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

Kazuki Nakaya, Akihiko Ishii and Norio Nakata

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S1. General

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a UNICO UL-1000A-UKF Glovebox under an inert atmosphere of argon. Anhydrous solvents were further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (C_6D_6) was dried and degassed over a potassium mirror by the freeze-thaw cycle prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AVANCE-400 (400, 101, and 162 MHz, respectively), and ^{29}Si NMR spectrum was recorded on a Bruker AVANCE-500 (99 MHz) spectrometer. All melting point points were determined on a Mel-temp capillary tube apparatus and were uncorrected. IR spectra were recorded on a TENSOR II. Elemental analysis was performed at Molecular Analysis and Life Science Center of Saitama University. All materials were obtained from commercial suppliers and used without further purification except *N,N'*-di-*tert*-butyl-diphenyliminophosphonamide,[1] lithium iminophosphonamide,[1] and $K[FeCp(CO)_2]$[2].

S.2 Experimental procedures characterization data

S2-1 Synthesis of iminophosphonamido aluminum(III) dichloride 1

In a Schlenk tube, lithium iminophosphonamide (886.9 mg, 2.65 mmol) and $AlCl_3$ (353.4 mg, 2.65 mmol) were dissolved into Et_2O (10 mL) at −78 °C. The mixture was gradually warmed up to room temperature and was kept stirring at this temperature for 1.5 h. All volatiles of the reaction mixture were removed under reduced pressure and the residue were extracted with toluene (15 mL). Recrystallisation from toluene at −10 °C gave the corresponding aluminum(III) dichloride **1** (1.13 g, 81%) as colorless crystals.

Mp: 187–188 °C. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 1.03 (s, 18H, CH_3), 7.03-7.05 (m, 4H, Ar), 7.10-7.14 (m, 2H, Ar), 7.92 (dd, J_{HH} = 12.4 and 7.2 Hz, Ar). ^{13}C{^{1}H} NMR (101 MHz, 25 °C, C_6D_6) δ 33.1 (d, J_{CP} = 6.9 Hz, CH_3), 52.5 (C_{tBu}), 129.0 (d, J_{CP} = 12.4 Hz, Ar(CH)), 130.2 (d, J_{CP} = 96.1 Hz, Ar(C)), 132.9 (d, J_{CP} = 2.9 Hz, Ar(CH)), 133.5 (d, J_{CP} = 11.1 Hz, Ar(CH)). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, C_6D_6) δ 29.3. Anal. Calcd for $C_{20}H_{28}N_2Cl_2AlP$: C, 56.48; H, 6.64; N, 6.59. Found: C, 55.61; H, 6.60; N, 6.29.

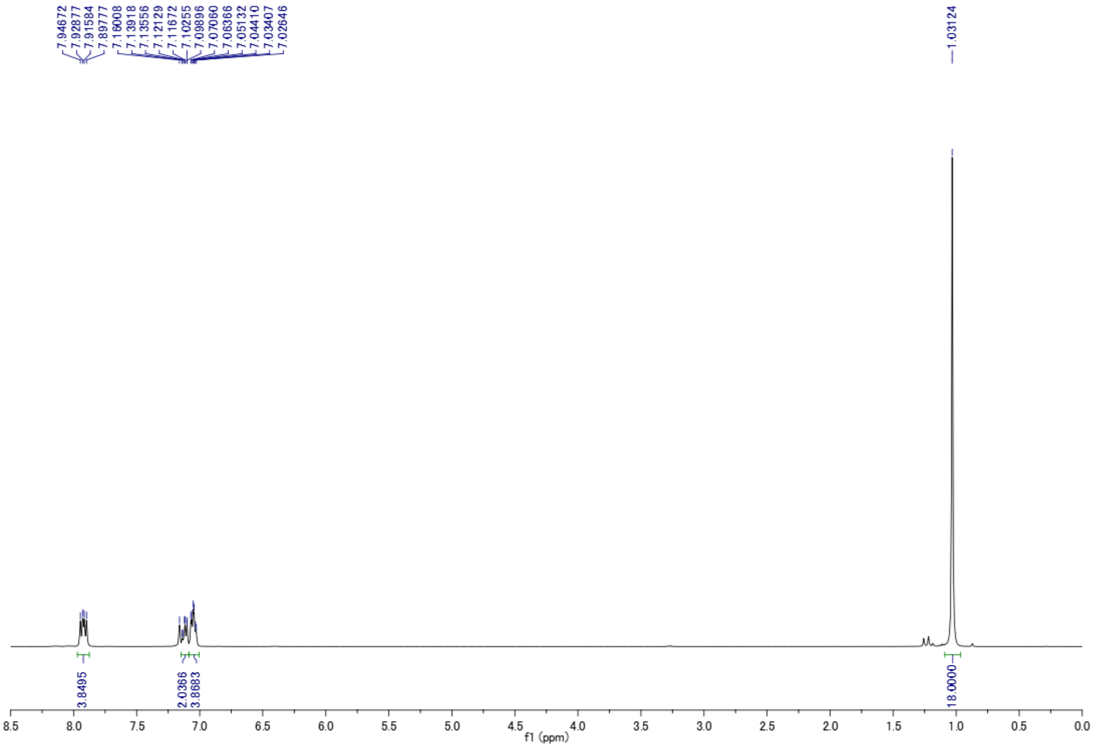

Figure S1. ^{1}H NMR spectrum of **1** (400 MHz, 25 °C, C_6D_6).

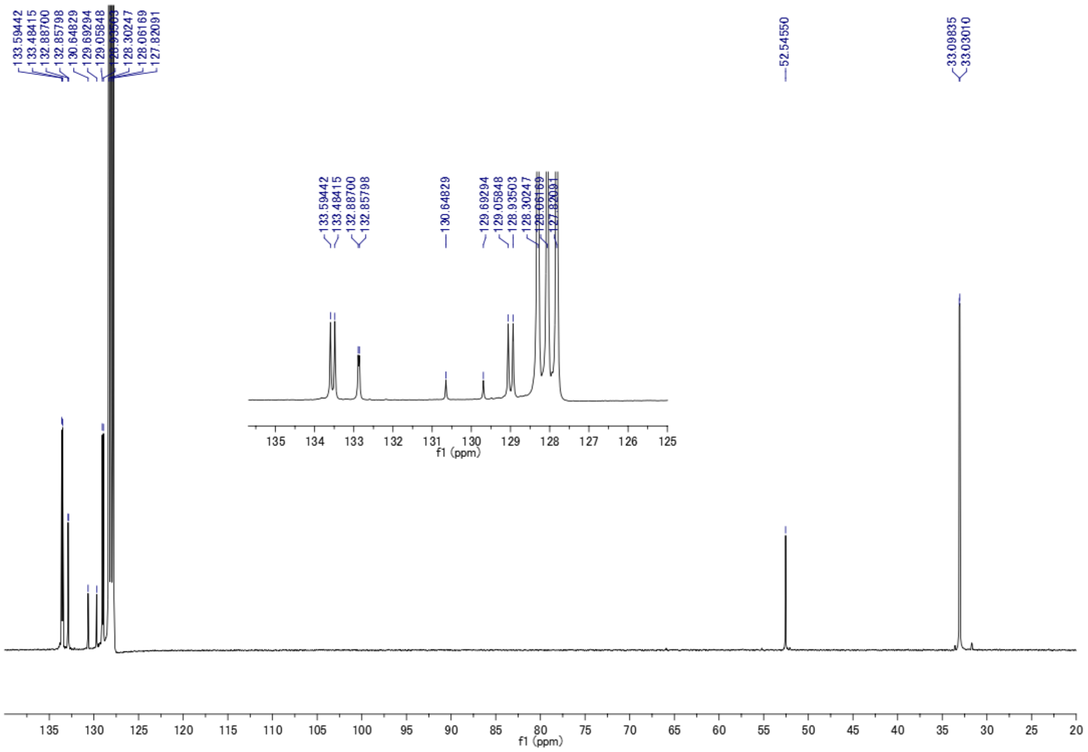

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (101 MHz, 25 °C, C_6D_6).

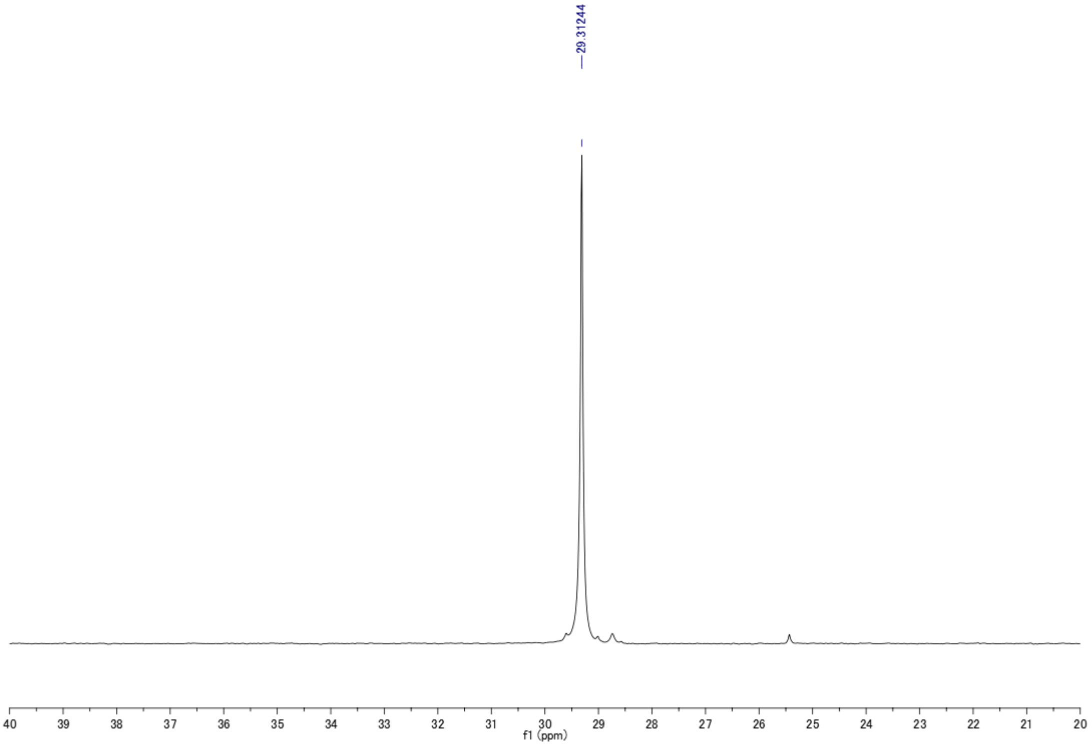

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (162 MHz, 25 °C, C_6D_6).

S2-2 Synthesis of iminophosphonamido amino(chloro)alumane 2

In a Schlenk tube, iminophosphonamido aluminum(III) dichloride **1** (112.8 mg, 0.265 mmol) and $KN(SiMe_3)_2$ (54.2 mg, 0.272 mmol) were dissolved into toluene (5 mL) at ambient temperature. The mixture was kept stirring at this temperature for 18.5 h. The reaction mixture was filtered and concentrated this filtrate. Recrystallisation from toluene at −10 ℃ gave an amino(chloro)alumane **2** (86.0 mg, 43%) as colorless crystals.

Mp: 169–170 ℃. ^1H NMR (400 MHz, 25 ℃, C_6D_6) δ 0.54 (s, 9H, $SiMe_3$), 0.72 (s, 9H, $SiMe_3$), 1.17 (s, 18H, CH_3), 7.06 (br, 6H, Ar), 7.94 (m, 2H, Ar), 8.10 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR (101 MHz, 25 ℃, C_6D_6) δ 7.0 ($SiMe_3$), 7.2 ($SiMe_3$), 33.6 (d, J_{CP} = 6.8 Hz, CH_3), 52.7 (C_{tBu}), 127.8 (d, J_{CP} = 12.4 Hz, Ar(CH)), 128.2 (d, J_{CP} = 12.4 Hz, Ar(C)), 130.3 (d, J_{CP} = 95.6 Hz, Ar(CH)), 132.3 (d, J_{CP} = 2.7 Hz, Ar(CH)), 132.3 (d, J_{CP} = 2.3 Hz, Ar(CH)), 133.1 (d, J_{CP} = 92.7 Hz, Ar(CH)), 135.0 (d, J_{CP} = 11.1 Hz, Ar(CH)), 135.1 (d, J_{CP} = 11.2 Hz, Ar(CH)). $^{31}P\{^1H\}$ NMR (162 MHz, 25 ℃, C_6D_6) δ 28.6. $^{29}Si\{^1H\}$ NMR (99 MHz, 25 ℃, C_6D_6) δ 0.4, 5.6.

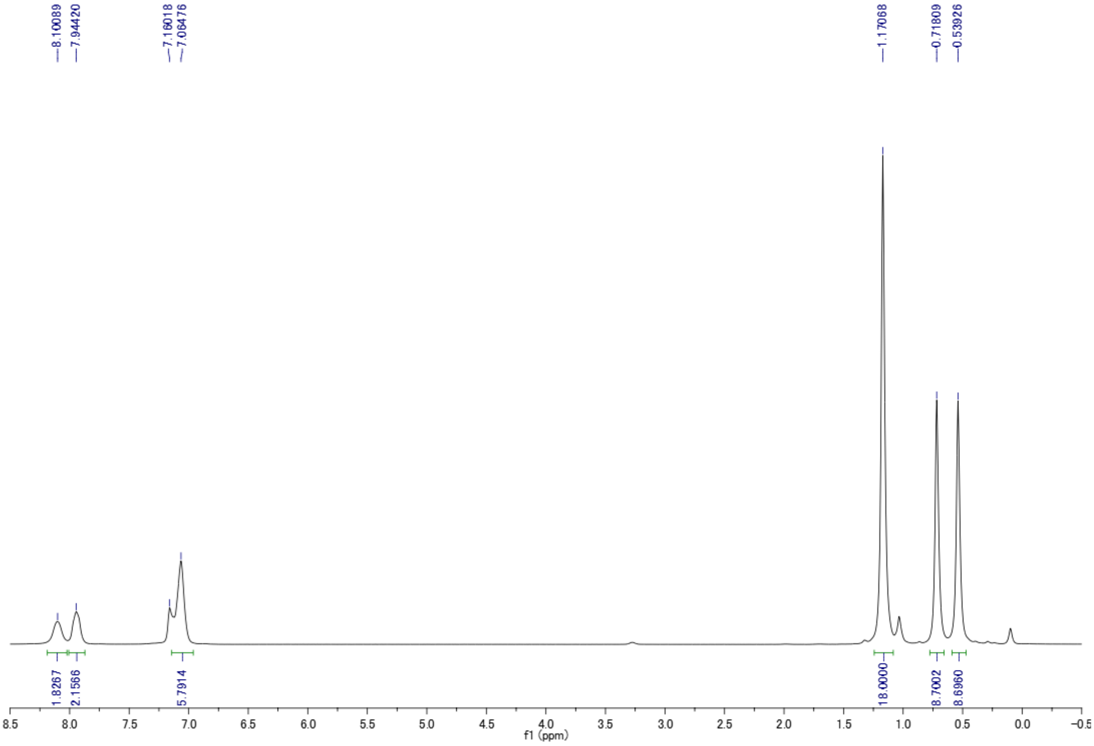

Figure S4. ^{1}H NMR spectrum of **2** (400 MHz, 25 °C, C_6D_6).

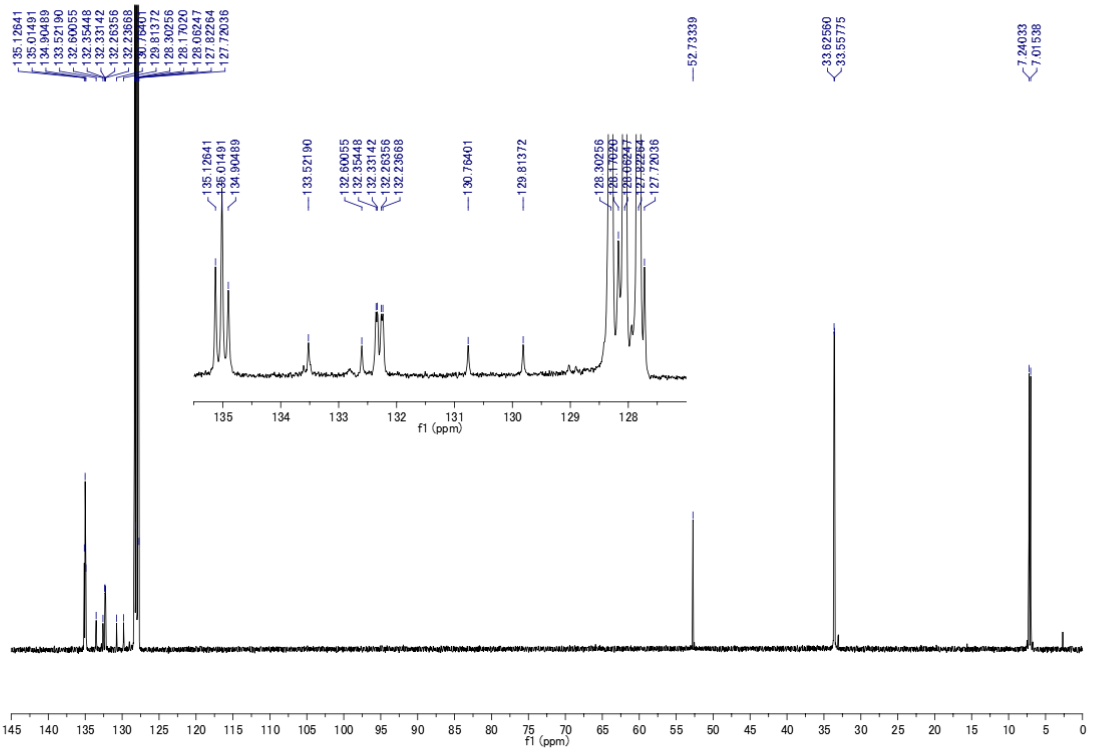

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (101 MHz, 25 °C, C_6D_6).

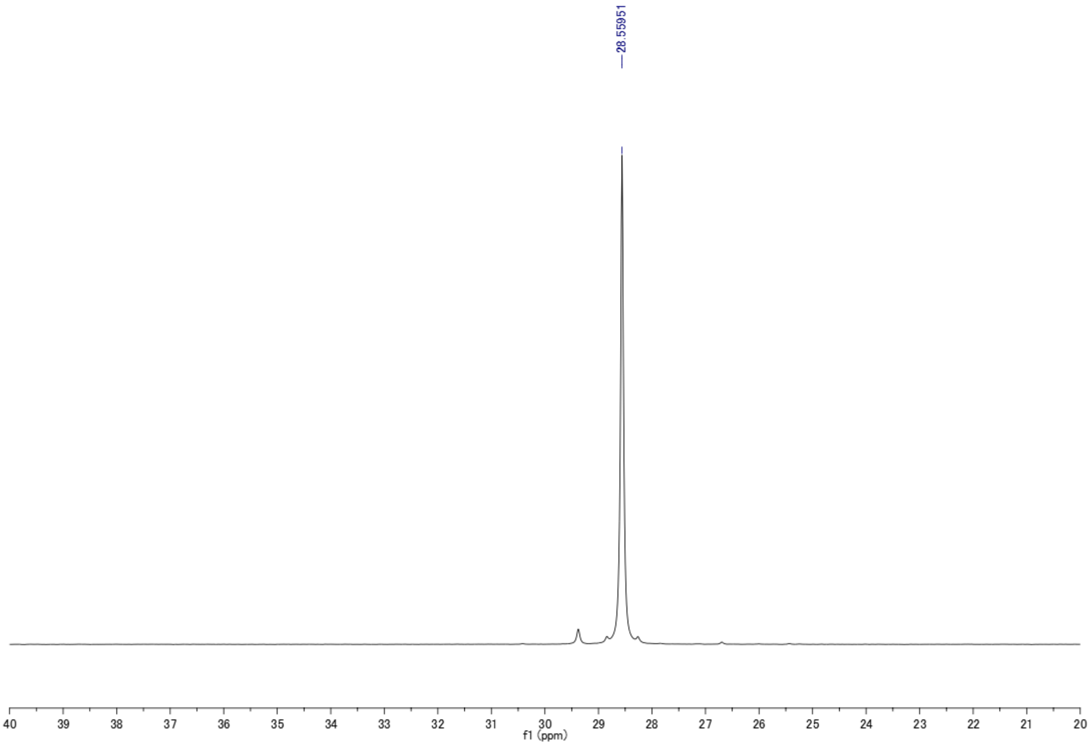

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (162 MHz, 25 °C, C_6D_6).

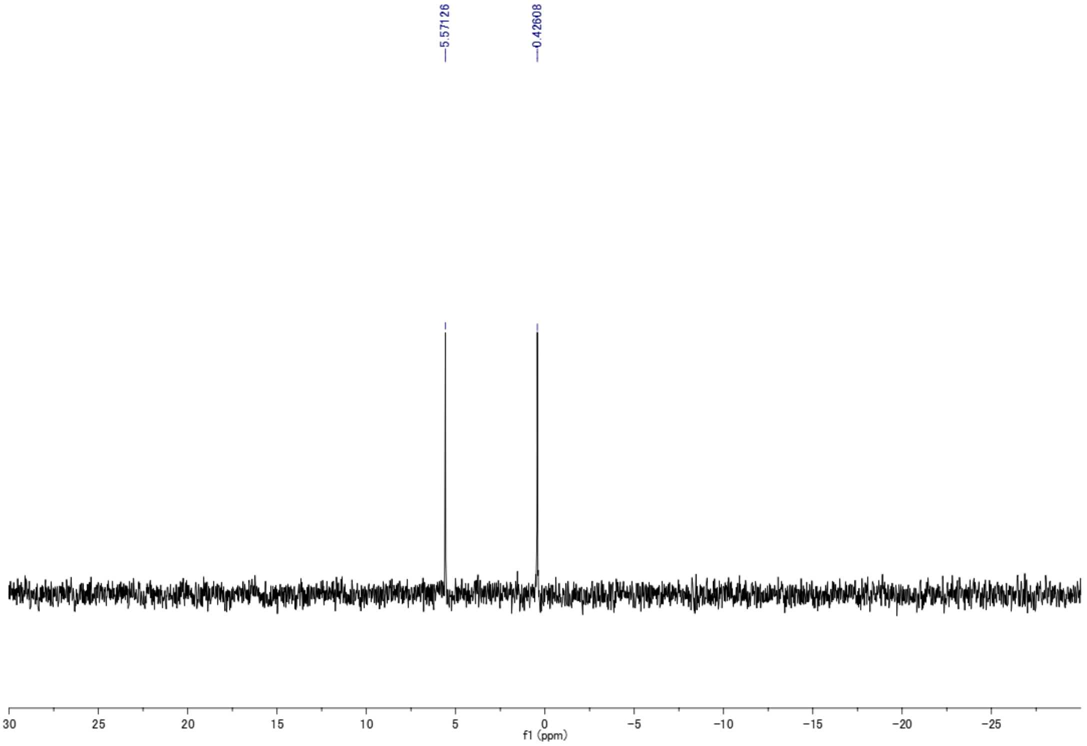

Figure S7. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** (99 MHz, 25 °C, C_6D_6).

S2-3 Synthesis of iminophosphonamido alumanyl-iron(II) complex 3

In a Schlenk tube, iminophosphonamido aluminum(III) dichloride **1** (150.0 mg, 0.353 mmol) and K[FeCp(CO)$_2$] (77.0 mg, 0.356 mmol) were dissolved into toluene (5 mL) at 60 ℃. The mixture was kept stirring at this temperature for 4 h. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Recrystallisation from toluene at −10 ℃ gave an alumanyl-iron(II) complex **3** (86.0 mg, 43%) as colorless crystals.

Mp: 104–106 ℃ (decomp.) ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 1.18 (s, 18H, CH_3), 4.52 (s, 5H, Cp), 7.03-7.12 (m, 6H, Ar), 8.06 (m, 2H, Ar), 8.26 (m, 2H, Ar). ^{13}C{^{1}H} NMR (101 MHz, 25 °C, C_6D_6) δ 33.6 (d, J_{CP} = 6.9 Hz, CH_3), 52.6 (C_{tBu}), 82.3 (Cp), 128.6 (d, J_{CP} = 11.8 Hz, Ar(CH)), 131.8 (d, J_{CP} = 47.9 Hz, Ar(C)), 132.2 (d, J_{CP} = 2.7 Hz, Ar(CH)), 132.3 (d, J_{CP} = 2.8 Hz, Ar(CH)), 132.7 (d, J_{CP} = 44.5 Hz, Ar(CH)), 133.5 (d, J_{CP} = 10.5 Hz, Ar(CH)), 134.5 (d, J_{CP} = 10.2 Hz, Ar(CH)). 217.9 (CO). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, C_6D_6) δ 30.2. IR (KBr): 1967 cm^{-1} (ν_{CO}), 1907 cm^{-1} (ν_{CO}).

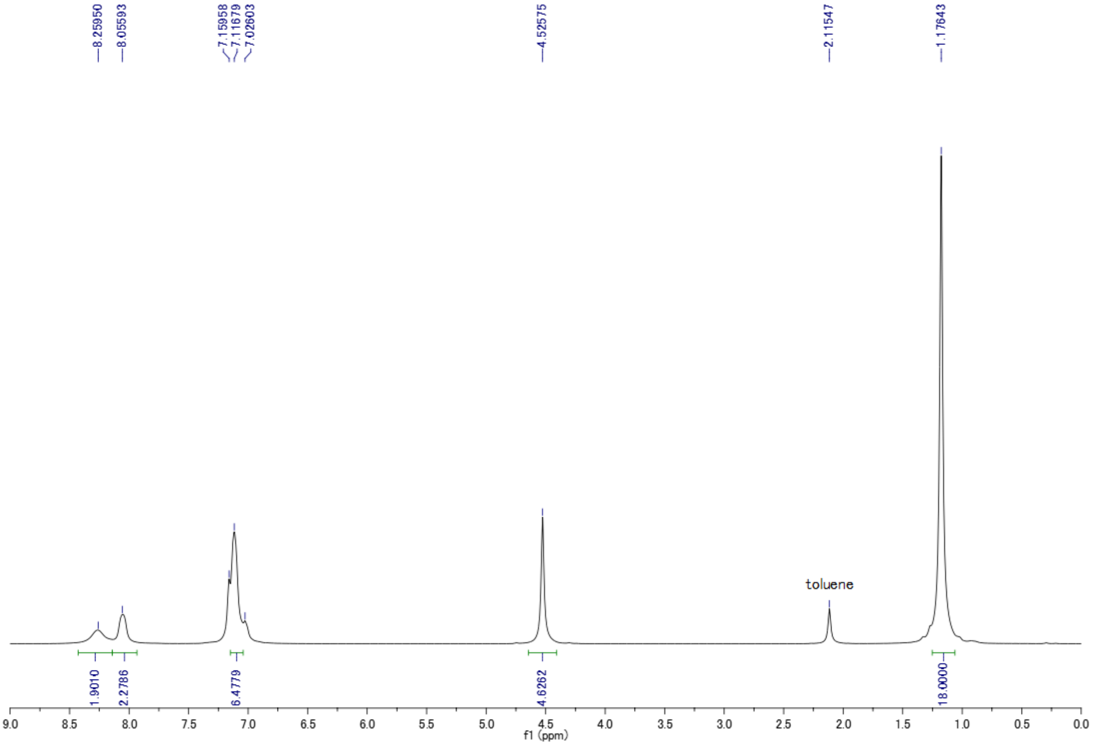

Figure S8. ^{1}H NMR spectrum of **3** (400 MHz, 25 °C, C_6D_6).

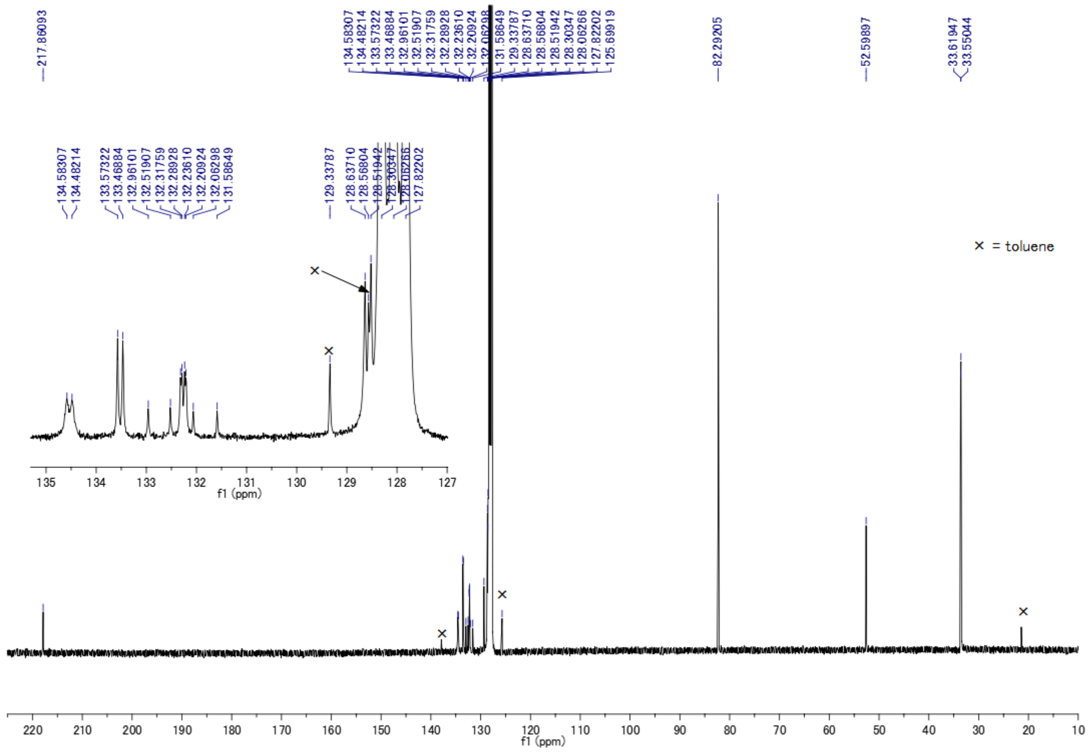

Figure S9. ^{13}C{^{1}H} NMR spectrum of **3** (101 MHz, 25 °C, C_6D_6).

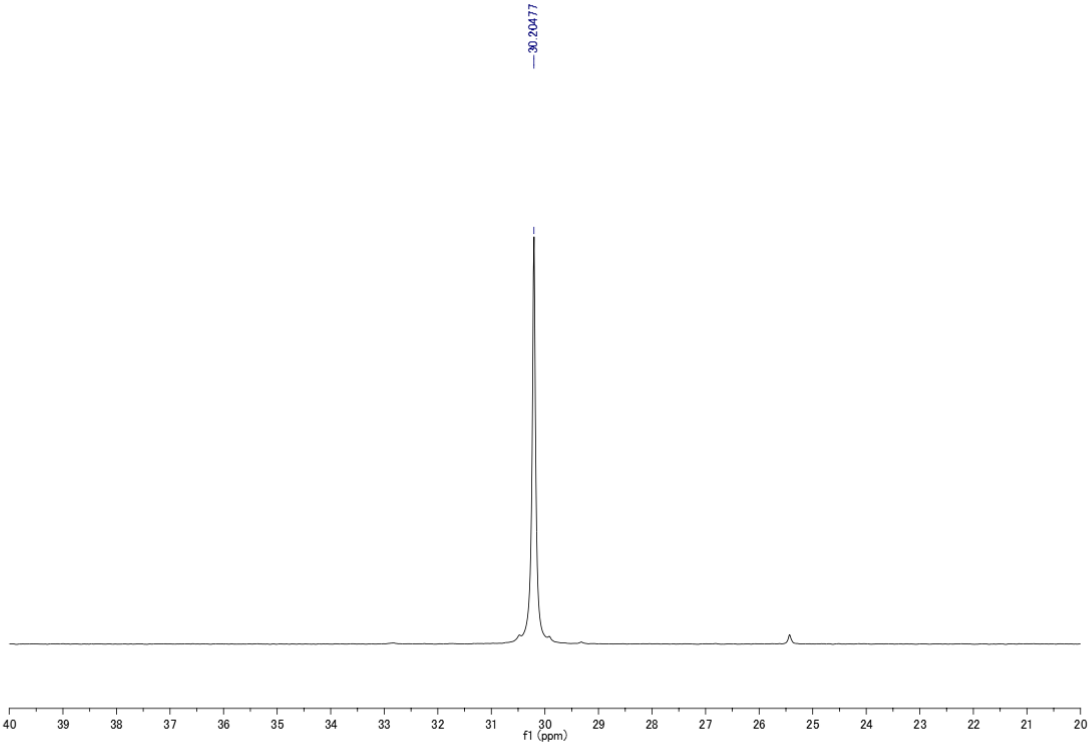

Figure S10. $^{31}P\{^1H\}$ NMR spectrum of **3** (162 MHz, 25 °C, C_6D_6).

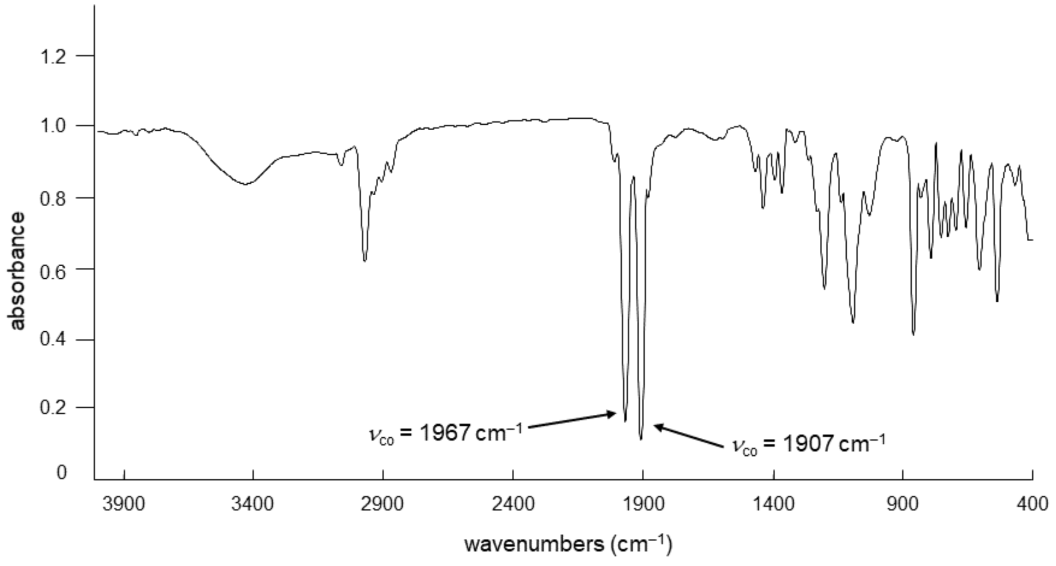

Figure S11. IR spectrum of **3** (KBr).

S2-4 Synthesis of iminophosphonamido Cp-substituted aluminum(III) 4

In a Schlenk tube, iminophosphonamido aluminum(III) **1** (174.3 mg, 0.410 mmol) was dissolved into toluene (3.0 mL), and CpNa in THF (2.4 M, 0.17 mL, 0.408 mmol) was added to the toluene solution at room temperature. The mixture was kept stirring at this temperature for 3 days. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Recrystallisation from toluene at –10 °C gave a Cp-substituted aluminum(III) **4** (95.1 mg, 51%) as colorless crystals.

Mp: 100–103 °C (decomp.) ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 0.94 (s, 18H, CH_3), 6.63 (s, 5H, Cp), 7.01-7.11 (m, 6H, Ar), 7.89-7.96 (m, 4H, Ar). ^{13}C{^{1}H} NMR (101 MHz, 25 °C, C_6D_6) δ 33.2 (d, J_{CP} = 7.1 Hz, CH_3), 52.0 (C_{tBu}), 115.1 (Cp), 128.6 (d, J_{CP} = 12.2 Hz, Ar(CH)), 128.7 (d, J_{CP} = 11.6 Hz, Ar(CH)), 130.5 (d, J_{CP} = 40.2 Hz, Ar(C)), 131.5 (d, J_{CP} = 37.7 Hz, Ar(C)), 132.5 (d, J_{CP} = 1.9 Hz, Ar(CH)), 132.5 (d, J_{CP} = 1.9 Hz, Ar(CH)), 133.6 (d, J_{CP} = 10.9 Hz, Ar(CH)), 133.9 (d, J_{CP} = 11.0 Hz, Ar(CH)). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, C_6D_6) δ 30.0.

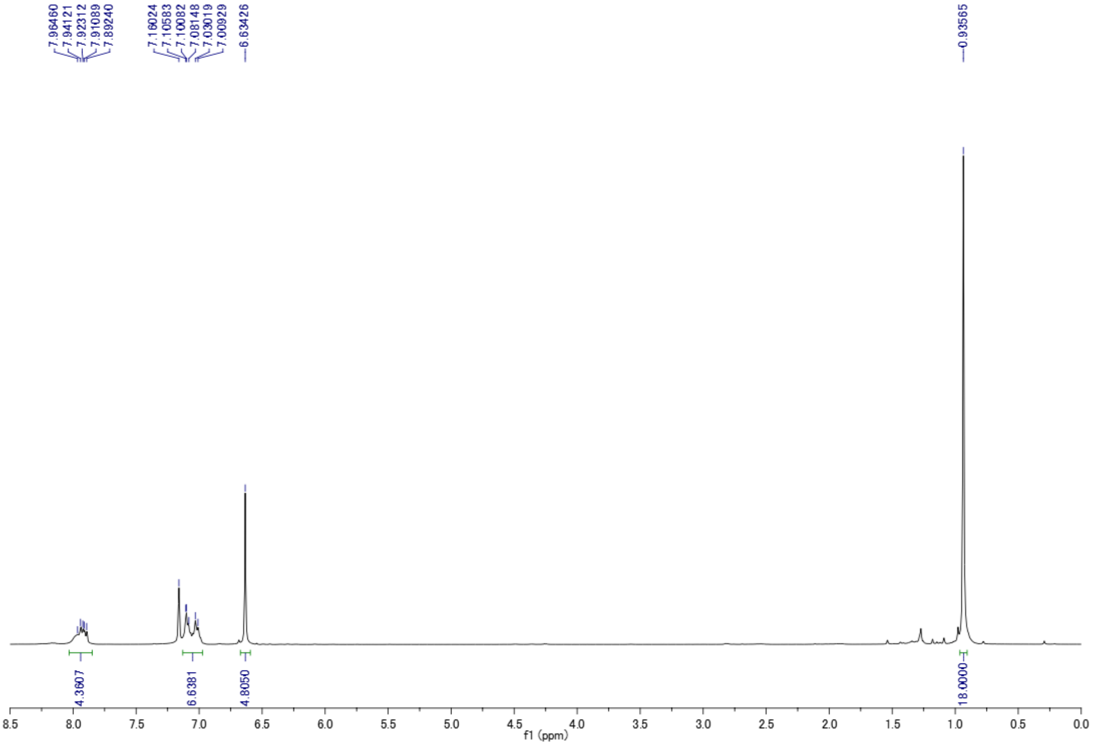

Figure S12. ^{1}H NMR spectrum of **4** (400 MHz, 25 °C, C_6D_6).

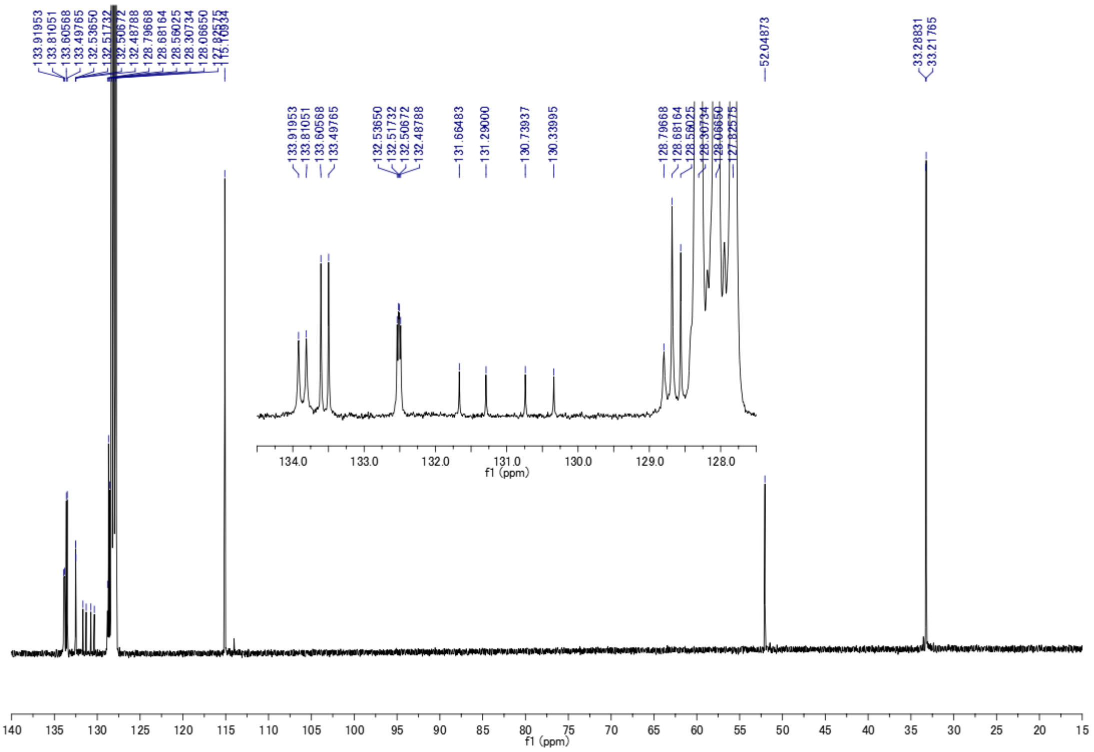

Figure S13. $^{13}C\{^1H\}$ NMR spectrum of **4** (101 MHz, 25 °C, C_6D_6).

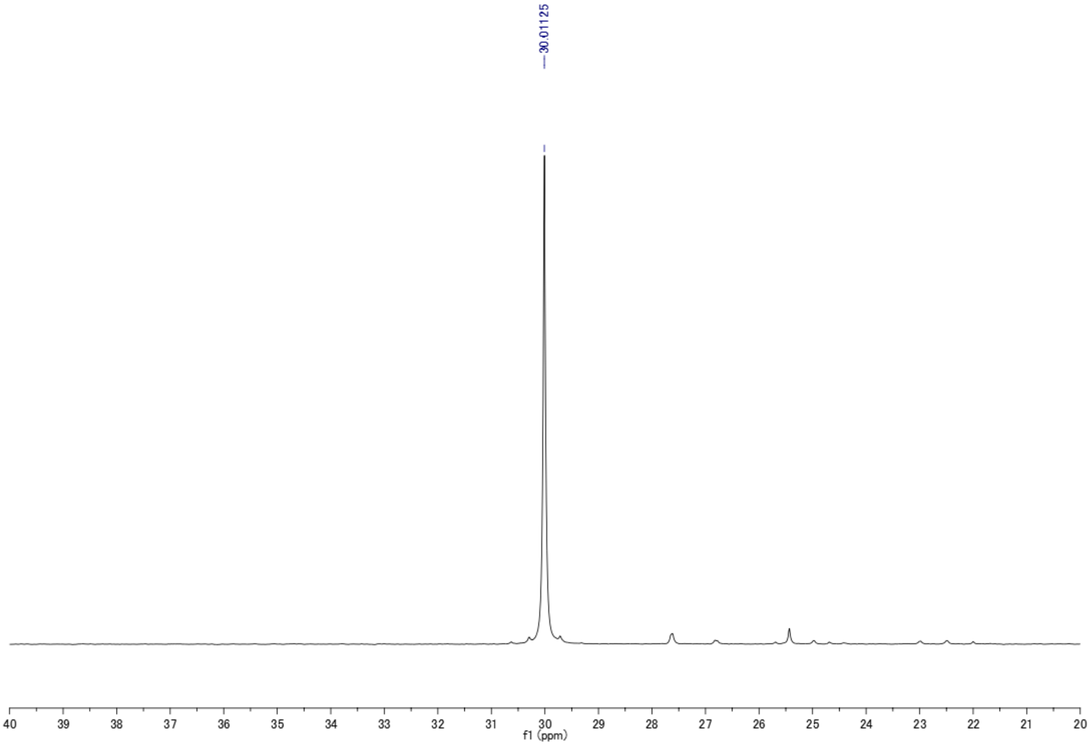

Figure S14. $^{31}P\{^1H\}$ NMR spectrum of **4** (162 MHz, 25 °C, C_6D_6).

S.3 X-ray crystallographic analyses

Colorless single crystals of **1**, **2**, and **4** were grown from each saturated toluene at −10 °C. Colorless single crystals of **3** were obtained from saturated C_6H_6 solution at 10 °C. The intensity data were collected at 120 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXT)[3] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL).[4] Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters.

S4. References

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