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A Comparative Study of Thermal- and Radiation-Induced Single Electron Transfer in Reactions of 1,4-Diaza-1,3-butadienes with Dialkylzinc Compounds

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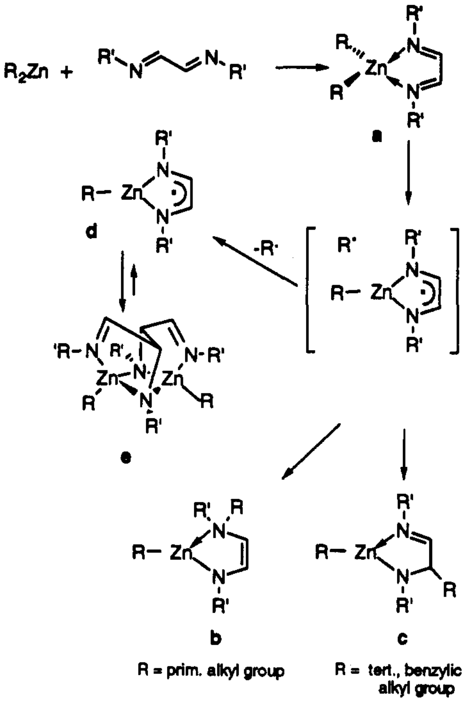
The reaction of R_2Zn with *t*-BuDAB (*t*-BuN=CH—CH=N-*t*-Bu) results in the quantitative formation of the red 1:1 coordination charge transfer complexes R_2Zn-*t*-BuDAB (R = Me (**1a**), CH_2SiMe_3 (**5a**)). Upon heating ($T > 35$ °C), both complexes undergo an inner-sphere single electron transfer (SET) leading to the radical pair [(RZn-*t*-BuDAB)$^\bullet$(R$^\bullet$)], that collapses, depending on R$^\bullet$, to several alkylation products, *i.e.* the N-alkylated product MeZn(*t*-BuN—CH=CH—N(Me)-*t*-Bu) (**1b**) and the exocyclic enamines RZn(*t*-BuN=CH—C(=CHR′)N-*t*-Bu) (R = Me (**1f**), CH_2SiMe_3 (**5f**/**5g**); R′ = H, $SiMe_3$). Alternatively, the alkyl radical R$^\bullet$ escapes from the organozinc radical (RZn-*t*-BuDAB)$^\bullet$, that subsequently dimerizes to the dinuclear species (RZn-*t*-BuDAB)$_2$ (R = Me (**1e**), CH_2SiMe_3 (**5e**)). The charge transfer complex Me_2-Zn-*t*-BuDAB was irradiated in order to induce a SET reaction within the complex. The irradiation reaction resulted in the formation of the symmetric dinuclear species **1e** (30%) and the unsymmetric dinuclear species [MeZn{*t*-Bu(H)NCH(Me)CH(N-*t*-Bu)–}{-CH(N-*t*-Bu)CMe=N-*t*-Bu}ZnMe] (**1h**) (70%). Product **1h** was independently prepared from MeZn(*t*-BuN—CH-(Me)–CH=N-*t*-Bu) (**1c**). The latter complex is in a tautomeric equilibrium with its enamine MeZn(*t*-BuN—CH(Me)=CH—N(H)-*t*-Bu), that reacts *via* a condensation reaction with a parent molecule **1c** to give **1h**.

Introduction

Recently, we reported on the regioselective N or C alkylation by dialkylzinc compounds (R_2Zn) of 1,4-disubstituted-1,4-diaza-1,3-butadienes (R′N=CH—CH=NR′ (R′DAB)).[1] These reactions are the result of an intramolecular electron shift from the R_2Zn moiety to the R′DAB ligand in an initially formed 1:1 coordination complex R_2ZnR′DAB. The so formed radical pair may collapse within the solvent cage to N- (**b**, cf. Scheme 1) (for primary alkyl groups) or C-alkylated (**c**) (for tertiary alkyl and benzylic groups) organozinc complexes, or the alkyl radical may escape from the organozinc radical. In that case, the remaining organozinc radical (**d**) is persistent and is in equilibrium with its C–C coupled dimer **e** (see Scheme 1).[2a,3]

The initially formed coordination complexes in the alkylation reaction are, like R_2ZnBpy complexes,[4,5] strongly colored with widely varying absorption maxima, that depend on the nature of R; see Table 1. It has been suggested that the intense color of the complexes **1a**–**4a** is caused by a $S_0 \rightarrow S_1$ LLCT transition σ(M-C) $\rightarrow \pi^*_{DAB}$.[2]

Scheme 1



Theoretical calculations on R_2Zn-*t*-BuDAB complexes, R = *t*-Bu, *i*-Pr, Et, and Me, show that the LUMO's of

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[●] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

(1) (a) Klerks, J. M.; Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1982**, *224*, 107. (b) van Koten, G. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987; p 277. (c) van Koten, G.; Wissing, E.; Kleijn, H.; Jastrzebski, J. T. B. H. In *Organic Synthesis via Organometallics* (*OSM 4*), *Proceedings of the Fourth Symposium in Aachen*; Enders, D., Gais, H.-J., Keim, W., Eds.; F. Wieweg Verlag: Wiesbaden, Germany, 1992; pp 175–190.

(2) (a) Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; van Koten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606. (b) Rossenaar, B. D.; Kleverlaan, C. J.; Stufkens, D. J.; Oskam, A. *Chem. Commun.* **1994**, 63.

(3) (a) van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, *250*, 49. (b) Spek, A. L.; Jastrzebski, J. T. B. H.; van Koten, G. *Acta Crystallogr.* **1987**, *C43*, 2006.

(4) Boersma, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, U. K., 1982; Vol. 2, p 823.

(5) (a) Noltes, J. G.; van der Hurk, J. W. G. *J. Organomet. Chem.* **1965**, *3*, 222. (b) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *9*, 1. (c) Rau, H.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1967**, *335*, 253.

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Table 1. Characteristic Features of R_2Zn-*t*-BuDAB Complexes

R_2Zn-*t*-BuDAB R group	color[a]	λ_{max} (nm)[b]	conversion temp (°C)[c]
Me (**1a**)	orange	390	room temp
Et (**2a**)	red	490	-50
i-Pr (**3a**)	blue	590	-70
t-Bu (**4a**)	purple	650	-90

[a] In diethyl ether. [b] Extinction coefficient ϵ was determined for Me_2Zn-*t*-BuDAB and was found to be 1200 M^{-1} cm^{-1}. [c] Conversion was monitored by ^1H NMR spectroscopy and starts above the temperature given.

these complexes, which are mostly localized within the chelated DAB ligand, have a comparable energy level, whereas the HOMO energies increase in the series R = Me < Et < *i*-Pr < *t*-Bu.[2a,6] This trend is also reflected by the decreasing stability of the coordination complexes, of which *t*-Bu_2Zn-*t*-BuDAB (**4a**) is only stable to -90 °C, whereas the Me_2Zn complex is stable at room temperature; see Table 1. When the temperature is raised above a critical temperature, an intramolecular single electron transfer (SET) from the R_2Zn to the DAB occurs, leading to the radical pair **a′**, that finally collapses to the alkylated products (see Scheme 1).

ESR experiments have shown that by irradiation in the charge transfer band of the coordination complexes, organozinc–DAB radicals are formed, indicating that the SET within the R_2Zn-*t*-BuDAB complexes can also be light-induced.[2a]

Recently, we have found that the bis((trimethylsilyl)methyl)zinc compound, $(Me_3SiCH_2)_2Zn$, like Me_2Zn forms a stable 1:1 coordination complex at room temperature.[7] In this paper we describe a study of the product formed by photochemical initiation of Me_2Zn-*t*-BuDAB and compare the results with those obtained in the thermally induced SET reaction of Me_2Zn-*t*-BuDAB and $(Me_3SiCH_2)_2Zn$-*t*-BuDAB.

Results

Both Me_2Zn and $(Me_3SiCH_2)_2Zn$ react with *t*-BuDAB in diethyl ether at room temperature to the corresponding 1:1 coordination complexes R_2Zn-*t*-BuDAB (R = Me (**1a**), R = CH_2SiMe_3 (**5a**)). Compounds **1a** and **5a** were crystallized from hexane to afford orange crystals. The UV–vis absorption spectrum of **5a** is comparable to that of **1a** (see Table 1) with λ_{max} at 390 nm.

Thermal Reaction. Solutions of **1a** and **5a** in benzene were heated for 6 h at 70 °C. Product analysis revealed that quantitative conversion into several products had occurred. Complex **1a** was converted into three products: the C–C coupled dinuclear species (MeZn-*t*-BuDAB)$_2$ (**1e**) (50%), the N-alkylated product [MeZn(*t*-BuN—CH=CH—N(Me)-*t*-Bu)] (**1b**) (25%), and the zinc–enamine [MeZn(*t*-BuN=CH—C(CH_2)—N-*t*-Bu)] (**1f**) (25%) (see Scheme 2, eq 1). Compound **1b** is similar to the products which are exclusively formed in the reaction of *t*-BuDAB with primary dialkylzinc compounds (see compound **b** in Scheme 1). The ^1H NMR spectrum of **1b** shows the same characteristic AB pattern in the olefin region ($^3J_{HH}$ = 4.4 Hz) as was observed for comparable N-alkylated products,[1,8] which is consistent with the presence of *cis* olefin H atoms. The ^1H NMR spectrum of the dimeric compound **1e** shows an AX pattern for the N=CH—CH—N moiety with a coupling constant ^3J of 2.7 Hz, characteristic for such dimers.[7] The ^1H NMR spectrum of the exocyclic zinc–enamine **1f** shows three singlet resonances for the N=CH—C=CH_2 moiety at 7.42, 4.59, and 4.18 ppm for the N=CH and the anisotropic C=CH_2 hydrogens, respectively. No geminal coupling was observed for the CH_2 hydrogens.

Thermal conversion of **5a** gave the dimeric species (Me_3SiCH_2Zn-*t*-BuDAB)$_2$ (**5e**) (65%) and the exocyclic enamines Me_3SiCH_2Zn(*t*-BuN=CH—C(CH_2)—N-*t*-Bu) (**5f**) (7%) and Me_3SiCH_2Zn(*t*-BuN=C($CHSiMe_3$)—N-*t*-Bu) (**5g**) (28%) (see Scheme 2, eq 2). The ^1H NMR spectrum of **5e** and **5f** shows the same characteristic signals as were found in **1e** and **1f**, respectively, whereas **5g** only contains two singlets at 8.11 and 5.04 ppm. The Si—C coupling constant in **5g**, $^1J_{Si-C}$ = 24.7 Hz, is significantly smaller than that of normal Si—C=C bonds in, *e.g.*, trimethylvinylsilane, $^1J_{Si-C}$ = 32.3 Hz. Also the ^{13}C chemical shift of the Si—*C*=C carbon in **5g**, 105.4 ppm, is much lower than that of the corresponding carbon in trimethylvinylsilane, 139.9 ppm, implying that this olefin carbon is strongly nucleophilic.[9]

The thermal decomposition of **5a** was followed by ^1H NMR in benzene-d_6 which showed the simultaneous formation of the products **5e**, **5f**, and **5g**, as well as a substantial amount of $Si(CH_3)_4$ and resonances that were ascribed to $Me_3SiCH_2SiMe_3$.

Irradiation Experiment. A solution of **1a** in diethyl ether or benzene was irradiated at approximately 20 °C with a high-pressure mercury lamp until no more starting material was detected by ^1H NMR spectroscopy. It appeared that the symmetric dinuclear species (MeZn-*t*-BuDAB)$_2$ (**1e**) (30%) and a new, unsymmetric dinuclear species [MeZn{*t*-Bu(H)NCH(Me)CH(N-*t*-Bu)–}{–CH(N-*t*-Bu)CMe=N-*t*-Bu}ZnMe] (**1h**) (70%) had formed (see eq 3). ^1H NMR measurements during the irradiation experiment showed that the C-alkylated product [MeZn(*t*-BuN—C(H)Me—CH=N-*t*-Bu)] (**1c**) and the dimer **1e** are formed first and **1h** is formed shortly thereafter. The relative amount of **1h** increases during the reaction, whereas the amount of **1e** and **1c** decreases and the latter eventually disappears.

Characterization and Independent Synthesis of 1h. The dinuclear structure of **1h** consists of two differently alkylated DAB skeletons, which are coupled *via* a newly formed C—C bond. The ^1H NMR spectrum shows four *t*-Bu— and two Me—Zn signals. Furthermore two CH_3 resonances were observed, *viz.* a singlet (1.75 ppm) and a doublet (0.82 ppm), which were assigned to a N=CMe and a N—C(H)Me entity, respectively. A characteristic ABX_3 pattern at 2.87 ppm was observed for the *t*-Bu(H)N—C(Me)*H*—CH—N-*t*-Bu hydrogen. The N—H resonance of this moiety was not observed in the ^1H NMR spectrum. However, simulation of the ABX_3 pattern (see Figure 1) enabled the determination of $^3J_{NH-CH}$, which was found to be 12.0 Hz. Finally, doublet (2.14 ppm) and singlet (3.18 ppm) resonances of the hydrogens bonded to the bridging carbons were found. No coupling between these two anisotropic hydrogens was observed.

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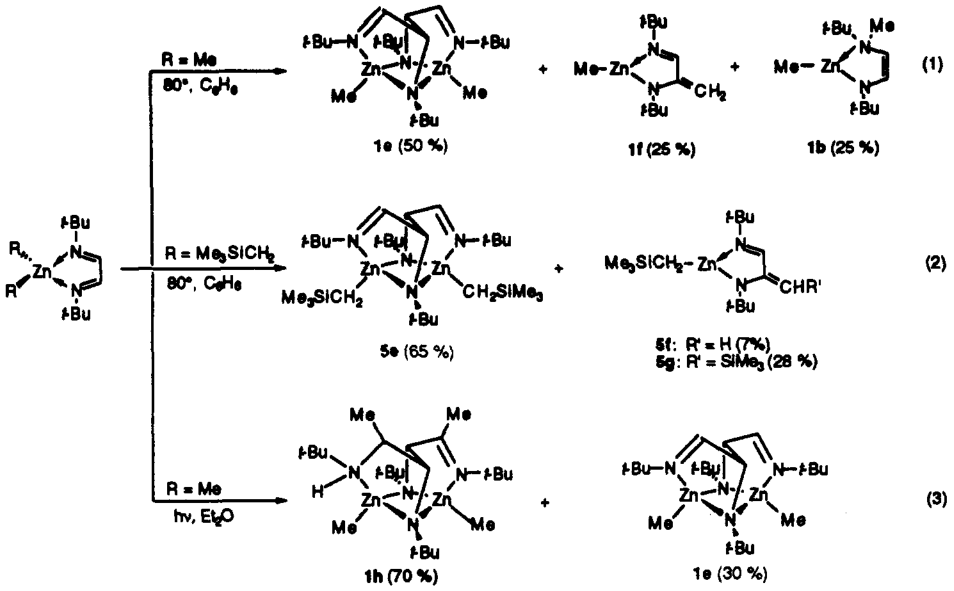
[6] Kaupp, M.; Stoll, H.; Preuss, H. *J. Comp. Chem.* **1990**, *11*, 1029.

[7] Wissing, E.; van der Linden, S.; Rijnberg, E.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics*, preceding article in this issue.

[8] Wissing, E.; Kleijn, H.; Boersma, J.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 618.

[9] The exocyclic zinc–enamines **1f**, **5f**, and **5g** are reactive toward electrophilic reagents.

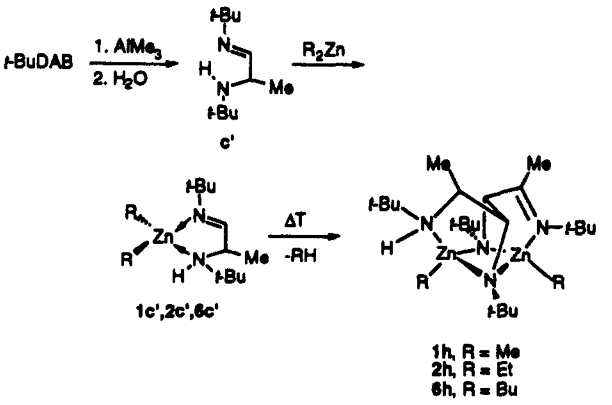
Scheme 2



Severe disorder made it impossible to refine the X-ray structure of **1h**, and no complete structure can therefore be presented. However a preliminary view of the structure shows that the two alkylated NCCN skeletons are coupled *via* a C–C bond similar to that found in the symmetric dinuclear structure of $(Me_3SiCH_2Zn\text{-}t\text{-}BuDAB)_2$ (**5e**).[7] In **5e** the dihedral angle between the hydrogens bonded to the bridging carbons is close to 90°, which would explain the lack of coupling between the two corresponding anisotropic hydrogens bonded to the bridging carbon atoms in **1h**.

We have been unable to separate the two dinuclear products, **1e** and **1h**, but they have each been prepared by independent syntheses. The dinuclear species **1e** was obtained by crystallization from the product mixture of the thermal reaction of $Me_2Zn\text{-}t\text{-}BuDAB$ (*vide supra*), whereas **1h** was obtained from the reaction of Me_2Zn with (t-BuN=CH—CH(Me)—N(H)-t-Bu) (**c′**).

The independent synthesis of **1h** was based upon the observation that in the irradiation reaction this dinuclear species was formed *via* the C-alkylated product **1c**. The necessary starting material t-BuN=CH—CH(Me)—N(H)-t-Bu (**c′**) was obtained by hydrolysis of Me_2Al(t-BuN=CH—CH(Me)—N-t-Bu), which is formed in the alkylation reaction of Me_3Al with t-BuDAB (see eq 4).[10]



(4)

The reaction of **c′** with Me_2Zn first gives the 1:1 coordination complex Me_2Zn(t-BuNH—CH(Me)—CH=N-t-Bu) (**1c′**),[11] which upon raising the temperature to 50 °C affords the dinuclear compound **1h** quantitatively. The intermediate MeZn(t-BuN—CH(Me)—CH=N-t-Bu) (**1c**) was never observed. The protonolysis of the R—Zn bond in the initial step of the reaction sequence (see Discussion), producing RH, was established with ^1H NMR.

This synthesis of **1h** is also applicable to other dialkylzinc compounds, and the Et–Zn (**2h**) and Bu–Zn (**6h**) analogs of **1h** were obtained from the reaction of **c′** with Et_2Zn and Bu_2Zn, respectively. The Bu–Zn derivative **6h** was prepared to increase the solubility of the product and to enable a molecular weight determination in solution (cryoscopy in benzene) in order to confirm its dinuclear nature (Calcd: 612. Found: 568).

Discussion

When it is accepted that the LUMO energy level of $(Me_3SiCH_2)_2Zn\text{-}t\text{-}BuDAB$ (**5a**) is at the same level as was calculated for R_2ZnDAB (R = Me, Et, i-Pr, t-Bu), then its λ_{max} of 390 nm indicates that its HOMO energy level must be comparable with that of $Me_2Zn\text{-}t\text{-}BuDAB$ (**1a**). This is in accord with the recent observation that $((Me_3Si)_2CH)_2ZnBpy$[14] has about the same λ_{max} as Me_2ZnBpy. Apparently, substitution of one or two of the hydrogens for $SiMe_3$ in Me_2Zn seems to have little or no influence on the LLCT charge transfer band and, accordingly, the stability of **5a** should be similar to that of **1a**. Indeed, upon heating both complexes decompose at the same critical temperature (about 35 °C) to three products, *i.e.*

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(10) Klerks, J. M.; Stufkens, D. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1978**, *181*, 271.

(11) Dialkylzinc compounds are known to react with secondary amines to form coordination complexes which, however, have only limited stability. Upon heating (T > 30 °C) these complexes decompose to give zinc amides.[12] The alkyl groups in alkylzinc halides (RZnX), however, are much more stable to acidic hydrogens.[13]

(12) (a) Thiele, K.-H.; Bendull, M. Z. *Anorg. Allg. Chem.* **1970**, *379*, 199. (b) Thiele, K.-H.; Zdunneck, P. *Organomet. Chem. Rev.* **1966**, *1*, 331. (c) Emptoz, G.; Huet, F. *J. Organomet. Chem.* **1974**, *82*, 139.

(13) Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974.

(14) Westerhausen, M.; Rademacher, B.; Schwarz, W. *J. Organomet. Chem.* **1992**, *427*, 275.

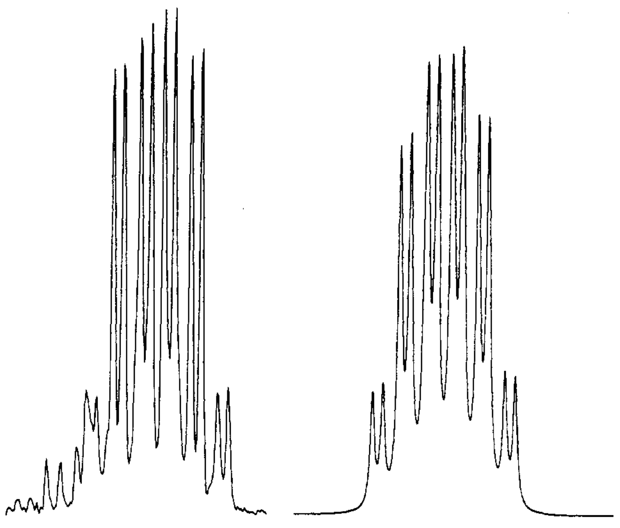
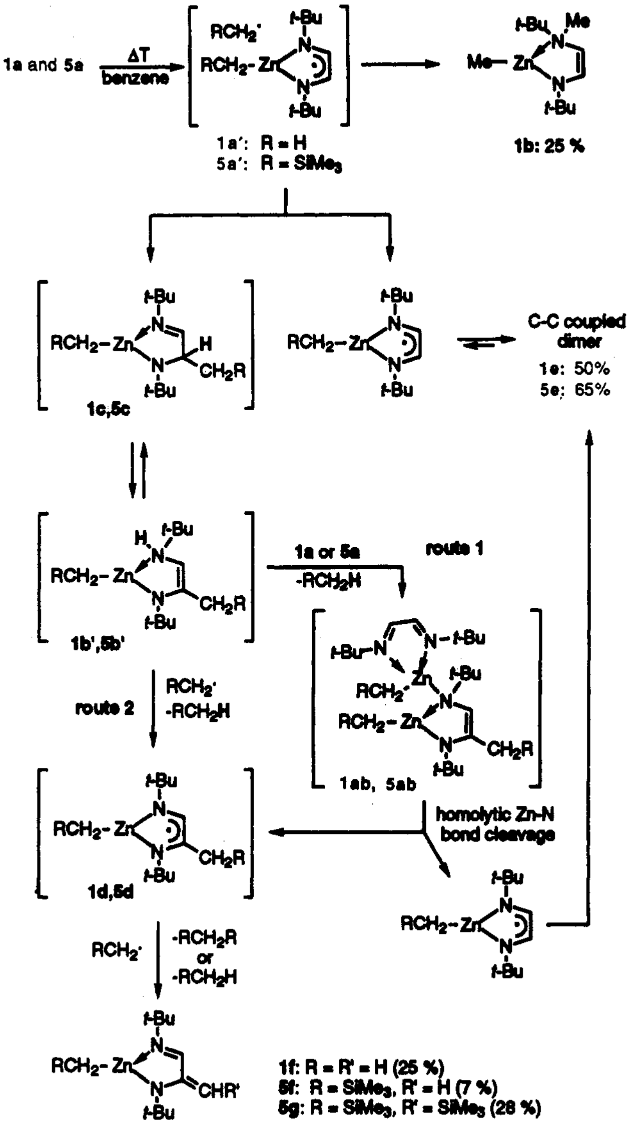


Figure 1. Observed (left) and simulated (right) 300-MHz ^1H NMR resonance for the ABX_3 pattern of the *t*-Bu(H)N–C(Me)*H*–CH–N-*t*-Bu hydrogen in **1h**.

1b, **1e**, and **1f** for **1a** and **5e**, **5f**, and **5g** for **5a**. Although $(Me_3SiCH_2)_2Zn$ is a primary dialkylzinc compound no N-alkylated product similar to **1b** was found. This was also observed in the reaction of $(Me_3CCH_2)_2Zn$ with *t*-BuDAB, that resulted in C alkylation only.[8]

The mechanism we propose for the formation of the products **1b**, **1e**, **1f**, **5e**, **5f**, and **5g** is outlined in Scheme 3. Upon heating, the coordination complexes **1a** and **5a** undergo a homolytical cleavage of one of the alkyl—zinc bonds, to give the radical pairs **1a′** and **5a′**, respectively. From this intermediate state the alkyl radicals can add to the NCCN skeleton of the organozinc radical, affording either the N-alkylated compound **1b** or the C-alkylated compounds **1c** and **5c**. Alternatively, the alkyl radicals can escape from the organozinc radical, leaving organozinc radicals that dimerize to **1e** and **5e**. The N-alkylated compound **1b** is the expected product in the reaction of **1a**, whereas the C-alkylated compounds **1c** and **5c** are not observed. However, we believe that **1f**, **5f**, and **5g** are formed from these intermediates. Earlier, we found that C-alkylated compounds like **1c** and **5c** are in equilibrium with their enamine tautomer RZn(*t*-BuN—CR=CH—N(H)-*t*-Bu) (**1b′** and **5b′**) and that the position of the equilibrium depends on the nature of the group bonded to the C atom of the NCCN skeleton.[8] When the shifted hydrogen is eliminated from the enamine tautomer, the organozinc radical species **1d** and **5d** are formed. This elimination process may occur in two ways. Firstly, when the tautomerization is faster than the initial C or N alkylation, a carbon—zinc bond in **1a** and **5a** may be hydrolyzed by the amine hydrogen of the enamine to form a N—Zn coupled dinuclear species (**1ab**, **5ab**) (route 1 in Scheme 3). Subsequent homolytic cleavage of the newly formed N—Zn bond leads to the radical species (RCH_2-Zn-*t*-BuDAB)$^•$ and **1d** (**5d**), of which the former dimerizes to **1e** (**5e**). When the rate of tautomerization is slower than the escape of an alkyl radical from the organozinc radical, then the shifted hydrogen in **1b′** (**5b′**) may be eliminated in a free alkyl radical process (route 2). Finally, a hydrogen (or a $SiMe_3$ group in the case of **5f**) is abstracted from the organozinc radicals **1d** and **5d** by a $RCH_2^•$ radical to give the products **1f**, **5f**, and **5g**. Because each of these $RCH_2^•$ radicals leaves behind a (RCH_2Zn-*t*-BuDAB)$^•$ radical that dimerizes to **1e**, these dimers **1e** and **1f** should be formed in a 2:1 ratio, which indeed has been observed (the same ratio was observed in the formation of **5e** and **5f**/**5g**). A similar reaction has been observed for analogous dimethylaluminum–iminoketone adducts.[15]

Scheme 3



The formation of $SiMe_4$ and $Me_3SiCH_2SiMe_3$ in the thermal decomposition of **5a** indicates that the escaped alkyl radicals take up two hydrogens, in the case of **1f** and **5g**, or one hydrogen and a trimethylsilyl group in the case of **5f**, from the initially formed C-alkylated products **1c** and **5c**.[16]

Irradiation Reaction. The irradiation of Me_2Zn-*t*-BuDAB basically gives 30% of the dinuclear species **1e** and 70% of the C-alkylated product **1c**, which was completely converted into the dinuclear species **1h** during the reaction. Since **1c** has been found to be thermally unstable, we believe that this subsequent conversion is caused thermally rather than photochemically. A plausible mechanism for the formation of **1h** would involve a condensation reaction (see Scheme 4). As mentioned above, the C-alkylated compound **1c**, which was independently generated from **1c′**, is in equilibrium with its zinc–enamine tautomer **1b′**; the latter being a nucleophilic

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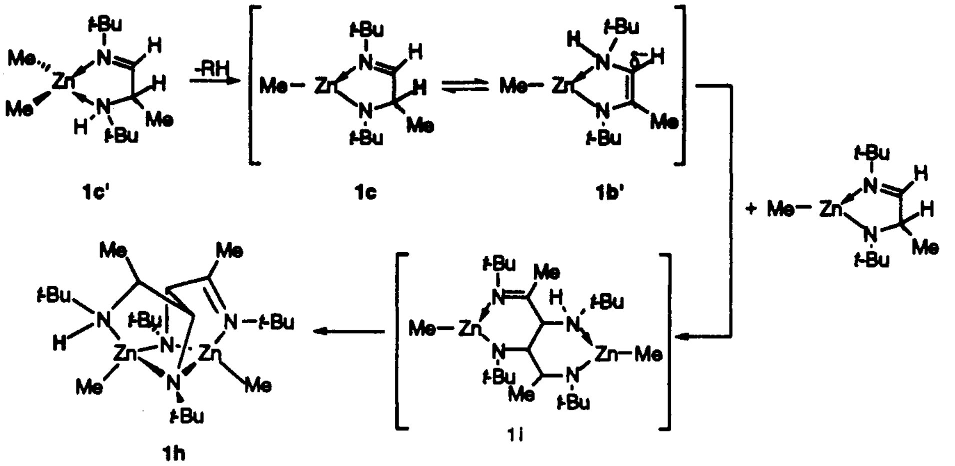
[15] van Vliet, M. R. P.; van Koten, G.; Buysingh, P.; Jastrzebski, J. T. B. H.; Spek, A. L. *Organometallics* **1987**, *6*, 537.

Scheme 4



reagent then undergoes a C—C coupling reaction with a parent molecule **1c** to give the zinc–aldolate **1i**. Finally, a hydrogen shift from one nitrogen to another gives the unsymmetric C—C coupled dinuclear compound **1h**. The hydrogen shift could formally be considered as self-rearrangement of the zinc–aldolate in order to reach a conformation wherein four-coordination of the zinc atoms is attained. The formation of **1h** is a nice example of double activation of the organic substrates by a zinc reagent. A comparable condensation reaction as mentioned above was found earlier in the regioselective alkylation reaction of Et_2Zn with imino esters (R'N=CH—COOEt) resulting in the formation of β-lactams.[18] The latter reaction involves condensation of the formed zinc enolate with the imine functionality of the Et_2Zn(R'N=CH—COOEt) complex.

The photochemically- and or thermally-induced SET reactions **1a** differ only in the degree of selectivity of the group transfer: in the thermal reaction a mixture of N- and C-alkylation products is formed, whereas the photochemical reaction resulted in C alkylation only. The highly regioselective C alkylation in the photochemical reaction supports the earlier suggestion that the T_1 state, obtained after a $S_0 \rightarrow S_1$ transition, followed by a fast heavy atom supported ISC process, is the starting point for the photochemistry in **1a**.[2] Calculations have shown an extremely low barrier to Zn–C dissociation in the T_1 state structure. The so formed radical pair, consisting of an organozinc and an alkyl radical, is a triplet and requires a spin flip before alkylation can take place; this increases the lifetime of the alkyl radical and favors alkylation at the least hindered center of the NCCN skeleton of the organozinc radical, *e.g.* a carbon center. In both reactions (thermal and photochemical) the initially formed C-alkylated product **1c** is the starting compound for subsequent reactions. The different amounts of second-order products formed is caused by the absence of large amounts of free alkyl radicals in the photochemical reaction. The higher temperature in the thermal reaction will enhance the formation of free radicals.

We have demonstrated that the β-aminozinc–enamido species **1b** are interesting intermediates for further synthesis, *i.e.* in condensation reactions with other imines and aldehydes, leading to, *e.g.*, indolizines,[19] 2- and 3-pyrrolidinones,[8] and 2-azetidinones.[7] Moreover, the dimeric zinc species **1e**, **1h**, and **5e** could be of interest in organometallic chemistry, since the newly formed tetradentate dianionic ligand may have some potential in stabilizing transition metal complexes.

Experimental Section

General Data. All experiments were carried out in a dry and oxygen-free nitrogen atmosphere, using standard

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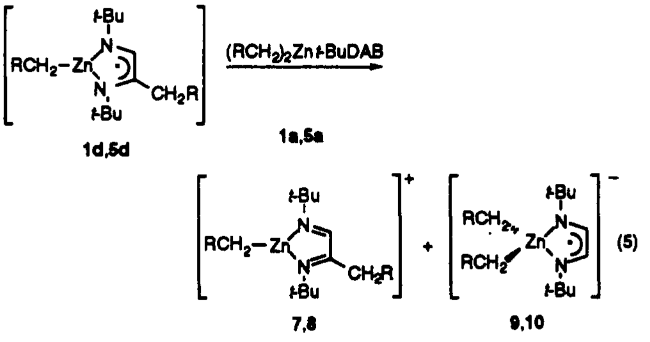
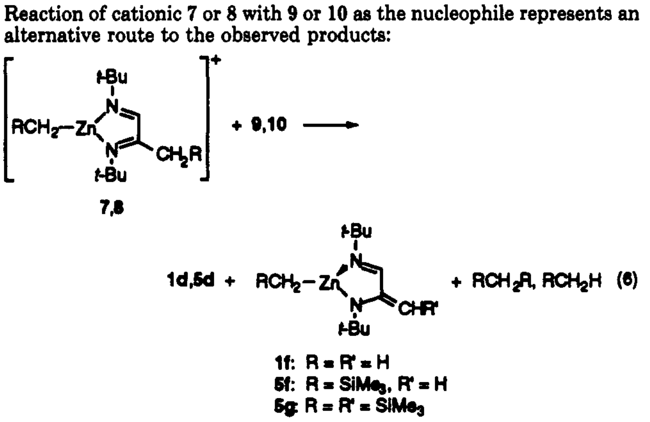
[16] It must be noted that the redox potential of radical **1d** or **5d** with respect to that of the 1:1 coordination complexes $(RCH_2)_2Zn$-*t*-BuDAB **1a** or **5a** is favorable for one-electron transfer (*cf.* the low ionization energy of RZn-*t*-BuDAB radicals (R = Me, Et)).[17] This would lead to the formation of cationic **7** or **8** as well as the diorganozinc radical-anion **9** or **10** according to



Reaction of cationic **7** or **8** with **9** or **10** as the nucleophile represents an alternative route to the observed products:



1f: R = R' = H
5f: R = $SiMe_3$, R' = H
5g: R = R' = $SiMe_3$

We thank one of the reviewers for this suggestion. However, recently, we found that radical-anion **9** or **10**, when generated separately, forms the heterozincate $[RCH_2Zn(t\text{-}BuN{-}CH{=}CH{-}N\text{-}t\text{-}Bu)]^-$ via the escape of a $RCH_2^{\bullet}$ radical.

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Schlenk techniques. Solvents were carefully dried and distilled from sodium/benzophenone prior to use. All starting chemicals were purchased from Aldrich Chemical Co. or Janssen Chimica. The starting materials *N,N'*-di-*tert*-butyl-1,4-diaza-1,3-butadiene (*t*-BuDAB),[20] Me_2Zn-*t*-BuDAB,[2] $(Me_3SiCH_2)_2Zn$,[21] and Bu_2Zn[22] were prepared according to literature procedures. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 or AC-300 spectrometers in C_6D_6, using $SiMe_4$ as an external standard (0.0 ppm). Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, FRG.

$(Me_3SiCH_2)_2Zn$-*t*-BuDAB (5a). To a stirred solution of *t*-BuDAB (1.68 g, 10 mmol) in diethyl ether (50 mL) was added 1 equiv of $(Me_3SiCH_2)_2Zn$ (2.39 g, 10 mmol). The solvent was removed *in vacuo* at ambient temperature to afford **5a** as an orange solid in quantitative yield; 4.07 g **5a** was crystallized from diethyl ether or hexane. ^1H NMR: δ 7.25 (s, 2H, N=CH), 1.14 (s, 18H, *t*-Bu), 0.27 (s, 18H, $SiCH_3$), −0.78 (s, 4H, $ZnCH_2$). ^{13}C NMR: δ 152.9 (N=CH), 58.7 ($C(CH_3)_3$), 30.1 ($C(CH_3)_3$), 4.0 ($Si(CH_3)_3$), 0.4 ($ZnCH_2$). UV–Vis: λ_{max} = 390 nm.

General Procedure for the Thermal Decomposition Reaction of R_2Zn-*t*-BuDAB. The coordination complex R_2Zn-*t*-BuDAB (R = Me, CH_2SiMe_3) (10 mmol) was dissolved in benzene (50 mL) and heated for 6 h at 80 °C. The solvent was removed *in vacuo*, leaving a dark brown sticky residue. The ^1H NMR spectrum of the residue obtained from **1a** showed that the product is a mixture of **1b** (25%), **1e** (50%), and **1f** (25%), whereas the ^1H NMR spectrum of the product obtained from **5a** revealed that the residue was a mixture of **5e** (65%), **5f** (7%), and **5g** (28%). The dimeric species were crystallized from the product mixtures in hexane at −20 °C as white crystals.[7]

^1H NMR of **1b**: δ 6.67 (d, *J* = 4.4 Hz, 1H, *CH*=CH), 4.29 (d, *J* = 4.4 Hz, 1H, CH=*CH*), 2.07 (s, 3H, N-CH_3), 1.22, 0.99 (s, 9H, *t*-Bu), −0.22 (s, 3H, $ZnCH_3$). ^{13}C NMR of **1b**: δ 139.7 (*CH*=CH), 100.3 (CH=*CH*), 56.2, 50.2 ($C(CH_3)_3$), 35.7 (N—Me), 31.2, 23.7 (*t*-Bu), −12.5 (Zn—Me). ^1H NMR of **1f**: δ 7.42 (s, 1H, N=*CH*), 4.59, 4.18 (s, 2 × 1H, C=*CHH'*), 1.48, 0.88 (s, 9H, *t*-Bu), −0.30 (s, 3H, $ZnCH_3$). ^{13}C NMR of **1f**: characteristic signals δ 168.2 (N=CH), not observed (*C*=CH_2), 94.7 (C=CH_2), −9.7 (Zn—Me).

^1H NMR of **1e**: δ 7.61 (d, *J* = 2.8 Hz, 2H, N=*CH*), 2.72 (d, *J* = 2.8 Hz, 2H, N—*CH*), 1.08, 1.04 (s, 2 × 18H, $C(CH_3)_3$), −0.01 (s, 6H, $ZnCH_3$). ^{13}C NMR of **1e**: δ 170.8 (N=CH), 60.1 (N—CH), 57.6, 52.2 ($C(CH_3)_3$), 32.6, 29.5 ($C(CH_3)_3$), −11.3 ($ZnCH_3$). Anal. Calcd for $C_{22}N_{46}N_4Zn_2$: C, 53.13; H, 9.32; N, 11.26. Found: C, 53.10; H, 9.38; N, 11.18.

^1H NMR of **5e**: δ 7.59 (d, *J* = 2.7 Hz, 2H, N=*CH*), 2.64 (d, *J* = 2.7 Hz, 2H, N—*CH*), 1.12, 1.04 (s, 18H, $C(CH_3)_3$), 0.46 (s, 18H, $Si(CH_3)_3$), −0.32, −0.44 (dd, *J* = 12.3, 2 × 2H, $ZnCHH'Si(CH_3)_3$). ^{13}C NMR of **5e**: δ 171.42 (N=CH), 59.6 (N—CH), 57.8, 52.4 ($C(CH_3)_3$), 32.8, 29.9 ($C(CH_3)_3$), 4.4 ($Si(CH_3)_3$), −3.4 ($ZnCH_2$). Anal. Calcd for $C_{28}H_{62}N_4Si_2Zn$: C, 52.40; H, 9.74; N, 8.73. Found: C, 51.93; H, 9.90; N, 8.85.

^1H NMR of **5f** (only characteristic signals): δ 7.48 (s, 1H, N=*CH*), 4.64 (s, 1H, C=*CH*H'), 4.27 (s, 1H, C=CH*H'*). ^{13}C signals not observed.

^1H NMR of **5g**: δ 8.11 (s, 1H, N=*CH*), 5.04 (s, 1H, C=*CH*$SiMe_3$), 1.53, 0.96 (s, 18H, $C(CH_3)_3$), 0.31 (s, 9H, $ZnCH_2Si(CH_3)_3$), 0.26 (s, 9H, $ZnCH_2Si(CH_3)_3$), −0.34 (s, 2H, $ZnCH_2Si(CH_3)_3$). ^{13}C NMR of **5g**: δ 166.4 (N=CH), 155.5 (N—C=CH), 105.0 (C=*C*(H)$SiMe_3$, $^1J_{Si-C}$ = 24.7 Hz) 57.7, 52.6 ($C(CH_3)_3$), 33.2, 30.6 ($C(CH_3)_3$), 4.5 ($Si(CH_3)_3$), −1.8 ($ZnCH_2$).

Independent Synthesis of the Dinuclear Species 1h (R = Me), 2h (R = Et), and 6h (R = Bu). To a stirred solution of *t*-BuN=CH—CH(CH_3)—NH(*t*-Bu)[11] (1.84 g, 10 mmol) in diethyl ether (25 mL) was added 1 equiv of R_2Zn (R = Me, Et, Bu). After stirring for 5 min the solvent was removed *in vacuo* at ambient temperatures, leaving the 1:1 coordination complexes **1c'**, **2c'**, and **6c'** as yellow solids in quantitative yield. (The products were obtained as white solids after crystallization from hexane.) Thermally instable **1c'**, **2c'**, and **6c'** were dissolved in hexane and heated at 60 °C for 30 min. The solvent was removed *in vacuo* to afford white solids. The products were crystallized from hexane to obtain analytically pure compounds.

^1H NMR of **1c'**: δ 6.88 (d, *J* = 2.1 Hz, 1H, N=*CH*), 2.96 (m, 1H, N—C(CH_3)*H*), 1.13, 0.93 (s, 2 × 9H, $C(CH_3)_3$), 0.82 (d, *J* = 7.2 Hz, 3H, N—CH(CH_3)), −0.31 (s, 6H, $ZnCH_3$). ^1H NMR of **2c'**: δ 6.83 (d, *J* = 2.0 Hz, 1H, N=*CH*), 2.90 (m, 1H, N—C(CH_3)*H*), 1.74 (t, 6H, $ZnCH_2CH_3$), 1.12, 0.93 (s, 2 × 9H, $C(CH_3)_3$), 0.78 (d, *J* = 7.2 Hz, 3H, N—C(CH_3)$_3$), 0.39 (q, 4H, $ZnCH_2CH_3$).

^1H NMR of **1h**: δ 3.18 (s, 1H, N—CH—C(CH_3)—N), 2.88 (ddq, *J* = 2.5 Hz, 6.3 Hz, 12 Hz, 1H, N—*CH*(CH_3)—CH—N), 2.04 (d, *J* = 2.5 Hz, 1H, N—CH(CH_3)—*CH*—N), 1.75 (s, 2H, N—CH—C(CH_3)=N), 1.26, 1.20, 1.09, 1.07 (s, 4 × 9H, $C(CH_3)_3$), 1.01 (d, *J* = 6.3 Hz, 3H, N—CH(CH_3)—CH—N), −0.04, −0.09 (s, 2 × 3H, $ZnCH_3$). ^{13}C NMR of **1h**: δ 183.3 (N=CCH_3), 66.2 (N—*CH*—CCH_3), 66.0 (N—CH(CH_3)—*CH*—N), 56.4, 53.4, 54.6, 52.6 ($C(CH_3)_3$), 53.5 (NCH(CH_3)—CH—N), 33.5, 32.2, 30.9, 30.4 ($C(CH_3)_3$), 21.7 (N—CH(CH_3)—CH—N), 19.6 (N=CCH_3), −8.4 ($ZnCH_3$). Anal. Calcd for $C_{24}H_{52}N_4Zn_2$: C, 54.65; H, 9.94; N, 10.62. Found: C, 54.82; H, 9.79; N, 10.45.

^1H NMR of **2h**: δ 3.11 (s, 21H, N—*CH*—C(CH_3)=N), 2.88 (ddq, *J* = 2.4 Hz, 6.2 Hz, 12 Hz, 1H, N—*CH*(CH_3)—CH—N), 2.02 (d, *J* = 2.4 Hz, 1H, N—CH(CH_3)—*CH*—N), 1.85 (q, 6H, $ZnCH_2CH_3$), 1.74 (s, 6H, N—CH—C(CH_3)=N), 1.24, 1.20, 1.07, 1.05 (s, 4 × 9H, $C(CH_3)_3$), 0.98 (d, *J* = 6.2 Hz, 3H, N—CH(CH_3)—CH—N), 0.79 (m, 4H, $ZnCH_2CH_3$). ^{13}C NMR of **2h**: δ 183.2 (N=CCH_3), 66.2 (N—*CH*—CCH_3), 66.1 (N—CH(CH_3)—CH), 56.1 ($C(CH_3)_3$), 54.4 (N—*CH*(CH_3)—CH—N), 53.2, 52.9, 52.0 ($C(CH_3)_3$), 33.6, 32.3, 30.7, 30.5 ($C(CH_3)_3$), 19.7 (N=CCH_3), 21.7 (N—CH(CH_3)—CH—N), 14.5, 14.3 ($ZnCH_2CH_3$), 4.7, 4.3 ($ZnCH_2CH_3$). Anal. Calcd for $C_{26}H_{56}N_4Zn_2$: C, 56.63; H, 9.50; N, 10.16. Found: C, 56.53; H, 10.06; N, 9.98.

^1H NMR of **6h**: δ 3.13 (s, 1H, N—*CH*—C(CH_3)=N), 2.86 (ddq, *J* = 2.3 Hz, 6.3 Hz, 12 Hz, 1H, N—*CH*(CH_3)—CH—N), 2.07 (m, 4H, butyl), 2.03 (d, *J* = 2.3 Hz, 1H, N—CH(CH_3)—*CH*—N), 1.79 (m, 4H, butyl), 1.75 (s, 3H, N—CH—C(CH_3)=N), 1.25 (m, 4H, butyl), 1.13 (m, 6H, butyl), 1.24, 1.21, 1.08, 1.07 (s, 4 × 9H, $C(CH_3)_3$), 0.99 (d, *J* = 6.3 Hz, 3H, N—CH(CH_3)—CH—N), 0.79–0.58 (m, 4H, $ZnCH_2$). ^{13}C NMR of **6h**: δ 183.1 (N=*C*—CH_3), 66.3 (N—*CH*—CCH_3), 66.1 (N—CH(CH_3)—CH), 56.1 ($C(CH_3)_3$), 54.4 (N—*CH*(CH_3)—CH—N), 53.2, 53.0, 52.1

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($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 33.2, 33.1 (CH_2), 32.3 ($C(CH_3)_3$), 31.2, 31.1 (CH_2), 30.7, 30.6 ($C(CH_3)_3$), 21.7 (N—CH(CH_3)—CH—N), 19.7 (N=CCH_3), 14.4 (CH_3), 13.9, 13.4 (ZnCH_2). Molecular weight determination in benzene: calcd weight, 610; found, 568.

Irradiation of Me_2Zn-*t*-BuDAB (1a). A stirred solution of **1a** (1.32 g, 5 mmol) in diethyl ether (50 mL) in a Pyrex tube at 20 °C was irradiated for 45 min with a 300-W high-pressure Hg lamp. The solvent was removed *in vacuo*, leaving a yellow solid. The ^1H NMR spectrum of the residue revealed that the product was a mixture of the symmetric dinuclear species **1d** (30%) and the unsymmetric dinuclear species **1h** (70%). We have been unable to separate the two products (see above for ^1H and ^{13}C NMR data for **1d** and **1h**).

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