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Mendeleev Commun., 2022, **32**, 71–73

Mendeleev Communications

Aluminum(III) di- and monochlorides incorporating an *N*,*N*′-chelating iminophosphonamide ligand: synthesis and structures

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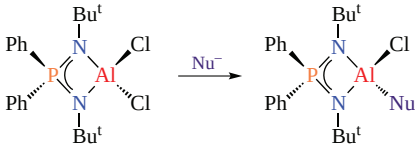
DOI: 10.1016/j.mencom.2022.01.023

Treatment of lithium iminophosphonamide with $AlCl_3$ in Et_2O led to the formation of an aluminum(III) dichloride complex as colorless crystals. The substitution reactions of aluminum(III) dichloride stabilized by an iminophosphonamide ligand with N- and Fe-nucleophiles gave the corresponding compounds of aluminum(III) monochloride. The reaction of the aluminum(III) dichloride complex with CpNa proceeded slowly at room temperature to form an aluminum(III) monochloride complex bearing an $\eta^1(\sigma)$-bonded cyclopentadienyl ring.

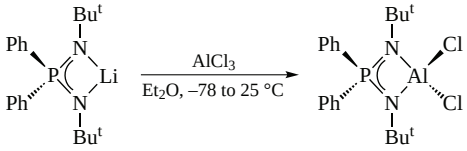


Keywords: aluminum, iminophosphonamide, *N*,*N*′-chelating ligand, nucleophilic substitution reaction, cyclopentadienide, X-ray crystallography.

Recent research on aluminum chemistry has focused on finding appropriate ancillary ligands for reactive organoaluminum compounds because of their increasing roles as catalysts and initiators for the polymerization and as suitable precursors for the synthesis of aluminum-based low-oxidation state species.[1] Much attention has been paid to monoanionic *N*,*N*′-chelating systems such as β-diketiminate,[2] amidinate[3,4] and guanidinate[5] ligands. Recently, organoaluminum compounds incorporating iminophosphonamide ligands, in which the central carbon moiety in amidinate ligands is replaced by a phosphorus one, have been intensively investigated. Representative examples of iminophosphonamide ligands have been reported including $[Ph_2P(Me_3SiN)_2]^-$,[6(a)] *rac*-[*trans*-1,2-$C_6H_{10}(NPPh_2NAr)_2]^{2-}$ (Ar = 2,4,6-$Me_3C_6H_2$ or 2,6-$Me_2C_6H_3$),[6(b)] $[Ph(H)P(Bu^tN)_2]^-$,[6(c)] $[Ph_2P(DipN)(Bu^tN)]^-$ (Dip = 2,6-$Pr^i_2C_6H_3$)[6(d)] and $[Ph_2P(MePhCHN)_2]^-$.[6(e)] However, the synthesis of aluminum(III) monochlorides bearing *N*,*N*′-chelating ligands by simple substitution reactions of dichloro precursors has scarcely been reported, probably due to the disproportionation of monochlorinated products. In this paper, we present the synthesis of aluminum(III) dichloride $[Ph_2P(Bu^tN)_2]AlCl_2$ **1** stabilized by a symmetrical iminophosphonamide ligand.[7] We also describe the reactivity of compound **1** with various nucleophiles to yield novel monochlorinated aluminum(III) compounds.

First, we synthesized a dichloroaluminum(III) complex with an iminophosphonamide ligand. The reaction of lithium iminophosphonamide[8] with $AlCl_3$ proceeded smoothly in Et_2O at –78 °C to furnish the desired aluminum(III) dichloride **1** as air- and moisture-sensitive colorless crystals in 81% yield (Scheme 1). In the ^1H NMR spectrum of complex **1**, equivalent *tert*-butyl groups were observed at 1.03 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum of complex **1** displayed a sharp signal at 29.3 ppm, which is in a similar region as those of the related iminophosphonamide derivatives (20.0–50.0 ppm).[6]

Compound **1** crystallized in the monoclinic space group $P2_1/c$ with two independent molecules in the unit cell, and one molecule is illustrated in Figure 1.† The crystal structure of compound **1** revealed that the four-coordinated aluminum center



1, 81%

Scheme 1

† *Crystal data for* **1**. $C_{20}H_{28}AlCl_2N_2P$, M = 425.29, monoclinic, space group $P2_1/c$, T = 120 K, a = 17.020(2), b = 15.735(2) and c = 18.055(2) Å, β = 111.791(2)°, Z = 8, V = 4489.7(10) Å^3, d_{calc} = 1.258 g cm^{-3}, R_1 = 0.0412 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1168 for 8138 reflections, 481 parameters, μ = 0.407, GOF = 1.019.

Crystal data for **2**. $C_{26}H_{46}AlClN_3PSi_2$, M = 550.24, monoclinic, space group $P2_1/n$, T = 120 K, a = 11.3257(11), b = 17.1890(16) and c = 15.9915(15) Å, β = 90.2660(10)°, Z = 4, V = 3113.2(5) Å^3, d_{calc} = 1.174 g cm^{-3}, R_1 = 0.0500 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1345 for 5745 reflections, 319 parameters, μ = 0.299, GOF = 1.016.

Crystal data for **3**. $C_{33}H_{39}AlClFeN_2O_2P$, M = 644.91, triclinic, space group $P\bar{1}$, T = 120 K, a = 10.692(2), b = 11.686(2) and c = 13.329(2) Å, α = 92.248(2), β = 96.890(2) and γ = 98.208(2)°, Z = 2, V = 1633.7(5) Å^3, d_{calc} = 1.311 g cm^{-3}, R_1 = 0.0414 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1168 for 5941 reflections, 401 parameters, μ = 0.651, GOF = 1.032.

Crystal data for **4**. $C_{25}H_{33}AlClN_2P$, M = 454.93, monoclinic, space group $P2_1/n$, T = 120 K, a = 11.3489(12), b = 16.5044(17) and c = 13.1839(14) Å, β = 92.0030(10)°, Z = 4, V = 2467.9(4) Å^3, d_{calc} = 1.224 g cm^{-3}, R_1 = 0.0504 [$I > 2\sigma(I)$], wR_2 (all data) = 0.1367 for 4571 reflections, 281 parameters, μ = 0.270, GOF = 1.015.

CCDC 2100003–2100006 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

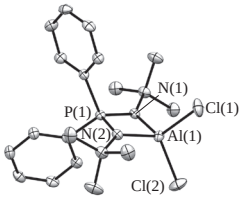


Figure 1 Molecular structure of complex **1** as ORTEP drawing with thermal ellipsoids at 50% probability level. All hydrogen atoms and one of the two independent molecules in the unit cell of complex **1** are omitted for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.861(2), Al(1)–N(2) 1.861(2), Al(1)–Cl(1) 2.1325(8), Al(1)–Cl(2) 2.1208(7), P(1)–N(1) 1.630(2), P(1)–N(2) 1.629(2). Selected angles (°): N(1)–Al(1)–N(2) 80.07(7), Cl(1)–Al(1)–Cl(2) 107.83(3), P(1)–N(1)–Al(1) 92.67(8), P(1)–N(2)–Al(1) 92.72(8), N(1)–P(1)–N(2) 94.54(8).

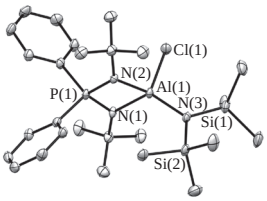


Figure 2 Molecular structure of complex **2** as ORTEP drawing with thermal ellipsoids at 50% probability level. All hydrogen atoms of complex **2** in the unit cell are omitted for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.885(2), Al(1)–N(2) 1.907(2), Al(1)–N(3) 1.829(2), Al(1)–Cl(1) 2.1573(9), P(1)–N(1) 1.626(2), P(1)–N(2) 1.630(2), Si(1)–N(3) 1.753(2), Si(2)–N(3) 1.735(2). Selected angles (°): N(1)–Al(1)–N(2) 78.23(8), Cl(1)–Al(1)–N(3) 107.78(7), P(1)–N(1)–Al(1) 93.75(9), P(1)–N(2)–Al(1) 92.80(9), N(1)–P(1)–N(2) 94.6(1).

is in a distorted tetrahedral environment. The Al–Cl bond lengths in compound **1** [2.1325(8) and 2.1208(7) Å] lie in the known range for iminophosphonamide aluminum(III) derivatives [2.1100(8)–2.134(1) Å][6(a),(c),(d)] and are slightly longer than those found in aluminum(III) dichlorides stabilized by amidinate ligands [2.1018(14)–2.110(1) Å].[3(a)–(c)]

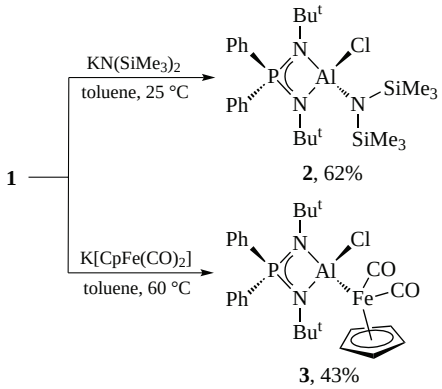
To synthesize functional monochlorinated aluminum(III) compounds from complex **1**, we performed its substitution reactions with various nucleophiles. Complex **1** was allowed to react with an N-nucleophile $KN(SiMe_3)_2$ in toluene at ambient temperature to obtain the corresponding amino(chloro)alumane **2** as colorless crystals in 62% yield (Scheme 2). Similarly, the reaction of complex **1** with a Fe-nucleophile $K[CpFe(CO)_2]$ proceeded in toluene at 60 °C to produce alumanyl-iron(II) complex **3** as colorless crystals in 43% yield (see Scheme 2).

In the ^1H NMR spectra of products **2** and **3**, the *tert*-butyl protons appeared as a sharp singlet at 1.17 and 1.18 ppm, respectively. Non-equivalent Me_3Si groups of complex **2** resonated at 0.54 and 0.72 ppm. The cyclopentadienyl (Cp) protons of complex **3** were observed as a sharp singlet at 4.52 ppm, indicating an η^5-coordination to the iron center. The $^{31}P\{^1H\}$ NMR spectra of products **2** and **3** exhibited singlets at 28.6 and 30.2 ppm, respectively. In the solid-state IR spectrum of complex **3**, two strong stretching vibrations of CO (ν_{CO}) were observed at 1967 and 1907 cm^{-1}. The average value of ν_{CO} (1937 cm^{-1}) is somewhat lower than those of the alumanyl complex of tri-coordinated iron(II), [Tbb(Br)AlFeCp(CO)$_2$] {Tbb = 4-Bu^t-2,6-[CH(SiMe$_3$)$_2$]$_2$C$_6$H$_2$}, (1956 cm^{-1})[9(b)] and the related amidinate-supported alumanyl-iron(II) complex (1944 cm^{-1}).[3(d)] This result distinctly reflects the strong σ-donor ability of the iminophosphonamide ligand for the aluminum center.

The crystal structures of aluminum(III) monochlorides **2** and **3** were unambiguously determined by single crystal X-ray diffraction analysis. The molecular structures of compounds **2** and **3** have a four-coordinated aluminum center, the coordination environment of which is distorted from the ideal tetrahedral shape due to the constraints of the four-membered AlN_2P ring [the N(1)–Al(1)–N(2) bond angles are 78.23(8) and 77.80(8)° for compounds **2** and **3**, respectively]. As shown in Figure 2, the AlN_2P ring in compound **2** is almost perpendicular to the SiNSi plane in the $N(SiMe_3)_2$ group (85.15°). The Al–N bond lengths [1.885(2) and 1.907(2) Å] in the AlN_2P ring of compound **2** are longer than the Al(1)–N(3) bond length [1.829(2) Å] because of the electronically delocalized iminophosphonamide ligand. X-ray diffraction analysis of compound **3** revealed that the piano-stool iron fragment adopts an *anti* configuration with respect to the chloride substituent on the aluminum atom (Figure 3). The Al(1)–Fe(1) bond length [2.3989(8) Å] of compound **3** is comparable to those of alumanyl-iron(II) complexes bearing amidinate ligands [2.340(1)–2.3699(8) Å],[3(d)–(f)] albeit that it is longer than those in alumanyl complexes of three-coordinated iron(II) [2.1319(1)–2.328(2) Å].[9] Moreover, the Al–Cl bond length [2.1870(9) Å] of compound **3** is slightly longer than those of compounds **1** [2.1325(8) and 2.1208(7) Å] and **2** [2.1573(9) Å], probably due to the steric effect.

The Cp ligand and its substituted derivatives have been well-established as versatile ligands in organometallic chemistry.[10] The normal coordination mode of the Cp ligand to transition metals is symmetric η^5. In contrast, main group elements exhibit various coordination modes from symmetric η^5 fashion *via* various slipped η^x-structures (x = 1, 2 or 3) to pure σ-bond.[11] As for the Cp-substituted aluminum(III) species, there have been only three reports so far, where the Cp group was in the η^1-coordination in all cases.[2(e),12] To verify the hapticity of the Cp ligand in the iminophosphonamido aluminum(III) compound, we prepared Cp-substituted chloro alumane **4**. Treatment of aluminum(III) dichloride **1** with CpNa in toluene at room temperature led to the formation of product **4** as colorless crystals in 51% yield (Scheme 3).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of product **4** displayed a sharp signal for the Cp moiety at 6.63 and 115.1 ppm,



Scheme 2

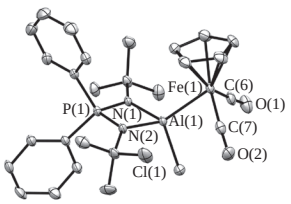
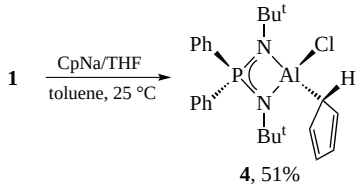


Figure 3 Molecular structure of complex **3** as ORTEP with thermal ellipsoids at 50% probability level. All hydrogen atoms of complex **3** and a benzene molecure in the unit cell are omitted for clarity. Selected bond lengths (Å): Al(1)–Fe(1) 2.3989(8), Fe(1)–C(6) 1.745(3), Fe(1)–C(7) 1.730(2), Al(1)–N(1) 1.901(2), Al(1)–N(2) 1.909(2), Al(1)–Cl(1) 2.1870(9), P(1)–N(1) 1.624(2), P(1)–N(2) 1.623(2). Selected angles (°): N(1)–Al(1)–N(2) 77.80(8), Fe(1)–Al(1)–Cl(1) 112.20(3), P(1)–N(1)–Al(1) 93.76(9), P(1)–N(2)–Al(1) 93.48(9), N(1)–P(1)–N(2) 94.93(9).



Scheme 3

respectively, indicating that all protons and carbon atoms in the ring are equivalent in the NMR time scale. Sergeyev proposed that the ^{1}H and ^{13}C NMR chemical shifts provide insight into the coordination mode of the Cp ligand in transition metal complexes.[13,14] In the ^{1}H NMR spectroscopy, the chemical shifts for the η^1-coordinated Cp ligand are observed between 5.6 and 6.2 ppm, while the shifts ranging from 4.0 to 4.8 ppm are indicative of η^5-coordination. In the case of ^{13}C NMR spectroscopy, chemical shifts for the η^1- and η^5-bound Cp ligands appear in the ranges 113–118 and 70–93 ppm, respectively. Thus, the chemical shifts for the Cp ligand in complex **4** are consistent with the range proposed by Sergeyev for the η^1-coordination. The ^{31}P{^{1}H} NMR spectrum of complex **4** shows a sharp singlet signal at 30.0 ppm, which is close to those of aluminum(III) chlorides **2** and **3** mentioned above.

As shown in Figure 4, X-ray diffraction analysis of complex **4** revealed that the Cp ring is located on the side of the four-membered AlN_2P ring to avoid electron repulsion with the Cl(1) chlorine atom. The Al(1)–C(1) bond length [2.016(2) Å] falls within the range reported for the Al–C bond lengths in Cp-substituted aluminum(III) compounds [1.984(3)–2.132(1) Å].[2(e),12] The hapticity of the Cp ring at the main group element center has been investigated using several criteria derived from crystallographic data. For example, the angle θ between the least-square plane of the Cp ring and the M–C_{ipso} bond can be conveniently distinguished between $\eta^1(\pi)$-(*ca.* 90°) and $\eta^1(\sigma)$-bonding fashions (*ca.* 109°).[11] Thus, the angle θ of complex **4** is 114.22°, which is consistent with the $\eta^1(\sigma)$-bonded Cp ring. Additionally, the Cp ring of complex **4** has the character of a 1,3-diene with alternating C–C bonds [C(1)–C(2) 1.458(3), C(2)–C(3) 1.356(3), C(3)–C(4) 1.434(3), C(4)–C(5) 1.365(3), C(5)–C(1) 1.461(3) Å], suggesting the $\eta^1(\sigma)$-coordination of the Cp ring.

In conclusion, we have demonstrated the synthesis and spectroscopic characterization of novel aluminum(III) di- and monochlorides stabilized by a Bu^t-substituted iminophosphonamide ligand. Further investigation of the reactivity, especially the reduction of the resulting halogenated aluminum(III) compounds, is forthcoming.

N.N. is grateful for the partial support from the Shorai Foundation for Science and Technology.

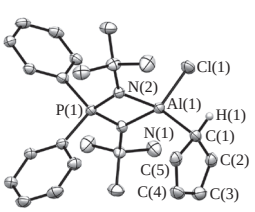


Figure 4 Molecular structure of complex **4** as ORTEP with thermal ellipsoids at 50% probability level. Hydrogen atoms except H(1) of complex **4** are omitted for clarity. Selected bond lengths (Å): Al(1)–N(1) 1.878(2), Al(1)–N(2) 1.885(2), Al(1)–Cl(1) 2.1573(8), Al(1)–C(1) 2.016(2), C(1)–C(2) 1.458(3), C(2)–C(3) 1.356(3), C(3)–C(4) 1.434(3), C(4)–C(5) 1.365(3), C(5)–C(1) 1.461(3). Selected angles (°): N(1)–Al(1)–N(2) 78.75(7), C(1)–Al(1)–Cl(1) 106.55(7), C(2)–C(1)–C(5) 104.8(2), C(2)–C(1)–H(1) 122(1), C(5)–C(1)–H(1) 119(1).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.023.

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Received: 30th July 2021; Com. 21/6633