Influence of bulky substituents on the regioselective group-transfer reactions of diorganozinc compounds with *N,N'*-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene

Elmo Wissing, Klaas van Gorp, Jaap Boersma and Gerard van Koten*
Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht (Netherlands)

(Received November 12, 1993)

Abstract

Diorganozinc compounds R_2Zn (R = alkyl or aryl) react with *N,N'*-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene, (i-Pr_2Ph)N=CHCH=N(i-Pr_2Ph) (i-Pr_2Ph-DAB) to give thermally unstable 1:1 coordination complexes R_2Zn(i-Pr_2Ph-DAB), which subsequently undergo a slow regioselective alkyl or aryl group-transfer reaction from the zinc atom to an imine-nitrogen or a carbon atom of the NCCN system of the i-Pr_2Ph-DAB ligand. In the case of R = methyl, n-propyl, n-butyl, s-butyl, neopentyl and benzyl, C-alkylation occurs with a subsequent 1,2-hydrogen shift in the amino-imino skeleton affording RZn[(i-Pr_2Ph)N–CH_2–CR=N(i-Pr_2Ph)], whereas for R = t-butyl the C-alkylated product t-BuZn[(i-Pr_2Ph)N–CH(t-Bu)–CH=N(i-Pr_2Ph)] is stable. Surprisingly, diphenylzinc reacts with i-Pr_2Ph-DAB exclusively to give the N-arylated product PhZn[(i-Pr_2Ph)N=CHCH=N(Ph)(i-Pr_2Ph)].

Key words: Organozinc reagents; Regioselective group transfer; Steric effects

Introduction

1,4-Disubstituted 1,4-diaza-1,3-butadienes (R'N=CH–CH=NR') have been extensively studied as ligands for transition and main-group metals [1, 2]. However, recent studies revealed that these heterodienes are versatile synthons in metal-mediated organic synthesis [3–7]. In these applications, reactions of diorganozinc compounds with R'DAB (R' = alkyl) [8, 9], which proceed with high regioselectivity, play an essential role. Some examples of such reactions are given in Scheme 1.

So far, our studies have been restricted to alkyl substituted 1,4-diaza-1,3-butadienes. Mechanistic studies showed that organozinc-R'DAB radical intermediates, [RZnR'DAB]', are likely key intermediates in the reactions shown in Scheme 1. When R' is an alkyl group, the LUMO occupied by the single electron will be primarily concentrated on the NCCN skeleton, as indicated by simple, well resolved, ESR spectra [9]. However, when R' is an aryl group, the LUMO may now be extended, through overlap with the π system of the aryl substituents.

In this paper we present the first results of reactions of R_2Zn compounds with aryl substituted DAB systems. Most of the reactions were performed with *N,N'*-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene, (i-Pr_2Ph)N=CHCH=N(i-Pr_2Ph) (2,6-i-Pr_2Ph-DAB), which was first reported by tom Dieck *et al.* [10]. A special structural feature of this aryl substituted α-diimine is the fixed perpendicular orientation of the aryl nuclei with respect to the C=N imine moieties as a result of the presence of two large *ortho* substituents in the aryl group. Also some experiments were carried out with a bis *ortho*-methyl substituted and a *para*-methyl substituted phenylDAB, i.e. 2,6-Me_2Ph-DAB and 4-MePh-DAB. In the latter aryl-DABs, the rotation around the phenyl C_{ipso}–N axis is less hindered (2,6-Me_2Ph-DAB) or not hindered at all (4-MePh-DAB). Consequently, with these aryl-DABs both steric and electronic effects on the group-transfer reaction with R_2Zn can be studied.

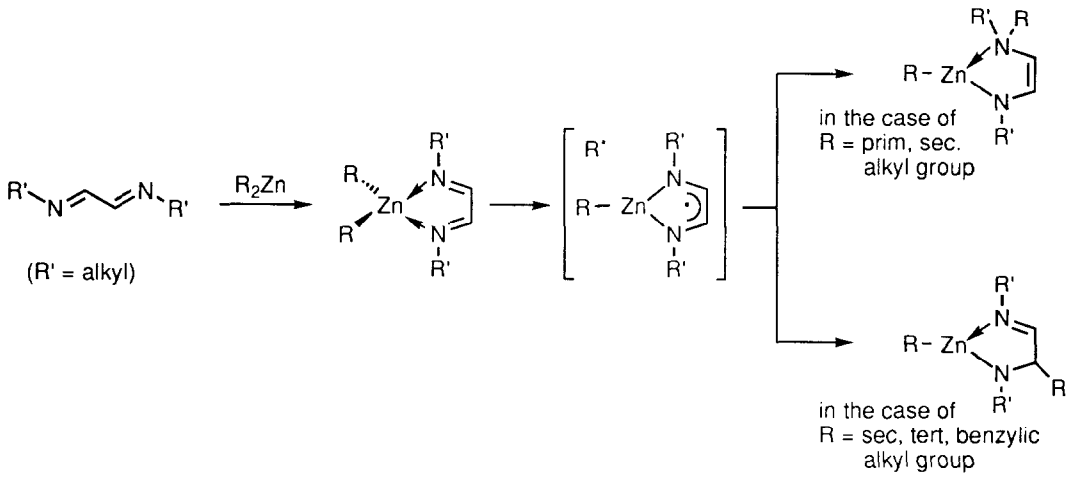
Experimental

General data

All experiments were carried out under a dry and oxygen-free nitrogen atmosphere, using standard

*Author to whom correspondence should be addressed.

SSDI 0020-1693(94)03854-H



Scheme 1.

Schlenk techniques. Solvents were carefully dried and distilled from sodium/benzophenone prior to use. The diorganozinc compounds n-Pr_2Zn (**2**), n-Bu_2Zn (**3**), s-Bu_2Zn (**4**), t-Bu_2Zn (**5**) and Ph_2Zn (**8**) were prepared from their corresponding Grignard reagent (**2**, **4** and **8**) or organolithium compound (**3** and **5**) with 0.5 equiv. of dry $ZnCl_2$, and purified by distillation at reduced pressure. The starting materials 2,6-i-Pr_2Ph-DAB, 2,6-Me_2Ph-DAB, 2,6-i-Pr_2Ph-Me_2DAB [10], 4-MePh-DAB [11], Me_2Zn (**1**) [12] and (Benzyl)$_2$Zn (**6**) [13] were prepared according to literature procedures. All other reagents were purchased from Aldrich Chemical Co. or Janssen Chimica. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

General procedure for the alkylation reactions of the R'DAB (R' = 2,6-i-Pr_2Ph, 2,6-Me_2Ph, 4-MePh) with R_2Zn

To a stirred solution of R'DAB (10 mmol) in Et_2O (50 ml) was added 1 equiv. of R_2Zn. The red solutions were stirred for 2 h in the case of **2**–**7**, **9** and **10**, and for 16 h in the case of **8**. The solvent was evaporated *in vacuo* affording the alkylated products as yellow–orange oils (**2d**, **3d**, **5c**, **6d** and **10**) or yellow solids (**4d**, **8b** and **9**) in quantitative yield. Relevant NMR data of these products and of **1d** (see below) are given in Tables 1 (^{1}H NMR) and 2 (^{13}C NMR).

Synthesis of MeZn(i-Pr_2Ph)N–CH_2–C(Me)=N(i-Pr_2Ph) (1d)

To a stirred solution of 2,6-i-Pr_2Ph-DAB (3.76 g, 10 mmol) in Et_2O (50 ml) was added 1 equiv. of Me_2Zn (10 ml of a 1 M solution in hexane). The red solution was heated at 34 °C for 36 h after which a second equivalent of Me_2Zn was added. The alkylation reaction was completed after an additional heating at 34 °C for 36 h. The solvent was evaporated *in vacuo* affording the alkylated product as an orange oil in quantitative yield.

General procedure for the hydrolyzed products

The alkylated products (**1d–4d**, **5c**, **6d**, **7b**, **8b**, **9** and **10**) were dissolved in Et_2O (50 ml) and 1 equiv. of H_2O was added. After stirring for 1 h the solid material was collected by centrifugation and 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 products in almost quantitative yield as yellow oils (**1d'**, **2d'**, **4d'**, **6d'**, **7d'**, **8b'**, **9'** and **10'**) or yellow solids (**3d'** and **5c'**).

Anal. Calc. for **1d'**, $C_{27}H_{40}N_2$: C, 82.60; H, 10.27; N, 7.13. Found: C, 82.78; H, 10.44; N, 7.26%. *Anal.* Calc. for **3d'**, $C_{30}H_{46}N_2$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.36; H, 11.10; N, 6.23%. *Anal.* Calc. for **4d'**, $C_{30}H_{46}N_2$: C, 82.89; H, 10.67; N, 6.44. Found: C, 80.10; H, 10.51; N, 6.27%. *Anal.* Calc. for **5c'**, $C_{30}H_{46}N_2$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.76; H, 10.80; N, 6.53%.

Relevant NMR data of these products are given in Tables 3 (^{1}H NMR) and 2 (^{13}C NMR).

Reaction of n-Pr_2Zn with 4-MePhDAB

The same experimental procedure as described above for the alkylation reactions of R_2Zn with 2,6-i-Pr_2PhDAB and 2.6-Me_2PhDAB was followed. The hydrolyzed reaction mixture consisted of the N-alkylated (**11b'**, 60%) and the C-alkylated products with (**11d'**, 30%) and without a 1,2-hydrogen shift (**11c'**, 10%).

Characteristic ^{1}H NMR data of the hydrolyzed N- (**11b'**) and C-alkylated (**11c'** and **11d'**) products: **11b'** δ 6.05 (dd, J=5.8 Hz, J=12.5 Hz, 1H, C*H*=CH), 5.46 (br d, J=12.5 Hz, 1H, N*H*), 5.02 (d, J=5.8 Hz, 1H,

TABLE 1. Relevant ^1H NMR data[a] of the alkylated organozinc complexes formed in the reactions of R_2Zn with *N,N'*-di-(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene

R=	ZnR[b]	N=C*R*	N=C*H*	N–CH_2	N–C*H*R	*H*C=C*H*	C*H*$(CH_3)_2$[c,d]
1d, Me	−0.34[e]	1.21[e]		4.32[3]			2.75, 3.79
2d, n-Pr	0.67[g,i]	[i]		4.39[e]			2.79, 3.70
3d, n-Bu	0.55[g,i]	[i]		4.45[e]			2.82, 3.82
4d, s-Bu	n.o.	[i]		4.41[e]			2.83, 3.85
5c, t-Bu	0.93[e]	1.20[e,j]	8.22[f,k]		4.28[f,k]		2.95, 3.10 3.51[o]
6d, Bn	2.12[e]	3.17[e]		4.38[e]			2.76, 3.64
7d, Np	0.71[e,l], 0.73[e,m]	1.02[e,l], 2.13[e,m]		4.68[e]			2.84, 3.69
8b, Ph						5.92[f,n] 4.98[f,n]	2.91, 3.61, 3.88[o]
9, Et[p]	0.55[h]	1.74[q]					2.90, 3.84, 3.96[o]
10, Pr[r]	0.65[g]			4.23[e]			1.95, 2.53[s,e]

[a] ^1H NMR spectra were recorded on a Bruker AC-200 or AC-300 MHz spectrometer. All values are in ppm using TMS as an external standard (0.0 ppm), in C_6D_6 at ambient temperature. [b]Only resonance of protons bonded to α-carbon (ZnC_α). [c]Resonances were observed as multiplets in a 1:1 ratio. [d]For all compounds the signals of the $CH(CH_3)_2$ are doublets between 1.0 and 1.5 ppm. [e]Singlet. [f]Doublet. [g]Triplet. [h]Quartet. [i]Most other resonances of R coincide with those of $CH(CH_3)_2$. [j]N–CH*t-Bu*. [k] $^3J = 1.7$ Hz. [l]CH_2CMe_3. [m]CH_2CMe_3. [n] $^3J = 5.4$ Hz, *Z*-configuration. [o]Resonances were observed as multiplets in a 2:1:1 ratio. [p]Product obtained from the reaction of Et_2Zn with *N,N'*-di-(2,6-di-methylphenyl)-1,4-diaza-2,3-di-methyl-1,3-butadiene. [q]One part of AB pattern of diastereotopic protons of CCH_2CH_3 (other part falls under i-Pr resonances). [r]Product obtained from the reaction of n-Pr_2Zn with *N,N'*-di-(2,6-di-methylphenyl)-1,4-diaza-1,3-butadiene. [s]Resonances of methyl groups.

TABLE 2. Relevant ^{13}C NMR data[a] of the alkylated organozinc products and hydrolyzed products (between brackets) of the reactions of R_2Zn with *N,N'*-di-(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene

Compound	Zn*C*	N=C*R*	N–CH_2	Other
1d (1d')	−15.9	184.8 (167.8)	66.9 (58.2)	18.0 (18.9) (N=C*Me*)
2d (2d')	11.6	187.6 (170.6)	66.0 (65.9)	
3d (3d')	8.5	187.9 (170.7)	64.9 (56.3)	
4d (4d')	17.2	191.9 (173.9)	60.7 (53.3)	
5c (5c')	40.2			182.9 (167.4)[b], 81.2 (71.9)[c], 28.4, 23.5 (27.2)[d]
6d (6d')	17.6	187.1 (168.5)	65.6 (56.7)	
7b (7b')	n.o.	187.1 (169.7)	66.9 (65.9)	46.6 (46.5)[e], 35.6, 30.4 (24.5)[f]
8b (8b')				132.5 (147.4)[g], 99.7 (106.3)[h]
9 (9')[i]	−1.8	191.0 (175.2)[j]		
10'[k]	11.9	187.8	61.2	

[a] ^{13}C NMR spectra were recorded on a Bruker AC-200 or AC-300 MHz spectrometer. All values are in ppm using TMS as an external standard (0.0 ppm), in C_6D_6 at ambient temperature. [b](N=C*H*). [c]N–*C*(H)CMe_3. [d]C*Me*$_3$. [e]N=CCH_2CMe_3. [f]N=CCH_2C*Me*$_3$. [g]Ar(Ph)NCH=CHNAr. [h]Ar(Ph)NCH=C*H*NAr. [i]Product obtained from the reaction of Et_2Zn with *N,N'*-di-(2,6-dimethylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (**b**). [j]N=*C*Me. [k]C-alkylated product obtained from the reaction of n-Pr_2Zn with *N,N'*-di-(2,6-di-methylphenyl)-1,4-diaza-1,3-butadiene (**c**).

CH=C*H*); **11c'** 7.53 (d, $J = 6.2$ Hz, N=C*H*); **11d'** δ 5.26 (br, 1H, N*H*), 4.68 (br d, 2H N–CH_2).

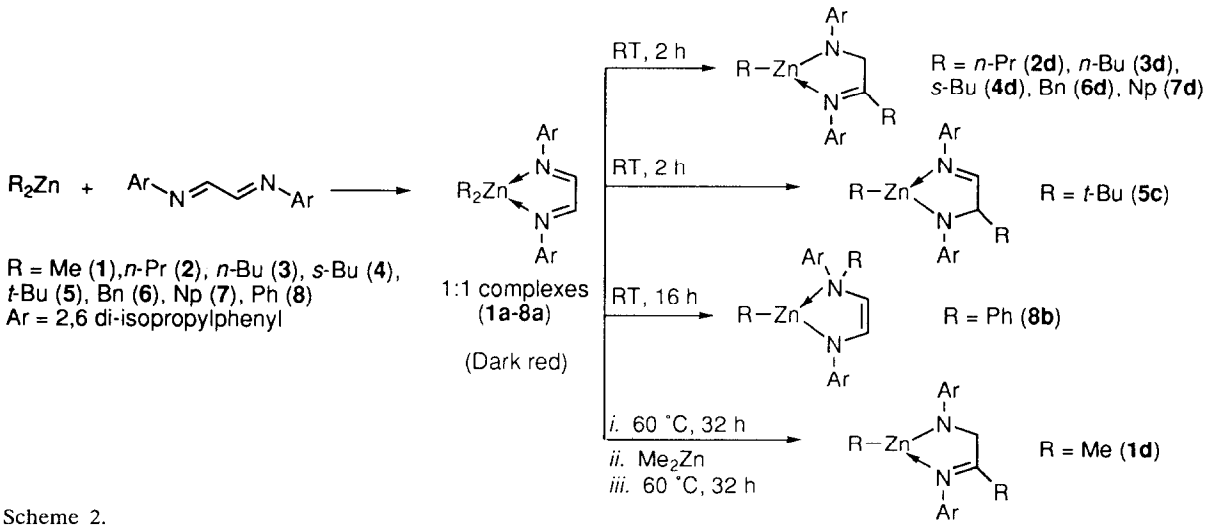
Results

The reactions of *N,N'*-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene (2,6-i-Pr_2Ph-DAB) with the diorganozinc compounds R_2Zn (R = methyl (**1**), n-propyl (**2**), n-butyl (**3**), sec-butyl (**4**), tert-butyl (**5**), benzyl (**6**), neopentyl (**7**) and phenyl (**8**) were performed in diethyl ether or hexane at room temperature and resulted in the immediate, quantitative, formation of the dark red 1:1 coordination complexes **1a–8a** (see Scheme 2). During the next 2 h, the color of the solutions slowly changed from red to yellow except for Me_2Zn(2,6-i-

TABLE 3. Relevant ^{1}H NMR data[a] of the hydrolyzed alkylated products formed in the reactions of R_2Zn with *N,N'*-di-(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene

R=	N=C*R*	N=C*H*	N-CH_2[b]	N-C*H*R	N*H*[b]	*HC=CH*	C*H*$(CH_3)_2$[c,d]
1d', Me	1.21[e]		3.70[f]		5.21[g]		2.84, 3.58
2d', n-Pr	0.48[g], 1.85[i,j]		3.88[f]		5.29[g]		2.90, 3.64
3d', n-Bu	0.60[g], 1.92[i,j]		3.93[f]		5.33[g]		2.92, 3.67
4d', s-Bu	0.55[g,j], 0.72[f], 2.33[i]		3.89[k], 4.02[k]		5.22[e]		2.88, 3.62
5c', t-Bu	1.19[e,l]	7.55[f,m]		4.15[h,m,n]	3.88[f,n]		2.49, 3.47
6d', Bn	3.17[e]		3.78[e]		5.18[e]		2.94, 3.46
7b', Np	0.67[e,o], 1.97[e,p]			3.94[e]	5.34[e]		2.90, 3.62
8b', Ph					4.43[f,q]	5.18[f,r], 5.39[h,q,r]	3.20, 3.38
9', Et[s]	1.55, 1.96[t,i]				5.41[e]		2.91, 3.06, 3.78[u]
10', n-Pr[v]	0.45[g]		3.78[e]		n.o.		2.37, 1.96[w]

[a] ^{1}H NMR spectra were recorded on a Bruker AC-200 or AC-300 spectrometer. All values are in ppm using TMS as an external standard (0.0 ppm) in C_6D_6 at ambient temperature. [b] ^3J = 6.2–6.4 Hz. [c]Resonances were found as multiplets in a 1:1 ratio. [d]For all compounds the signals of the $CH(CH_3)_2$ are doublets between 1.0 and 1.5 ppm. [e]Singlet. [f]Doublet. [g]Triplet. [h]Double doublet. [i]Multiplet. [j]Rest of signals coincides with those of $CH(CH_3)_2$. [k]AB pattern, ^2J = 18.5 Hz. [l]N-CH*t-Bu*. [m] ^3J = 5.9 Hz. [n] ^3J = 11.4 Hz. [o]CH_2CMe_3. [p]CH_2CMe_3. [q] ^3J = 11.1 Hz. [r] ^3J = 6.8 Hz., indicating a *Z*-configuration. [s]Hydrolyzed product from the reaction of Et_2Zn with *N,N'*-di-(2,6-dimethylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene. [t]Diastereotopic CCH_2CH_3 protons. [u]Resonances were found as multiplets in a 1:1:2 ratio. [v]C-alkylated product obtained from the reaction of n-Pr_2Zn with *N,N'*-di-(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene. [w]Resonances of methyl groups.



Scheme 2.

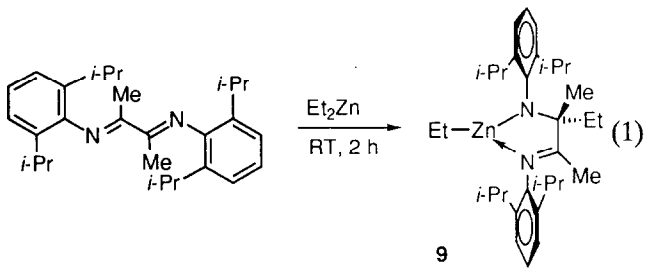
Pr_2Ph-DAB) (**1a**) and Ph_2Zn(2,6-i-Pr_2Ph-DAB) (**8a**), in which cases the red color remained. This color change is indicative of the occurrence of an alkyl group transfer from zinc to the chelate-bonded DAB system [8, 9]. This alkyl group transfer resulted in C-alkylated products for the primary (**2**, **3** and **7**) and secondary alkyl (**4**) and benzyl (**6**) zinc compounds. In these cases, products are also formed that originate from a subsequent hydrogen shift from the alkylated carbon of the DAB skeleton to the neighboring imine C atom, i.e. products **2d–4d**, **6d** and **7d** (see Scheme 2).

The coordination complex Me_2Zn(2,6-i-Pr_2Ph-DAB) (**1a**) formed in the reactions with dimethylzinc, is stable at room temperature. Quantitative conversion of this complex to the C-alkylated product **1d** could only be brought about by boiling it in diethyl ether for at least 72 h, provided that after about 36 h a second equivalent of Me_2Zn was added to the solution. The corresponding

complex with diphenylzinc, **8a**, is less stable and is quantitatively converted into the N-alkylated product **8b** already after 16 h at room temperature. The tertiary dialkylzinc compound t-Bu_2Zn reacted with 2,6-i-Pr_2Ph-DAB to give the C-alkylated product **5c** only, i.e. without a subsequent hydrogen shift. Even prolonged boiling in hexane (16 h at 70 °C) did not cause such a shift.

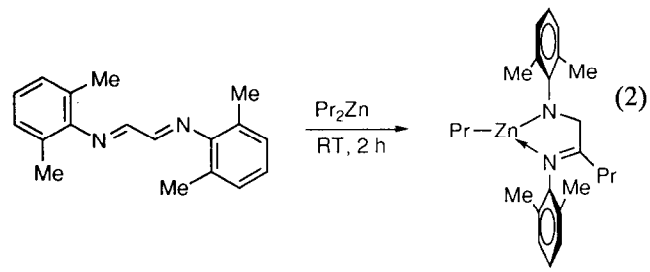
The conversion of the dibutylzinc complex of **3a** into **3d** was followed by means of ^{1}H NMR spectroscopy in benzene. It appeared that **3d** was formed directly and an intermediate C-alkylated species without subsequent H shift, cf. **5c**, was not detected.

In contrast to the other primary dialkylzinc compounds **1–3**, Et_2Zn did not react with 2,6-i-Pr_2Ph-DAB to give a stable alkylated product but instead only decomposition products were formed. However, the reaction of Et_2Zn with the methyl-substituted derivative of 2,6-i-Pr_2Ph-DAB, i.e. (i-Pr_2Ph)N=CMeCMe=N(i-Pr_2Ph) (i-Pr_2Ph-Me_2DAB), resulted in the formation of the C-alkylated product **9** (eqn. (1)).

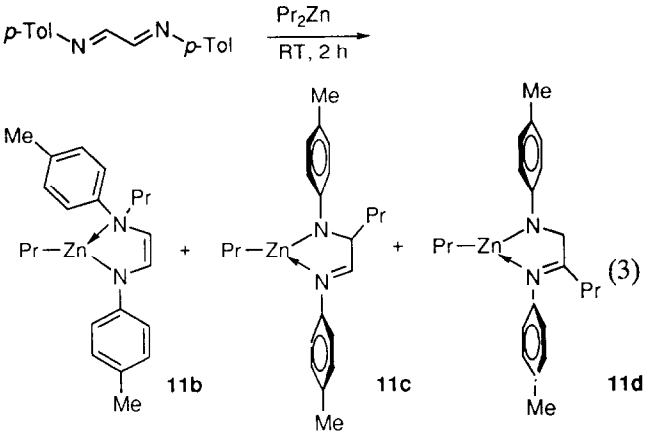


9

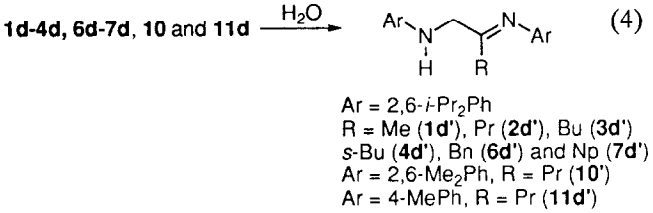
In order to study whether C-alkylation of 2,6-i-Pr_2Ph-DAB by dialkylzinc compounds is the result of steric or electronic effects, we studied the reactions of n-Pr_2Zn with two other aryl substituted R'DAB (R' = 2,6-dimethylphenyl, R' = 4-methylphenyl) ligands which have *ortho* substituents of different sizes. In the case of 2,6-Me_2Ph-DAB, a quantitative formation of the C-alkylated product **10** with hydrogen shift was observed (eqn. (2)), while 4-MePh-DAB gave a mixture of the N-alkylated product **11b** (60%), and two C-alkylated products, one, **11d**, with a subsequent hydrogen shift and a second, **11c**, without such a shift (30 and 10% yield, respectively) (eqn. (3)).



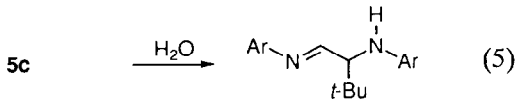
10



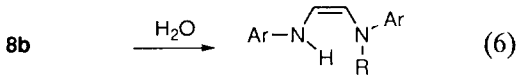
Hydrolysis of the alkylated organozincDAB compounds with H_2O gave the organic alkylated products **1d'–4d'**, **5c'**, **6–7d'**, **8b'**, **9'** and **10'** in excellent yield (eqns. (4)–(7)).



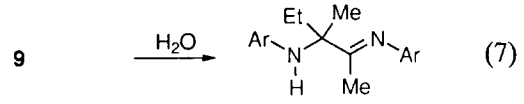
Ar = 2,6-*i*-Pr_2Ph
R = Me (**1d'**), Pr (**2d'**), Bu (**3d'**)
s-Bu (**4d'**), Bn (**6d'**) and Np (**7d'**)
Ar = 2,6-Me_2Ph, R = Pr (**10'**)
Ar = 4-MePh, R = Pr (**11d'**)



5c': R = *t*-Bu, Ar = 2,6-*i*-Pr_2Ph
11c': R = Pr, Ar = 4-MePh



8b': R = Ph, Ar = 2,6-*i*-Pr_2Ph
11b': R = Pr, Ar = 4-MePh



9': Ar = 2,6-*i*-Pr_2Ph

Discussion

Steric effects

Our results show that replacement of N-alkyl by N-aryl substituents in DAB systems has a large influence on the course of group-transfer reactions with diorganozinc reagents. The most outstanding fact is that reactions of i-Pr_2Ph-DAB with dialkylzinc compounds

result in the exclusive formation of C-alkylated products. We believe that this is caused by the steric effects of the bis-*ortho*-substituted 2,6-di-isopropylphenyl substituents on the imine-N atoms. These effects have been described earlier by Vrieze and co-workers [14] for the reactions of N-substituted DAB ligands with $Ru_3(CO)_{12}$. They found that the introduction of *ortho*-methyl substituents (2,6-xylyl or mesityl) in *N*-aryl-DAB, or of methyl substituents in the β or γ positions of *N*-alkyl-DAB, gives rise to a fixed orientation of the aryl rings and alkyl chain perpendicular to the Ru–NCCN chelate plane. Similarly, the bis *ortho*-isopropyl substituted aryl-DAB ligand used in the present study, i.e. *N*,*N'*-bis(2,6-di-isopropylphenyl)-1,4-diaza-1,3-butadiene, can be expected to have its N-aryl groups fixed perpendicularly to the NCCN chelate ring plane. In this way, the reactivity of the i-Pr_2Ph-DAB ligand towards dialkylzinc compounds, as compared with that of the previously studied alkyl-group-substituted DAB ligands, will be changed because alkylation at the N atoms is prevented. In fact, the reaction of n-Pr_2Zn with Me_2Ph-DAB shows that the steric hindrance caused by *ortho*-methyl substituents is already sufficient to direct the group transfer entirely to the neighboring C atom.

Electronic effects

The reaction of n-Pr_2Zn with 4-MePh-DAB which is electronically comparable to i-Pr_2Ph-DAB and Me_2Ph-DAB but lacks the *ortho* substituents in the aryl ring, gave 60% N-alkylation and 40% C-alkylation. This mixture of products indicates that steric effects no longer determine the alkylation of the NCCN skeleton, but that electronic effects are coming into play. Two electronic effects can be recognized which may influence the regioselectivity of the alkyl-group transfer. In the first place, the electron-withdrawing character of the N-aryl substituents will increase the electrophilicity of the N atoms and therefore their susceptibility to alkylation. Secondly, the delocalization of the electron-spin density within the intermediate organozinc radicals, [RZnAr-DAB]$^{\cdot}$ (see Scheme 1), will lower the spin density on the N atom. In the case of i-Pr_2Ph-DAB and Me_2Ph-DAB ligands, spin delocalization into the phenyl rings is unlikely, since the *ortho* substituents of the aryl rings force them in a perpendicular position relative to the Zn–NCCN–chelate ring (*vide supra*).

However, rotation of the aryl ring around the C_{ipso}–N bond in 4-MePh-DAB has a lower rotation barrier and the rotamer in which this ring is coplanar with the Zn–NCCN chelate ring will be more likely. This rotamer allows overlap between the π-aryl MOs and the NCCN LUMO and as a consequence the spin density at the N atoms (the spin density in [RZnt-BuDAB]$^{\cdot}$ radicals is *c.* 60% at the N atoms and 40% at the C atoms) will decrease because of delocalization in the aryl rings and the susceptibility of the N atoms for alkylation will decrease, cf. ESR spectra and computational data in ref. 9. We believe that this electronic effect is responsible for the observed 40% C- and 60% N-alkylation. (In the case of t-BuDAB primary alkyl radicals give rise to quantitative N-alkylation [9]). We recently observed such conjugation in two solid-state structures of two organoaluminum–DAB complexes, i.e. $Me_2Al(ArN–CH_2–C(Me)=NAr)$ (Ar = *p*-tolyl or *p*-methoxyphenyl). In each of these, one of the aryl rings was found to be planar to the five-membered aluminium–NCCN chelate ring [15].

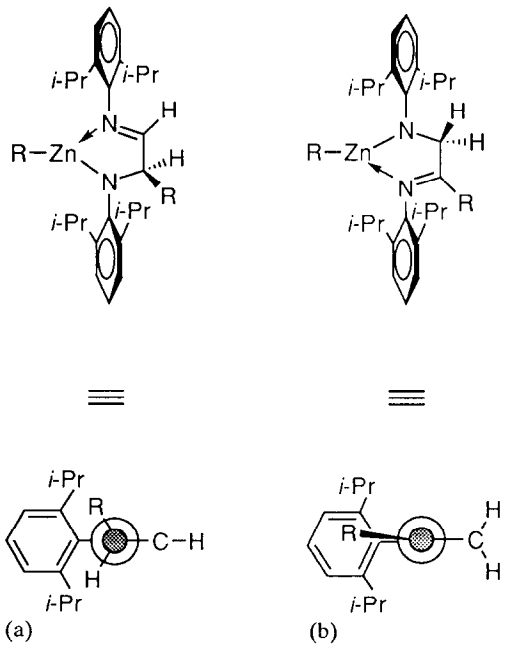
The reaction of t-Bu_2Zn with i-Pr_2Ph-DAB gives the C-alkylated product **5c**, analogous to the reaction of t-Bu_2Zn with t-BuDAB [8]. In the latter case, steric interference between the t-Bu substituents on the N atoms and the bulky alkyl groups already prevent N-alkylation and a further increase of steric strain will have no effect.

The products **1d–4d**, **6d** and **7d** are formally the result of C-alkylation followed by a hydrogen shift. However, the initial C-alkylated products have never been observed, which leaves open the question of the sequence of the steps. Also the hydrogen shifts have never been observed in reactions of R'DAB (R' = alkyl) with dialkylzinc compounds. Products like **1d–4d**, **6d** and **7d**, however, have been commonly isolated from reactions of R'DAB (R' = alkyl or aryl) with R_3Al (R = Me, Ph), and in some cases the initially formed C-alkylated intermediate was detected [16]. It, therefore, seems plausible that the products **1d–4d**, **6d** and **7d** are likewise formed via the initial formation of such intermediates. The subsequent hydrogen shift may be explained in terms of release of steric strain. Within an initially formed C-alkylated intermediate, much steric interference exists between the introduced alkyl group and the *ortho*-aryl substituents (Fig. 1(a)). After a hydrogen shift, the alkyl group is now bonded to a sp^2 carbon, and points in a direction between the *ortho*-aryl substituents, which alleviates steric strain (Fig. 1(b)).

In the case of **5c**, a large tert-butyl group is introduced in the alkylation reaction. A hydrogen shift in this case would result in an increase of steric interference with the aryl substituents in the product, and consequently it does not occur.

In the two alkylated organoaluminum–DAB derivatives mentioned before, i.e. $Me_2Al(ArN–CH_2–C(Me)=NAr)$, (Ar = *p*-tolyl or *p*-methoxyphenyl), the aryl substituents bound to the nitrogen atoms lack large groups in the *ortho* positions but even there the least steric interference occurs within the hydrogen-shift products.

The reaction of Ph_2Zn with i-Pr_2Ph-DAB, resulting in the N-arylated product **8b**, is extraordinary for two



(a) (b)

Fig. 1. Newman projections: (a) view along the C(R)H–N_{amino} bond of a C-alkylation product before a hydrogen shift; (b) view along the CR=N_{imino} bond of a C-alkylation product after a hydrogen shift.

reasons. In the first place, it completely differs from the reaction of Ph_2Zn with t-BuDAB, which gives a thermally stable 1:1 coordination complex Ph_2Znt-BuDAB that does not convert into a subsequent product [8, 9]. Secondly, in all reactions of 2,6-i-Pr_2Ph-DAB with dialkylzinc compounds we only observe C-alkylation. These facts suggest that the reactivity of Ph_2Zn towards 2,6-i-Pr_2Ph-DAB is not determined by steric effects as discussed above, but by electronic effects. It remains unclear why arylation takes place at the nitrogen atom, leading to a highly crowded nitrogen atom.

Conclusions

The alkylation of R'DAB systems by means of R_2Zn can be regioselectively directed (i) by controlling the nature of the dialkylzinc compounds in the case of R' = alkyl, or (ii) by introducing bulky *ortho*-aryl substituents on the nitrogen atoms of the DAB system. In the first case, tertiary, benzylic and some secondary dialkylzinc compounds give C-alkylation in the reaction with R'DAB systems, whereas primary dialkylzinc compounds give N-alkylation. This opens the possibility of introducing primary and secondary alkyl groups selectively at the carbon atom of the DAB as well. In the DAB system, 2,6-i-Pr_2Ph-DAB, phenyl groups may also be introduced at the nitrogen atom via Ph_2Zn. So far, this N-selectivity is not understood.

Acknowledgements

This work was supported in part (E.W.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (NWO).

References

1 G. van Koten and K. Vrieze, *Adv. Organomet. Chem., 21* (1981) 151.
2 K. Vrieze and G. van Koten, *Inorg. Chim. Acta, 100* (1985) 79; B.D. Rossenaar, C.J. Kleverlaan, D.J. Stufkens and A. Oskam, *Chem. Commun.*, (1994) 63.
3 E. Wissing, J. Boersma, H. Kleÿn and G. van Koten, *Recl. Trav. Chim. Pays-Bas, 112* (1993) 618.
4 H.-W. Frühauf and F. Seils, *J. Organomet. Chem., 323* (1987) 67.
5 P.P.M. de Lange, H.-W. Frühauf, M. Kraakman, M. van Wijnkoop, M. Kranenburg, A.H.J.P. Groot, K. Vrieze, J. Fraanje, Y. Wang and M. Numan, *Organometallics, 12* (1993) 417.
6 E. Wissing, R.W.A. Havenith, J. Boersma and G. van Koten, *Tetrahedron Lett., 33* (1992) 7933.
7 H. tom Dieck and E. Haupt, *Chem. Ber., 116* (1983) 1540.
8 G. van Koten, in A. de Meijere and H. tom Dieck (eds.), *Organometallics in Organic Synthesis,* Springer, Heidelberg, 1987, p. 277.
9 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W.J.J. Smeets and A.L. Spek, *J. Am. Chem. Soc., 113* (1991) 5606.
10 H. tom Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch., Teil B, 36* (1981) 823.
11 H. tom Dieck and I.W. Renk, *Chem. Ber., 104* (1971) 92.
12 A.L. Galyer and G. Wilkinson, *Inorg. Synth., XIX* (1979) 253.
13 V. Weissig, R. Beckhaus, U. Banasiak and K.H. Thiele, *Anorg. Allg. Chem., 467* (1980) 61.
14 (a) L.H. Staal, L.H. Polm, K. Vrieze, F. Ploeger and C.H. Stam, *Inorg. Chem., 20* (1981) 3590; (b) H. van der Poel, G. van Koten, K. Vrieze, M. Kokkes and C.H. Stam, *Inorg. Chim. Acta, 39* (1980) 197.
15 J.A. Kanters, G.P.M. van Mier, R.L.L.M. Nijs, F.H. van der Steen and G. van Koten, *Acta Crystallogr., Sect. C, 44* (1988) 1391.
16 J.M. Klerks, D.J. Stufkens, G. van Koten and K. Vrieze, *J. Organomet. Chem., 181* (1979) 271.