 (m), 752 (w), 747 (m), 693 (vs), 651 (vw), 617 (w), 599 (w), 518 (vs), 478 (m), 439 (vw).

**Synthesis of [L₂Ga][AlCl₄]⁻ (5)**

Following the procedure described above for 4, the reaction of 3 (150 mg, 0.16 mmol, 1.00 eq.) and AlCl₃ (7 mg, 0.16 mmol, 1.00 eq.) afforded white powder. Single crystals suitable for X-ray structure analysis were grown from concentrated benzene solution at room temperature.

**Yield** (based on crystals): 104 mg (60%). **Elemental analysis** calcd (%) for [C₆₆H₆₆N₄P₂AlGaCl₄]: C 61.96, H 5.20, N 5.16. Found: C 61.98, H 5.17, N 5.22.

**¹H NMR** (CDCl₃, 400 MHz): δ [ppm] = 7.64 (4H, Ar-H), 7.58 (s), 7.50 (d, 3H, Ar-H), 7.42 (d, 3H, Ar-H), 7.35 (t, 1H, Ar-H), 7.28 (t, 1H, Ar-H), 7.22 (t, 1H, Ar-H), 7.18 (t, 1H, Ar-H), 7.15 (d, 3H, Ar-H), 7.05 (d, 3H, Ar-H), 7.00 (m, 8H, Ar-H), 6.79 (d, 2H, Ph(CH)₂CH₃), 6.50 (d, 2H, Ph(CH)₂CH₃), 4.31 (s, 3H, CH₃), 1.50 (s, 9H, (CH₃)₃P). **¹³C[¹H] NMR** (CDCl₃, 100 MHz): δ [ppm] = 143.9 (d, JₚC = 3.8 Hz, Ar-C₆), 133.9 (Ar-C₆), 132.9 (d, JₚC = 11.3 Hz, Ar-C₆), 129.2 (d, JₚC = 12.8 Hz, Ar-C₆), 128.8 (Ar-C₆), 127.9 (Ar-C₆), 126.8 (Ar-C₆), 125.1 (d, JₚC = 99.6 Hz, Ar-C₆), 54.4 (Ph(CH)₂CH₃), 27.9 (d, JₚC = 12.4 Hz, Ph(CH)₂CH₃).

**Conclusions of interest**

There are no conflicts to declare.

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**Notes and references**


41 B. Prashanth, N. Srungavruksham and S. Singh, ChemistrySelect, 2016, 1, 3601–3606.


