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REGIOSELECTIVE ETHYL TRANSFER REACTIONS BETWEEN DIETHYLZINC AND 1,4-DIALKYL-1,4-DIAZA-1,3-BUTADIENES: SYNTHESIS OF Et$\overline{\text{Zn[R(Et)NCH=CHN}}$R]

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Summary

The 1/1 reaction of diethylzinc with 1,4-dialkyl-1,4-diaza-1,3-butadienes (R-DAB = R—N=C(R′)—C(R′)=N—R) below —50°C results in formation of the 1/1 complex Et_2Zn(R-DAB) (R = alkyl), containing σ,σ-N,N′ chelate bonded R-DAB. Above —50°C these complexes are unstable and undergo selective transfer of an ethyl group from Zn to the adjacent N atom, thus producing the novel species Et$\overline{\text{Zn[R(Et)NCR′=CR′N}}$R] in quantitative yield. The proposed monomeric structure consists of a three-coordinate zinc atom bound to a 1-amino-2-amidoethylene mono-anionic ligand via the N atoms. Reaction of these zinc complexes with t-BuOH(D) affords an equilibrium mixture of the ene-diamine and the 1-amino-2-iminoethane tautomers, which upon reaction with diethylzinc re-forms the Et$\overline{\text{Zn[R(Et)NCR′=CR′N}}$R] compound. The tautomer equilibrium is dependent on the nature of R and R′. Branching at C^β in R shifts the equilibrium towards the 1-amino-2-iminoethane tautomer, while introduction of an Me(R′) group stabilizes the ene-diamine tautomer.

Introduction

The 1,4-diaza-1,3-butadiene ligand, RN=C(R′)—C(R′)=NR **, has a versatile coordination chemistry. This is due to the fact that the R-DAB molecule can act not only as a σ-N but also as a η^2-C=N donor ligand. Accordingly, metal-R-DAB complexes have been isolated in which the R-DAB ligand is bonded as either a two-, four-, six- or eight-electron donating ligand [1].

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** Abbreviated as R-DAB.

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Reactions between the R-DAB ligands and organometallic species containing reactive M—C bonds are particularly interesting because after complex formation, reaction of the M—C bond with one or both C=N bonds may occur. The latter type of bond has been shown to be highly susceptible to addition reactions [2].

In general, reactions of organolithium and organomagnesium reagents with 1,4-diaza-1,3-butadiene ligands proceed with low selectivity and so give intractable product mixtures. However, the reactions of trimethylaluminium dimer with R-DAB ligands initially give the 1/1 complex $Me_3Al(RN{=}CR'CR'{=}NR)$, which subsequently undergoes a selective addition leading to quantitative formation of $\overline{Me_2Al\{N(R)CR'(Me)CR'{=}N}R\}$ [3,4]. This novel type of 1-imino-2-amidoethane-metal complex results from the selective reduction of one of the C=N bonds in the N=C—C=N skeleton to a C—N bond, with transfer of the R group from aluminium to carbon [3].

Recently we found that in the reaction of diethylzinc with R-DAB one of the ethyl groups bound to zinc is not transferred to carbon but to nitrogen, leading to 1-amino-2-amidoethylene-metal complexes [5]. In particular the observation of this completely opposite regioselectivity in the reactions of 1,4-diaza-1,3-butadienes with Al and Zn derivatives prompted us to investigate the organozinc chemistry further.

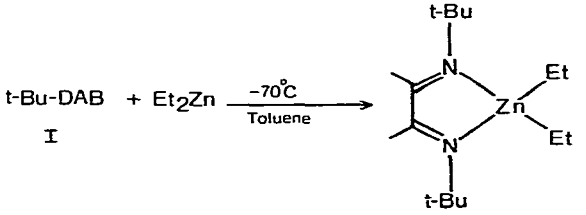
In this paper we describe the synthesis and characterization of the ethylzinc derivatives obtained from the reactions of diethylzinc with 1,4-dialkyl-1,4-diaza-1,3-butadienes. In a forthcoming paper the results of a study into the detail of the mechanism of the ethyl transfer from zinc to the nitrogen atom of a σ-N coordinated C=N bond will be described [6].

Results

Synthesis

The reactions of Et_2Zn with the 1,4-dialkyl-1,4-diaza-1,3-butadienes I—VII (see Experimental) follow a very distinct reaction course in which product formation at each step is almost quantitative. As a representative example the 1/1 molar reaction of Et_2Zn with t-Bu-DAB will be described.

When Et_2Zn and t-Bu-DAB are mixed in a 1/1 molar ratio in toluene at —70°C only one product (Ia) is formed, and this, according to the ^1H NMR spectra, has an 1/1 Et_2Zn to t-Bu-DAB stoichiometry (see eqn. 1). The observation that both the t-Bu protons and the imine protons appear in these spectra as singlets (1.20 and 7.50 ppm, respectively) indicates that the t-Bu-DAB ligand is σ,σ-N,N' chelate bonded, and thus we propose a tetrahedral coordination geometry at the zinc atom.



I

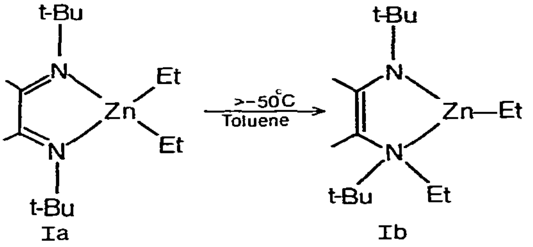
Ia

eqn-1

Like the other 1/1 complexes IIa—VIIa, Ia is thermally unstable, and no attempts have been undertaken to isolate any of these complexes. All the complexes are very soluble in toluene, but in n-pentane they separate as orange red solids.

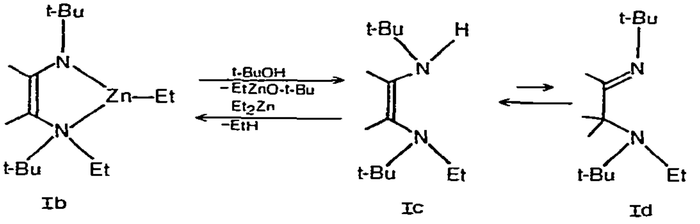
When the red toluene solution containing Ia is gradually warmed a sharp colour change occurs at about —50°C, indicating further reaction. The ^1H NMR spectra showed that a new organozinc species (Ib) had been formed in almost quantitative yield (>98%). When Et_2Zn and t-Bu-DAB were brought into direct reaction at room temperature a mixture with essentially the same ^1H and ^{13}C NMR spectra was obtained. In fact, since this reaction is quantitative, it is possible to use it for the determination of the concentration of solutions of Et_2Zn in hydrocarbons (see Experimental).

The compounds obtained from the reactions of diethylzinc with the R-DAB ligands with the smaller alkyl groups (i.e. Ib, IIb and VIIb) were distillable oils. All the compounds Ib—VIIb are extremely sensitive towards air and moisture. The ^1H and ^{13}C NMR spectra of Ib—VIIb were in accord with the 1-amino-2-amidoethylene-zinc structure (shown for Ib in eqn. 2) arising from transfer of one ethyl group from Zn to a coordinated N atom within the 1/1 complex (Ia—VIIa).



eqn-2

Careful protonolysis of pentane solutions of Ib—VIIb with t-BuOH (1/1 organozinc/t-BuOH molar ratio) gives the corresponding ene-diamine compounds Ic—VIIc, which are in equilibrium with their respective tautomers, the imine-amine compounds Id—VIId, see eqn. 3.



eqn 3

It is important to note that the organozinc compounds Ib—VIIb can be reformed quantitatively from these tautomer mixtures by treatment with diethylzinc, as indicated for Ic and Id in eqn. 3.

Structure of $Et\overline{ZnN(R)C(R'')=C(R')N}(R)Et$ *(Ib—VIIb) in solution*

The ^1H and ^{13}C NMR spectra of Ib—VIIb (see Tables 1 and 2) are in agreement with structures consisting of an EtZn entity coordinated to a *cis*-RNC-(R″)=C(R′)N(R)Et, potentially bidentate, monoanion. A representative exam-

TABLE 1

^{1}H NMR DATA FOR Et$\overline{\text{ZnN(R)C(R}'')\text{=C(R}')\text{N}}$(R)Et, Ib—VIIb [a, b, c]

Compound (R)			H_A [d]	H_B [d]	H(R′)	H(R″)	R
R=C(CH$_3$)$_3$	R′ = R″ = H	Ib	2.05(m)	2.95(m)	4.05(d) [e]	6.85(d) [e]	C(CH$_3$)$_3$ 1.15(s), C(CH$_3$)$_3$ 1.25(s)
R=CH(CH$_3$)$_2$	R′ = R″ = H	IIb	2.20(m)	2.55(m)	3.85(d) [e]	6.64(d) [e]	C*H*(CH$_3$)$_2$ 2.80(m) and 3.30(m), CH(C*H*$_3$)$_2$ 1.15(d), CH(C*H*$_3$)$_2$ 0.8(d) and 1.10(d)
R=CH$_2$C(CH$_3$)$_3$	R′ = R″ = H	IIIb	2.09(m)	2.66(m)	3.73(d) [e]	6.31(d) [e]	C*H*$_2$C(CH$_3$)$_3$ 2.98(s), C*H*$_2$C(CH$_3$)$_3$ 2.10 and 2.48 ^2J(HH) 13.5 Hz, CH$_2$C(C*H*$_3$)$_3$ 0.92(s) and 1.00(s)
R=c-C$_6$H$_{11}$	R′ = R″ = H	IVb	2.29(m)	2.63(m)	3.97(d) [e]	6.70(d) [e]	NC*H*(CH$_2$)$_5$ 2.45(m) and 2.85(m)
R=CH(CH(CH$_3$)$_2$)$_2$	R′ = R″ = H	Vb	2.28(m)	2.75(m)	4.03(d) [e]	6.33(d) [e]	Broad signals between 0.5 and 2.3 ppm
R=c-C$_6$H$_{11}$	R′ = R″ = CH$_3$	VIb	2.14(m)	2.91(m)	1.47(s)	1.85(s)	NC*H*(CH$_2$)$_5$ 2.30(m) and 3.20(m)
R=CH(CH$_3$)$_2$	R′ = H R″ = CH$_3$	VIIb	2.30(m)	2.56(m)	3.72(q) [f]	1.78(d) [f]	C*H*(CH$_3$)$_2$ 2.80(m) and 3.55(m), CH(CH$_3$)$_2$ complex multiplets 0.8—1.30 ppm

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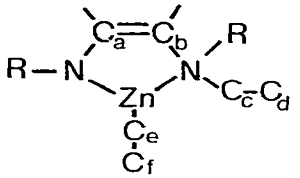
[a] All values are in ppm relative to TMS internal, in C$_6$D$_6$ solvent at ambient temperature. [b] For all compounds the signal for the CH$_3$ group in NCH$_2$CH$_3$ was observed as a triplet at about 1.0 ppm; [c] The CH$_2$ group in ZnCH$_2$CH$_3$ was observed as a multiplet at about 0.6 ppm and the CH$_3$ group as a triplet at about 1.45 ppm. [d] The diastereotopic protons in the NC*H*$_2$CH$_3$ group are labelled H_A and H_B. [e] ^3J(HH) 5 Hz. [f] ^4J(HH) 1.5 Hz.

TABLE 2

^{13}C NMR DATA FOR $\mathrm{Et\overline{ZnN(R)C(H)=C(H)N}(R)Et}$, R = $\mathrm{C(CH_3)_3}$ (Ib) AND R = $\mathrm{CH(CH_3)_2}$ (IIb) [a]



Compound	C_a	C_b	C_c	C_d	C_e	C_f	R
Ib	143.98(d)	97.66(d)	44.61(t)	11.98(q)	2.88(t)	12.39(q)	two different $\mathrm{C(CH_3)_3}$ groups; $\mathit{C}\mathrm{(CH_3)_3}$ 51.51(s) and 58.77(s), $\mathrm{C(\mathit{C}H_3)_3}$ 25.94 (q) and 32.90(q).
IIb	148.39(d)	95.56(d)	49.93(t)	11.63(q)	0.17(t)	12.31(q)	two different $\mathrm{CH(CH_3)_2}$ groups; $\mathit{C}\mathrm{H(CH_3)_2}$ 52.36(d) and 56.94(d), $\mathrm{CH(\mathit{C}H_3)_2}$ 27.65(q) (not diastereotopic); 16.19(q) and 20.08(q) (diastereotopic).

[a] All values are in ppm relative to internal TMS, in C_6D_6 at ambient temperature. Multiplicity, obtained from off-resonance spectra, between parentheses.

ple of an observed ^{1}H NMR spectrum is shown in Fig. 1a.

In contrast to the isochronous t-Bu and imine H resonances in symmetric $\mathrm{Et_2Zn}$(t-Bu-DAB), Ia, the t-Bu- and imine-H resonances in Ib are clearly anisochronous, reflecting the asymmetry within the mono-anionic ligand. The resonances of hydrogen atoms connected to the C atoms of the N—C=C—N skeleton are shifted from the low field region, which is characteristic for imine-H resonances, to the region for H atoms of the olefinic type. The asymmetry in the ligand system gives rise to an AX pattern for these two protons with a ^3J(HH) of ca. 5 Hz, a value which is consistent with *cis* olefinic H atoms [7]. In the compound containing i-PrNC=C(Me)N(Et)i-Pr, VIIb, only one olefinic proton is observed, with a ^4J(HH) of 1.5 Hz, a typical value for an allylic system [7]. The ^{13}C NMR spectra of Ib and IIb each show two different olefinic carbon atoms at ca. 145 and ca. 95 ppm (see Table 2).

Each of the organozinc compounds Ib—VIIb contains one tetrahedral and one trigonal N centre. The tetrahedral N atom, containing the transferred Et group, is a stable chiral centre since coordination of this N atom to Zn prevents the occurrence of pyramidal inversion. As a consequence the ^{1}H resonances of the ethyl-$\mathrm{CH_2}$ groups bonded to this N centre give rise to a complex $\mathrm{ABX_3}$ pattern that was unambiguously characterised by the observation of invariant coupling constant values obtained from NMR spectra recorded at different field strengths. The calculated and observed spectra for these protons in Ib are shown in Fig. 1b.

TABLE 3

^{1}H NMR DATA FOR HN(R)C(R″)=C(R′)N(R)Et, Ic—VIIc [a]

Compound		Relative abundance (%) [g]	H(R′)	H(R″)	N*H*	$\mathrm{NC}H_2\mathrm{CH}_3$ [b]	R
R = $C(CH_3)_3$ R′ = R″ = H	Ic	86	4.40(d) [c]	5.80(d of d) [c, d]	4.1(d)	2.40(q)	$C(CH_3)_3$ 1.00(s) and 1.04(s)
R = $CH(CH_3)_2$ R′ = R″ = H	IIc	78	4.40(d) [c]	5.60(d of d) [c, d]	3.8(m)	2.45(q)	$CH(CH_3)_2$ 2.80(m) and 3.10(m), $CH(CH_3)_2$ multiplets at 0.8/1.2
R = $CH_2C(CH_3)_3$ R′ = R″ = H	IIIc	59	4.45(d) [c]	5.35(d of d) [c, d]	3.8(m)	2.60(q)	$CH_2C(CH_3)_3$ 2.10(s) and 2.50(d) [e], $CH_2C(CH_3)_3$ multiplets at 1 ppm.
R = c-C_6H_{11} R′ = R″ = H	IVc	29	4.45(d) [c]	5.70(d of d) [c, d]	3.9 (d of d)	2.55(q)	c-C_6H_{11} complex multiplets 1.0—2.5 ppm
R = $CH(CH(CH_3)_2)_2$ R′ = R″ = H	Vc	78	4.60(d) [c]	5.30(d of d) [c, d]	3.5(m)	2.65(q)	$CH(CH(CH_3)_2)_2$ complex multiplets 1.0—2.5 ppm
R = c-C_6H_{11} R′ = R″ = CH_3	VIc	100	1.50(s)	1.65(s)	4.9(d)	2.75(q)	c-C_6H_{11} complex multiplets 1.0—2.5 ppm.
R = $CH(CH_3)_2$ R′ = H R″ = CH_3	VIIc	22	4.30(q) [f]	1.55(d) [f]	4.2(d)	2.45(q)	$CH(CH_3)_2$ complex multiplets 1.0—2.5 ppm.

[a] All values are in ppm relative to TMS, internal, in C_6D_6, at ambient temperature. [b] For all compounds the signal for the CH_3 group in NCH_2CH_3 was observed as a triplet at about 1 ppm. [c] ^3J(HH) 6 Hz (*cis* olefinic). [d] ^3J(HH) 13 Hz (*H*NC*H*). [e] ^3J(HH) 8 Hz (*H*NC*H*$_2$). [f] ^4J(HH) 1.3 Hz (allylic). [g] Tautomers c + d = 100%.

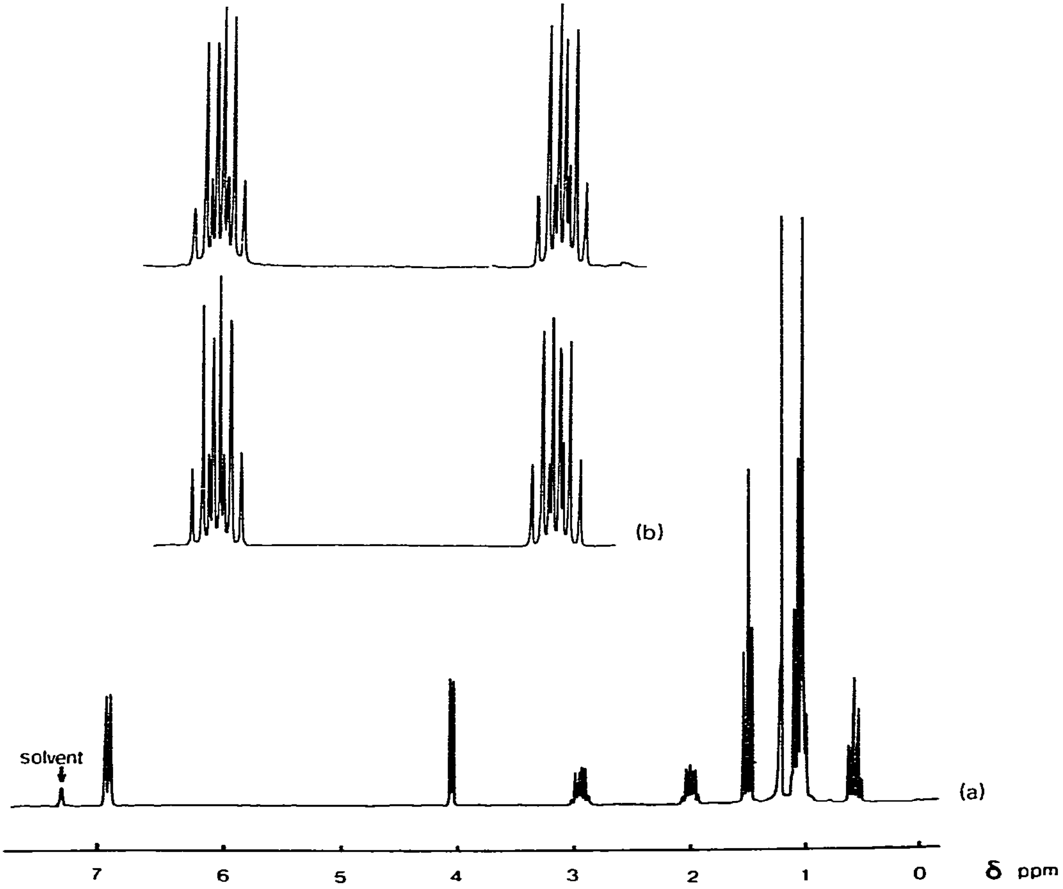


Fig. 1. a. ^{1}H NMR spectrum of Ib in C_6D_6 at 250 MHz. b. Observed (top) and calculated (bottom) ^{1}H NMR spectrum (1.8 to 3.2 ppm region) at 250 MHz of H_A and H_B of Ib in C_6D_6 (see text).

The chirality of the tetrahedral N centre is also clearly reflected in the ^{1}H NMR spectra of IIb and Vb (see Table 1) which contain alkyl-N groups with one and two prochiral groupings, respectively. Apart from the fact that in each compound the two N groups have different chemical shifts, the C and H atoms in these prochiral groupings become diastereotopic, resulting in spectra with complex resonance patterns.

^{1}H and ^{13}C NMR spectra of the tautomers Ic—VIIc and Id—VIId

The reactions of the novel organozinc compounds Ib—VIIb with t-BuOH to form Ic—VIIc and Id—VIId were monitored by ^{1}H NMR spectroscopy. The signals assignable to the ene-diamine compounds appear first and these decrease in intensity as those from the amine-imine tautomer increase (see eqn. 3), at a rate which depends on the substituents present. Equilibrium is reached within 24 h (see Tables 3 and 4).

The ^{1}H NMR spectra of the ene-diamine compounds Ic—Vc show the presence of two different olefinic protons at ca. 4.5 and ca. 5.5 ppm, the former

TABLE 4

^{1}H NMR DATA FOR RN=C(R″)—CHR′N(R)Et, Id—VIId [a]

Compound		Relative abundance (%) [d]	$H_2(R')$	$H(R'')$	$NC\mathit{H}_2CH_3$ [b]	R
$R = C(CH_3)_3$ $R' = R'' = H$	Id	14	3.20(d) [c]	7.65(t) [c]	2.40(q)	$C(CH_3)_3$ groups at about 1 ppm
$R = CH(CH_3)_2$ $R' = R'' = H$	IId	22	3.10(d) [c]	7.55(t) [c]	2.35(q)	$CH(CH_3)_2$ groups not assigned
$R = CH_2C(CH_3)_3$ $R' = R'' = H$	IIId	41	3.20(d) [c]	7.55(t) [c]	2.50(q)	$C\mathit{H}_2C(CH_3)_3$ 2.10(s) and 3.05(s), $CH_2C(C\mathit{H}_3)_3$ about 1 ppm.
$R = c\text{-}C_6H_{11}$ $R' = R'' = H$	IVd	71	3.20(d) [c]	7.55(t) [c]	2.45(q)	$c\text{-}C_6H_{11}$ complex multiplets 1.0—2.5 ppm
$R = CH(CH(CH_3)_2)_2$ $R' = R'' = H$	Vd	22	3.40(d) [c]	7.55(t) [c]	2.45(q)	$CH(CH(CH_3)_2)_2$ complex multiplets 1.0—2.5 ppm
$R = CH(CH_3)_2$ $R' = H$ $R'' = CH_3$	VIId	78	3.00(s)	1.70(s)	2.35(q)	$CH(CH_3)_2$ complex multiplets 1.0—1.5 ppm

[a] All values are in ppm relative to TMS internal, in C_6D_6, at ambient temperature. [b] For all compounds the CH_3 group in NCH_2CH_3 was observed as a triplet at about 1 ppm. [c] $^3J(HH)$ 7 Hz. [d] Tautomers c + d = 100%.

with a coupling of 6 Hz and the latter with couplings of 6 Hz and 13 Hz. This last 13 Hz coupling was not observed in the *N*-monodeuterated ene-diamines, pointing to a HNCH interaction. This was confirmed by H—H spin decoupling experiments, irradiation of the amine proton at 4.0 ppm resulting in the lower field olefinic proton appearing as a doublet with 6 Hz separation. The observed resonance pattern and the absence of other olefinic resonances indicate that exclusively the *cis*-olefinic ene-diamine is formed.

The resonance due to the amine-H atom (see Table 3) could be unambiguously assigned because of its decreased intensity or absence in the deuterolysis products formed in the reaction of Ib—VIIb with t-BuOD. A more detailed ^{1}H NMR investigation of the reaction of IVb with t-BuOD showed that at least two processes are involved in the ene-diamine/imine-amine equilibrium (see Fig. 2). First mono-deuterated IVc is formed in a very fast reaction, and this is followed by a much slower reaction which reaches equilibrium after about ten minutes. This equilibrium mixture consists of monodeuterated IVc and monodeuterated IVd. The second process involves random exchange of all hydrogen and deuterium involved in the isomerisation. After about one hour fully protonated, mono- and di-deuterated IVc and IVd are present in a statistical ratio. Since these ^{1}H NMR spectra show a constant value for the sum of the intensities of the low field olefinic proton of both IVc and IVc′, together with the imine proton of IVd, this indicates that proton H_A is not involved in the isomerisation and the H—D exchange reactions. This is also confirmed by the fact that the high field olefinic proton H_B of IVc is always observed as a perfect doublet.

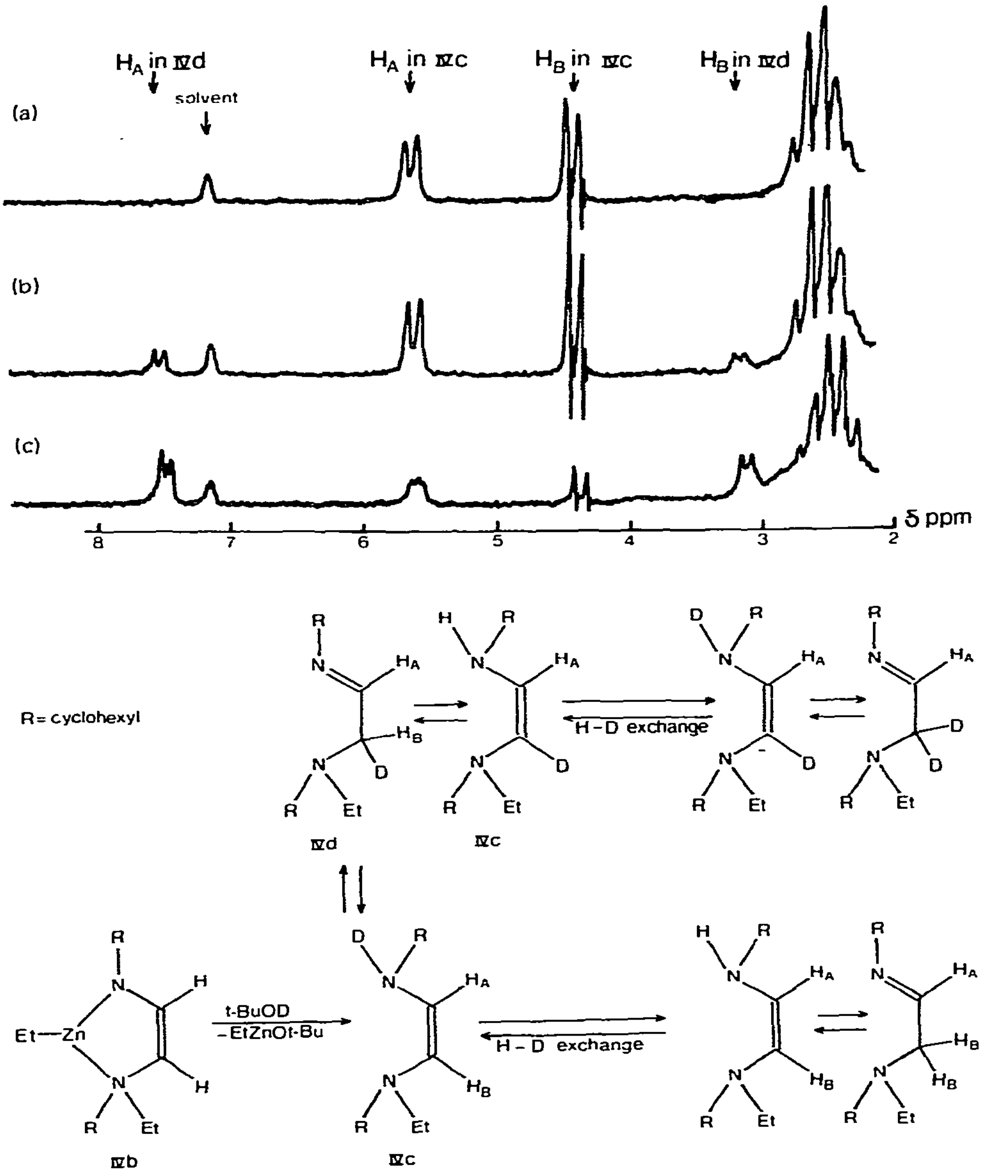


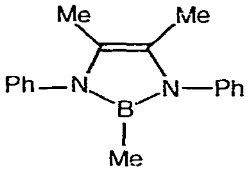
Fig. 2. ^1H NMR spectra (2 to 8 ppm region) of the reaction mixture of IVb with one equivalent of t-BuOD: after: a, 1 min; b, 10 min and c, 1 h.

The observed ^1H and ^{13}C NMR data of the ene-diamine- and imine-amine compounds are in agreement with the data reported by Bruder [8] for this type of compound.

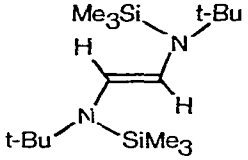
Discussion

In general, diorganozinc compounds form stable 1/1 complexes, R_2ZnL_2, with bidentate ligands L_2 such as TMED [9] or 2,2'-bipy and related chelating heterocyclic N-donor ligands [10]. The L_2 ligand in these complexes is bound to the R_2Zn moiety via the N-donor atoms, forming a five-membered chelate ring. Similarly, in the recently reported p-Tol_2Zn(R-DAB) complexes, which are stable up to 140°C [6], the R-DAB ligand is σ,σ-N,N′ bonded.

This general stability of R_2ZnL_2 complexes contrasts with the instability of the Et_2Zn(R-DAB) (R = alkyl) complexes reported in this paper. The observed quantitative conversion above −50°C of the 1,4-diaza-1,3-butadiene skeleton in the latter complexes into an 1,4-diaza-2-butene skeleton is to our knowledge unprecedented. The few compounds containing the 1,4-diaza-2-butene skeleton, cf. VIII and IX, were obtained by a very different route, viz. the reaction of the R-DAB radical anion with Me_3SiX [8] and $MeBBr_2$ [11].



VIII



IX

The compounds Ib—VIIb differ from VIII and IX in respect of the nature of the N-donor sites. In the former compounds an amino-amido monoanionic ligand is present, while in the latter the di-anionic ligand is bound to the metal centre via a diamido combination. The monomers Ib—VIIb do not react further with N-donor ligands such as pyridine or 2,2′-bipy, indicating that the planar three-coordinate geometry at zinc is comparatively stable. This is probably due to the bulkiness of the coordinated N(Et)R groups. The degree of branching at C^α or C^β in the R group is obviously unimportant in this respect. It would be interesting to know whether the amido-N centre in these complexes has a planar trigonal geometry, as often encountered for secondary N groups connected to a C=C double bond system [12a]. This would imply the possibility of delocalization of the amido-N lone pair and the C=C π electrons into the remaining empty $4p$ orbital of zinc. In a recent X-ray structural investigation [12b] of $Cl_2\overline{AlN(Et)C_2H_4N}Me_2$ [12c] donations of the nitrogen lone pair to aluminium $3d_\pi$ orbitals was suggested on the basis of an extremely short AlN(Et) distance and a planar geometry around N(Et).

Although a detailed mechanistic study is required to elucidate the reasons for the difference in product formation in the reaction of R-DAB molecules with organo-aluminium and -zinc reagents, at the present stage of our study the following suggestions can be put forward.

The overall result in the R-DAB/Et_2Zn reactions, i.e. transfer of an ethyl group from Zn to the coordinated N atom [*], which results in the formation of a new C—N bond, seems to exclude a polar mechanism. If such a mechanism

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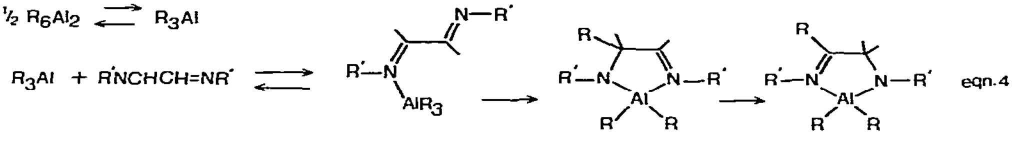
[*] Escape of an Et radical from the solvent cage produces in low yield (<1%) a persistent organozinc radical EtZn[t-BuN=C(H)C(H)=Nt-Bu]; which is in equilibrium with its C—C coupled dimer [EtZn{t-BuN=C(H)(t-BuN)CH}]$_2$ [5].

were operative the nucleophilic (M)—C centre would attack the imino-C atom of the C=N bond and thus form a new C—C bond. This has been observed in the related reactions of trimethylaluminium dimer with 1,4-dialkyl- and -diaryl-1,4-diaza-1,3-butadienes, see eqn. 4 [3].



Xa Xb Xc

The driving force in the reaction sequence shown in eqn. 4 is probably a reduction of steric interaction between vicinal groups about the various bonds. By the addition of one of the R—Al bonds across the C=N bond (Xa to Xb) the potentially bidentate ligand becomes attached to the Al centre via both N-donor sites. In the final H^- shift (Xb to Xc) the tetrahedral C atom group becomes a $>CH_2$ group.

It is interesting to note that in contrast to organoaluminium compounds, dialkyl- and diarylzinc compounds normally display little reactivity towards aldimines, R(R')C=NR". An exception is the mixed 2 RMgX, ZnX_2 reagent, which readily adds across the C=N double bond with formation of a new R—C bond [13]. This has been ascribed to enhancement, by N—Mg coordination, of polarization in the C=N bond, which is thus activated towards nucleophilic attack at the C centre [13].

The fact that with the complexes Ia—VIIa an Et—N bond is formed instead of an Et—C bond, even though the N=C—C=N skeleton is connected to the Zn atom via both N atoms indicates that the ethyl transfer in Et_2Zn(R-DAB) is induced for other reasons. Earlier work on the bonding in R_2Zn(2,2'bipy) complexes has shown that extensive electron transfer from Zn into the π^* system of the 2,2'-bipy ligand takes place in these complexes [14]. A similar back-bonding is also expected to be important in the Et_2Zn(R-DAB) complexes, particularly since the R-DAB ligand is a better electron acceptor than 2,2'-bipy [15]. This implies that the LUMO of the M—N=C—C=N entity, which is bonding between the central C atoms but antibonding for the adjacent C—N bonds, is filled. Accordingly back donation concentrates spin density on the N-centres, which would be consistent with a mechanism involving an intramolecular 1,2-shift of an ethyl radical from Zn to N and formation of an Et—N bond.

This entirely different activation of C=N bonds for a subsequent reaction with the R—Zn bond is probably not restricted to 1,4-diaza-1,3-butadienes. Similar reactions have been found for 1,4-dioxo-1,3-butadienes (ortho-chinones) [16] and are anticipated for compounds containing the 1-oxo-4-aza-1,3-butadiene skeleton [6].

Finally, the interesting 1,4-diaza-2-butene compounds (Ic—VIIc; ene-diamines) can be synthesized in high yields via the R-DAB/Et_2Zn route because protonolysis of the complexes Ib—VIIb occurs quantitatively. The relative stability of the respective tautomers (see eqn. 3 for Ib) depends on the nature of the R—N and R'—C substituents (see Tables 3 and 4). Branching at C^β shifts the equilibrium towards the 1-amino-2-iminoethane tautomer (cf. IIIc, R = CH_2(t-Bu) and IVc, R = cyclohexyl). When R′ is CH_3 instead of H a complete inversion of the tautomer equilibrium is observed (cf. IIc, R = i-Pr, R′ = H with VIIc, R = i-Pr, R′ = Me). In each of the equilibria the ene-diamine tautomer is present with a *cis*-configuration at the C═C double bond, probably a result of the stabilizing effect of the N—H···N bridge. This latter hydrogen bridge cannot be present in the *trans*-isomer. The observation that reaction of Et_2Zn with the individual tautomer mixtures quantitatively produces the parent complexes, Ib—VIIb, indicates that a new route for the synthesis of organometallic complexes containing the 1,4-diaza-2-butene skeleton is now available [6].

Experimental

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully dried and distilled before use. The 1,4-diaza-1,3-butadienes were prepared by published methods [1].

^1H NMR spectra were recorded on Bruker WM250 and Varian T60 NMR spectrometers and ^{13}C NMR spectra on a Bruker WP80 NMR spectrometer.

Determination of the exact concentration of Et_2Zn in hexane solution

A solution containing 1,4-diaza-1,3-butadiene (10.00 mmol) in n-pentane (40 ml) was titrated with a solution of Et_2Zn in hexane (about 1.5 molar). The equivalence point was reached when the last added drop of Et_2Zn solution did not cause a red colouration (accuracy 0.05 ml). In this way, 10.00 mmol 1,4-ditert-butyl-1,4-diaza-1,3-butadiene consumed 6.85 ml Et_2Zn solution, so the concentration of Et_2Zn was 1.46 *M*.

Preparation of $Et\overline{ZnN(R)C(R'')=C(R')N}(R)Et$, Ib—VIIb

A solution of Et_2Zn in hexane containing 10 mmol of Et_2Zn was added dropwise to a solution of 10 mmol of the corresponding 1,4-diaza-1,3-butadiene (R-DAB{R′,R″}: R′,R″ = H; R = t-Bu (I), i-Pr (II), CH_2 t-Bu (III), cyclohexyl (IV), $CH(i\text{-}Pr)_2$ (V), R′,R″ = Me, R = cyclohexyl (VI) and R′ = H, R″ = Me, R = i-Pr (VII)) in pentane (15 ml). An immediate exothermic reaction took place, resulting in a dark red coloured mixture, the colour of which rapidly changed to pale yellow. The solvent was evaporated off in vacuo at ambient temperature to leave a yellow oil, the ^1H NMR spectrum of which indicated that it was the pure organozinc compound Ib—VIIb (see eqn. 2). In all cases the yield was better than 98%. Analytically pure samples of Ib were obtained by distillation, b.p. 92°C/0.1 mmHg. Mol. wt. (by cryoscopy in benzene): found (calcd.) 280 (291.4).

Alcoholysis of $Et\overline{ZnN(R)C(R'')=C(R')N}(R)Et$ (Ib—VIIb) with t-BuOH; ^1H NMR experiments

A known amount of each of the organozinc compounds Ib—VIIb was dissolved in C_6D_6 in an NMR tube. An equimolar amount of t-BuOH was added to give a clear solution. The ^1H NMR spectrum was recorded immediately and after one hour, one day, and two days.

Isolation of the alcoholysis products Ic, H(t-Bu)NC(H)═C(H)N(t-Bu)Et, and Id, t-BuN═C(H)C(H)$_2$N(t-Bu)Et

The organozinc compound Ib (5 g; 17.1 mmol) was dissolved in n-pentane (25 ml). An equimolar amount of t-BuOH was added dropwise, giving an immediate white precipitate (EtZnOt-Bu) and a colourless solution. This mixture was set aside at −70°C for 24 h to permit the EtZnOt-Bu to separate quantitatively. The cold mixture was filtered, and the white solid was washed with 5 ml of cold pentane. This solid (2.5 g; 87%), which was dried in vacuo, and shown by its ^{1}H and ^{13}C NMR spectra to be pure EtZnOt-Bu [17]. The combined pentane solutions were concentrated to leave a pale yellow distillable oil (b.p. 61—62°C/5 mmHg), consisting of Ic and Id in a 86/14 molar ratio (^{1}H and ^{13}C NMR, see Table 3 and 4) (yield 88%).

Reaction of the alcoholysis products Ic and Id with Et$_2$Zn; re-formation of Ib

The mixture of Ic and Id (2 mmol) was dissolved in pentane. A solution of 2 mmol of Et$_2$Zn in hexane (1.4 ml) was added and the resulting pale yellow solution was stirred for 1 h. The solvent was removed from the mixture in vacuo to leave a pale yellow oil. The ^{1}H and ^{13}C NMR spectra of this oil were identical to those of pure Ib obtained by the direct t-Bu-DAB/Et$_2$Zn reaction (see above) (yield >96%).

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