Electron Paramagnetic Resonance Study of the Mononuclear Al Species Formed in the Reaction of Al Atoms and Cyclopropylamine at 77 K in an Adamantane Matrix

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Ground-state Al atoms have been reacted with cyclopropylamine ($CpNH_2$) in an adamantane matrix at 77 K. The four paramagnetic species generated in the reaction have been studied by electron paramagnetic resonance (EPR) spectroscopy and their magnetic parameters extracted from the EPR spectra. The isotropic Al hyperfine interactions (hfis) for these radicals vary from 801 to 962 MHz and are consistent with values previously reported for structurally similar Al-centered radicals. The major species formed in the reaction has a highly anisotropic *a* tensor indicative of an Al-centered radical with a substantial amount of the unpaired spin density residing in the Al 3p orbital. In addition, there is EPR evidence that the insertion products, CpNH(AlH) and $CpAlNH_2$, are formed in the reaction, suggesting that Al atoms can activate the N−H and C−N bonds of amines. It has been shown that a molecule of $CpNH_2$ coordinates to CpNH(AlH), causing the Al, N and H hfi of the N−H insertion product to decrease. The values of the nuclear hfis calculated for the insertion products, using a density functional theory (DFT) method, are comparable to the experimental values.

I. Introduction

The oxidative addition of C−N bonds is thought to be involved in the hydrodenitrogenation of petroleum[1] whereas the oxidative addition of N−H bonds can be used to functionalize alkenes[2] and alkynes[2] via hydroamination. Although there are well characterized examples of C−N and N−H bond activation by low-valent transition metal centers[3] there are relatively few reports[4−8] involving the Group 13 metal atoms despite their ability to insert into many different types of bonds, i.e., C−Br,[9] C−H,[10] H−H,[11] C−O,[12,13] C−C,[12] O−H,[14,15] H− S,[15] H−Se,[15] H−Cl,[16] and P−H.[17]

The products of the reaction of Al atoms with ammonia under matrix-isolation conditions have been studied by both IR[5−7] and EPR[4,8] spectroscopy. At low ammonia concentration, the major products detected by IR spectroscopy in an Ar matrix at 4 K were $AlNH_3$,[6] $AlNH_2$[5,6] and $HAlNH_2$.[5,6] The insertion product formed after photoirradiation of the deposit at $\lambda = 436$ nm and exposure to broad band UV−visible light caused $HAlNH_2$ to decompose to $AlNH_2$. At high ammonia concentrations,[7] $HAlNH_2(NH_3)$ and $Al(NH_2)_2$ were also formed.

The paramagnetic products detected when Al atoms were reacted with NH_3 in adamantane[4] at 77 K were $Al(NH_3)_2$, $Al(NH_3)_4$ and the N−H insertion product $HAlNH_2$. On the other hand, the EPR study of the Al−ammonia reaction products in Ar[8] at 4 K showed that mainly the dative complex $Al(NH_3)$ formed spontaneously. Formation of the insertion radical required irradiation of the deposit with near-IR light, i.e., $\lambda =$ 700 nm. In experiments where the ammonia concentration was ≥2%, $HAlNH_2(NH_3)$ was also formed. Irradiation of the complexed insertion product at $\lambda = 450$ nm resulted in the formation of $Al(NH_2)_2$. On the basis of the results of a semiempirical SCF molecular orbital method, the mechanism shown in Scheme 1 was proposed to account for the Al−ammonia reaction products. The first step involves the spontaneous formation of a dative complex, $Al{:}NH_3$, which acts as the precursor for the formation of the insertion product. Cleavage of one of the N−H bonds proceeds bond formation between the hydrogen atom and Al. Under the appropriate reaction conditions, the insertion product can be complexed by a second NH_3 molecule. Irradiation of $HAlNH_2$ and $HAlNH_2(NH_3)$ results in the formation of $AlNH_2$ and $Al(NH_2)_2$, respectively. Finally, hydrogen atoms, released during the course of the reaction can combine with $HAlNH_2$ to give H_2AlNH_2.

This paper deals with the EPR characterization of the products formed in the reaction of Al atoms with cyclopropylamine ($CpNH_2$) in an adamantane matrix at 77 K. Four Al-centered radicals have been detected. They include the N−H insertion products, CpNH(AlH) and $CpNH(AlH){:}CpNH_2$, the C−N insertion product, $CpAlNH_2$, and an $Al{:}(CpNH_2)_n$ adduct. The Al hfi of the insertion radicals has been calculated using a DFT method for comparison with the experimental values. Although a few EPR spectra[8,13] have been assigned to Al atom insertion products complexed to a substrate molecule via the heteroatom (N or O), none is as convincing as that obtained in the present study for $CpNH(AlH){:}CpNH_2$ where the Al, N and H hfis are clearly seen. In addition, this is to our knowledge the first report of the insertion of Al atoms into C−N bonds.

II. Experimental Section

The rotating cryostat, used to investigate the reaction of ground-state Al atoms with cyclopropylamine, has been described in detail elsewhere.[18] Al atoms were produced by resistively heating Al wire (Alpha Products) in a tungsten basket (No. 12070, Ernest F. Fullam, Inc., Schenectady, NY) suspended between the electrodes of a furnace and were condensed, along with cyclopropylamine or *N*,*N*-dideuteriocyclopropylamine and adamantane, on the surface of the liquid nitrogen-filled drum of the rotating cryostat maintained at $<10^{-5}$ Torr. The cyclopropylamine and adamantane were the purest available commercial products and were used as received after thorough

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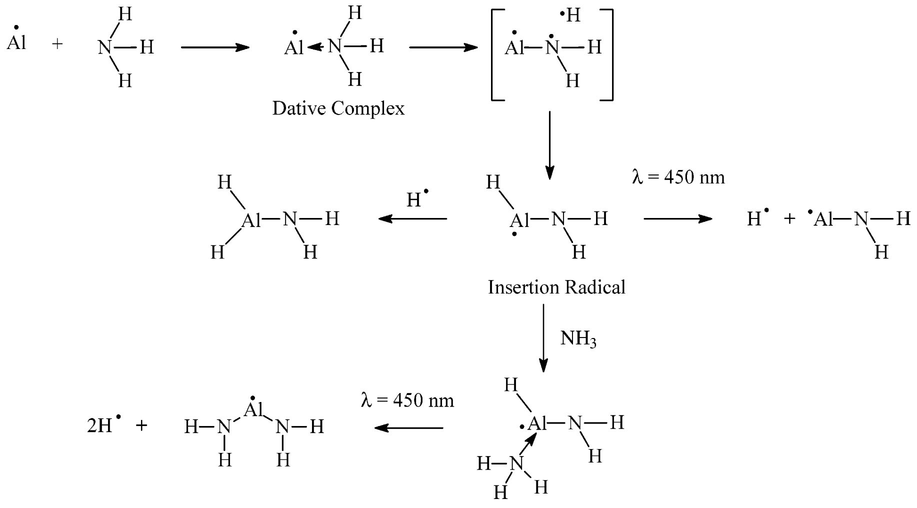
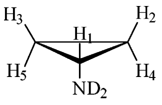
SCHEME 1



degassing. *N*,*N*-dideuteriocyclopropylamine was synthesized as described below. The total deposition times for Al−cyclopropylamine−adamantane reaction mixtures were ca. 10−12 min. EPR X-band spectra were recorded between 77 and 298 K on a Varian E line spectrometer. The spectra were calibrated with the aid of a Varian gaussmeter and microwave frequencies were measured with a Systron-Donner 6016 frequency counter. The magnetic parameters were determined from exact solutions of the spin Hamiltonian by using the computer programs, BRABI and ESRLSQ written by Drs. J. R. Morton and K. F. Preston (NRCC).

Synthesis of *N,N*-Dideuteriocyclopropylamine. Deuterium oxide (8 mL) and cyclopropylamine (4 mL) were combined in a round-bottomed flask. The solution was vigorously stirred with the aid of a stir bar. The *N*,*N*-dideuteriocyclopropylamine (**1**, 3 mL, 75% yield) was slowly distilled from the reaction mixture through a distillation apparatus equipped with a Vigreux column. This procedure was repeated using the *N*,*N*-dideuteriocyclopropylamine recovered above to ensure maximum exchange. NMR (DMSO-d_6, 200 MHz): δ 0.14 ppm (m, H_2 and H_3), 0.32 ppm (m, H_4 and H_5) and 2.16 ppm (t of t, H_1, $J_{14} = J_{15} = 3.8$ Hz, $J_{12} = J_{13} = 6.4$ Hz). This analysis is consistent with that reported in the literature[19] for the undeuterated cyclopropylamine. It should be noted that there was no absorption at 1.68 ppm due to amino protons.



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Computational Methods. Gaussian 98[20] was used to calculate the Al, H and N hfis for the C−N and N−H Al atom insertion products of cyclopropylamine. Several conformational isomers were considered for each of the radicals. The geometry of the isomers was optimized using the B3LYP[21] functional and the split valence 6-31G(d,p) basis set. The species were characterized using frequency analysis. The nuclear hyperfine interactions (hfis) were determined from single point calculations using the 6-311+G(2df, p) basis set and the B3LYP functional.

III. Results

Al/Cyclopropylamine/Adamantane. The EPR spectrum of the major product, species A, formed in the reaction of Al atoms with cyclopropylamine in adamantane at 77 K is shown in Figure 1a. The spectrum consists of 6 lines and is typical of a mononuclear Al ($I = {}^5/_2$) species with a highly anisotropic Al hfi. The spacing between the six parallel features was readily measured to give an average $a_\parallel = 137$ MHz and $g_\parallel = 2.0025$. The perpendicular parameters were estimated using a simulation program. The simulation presented in Figure 1b was obtained with $a_\parallel(\text{Al}) = 137$ MHz, $g_\parallel = 2.0025$, $a_\perp(\text{Al}) = 25$ MHz, $g_\perp = 2.000$ assuming that the unpaired electron interacts with four hydrogen nuclei with an isotropic H hfi of 22 MHz whereas Figure 1c assumes the interaction with only two hydrogen nuclei with an isotropic H hfi of 28 MHz.

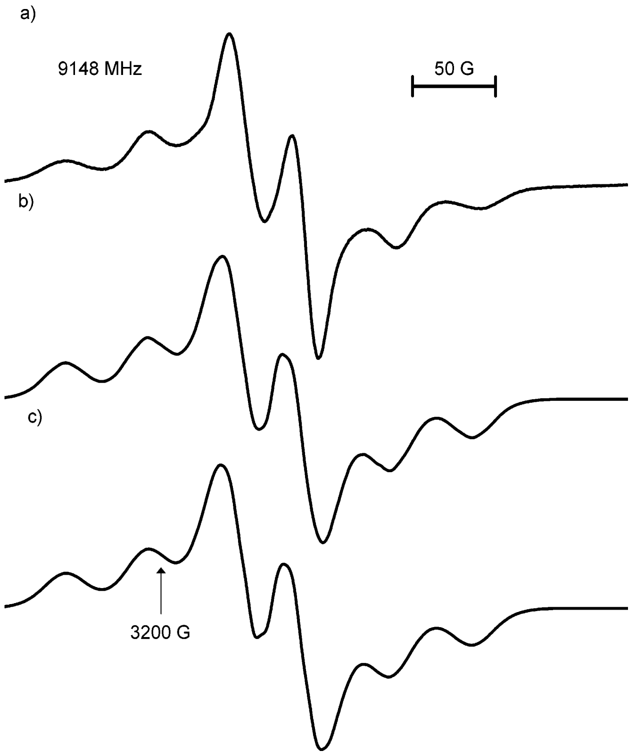


Figure 1. (a) Central feature (A) of the EPR spectrum (microwave power (mp) = 2 mW) of the Al−cyclopropylamine−adamantane reaction mixture recorded at 77 K. (b) Simulation of the central feature using the parameters $a_\parallel(\text{Al}) = 137$ MHz, $g_\parallel = 2.0025$, $a_\perp(\text{Al}) = 25$ MHz, $g_\perp = 2.000$ and assuming the interaction of the unpaired electron with four H nuclei with $a_\parallel(\text{H}) = a_\perp(\text{H}) = 22$ MHz. (c) Simulation of the central feature using the same parameters used in (b) except the interaction of the unpaired electron with two H nuclei where $a_\parallel(\text{H}) = a_\perp(\text{H}) = 28$ MHz is assumed.

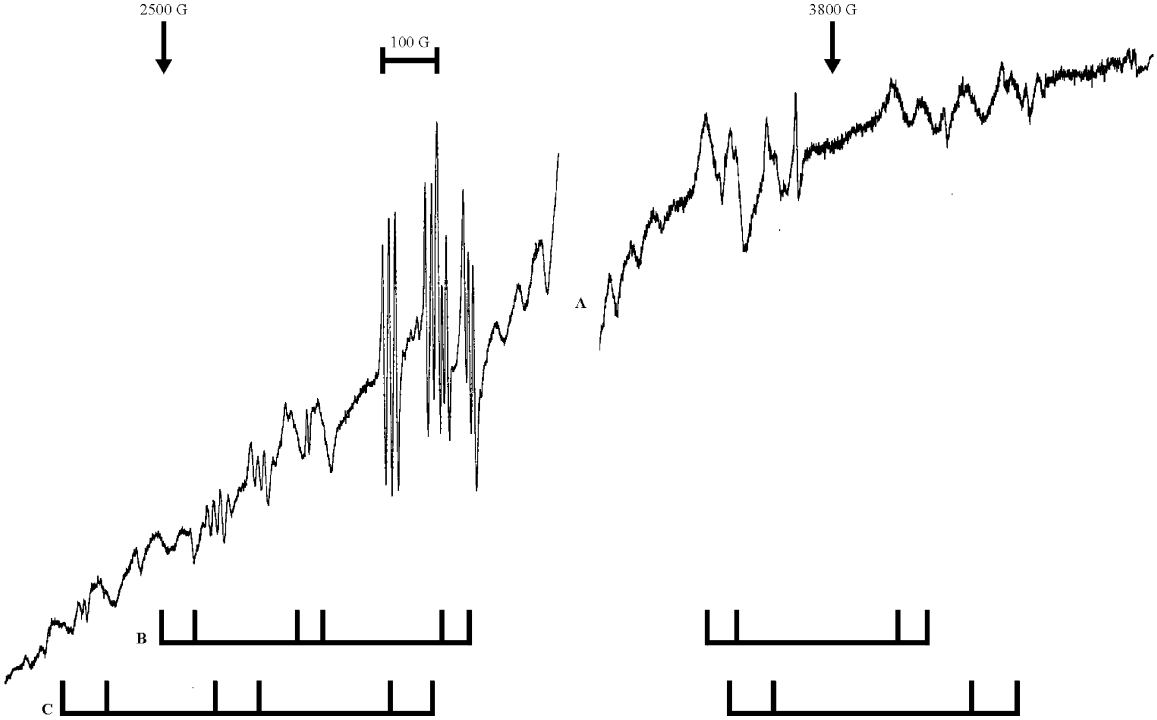


Figure 2. EPR spectrum recorded at 150 K for the products of the Al−cyclopropylamine-adamantane reaction (ν = 9139 MHz, mp = 2 mW). Note that A represents the central features that were off scale at the receiver gain used to record B and C.

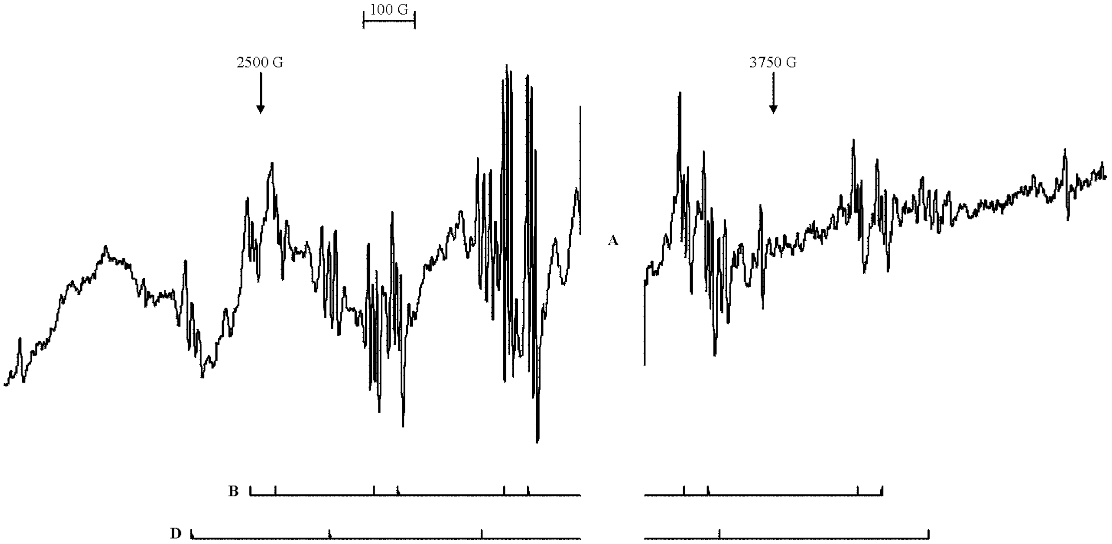


Figure 3. EPR spectrum recorded at 200 K for the products of the Al−cyclopropylamine−adamantane reaction (ν = 9115 MHz, mp = 15 mW). Note that A represents the central features that were off scale at the receiver gain used to record B and D.

Annealing the sample to 150 and 200 K in the cavity of the EPR spectrometer gave the spectra shown in Figures 2 and 3, respectively. In addition to the strong central features of species A, transitions belonging to at least three mononuclear Al products (B, C and D) were detected. Examination of the $M_I = {}^1/_2$ transitions of species B, C and D revealed additional super hfi; i.e., species B and C give a sextet of doublets of triplets whereas D produces a sextet of triplets, Figures 4a ($T = 150$ K) and 5 ($T = 200$ K). We would like to note that the $M_I = -{}^1/_2$ transitions of B, C and D are masked by the spectrum of species A and the spectrum for species C is no longer detectable at 200 K. The sextet of doublets of triplets belonging to species B is centered at $g = 2.0018(5)$; the sextet, doublet and triplet splittings are 801(1), 133(4) and 23(2) MHz, respectively. Spectrum C is centered at $g = 2.0023(6)$ with sextet, doublet and triplet spacings of 962(2), 216(1) and 32(2) MHz, respectively. The doublet splitting in B and C originates from the interaction of the unpaired electron with a hydrogen ($I = {}^1/_2$) nucleus whereas the triplet splitting is thought to involve the interaction of the nitrogen ($I = 1$) nucleus.

The sextet of triplets assigned to species D is centered at 2.0016(3); the sextet and triplet splittings are 943(1) and 37(2) MHz, respectively. The triplet splitting is thought to originate from the interaction of the unpaired electron with N ($I = 1$). The $M_I = {}^1/_2$ transitions for species B, C and D were simulated using the magnetic parameters mentioned above, Figure 4b.

Al/*N*,*N*-Dideuteriocyclopropylamine/Adamantane. The experiment was repeated using *N*,*N*-dideuteriocyclopropylamine. EPR analysis of the reaction mixture indicated that several mononuclear Al species were formed. The major species is characterized by a six-lined spectrum centered at $g = 2.0006$. The spectrum closely ressembles that assigned to species A

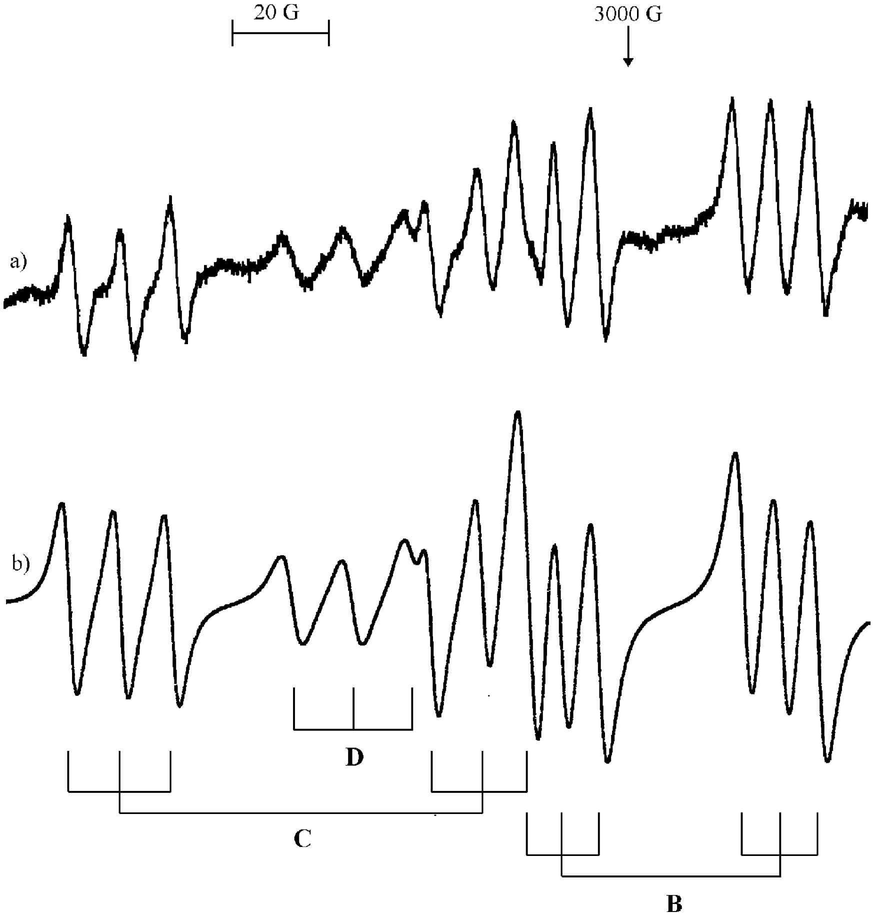


Figure 4. (a) $M_I = {}^1/_2$ region of the spectrum shown in Figure 2 ($T = 150$ K, $\nu = 9115$ MHz, mp = 2 mW. (b) Spectral simulation of the $M_I = {}^1/_2$ region using the magnetic parameters given in the text for species B, C and D.

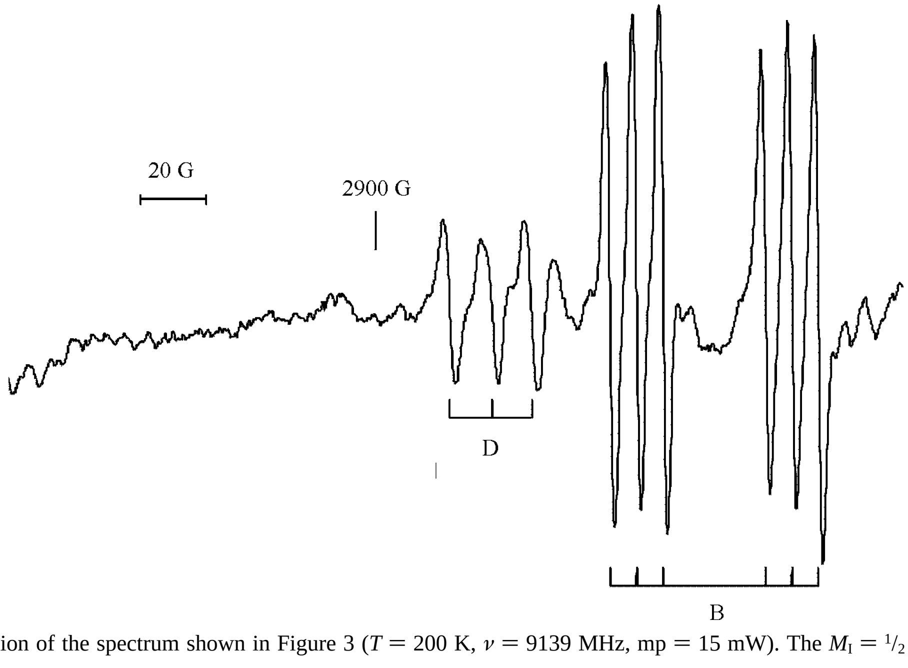


Figure 5. $M_I = {}^1/_2$ region of the spectrum shown in Figure 3 ($T = 200$ K, $\nu = 9139$ MHz, mp = 15 mW). The $M_I = {}^1/_2$ transitions of species B and D are indicated.

formed in the Al−*N*,*N*-cyclopropylamine reaction; the only difference being the slight narrowing of the spectral lines upon deuteration.

The $M_I = {}^1/_2$ region of the EPR spectrum of the mononuclear Al radicals formed in the Al atom−*N*,*N*-dideuteriocyclopropylamine reaction is shown in Figure 6 a. The reaction mixture contains four radicals. The magnetic parameters of two of the radicals were identical within experimental error to those determined for B and C identified in the reaction of Al atoms with cyclopropylamine. The transitions belonging to B and C have been indicated with the aid of a stick diagram. Transitions belonging to two other Al-centered radicals, B′ and C′ were detected, Figure 6. The spectra for B′ and C′ are centered at $g \approx 2.002$ and $g \approx 2.000$, respectively. The sextet splitting

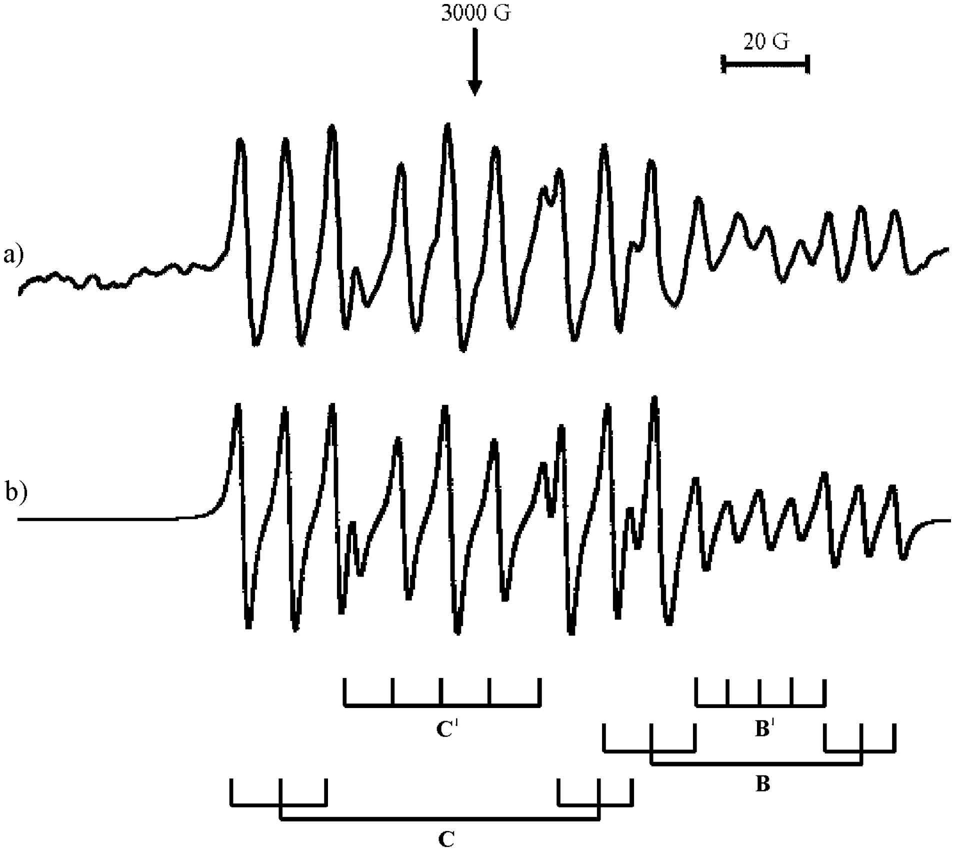


Figure 6. (a) $M_I = {}^1/_2$ region of the EPR spectrum recorded at 200 K for the products given by the reaction of Al atoms and *N*,*N*-dideuteriocyclopropylamine in adamantane at 77 K ($\nu = 9293$ MHz, mp = 2 mW). (b) Spectral simulation of the $M_I = {}^1/_2$ region using the magnetic parameters given in the text for species B, B′, C and C′.

corresponding to the interaction of the unpaired electron with the Al nucleus was found to be 804 MHz for B′ and 968 MHz for C′ suggesting that B′ and C′ are the deuterated analogues of B and C. The transition lines for both species B′ and C′ showed super hfi. The quintet spacing is due to the interaction of the unpaired electron with a deuterium nucleus ($I = 1$) and a nitrogen nucleus ($I = 1$). The a_D and a_N were 20.4 and 22.7 MHz for B′ and 33.3 and 31.6 MHz for C′. The a_D values of B′ and C′ are approximately 6.5 times smaller than the a_H values determined for B and C. This observation confirms that B′ and C′ are deuterated analogues of B and C. A simulation of the $M_I = {}^1/_2$ region of the EPR spectrum, Figure 6b, was obtained by assuming four species are formed in the reaction, i.e., B, C, B′ and C′. For B and B′, an a_N value of 22.7 MHz was used in the simulation along with $a_H = 133$ MHz for B and $a_D = 20.4$ MHz for B′. For the simulation of the spectra of species C and C′, an $a_N = 31.6$ MHz was used along with $a_H = 218$ MHz for C and $a_D = 33.3$ MHz for C′. The ratios of C:C′ and B:B′ are approximately 1.8:1 and 2:1, respectively. C and C′ are easily detectable at 77 K whereas the EPR spectra for B and B′ become more prominent as the temperature is increased. At temperatures ≥210 K only B and B′ persist.

IV. Discussion

Al atoms react with cyclopropylamine to give four different Al-centered radicals. The magnetic parameters of species A, B, C and D, extracted from the EPR spectra, are summarized in Table 1.

Species A. Species A is the major product formed in the reaction between Al atoms and cyclopropylamine in adamantane at 77 K. It is characterized by the spectrum shown in Figure 1 (vide supra), which persists to ≈140 K. Although a good estimate of $a_{\|}$ (137 MHz) and $g_{\|}$ (2.0025) was possible, the perpendicular features were not evident, indicating the species has a highly anisotropic Al hfi. This type of spectrum has been observed for $Al(CO)_2$,[22] $Al(H_2C{=}CH_2)$[23] and $Al(H_2C{=}CH_2)_2$,[23] radicals possessing a large degree of spin density in the Al 3p orbital. The number of ligands in many Al complexes, e.g., $Al(CO)_2$,[22] $Al(H_2C{=}CH_2)$ and $Al(H_2C{=}CH_2)_2$,[23] $Al(PMe_3)_2$[24] and $Al(P(OMe)_3)_2$,[24] could be identified definitively because of the presence of super hfi in the EPR spectra resulting from the interaction of the unpaired electron with nuclei such as ^{13}C ($I = {}^1/_2$), H ($I = {}^1/_2$) or ^{31}P ($I = {}^1/_2$), Table 2. Unfortunately, we were not able to detect super hfi in the EPR spectrum of A and therefore are not able to determine whether Al complexes one or two $CpNH_2$ molecules. However, we did notice a slight narrowing of the spectral lines upon deuteration, indicating the unpaired electron interacts with the hydrogen nuclei. A good simulation was obtained assuming $a_{\|} = 137$ MHz, $g_{\|} = 2.0025$, $a_{\perp}(Al) = 25$ MHz, $g_{\perp} = 2.0000$ and an isotropic $a_H = 22$ MHz

TABLE 1: EPR Parameters of the Products from Reaction of Al Atoms with Cyclopropylamine in Adamantane at 77 K[a]

species	a_{Al}	a_H	a_N	g_{iso}
A	137 (∥)[b] 25 (⊥)	22[d]–28[e]		2.0025 (∥) 2.0000 (⊥)
B	801 (1)[c]	133 (4)	23 (2)	2.0018 (5)
C	962 (2)	216 (1)	32 (2)	2.0023 (6)
D	943 (1)		37 (2)	2.0016 (3)

[a] The hfis are in MHz. [b] The magnetic parameters for species A are $a_{\|}$, $a_{\perp}$, $g_{\|}$ and $g_{\perp}$. [c] The value in parentheses represents the error. [d] Assuming the interaction of four hydrogen nuclei with an isotropic $a_H = 22$ MHz. [e] Assuming the interaction of two hydrogen nuclei with an isotropic $a_H = 28$ MHz.

TABLE 2: Magnetic Parameters of Al Mono- and Diligand Complexes[a]

	$Al(CO)_2$	$Al(H_2C{=}CH_2)$	$Al(H_2C{=}CH_2)_2$	$Al(PMe_3)_2$	$Al(POMe_3)_2$	$Al{:}NH_3$	$Al(NH_3)_2$	species A
$a_{\parallel}(Al)$	108.7	124.7	71.5	150	157	131.6	131.5	137
$a_{\perp}(Al)$	54.6	14	11	0	0	86.6; 82.2	20	25
A_{iso}	72.6[b]	50.9[c] (32.2)[d]	31.2[c] (16.5)[d]	50	52	−12.4	57.2[c] (30.5)[d]	62.3[c] (29)[d]
A_{dip}	36.6	36.9[c] (46.2)[d]	20.2[c] (27.5)[d]	50	52	72	37.2[c] (50.5)[d]	37.3[c] (54)[d]
$a_{\parallel}(L)$	<2.8	14	11	59.8	44.9			22 or 28[e]
$a_{\perp}(L)$	25.0	14	11	68.1	70.2			22 or 28[e]
$g_{\parallel}$	2.0021	2.0025	2.0023	1.9973	2.0071	2.001	1.999	2.0025
$g_{\perp}$	2.0021	2.0097; 1.9965	2.0083; 1.9993	2.0023	2.0071	1.995; 1.957	1.999	2.000
ρ_{3s}	0.019	0.013[c] (0.008)[d]	0.008[c] (0.004)[d]	≈0.013	≈0.013		0.015[c] (0.008)[d]	0.016[c] (0.007)[d]
ρ_{3p}	0.44	0.44[c] (0.56)[d]	0.24[c] (0.33)[d]	0.60	0.63	0.86	0.45[c] (0.61)[d]	0.45[c] (0.65)[d]
ref	22	23	23	24	24	8	4	this work

[a] The hfis are in MHz. [b] Experimental value. [c] Values calculated assuming $a_{\parallel}$ and $a_{\perp}$ are of the same sign. [d] Values calculated assuming $a_{\parallel}$ and $a_{\perp}$ are of opposite sign. [e] Values estimated from spectral simulations (see text).

for four hydrogen nuclei consistent with $Al(CpNH_2)_2$, Figure 1b, or with an isotropic $a_H = 28$ MHz for two hydrogen nuclei consistent with $Al(CpNH_2)$, Figure 1c.

Values of A_{iso} and A_{dip} for species A were determined by substituting $a_{\parallel}(Al)$ and $a_{\perp}(Al)$ into eqs 1 and 2,[25] respectively.

$$A_{iso} = (a_{\parallel} + 2a_{\perp})/3 \tag{1}$$

$$A_{dip} = (a_{\parallel} - a_{\perp})/3 \tag{2}$$

If $a_{\parallel}$ and $a_{\perp}$ are assumed to have the same sign, A_{iso} and A_{dip} are 62.3 and 37.3 MHz, respectively. Should $a_{\parallel}$ and $a_{\perp}$ be of opposite sign, A_{iso} and A_{dip} are 29 and 54 MHz, respectively. An estimate of the Al 3s-spin contribution, ρ_{3s}, to the SOMO is obtained by dividing the values calculated for A_{iso} by the one electron atomic parameter for Al 3s orbital (3911 MHz).[26] Dividing A_{dip} by αP (where α is the angular factor of 0.4 for a p orbital and P is the atomic parameter for an electron in the Al 3p orbital (207.7 MHz)[26]) gives an estimate of the Al 3p-spin contribution, ρ_{3p}, to the SOMO. Therefore ρ_{3s} and ρ_{3p} are 0.016 and 0.45 if $a_{\parallel}$ and $a_{\perp}$ are positive and 0.007 and 0.65 if $a_{\parallel}$ and $a_{\perp}$ are of opposite sign.

These values can be compared to those reported for a number of mono- and diligand Al complexes, Table 2. A species with magnetic parameters similar to those found for A was detected in the Al−ammonia reaction in adamantane at 77 K.[4] Although no N hfi was detected, the spectrum was assigned to $Al(NH_3)_2$ because (a) the Al 3s and 3p spin density contribution to the SOMO of the radical was similar to that of $Al(CO)_2$ and (b) the same radical was formed in neat ammonia. When the reaction was carried out in Ar at 4 K, a radical with different magnetic parameters was detected, i.e., $a_1 = 131.6$ MHz, $a_2 = 86.6$ MHz, $a_3 = 82.2$ MHz, $g_1 = 2.001$, $g_2 = 1.995$ and $g_3 = 1.957$. This spectrum has been assigned to the dative complex $Al{:}NH_3$.

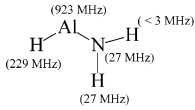
One can therefore conclude that the species formed in adamantane for both of the N-donor ligands studied, NH_3 and $CpNH_2$, are very similar in character. The fact that $Al{:}NH_3$, formed in rare gas matrixes, has magnetic parameters very different from those of the species isolated in adamantane suggests that $Al(NH_3)_2$ and $Al(CpNH_2)_2$ are formed in adamantane. This assignment is tentative and must be confirmed by an auxiliary method that would allow the determination of the number of ligands.

Species C. The EPR spectrum for species C is a sextet of doublets of triplets centered at $g = 2.0023$, which indicates the unpaired electron interacts with an Al, H and N nucleus. The large doublet spacing of 216 MHz is typical of Al-centered radicals with the structure HAlX, where X is an electron withdrawing group, Table 3. Species C is therefore thought to be the N−H insertion product CpNH(AlH). The reaction of Al atoms with ammonia in adamantane also resulted in the formation of an N−H insertion product, $HAlNH_2$. The magnetic parameters for $HAlNH_2$, $a_{Al} = 923$ MHz, $a_H = 229$ MHz and $a_N = 27$ MHz are similar to those of CpNH(AlH); cf. Table 1. Dividing the observed Al hfi by 3911 MHz, the one electron atomic parameter for the Al 3s orbital, gives an estimate of the Al 3s unpaired spin population (ρ_{3s}) of 0.25. The ρ_{3s} for divalent mononuclear Al radicals ranges from 0.20 to 0.29 depending on the electron withdrawing nature of the ligands attached to Al, Table 3.

TABLE 3: Hfis (in MHz) and Al 3s Unpaired Spin Population (ρ_{3s}) of Several Mononuclear Al Insertion Products

radical	a_{Al}	a_H	a_X	ρ_{3s}	ref
CH_3AlH	772	152		0.20	10
HAlH	834	128		0.21	11
HAlOH	911	286		0.23	14, 15
HAlSH	984	210		0.25	15
HAlCl	1115	279	31 (Cl)	0.29	16
$HAlNH_2$	923	229	27 (N) 27 (H)	0.24	4
CpNH(AlH)	962	216	32 (N)	0.25	this work
$CpAlNH_2$	943		37 (N)	0.24	this work

The amino hydrogen does not interact with the unpaired electron. This is not unexpected, as it has been previously demonstrated for $HAlNH_2$ that significant unpaired electron density is only found on the hydrogen trans to the main spin density lobe (**2**).[8] Because an amino hydrogen hfi was not observed for CpNH(AlH), it would suggest that predominant conformation of the radical has the hydrogen atoms attached to Al and N arranged trans to one another, **3**.



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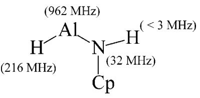

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The Al hfi of a number of divalent organoaluminum radicals were calculated using a DFT method.[27] The best agreement between theory and experiment occurred at the B3LYP[21] level using a 6-311+G(2df,p) basis set. In all cases, the calculated values underestimated the Al hfi slightly with deviations ranging from 1% to 8%. This method was used to calculate the Al hfi of the N−H insertion product of cyclopropylamine. A single point calculation using the B3LYP functional[21] and the split valence 6-311+G(2df,p) basis set was used to determine the energies and the nuclear hfis for a number of different conformations of the N−H insertion product. The geometry of the different conformations was optimized using the B3LYP

CHART 1

	Cis	Trans
H_1-Al	1.608 Å	1.605 Å
Al-N	1.799 Å	1.799 Å
N-C	1.438 Å	1.442 Å
N-H_2	1.017 Å	1.016 Å
∠CNAl	131.3°	130.2°
∠NAlH_1	112.7°	117.5°
∠H_2NAl	117.1°	118.3°

TABLE 4: Experimental Hfi, Calculated Hfi and Potential Energies (E) of the cis and trans Conformers of the N−H Insertion Product

	cis conformer	trans conformer	exp
a_{Al}	914[a]	891[a]	962[b]
a_N	21	31	32
a_{H_1}	227	226	216
a_{H_2}	24	−2	
E^c	−415.7432	−415.7430	

[a] Calculated isotropic hfi in MHz. [b] Experimental isotropic hfi in MHz. [c] Energies in hartrees.

functional and the split valence 6-31(d,p) basis set. The optimized geometries of the two lowest energy conformations (cis and trans conformations) are shown in Chart 1; their energies and nuclear hfis are in Table 4 along with the experimental hfis.

The magnitude of the Al, N, H_1 and H_2 hfi is dependent on the conformation of the radical. Stepwise rotation about the C−N bond showed that the a_{Al}, a_N, a_{H_1} and a_{H_2} values vary by a maximum of 0.5%, 1%, 8% and 12%, respectively. Greater deviations were observed for rotation about the Al−N bond; i.e., a_{H_2} varies from −2 to 24 MHz, a_N from 14 to 40 MHz, a_{Al} from 828 to 914 MHz and a_{H_1} from 226 to 255 MHz. The maximum difference in potential energy for the conformers tested was found to be ≈5 kcal/mol. The cis isomer is only 0.1 kcal/mol more stable than the trans isomer.

The best agreement between the calculated and experimental hfis occurs for the trans isomer, which would indicate that it is the preferred conformation. The deviations in hfi are ≈7% for a_{Al}, ≈3% for a_N, and ≈5% for a_{H_1}. The small hfi of −2 MHz calculated for H_2 is consistent with our inability to extract the experimental value.

The assignment was confirmed by the experiments involving *N*,*N*-dideuteriocyclopropylamine. Insertion of the Al atoms into the N−D bond results in a change in the appearance of the EPR spectrum with respect to that obtained for CpNH(AlH). The spectrum was best described as a sextet of triplets of triplets originating from the interaction of the unpaired electron with an Al, N and D nucleus. The Al and N hfis are 968 and 31.6 MHz, respectively. These values are identical within experimental error to those determined for CpNH(AlH). The a_D of 33.3 MHz is approximately 6.5 times smaller than that of the a_H; this is expected on the basis of the ratio of the gyromagnetic ratios of H and D. Despite having taken precautions to eliminate all H_2O, a radical with the same magnetic parameters as CpNH(AlH) was observed indicating that exchange must occur with adventitious water. The reaction mixture therefore contains CpND(AlH), CpNH(AlD) and CpND(AlD). The ratio of the Al atom NH to ND insertion products is approximately 1.8:1, suggesting that there is an isotope effect and N−H bond insertion is more facile than N−D insertion.

A possible mechanism for the insertion reaction involves (1) the formation of a dative complex, $CpNH_2$:Al, via the interaction of Al with the lone pair of electrons on N, (2) the homolytic cleavage of the N−H bond and (3) bond formation between Al and the hydrogen atom. This three-step process was modeled after the scheme proposed by Kasai and Himmel[8] for the formation of $HAlNH_2$. in the Al−ammonia reaction.

Species B. The spectrum for species B is also a sextet of doublets of triplets centered at $g = 2.0018$. The nuclear hfis extracted from the EPR spectrum, i.e., $a_{Al} = 801$ MHz, $a_H = 133$ MHz and $a_N = 23$ MHz, are smaller than those observed for CpNH(AlH) by 17%, 38% and 28%, respectively.

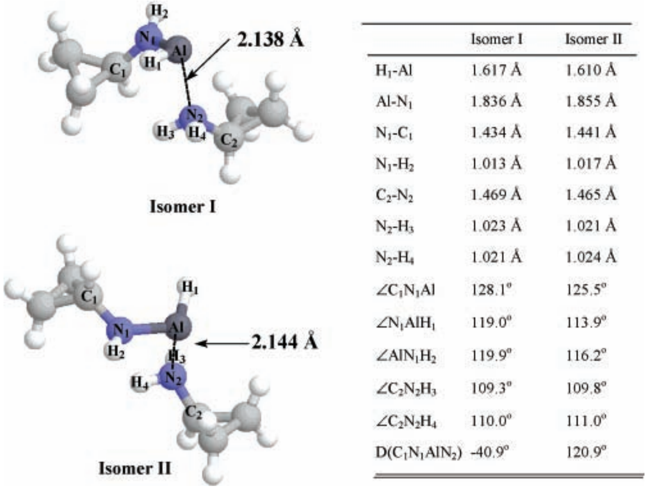
Complexation on the vacant coordination sites of divalent Al complexes causes a decrease in the isotropic hfi of the radical; e.g., coordination of the vacant sites on AlH_2[28] by two $N(CH_3)_3$ molecules causes the magnetic parameters to change from $a_{Al} = 834$ MHz and $a_H = 128$ MHz to $a_{Al} = 716$ MHz and $a_H = 28$ MHz. This represents a 14% and 78% decrease in a_{Al} and a_H, respectively. The C−O insertion product, CH_3AlOCH_3 and the coordinated compound CH_3AlOCH_3:$O(CH_3)_2$ have also been studied by EPR.[13] Complexation of the insertion product causes the a_{Al} to decrease by 4%.

Himmel and Kasai,[8] in a study of Al atoms and ammonia in Ar have recently shown evidence for the complexed insertion product $(HAlNH_2)$:NH_3 where the a_{Al} differs from the uncomplexed insertion product by 18%. They were not able to obtain precise values for a_H and a_N of the complexed product because of poor resolution of the spectral lines. However, these were estimated from the line width to be ≈28 MHz. Therefore, coordination of NH_3 to the insertion radical causes the a_H to decrease by 55% and a_N to increase by 5%. Because species B behaved in a similar fashion, it is thought to be the complexed insertion product, CpNH(AlH):$CpNH_2$.

The study involving the deuterated substrate confirmed that Al inserts itself into the N−D bond. The $M_I = {}^1/_2$ line of B′ shows additional hfi. The five-lined motif is due to the interaction of the unpaired electron with deuterium ($I = 1$) and nitrogen ($I = 1$). The triplet splitting (20.4 MHz) resulting from the interaction with D is approximately 6.5 times smaller than the a_H. The a_{Al} and a_N are the same within experimental error to that of the undeuterated compound, CpNH(AlH):$CpNH_2$. This suggest that B′ is CpND(AlD):$CpND_2$.

The possibility that the insertion radical is coordinated to a $CpNH_2$ molecule was tested by carrying out an exploratory DFT calculation. This was done by first optimizing the geometry of CpNH(AlH) using the B3LYP and split valence 6-31G(d,p) basis set. Next, a $CpNH_2$ molecule was introduced below the H_1AlNH_2 plane of the CpNH(AlH) radical and the geometry was reoptimized. The nuclear hfis of the two conformers shown in Chart 2 were obtained from a single point calculation using the 6-311+G(2df,p) basis set and the B3LYP functional. For isomer I, the Al, H and N hfi were estimated to be 791, 120 and 27 MHz, respectively, whereas for isomer II values of 772, 106 and 15 MHz were obtained. Coordination of $CpNH_2$ causes the Al and H hfi to decrease by 11−13% and 47−53%, respectively, with respect to the values calculated for *trans*-CpNH(AlH). The calculated N hfi of isomers I and II differed

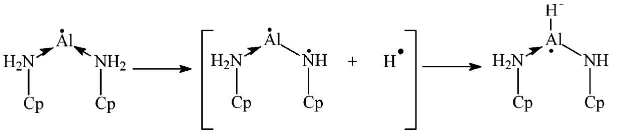
CHART 2



	Isomer I	Isomer II
H_1-Al	1.617 Å	1.610 Å
Al-N_1	1.836 Å	1.855 Å
N_1-C_1	1.434 Å	1.441 Å
N_1-H_2	1.013 Å	1.017 Å
C_2-N_2	1.469 Å	1.465 Å
N_2-H_3	1.023 Å	1.021 Å
N_2-H_4	1.021 Å	1.024 Å
∠C_1N_1Al	128.1°	125.5°
∠N_1AlH_1	119.0°	113.9°
∠AlN_1H_2	119.9°	116.2°
∠$C_2N_2H_3$	109.3°	109.8°
∠$C_2N_2H_4$	110.0°	111.0°
D(C_1N_1AlN_2)	-40.9°	120.9°

from that of *trans*-CpNH(AlH) by 13% and 52%, respectively. The two isomers differ in energy by 0.02 kcal/mol with I being slightly more stable than II.

Formation of CpNH(AlH):CpNH$_2$ could occur by one of two pathways. The first mechanism suggested by Kasai and Himmel[8] for the Al–NH$_3$ reaction involves direct coordination of the insertion product, CpNH(AlH). Alternatively,[7] one could envision Al(CpNH$_2$)$_2$ acting as a precursor for CpNH(AlH):CpNH$_2$ formation. The homolytic cleavage of an N–H bond with the subsequent formation of an Al–H bond would yield CpNH(AlH):CpNH$_2$, eq 3.



[3]

Species D. The spectrum for species D is a sextet of triplets centered at $g = 2.0016$. The sextet and triplet splittings were found to be 943 and 37 MHz, respectively. A possible carrier of the spectrum is the C–N insertion product, CpAlNH$_2$. Information concerning the C–N insertion product could not be obtained from the experiment using the deuterated amine because its spectrum is obscured by that of CpND(AlD) and it is not present in high concentration. The magnitude of the Al hfi for species D is what one would expect for divalent Al species; cf. Table 3 (vide infra).

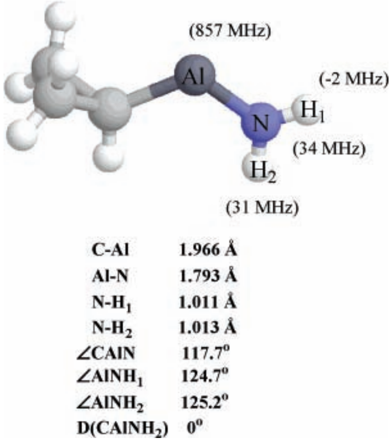
The Al hfi of the C–N insertion product is 2% larger than that reported[4,8] for HAlNH$_2$ and 2% smaller than that observed for the N–H insertion product of cyclopropylamine. The N hfi of the C–N insertion product is larger than that found for CpNH(AlH) (14%) and HAlNH$_2$ (27%). As far as we know, there are no other reports of Al C–N insertion products so comparison of nuclear hfi values with similar radicals was not possible.

The nuclear hfis for CpAlNH$_2$ were estimated using the DFT method described above. The lowest energy conformation, Chart 3, has an Al, N and H hfi of 857, 34 and 31 MHz, respectively. We calculated the nuclear hfis for several conformations resulting from the stepwise rotation about the C–Al and Al–N bonds of CpAlNH$_2$, Tables 5 and 6.

The Al, N, and H hfis are not affected significantly upon rotation about the C–Al bond of CpAlNH$_2$. The maximum difference in energy between the conformers of CpAlNH$_2$ is only 0.89 kcal/mol. However, rotation about the Al–N bond causes the hfi of the amino hydrogens to fluctuate considerably. As the dihedral angle is changed from 0 to 180°, the hfis of H$_1$ and H$_2$ vary from +31 to −3 MHz and −3 to +31 MHz, respectively. The difference in energy between these conformers is relatively small and free rotation about the Al–N bond would result in an averaging of the H hfis of H$_1$ and H$_2$. Because the experimental spectrum showed no evidence of the H hyperfine splitting, one could conclude that this is a consequence of rapid rotation about the Al–N bond of CpNH$_2$ with respect to the EPR time scale. The N hfi is also dependent on the conformation of the radical; a variation of 19 MHz was calculated as the dihedral angle was swept from 0 to 180°. The experimental N hfi would be expected to be an average of the values determined for individual conformers because of the relatively small difference in their energies. The calculated Al hfi for the different conformations varies slightly (7%) as the dihedral angle is changed from 0 to 180°.

The DFT calculations for the Al atom C–N insertion product support the assignment of the EPR spectrum to CpAlNH$_2$ as the Al and N hfi values are within 9–10% of the experimental values. The absence of H hfi in the experimental spectrum is

CHART 3



C-Al	1.966 Å
Al-N	1.793 Å
N-H_1	1.011 Å
N-H_2	1.013 Å
∠CAlN	117.7°
∠AlNH_1	124.7°
∠AlNH_2	125.2°
D(CAlNH_2)	0°

TABLE 5: Effect of Rotation about the C–Al Bond on the Al, H and N Hfis Calculated for CpAlNH$_2$

dihedral angle (deg)	isotopic hyperfine interaction (MHz)				energy difference[a] (kcal/mol)
	H(1)	N	Al	H(2)	
0	31	34	857	−2	0
20	31	34	855	−2	0.15
60	31	36	849	−2	0.89
120	30	37	858	−3	0.83
160	31	36	857	−2	0.26
180	31	35	856	−2	0.18

[a] Energy relative to that calculated for conformation with a dihedral angle = 0°.

TABLE 6: Effect of Rotation about the Al–N Bond on the Al, H and N Hfis Calculated for CpAlNH$_2$

dihedral angle (deg)	isotopic hyperfine interaction (MHz)				energy difference[a] (kcal/mol)
	H(1)	N	Al	H(2)	
0	31	34	857	−2	0
20	29	32	848	−2	0.32
60	14	22	795	−3	2.84
120	−3	41	858	29	0.83
160	−3	34	857	31	0.50
180	−2	34	857	31	0.00

[a] Energy relative to that calculated for the conformation with dihedral angle = 0°.

thought to occur because of the rotation about the Al−N bond causing the hfi of the amino hydrogens to vary from +31 to −3 MHz.

The mechanism used to explain the formation of the N−H insertion product can be adapted to explain the formation of the C−N insertion product. More specifically, the Al atom first interacts with the lone pair of electrons on N in cyclopropylamine. This is followed by the homolytic cleavage of the C−N bond and bond formation between Al and the C atom of the cyclopropyl ring.

V. Summary

Al atoms were reacted with cyclopropylamine in an adamantane matrix at 77 K. Four mononuclear Al radicals were identified. The major complex formed and characterized by EPR spectroscopy is $Al(CpNH_2)_n$. In addition, EPR evidence for the formation of the N−H insertion radical, CpNH(AlH) and the complexed N−H insertion radical $CpNH(AlH){:}CpNH_2$ was obtained. Although the possibility of the complexation of divalent radicals has been previously mentioned, this is the first report where the Al and H hfi for such a radical are clearly resolved. As expected, complexation of the N−H insertion product causes the values for the Al, N and H hfi to decrease. Al atoms were also shown to activate C−N bonds producing $CpAlNH_2$. Finally, good estimates of the nuclear hfis were obtained for the divalent N−H and C−N Al atom insertion products using the DFT method.

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References and Notes

(1) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678 and references within.

(2) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675 and references within.

(3) (a) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc*. **2004**, *126*, 4792. (b) Ozerov, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573.

(4) Howard, J. A.; Joly, H. A.; Edwards, P. P.; Singer, R. J.; Logan, D. E. *J. Am. Chem. Soc*. **1992**, *114*, 474.

(5) Lanzisera, D. V.; Andrews, L. *J. Phys. Chem. A* **1997**, *101*, 5082.

(6) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc*. **2000**, *122*, 9793.

(7) Gaertner, B.; Himmel, H.-J. *Inorg. Chem.* **2002**, *41*, 2496.

(8) Kasai, P. H.; Himmel, H.-J. *J. Phys. Chem. A* **2002**, *106*, 6765.

(9) Tanaka, Y.; Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc*. **1982**, *104*, 1013.

(10) Parnis, J. M.; Ozin, G. A. *J. Phys. Chem.* **1989**, *93*, 1204.

(11) Knight, L. B., Jr.; Woodward, J. R.; Kirk, T. J.; Arrington, C. A. *J. Phys. Chem.* **1993**, *97*, 1304.

(12) (a) Howard, J. A.; Joly, H. A.; Mile, B. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 219. (b) Chenier, J. H. B.; Howard, J. A.; Joly, H. A.; LeDuc, M.; Mile, B. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3321.

(13) Kasai, P. H. *J. Phys. Chem. A* **2002**, *106*, 83.

(14) Knight, L. B., Jr.; Gregory, B.; Cleveland, J.; Arrington, C. A. *Chem. Phys. Lett.* **1993**, *204*, 168.

(15) Joly, H. A.; Howard, J. A.; Tomietto, M.; Tse, J. S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3145.

(16) Fängström, T.; Lunell, S.; Kasai, P. H.; Eriksson, L. A. *J. Phys. Chem. A* **1998**, *102*, 1005.

(17) (a) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *Inorg. Chem.* **2001**, *40*, 396. (b) Himmel, H.-J.; Downs, A. J.; Green, J. C.; Greene, T. M. *J. Chem. Soc., Dalton Trans.* **2001**, 535.

(18) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381.

(19) Wilberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **1973**, *38*, 378.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Lui, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(22) Chenier, J. H. B.; Hampson, C. A.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Phys. Chem.* **1986**, *90*, 1524.

(23) Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165.

(24) Histed, M.; Howard, J. A.; Joly, H. A.; Mile, B. *Chem. Phys. Lett.* **1989**, *161*, 122.

(25) Weltner, W., Jr. *Magnetic Atoms and Molecules*. Dover: New York, 1989.

(26) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(27) Joly, H. A.; Howard, J. A.; Arteca, G. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 750.

(28) Hudson, L.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1194.