

Review

STABLE 1,4-DIAZA-1,3-BUTADIENE(α -DIIMINE)-ZINC AND -ALUMINIUM RADICALS FORMED IN SINGLE ELECTRON TRANSFER REACTIONS: THEIR CONSEQUENCES FOR ORGANIC SYNTHESSES

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Summary

A discussion is given of the formation of complexes of the reaction of 1,4-di-*t*-butyl-1,4-diaza-1,3-butadiene *t*-Bu-N=CH-CH=N-*t*-Bu (*t*-Bu-DAB) or of *t*-Bu-N=CH-2-C₅H₄N (*t*-Bu-Pyca) with Et₂Zn or Et₃Al. It is shown that after the initial formation of four-coordinate complexes Et₂Zn(*t*-Bu-DAB) and Et₂Zn(*t*-Bu-Pyca) with chelated diimine groups and of Et₃Al(*t*-Bu-DAB) and Et₃Al(*t*-Bu-Pyca) with monodentate bonded diimine groups a variety of reactions may occur. These reactions involve ethyl transfer to either the C- or the N-atoms of the ligand N=C-C=N skeleton, and the formation of persistent organo-zinc and -aluminium radical complexes was also observed. The latter radical complexes have been studied by ESR spectroscopy. In the case of zinc the radical complex [EtZn(*t*-Bu-DAB)·] is in equilibrium with a dinuclear complex in which the two *t*-Bu-DAB ligands are coupled via a C-C bond. The mechanistic aspects of the reaction are briefly discussed.

Introduction

Research in our laboratory on metal-diimine complexes has mainly concentrated on the 1,4-disubstituted 1,4-diaza-1,3-butadienes RN=C(H)-(H)C=NR (= R-DAB) and on the N-substituted pyridine-2-carbaldimines RN=CH-2-C₅H₄N (= R-Pyca) as ligands. The aim is to study the relation between the type of coordination of the diimine ligands to metal atoms and the reactions of the coordinated diimine ligand [1,2].

It is now clear that 1,4-diaza-1,3-butadienes may coordinate as 2e, 4e, 6e and 8e donor ligands [1-3], while the R-Pyca ligands show only 2e, 4e, and 6e donation. The reactions of the coordinated R-DAB and R-Pyca ligands have been studied mainly for the 6e-donor type of bonding, such as that present in [Ru₂(CO)₆-(R-DAB)]. The η^2 -bonded imine N=C group of the R-DAB ligand may couple via

C-C bond formation to other unsaturated substrates, e.g. R-DAB, alkynes, etc. [4].

In this paper we survey very recent work on the activation of 2e- and 4e-bonded R-DAB and R-Pyca groups by coordinated Et_2Zn and Et_3Al moieties. This activation may result in C-C and C-N bond formation and in some cases the production of stable radical complexes [5-7]. The implications for organic synthesis are indicated. Full details of this work, including the reactions of other R_2Zn and R_3Al compounds with R-DAB and R-Pyca, will be reported shortly.

Organometallic aspects

The reactions of both Et_2Zn and Et_3Al with the diimine t-Bu-DAB take well-defined, but quite distinct routes. The initial step in both reactions is the formation of the 1/1 complexes $\text{Et}_n\text{M}(\text{t-Bu-DAB})$ (I) which are, however, not stable at room temperature and are converted completely into secondary complexes. The overall reaction is virtually quantitative transfer of one Et group from the metal to either the N or the C centre of the ligand $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton. Accordingly the neutral hetero-1,3-butadiene ligand is reduced to the hetero-2- or -1-butene mono-anionic ligands present in the products II and III respectively (see Fig. 1). Interestingly, the ESR spectra of the reaction mixtures reveal that this reduction is accompanied by the formation of trace amounts of the stable organometallic radical complexes IV having 1/1 metal to t-Bu-DAB stoichiometry [5].

Distinct differences between the reactions of Et_2Zn and Et_3Al with t-Bu-DAB are (i) the exclusive formation of the N-alkylated product IIa with Et_2Zn [6] compared with the formation of a mixture of N- (IIb) and C-alkylated (IIIb) products from Et_3Al [7], and (ii) the hydride shift of IIIb to form IIIb' when the

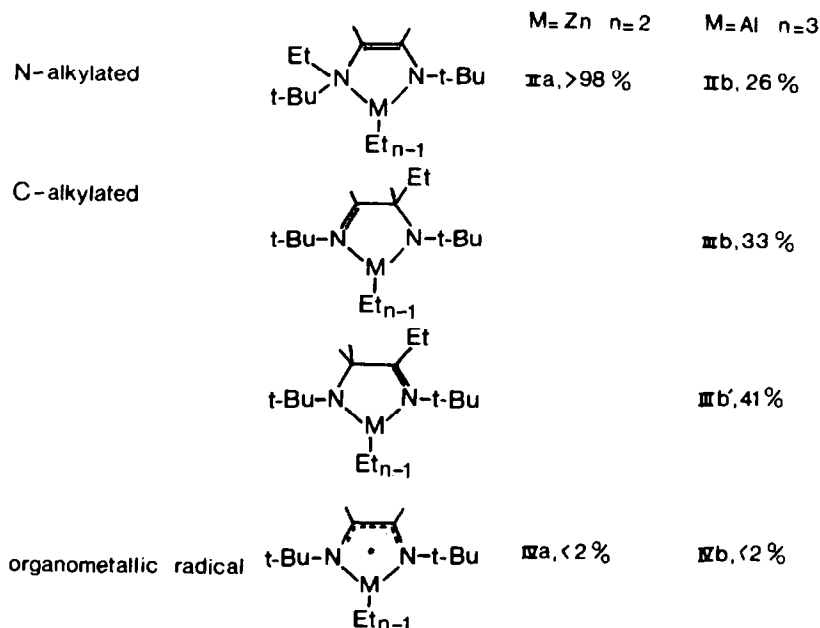


Fig. 1. Secondary products emerging from the $\text{Et}_n\text{M}(\text{t-Bu-DAB})$ complexes Ia and Ib.

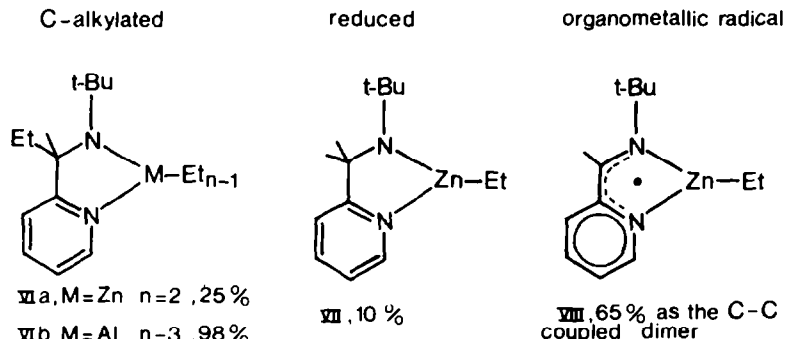


Fig. 2. Secondary products arising from heating of $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ (V) or the 1/1 molar reaction of Et_3Al with t-Bu-Pyca at RT.

C-alkylated product is coordinated to a Et_2Al^+ grouping [7]. Since in this paper only the $\text{Et}_n\text{M}/\text{t-Bu-DAB}$ system is discussed, it must be recalled that product formation in the $\text{R}_n\text{M}/\text{R}'\text{-DAB}$ system is strongly dependent on both the nature of R and R' as well as their combination in a given reaction [2]. For example, a C-phenylated product (IIIb) is formed exclusively in the $\text{Ph}_3\text{Al}/\text{t-Bu-DAB}$ reaction [7]. Furthermore, quantitative C-alkylation is likewise observed in the $\text{t-Bu}_2\text{Zn}/\text{t-Bu-DAB}$ system instead of N-alkylation as seen in the $\text{Et}_2\text{Zn}/\text{t-Bu-DAB}$ reaction.

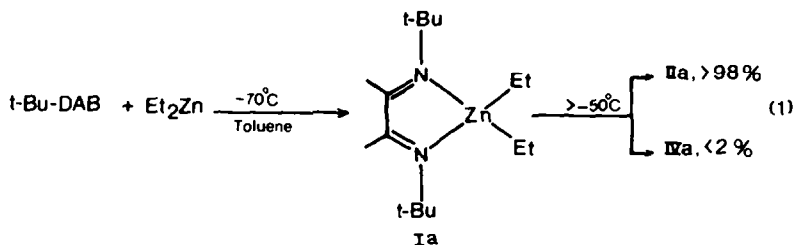
The reactions of Et_2Zn and Et_3Al with pyridine-2-N-t-butylcarbalimine (t-Bu-Pyca), as with t-Bu-DAB , show several contrasting features. The reaction of Et_2Zn with t-Bu-Pyca yields the 1/1 complex $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ (V). This complex is stable at room temperature but is converted slowly above this temperature into the C-alkylated product VIa, the reduced product VII, and a relatively large amount of the ethylzinc radical VIII, see Fig. 2. The latter radical VIII is isolated as its diamagnetic dimer (see below). By contrast, the reaction of Et_3Al with t-Bu-Pyca affords the C-alkylated product VIb in nearly quantitative yield.

These results show that the Et_2Zn and Et_3Al reagents exhibit greatly differing reactivities towards t-Bu-DAB and t-Bu-Pyca ligands, but have as common features (i) the initial complex formation between the organometallic species and the heterobutadiene ligand, and (ii) the formation of stable organometallic radicals. In the next two sections these features will be discussed in more detail.

(i) *Complex formation of Et_2Zn and Et_3Al with t-Bu-DAB and t-Bu-Pyca*

In general, diorganozinc compounds form 1/1 complexes, R_2ZnL_2 , with bidentate ligands (L_2) such as TMED [8] or 2,2'-bipy and related chelating N-donor ligands [9]. These complexes contain a tetrahedrally surrounded Zn centre with the L_2 ligand bonded to the R_2Zn moiety via the N-donor atoms.

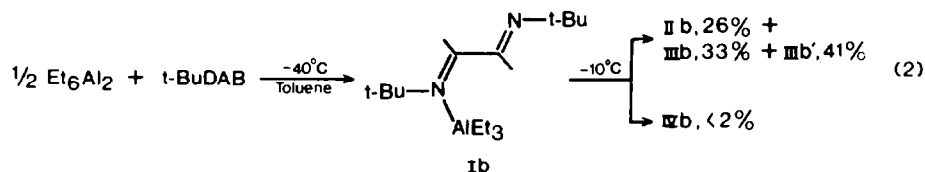
The ^1H NMR spectra show that the $\text{Et}_2\text{Zn}(\text{t-Bu-DAB})$ complex (Ia) is stable below -50°C and contains a $\sigma, \sigma\text{-N, N}'$ chelate bonded t-Bu-DAB ligand [6].



The low stability of Ia contrasts with the observation that *p*-tolyl₂Zn(t-Bu-DAB) (IX) can be heated to 140°C without any observable decomposition [6]. Although both zinc complexes contain the strongly σ -donating t-Bu-DAB group, this difference in stability may arise from the fact that only the *p*-tolyl₂Zn moiety can compensate for the enhanced electron density on the metal by backdonation into the π^* levels of the *p*-tolyl groups (see below).

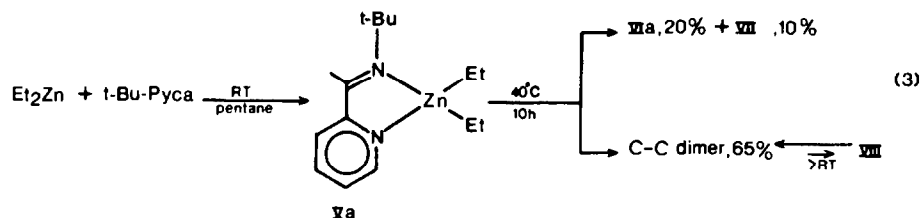
The dimeric Et₆Al₂ readily breaks down on reaction with monodentate nitrogen ligands L (e.g. NMe₃) into mononuclear complexes Et₃Al · L [10]. Chelate bonding of bidentate ligands to Et₃Al units, which would lead to a five-coordinate species, is less favourable [10] when the coordinating N-atoms bear bulky substituents.

We observed that t-Bu-DAB coordinates to the Et₃Al moiety in the monodentate bonding mode via one N-donor site [6]. The ligand has the *s-trans* configuration (see eq. 2) which is also the most stable configuration for a free R-DAB molecule [11].

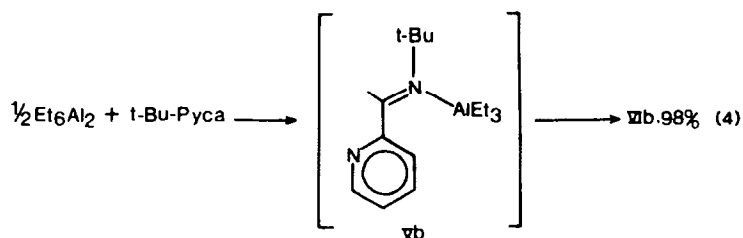


This conformation in Ib was deduced from the resonance pattern of the t-Bu-DAB ligand in the ¹H NMR spectrum of an in situ prepared solution at -40°C. The observation of an AB pattern for the imine protons ($\delta(\text{H})$ 7.65 and 8.90 ppm, ³*J*(H_A-H_B) 8 Hz) and two singlets for the t-Bu groups are in agreement with data for other R-DAB-metal complexes, for which σ -N monodentate bonding has been firmly established (e.g. *trans*-[PdCl₂(PPh₃)(t-Bu-DAB)] [11–13]).

The 1/1 complex of Et₂Zn with t-Bu-Pyca (Va) can be isolated as an orange crystalline solid in nearly quantitative yield. Like Ia, a four-coordinate structure for Va is proposed containing a σ, σ -N,N' bonded t-Bu-Pyca ligand (see eq. 3).



The reaction to form Et₃Al(t-Bu-Pyca), which like Ib is expected to contain a σ -N monodentate bonded ligand is still under study (see eq. 4):



It is now possible to compare these novel Et_2Zn complexes of *t*-Bu-DAB and *t*-Bu-Pyca with those of an other important α -diimine ligand, 2,2'-bipy. It has been shown, by considering the relative donor/acceptor properties of the α -diimine molecules, that the π -acceptor capacity increases on going from 2,2'-bipy via R-Pyca to R-DAB [14]. We have found that the stability of the zinc complexes decreases from 2,2'-bipy via *t*-Bu-Pyca to *t*-Bu-DAB. Most probably we are dealing here with the order of kinetic stability of the complexes with regard to their further reaction via a single electron transfer (SET) reaction and/or transfer of the organo group or hydride (resulting from prior β -elimination) from the zinc to the $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton [15,16] (*vide infra*).

(ii) *The organometallic radical complexes $\text{Et}_{n-1}\text{M}(\textit{t}\text{-Bu-DAB})$ (I) and $\text{Et}_{n-1}\text{M}(\textit{t}\text{-Bu-Pyca})$ (VIII)*

Interesting products emerging from warming solutions of the 1/1 complexes $\text{Et}_2\text{Zn}(\textit{t}\text{-Bu-DAB})$ ($> -50^\circ\text{C}$), $\text{Et}_2\text{Zn}(\textit{t}\text{-Bu-Pyca})$ ($>$ room temperature) and $\text{Et}_3\text{Al}(\textit{t}\text{-Bu-DAB})$ ($> -10^\circ\text{C}$) are the organometallic radical complexes IV and VIII. The presence of these radicals gives important information about the operative mechanisms (*vide infra*).

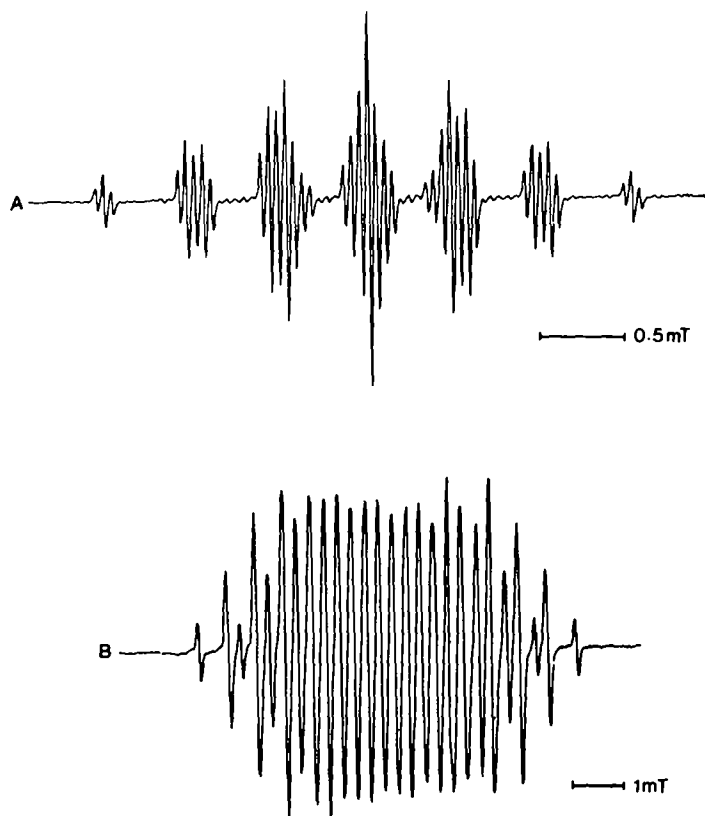


Fig. 3. (a) The observed ESR spectrum of the persistent $\text{EtZn}(\textit{t}\text{-Bu-DAB})$ radical IVa (for the calculated spectrum, see ref. 5.) (b) The observed ESR spectrum of the persistent $\text{Et}_2\text{Al}(\textit{t}\text{-Bu-DAB})$ radical IVb.

TABLE I

ESR DATA OF SOME PERSISTENT ETHYLZINC AND DIETHYLALUMINIUM- α -DIIMINE RADICALS^a

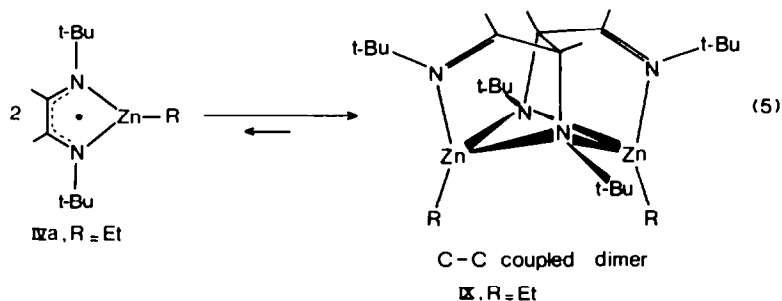
Radical	a_N	a_H^b	$a_{H(ET)}^c$	a_X	g
MeZn(t-Bu-DAB) ^e	0.487	0.587	0.051		2.0021
EtZn(t-Bu-DAB) ^e	0.487	0.587	0.048		2.0021
i-PrZn(t-Bu-DAB) ^e	0.487	0.587	0.030		2.0021
ClZn(t-Bu-DAB) ^d	0.56	0.56	–	0.058 ^e 0.44 ^f	2.0024
PhZn(2,2'-bipy) ^g	0.318	–	–		2.0029
Et ₂ Al(t-Bu-DAB) ^e	0.537	0.563	n.o.	0.793 ^h	2.0028
Et ₂ Al(2,2'-bipy) ^e	0.300	–	n.o.	0.436	2.0030
EtZn(t-Bu-Pyca) ⁱ					

^a Coupling constants in mT, n.o. not observed. ^b Imine hydrogen. ^c Methylene hydrogen of the Et group. ^d Ref. 17. ^e Average value for ³⁵Cl and ³⁷Cl. ^f X = ⁶⁷Zn. ^g Ref. 18. ^h X = ²⁷Al. ⁱ Very complex pattern which so far could not be assigned.

Freshly prepared solutions of the Et₂Zn(t-Bu-DAB) complex (Ia) at -70°C do not show an ESR signal. However, at room temperature, i.e. after Ia has been converted into the N-alkylated product IIa (see eq. 1), the ESR signal of a persistent radical present in low concentration is observed, see Fig. 3a [6]. This spectrum (see Table 1) can be assigned to the three-coordinate organozinc radical IVa having a planar five-membered chelate ring.

Likewise ESR spectra of the reaction mixture of Et₃Al and t-Bu-DAB indicate the presence of the Et₂Al(t-Bu-DAB) (IVb) radical, see Fig. 3b. These data (see Table 1) are consistent with a chelate bonded t-Bu-DAB ligand, and thus a four-coordinate aluminium atom.

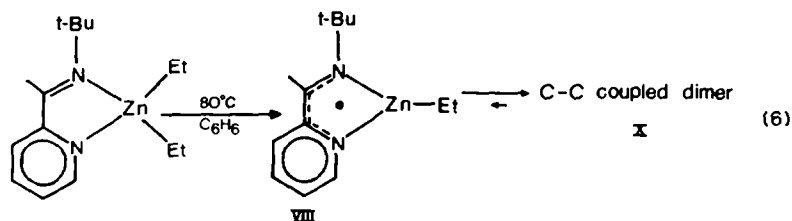
These ethylmetal-t-Bu-DAB radicals can also be prepared directly from the reaction of (t-Bu-DAB)K [19] with either EtZnCl-tetramer (4/1 molar ratio) or Et₂AlCl-dimer (2/1 molar ratio). The radical complexes RZn(t-Bu-DAB)^e (R = Me, Et, i-Pr) (see Table 1) have been isolated as white crystalline solids in 80–90% yields. Molecular weight determinations indicate that these compounds exist in benzene as the dimeric species [RZn(t-Bu-DAB)]₂. On dissolution these dimers dissociate to a very small extent into paramagnetic monomers, thus forming an equilibrium mixture (see eq. 5). The equilibrium between IVa and its dimer IX lies predominantly on the



side of the dimer. This is indicated by the following evidence: (i) a dimeric molecular

weight; (ii) the ^1H and ^{13}C NMR patterns (which support the schematic structure shown in eq. 5) show narrow lines: i.e. the rates of paramagnetic IVa \rightarrow diamagnetic IX and the reverse process are slow on the NMR timescale; and (iii) the fact that below -60°C no ESR spectrum is observed while above this temperature signals appear whose intensity increases with the temperature.

The proposed structure for IX with two C-C coupled t-Bu-DAB ligands is strongly supported by the X-ray structure of dinuclear X which was isolated after heating $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ (see eq. 6) [6]. The structure of X is shown in Fig. 4.



Important structural features of X are the four-coordinate geometry of the Zn atoms and the newly formed quadridentate dianionic ligand (t-Bu-IAE) comprising two C-C coupled t-Bu-Pyca ligands. This t-Bu-IAE ligand is bonded to the two Zn centres via two amido and two imino Zn-N interactions thus acting as a 10-electron donor. It is important to note that a similar C-C coupling and hence dimeric ligand

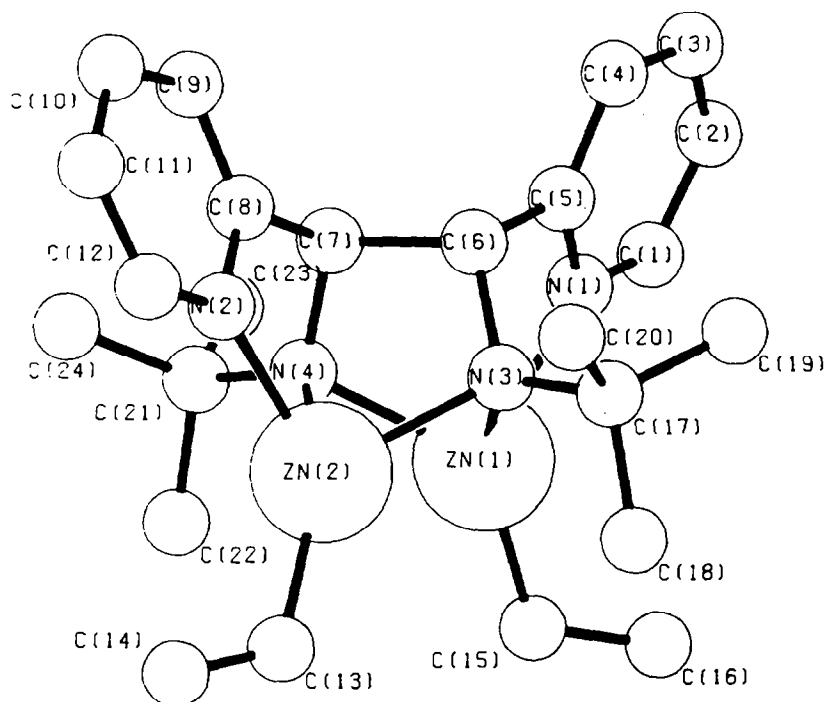
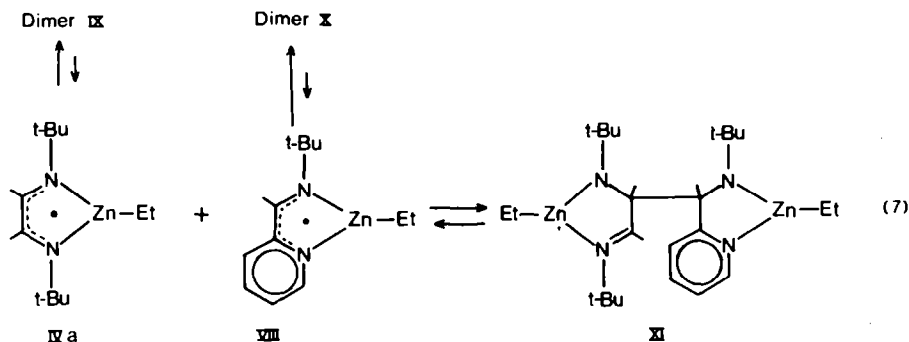


Fig. 4. Molecular geometry of dimeric $[\text{EtZn}(\text{t-Bu-Pyca})_2]$ (X). Relevant distances are $\text{C}_{\text{imine}}-\text{C}'_{\text{imine}}$ 1.570(8) Å and $\text{Zn}\dots\text{Zn}$ 2.749(1) Å.

structure has been observed in $(\text{Mo}(\text{CO})_3)_2(\text{t-Bu-IAE})$ [20] and $\text{Ru}_2(\text{CO})_5(\text{t-Bu-IAE})$ [21]. In X the C–C' bond is most probably stabilized by the bridging amido groups.

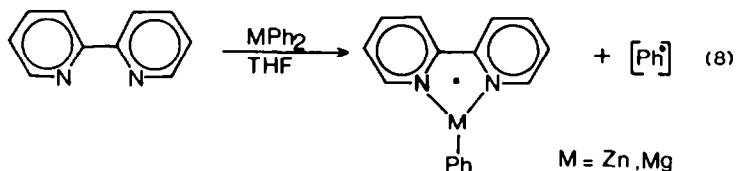
Knowing the dinuclear structure of IX and X a plausible explanation can be given for the observation that $\text{Et}_2\text{Al}(\text{t-Bu-DAB})'$ (isolated as a green-yellow oil) according to its intense ESR spectrum and broad (500 Hz) lines in the NMR spectra consists mainly of the persistent radical. Since the Al centre, when compared with the Zn centre, contains one ethyl group more, a dinuclear structure for IVb, which would render the Al centres five-coordinate, is not very likely. Steric effects arising from the presence of the bulky *t*-butyl groups may also play a very important role in destabilizing the dinuclear structure with respect to the paramagnetic monomer IVb.

A fascinating observation is the formation of the asymmetric dinuclear C–C coupled XI on mixing the symmetric IX and X (see eqn. 7). The ^1H NMR spectra



(250 MHz) show the presence of the three dinuclear compounds IX–XI in a statistical ratio (1/1/2), which further supports the existence of the monomer–dimer equilibria.

The organometallic radicals IV and VIII are the result of homolytic cleavage of an Et–M bond in the corresponding 1/1 complexes and escape of the Et radical from the solvent cage. This explains why these radicals are formed only in trace amounts, since most ethyl groups are captured intramolecularly (*vide infra*). Consequently, the overall result is the transfer of an electron from the R_2Zn or R_3Al entity to the coordinated ligand $\text{N}=\text{C}=\text{N}$ skeleton. Similar electron transfer reactions between a whole range of organometallics including R_2Mg , R_3Al and R_2Zn have been reported for the α -diimines 2,2'-bipy and phenanthroline. Accordingly, species such as those shown in eq. 8 and Table 1 have been characterized by ESR spectroscopy [18,22,23].



A striking feature of the organozinc radicals discussed in this paper is the monomeric nature of these organometallic-2,2'-bipy radicals. The C–C coupling of these monomers, which is the predominant feature of the organozinc-*t*-Bu-DAB and

-t-Bu-Pyca radicals, is sterically and also electronically (loss of resonance energy) unfavourable.

It can be calculated from the data for the RZn(t-Bu-DAB) radicals (Table 1) that the spin density on the N atoms is about 0.3 and that on the C atoms about 0.2. Thus only a little spin density is present on Zn, a fact which is reflected in the small methylene hydrogen splittings [24]. This information appears to be very useful for the understanding of the product formation from $\text{Et}_2\text{Zn}(\text{t-Bu-DAB})$ and $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$. Although the ESR pattern could not be reliably assigned of the t-Bu-Pyca complex, it may be anticipated that the spin density at the pyridine-N atom is spread out over the pyridyl ring atoms (cf. 2,2'-bipy-metal complexes [22]). A similar delocalization of spin density is found for the $\text{EtZn}(\text{aryl-DAB})$ complexes.

Mechanistic aspects

Extensive studies of reactions of alkylmetal reagents with carbonyl and imine compounds, i.e. with hetero-olefins >C=X ($\text{X} = \text{O}$ or NR) [16,25], nitriles [15], alcohols [16,26,27] and alkyl halides [28], have revealed the importance of single electron transfer (SET) mechanisms in addition to polar reactions.

The 1,4-dihetero-1,3-butadienes, X=C-C=Y , which we are concerned with can either react with the organometallic reagent as isolated hetero-olefinic >C=X and >C=Y units or as the conjugated system having the X=C-C=Y skeleton in either the planar *s-trans* or *s-cis* configuration. From the results obtained we conclude that both t-Bu-DAB containing two >C=N units and t-Bu-Pyca (in which one of the C=N units is part of a resonance-stabilized pyridyl ring system) react with the diethylzinc species in the chelate bonding mode (*s-cis* configuration: i.e., complexes of type Ia or Va).

Although further detailed mechanistic studies are under way the currently available information for the $\text{Et}_2\text{Zn}/\text{t-Bu-DAB}$ and $\text{Et}_2\text{Zn}/\text{t-Bu-Pyca}$ systems illustrate nicely the intimate steps operative in these reactions, see Scheme 1.

Starting from a $\sigma,\sigma\text{-N,N}'$ complex (Ia or Va) two major routes are available for further reaction depending on whether the chelate bonded hetero-butadiene is t-Bu-DAB or t-Bu-Pyca. In the case of $\text{Et}_2\text{Zn}(\text{t-Bu-DAB})$ the N-alkylated product IIa is formed almost quantitatively. This can be explained by a SET reaction giving the transition state A followed by a fast intramolecular 1,2 shift of the ethyl group. Competitive escape of an ethyl radical from the solvent cage as the minor pathway ($k_{\text{N}} \gg k_{\text{esc}}$) can also produce the EtZn radical IVa. The observation that the C-alkylated product is not formed indicates that $k_{\text{N}} \gg k_{\text{esc}} \gg k_{\text{C}}$, in line with the higher spin density on the N atoms than on the imine-C atoms (vide supra).

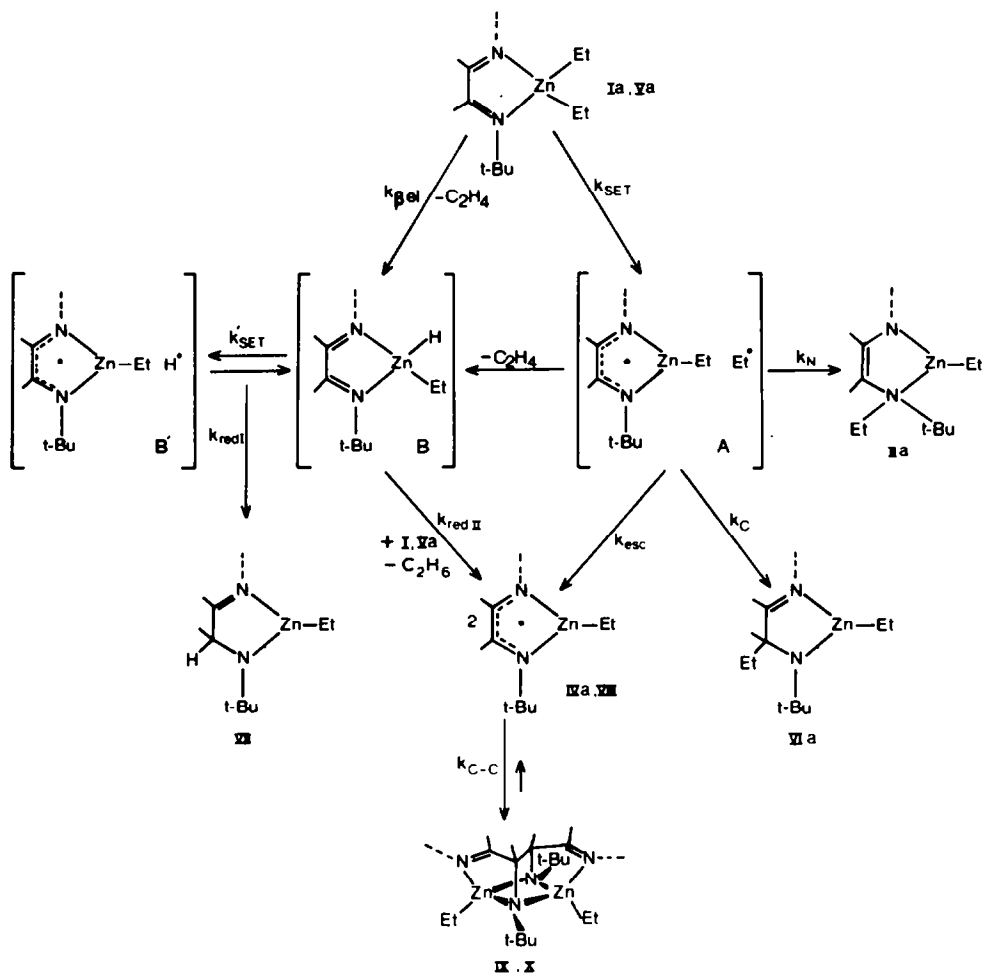
The reaction starting from $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ takes an entirely different course. The fast N-alkylation route is blocked because this would require break-up of the conjugation in the pyridyl ring. Thus a different route, possibly involving a zinc hydride intermediate or transition state (B or B'), becomes the major pathway. The fact that 75% of one Et group is identifiable as a 1/1 molar mixture of ethylene and ethane, whereas butane is absent excludes the participation of free ethyl radicals. Likewise, the formation of VIII via a SET reaction leading to A and subsequent reaction of A with unreacted $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ seems unlikely, because this would also lead to butane. Therefore, we propose that the $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$ complex is converted into an intermediate or transition state (B or B') from which further

SCHEME 1. Stoichiometry of the $\text{Et}_2\text{Zn}/t\text{-Bu-Pyca}$ reaction and the proposed steps for the $\text{Et}_2\text{Zn}/t\text{-Bu-DAB}$ ($\text{C}=\text{N}\dots$ is $\text{C}=\text{N}-t\text{-Bu}$) and $\text{Et}_2\text{Zn}/t\text{-Bu-Pyca}$ ($\text{C}=\text{N}\dots$ is the 2-pyridyl ring).

Stoichiometry :



Proposed Steps:



product formation then takes place. B (or B') may be formed via either a β elimination route (this would require a free coordination site at Zn!) or a transition state A with subsequent elimination of ethylene from the ethyl radical and formation of the $[\text{EtZn}(t\text{-Bu-Pyca})\text{H}^\bullet]$ radical pair B' (or B).

That A is indeed formed in this reaction may be deduced from the presence of the C-alkylated product VIa. Although this compound can also originate from a direct polar reaction, this is very unlikely in view of the strong $\sigma, \sigma\text{-N, N}'$ chelation.

B (or B' as a result of SET) reacts either intramolecularly to the reduced product VII or with unreacted $\text{Et}_2\text{Zn}(t\text{-Bu-Pyca})$ to the EtZn radical VIII. The product ratio shows that $k_{\text{red II}} \gg k_{\text{red I}}$. Support for the intermediacy of B (or B') comes from two

observations; (i) the 1/1 reaction of $\text{EtZnH} \cdot \text{pyridine}$ with *t*-Bu-Pyca affords VII in quantitative yield; and (ii) when the same reaction is carried out in the presence of 1 equivalent of $\text{Et}_2\text{Zn}(\text{t-Bu-Pyca})$, the products VII, VIa and VIII are formed in the same yields as shown in Scheme 1, but now exclusively ethane (1 equivalent) is formed and no ethylene. The presence of VIa is particularly interesting, and again seems to support the presence of A in addition to B (or B').

It is important to realize that the reactions discussed here have many parallels with the reported reactions of Grignard reagents with ketones [16]. A difference, however, is the preponderant position of transition states of type A or B' in which the molecular conformation has already been well developed along the reaction coordinate in the direction of the stabilized EtZn radical. Comparative studies in which primary, secondary and tertiary alkylzinc compounds have been used, show characteristic changes in the products formed (*vide infra*). These reactions as well as those involving triorgano-aluminium reagents will be described in full detail elsewhere.

Relevance for organic synthesis

The previous sections have shown that 1,4-dihetero-1,3-butadienes can be activated for subsequent (selective) conversion by coordination to a metal centre. In general, 1,4-dihetero-1,3-butadienes, $\text{X}=\text{C}(\text{R})\text{C}(\text{R}')=\text{Y}$, which in most cases are easily made [1,2], can be attractive starting materials for the synthesis of organic skeletons containing hetero-atoms. Scheme 2 shows some reactions we have carried out for the $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton which involve stepwise conversion of the diene into a monoene. For many combinations of R and R' the reaction of R_2Zn with R'-DAB, selective N-alkylation is observed, see Scheme 2A [6]. This step is quantitative, and subsequent protonolysis afford *cis*-enediamino compounds which are in equilibrium with the tautomeric aminoimines.

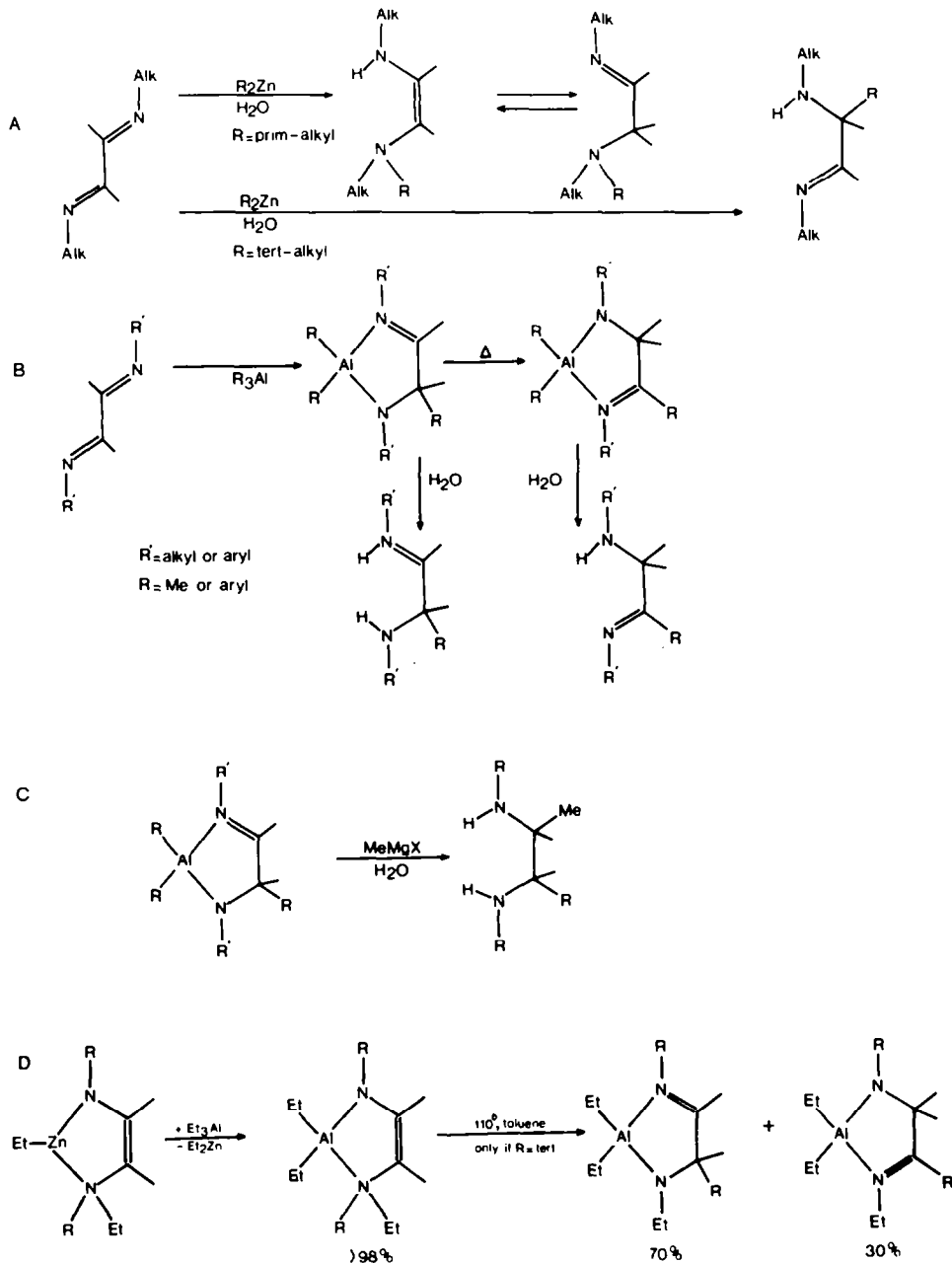
In the case of R_3Al , selective C-alkylation of alkyl- or aryl-DAB compounds has been observed when R is methyl or aryl. Depending on the conditions employed one obtains either the 3-substituted 1,4-diaza-1-butene or, as a result of subsequent H-shift, the 2-substituted derivative (both are aminoimines), see Scheme 2B [7].

When the organo-zinc or -aluminium compounds shown in Scheme 2B are treated before protonolysis with another equivalent of organometallic reagent (R_3Al or R_2Mg), further reduction of the monoene to a fully saturated $\text{X}-\text{C}-\text{C}-\text{X}$ or $\text{X}-\text{C}-\text{C}-\text{Y}$ skeleton can be achieved, see Scheme 2C. Most of these N- and C-substituted 1,2-diaminoethane compounds have been isolated in nearly quantitative yields.

A further example of the versatility of these reactions is the conversion of symmetric 1,4-diaza-1,3-butadiene into unsymmetrically substituted derivatives by the reaction shown in Scheme 2D. This novel reaction involves a 1,2 shift of the *t*-alkyl group R from the N to the C centre.

Finally we draw attention to the fact that reduction of the prochiral $\text{X}=\text{C}$ and $\text{Y}=\text{C}$ groupings in the heterobutadienes produces one or two chiral centres. We are now examining with the aid of chiral N-substituents whether these reductions can be carried out with a high degree of enantioselectivity.

SCHEME 2. Synthesis of 1,4-diaza-butene and 1,2-diaminoethane derivatives from 1,4-diaza-1,3-butadiene compounds.



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