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SUPPLEMENTARY MATERIAL

Formation of an Unusual *Bis*(diguanidinate) Ligand *via* Nucleophilic Attack of a Guanidinate onto a Carbodiimide

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General Experimental Details of NMR Spectroscopic Studies

NMR spectra were obtained in deuterated NMR solvents (d_6-benzene, d_8-toluene) which had been dried over a sodium mirror. A Bruker 500 MHz TCI Cryoprobe Spectrometer was used and all spectra were recorded at +25°C. The frequencies of the nuclei and external reference standards are as follows: ^{1}H – 500.20 MHz, (Me_4Si, $CDCl_3$, 1%), ^{71}Ga NMR – 152.54 MHz, ($Ga(H_2O)_6^{3+}$,D_2O), ^{13}C NMR - 125.79 MHz, (Me_4Si, $CDCl_3$, 1%).

1. Synthesis and analytical data for compound 1 [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}Li·Et$_2$O]

^{n}BuLi (2.334 ml, 3.75 mmol) was added dropwise to a solution of diisopropylamine (0.523 ml, 3.75 mmol) in ether (15 ml) at -78°C and the resulting solution was stirred for 30 minutes. N,N'-diisopropylcarbodiimide (0.6 ml, 3.75 mmol) in ether (10 ml) was then added dropwise at -78°C, the solution was warmed to room temperature and stirred overnight. The solvent volume was reduced *in vacuo* until a precipitate formed, which was heated back into solution. Storage of the resulting solution at -20°C for 24 hours afforded colourless blocks of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}Li·Et$_2$O] (314 mg, 0.51 mmol, 27%).

NMR:

^{1}H NMR (500.1 MHz, δ /ppm, d$_6$-benzene, +25 ^{o}C): 3.73 (septet, 2H), 3.54 (septet, 2H), 3.48 (septet, 2H), 3.30 (q., ether), 3.07 (septet, 2H), 1.35 (d., 12H), 1.27 (d., 12H), 1.14 (t., ether), 1.04 (d., 12H), 0.95 (d., 12H).

^{13}C NMR (125.8 MHz, δ /ppm, d$_6$-benzene, +25 ^{o}C): 128.2, 127.8, 65.9 (ether), 47.8, 47.2, 46.0, 45.5, 23.7, 22.8, 22.1, 21.6, 15.5 (ether).

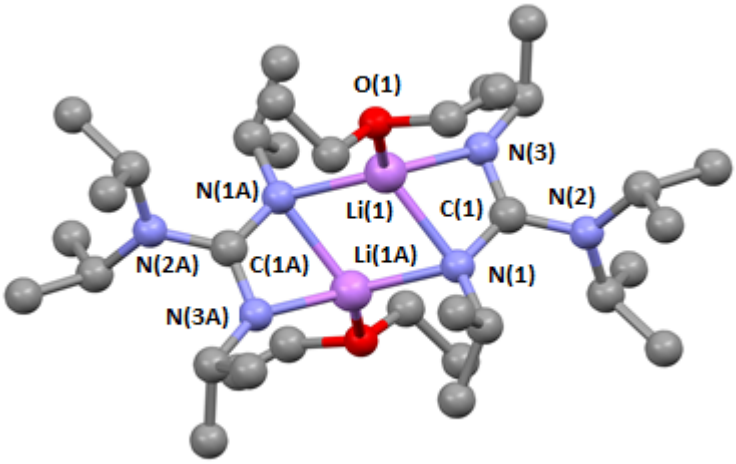

Figure 1.1 Crystal structure of compound **1** [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}Li·Et$_2$O]. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Li-N 2.017(3)-2.182(4), Li-O 1.986(3), N-C(ring) 1.347(2)-1.433(2), N-C(^{i}Pr) 1.463(2)-1.470(2), N(1)-Li-N(3) 65.4(1), N(1)-Li-N(1A) 108.2(1), Li-N-Li 71.8(1), N-C-N 117.1(1)-122.1(1), Li-N-C(ring) 90.6(1), Li-N-C(^{i}Pr) 148.7(1), C(ring)-N-C(^{i}Pr) 117.0(1)-120.7(1).

Crystal data:

$C_{34}H_{76}Li_2N_6O_2$, M = 614.89, *monoclinic*, space group $P21/n$, Z = 2, a = 9.8005(2), b = 19.6311(5), c = 10.9117(4) Å, α = 90.00, β = 103.947(2), γ = 90.00°, V = 2037.5(1) Å^3, μ(Mo–Kα) = 0.061 mm^{-1}, ρ_{calc} = 1.002 Mg m^{-3}, T = 180(2) K. Total reflections 13390, unique 4585 (R_{int} = 0.085). $R1$ = 0.056 [$I>2\sigma(I)$] and $wR2$ = 0.158 (all data). H-atoms were not located and were fixed geometrically.

2. NMR spectra for compound 1

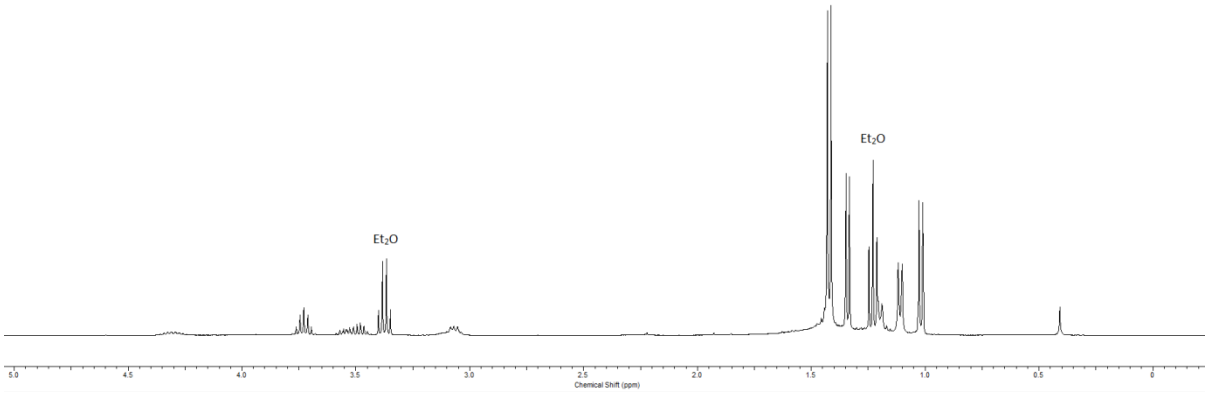

Figure 1.2 ^{1}H NMR Spectrum of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}Li·Et$_2$O] (**1**) in d$_6$-benzene.

Note: the above proton NMR spectrum was taken on a 400.14 MHz spectrometer.

3. NMR spectra for compound 2

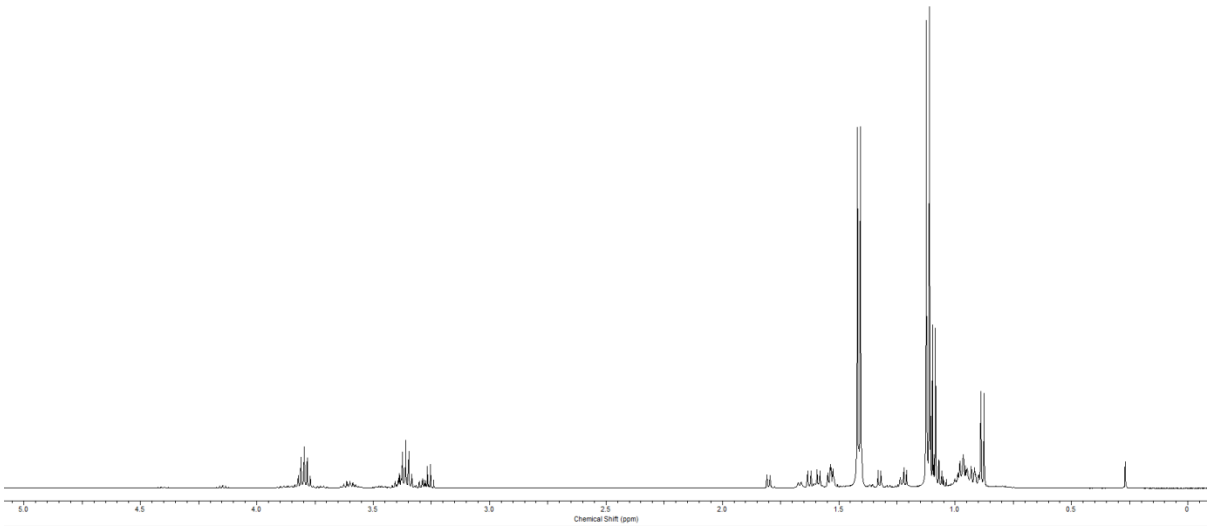

Figure 1.3 ^{1}H NMR Spectrum of [{^{i}Pr$_2$NC(=N^{i}Pr)$_2$}GaCl$_2$] (**2**) in d$_6$-benzene. Peaks for both the carbodiimide ^{i}PrN=C=N^{i}Pr and the *bis*(diguanidinate) complex [^{i}PrN{C(N^{i}Pr)=N^{i}Pr}{C(=N^{i}Pr)N^{i}Pr$_2$}GaCl$_2$] (**4**) can be seen along with the expected doublets and septets for **2**.

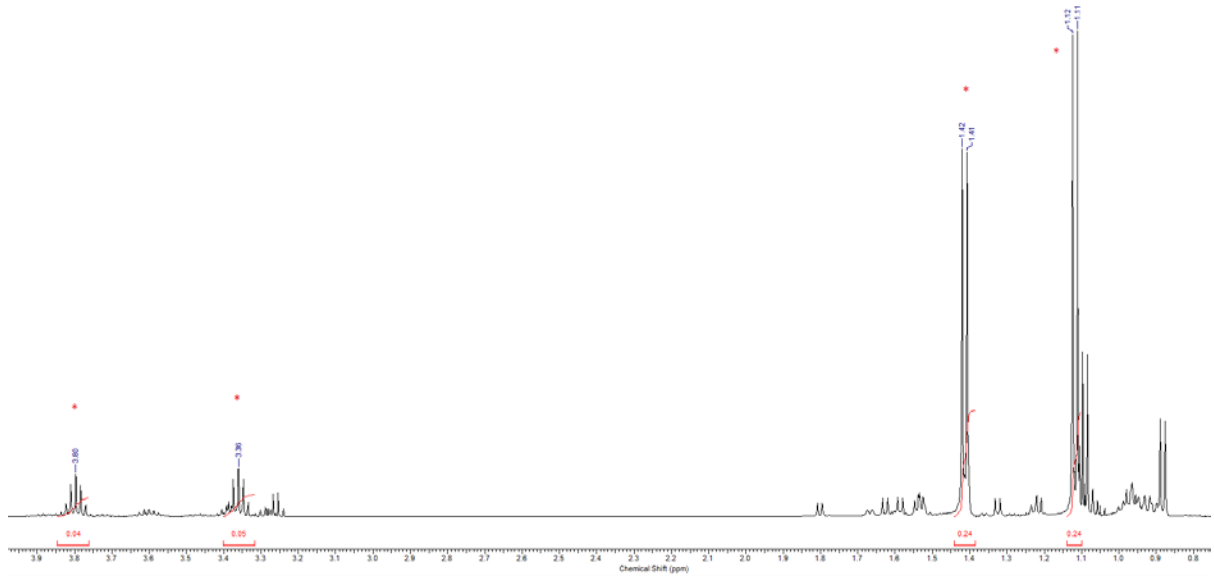

Figure 1.4 Zoomed-in ^{1}H NMR Spectrum of **2** showing integration of septets to doublets.

The major peaks corresponding to compound **2** are septets at δ = 3.80 and 3.36 ppm and doublets at δ = 1.42 and 1.12 ppm (indicated * on the above spectrum). The integration of these peaks shows a

ratio of 1 : 6, as expected (the septet at δ = 3.36 ppm is difficult to integrate as there is a minor overlapping septet at δ = 3.37 ppm corresponding to compound **4**).

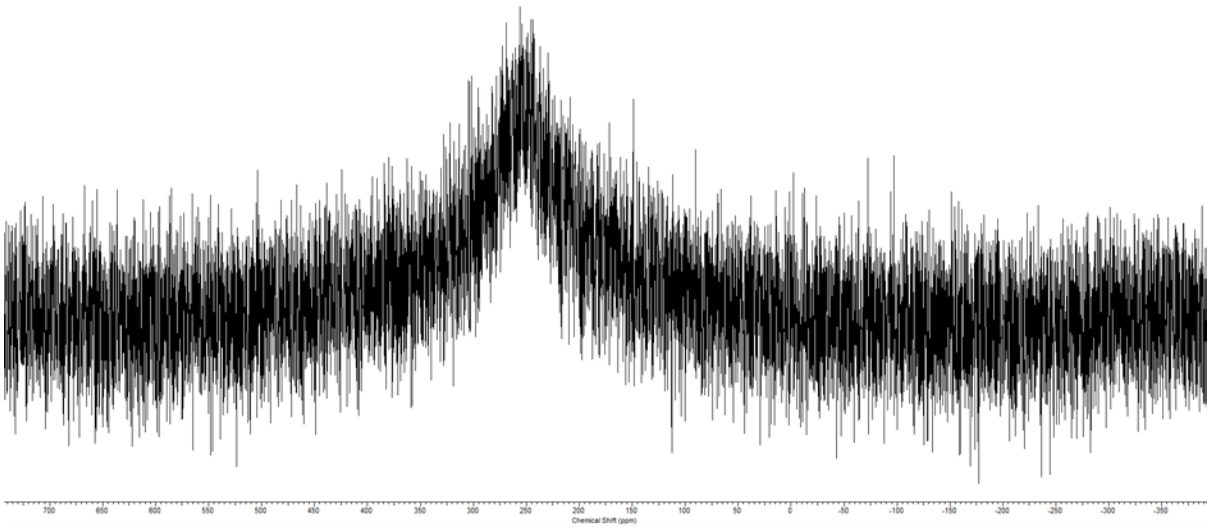

Figure 1.5 ^{71}Ga NMR Spectrum of [{^{i}Pr$_2$NC(=N^{i}Pr)$_2$}GaCl$_2$] (**2**) in d$_6$-benzene.

4. NMR spectra for compound 3

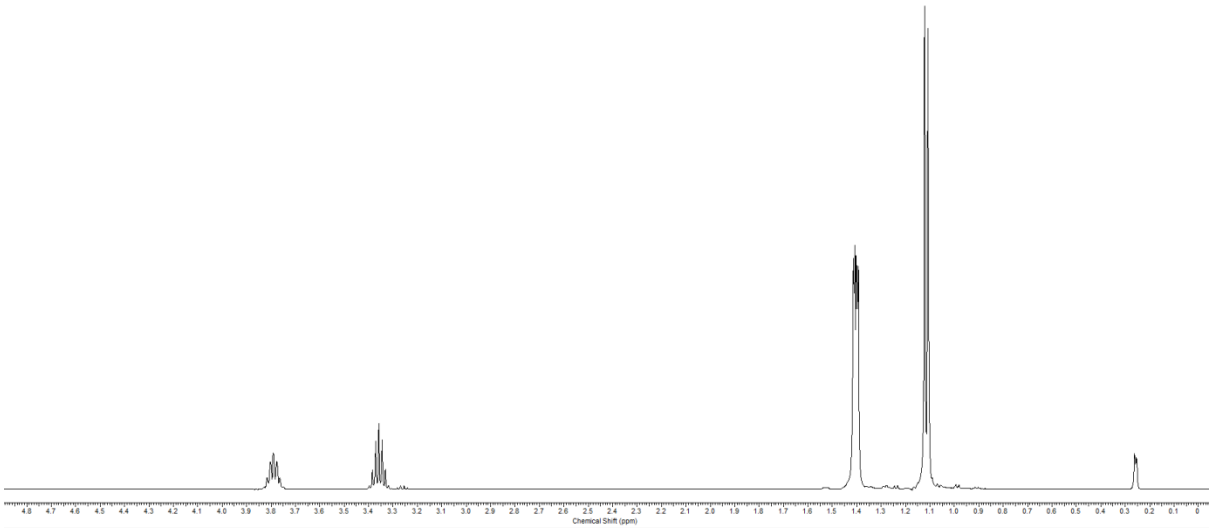

Figure 1.6 ^{1}H NMR Spectrum of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}$_2$GaCl] (**3**) in d$_6$-benzene.

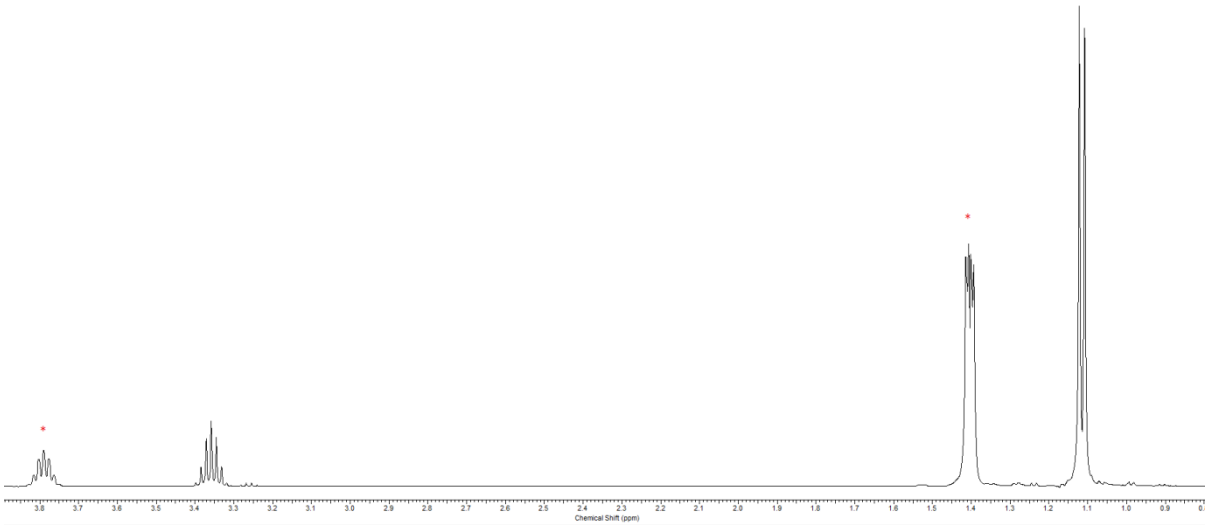

Figure 1.7 Slightly zoomed-in version of the ^{1}H NMR Spectrum of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}$_2$GaCl] (**3**) in d$_6$-benzene. It can be seen that the doublet at δ = 1.41 ppm is actually split into two doublets and the septet at δ = 3.79 ppm has broad peaks indicating that it may also actually be two septets (peaks in question are marked *). This is consistent with the solid-state structures of **3** which shows that the ^{i}Pr$_2$N groups are approximately perpendicular to the CN$_3$ ligand plane and are therefore inequivalent.

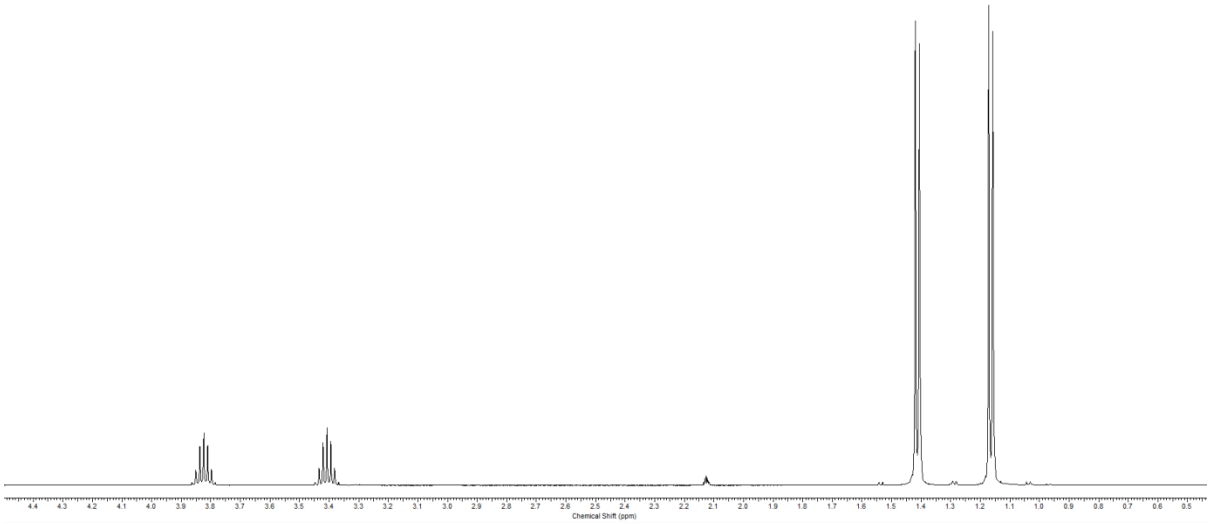

Figure 1.8 ^{1}H NMR Spectrum of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}$_2$GaCl] (**3**) in d$_8$-toluene at +40°C. It can be seen that at high temperature the septet at δ = 3.79 ppm is much sharper and also that there is only one doublet at δ = 1.41 ppm, rather than the two that appear at room temperature.

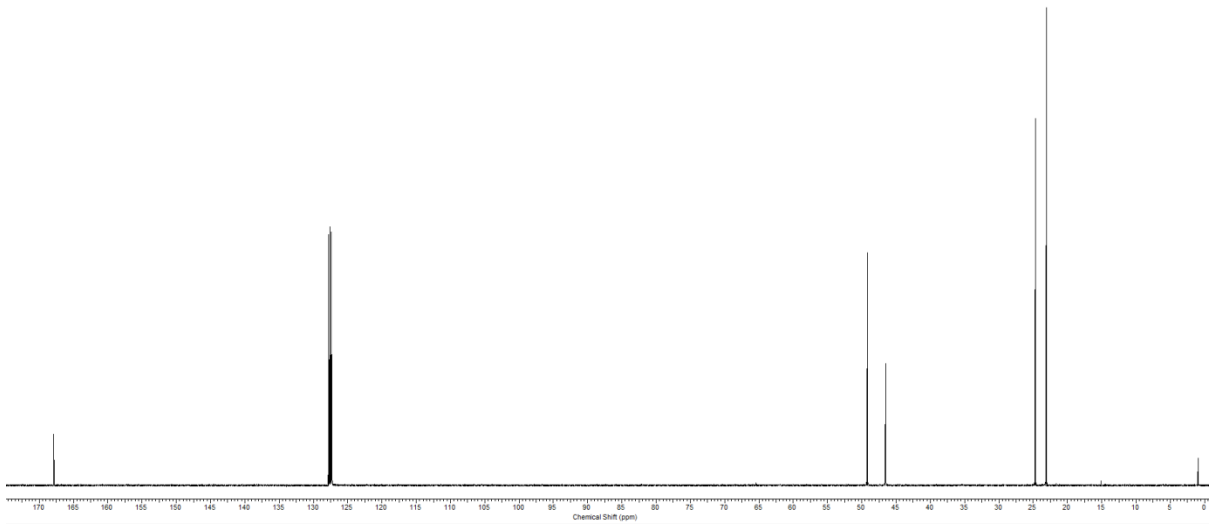

Figure 1.9 ^{13}C NMR Spectrum of [{^{i}Pr$_2$NC(N^{i}Pr)$_2$}$_2$GaCl] (**3**) in d$_6$-benzene.

5. NMR spectra for compound 4

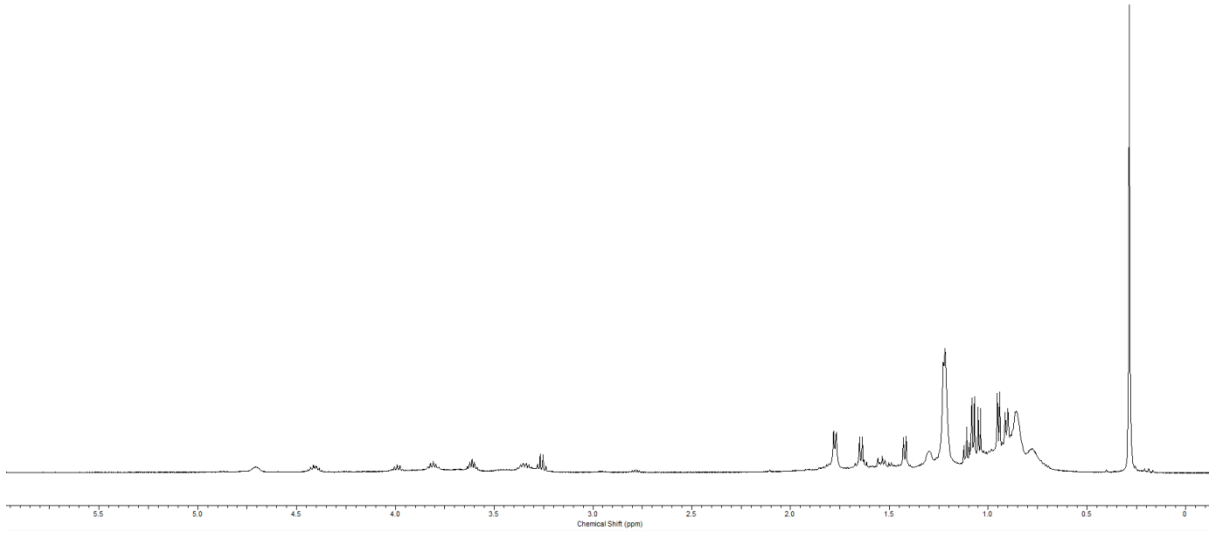

Figure 1.10 ^{1}H NMR Spectrum of [^{i}PrN{C(N^{i}Pr)=N^{i}Pr}{C(=N^{i}Pr)N^{i}Pr$_2$}GaCl$_2$] (**4**) in d$_6$-benzene. Present in the spectrum are peaks for both compounds **2** and **4**, as well as peaks for the carbodiimide, ^{i}PrN=C=N^{i}Pr.

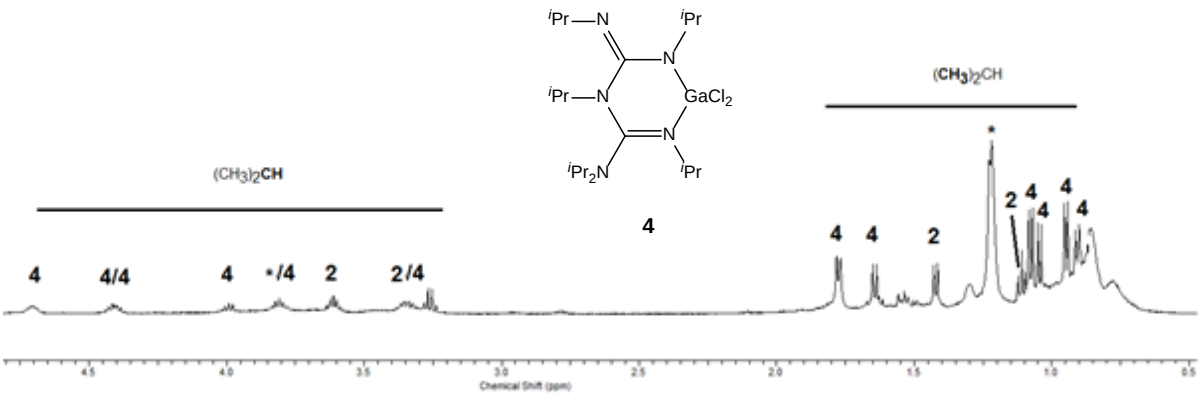

Figure 1.11 ^{1}H NMR Spectrum of [^{i}PrN{C(N^{i}Pr)=N^{i}Pr}{C(=N^{i}Pr)N^{i}Pr$_2$}GaCl$_2$] (**4**) in d$_6$-benzene with the peaks labelled to indicate which compound each shift is due to. Peaks marked * are those for the carbodiimide.

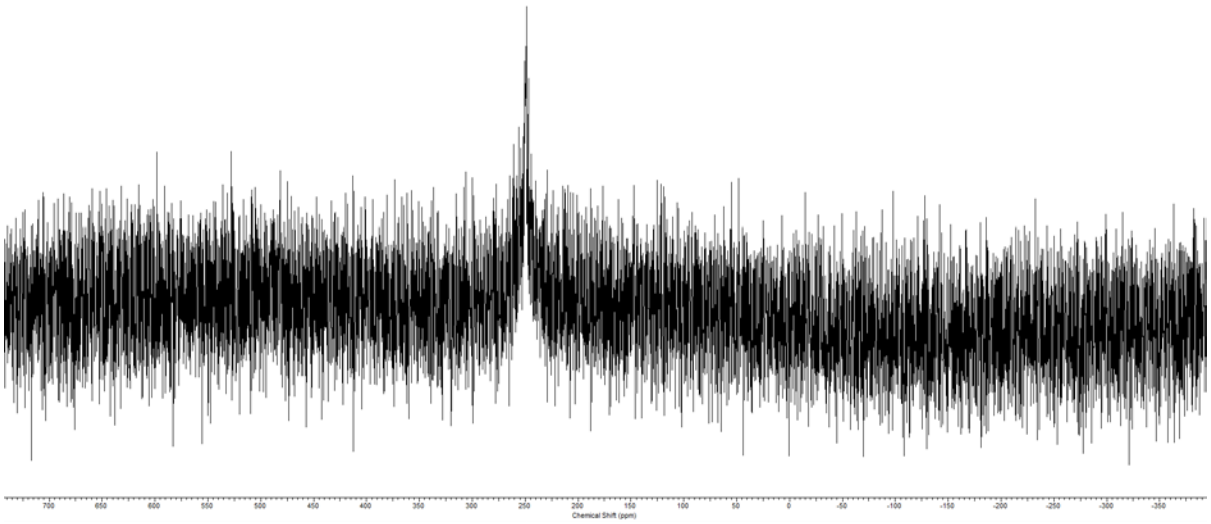

Figure 1.12 ^{71}Ga NMR Spectrum of [^{i}PrN{C(N^{i}Pr)=N^{i}Pr}{C(=N^{i}Pr)N^{i}Pr$_2$}GaCl$_2$] (**4**) in d$_6$-benzene.