Recl. Trav. Chim. Pays-Bas **112**, 618–626 (1993) 0165–0513/93/12618–09$6.00

Regioselective introduction of functional groups in α-diimines by means of dialkylzinc compounds. Synthesis of functionalized 2- and 3-pyrrolidinone derivatives

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(Received April 7, 1993)

Abstract. Alkylation of the 1,4-diaza-1,3-butadiene *t*-BuN=CH–CH=N*t*-Bu (*t*-BuDAB) by functionally substituted diorganozinc compounds $Zn[(CHR^1)(CH_2)_nXR^2]_2$ ($n = 1$–3, $R^1 = H$, Me, $XR^2 = OMe$, OBn, SEt, NMe_2, COOEt) occurs regioselectively. Alkylation occurs at the nitrogen atom of the N=C–C=N skeleton of *t*-BuDAB when primary diorganozinc compounds are used ($R^1 = H$), but at the carbon atom when secondary and benzylic diorganozinc compounds are employed. The functional groups in the diorganozinc reagents proved to be important for the alkylation reaction only in the case of $Zn[(CH_2)_3NMe_2]_2$ (**7**) and $Zn(C_6H_4CH_2NMe_2\text{-}2)_2$ (**16**), in which the strongly coordinating NMe_2 groups give either a decrease of the alkylation rate (**7**), or no reactivity at all (**16**). When *t*-BuDAB is reacted with $Zn[(CH_2)_2COOEt]_2$ (**10**) alone, a 3-pyrrolidinone (**10c**) is formed, whereas the same reaction with a mixture of **10** and $ClZn(CH_2)_2COOEt$ affords a 2-pyrrolidinone (**10b**). The reactions involve a two-step process involving prior regioselective introduction of the alkyl group either at the N or C atom of an imine unit followed by an intramolecular nucleophilic substitution leading to **10b** or **10c**, respectively. The molecular structure of **10c** shows the functionalized heterocycle to be part of a conjugated enamine system.

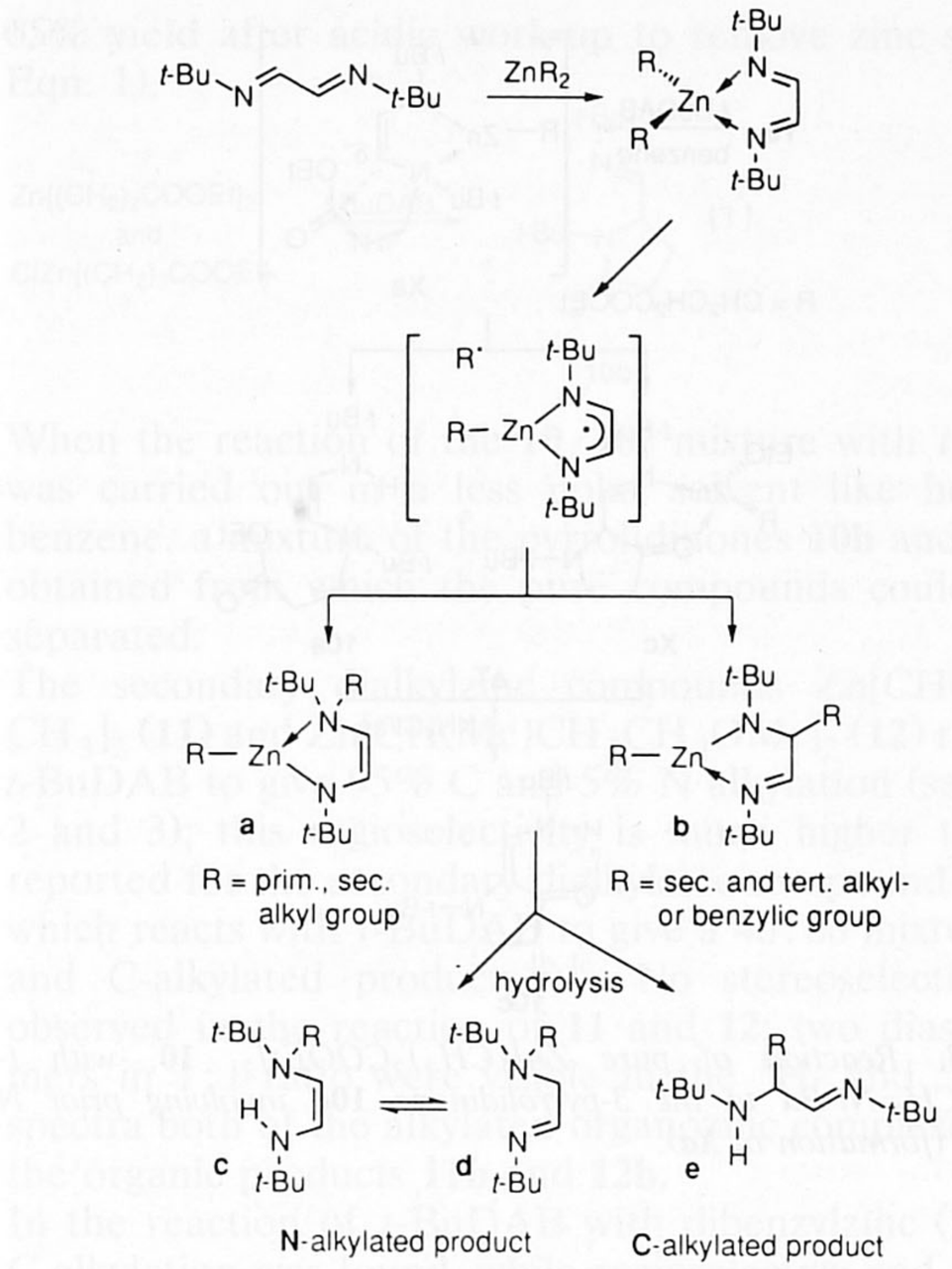
Introduction

Diorganozinc compounds have proven to be useful reagents in organic synthesis, *e.g.* in the diastereoselective synthesis of *trans*-β-lactams[1], in the preparation of optically active secondary alcohols from aldehydes with high enantioselectivity[2] and in the synthesis of imino alcohols from imino ketones[3]. The reactions of diorganozinc compounds with α-diimines, especially 1,4-diaza-1,3-butadiene systems (R′N=CH–CH=NR′, R′DAB, 1,2-ethanediimines) have received much attention in our laboratory, as the N=C–C=N skeleton could be an interesting building block for organic synthesis. We found that dialkylzinc compounds can alkylate the R′DAB skeleton with very high regioselectivity to generate zinc-bonded alkylated monoanionic systems[4]. Whether the alkylation takes place on a nitrogen or a carbon atom of this skeleton is determined by the nature of the alkyl group bound to zinc. Primary dialkylzinc compounds give almost quantitative (> 99%) N alkylation (**a**), secondary dialkylzinc compounds give a mixture of N (**a**) and C alkylation (**b**), and tertiary dialkylzinc compounds give exclusively C alkylation (see Scheme 1). Hydrolysis of these alkylated organozinc complexes give organic products which are a mixture of the N-alkylated tautomers **c** and **d** and/or the C-alkylated amino-imine **e**.

We currently use this regioselective alkylation method to introduce functionalized alkyl and benzyl groups via $Zn[CHR^1(CH_2)_nXR^2]_2$ ($R^1 = H$, Me; $n = 1$, 2, 3; $XR^2 =$ SEt, OMe, OCH_2Ph, NMe_2, COOEt)[5,6] and $Zn(CH_2C_6H_4NMe_2\text{-}2)_2$[7] onto the diimine unit of 1,4-diaza-1,3-butadienes. This work has led to the development of new synthetic routes for functionalized (*Z*)-1,2-ethenediamines (**c**) and 2-imino-ethanamines (**d** and **e**).

In this paper we present the results of a study of the alkylation of 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene [a] (*t*-BuDAB) by hetero-atom-functionalized diorganozinc compounds, with particular emphasis on the influence of the intramolecular heteroatom–zinc coordination present in these reagents[5] (see Figure 1) on the regioselectivity of the reaction. In this study, most alkylated R′DAB moieties have been isolated as their easily storable organozinc derivatives; the free organic products obtained by hydrolysis of these organozinc derivatives often have only limited stability.

[a] *Chem. Abstr. name*: *N*,*N*′-bis(1,1-dimethylethyl)-1,2-ethanediimine.



Scheme 1. The proposed reaction scheme for the group transfer reaction between ZnR_2 and the α-diimine, t-BuN=CHCH=Nt-Bu, involving intramolecular ligand-to-ligand electron transfer followed by collapse of the radical pair to either N- (primary alkyl) or C-alkylated (secondary alkyl or benzyl) products (cf. Ref. 4c).

Results

Most of the diorganozinc compounds used in this work (**1–16**, Table I) were prepared by the reaction of the corresponding Grignard or lithium reagents with half an equivalent of dry $ZnCl_2$[5,7,8] and were purified by either distillation or crystallization.

Alkylation reactions of t-BuDAB

The reactions of the dialkylzinc compounds **1–14** and *t*-BuDAB in 1:1 molar ratio, fit the reaction pattern found in earlier reactions of R′DAB systems with dialkylzinc compounds; the reaction of $Zn[(CH_2)_3NMe_2]_2$ (**7**) is exceptional[4]. On mixing *t*-BuDAB and the dialkyl-

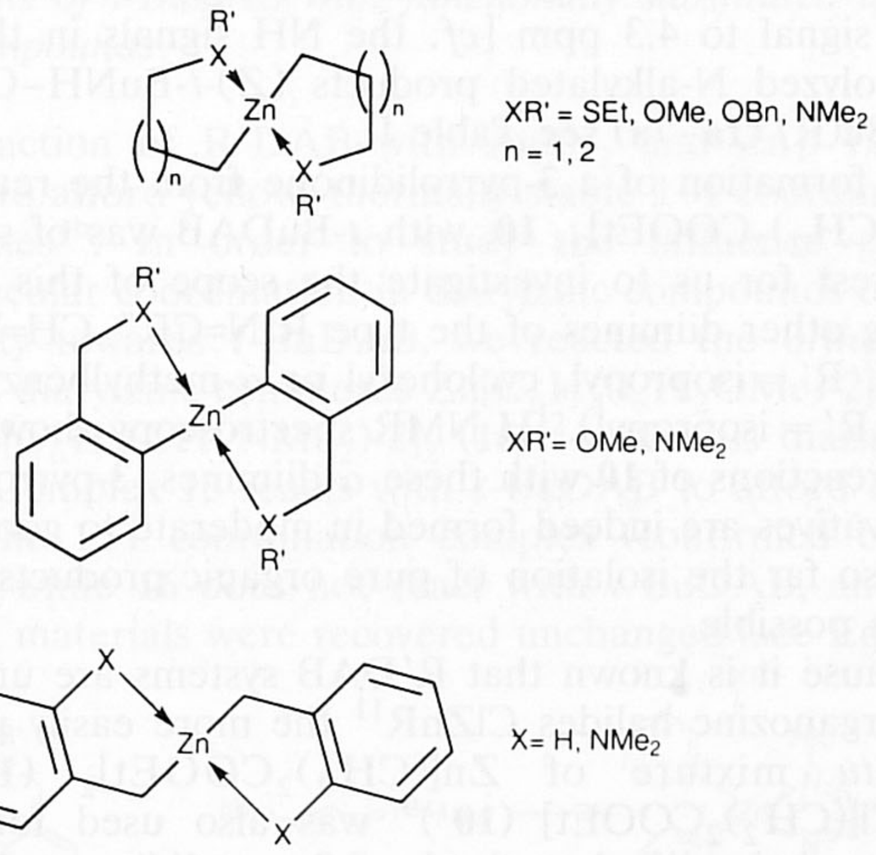


Figure 1. Functionally substituted ZnR_2 compounds with intra-molecular coordination (see Table I for compound numbers). The Zn–XR′ coordinative interaction decreases in the series Zn–NMe₂ > Zn–OR > Zn–SR.

Table I Results of the alkylation reactions of R_2Zn compounds with t-BuDAB.

ZnR_2 compound	N alkylation (%) [a]	C alkylation (%)
$Zn[(CH_2)_2CH_3]_2$ (**1**)	100	0
$Zn[(CH_2)_3CH_3]_2$ (**2**)	100	0
$Zn[(CH_2)_3OMe]_2$ (**3**)	100	0
$Zn[(CH_2)_3OCH_2Ph]_2$ (**4**)	100	0
$Zn[(CH_2)_4OMe]_2$ (**5**)	100	0
$Zn[(CH_2)_3SEt]_2$ (**6**)	100	0
$Zn[(CH_2)_3NMe_2]_2$ (**7**) [b]	68	21
$Zn(CH_2CMe_3)_2$ (**8**)	0	100
$Zn(CH_2CMe_2Ph)_2$ (**9**) [c]	0	100
$Zn[(CH_2)_2COOEt]_2$ (**10**)	100	0
$Zn[CH(Me)CH_2CH_3]_2$ (**11**)	5	95
$Zn[CH(Me)(CH_2)_2OMe]_2$ (**12**)	3	97
$Zn(CH_2Ph)_2$ (**13**)	5	95
$Zn(CH_2C_6H_4NMe_2\text{-}2)_2$ (**14**)	0	100
$Zn[C_6H_4(CH_2OMe)\text{-}2]_2$ (**15**)	1:1 coordination complex [d]	
$Zn[C_6H_4(CH_2NMe_2)\text{-}2]_2$ (**16**)	no reaction [e]	

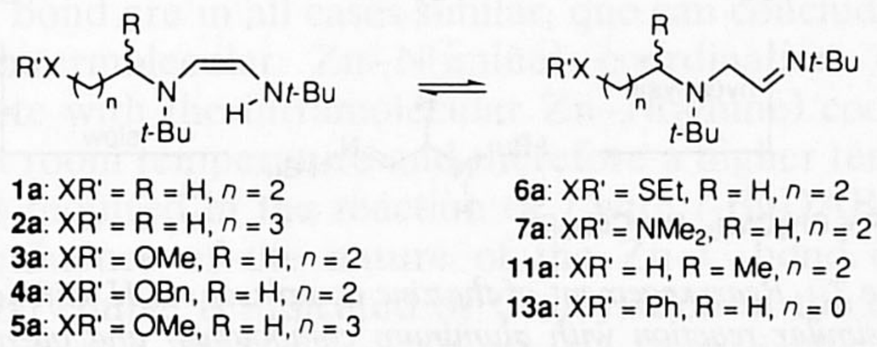
[a] Percentage N and C alkylation after hydrolysis, determined by ^1H NMR integration of characteristic proton signals. [b] Complete conversion after heating for 48 h at 70°C. [c] N- and C-alkylation percentages of the crude reaction product. [d] A thermally stable 1:1 coordination complex was isolated. [e] The starting materials were recovered unchanged.

zinc reagents at −78°C the reaction solution turns dark red, indicative of the formation of a 1:1 coordination complex $[R_2Znt\text{-BuDAB}]$[4b,4c]. On raising the temperature to room temperature, the color of the solution gradually changes from red to yellow, which is indicative of an alkyl shift from zinc to the chelating N=C–C=N skeleton of the *t*-BuDAB ligand. Hydrolysis of the resulting N- and/or C-alkylated organozinc complexes affords the free organic products. The reaction can also be carried out at room temperature; it is then complete within a few seconds.

The reactions of the primary dialkylzinc compounds **1–6** with *t*-BuDAB in all cases resulted in the exclusive formation of N-alkylated organozinc species which, upon hydrolysis, afforded the organic products **1a–6a** in good yields (see Figure 2). These products are first isolated as the enamine tautomer but after a few days small amounts of the amine–imine tautomer could be detected by ^1H NMR spectroscopy.

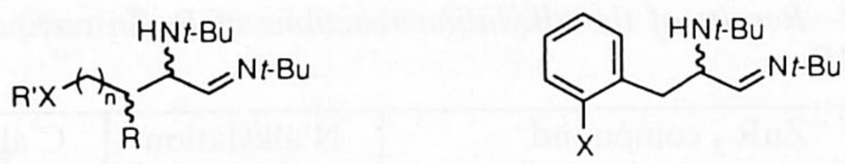
Compared to similar reactions with non-functionalized R_2Zn compounds, the intramolecular coordination of the donor atoms in the dialkylzinc reagent **3–6** influences neither the rate of the reaction nor the type of alkylation. However, the reaction mixture of $Zn[(CH_2)_3NMe_2]_2$ (**7**) with *t*-BuDAB had to be heated at 70°C for 48 h in order to obtain complete transfer of the alkyl group from zinc to the α-diimine substrate *t*-BuDAB. After hydrolysis, this reaction resulted in a mixture of 68% N- and 21% C-alkylated products together with two unidentified minor products.

In contrast to **1–6**, that give N-alkylated products, the two other primary dialkylzinc reagents, $Zn(CH_2CMe_3)_2$ (**8**) and $Zn(CH_2CMe_2Ph)_2$ (**9**) reacted with *t*-BuDAB at room



1a: XR′ = R = H, *n* = 2
2a: XR′ = R = H, *n* = 3
3a: XR′ = OMe, R = H, *n* = 2
4a: XR′ = OBn, R = H, *n* = 2
5a: XR′ = OMe, R = H, *n* = 3
6a: XR′ = SEt, R = H, *n* = 2
7a: XR′ = NMe_2, R = H, *n* = 2
11a: XR′ = H, R = Me, *n* = 2
13a: XR′ = Ph, R = H, *n* = 0

Figure 2. Organic products resulting from N-alkylation of t-BuNCHCHNt-Bu by $Zn[(CH_2)_nXR']_2$; the imine–enamine tautomer equilibrium is shown.



7b: XR' = NMe_2, R = H, *n* = 2
8b: XR' = *t*-Bu, R = H, *n* = 0
9b: XR' = CMe_2Ph, R = H, *n* = 0
11b: XR' = H, R = Me, *n* = 2
12b: XR' = OMe, R = Me, *n* = 2

13b: X = H
14b: X = NMe_2

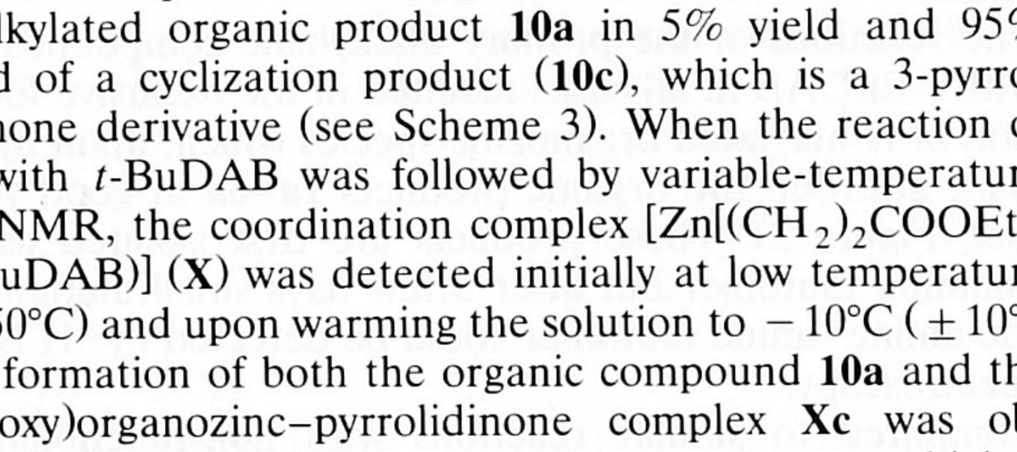
Figure 3. Organic products resulting from C alkylation of t-BuNCHCHNt-Bu by $Zn[(CH_2)_nXR']_2$ *and* $Zn[CH_2C_6H_4X\text{-}2]_2$*, respectively.*

temperature to give > 99% of C-alkylated products (**8b** and **9b**) (see Figure 3). It is noteworthy that the C/N alkylation ratio was found to be 95 : 5 when the reaction was carried out at −78°C.

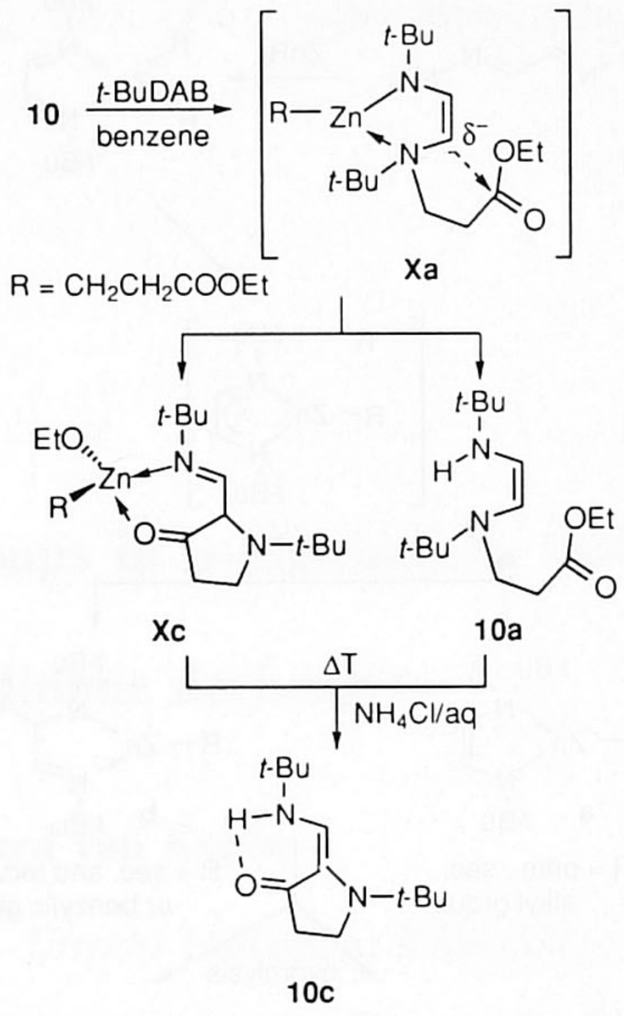
The C-alkylated organozinc complexes obtained from the reaction of *t*-BuDAB with **8** and **9** are not stable and convert to secondary complexes within 24 h. The resonances in ^{1}H- and ^{13}C-NMR spectra of these newly formed organozinc complexes indicate the formation of the organozinc enamines RZn[*t*-BuN–C(R)=CH–N(H)*t*-Bu] (R = CH_2CMe_3, CH_2CMe_2Ph) (see Scheme 2), containing a zinc–secondary-amine donative bond. Hydrolysis of the initial C-alkylated organozinc complexes, before rearrangement has taken place, afforded the expected C-alkylated product, that slowly rearranges to its enamine tautomer, while hydrolysis of the rearranged complex resulted directly in the hydrolyzed enamine tautomer.

In the reaction of the primary dialkylzinc compound, $Zn[(CH_2)_2COOEt]_2$[6,9] (**10**) with *t*-BuDAB in a 1 : 1 molar ratio, the normal color change from red to yellow was observed and 100% N alkylation was anticipated, *i.e.* complex **Xa**. However, hydrolysis of the alkylated organozinc species formed, gave a mixture of the expected N-alkylated organic product **10a** in 5% yield and 95% yield of a cyclization product (**10c**), which is a 3-pyrrolidinone derivative (see Scheme 3). When the reaction of **10** with *t*-BuDAB was followed by variable-temperature ^{1}H NMR, the coordination complex [$Zn[(CH_2)_2COOEt]_2$ (t-BuDAB)] (**X**) was detected initially at low temperature (−50°C) and upon warming the solution to −10°C (±10°), the formation of both the organic compound **10a** and the (alkoxy)organozinc–pyrrolidinone complex **Xc** was observed. The N-alkylated organozinc complex **Xa**, which is the expected precursor of **10a** (*vide infra*), was not detected. The best method to obtain **10c** without **10a** is to perform the alkylation reaction in an aromatic solvent like benzene or toluene and to heat the reaction mixture for a few hours at 60°C before hydrolysis.

Although the formation of **10c** is almost quantitative under these conditions it could only be isolated pure as a yellow solid in 15% yield. This low yield results from the



Scheme 2. Rearrangement of the zinc complexes via H shift (cf. Ref. 4 for a similar reaction with aluminum compounds) and quenching of the zinc complexes to the respective amine–imine and enamine hydrolysis products: the amine–imine tautomer is completely converted into an enamine one.



Scheme 3. Reaction of pure $Zn[(CH_2)_2COOEt]_2$*,* **10***, with t-BuN=CHCH=Nt-Bu to the 3-pyrrolidinone* **10c** *involving prior N alkylation (formation of* ***Xa****).*

decomposition of **10c** that occurs during the acidic work-up which is necessary to remove zinc salts formed in the hydrolysis step. Compound **10c** was identified by ^{1}H and ^{13}C NMR and the proposed structure was confirmed by an X-ray structure determination[10].

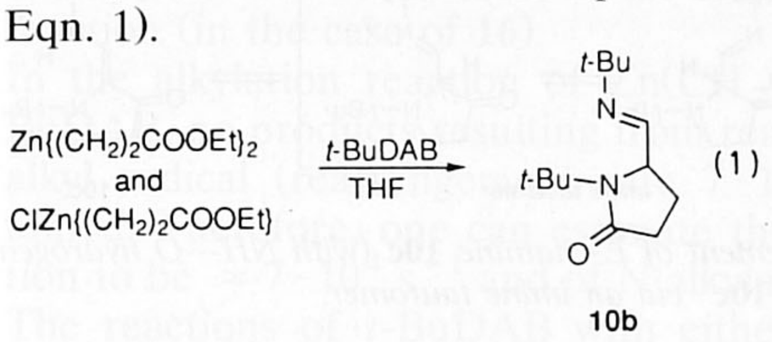
The molecular structure of **10c** shows this compound to have a pyrrolidine ring with the enamine fragment in the *E* configuration stabilized by a NH---O hydrogen bond. The enamine system is fully conjugated with the carbonyl function as indicated by a short *t*-Bu(H)N–C single bond of 1.334 (3) Å and a relatively long olefinic C=C bond of 1.360 (4) Å. As a result, the H–N–C=C–C=O moiety is planar.

In the ^{1}H NMR spectrum of **10c** (C_6D_6, room temp.) there is a large downfield shift for the NH signal (δ 9.5 ppm) that is consistent with the presence of the NH---O hydrogen bridge in solution. When **10c** is first dissolved in C_6D_6, it is the isomer with the E configuration which is present but this converts slowly into the isomer with the Z configuration (**10d**) until an equilibrium mixture with an E/Z ratio of 4 : 1 is formed. In the *Z* isomer, **10d**, the NH---O bond of the *E*-isomer has been replaced by a NH---N bond and this results in a high-field shift of the NH signal to 4.3 ppm [*cf.* the NH signals in the other hydrolyzed N-alkylated products (*Z*)-*t*-BuNH–CH=CH–N*t*-Bu(R) (**1a–7a**) see Table I].

The formation of a 3-pyrrolidinone from the reaction of $Zn[(CH_2)_2COOEt]_2$, **10**, with *t*-BuDAB was of sufficient interest for us to investigate the scope of this reaction using other diimines of the type R′N=CR″–CH=NR′ (R″ = H, R′ = isopropyl, cyclohexyl or α-methylbenzyl; R″ = Me, R′ = isopropyl). ^{1}H NMR spectroscopy shows that in the reactions of **10** with these α-diimines, 3-pyrrolidinone derivatives are indeed formed in moderate to good yields, but so far the isolation of pure organic products has not been possible.

Because it is known that R′DAB systems are unreactive to organozinc halides ClZnR[11] the more easily prepared *in-situ* mixture of $Zn[(CH_2)_2COOEt]_2$ (**10**) and $ZnCl[(CH_2)_2COOEt]$ (**10′**)[9] was also used for an attempted simplified synthesis of 3-pyrrolidinone derivative **10c**. Surprisingly, in this case, when THF was used as solvent, the 2-pyrrolidinone derivative **10b** is formed directly (without a hydrolysis step) and could be isolated in

65% yield after acidic work-up to remove zinc salts (see Eqn. 1).



(1)

10b

When the reaction of the **10**/**10′** mixture with *t*-BuDAB was carried out in a less polar solvent like hexane or benzene, a mixture of the pyrrolidinones **10b** and **10c** was obtained from which the pure compounds could not be separated.

The secondary dialkylzinc compounds $Zn[CH(Me)CH_2CH_3]_2$ (**11**) and $Zn[CH(Me)CH_2CH_2OMe]_2$ (**12**) react with *t*-BuDAB to give 95% C and 5% N alkylation (see Figure 2 and 3); this regioselectivity is much higher than that reported for the secondary dialkylzinc compound Zn*i*-Pr_2, which reacts with *t*-BuDAB to give a 40 : 60 mixture of N- and C-alkylated products[4b,4c]. No stereoselectivity was observed in the reaction of **11** and **12**; two diastereoisomers in 1 : 1 ratio were visible in the ^{1}H- and ^{13}C-NMR spectra both of the alkylated organozinc complexes and of the organic products **11b** and **12b**.

In the reaction of *t*-BuDAB with dibenzylzinc (**13**), 95% C alkylation was found, while regioselective and quantitative C alkylation of *t*-BuDAB was obtained with the *ortho*-functionalized dibenzylic zinc reagent **14**.

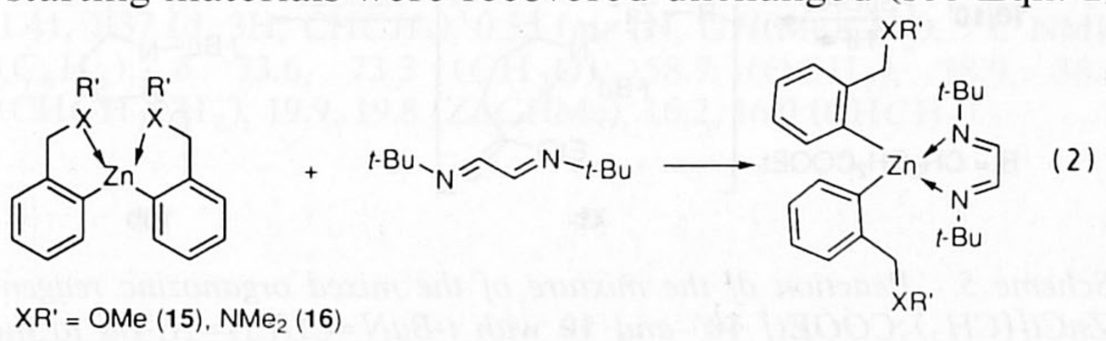
Hydrolysis of the alkylated organozinc complexes

With the exception of **4a**, **9b** and **14b**, the organic products **1a–3a, 5a–7a, 8b, 11b–13b**, can easily be obtained by careful hydrolysis of the corresponding alkylated organozinc complexes with one equivalent of H_2O. In the case of the organozinc complexes RZn[*t*-BuN–CH=CH–N(R)*t*-Bu] [R = $(CH_2)_3OBn$] and RZn[*t*-BuN–CH(R)–CH=N*t*-Bu] (R = CH_2CMe_2Ph, $CH_2C_6H_4NMe_2$-2) the best results were obtained when hydrolysis was carried out with a solution of 2.5 M *t*-BuOH in hexane. In the case of **9b** and **14b**, additional purification was achieved by hydrolysis of their recrystallized $ZnMe_2$ adducts, Me_2Zn[*t*-BuNH–CH(R)–CH=N*t*-Bu] [R = CH_2CMe_2Ph (**17**), $CH_2C_6H_4NMe_2$-2 (**18**)].

The organic products are stable for only a few days at room temperature, and for a few months at −20°C, while the alkylated organozinc precursors of these compounds are stable for many years when stored at −20°C.

Reactions of t-BuDAB with functionally substituted diarylzinc compounds

The reaction of R′DAB with $ZnPh_2$ and Zn*p*-Tol_2 is known to afford yellow, thermally stable 1 : 1 coordination complexes[4b]. In order to study the influence of intramolecular coordination in diarylzinc compounds on the reactivity towards *t*-BuDAB, we reacted the *ortho*-substituted diarylzinc complexes $Zn[C_6H_4(CH_2OMe)\text{-}2]_2$ (**15**) and $Zn[C_6H_4(CH_2NMe_2)\text{-}2]_2$ (**16**)[12] with this diazabutadiene. Complex **15** reacts with *t*-BuDAB to afford exclusively the 1 : 1 coordination complex (confirmed by ^{1}H NMR), while **16** does not react with *t*-BuDAB, and the starting materials were recovered unchanged (see Eqn. 2).



XR′ = OMe (**15**), NMe_2 (**16**)

only in the case of XR′ = OMe

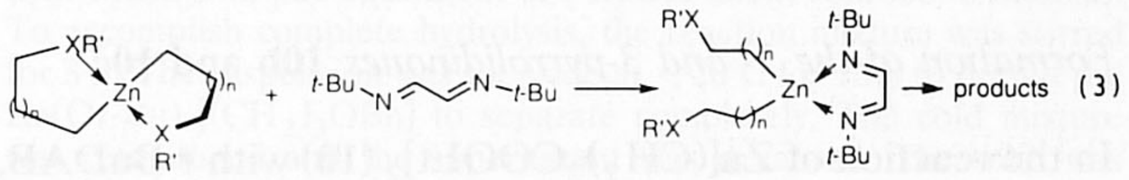
(2)

Discussion

The course of the reactions of the diorganozinc reagents **1–14** with *t*-BuDAB can best be discussed in terms of the mechanism we suggested in 1987 (shown in Scheme 1)[4b]. In the first step a thermally unstable 1 : 1 coordination complex [ZnR_2(*t*-BuDAB)] is formed. Above a critical temperature, which is characteristic for each initially formed 1 : 1 coordination complex, one of the Zn–C bonds breaks homolytically, leading to a organozinc radical (RZn*t*-BuDAB)$^{\cdot}$ and alkyl radical pair, which subsequently collapses to the alkylated organozinc complex[13]. The less stable primary alkyl radicals, which are also the least sterically demanding, from the dialkylzinc compounds **1–6**, give N alkylation, while the more stable tertiary alkyl and benzylic radicals give almost exclusively C alkylation. In the reactions of $Zn(CH_2CMe_3)_2$ (**8**) and $Zn(CH_2CMe_2Ph)_2$ (**9**) with *t*-BuDAB, during which the relatively stable $Me_3CCH_2^{\bullet}$ and $Me_2PhCCH_2^{\bullet}$ radicals[14] are formed, only C alkylation occurs. In these cases the absence of products resulting from rearrangements of the latter radicals to $^{\bullet}CMe_2CH_2Me$ and $^{\bullet}CMe_2CH_2Ph$ (rearrangement rate $7 \cdot 10^2$ s^{-1})[15], implies that the rate of alkylation is faster. Furthermore, the observation that in the low temperature reaction of **8** and **9** with *t*-BuDAB 5% N alkylation is found, confirms our view that the N-alkylated product is the kinetically determined product[16].

In the alkylation reactions of *t*-BuDAB with the secondary dialkylzinc compounds **11** and **12** high regioselectivity was obtained, though no diastereoselectivity was found. This lack of diastereoselectivity seems to corroborate the radical mechanism proposed. The alkyl radicals formed in these reactions will have no preferred mode of attack on the flat organozinc radical (RZn*t*-BuDAB)$^{\bullet}$ [4c], resulting in an equal probability for the formation of the two possible diastereoisomers.

Except for the reaction of $Zn[(CH_2)_3NMe_2]_2$ (**7**) with *t*-BuDAB, the presence of a hetero-atom functionality has no influence on the reactions of the dialkylzinc compounds **3–6**, **12** and **14** with this 1,4-diaza-1,3-butadiene. While these latter dialkylzinc reagents react instantaneously with *t*-BuDAB at room temperature, the same reaction of **7** took 48 hours for completion at 70°C (68% N and 21% C alkylation products). A possible explanation for this slow reaction is the strength of the intramolecular Zn–N coordination bonds in **7**[5b]; prior dissociation of these bonds is necessary for formation of the initial 1 : 1 R_2Zn*t*-BuDAB coordination complexes (see Eqn. 3).



(3)

The functionally substituted dialkylzinc reagents **3–7** contain either 5- (**3**, **4**, **6** and **7**) or 6-membered (**5**) chelate rings as a result of intramolecular Zn–hetero-atom coordination. It is this latter interaction that markedly differs in the species **3–7**, *i.e.* the Zn–NMe_2 bond is much stronger than either the Zn–OR or Zn–SR bonds[5]. Since the alkanediyl chain of the chelate that connects the carbon and donor hetero-atom and the nature of the Zn–C bond are in all cases similar, one can conclude for **7** that intermolecular Zn–N(imine) coordination cannot compete with the intramolecular Zn–N(amine) coordination at room temperature and therefore a higher temperature is required in the reaction of **7** with *t*-BuDAB.

The influence of the nature of the Zn–C bond on the reaction course is indicated by C alkylation in the case of **12** (secondary alkyl carbon atom) and **14** (benzylic carbon atom). The formation of some C-alkylated product in the reaction of **7** with *t*-BuDAB is ascribed to the higher

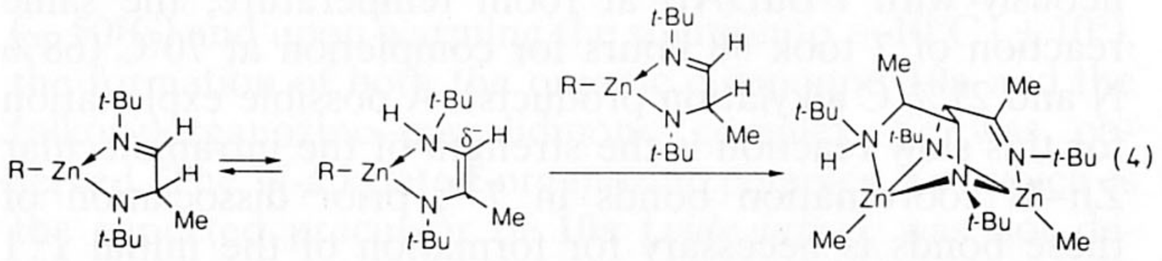
temperature required (80°C) and is in accord with previous results[4].

The less flexible C–N-chelated chain in **14** (two sp^2 and two sp^3 carbon atoms), as compared with the alkanediyl chains in **3–7** (all sp^3 carbon atoms), obviously does not interfere with the *t*-BuDAB complexation and product formation reaction steps (see Table I). The Zn–N(amine) interaction in **14** is distinctly weaker than that in **7** due to the lower Lewis basicity of the aryl amine *versus* the alkylamine N-donor atoms. Consequently, formation of the intermolecular Zn–N(imine) bond [formation of the 1:1 complex [ZnR_2(*t*-BuDAB)]] competes successfully with the weaker intramolecular Zn–N(amine) coordination process.

Finally, it is interesting to compare the reactivity of the *ortho*-hetero-atom substituted diarylzinc complexes $Zn(C_6H_4CH_2XR\text{-}2)_2$ (XR = OMe (**15**)) and (XR = NMe_2 (**16**)) and that of the parent $ZnPh_2$; all three fail to give rise to arylated *t*-BuDAB products. In agreement with the above discussion of the intramolecular hetero-atom–Zn bond strength of these two aryl zinc complexes, only **15**, with a OMe functionality, forms a 1:1 coordination complex with *t*-BuDAB. In contrast, the strong intramolecular coordination of the NMe_2 group in **16** hampers the formation of a 1:1 complex of this diorganozinc reagent with *t*-BuDAB (see Eqn. 2)[17].

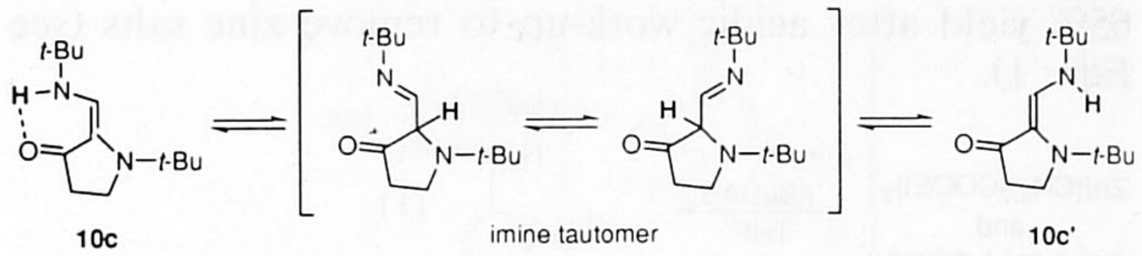
Imine–enamine tautomerization

The imine–enamine tautomerization reaction within the C-alkylated organozinc complexes obtained from the reaction of **8** and **9** with *t*-BuDAB (see Scheme 2) was previously observed in a study of the C-alkylated organozinc complex MeZn[*t*-BuN–CH(Me)–CH=N*t*-Bu]. This complex is in equilibrium with its organozinc enamine, that with a parent molecule undergoes a condensation reaction to an unsymmetric dinuclear species, which was the subject of an X-ray structure determination (see Eqn. 4)[18]. Such a C–C coupling reaction was not observed with the organozinc enamines obtained in the reaction of **8** and **9**, probably because of steric effects of the large neopentyl and neophyl groups.



Formation of the 2- and 3-pyrrolidinones **10b** and **10c**

In the reaction of $Zn[(CH_2)_2COOEt]_2$ (**10**) with *t*-BuDAB, the 3-pyrrolidinone **10c** was formed almost quantitatively. Although the N-alkylated organozinc complex **Xa** was never observed it is plausible to assume that this is the intermediate for the ring-closed product **10c**. Intermediate **Xa** is an organozinc enamine and recent theoretical calculations on the structure of these N-alkylated organozinc complexes (**a** in Scheme 1, Refs. 4c, 19, 20) indicate that delocalization of charge in the enamine results in a nucleophilic β-carbon[21]. Accordingly, an intramolecular nucleophilic attack of such enamine carbon on the carbonyl carbon in **Xa** (see Scheme 3) is possible, and this will lead to the formation of the 5-membered 3-pyrrolidinone derivative **Xb**. Simultaneously with this C–C bond formation, an ethoxide group migrates to the zinc atom to give an alkylzinc-ethoxide moiety which is coordinated to the newly formed pyrrolidinone compound (**Xc**). The formation of **Xc** may thus be considered a Dieckmann-like cyclization reaction[22].



Scheme 4. Rearrangement of E-enamine **10c** *(with NH---O hydrogen bond) to its Z isomer* **10c**′ *via an imine tautomer.*

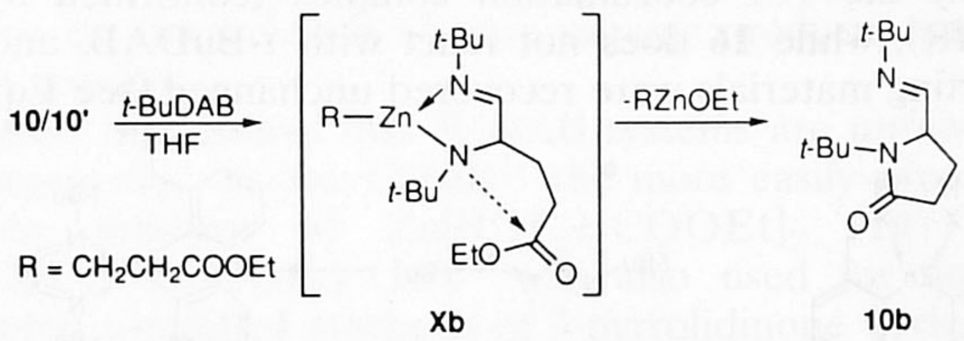
The *E*-enamine tautomer **10c** has a NH---O hydrogen bond and in solution it slowly converts, but only to a small extent, into its *Z* isomer (**10c**′). The *Z* isomer can only be formed when the imine tautomer (see Scheme 4) is accessible as an intermediate, because in this intermediate a rotation around the exocyclic single C–C bond can take place, resulting in the formation of either the E- or the thermodynamically less favorable *Z* configuration. The imine tautomer was never observed by ^{1}H NMR.

In the reaction of *t*-BuDAB with a mixture of **10** and the mixed organozinc reagent $ClZn(CH_2)_2COOEt$ **10**′ exclusively C alkylation instead of N alkylation occurs to give the 2-pyrrolidinone **10b** (see Eqn. 1). We have no explanation for this surprising result. Attempts to reproduce this exceptional behavior with a mixture of $ZnEt_2$ (which gives rise to exclusive N-alkylation) and EtZnCl were unsuccessful.

The formation of **10b** is probably the result of an intramolecular substitution reaction in the C-alkylated product **Xb** (see Scheme 5). The highly nucleophilic amide nitrogen in **Xb** may attack the electrophilic ester function, resulting in a new N–C bond. There then follows elimination of the organozinc alkoxide $EtOZn(CH_2)_2COOEt$. In contrast to the 3-pyrrolidinone (**10c**), the 2-pyrrolidinone **10b** is only present in the imine configuration. The heterocyclic compound **10b** is only formed when the reaction is carried out in THF, in which a homogenous reaction mixture is maintained. When less polar hexane or benzene is used, a suspension is formed, and the 1:1 coordination complex [ClZnR(*t*-BuDAB)] precipitates[11]. In this way **10**′ is removed from the reaction mixture, leaving **10** in solution. The latter then reacts normally with *t*-BuDAB to afford the 3-pyrrolidinone **10c**.

Concluding remarks

Regioselective introduction of functional substituents at either the N or C center of the N=C–C=N skeleton of *t*-BuDAB has been achieved by using functionally substituted diorganozinc compounds. The nature of the α-carbon atom bonded to the zinc atom governs the alkylation process. Quantitative alkylation on a nitrogen or carbon atom of the *t*-BuDAB system is obtained by using primary, secondary or benzylic diorganozinc compounds. These reactions are general for other R′DAB systems, R′ = *i*-Pr, cyclohexyl, neopentyl, etc., but isolation of the alkylated organic products was difficult in some cases. The presence of strong donating groups like NMe_2 in the diorganozinc reagents may disturb the regioselectivity of



Scheme 5. Reaction of the mixture of the mixed organozinc reagent $ZnCl[(CH_2)_2COOEt]$ **10**′ *and* **10** *with t-BuN=CHCH=Nt-Bu to the 2-pyrrolidinone* **10b**, *involving prior C alkylation (formation of* **Xb**).

the alkylation reaction (in the case of **7**) or even prevent a reaction (in the case of **16**).
In the alkylation reaction of $Zn(CH_2CMe_2Ph)_2$ with *t*-BuDAB, no products resulting from rearrangement of the alkyl radical (rearrangement rate $7 \cdot 10^2$ s^{-1}) were obtained. Therefore, one can estimate the rate of C alkylation to be $\approx 7 \cdot 10^4$ s^{-1} and of N alkylation $\approx 7 \cdot 10^6$ s^{-1}.
The reactions of *t*-BuDAB with either a mixture of **10** and **10′** or with **10** alone lead to very reactive, functionalized intermediates which, in a subsequent intramolecular substitution reaction, give the 2- and 3-pyrrolidinone derivatives **10b** and **10c**, respectively.

Experimental

General

All experiments were carried out under dry and oxygen-free nitrogen, using standard Schlenk techniques. Solvents were carefully dried and distilled prior to use. The starting materials *N,N′*-di-*tert*-butyl-1,4-diaza-1,3-butadiene (*t*-BuDAB)[30], $ZnPr_2$ (**1**)[31], $ZnBu_2$ (**2**)[32], Zn*s*-Bu_2 (**11**)[33], $ZnBn_2$ [b] (**13**)[34], $Zn(CH_2C_6H_4NMe_2\text{-}2)_2$ (**14**)[7], $Zn[(CH_2)_3OMe]_2$ (**3**)[5b], $Zn[(CH_2)_4OMe]_2$ (**5**)[5a-b], $Zn[(CH_2)_3NMe_2]_2$ (**7**)[5b-c], $Zn[(CH_2)_3SEt]_2$ (**6**)[5b], and $Zn[C_6H_4(CH_2NMe_2)\text{-}2]_2$ (**16**)[9,11] were prepared according to procedures described in the literature. $Zn(CH_2CMe_3)_2$ (**8**) and $Zn(CH_2CMe_2Ph)_2$ (**9**) were prepared via the corresponding organolithium compounds with 0.5 equiv. of $ZnCl_2$. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AC-200 or Bruker AC-300 instrument using C_6D_6 or $CDCl_3$ as solvent. Elemental analyses were performed by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands, and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of $Zn[(CH_2)_3OBn]_2$ (**4**)

The preparation of $Zn[(CH_2)_3OBn]_2$ is similar to that of $Zn[(CH_2)_3OMe]_2$ (**3**). The starting material $Br(CH_2)_3OBn$ was prepared according to a published method[35]. ^1H NMR (C_6D_6): δ 7.2 (m, 5H, aryl), 4.36 (s, 2H, CH_2Ph), 3.14 (t, 2H, CH_2O), 1.87 (m, $CH_2CH_2CH_2$), 0.28 (t, 2H, $ZnCH_2$).

Synthesis of $Zn(CH_2CH_2COOEt)_2$ (**10**)

To a stirred solution of dry $ZnCl_2$ (6.8 g, 50 mmol) in Et_2O (70 ml) was added dropwise 1-ethoxy 1-(trimethylsiloxy)cyclopropane[36] (17.4 g, 100 mmol). After further stirring for 16 h at room temperature (rt), the solvent and the Me_3SiCl which was formed in the reaction were removed *in vacuo*, affording a viscous oil in 85% yield. Distillation at low pressure (0.01 mmHg), gave **10** as a colorless, flammable liquid (b.p. 120–150°C) in 65% yield. ^1H NMR ($CDCl_3$): δ 4.12 (q, *J* 7.2 Hz, 4H, 2 OCH_2CH_3), 2.50 (t, *J* 7.6 Hz, 4H, 2 CH_2CH_2CO), 1.21 (t, *J* 7.2 Hz, 6H, 2 OCH_2CH_3), 0.21 (t, *J* 7.6 Hz, 4H, 2 $ZnCH_2$). ^{13}C NMR ($CDCl_3$): δ 183.8 (*C*=O), 61.5 (OCH_2), 32.4 (OCH_2CH_3), 14.2 (CH_2CH_2CO), 2.7 ($ZnCH_2$).

Synthesis of $Zn[CH(Me)CH_2CH_2OMe]_2$ (racemic mixture) (**12**)

$Zn[CH(Me)CH_2CH_2OMe]_2$ was prepared in the same way as Zn*s*-Bu_2 via the Grignard reaction of $BrCH(Me)CH_2CH_2OMe$[37] with half an equivalent of $ZnCl_2$. Compound **12** was purified by distillation at reduced pressure. Highly flammable **12** decomposes slowly at room temperature and must be stored under nitrogen atmosphere at −20°C. Two different diastereoisomers of **12** can be seen in its ^1H NMR and ^{13}C NMR spectra. ^1H NMR (C_6D_6): δ 3.20, 3.05 (m, 2H, CH_2O), 2.98 (s, 3H, OCH_3), 1.90, 1.65 (m, 2H, $CH(Me)CH_2CH_2$), 1.41, 1.37 (d, 3H, $CHCH_3$), 0.55 (m, 1H, $CH(Me)CH_2$). ^{13}C NMR (C_6H_6): δ 73.6, 73.3 (CH_2O), 58.7 (OCH_3), 38.9, 38.8 ($CHCH_2CH_2$), 19.9, 19.8 ($ZnCHMe$), 16.2, 16.0 ($CHCH_3$).

[b] Bn = benzyl = C_6H_5–CH_2–.

General procedure for the alkylation reactions

To a stirred solution of *t*-BuDAB (1.68 g, 10 mmol) in Et_2O (25 ml) at −78°C a solution of ZnR_2 (10 mmol) in Et_2O (10 ml) was added. Immediately a dark red solution was formed. NMR spectroscopy was in accord with the formation: of the 1:1 coordination complex R_2Zn(*t*-BuDAB). When the solution was warmed to room temperature, a slow color change of the solution from red to yellow occurred between −60 and −10°C, depending on R (see Table I of Ref. 4b). The reaction mixture was stirred for an additional 5 min at room temp. and then hydrolyzed with H_2O (0.09 ml, 5 mmol). To accomplish complete hydrolysis of the organozinc intermediate the mixture was stirred for 1 h after which the solid material was collected by centrifugation with subsequent decantation of the clear solution. The solid was extracted with Et_2O (2×10 ml). The combined ethereal extracts were concentrated *in vacuo*, affording the organic product as a fluid oil.

(Z)-N,N′-Bis(1,1-dimethylethyl)-N-propyl-1,2-ethenediamine (**1a**). $ZnPr_2$ (1.51 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. Compound **1a**, a colorless oil, 2.08 g yield (98%). ^1H NMR (C_6D_6): δ 5.83 (dd, *J* 12.9 Hz, *J* 5.7 Hz, 1H, *CH*=CH), 4.43 (d, *J* 5.7, 1H, CH=*CH*), 4.12 (br d, *J* 12.9 Hz, 1H, *NH*), 2.39 (t, 2H, NCH_2), 1.51 (m, 2H, $CH_2CH_2CH_3$), 1.09, 1.03 [s, 9H, $C(CH_3)_3$], 0.93 (t, 3H, CH_2CH_3). ^{13}C NMR (C_6D_6): δ 131.7 (NH–*CH*=C), 110.2 (C=*CH*–N), 55.1 [*C*(CH_3)$_3$], 52.1 (NCH_2), 49.8 [*C*(CH_3)$_3$], 30.2, 29.4 [C(*CH*$_3$)$_3$], 22.8 ($CH_2CH_2CH_3$), 12.5 ($CH_2CH_2CH_3$).

N-Butyl-N,N′-bis(1,1-dimethylethyl)-1,2-ethenediamine (**2a**). $ZnBu_2$ (1.79 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. Compound **2a**, a pale yellow oil, 2.21 g yield (98%). ^1H NMR (C_6D_6): δ 5.79 (dd, *J* 5.7 Hz, *J* 12.5 Hz, 1H, *CH*=C), 4.37 (d, *J* 5.7 Hz, 1H, C=*CH*), 4.04 (d, *J* 12.5 Hz, 1H, *NH*), 2.39 (t, 2H, NCH_2), 1.38 (m, 4H, CH_2CH_2), 1.05 [s, 9H, $C(CH_3)_3$], 1.02 [s, 9H, $C(CH_3)_3$], 0.89 (t, 3H, CH_2CH_3). ^{13}C NMR (C_6D_6): δ 131.6 (NH–*CH*=C), 110.0 (C=*CH*–N), 55.1, 49.8 [*C*(CH_3)$_3$], 49.6 (NCH_2), 31.9 ($CH_2CH_2CH_2$), 30.2, 26.7 [C(*CH*$_3$)$_3$], 21.2 (CH_2CH_3), 14.4 (CH_3).

(Z)-N,N′-Bis(1,1-dimethylethyl)-N-(3-methoxypropyl)-1,2-ethenediamine (**3a**). $Zn[(CH_2)_3OMe]_2$ (1.79 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. Compound **3a**, a pale yellow oil, 2.43 g yield (98%). ^1H NMR (C_6D_6): δ 5.93 (dd, *J* 6.0 Hz, *J* 13.0 Hz, 1H, *CH*=CH), 4.52 (d, *J* 6.0 Hz, 1H, CH=*CH*), 4.2 (br d, *J* 13 Hz, 1H, *NH*), 3.45 (t, 2H, OCH_2), 3.24 (s, 3H, OCH_3), 2.65 (t, 2H, NCH_2), 1.88 (m, 2H, $CH_2CH_2CH_2$), 1.17 [s, 9H, $C(CH_3)_3$], 1.05 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 131.9 (NH–*CH*=C), 110.0 (C=*CH*–N), 71.5 (CH_2O), 58.3 (OCH_3), 55.3 [*C*(CH_3)$_3$], 49.9 [*C*(CH_3)$_3$], 47.0 (NCH_2), 30.2 [C(*CH*$_3$)$_3$], 29.9 (CH_2), 26.7 [C(*CH*$_3$)$_3$]. An analytically pure product was obtained as a colourless oil by distillation. Anal. calcd. for $C_{14}H_{30}N_2O$: C 69.42, H 12.40, N, 11.57, found: C, 69.63, H, 12.09, N, 11.87%.

(Z)-N,N′-Bis(1,1-dimethylethyl)-N-[3-(benzyloxy)propyl]-1,2-ethenediamine (**4a**). $Zn[(CH_2)_3OBn]_2$ (3.63 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in hexane. The alkylated organozinc complex was hydrolyzed with one equivalent of *t*-BuOH (2.5M solution in hexane). To accomplish complete hydrolysis, the reaction mixture was stirred for 3 h. The suspension was set aside at −20°C for 16 h to permit the Zn(O*t*-Bu) [$(CH_2)_3OBn$] to separate completely. The cold mixture was centrifuged and the supernatant was decanted. The solid was extracted with cold hexane (2×10 ml). Concentration of the combined hexane solutions *in vacuo*, afforded **4a** as a pale yellow oil, 3.02 g yield (95%). ^1H NMR (C_6D_6): δ 7.23 (m, 5H, aryl), 5.87 (dd, *J* 6.0 Hz, *J* 12.9 Hz, 1H, *CH*=C), 4.45 (d, *J* 6.0 Hz, 1H, C=*CH*), 4.38 (s, 2H, $OCH_2C_6H_5$), 4.12 (d, *J* 12.9 Hz, 1H, *NH*), 3.52 (t, 2H, CH_2CH_2O), 2.61 (t, 2H, CH_2N), 1.85 (m, 2H, $CH_2CH_2CH_2$), 1.10 [s, 9H, $C(CH_3)_3$], 1.02 [s, 9H, $C(CH_3)_3$].

(Z)-N,N-Bis(1,1-dimethylethyl)-N-(4-methoxybutyl)-1,2-ethenediamine (**5a**). $Zn[(CH_2)_4OMe]_2$ (2.39 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. Compound **5a**, a pale yellow oil, 2.49 g yield (97%). ^1H NMR (C_6D_6): δ 5.85 (dd, *J* 6.0 Hz, *J* 13.0 Hz, 1H, *CH*=C), 4.47 (d, *J* 6.0 Hz, 1H, C=*CH*), 4.14 (d, *J* 13.0 Hz, 1H, *NH*), 3.28 (t, 2H, OCH_2), 3.17 (s, 3H, OCH_3), 2.45 (t, 2H, NCH_2), 1.63 (m, 4H, CH_2CH_2), 1.11 [s, 9H, $C(CH_3)_3$], 1.05 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR (C_6H_6): δ 131.8 (NH–*CH*=C), 109.3 (C=*CH*–N), 73.2 (OCH_2), 58.3 (CH_3O), 55.2 [*C*(CH_3)$_3$], 49.9 (NCH_2), 49.9 [*C*(CH_3)$_3$], 30.2 [C(*CH*$_3$)$_3$], 28.5 (CH_2CH_2), 26.7 [C(*CH*$_3$)$_3$], 26.5 (CH_2CH_2). An analytically pure product was obtained as a colorless oil by distillation. Anal. calcd for $C_{15}H_{32}N_2O$: C 70.31, H 12.5, N 10.94; found: C 70.54, H 12.43, N 11.18%.

(Z)-N,N'-Bis(1,1-dimethylethyl)-N-[3-(ethylthio)propyl]-1,2-ethenediamine (**6a**). $Zn[(CH_2)_3SEt]_2$ (2.71 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. Compound **6a**, a pale yellow oil, 2.66 g yield (98%). ^1H NMR (C_6D_6): δ 5.81 (dd, *J* 5.8 Hz, *J* 12.5 Hz, 1H, C*H*=C), 4.37 (d, *J* 5.8 Hz, 1H, C=C*H*), 4.03 (br d, *J* 12.5 Hz, 1H, N*H*), 2.30 (m, 6H, NCH_2, CH_2SCH_2), 1.72 (m, 2H, $CH_2CH_2CH_2$), 1.09 [s, 9H, C(CH_3)$_3$], 1.08 (t, 3H, SCH_2CH_3), 1.02 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 131.8 (NH*C*H=C), 109.8 (C=*C*H–N), 55.3, 49.8 [*C*(CH$_3$)$_3$], 49.0 (N*C*H$_2$), 29.5 (CH_2CH_2S), 25.9 (SCH_2CH_3), 30.2, 26.7 [C(*C*H$_3$)$_3$], 15.0 (CH_2CH_3).

Reaction of $Zn[(CH_2)_3NMe_2]_2$ with t-BuDAB leading to N-[3-(Dimethylamino)propyl]-N,N'-bis(1,1-dimethylethyl)-1,2-ethenediamine (**7a**) *and 5-(dimethylamino)-1-[1,1-dimethylethyl)imino]-2-pentanamine* (**7b**). A 1:1 mixture of *t*-BuDAB (1.68 g, 10 mmol) and $Zn[(CH_2)_3NMe_2]_2$ (2.37 g, 10 mmol) in hexane was heated at 70°C for 72 h. The mixture was hydrolyzed with half an equivalent of H_2O, which resulted directly in the formation of a white precipitate. After work-up (*vide supra*), a colorless oil was obtained. According to ^1H-NMR and GC analysis (capillary column) the oil was of a mixture of four products; 68% of **7a**, 21% of **7b**, and 11% of unknown products. ^1H NMR of **7a** (C_6D_6): δ 5.88 (dd, *J* 5.9 Hz, *J* 12.4 Hz, 1H, C*H*=C), 4.48 (d, *J* 5.9 Hz, 1H, C=C*H*), 4.17 (br d, *J* 12.4 Hz, 1H, N*H*), 2.56 (t, 2H, NCH_2), 2.32 [t, 2H, CH_2N(CH$_3$)$_2$], 2.16 [s, 6H, N(CH_3)$_2$], 1.69 (m, 2H, $CH_2CH_2CH_2$), 1.13 [s, 9H, C(CH_3)$_3$], 1.05 [s, 9H, C(CH_3)$_3$]. ^1H NMR of **7b** (C_6D_6): δ 7.41 (d, *J* 4.47 Hz, 1H, N=C*H*), 3.31 (m, 1H, N–C*H*), 2.14 [s, 6H, N(CH_3)$_2$].

N-(1,1-Dimethylethyl)-1-[(1,1-dimethylethyl)imino]-4,4-dimethyl-2-pentanamine (**8b**). To a stirred solution of *t*-BuDAB (1.68 g, 10 mmol) in Et_2O (25 ml) a solution of $Zn(CH_2CMe_3)_2$ (2.07 g, 10 mmol) in Et_2O (10 ml) was added. The reaction mixture was stirred for 2 h during which time the initial red color of the solution slowly changed to yellow. After work-up (*vide supra*), compound **8b** was isolated as a pale yellow oil in 2.35 g yield (98%). ^1H NMR (C_6D_6): δ 7.35 (d, *J* 5.7 Hz, 1H, N=C*H*), 3.54 (m, 1H, N–C*H*), 1.45 (dd, ^2J 14.0 Hz, ^3J 6.9 Hz, 1H, CH–C*H*H'), 1.25 (dd, ^2J 14.0 Hz, ^3J 6.9 Hz, 1H, CH–CH*H'*), 1.13, [1.06, 0.97 C(CH_3)$_3$], no N*H* signal was observed. ^{13}C NMR (C_6D_6): δ 163.6 (N=*C*H), 56.0 [*C*(CH$_3$)$_3$], 55.0 (N*C*H), 52.9, 51.3 [*C*(CH$_3$)$_3$], 31.6, 30.8 [C(*C*H$_3$)$_3$], 29.8 [$CH_2C(CH_3)_3$], 29.3 [C(*C*H$_3$)$_3$].

N-(1,1-Dimethylethyl-α-[[(1,1-dimethylethyl)imino]methyl]-β,β-dimethylbenzenepropanamine (**9b**). The same experimental procedure as for **4a**. $Zn(CH_2CMe_2Ph)_2$ (3.31 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in hexane. Compound **9b**, an orange oil, 2.87 g yield (95%). To obtain an analytically pure product the oil was dissolved in hexane (15 ml) and one equivalent of Me_2Zn (1M solution in hexane) was added. After stirring for 10 min, the solution was concentrated and set aside at −20°C for 16 h. The clear hexane solution was decanted and the remaining solid was washed with cold hexane (10 ml) affording the off-white solid Me_2Zn[*t*-BuNH-CH(CH_2CMe_2Ph)–CH=N*t*-Bu] (**9c**). Compound **9c** was dissolved in hexane (15 ml) and hydrolyzed with two equivalents of H_2O. To accomplish complete hydrolysis the mixture was stirred for 1 h after which the solid material was separated by centrifugation and the supernatant hexane collected by decantation. The solid was extracted with hexane (10 ml). The combined hexane solutions were concentrated *in vacuo*, affording **9b** as a colorless oil in 2.66 g yield (overall 88%). ^1H NMR of **9b** (C_6D_6): δ 7.15 (m, 6H, aryl, N=C*H*), 3.42 (m, 1H, N–C*H*), 1.85 (d, *J* 6.4 Hz, 2H, CH–CH_2), 1.13 [s, 6H, C(CH_3)$_2$], 1.05 [s, 9H, C(CH_3)$_3$], 0.90 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR of **9b** (C_6D_6): δ 163.4 (N=*C*), 150.2 (C_{ipso}), 128.4, 126.9, 126.4 (aryl), 56.3 [*C*(CH$_3$)$_3$], 55.1 (*C*HN), 50.9 [*C*(CH$_3$)$_3$], 50.7 [$CH_2C(CH_3)_2$], 38.2 [$CH_2C(CH_3)_2$], 31.8 [$CH_2C(CH_3)CH_3$], 30.4 [C(*C*H$_3$)$_3$], 29.9 [$CH_2C(CH_3)CH_3$], 29.4 [C(*C*H$_3$)$_3$]. Anal. calcd for $C_{20}H_{34}N_2$: C 79.41, H 11.33, N 9.26; found: C 79.28, H 11.24, N 9.18%. ^1H NMR of **9c** (C_6D_6): δ 7.10 (m, 5H, aryl), 6.80 (d, *J* 2.5 Hz, 1H, N=C*H*), 3.32 (m, 1H, N–C*H*-CH$_2$), 2.20 [br resonance, 1H, CH*H'*–C(CH$_3$)$_2$], 1.77 [dd, ^2J 13.0 Hz, ^3J 5.9, 1H, C*H*H'–C(CH$_3$)$_2$], 1.20 (s, 3H, CH$_2$–CCH_3), 1.12 (s, 3H, CH$_2$–CCH_3), under 1.12 (br d, 1H, N*H*), 0.95, 0.88 [s, 9H, C(CH_3)$_3$], −0.33 [s, 6H, Zn(CH_3)$_2$]. ^{13}C NMR of **9c** (C_6D_6): δ 162.3 (N=C), 148.0 (C_{ipso}), 129.0, 126.6, 126.2 (aryl), 58.6 [*C*(CH$_3$)$_3$], 54.8 (N–*C*H), 53.5 [*C*(CH$_3$)$_3$], 50.8 [$CH_2C(CH_3)_2$], 37.4 [$CH_2C(CH_3)_2$], 32.1 (CH_2CCH_3), 29.2 [C(*C*H$_3$)$_3$], 28.8 (CH_2CCH_3), 28.0 [C(*C*H$_3$)$_3$], −5.4 [Zn(*C*H$_3$)$_2$].

1-(1,1-Dimethylethyl)-5-[[(1,1-dimethylethyl)imino]methyl]-2-pyrrolidinone (**10b**). To a stirred solution of crude (undistilled) $Zn[(CH_2)_2COOEt]_2$ (27 mmol) in THF (40 ml) at −60°C, was added dropwise a solution of *t*-BuDAB (4.54 g, 27 mmol) in THF (10 ml). Immediately a dark red solution was formed. The color of the solution changed on warming from red to yellow between −20 and −10°C. The reaction mixture was continuously heated at 55°C for 16 h. The resulting mixture was quenched at room temp. with satd. aqueous NH_4Cl solution (30 ml). The water layer was separated and extracted twice with Et_2O/pentane (80/20) (30 ml). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, to afford the 2-pyrrolidinone (65% yield) as a dark yellow solid. ^1H NMR (C_6D_6): δ 7.28 (d, J 6.2 Hz, 1H, N=C*H*), 4.09 (m, *J* 8.5 Hz, *J* 6.2 Hz, *J* 1.4 Hz, 1H, N=C–C*H*), 2.29–1.94 (m, 2H, CH_2–C=O), 1.76–1.52 (m, 1H, C*H*H'–CH$_2$C=O), 1.41 [s, 9H, C(CH_3)$_3$], 1.35–1.09 (m, 1H, CH*H'*–CH$_2$C=O), 1.04 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 174.5 (*C*=O), 158.3 (N=*C*H), 62.3 (N–*C*H), 56.7, 54.3 [*C*(CH$_3$)$_3$], 31.3 (*C*H$_2$–C=O), 29.3, 28.5 [C(*C*H$_3$)$_3$], 23.9 (*C*H$_2$–CH$_2$C=O). The product was purified by crystallization from pentane at −78°C; m.p. 40°C. IR (KBr): 1685 cm^{-1} ν(C=O). Anal. calcd for $C_{13}H_{24}N_2O$: C 69.60, H 10.78, N 12.49; found: C 68.09, H 10.35, N 12.25%

1-(1,1-Dimethylethyl)-2-[[(1,1-dimethylethyl)amino]methylene]-3-pyrrolidinone (**10c**). To a stirred solution of $Zn[(CH_2)_2COOEt]_2$ (2.67 g, 10 mmol) in benzene (50 ml) was added a solution of *t*-BuDAB (1.68 g, 10 mmol) in benzene (5 ml). A clear dark red solution was formed immediately and the color changed gradually to yellow. The reaction mixture was heated for 3 h at 70°C then cooled to room temp. and quenched with H_2O (0.015 mol). The resulting mixture was shaken vigorously in order to get complete hydrolysis. The clear yellow solution was decanted and the precipitate was extracted twice with Et_2O (10 ml). The combined organic solutions were dried (Mg_2SO_4) and concentrated *in vacuo* to afford the crude 3-pyrrolidinone product in 80% yield. ^1H NMR (C_6D_6): δ 9.05 (br d, *J* 12.8 Hz, 1H, N*H*), 6.71 (d, *J* 12.8 Hz, 1H, N–C*H*=C), 3.05 (t, *J* 7.5 Hz, 2H, N–CH_2–C), 2.20 (t, *J* 7.5 Hz, 2H, C–CH_2–C=O), 1.02, 0.88 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 201.9 (*C*=O), 137.8 (N–*C*H=C), 116.9 (N–CH=*C*), 56.3, 50.9 [*C*(CH$_3$)$_3$], 45.8 (N–*C*H$_2$), 37.7 (*C*H$_2$–C=O), 29.7, 27.7 [C(*C*H$_3$)$_3$]. Pure **10c** was isolated by sublimation, followed by repeated crystallization from cold (−30°C) Et_2O. Yield 0.22 g (10%), m.p. 66°C. Compound **10c** is very sensitive to O_2 and is stable when stored under N_2 at −25°C. IR (KBr): 3425 cm^{-1} ν(NH), 1658 cm^{-1} ν(C=C), 1578 cm^{-1} ν(C=O). Anal. calcd. for $C_{13}H_{24}N_2O$: C 69.60, H 10.78, N 12.49, found: C 69.48, H 10.73, N 12.36%.

N,N'-Bis(1,1-dimethylethyl)-N-(1-methylpropyl)-1,2-ethenediamine (**11a**) *and N-(1,1-dimethylethyl)-1-[1,1-dimethylethyl)imino]-3-methyl-2-pentanamine* (**11b**). To a stirred solution of *t*-BuDAB (1.68 g, 10 mmol) in Et_2O (25 ml), a solution of Zn [CH(Me)CH_2CH_3]$_2$ (1.79 g, 10 mmol) in Et_2O (25 ml) was added. After stirring for 5 min, H_2O (0.09 ml) was added, which resulted in the direct formation of a white precipitate. According to ^1H-NMR data the isolated pale yellow oil (2.21 g, 98% yield) consisted of three isomeric compounds, in a molar ratio of 12:12:1, two diastereoisomers of **11b** and one of **11a**, which we could not separate. ^1H NMR **11a** (C_6D_6): δ 5.85 (dd, *J* 5.9 Hz, *J* 12.9 Hz, 1H, C*H*=C), 4.63 (d, *J* 5.9, 1H, C=C*H*), 4.10 (d, *J* 12.9, 1H, N*H*), 2.91 (m, 1H, NC*H*CH$_3$). ^{13}C NMR **11a** (C_6D_6): δ 133.2 (NH–C*H*=C), 104.3 (C=*C*H–N).
11b and **11b'**. ^1H NMR (C_6D_6): δ 7.47, 7.43 (d, *J* 3.9 Hz, 2×1H, N=C*H*), 3.08 (m, 2×1H, N–C*H*), 1.93 (d, 2×1H, N*H*), 1.30 (m, 6H, 2×C*H*CH$_3$, 2×CH_2CH$_3$), 1.10 [s, 2×9H, C(CH_3)$_3$], 1.02 [s, 2×9H, C(CH_3)$_3$], 0.89 [d, 2×3H, CHCH_3), 0.84 (t, 2×3H, CH_2CH_3). ^{13}C NMR (C_6D_6): δ 161.0, 160.7 (N=*C*H), 59.9, 59.4 (N*C*H), 56.4, 56.3, 50.7, 50.5 [*C*(CH$_3$)$_3$], 40.9, 39.5 (*C*HCH$_3$), 30.3, 29.7 [C(*C*H$_3$)$_3$], 26.6, 25.7 (*C*H$_2$), 15.9, 14.3 (*C*H$_3$CH), 12.4 (*C*H$_3$CH$_2$). An analytically pure product was obtained as a colorless oil by distillation. Anal. calcd for $C_{14}H_{30}N_2$: C 74.27, H 13.36, N 12.37, found: C 74.21, H 13.29, N 12.42%.

N-(1,1-Dimethylethyl)-1-[(1,1-dimethylethyl)imino]-5-methoxy-3-methyl-2-pentanamine (**12b**) The same experimental procedure as for **11a/11b** using Zn[CH(Me)(CH$_2$)$_2$OMe]$_2$ (2.39 g, 10 mmol) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O. According to ^1H- and ^{13}C-NMR data the isolated pale yellow oil (2.48 g, 97% yield) consists of three isomers; 96.5% of two diastereomers of compounds **12b** in a molar ratio of 1:1 and 3.5% of isomer **12a**, which we could not separate. ^1H NMR of **12a** (C_6D_6): δ 5.88 (dd, *J* 12.6 Hz, *J* 5.8 Hz, 1H, C*H*=C), 4.67 (d, *J* 5.8 Hz, 1H, C=C*H*), 4.52 (br d, *J* 12.6 Hz, 1H, N*H*). ^1H NMR of **12b** (C_6D_6): δ 7.48, 7.43 (d, *J* = 3.8 Hz, 2×1H, N=C*H*), 3.32 (m, 2×2H, CH_2OCH$_3$), 3.16, 3.12 (s, 2×3H, OCH_3), N–C*H* under OCH$_3$ signals, 2.1–1.3 (m, 8H, 2×CH–C*H*–CH$_3$, 2×CH_2CH$_2$O, 2×N–*H*), 1.11, 1.09, 1.05, 1.03 [s, 4×9H, C(CH_3)$_3$], 0.98, 0.88 (d, *J* = 6.7 Hz, 2×3H, CH–CH_3). ^{13}C NMR of **12b** (C_6D_6): δ 160.9, 160.8 (N=*C*H), 71.3 (*C*H$_2$O), 60.1, 59.7 (OCH$_3$), 58.3, 58.2 (N–*C*H), 56.4, 56.3, 50.7, 50.5 [*C*(CH$_3$)$_3$], 35.5, 34.3 (CH*C*H–CH$_3$), 34.0, 32.6 (*C*H$_2$CH$_2$O), 30.3, 30.2, 29.7 [C(*C*H$_3$)$_3$],

16.8, 14.5 (CH–CH_3). An analytically pure product was obtained as a colorless oil by **short-path distillation**. Anal. calcd. for $C_{15}H_{32}N_2O$: C 70.26, H 12.58, N 10.92; found: C 70.98, H 13.02, N 10.78%

N-(1,1-Dimethylethyl)-α-[[1,1-dimethylethyl)imino]methyl]benzeneethanamine (**13b**). The same experimental procedure as for **11a/11b** was used with $ZnBn_2$ (2.47 g, 10 mmol) in Et_2O (25 ml) and *t*-BuDAB (1.68 g, 10 mmol) in Et_2O (10 ml). After work-up (*vide supra*) **13b** was obtained as a pale yellow oil in 2.52 g (97%) yield. ^{1}H NMR (C_6D_6): δ 7.47 (d, *J* 4.6 Hz, 1H, N=C*H*), 7.16 (m, 5H, aryl), 3.60 (m, 1H, NC*H*), 0.95 [s, 9H, C(CH_3)$_3$], 2.79 (dd, ^2J 13.2 Hz, ^3J 5.9 Hz, 1H, C*H*H′–C_6H_5), 2.62 (dd, ^2J 13.2 Hz, ^3J 8.2 Hz, 1H, CH*H′*–C_6H_5), 1.67 (s, 1H, N*H*), 1.09 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 162.2 (N=*C*H), 139.1 (*ipso-C*), 130.1, 128.4, 126.5 (aryl), 58.2 (N–*C*H), 56.3, 50.8 [*C*(CH$_3$)$_3$], 42.5 (*C*H$_2$Ph), 30.0 [C(C*H*$_3$)$_3$], 29.6 [C(C*H*$_3$)$_3$]. Anal. calcd for $C_{17}H_{28}N_2$: C 78.41, H 10.84, N 10.76, found: C 78.37, H 10.93, N 10.97%.

2-(Dimethylamino)-N-(1,1-dimethylethyl)-α-[[1,1-dimethylethyl)imino]methyl]benzeneethanamine (**14b**). To a stirred suspension of Zn[2-(dimethylamino)benzyl]$_2$ (ZnDMAT$_2$) (3.33 g, 10 mmol) in hexane (50 ml) *t*-BuDAB (1.68 g, 10 mmol) in hexane (10 ml) was added. This resulted directly in a yellow solution. The solution was stirred for 10 min after which the alkylated organozinc complex was hydrolyzed by an equimolar amount of *t*-BuOH (2.5M solution in hexane) resulted in the direct formation of a white precipitate of (Zn(O*t*-Bu)(DMAT)). The reaction mixture was set aside at −20°C for 16 h to permit this solid to separate quantitatively. The cold mixture was centrifuged and the supernatant collected by decantation. The solid was extracted with cold hexane (10 ml). Concentration of the combined hexane solutions *in vacuo*, afford **14b** as a yellow oil in 2.87 g (95%) yield. To obtain a pure product, the same experimental procedure as for **9b** was followed. The intermediate Me_2Zn[*t*-BuNH–CH($CH_2C_6H_4NMe_2$-2)-CH=N*t*-Bu] (**14c**) was obtained as a colorless solid.

^{1}H NMR of **14b** (C_6D_6): δ 7.59 (d, *J* 4.7 Hz, 1H, N=C*H*), 7.22–6.87 (m, 4H, aryl), 3.06 (dd, ^2J 12.9 Hz, ^3J 8.6 Hz, 1H, CH–CH*H′*), 3.77 (m, 1H, NC*H*), 2.85 (dd, ^2J 12.9 Hz, ^2J 5.8 Hz, 1H, CH–C*H*H′), 2.43 [s, 6H, N(CH_3)$_2$], 2.12 (s, 1H, N*H*), 1.20 [s, 9H, C(CH_3)$_3$], 0.98 [s, 9H, C(CH_3)$_3$]. ^{13}C NMR of **14b** (C_6D_6): δ 163.1 (N=C), 153.6, 134.6, 131.9, 127.4, 124.0, 119.8 (aryl), 58.6 (N–*C*H), 56.0 [*C*(CH$_3$)$_3$], 50.7 [*C*(CH$_3$)$_3$], 45.2 [N(*C*H$_3$)], 37.7 (*C*H$_2$), 30.0, 29.7 [C(*C*H$_3$)$_3$]. ^{1}H NMR of **14c** (C_6D_6): δ 7.25 (d, ^3J 2.5 Hz, 1H, N=C*H*), 6.97 (m, 4H, aryl), 3.39 (m, 1H, NC*H*), 3.02 (dd, ^2J 13.2 Hz, ^3J 9.4 Hz, 1H, C*H*H′), 2.54 (dd, ^2J 13.2 Hz, ^3J 4.1 Hz, 1H, CH–CH*H′*), 2.42 (s, 6H, NCH_3), N*H* under NCH_3 signal, 1.17 [s, 9H, C(CH_3)$_3$], 0.84 [s, 9H, C(CH_3)$_3$], −0.21 (s, 6H, CH_3Zn). ^{13}C NMR of **14**C (C_6D_6): δ 162.5 (N=*C*), 153.8, 133.9, 131.8, 128.2, 124.4, 120.2 (aryl), 59.4 (NCH), 58.6, 52.4 [*C*(CH$_3$)$_3$], 45.3 [N(*C*H$_3$)], 35.6 (*C*H$_2$), 29.7, 28.1 [C(*C*H$_3$)$_3$], −5.5 (*C*H$_3$Zn).

Coordination complex Zn[C$_6$H$_4$(CH$_2$OMe)-2]$_2$(t-BuDAB) (**15**). To a stirred solution of *t*-BuDAB (1.68 g, 10 mmol) in Et_2O (25 ml) at room temp. a solution of Zn[C_6H_4(CH$_2$OMe)-2]$_2$ (3.07 g, 10 mmol) in Et_2O (10 ml) was added resulting in a yellow solution. The solvent was removed *in vacuo* leaving **15** as a yellow solid in 5.75 g (100%) yield. ^{1}H NMR of **15** (C_6D_6): δ 8.12 (s, 2H, N=C*H*), 7.91 (m, 2H, aryl), 7.33 (m, 4H, aryl), 6.97 (m, 2H, aryl), 4.25 (s, 4H, CH_2OCH$_3$), 2.94 (s, 6H, CH$_2$OCH_3), 1.17 [s, 18H, C(CH_3)$_3$]. ^{13}C NMR of **15**: δ 157.5 (N=*C*H), 149.0, 146.5, 126.6, 126.4, 123.0 (aryl), 76.3 (*C*H$_2$OCH$_3$), 58.1 (CH$_2$O*C*H$_3$), 57.9 [*C*(CH$_3$)$_3$], 29.4 [C(*C*H$_3$)$_3$].

Acknowledgements

This work was supported in part (E.W.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Advancement of Pure Research (NWO). The authors of this paper thank Dr. *J.T.B.H. Jastrzebski* for helpful discussions and Dr. *P.A. van der Schaaf* for providing a sample of Zn[C_6H_4(CH$_2$OMe)-2]$_2$.

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