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

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## Summary

Whereas *p*-$Tol_2Zn$ reacts with t-BuN=CHCH=N-t-Bu (t-BuDAB) to give a stable 1/1 complex [*p*-$Tol_2Zn$(t-BuDAB)], $Et_2Zn$ gives EtZnN(Et)(t-Bu)CH=CHN-(t-Bu) via intramolecular ethyl transfer in the unstable $Et_2Zn$(t-BuDAB) complex. In solution the stable persistent organozinc radical EtZn(t-BuDAB)$^{\cdot}$, which is formed in trace amounts in the $Et_2Zn$/t-BuDAB reaction, is in equilibrium with its stable C—C coupled dimer [EtZn-t-BuN=CH(t-BuN)CH]$_2$. The dimer can be prepared in quantitative yield by the reaction of $(EtZnCl)_4$ 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. $\sigma$-*N* monodentate (2*e*), $\sigma,\sigma$-*N,N'* chelate (4*e*), $\sigma$-*N*, $\sigma$-*N'* bridging (2*e*+2*e*) as well as $\sigma$-*N*,$\mu_2$-*N'*,$\eta^2$-*CN'* (6*e*) and even $\sigma,\sigma$-*N,N'*, $\eta^2$-*CN*, $\eta^2$-*CN'* (8*e*) 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 $Mo_2(CO)_6$ and $Ru_2(CO)_6$ units [4], for which $\eta^2$-CN coordination is the activating step, and *ii*, the selective addition of a R—Al bond in $R_6Al_2$ 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 [t-BuDAB]$^{\cdot-}$.

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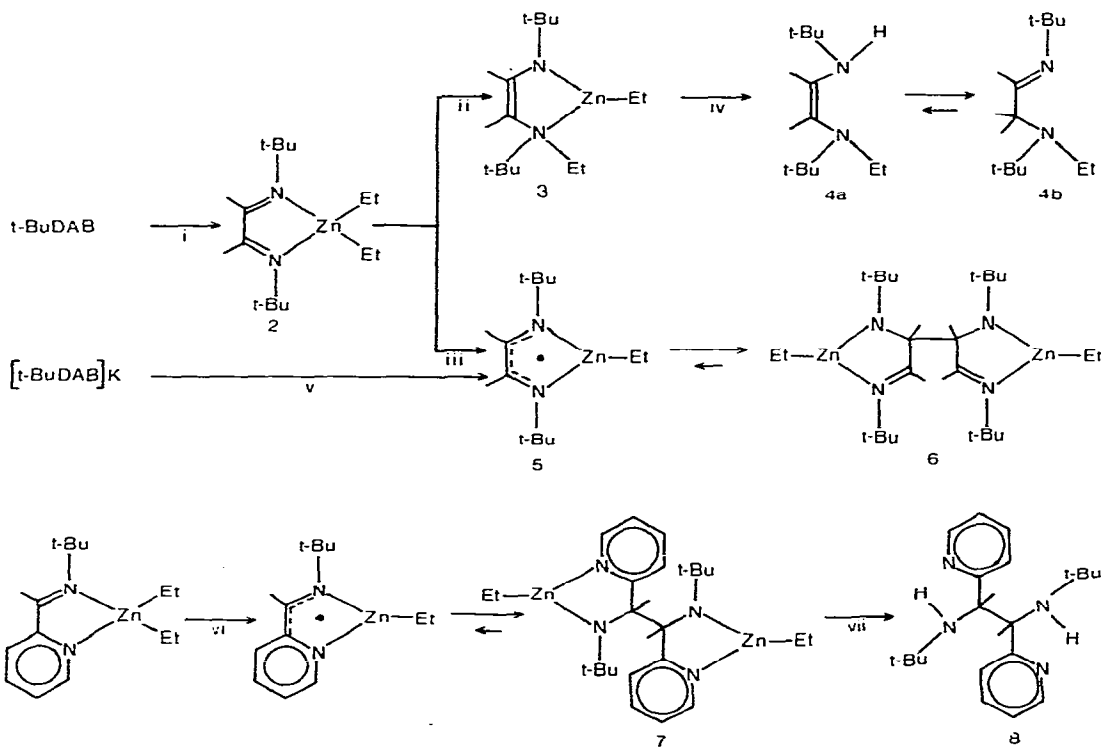
The 1/1 molar reaction of t-BuDAB with $p$-$Tol_2Zn$ in diethyl ether immediately gave the yellow 1/1 complex $p$-$Tol_2Zn$·t-BuDAB (1) (monomeric in benzene by cryoscopy mol. wt. found (calcd.) 405 (415.4)). The $^1H$ and $^{13}C$ NMR spectra revealed that 1 is a four coordinate Zn compound containing $\sigma,\sigma$-$N,N'$ chelate bonded t-BuDAB. This is the expected coordination behaviour for bidentate ligands $L_2$ in $R_2ZnL_2$ compounds; e.g. $L_2$ is $Me_2NCH_2CH_2NMe_2$ [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 $^{13}C$ NMR spectra.

An entirely different and unexpected reaction is observed to take place in the 1/1 reaction of $Et_2Zn$ 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 $Et_2Zn$·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 organozinc species 3 had been formed in almost quantitative yield (>98%), and this was isolated as a distillable oil (b.p. 91°C/0.1 mmHg).

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




SCHEME 1. *i*, $Et_2Zn$, pentane, −70°C; *ii*, >−50°C, $Et^{\bullet}$ transfer, >98%; *iii*, $Et^{\bullet}$ loss, trace; *iv*, t-BuOH, pentane, −EtH; *v*, EtZnCl, THF/$Et_2O$, −40°C; *vi*, toluene, 110°C, $C_2H_4$ and $C_2H_6$ also are formed; *vii*, $H_2O$, −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 $^1$H 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 $^3J$(HH) of 5 Hz, consistent with *cis*-olefinic H atoms. The $CH_2$ hydrogen atoms of the NEt group are diastereotopic ($\delta$(NC$\underline{H}_2$Me) 2.05 and 2.95 ppm, $^2J$(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, $Me_3Al \cdot$t-BuDAB ($\sigma$-*N* monodentate) and $Et_2Zn \cdot$t-BuDAB (2) ($\sigma,\sigma$-*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, $a_{H\alpha}$ 5.87 G, $a_{H\beta}$ 0.48 G). Radical 5 is formed from 2 by escape of the Et radical from the solvent cage. Similar radical species [R-DABZnX]$^\cdot$ (X = Cl, Br, I, CN) have been reported by Clopath et al. [11] and the thermally very unstable [EtZnBipy]$^\cdot$ (dec. above −60°C) was studied by Boersma et al. [12].

In order to prepare 5 directly the reaction of $(EtZnCl)_4$ with [t-BuDAB]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 [EtZn(t-BuDAB)] (by cryoscopy, found (calcd.) 505

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*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].

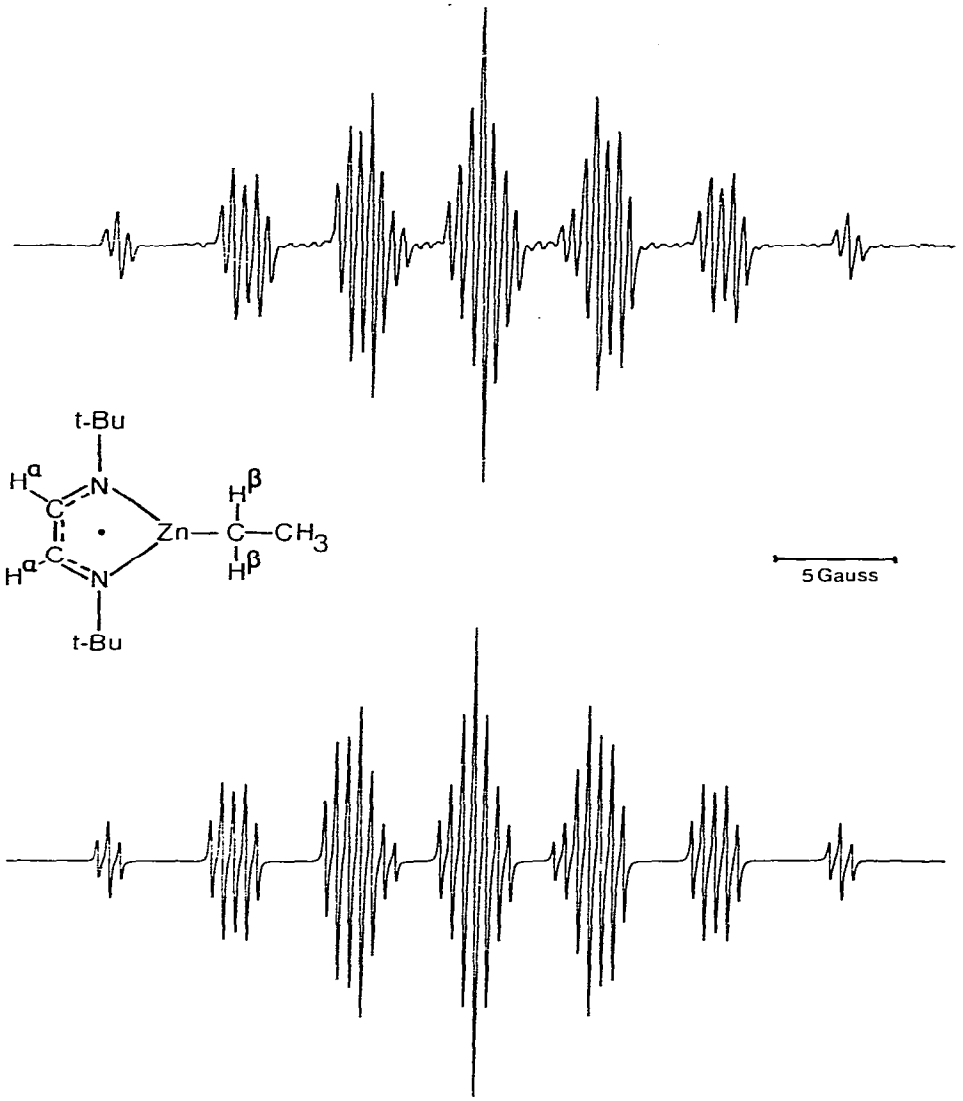


Fig. 1. Observed (top) and calculated (bottom) ESR spectrum of the persistent [EtZn(t-BuDAB)] radical 5.

(524.8)). $^{1}H$ and $^{13}C$ NMR data* pointed to structure **6** consisting of two [EtZn(t-BuDAB)]$^{\cdot}$ moieties coupled together via a C—C bond. Moreover, these data are in agreement with the data of $[Mo_2(CO)_6(t\text{-BuDAB})_2]$ 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

*$^{1}H$ NMR (250 MHz) in toluene-$d_8$: δ(t-Bu) 1.10 and 1.19, δ(CH=N) 7.78, δ(NCH) 2.78 ppm ($^{3}J$(H—H)3 Hz); $^{13}C$ NMR (20.115 MHz) in toluene-$d_8$: δ(t-Bu) 29.4 and 32.6, δ(CH=N) 170.9, δ(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 $^{1}H$ 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-BuN=CH-2-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 $M_2(CO)_6$ 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-diimines where R is either a primary, secondary or tertiary alkyl group.