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ARTICLE

Liquid coordination complexes of Lewis acidic metal chlorides: Lewis acidity and insights into speciation

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Coordination complexes of Lewis acidic metal chlorides: AlCl₃, GaCl₃, InCl₃, SbCl₃, SnCl₄, SnCl₂, ZnCl₂ and TiCl₄ with trioctylphosphine (P₈₈₈) and with trioctylphosphine oxide (P₈₈₈O) were synthesised. All compounds formed liquid coordination complexes (LCCs) at ambient temperature, although decomposition *via* redox mechanism was detected in some cases. Lewis acidity of the metal chlorides (measured as 1,2-dichloroethane solutions) and the LCCs (measured neat) was quantified by Gutmann acceptor number (AN). In general, LCCs were equally or more Lewis acidic than the corresponding metal chlorides. The AN values were compared with the catalytic activity of selected LCCs in a model Diels-Alder reaction. Insights into speciation of LCCs was gained using multinuclear NMR spectroscopy, revealing that most LCCs comprised charge-neutral complexes, rather than ionic ones. The relationship between the speciation, Lewis acidity (AN scale) and catalytic activity was discussed in detail. This approach revealed several new, promising catalytic systems, such as P₈₈₈O-InCl₃, with Lewis acidity enhanced compared to chloroindate ionic liquids, and P₈₈₈O-TiCl₄, with hydrolytic stability enhanced with respect to neat TiCl₄.

Introduction

Lewis acidic ionic liquids, in particular those with chloroaluminate(III) anions, are the oldest and are the most thoroughly studied group of ionic liquids to gain widespread interest.¹⁻³ Their catalytic applications (Friedel-Crafts chemistry, olefin isomerisation and oligomerisation, activation of transition metal catalysts) have been extensively researched in the academia, leading to the emergence of several full-scale industrial processes. In Difasol (IFP) chloroaluminate(III) ionic liquids were used as solvent and co-catalyst for nickel-catalysed dimerisation of alkenes.⁴ IONIKYLATION by Petrochina,⁵ CILA by Shell/Petrochina,⁶ and ISOALKYL by Chevron (licenced by Honeywell/UOP)⁷ are all recently-demonstrated refinery alkylations (alkylation of isobutene with butenes, to produce high-octane gasoline), and all are catalysed with chloroaluminate(III) ionic liquids.

Despite this widespread interest, chlorometallate(III) ionic liquids have some key drawbacks: (i) the organic cation, which plays a spectator role in Lewis acid chemistry, is also the cost-incurring component, and (ii) the comprises a metal surrounded exclusively by halide ligands (typically chlorides),

which leaves little room for modification of the catalytic activity. These shortcomings are driving the development of new generations of ionic liquid-like Lewis acids, such as liquid coordination complexes (LCCs). LCCs is a recently-coined term for eutectic mixtures of metal halides and organic donors.⁸ In fact, combinations of AlCl₃ with donor molecules have long been used as Lewis acidic reactants in organic chemistry - always in solutions of organic solvents.^{9,10} Physical chemists have suggested that such combinations form ionic mixtures of coordination complexes, rather than solvated salts.^{11,12} However, only recently these systems were researched in the context of ionic liquid applications.

Abbott *et al.* reported liquid mixtures of urea/amides and AlCl₃, postulating that they form ionic liquids.¹³ Coleman *et al.* studied the speciation of eutectics formed by AlCl₃ or GaCl₃ with a range of donors (urea, thiourea, acetamide, phosphine oxide, or phosphine), and reported them to contain equilibrated cationic, anionic and neutral coordination complexes of the corresponding metals. A detailed study on amide-AlCl₃ by Liu and co-workers demonstrated that urea (Ur) and acetamide (AcA) coordinate to AlCl₃ through oxygen, whereas methylacetamide (NMA) and dimethylacetamide (DMA) have a tendency for bidentate coordination through both *O*- and *N*-donation, increasing as a function of degree of methylation.¹⁴ LCCs of other metal chlorides were merely touched upon: Abbott *et al.* reported that urea and ZnCl₂, SnCl₂ or FeCl₃ form liquids at ambient temperature.¹⁵ Coleman *et al.* stated the same for trioctylphosphine or trioctylphosphine oxide combined with SnCl₄, SnCl₂, ZnCl₂ or FeCl₃.⁸ However, no speciation studies were provided.

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In catalytic applications of LCCs, their speciation was found to have a crucial impact on the catalytic performance. In oligomerisation of 1-decane, DMA-MCl₃ (M = Al or Ga) yielded significantly higher proportion of heavy oligomer products compared to Ur-MCl₃ or AcA-MCl₃.¹⁶ In Friedel-Crafts alkylation of benzene with 1-decene, DMA-GaCl₃ gave much higher reaction rate than Ur-GaCl₃.¹⁷ In refinery alkylation catalysed with L-AlCl₃ (L = AcA, NMA, DMA, among others) the catalytic performance changed as a function of the methylation in the amide ligand.¹⁸ All these can be explained in terms of differing coordination modes, as demonstrated by Liu and co-workers.¹⁴ Despite increasing interest in LCCs as Lewis acidic catalysts, only systems based on AlCl₃ or GaCl₃ have been wider explored.

In this scoping study, we screened a wide range of Lewis acidic metal chlorides for their LCC-forming potential, and investigated their Lewis acidity in order to identify promising catalytic systems.

Experimental

Materials

Aluminium(III) chloride (99.999%) and gallium(III) chloride (99.999%) were purchased in sealed ampules, under argon from Alfa Aesar. Titanium tetrachloride (99%), tin tetrachloride (99.999%), tin dichloride (99.99%), indium trichloride (99%), zinc dichloride (98 %) and antimony trichloride (99.95%) were all purchased from Sigma Aldrich and used as received. Trioctylphosphine oxide (99.5%) was provided by Cytec and dried under reduced pressure (80 °C, < 1 mbar, 48 h) before use. Trioctylphosphine (99.5%) was provided by Cytec in a sealed canister under an inert atmosphere and used as received. Triethylphosphine oxide (99%) and ethyl acrylate were purchased from Sigma Aldrich and was used as received. Cyclopentadiene (ex. Sigma Aldrich) was supplied as a dimer and was distilled immediately before use.

Synthesis of liquid coordination complexes

LCCs were synthesised on a 2 g scale, following the literature procedure.⁸ All syntheses were carried out in a argon-filled glovebox (MBraun LabMaster dp, <0.6 ppm O₂ and H₂O). To a neutral donor ligand (0.25 - 1.00 mol eq.) a metal chloride was added in small aliquots. Heat was typically evolved. The reaction mixture was stirred until the flask was cool to touch before additional aliquots were added. This was repeated until the desired molar ratio of metal chloride of ($\chi_{MCl_x} = 0.50 - 0.75$) was reached. Heat was typically evolved. Afterwards, the reaction mixture was stirred (0.5 - 24 h, 30 - 80 °C), until homogeneous liquid was obtained. All LCCs were stored in the glovebox until used.

Multinuclear NMR spectroscopy

³¹P, ⁶⁷Zn, ¹¹⁵In and ¹²¹Sb NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer, at 162, 25, 88 and 96 MHz, respectively. ⁴⁹Ti and ¹¹⁹Sn NMR spectra were recorded on a Bruker Avance DPX 600 MHz spectrometer, at 34 and 224 MHz, respectively. All samples were studied neat, using a DMSO-filled, sealed capillary as an external lock.

Gutmann AN measurements

The Gutmann acceptor numbers of metal chlorides were measured as 1:1 adducts of MCl_x and triethylphosphine oxide (P₂₂₂O) as described by Gutmann.¹⁹ Solutions of accurately weighed metal chlorides (ca. 0.58 mmol) in accurately known volumes of 1,2-dichloroethane (ca. 1.5 ml) were prepared, to achieve concentrations of ca. 0.35 mol dm⁻³. To each solution, 1 mol eq. of P₂₂₂O (ca. 0.58 mmol) was added, and the mixture was stirred for 30 min. All solids dissolved readily upon the addition of P₂₂₂O. The ³¹P NMR spectra of the solutions were recorded, and then the solutions were diluted to ca. 0.25 mol dm⁻³, and subsequently to ca. 0.20 mol dm⁻³, with ³¹P NMR spectra recorded for each concentration. Recorded ³¹P NMR chemical shifts were plotted as a function of concentration and extrapolated to infinite dilution of P₂₂₂O in the studied sample (δ_{inf}). The acceptor number was calculated according to Eq 1, where $\delta_{hex inf}$ is the ³¹P NMR chemical shift for infinite dilution of P₂₂₂O in hexane.

$$AN = 2.348 \cdot (\delta_{inf} - \delta_{hex inf}) \quad \text{Eq 1}$$

For each LCC, three samples (ca. 1 g each) were weighed out accurately into samples vials. P₂₂₂O was weighed accurately into each sample (ca. 1, 2 and 3 wt %). ³¹P NMR spectra were recorded for the three concentrations, and the chemical shift value was extrapolated to the value of infinite dilution. The AN values were calculated from Eq 1.

General procedure for Diels-Alder reaction

All reactions were carried out under dry argon. In a typical procedure, the LCC catalyst (0.1 - 1.0 mol% per 1.0 mole of dienophile) was placed in a two-neck round-bottomed flask equipped with stirring bar. Then, a mixture of dienophile (16 mmol) and diene (24 mmol) was added drop-wise to the vigorously stirred (1500 rpm) reaction mixture in an ice bath. The reaction was carried out for 5 - 120 min, and its progress monitored by gas chromatography. Afterwards, the reaction was quenched with few drops of water, and 1 cm³ of dichloromethane was added to homogenise the mixture prior to GC analysis.

GC analysis was performed using a Perkin Elmer Clarus 500 gas chromatograph equipped with an SPB™-5 column (30 m x 0.2 mm x 0.2 μm) with *n*-decane as internal standard.

Results and discussion

Synthetic strategy

Liquid coordination complexes were prepared from a range of Lewis acidic metal chlorides: AlCl₃, GaCl₃, InCl₃, SbCl₃, SnCl₄, SnCl₂, ZnCl₂ and TiCl₄, combined with either of the two ligands: trioctylphosphine (P₈₈₈) or trioctylphosphine oxide (P₈₈₈O). The 6 - 8 carbon alkyl chain length is considered optimal for generating liquids, rather than solids (shorter chains promote crystallisation, whereas longer ones - wax formation).²⁰ Indeed, in our earlier work on the AlCl₃ and GaCl₃-LCCs, these two ligands yielded LCCs that were liquid at ambient conditions for the widest range of compositions.⁸ Furthermore, comparison between P₈₈₈ and P₈₈₈O was

potentially offering insight into the influence of the donor hardness on speciation and Lewis acidity.

The compositional range (metal chloride to ligand ratio, reported as the molar ratio of the former, χ_{MCl_x}) was also varied. In our preliminary work, we reported the L-AlCl₃ (L = P₈₈₈O or P₈₈₈) systems to be liquid for $\chi_{\text{AlCl}_3} = 0.50 - 0.60$, and the L-GaCl₃ (L = P₈₈₈O or P₈₈₈) LCCs to be liquid at $\chi_{\text{GaCl}_3} = 0.50 - 0.75$.⁸ In this work, the equimolar composition ($\chi_{\text{MCl}_x} = 0.50$) was the starting point; whenever homogenous liquids had been obtained, a composition with the excess of metal chloride ($\chi_{\text{MCl}_x} = 0.60$, corresponding to MCl_x:L ratio of 1.5:1) was synthesised.

All metal chlorides, combined with either of the two ligands at $\chi_{\text{MCl}_x} = 0.50$, formed homogenous liquids (Table 1). At $\chi_{\text{MCl}_x} = 0.60$, homogenous LCCs were generated by combining GaCl₃, SbCl₃, SnCl₄, TiCl₄ or ZnCl₂ with at least one of the two ligands. As previously reported, L-GaCl₃ LCCs were homogenous liquids up to $\chi_{\text{MCl}_x} = 0.75$.⁸

Table 1. Combinations of metal chlorides and P₈₈₈ or P₈₈₈O ligands that formed LCCs, at given χ_{MCl_x} values.

| MCl _x | χ_{MCl_x} | P ₈₈₈ O | P ₈₈₈ |
|-------------------|-----------------------|---------------------------------------------------|--------------------------------------------------------|
| AlCl ₃ | 0.50 | Colourless liquid [§] | Yellow liquid [§] |
| | 0.60 | Yellow liquid [§] | Yellow liquid [§] |
| | 0.67 | Yellow liquid with white precipitate [§] | Yellow liquid with white precipitate [§] |
| GaCl ₃ | 0.50 | Colourless liquid [§] | Colourless liquid [§] |
| | 0.60 | Colourless liquid [§] | Colourless liquid [§] |
| | 0.67 | Colourless liquid [§] | Colourless liquid [§] |
| | 0.75 | Colourless liquid [§] | Colourless liquid [§] |
| InCl ₃ | 0.50 | Colourless liquid | Colourless liquid with white precipitate ^{§§} |
| | 0.60 | Colourless liquid with white precipitate | Colourless liquid with white precipitate |
| SbCl ₃ | 0.50 | Colourless liquid | Liquid, redox reaction |
| | 0.60 | Colourless liquid | - |
| SnCl ₂ | 0.50 | Colourless liquid | Colourless liquid |
| | 0.60 | Colourless liquid with white precipitate | Colourless liquid with white precipitate |
| SnCl ₄ | 0.50 | Colourless liquid | Liquid, redox reaction |
| | 0.60 | Colourless liquid | - |
| TiCl ₄ | 0.50 | Yellow liquid | Red liquid |
| | 0.60 | Yellow solid with white powder | Red liquid |
| ZnCl ₂ | 0.50 | Colourless liquid | Colourless liquid |
| | 0.60 | Colourless liquid | Colourless liquid with white precipitate |

[§] - previously reported; ^{§§} - a very small amount of precipitate

The presence of a hydrophobic ligand (P₈₈₈O or P₈₈₈) increased the hydrolytic stability of halides such as SnCl₄ or TiCl₄; the corresponding LCCs did not fume/hydrolyse violently when exposed to air. Although they hydrolysed over prolonged exposure to the atmosphere, the lack of rapid HCl release

upon exposure to air is a significant advantage in terms of ease and safety of handling.

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Lewis acidity of the LCCs, similarly to that of halometallate ionic liquids, depends on the metal centre, and on speciation.²¹ In LCCs however, added complexity arose from the presence of a ligand (soft P₈₈₈ vs. hard P₈₈₈O), expected to influence electrophilicity on the metal.

Insights into speciation

To enable meaningful interpretation of the AN studies, knowledge of the LCCs speciation was indispensable. At the same time, a full speciation study of every system (comprising minimum three techniques, such as multinuclear NMR spectroscopy, Raman and FT-IR spectroscopies, XPS or EXAFS, and supporting studies, *e.g.* conductivity measurements) was not feasible for a single publication. Therefore, in this work, preliminary speciation of LCCs was proposed, based on multinuclear NMR studies combined with a thorough literature research. Systems of particular interest were identified, and their detailed speciation will be published in separate contributions.

Amongst the LCCs in this study here, AlCl₃ and GaCl₃-LCCs have already been characterised by ²⁷Al NMR and Raman spectroscopies (⁷¹Ga NMR signals were too broad to be interpretable).⁸ In this work, it was attempted to record ¹¹⁵In, ¹²¹Sb, ¹¹⁹Sn, ⁴⁹Ti and ⁶⁷Zn NMR spectra of the relevant LCCs, but only the ¹¹⁹Sn NMR spectra contained well-defined signals. The remaining nuclei are quadrupolar (in contrast to spin 1/2 ¹¹⁹Sn), thus generally give wider signals, which broaden further with decreasing symmetry around the studied nuclei. Fortunately, the ³¹P{¹H} NMR spectra for all LCCs gave interpretable signals (δ ³¹P, Table 2), with signals shifted upfield in comparison to uncoordinated ligand ($\Delta\delta$ ³¹P, Table 2). The corresponding ³¹P NMR spectra are reported in Supplementary Information, Figure 1 SI - 4 SI.

Table 2. ^{31}P NMR chemical shifts ($\delta^{31}\text{P}$ / ppm) for free P_{888} and P_{888}O , and for ligands in the corresponding LCCs with different metal halides and χ_{MCl_x} values. Changes in ^{31}P NMR chemical shift upon ligand complexation to a metal ($\Delta\delta^{31}\text{P}$ / ppm) are also listed.

| MCl _x | χ_{MCl_x} | P_{888}O | | P_{888} | |
|------------------|-----------------------|--------------------------|-----------------------------|-----------------------|-----------------------------|
| | | $\delta^{31}\text{P}$ | $\Delta\delta^{31}\text{P}$ | $\delta^{31}\text{P}$ | $\Delta\delta^{31}\text{P}$ |
| / ppm | | | | | |
| - | 0.00 | 49.91 | - | -29.44 | - |
| AlCl_3 | 0.50 | 75.20 | 25.29 | -26.65 | 2.79 |
| | | 77.38 | 27.47 | -22.16 | 7.28 |
| | 0.60 | 76.57 | 26.66 | -23.29 | 6.15 |
| GaCl_3 | 0.50 | 76.50 | 26.59 | -9.87 | 19.57 |
| | | 80.15 | 30.24 | | |
| | 0.60 | 79.97 | 30.06 | -5.99 | 23.45 |
| | | 81.23 | 31.32 | | |
| | 0.67 | 81.31 | 31.40 | -2.61 | 26.83 |
| | | 83.41 | 33.50 | | |
| | 0.75 | 84.37 | 34.46 | -0.86 | 28.58 |
| 85.21 | | 35.30 | | | |
| 86.02 | 36.11 | | | | |
| InCl_3 | 0.50 | 72.04 | 22.13 | 11.49 | 40.93 |
| SbCl_3 | 0.50 | 70.91 | 21.00 | -2.77 | 26.67 |
| | 0.60 | 69.60 | 19.69 | - | - |
| SnCl_2 | 0.50 | 70.96 | 21.05 | -3.89 | 25.55 |
| SnCl_4 | 0.50 | 68.74 | 18.83 | 102.7 | 132.14 |
| | | 71.40 | 21.49 | (redox) | (redox) |
| | 0.60 | 68.88 | 18.97 | - | - |
| | | 71.38 | 21.47 | | |
| TiCl_4 | 0.50 | 87.27 | 37.36 | 27.68 | 57.12 |
| | 0.60 | - | - | 34.50 | 63.94 |
| ZnCl_2 | 0.50 | 65.56 | 15.65 | -20.03 | 9.41 |
| | 0.60 | 68.23 | 18.32 | | |

AlCl_3 -LCCs. Both $\chi_{\text{MCl}_x} = 0.50$ and 0.60 compositions were liquids, irrespective of the ligand (Table 1). Speciation of L-AlCl_3 ($\text{L} = \text{P}_{888}$ or P_{888}O), has been already studied as a function of composition, using ^{27}Al NMR and Raman spectroscopies.⁸ It was proposed that, at $\chi_{\text{MCl}_3} = 0.50$, these LCCs contain equilibrated mononuclear complexes (Eq 2).



The ^{31}P NMR spectrum of $\text{P}_{888}\text{O-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.50$ (Figure 1 a, Table 2) featured two ^{31}P NMR signals, corresponding to two phosphorus-containing complexes proposed in Eq 2, 25.29 ppm - $[\text{AlCl}_3(\text{P}_{888}\text{O})]$ and 27.47 ppm - $[\text{AlCl}_2(\text{P}_{888}\text{O})_2]^+$.

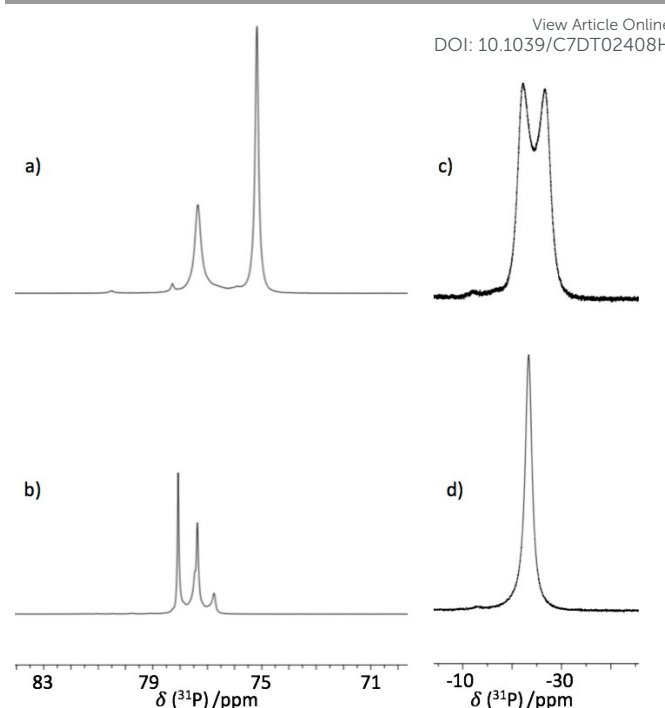
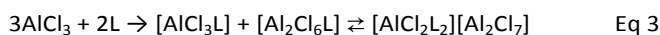


Figure 1. ^{31}P NMR spectra of a) $\text{P}_{888}\text{O-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.50$, b) $\text{P}_{888}\text{O-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.60$, c) $\text{P}_{888}\text{-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.50$, d) $\text{P}_{888}\text{-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.60$.

For $\chi_{\text{AlCl}_3} = 0.60$, binuclear complexes were detected (Eq 3).⁸ The $[\text{Al}_3\text{Cl}_{10}]^-$ anion is not stable at ambient conditions and decomposes to precipitate AlCl_3 ,^{1,22} therefore $\chi_{\text{AlCl}_3} = 0.60$ was the upper compositional limit for AlCl_3 -LCCs.



In agreement with this assignment, ^{31}P NMR spectrum of $\text{P}_{888}\text{O-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.60$ (Figure 1 b) contained three signals, 26.66, 27.46 and 28.16 ppm, corresponding to $[\text{AlCl}_3(\text{P}_{888}\text{O})]$, $[\text{AlCl}_2(\text{P}_{888}\text{O})_2]^+$, and $[\text{Al}_2\text{Cl}_6(\text{P}_{888}\text{O})]$, respectively. This supports the speciation proposed currently for all O-donor-AlCl_3 LCCs (with monodentate ligands) studied to date.^{8,14}

The ^{31}P NMR spectrum of the $\text{P}_{888}\text{-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.50$, featured two broad overlapping singlets at -26.65 and -22.16 ppm (Figure 1 c). It could be mistaken for a doublet because the two signals are of similar intensity, but the coupling of $^1J_{\text{P-Al}} = 467$ Hz is exceedingly high for Al-phosphine complex, with reported values always $^1J_{\text{P-Al}} < 300$ Hz.²³⁻²⁵ The change in ^{31}P NMR chemical shifts, compared to that of neat P_{888} ($\Delta\delta^{31}\text{P} = 2.79 - 7.28$ ppm), is quite small, when compared to other data in Table 2, and to $\Delta\delta^{31}\text{P} = 19.4$ ppm reported for $[\text{AlCl}_3(\text{P}_{111})]$.²⁵ This however is in agreement with the literature: in Al-phosphine adducts, $\Delta\delta^{31}\text{P}$ decreases with increasing bulkiness of the phosphine, and even may assume negative values.²⁶ Finally, Raman spectra of $\text{P}_{888}\text{-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.50$, featured bands characteristic of the $[\text{AlCl}_4]^-$ anion.⁸ This points towards speciation consistent with Eq 2, with equilibrated $[\text{AlCl}_3(\text{P}_{888})]$, $[\text{AlCl}_2(\text{P}_{888})_2]^+$, and $[\text{AlCl}_4]^-$.

The ^{31}P NMR spectrum of the $\text{P}_{888}\text{-AlCl}_3$, $\chi_{\text{AlCl}_3} = 0.60$, contains a singlet at -23.29 ppm (Figure 1 d). With the reported Raman spectrum being inconclusive,⁸ the ^{27}Al NMR spectrum features

a broad signal with a maximum at 107.8 ppm, consistent with AlCl_3 -phosphine adducts.^{23,25} This may be interpreted as the equilibrium in Eq 3 being strongly left-shifted (towards molecular adduct), or as a very rapid exchange between charged and neutral complexes. AlX_3 -phosphine complexes are rare,²⁴ and systems with aluminium halide in excess is quite unique, which offers no literature backing of either hypothesis.

GaCl₃-LCCs. L-GaCl₃ LCCs were liquid for $\chi_{\text{MClx}} = 0.50 - 0.75$, irrespective of the ligand (Table 1).⁸ This derives from propensity of chlorogallate(III) ions to form oligomeric chains, as reported for chlorogallate(III) ionic liquids.²⁷⁻²⁹ Raman studies of L-GaCl₃, $\chi_{\text{MClx}} = 0.50 - 0.75$, have been reported in our earlier work.⁸

The ³¹P NMR spectrum of $\text{P}_{888}\text{O-GaCl}_3$, $\chi_{\text{GaCl}_3} = 0.50$ (Figure 2 a, left; Table 2) featured two ³¹P NMR signals at 76.50 and 80.15 ppm, corresponding to two phosphorus-containing complexes: $[\text{GaCl}_3(\text{P}_{888}\text{O})]$ and $[\text{GaCl}_2(\text{P}_{888}\text{O})_2]^+$, respectively, in analogy to Eq 2. Compared to AlCl_3 -based analogue (Figure 1 a), the signal for the neutral adduct was much more prominent.

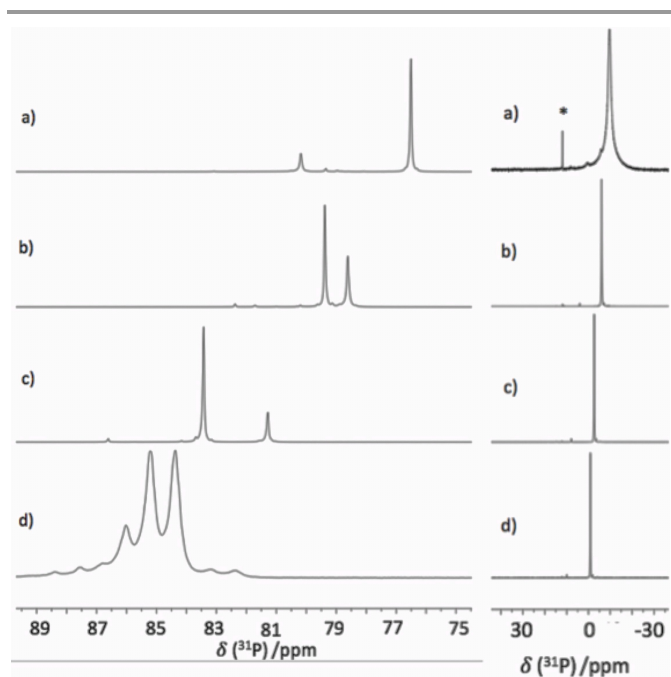
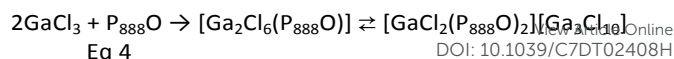


Figure 2. ³¹P NMR spectra of L-GaCl₃, where L = P_{888}O (left) or P_{888} (right) a) $\chi_{\text{GaCl}_3} = 0.50$, b) $\chi_{\text{GaCl}_3} = 0.60$, c) $\chi_{\text{GaCl}_3} = 0.67$, d) $\chi_{\text{GaCl}_3} = 0.75$ (*= artefact)

The ³¹P NMR spectrum of $\text{P}_{888}\text{O-GaCl}_3$, $\chi_{\text{GaCl}_3} = 0.60$ (Figure 2 b, left; Table 2), is similar to that of the AlCl_3 analogue (Figure 1 b), but only two signals are visible, with the lowest intensity signal either absent, or merged with the baseline. However, in combination with Raman studies,⁸ speciation analogous to that in Eq 3 can be confirmed.

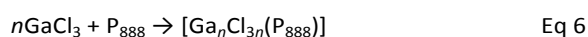
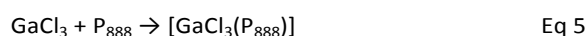
The presence of two signals at 81.31 and 83.41 ppm for $\text{P}_{888}\text{O-GaCl}_3$, $\chi_{\text{GaCl}_3} = 0.67$ (Figure 2 c, left; Table 2) corresponds well to $[\text{GaCl}_2(\text{P}_{888}\text{O})_2]^+$ and $[\text{Ga}_2\text{Cl}_6(\text{P}_{888}\text{O})]$ - see Eq 4. This assignment is in agreement with the reported Raman spectra, which (in the Ga-Cl stretching frequency region) are very similar of all O-donor-GaCl₃ LCCs.⁸



Finally, the spectrum for $\chi_{\text{GaCl}_3} = 0.75$ is complex (Figure 2 d, left; Table 2), with three major signals and some low-intensity features, suggesting a number of equilibrated oligomeric chlorogallate species.

Speciation of $\text{P}_{888}\text{-GaCl}_3$ system appears to deviate from that proposed in our earlier work (Coleman *et al.*).⁸ All compositions, $\chi_{\text{GaCl}_3} = 0.50 - 0.75$, gave singlets in their ³¹P NMR spectra (Figure 2, right; Table 2). The signal at $\chi_{\text{GaCl}_3} = 0.50$ is relatively broad, which could indicate several species in an equilibrium (Figure 2 a, right), however, the peaks for $\chi_{\text{GaCl}_3} = 0.60 - 0.75$ are very narrow, suggesting belonging to a single species (Figure 2 b-d, right).

Previously-reported Raman spectra feature less bands in the Ga-Cl stretching frequency region, compared to other L-GaCl₃ LCCs, which suggests lower number of complexes present.⁸ The band at 349 cm^{-1} is dominant for $\chi_{\text{GaCl}_3} = 0.50$, and the band at 372 cm^{-1} dominates for $\chi_{\text{GaCl}_3} = 0.60 - 0.75$. The Ga-Cl vibrational frequency of 349 cm^{-1} is in close agreement with the band at 349 cm^{-1} , reported for a neutral adduct, $[\text{GaCl}_3(\text{PPh}_3)]$, by Reid and co-workers.³⁰ The same group reported several failed attempts to synthesise $[\text{GaCl}_2\text{L}_2]^+$ cations (L = phosphine), with GaCl_3 having a strong preference towards molecular adduct with monodentate phosphines,³¹ in contrast to findings for AlCl_3 .²⁵ The band at 372 cm^{-1} was recorded also in other L-GaCl₃ LCCs, and may thus be assigned to Ga-Cl stretching frequency in oligomeric neutral Ga^{III} complex, $[\text{Ga}_n\text{Cl}_{3n}(\text{P}_{888})]$, forming in the excess of GaCl_3 . Combining the ³¹P NMR spectra recorded in this work with the literature Raman spectra,⁸ and with the literature data,^{25,30,31} the $\text{P}_{888}\text{-GaCl}_3$ LCCs appear to be molecular adducts (Eq 5 and 6).

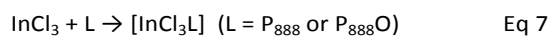


The difference in the action of P_{888}O and P_{888} on the dimeric ' Ga_2Cl_6 ' unit can possibly be interpreted in analogy to work of Gandon and co-workers.³² In their study of GaX_3 adducts with NHC-donors, they found that strong donors (such as P_{888}O) induce heterolytic splitting, whereas homogenous splitting is caused by weaker donors (here - P_{888}).

InCl₃-LCCs. LCCs with equimolar composition, L-InCl₃, $\chi_{\text{InCl}_3} = 0.50$ (L = P_{888}O or P_{888}), contained very small amounts of precipitate, which was filtered off before further studies. For $\chi_{\text{InCl}_3} > 0.50$, InCl₃ was found to precipitate in significant quantities (Table 1). Similarly, in chloroindate(III) ionic liquids, dimeric or oligomeric chloroindate(III) anions were not observed, with excess of InCl₃ precipitating.^{29,33,34}

³¹P NMR signals recorded for the two InCl₃-LCCs studied here revealed broad singlets, at 72.04 ppm for $\text{P}_{888}\text{O-InCl}_3$, $\chi_{\text{InCl}_3} = 0.50$ and at 11.49 ppm for $\text{P}_{888}\text{-InCl}_3$, $\chi_{\text{InCl}_3} = 0.50$ (Table 2). Whereas chloroindate(III) ionic liquids gave broad but well-defined signals for the tetrahedral $[\text{InCl}_4]^-$ anion in their ¹¹⁵In

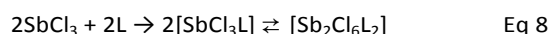
NMR spectra,³⁴ no ¹¹⁵In NMR signals could be distinguished for either LCC. Single peaks in ³¹P NMR spectra and no evidence for [InCl₄]⁻ in ¹¹⁵In NMR spectra suggest that simple molecular adducts, liquid at ambient temperatures, are formed in both cases (Eq 7).



This is supported by the literature on coordination chemistry of In^{III}. Indium has significantly larger covalent radius, compared to gallium and aluminium, easily adopting 4-, 5- or 6-coordinate environment.²⁴ Hence, chloroindate(III) ionic liquids contain equilibrated [InCl₆]³⁻, [InCl₅]²⁻ and [InCl₄]⁻ anions, depending on the composition, χ_{InCl_3} .^{29,33,34} In adducts with phosphine oxides, the formation of a molecular or ionic compound depended on the ligand bulkiness, e.g. [InCl₃(P₁₁₁O)₃] vs. [InCl₂(PPh₃O)₄][InCl₄].³⁵ Nevertheless, the ligand size did not decrease the coordination number of the cationic indium, and always excess of ligand was required to induce heterolytic splitting (which is never the case in this study). In adducts of InX₃ with phosphines, 4- and 5-coordinate molecular adducts are common, with some 6-coordinate species known, but heterolytic splitting is rare, only with extremely bulky ligands.²⁴

SbCl₃-LCCs. Both ligands gave homogenous liquids for $\chi_{\text{SbCl}_3} = 0.50$. The P₈₈₈O-SbCl₃, $\chi_{\text{SbCl}_3} = 0.60$, LCC was also a liquid.

The ³¹P NMR spectrum of P₈₈₈-SbCl₃, $\chi_{\text{SbCl}_3} = 0.50$, featured a singlet at -2.77 ppm (Table 2). Burford and co-workers reported that reactions of SbCl₃ with three different phosphines, at $\chi_{\text{SbCl}_3} = 0.50$, yield the corresponding neutral adducts, [SbCl₃(phosphine)], characterised by ³¹P NMR singlets at 5.6 - 25.1 ppm.³⁶ In the crystal structure, [SbCl₃(P₁₁₁)] formed a Cl-bridged polymeric chain (Figure 3 a), whereas complexes with bulkier phosphines, [SbCl₃(PPh₃)] and [SbCl₃(PCy₃)], formed dimers with two Cl-bridges (Figure 3 b). In all cases, the complex adopted square based pyramidal geometry around the Sb^{III} centre. In analogy, the formation of a molecular adduct was assumed, with the caveat that it may be assuming a dimeric structure also in solution (Eq 8).



However, after two days (sample stored in the glovebox under ambient conditions, argon atmosphere), a weak signal corresponding to [P^V₈₈₈Cl]⁺ appeared at 103 ppm (Figure 5 SI b).³⁷ In an older sample, a dark precipitate (likely antimony black) appeared, indicating that the LCC is unstable, and undergoes a complex redox reaction, which was further confirmed by ³¹P NMR spectroscopy of the remaining liquid (Figure 5 SI c). A fresh sample of the LCC was synthesised for acceptor number and Diels-Alder studies, but the P₈₈₈-SbCl₃, $\chi_{\text{SbCl}_3} = 0.60$, composition was not studied, owing to this decomposition.

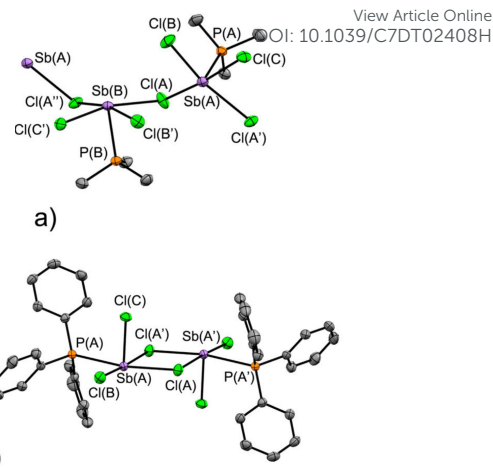


Figure 3. Crystal structures for a) [SbCl₃(P₁₁₁)] (a polymeric array), and b) [SbCl₃(PPh₃)] (dimeric structure).³⁶

The ³¹P NMR spectra of the P₈₈₈O-SbCl₃ system featured a singlet at 70.91 ppm ($\Delta\delta^{31}\text{P} = 21.0$ ppm) for $\chi_{\text{SbCl}_3} = 0.50$, and a singlet at 69.60 ppm ($\Delta\delta^{31}\text{P} = 19.69$ ppm) for $\chi_{\text{SbCl}_3} = 0.60$ (Table 2). These are comparable with the ³¹P NMR spectrum of the [SbCl₃(PCy₃O)] adduct, which also contained a singlet at 65.3 ppm ($\Delta\delta^{31}\text{P} = 15.6$ ppm).³⁸ The crystal structure for this adduct, published by Burford and co-workers, revealed a dimer with pentacoordinate Sb^{III}, which was remarkably similar to the structure of [SbCl₃(PPh₃)], Figure 3 b.³⁸

The liquid-phase speciation of the P₈₈₈O-SbCl₃ system is proposed to contain neutral adducts, possibly in the dimeric form, for $\chi_{\text{SbCl}_3} = 0.50$ (Eq 8). The P₈₈₈O-SbCl₃, $\chi_{\text{SbCl}_3} = 0.60$ composition likely contain charge-neutral Cl-bridged oligomers, with bridging modes like these in Figure 3, but further studies would be required to confirm this.

SnCl₂-LCCs. The L-SnCl₂ LCCs (L = P₈₈₈O or P₈₈₈) were liquid for $\chi_{\text{SnCl}_2} = 0.50$, and contained unreacted SnCl₂ for $\chi_{\text{SnCl}_2} > 0.50$ (Table 1). This was in contrast to chlorostannate(II) ionic liquids, which were homogenous up to $\chi_{\text{SnCl}_2} = 0.67$ due to the formation of [Sn₂Cl₅]⁻.³⁹ This was the first indication that molecular adducts, rather than ionic species, should be expected in L-SnCl₂ LCCs.

The ¹¹⁹Sn NMR spectrum of P₈₈₈-SnCl₂, $\chi_{\text{SnCl}_2} = 0.50$, featured a broad singlet at -70.9 ppm (Figure 4 a), and the corresponding ³¹P NMR spectrum had a sharp singlet at -3.89 ppm (Figure 4 c, Table 2). These are in a good agreement with spectroscopic data reported for the neutral adduct, [SnCl₂(P₂₂₂)], which a broad ¹¹⁹Sn NMR signal at -82.5 ppm, and a ³¹P NMR singlet at -3.7 ppm.⁴⁰ In its crystal structure, the bond angles around tin at ca. 90° angle due to very strong inert pair effect.

In conclusion, tricoordinate [SnCl₂(P₈₈₈)] adduct, liquid at ambient temperature, was formed (Eq 9).



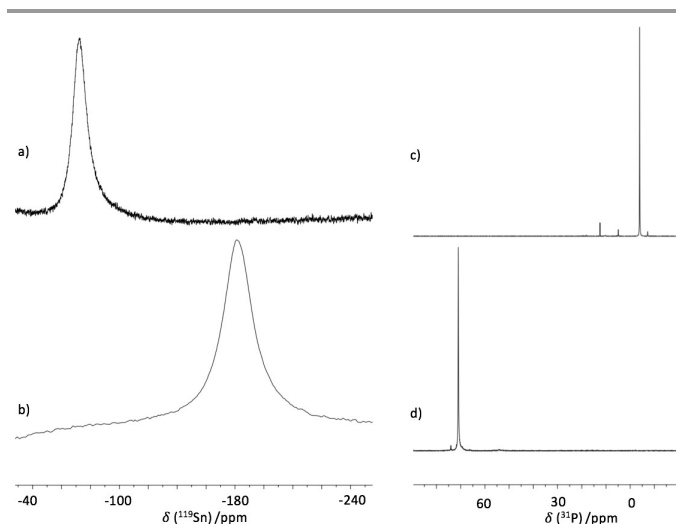
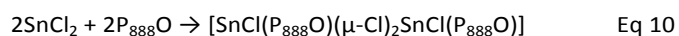


Figure 4. NMR spectra of L-SnCl₂ LCCs at $\chi_{\text{SnCl}_2} = 0.50$ a) ^{119}Sn NMR spectrum of P₈₈₈-SnCl₂, b) ^{119}Sn NMR spectrum of P₈₈₈O-SnCl₂, c) ^{31}P NMR spectrum of P₈₈₈-SnCl₂, d) ^{31}P NMR spectrum of P₈₈₈O-SnCl₂

Crystal structures of a general formula [SnCl₂L], where L = trialkylphosphine oxide, or triarylphosphine oxide, are not known,[‡] in contrast to [SnCl₂L₂] adducts. For example, Reid and co-workers reported on crystal structures of [SnCl₂(P₁₁₁O)₂] and [SnCl₂(PPh₃O)₂], crystallised from solutions with SnCl₂:L ratio of $\chi_{\text{SnCl}_2} = 0.33$.⁴¹ The ^{31}P NMR spectra featured broad singlets at 51.2 and 36.3, respectively. The ^{119}Sn NMR spectrum of [SnCl₂(P₁₁₁O)₂] had a singlet at -204 ppm, but no signal was recorded for [SnCl₂(PPh₃O)₂].

The ^{119}Sn NMR spectrum of P₈₈₈O-SnCl₂, $\chi_{\text{SnCl}_2} = 0.50$, reported in this work, featured a broad, low intensity singlet at -179.5 ppm (Figure 4 b), with the ^{31}P NMR spectrum featuring a sharp singlet at 70.96 ppm (Figure 4 d, Table 2). The ^{119}Sn NMR signal corresponds to a tetracoordinate tin^{II} complex, with no signals either in the tricoordinate region (downfield from -100 ppm), nor for SnCl₂ (>0 ppm).²³ Combining the requirement for tetracoordinate environment, equimolar ligand to tin ratio and single peak in ^{31}P NMR spectrum, a charge-neutral dimer, [Sn₂Cl₄(P₈₈₈)₂], with two bridging chlorides, is proposed as the main species (Eq 10).



SnCl₄-LCCs. The P₈₈₈O-SnCl₄, $\chi_{\text{SnCl}_4} = 0.50$ and 60, formed homogenous liquids (Table 1). Their ^{119}Sn NMR spectra both contained three groups of signals: -336.3, -449.2 and -710 ppm for $\chi_{\text{SnCl}_4} = 0.50$ (Figure 5 a), and -211.1, -449.2 and -710 ppm for $\chi_{\text{SnCl}_4} = 0.60$ (Figure 5 b). In the multiplet at -710 ppm, two poorly resolved doublets (or multiplet fragments) could be identified, at -709.5 ppm ($^2J_{119\text{Sn}-31\text{P}} = 149.4$ Hz) and at -711.7 ppm ($^2J_{119\text{Sn}-31\text{P}} = 109.2$ Hz) - see insert in Figure 5. Otherwise, all signals were broad singlets.

The corresponding ^{31}P NMR spectra both contained two groups of signals: at 68.74 and 71.40 ppm for $\chi_{\text{SnCl}_4} = 0.50$, and at 68.88 and 71.38 ppm for $\chi_{\text{SnCl}_4} = 0.6$ (Table 2, Figure 5 c and d).

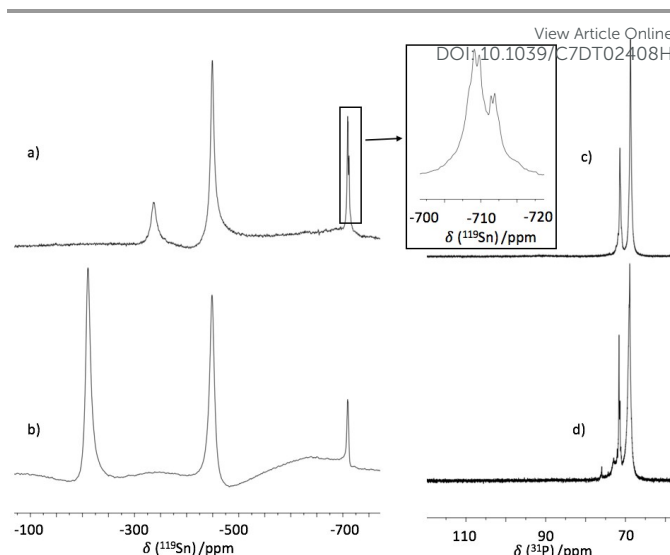
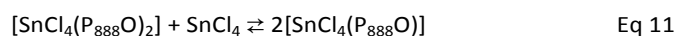
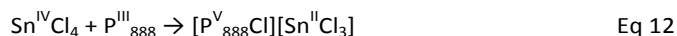


Figure 5. NMR spectra of SnCl₄-LCCs a) ^{119}Sn NMR spectrum of P₈₈₈O-SnCl₄, $\chi_{\text{SnCl}_4} = 0.50$, b) ^{119}Sn NMR spectrum of P₈₈₈O-SnCl₄, $\chi_{\text{SnCl}_4} = 0.60$ c) ^{31}P NMR spectrum of P₈₈₈O-SnCl₄, $\chi_{\text{SnCl}_4} = 0.50$, d) ^{31}P NMR spectrum of P₈₈₈O-SnCl₄, $\chi_{\text{SnCl}_4} = 0.60$.

This highly shielded signal at -710 ppm can be identified as belonging to the hexacoordinate [SnCl₄(P₈₈₈O)₂],⁴² with the two multiplets likely corresponding to *cis*- and *trans*-conformations of the P₈₈₈O ligand in the octahedron. Coupling constants are slightly lower than these reported in the literature ($^2J_{119\text{Sn}-31\text{P}} = 144 - 216$ Hz). The less shielded peak at -449.2 ppm is assigned to [SnCl₄(P₈₈₈O)], which is the stoichiometric composition for $\chi_{\text{SnCl}_4} = 0.50$. The chemical shift for the least shielded signal changed from -336.3 ppm for $\chi_{\text{SnCl}_4} = 0.50$, to -211.1 ppm for $\chi_{\text{SnCl}_4} = 0.60$, compared to -150 ppm for neat SnCl₄. Also, its area visibly increased with increasing χ_{SnCl_4} value. This signal is assigned to tin(IV) chloride, in a dynamic equilibrium with its complexes (Eq 11).



The P₈₈₈-SnCl₄ $\chi_{\text{SnCl}_2} = 0.50$ system was a homogenous liquid at ambient temperature, but both ^{119}Sn and ^{31}P NMR spectroscopy of the fresh sample revealed a redox reaction (Eq 12). Consequently, higher loadings of SnCl₄ were not tested.



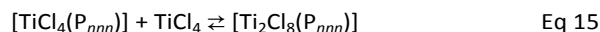
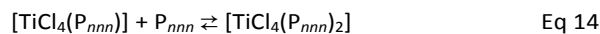
This contrasts with reports of Burford and co-workers, who synthesised [SnCl₄(P₁₁₁)₂] with no evidence of redox reaction, even despite pyrophoric nature of P₁₁₁.⁴³ This might be attributed to very different reaction conditions: after 1 h reaction in dichloromethane, the solid product was isolated.

TiCl₄-LCCs. Both P₈₈₈-TiCl₄ compositions were bright red liquids (Table 1). The colour is characteristic of phosphine complexes of Ti^{IV} and arises due to phosphine→Ti^{IV} LMCT absorption; for example, both [TiCl₄(PPh₃)] and [TiCl₄(PPh₃)₂] absorb *ca.* 480 nm.⁴⁴

In ^{31}P NMR spectra of P₈₈₈-TiCl₄, $\chi_{\text{TiCl}_4} = 0.50$ and 0.60, singlets at 27.68 and 34.50 ppm, respectively, were found (Table 2). Very strong deshielding of the nuclei compared to the neat

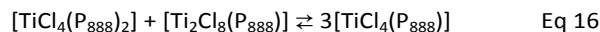
ligand ($\Delta\delta^{31}\text{P} = 57.12$ and 63.94 , respectively) is in agreement with the literature reports for phosphine complexes of Ti^{IV} ($\Delta\delta^{31}\text{P} = 26$ ppm for PPh_3 , 71.2 ppm for PMe_3).⁴⁵

The TiCl_4 -phosphine adducts in solution are characterised by complex equilibria between molecular complexes: $[\text{TiCl}_4(\text{P}_{nnn})]$ and $[\text{TiCl}_4(\text{P}_{nnn})_2]$ - see Eq 13 and 14, in addition to a dimer with two bridging chlorides, $[\text{Ti}_2\text{Cl}_8(\mu\text{-Cl})_2\text{TiCl}_2]$, (Eq 15), in excess of TiCl_4 .⁴⁵⁻⁴⁷



Depending on the solvent, temperature and phosphine, ^{31}P NMR spectra of the solutions may feature either a single peak,⁴⁵ or separate signals for each of the three proposed species are seen.⁴⁷ For example, studies of TiCl_4 adducts with P_{222} or P_{444} in C_6D_6 afforded three distinguishable ^{31}P NMR signals for $[\text{TiCl}_4(\text{P}_{nnn})_2]$, $[\text{TiCl}_4(\text{P}_{nnn})]$ and $[\text{Ti}_2\text{Cl}_8(\text{P}_{nnn})]$. Irrespective of the phosphine, and for a wide range of TiCl_4 loadings (from $\chi_{\text{TiCl}_4} = 0.50$ to $\chi_{\text{TiCl}_4} > 0.67$), these three signals were present, indicating the presence of all three species in all compositions.⁴⁷ The same was suggested for other phosphines, even if singlets were found in ^{31}P NMR spectra.^{45,46}

The ^{31}P NMR signals recorded in this work are within the same range as in the literature, and liquids are formed even with excess of TiCl_4 , thus analogous speciation is concluded, *i.e.* equilibrated $[\text{TiCl}_4(\text{P}_{888})_2]$, $[\text{TiCl}_4(\text{P}_{888})]$ and $[\text{Ti}_2\text{Cl}_8(\text{P}_{888})]$ in both studied compositions (Eq 16).



The $\text{P}_{888}\text{O-TiCl}_4$ $\chi_{\text{TiCl}_4} = 0.50$ formed a yellow liquid, but the $\chi_{\text{TiCl}_4} = 0.60$ composition solidified, and was not studied further (Table 1). A single ^{31}P NMR signal at 87.27 ppm was recorded for the $\chi_{\text{TiCl}_4} = 0.50$ composition. With $\Delta\delta^{31}\text{P} = 37.36$ ppm, it is the most deshielded signal for P_{888}O recorded in this study (Table 2), giving the promise of high Lewis acidity.

A yellow crystalline $[\text{TiCl}_4(\text{OPPh}_3)_2]$ complex was reported, but no crystal structures of equimolar adducts are known.⁴⁸ P_{888}O , often abbreviated as TOPO (trioctylphosphine oxide), is commonly studied extracting agents for Ti^{IV} species from acidic aqueous solutions, with $[\text{TiCl}_4(\text{P}_{888}\text{O})_2]$ as the proposed adduct structure.⁴⁹ Furthermore, P_{888}O was used as solvent/capping agent in the synthesis of titania nanoparticles from TiCl_4 and titanium alkoxides.⁵⁰ Despite many uses, coordination chemistry of Ti^{IV} with phosphine oxides in solution is not well studied, especially with equimolar or excess amount of TiCl_4 . Based on the available ^{31}P NMR spectrum, and evidently strong bonding of the ligand, an equimolar adduct $[\text{TiCl}_4(\text{P}_{888}\text{O})]$ is tentatively assumed as the dominant species. Oligomers similar to those postulated for $\text{TiCl}_4\text{-P}_{888}$ (Eq 16) are conceivable, but considering very strong O-Ti interaction, the ligand is expected to be much less labile. Given interest in this system, speciation of $\text{P}_{888}\text{O-TiCl}_4$ as a function of χ_{TiCl_4} will be the subject of a separate study, supported with vibrational spectroscopy and crystallography.

ZnCl₂-LCCs. The L-ZnCl₂ LCCs, $\chi_{\text{ZnCl}_2} = 0.50$, formed homogenous liquids for both L = P_{888}O and P_{888} (Table 1). With increasing zinc chloride loading to $\chi_{\text{ZnCl}_2} = 0.60$, $\text{P}_{888}\text{O-ZnCl}_2$ formed a homogenous liquid, whereas $\text{P}_{888}\text{-ZnCl}_2$ contained white precipitate.

The ^{31}P NMR spectrum of $\text{P}_{888}\text{-ZnCl}_2$, $\chi_{\text{ZnCl}_2} = 0.50$, gave a singlet at -20.03 ppm. In the crystal structures of adduct of ZnX_2 with neutral ligands, the most common are $[\text{ZnX}_2\text{L}_2]$ motifs ($\chi_{\text{ZnCl}_2} = 0.33$), but with higher χ_{ZnCl_2} values bridged structures are reported, without decreasing the coordination number.²⁴ Indeed, equimolar adducts of zinc(II) halides with phosphines are known to form $[\text{ZnX}(\text{PR}_3)(\mu\text{-X})_2\text{ZnX}(\text{PR}_3)]$,²⁴ for example recently-reported $[\text{ZnCl}(\text{P}^t\text{Bu})(\mu\text{-Cl})_2\text{ZnCl}(\text{P}^t\text{Bu})]$, Figure 6.⁵¹

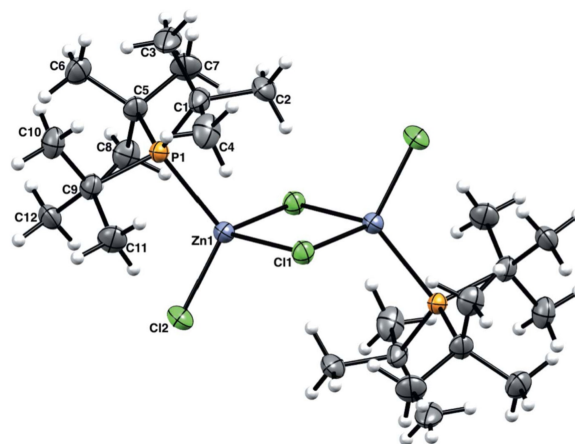
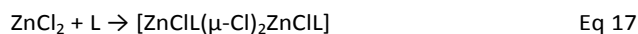


Figure 6. The structure of $[\text{ZnCl}(\text{P}^t\text{Bu})(\mu\text{-Cl})_2\text{ZnCl}(\text{P}^t\text{Bu})]$, with ellipsoids at 50% probability level and arbitrary size for hydrogens.⁵¹

The existence of large, Cl-bridged structures in the liquid phase is feasible; for example, chlorozincate(II) ionic liquids may contain $[\text{ZnCl}_4]^{2-}$, $[\text{Zn}_2\text{Cl}_6]^{2-}$, and larger anionic clusters such as $[\text{Zn}_4\text{Cl}_{10}]^{2-}$.^{52,53} In consistence with a singlet in ^{31}P NMR spectrum, and known chemistry of zinc(II) chloride with phosphines, the structure of $\text{P}_{888}\text{-ZnCl}_2$, $\chi_{\text{ZnCl}_2} = 0.50$ is postulated (Eq 17).



Adducts of zinc halides with phosphine oxides are far less studied in inorganic chemistry, although in general with both halides and O-donors zinc forms tetrahedral complexes.⁵⁴ Again, in analogy to Ti^{IV} , P_{888}O and other phosphine oxides are commonly studied for Zn^{II} extraction from the aqueous layer, with $[\text{ZnX}_2(\text{P}_{nnn}\text{O})_2]$ stoichiometry suggested, but no studies on equimolar compositions.⁵⁵ Also in this case, a tentative structure postulated in Eq 17 is proposed, $[\text{ZnCl}(\text{P}_{888}\text{O})(\mu\text{-Cl})_2\text{ZnCl}(\text{P}_{888}\text{O})]$, but this system lends itself onto further study.

The summary of plausible speciation of the synthesised LCCs is gathered in Table 3. Compared to the L- AlCl_3 and L- GaCl_3 LCCs, in liquid coordination complexes of other metals molecular species are preferred over the ionic ones.⁵⁶ A possible

explanation might be derived from the study on the formation of ammonia borane, $[\text{NH}_3\text{BH}_3]$, vs. diammoniate of diborane, $[\text{BH}_2(\text{NH}_3)_2][\text{BH}_4]^{56}$. The formation of the ionic product was found to be less energetically favourable compared to the molecular adduct. In general terms, several conditions needed to be met *en route* to the charged species, including a pathway

to form a dimeric intermediate, and the presence of sufficient weak interactions stabilising the opposing charges. Although, for many of the newly-reported LCCs, further studies would be required to confirm the proposed speciation, the charge-neutral coordination complexes, mono- or oligonuclear, appear to be the norm.

Table 3. Suggested speciation in LCCs studied in this work, based on the available NMR spectroscopic data and the literature.

| MCl_x | χ_{MCl_x} | P_{888}O | P_{888} |
|-----------------|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| AlCl_3 | 0.50 | $2[\text{AlCl}_3(\text{P}_{888}\text{O})] \rightleftharpoons [\text{AlCl}_2(\text{P}_{888}\text{O})_2][\text{AlCl}_4]$ | $2[\text{AlCl}_3(\text{P}_{888})] \rightleftharpoons [\text{AlCl}_2(\text{P}_{888})_2][\text{AlCl}_4]$ |
| | 0.60 | $[\text{AlCl}_3\text{L}] + [\text{Al}_2\text{Cl}_6(\text{P}_{888}\text{O})] \rightleftharpoons [\text{AlCl}_2(\text{P}_{888}\text{O})_2][\text{Al}_2\text{Cl}_7]$ | $[\text{AlCl}_3\text{L}] + [\text{Al}_2\text{Cl}_6(\text{P}_{888})] \rightleftharpoons [\text{AlCl}_2(\text{P}_{888})_2][\text{Al}_2\text{Cl}_7]$ |
| GaCl_3 | 0.50 | $2[\text{GaCl}_3(\text{P}_{888}\text{O})] \rightleftharpoons [\text{GaCl}_2(\text{P}_{888}\text{O})_2][\text{GaCl}_4]$ | $[\text{GaCl}_3(\text{P}_{888})]$ |
| | 0.60 | $[\text{GaCl}_3(\text{P}_{888}\text{O})] + [\text{Ga}_2\text{Cl}_6(\text{P}_{888}\text{O})] \rightleftharpoons [\text{GaCl}_2(\text{P}_{888}\text{O})_2][\text{Ga}_2\text{Cl}_7]$ | $[\text{Ga}_2\text{Cl}_6(\text{P}_{888})]$ |
| | 0.67 | $[\text{Ga}_2\text{Cl}_6(\text{P}_{888}\text{O})] \rightleftharpoons [\text{GaCl}_2(\text{P}_{888}\text{O})_2][\text{Ga}_3\text{Cl}_{10}]$ | $[\text{Ga}_3\text{Cl}_9(\text{P}_{888})]$ |
| | 0.75 | complex oligomers | complex oligomers |
| InCl_3 | 0.50 | $[\text{InCl}_3(\text{P}_{888}\text{O})]$ | $[\text{InCl}_3(\text{P}_{888})]$ |
| SbCl_3 | 0.50 | $2[\text{SbCl}_3(\text{P}_{888}\text{O})] \rightleftharpoons [\text{Sb}_2\text{Cl}_6(\text{P}_{888}\text{O})_2]$ | $2[\text{SbCl}_3\text{L}] \rightleftharpoons [\text{Sb}_2\text{Cl}_6\text{L}_2] \rightarrow \text{redox}$ |
| | 0.60 | oligonuclear Cl-bridged complexes | - |
| SnCl_2 | 0.50 | $[\text{Sn}_2\text{Cl}_4(\text{P}_{888}\text{O})_2]$ | $[\text{SnCl}_2(\text{P}_{888})]$ |
| SnCl_4 | 0.50 | $[\text{SnCl}_4(\text{P}_{888}\text{O})_2] + \text{SnCl}_4 \rightleftharpoons 2[\text{SnCl}_4(\text{P}_{888}\text{O})]$ | redox |
| | 0.60 | $[\text{SnCl}_4(\text{P}_{888}\text{O})_2] + \text{SnCl}_4 \rightleftharpoons 2[\text{SnCl}_4(\text{P}_{888}\text{O})]^a$ | - |
| TiCl_4 | 0.50 | $[\text{TiCl}_4(\text{P}_{888}\text{O})]$ | $[\text{TiCl}_4(\text{P}_{888})_2] + [\text{Ti}_2\text{Cl}_8(\text{P}_{888})] \rightleftharpoons 3[\text{TiCl}_4(\text{P}_{888})]$ |
| | 0.60 | - | $[\text{TiCl}_4(\text{P}_{888})_2] + [\text{Ti}_2\text{Cl}_8(\text{P}_{888})] \rightleftharpoons 3[\text{TiCl}_4(\text{P}_{888})]^a$ |
| ZnCl_2 | 0.50 | $[\text{Zn}_2\text{Cl}_4(\text{P}_{888}\text{O})_2]$ | $[\text{Zn}_2\text{Cl}_4(\text{P}_{888})_2]$ |
| | 0.60 | oligonuclear Cl-bridged complexes | - |

^a - the equilibrium reaction does not reflect the actual stoichiometry at the given composition

Gutmann acceptor number of metal chlorides

Methodology. The literature data on ANs of metal chlorides used in this work were incomplete. Moreover, even if the AN values were reported, they were measured in different solvents, for example Gutmann and co-workers used 1,2-dichloroethane (DCE),¹⁹ but Beckett *et al.* selected diethyl ether (Et_2O).⁵⁷ For the sake of reliable comparison, we measured AN values for all metal chlorides used in this work, adhering to the Gutmann's procedure,¹⁹ whereby ^{31}P NMR spectra of equimolar mixtures of P_{222}O and a metal chloride in DCE were recorded.

Although most ^{31}P NMR spectra featured a single peak (Figure 6 SI b), in some cases - several signals were observed (Figure 6 SI a). A weighted average of chemical shifts (taking into account chemical shifts and peak areas) was initially considered as the most accurate method of reporting the AN value. However, this methodology would not be suitable for LCCs, where partial overlap with signals from P_{888}O was anticipated, preventing meaningful integration of signals. Thus, AN was calculated based on the chemical shift of the signal with the largest peak area, related to the Lewis acidic species of highest concentration. ^{31}P NMR chemical shifts of P_{222}O and metal chloride solutions in DCE are listed in Table 1 SI, with

samples where multiple ^{31}P NMR signals occurred marked with asterisk.

AN scale for metal chlorides. Acceptor numbers of metal chlorides followed the order: $\text{TiCl}_4 > \text{SbCl}_5 > \text{AlCl}_3 > \text{SnCl}_4 > \text{GaCl}_3 \approx \text{InCl}_3 \approx \text{SnCl}_2 > \text{ZnCl}_2 > \text{SbCl}_3$ (Figure 7).

Besides this work, the most comprehensive classification of Lewis acidic metal chlorides in the literature appears to have been provided by Kobayashi and co-workers.⁵⁸ Metal chlorides were divided into categories with respect to their catalytic strength: A (active), B (weak) and C (inactive), and with respect to the aldehyde/aldimine selectivity: 1 (aldehyde-selective), 2 (aldimine-selective) and 3 (neutral).⁵⁸ ANs measured here were in a relatively good agreement with the Kobayashi classification (Figure 7), with a marked exception of SbCl_3 , which is a moderate acid by AN = 61.4, but was found very active (A-1) by Kobayashi.

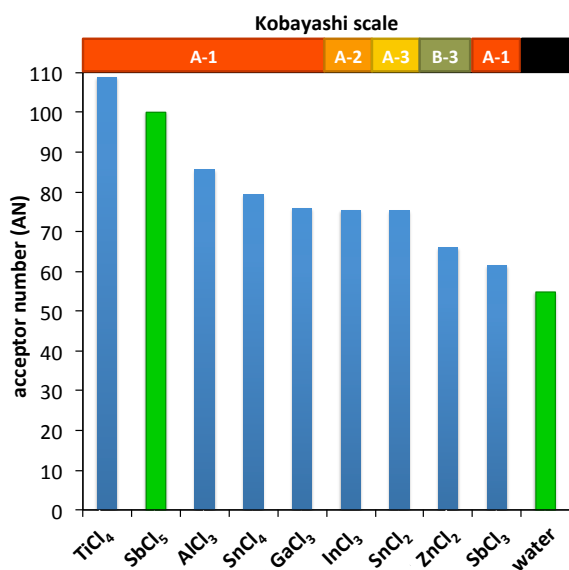


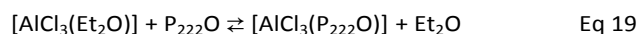
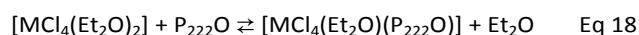
Figure 7. Acceptor Numbers of metal halides, measured as 1,2-dichloroethane solutions, and water, compared to classification by Kobayashi.⁵⁸ ANs of SbCl₅ and water cited after Gutmann and co-workers.¹⁹

AN values of metal chlorides measured in DCE (this work) and in Et₂O (Beckett *et al.*)⁵⁹ are compared in Table 4. Acceptor number for AlCl₃ was independent of solvent (AN = *ca.* 86), in contrast to AN values for TiCl₄ and SnCl₄, which were significantly lower when measured in Et₂O compared to DCE (Table 4).

Table 4. Comparison of ANs measured for selected metal chlorides in 1,2-dichloroethane solution, AN_{DCE} (this work) or diethyl ether solution, AN_{Et₂O} (Beckett *et al.*)⁵⁷

| MCl _x | AN _{DCE} | AN _{Et₂O} |
|-------------------|-------------------|-------------------------------|
| TiCl ₄ | 108.8 | 70 |
| AlCl ₃ | 85.6 | 87 |
| SnCl ₄ | 79.2 | 59 |

This can be justified through differences in coordination chemistry of the three metal chlorides. Diethyl ether is known to coordinate weakly to Lewis acidic metal centres, forming hexacoordinate [MCl₄(Et₂O)₂] adducts with Ti or Sn^{IV} chlorides,^{60,61} and a tetracoordinate [AlCl₃(Et₂O)] adduct with aluminium chloride.⁶² Since equimolar amounts of the phosphine oxide probe were used, it is possible that Lewis acidity of TiCl₄ and SnCl₄ was weakened and softened by the remaining Et₂O ligand (Eq 18). In contrast, in the [AlCl₃(Et₂O)] adduct, ether was likely to be entirely substituted by P₂₂₂O (Eq 19).



This may suggest that using DCE as a non-coordinating solvent may give results that are more true to 'neat' metal chlorides.

Lewis acidity by Gutmann acceptor number approach

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Methodology. To measure acceptor numbers of LCCs, small quantities (1 - 3 wt %) of P₂₂₂O were dissolved in neat LCCs and ³¹P NMR spectra were recorded (Table 1 SI). This methodology, developed and optimised for halometallate ionic liquids, was shown to be sensitive to their speciation (with the exception of chloroaluminate ionic liquids).^{21,63}

With regards to P₈₈₈O-MCl_x LCCs studied in this work, a potential difficulty might have been in the signal from the ligand (P₈₈₈O) obscuring the signal of the probe (P₂₂₂O). To establish the relative difference in ³¹P NMR chemical shifts between signals from P₈₈₈O and P₂₂₂O complexes, an LCC based on the probe itself, P₂₂₂O-AlCl₃, $\chi_{\text{AlCl}_3} = 0.50$, was synthesised, and its ³¹P NMR spectrum was compared to P₈₈₈O-AlCl₃, $\chi_{\text{AlCl}_3} = 0.50$. The ³¹P NMR signals for P₂₂₂O-AlCl₃, $\chi_{\text{AlCl}_3} = 0.50$ (80.37 and 82.28 ppm, recorded at 55 °C) were *ca.* 5 ppm downfield with respect to the analogous peaks from P₈₈₈O-AlCl₃, $\chi_{\text{AlCl}_3} = 0.50$ (75.20 and 77.38 ppm - see Table 2). This difference was expected to be sufficient for the detection of a probe signal in P₈₈₈O-MCl_x LCCs. Indeed, low intensity peaks originating from the probe were easily distinguished in all P₈₈₈O-MCl_x LCCs, upfield from the high intensity signals from the ligand. These signals were easily identified, as they were not present in ³¹P NMR spectra of neat LCCs, and their intensity was increasing with the increasing probe concentration (Figure 7 SI).

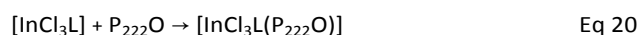
Reactions of LCCs with a base/spectroscopic probe. Acceptor numbers for LCCs and their corresponding metal chlorides are listed in Table 5. To facilitate the discussion, data were additionally plotted on two separate bar charts (Figure 8).

In general, although LCCs are adducts of Lewis acidic metal chlorides with either a hard base (P₈₈₈O) or a soft base (P₈₈₈), these adducts have the same or higher AN values as neat metal chlorides. An in-depth analysis is required to analyse the meaning of the AN number, considering a wide variety of Lewis acidic centres and species compared here. Bearing in mind a very large excess of LCC compared to the probe, three modes of interaction between LCCs and P₂₂₂O may be envisaged, as detailed below.

Table 5. Gutmann AN values for metal chlorides, and for LCCs based on $P_{888}O$ or P_{888} ligands, combined with a range of metal halides at different χ_{MCl_x} values.

| MCl_x | χ_{MCl_x} | AN | | |
|----------|----------------|--------------|------------|-----------|
| | | neat MCl_x | $P_{888}O$ | P_{888} |
| $AlCl_3$ | 0.50 | | 85.4 | 83.3 |
| | 0.60 | | 94.7 | 101.9 |
| | 1.00 | 85.6 | | |
| $GaCl_3$ | 0.50 | | 87.4 | 87.8 |
| | 0.60 | | 96.3 | 95.6 |
| | 0.67 | | 105.0 | 102.3 |
| | 0.75 | | 107.3 | 104.9 |
| | 1.00 | 75.9 | | |
| $InCl_3$ | 0.50 | | 75.3 | 67.5 |
| | 1.00 | 74.3 | | |
| $SbCl_3$ | 0.50 | | 69.3 | 58.3 |
| | 0.60 | | 76.2 | - |
| | 1.00 | 61.4 | | |
| $SnCl_2$ | 0.50 | | 74.9 | 77.6 |
| | 1.00 | 75.2 | | |
| $SnCl_4$ | 0.50 | | 79.6 | - |
| | 0.60 | | 77.0 | - |
| | 1.00 | 79.2 | | |
| $TiCl_4$ | 0.50 | | 109.80 | 122.1 |
| | 0.60 | | - | 135.9 |
| | 1.00 | 108.8 | | |
| $ZnCl_2$ | 0.50 | | 63.3 | 64.3 |
| | 0.60 | | 65.8 | - |
| | 1.00 | 66 | | |

In the simplest mode, coordinationally unsaturated Lewis acids undergo a simple acid-base addition, exemplified in Eq 20.



This reactivity was anticipated for $P_{888}O-MCl_x$ LCCs ($M = In^{III}$, Sn^{IV} or Ti^{IV}), and for $P_{888}-MCl_x$ LCCs ($M = In^{III}$ or Sn^{II}), which exist as coordinationally unsaturated monomeric complexes - see Table 3. All but one LCCs from this group had AN values the same (within error bars) as the corresponding metal chloride (Figure 8, top). The exception was $[InCl_3(P_{888})]$, with its AN value lower than that of $InCl_3$ (67.5 vs. 74.3 - see Figure 8, bottom). It can be attributed to a very good orbital overlap between In^{III} and the phosphorus, which leads to lowering electrophilicity of this LCC. Noteworthy, AN value for another tetracoordinate indium species, $[InCl_4]^-$, was reported at a much lower value of AN = 57.1,²¹ which may be attributed to the negative charge on the tetrachloroindate(III) anion. Chloroindate(III) ionic liquids have been used as water stable, mild Lewis acids.^{64,65}

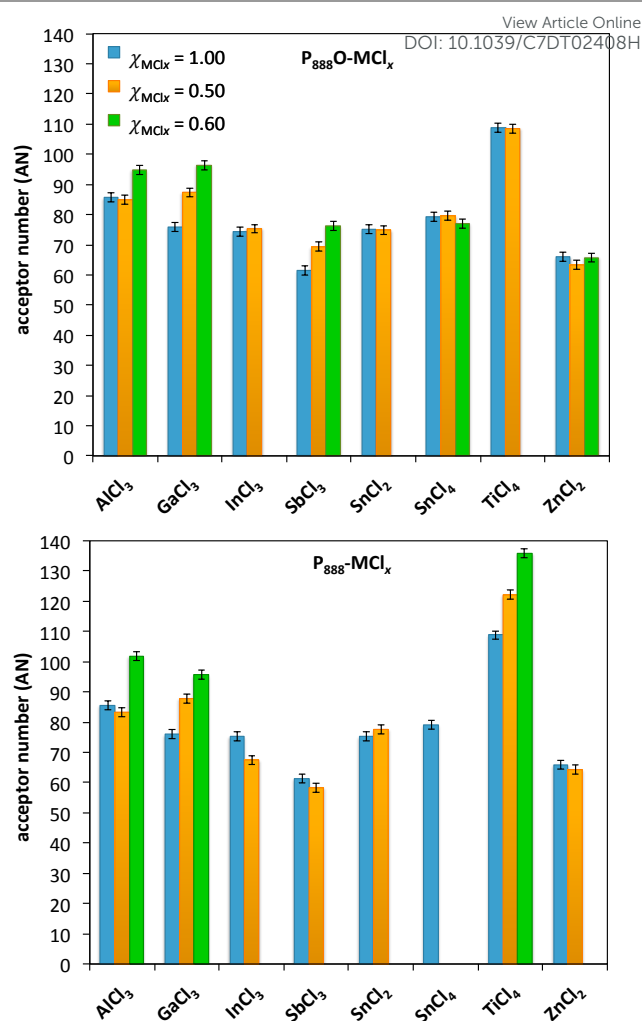
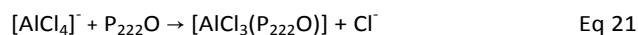


Figure 8. ANs of metal halides (MCl_x , $\chi_{MCl_x} = 1.00$), measured as 1,2-dichloroethane solutions, and LCCs of a general formula $L-MCl_x$, $\chi_{MCl_x} = 0.50$ and 0.60 , measured neat. L = trioctylphosphine oxide, $P_{888}O$ (top) or trioctylphosphine, P_{888} (bottom).

Another mode of reaction between an LCC and the probe is the substitution of a ligand in the coordinationally saturated complex. In halometallate ionic liquids, such case reported was only in chloroaluminate(III) system, where $P_{222}O$ replaced the chloride in $[AlCl_4]^-$, owing to high oxophilicity of Al^{III} (Eq 21).^{21,63}



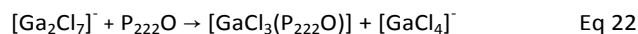
The $[AlCl_3(P_{222}O)]$ complex was formed, resulting in high acceptor number (AN = 96), despite the fact that ionic liquids with $[AlCl_4]^-$ anion are typically catalytically inactive - in contrast to very active ionic liquids with the $[Al_2Cl_7]^-$ anion.¹ In this context, high AN reported for $[AlCl_4]^-$ was considered a 'fake reading',^{21,63} where interaction with the probe was not reflected in interaction with most substrates in catalytic reactions. In $L-AlCl_3$, $\chi_{AlCl_3} = 0.50$ LCCs, $P_{222}O$ may replace either a chloride in $[AlCl_4]^-$ or L in $[AlCl_3L]$, both resulting in the formation of $[AlCl_3(P_{222}O)]$, and in consequence - in AN value the same as $AlCl_3$ (Figure 8). It is not immediately obvious whether this value corresponds to actual catalytic activity.

Ionic liquids based on $[\text{GaCl}_4]^-$ gave low acceptor number (AN = 45),²¹ indicating that P_{222}O is neither displacing the chloride, nor does it form a pentacoordinate adduct in an easy manner. However, ANs for L-GaCl₃ $\chi_{\text{GaCl}_3} = 0.50$ LCCs are even higher than that recorded for GaCl₃ (Figure 8). It is unclear whether the ligand (L) be replaced by P_{222}O to form $[\text{GaCl}_3(\text{P}_{222}\text{O})]$, or a pentacoordinate $[\text{GaCl}_3\text{L}(\text{P}_{222}\text{O})]$ is formed (Eq 20) - in either case the AN values are unexpectedly high, especially in the light of earlier-reported lack of catalytic activity of L-GaCl₃ $\chi_{\text{GaCl}_3} = 0.50$ LCCs in carbocationic reactions. {Matuszek:2015ir, Hogg:2015co}

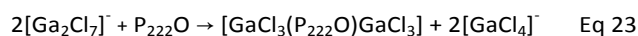
Finally, the third case of P_{222}O interaction with LCCs is the reaction with bi- and oligonuclear complexes with chloride bridges. They are nominally coordinatively saturated, but bridging chloride bonds are easily broken by any base (*viz.* 'masked' Lewis acids⁶⁶). This type of Lewis acidity is prevalent in chlorometallate ionic liquids with oligomeric anions, such as $[\text{Al}_2\text{Cl}_7]^-$ or $[\text{Zn}_2\text{Cl}_6]^{2-}$.

In LCCs, oligomeric species were postulated for LCCs based on AlCl₃, GaCl₃, SbCl₃ and ZnCl₂ (Table 3). Furthermore, the existence of bridging structures was suggested for $\text{P}_{888}\text{O-SnCl}_2$ and $\text{P}_{888}\text{-TiCl}_4$ LCCs.

It could be envisaged that P_{222}O breaks the chloride bridge to form a simple adduct, as exemplified in Eq 22. In this case, the Lewis acidity measured by AN should be the same as for the corresponding metal chloride, which is the case for L-SbCl₃ and L-ZnCl₂ LCCs.



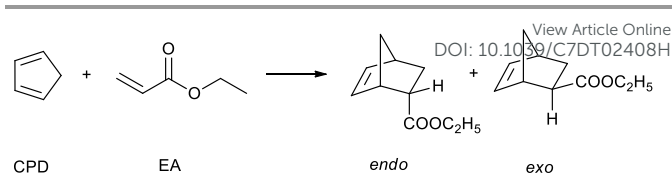
However, in other cases AN values increase from metal chloride, to $\chi_{\text{MCl}_x} = 0.50$, and further to $\chi_{\text{MCl}_x} = 60$ (Figure 8). For example, there is a marked increase in AN values for the $\text{P}_{888}\text{-TiCl}_4$ LCCs, with dinuclear complexes present, but AN for $\text{P}_{888}\text{O-TiCl}_4$ LCC, with mononuclear complexes, remains the same as TiCl₄. Similar behaviour was reported for chlorometallate ionic liquids, where AN was increasing with χ_{MCl_x} in a step-wise fashion, correlated with the appearance of different Lewis acidic species.^{21,39,53} Evidently, the probe must have the ability to detect the oligomeric species, for example following reaction as per Eq 23.



In conclusion, numerical AN values are underpinned by the probe partaking in several different reactions, and being in different coordination environment. With such variety of Lewis acids, it was interesting to investigate whether there would be any correlation of AN with catalytic activity of the LCCs.

LCCs as catalysts in a model Diels-Alder reaction

LCCs of the general formula $\text{P}_{888}\text{O-MCl}_x$ $\chi_{\text{MCl}_x} = 0.50$ were selected for the catalytic study, being the most numerous group, with relatively easy to understand speciation. The cycloaddition of cyclopentadiene (CPD) to ethyl acrylate (EA) was used as the model Diels-Alder reaction (Scheme 2). It was carried out solventless, in ice-bath, with diene in excess. The LCC catalyst (10 mol% per EA) was dissolved in neat reactants.



Scheme 1. The model Diels-Alder reaction of cyclopentadiene (CPD) and ethyl acrylate (EA) used in this study.

Both the reaction rate and the *endo:exo* selectivity are sensitive to Lewis acid strength, therefore Diels-Alder reaction is amongst the more popular test reactions for grading catalytic activity of Lewis acids.⁶⁷ Amongst the studied LCCs, a wide spectrum of catalytic performance was observed, from lack of reactivity and selectivity, through to moderate activity, to full conversion and high *exo:endo* selectivity (Figure 9). It was concluded that the type of the reaction, and reaction conditions, are indeed suitable to distinguish between different Lewis acid strengths.

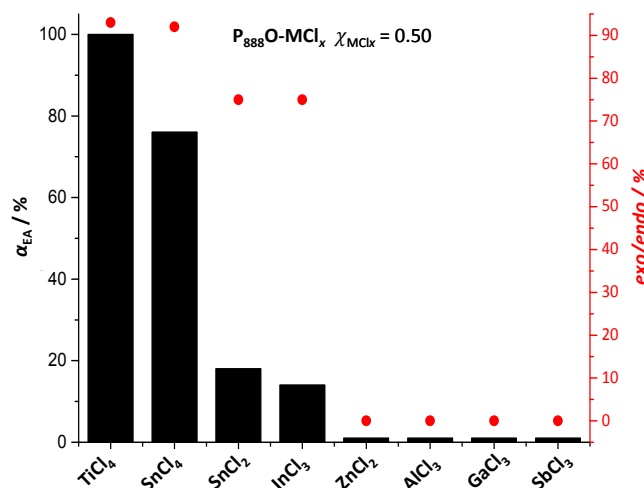


Figure 9. Catalytic performance of LCCs of a general formula $\text{P}_{888}\text{O-MCl}_x$ $\chi_{\text{MCl}_x} = 0.50$ in Diels-Alder reaction, in terms of conversion and stereoselectivity. Reaction conditions: cyclopentadiene (1.586 g, 24 mmol), ethyl acrylate (1.602 g, 16 mmol), catalyst 10 mol% per EA, ice bath, 1500 rpm, 5 min, conversion and selectivity determined by GC.

Conversion of dienophile in the Diels-Alder reaction catalysed with LCCs based on different metals was plotted against AN values measured for these LCCs (Figure 10). Despite limited number of data points, most results fit well to Boltzmann sigmoidal curve. The same type of AN-conversion correlation has been reported for Diels-Alder reaction catalysed with Lewis acidic borenium ionic liquids.⁶⁸ There are, however, two outliers: $\text{P}_{888}\text{O-AlCl}_3$ $\chi_{\text{AlCl}_3} = 0.50$ and $\text{P}_{888}\text{O-GaCl}_3$ $\chi_{\text{GaCl}_3} = 0.50$, which had no catalytic activity despite high AN values. This is also in agreement with earlier studies, where L-AlCl₃ and L-GaCl₃ LCCs at $\chi_{\text{MCl}_3} = 0.50$ were catalytically inactive, in contrast to $\chi_{\text{MCl}_3} > 0.50$ compositions.^{16,17,69}

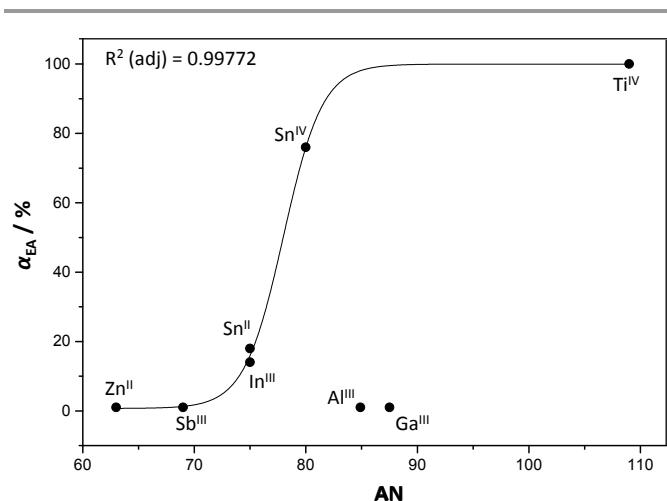


Figure 10. Dienophile conversion in Diels-Alder reaction catalysed with LCCs of a general formula $P_{888}O-MCl_x$, $\chi_{MCl_x} = 0.50$, plotted against AN values of these LCCs.

In conclusion, when the $P_{222}O$ probe reacts with LCCs by a simple addition to coordinationally unsaturated Lewis acid (Eq 20), or by breaking of the bridging halide bond (Eq 22 and 23), the AN values correspond well to the catalytic activity of LCCs. In contrast, in exceptional cases where the probe substitutes the ligand (Eq 21), the AN values reported are artificially high and do not correspond to the actual catalytic activity. This is backed by our studies on borenium ionic liquids (containing coordinationally unsaturated Lewis acidic centres), where very good correlation between AN values and catalytic activity was reported, with no outliers.⁶⁸

Conclusions

The strategy of generating liquid coordination complexes by using ligands with octyl alkyl chains was successful for all tested metal chlorides, and is likely to be applicable for a wide array of metal salts. Notably, several $P_{888}-MCl_x$ LCCs underwent a redox reaction, therefore the $P_{888}O$ ligand appears to be a more robust choice.

Multinuclear NMR spectroscopy was used to gain some insight into the speciation. Spectra of most metals were not informative due to strong quadrupole effect. However, building on ^{31}P NMR spectroscopy and on the literature data, it was suggested that most LCCs contain charge-neutral coordination complexes. Earlier-reported $L-AlCl_3$ and $P_{888}O-GaCl_3$ systems, comprising cationic, anionic and neutral species, appear to be the exception rather than the rule. Furthermore, many complexes are inferred to be di- or oligonuclear (Table 3). Further multi-technique studies are required to confirm these preliminary conclusions.

Lewis acidity of both metal chlorides and corresponding LCCs was quantified using Gutmann acceptor number approach. A scale established for metal chlorides followed the order: $TiCl_4 > SbCl_5 > AlCl_3 > SnCl_4 > GaCl_3 \approx InCl_3 \approx SnCl_2 > ZnCl_2 > SbCl_3$ was in a reasonable agreement with the Kobayashi scale. LCCs were found to be equally or more acidic than the corresponding metal chlorides.

The relationship between the speciation and Lewis acidity (AN) in LCCs was analysed by considering reaction of the $P_{222}O$ probe with species present in each LCC. To form an adduct with a Lewis acid, the probe must undergo one of three reactions: (1) addition to coordinationally unsaturated Lewis acid, (2) substitution of a ligand in a coordinationally saturated Lewis acid and (3) addition to a Lewis acidic centre by breaking a weak bridging chloride bond. It was observed that AN values obtained following reaction (1) or (3) were in good correlation with the dienophile conversion in Diels-Alder reaction (used as an alternative measure of Lewis acidity), whereas AN values obtained through reaction (2) were overestimated.

In this scoping study, several potentially interesting catalytic LCCs were identified. For example, the $P_{888}O-InCl_3$ system was more acidic than chloroindate(III) ionic liquids (AN = 75.3 vs. 57),²¹ and could replace them as mild and water-stable Lewis acidic catalyst. The $P_{888}O-TiCl_4$ system (albeit still moisture-sensitive) was of much higher stability compared to neat $TiCl_4$, whilst retaining very high Lewis acidity, and could be used as a safer and less hazardous alternative. In summary, this contribution opens up new avenues of research into LCCs, both on speciation and applications in Lewis acid catalysis.

Acknowledgements

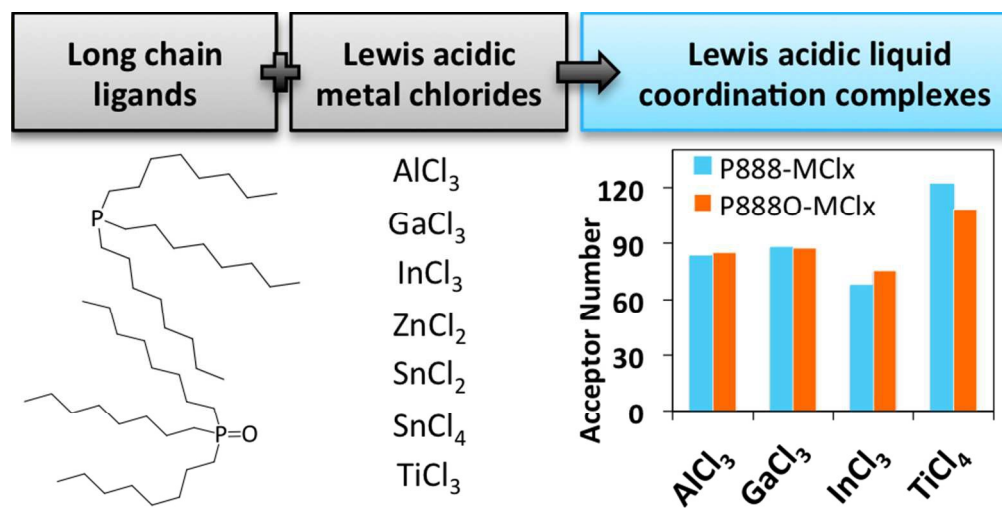
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TOC figure: Lewis acidity of metal chlorides and their liquid coordination complexes was measured, and related to their speciation and catalytic activity.

352x176mm (72 x 72 DPI)