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COORDINATION OF 3-SUBSTITUTED 1-AZA-4-OXO-1,3-BUTADIENES (α-IMINOESTERS AND AMIDES) TO ALUMINUM AND ZINC CHLORIDE AND TO DIMETHYLZINC. SELECTIVE REDUCTION IN THE $ZnEt_2-R^1N{=}CHC(NEt_2){=}O$ SYSTEM, AND CRYSTAL STRUCTURE OF $[EtZn(t\text{-}Bu)NCH_2C(NEt_2){=}O]_2$

M. ROBERT P. VAN VLIET, GERARD VAN KOTEN *, JOHAN F. MODDER,
JOHANNUS A.M. VAN BEEK, WIM J. KLAVER

*Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

KEES GOUBITZ and CASPAR H. STAM

*Laboratorium voor Kristallografie, J.H. van 't Hoff Instituut, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

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Summary

Reactions of $ZnCl_2$ and $AlCl_3$ with 3-substituted 1-aza-4-oxo-1,3-butadienes (α-iminoesters and amides) have given the corresponding 1 : 1 complexes $MCl_n[(t\text{-}Bu)N{=}CHC(R^3){=}O]$ (R^3 = OMe, OEt or NEt_2). The α-iminoester and amide ligands in these complexes are chelate-bonded via the imino-N and carbonyl-O atoms, except for the $AlCl_3$-α-iminoamide complex in which the α-iminoamide is monodentate-N coordinated. Stable 1 : 1 coordination complexes, $ZnMe_2[(t\text{-}Bu)N{=}CHC(R^3){=}O]$ (R^3 = OMe, OEt or NEt_2), have also been isolated from the reaction of $ZnMe_2$ with these α-iminoesters and amides. The α-iminoesters are chelate bonded to the zinc centre via the imino-N and the alkoxy-O atoms, whereas the α-imino-amides are bonded via the imino-N and carbonyl-O atoms.

Similar 1 : 1 complexes could not be isolated from the reaction of $ZnEt_2$ with α-iminoamides. Instead, products formed by N-addition as well as by N=C reduction and C–C dimerization reactions were obtained. The occurrence of reduction in these reactions was demonstrated by an X-ray crystal structure determination of $[EtZn(t\text{-}Bu)NCH_2C(NEt_2){=}O]_2$ (**12**). The crystals are monoclinic, with cell dimensions *a* 20.413(2), *b* 8.445(2), *c* 19.177(2) Å and β 115.59(1)°. The final *R*-value was 0.055 for 2222 reflexions. The dimeric molecule consists of a central four-membered Zn_2N_2 ring which links the two halves of the dimer. Coordination of the amide-O

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* Author to whom correspondence should be addressed.

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atom to zinc results in formation of a five-membered $\overline{\mathrm{ZnOCCN}}$ ring and completes the four coordination at zinc.

Comparison of the products formed in the reaction of $ZnEt_2$ with various 1-aza-4-oxo(aza)-1,3-butadienes, i.e. α-iminoketones, α-iminoamides, 1,4-disubstituted 1,4-diaza-1,3-butadienes (R-DAB and pyridylcarbaldehyde imine (R-Pyca)) pointed to a striking mechanistic similarity of these reactions with respect to chelate coordination as the initial step, SET activation, single electron transfer, and inter- and intramolecular transfer of the organo group from zinc to the organic moiety.

Introduction

Organozinc and aluminum compounds undergo interesting reactions with ligands with a conjugated N=C–C=O skeleton, viz. α-imino-ketones, -esters, and -amides [1]. Depending on the nature of the substituents of the N=C–C=O skeleton and the organo groups bound to zinc or aluminum the reaction stops either at the stage of the 1 : 1 or 1 : 2 coordination complexes or proceeds after complex formation by a regioselective conversion of the N=C–C=O skeleton.

Only a few coordination complexes have so far been isolated, of which the 2 : 1 complex $[(AlMe_3)_2\{\sigma,\sigma\text{-N,O-(MeN=C(Ph)C(Ph)=O)}\}]$ is a representative [1]. An important feature of this complex is the non-planar *gauche* conformation of the ligand skeleton of the bridge bonded α-iminoketone molecule. The quantitative conversion of this 2 : 1 complex at higher temperatures into the ketone-C alkylated product, $Me_2\overline{\mathrm{Al(Me)N{=}C(Ph)C(Me,Ph)O}}AlMe_3$, is an example of the type of reaction generally observed for most of the α-iminoketone ligands studied.

Stable coordination complexes of organozinc compounds with α-iminoketones have not previously been made. Reactions of ZnR_2 with α-iminoketones $[R^1N{=}C(R^2)C(R^3){=}O]$ gave directly $[R\overline{\mathrm{Zn(R)(R^1)NC(R^2){=}C(R^3)O}}]_2$ (for R is a primary or secondary, alkyl group) and $[R\overline{\mathrm{Zn(R^1)N{=}C(R^2)C(R^3,R)O}}]_2$ (for R is an aryl, methyl or tertiary alkyl group) [1f,1g].

In order to understand this seemingly complex reaction pattern we have concentrated our research on the study of the initial stages of the interaction of the zinc centre with the 1-aza-4-oxo-1,3-butadiene ligands. In an attempt to reduce the reactivity of the metal reagent we treated α-iminoesters and -amides with $ZnCl_2$ and, for comparison, also with $AlCl_3$. For the α-iminoamide ligands stable 1 : 1 complexes were formed not only with $ZnCl_2$ and $AlCl_3$, but with $ZnMe_2$ also a stable 1 : 1 coordination complex could be isolated and characterized. Finally, the reactions of $ZnEt_2$ with α-iminoamides were studied. In these reactions no formation of coordination complexes was detected. Products arising from reduction of the N=C bond, from transfer of the organo group from zinc to nitrogen or carbon, and from dimerization reactions were found. The reduction of the N=C bond has been confirmed by the isolation and structural characterization of $[Et\overline{\mathrm{Zn(t\text{-}Bu)NCH_2C(NEt_2){=}O}}]_2$ (**12**).

Experimental

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully dried and distilled before use. Commercially available $ZnCl_2 \cdot 6H_2O$ was dehydrated in refluxing $SOCl_2$. The $ZnCl_2$ precipitate was collected by filtration, washed with hexane, then stored under nitrogen. Al_2Cl_6 was freshly sublimed before use. $ZnMe_2$ and $ZnEt_2$ were synthesized and isolated by published methods [1f].

The 1-aza-4-oxo-1,3-butadienes [t-BuN=CHC(R^3)=O]* with R^3 = Me (**L1**), OMe (**L2**), or NEt_2 (**L7**) were prepared by published methods [1c,2]. The new α-iminoesters R^1N=CHCOOEt with R^1 = i-Pr (**L3**), t-Bu (**L4**), 2,6-dimethylPh (**L5**) and α-iminoamides R^1N=CHC(NEt_2)=O with R^1 = i-Pr (**L6**) and 2,4-dimethyl-3-pentyl (**L8**) were synthesized from ethyl glyoxylate and the corresponding amines by the procedures previously described for **L2** and **L7** [1c]. Yield (%) and b.p. (°C/0.01 mmHg) for **L3**, **L4**, **L5**, **L6**, and **L8**, respectively: 61 (135), 85 (117), 35 (186), 58 (112), and 60 (124).

IR (Nujol, NaCl, cm^{-1}). (**L3**) ν(COOEt) 1749vs, ν(C=N) 1646s, (**L4**) ν(COOEt) 1760vs, ν(C=N) 1648m, (**L6**) ν($CONEt_2$) 1627vs, ν(C=N) 1655s, (**L8**) ν($CONEt_2$) 1627vs, ν(C=N) 1655m.

^1H NMR (in $CDCl_3$, RT, TMS internal, δ ppm). **L3**: 1.32 (d, 6H, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 3.68 (sept, 1H, $\mathrm{(CH_3)_2C}\mathit{H}$), 1.39 (t, 3H, $\mathrm{OCH_2C}\mathit{H}_3$), 4.36 (q, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 7.70 (s, 1H, N=CH); **L4**: 1.21 (s, 9H, $\mathrm{(CH_3)_3}$), 1.22 (t, 3H, $\mathrm{OCH_2C}\mathit{H}_3$), 4.23 (q, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 7.68 (s, 1H, N=CH); **L5**: 1.24 (t, 3H, $\mathrm{OCH_2C}\mathit{H}_3$), 4.26 (q, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 2.18 (s, 6H, $\mathrm{(C}\mathit{H}_3\mathrm{)_2C_6H_3}$), 7.07 (m, 3H, $\mathrm{C_6H_3}$), 7.53 (s, 1H, N=CH); **L6**: 1.20 (d, 6H, $\mathrm{(C}\mathit{H}_3\mathrm{)_2CH}$), 3.45 (m, 1H, $\mathrm{(CH_3)_2C}\mathit{H}$), 1.11/1.22 (t, 6H, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$), 3.41/3.51 (q, 4H, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 7.75 (s, 1H, N=CH); **L8**: 0.95 (d, 12H, $\mathrm{[HC(C}\mathit{H}_3\mathrm{)_2]_2}$), 2.06 (m, 2H, $[\mathit{H}\mathrm{C(CH_3)_2]_2}$), 2.34 (d/d, 1H, NCH), 0.95/1.19 (t, 6H, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$), 3.42/3.59 (q, 4H, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 7.70 (s, 1H, N=CH).

^{13}C NMR (in $CDCl_3$, RT, TMS internal, δ ppm). **L3**: 23.1 (q, $\mathrm{HC(CH_3)_2}$), 61.2 (d, $\mathrm{H}\mathit{C}\mathrm{(CH_3)_2}$), 13.8 (q, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 61.3 (t, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 150.8 (d, N=C), 163.0 (s, C=O); **L4**: 29.8 (q, $\mathrm{(CH_3)_3}$), 61.7 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 15.0 (q, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 65.7 (t, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 149.3 (d, N=C), 164.7 (s, C=O); **L6**: 24.5 (q, $\mathrm{HC(}\mathit{C}\mathrm{H_3)_3}$), 62.5 (d, $\mathrm{H}\mathit{C}\mathrm{(CH_3)_3}$), 13.7/15.5 (q, $\mathrm{N(CH_2}\mathit{C}\mathrm{H_3)_2}$), 41.5/43.2 (t, $\mathrm{N(}\mathit{C}\mathrm{H_2CH_3)_2}$), 155.3 (d, N=C), 165.8 (s, C=O); **L8**: 19.0/21.1 (q, $\mathrm{HC(}\mathit{C}\mathrm{H_3)_2}$), 30.3 (d, $\mathrm{H}\mathit{C}\mathrm{(CH_3)_2}$), 84.6 (d, NCH), 13.7/15.6 (q, $\mathrm{N(CH_2}\mathit{C}\mathrm{H_3)_2}$), 41.5/42.9 (t, $\mathrm{N(}\mathit{C}\mathrm{H_2CH_3)_2}$, 157.6 (d, N=C), 165.3 (s, C=O).

*Synthesis of MCl_n[t-BuN=CHC(R^3)=O] (M = Zn, n = 2, R^3 = Me (**1**), R^3 = OMe (**2**), R^3 = NEt_2 (**3**); M = Al, n = 3, R^3 = OMe (**4**), R^3 = NEt_2 (**5**))*

The synthesis of $ZnCl_2$(t-BuN=CHCOOMe) (**2**) is described as a typical example.

A solution of 1.0 g of α-(t-butyl)iminomethyl ester (7 mmol) in diethyl ether (10 ml) was slowly added to a stirred suspension of 0.95 g of zinc dichloride (7 mmol) in diethyl ether (30 ml) at room temperature. The mixture was stirred for 30 min and the diethyl ether distilled off in vacuo. The residue was dissolved in dichloromethane (100 ml) and the solution filtered. The new product **2** separated from the filtrate, at −20°C, as small white crystals. Yield 1.75 g (90%). Compound **1** was obtained by filtration of the crude reaction mixture and crystallization of the product from the filtrate. The elemental analytical data for **1**–**5** are; **1**, found: C, 32.22; H, 5.34; N, 5.04, O, 6.68. $C_7H_{13}Cl_2NOZn$ calc: C, 31.91; H, 4.97; N, 5.32;

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* R^1N=C(R^2)C(R^3)=O is used as a general abbreviation for the 1-aza-4-oxo-1,3-butadienes used in this study.

O, 6.07%. **2**, found: C, 30.09; H, 5.11; N, 5.31. $C_7H_{13}Cl_2NO_2Zn$ calc: C, 30.40; H, 4.74; N, 5.07%. **3**, found: C, 37.44; H, 6.67; N, 8.32. $C_{10}H_{20}Cl_2N_2OZn$ calc: C, 37.81; H, 6.35; N, 8.82%. **4**, found: C, 37.27; H, 6.63; N, 8.71; O, 5.25. $C_7H_{13}AlCl_3NO_2$ calc: C, 37.47; H, 6.29; N, 8.74; O, 4.99%. **5**, found: C, 38.10; H, 6.41. $C_{10}H_{20}AlCl_3N_2O$ calc: C, 37.81; H, 6.35%.

*Syntheses of $ZnMe_2(R^1N{=}CHC(R^3){=}O)$ (R^3 = OEt and R^1 = i-Pr (**6**), t-Bu (**7**), 2,6-dimethylPh (**8**) and R^3 = NEt_2 and R^1 = i-Pr (**9**), t-Bu (**10**), 2,4-dimethyl-3-pentyl (**11**))*

The synthesis of $ZnMe_2$(t-BuN=CHCOOEt) (**7**) is described as an example of the general procedure. A hexane solution of dimethylzinc (20 mmol, 1 *M* solution) was slowly added to a stirred solution of α-(t-butyl)iminoethyl ester (19 mmol) in 100 ml of hexane at −60 °C, which resulted in the immediate precipitation of a light yellow solid. The mixture was stirred for 30 min then warmed to 10 °C during 1 h, to give an almost clear yellow solution. This was filtered and concentrated to 50 ml, at 0 °C. At −30 °C the new complex crystallized out as yellow needles; m.p. about 10 °C. Yield 2.8 g (58% calculated on the starting amount of the α-iminoester). The elemental analytical data for **6**, **7**, **9** and **11** are; **6**, found: C, 45.31; H, 7.91. $C_9H_{19}NO_2Zn$ calc: C, 45.30; H, 8.03%. **7**, found: C, 46.85; H, 8.11. $C_{10}H_{21}NO_2Zn$ calc: C, 47.53, H, 8.38%. **9**, found: C, 49.89; H, 8.93. $C_{11}H_{24}N_2OZn$ calc: C, 49.72; H, 9.03%. **11**, found: C, 55.76; H, 9.98. $C_{15}H_{32}N_2OZn$ calc: C, 55.98; H, 10.02%.

Synthesis of dimeric α-(amino)methylamido (ethyl)zinc (12 and 13)

$[EtZn(R^1)NCH_2C(NEt_2){=}O]_2$ (R^1 = t-Bu (**12**), 2,4-dimethyl-3-pentyl (**13**)). Addition of a solution of $ZnEt_2$ in hexane (10 ml, 1 *M*) to a solution of an equimolar amount of the α-iminoamide in hexane (100 ml) at −60 °C, produced complexes **12** and **13**, respectively. The solution was stirred for 1 h then warmed to room temperature and concentrated to 50 ml. The new complexes crystallized from the cooled (4 °C) solution as white needles, which are stable at room temperature. Yields 20 and 28% for **12** and **13**, respectively. The elemental analytical data for **12** and **13** are; **12**, found: C, 51.40; H, 8.97. $C_{12}H_{26}N_2OZn$ calc: C, 51.54; H, 9.37%. **13**, found: C, 55.23; H, 9.44. $C_{15}H_{32}N_2OZn$ calc: C, 56.00; H, 9.96%.

Physical measurements

The ^1H NMR spectra were recorded on Bruker WM 250, Varian T 60, Varian A 60 and Varian XL 100 NMR spectrometers and ^{13}C NMR spectra on Bruker WM 250 and WP 80 and Varian CFT 20 NMR spectrometers. Off-resonance ^{13}C NMR spectra were recorded for all compounds to aid assignment of the resonance patterns. IR spectra were obtained with a Perkin–Elmer 283 spectrophotometer and FT-IR spectra were recorded on a Nicolet 7199B FT-IR interferometer. The IR, ^1H and ^{13}C NMR spectroscopic data are summarized in Tables 1–5. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO Zeist, The Netherlands.

X-Ray data collection, structure determination and refinement for $EtZn(t\text{-}Bu)NCH_2C(NEt_2){=}O$ dimer (12)

Crystals of the title compound ($Zn_2C_{24}H_{52}N_4O_2$; M_n = 559.62) are monoclinic, space group $P2_1/c$ with 4 molecules in a unit cell of dimensions: *a* 20.413(2), *b*

8.445(2), c 19.177(2) Å and β 115.59(1)°, $Z = 4$, V 2981.55 Å^3, D_{calc} 1.24 g cm^{-3}. 2222 Reflections with intensities above the 2.5$\sigma(I)$ level were measured on a Nonius CAD4 diffractometer using graphite monochromatised Cu-K_α radiation (μ 21.77

TABLE 1

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE NON-HYDROGEN ATOMS WITH STANDARD DEVIATION IN PARENTHESES, FOR $[\mathrm{Et}\overline{\mathrm{Zn(t\text{-}Bu)NCH_2C(NEt_2)=O}}]_2$ (**12a**)

Zn(1)-Zn(2)	2.864(6)	N(4)-C(14)	1.355(8)
Zn(1)-O(1)	2.118(5)	N(4)-C(9)	1.491(11)
Zn(1)-N(1)	2.069(4)	N(4)-C(21)	1.498(10)
Zn(1)-N(3)	2.086(9)	C(1)-C(2)	1.523(7)
Zn(1)-C(11)	1.991(7)	C(3)-C(4)	1.513(8)
Zn(2)-O(2)	2.123(4)	C(3)-C(5)	1.535(8)
Zn(2)-N(1)	2.090(8)	C(3)-C(6)	1.507(10)
Zn(2)-N(3)	2.093(4)	C(7)-C(8)	1.508(11)
Zn(2)-C(23)	1.978(10)	C(9)-C(10)	1.493(15)
O(1)-C(2)	1.242(6)	C(11)-C(12)	1.524(11)
O(2)-C(14)	1.239(7)	C(13)-C(14)	1.497(8)
N(1)-C(1)	1.487(7)	C(15)-C(16)	1.524(13)
N(1)-C(3)	1.506(6)	C(15)-C(17)	1.534(8)
N(2)-C(2)	1.346(8)	C(15)-C(18)	1.549(8)
N(2)-C(7)	1.462(7)	C(19)-C(20)	1.317(22)
N(2)-C(9)	1.477(8)	C(21)-C(22)	1.423(19)
N(3)-C(13)	1.469(7)	C(23)-C(24)	1.486(14)
N(3)-C(15)	1.486(8)		
O(1)-Zn(1)-N(1)	82.04(25)	C(14)-N(4)-C(19)	119.4(7)
O(1)-Zn(1)-N(3)	98.4(4)	C(14)-N(4)-C(21)	123.6(7)
O(1)-Zn(1)-C(11)	110.5(3)	C(17)-N(4)-C(21)	116.4(9)
N(1)-Zn(1)-N(3)	93.4(3)	N(1)-C(1)-C(2)	112.1(6)
N(1)-Zn(1)-C(11)	131.4(3)	O(1)-C(2)-N(2)	120.8(6)
N(3)-Zn(1)-C(11)	128.2(4)	O(1)-C(2)-C(1)	121.5(5)
O(2)-Zn(2)-N(1)	97.8(4)	N(2)-C(2)-C(1)	117.8(6)
O(2)-Zn(2)-N(3)	81.42(24)	N(1)-C(3)-C(4)	107.2(5)
O(2)-Zn(2)-C(23)	114.7(4)	N(1)-C(3)-C(5)	111.6(5)
N(1)-Zn(2)-N(3)	92.6(4)	N(1)-C(3)-C(6)	112.9(6)
N(1)-Zn(2)-C(23)	126.6(5)	C(4)-C(3)-C(5)	107.2(6)
N(3)-Zn(2)-C(23)	131.7(3)	C(4)-C(3)-C(6)	108.1(7)
Zn(1)-O(1)-C(2)	112.7(4)	C(5)-C(3)-C(6)	109.6(7)
Zn(2)-O(2)-C(14)	112.7(4)	N(2)-C(7)-C(8)	115.4(7)
Zn(1)-N(1)-Zn(2)	87.0(4)	N(2)-C(9)-C(10)	111.6(8)
Zn(1)-N(1)-Cl	110.2(4)	Zn(1)-C(11)-C(12)	114.0(6)
Zn(1)-N(1)-C(3)	117.2(3)	N(3)-C(13)-C(14)	112.8(5)
Zn(2)-N(1)-Cl	113.4(6)	O(2)-C(14)-N(4)	119.8(6)
Zn(2)-N(1)-C(3)	117.6(5)	O(2)-C(14)-C(13)	122.3(6)
C(1)-N(1)-C(3)	109.8(5)	N(4)-C(14)-C(13)	117.8(6)
C(2)-N(2)-C(7)	125.1(6)	N(3)-C(15)-C(16)	113.3(8)
C(2)-N(2)-C(9)	118.4(6)	N(3)-C(15)-C(17)	111.7(7)
C(7)-N(2)-C(9)	116.3(6)	N(3)-C(15)-C(18)	106.5(6)
Zn(1)-N(3)-Zn(2)	86.5(4)	C(16)-C(15)-C(17)	110.3(8)
Zn(1)-N(3)-C(13)	109.5(6)	C(16)-C(15)-C(18)	107.3(8)
Zn(1)-N(3)-C(15)	118.2(6)	C(17)-C(15)-C(18)	107.4(6)
Zn(2)-N(3)-C(13)	110.0(4)	N(4)-C(19)-C(20)	109.1(14)
Zn(2)-N(3)-C(15)	120.3(4)	N(4)-C(21)-C(22)	114.8(11)
C(13)-N(3)-C(15)	110.1(6)	Zn(2)-C(23)-C(24)	117.9(8)

TABLE 2

ATOMIC COORDINATES FOR **12a**

Atom	*x*	*y*	*z*
Zn(1)	0.68137(4)	0.2479(1)	0.25952(5)
Zn(2)	0.78852(5)	0.4528(1)	0.24911(5)
O(1)	0.6827(2)	0.3629(5)	0.3582(2)
O(2)	0.8314(3)	0.5176(6)	0.3674(3)
N(1)	0.6787(3)	0.4793(6)	0.2227(3)
N(2)	0.6604(3)	0.5955(7)	0.4011(3)
N(3)	0.7930(3)	0.2271(6)	0.2963(3)
N(4)	0.8645(5)	0.4242(9)	0.4874(4)
C(1)	0.6652(4)	0.590(1)	0.2754(4)
C(2)	0.6703(3)	0.507(1)	0.3481(3)
C(3)	0.6275(4)	0.516(1)	0.1402(4)
C(4)	0.6469(4)	0.407(1)	0.0895(4)
C(5)	0.6370(4)	0.687(1)	0.1183(4)
C(6)	0.5491(4)	0.488(1)	0.1229(4)
C(7)	0.6421(4)	0.764(1)	0.3931(4)
C(8)	0.7044(5)	0.875(1)	0.4360(5)
C(9)	0.6615(5)	0.515(1)	0.4700(4)
C(10	0.5876(6)	0.461(1)	0.4571(6)
C(11)	0.6068(4)	0.077(1)	0.2240(4)
C(12)	0.5474(4)	0.098(1)	0.2512(5)
C(13)	0.8299(4)	0.235(1)	0.3810(4)
C(14)	0.8426(4)	0.402(1)	0.4107(4)
C(15)	0.8205(4)	0.090(1)	0.2683(4)
C(16)	0.8987(4)	0.110(1)	0.2802(6)
C(17)	0.8118(5)	−0.066(1)	0.3043(5)
C(18)	0.7727(4)	0.079(1)	0.1802(4)
C(19)	0.8695(7)	0.588(2)	0.5179(6)
C(20)	0.9374(10)	0.637(3)	0.5454(15)
C(21)	0.8743(7)	0.292(1)	0.5432(5)
C(22)	0.9421(9)	0.212(2)	0.5698(8)
C(23)	0.8399(5)	0.545(1)	0.1920(5)
C(24)	0.9177(6)	0.587(1)	0.2364(7)

cm^{-1}). The Zn atoms were determined by means of direct methods using the symbolic addition program set SIMPEL [3]. The C, N and O atoms were found in a ΔF-synthesis during isotropic block-diagonal least-squares refinement. The H atoms were calculated and kept fixed at their calculated positions during anisotropic refinement of the other atoms. An empirical absorption correction was applied (DIFABS) [4]. The final R-value was 0.055. A weighting scheme was applied and the anomalous scattering of Zn taken into account, $w = 1/[7.92 + F_{obs} + 0.0097F_{obs}^2]$ [5].

The bond distances, bond angles for $[\mathrm{EtZ}\overline{\mathrm{n(t\text{-}Bu)NCH_2C(NEt_2)\!=\!O}}]_2$ (**12**) are listed in Table 1, and the atomic coordinates in Table 2. Lists of thermal parameters and structure factors are available from the authors.

Results and discussion

For a better understanding of the complex reaction pattern observed for the ZnR_2-$R^1N{=}C(R^2)C(R^3){=}O$ (R^3 = OR or NR_2) system information on the initial complex formation of α-imino-ester and -amide ligands with organozinc species is required. This study appeared to be difficult because of fast subsequent reactions that generally occur after initial complexation. Therefore we also examined the coordination modes of these ligands on less reactive metal centres, viz. $ZnCl_2$, $AlCl_3$, and $ZnMe_2$. The coordination complexes of the dimethylzinc compound are much less reactive than the complexes of higher dialkylzinc homologues. For example, the Me_2Zn(α-iminoamide) complex is stable in toluene solution up to 110°C, and it is only after reflux for several hours that it decomposes to give a range of unidentified organic products.

The question which arises with respect to the coordination mode of the $R^1N{=}CR^2C(R^3){=}O$ molecules in these initial complexes is whether they are monodentate bonded, through the nitrogen or oxygen donor atoms, or are bidentate bonded.

The metal chloride complexes $MCl_n(t\text{-}BuN{=}CHC(R^3){=}O)$ (1–5)

These complexes with M, n and R^3 as indicated in eq. 1 have been obtained in almost quantitative yields from the reactions of $t\text{-}BuN{=}CHC(R^3){=}O$ with the corresponding metal chlorides in a 1/1 molar ratio. They are yellow crystalline solids which are soluble in dichloromethane, slightly soluble in diethyl ether, and insoluble in hexane and benzene. Elemental analytical data pointed to a 1 : 1 MCl_n-$t\text{-}BuN{=}CHC(R^3){=}O$ stoichiometry. It must be noted that attempts to synthesize the 2/1 or 1/2 metal/ligand complexes were unsuccessful.

The new zinc and aluminum complexes **1**–**5** are very air- and moisture-sensitive, and this, for example, hampered a detailed study of compound **1** by spectroscopic techniques. The compounds are hydrolysed easily to give polymeric organic products.

$$MCl_n + t\text{-}BuN{=}CHC(R^3){=}O \rightarrow MCl_n(t\text{-}BuN{=}CHC(R^3){=}O) \qquad (1)$$

$$\big(M = Zn,\ n = 2;\ R^3 = Me\ (\mathbf{1}),\ OMe\ (\mathbf{2}),\ NEt_2\ (\mathbf{3});$$

$$M = Al,\ n = 3;\ R^3 = OMe\ (\mathbf{4}),\ NEt_2\ (\mathbf{5})\big)$$

IR data for **2**–**5** are given in Table 3. The observation of characteristic functional group absorptions (imine, ester and amide) established the presence of an unchanged ligand skeleton in these complexes. The imine stretching frequency, ν(C=N),

TABLE 3

INFRARED DATA[a] $MCl_n(t\text{-}BuN{=}CHC(R^3){=}O)$ (**2**–**5**) AND FOR $ZnMe_2(t\text{-}BuN{=}CHCOOEt)$ (**7**)

Compound		ν(C=N)	Δν[b]	ν(C=O)	Δν[b]
$ZnCl_2$(t-BuN=CHCOOMe)	(**2**)	1645m	−7	1698vs	−57
$ZnCl_2$(t-BuN=CHC(NEt_2)=O)	(**3**)	1650s	−10	1611vs	−19
$AlCl_3$(t-BuN=CHCOOMe)	(**4**)	1640m	−12	1650s	−105
Al_3Cl(t-BuN=CHC(NEt_2)=O)	(**5**)	1650m	−10	1628s	−2
$ZnMe_2$(t-BuN=CHCOOEt)	(**7**)[c]	1638m	−10	1772s	+12

[a] Recorded as KBr pellets, ν in cm^{-1}; vs = very strong, s = strong, m = medium relative to the most intensive peak. [b] Shift compared with the free ligands (Δν = ν(complex) − ν(free)). The ν(C=N) and ν(C=O) data for the free ligands are; t-BuN=CHCOOMe (**L2**) 1652 and 1755 cm^{-1}, t-BuN=CHOOEt (**L4**) 1648 and 1760 cm^{-1}, and t-BuN=CHC(NEt_2)=O (**L7**) 1660 and 1630 cm^{-1}. [c] Solution in hexane, *T* −20°C.

TABLE 4

^{1}H AND ^{13}C NMR DATA FOR MCl_n(t-BuN=CHC(R^3)=O) (**2–5**)

Compound		R^3				δ(t-Bu)	δ(N=CH), Δδ [b]
		δ(CH_3)	Δδ [b]	δ(CH_2)	Δδ [b]		
$ZnCl_2$(t-BuN=CHCOOMe)	(**2**)	4.19s	+0.31			1.51s	7.85s, +0.17
$ZnCl_2$(t-BuN=CHC(NEt_2)=O)	(**3**)	1.30/1.38t		3.69q	+0.24	1.54s	8.19s, +0.47
$AlCl_3$(t-BuN=CHCOOMe)	(**4**)	4.37s	+0.49			1.73s	8.03s, +0.35
$AlCl_3$(t-BuN=CHC(NEt_2)=O)	(**5**)	1.19/1.27t		3.46/3.56q	+0.05	1.45s	8.32s, +0.58

[a] In $CDCl_3$. All values are in ppm relative to external TMS: s = singlet, t = triplet, q = quartet. [b] Compared with the δ(OCH_3) and δ(NCH_2) in the corresponding free ligands (Δδ = δ(complex) − δ(free)).

is shifted on complexation to $ZnCl_2$ or $AlCl_3$ towards lower values by about the same amount, viz. 7–12 cm^{-1}. The extent of this frequency decrease is comparable to that observed for the t-BuN=CHC(Me)=O ligand in *trans*-[$PtCl_2(PEt_3)${σ-N-(t-BuN=CHC(Me)=O)}], Δν * −13 cm^{-1} [1c], and for t-Bu-DAB in, for example, [$PtCl_2(PBu_3)]_2$(t-Bu-DAB), Δν 13 cm^{-1} [6]. In the latter compound coordination of the imino-N atom has been established unambiguously. Consequently, it can be concluded that in the coordination of the α-imino-esters and -amides also, at least the imino-N atom takes part. This conclusion is confirmed by the downfield shift of both the imine and t-butyl protons (see Table 4) on coordination of the ligands to the zinc and aluminum chlorides.

Further coordination may then involve either the carbonyl- or alkoxy-O atom in the case of **2** and **4**, while in **3** and **5** either the carbonyl-O atom or the amide-N atom can be the second donor atom bound to the metal centre. It is therefore of interest to observe that the change of the ν(C=O) value seems to be very dependent on the type of metal halide involved as well as on the nature of the donor atom set available (ester versus amide).

Coordination of t-BuN=CHC(NEt_2)=O to either zinc (in **3**) or aluminum chloride (in **5**) shifts the ν(C=O) only slightly (−19 and −2 cm^{-1}, respectively). However, a significantly larger decrease in this carbonyl stretching frequency was observed for the complexes of t-BuN=CHCOOMe (**2**, −57 and **4**, −105 cm^{-1}, respectively). On the basis of the latter observations, the coordination modes for the 1-aza-4-oxo-1,3-butadiene ligands depicted in Fig. 1 are proposed [7].

The α-iminoester in compounds **2** and **4** is chelate-bonded via the imino-N and carbonyl-O atom. It must be noted that the molecular weights of **2–5** in solution could not be measured due to their low solubility and their extreme sensitivity towards moisture, and so the coordination geometry of the metal centres in these compounds is not known in detail. In the case of **2** the zinc atom is at least four-coordinate when the compound is a monomer, but higher coordination numbers up to six are possible when it forms a higher aggregate, for example via intermolecular Cl–Zn–Cl bridges [8]. The Al centre in compound **4** will be five-coordinate as a result of the chelate bonding of the α-iminoester. Five-coordination at aluminum is commonly encountered, particularly in aluminum trichloride-bidentate ligand complexes [9].

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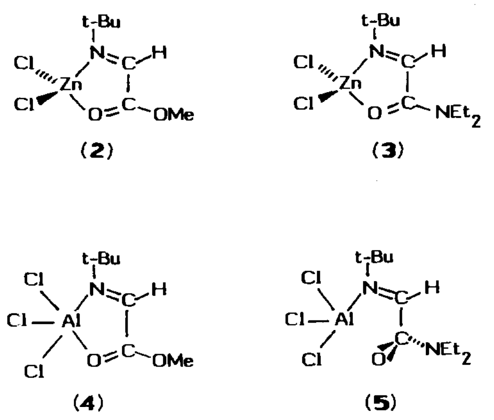
* Δ = ν(complex) − ν(free ligand).



(2) (3) (4) (5)

Fig. 1. Proposed structures for the $ZnCl_2$ and $AlCl_3$ coordinated α-iminoester and α-iminoamides; **2**, **3**, and **4**, 4e, σ-N, σ-O, chelating; **5**, 2e, σ-N monodentate. The metals may have a higher coordination number than indicated, see text.

Bidentate N,O-coordination of the α-iminoamide, t-BuN=CHC(NEt_2)=O, to zinc is similarly proposed for complex **3** (see Fig. 1). In particular the downfield shifts of the imine and t-butyl protons (see Table 4) similar to those observed for **2** and **4** supports the proposed bonding mode. Furthermore, the ν(C=O) is significantly lowered, by 19 cm^{-1}, which can be taken as a clear indication for involvement of the carbonyl-O atom of the amido group in the coordination to zinc [10]. It should be noted that the alternative coordination mode of the group, i.e. through the amido-N atom, is not very likely since the carbonyl-O atom is the stronger donor [11,12].

In contrast to the chelate bonding of t-BuN=CHC(NEt_2)=O to zinc dichloride, there is probably monodentate N-bonding of this ligand to $AlCl_3$ in compound **5**. Indications for this coordination mode are provided by the almost unchanged ν(C=O) frequency for the complex (see Table 3), and furthermore the shift of the NCH_2CH_3 protons of the amide group is very small ($\Delta\delta$ 0.05 ppm) compared with those in the other compounds ($\Delta\delta$ 0.24–0.49 ppm) (see Table 4). We have shown that the ligand skeleton of 1-aza-4-oxo-1,3-butadienes in monodentate-N (cf. *trans*-[$PtCl_2(PEt_3)$\{σ-N-(t-BuN=CHC(Me)=O)\}] or bidentate bridge bonding (cf. [$(AlMe_3)_2$ \{σ,σ′-N,O-(MeN=C(Ph)C(Ph)=O)\}]) has a non-planar *gauche* conformation with an N=C/C=O torsion angle of about 90° [1c,d]. Consequently, the monodentate imino-N coordination of the α-iminoamide in **5**, in which the carbonyl-O atom is in the neighbourhood of the Al centre, is very close to the chelate bonding mode found in the other compounds **2**–**4**. It must be noted, however, that this conformational preference of 3-functionally substituted 1-aza-4-oxo-1,3-butadienes is the result of a balance between the conformation with minimal steric interaction between the skeleton substituents (non-planar *gauche*) and the conformation with maximum resonance stabilization by orbital overlap between the N=C and C=O chromophores (planar *syn* or *anti*) [13]. It was demonstrated that in the case of α-iminoketones the influence of steric factors is predominant, as is reflected by the observed non-planar *gauche* conformation of the ligands both as free molecules and in the complexes [1c,d]. For the α-iminoesters the resonance stabilization effect is probably much more important. Crystal structure determinations on α-iminoesters and α-iminoamides have shown that the imino and ester or amide groupings in such species are nearly coplanar [14] and also in coordination complexes, viz. $Fe_2(CO)_6(R^1N{=}C(R^2)COOR^3)$, these ligands seems to prefer an almost planar N=C–C=O skeleton [15]. Our proposed structures involving chelate-bonded ligands for **2–4** are in keeping with these observations.

The dimethylzinc complexes $ZnMe_2(R^1N{=}CHC(R^3){=}O)$ *(6–11)*

The 1 : 1 coordination complexes with dimethylzinc appear to be fairly stable, in contrast with the instability of the precursor complexes formed in reactions of higher dialkylzinc reagents with α-iminoester and α-iminoamide ligands. The compounds $ZnMe_2(R^1N{=}CHC(R^3){=}O)$ (**6–11**) with R^1 and R^3 as indicated in eq. 2, have been obtained as yellow, low melting, crystalline solids from the reaction of $ZnMe_2$ with the respective α-imino substrates in 1/1 molar ratio in hexane. The ^1H NMR data show complexes **6–11** to have 1/1 $ZnMe_2$/ligand stoichiometry. The complexes, which have good solubility in hydrocarbon solvents, are very air- and moisture-sensitive, and consequently had to be prepared immediately before each measurement.

$$ZnMe_2 + R^1N{=}CHC(R^3){=}O \rightarrow ZnMe_2(R^1N{=}CHC(R^3){=}O) \qquad (2)$$

(R^1 = i-Pr (**6**), t-Bu (**7**), 2,6-dimethylPh (**8**) and R^3 = OEt;

R^1 = i-Pr (**9**), t-Bu (**10**), 2,4-dimethyl-3-pentyl (**11**) and R^3 = NEt_2)

The combined ^1H and ^{13}C NMR data are summarized in Table 5 and the IR data of **7** in Table 3. The NMR spectra for the zinc compounds **6–11** confirmed the 1/1 $ZnMe_2$/ligand stoichiometry in the products **6–11**. The ^{13}C NMR spectra show two different low field carbon atom resonances at ca. 150 ppm (N=*C*) and ca. 165 ppm

TABLE 5

^1H AND ^{13}C NMR DATA [a] FOR $ZnMe_2(R^1N{=}CHC(R^3){=}O)$ (**6–11**)

Compound	δ(Me-Zn)	R^1	δ(R^1)	δ(N=CH)	R^3	δ(R^3)	
^1H NMR							
6	−0.26s	i-Pr	1.27d, 3.40m	7.76	OEt	1.13t, 4.27q	
7	−0.23s	t-Bu	1.24s	7.47	OEt	1.19t, 4.15q	
8	−0.04s	2,6-dimethylPh	2.19s, 7.05s	6.81	OEt	1.03t, 3.95q	
9	−0.25s	i-Pr	1.36d, 3.51m	7.75	NEt_2	0.92/1.09t, 3.05/3.26q	
10	−0.16s	t-Bu	1.38s	7.85	NEt_2	0.92/1.12t, 3.04/3.27q	
11	−0.32s	2,4-dimethyl-3-pentyl	1.02d, 2.14m, 2.48d/d	7.73	NEt_2	0.93/1.13t, 3.26/3.19q	
^{13}C NMR							δ(C=O)
7	−7.3		30.0, 61.3	149.3		14.7, 63.4	164.4
9	−8.0		24.7, 62.2	151.1		13.5/15.9, 42.9	163.2
10	−7.7		30.4, 61.0	148.5		13.6/16.0, 43.2	163.4
11	−7.0		19.2/20.8, 30.2, 85.4	155.1		13.6/15.8, 42.5/42.9	164.0

[a] In C_7D_8. All values are in ppm relative to external TMS: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The multiplicities of the ^{13}C resonances were obtained from off-resonance spectra, and are in agreement with the proposed assignments.

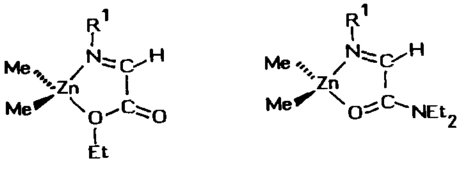
(*C*=O) which indicates that the N=C–C=O skeleton is present unchanged. Furthermore the IR data for **7** in hexane with absorptions at 1638 [ν(C=N)] and 1762 [ν(COOEt)] cm^{-1} establish the presence of a N=C–COOR ligand skeleton in **7**. These data are in agreement with structures for **6–11** which involve a dimethylzinc entity and a coordinated α-iminoester or amide substrate.

It is obvious from the IR and NMR data that zinc binds at the same time to the imine-N atom as well as to either one of the donor atoms in the ester or amide moiety. However, we observed a remarkable difference in behaviour of the ν(C=O) in the $ZnMe_2/\alpha$-iminoester complexes (**6–8**) compared with that in the $ZnCl_2/\alpha$-iminoester compounds (**2** and **4**). Again, the shift of the [ν(C=N)] of **6–8** to lower frequencies by 12 cm^{-1} confirms the imine-N coordination of the ligand. The ester carbonyl frequency, which for the metal halide-α-iminoester complexes **2** and **4** shifted to lower values, appears in **7** at 1772 cm^{-1}; i.e., rather than the expected decrease of the ν(C=O), which would point to involvement of the carbonyl-O atom in a chelate coordination [16], there is an increase to higher frequencies by 12 cm^{-1} relative to that for the free ligand (ν(C=O) 1760 cm^{-1}). This most unusual shift of the carbonyl absorption to a higher frequency can be interpreted in terms of coordination via the alkoxy-O atom [17]. Kobayaski et al. similarly proposed for the coordination complexes formed in the reaction of β-carbomethoxypropionaldehyde with trimethylaluminum bonding through the alkoxy-oxygen atom [18]. An important factor is that in this complex alkoxy-O coordination is preferred over carbonyl-O coordination because of steric effects in the complex.

Although unambiguous interpretation of the NMR data (see Table 5) of the $ZnMe_2/\alpha$-iminoamide complexes (**9–11**) reported here is not yet possible, it seems likely that the metal is chelate bonded through the imine-N and the amide-O atoms. The preference for amide-O atom coordination to organozinc moieties is also demonstrated by the structure of $[\overline{EtZn(t\text{-}Bu)NCH_2C(NEt_2)=O}]_2$, see Fig. 3. On the basis of these observations we propose the coordination modes for the α-imino-ester and -amide ligands in the dimethylzinc complexes **6–11** depicted in Fig. 2.

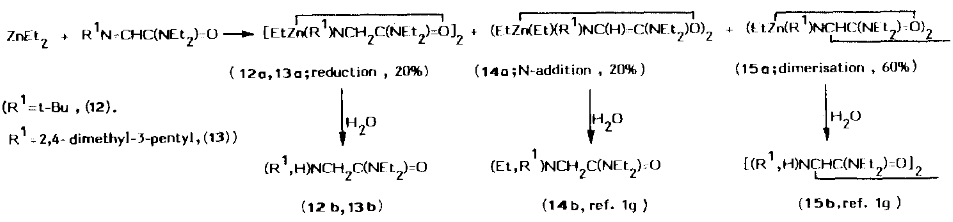
Selective reduction in the $ZnEt_2$– $R^1N=CHC(NEt_2)=O$ system and molecular geometry of 12

The reactions of diethylzinc with α-iminoamides follow a distinct reaction course (see Scheme 1). Isolation and characterization of the coordination products $ZnEt_2(R^1N=CHC(NEt_2)=O)$ was impossible because of the much higher reactivity of these complexes than of the dimethylzinc analogues, $ZnMe_2(R^1N=CHC(NEt_2)=O)$ (**9–11**). Just as in the ZnR_2/α-iminoketone system, the nature of the organo groups



(6-8) **(9-11)**

Fig. 2. Proposed structures for the $ZnMe_2$ coordinated α-iminoesters and α-iminoamides; **6–8**, 4e σ-N, σ-O (alkoxy), chelating; **9–11**, 4e, σ-N, σ-O, chelating.



SCHEME 1

R bonded to zinc, appeared to be an important factor involved in determining the type of the organozinc species formed [1a,f].

From the reaction of $ZnEt_2$ with the α-iminoamides the reduction products **12a** and **13a** were isolated as crystalline solids in moderate yields up to 20%. Both N-addition products **14b** and (imino)-C-(imino)-C dimerisation products **15b**, formed in an important side reaction, were identified after hydrolysis of the reaction mixture, see ref. 1g.

Both **12a** and **13a**, which are soluble in hexane, dichloromethane, and aromatic solvents, are sensitive towards moisture and oxygen. Elemental analytical data confirmed the stoichiometries for the products **12a** and **13a** shown in Scheme 1.

Unambiguous proof for the (dimeric) structure in the solid state of the new ethylzinc (β-amino)amides **12a** and **13a** comes from the X-ray structure determination on compound **12a**, $[EtZn(t\text{-}Bu)NCH_2C(NEt_2)=O]_2$. The molecular structure is shown in Fig. 3. Relevant bond lengths, bond and torsion angles for the non-hydrogen atoms are listed in Table 1.

The molecule has a dimeric structure in the solid state. It consists of a central four-membered Zn_2N_2 ring which links the two halves of the dimer, while coordination of the amide-O atom to zinc results in formation of a five-membered $\overline{ZnNCCO}$ ring and completes the four coordination at the zinc atom. The central Zn_2N_2 ring is flat (Σ angles 359.5°). Both five-membered chelate rings are slightly puckered and are on the same side of the Zn_2N_2 plane with an angle between best planes through the five- and four-membered rings of 98°. The Zn and N atoms involved in the central ring are four-coordinate, and in terms of bonding geometry may formally be considered to be sp^3-hybridized. The Zn(1)–N(1)–C(3) angle of 117.2(3) and the N(1)–Zn(1)–C(11) angle of 131.4(3)° are considerable larger than the tetrahedral value, no doubt as a result of the strain in the four- and five-membered chelate rings. The Zn–N–Zn and the N–Zn–N angles (mean 86.7 and 93.0°, respectively) are in good agreement with the corresponding angles of 89.3(3) and 90.6° mean in dimeric $(MeZnNPh_2)_2$, which is the only other structure known that contains a Zn_2N_2 fragment [11]. The Zn–N bond lengths in the Zn_2N_2 ring of 2.069–2.093 Å are not significantly different from the lengths (2.062–2.081 Å) found in the Zn_2N_2 rings of dimeric methyl(diphenylamino)zinc [19]. The Zn(1)–C(11) distance (1.991(7) Å) resembles the Zn–C value of 2.00 Å for $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$. The N(1)–C(1) bond is considerably lengthened in **12** to 1.487(7) Å, which is consistent with a reduction of a formerly C=N double bond to a N–C single bond. This is in accord with the presence of a mono-anionic α-amido-β-amino moiety. The C(2)–N(2) bond distance in the amido grouping is 1.346(8) Å, and is intermediate between the value for a C–N single bond (1.47 Å) and a C=N double bond (1.24 Å). This partial

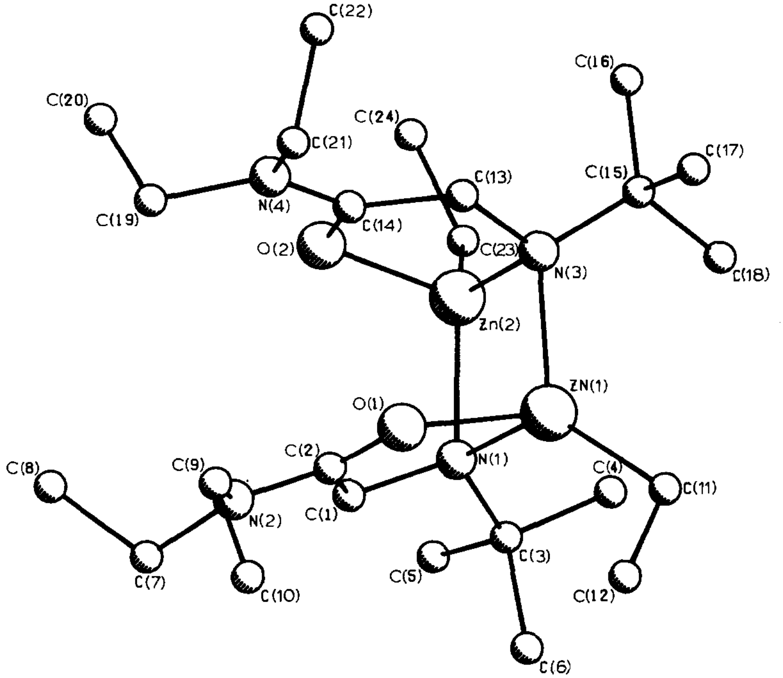


Fig. 3. PLUTO drawing of $[\overline{EtZn(t\text{-}Bu)NCH_2C(NEt_2)=O}]_2$ (**12a**) (40% level), with atom numbering scheme.

double bond character of the C(2)N(2) bond may result from delocalization of the nitrogen lone-pair electrons into the π-system of the carbonyl bond [20,21]. The C(2)–O(1) bond length of 1.242(6) Å is close to the expected double bond value. All atoms of the amide group O(1), C(2), C(1), N(2), C(7) and C(9) are essentially coplanar (Σ angles C(2) 360.1° and Σ angles N(2) 359.8°). The Zn(1)–O(1) bond length (2.118(5) Å) is slightly shorter than this bond in $Et_2Zn_4[N(Ph)COOMe]_6$ (2.180(2) Å) [22], close to the value of 2.078 Å (mean) for the bonds in $(MeZnOMe)_4$ [24] but larger than the Zn–O bond in the Reformatsky reagent (2.01 Å) [23].

The combined NMR spectra of **12a** and **13a**, see Table 6, point to a molecular geometry similar to that in the solid. The ^1H NMR spectra are in agreement with structures consisting of an ethylzinc entity to which a $(t\text{-}BuNCH_2C(NEt_2)=O)$ monoanion is bidentate bonded. The imino-hydrogen resonances, $N=CH$, are shifted from the low field region of this proton in α-iminoamides (ca. 7.5 ppm) to the region characteristic for α-amino CH_2 hydrogen atoms (ca. 4.0 ppm).

The ^{13}C NMR spectra (Table 6) show two different NCCO skeleton carbon atom resonances, at 64.7 (NCH_2) and 182.3 (C=O) ppm. The bridging nitrogen atom in the organozinc compounds **12a** and **13a** is a stable chiral centre, since coordination of this N-atom to both zinc prevents pyrimidal inversion at the nitrogen atom. The chirality of the tetrahedral N centres is reflected in the resonance pattern for $[(CH_3)_2CH]_2CH$ protons and 13-carbon centres in the ^1H and ^{13}C NMR spectra of **13a**, respectively. The prochiral methyl groups in the Me_2CH nitrogen substituent are diastereotopic with complex resonance patterns. Furthermore, the α-amido CH_2 protons and the N,N-diethyl proton in **12a** are non-equivalent.

TABLE 6

^{1}H AND ^{13}C NMR DATA^a FOR $[\overline{\mathrm{EtZn(R^1)NCH_2C(NEt_2)=O}}]_2$ (**12a** and **13a**)

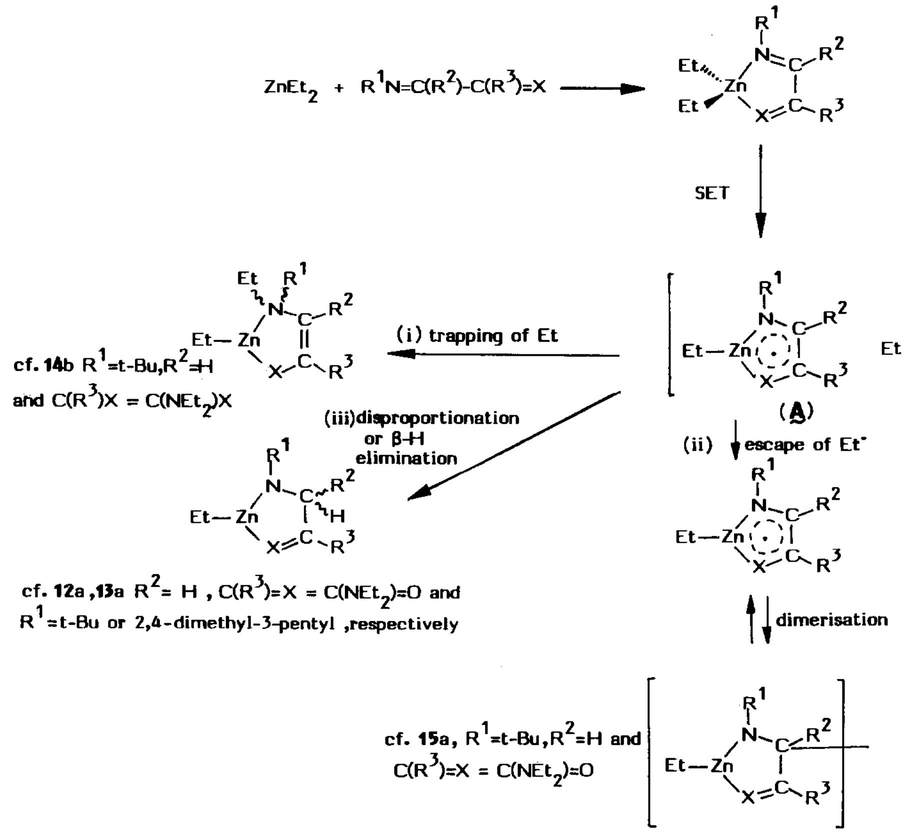
Compound	δ(Et-Zn)	δ(R^1)	δ(CH$_2$)	δ(NEt$_2$)
^{1}H NMR				
12a	1.2m, 1.96t	δ(t-Bu)1.66s	3.85/4.02 d^b	0.94t, 1.02t, 2.97q
13a	1.2m, 1.99t	2,4-dimethyl-3-pentyl 1.33/1.47d, 2.16m, 2.4d	4.01m	1.07t, 1.11t, 3.30q, 3.43q
^{13}C NMR				δ(C=O)
13a	3.7, 13.5	20.1/21.4/22.8^b, 34.2/35.4^b, 72.0	64.7	14.3/15.6, 182.3 42.2/43.2

^{a} In C_7D_8. All values are in ppm relative to external TMS: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Multiplicity (for ^{13}C NMR), obtained from off-resonance spectra, is in agreement with the proposed assignments. ^{b} Diastereotopic groups.

Further evidence for the structure of the organozinc compounds **12a** and **13a** came from the results of hydrolysis. Hydrolysis of the isolated, pure organozinc compounds **12a** and **13a** gave quantitative yields of the new α-aminoamides, according to Scheme 1. However, hydrolysis of the crude reaction mixture in an one-pot reaction gave, besides the reduction products **12b** (and **13b**), the N-addition products **14b** (in up to 20% yield) and the (imino)C–(imino)C coupled dimerization products **15b**, formed in up to 60% yield, see ref. 1g. This shows that in the reaction of $ZnEt_2$ with the α-iminoamides in addition to the α-aminoamide reduction products (**12a** and **13a**), the N-addition product **14a** and the C–C coupled product **15a** are formed in a competing reaction. The organic aspects of these reactions as well as of the formation of new organic products by hydrolysis of the formed zinc complexes will be discussed in a separate paper.

Mechanistic aspects

The striking difference in stability of the α-iminoamide complexes of $ZnMe_2$ (isolable) and $ZnEt_2$(not-detectable) probably arises from a difference in kinetic stability of the complexes in respect to the further reactions of the type shown in Scheme 1 for the $ZnEt_2$ complexes. The formation of **12a**, **14a** and **15a** indicates that also these reactions occur via a process that which has many similarities with those found for reactions with α-diimines and R-Pyca compounds: i.e. concomitant homolytic Zn–C^{Et} bond cleavage and intramolecular single electron transfer in the chelate bonded 1/1 complex thus generating an intermediate radical pair comprising an EtZn(R^1)NCHC(NEt$_2$)O radical and an Et radical (see Scheme 2). The formation of the N-ethylated product **14a** recalls the almost quantitative formation of the N-ethylated product $[\overline{\mathrm{EtZn(Et,R^1)NC(H)=C(R^3)O}}]_2$ in the $ZnEt_2$-α-iminoketone reaction [1f]. In the latter reaction the homolytic cleavage of the Zn–Et bond and intramolecular SET is followed by capture of the produced Et radical by the N-atom within the first formed radical pair. The observation that **14a** is formed in only 20% yield whereas the reaction of $ZnEt_2$ with t-BuN=CH-C(Me)=O proceeds quantitatively points to a large influence of the substituent on the carbonyl carbon centre (NEt$_2$ vs. Me) on the spin density distribution in the ZnNCCO chelate ring of the organozinc radical. Evidently, in radical pair **A** the spin density on the endocyclic N atom is considerably lowered by the NEt$_2$ substituent, thus allowing



SCHEME 2. Proposed steps for the $ZnEt_2/R^1N{=}C(R^2){-}C(R^3){=}X$ systems in which $-C(R^3){=}X$ is $-C(H){=}NR$, $-C_5H_4N$, $-C(R){=}O$ or $-C(NEt_2){=}O$.

the Et radical to diffuse apart from the organozinc radical. Firm prove of this possibility was obtained from the study of the reaction of $ZnEt_2$ with t-Bu-DAB, which likewise produces almost exclusively the N-ethylated product $Et\overline{Zn(Et)(t\text{-}Bu)\text{-}NC(H){=}C(H)N}\text{-}t\text{-}Bu$ [25]. In this reaction also trace amounts of the stable organozinc radical $Et\overline{Zn(t\text{-}Bu)NC(H)C(H)N}\text{-}t\text{-}Bu$ could be detected by ESR. This radical is in equilibrium with the C–C coupled product (see Scheme 2 where $-C(R^3){=}X$ is $-C(H){=}N\text{-}t\text{-}Bu$). It is this product that is similar to the C–C coupled product **15a**, and this establishes the formation of $Et\overline{Zn(R^1)NC(H)C(NEt_2)O}$ radical as a key intermediate in the $ZnEt_2$-α-iminoamide reaction.

The formation of the reduced product **12a** (or **13a**) is comparable with that of such products in the reaction of $ZnEt_2$ with t-Bu-Pyca [26]. A possible rationale for the formation of **12a** is the formation of a zinc hydride species $H\overline{ZnEt(R^1N\text{-}{=}CHC(NEt_2){=}O})$ either via (i) a radical disproportionation reaction within the radical pair between $Et\overline{Zn(R^1)NC(H)C(NEt_2)O}$ radical and Et radical followed by transfer of the hydride to the imino-carbon atom, or (ii) direct β-hydride elimination. The feasibility of pathway (i) has beeen unambiguously established in the $ZnEt_2$(R-Pyca) reactions [27].

The available information for the $ZnEt_2$/1-aza-4-oxo(or aza)-1,3-butadiene systems discussed, i.e., $ZnEt_2$(t-Bu-DAB), $ZnEt_2$(t-Bu-Pyca), $ZnEt_2$(α-iminoketone), and $ZnEt_2$(α-iminoamide), suggest a striking similarity of the mechanisms of all these reactions, as illustrated in Scheme 2. Starting from the σ,σ-N,X chelate complex, a single electron transfer gives rise to the intermediate radical pair **A**. Depending on the spin density of the various chelate ring atoms as well as on the reactivity of the R radical the radicals in **A** can either diffuse apart or collapse to products. The relative rates of these processes will depend greatly on the actual spin density on the chelate ring atoms, which is determined by the LUMO level of the various N=C(H)–C(R)=X chelates. Substitution at the central C atoms (e.g. R = Me [1f] or NEt_2 [present study]) will further influence this distribution. Further study of the organozinc radicals (cf. ref. 27) will be needed to gain more quantitative information.

Finally, we note that the relatively high stability of the Me_2Zn(α-iminoamide) complex is surprising. The results suggest that the NEt_2 substituent changes the LUMO level of the N=C–C=O system, relative to the HOMO level of Me_2Zn, to such an extent that single electron transfer leading to the radical pair of type **A** becomes less likely. This aspect is also now under investigation.

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