Reactivity of Zn(II), Mg(II) and Al(III) chlorides with a phosphinimine ligand: new tetrameric inverse crown ether structures†

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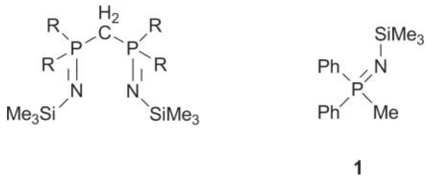
Reaction of [$Me_3SiNPPh_2CH_3$] **1** with $ZnCl_2$ yields the dimer [$ClZn(\mu\text{-}Cl)(Me_3SiNPPh_2CH_3)]_2$ **2** whereas treatment of **1** with $AlCl_3$ in THF leads to the monomeric *N* adduct [$Cl_3Al(Me_3SiNPPh_2CH_3)$] **3**. Compounds **2** and **3** were found to be thermally stable and were fully characterized by NMR spectroscopy, X-ray diffraction, and elemental analysis. On the other hand, treatment of phosphinimine **1** with $^nBuLi/ZnCl_2$ or $(CH_3)_2CHMgCl$ yields the zinc and magnesium complexes [$M_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2$] **5** (M = Zn) and **6** (M = Mg), respectively. These compounds can be considered as new examples of inverse crown ethers in which the oxygen atom is encapsulated by polar organometallic complexes in a tetrameric arrangement. In contrast, reaction of **1** with $^nBuLi/AlCl_3$ in Et_2O under inert atmospheric conditions leads to the formation of the dimeric species [$Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ **7**, which displays oxygen insertion into the C–Al bond, while the same reaction in the presence of air yields the compound [$\mu\text{-}(AlCl_2)(NPPh_2CH_3)]_2$ **8** with loss of $ClSiMe_3$ and without oxygen insertion into the C–Al bond.

1 Introduction

Since the first report of an organometallic complex stabilized by a phosphinimine ligand in 1962,[1] the subject has attracted much interest and a wide variety of compounds and their applications have been reported.[2] The bis(phosphinimine)methane ligand $CH_2(PR_2{=}NR')_2$ (Scheme 1) has been one of the most studied members of this family. It contains two N atoms that are prompt to bind metal centers in high oxidation states with usual coordination environments[3,4] and few unusual geometries.[5–7]

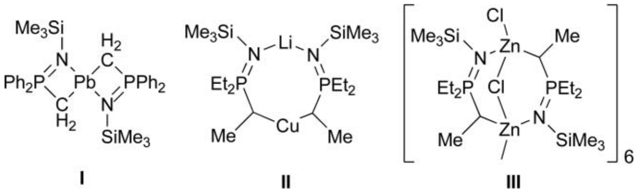


Scheme 1 Structure of a bis(phosphinimine) ligand (left) and the *P*-methyl phosphinimine ligand **1** (right).

However, published information on phosphinimine chemistry is limited and in particular, only a few reports refer to the *P*-methyl phosphinimine **1**. Apart from its ability to undergo the common *N*-coordination to Lewis acid metal halides,[8] this compound can endure α-metalation when reacted with simple organolithium reagents.

For example the groups of López-Ortiz and Elsevier have shown that the Li complex [$Li(PhNPPh_2CH_2)$] is extremely reactive and forms a four-membered LiCPN ring in solid state.[9–11]

Subsequently, two research groups simultaneously published the use of α-lithiated phosphinimines in transmetallation reactions to obtain new organometallic derivatives. Lappert *et al.* reported the monometallic complex **I** [$Pb(Me_3SiNPPh_2CHSiMe_3)_2$][12] in which two phosphinimine carbanions coordinate to one Pb^{II} cation, forming two four-membered rings in a spiro arrangement. Furthermore, Dehnicke *et al.* reported the bimetallic complexes **II** and **III** (Scheme 2). In the heterobimetallic complex **II**, two ligands in *cis* arrangement are coordinated to one Cu^I center through their carbon atoms and to one Li center through their N atoms, forming an eight-membered ring. In the homobimetallic complex **III**, two ligands in *trans* arrangement coordinate to two different Zn^{II} centers, each to one C and one N atom, forming an eight-membered ring.[13] This complex obtains a higher degree of organization in solid state through the formation of bridges between Cl and Zn centers, which lead to a dodecameric structure of six eight-membered rings.



Scheme 2 Structure of some α-metalated phosphinimine complexes.

Additionally, Muller *et al.* later demonstrated the high reactivity of α-metallated phosphinimines when investigating the reaction between [$Me_3SiNPMe_3$] and the Grignard reagent EtMgI. They found that byproduct **IV** (Scheme 3) resulted from the rupture of a diethylether solvent molecule, followed by the insertion of the CH_3CHO fragment into the C–Mg bond. The X-ray structure shows a three coordinated O atom encapsulated by two Mg centers and one C atom.[14,15]

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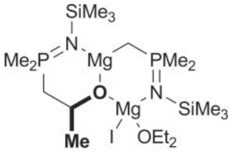


IV

Scheme 3 Structure of **IV** showing the insertion of the CH_3CHO fragment into the C–Mg bond.

These results demonstrate potential uses of iminophosphoranes in ethereal solvents for the synthesis of *inverse crown ether* (ICE) complexes; a family of compounds which exhibit a topological (anti) relationship to crown ether complexes, *i.e.* metal atoms that act as a host, whereas the oxygen occupies the guest position.[16,17] The interest in ICE complexes has continuously grown during the last decade and recently, they have found new applications in organometallic chemistry. The majority of the ligands that have been used to synthesize such complexes are amidinates and it has been shown that the combination of Na and Mg into a heterobimetallic ICE provides hyperbasic properties, which have been used to convert a metallocene into an unprecedented polymetallated form.[18]

In this report, we show our results on the reactivity between the ligand $[Me_3SiNPPh_2CH_3]$ **1** and its carbanionic form $[Me_3SiNPPh_2CH_2]^-$ **4** with $MgCl_2$, $ZnCl_2$, and $AlCl_3$. The neutral ligand **1**, reacted with these Lewis acids, yielded complexes $[ClZn(\mu\text{-}Cl)(Me_3SiNPPh_2CH_3)]_2$ **2** and $[Cl_3Al(Me_3SiNPPh_2CH_3)]$ **3** in THF, whereas **4** with different reaction conditions gave complexes $[Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ **7** and $[\mu\text{-}(AlCl_2)(NPPh_2CH_3)]_2$ **8**. Interestingly, the reaction of **1** with ${}^tBuLi/ZnCl_2$ and ${}^iPrMgCl$, yielded the novel "inverse crown ethers" $[M_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2]$ **5** (M = Zn) and **6** (M = Mg) by reaction with an unidentified source of chalcogen.

2 Experimental

2.1 Materials and methods

All manipulations of air and moisture-sensitive compounds were performed under an atmosphere of argon or dry nitrogen gas using standard high vacuum Schlenk and cannula techniques or in an inert atmosphere glovebox. Solvents were dried over sodium/benzophenone and freshly distilled prior to use. NMR spectra were recorded on a Varian-Inova-400 MHz and a Varian-Gemini-200 MHz instruments. Chemical shifts were referenced to TMS for ^1H and ^{13}C. ^{31}P NMR spectra were referenced to external 85% H_3PO_4, while ^7Li was referenced to LiCl. Elemental analyses (C, H, and N) were run on an Elemental microanalysis instrument using the CHN mode. $(CH_3)_3SiN_3$, $ZnCl_2$, $MgCl_2$, $AlCl_3$, ${}^tBuLi$ 1.47 M in hexane and ${}^iPrMgCl$ 2 M in Et_2O solution were purchased from the Aldrich Chemical Co.

2.2 Synthesis of $[Me_3SiNPPh_2CH_3]$ (1)

$(CH_3)_3SiN_3$ (4.82 mL, 36.66 mmol) was added to Ph_2PCH_3 (7.34 g, 36.66 mmol) prepared in the laboratory using a reported procedure.[19] The mixture was heated to 110–120 °C for 4 h, until no more N_2 evolution could be observed. After distillation of the crude reaction under reduced pressure compound **1** was obtained as colorless oil. Yield, 6.7 g, 90%. Bp 90–100 °C/10^{-2} mm Hg. Spectroscopic data of **1**: ^1H NMR (200 MHz, $CDCl_3$): δ 0.01 (s, 9H, $Si(CH_3)_3$), 1.90 (d, $^2J_{P\text{–}H}$ = 3.2 Hz, 3H, PCH_3), 7.39–7.72 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, $CDCl_3$): δ 4.30 ($Si(CH_3)_3$), 18.82 (d, $^1J_{C\text{–}P}$ = 72 Hz, PCH_3), 128.37–137.55 (Ph). ^{31}P NMR (80.81 MHz, $CDCl_3$): δ –2.57; ^{31}P NMR (80.81 MHz, THF): δ –2.5. ^{29}Si NMR (39.74 MHz, $CDCl_3$): δ –11.81. ^{15}N NMR (40.52 MHz, C_6D_6): δ 42.12. Anal. Calcd. for $C_{16}H_{22}NPSi$ (287.13): C 66.87, H 7.72, N 4.87. Found: C 66.29, H 7.71, N 4.87%.

2.3 Synthesis of $[ClZn(\mu\text{-}Cl)(Me_3SiNPPh_2CH_3)]_2$ (2)

A solution of **1** (0.53 g, 2 mmol) in THF (5 mL) was added under stirring and at room temperature to a suspension of $ZnCl_2$ (0.27 g, 2 mmol) in THF and a white precipitate immediately formed. After stirring overnight the reaction medium was filtered through cannula and all volatile components eliminated under reduced pressure. The resulting yellowish powder was dissolved in a small volume of benzene and after several days at room temperature pale yellow crystals which were suitable for X-ray diffraction analysis formed. Yield, 0.2 g, 38%. Mp 85 °C. Spectroscopic data of **2**: ^1H NMR (200 MHz, THF): δ –0.30 (s, 9H, $Si(CH_3)_3$), 1.62 (d, $^2J_{H\text{–}P}$ = 12.8 Hz, 3H, PCH_3), 7.12–7.44 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, THF): δ 2.25 ($Si(CH_3)_3$), 14.52 (d, $^1J_{C\text{–}P}$ = 37.95 Hz, PCH_3), 129.10–133.05 (Ph). ^{31}P NMR (80.81 MHz, THF): δ 35.7. Anal. Calcd. for $C_{32}H_{44}Cl_4N_2P_2Si_2Zn_2$ (847.42): C 45.36, H 5.23, N 3.31. Found: C 45.35, H 5.40, N 3.15%.

2.4 Synthesis of $[Cl_3Al(Me_3SiNPPh_2CH_3)]$ (3)

A solution of **1** (0.53 g, 2 mmol) in THF (5 mL) was added at –78 °C to a stirred suspension of $AlCl_3$ (0.26 g, 2 mmol) in THF. After further stirring of the reaction overnight, a white precipitate was formed in small quantity and filtered off by means of a cannula. The resulting clear solution was stored at –30 °C and after several days crystals suitable for X-ray diffraction formed in substantial quantities. Yield, 0.175 g, 33%. Mp 188 °C. Spectroscopic data of **3**: ^1H NMR (200 MHz, $CDCl_3$): δ 0.15 (s, 9H, $Si(CH_3)_3$), 2.53 (d, $^2J_{P\text{–}H}$= 12.6 Hz, 3H, PCH_3), 7.62–7.79 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, $CDCl_3$): δ 5.36 (s, $Si(CH_3)_3$), 20.08 (d, $^1J_{C\text{–}P}$ = 69.7 Hz, PCH_3), 129.60–133.83 (Ph). ^{31}P NMR (80.81 MHz, THF): δ 38.2. Anal. Calcd. for $C_{16}H_{22}AlCl_3NPSi$ (420.75) C 45.67, H 5.27, N 3.33. Found: C 45.67, H 5.38, N 3.25%.

2.5 Synthesis of $[Li(Me_3SiNPPh_2CH_2]\cdot 2Et_2O$ (4)

By means of a syringe, commercial ${}^tBuLi$ 1.47 M in hexane (1.25 mL, 2 mmol) was added dropwise under stirring conditions to a solution of **1** (0.53 g, 2 mmol) in ether (5 mL) at room temperature. The reaction medium, which immediately turned yellow, was further stirred for two hours. The crude solution was consistently of high enough purity to be used in the following synthesis without additional purification. Furthermore, the elimination of all volatile components of a sample under reduced pressure led to a yellow powdery substance which could be analyzed by NMR. Spectroscopic data of **4**: ^1H NMR (200 MHz, C_6D_6): δ 0.07 (s, 9H, $Si(CH_3)_3$), 2.89 (d, $^2J_{H\text{–}P}$ = 7.0 Hz, 2H, PCH_2), 7.05–7.67 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, C_6D_6): δ 4.86 ($Si(CH_3)_3$), 6.59 (d, $^1J_{C\text{–}P}$ = 64.4 Hz, PCH_2), 127.93–143.82

(Ph). ^{31}P NMR (80.81 MHz, C_6D_6): δ 30.5. ^{29}Si NMR (39.74 MHz, C_6D_6): δ 0.44. ^{7}Li NMR (77.75 MHz, C_6D_6): δ 0.88. Anal. Calcd. for $C_{24}H_{41}NLiO_2PSi$ (441.59): C 65.28, H 9.36, N 3.17 Found: C 65.35, H 9.40, N 3.29%.

2.6 Synthesis of $[Zn_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2]$ (5)

A freshly prepared solution of **4** (2 mmol) in Et_2O was added *via* cannula to a stirred suspension of $ZnCl_2$ (0.27 g, 2 mmol) in ether at room temperature. A white precipitate rapidly formed and the mixture was left under stirring conditions overnight. The solution was then filtered through cannula and stored at −30 °C. Large hexagonal crystals suitable for X-ray crystallography were formed after several days of storage. Yield, 0.22 g, 42%. Mp 103 °C. Spectroscopic data of **5**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.28 (s, 9H, $Si(CH_3)_3$), 2.28 (d, $^{2}J_{P\text{–}H} = 13.6$ Hz, PCH_2), 6.93–8.19 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, $CDCl_3$): δ 4.85 ($Si(CH_3)_3$), 13.01 (d, $^{1}J_{P\text{–}C} = 60.6$ Hz, PCH_2), 128.35–139.62 (Ph). ^{31}P NMR (80.81 MHz, $CDCl_3$): δ 42.4. Anal. Calcd. for $C_{64}H_{84}Cl_2N_4OP_4Si_4Zn_4$ (1494.10): C 51.45, H 5.67, N 3.75. Found: C 50.96, H 6.10, N 3.56%.

2.7 Synthesis of $[Mg_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2]$ (6)

A solution of **1** (0.53 g, 2 mmol) in ether (10 mL) was cooled down to −78 °C and ^{i}PrMgCl (1 mL, 2 mmol) was added dropwise by means of a syringe under stirring conditions. A substantial quantity of white solid immediately precipitated and subsequently disappeared after warming to room temperature. The solution was reduced to a small volume under reduced pressure and stored at −30 °C. After two days large hexagonal colorless crystals were formed and were deemed suitable for X-ray diffraction analysis. Yield, 0.22 g, 42%. Mp 208 °C. Spectroscopic data of **6**: ^{1}H NMR (200 MHz, C_6D_6): δ 0.39 (s, 9H, $Si(CH_3)_3$), 1.51 (d, $^{2}J_{P\text{–}H} = 12.8$ Hz, 2H, PCH_2), 7.08–7.56 (m, 10H, 2 Ph). ^{13}C NMR (50 MHz, C_6D_6): δ 4.98 ($Si(CH_3)_3$), 11.86 (d, $^{1}J_{P\text{–}C} = 62$ Hz, PCH_2), 130.5–133.65 (Ph). ^{31}P NMR (80.81 MHz, C_6D_6): δ 42.1. Anal. Calcd. for $C_{64}H_{84}Cl_2Mg_4N_4OP_4Si_4$ (1329.76): C 57.81, H 6.37, N 4.21. Found: C 57.96, H 6.45, N 4.56%.

2.8 Synthesis of $[Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ (7)

A freshly prepared solution of **4** (2 mmol) in THF (10 mL) was added at room temperature to a stirred suspension of $AlCl_3$ (0.26 g, 2 mmol) in Et_2O (10 mL). After the mixture was stirred for 30 min and a white precipitate formed, the solution was filtered *via* cannula and concentrated under reduced pressure to a small volume. After storage at −30 °C for two weeks, a few crystals that were suitable for X-ray diffraction analysis were formed. Anal. Calcd. for $C_{32}H_{42}Al_2Cl_4N_2O_2P_2Si_2$ (800.59): C 48.01, H 5.29, N 3.50. Found: C 48.26, H 5.43, N 3.58%.

2.9 Synthesis of $[\mu\text{-}(AlCl_2)(NPPh_2CH_3)]_2$ (8)

A freshly prepared solution of **4** (2 mmol) in THF (10 mL) was added at room temperature to a stirred suspension of $AlCl_3$ (0.26 g, 2 mmol) in Et_2O (10 mL). After the mixture was stirred for 30 min under inert atmosphere and a white precipitate formed, the flask was left open for a short time in order to replace N_2 atmosphere by air. The solution was filtered *via* cannula and concentrated under reduced pressure to a small volume. After storage at −30 °C for several weeks, a few crystals that were suitable for X-ray diffraction analysis were obtained. Anal. Calcd. for $C_{26}H_{26}Al_2Cl_4N_2P_2$ (624.23): C 50.03, H 4.20, N 4.49. Found: C 50.17, H 4.26, N 4.62%.

2.10 X-Ray diffraction measurements

Crystals of **2**, **3**, and **5–8** were mounted directly from solution under argon using inert oil to protect them from atmospheric oxygen and moisture. X-Ray intensity data were collected using the SMART[20] program, on a Bruker APEX CCD diffractometer with monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were carried out with the use of the SAINT program using intensity data up to $2\theta = 25°$. The SADABS program was used to make incident beam, decay and absorption corrections in the SAINT-Plus v. 6.0 suite.[21] Subsequently, the structures were solved by direct methods with the SHELXS program and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite.[22] Further details of the structure analyses are given in Table 1. For **7**, two THF solvate molecules were positional disordered giving two split positions of the rings. Refinement including restraints to obtained satisfactory anisotropic displacement parameters for the C and O atoms, gave an occupancy factor level of 0.63. In the case of **8**, diethyl ether solvate was near an inversion center, refinement including restraints and taking into account the special position gave satisfactory anisotropic displacement parameters for the C and O atoms. All hydrogen atoms were generated in calculated positions for all complexes and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms.

3. Results and discussion

3.1 Synthesis of 1

Synthesis of compound **1** occurred by oxidation of the corresponding methyl diphenylphosphine *via* Staudinger reaction with trimethylsilylazide. After distillation under reduced pressure, the expected phosphinimine was obtained as a colorless oily liquid which was of very high purity and near quantitative yield. The liquid was stored under inert atmosphere and low temperature for months without any sign of decomposition. Before exploring the σ–C coordination ability of ligand **1**, which is expected to involve intramolecular coordination of the imino function, we decided to first study its simple reaction with the chloride derivatives of Zn(II), Mg(II) and Al(III).

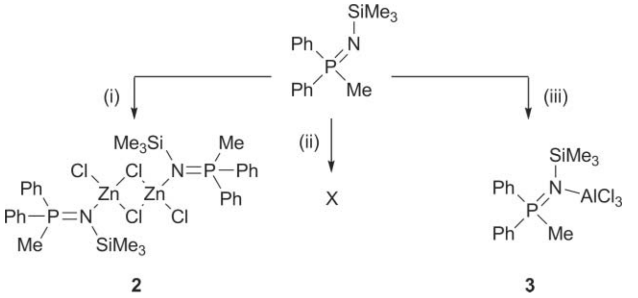
3.2 Reaction of 1 with $ZnCl_2$, $MgCl_2$ and $AlCl_3$

Phosphinimines usually react with Lewis acids to form the corresponding donor–acceptor adducts. In our study the reaction of **1** with $ZnCl_2$ and $AlCl_3$ in THF yielded the expected complexes **2** and **3**, whereas the reaction with $MgCl_2$ after workup resulted in the isolation of unreacted **1** and $MgCl_2$ (Scheme 4). Possible reasons for this lack of reactivity may be the weaker Lewis acidity and lower solubility in THF of $MgCl_2$ compared to $ZnCl_2$.

These reactions were monitored by ^{31}P NMR in THF. On time, the resonance due to **1** at δ −2.5 ppm disappeared and

Table 1 Crystallographic data for complexes **2**, **3**, **5**, **6**, **7** and **8**

Compound	**2**	**3**	**5**	**6**	**7**	**8**
Empirical formula	$C_{32}H_{44}Cl_4N_2P_2Si_2Zn_2$	$C_{16}H_{22}Cl_3AlNPSi$	$C_{64}H_{84}Cl_2N_4OP_4Si_4Zn_4$	$C_{64}H_{84}Cl_2Mg_4N_4OP_4Si_4$	$C_{32}H_{42}Cl_4Al_2N_2O_2P_2Si_2{\cdot}4(C_4H_8O)$	$C_{26}H_{26}Al_2Cl_4N_2OP_2{\cdot}(C_4H_{10}O)$
M	847.39	420.74	373.49	1329.73	544.49	694.28
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	150(2)
Crystal system	Triclinic	Monoclinic	Tetragonal	Tetragonal	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{4}2_1c$	$P\bar{4}2_1c$	$P\bar{1}$	$P\bar{1}$
a/Å	8.6468(11)	9.7388(13)	14.8254(19)	14.8622(16)	9.3733(9)	8.4330(15)
b/Å	11.1936(14)	14.3203(19)	14.8254(19)	14.8622(16)	11.8131(12)	9.7126(17)
c/Å	11.3940(14)	14.5442(19)	16.278(3)	16.258(2)	14.4903(14)	11.539(2)
β/°	74.323(2)	94.085(4)	90	90	91.232	94.033(3)
V/Å^3	974.1(2)	2023.2(5)	3577.8(9)	3591.1(7)	1409.7(2)	873.0(3)
Z	1	4	2	2	1	1
D_c/Mg m^{-3}	1.444	1.381	1.387	1.23	1.283	1.347
μ(Mo-Kα)/mm^{-1}	1.674	0.633	1.597	0.323	0.386	0.511
F(000)	436	872	1548	1404	576	364
No. reflections collected	4786	3390	12 415	9585	11 567	8486
No. independent reflections (R_{int})	3194 (0.0235)	2247 (0.0501)	3156 (0.0610)	2704 (0.0849)	4930 (0.0235)	3059 (0.1161)
Final R_1 ($I > 2\sigma(I)$)	0.0459	0.0387	0.0364	0.0417	0.0478	0.0417
wR_2 indices (all data)	0.1076	0.1110	0.0581	0.0957	0.1390	0.1254



Scheme 4 Formation of donor–acceptor adducts between **1** and Lewis acids. *Reagents and conditions*: (i) $ZnCl_2$, THF; (ii) $MgCl_2$, THF; (iii) $AlCl_3$, THF.

was replaced by a new resonance at δ 35.7 and δ 38.2 ppm for **2** and **3**, respectively. The resulting downfield shift in both cases is typical for the coordination of the phosphinimine nitrogen atom to Lewis acid centers and in addition, all others NMR spectroscopic data are consistent with the formulation of the corresponding complexes.

An X-ray crystallographic study of **2** (Fig. 1) shows a symmetrical dimeric structure in which μ_2-chloro bridges bind two Zn atoms in a tetrahedral geometry and both iminophosphorane groups and exocyclic Cl atoms are arranged *trans* to each other. The four membered core is almost perfectly square and planar with Zn–Cl–Zn and Cl–Zn–Cl bond angles of 89.98(4)° and 90.02(4)°, respectively. The cyclic Zn–Cl bond lengths are slightly different [2.3393(10) Å and 2.3939(11) Å], although longer than the exocyclic Zn–Cl bond lengths [2.2076(11) Å]. Both N atoms are in a trigonal planar environment around the Zn atom with a P–N–Zn bond angle of 113.85(16)°, thus they may be seen as sp^2 hybridized. In each monomeric unit, the Zn atom bound to N arranges *trans* to one of the phenyl substituents on P, and both the CH_3 substituents and the exocyclic Cl atoms are oriented towards the same side of the dimer. The Zn–N bond lengths [2.005(3) Å] as well as the P–N bond lengths [1.601(3) Å] are similar to those found in $[Cl_2Zn\{Me_3SiNP(C_4H_8)^tBu\}]_2$.[23] The P–N bond length is

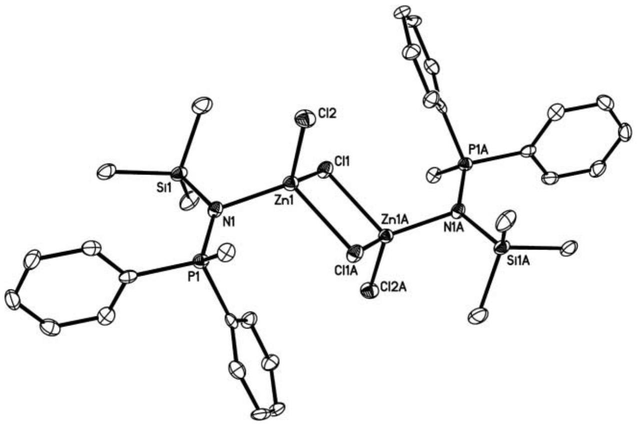


Fig. 1 Molecular structure of dimeric complex $[ClZn(\mu\text{-}Cl)(Me_3SiNPPh_2CH_3)]_2$ **2**. Selected bonds lengths (Å) and angles (°): Zn(1)–Cl(1) 2.3393(10), Zn(1)–Cl(2) 2.2076(11), Zn(1)–N(1) 2.005(3), P(1)–N(1) 1.601(3), Si(1)–N(1) 1.755(3); Zn(1)–Cl(1)–Zn(1A) 89.98(4), Cl(1)–Zn(1)–Cl(1A) 90.02(4), Cl(1)–Zn(1)–Cl(2) 117.54(4), Zn(1)–N(1)–P(1) 113.85(16), Zn(1)–N(1)–Si(1) 113.55(17). Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$.

indicative of a double bond character. Therefore, the P=N bond in **2** is not affected upon coordination to Zn.

The crystal structure of compound **3** presented in Fig. 2 shows a monomeric Lewis acid–base adduct in which the Al atom adopts a pseudo tetrahedral geometry and arranges *trans* to the CH_3 substituent on P. This situation contrasts with **2**, in which the Zn atom is located *trans* to a phenyl substituent. The Al–N bond length [1.875(3) Å] and the average Al–Cl bond lengths [2.1389(8) Å], are in the range found for similar compounds.[24] The geometry around N is approximately trigonal planar with P–N–Si, P–N–Al and Si–N–Al bond angles of 121.66 (15)°, 119.70(11)° and 118.56(12)°, respectively. The P–N bond length [1.620(2) Å] is marginally longer than the one observed for the Zn adduct **2**, but still in the expected range for phosphinimine adducts with Al [$Me_3Al(Me_3SiNPPh_3)$, d(P–N) = 1.646(2) Å].[8]

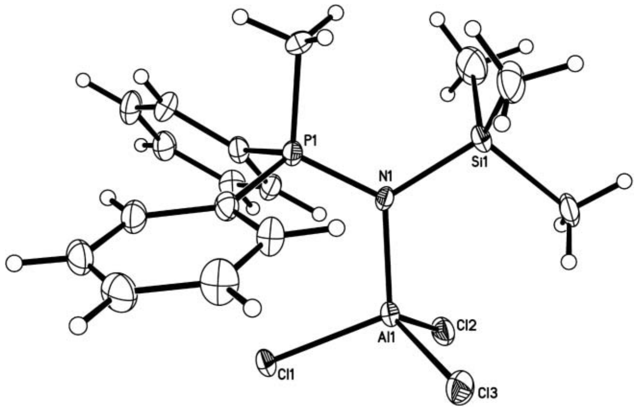


Fig. 2 Molecular structure of complex [$Cl_3Al(Me_3SiNPPh_2CH_3)$] **3**. Selected bonds lengths (Å) and angles (°): Al(1)–N(1) 1.875(3), Al(1)–Cl(1) 2.1389(8), Al(1)–Cl(2) 2.1381(12), Al(1)–Cl(3) 2.1296(12), P(1)–N(1) 1.620(2), Si(1)–N(1) 1.7863(19); P(1)–N(1)–Al(1) 119.70(11), P(1)–N(1)–Si(1) 121.66(15), Si(1)–N(1)–Al(1) 118.56(12), N(1)–Al(1)–Cl(1) 109.65(7), N(1)–Al(1)–Cl(2) 111.20(9), N(1)–Al(1)–Cl(3) 111.22(8), Cl(3)–Al(1)–Cl(1) 109.21(4), Cl(2)–Al(1)–Cl(1) 104.83(4), Cl(3)–Al(1)–Cl(2) 110.52(5).

In contrast to the straightforward formation of the Lewis acid–base complexes **2** and **3**, all attempts to obtain the corresponding adduct with $MgCl_2$ resulted in no reaction under a variety of conditions.

3.1 Reaction of 4 with $ZnCl_2$

α-Lithiated phosphinimines are readily accessible by metallation with ^nBuLi and may be used as reagents in metathesis reactions with metal halides.[25] Thus, the reaction between [$Me_3SiNPPh_2CH_3$] **1** with ^nBuLi or ^tBuLi occurred rapidly and was straightforward (monitored by ^{31}P NMR), yielding [$Li(Me_3SiNPPh_2CH_2)$] **4** in near quantitative yield. Even though the α-lithiation was fully established by elemental analysis and NMR spectroscopy of the product, all attempts to obtain crystals of sufficient quality for X-ray crystallography were unsuccessful. The ^{31}P NMR spectrum of **4** revealed a singlet at δ 30.5 ppm and a DEPT 135 experiment clearly demonstrated the presence of the carbanionic CH_2^- group through the emergence of an inverse doublet at 7.9 ppm. The characterization was completed with ^1H, ^{13}C, and ^7Li NMR spectra. Solutions of **4** showed slow decomposition on time, consequently they were used in the following metathesis reactions immediately after their production.

Monitoring of the metathesis reaction between **4** and $ZnCl_2$ by ^{31}P NMR in diethyl ether revealed the complete conversion of **4** into merely one compound (**5**) by the emergence of a single resonance at δ 42.4 ppm. After filtration of the precipitate and storage of the resulting solution at −30 °C for several days, crystals of quality suitable for an X-ray diffraction study were obtained. The spectroscopic study of the crystals in $CDCl_3$ solution displayed a single ^{31}P NMR resonance at δ 42.4 ppm and a doublet signal with negative phase at 13.6 ppm in a DEPT 135 experiment, which confirmed the presence of a carbanionic CH_2^- bound to Zn ($^1J_{C\text{–}P}$ = 61.8 Hz). The characterization was completed with ^1H and ^{13}C NMR spectroscopy and elemental analysis.

As seen in Fig. 3, complex **5** is a tetramer of [$Zn(Me_3SiNPPh_2CH_2)$]$^+$ organometallic units in which each Zn atom coordinate a central O^{2-} and one of two outer Cl^- ions. It shows the structure of an ICE that contains four six-membered ZnNPCZnO rings in boat conformation and connected through the central O atom. In the central Zn_4O cluster, the four Zn^{2+} ions span a tetrahedron around the central O^{2-} ion. The Zn atom is in a usual tetracoordinated environment with Zn–O [1.9712(5) Å], Zn–C [2.047(4) Å] and Zn–N [2.048(3) Å] bond lengths close to the values reported for related compounds [Zn–O (1.9 to 2.02 Å)].[26–28] The two outer Cl atoms bridge pairs of Zn centers and form two four-membered perpendicular ZnOZnCl rings with normal Zn–Cl bond lengths [2.4803(5) Å]. The phosphinimine P–N bond length

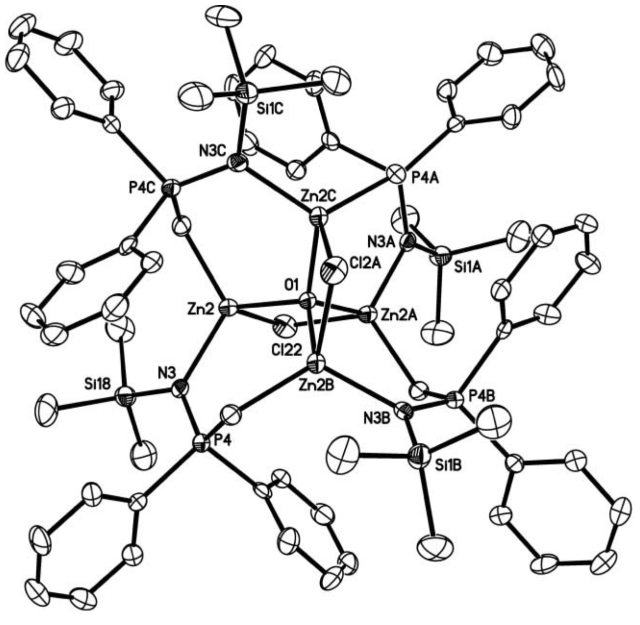


Fig. 3 Molecular structure of [$Zn_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2$] **5**. Selected bonds lengths (Å) and angles (°): Zn(2)–O(1) 1.9712(5), Zn(2)–C(5) 2.047(4), Zn(2)–N(3) 2.048(3), Zn(2)–Cl(22) 2.4803(15), P(4)–N(3) 1.600(3), Si(18)–N(3) 1.744(3); Zn(2)–Cl(22)–Zn(2A) 76.90(6), Zn(2)–O(1)–Zn(2A) 102.96(3), Zn(2C)–O(1)–Zn(2) 112.821 (17), C(5)–Zn(2)–Cl(22) 116.58(12), C(5)–Zn(2)–N(3) 119.10(14), O(1)–Zn(2)–C(5) 109.48(12), O(1)–Zn(2)–N(3) 118.46(9), O(1)–Zn(2)–Cl(22) 90.07(3). Symmetry transformations used to generate equivalent atoms: #1 − x, −y, z #2 y, −x, −z #3 −y, x, −z.

[1.600(3) Å] is typical for a double bond and then the N atom is sp^2 hybridized.

3.3 Reaction of 1 with ^{i}PrMgCl

All attempts to prepare the organomagnesium derivative by means of a metathesis reaction between **4** and $MgCl_2$ were unsuccessful. However, we assumed that organomagnesium nucleophiles should be sufficiently reactive to form the organomagnesium derivative by direct abstraction of a proton from phosphinimine **1**. In our first attempt, we discovered that the EtMgCl was not basic enough, however, the reaction with ^{i}PrMgCl in ether at −70 °C instantaneously lead to the formation of copious amounts of solid. The immediate monitoring of the solution by ^{31}P NMR spectroscopy showed the complete conversion of **1** into a new compound (**6**) that exhibits a single resonance at δ 42.1 ppm, the expected chemical shift for the corresponding α-metallated derivative. The solution was stored at −30 °C and after several days crystals of quality suitable for X-ray crystallography were formed. Compound **6** was fully characterized by multinuclear NMR spectroscopy and elemental analysis. A DEPT 135 experiment exhibited a doublet signal with a negative phase centered at δ 11.9 ppm ($^1J_{C-P} = 65.5$ Hz) which was unambiguously assigned to the methylene group bound to Mg.

The crystal structure of compound **6** shown in Fig. 4, displays an ICE isostructural to compound **5**, *i.e.* a tetramer of $[Mg(Me_3SiNPPh_2CH_2)]^+$ organometallic units in which each metal center coordinates to a central O^{2-} and one of two outer Cl^- ions. It forms four six-membered MgNPCMgO rings in a boat conformation and linked through the central O atom. In the central Mg_4O cluster the four Mg^{2+} ions span a tetrahedron around the central O^{2-} ion. The Mg atom is tetracoordinated, which is the usual coordination mode for this atom, and the Mg–O [1.9598(11) Å], Mg–C [2.186(3) Å] and Mg–N [2.073(3) Å] bond lengths are similar to the values reported for related compounds [Mg–O (1.95 Å),[29,30] Mg–C(2.191 Å), Mg–N(2.073 Å)]. The two outer Cl atoms bridge pairs of Mg centers such that two four-membered perpendicular MgOMgCl rings are formed. The Mg–Cl bond length [2.4652(16) Å][31,32] is typical for magnesium chloride derivatives with a tetracoordinated Mg center. As previously observed in the former complexes, the coordination of the imine N to the Mg center does not affect the phosphinimine P–N bond distance [1.611(3) Å], which is a hallmark for double bonding and the N atom is sp^2 hybridized.

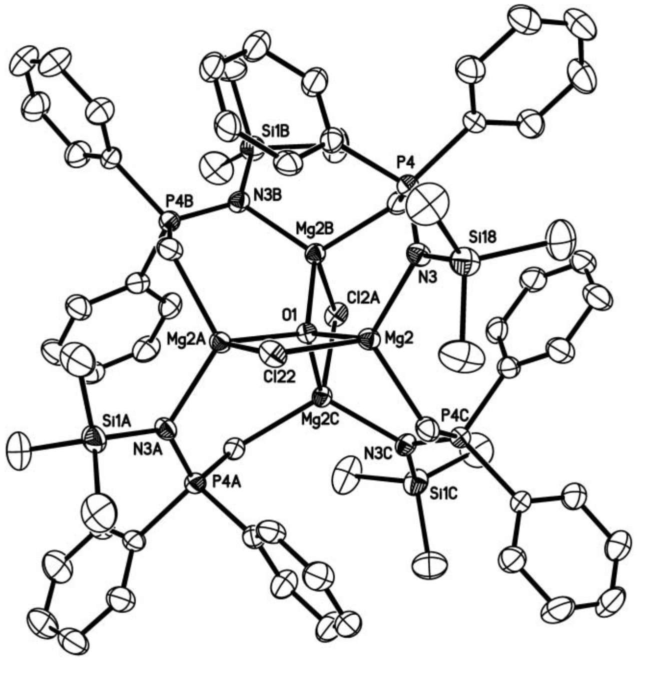


Fig. 4 Molecular structure of $[Mg_4(Me_3SiNPPh_2CH_2)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2]$ **6**. Selected bonds lengths (Å) and angles (°): Mg(2)–O(1) 1.9598(11), Mg(2)–C(5) 2.186(3), Mg(2)–N(3) 2.073(3), Mg(2)–Cl(22) 2.4652(16), P(4)–N(3) 1.611(3), Si(18)–N(3) 1.731(1); Mg(2)–Cl(22)–Mg(2A) 76.48(6), Mg(2)–O(1)–Mg(2A) 102.26(7), Mg(2C)–O(1)–Mg(2) 113.19(4), C(5)–Mg(2)–Cl(22) 115.00(11), C(5)–Mg(2)–N(3) 118.35(12), O(1)–Mg(2)–C(5) 105.68(11), O(1)–Mg(2)–N(3) 122.90(9), O(1)–Mg(2)–Cl(22) 90.63(4). Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+2, z$ #2 $-y+2, x, -z+2$ #3 $y, -x+2, -z+2$.

Interestingly for **5** and **6**, the M–O, M–N and M–Cl bond lengths and bond angles around O and the metal centers are almost equivalent. The only noticeable difference is that the Mg–C bond length in **6** [2.191(3) Å] is slightly longer than the Zn–C bond length in **5** [2.043(4) Å].

The chalcogen source for the obtention of **5** and **6** could be attributed to air contamination (O_2 or H_2O) of the reaction medium, to the presence of traces of metal oxide or hydroxide in the metallic starting material or finally, to cleavage of the diethylether solvent used in the reaction. In these particular cases the last supposition is not likely, due to the fact that the oxygen in **5** and **6** is not inserted into the metal–carbon bond of the ligand. However, we observed that the result is reproducible under stringent inert atmosphere conditions using freshly and cautiously distilled solvent, and always with good yields (> 40%).

3.4 Reaction of 4 with $AlCl_3$

In an attempt to prepare the organoaluminium derivative of phosphinimine **1** *via* a metathesis reaction, $[Li(Me_3SiNPPh_2CH_2)]$ and $AlCl_3$ were combined in THF. ^{31}P NMR spectroscopy of the reaction medium showed a unique signal at δ 24.1 ppm which is in the expected region for the anticipated compound. Nevertheless, the ^{31}P NMR spectroscopy monitoring of the reaction showed rapid decomposition of the main product into several compounds, yielding to various broad signals in the narrow region between 24 and 30 ppm. After two weeks of storage at −30 °C the ^{31}P analysis of the reaction remain unchanged and few crystals were formed. The measurement of one of these by X-ray diffraction showed the structure of compound $[Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ (**7**), product of oxygen insertion into the Al–C bond (Fig. 5). In addition, the X-ray crystal structure showed two molecules of THF solvate.

As seen in Fig. 5, compound **7** is a dimer of $[Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ units with inversion symmetry. It shows a tricycle structure consisting of two five-membered OAlNPC rings bridged through O–Al coordination which leads to the formation of a central four-membered Al_2O_2 ring. The O atoms are tricoordinated in a tetrahedral geometry and the angles and bond lengths they formed with their substituents are comparable to those found for tricoordinated O atoms.[33] The Al centers are pentacoordinated with distorted trigonal bipyramidal geometry. The axial positions are occupied by one of the O and the N atoms,

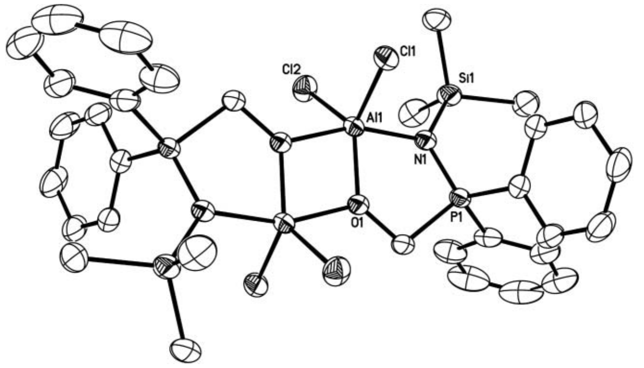


Fig. 5 Molecular structure of $[Cl_2Al(Me_3SiNPPh_2CH_2O)]_2$ **7**. Selected bonds lengths (Å) and angles (°): Al(1)–O(1) 1.869(17), O(1)–C(1) 1.411(3), O(1)–Al(1A) 1.9205(18), Al(1)–N(1) 1.969(2), Al(1)–Cl(1) 2.1720 (9), Al(1)–Cl(2) 2.1698(9), P(1)–N(1) 1.601(2), Si(1)–N(1) 1.764(2); Al(1)–O(1)–Al(1A) 107.08(8), O(1)–Al(1)–O(1A) 72.92(8), P(1)–N(1)–Si(1) 123.18(12), Al(1)–N(1)–Si(1) 124.85(11), O(1A)–Al(1)–N(1) 160.34(9), C(1)–O(1)–Al(1) 124.57(15), C(1)–O(1)–Al(1A) 127.95(14), O(1)–Al(1)–N(1) 88.25(8), O(1)–Al(1)–O(1A) 72.92(8). Symmetry transformations used to generate equivalent atoms: −*x* + 2, −*y*, −*z* + 1.

while the second O and the two Cl atoms occupy the equatorial positions. The Al–O_{axial} [1.9205(18) Å], Al–O_{equat} [1.8269(17) Å] and Al–N [1.969(2) Å] bond lengths and the N–Al–O_{axial} bond angle [160.34(9)°] are in close agreement with the values reported (range 158–162°) for comparable compounds.[34] The geometry around N is approximately trigonal planar with a P–N–Si angle of 123.18(12)° (normal range 121.8–126.6) and a P–N bond distance [1.601(2) Å] characteristic for a multiple bond.

Although the composition of **7** could be confirmed by elemental analysis, no interpretable NMR data could be obtained from the few crystals isolated from this reaction. As seen by the complexity of the spectra in deuterated THF, this compound likely engages in complicated equilibrium processes and decomposes in solution.

Compound **7** has a structure very similar to the one reported by Schumann *et al.*[35] for the organoaluminium chloride $[Cl_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ from which the diallyl derivative was synthesized and found to be a useful reagent for the transfer of one allyl group to aldehydes, imines, and enones. Similarly, **7** might also posses such properties which lead us to further improve its synthesis and complete its characterization by NMR methods. As the insertion of an O atom into the C–Al bond suggested inconspicuous exposure to air, it seemed reasonable to reproduce the synthesis by deliberated exposure of the reaction medium to air for a short time. The monitoring of the solution by ^{31}P NMR showed a set of broad signals in the region between 25 and 30 ppm, very similar to the results obtain in the previous reaction. However, the mixture was stored at −30 °C and after several weeks few crystals were grown while the ^{31}P NMR spectroscopy study of the solution remained unchanged. An X-ray diffraction measurement of one crystal of suitable quality showed the structure of compound $[\mu\text{-}(AlCl_2)(NPPh_2CH_3)]_2$ (**8**) resulting from $SiMe_3$ substitution by $AlCl_2$.

In Fig. 6, the solid state structure of compound **8** determined by X-ray crystallography shows a dimer of $[\mu\text{-}(AlCl_2)(NPPh_2CH_3)]$ units in which two Al centers bridge two phosphinimine ligands by coordination to the N atom. The geometry around Al is significantly distorted from tetrahedral with average bond lengths [Al–N 1.852(2) Å and Al–Cl 2.1340(10) Å] and bond angles [Cl–Al–Cl 108.32(4)° and N–Al–N 88.39(9)°] which are in agreement with those reported for similar compounds.[36] The four-membered Al_2N_2 ring is almost perfectly square with angles close to 90° [N–Al–N 88.39(9)° and Al–N–Al 91.61(9)°] and generates an Al–Al separation of 2.656(14) Å. The P–N bond distance [1.5853(19) Å] agrees with double bonding and the N atom is sp^2 hybridized.

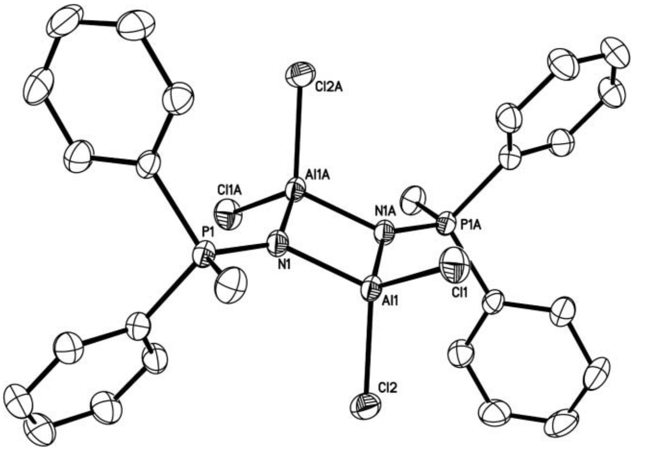
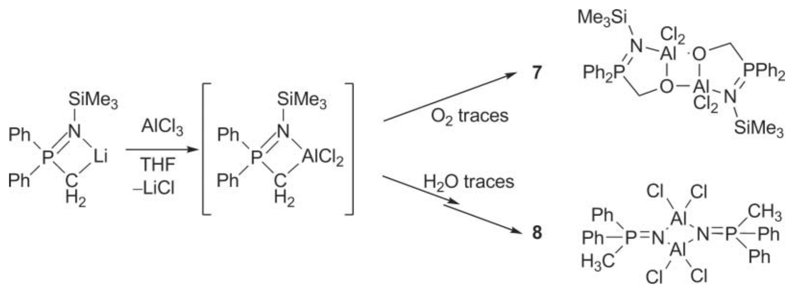


Fig. 6 Molecular structure of $[\mu\text{-}Al(Cl)_2(NPPh_2CH_3)]_2$ **8**. Selected bonds lengths (Å) and angles (°): Al(1)–N(1) 1.852(2), Al(1)–N(1A) 1.8526(2), Al(1)–Cl(1) 2.1349(9), Al(1)–Cl(2) 2.1340(10), P(1)–N(1) 1.5853(19), N(1)–Al(1A) 1.852(2), Al(1)–Al(1A) 2.6560(14); N(1)–Al(1)–N(1A) 88.39(9), Al(1)–N(1)–Al(1A) 91.61(9), N(1)–Al(1)–Cl(1) 114.83(7), N(1)–Al(1)–Cl(2) 113.35(7), Cl(1)–Al(1)–Cl(2) 108.28(4), P(1)–N(1)–Al(1) 133.97(13), P(1)–N(1)–Al(1A) 134.30(11). Symmetry transformations used to generate equivalent atoms: #1 −*x* + 1, −*y* + 1, −*z* + 1 #2 −*x* + 2, −*y*, −*z*.



Scheme 5 Formation of **7** and **8** in reactions between α-lithiated phosphinimine **4** and $AlCl_3$.

It is worth noting that compound **8**, formed as a side product in this last reaction, could not be obtained by thermolysis of $ClSiMe_3$ from **3**. Additionally, the production of **8** can only be explained by reaction of the organometallic species with moisture. In contrast, the insertion of oxygen into the metal carbon bond of **7** suggests in this case that the chalcogen source is more likely a contamination of the reaction medium by traces of molecular oxygen or eventually solvent activation (Scheme 5).

Conclusions

The formation of *N*-donor adducts thermally stable from phosphinimines **1** and **4** with metallic halides and the reactivity of organometallic phosphinimine compounds towards oxygen is demonstrated in this study. The solid state structures of **5** and **6** showed oxygen encapsulation with tetrahedral coordination of the chalcogenide center, opening the way to new ICE chemistry. The deliberate and controlled exposure to air of the reaction medium with aluminium chloride and **4** leads to hydrolysis and no oxygen insertion was observed.

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