

Preliminary communication

AN UNEXPECTED ETHYL TRANSFER REACTION BETWEEN Et_2Zn AND DI(*t*-BUTYL)-GLYOXALDIIMINE (*t*-BuDAB). STUDIES OF THE PERSISTENT $[\text{EtZn}(\text{t-BuDAB})]$ RADICAL WHICH IS IN EQUILIBRIUM WITH ITS C—C COUPLED DIMER

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Summary

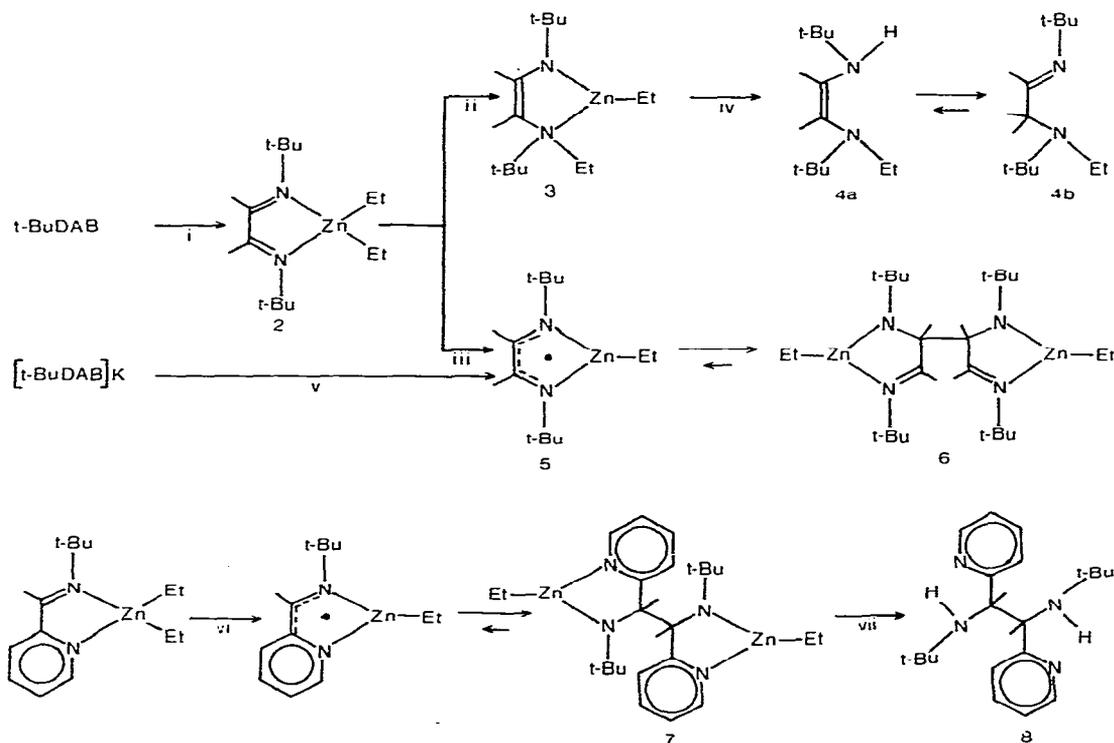
Whereas *p*-Tol₂Zn reacts with *t*-BuN=CHCH=N-*t*-Bu (*t*-BuDAB) to give a stable 1/1 complex [*p*-Tol₂Zn(*t*-BuDAB)], Et_2Zn gives $\text{EtZnN}(\text{Et})(\text{t-Bu})\text{CH}=\text{CHN}(\text{t-Bu})$ via intramolecular ethyl transfer in the unstable $\text{Et}_2\text{Zn}(\text{t-BuDAB})$ complex. In solution the stable persistent organozinc radical $[\text{EtZn}(\text{t-BuDAB})^\cdot]$, which is formed in trace amounts in the $\text{Et}_2\text{Zn}/\text{t-BuDAB}$ reaction, is in equilibrium with its stable C—C coupled dimer $[\text{EtZn-t-BuN}=\text{CH}(\text{t-BuN})\text{CH}]_2$. The dimer can be prepared in quantitative yield by the reaction of $(\text{EtZnCl})_4$ with K(*t*-BuDAB).

Recent reports have shown that the N=C—C=N skeleton of substituted 1,4-diaza-1,3-dienes (R-DAB) can interact with metal centres in a variety of modes: viz. σ -N monodentate (2e), σ, σ -N,N' chelate (4e), σ -N, σ -N' bridging (2e+2e) as well as σ -N, μ_2 -N', η^2 -CN' (6e) and even σ, σ -N,N', η^2 -CN, η^2 -CN' (8e) bridging [1–3]. This suggests that the N=C—C=N skeleton in the R-DAB molecule might be activated for a particular conversion by coordination to a metal, and so study of this heteroolefin as a synthon for novel organic chemistry holds promise [3]. Examples illustrating this idea are *i*, the C—C coupling of two R-DAB molecules on Mo₂(CO)₆ and Ru₂(CO)₆ units [4], for which η^2 -CN coordination is the activating step, and *ii*, the selective addition of a R—Al bond in R₆Al₂ across one N=C bond of a R-DAB molecule to give imino-amino-aluminium compounds; the latter upon subsequent hydrolysis give quantitative yields of the corresponding imino-amine derivatives [5]. In this paper we describe reactions of organozinc derivatives R_nZnX_{2-n} (*n* = 1 or 2; R = Et or *p*-tolyl; X = Cl) with either *t*-BuDAB or its radical anion $[\text{t-BuDAB}]^\cdot$.

The 1/1 molar reaction of *t*-BuDAB with *p*-Tol₂Zn in diethyl ether immediately gave the yellow 1/1 complex *p*-Tol₂Zn·*t*-BuDAB (1) (monomeric in benzene by cryoscopy mol. wt. found (calcd.) 405 (415.4)). The ¹H and ¹³C NMR spectra revealed that 1 is a four coordinate Zn compound containing σ, σ -*N,N'* chelate bonded *t*-BuDAB. This is the expected coordination behaviour for bidentate ligands L₂ in R₂ZnL₂ compounds; e.g. L₂ is Me₂NCH₂CH₂NMe₂ [6,7], 2,2'-bipy [8] or tetramethyltetraazene [7]. Compound 1 is thermally very stable; heating a solution of 1 in xylene for six hours did not affect the ¹H or ¹³C NMR spectra.

An entirely different and unexpected reaction is observed to take place in the 1/1 reaction of Et₂Zn with *t*-BuDAB (see Scheme 1). Mixing the two reactants in toluene at -70°C resulted in formation of an orange red solution, which according to the ¹H NMR spectrum contained the 1/1 complex Et₂Zn·*t*-BuDAB (2). A subsequent reaction of this unstable complex occurred, when the solution was heated, as indicated by a sharp colour change to pale yellow (at about -50°C). The ¹H NMR spectrum showed that a new organo-zinc species 3 had been formed in almost quantitative yield (>98%), and this was isolated as a distillable oil (l.p. 91°C/0.1 mmHg).

The ¹H and ¹³C NMR spectra of 3 are in agreement with a structure consist-



SCHEME 1. *i*, Et₂Zn, pentane, -70°C; *ii*, >-50°C, Et⁺ transfer, >98%; *iii*, Et⁺ loss, trace; *iv*, *t*-BuOH, pentane, -EtH; *v*, EtZnCl, THF/Et₂O, -40°C; *vi*, toluene, 110°C, C₂H₄ and C₂H₆ also are formed; *vii*, H₂O, -EtH.

ing of an EtZn species coordinated by the (t-Bu)EtNCH=CHN(t-Bu) bidentate anion. Cryoscopic molecular weight determinations revealed that **3** is monomeric in benzene (found(calcd.) 280(291.4)).

The asymmetry in this new ligand is reflected by the observation in the ^1H NMR spectrum of **3** of two singlets for the t-Bu groups (1.10 and 1.35 ppm) and two anisochronous resonance patterns for the two Et groups. The resonances due to the NCH=CHN hydrogen atoms, which are isochronous in **2** (7.50 ppm), appear in **3** in the olefinic region as an AX pattern (4.05 and 6.85 ppm) with $^3J(\text{HH})$ of 5 Hz, consistent with *cis*-olefinic H atoms. The CH_2 hydrogen atoms of the NEt group are diastereotopic ($\delta(\text{NCH}_2\text{Me})$ 2.05 and 2.95 ppm, $^2J(\text{HH})$ 11.5 Hz) as a result of coordination of the Et(t-Bu)N group to zinc which renders this N atom a stable chiral centre. Likewise the methylene protons of the ZnEt group are diastereotopic. Further proof for the structure of **3** comes from alcoholysis experiments with t-BuOH which gave a EtZnO-t-Bu [**9**] quantitatively and a 4/1 equilibrium mixture of **4a** and **4b***. Treatment of this mixture with Et_2Zn gave **3** and ethane in almost quantitative yields.

Compound **3** does not react further with N donor ligands (pyridine and 2,2'-bipyridine) indicating that its three-coordinate geometry at Zn is stable. This is most probably due to the bulk at the N centre of the coordinated Et(t-Bu)N group, which is adjacent to the Zn centre.

A remarkable difference exists between the reactions of t-BuDAB with Et_2Zn and Me_6Al_2 . While in the former reaction an Et-N bond is formed, the latter reaction gives rise to a new Me-C bond [**5**]. This difference might be due to different bondings of the t-BuDAB ligand in the precursor complexes, $\text{Me}_3\text{Al}\cdot\text{t-BuDAB}$ ($\sigma\text{-N}$ monodentate) and $\text{Et}_2\text{Zn}\cdot\text{t-BuDAB}$ (**2**) ($\sigma, \sigma\text{-N, N}'$ chelating), resulting in different polarizations of the N=C-C=N skeleton. The Zn-Et bond in **2** is obviously activated for homolytic cleavage, resulting in formation of an Et radical which is intramolecularly trapped by a N centre of the N=C-C=N skeleton. This trapping is extremely efficient (cf. >98% yield of **3**).

ESR spectra recorded on freshly prepared solutions of **2** (at -70°C) did not show an ESR signal. However, at room temperature, i.e. after **2** had been converted into **3**, the ESR spectrum of a persistent radical present in low concentration was recorded, and could be assigned to the three-coordinate organozinc radical **5**, see Fig. 1 (g 2.0021, a_{N} 4.87 G, $a_{\text{H}\alpha}$ 5.87 G, $a_{\text{H}\beta}$ 0.48 G). Radical **5** is formed from **2** by escape of the Et radical from the solvent cage. Similar radical species $[\text{R-DABZnX}]^\cdot$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$) have been reported by Clopath et al. [**11**] and the thermally very unstable $[\text{EtZnBipy}]^\cdot$ (dec. above -60°C) was studied by Boersma et al. [**12**].

In order to prepare **5** directly the reaction of $(\text{EtZnCl})_4$ with $[\text{t-BuDAB}]\text{K}$ in 1/4 molar ratio was studied and this gave a white crystalline solid in 85% yield. Surprisingly molecular weight determinations indicated that this compound was a dimer of $[\text{EtZn(t-BuDAB)}]$ (by cryoscopy, found (calcd.) 505

* **4a**: *cis-N, N'*-di(t-butyl)-*N*-ethyl-1,2-diaminoethene and

4b: *N, N'*-di(t-butyl)-*N'*-ethyl-1,4-diaza-1-butene; a similar equilibrium between this type of ene-diamine and imine-amine was observed by Bruder et al. [**10**].

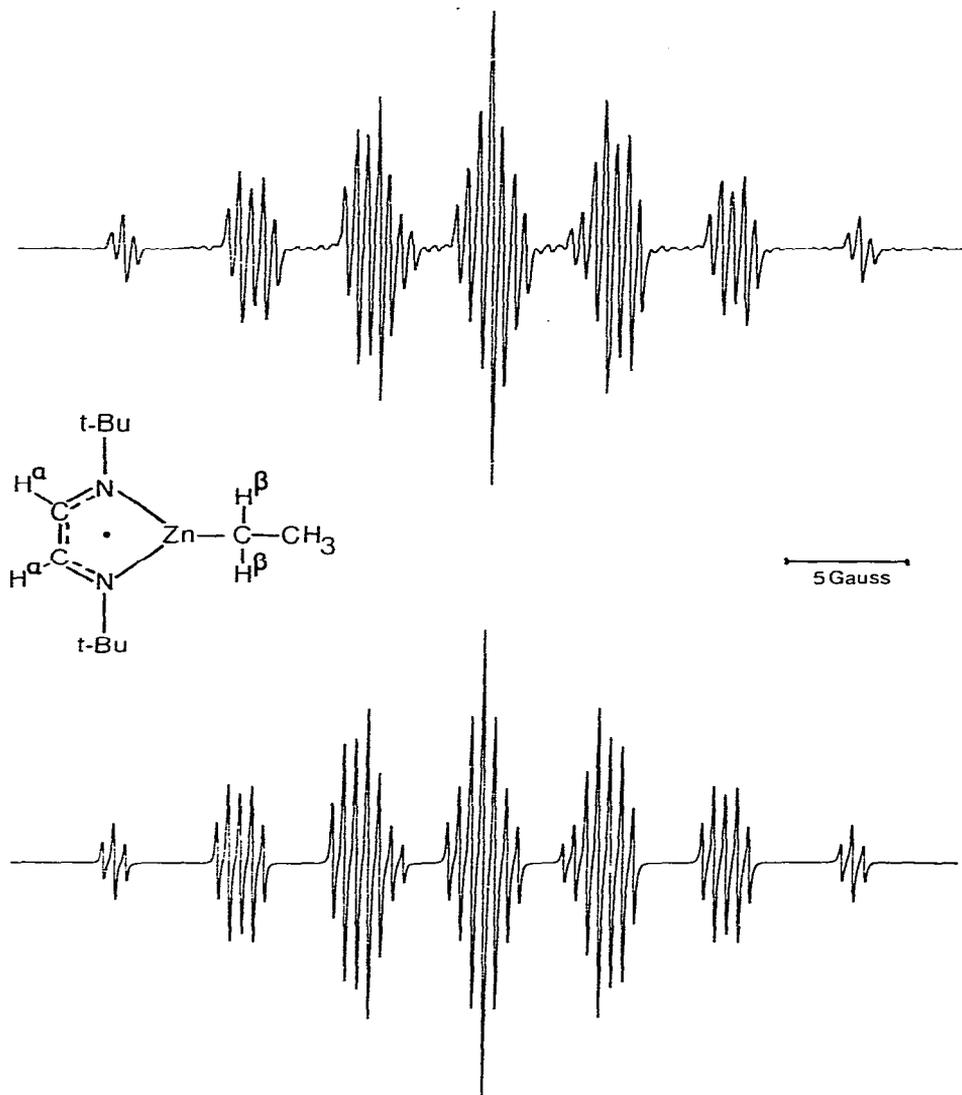


Fig. 1. Observed (top) and calculated (bottom) ESR spectrum of the persistent $[\text{EtZn}(\text{t-BuDAB})]$ radical 5.

(524.8). ^1H and ^{13}C NMR data* pointed to structure 6 consisting of two $[\text{EtZn}(\text{t-BuDAB})]^\cdot$ moieties coupled together via a C—C bond. Moreover, these data are in agreement with the data of $[\text{Mo}_2(\text{CO})_6(\text{t-BuDAB})_2]$ which likewise contains a C—C coupled t-BuDAB dimer ligand [4].

The dimer 6 dissociates in solution to a very small extent, providing the persistent radical 5. That the equilibrium between 6 and 5 lies predominantly to the side of the dimer is indicated by *i*, the molecular weight data for 6; *ii*, the fact that the signal intensities in the NMR spectra of 6 are not noticeably

* ^1H NMR (250 MHz) in toluene- d_6 : $\delta(\text{t-Bu})$ 1.10 and 1.19, $\delta(\text{CH}=\text{N})$ 7.78, $\delta(\text{NCH})$ 2.78 ppm ($^3J(\text{H}-\text{H})$ 3 Hz); ^{13}C NMR (20.115 MHz) in toluene- d_6 : $\delta(\text{t-Bu})$ 29.4 and 32.6, $\delta(\text{CH}=\text{N})$ 170.9, $\delta(\text{NCH})$ 60.1 ppm.

temperature dependent, and *iii*, the fact that no ESR spectrum could be obtained below -60°C . Moreover the absence of significant line broadening in the ^1H and ^{13}C NMR spectra indicates that the dissociation—association process is slow on the NMR time scale.

Attempts to isolate the novel tetraamine ligand in **6** by hydrolysis of the dimer failed, probably because this ligand is not stable on its own. In this respect it is interesting to note that the reaction of Et_2Zn with $t\text{-BuN}=\text{CH}-2\text{-Py}$ afforded the dimer **7** in almost quantitative yield (see Scheme 1), and the latter upon hydrolysis gave the free ligand **8**. The observation that solutions of **7** give an ESR spectrum only above 50°C indicates that dimer **7** is much more stable than **6**.

The scope of these unusual alkyl transfer reactions of alkylzinc compounds with R-DAB systems* will be further explored because they offer a convenient route to the synthesis of novel types of ene-diamine compounds, (e.g. **4a**) and tetradentate nitrogen ligands (e.g. **8**). In addition, to aid interpretation of the mechanism of the coupling reactions between R-DAB molecules on $\text{M}_2(\text{CO})_6$ units, studies of the influence of the R substituent on the equilibrium between the unusually stable organozinc radicals and their respective dimers are planned.

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*The same reaction pattern and selective product formation has been found for other alkyl-diamines where R is either a primary, secondary or tertiary alkyl group.