

ZINC ENOLATES: C- OR O-METALLATION?

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Summary

Two methods have been used for the generation of zinc enolates: the reaction of EtZnOMe with enol acetates, and that of lithium enolates with zinc chloride. Most of the zinc compounds prepared proved to be very reactive towards carbonyl functions, and so they cannot be isolated from the EtZnOMe/enol acetate system. The final products of these reactions are polymerisation and self-condensation products and β -diketonates, the latter being formed by condensation reactions of the zinc enolates with an acetate molecule. The structure of $[\text{EtZnOMe} \cdot \text{Zn}(\text{Pac})_2]_2$ (HPac = pivaloylacetone, $(\text{CH}_3)_3\text{CCOCH}_2\text{COCH}_3$), isolated in 20% yield from the reaction of EtZnOMe with $\text{CH}_3\text{COOC}(\text{t-Bu})=\text{CH}_2$, was determined by X-ray diffraction analysis. The compound forms monoclinic crystals, space group $P2_1/c$, with two dimers in a cell of dimensions a 11.677(4), b 18.299(9) and c 12.719(5) Å and β 117.26(3)°. The structure closely resembles that of the known complex $[\text{PhZnOPh} \cdot \text{Zn}(\text{Pac})_2]_2$.

The complications involving reactions of zinc enolates with enol acetates were avoided by treating lithium enolates with zinc chloride. Polymerization and self-condensation could be prevented by using the very bulky enolate $\text{LiOC}(\text{t-Bu})=\text{CMe}_2$. In this way, the corresponding stable zinc enolate $\text{RZnCl} \cdot \text{THF}$ was obtained as a dissociating dimer. No replacement of the second chlorine atom by an enolate group occurred even when a large excess of lithium enolate was used.

The reactivity of the zinc enolates suggests that they contain both zinc-carbon and zinc-oxygen bonds. They are assumed to have a cyclic structure which resembles that of the Reformatsky reagent.

Introduction

Organic compounds with a hydrogen atom α to a carbonyl function can occur in two tautomeric forms: a keto form and an enol form. Metal derivatives of such compounds, in which the relatively acidic hydrogen atom is replaced by a metal, can occur in corresponding forms, depicted in Fig. 1 (a and b), but also in a third form: an η -3 oxa-allyl coordination mode (c), recently reported for some transition-metal compounds [1].

Most known metal-organic compounds derived from ketones are based on Group I or II metals. Structure determinations of lithium enolates have been reported. In the solid state and in solution these compounds are associated. For the solid state, tetramers [2] and higher associates [3] of O-metallated species have been reported. For a number of lithium compounds, including enolates [4], cryoscopic measurements in THF indicate a mixture of dimeric and tetrameric species in this solvent. In the infrared spectra of solutions of alkali-metal enolates, the C=O vibration is replaced by a C=C vibration [5], showing that in solution also the compounds are O-metallated.

Derivatives of the second group of the Periodic Table have been studied less extensively. On the basis of infrared and ^{13}C NMR spectroscopy, Meyer et al. [6] and Pinkus et al. [7] concluded that magnesium enolates are dimeric O-metallated species, with the oxygen atoms bridging between the metal atoms. In their study Meyer et al. [6] included several mercury compounds, for which they reported a carbonyl vibration in the infrared spectra between 1660 and 1710 cm^{-1} . Furthermore, in the ^{13}C NMR spectra a carbonyl-carbon resonance was found between 200 and 220 ppm. These data were interpreted in terms of a C-metallated species. For mercury derivatives of ketones, only one crystal structure determination has been carried out [8], and this shows that bromomercurio acetone exists as the C-metallated form. The weak intermolecular interaction of the mercury atom with the carbonyl group of adjacent molecules accounts for the slight lowering of the C=O vibration in the infrared spectrum [8].

Zinc compounds derived from ketones reported hitherto in the literature were considered to be O-metallated [6,9] on the basis of an absorption in the infrared spectra at 1655 cm^{-1} attributed to a C=C vibration [6]. The small difference ($\sim 5 \text{ cm}^{-1}$) between the carbonyl vibration observed in the mercury compounds and the assumed C=C vibration in the zinc compounds raises the question of whether the latter assignment is unequivocal. Also, the carbonyl vibrations in the monomeric Reformatsky reagent [10] (a zinc derivative of an ester) and in zinc homoenolates [11] are found considerably below 1700 cm^{-1} .

The question of whether zinc enolates are O-metallated or C-metallated species is closely related to the corresponding discussion on the nature of the Reformatsky

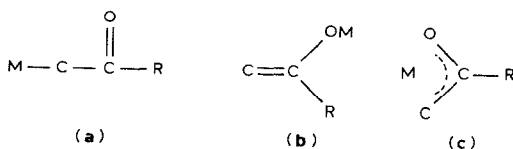


Fig. 1. Possible structures for metal derivatives of ketones (R = alkyl, aryl).

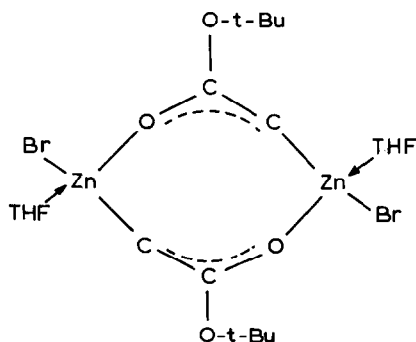
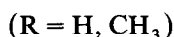
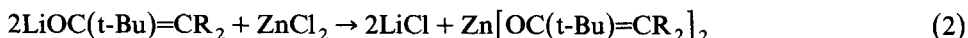
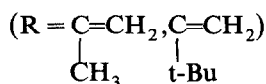
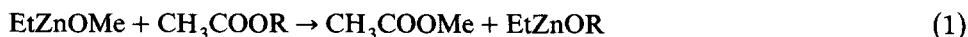


Fig. 2. Schematic drawing of the Reformatsky dimer.

reagent. Formally, the replacement of the OR group in the latter reagent by an alkyl or aryl group results in an enolate (C- or O-metallated). We recently elucidated the structure of the Reformatsky reagent, showing it to be a cyclic dimer, containing both zinc-carbon and zinc-oxygen bonding interactions [12] (cf. Fig. 2).

In the present paper we describe the formation and properties of a number of zinc enolates. The structure and reactivities of these compounds are compared with those of the Reformatsky reagent.

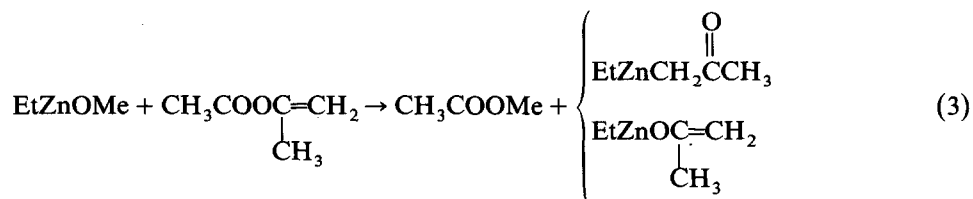
The syntheses of zinc enolates involved reactions of EtZnOMe with enol acetates (eq. 1) and those of lithium enolates with zinc chloride (eq. 2).



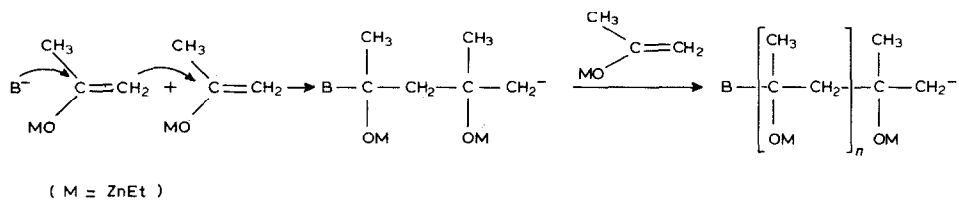
Results and discussion

Formation of zinc enolates

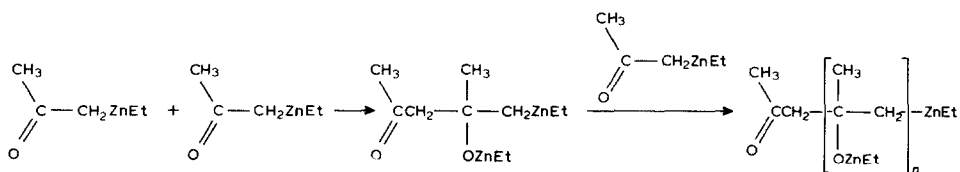
In the reaction of EtZnOMe with isopropenyl acetate, the formation of a zinc derivative of acetone via a transesterification was expected* (eq. 3).



* Whether this compound exists in the C- or O-metallated form is unknown, since the relevant part of the infrared spectrum of the reaction mixture ($1600\text{--}1800\text{ cm}^{-1}$) is obscured by acetate absorptions.



SCHEME 1. Proposed mechanism of the anionic polymerization of $\text{MOC}(\text{CH}_3)=\text{CH}_2$ (M = metal), catalysed by a base (B^-).

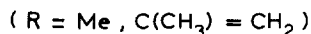
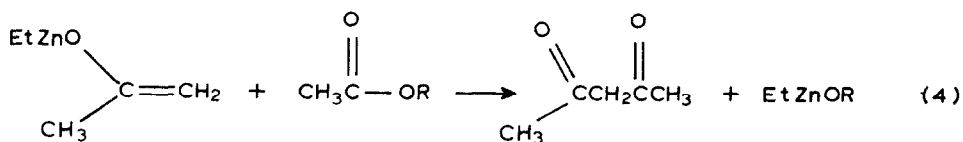


SCHEME 2. Proposed mechanism for the Grignard-like addition of a C-metallated zinc enolate over the $\text{C}=\text{O}$ of another C-metallated zinc enolate.

However, upon hydrolysis of the reaction mixture only a small quantity of acetone was detected. Acetyl acetone was also identified as a minor hydrolysis product, the main organic product being a polymeric material. The ^1H NMR spectrum of this material suggests that it is a polymer of the enol form of acetone. Formation of this product indicates that the zinc compound once formed, is unstable and tends to polymerize. This polymerization could proceed via two different routes. The first involves an anionic polymerization of the O-metallated form of the zinc compound (Scheme 1).

Since the polarity of the $\text{C}-\text{OM}$ fragment in the monomer already provides a partly negative charge on the centre of attack, this route is rejected in favour of the second route, viz. a Grignard-like addition of the $\text{Zn}-\text{C}$ bond of a C-metallated species to a carbonyl function of another C-metallated enolate (Scheme 2).

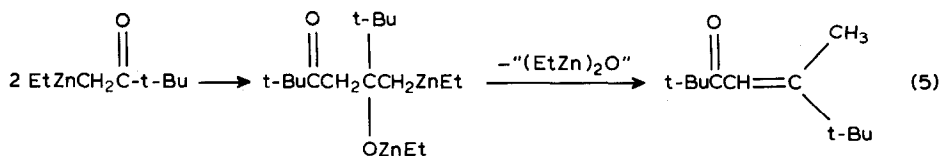
The presence of acetyl acetone among the hydrolysis products can be accounted for in terms of an aldol condensation of the initially formed enolate with the ester function of an acetate molecule (eq. 4). This type of reaction is common for alkali-metal enolates, which are O-metallated species.



The nature of the products shows that the zinc compound can react both as a C-metallated reagent (polymerization) and as an O-metallated reagent (condensation reaction).

The use of a more bulky enolate group prevented the polymerization reaction of the primary zinc compound. In the reaction of EtZnOMe with $\text{CH}_3\text{COOC}(\text{t-Bu})=\text{CH}_2$ no polymeric material was formed, but a white crystalline material was isolated, and identified as $[\text{EtZnOMe} \cdot \text{Zn}(\text{Pac})_2]_2$, the EtZnOMe complex of zinc pivaloylacetate. The molecular structure of this complex was established by an X-ray diffraction study (*vide infra*).

Hydrolysis of the reaction mixture after removal of the crystalline complex yielded $\text{CH}_3\text{CO-t-Bu}$ (identified by ^1H NMR), indicating that the expected zinc compound had been formed. The ^1H NMR spectrum also showed signals due to an unsaturated carbonyl compound. Ageing of the reaction mixture resulted in an increase of the latter signals. Analysis of the hydrolysis products of the reaction mixture showed this second compound to be $\text{t-BuC}(\text{CH}_3)=\text{CHCO-t-Bu}$. It seems reasonable to assume a self-condensation reaction of the initially formed zinc compound in order to account for the formation of this second product.



The first step in the formation of this compound is analogous to that in the polymerization of the less bulky acetone derivative (Scheme 2). The fact that no polymeric material was isolated from the reaction mixture indicates that the bulk of the t-butyl group prevents this reaction from continuing beyond dimers.

The reactions described above show that the desired zinc compounds are actually formed, but that subsequent reactions with acetates and self-condensation reactions prevent their isolation. To avoid these complications, the route via lithium enolates was investigated further.

The reaction of the lithium enolate $\text{LiOC}(\text{t-Bu})=\text{CH}_2$ with half an equivalent of zinc chloride in THF afforded a product mixture, the ^1H NMR spectrum of which resembled that of the initial product mixture from EtZnOMe and $\text{CH}_3\text{COOC}(\text{t-Bu})=\text{CH}_2$. Hydrolysis of the reaction mixture yielded mainly $\text{CH}_3\text{CO-t-Bu}$. Like its ethylzinc analogue, the compound underwent self-condensation; after a few hours at room temperature appreciable amounts of the unsaturated carbonyl compound $\text{t-BuC}(\text{CH}_3)=\text{CHCO-t-Bu}$ were detected among the hydrolysis products.

The first stable zinc enolate was isolated from the reaction of the lithium enolate from $\text{t-BuCOCH}(\text{CH}_3)_2$ and zinc chloride. No self-condensation product could be detected after several days in non-polar or weakly-polar solvents. Hydrolysis of the reaction mixture yielded only the starting ketone. After removal of the precipitated LiCl and evaporation of the solvent in *vacuo* a foamy mass resulted, which analysed as $\text{ClZnC}_8\text{H}_{15}\text{O} \cdot \text{THF}$, ($\text{C}_8\text{H}_{15}\text{O}$ corresponding to the 2,2,4-trimethylpentane-3-one fragment). Experiments with an excess of lithium enolate showed that the second chlorine atom in zinc chloride could not be replaced by an enolate group. Molecular weight determinations of the foamy product showed that the compound forms dissociating dimers in boiling THF, the observed degrees of association being 1.3, 1.5, and 1.6 at concentrations of 29, 53, and 70 mmol/l respectively. Attempts to grow single crystals suitable for X-ray diffraction analysis by crystallization from various organic solvents failed.

Experiments with $C_6H_5COCH(CH_3)_2$ as the starting ketone led to the same results: under the conditions used, zinc chloride was only mono-alkylated, and no single crystals of the zinc enolate could be obtained.

The structure of $[EtZnOMe \cdot ZnPac_2]_2$

Suitable crystals of the complex were grown by evaporating the reaction mixture formed from $EtZnOMe$ and $CH_3COO(t-Bu)=CH_2$, and recrystallizing the residue from pentane at $-30^\circ C$. The compound, $[EtZnOMe \cdot Zn(Pac)_2]_2$, forms monoclinic crystals, space group $P2_1/c$, with two centrosymmetric dimers in the unit cell. Figure 3 shows a PLUTO drawing of the molecule.

The molecular structure of the compound closely resembles that of the corresponding phenylzinc phenoxide complex $[PhZnOPh \cdot ZnPac_2]_2$, which we reported some years ago [13]. The core of the molecule consists of a Zn_4O_6 unit, which is built up from two slanted zinc-oxygen cubes, fused along one face, and missing a zinc atom at the vertex of each cube (Fig. 4). For the cores in both pivaloylacetate complexes, an approximate C_{2h} symmetry is observed. The average bond lengths for both complexes are compared in Fig. 4. The fact that the $Zn(2)-O(3)$ bond in the $EtZnOMe$ complex is relatively short is probably due to the better coordinating properties of the methoxy group compared with those of the phenoxy group.

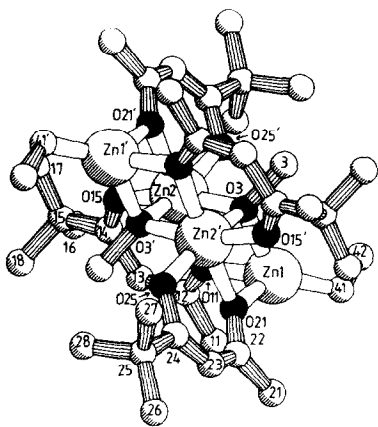


Fig. 3. PLUTO drawing of $[EtZnOMe \cdot ZnPac_2]_2$. Hydrogen atoms have been omitted for clarity.

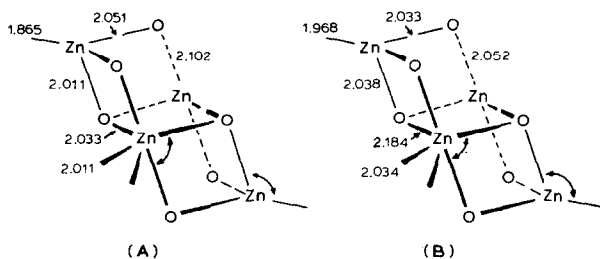


Fig. 4. Cores of zinc pivaloylacetate complexes. (a) $EtZnOMe$ complex. (b) $PhZnOPh$ complex [13].

A further noteworthy difference between the two structures is the orientation of the *t*-Bu groups of the pivaloyl ligands. In the PhZnOPh compound both *t*-Bu groups are approximately eclipsed with respect to the carbonyl C=O bond (torsion angles 11(1) and 21(1)°). In the EtZnOMe compound, one of these groups is eclipsed (7(1)°), while the other is staggered (178(1)°). This difference between the two structures is probably due to packing effects. The formation of this complex shows the flexibility of zinc acetylacetonates in accommodating quite different organozinc alkoxides.

Zinc enolates: C- and / or O-metallation

For the Reformatsky reagent, a crystal structure determination showed it to be a dimer, with both zinc–carbon and zinc–oxygen bonding interactions [12]. This structure was shown to persist in the most commonly used weakly polar solvents. For the corresponding zinc enolates no structure determination has been carried out, and attempts to grow suitable single crystals of our stable zinc enolates were unsuccessful.

A decrease in the electronegativity of a metal will increase its tendency to form metal–oxygen bonds. The very electropositive alkali- and alkaline-earth metals will therefore form O-enolates, stabilized by bridging oxygen atoms. In bromomercurioacetone, only a weak residual interaction between mercury and the oxygen atoms of adjacent molecules is observed [8]. The more electropositive zinc is expected to give a stronger interaction. Besides the fact that zinc is more electropositive than mercury, it also has a preference for higher coordination numbers. Thus, zinc enolates are expected to have both zinc–carbon and zinc–oxygen bonds, and so a dimeric structure for zinc enolates closely related to the structure of the Reformatsky reagent (cf. Fig. 5) seems plausible. Such a structure would also be in accord with the observed reactivity of zinc enolates.

Ebulliometric experiments showed that these dimeric associates dissociate to some extent in THF, although the nature of the monomers has not been established.

Whereas the Reformatsky reagent does not react with ester carbonyls, zinc enolates yield β -diketonates in an aldol condensation. Apparently, the OR group in the Reformatsky reagent deactivates it sufficiently to prevent this reaction.

Polymerization reactions of the zinc enolates are largely determined by the bulk of the group R adjacent to the carbonyl function. With R = H [14] and R = Me the compounds polymerize, whereas with R = *t*-Bu the polymerization does not proceed beyond dimers. Apparently, steric strain prevents incorporation of a third monomeric unit. Dimerization can be prevented by branching in the carbon atom directly

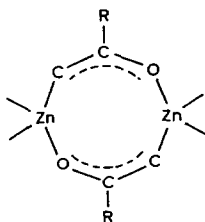


Fig. 5. Proposed dimeric structure for zinc enolates (R = alkyl, aryl).

bound to zinc; the zinc enolate from 2,2,4-trimethylpentane-3-one, $\text{ClZnC}_8\text{H}_{15}\text{O} \cdot \text{THF}$, which contains two methyl groups instead of hydrogens, is the first isolated stable zinc enolate.

Experimental

All manipulations were carried out under pure nitrogen. The solvents used were distilled from sodium/benzophenone prior to use. The ^1H NMR spectra were recorded on Varian EM-360 and EM-390 spectrometers. Chemical shifts are relative to internal Me_4Si . ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. GC/MS analysis was carried out on a Kratos MS80 with a 3% OV101 column. Micro-analysis was performed at the Institute for Applied Chemistry (TNO) under the supervision of Mr. G.J. Rothscheid.

Starting materials

2-Acetoxy-3,3-dimethyl-butene [9], 2,2,4-trimethylpentane-3-one [15], 1-phenyl-2-methylpropane-1-one [16], EtZnOMe [17] and lithium enolates [2] were prepared by published methods.

Reaction of EtZnOMe with $\text{CH}_3\text{COOC}(\text{CH}_3)=\text{CH}_2$

A solution of 26.3 mmol (3.3 g) of EtZnOMe and 26.5 mmol (2.65 g) of isopropenyl acetate in 10 ml benzene was slowly heated to 60°C . In the ^1H NMR the signals of isopropenyl acetate (4.6 and 1.7 ppm) disappeared, as did the OCH_3 signal of EtZnOMe at 3.5 ppm. The new signals of methyl acetate (3.4 and 1.6 ppm) could clearly be recognized. After about 1 h, the NMR spectra showed no further change, indicating that the reaction was complete. Volatile compounds were removed in vacuo, and collected in a cold trap. The amount of methyl acetate detected corresponded to 70% conversion. Hydrolysis of the foamy residue with aqueous hydrochloric acid and subsequent analysis of the mixture formed yielded (based on isopropenyl acetate) 6% of acetone (detected with GLC), 35% of acetyl acetone (estimated from ^1H NMR) and 40% (by weight) of a polymeric material, which gives a broad signal in the ^1H NMR spectrum between 1 and 2 ppm. This is probably a polymer of the enol form of acetone.

Reaction of EtZnOMe with $\text{CH}_3\text{COOC}(t\text{-Bu})=\text{CH}_2$

This reaction was carried out similarly with 80.3 mmol of EtZnOMe and 86 mmol of $\text{CH}_3\text{COOC}(t\text{-Bu})=\text{CH}_2$ in 20 ml benzene. Again the disappearance of the signals of the enol acetate [4.8 ppm (CH_2), 1.8 ppm (CH_3) and 1.0 ppm ($t\text{-Bu}$)] and of the OCH_3 of EtZnOMe (3.5 ppm) was monitored by ^1H NMR spectroscopy. In the reaction mixture, the new peaks of methyl acetate (3.4 and 1.6 ppm) could be recognised along with those of zinc pivaloyl acetonate (5.4 ppm, 1H; 1.9 ppm, 3H and 1.1 ppm, 9H). After 1 h the volatile compounds, among which methyl acetate and diethylzinc were identified by ^1H NMR spectroscopy, were removed and the residue was dissolved in 20 ml pentane. Cooling to -30°C afforded colourless crystals of $[\text{EtZnOMe} \cdot \text{Zn}(\text{Pac})_2]_2$ in 20% yield (based on the enol acetate). This product was characterised by X-ray diffraction analysis. The pentane layer was shaken with water. The presence of $t\text{-BuC}(\text{CH}_3)=\text{CHCO}-t\text{-Bu}$ and $\text{CH}_3\text{CO}-t\text{-Bu}$ was inferred from ^1H and ^{13}C NMR data and GC/MS analysis. (NMR data for

t-BuC(CH₃)CHCO-t-Bu: ¹H NMR (CDCl₃) 1.1 ppm, 18H; 2.0 ppm, 3H; 6.3 ppm 1H. ¹³C NMR (CDCl₃): 206.8; 164.3; 116.1; 43.7; 37.6; 28.3; 26.9 and 26.4 ppm).

Reaction of LiOC(t-Bu)=CH₂ with ZnCl₂

A solution of 5.7 mmol of ZnCl₂ in 18 ml THF was added dropwise to a stirred solution of 10.8 mmol of LiOC(t-Bu)=CH₂ in 10 ml of the same solvent. After stirring for about 1 h, the volatile compounds were removed in vacuo, and the residue was dissolved in 20 ml benzene. The LiCl was removed by centrifugation. Evaporation of the solvent yielded a glassy residue, which, upon hydrolysis gave CH₃CO-t-Bu and t-BuC(CH₃)=CHCO-t-Bu, detected by NMR spectroscopy.

Reaction of LiOC(t-Bu)=C(CH₃)₂ with ZnCl₂

This reaction was carried out similarly with 20 mmol of lithium enolate and 20 mmol of zinc chloride in THF, and also yielded a glassy solid. Upon hydrolysis only (CH₃)₂CHCO-t-Bu was detected. The glassy material analysed as ClZnC₈H₁₅O·

TABLE 1
CRYSTAL DATA AND DETAILS OF THE STRUCTURE DETERMINATION

<i>Crystal data</i>	
Formula	C ₃₈ H ₆₈ O ₁₀ Zn ₄
Mol wt	646.4
Crystal system	monoclinic- <i>b</i>
Space group	No. 14, <i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.677(4)
<i>b</i> (Å)	18.299(9)
<i>c</i> (Å)	12.719(5)
β (°)	117.26(3)
<i>V</i> (Å ³)	2416(2)
<i>Z</i>	2 (dimers)
<i>D</i> _{calc} (g cm ⁻³)	1.301
<i>F</i> (000), electrons	992
μ(Cu- <i>K</i> _α) (cm ⁻¹)	24.28
Crystal size (mm)	0.15 × 0.35 × 0.35
<i>Data collection</i>	
θ _{min} , θ _{max} (°)	1.3, 50
Radiation (Å)	Cu- <i>K</i> _α (Ni-filtered), 1.5418
ω/2θ scan (°)	Δω = 0.6 + 0.14tanθ
Max time per refl. (s)	90
Horizontal and vertical aperture (mm)	2, 2
Distance to crystal (mm)	173
Reference reflections	1 - 3 - 2
Data set	<i>h</i> -11:11; <i>k</i> 0:18; <i>l</i> -12:0
Total data	1899
Observed data (<i>I</i> > 2.5σ(<i>I</i>))	1530
Total X-ray exposure time (h)	55.3
<i>Refinement</i>	
<i>NO</i> , <i>NV</i> , <i>S</i>	1530, 149, 4.54
<i>R</i> , <i>R</i> _w	0.146, 0.156
Weighting scheme	w ⁻¹ = σ ² (<i>F</i>) + 0.03 <i>F</i> ²
(Δ/σ) _{av}	0.2

THF, indicating that only one organic group was transferred to the zinc (Found: Zn, 21.31; Cl, 13.46; C, 46.83 and 46.94; H 7.70 and 7.90; O, 12.17; $C_{12}H_{23}ClO_2Zn$ calc: Zn, 21.79; Cl, 11.83; C, 48.04; H, 7.67 and O, 10.67%). Molecular weight determinations by ebulliometry in THF gave molecular weights of 363, 424, and 460 (at concentrations of 29, 53 and 70 mmol/l, respectively), corresponding to a degree of association of 1.3, 1.5, and 1.6, respectively.

Reaction of $LiOC(C_6H_5)=C(CH_3)_2$ with $ZnCl_2$

The reaction of 120 mmol of $LiOC(C_6H_5)=C(CH_3)_2$ with 60 mmol of $ZnCl_2$ was carried out as described above, and also yielded a glassy residue. A Beilstein test showed the presence of chlorine in the product mixture.

Data collection and structure determination for $[EtZnOMe \cdot Zn(Pac)_2]_2$

X-ray data were collected on an Enraf–Nonius CAD4 diffractometer for a poorly reflecting colourless crystal mounted under nitrogen in a Lindemann glass capillary. Details of the structure determination are given in Table 1. Unit cell parameters and standard deviations were determined in the usual way from the setting angles of 15 carefully-centered reflections [18]. The space group was determined as $P2_1/c$ from

TABLE 2.

FRACTIONAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	U or U_{eq}^a
Zn(1)	0.2275(3)	-0.0366(2)	0.0032(3)	0.084(2)
Zn(2)	0.0722(3)	0.0106(2)	0.1381(3)	0.077(1)
O(3)	-0.064(1)	0.0619(7)	-0.011(1)	0.067(4)
O(11)	0.234(1)	0.0439(8)	0.120(1)	0.070(4)
O(15)	0.111(1)	0.0958(9)	0.251(1)	0.083(5)
O(21)	-0.100(1)	-0.0174(8)	0.144(1)	0.071(4)
O(25)	0.162(1)	-0.0595(9)	0.272(1)	0.088(5)
C(3)	-0.044(3)	0.142(1)	-0.027(3)	0.104(9)
C(11)	0.427(2)	0.102(1)	0.152(2)	0.087(8)
C(12)	0.311(2)	0.093(1)	0.172(2)	0.069(7)
C(13)	0.303(2)	0.140(2)	0.256(2)	0.097(9)
C(14)	0.202(2)	0.137(1)	0.294(2)	0.082(7)
C(15)	0.210(3)	0.190(2)	0.390(3)	0.124(11)
C(16)	0.340(5)	0.194(3)	0.492(4)	0.231(22)
C(17)	0.107(4)	0.177(3)	0.424(4)	0.182(17)
C(18)	0.217(4)	0.270(2)	0.362(2)	0.210(19)
C(21)	-0.235(2)	-0.039(2)	0.230(3)	0.101(9)
C(22)	-0.100(2)	-0.042(1)	0.241(2)	0.078(7)
C(23)	0.004(2)	-0.069(1)	0.327(2)	0.080(7)
C(24)	0.125(2)	-0.080(1)	0.351(2)	0.077(7)
C(25)	0.230(3)	-0.119(2)	0.453(3)	0.123(11)
C(26)	0.189(4)	-0.146(2)	0.548(3)	0.172(15)
C(27)	0.352(4)	-0.070(2)	0.504(3)	0.158(14)
C(28)	0.279(4)	-0.182(2)	0.409(4)	0.172(16)
C(41)	-0.369(3)	0.095(2)	-0.029(3)	0.113(10)
C(42)	-0.431(3)	0.133(2)	-0.136(3)	0.154(13)

^a $U_{eq} = 1/3 \sum_i U_{ij} \cdot a_i^* \cdot a_j^* \cdot \bar{a}_i \cdot \bar{a}_j$.

TABLE 3

SELECTED DATA ON THE GEOMETRY OF $[\text{EtZnOMe} \cdot \text{Zn}(\text{Pac})_2]_2$ (Atoms related by the symmetry operation $-x, -y, -z$ are indicated with a prime)

<i>Bond distances (Å)</i>			
Zn(1)–O(11)	2.07(2)	Zn(1)–O(21)	2.04(2)
Zn(1)–O(3)	2.01(1)	Zn(1)–C(41)	1.87(3)
Zn(2)–O(11)	2.10(2)	Zn(2)–O(15)	2.02(2)
Zn(2)–O(21)	2.11(2)	Zn(2)–O(25)	2.00(2)
Zn(2)–O(3)	2.06(2)	Zn(2)–O(3')	2.06(1)
O(3)–C(3)	1.51(3)	C(41)–C(42)	1.39(6)
<i>Bond angles (°)</i>			
O(11)–Zn(1)–O(21)	94.8(6)	O(21)–Zn(1)–O(3)	80.9(6)
O(11)–Zn(1)–O(3)	81.7(6)	O(21)–Zn(1)–O(41)	131.2(13)
O(11)–Zn(1)–C(41)	122.8(12)	O(3)–Zn(1)–C(41)	130.1(12)
O(11)–Zn(2)–O(15)	86.2(7)	O(11)–Zn(2)–O(21')	175.1(6)
O(21')–Zn(2)–O(25)	87.2(7)	O(11)–Zn(2)–O(3)	79.6(6)
O(11)–Zn(2)–O(25)	97.7(7)	O(21')–Zn(2)–O(3)	99.6(6)
O(25)–Zn(2)–O(3)	94.2(7)	O(15)–Zn(2)–O(25)	91.9(7)
O(15)–Zn(2)–O(21')	94.1(7)	O(21')–Zn(2)–O(3')	78.2(6)
Zn(1)–O(11)–Zn(2)	97.7(6)	Zn(1)–O(21)–Zn(2')	99.2(7)
Zn(2)–O(3)–Zn(2')	99.7(6)	Zn(1)–C(41)–C(42)	118.7(29)
Zn(1)–O(3)–C(3)	116.1(13)	Zn(2)–O(3)–C(3)	118.0(16)
Zn(2')–O(3)–C(3)	117.7(14)		

observed systematic extinctions. A transformation of the monoclinic unit cell by (100/010/102) results in a *B*-centered lattice that is metrically orthorhombic. However, this symmetry was not confirmed by a corresponding Laue symmetry. The *A*-vector method [19] was applied to calculate Ψ -values that minimize the observed reflection splitting. The data were corrected for Lp but not for absorption. The structure was solved by standard Patterson and Fourier techniques, and refined on *F* by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions [C–H 1.08 Å, *U* 0.07 Å²] and refined with fixed geometry. The large thermal parameters of the *t*-Bu carbon atoms suggest the presence of some disorder in these groups, but this was not investigated further in view of the fairly poor quality of the data. Similar large thermal parameters were observed in $[\text{PhZnOPh} \cdot \text{Zn}(\text{Pac})_2]_2$ [13]. The refinement, with anisotropic thermal parameters for the Zn atoms and isotropic thermal parameters for the other non-hydrogen atoms, converged at $R = 0.15$ ($R_w = 0.16$) for 1530 observed reflections. Final positional parameters for the non-hydrogen atoms are given in Table 2, and selected parameters are listed in Table 3. Neutral atoms scattering factors were taken from ref. 20 and corrected for anomalous dispersion [21]. All calculations were carried out on the CYBER-175 of the University of Utrecht Computer Centre. Programs used include SHELX76 (structure refinement [22]) and PLATO (geometry calculation and analysis [23]) and PLUTO (molecule plotting program [23]).

Supplementary data (all positional and thermal parameters, a full list of bond distances, angles and torsion angles, and an $F(\text{obs}) - F(\text{calc})$ -listing, are available from the authors.

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References

- 1 J.J. Doney, R.G. Bergman and C.H. Heathcock, *J. Am. Chem. Soc.*, 107 (1985) 3724.
- 2 R. Amstutz, W.B. Schweizer, D. Seebach and J.D. Dunitz, *Helv. Chim. Acta*, 64 (1981) 2617.
- 3 P.G. Willard and G.B. Carpenter, *J. Am. Chem. Soc.*, 107 (1985) 3345.
- 4 W. Bauer and D. Seebach, *Helv. Chim. Acta*, 67 (1984) 1972.
- 5 L. Lochman, L. De Rajib and J. Trekoval, *J. Organomet. Chem.*, 156 (1978) 307.
- 6 R. Meyer, L. Gorrichon and P. Maroni, *J. Organomet. Chem.*, 129 (1977) C7; R. Meyer, L. Gorrichon-Gaigon and P. Maroni, *ibid.*, 188 (1980) 11; R. Meyer, L. Gorrichon, J. Bertrand and P. Maroni, *Organometallics Fonct. Ambidents, Recl. Commun., Colloq. Fr.-Bulg.*, (1980) 224.
- 7 A.G. Pinkus, J.E. Linberg and A.-B. Wu, *J. Chem. Soc., Chem. Commun.*, (1969) 1350; A.G. Pinkus, J.E. Linberg and A.-B. Wu, *ibid.*, (1970) 859; A.G. Pinkus and A.-B. Wu, *J. Org. Chem.*, 40 (1975) 2816.
- 8 J.A. Potenza, L. Zyontz, J. San Filippo Jr. and R.A. Lancette, *Acta Cryst.*, B34 (1978) 2624.
- 9 H.O. House, D.S. Crumrine, A.Y. Teranishi and H.D. Olmstead, *J. Am. Chem. Soc.*, 95 (1973) 3310.
- 10 M. Gaudemar and M. Martin, *C.R. Acad. Sci. Paris Ser. C*, 267 (1968) 1053.
- 11 E. Nakamura and I. Kuwajima, *J. Am. Chem. Soc.*, 106 (1984) 3368; E. Nakamura, J.-I. Shimuda and I. Kuwajima, *Organometallics*, 4 (1985) 641.
- 12 J. Dekker, J. Boersma and G.J.M. van der Kerk, *J. Chem. Soc., Chem. Commun.*, (1983) 553; J. Dekker, P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk and A.L. Spek, *Organometallics*, 3 (1984) 1403.
- 13 J. Boersma, A.L. Spek and J.G. Noltes, *J. Organomet. Chem.*, 81 (1974) 7.
- 14 J.C. de Souza Barbosa, C. Pétrier and J.L. Luche, *Tetrahedron Lett.*, (1985) 829.
- 15 M.F. Ansell, M.A. Davis, J.W. Humcock, W. Hickenbottom, P.G. Holton and A.A. Hyatt, *J. Chem. Soc.*, (1955) 2705.
- 16 C. Schmidt, *Ber. Deutsch. Chem. Gesell.*, 22 (1889) 3249.
- 17 G.E. Coates and D. Ridley, *J. Chem. Soc.*, (1965) 1870.
- 18 F.A.J.J. van Santvoort, H. Krabbendam, A.L. Spek and J. Boersma, *Inorg. Chem.*, 17 (1978) 338.
- 19 A.J.M. Duisenberg, *Acta Crystallogr. Sect A*, A39 (1983) 211.
- 20 D.T. Cromer and J.B. Mann, *Acta Crystallogr. Sect A*, A24 (1968) 321.
- 21 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
- 22 G.M. Sheldrick "SHELX-76, a program for crystal structure determination"; Cambridge, England, 1976.
- 23 A.L. Spek in D. Sayre (Ed.), *Computational Crystallography; The EUCLID-package* Clarendon Press, Oxford, 1982, p. 528.