Electronic Supplementary Information for Dalton Transactions


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***Electronic Supplementary Information* for:**

# *The Synthesis of a Dichloroalane Complex and its Reaction with an α-Diimine.*

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## Experimental

The NHC IMes was prepared using a literature procedure.[1] Diethyl ether, THF and hexane were dried over sodium and freshly distilled from sodium diphenylketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. $^1$H NMR spectra were recorded at 300.13 MHz using a Varian 2000 spectrometer with chemical shifts referenced to the residual $^1$H resonances of the *deutero*-benzene solvent ($\delta$ 7.16 ppm). Melting points were determined in sealed glass capillaries under argon and are uncorrected. All microanalyses (**1** and **4**) were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand. The single crystal X-ray data collection for **4** was undertaken at Monash Univeristy. Further details are listed in a separate section below.

## $[AlCl_2H(NMe_3)_2]$, 2

A slurry of trimethylamine hydrochloride (0.18 g, 1.88 mmol) in diethyl ether (50 $cm^3$) was added to a solution of $[AlH_3(NMe_3)]$ (0.17 g, 1.91 mmol) in diethyl ether (50 $cm^3$) at -78 °C. The resulting effervescent solution was gradually warmed to room temperature over a period of 3 hours. A further equivalent of trimethylamine hydrochloride was added to the solution in the same manner (-78 °C to RT) and the solvent removed by distillation. The product was collected by sublimation (40 °C at 1.0 x $10^{-4}$ bar) to afford a white crystalline solid (0.37 g, 91%), m.p. 105-107 °C, dec. 154 °C; $^1H$ NMR ($C_6D_6$): δ 2.11 (s, 18H; $NCH_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ 46.1 ($NCH_3$); IR (Nujol), $cm^{-1}$: 1802 br s (Al-H stretch). A microanalysis of **2** could not be undertaken due to its significant air- and moisture sensitivity as-well-as pyrophoric nature. The latter precluded transport.

## X-Ray Structure Determination

A crystalline sample of **4** was mounted on a glass fibre in silicone oil at – 150(2) °C (123 (2) K). A summary of crystallographic data can be found in Table 1. Hydrogen atoms were refined in calculated positions (Riding model). Data were collected using graphite monochromated $Mo_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) on an Enraf-Nonius Kappa CCD diffractometer, and were corrected for absorption using SADABS.[2] Quality of data is poor as reflected by high R-factor of 9.61%. A significant void space (49 $Å^3$) is present in the crystal lattice, however there is no evidence of solvent inclusion (no unassigned peaks of electron density) and spectroscopic data for **4** is inconsistent with solvation. Structural solution and refinement was carried out using the SHELX suite of programs[3] with the graphical interface X-seed.[4]

Crystallographic data (excluding structure factors) **4** has been deposited with the Cambridge Crystallographic Data Centre as supplementary number 693606.

**TABLE 1:** Summary of crystallographic data for compound **4**.

| | [$AlCl_2${MesNC(=IMes)C(H)NMes}] (**4**) |
|---|---|
| Mol. Formula | $C_{41}H_{47}AlCl_2N_4$ |
| Mol. Weight | 693.71 |
| Temperature (K) | 123(2) |
| Space Group | $P2_1/n$ |
| a, Å | 10.0810(2) |
| b, Å | 18.3266(4) |
| c, Å | 21.1938(4) |
| α, deg | 90 |
| β, deg | 91.942(1) |
| γ, deg | 90 |
| Volume, Å$^3$ | 3913.32(14) |
| Z | 4 |
| $D_c$, g cm$^{-3}$ | 1.177 |
| μ, mm$^{-1}$ | 0.221 |
| reflections collected | 47016 |
| unique reflections | 9591 |
| parameters varied | 445 |
| R(int) | 0.1163 |
| $R_1$ | 0.0961 |
| $wR_2$ | 0.2571 |

**TABLE 2:** Selected bond lengths (Å) and angles (°) for compounds **4** and **5**:

| | (**4**) | $[(AlCl_2)_2\{2,6\text{-}^iPr_2C_6H_3N{=}C(H)\text{-}C(=NC_6H_3\text{-}2,6\text{-}^iPr_2)\}_2]$ (**5**)[5] |
|---|---|---|
| Al(1)-C(1)/N(1) | 1.846(3) | 1.824(4) |
| Al(1)-N(2) | 1.856(3) | 1.953(4) |
| Al(1)-Cl(1) | 2.1346(15) | 2.115(2) |
| Al(1)-Cl(2) | 2.1524(15) | 2.100(2) |
| C(1)-N(1) | 1.424(5) | 1.462(6) |
| C(2)-N(2) | 1.365(4) | 1.286(6) |
| C(1)-C(2) | 1.364(5) | 1.498(7) |
| C(1)-C(21) | 1.454(5) | 1.585(9) ($sp^3$-$sp^3$) |
| C(3) oop [N(1),C(1),C(2),C(21)] | 0.823(5) | unavailable |
| Sum of angles about N(1) | 349.7(7) | 355.2(5) |
| C(1),N(1),C(2):C(21),N(3),N(4) | 34.5(2) | unavailable |
| N(1)-C(1)-C(2) | 115.1(3) | 109.0(4) |
| N(1)-C(1)-C(21) | 122.6(3) | 113.6(5) |
| C(2)-C(1)-C(21) | 120.9(3) | 107.0(5) |
| C(2)-N(2)-C(12) | 118.4(3) | 118.8(4) |
| N(3)-C(21)-N(4) | 105.8(3) | not applicable |

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