1st Row Transition Metal Aluminylene Complexes: Preparation, Properties and Bonding Analysis

Electronic Supporting Information

Richard Y. Kong, Mark R. Crimmin

Department of Chemistry, Imperial College London, White City, London, W12 0BZ
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1 General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. A MBraun Labmaster glovebox was employed, operating at <0.1 ppm O₂ and <0.1 ppm H₂O. Solvents were dried over activated alumina from a SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120°C prior to use. C₆D₆ was dried over 3 Å molecular sieves and freeze-pump-thaw degassed thrice before use.

NMR Spectra were recorded on Bruker 400 MHz or 500 MHz at 298 K unless otherwise stated and values recorded in ppm. Data were processed in MestReNova software. Where needed, chemical shifts were assigned with the assistance of 2D NMR (HSQC, HMBC, COSY) spectra. 1¹, and 2f-h²-⁴ were synthesized according to literature procedures. IR spectra were recorded on an Agilent Cary630 ATR FTIR spectrometer. Photolysis experiments were conducted using a 400W Hg lamp. Chemicals were purchased from Sigma Aldrich, Fluorochem, Alfa Aesar, and VWR. Elemental analyses were performed by Elemental Labs (https://www.elementallab.co.uk/).
2 Synthetic Methods

2.1 – Preparation of compounds

In a glovebox, 1 (18 mg, 0.04 mmol) was suspended in toluene (~ 0.5 mL) in a 20 mL scintillation vial. To this solution, a suspension of [Cr(CO)₆] (10 mg, 0.045 mmol) in toluene (~ 0.5 mL) was added at 25°C and the resultant mixture was placed under reduced pressure (static vacuum). The reaction mixture was swirled within the vial and evolution of CO gas was observed during the reaction. The vacuum atmosphere was refreshed periodically to remove the evolved CO gas. Upon dissolution of 1, the reaction is assumed to be complete and formed a beige suspension of 3a in toluene. The solvent was partially removed in vacuo until approximately 0.1 mL of toluene remained. The resultant crude mixture was diluted with ~2 mL of n-pentane and the solution was agitated to create a suspension of 3a. The beige solid was collected by suction filtration and the residue was washed thrice with n-pentane. 3a was transferred to a vial and dried briefly (~2 minutes) in vacuo. X-ray quality crystals were obtained from recrystallizing 3a using a mixture of toluene, n-pentane, and the minimum amount of THF. Yield: 14 mg, 0.22 mmol, 55%.

1H NMR (400 MHz, C₆D₆, 298 K) δ 0.99 (d, 3J_HH = 6.8 Hz, 12H, (CH₃)₂CH), 1.43 (s, 6H, (CH₃)₂C)₂CH), 1.46 (d, 3J_HH = 6.8 Hz, 12H, (CH₃)₂CH), 3.09 (hept, 3J_HH = 6.6 Hz, 4H, 4x (CH₃)₂CH), 5.07 (s, 1H, (CH₃)C)₂CH), 7.10-7.23 (6H, Ar-H).

13C NMR (101 MHz, C₆D₆, 298 K) δ 24.2 (2x (CH₃)₂CH), 24.3 (4x (CH₃)₂CH), 30.2 (4x (CH₃)₂CH), 100.3 (4x (CH₃)₂CH), 144.3 (ArC), 171.1 (4x (CH₃)₂CH). 3a is poorly soluble in C₆D₆ and some quaternary carbon resonances were not observed.

IR (ATR), νCO (cm⁻¹): 2027, 1946, 1919, 1897, 1887.

Due to the instability of 3a to vacuum accurate CHN analysis could not be obtained. Anal. Calc. (C₃₄H₄₃AlCrN₂O₅): C, 64.40; H, 6.49; N, 4.40. Found: C, 60.13; H, 6.49; N, 4.53.
In a glovebox, 1 (18 mg, 0.04 mmol) was suspended in C₆D₆ (0.6 mL) and transferred to a J-Young NMR tube. To this solution, [(η⁵-C₅H₄Me)Mn(CO)]₃ (7 μL, 9.7 mg, 0.044 mmol) was added via micropipette. The J-Young NMR tube was sealed and removed from the glovebox. The reaction mixture was heated at 80°C and shaken to ensure dissolution of 1. Upon complete dissolution, the homogeneous reaction mixture was heated at 80°C for 16 h. The reaction was complete upon complete consumption of 1 as monitored by ¹H NMR spectroscopy. At this point, the NMR tube was returned to the glovebox and the headspace of the NMR tube was evacuated to remove the evolved CO gas. The solution was decanted into a 20 mL scintillation vial and diluted with ~ 2 mL of toluene. The resultant red-orange solution was concentrated in vacuo until ~ 0.4 mL of solution remained. The solution was filtered into a 4 mL vial, n-pentane layered on top, and 3b allowed to crystallise at –35°C. 3b crystallised as bright yellow crystals. The supernatant was decanted and the crystals were washed with cold (-35°C) n-pentane thrice (3x 0.5 mL) before the solid was dried briefly in vacuo (~ 2 minutes). Yield: 11 mg, 0.017 mmol, 43%.

¹H NMR (400 MHz, C₆D₆, 298 K) δ 1.05 (d, ᵃ_JHH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.48 (d, ᵃ_JHH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.51 (s, 6H, {((CH₃)₂C)₂CH}), 1.81 (s, 3H, C₅H₄CH₂), 3.22 (hept, ᵃ_JHH = 6.8 Hz, 4H, 4x (CH₃)₂CH), 3.49 (apparent t, ᵃ_J = 2.0 Hz, 2H, Cp'CH₂), 3.98 (apparent t, ᵃ_J = 2.0 Hz, 2H, Cp'CH₂), 5.10 (s, 1H, {((CH₃)C)CH}), 7.10 – 7.23 (m, 6H, Ar-₇₈).

¹³C NMR (101 MHz, C₆D₆, 298 K) δ 14.2 (CH₃C₅H₄), 24.2 {((CH₃)₂C)₂CH), 24.5 (2x (CH₃)₂CH), 24.5 (2x (CH₃)₂CH), 29.6 (4x (CH₃)₂CH), 76.2 (2x CH³), 79.0 (2x CH¹), 96.9 (Cp'-CCH₃), 101.5 {((CH₃)₂C)₂CH}, 124.9 (Ar-peated), 128.5 (Ar-peated), 141.1 (Ar-peated), 143.7 (Ar-peated), 170.2 {((CH₃)₂C)₂CH), 233.3 (Mn(CO)₂).

IR (ATR), ν(CO) (cm⁻¹): 1886, 1813.

Anal. Calc. (C₃₈H₄₈AlMnN₂O₂): C, 70.02, H, 7.62; N, 4.41. Found: C, 69.77; H, 7.60; N, 4.35.
Synthesis of 3c:

In a glovebox, 1 (18 mg, 0.04 mmol) was suspended in toluene (0.6 mL) and transferred to a J-Young NMR tube. To this solution Fe(CO)₅ (7.5 μL, 11 mg, 0.055 mmol) was added via micropipette. The J-Young NMR tube was sealed and removed from the glovebox. The mixture was heated at 80°C briefly and shaken to ensure the complete dissolution of 1. The reaction was complete within 5 minutes, and 3c formed as a bright yellow precipitate. The NMR tube was returned to the glovebox and the headspace of the NMR tube was evacuated to purge the evolved CO gas from the reaction. The contents of the NMR tube were emptied into a 20 mL scintillation vial and the mixture was concentrated in vacuo until approximately ~0.5 mL of solvent remained. n-Pentane (2 mL) was added to the resultant crude mixture and the vial was placed in the freezer (−35°C) for 18 h. The supernatant was decanted and the bright yellow powder 3c was washed with n-pentane thrice (3x 0.5 mL) before being dried briefly under vacuum. X-ray quality crystals can be grown from a concentrated toluene solution at −35°C. Yield: 19 mg, 0.31 mmol, 78%.

1H NMR (400 MHz, C₆D₆, 298 K) δ 1.05 (d, 3J_HH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.45 (s overlapping, 6H, (((CH₃)₂C)₂CH), 1.46 (d, 3J_HH = 6.5 Hz, 12H, 2x (CH₃)₂CH), 3.03 (hept, 3J_HH = 6.8 Hz, 4H, 4x (CH₃)₂CH), 5.03 (s, 1H, (((CH₃)₂C)₂CH), 7.09-7.24 (m, 6H, Ar-H).

13C NMR (101 MHz, C₆D₆, 298 K) δ 24.0 (((CH₃)₂C)₂CH), 24.6 (2x (CH₃)₂CH), 24.7 (2x (CH₃)₂CH), 29.5 (4x (CH₃)₂CH), 102.6 (((CH₃)₂C)₂CH), 125.3 (Ar-C), 129.3 (Ar-C), 138.3 (Ar-C), 143.8 (Ar-C), 172.8 (((CH₃)₂C)₂CH), 215.7 (4x FeCO).

IR (ATR), ν_CO (cm⁻¹): 2007, 1901, 1873.

Anal. Calc. (C₃₃H₄₁AlFeN₂O₄): C, 64.71, H, 6.75; N, 4.57. Found: C, 64.63; H, 6.45; N, 4.20.
Synthesis of 3d

In a glovebox, to a suspension of 3c (18 mg, 0.029 mmol) in C₆D₆ (0.600 mL), was added PCy₃ (10 mg, 0.035 mmol) as a solid. The mixture was transferred to a borosilicate J-Young NMR tube, removed from the glovebox, and photolyzed at 25°C for 7 hours (400 W, Hg-lamp). The J-Young NMR tube was returned to the glovebox and exposed to vacuum, and refreshed with N₂ at the 2-hour and 4-hour timepoint to remove evolved CO gas. The reaction was monitored by ¹H NMR spectroscopy. Upon complete consumption of 3c, the NMR-tube was returned to the glovebox, diluted with approx. 1 mL of toluene, and decanted into a 4 mL vial. The crude mixture was concentrated in vacuo until approximately 0.4 mL of solvent remained. n-Pentane was layered on top of toluene solution and the vial placed in the glovebox freezer at −35°C. 3d crystallised as orange blocks. The supernatant was decanted, and the crystals were washed thrice with n-pentane (3x 0.5 mL), before the solid was dried briefly in vacuo (~ 2 minutes). Yield: 10 mg, 0.012 mmol, 40%.

¹H NMR (400 MHz, C₆D₆, 298 K) δ 1.12 (d, 3J_HH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.15-1.26 (m, 9H, Cy-H), 1.54 (s, 6H, (CH₃)₂C₂CH), 1.49-1.62 (m overlapping, 9H, Cy-H), 1.65 (d, 3J_HH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.68-1.77 (m, 6H, Cy-H), 1.96 – 2.20 (m, 9H, Cy-H), 3.29 (hept, 3J_HH = 6.7 Hz, 4H, 4x (CH₃)₂CH), 5.13 (s, 1H, (CH₃)₂CH), 7.19 – 7.29 (m, 6H, Ar-H).

¹³C NMR (101 MHz, C₆D₆, 298 K) δ 24.3 ((CH₃)₂C₂CH), 24.7 (2x (CH₃)₂CH), 25.0 (2x (CH₃)₂CH), 27.0 (Cy-CH₂), 28.3 (d, 2J_CP = 9.9 Hz, Cy-CH₂), 29.6 (4x (CH₃)₂CH), 30.1 (Cy-CH₂), 39.15 (d, 1J_CP = 18.1 Hz, Cy-CH), 101.9 ((CH₃)₂C₂CH), 124.9 (Ar-C), 128.6 (Ar-C), 140.1 (Ar-C), 143.9 (Ar-C), 171.6 ((CH₃)₂CH), 216.8 (3x FeCO).

³¹P NMR (162 MHz, C₆D₆) δ 85.46.

IR (ATR), ν_CO (cm⁻¹): 1916, 1843, 1806.

Anal. Calc. (C₅₀H₇₄AlFeN₂O₃P): C, 69.43, H, 8.62; N, 3.24. Found: C, 69.44; H, 8.55; N, 2.90.
**Synthesis of 3e:**

In a glovebox, a solution of 1 (18 mg, 0.040 mmol) and [CoCp(PCyPh2)(CO)] (18 mg, 0.046 mmol) in benzene (~0.6 mL) was transferred to a J-Young NMR tube. n-Hexane was layered on top of this solution and the mixture was allowed to stand at 25°C undisturbed for 18 h. (3e)2 crystallised directly from the reaction mixture as a bright orange solid. The contents of the NMR tube were emptied into a vial and the crystals collected by decanting the supernatant. The orange solid was washed thrice with n-pentane (3x 1 mL) and dried briefly under vacuum (~ 2 minutes). Yield: 23 mg, 0.019 mmol, 96%.

3e is insoluble in common NMR solvents (toluene, benzene, THF) and so solution-state NMR spectra could not be attained.

IR (ATR), νCO (cm⁻¹): 1640

Anal. Calc. (C₇₀H₉₂Al₂Co₂N₄O₂): C, 70.45, H, 7.77; N 4.69. Found: C, 70.91; H, 8.12; N, 4.43.
**Synthesis of 3f:**

In a glovebox, 1 (20 mg, 0.045 mmol) and 2f (21 mg, 0.038 mmol) were dissolved in toluene (~1 mL) in a 20 mL scintillation vial. The mixture was agitated at 25°C until the total dissolution of 1 was observed. A colour-change of the solution from the characteristic orange-red of 1 to a bright orange was observed. The vial was placed in the glovebox freezer (–35°C) and 3f was allowed to recrystallise as a bright orange solid over 18 h. n-Pentane (~5 mL) was added to the mixture and the vial was returned to the freezer) for a further 18 h. The supernatant was decanted, and the resultant solid 3f was washed thrice with n-pentane (3x 2 mL) and dried briefly *in vacuo* (~2 minutes). Yield: 30 mg, 0.031 mmol, 83%.

\[ ^1H \text{ NMR (400 MHz, C}_6\text{D}_6, 298 K) \delta 0.93 (d, ^3J_{HH} = 6.9 \text{ Hz}, 12H, 2x (CH}_3)_2\text{CH}), 0.98 (d, ^3J_{HH} = 6.8 \text{ Hz}, 12H, 2x (CH}_3)_2\text{CH}), 1.32 (s, 6H, \{(CH}_3)_2\text{C}_2\text{CH}), 1.94 (s, 12H, 4x Mes-CH}_3)_2\text{CH}), 2.23 (s, 6H, 2x Mes-CH}_3)_2\text{CH}), 2.70 (hept, ^3J_{HH} = 6.8 \text{ Hz}, 4H, 4x (CH}_3)_2\text{CH}), 4.96 (s, 1H, \{(CH}_3)_2\text{CH}), 5.15 (s, 1H, \{(CH}_3)_2\text{CH}), 6.17 (s, 4H, Mes-CH}_3)_2\text{CH}), 6.65 (s, 4H, 2x Mes-CH}_3)_2\text{CH}), 6.99-7.14 (m, 6H, ArH).]

\[ ^{13}C \text{ NMR (101 MHz, C}_6\text{D}_6, 298 K) \delta 19.1 (4x Mes-CH}_3)_2\text{CH}), 21.1 (2x Mes-CH}_3)_2\text{CH}), 23.3 (2x (CH}_3)_2\text{CH}), 23.9 (\{(CH}_3)_2\text{C}_2\text{CH}), 24.8 (2x (CH}_3)_2\text{CH}), 29.7 (4x (CH}_3)_2\text{CH}), 84.6 (\{(CH}_3)_2\text{C}_2\text{CH}), 102.5 (\{(CH}_3)_2\text{C}_2\text{CH}), 125.3 (ArC), 128.8 (ArC), 130.6 (ArC), 131.5 (ArC), 140.8 (ArC), 143.0 (2x ArC), 147.9 (ArC), 169.6 (\{(CH}_3)_2\text{C}_2\text{CH}). \text{Some quaternary carbon resonances cannot be observed due to coupling to } ^{19}\text{F.}

\[ ^{19}F \text{ NMR (377 MHz, C}_6\text{D}_6, 298 K) \delta -63.08 .

\text{Anal. Calc. (C}_{52}\text{H}_{64}\text{AlCuF}_6\text{N}_4): C, 65.77, H, 6.79; N, 5.90. Found: C, 67.03; H, 6.94; N, 5.71.}
Synthesis of 3g:

In a glovebox, 1 (20 mg, 0.045 mmol) and 2g (19 mg, 0.038 mmol) were dissolved in toluene (~1 mL) in a 20 mL scintillation vial. The mixture was agitated at 25°C until the dissolution of 1 was observed. A colour-change of the solution from the characteristic orange-red of 1 to a bright yellow was observed. The solution was concentrated until approximately 0.4 mL remained. The vial was placed in the glovebox freezer (–35°C) and 3f was allowed to recrystallise as a bright yellow solid over 18 h. The supernatant was decanted, and the resultant solid was washed thrice with n-pentane (3x 2 mL) and dried briefly in vacuo (~2 minutes). Yield: 20 mg, 0.022 mmol, 58%.

**H NMR** (400 MHz, C₆D₆, 298 K) δ 1.05 (d, 3J_HH = 6.9 Hz, 12H, 2x (CH₃)₂CH), 1.15 (d, 3J_HH = 6.8 Hz, 12H, 2x (CH₃)₂CH), 1.39 (s, 6H, {(CH₃)₂C}₂CH), 1.62 (s, 6H, {(CH₃)₂C}₂CH), 2.86 (hept, 3J_HH = 6.9 Hz, 4H, 4x (CH₃)₂C₄H), 4.90 (s, 1H, {(CH₃)C}₂CH), 5.06 (s, 1H, {(CH₃)C}₂CH), 6.42 (apparent t, J = 7.9 Hz, 2H, Ar-CH), 6.90 – 7.32 (m, 10H, Ar-CH).

**C NMR** (101 MHz, C₆D₆, 298 K) δ 23.3 (2x (CH₃)₂CH), 23.6 ({{(CH₃)C}₂CH}, 24.0 ({{(CH₃)C}₂CH}), 24.8 (2x (CH₃)₂CH), 29.6 (4x (CH₃)₂CH), 96.1 ({{(CH₃)C}₂CH}, 102.4 ({{(CH₃)C}₂CH}, 122.3 (ArC), 125.2 (ArC), 127.9 (ArC), 128.4 (ArC), 131.4 (ArC), 141.3 (ArC), 142.4 (ArC), 151.1 (ArC), 162.8 ({{(CH₃)C}₂CH}, 169.4 ({{(CH₃)C}₂CH}).

Anal. Calc. (C₄₆H₅₄AlCl₄CuNa): C, 61.71, H, 6.08; N, 6.26. Found: C, 61.62; H, 5.80; N, 6.13.
**Synthesis of 3h:**

In a glovebox, 1 (20 mg, 0.045 mmol) and 2h (18 mg, 0.038 mmol) were suspended in toluene (~0.6 mL) and transferred to a J-Young NMR tube. The NMR tube was removed from the glovebox and heated at 100°C briefly to dissolve the reagents, at which point the reaction is likely complete. The J-Young NMR tube was returned to the glovebox and the reaction mixture was decanted into a 20 mL scintillation vial. The vial was placed in the glovebox freezer (~35°C) and 3h was allowed to recrystallize as green-brown needles. The supernatant was decanted, and the solid was washed thrice with n-pentane (3x 2 mL) before the crystals were dried briefly *in vacuo* (~2 minutes). Yield: 26 mg, 0.030 mmol, 79%.

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 1.07 (d, $^3$J$_{HH}$ = 6.8 Hz, 12H, 2x (CH$_3$)$_2$CH), 1.11 (d, $^3$J$_{HH}$ = 6.8 Hz, 12H, 2x (CH$_3$)$_2$CH), 1.38 (s, 6H, ((CH$_3$)$_2$C)$_2$CH), 1.96 (s, 6H, ((CH$_3$)$_2$C)$_2$CH), 3.00 (hept, $^3$J$_{HH}$ = 6.8 Hz, 4H, 4x (CH$_3$)$_2$CH), 3.33 (s, 12H 4x OCH$_3$), 4.91 (s, 1H, ((CH$_3$)C)$_2$CH), 5.00 (s, 1H, ((CH$_3$)C)$_2$CH), 6.49 (apparent d, $J$ = 8.2 Hz, 4H, Ar-CH), 6.73 – 6.88 (m, 2H, Ar-CH), 6.97 – 7.18 (m, 6H, Ar-CH).

$^{13}$C NMR (101 MHz, C$_6$D$_6$, 298 K) δ 23.5 (((CH$_3$)$_2$C)$_2$CH), 23.6 (((CH$_3$)$_2$C)$_2$CH), 24.1 (2x (CH$_3$)$_2$CH), 25.4 (2x (CH$_3$)$_2$CH), 29.2 (4x (CH$_3$)$_2$CH), 56.4 (4x OCH$_3$), 96.7 (((CH$_3$)$_2$C)$_2$CH), 101.1 (((CH$_3$)$_2$C)$_2$CH), 108.5 (Ar-CH), 121.1 (Ar-CH), 124.4 (Ar-CH), 127.4 (Ar-CH), 128.3 (Ar-CH), 136.9 (Ar-CH), 140.3 (Ar-CH), 144.2 (Ar-CH), 154.1 (Ar-CH), 162.7 (((CH$_3$)$_2$C)$_2$CH), 167.7 (((CH$_3$)$_2$C)$_2$CH).

Anal. Calc. (C$_{50}$H$_{66}$AlCuN$_4$O$_2$): C, 68.43, H, 7.58; N, 6.38. Found: C, 65.44; H, 7.50; N, 6.12.
3. X-ray Data

The X-ray crystal structure of 3a

Figure S1: The X-ray crystal structure of 3a. Hydrogen atoms and included solvent omitted for clarity.

3a was found to crystallise in the space group P2₁/n, with an included toluene molecule in the asymmetric unit.

Crystal Data for C₄₅H₅₇AlCrN₂O₆, \( M = 800.90 \), monoclinic, space group P2₁/n (no. 14), \( a = 10.9861(6) \) Å, \( b = 25.9752(14) \) Å, \( c = 15.2738(10) \) Å, \( \beta = 99.548(6)^\circ \), \( V = 4298.2(4) \) Å³, \( Z = 4 \), \( \rho_{\text{calc}} \) g/cm³ = 1.238, \( \mu(\text{CuKα}) = 2.771 \) mm⁻¹, \( T = 173.0(3) \), yellow needles, \( F^2 \) refinement, \( R_1(\text{obs}) = 0.0838 \), \( wR_2(\text{all}) = 0.2867 \), 8300 independent observed reflections \( (R_{\text{int}} = 0.1021) \), 3608 independent measured reflections \( [|F_o| > 4\sigma(|F_o|), 2\theta_{\text{full}} = 147.318] \), 507 parameters. CSD 2071011.
**The X-ray crystal structure of 3b**

![Image of X-ray crystal structure](image)

**Figure S2**: The X-ray crystal structure of 3b. One of two independent molecules. Hydrogen atoms omitted for clarity.

3b was found to crystallise in the space group P2_1/n.

**Crystal Data for C_{37}H_{48}AlMnN_{2}O_{2}, M =634.69, monoclinic, space group P2_1/n (no. 14), a = 8.86240(19) Å, b = 20.6632(3) Å, c = 18.2680(3) Å, β = 94.2925(17)°, V = 3335.95(10) Å³, Z = 4, ρ_{calc}/g/cm³ = 1.264, μ(CuKα) = 3.733 mm⁻¹, T = 173.00(14), yellow prisms, F² refinement, R1(obs) = 0.0413, wR2(all) = 0.1124, 6343 independent observed reflections (R_{int} = 0.0301), 5120 independent measured reflections [||F_o|| > 4σ(|F_o|)], 2θ_{full} = 146.57], 399 parameters. CSD 2071012.
The X-ray crystal structure of 3c

**Figure S3**: The X-ray crystal structure of 3c. Hydrogen atoms, disorder, and included solvent omitted for clarity.

3c was found to crystallise in the space group Pnma. The unit cell of the crystal was found to contain four full molecules of 3c, and four full molecules of toluene. Accordingly, the asymmetric unit of the crystal contains half a molecule of 3c, and half a molecule of toluene. Both molecules are disordered along a mirror plane defined by the Al1–Fe1–C1 atoms.

The included toluene is disordered over this mirror plane. The toluene is modelled in two orientations in the Part -1 and Part -2 with major and minor occupancies ca. 34% and 16%, summing to one half occupancy toluene molecule, with the symmetry element generating the other half. The thermal parameters of adjacent atoms in the major and minor components were restrained to be similar, their geometries optimized, and only the non-hydrogen atoms in the major orientation were refined anisotropically (those in the minor orientation were refined isotropically).

_Crystal Data for_ C_{40}H_{49}AlFeN_{2}O_{4}, M = 704.64, orthorhombic, space group Pnma (no. 62), a = 21.9278(9) Å, b = 16.6105(8) Å, c = 10.6008(6) Å, V = 3861.2(3) Å³, Z = 4, ρ_{calc}g/cm³ = 1.212, μ(MoKα) = 0.454 mm⁻¹, T = 173.00(14), yellow plates, F² refinement, R₁(obs) = 0.0450, wR₂(all) = 0.1310, 4086 independent observed reflections (R_{int} = 0.0314), 2941 independent measured reflections [|Fo| > 4σ(|Fo|), 2θ_{null} = 56.668], 271 parameters. CSD 2071013.
The X-ray crystal structure of 3d

**Figure S4**: The X-ray crystal structure of 3d. Hydrogen, included solvent, and disorder omitted for clarity.

3d was found to crystallise in the P2₁/n space group with an included toluene molecule in the asymmetric unit.

The cyclohexyl ring (C39-C44) was modelled as disordered over two sites in ca. 77:23 occupancies for the major and minor orientations respectively. The two orientations are related by ring-flip isomerisation of the cyclohexyl group. The carbon atom C39 occupies the same position in both ring conformations and so was not included in the disorder model. The thermal parameters of adjacent atoms in the major and minor components were restrained to be similar, their geometries optimized, and only the non-hydrogen atoms in the major orientation were refined anisotropically (those in the minor orientation were refined isotropically).

The included toluene was found to be disordered over two sites in ca. 51:49 occupancies for the major and minor occupancies respectively. The thermal parameters of adjacent atoms in the major and minor components were restrained to be similar, their geometries optimized, and both orientations were refined anisotropically.

*Crystal Data for* C₅₇H₈₂AlFeN₂O₃P, *M* = 957.04, monoclinic, space group P2₁/c (no. 14), *a* = 14.0053(4) Å, *b* = 16.6674(5) Å, *c* = 23.4517(10) Å, *β* = 102.825(4)°, *V* = 5337.8(3) Å³, *Z* = 4, *ρ*calcd g/cm³ = 1.191, *μ*(MoKα) = 0.373 mm⁻¹, *T* = 173.05(10), yellow prisms, *F*² refinement, *R*₁(obs) = 0.0598, *wR*₂(all) = 0.1649, 10728 independent observed reflections (*R*¹int = 0.0318), 7543 independent measured reflections ([|*F*₀| > 4σ(|*F*₀|), 2θfull = 56.614], 659 parameters. CSD 2071014.
The X-ray crystal structure of \((3\text{e})_2\)

\(\textbf{Figure S5}:\) The X-ray crystal structure of \((3\text{e})_2\). Hydrogen atoms and included solvent omitted for clarity.

\((3\text{e})_2\) was found to crystallise in the space group P2\(_1\)/c. The unit cell contains two full molecules of \((3\text{e})_2\) and four molecules of benzene, corresponding to half a molecule of \((3\text{e})_2\) and a full benzene molecule in the asymmetric unit. A full molecule of \((3\text{e})_2\) can be generated from the asymmetric unit by \(C_2\) rotation.

The included benzene molecule (C36–C41) was modelled as disordered over two sites in ca. 63:37 ratio for the major and minor components respectively. The thermal parameters of adjacent atoms in the major and minor components were restrained to be similar, their geometries optimized, and only the non-hydrogen atoms in the major orientation were refined anisotropically (those in the minor orientation were refined isotropically).

\textit{Crystal Data for \(\text{C}_{82}\text{H}_{104}\text{Al}_2\text{Co}_2\text{N}_4\text{O}_2, M = 1349.51\), monoclinic, space group P2\(_1\)/c (no. 14),} \(a = 13.1004(2)\) Å, \(b = 24.5243(3)\) Å, \(c = 12.29286(17)\) Å, \(\beta = 111.8523(19)^\circ\), \(V = 3665.66(10)\) Å\(^3\), \(Z = 2\), \(\rho\) (calc) g/cm\(^3\) = 1.223, \(\mu\) (CuK\(\alpha\)) = 4.145 mm\(^{-1}\), \(T = 173.00(14)\), yellow needles, \(F^2\) refinement, \(R_1\) (obs) = 0.0428, \(wR_2\) (all) = 0.1076, 7023 independent observed reflections \((R_{int} = 0.0293)\), 5595 independent measured reflections \([|F_o| > 4\sigma(|F_o|), 2\theta_{\text{full}} = 146.77]\), 426 parameters. CSD 2071015.
The X-ray crystal structure of 3f

3f was found to crystallise in the P-1 space group.

Figure S6: The X-ray crystal structure of 3f. Hydrogen atoms omitted for clarity.

Crystal Data for C_{26}H_{32}Al_{0.5}Cu_{0.5}F_{3}N_{2}, M =474.79, triclinic, space group P-1 (no. 2), a = 11.1165(4) Å, b = 12.5995(5) Å, c = 19.3405(8) Å, α = 88.586(3)°, β = 88.722(3)°, γ = 67.821(4)°, V = 2507.43(18) Å³, Z = 4, ρ_{calc} = 1.258 g/cm³, μ(MoKα) = 0.513 mm⁻¹, T = 173.00(14), orange plates, F² refinement, R₁(obs) = 0.0412, wR₂(all) = 0.1149, 9920 independent observed reflections (R_{int} = 0.0182), 7902 independent measured reflections [[|F_o| > 4σ(|F_o|), 2θ_{full} = 56.536]], 593 parameters. CSD 2071016.
The X-ray crystal structure of 3g

Figure S7: The X-ray crystal structure of 3g. Hydrogen atoms omitted for clarity.

3g was found to crystallise in the P2₁/n space group.

Crystal Data for C₄₆H₅₄AlCl₄CuN₄, M = 895.25, monoclinic, space group P2₁/n (no. 14), a = 11.11938(13) Å, b = 20.2656(2) Å, c = 20.5958(2) Å, β = 96.1813(10)°, V = 4614.09(9) Å³, Z = 4, ρcalc = 1.289 g/cm³, μ(CuKα) = 3.252 mm⁻¹, T = 173.00(14), yellow needles, F² refinement, R₁(obs) = 0.0443, wR²(all) = 0.1177, 8930 independent observed reflections (Rint = 0.0645), 6828 independent measured reflections [|Fo| > 4σ(|Fo|), 2θfull = 147.702], 517 parameters. CSD 2071017.
The X-ray crystal structure of \(3h\)

\(3h\) was found to crystallise in the \(P2_1/n\) space group. Two toluene molecules were found in the asymmetric unit, for a total of eight within the unit cell.

The included toluene molecule (C58–C64) was modelled as disordered over two sites in \(ca.\ 71:29\) ratio for the major and minor components respectively. The thermal parameters of adjacent atoms in the major and minor components were restrained to be similar, their geometries optimized, and only the non-hydrogen atoms in the major orientation were refined anisotropically (those in the minor orientation were refined isotropically).

\textit{Crystal Data for C}_{64}\text{H}_{82}\text{AlCuN}_{4}\text{O}_{4}, M =1061.85,\) monoclinic, space group \(P2_1/n\) (no. 14), \(a = 12.1523(2)\) Å, \(b = 27.1205(6)\) Å, \(c = 17.9897(4)\) Å, \(\beta = 97.1641(19)^\circ\), \(V = 5882.7(2)\) Å³, \(Z = 4, \rho_{\text{calc}}/\text{cm}^3 = 1.199, \mu(\text{CuK}\alpha) = 1.048 \text{ mm}^{-1}, T = 173.0(3), \) yellow needles, F² refinement, \(R_1(\text{obs}) = 0.0573, wR_2(\text{all}) = 0.1284, \) 10285 independent observed reflections \((R_{\text{int}} = 0.0532), \) 6665 independent measured reflections \([|F_o| > 4\sigma(|F_o|), 2\theta_{\text{full}} = 133.186], \) 691 parameters.
4. Density Functional Theory Calculations

4.1 Computational Methods

DFT calculations were run using Gaussian 09 (Revision D.01)\textsuperscript{5} using the M06l Minnesota functional.\textsuperscript{6} Al and Mg centres were described with Stuttgart SDDAll ECP and associated basis sets, and the 6-31G** basis sets were used for all other atoms. M06l has been previously benchmarked against other functionals (ωB97x, B3PW91, M062x) to provide the best agreement with experimental data for closely related systems.\textsuperscript{7,8} Geometry optimisation calculations were performed without symmetry constraints. Frequency analyses for all stationary points were performed using the enhanced criteria to confirm the nature of the structures as either minima (no imaginary frequency) or transition states (only one imaginary frequency). Single point solvent corrections (benzene, $\varepsilon = 2.2706$) were applied using the polarizable continuum model (PCM) to free energies reported in the main text. Single point dispersion corrections were applied to the free energies to the Minnesota functional (M06l) energies using Grimme’s D3 correction.\textsuperscript{9}

ETS-NOCV calculations were performed in the Orca 4.2.1 quantum chemistry software package\textsuperscript{10–12} with optimised geometries attained above. The calculations were run using the M06l Minnesota functional with the def2-tzvpp basis set. Calculations were performed with the resolution of identity approximation for the Coulomb integrals, and chain of spheres approximation for the exchange integrals (RIJCOSX) with the def2/j auxiliary basis set.\textsuperscript{13}

LED calculations were performed in the Orca 4.2.1 quantum chemistry software with optimized geometries attained above.\textsuperscript{14,15} The calculations were performed at the DLPNO-CCSD(T)\textsuperscript{16} level with the def2-tzvpp basis set, def2/jk, and def2-tzvpp/c auxiliary basis sets. TightPNO settings were used for the DLPNO-CCSD(T) calculations. The Foster-Boys method was used to localize orbitals. Calculations were performed with the resolution of identity approximation for the Coulomb integrals, and chain of spheres approximation for the exchange integrals (RIJCOSX) with the def2/j auxiliary basis set. Dispersion interaction density plots were generated as described by Pollice and Chen\textsuperscript{17} and as implemented in Orca 4.2.1. The perturbative triples correction was decomposed to dispersive and non-dispersive components using the scheme recommended by Bistoni and co-workers.\textsuperscript{14}
4.2 ETS-NOCV Deformation Density Plots

|        | $\Delta E_{\text{orb}}$ | $\Delta \rho_1$ | $\Delta \rho_2$ | $\Delta \rho_3$ |
|--------|-------------------------|-----------------|-----------------|-----------------|
| 3a     | -84.4                   | -64.6           | -7.1            | -5.9            |
| 3b     | -93.3                   | -64.2           | -13.0           | -8.5            |

*Table S1: Deformation densities of the first three contributions. Energies in kcal mol$^{-1}$, charge flow from red to blue.*
| \( \Delta E_{\text{orb}} \) | \( \Delta \rho_1 \) | \( \Delta \rho_2 \) | \( \Delta \rho_3 \) |
|-----------------|-----------------|-----------------|-----------------|
| 3c              | –128.1          | –103.0          | –9.7            |
|                 |                 |                 |                 |
| 3d              | –129.7          | –102.1          | –10.9           |

**Table S2:** Deformation densities of the first three contributions. Energies in kcal mol\(^{-1}\), charge flow from red to blue.
| $\Delta E_{\text{orb}}$ | $\Delta \rho_1$ | $\Delta \rho_2$ | $\Delta \rho_3$ |
|------------------------|----------------|----------------|----------------|
| 3e                     | -86.1          | -55.3          | -16.4          |
| [Ni(CO)$_3$]           | -65.5          | -46.1          | -7.2           |
|                        |                |                |                |

Table S3: Deformation densities of the first three contributions. Energies in kcal mol$^{-1}$, charge flow from red to blue.
| $\Delta E_{\text{orb}}$ | $\Delta \rho_1$ | $\Delta \rho_2$ | $\Delta \rho_3$ |
|-----------------|--------------|--------------|--------------|
| $3f$            | -47.5        | -22.5        | -8.0         |
| $3g$            | -43.4        | -21.3        | -7.0         |

Table S4: Deformation densities of the first three contributions. Energies in kcal mol$^{-1}$, charge flow from red to blue.
| $\Delta E_{\text{orb}}$ | $\Delta \rho_1$ | $\Delta \rho_2$ | $\Delta \rho_3$ |
|----------------|----------------|----------------|----------------|
| 3h            | –47.4          | –18.6          | –9.9           | –4.9           |

Table S5: Deformation densities of the first three contributions. Energies in kcal mol$^{-1}$, charge flow from red to blue.
### 4.3 Local energy decomposition calculations

#### 4.3.1 Local energy decomposition components

|        | $\Delta E_{\text{int}}$ | $\Delta E_{\text{int}}^{HF}$ | $E_{\text{el-stat}}^{HF}$ | $E_{\text{exchange}}^{HF}$ | $\Delta E_{\text{el-prep}}^{HF}$ | $\Delta E_{\text{int}}^{C}$ | $E_{\text{CCSD(T)}}^{C-\text{disp}}$ | $\Delta E_{\text{non-disp}}^{C-\text{CCSD(T)}}$ |
|--------|--------------------------|-------------------------------|----------------------------|----------------------------|---------------------------------|-----------------------------|---------------------------------|---------------------------------|
| 3a     | -77.2                    | -27.4                         | -719.4                     | -155.1                    | +847.1                         | -49.7                       | -38.5                           | -11.2                           |
| 3b     | -78.5                    | -5.5                          | -905.4                     | -173.4                    | +1073.3                        | -73.0                       | -42.7                           | -30.3                           |
| 3c     | -95.7                    | -20.0                         | -1056.1                    | -187.8                    | +1224.0                        | -75.6                       | -42.1                           | -33.6                           |
| 3d     | -95.5                    | -12.3                         | -1108.1                    | -197.3                    | +1293.1                        | -83.3                       | -44.8                           | -38.5                           |
| 3e     | -78.6                    | -5.5                          | -855.8                     | -144.9                    | +995.2                         | -73.1                       | -40.5                           | -32.7                           |
| [Ni(CO)$_3$1] | -54.1                    | -18.3                         | -791.7                     | -163.3                    | +936.7                         | -35.8                       | -27.5                           | -8.3                            |
| 3f     | -61.6                    | -8.1                          | -450.6                     | -79.2                     | +521.1                         | -53.5                       | -42.5                           | -11.3                           |
| 3g     | -62.3                    | -8.7                          | -431.7                     | -75.8                     | +499.4                         | -53.6                       | -42.3                           | -11.1                           |
| 3h     | -63.0                    | -0.2                          | -460.3                     | -85.2                     | +545.3                         | -62.8                       | -50.3                           | -12.6                           |

Table S6: Local energy decomposition results. All energies in kcal mol$^{-1}$. 

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4.3.2 Dispersion interaction density plots

Figure S9: Dispersion interaction density plots for complexes explored computationally.
4.4 Comparison of calculated DFT M–M bond lengths to XRD data

| Complex     | XRD      | DFT  |
|-------------|----------|------|
| 3a·THF      | 2.557(2) | 2.46*|
| 3b          | 2.3094(7)| 2.30 |
| 3c          | 2.2762(10)| 2.30 |
| 3d          | 2.2547(9)| 2.25 |
| (3e)₂       | 2.3152(7)| 2.31 |
| 3f          | 2.3021(7)| 2.32 |
| 3g          | 2.3132(7)| 2.34 |
| 3h          | 2.2670(9)| 2.28 |

Table S7: Comparison of DFT calculated Al–M bond lengths to the XRD data. All values in Å. *Compared to the solvent free calculated structure of 3a.
4.5 Computational Coordinates

3a.log

SCF (m06l) = -1895.06560092
E(SCF)+ZPE(0 K) = -1894.381086
H(298 K)= -1894.333229
G(298 K)= -1894.458599
Lowest Frequency = 21.1450 cm⁻¹

C  7.810394  26.072157  4.859070
H  8.088529  26.633322  3.971590
C  6.588566  16.388574  6.222759
H  6.295750  15.667045  6.980060
C  7.120306  18.027509  8.082311
H  7.976327  18.699795  8.280856
C  6.471244  16.056060  4.879731
H  6.095867  15.077646  4.593953
C  7.010363  18.961358  1.817520
H  7.453868  18.080206  1.340121
H  7.152626  19.808383  1.141163
H  5.934517  18.794099  1.913539
C  7.137619  26.714366  5.891185
H  6.899829  27.770981  5.808189
C  9.176334  19.404706  2.979026
H  9.673147  19.810204  3.864925
H  9.392733  20.082498  2.146790
H  9.636544  18.437838  2.744390
C  5.868808  18.819051  8.460205
H  5.750575  19.704111  7.826596
H  5.906525  19.155851  9.501197
H  4.965569  18.214253  8.326387
C  7.704707  23.712940  9.404612
H  8.554661  23.143144  9.017486
H  7.337218  23.190307  10.293396
H  8.074545  24.694138  9.724362
C  7.312445  16.842542  9.020987
H  6.429238  16.195926  9.045092
H  7.476746  17.192396  10.044079
H  8.168697  16.223721  8.733050
C  9.674274  24.911628  2.926121
H  10.233936  24.322017  2.194511
H  10.393527  25.480026  3.524650
H  9.071716  25.630130  2.360922
C  5.340731  24.453078  9.021985
H  5.556832  25.402132  9.524913
H  4.949571  23.765330  9.775421
H  4.548017  24.630676  8.289079
C  4.236389  19.630534  5.398214
O  4.636055  24.535149  4.967432

3b.log

SCF (m06l) = -1805.23965386
E(SCF)+ZPE(0 K) = -1804.468435
H(298 K)= -1804.421230
G(298 K)= -1804.454513
Lowest Frequency = 19.2388 cm⁻¹

H(298 K)=
E(SCF)+ZPE(0 K)=
SCF (m06l)=

Mn  1.209133  15.667263  4.754936
Al  2.451264  15.443200  6.673364
O  0.270485  12.893901  4.908336
N  3.279600  16.718973  7.886633
N  3.114642  13.926540  7.680145
| Atom  | X     | Y     | Z     |
|-------|-------|-------|-------|
| O     | 0.712301 | 13.985216 | 4.882943 |
| C     | 5.992075 | 19.576413 | 6.414477 |
| H     | 5.756072 | 20.537050 | 5.940120 |
| H     | 6.907206 | 19.198684 | 5.949054 |
| H     | 6.208300 | 19.777752 | 7.469341 |
| C     | -0.218126 | 16.414441 | 3.383351 |
| C     | -0.499224 | 15.899511 | 2.474145 |
| H     | -0.679365 | 17.859128 | 9.283122 |
| C     | -0.776321 | 18.703011 | 9.975462 |
| H     | -1.258137 | 17.032227 | 9.704951 |
| C     | -1.150196 | 18.150970 | 8.339658 |
| H     | 3.982900 | 11.879096 | 3.994240 |
| C     | 4.243680 | 10.816608 | 3.927891 |
| H     | 4.665745 | 12.473797 | 3.340691 |
| C     | 2.970183 | 12.006660 | 3.600876 |
| C     | -2.035760 | 15.404602 | 4.956519 |
| C     | -2.051580 | 14.502624 | 4.339840 |
| C     | -2.966245 | 15.952805 | 4.769304 |
| C     | -2.043871 | 15.088275 | 6.004015 |
| C     | -0.404619 | 13.891561 | 8.575539 |
| C     | -0.095377 | 14.468540 | 7.693429 |
| C     | -0.865221 | 14.580344 | 9.294138 |
| H     | -1.173222 | 13.186547 | 8.238323 |
| C     | 5.487416 | 12.118497 | 5.988750 |
| C     | 6.565872 | 12.622393 | 6.945561 |
| C     | 6.262123 | 12.462625 | 5.296252 |
| C     | 5.633605 | 11.043044 | 6.145202 |
| C     | 2.682992 | 15.277901 | 3.872294 |
| C     | 0.328597 | 12.407703 | 10.466562 |
| H     | -0.503331 | 11.724092 | 10.267775 |
| H     | -0.018369 | 13.120340 | 11.221568 |
| C     | 1.139940 | 11.816858 | 10.906165 |

### 3c.log

SCF (m06L) = -1818.65433413
E(SCF)+ZPE(0 K) = -1817.978399
H(298 K) = -1817.932552
G(298 K) = -1818.054653
Lowest Frequency = 25.7566cm-1

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Fe   | 5.456569 | 4.136094 | 8.363229 |
| Al   | 7.611042 | 4.142815 | 9.169596 |
| N    | 8.857154 | 2.738054 | 9.507364 |
| O    | 2.754364 | 4.023287 | 7.216408 |
| C    | 10.765560 | 4.166771 | 9.867469 |
| C    | 11.831291 | 4.176022 | 10.063931 |
| O    | 6.789995 | 4.179699 | 5.743547 |
| C    | 8.329531 | 1.395858 | 9.582555 |
| C    | 8.111853 | 0.832048 | 10.855918 |
| C    | 5.255630 | 2.623050 | 9.277060 |
| C    | 10.170596 | 2.907221 | 9.746130 |
| C    | 11.047315 | 1.706854 | 9.944079 |
| H    | 10.889560 | 1.271509 | 10.937100 |
3d.log

SCF (m06l) = -2752.45161086
E(SCF)+ZPE(0K) = -2751.296646
H(298K) = -2751.237293
G(298K) = -2751.391803
Lowest Frequency = 12.8830cm-1

Fe  2.171956  9.093484  6.063447
P  0.395919  7.836637  6.523847
Al  3.825596 10.626545  5.799107
O  0.379157 11.414931  6.208732
N  4.558165 11.530154  4.278052
N  4.908104 11.597049  7.064614
C  5.483161 12.505269  4.296519
C  5.783244 10.269724  8.933876
C  2.830838 11.479612  2.542420
C  5.762709 12.592993  6.786477
C  6.526805 13.263342  7.892394
C  5.961458 13.288380  8.825805
H  6.799552 14.281074  7.607139
H  7.456575 12.727226  8.102796
C  4.092513 11.051859  3.000232
C  4.876299 10.135642  2.277690
C  4.385868  9.679943  1.052519
H  4.969533  8.963369  0.478811
H  6.012577 13.028680  5.479893
H  6.727217 13.836633  5.371444
C  4.788465 11.121826  8.418609
C  3.628549 11.449288  9.147625
C  1.991783 12.457287  3.344286
H  2.132507 12.220401  4.408784
C  6.174201  9.576298  2.830026
H  6.535604 10.246845  3.621822
C  7.000593  9.882720  8.111578
H  7.233239 10.710371  7.430862
C  5.586965  9.739944 10.210344
H  6.333190  9.070988  10.629949
\[ E_{\text{SCF}} + ZPE(0 K) = \]
| Atom | X    | Y    | Z    |
|------|------|------|------|
| Co   | 2.726668 | 1.197846 | 7.936191 |
| Al   | 4.416966  | 0.649727  | 3.665669  |
| O    | 3.772801  | 1.330149  | 5.265916  |
| N    | 2.803026  | 0.595268  | 2.584461  |
| N    | 5.073118  | 2.325684  | 2.963144  |
| C    | 4.919929  | 2.534391  | 1.647763  |
| C    | 1.750190  | 0.642367  | 9.711193  |
| H    | 1.639771  | -0.365724 | 10.093828 |
| C    | 5.761572  | 3.330118  | 3.733003  |
| C    | 2.837759  | 1.524951  | 10.008684 |
| H    | 3.683871  | 1.827524  | 10.642866 |
| C    | 0.505438  | 0.794025  | 3.426974  |
| C    | 3.996802  | 1.180135  | 0.868649  |
| H    | 4.009738  | 2.031900  | -0.194020 |
| C    | 1.546689  | -0.024882 | 2.940982  |
| C    | 5.724853  | 5.481405  | 4.822845  |
| H    | 5.175212  | 6.370777  | 5.133320  |
| C    | 2.457583  | -2.370342 | 2.434622  |
| C    | 3.384431  | -1.797384 | 2.342090  |
| C    | -0.775624 | 0.246948  | 3.508115  |
| H    | -1.593706 | 0.875740  | 3.871844  |
| C    | 2.610393  | 2.747078  | 9.323930  |
| H    | 3.263407  | 3.610438  | 9.320470  |
| C    | 0.747242  | 2.230751  | 3.845913  |
| H    | 1.809080  | 2.314879  | 4.104744  |
| C    | 5.741421  | 3.588702  | 0.967486  |
| H    | 5.505653  | 4.586701  | 1.349955  |
| H    | 5.580120  | 3.584054  | -0.110923 |
| H    | 6.806655  | 3.435629  | 1.172620  |
| C    | 2.923472  | 1.024640  | 1.317757  |
| C    | 9.089589  | 2.251669  | 2.779959  |
| H    | 9.815665  | 2.926188  | 3.248589  |
| H    | 8.763569  | 2.722461  | 1.845942  |
| H    | 9.621350  | 1.330518  | 2.517259  |
| C    | 3.303996  | 1.229075  | 6.412172  |
| C    | 7.919484  | 1.951448  | 3.714611  |
| H    | 7.248000  | 1.250932  | 3.212250  |
| C    | 3.556443  | 4.638192  | 3.901079  |
| C    | 3.816490  | 3.726069  | 4.320247  |
| C    | 0.845345  | 1.322050  | 8.851510  |
| H    | -0.070949 | 0.920417  | 8.438162  |
| C    | 5.041846  | 4.470530  | 4.147327  |
| H    | -1.021713 | -1.084327 | 3.222292  |
| C    | -2.028190 | -1.487065 | 3.300353  |
| C    | 2.635648  | -3.322115 | 3.618244  |
| H    | 2.803662  | -2.777852 | 4.554730  |
| C    | 3.496493  | -3.983672 | 3.467847  |
| H    | 1.749149  | -3.951354 | 3.759398  |
| C    | 0.038905  | -1.906528 | 2.875868  |
| H    | -0.129453 | -2.968888 | 2.708285  |
| C    | 1.335503  | -1.402962 | 2.735382  |

G(298 K) = -3386.838458
Lowest Frequency = 22.285 cm⁻¹
H 3.740163 -4.998373 11.159079
H 2.302768 -4.211113 10.469316
C 6.189037 -2.022436 10.324968
C 1.820223 -1.298221 10.919064
H 0.991614 -1.909977 11.286530
H 2.748170 -1.856783 11.052062
H 1.881536 -0.406580 11.544361
C 1.575336 -0.891575 9.455347
H 2.473854 -0.354755 9.101302
C 3.487406 -4.832293 6.818387
H 4.303318 -4.707875 7.540799
C 2.310892 -3.992708 7.278591
C 8.449042 2.306261 9.242564
H 9.055785 3.207167 9.223034
C 4.089517 2.350114 9.360480
H 4.093283 2.090864 8.295218
H 3.048564 2.375160 9.703848
C 4.495094 3.361795 9.471266
C 7.126271 2.367707 9.655146
H 6.698288 3.319987 9.961903
C 6.325463 1.223056 9.685384
C 3.996216 -4.320721 5.468625
H 4.304784 -3.269334 5.525713
H 4.852107 -4.910282 5.123953
H 3.209789 -4.392730 4.707470
C 0.420966 0.104119 9.416300
H 0.680548 0.997395 9.991684
H 0.168065 0.422625 8.400869
C -0.485841 -0.315428 9.867094
C 8.568754 -1.523806 6.834605
H 8.420559 -0.693942 6.283849
C 8.991322 -2.461785 6.458736
H 7.498757 -1.511699 6.597414
C 7.226727 -1.776181 11.385019
H 7.129100 -0.764881 11.792238
H 7.136150 -2.495258 12.199671
H 8.240642 -1.838103 10.977558
C -0.029514 -3.399519 7.052905
H -1.004680 -3.580797 6.609988
C 1.386507 -2.078216 8.521456
C 10.306355 -1.538398 8.648519
H 10.523851 -1.376904 9.709619
H 10.646757 -2.543590 8.382724
H 10.918846 -0.834857 8.075088
C 3.160006 -6.321268 6.746687
H 2.430417 -6.539801 5.959867
H 4.059469 -6.900072 6.516860
H 2.747200 -6.698758 7.688541
C 4.830841 1.650363 11.669382
C 3.801959 1.726397 12.010942
C 5.533591 0.879676 12.262303
C 5.533028 2.605182 11.880669
C 0.144459 -2.342120 7.938481
H -0.701880 -1.703617 8.171432

SCF (m06l) = -3037.46377478
E(SCF)+ZPE(0 K) = -3036.405027
H(298 K) = -3036.336480
G(298 K) = -3036.650541

Lowest Frequency = 33.9481 cm⁻¹
| Element | U (m06l) | E(SCF) | ZPE(DM) |
|---------|----------|--------|---------|
| C       | 2.207453 | 1.525745 | 5.766883 |
| C       | 2.876850 | 1.815171 | 2.031685 |
| H       | 3.930057 | 2.126048 | 2.091020 |
| H       | 2.399095 | 2.438963 | 1.275568 |
| H       | 2.881922 | 0.781598 | 1.674764 |
| C       | 8.715747 | 3.835324 | 9.248819 |
| H       | 8.817121 | 4.921806 | 9.345957 |
| C       | 9.127737 | 3.416291 | 9.082294 |
| H       | 8.365327 | 3.454868 | 10.21417 |
| C       | 4.390611 | 6.174037 | 2.195159 |
| H       | 4.989034 | 6.266171 | 3.110550 |
| C       | 9.210610 | 0.204996 | 4.138806 |
| H       | 10.210814 | 0.644002 | 4.083851 |
| H       | 6.396987 | 0.273676 | 6.904579 |
| C       | 2.876850 | 1.815171 | 2.031685 |
| C       | 2.876850 | 1.815171 | 2.031685 |
| C       | 2.876850 | 1.815171 | 2.031685 |
| C       | 2.876850 | 1.815171 | 2.031685 |

3g.log

SCF (m06l) = -2263.74373791
E(SCF)+ZPE(0 K) = -2262.844953
H(298 K) = -2262.783644
G(298 K) = -2262.941605
Lowest Frequency = 8.0103 cm⁻¹

Cu: -1.391690 18.098680 6.597840
Al: 0.595983 16.862405 6.473327
Cl: -3.101649 18.017138 10.648862
Cl: -3.399944 15.337223 5.816812
Cl: -2.242396 18.806133 3.079603
Cl: -0.161343 22.101983 6.978539
N: -1.958506 19.883560 5.870491
N: 1.619658 15.947293 7.855387
N: -3.124844 17.776844 7.584400
N: 1.907164 16.391931 5.112340
C: 2.853314 15.433573 7.758752
C: -3.159281 20.428147 6.081920
C: -3.437414 15.346229 7.629524
C: 3.036767 15.680545 5.275649
C: 3.447773 18.681793 4.302083
C: 3.946526 17.893700 4.879645
SCF (m06l) = -2664.24375395
E(SCF) + ZPE(0K) = -2663.175678
H(298 K) = -2663.109943
G(298 K) = -2663.272354
Lowest Frequency = 17.0283 cm⁻¹

Cu  4.688885  17.378493  14.643531
Al  6.955952  17.445060  14.900821
N  8.484805  18.158483  13.944445
N  8.078461  16.206934  15.915305
N  3.456865  16.237407  13.583954
|  | X  | Y  | Z     |
|---|----|----|-------|
| H | 6.962162 | 13.482927 | 11.843511 |
| C | 6.697371  | 12.660366  | 15.554261 |
| H | 7.789136  | 12.698294  | 15.459608 |
| H | 6.293657  | 12.262911  | 14.616712 |
| H | 6.462010  | 11.941166  | 16.347630 |
| C | 7.617775  | 18.759849  | 18.446361 |
| H | 6.908490  | 18.724749  | 17.606117 |
| H | 8.083394  | 19.751456  | 18.448229 |
| H | 7.019751  | 18.667189  | 19.360714 |
| C | 10.547470 | 20.122496  | 15.749681 |
| H | 10.813843 | 19.156592  | 15.311309 |
| H | 10.798977 | 20.075625  | 16.815316 |
| H | 11.182171 | 20.890582  | 15.292297 |
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