Recl. Trav. Chim. Pays-Bas **107**, 263–266 (1988) 0165–0513/88/03263–04$1.50

X-Ray crystal structure of the ethylzinc enolate of 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone, the unexpected reaction product from cyclopentadienyl(ethyl)zinc and ethyl *N,N*-diethylglycinate

Johann T. B. H. Jastrzebski[a], Jaap Boersma[a], Gerard van Koten[a]*, Wilberth J. J. Smeets[b] and Anthony L. Spek[b]

[a] *University of Utrecht, Laboratory of Organic Chemistry, Dept. of Metal-Mediated Synthesis, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b] *University of Utrecht, Dept. of Crystal and Structure Chemistry, Padualaan 8, 3584 CH Utrecht, The Netherlands*
(Received October 9th, 1987)

Abstract. Reaction of cyclopentadienyl(ethyl)zinc with ethyl *N,N*-diethylglycinate affords the dimeric ethylzinc enolate (**2**) of 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone in quantitative yield. Its molecular structure was determined by X-ray crystallography. Crystals of **2** $C_{26}H_{42}N_2O_2Zn_2$ are monoclinic, space group $P2_1/c$, with unit cell parameters a = 7.972(1) Å, b = 15.741(2) Å, c = 11.062(2) Å, β = 91.85(2)°. The crystal structure was solved using standard *Patterson* methods (Zn) and subsequent difference *Fourier* techniques. Anisotropic full-matrix least-squares refinement with 1989 observed reflections and 160 parameters converged at R = 0.0335.

Introduction

Recently, we described a new method for the selective synthesis of *trans*-β-lactams, either starting from α-imino esters and diethylzinc[1] or from *in situ* prepared zinc enolates and imines[2] (see Scheme 1). Zinc ester enolates appear to play a key role in this new route to β-lactam formation. To obtain further insight into the mechanisms involved in these reactions we have tried to obtain structural information about zinc ester enolates of this type.

Although the ethyl- and chlorozinc ester enolates **1a** and **1b** have been isolated[2], it was not possible to obtain single crystals suitable for an X-ray crystal structure determination of either of these compounds. This failure may be due to the formation in solution of complex aggregates in which LiCl is also present. To avoid these complications, we tried an alternative route to the preparation of zinc ester enolates, *i.e.* the direct deprotonation of ethyl *N,N*-diethylglycinate by a suitable reactive organozinc compound. Our experience with the high reactivity of cyclopentadienylzinc derivatives towards proton acids, exemplified by their reactions with extremely weak acidic transition-metal hydrides[3], suggested cyclopentadienyl(ethyl)zinc as deprotonating agent. As an added benefit, these reactions might provide some insight into the virtually unexplored organic chemistry of cyclopentadienylzinc compounds.

While diethylzinc or ethylzinc ethoxide did not react with ethyl *N,N*-diethylglycinate, not even under forcing conditions (8h, 120°C), with cyclopentadienyl(ethyl)zinc a fast and exothermic reaction took place at room temperature. The formation, isolation and X-ray crystallographical characterisation of the unexpected product obtained from this reaction are described here.

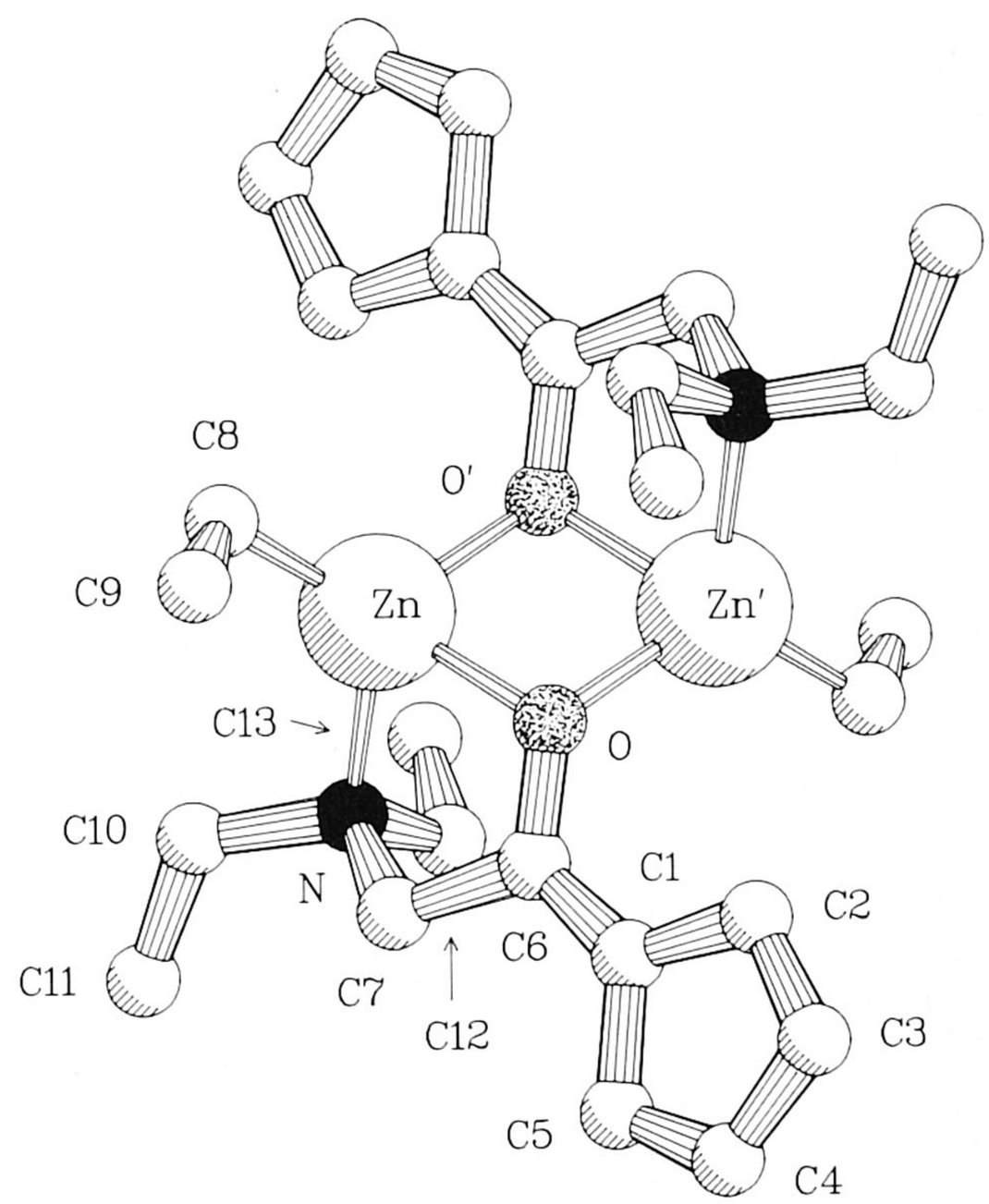
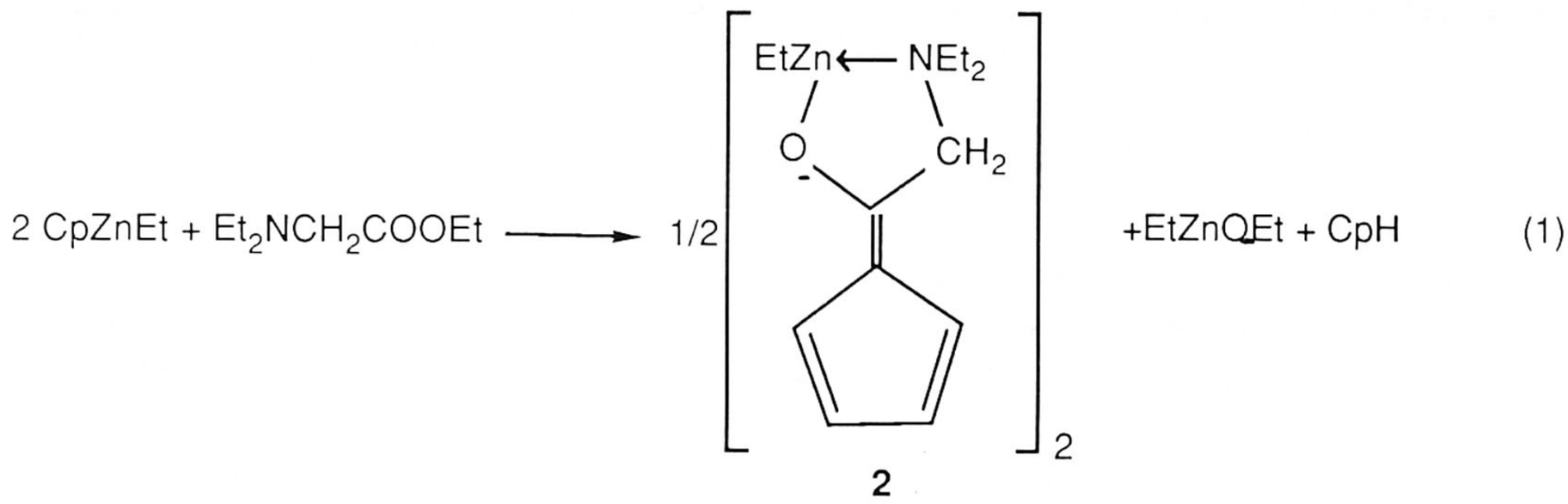


Fig. 1. View of the molecular structure of **2** *showing the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.*

Dedicated to Professor Dr. *G. J. M. van der Kerk* on the occasion of his 75th birthday.



Results and discussion

Addition of ethyl *N,N*-diethylglycinate to a solution of cyclopentadienyl(ethyl)zinc in a 1:2 molar ratio at room temperature affords, after work-up, the ethylzinc enolate (**2**) of 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone in quantitative yield as a yellow microcrystalline powder (Eqn. 1).

Yellow crystals of **2** were obtained by recrystallization from hot benzene, and one of suitable size was chosen for an X-ray single-crystal diffraction study. The results of the structure determination and refinement showed these crystals to be $[EtZnOC(CH_2NEt_2)=(c\text{-}C_5H_4)]_2$, the dimeric **2**. Fig. 1 presents an overview of the molecule together with the adopted numbering scheme. Coordinates are given in Table I. Bond distances and angles are given in Table II. The molecule contains a central four-membered Zn_2O_2 ring which links two monomeric units across a centre of symmetry. Coordination of the amino nitrogen atoms to the zinc atoms results in the formation of five-membered ZnOCCN chelate rings and completes the four-coordination of the zinc atoms, while the O atoms remain three coordinate. The Zn–O–Zn′ and the O–Zn–O′ angles of 98.99(7)° and 81.01(8)°, respectively, are in agreement with the corresponding angles of 95.8(5)° and 84.2(5) found in dimeric $[EtZn(t\text{-}Bu)(Et)NC(H)=C(Me)O]_2$[4]. The Zn–O bond lengths in the Zn_2O_2 ring of 2.075(2) and 2.041(2) Å are not significantly different from the bond lengths 2.12(1) and 2.02(1) Å found in the Zn_2O_2 ring of $[EtZn(t\text{-}Bu)(Et)NC(H)=C(Me)O]_2$[4]. The alternating short (1.35 Å) and longer (1.45 Å) C–C bond lengths in the five-membered ring in **2** indicate a fulvene type of structure with alternating double and single C–C bonds, as shown schematically in Eqn. 1.

Table I Fractional atomic coordinates and equivalent isotropic thermal parameters, with esd's shown in parentheses, for $C_{26}H_{42}N_2O_2Zn_2$.

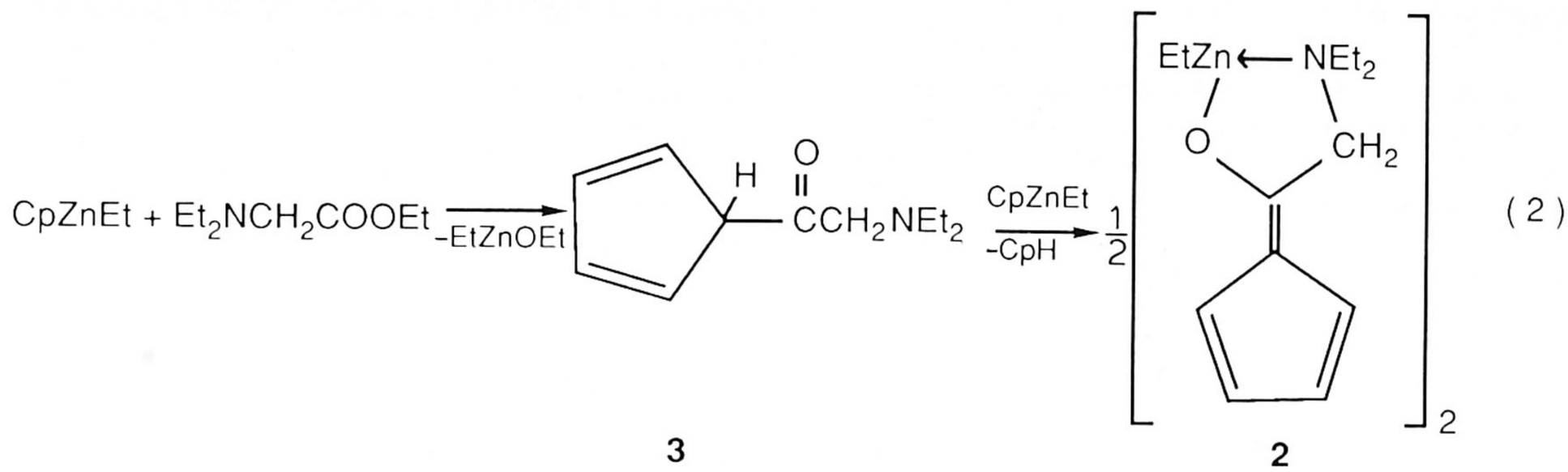
Atom	*x*	*y*	z	U_{eq}[a] or U (Å^2)
Zn	0.00378(5)	0.02162(2)	0.13813(3)	0.0543(1)
O	0.1239(2)	−0.0564(1)	0.0169(2)	0.0522(6)
N	−0.0834(3)	−0.0985(1)	0.1962(2)	0.0520(6)
C(1)	0.2273(3)	−0.1958(2)	−0.0037(3)	0.052(1)
C(2)	0.3128(4)	−0.1844(2)	−0.1156(3)	0.062(1)
C(3)	0.3918(4)	−0.2581(2)	−0.1408(3)	0.076(1)
C(4)	0.3608(4)	−0.3183(2)	−0.0482(3)	0.076(1)
C(5)	0.2617(4)	−0.2828(2)	0.0340(3)	0.065(1)
C(6)	0.1426(3)	−0.1352(2)	0.0564(2)	0.0481(8)
C(7)	0.0704(4)	−0.1501(2)	0.1792(3)	0.057(1)
C(8)	0.1171(5)	0.1024(2)	0.2477(3)	0.077(1)
C(9)	0.2936(5)	0.0811(3)	0.2815(5)	0.121(2)
C(10)	−0.1196(5)	−0.0936(2)	0.3288(3)	0.075(1)
C(11a)	−0.1527(6)	−0.1708(3)	0.3949(4)	0.075(2)
C(12)	−0.2227(4)	−0.1357(2)	0.1215(3)	0.067(1)
C(13)	−0.3827(4)	−0.0845(3)	0.1219(4)	0.091(2)
Minor disorder component [s.o.f. = 0.276(7)]				
C(11b)	−0.228(3)	−0.038(1)	0.368(2)	0.132(8)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Table II Bond distances and angles for the non-hydrogen atoms of $C_{26}H_{42}N_2O_2Zn_2$[a].

Bond distances (Å)	
Zn–O	2.075(2)
Zn–O′	2.041(2)
Zn–N	2.121(2)
Zn–C(8)	1.957(3)
O–C(6)	1.322(3)
N–C(7)	1.488(4)
N–C(10)	1.506(4)
N–C(12)	1.483(4)
C(1)–C(2)	1.443(5)
C(1)–C(5)	1.455(5)
C(1)–C(6)	1.355(4)
C(2)–C(3)	1.353(5)
C(3)–C(4)	1.423(5)
C(4)–C(5)	1.345(5)
C(6)–C(7)	1.511(4)
C(8)–C(9)	1.483(6)
C(10)–C(11)	1.447(6)
C(12)–C(13)	1.509(5)
Bond angles (°)	
O–Zn–O′	81.01(8)
O–Zn–N	80.25(8)
O–Zn–C(8)	124.8(1)
O′–Zn–N	109.53(8)
O′–Zn–C(8)	123.6(1)
N–Zn–C(8)	122.7(1)
Zn–O–Zn′	98.99(7)
Zn–O–C(6)	113.0(2)
Zn′–O–C(6)	125.3(2)
Zn–N–C(7)	99.7(2)
Zn–N–C(10)	108.9(2)
Zn–N–C(12)	115.5(2)
C(7)–N–C(10)	109.6(2)
C(7)–N–C(12)	108.6(2)
C(10)–N–C(12)	113.5(2)
C(2)–C(1)–C(5)	105.8(3)
C(2)–C(1)–C(6)	126.1(3)
C(5)–C(1)–C(6)	127.9(3)
C(1)–C(2)–C(3)	107.8(3)
C(2)–C(3)–C(4)	109.3(3)
C(3)–C(4)–C(5)	109.2(3)
C(1)–C(5)–C(4)	107.9(3)
O–C(6)–C(1)	123.4(2)
O–C(6)–C(7)	113.6(2)
C(1)–C(6)–C(7)	122.8(3)
N–C(7)–C(6)	111.6(2)
Zn–C(8)–C(9)	115.1(3)
N–C(10)–C(11)	119.5(3)
N–C(12)–C(13)	113.9(3)

[a] [′] indicates symmetry operation: $-x, -y, -z$.



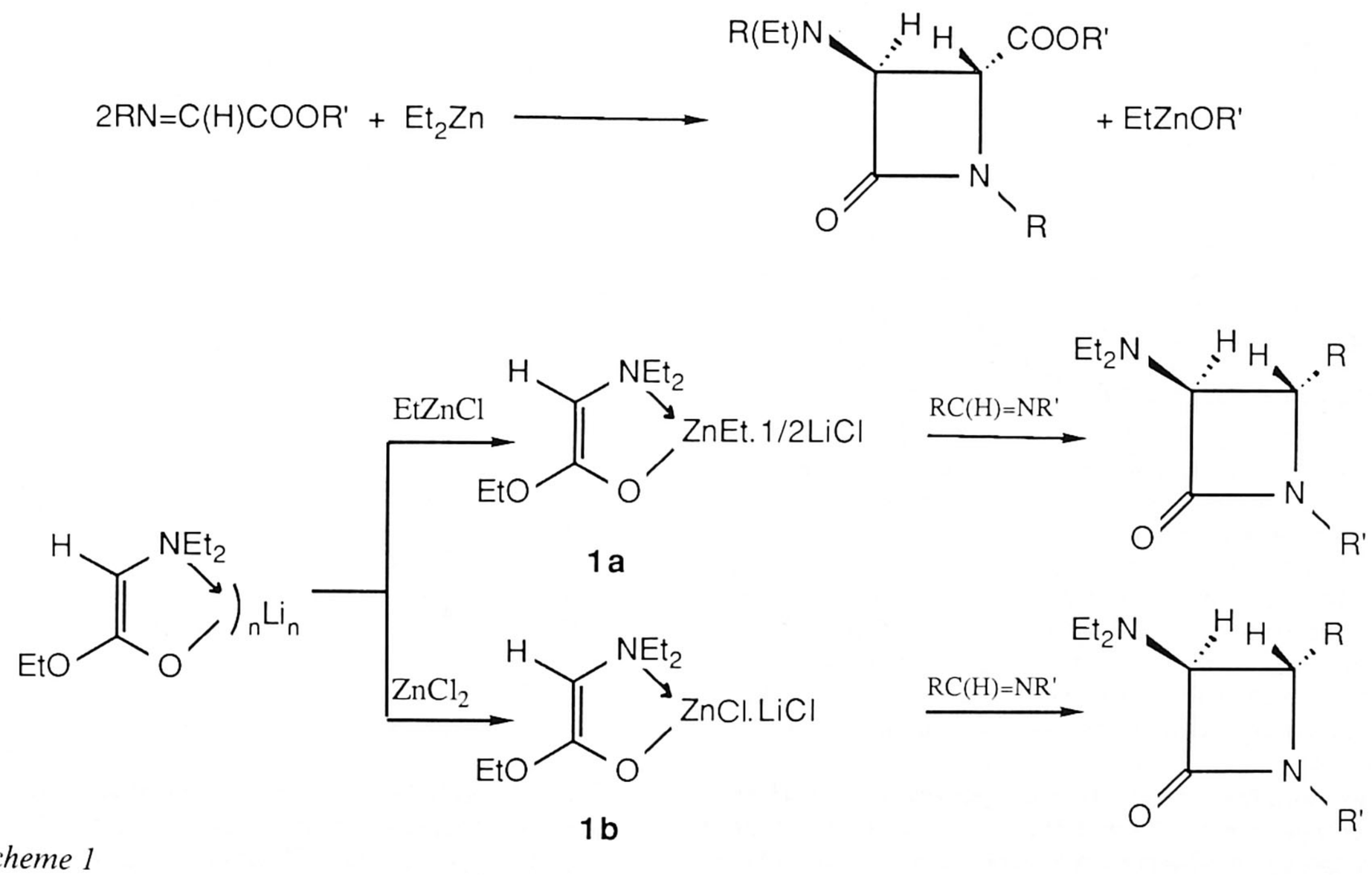
(2)

At 30°C, the ^{1}H and ^{13}C NMR data (toluene-d_8, see experimental) of **2**, which has a dissymmetric structure, suggest that a fluxional process, probably involving Zn–N dissociation/association, is operative. At −20°C in the ^{1}H NMR spectrum, the $N(C\underline{H}_2CH_3)_2$ and $C\underline{H}_2N(CH_2CH_3)_2$ resonances are observed as a complicated pattern between 2.00 and 4.00 ppm, indicating that the process at this temperature is in the slow exchange limit. This is even better illustrated in the ^{13}C NMR spectra. At 30°C, the $N(\underline{C}H_2CH_3)_2$ and $N(CH_2\underline{C}H_3)_2$ resonances are observed at 46.8 and 8.9 ppm, respectively, whereas at −20°C, both resonances are split into two sets of resonances at 44.3 and 47.6 and at 8.8 and 10.7 ppm, respectively. This observation indicates that, at the latter temperature, the $N(CH_2CH_3)_2$ group is diastereotopic and Zn–N coordination is inert on the NMR time scale. It is therefore most likely that the dimeric structure of **2** is retained in solution.

Ester functions are normally completely inert towards dialkyl- or diarylzinc compounds, with the exception of β-propiolactone, which is in fact an activated ester due to strain in the four-membered ring and which reacts via acyl–oxygen cleavage of the lactone ring with ethylzinc methoxide[5], ethylzinc diphenylamide[5] and ethylzinc diphenylphosphide[6]. It is surprising therefore, that the reaction between ethyl *N,N*-diethylglycinate and cyclopentadienyl(ethyl)zinc proceeds so easily and with high selectivity.

Most likely, the first step in this reaction involves a substitution of the ethoxy group by the cyclopentadienyl group leading to 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone **3** and ethylzinc ethoxide (see Eqn. 2). The organic molecule **3** is immediately trapped by the excess of cyclopentadienyl(ethyl)zinc present in solution, leading to **2** and cyclopentadiene. Unfortunately, we were unable to isolate the free organic molecule **3**. When the reaction of cyclopentadienyl(ethyl)zinc with ethyl *N,N*-diethylglycinate is carried out in a 1:1 molar ratio, only 50% of the ethyl *N,N*-diethylglycinate is converted according to Eqn. 2 and the other 50% of ethyl *N,N*-diethylglycinate remains unchanged in solution. Furthermore, careful hydrolysis of **2** does not lead to free **3**, but results in a complete decomposition or polymerisation of the organic molecule.

That the formation of **2** most likely proceeds as indicated in Eqn. 2 and that the ethylzinc enolate of ethyl *N,N*-diethylglycinate is not an intermediate in this reaction is indicated by the observation that cyclopentadienyl(ethyl)zinc is unreactive towards the ethylzinc enolate of ethyl *N,N*-diethylglycinate. The latter was prepared via a different route (*cf.* compounds **1** in Scheme 1). Its synthesis, characterisation and reactivity with respect to the formation of *trans*-β-lactams will be the subject of a forthcoming paper[7]. We are currently also exploring reactions of cyclopentadienyl(ethyl)zinc with other β-heteroatom-substituted esters for the synthesis of zinc enolates related to **2** as well as the subsequent conversion of **2** by *Diels–Alder* type reactions.



Scheme 1

Experimental

All solvents were carefully dried and distilled from sodium prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 200 spectrometer. Since the procedure for the synthesis of cyclopentadienyl(ethyl)zinc given by *Strohmeier*[8] is time consuming and gives only a moderate yield, we prepared cyclopentadienyl(ethyl)zinc via a different route. Pure diethylzinc and bis(cyclopentadienyl)zinc were mixed in a 1:1 molar ratio and warmed at 60°C for 1 h giving almost pure cyclopentadienyl(ethyl)zinc in quantitative yield. The product was purified by sublimation *in vacuo* at 60°C. Yield 85%. ^{1}H NMR (C_6D_6): 0.30 (q, 2H, $ZnC\underline{H}_2CH_3$), 1.20 (t, 3H, $ZnCH_2C\underline{H}_3$), 6.10 (s, 5H, C_5H_5).

Synthesis of the ethylzinc enolate of 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone **2**

To a solution of 20 mmol of cyclopentadienyl(ethyl)zinc dissolved in 15 ml of benzene was added 10 mmol of ethyl *N,N*-diethylglycinate. An immediate exothermic reaction occurred while the colour of the solution turned from colourless to yellow. ^{1}H NMR spectroscopy of this solution showed the presence of **2**, ethylzinc ethoxide and cyclopentadiene in a 1:1:1 molar ratio. All volatile material was evaporated *in vacuo* at 50°C yielding a yellow solid. This solid was washed with three 20-ml portions of diethyl ether to remove ethylzinc ethoxide and three 20-ml portions of pentane and dried *in vacuo* to yield 95% of **2** as a yellow solid. ^{1}H NMR (C_6D_6): 0.60 (q, 2H, Zn $C\underline{H}_2CH_3$), 0.95 (t, 6H, $N(CH_2C\underline{H}_3)_2$), 1.45 (t, 3H, $ZnCH_2C\underline{H}_3$), 2.5 (m, 4H,$N(C\underline{H}_2CH_3)_2$), 3.45 (s, 2H, $C\underline{H}_2N(CH_2CH_3)_2$), olefinic resonances at 6.80, 6.90 and 7.10 ppm (2H, 1H and 1H). ^{13}C NMR (C_6D_6): −0.9 ($Zn\underline{C}H_2CH_3$), 8.9 ($N(CH_2\underline{C}H_3)_2$), 13.9 ($ZnCH_2\underline{C}H_3$), 46.8 ($N(\underline{C}H_2CH_3)_2$), 58.5 ($CH_2N(\underline{C}H_2CH_3)_2$), olefinic resonances at 118.4, 120.4, 125.9, 127.4, 128.3 and 166.7 ppm. Analysis found (calc.); C 57.14 (57.26), H 7.76 (7.97), N 4.96 (5.14), O 5.63 (5.87), Zn 23.81 (23.98).

Structure determination and refinement of the ethylzinc enolate of 1-(2,4-cyclopentadienyl)-2-(diethylamino)-1-ethanone **2**

A yellow block-shaped crystal suitable for an X-ray structure determination was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Crystal data and details of the structure determination are given in Table III. Unit-cell parameters were determined from a least-squares treatment of the setting angles of 12 reflections in the range $9.8 < \Theta < 15.8°$. The monoclinic unit cell was checked for the presence of higher lattice symmetry[9]. Data were collected for one hemisphere ($-9 \leq h \leq 9$; $-19 \leq k \leq 19$;$0 \leq l \leq 13$) and corrected for *Lp* and a linear decay of 11.3% during the 113 h of X-ray exposure time. Standard deviations based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + [0.015(I)]^2$ [10]. The equivalent reflections (*hkl* and $h\bar{k}l$) were merged with a consistency index (on *I*) of 5.41%. Space group $P2_1/c$ was determined from the systematic extinctions $h0l$: $l = 2n + 1$ and $0k0$: $k = 2n + 1$. The Zn atom was found using *Patterson* methods (SHELXS86)[11]. Other non-H atoms were located from the subsequent difference *Fourier* maps. The C(11) atom was found to be disordered over two positions: 72.4(7) and 27.6(7)%, respectively. Refinement on *F* was carried out by full-matrix least-squares techniques. All non-hydrogen atoms, with the exception of the minor disordered C(11b) atom, were refined using anisotropic thermal parameters. Hydrogen atoms were introduced on calculated positions [*d*(C−H) 0.98 Å] and included in the refinement, riding on their carrier atom with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.0335$. A final difference *Fourier* synthesis reveals residual density between 0.20 and −0.31 e/Å^3. Neutral atom scattering factors were taken from ref. 12 and corrected for anomalous dispersion[13]. Data collection was carried out using a modified CAD-4F software package[14]. All calculations were performed with SHELX76[15] and the EUCLID package[16] (geometrical calculations and illustrations) on a Micro VAX-II computer.

Supplementary data (anisotropic thermal parameters, all H-atom parameters, complete lists of bond lengths, bond angles, torsion angles and a listing of observed and calculated structure-factor amplitudes) are available from one of the authors (A. L. S.).

Table III Crystal data and details of the structure analysis.

(a) Crystal data	
Formula	$C_{26}H_{42}N_2O_2Zn_2$
Mol. wt.	545.39
Crystal system	monoclinic
Space group	$P2_1/c$ (Nr. 14)
a, b, c (Å)	7.972(1), 15.741(2), 11.062(2)
β (°)	91.85(2)
V (Å^3)	1387.4(4)
Z	2
D_{calc} (g·cm^{-3})	1.305
F(000)	576
μ(CuKα) (cm^{-1})	23.1
Crystal size (mm)	0.38 × 0.30 × 0.25
(b) Data collection	
θ_{min}, θ_{max} (°)	2.8, 70.0
Radiation	CuKα (Ni-filtered), 1.54184 Å
ω/2θ scan (°)	0.60 + 0.15 tanθ
Horizontal and vert. aperture (mm)	3.0, 6.0
Distance crystal to detector (mm)	173
Reference reflections	004; 202
Total data	5563
Total unique data	2633
Observed data ($I > 2.5\sigma(I)$)	1989
(c) Refinement	
No. of refined parameters	160
Weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000243F^2]$
Final *R*, *wR*, *S*	0.0335, 0.0396, 0.64
$(\Delta/\sigma)_{max}$ in final cycle	0.069

Acknowledgements

X-ray data were kindly collected by *A. J. M. Duisenberg*. This work was supported in part (WJJS & ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Advancement of Pure Research (ZWO).

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