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# DIAZABUTADIENES AS LIGANDS

# I. COMPOUNDS OF ALUMINIUM: COORDINATION OF DIAZABUTADIENES TO $Al(CH_3)_3$ AND SUBSEQUENT INTRAMOLECULAR INSERTION AND REARRANGEMENT REACTIONS LEADING TO $(CH_3)_2AlR{-}N{-}CH(CH_3){-}C(R'){=}N{-}R$ (R′ = H, $CH_3$) AND $(CH_3)_2AlR{-}N{-}CH_2{-}C(CH_3){=}N{-}R$

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## Summary

Reaction of R—N=CH—CH=N—R with $[(CH_3)_3Al]_2$ affords the coordination product $(CH_3)_3AlRN{=}CH{-}CH{=}NR$ (A) for R = 2,6-$(CH_3)_2C_6H_3$ and 2,4,6$(CH_3)_3$-$C_6H_2$. For R = 4 $ClC_6H_4$, 4-$CH_3C_6H_4$ and 4-$CH_3OC_6H_4$, insertion takes place, giving the complexes $(CH_3)_2AlRN{-}CH(CH_3){-}CH{=}N{-}R$ (B), in which Al is part of a five-membered chelate ring. Depending on the temperature both the addition and insertion products rearrange intramolecularly to the complexes $(CH_3)_2$-$AlR{-}N{-}CH_2{-}C(CH_3){=}N{-}R$ (C), in which Al is also part of a five-membered chelate ring. Reactions of the asymmetric $(CH_3)_2HC{-}N{=}CH{-}C(CH_3){=}N{-}CH$-$(CH_3)_2$ with $[Al(CH_3)_3]_2$ also leads to an insertion product, $(CH_3)_2AlRN{-}$ $CH(CH_3){-}C(CH_3){=}N{-}R$ (B′) (R = $(CH_3)_2CH$), but there is no subsequent rearrangement in this case.

A mechanism involving hydrogen migration is tentatively proposed to account for the observed isomerization, which increases in rate in the order:

R = $(CH_3)_3C$ > 2,4,6-$(CH_3)_3C_6H_2$ > 2,6-$(CH_3)_2C_6H_3$ (A → C)

and

R = 4-$CH_3OC_6H_4$ > 4-$CH_3C_6H_4$ > 4-$ClC_6H_4$ (B → C)

Hydrolysis of isomer C gives the unknown imino amines $R{-}NH{-}CH_2{-}$ $C(CH_3){=}N{-}R$ in quantitative yield.

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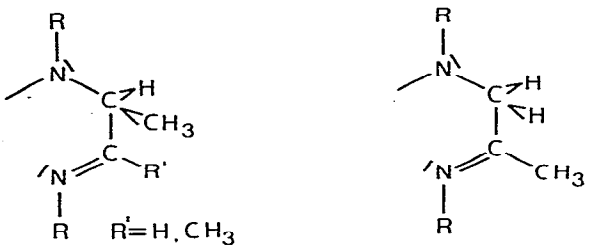


Fig. 1. Structures of the imino-amine ligands $[R{-}N{-}CH(CH_3){-}C(R'){=}N{-}R]^-$ and $[R{-}N{-}CH_2{-}C(CH_3){=}N{-}R]^-$ ($R' = H, CH_3$).

## Introduction

The chemistry of diazabutadienes (R—N=CH—CH=N—R) [1—4] and the related sulfurdiimines (R—N=S=N—R) [5,6] has received much attention because of their interesting coordination characteristics. It has further been shown that alkyllithium, aryllithium and Grignard reagents can react quantitatively with R—N=S=N—R [7] to form the $[R{-}N{=}S(R'){-}N{-}R]^-$ anion, which may bind as a pseudoallyl ligand to $Cu^I$, $Ag^I$, $Rh^I$ [7] and $Pd^{II}$ [8].

These results prompted us to attempt the insertion of diazabutadienes and sulfurdiimines into the Al—$CH_3$ bonds. If successful, the products would, in principle, be convenient starting compounds for further interesting chemistry.

We describe below the reaction of $[(CH_3)_3Al]_2$ with some diazabutadienes which gives the new imino-amino ligands $[R{-}N{-}CH(CH_3){-}C(R'){=}N{-}R]^-$ and $[R{-}N{-}CH_2{-}C(CH_3){=}N{-}R]^-$ ($R' = H, CH_3$) (Fig. 1).

## Experimental

All manipulations were carried out under dry, oxygen-free nitrogen. All solvents solvents were carefully dried and purified before use. The diazabutadienes were prepared by published methods [9].

*Preparation of $(CH_3)_3AlRN{=}CH{-}CH{=}NR$ (A), $(CH_3)_2Al\overline{R{-}N{-}CH(CH_3){-}CH{=}N}{-}R$ (B) and $(CH_3)_2Al\overline{R{-}N{-}CH(CH_3){-}C(CH_3){=}N}{-}R$ (B')*

A solution of 25% $[(CH_3)_3Al]_2$ in hexane containing 5 mmol of $[(CH_3)_3Al]_2$ (4.2 $cm^3$) was added dropwise to a suspension of 10 mmol of diazabutadiene in pentane (20 $cm^3$). A colour change was immediately observed. After 5 min the precipitate was filtered off and washed with pentane (Yield ~90%).

Products IB, (R = 4-$ClC_6H_4$), IIB, (R = 4-$CH_3C_6H_4$) and IIIB, (R = 4-$CH_3OC_6H_4$) were prepared at 0°C, while for the products IVA (R = 2,6$(CH_3)_2C_6H_3$), VA (R = 2,4,6-$(CH_3)_3C_6H_2$ and VIIB' (R = $(CH_3)_2CH$) temperatures of —40°C were used. In the latter cases filtration of the reaction mixture was also carried out at —40°C. Products IB, IIB and IIIB can be recrystallized from toluene at —30°C (Yield ~95%).

All the products are pyrophoric in air and very susceptible to hydrolysis.

*Preparation of $(CH_3)_2Al\overline{R{-}N{-}CH_2{-}C(CH_3){=}N}R$ (C)*

A solution of IB, IIB or IIIB in toluene was allowed to stand at room temper-

ature for 24 h. The pure isomer C crystallized. The crystals were filtered off, washed with pentane, and dried under vacuum (Yield ~90%).

The products IVC and VC were prepared from a solution of IVA and VA in toluene/pentane. After 0.5 h at room temperature the solution was stored at —80° C for about 48 h. The crystalline isomer C was collected on a filter at —40° C, washed with pentane and dried under vacuum (Yield ~90%).

Product VIC was prepared from 4.2 $cm^3$ of a solution of 25% $[(CH_3)_3Al]_2$ in hexane (5 mmol) and a suspension of 10 mmol of $(CH_3)_3C—N=CH—CH=N—C(CH_3)_3$ in 20 $cm^3$ of pentane at —40° C. The precipitate was filtered off at —40° C, after which the temperature was slowly raised until, at approximately —20° C, a rapid reaction occurred. The resulting oily product was dissolved in pentane and stored at —80° C. After 24 h the crystals of VIC were filtered off at —40° C, washed with cold pentane, and dried under vacuum (Yield ~80%).

All the products are pyrophoric and very susceptible to hydrolysis.

*Reactions of IVA, VA and IC and IIC with $H_2O$: isolation of the ligands*

$H_2O$ was added to a solution of IVA or VA in acetone at —30° C. After filtration the solvent was removed from the filtrate under vacuum. The remaining product, free diazabutadiene, was collected and identified by $^1H$ NMR (Yield 95%).

TABLE 1

ANALYTICAL DATA FOR $(CH_3)_3AlRN=CHCH=NR$ (A), $(CH_3)_2AlRNCH(CH_3)CH=NR$ (B) $(CH_3)_2AlRNCH(CH_3)C(CH_3)=NR$ (B') AND $(CH_3)_2AlRNCH_2C(CH_3)=NR$ (C)

| Compound (R) | Code | Colour | Analysis (% found (calcd)) | | | Molecular Weight Found (calcd) |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| $4\text{-}ClC_6H_4$ | IB | yellow | 58.50 (58.46) | 5.73 (5.48) | 7.98 (8.02) | 342 (349) |
| $4\text{-}ClC_6H_4$ | IC | yellow | 58.60 (58.46) | 5.81 (5.48) | 7.93 (8.02) | [a] |
| $4\text{-}CH_3C_6H_4$ | IIB | yellow | 74.64 (73.99) | 7.89 (8.17) | 9.53 (9.09) | 305 (308) |
| $4\text{-}CH_3C_6H_4$ | IIC | yellow | 73.67 (73.99) | 8.37 (8.17) | 9.12 (9.09) | 290 (308) |
| $4\text{-}CH_3OC_6H_4$ | IIIB | yellow | 66.83 (67.04) | 7.45 (7.40) | 8.20 (8.23) | 337 (340) |
| $4\text{-}CH_3OC_6H_4$ | IIIC | yellow | 67.02 (67.04) | 7.43 (7.40) | 8.22 (8.23) | 332 (340) |
| $2,6\text{-}(CH_3)_2C_6H_3$ | IVA | orange | 74.24 (74.96) | 8.91 (8.69) | 8.08 (8.33) | [b] |
| $2,6\text{-}(CH_3)_2C_6H_3$ | IVC | orange | 74.79 (74.96) | 8.87 (8.69) | 8.08 (8.33) | 333 (337) |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | VA | orange | 75.13 (75.78) | 8.91 (9.13) | 7.63 (7.69) | [b] |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | VC | orange | 74.97 (75.78) | 9.18 (9.13) | 7.70 (7.69) | 360 (365) |
| $C(CH_3)_3$ | VIC | white | 65.03 (64.96) | 11.98 (12.16) | 11.51 (11.66) | 239 (240) |
| $(CH_3)_2CH$ | VIIB' | white | 63.70 (63.68) | 12.07 (12.02) | 12.31 (12.38) | 213 (226) |

[a] Solubility too low. [b] Reacts to give isomer C at temperatures >—30° C.

TABLE 2

$^1$H NMR DATA FOR R—N=CH—CH=N—R AND R—N=CH—C($CH_3$)=N—R [a]

| R | Temp. [b] | Solvent | 1 | 2 | 3 |
|---|---|---|---|---|---|
| 4-$ClC_6H_4$ | P.T. | $CDCl_3$ | — | 7.34 | 7.11 |
| 4-$CH_3C_6H_4$ | P.T. | $CDCl_3$ | — | 7.18 | 7.18 |
| 4-$OCH_3C_6H_4$ | P.T. | $CDCl_3$ | — | 7.28 | 6.87 |
| 2,6-$(CH_3)_2C_6H_3$ | P.T. | $CDCl_3$ | — | — | 6.99 |
| 2,4,6-$(CH_3)_3C_6H_2$ | P.T. | $CDCl_3$ | — | — | 6.83 |
| $(CH_3)_3C$ | P.T. | $CDCl_3$ | 1.27 | — | |

| R | Temp. [b] | Solvent | 1 | 1' | 2 | 2' | 3 | 3' |
|---|---|---|---|---|---|---|---|---|
| *$(CH_3)_2CH$(assym.) | P.T. | $CDCl_3$ | 1.21 | 1.21 | 3.86 | 3.51 | — | — |

[a] All values are in ppm relative to TMS. See Fig. 2 for the numbering of the protons. [b] P.T. = Probe Temperature.

$H_2O$ was added to a suspension of IC or IIC in pentane. After 3 h the pentane was removed under vacuum. Subsequently $CH_2Cl_2$ was added to the precipitate and the resulting suspension was filtered. The solvent was removed from the filtrate under vacuum and the resulting white powder 4-$XC_6H_4$—NH—$CH_2$-C($CH_3$)=N—$C_6H_4$X-4 (X = $CH_3$, Cl) was collected (Yield ~90%). The products were identified by $^1$H and $^{13}$C NMR spectroscopy. The products are air-stable as solids and in solution.

*Molecular weight determinations and NMR spectroscopy*

Molecular weights were determined by cryoscopy in benzene (Table 1). $^1$H-NMR spectra were recorded on a Varian A 60 or T 60D spectrometer (Tables 2, 3 and 6). $^{13}$C-NMR spectra were recorded on a Varian CFT 20 or a Bruker WP 80 spectrometer (Tables 4, 5 and 6). Off-resonance $^{13}$C spectra were recorded for all the compounds to assist in assignment of the $^{13}$C spectra.

## Results

*1. Coordination products $(CH_3)_3AlR$—N=CH—CH=N—R (A) (Figs. 2 and 3)*

When the R groups are bulky and the reaction temperature is kept low (—40°C) the complexes A are formed according to:

$$\tfrac{1}{2}[(CH_3)_3Al]_2 + R—N=CH—CH=N—R \xrightarrow{-40°C} (CH_3)_3AlR—N=CH—CH=N—R \quad (A)$$

The products are stable as solids at room temperature, but only below —30°C in solution.

$^1$H and $^{13}$C NMR spectra show that the ligand is coordinated to the metal by a dative bond. The R groups are equivalent, even at —90°C in toluene, and the ratio $(CH_3)_3$Al/ligand is 1/1. The Al—$CH_3$ groups appear as a single resonance —90°C, which shows that no free $[(CH_3)_3Al]_2$ is present in solution. Addition of free ligand to a solution of complex (A) in $C_7D_8$ shows that even at —90°C there is intermolecular exchange between the free ligand and complex (A) which is fast on the NMR time scale.

| 4 | 4' | 5 | 5' | Methyl groups 2 | 2' | 4 | 4' | 5 | 5' | Coupling constants J (Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| — | | 8.27 | | — | | — | | — | | J(2—3) = 8 |
| — | | 8.34 | | — | | 2.34 | | — | | |
| — | | 8.33 | | — | | 3.80 | | — | | J(2—3) = 9 |
| 6.99 | | 8.03 | | 2.14 | | — | | — | | |
| — | | 8.05 | | 2.11 | | 2.23 | | — | | |
| | | 7.92 | | | | | | — | | |
| — | — | | 7.83 | — | — | — | — | | 2.07 | J(1—2) = J(1'—2') = 6—7<br>J(5'—Me(5)) = 0 |

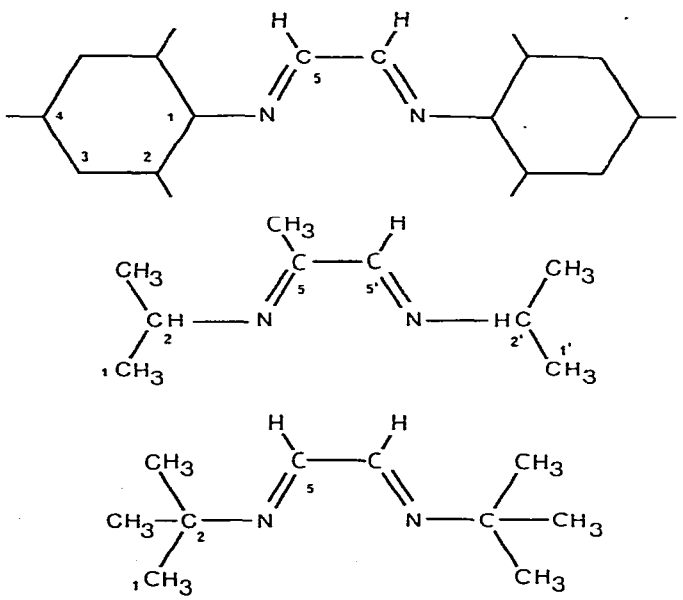
*2. Insertion products $(CH_3)_2Al\overline{R—N—CH(CH_3)—CH=N}—R$ (B) and $(CH_3)_2AlR—N—CH(CH_3)—C(CH_3)=N—R$ (B').*

The complexes B and B' were formed almost quantitatively at 0°C by the reaction:

$$\tfrac{1}{2}[(CH_3)_3Al]_2 + R—N=CH—C(R')=N—R \xrightarrow{0^\circ C} (CH_3)_2AlR—N—CH(CH_3)—C(R')=N—R$$

R = 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-$ClC_6H_4$ ; R' = H (B)

R = $(CH_3)_2CH$ ; R' = $CH_3$ (B')



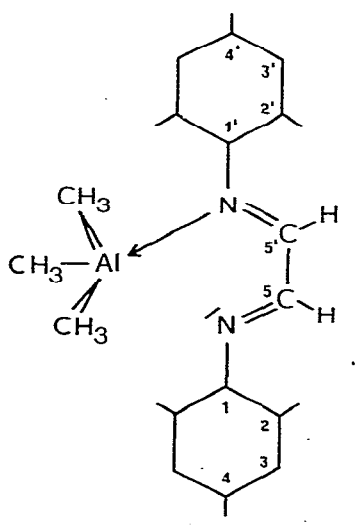



Fig. 2. Structures of some diazabutadienes.

Fig. 3. Structure of isomer A, $(CH_3)_3AlR—N=CH—CH=N—R$ (R = 2,4,6-$(CH_3)_3C_6H_2$).

*(Continued on p. 279)*

TABLE 3

$^1$H NMR DATA FOR $(CH_3)_3AlRN{=}CH{-}CH{=}N{-}R$ (A), $(CH_3)_2AlR{-}N{-}CH(CH_3){-}CH{=}N{-}R$ (B), $(CH_3)_2AlR{-}N{-}CH(CH_3){-}C(CH_3){=}N{-}R$ (B') AND $(CH_3)_2AlR{-}N{-}CH_2{-}C(CH_3){=}N{-}R$ (C)

| Compound (R) | | Temp. (°C) | Solvent | Protons | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 1′ | 2 | 2′ | 3 | 3′ | 4 | 4′ | 5 | 5′ |
| 4-$ClC_6H_4$ | IB | P.T. | $CDCl_3$ | — | — | 7.42 | 7.07 | 7.23 | 6.06 | — | — | 8.30 | 4.62 |
| 4-$ClC_6H_4$ | IC | P.T. | $CDCl_3$ | — | — | 7.07 | 7.07 | 6.06 | 6.06 | — | — | — | 4.15 |
| 4-$CH_3C_6H_4$ | IIB | P.T. | $CDCl_3$ | — | — | 7.33 | 7.05 | 7.33 | 7.58 | — | — | 8.42 | 4.77 |
| 4-$CH_3C_6H_4$ | IIC | P.T. | $CDCl_3$ | — | — | 7.20 | 6.93 | 6.81 | 6.45 | — | — | — | 4.25 |
| 4-$CH_3OC_6H_4$ | IIIB | P.T. | $CDCl_3$ | — | — | 7.29 | 6.77 | 6.89 | 6.47 | — | — | 8.23 | 4.63 |
| 4-$CH_3OC_6H_4$ | IIIC | P.T. | $CDCl_3$ | — | — | 6.98 | 6.86 | 6.98 | 6.57 | — | — | — | 4.28 |
| 2,6-$(CH_3)_2C_6H_3$ | IVA | −50 | $CDCl_3$ | — | — | — | — | 7.25 | 7.25 | 7.25 | 7.25 | 8.57 | 8.57 |
| 2,6-$(CH_3)_2C_6H_3$ | IVC | P.T. | $CDCl_3$ | — | — | — | — | 7.10 | 7.10 | 6.98 | 6.90 | — | 4.37 |
| 2,4,6-$(CH_3)_3C_6H_2$ | VA | −90 | $CH_2Cl_2$ | — | — | — | — | 7.07 | 7.03 | — | — | 8.60br | 8.60br |
| 2,4,6-$(CH_3)_3C_6H_2$ | VA | −60 | $CDCl_3$ | — | — | — | — | 6.95 | 6.95 | — | — | 8.42 | 8.42 |
| 2,4,6-$(CH_3)_3C_6H_2$ | VC | P.T. | $CDCl_3$ | — | — | — | — | 6.93 | 7.00 | — | — | — | 4.37 |
| $(CH_3)_3C$ | VIC | P.T. | $CDCl_3$ | 1.46 | 1.10 | — | — | — | — | — | — | — | 3.90 |
| $(CH_3)_2CH$ | VIIB′ | P.T. | $CDCl_3$ | 1.19 | 1.31 | 3.93 | 3.12 | — | — | — | — | — | 3.98 |

| Compound (R) | | Temp. (°C) | Solvent | Methyl groups | | | | | | | Coupling constants $J$ (Hz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Al Me | 2 | 2′ | 4 | 4′ | 5 | 5′ | |
| 4-$ClC_6H_4$ | IB | P.T. | $CDCl_3$ | −0.64<br>−0.70 | — | — | — | — | — | 1.42 | $J(2{-}3) = J(2'{-}3') = 8$<br>$J(5'{-}Me(5')) = 7$ |
| 4-$ClC_6H_4$ | IC | P.T. | $CDCl_3$ | −0.79 | — | — | — | — | 2.03 | — | $J(2{-}3) = J(2'{-}3') = 8$ |
| 4-$CH_3C_6H_4$ | IIB | P.T. | $CDCl_3$ | −0.63<br>−0.68 | — | — | 2.43 | 2.27 | — | 1.48 | $J(2{-}3) = 0$ $J(2'{-}3') = 8$<br>$J(5'{-}Me(5')) = 7$ |
| 4-$CH_3C_6H_4$ | IIC | P.T. | $CDCl_3$ | −0.77 | — | — | 2.36 | 2.20 | 2.03 | — | $J(2{-}3) = J(2'{-}3') = 8$ |
| 4-$CH_3OC_6H_4$ | IIIB | P.T. | $CDCl_3$ | −0.60<br>−0.65 | — | — | 3.80 | 3.76 | — | 1.40 | $J(2{-}3) = J(2'{-}3') = 9$<br>$J(5')-Me(5')) = 7$ |
| 4-$CH_3OC_6H_4$ | IIIC | P.T. | $CDCl_3$ | −0.78 | — | — | 3.83 | 3.76 | 2.08 | — | $J(2{-}3) = 0$ $J(2'{-}3') = 9$ |
| 2,6-$(CH_3)_2C_6H_3$ | IVA | −50 | $CDCl_3$ | −0.90 | 2.27 | 2.27 | — | — | — | — | — |
| 2,6-$(CH_3)_2C_6H_3$ | IVC | P.T. | $CDCl_3$ | −0.88 | 2.17 | 2.33 | — | — | 1.83 | — | $J(5'{-}Me(5)) = 0.7$ |
| 2,4,6-$(CH_3)_3C_6H_2$ | VA | −90 | $CH_2Cl_2$ | −0.99 | 2.22 | 2.22 | 2.35 | 2.35 | — | — | — |
| 2,4,6-$(CH_3)_3C_6H_2$ | VA | −60 | $CDCl_3$ | −1.0 | 2.20 | 2.20 | 2.27 | 2.27 | — | — | — |
| 2,4,6-$(CH_3)_3C_6H_2$ | VC | P.T. | $CDCl_3$ | −0.86 | 2.18 | 2.18 | 2.35 | 2.35 | 1.84 | — | $J(5'{-}Me(5)) = 0.7$ |
| $(CH_3)_3C$ | VIC | P.T. | $CDCl_3$ | −0.80 | — | — | — | — | 2.20 | — | $J(5'{-}Me(5)) = 0.7$ |
| $(CH_3)_2CH$ | VIIB′ | P.T. | $CDCl_3$ | −0.80<br>−0.88 | — | — | — | — | 2.10 | 0.94 | $J(1{-}2) = J(1'{-}2') = 7$<br>$J(5'{-}Me(5')) = 6$ |

All values are in ppm relative to TMS. See Figs. 3, 4 and 5 for the numbering of the protons.

TABLE 4

$^{13}C$ NMR DATA FOR R—N=CH—CH=N—R AND R—N=CH—C($CH_3$)=N—R*

| R | Temp. (°C) | Solvent | 1 | 1′ | 2 | 2′ | 3 | 4 | 5 | 5′ | Methyl groups | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | 2 | 4 | 5 |
| 4-$ClC_6H_4$ | P.T. | $CDCl_3$ | 148.31 | | 122.39 | | 129.42 | 133.59 | 159.64 | | — | — | — |
| 4-$CH_3C_6H_4$ | P.T. | $CDCl_3$ | 147.40 | | 121.00 | | 129.66 | 137.65 | 158.73 | | — | 20.88 | — |
| 4-$OCH_3C_6H_4$ | P.T. | $CDCl_3$ | 142.92 | | 122.75 | | 114.46 | 159.58 | 157.34 | | — | 55.34 | — |
| 2,6-$(CH_3)_2C_6H_3$ | P.T. | $CDCl_3$ | 149.71 | | 124.51 | | 128.08 | 126.14 | 163.15 | | 18.04 | — | — |
| 2,6-$(CH_3)_2C_6H_3$ | −50 | $CDCl_3$ | 149.21 | | 124.56 | | 127.98 | 126.25 | 163.25 | | 18.28 | — | — |
| 2,4,6-$(CH_3)_3C_6H_2$ | P.T. | $CDCl_3$ | 147.28 | | 126.21 | | 128.75 | 133.84 | 163.15 | | 17.97 | 20.52 | — |
| $(CH_3)_3C$ | P.T. | $CDCl_3$ | 28.64 | | 57.28 | | — | — | 157.10 | | — | — | — |
| | | | 1 | 1′ | 2 | 2′ | | | 5 | 5′ | | | 5 |
| *$(CH_3)_2CH$(assym.) | P.T. | $CDCl_3$ | 23.61 | 23.00 | 60.37 | 51.16 | | | 161.88 | 164.30 | | | 12.60 |

All values are in ppm relative to TMS. See Fig. 2 for the numbering of the carbon atoms.

TABLE 5

$^{13}C$ NMR DATA FOR $(CH_3)_3AlR{-}N{=}CH{-}CH{=}N{-}R$ (A), $(CH_3)_2AlR{-}N{-}CH(CH_3){-}CH{=}N{-}R$ (B), $(CH_3)_2AlR{-}N{-}CH(CH_3){-}C(CH_3){=}N{-}R$ (B') AND $(CH_3)_2AlR{-}N{-}CH_2{-}C(CH_3){=}N{-}R$ (C)

| Compound (R) | | Temp. (°C) | Solvent | Carbon atoms | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 1' | 2 | 2' | 3 | 3' | 4 | 4' | 5 | 5' |
| $4\text{-}ClC_6H_4$ | (IB) | −40 | $CDCl_3$ | 148.84 | 140.73 | 122.59 | 130.04 | 128.86 | 114.38 | 134.98 | 118.33 | 178.76 | 56.45 |
| $4\text{-}ClC_6H_4$ [a] | (IC) | — | — | — | — | — | — | — | — | — | — | — | — |
| $4\text{-}CH_3C_6H_4$ | (IIB) | −40 | $CDCl_3$ | 147.98 | 139.96 | 121.02 | 130.29 | 129.66 | 113.26 | 139.26 | 121.89 | 177.46 | 56.18 |
| $4\text{-}CH_3C_6H_4$ | (IIC) | −10 | $CDCl_3$ | 149.39 | 139.19 | 121.99 | 130.16 | 129.73 | 112.71 | 137.25 | 122.95 | 187.17 | 57.41 |
| $4\text{-}CH_3OC_6H_4$ | (IIIB) | −40 | $CDCl_3$ | 145.38 | 135.19 | 122.41 | 113.50 | 114.56 | 115.89 | 159.59 | 148.13 | 175.78 | 57.35 |
| $4\text{-}CH_3OC_6H_4$ [b] | (IIIC) | 25 | $CDCl_3$ | — | — | — | — | — | — | — | — | 187.09 | 57.22 |
| $2,6\text{-}(CH_3)_2C_6H_3$ | (IVA) | −50 | $CDCl_3$ | 147.38 | 147.38 | 127.36 | 127.36 | 128.28 | 128.28 | 126.69 | 126.69 | 164.77 | 164.77 |
| $2,6\text{-}(CH_2)_2C_6H_3$ | (IVC) | −40 | $CDCl_3$ | 148.30 | 140.07 | 129.63 | 137.99 | 128.65 | 127.73 | 126.53 | 122.79 | 190.24 | 61.37 |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | (VA) | −55 | $CDCl_3$ | 145.01 | 145.01 | 127.68 | 127.68 | 128.96 | 128.96 | 136.53 | 136.53 | 164.59 | 164.59 |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | (VC) | P.T. | $CDCl_3$ | 145.44 | 137.44 | 129.31 | 137.88 | 128.41 | 129.31 | 132.33 | 136.84 | 190.84 | 61.59 |
| $(CH_3)_3C$ | (VIC) | P.T. | $CDCl_3$ | 29.77 | 29.77 | 59.79 | 49.79 | — | — | — | — | 186.03 | 57.48 |
| $(CH_3)_2CH$ | (VIIB') | −40 | $CDCl_3$ | 22.09 | 22.34 | 62.44 | 50.52 | — | — | — | — | 188.84 | 44.19 |

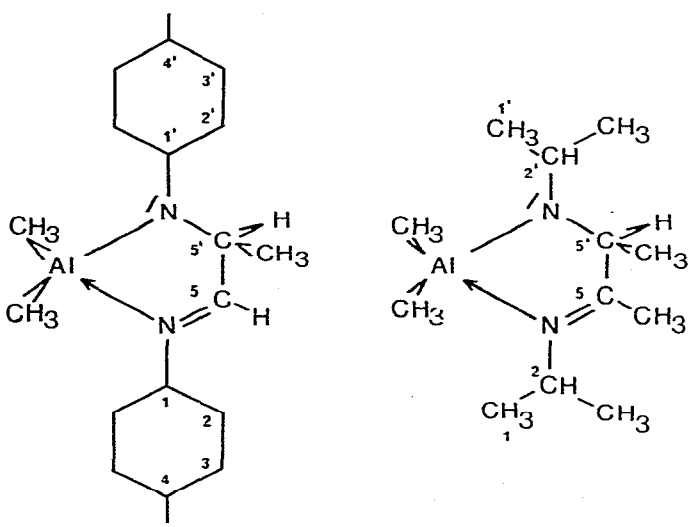
| | | | | Methyl groups | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Al Me | 2 | 2' | 4 | 4' | 5 | 5' |
| $4\text{-}ClC_6H_4$ | (IB) | −40 | $CDCl_3$ | −7.83<br>−10.21 | — | — | — | — | | 16.28 |
| $4\text{-}ClC_6H_4$ [a] | (IC) | — | — | — | — | — | — | — | — | — |
| $4\text{-}CH_3C_6H_4$ | (IIB) | −40 | $CDCl_3$ | −7.93<br>−10.07 | — | — | 21.07 | 20.19 | | 16.47 |
| $4\text{-}CH_3C_6H_4$ | (IIC) | −10 | $CDCl_3$ | −10.08 | — | — | 20.81 | 20.12 | 18.34 | — |
| $4\text{-}CH_3OC_6H_4$ | (IIIB) | −40 | $CDCl_3$ | −7.73<br>−10.00 | — | — | 55.37 | 56.23 | — | 16.49 |
| $4\text{-}CH_3OC_6H_4$ [b] | (IIIC) | 25 | $CDCl_3$ | −9.96 | — | — | 55.34 | 57.66 | 18.58 | — |
| $2,6\text{-}(CH_3)_2C_6H_3$ | (IVA) | −50 | $CDCl_3$ | −6.66 | 18.54 | 18.54 | — | — | — | — |
| $2,6\text{-}(CH_2)_2C_6H_3$ | (IVC) | −40 | $CDCl_3$ | −7.49 | 18.55 | 17.87 | — | — | 18.16 | — |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | (VA) | −55 | $CDCl_3$ | −6.75 | 18.60 | 18.60 | 20.82 | 20.82 | — | — |
| $2,4,6\text{-}(CH_3)_3C_6H_2$ | (VC) | P.T. | $CDCl_3$ | −7.50 | 17.76 | 18.42 | 20.74 | 20.74 | 18.12 | — |
| $(CH_3)_3C$ | (VIC) | P.T. | $CDCl_3$ | −4.32 | — | — | — | — | 20.93 | — |
| $(CH_3)_2CH$ | (VIIB') | −40 | $CDCl_3$ | −5.44 | — | — | — | — | 17.20 | 17.97 |

All values are in ppm relative to TMS. See Figs. 3, 4 and 5 for the numbering of the carbon atoms. [a] Solubility too low. [b] Broadening of some of the resonances made a complete assignment impossible.

The NMR data show that the groups R in isomer B and B′ are inequivalent. $^1$H NMR of isomer B shows only one N=CH proton at 8—9 ppm, while a quartet of one hydrogen atom at 4—5 ppm and a doublet of three hydrogen atoms at about 1.4 ppm are present. This pattern is compatible with the formation of a —N—CH($CH_3$)—CH=N—fragment. $^1$H NMR of isomer B′ shows that the N=CH proton has disappeared, while a quartet of one hydrogen atom at 4—5 ppm and a doublet of three hydrogen atoms at about 1.4 ppm have appeared. $^{13}$C NMR shows that a N=C bond is still present. The presence of a N—CH($CH_3$)—C($CH_3$)=N fragment in isomer B′ could account for these spectroscopic data. This information, together with the monomeric nature of both isomer B and B′ and the observation that the products do not react with coordinating solvents such as ether, leads to the structures shown in Fig. 4.
The nonequivalence of the Al—$CH_3$ groups and the R groups is caused by the presence of the chiral —CH($CH_3$)—fragment in the chelate ring. Broadening of the Al—C resonances in $^{13}$C NMR shows that the structure is not rigid.

*3. Rearrangement products* $(CH_3)_2Al\overline{R—N=CH_2—C(CH_3)=N—R}$ *(C)*

Isomer C is formed from a solution of isomer A or B in toluene. The isomerization also takes place in other solvents such as $CH_2Cl_2$ and $CHCl_3$. The rate of the reaction B → C at 30° C increases in the order: R = 4-$ClC_6H_4$ < 4-$CH_3C_6H_4$ < 4-$CH_3OC_6H_4$. For R = 2,6-$(CH_3)_2C_6H_3$ and 2,4,6-$(CH_3)_3C_6H_2$ isomer C is directly formed from the coordination product A without the intermediate formation of a stable isomer B, as was shown by following the change in the $^1$H NMR spectrum with time at —20° C. The rate of the reaction A → C at —20° C increases



ISOMER B ISOMER B'

Fig. 4. Structures of isomers B and B′.

TABLE 6

$^1H$ AND $^{13}C$ NMR DATA FOR R—NH—$CH_2$—$C(CH_3)$=NR

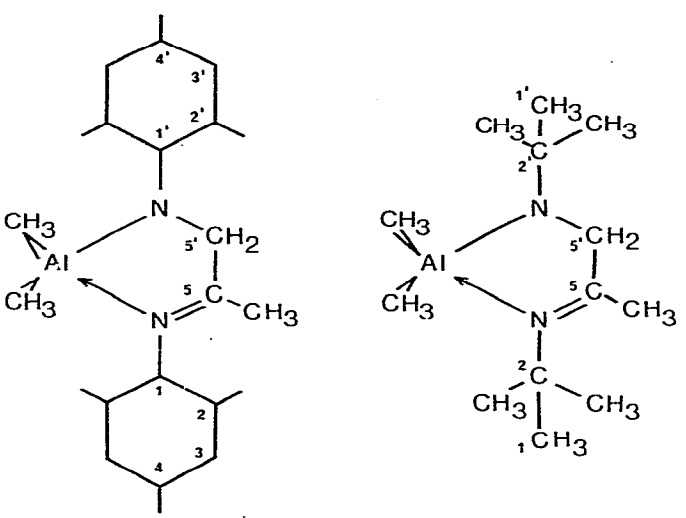
| Compound (R) | | Temp. | Solvent | 1 | 1′ | 2 | 2′ | 3 | 3′ |
|---|---|---|---|---|---|---|---|---|---|
| 4-$CH_3C_6H_4$ | ($^1H$) | P.T. | $CDCl_3$ | — | — | [ 6.4 | — | 7.4 | ] |
| 4-$CH_3C_6H_4$ | ($^{13}C$) | P.T. | $CDCl_3$ | 147.76 | 145.32 | 119.26 | 129.62 | 129.39 | 112.86 |
| 4-$ClC_6H_4$ | ($^1H$) | P.T. | $CDCl_3$ | — | — | [ 6.4 | — | 7.4 | ] |
| 4-$ClC_6H_4$ | ($^{13}C$) | P.T. | $CDCl_3$ | 148.69 | 145.96 | 120.77 | 129.03 | 129.03 | 113.80 |

The numbering of the atoms is the same as for complex C (see Fig. 5). All values are in ppm relative to TMS.

with R = 2,6-$(CH_3)_2C_6H_3$ < 2,4,6-$(CH_3)_3C_6H_2$. Finally, for R = $(CH_3)_3C$ the isomerization takes place even in the solid state at —20°C.

NMR data for isomer C show that the R groups are nonequivalent. In the $^1H$ NMR spectrum the N=CH hydrogen atom found in isomer A or B has disappeared together with the quartet at 4—5 ppm of isomer B, while a broad resonance of two hydrogen atoms at about 4 ppm has appeared. In some cases (VC and VIC) this resonance could be resolved into a quartet with $J$ 0.7 Hz. In these cases the resonance at 2 ppm (three hydrogen atoms) appeared to be a triplet with the same coupling constant. On the other hand the $^{13}C$ spectra show that a N=C carbon atom at about 180 ppm is still present.

These data indicate the formation of a R—N—$CH_2$—$C(CH_3)$=N—R fragment. Further evidence for this structure is provided by the hydrolysis products obtained from the reaction of isomer C with $H_2O$. The $^1H$ and $^{13}C$ NMR spectra




ISOMER C

Fig. 5. Structures of isomers C.

| 4 | 4′ | 5 | 5′ | NH | Methyl groups | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 2 | 2′ | 4 | 4′ | 5 | 5′ |
| — | — | — | 3.94 | 4.90 | — | — | 2.30 | 2.23 | 1.87 | — |
| 132.69 | 126.22 | 166.68 | 51.80 | — | — | — | 20.63 | 20.21 | 18.13 | — |
| — | — | — | 3.90 | 5.00 | — | — | — | — | 1.84 | — |
| 129.63 | 114.40 | 167.26 | 51.23 | — | — | — | — | — | 18.21 | — |

of these hydrolysis products are consistent with the structure R—NH—$CH_2$—$C(CH_3)$=NR (Table 6). From this information, combined with the measured molecular weights (monomeric) and the observation that coordinating solvents such as ether do not react with C, it can be concluded that the structure of C is as depicted in Figure 5.

## Discussion

The novel reaction of $[Al(CH_3)_3]_2$ with R—N=CH—CH=N—R affords the addition compound $(CH_3)_3$AlR—N=CH—CH=N—R (A), which can subsequently rearrange intramolecularly to give $(CH_3)_2\overline{AlR—N—CH_2—C(CH_3)=N}$—R (C) via $(CH_3)_2\overline{AlR—N—CH(CH_3)—CH=N}$—R (B).

There are three possibilities for the structure of isomer A which can account for the observed equivalence of the R groups in the $^1$H NMR spectra in the temperature range measured: i) a structure in which the ligand acts as a *N,N*-chelate with a four electron-three center bond; ii) a structure in which the ligand coordinates to the metal by means of its conjugated $\pi$-system; iii) a structure in which the ligand is coordinated to the metal by only one $\sigma(N)$ dative bond with equivalence caused by a rapid ligand exchange.

We prefer the third possibility for the following reasons: Firstly, $\sigma(N)$ coordination results in the formation of a strong Al—N bond, as can be seen, for example from the stability of the complexes $(CH_3)_3$Al NRR′R″ [11]. Furthermore, the ligand exchange was in fact found in the form of an intermolecular exchange between the free ligand and A. Finally structure A would explain why only one N=C double bond is reduced in the reaction which converts A to B.

Unlike the structure of isomer A, the structures of isomer B and C could be established unambiguously on basis of NMR and molecular weight data. The following reaction path is tentatively proposed for their formation:

Rotation of the $(CH_3)_3$Al fragment around the Al—N bond brings one of the Al—$CH_3$ methyl groups in the proximity of the N$p_\pi$ orbital at the non-coordinated end of the molecule. CNDO/s calculations show [12] that this results in a strong bonding interaction between the non-coordinated nitrogen atom and both the aluminium and the Al—$CH_3$ carbon atoms. At the same time the Al—C bond is drastically weakened. Subsequently, isomer B is formed by migration of the methyl group to the N—C carbon atom and formation of the Al—N bond.

The subsequent rearrangement B → C is suggested to involve a concerted reaction process initiated by attack of the metal on the N=C $\pi$ bond, which will

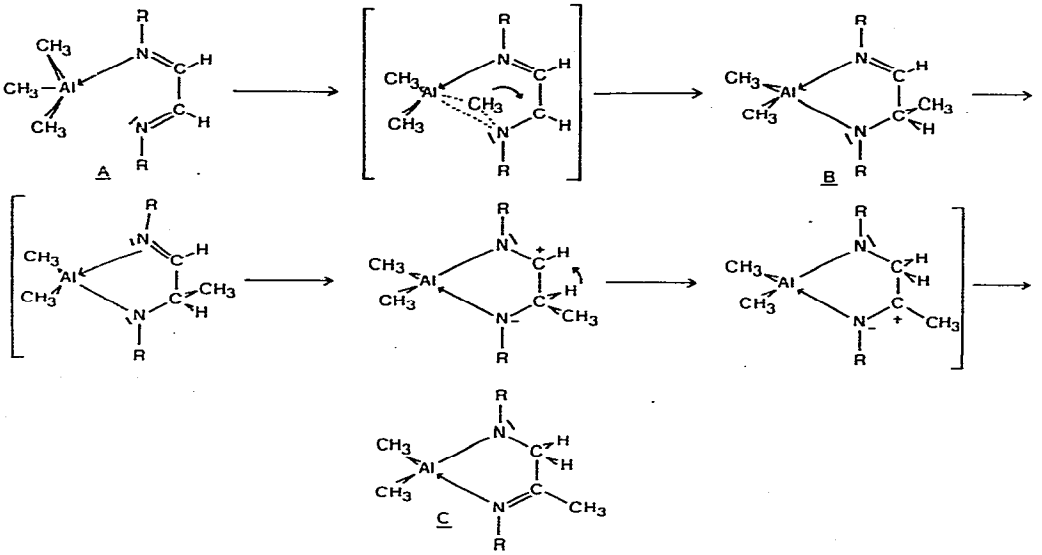


Fig. 6. Proposed mechanism for the reaction A → B → C.

be the most reactive end of the molecule. An Al—N bond is thus formed at this end of the molecule and this induces an excess of electron density on the metal, which is passed on to the nitrogen atom on the other side of the molecule. The resulting polarisation of the ligand induces a $H^-$ migration, after which isomer C is formed.

This mechanism accounts for the observed order of the rate of the reaction B → C in terms of Frontier Orbital Theory [10]. Introduction of an electron donating group into the R groups of the ligand will increase the energy of the N=C $\pi$ orbital (HOMO) relative to the empty Al $sp^3$ orbital (LUMO). As a result the activation energy for the attack of the Al atom on the N=C bond will be lowered, with an increase in the rate of reaction. This mechanism also explains why in the case of isomer B' no different rearrangement product is found because in this case the process is regenerative.

The observation that bulky R groups stabilize isomer A and at the same time destabilize isomer B, can be explained by the increase in energy of isomer B caused by steric hindrance from the R groups on the N—$CH(CH_3)$ methyl group *.

An interesting consequence of this novel aluminium-diazabutadiene chemistry is the possibility of producing, in quantitative yield, wholly novel iminoamino

* The reaction of $[CpMo(CO)_2NN']Cl$ (NN' = 2-pyridinecarbaldehyde) with methyllithium in THF at 65° C gives two neutral products with the general formula $CpMo(CO)_2L$, in which L is either (RHN)(2-py)$(CH_3)$C— or (RHN)(2-py)HC—. The formation of the former product formally involves H/methyl exchange at the azomethyne carbon atom and formation of new N—H and Mo—C bonds [13]. On the basis of the present results the H/methyl exchange and NH bond formation could also be accounted for by a proton shift and concomitant Mo—N bond cleavage and Mo—C bond formation.

compounds, according to the reaction:

$$(CH_3)_3Al + R{-}N{=}CH{-}CH{=}N{-}R \rightarrow (CH_3)_2\overline{AlR{-}N{-}CH(CH_3){-}CH{=}N{-}R} \rightarrow$$

$$(CH_3)_2\overline{AlR{-}N{-}CH_2{-}C(CH_3){=}N{-}R} \xrightarrow{3\,H_2O} Al(OH)_3 + 2\,CH_4$$

$$+ R{-}NH{-}CH_2{-}C(CH_3){=}N{-}R$$

To our knowledge such organic compounds are unknown.

The use of the reported aluminium compounds for the synthesis of other metal iminoamino compounds by ligand exchange is currently being explored in our laboratory e.g.:

$$(CH_3)_2AlR{-}N{-}CH(CH_3){-}CH{=}N{-}R + HgCl_2 \rightarrow Me_2Hg$$

$$+ Cl_2AlRN{-}CH(CH_3){-}CH{=}N{-}R \xrightarrow[-AlCl_3]{MCl_n} Cl_{n-1}M(R{-}N{-}CH(CH_3){-}CH{=}N{-}R)$$

## Acknowledgement

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