ZINC AND CADMIUM

LITERATURE SURVEY COVERING THE YEAR 1980 [*]

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Contents

Introduction

This year, about fifty papers have appeared dealing with organozinc- and
organocadmium chemistry. Apart from the established research interests,
some new, interesting topics have emerged. The first, stable organozinc
compounds containing direct zinc-transition metal bonds have been
·rted. These compounds may have interesting catalytical properties
.ause of their dual-metal character. The chemistry of the zinc-hydrogen
bond is being developed and the first stable organo-zinc hydrides have
been prepared.
In the field of applications of organozinc compounds as intermediates, the
transition-metal catalyzed cross-coupling reaction of organo-zinc reagents

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[*] Previous review see J. Organometal. Chem., 207 (1981) 1 - 12.

with organic halides is growing into a very useful synthetic pathway
to complex conjugated olefines.
Two reviews dealing with the preparation and reactions of organozinc
compounds in organic synthesis have appeared [1,2].
The organometallic chemistry of zinc, together with that of the alka-
line-earth metals, has been reviewed [3].

I. Preparation of organozinc- and organocadmium compounds

Di[tris(trimethylsilyl)methyl]-zinc and -cadmium have been prepared
from the metal halides and the corresponding lithium compound [4]. Both
compounds are extremely thermally stable, decomposing only above 300°C,
and are unusually unreactive. They can be handled in air and do not react
with reagents like bromine in boiling carbontetrachloride. Their most
striking property is their ability to withstand boiling aqueous THF. The
zinc compound can even be steam-distilled unchanged. The hydrolytic
stability is associated with the presence of the third trimethylsilyl
groups, di[bis(trimethylsilyl)methyl]-zinc and -cadmium being both readily
hydrolyzed and oxidized. No reason for this extraordinary behaviour has
been given.
Bushnell and Stobart have determined the crystal and molecular structure
of the curious adduct of di[trimethylsilylmethyl]cadmium with 2,2'-bipy-
ridyl (cf. A.S. 1978, p.4)[5]. The crystal structure of this complex, which
has the composition $(Me_3SiCH)_2Cd.1.5$ Bipy, appears to consist of normal
1:1 complex molecules with intercalating, non-bonded Bipy molecules. The
long (253 pm) cadmium-nitrogen bond lengths and the small (65°) N-Cd-N
angle suggest only weak coordinate bonding. This also agrees with the
C-Cd-C angle of 156°, which indicates that the coordination geometry
around cadmium is closely related to a linear cadmium dialkyl.
The perfluoroalkylzinc compound $(CF_3)_2Zn$, for which ^{19}F-NMR evidence was
given by Liu last year (cf. A.S. 1979, p.3), has been isolated as its
pyridine complex [6]. The complex was prepared in 82% yield by reacting
bis(trifluoromethyl)mercury with dimethylzinc in pyridine and evaporating
the volatile materials:

$$(CF_3)_2Hg + Me_2Zn \xrightarrow{Py} (CF_3)_2Zn + Me_2Hg$$

$$82\%$$
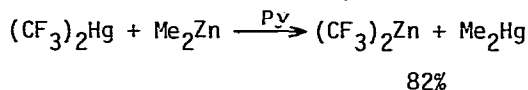
The dimethoxyethane complex of bis(trifluoromethyl)cadmium, $(CF_3)_2Cd.DME$ (I), has been isolated from the reactions between bis(trifluoromethyl)mercury and dimethylcadmium in dimethoxyethane [7]. Colourless, solid (I), which is air stable, was found to be by far the most convenient reagent known for the preparation of trifluoro-methyl-substituted metal compounds (cf. Section II D). In the presence of aryl halides, (I) acts as a low-temperature source of difluorocarbene (cf. Section II B).

According to Thiele and co-workers, diarylzinc compounds prepared from zinc chloride and aryl Grignards using literature procedures, contain appreciable amounts of diarylmagnesium compounds as impurities [8]. When e.g. benzylmagnesium chloride is reacted with zinc chloride in 3:1 molar ratio, the dibenzylzinc obtained after precipitation of the magnesium salts with 1,4-dioxane, contains up to 30 mole % of dibenzylmagnesium. This is caused, according to the authors, through a shift in the Schlenk equilibrium

$$2 \ C_6H_5CH_2 \ MgCl \ \rightleftharpoons \ (C_6H_5CH_2)_2Mg + MgCl_2$$
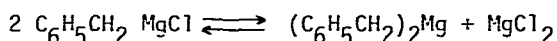
by dioxane, the dibenzylmagnesium formed co-precipitating along with the dibenzylzinc. The latter compound can be obtained magnesium-free by reacting the impure product with sufficient zinc chloride in a second step to convert the dibenzylmagnesium completely into dibenzylzinc. In this way, a series of substituted dibenzylzinc compounds have been pre-pared in pure form. The UV-VIS absorption spectra of the Bipy complexes have been recorded and the positions of the charge-transfer bands in these spectra have been correlated with the electronegativities of the substituent atoms or groups.

Bis(dienyl)zinc compounds (II-VI) have been prepared by metal-exchange reactions and isolated as crystalline TMEDA complexes [9].
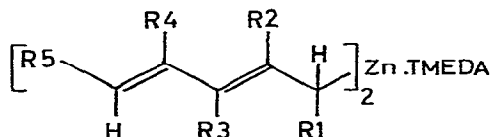
II: R_{1-6}=H; III, R_3=Me, $R_{1,2,4,5}$=H; IV, R_4=Me, $R_{1,2,3,5}$=H;

V, R_5=Me, $R_{1,2,3,4}$=H; VI, $R_{2,4}$=Me, $R_{1,3,5}$=H

II-VI are monomeric in benzene and are thermolabile. Bis(pentadienyl)
zinc.TMEDA (II) exists as a mixture of (E) and (Z)isomers in a 4:1
ratio, but pentadienylzinc chloride.TMEDA has only the (E) structure
in solution below 80°. A crystal structure determination of the latter
compound shows that the pentadienyl group is σ-bonded to zinc by the
terminal carbon atom and has the 5-trans(E) conformation. Rapid 1,5-
metallotropic rearrangement was detected for bis(2,4-dimethylpentadie-
nyl)zinc (VI):
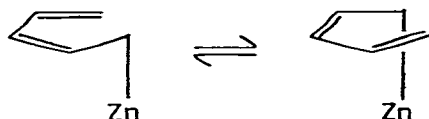
The absence of a corresponding 1,3-shift has been interpreted in terms
of the unimportance of ionic character and d orbital participation in
the zinc-dienyl bond.

The electrochemical synthesis method developed by Tuck and co-workers
(cf. A.S. 1979 p.2), has been extended to the preparation of neutral
and anionic organozinc halides [10]. Also arylzinc halides which hitherto
could not be obtained from the corresponding aryl halides and zinc,
are accessible via this route. The organozinc halides have been iso-
lated as their Bipy complexes. Tha anionic species $RZnX_2^{\ominus}$ have tetra-
-n-propylammonium cations as counter ions.

A Ph.D. thesis dealing with the electrochemical synthesis of selected
group IIB organometallic compounds has appeared [11].

In continuation of their work on dialkylaminopropylzinc compounds,
Thiele and co-workers have prepared dimeric N,N-dialkylaminopropylzinc
chlorides from zinc chloride and the corresponding lithium compounds [12]:

$$R_2N(CH_2)_3Li + ZnCl_2 \xrightarrow{\text{Et}_2O} R_2N(CH_2)_3ZnCl$$
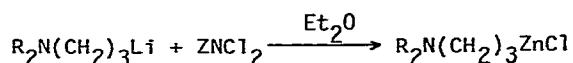
R=Me,Et

These organozinc halides are involatile, weakly oxidation-sensitive,
rather insoluble solids and do not interact with esters and methyliodide.
They have been formulated as chlorine-bridged dimers:
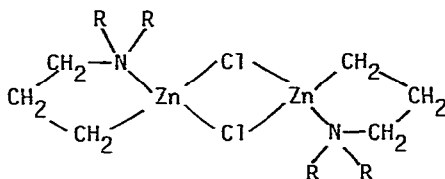
Organozinc hydride complexes containing pyridine as ligands, have been prepared by the reaction of zinc hydride with diethylzinc or diphenylzinc in pyridine [13]:
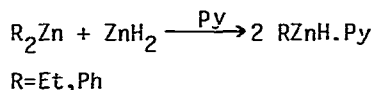
$$R_2Zn + ZnH_2 \xrightarrow{Py} 2\ RZnH.Py$$

$$R=Et,Ph$$

Alternatively, the compounds are formed when pre-formed pyridine complexes of the parent diorganozinc compounds are reacted with zinc hydride. The complexes have been characterized by ^{1}H- and ^{13}C-NMR and IR spectroscopy and appear to be associated into trimeric species in benzene. The authors have proposed the following structure for the trimers:

R= Et or Ph
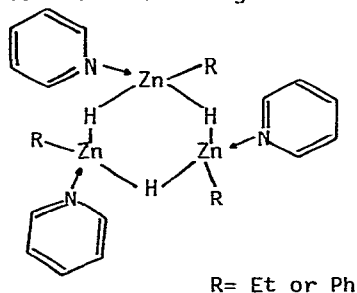
Upon reaction with TMEDA, the corresponding TMEDA complexes are formed which, however, tend to disproportionate, e.g.:

$$(PhZnH)_2TMEDA \rightleftharpoons Ph_2Zn_3H_4.TMEDA + Ph_2Zn.TMEDA$$
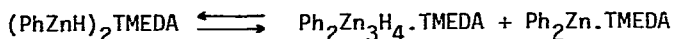
Similar reactions with methoxy- or dimethylamino-substituted dialkylzinc compounds show that also in those cases organozinc hydrides are formed, but these dissociate to varying degrees depending on the donor strength of the substituent group.

Like zinc hydride itself, organozinc hydrides reduce pyridine and
carbonyl derivatives, but do not show unusual stereoselectivities in
these reductions.

In a preliminary communication, Budzelaar and co-workers have reported
on the first examples of stable organozinc compounds containing direct
zinc-transition metal bonds [14]. Whereas simple alkyl- or arylzinc com-
pounds of this type disproportionate completely or nearly so into
symmetric species:

$$2 \; RZnTM \longrightarrow R_2Zn + Zn(Tm)_2$$
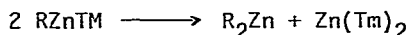
cyclopentadienylzinc derivatives are completely stable in this respect.
The transition-metal derivatives have been prepared via two alternative
routes:

$\underline{1}$. $Cp_2Zn + TmH \longrightarrow CpZnTm + CpH$

$\underline{2}$. $Cp_2Zn + Zn(Tm)_2 \longrightarrow 2 \; CpZnTm$
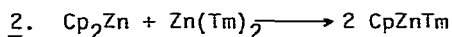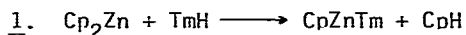
$Tm= -Mn(CO)_5, -Co(CO)_4, -CpMO(CO)_3, -CpFe(CO)_2, -CpCr(CO)_2; Cp_2W<, Cp_2Mo<$

Thermally stable complexes of zinc- and cadmium chloride with alkylidene-
triphenylphosphoranes (VII) have been prepared by Yamamoto and Sugimoto [15]:

$$2 \; Ph_3P=CH-R + MCl_2 \longrightarrow [Ph_3\overset{\oplus}{P}-\overset{\overset{\displaystyle R}{|}}{C}H-M-\overset{\overset{\displaystyle R}{|}}{C}H-\overset{\oplus}{P}Ph_3].2Cl^{\ominus} \quad VII$$
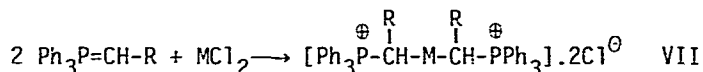
R= H,Me,i-Pr; M= Zn,Cd.

The presence of a sp-hybridized metal-carbon bond in the cadmium complex
VII (R= H; M= Cd) was indicated by the observation of a large J_{H-C-Cd}
coupling constant. With the exception of VII (R=H; M=Zn,Cd) all complexes
are insoluble in organic solvents.

Boranatobis(dimethylphosphoniummethylide) complexes of zinc and cadmium
have been obtained from the reactions of the metal chlorides with the
lithium derivative of the ylide [16].

II. Reactions of organozinc and organocadmium compounds

A. The Reformatsky reaction and related reactions.

Lucas and Guette have compared the asymmetric induction and selectivity in the Reformatsky reaction of α-bromoesters with α-aminoketones, with those observed earlier in reactions with β-aminoketones [17].

$$RCHBrCOOMe + PhCOCH_2NR_2^1 \xrightarrow[\text{2)H}_2\text{O}]{\text{1)Zn}}$$
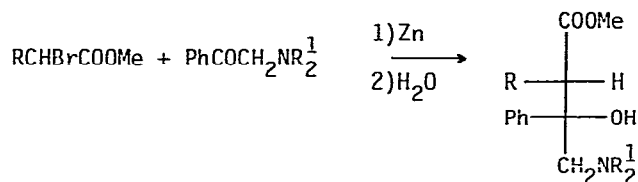
R= Me,Et,i.Pr,t.Bu

NR_2^1 = piperidino, morpholino,·dimethylamino

In both cases, the kinetically controlled products predominate. The stereo-selectivity attains a maximum for R=i.Pr and increases with increasing nucleophilicity of the amino group (Me_2N > piperidino >morpholino). The stereoselectivity in the reactions with α-aminoketones is less than in those with β-aminoketones. The authors assume that a cyclic transition state occurs, the stability of which is discussed in terms of the nature of chelation, the steric interaction between various groups, and the donor capacity of the amino group.

When azirines (VIII) were reacted with α-bromoesters and zinc, diastereo-meric pairs (IX) were formed which were cyclized by reaction with HF in pyridine to give the aminolactones (X) [18]:
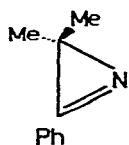
VIII
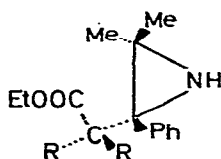
a: R=H, R^1=Me
b: R=Me, R^1=H

IX

a: R=H, R^1=Me
b: R=Me, R^1=H

X

The stereochemistry and the mechanism of these reactions have been discussed.

The ^{14}C-labelled butyrolactones (XI) and (XII) have been prepared by the Reformatsky reaction of the ^{14}C-labelled bromoacrylates (XIII) and (XIV) with acetone and cyclohexanone [19]:

$CH_2=C(^{14}CH_2Br)COOEt$ (XIII) $\longrightarrow$

$^{14}CH_2=C(CH_2Br)COOEt$ (XIV) $\longrightarrow$

R,R= Me; Cyclohexyl

In a new approach to the synthesis of 3β, 23-diacetoxy-24-nor-5-cholane from 3β, 21-diacetoxy-5-pregnen-20-one (XV), the Reformatsky reaction of (XV) with ethylbromoacetate was used to prepare lactones of the type (XVI) [20].

$BrZnCH_2COOEt$

(XV)

R^1=H, acetyl.

(XVI)

Bogavac and co-workers have developed a new and easy synthesis of β-hydroxy acids using the readily accessible tetrahydropyranyl esters of α-bromoacids as starting materials in Reformatsky reactions [21]. The reactions are best carried out in THF at low (< 0°) temperatures. Under these conditions, yields of 65-91% were obtained in reactions with various aldehydes. It is not necessary to use activated zinc, in fact the use of zinc/copper couple

appears to be ineffective in cold THF. In all cases studied, the
acid hydrolysis of the product β-hydroxyesters of tetrahydropyran
went very easily and under mild conditions.

2,2-Dimethyl-4-hydroxy-4-carbethoxymethyltetrahydropyran (XVII) has
been obtained from the Reformatsky reaction of the corresponding
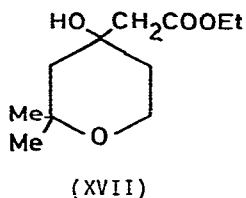dimethylpyranone [22].

(XVII)

B. Carbenoid reactions

The dimethoxyethane complex of bis(trifluoromethyl)cadmium has been
found to be an efficient low-temperature source of difluorocarbene
in the presence of acyl halides [23]. This is illustrated by the formation
of the difluorocyclopropane derivative (XVIII) from the reaction with
2,3-dimethyl-2-butene in the presence of acetylbromide:

(XVIII)
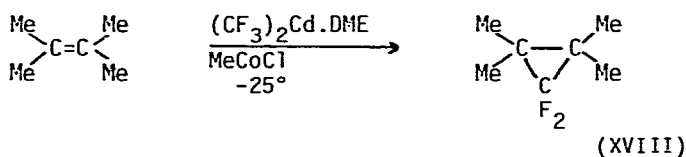
Isomeric 3-hydroxy-4,5-cyclopropano derivatives of 19-hydroxycholestane
have been prepared by the Simmons-Smith reaction from the epimeric alco-
hols (XIX) and (XX) [24]. It appeared that in both cases the stereochemistry
of the addition was directed by the configuration of the hydroxyl group at
C (3):

The Simmons-Smith reaction of the allylic hydroxylated α,β-unsaturated ·
ester (XXI) yielded both the cyclopropanation product (XXII) and the
ether (XXIII), illustrating the dual character of the reagent in the
reaction with a hydroxylated olefine [25]:

$$n \; C_{11}H_{23}\text{-CHOH-CH=CH-CH}_2\text{-COOMe} \qquad (XXI)$$

$$\downarrow CH_2I_2/Zn/Cu$$

$$n \; C_{11}H_{23}\text{-CHOMe-}\underset{\underset{CH_2}{\diagdown \diagup}}{CH}\text{-}CH\text{-CH}_2\text{-COOMe} \qquad\qquad n \; C_{11}H_{23}\text{-CHOH-}\underset{\underset{CH_2}{\diagdown \diagup}}{CH}\text{-}CH\text{-CH}_2\text{-COOMe}$$

$$70\% \; (XXIII) \qquad\qquad\qquad\qquad 20\% \; (XXII)$$

The Simmons-Smith methylenation of scillarenin has been used in the first
step of the synthesis of 4,5-methanobufadienolides [26].

C. Reaction of alkenyl- and alkynylzinc compounds

L. Miginiac and co-workers have made a systematic study of the best methods
of preparing β-acetylenic, α-allenic, and β-ethylenic tertiary amines using
various organometallic reagents including alkynyl- and alkenylzinc deriva-
tives [27]. In several cases, the organozinc reagents were found to be good
alternatives for organolithium,-magnesium, or -aluminiun reagents. However,
in no case the zinc reagents offer decisive advantages over the other
reagents.
The regioselectivity of the addition of bis(2-methallyl)zinc to para- and
meta-substituted styrenes has been investigated by Lehmkuhl and McLane [28].
It was found that electron-donating substituents (OMe, Me) enhance metal
attack on the primary carbon atom, whereas electon-withdrawing substituents
(halogens, CF_3) favour metal attack on the secondary carbon atom:

X= OMe, Me   X= halogen, CF_3

A linear relation was found between log $(M \rightarrow C_{prim.} / M \rightarrow C_{sec})$ and the Hammett σ constants of the substituent atoms or groups.

The palladium-catalyzed coupling reaction of alkylzinc halides with alkenyl halides has been used to effect substitution on the β-carbon atom of α,β-unsaturated carbonyl derivatives [29]:
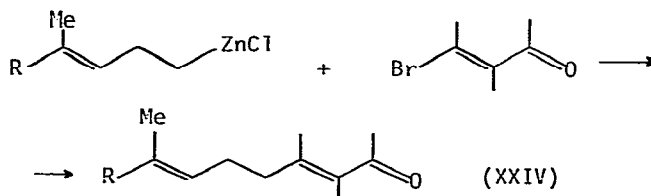

(XXIV)

This reaction, which proceeds with > 98% stereoselectivity, has been applied to the synthesis of butenolides and furans of terpenoid origin such as mokupalide (XXIV) and dendrolasin (XXV)

(XXV)
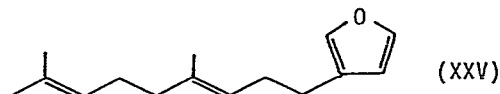
Also the reaction conditions necessary to convert homoallylic bromides stereospecifically (> 98%) into the corresponding organozinc starting materials, have been described.

Gaudemar and co-workers have examined the stereochemistry of the reactions of Schiff bases with various allylic organometallic compounds, including allylzinc bromides [30]. The reactions yield mixtures of erythro- and threo-products:

$PhCH=NR + R^1CH=CHCH_2ZnBr \longrightarrow$

R= Me,Et,iPr,iBu,Ph

R^1= Me,Pr
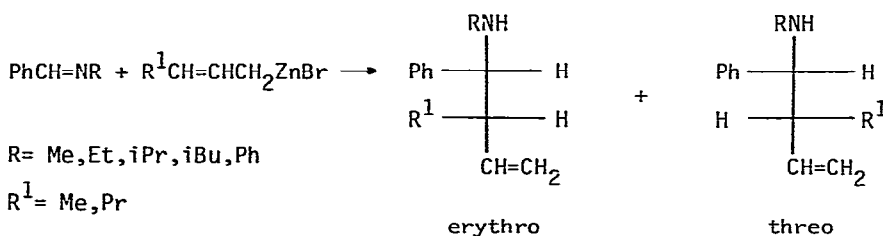
erythro   threo

It was shown that the erythro form was favoured in reactions with Schiff bases containing a small R-substituent group. Independent of the nature of the metal or the aldimine, the proportion of threo product decreases as R^1 goes from methyl to propyl. The reaction mechanism and the possible transition state were discussed.

D. Miscellaneous reactions of organozinc and organocadmium compounds

Dialkyl- and diarylzinc compounds, in particular dimethylzinc, were
found to be attractive reagents in the alkylation or arylation of
tertiary alkyl halides [31]. The nature of the solvent in these reactions
appears to be of prime importance, methylene chloride giving the best
results, e.g.:

quantitative yield
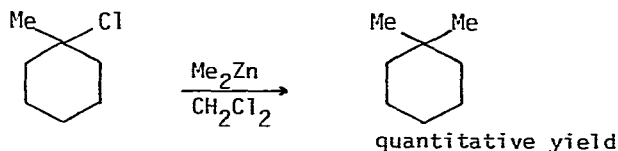
With other dialkylzinc compounds, these reactions give generally less
satisfactory results, reduction of the tertiary halide by hydride
abstraction occurring as a side-reaction. The ready availability of
dimethylzinc and the high positional specificity are claimed as the main
advantages of this reaction system.

Dimethylzinc has been used successfully in the preparation of molybdenum
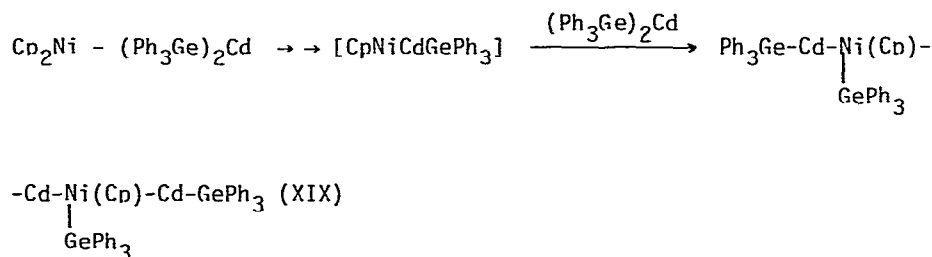and tungsten complexes containing methyl- and imido ligands bound to
the same metal atom [32]:

$$2(tBuN)_2M(OR)_2 + 4Me_2Zn \rightarrow [(tBuN)_2MMe_2]_2 \ (XXVI) + 4MeZnOR$$
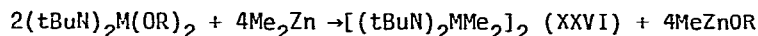
M= Mo,W

In a similar reaction, i.e. that of diphenylzinc with $(tBuN)_2Cr(OSiMe_3)_2$,
$PhZnOSiMe_3$ was formed, but no complexes analogous to (XXVI) were found.
Instead, monophenylation seems to occur to give an intermediate (XXVII)
which can either undergo phenyl-migration to the imido-nitrogen, or may
react further with diphenylzinc to the expected diphenyl chromium
derivative which then reductively eliminates biphenyl:
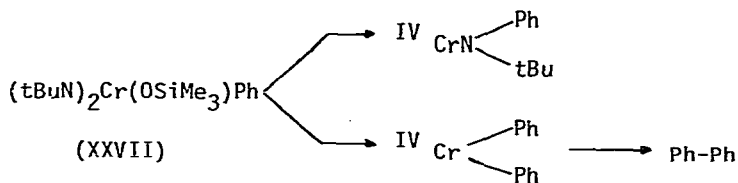
The reaction of bis(triphenylgermyl)cadmium with nickelocene was
found to proceed via the displacement of a cyclopentadienyl group
from the nickelocene to give intermediate (XXVIII), containing bivalent
coordinatively unsaturated nickel [33]. (XXVIII) Is supposed to insert
into the Cd-Ge bonds of initial $(Ph_3Ge)_2Cd$ to give the final product
(XIX):

$$Cp_2Ni - (Ph_3Ge)_2Cd \rightarrow \rightarrow [CpNiCdGePh_3] \xrightarrow{(Ph_3Ge)_2Cd} Ph_3Ge-Cd-\underset{\underset{GePh_3}{|}}{Ni}(Cp)-$$

$$-Cd-\underset{\underset{GePh_3}{|}}{Ni}(Cp)-Cd-GePh_3 \quad (XIX)$$

An X-ray analysis of (XIX) has been carried out. The compound contains
the longest known polymetallic chain, consisting of seven metal atoms
with branching at the Ni atoms to include nine metal atoms in all.
In a preliminary study on the reactions of diphenylcadmium with diborane,
Bullen and co-workers have shown that mixtures of triphenylboron and
monophenylboron compounds are formed [34]. The triphenylboron can be isolated
as a complex with pyridine or triphenylphosphine and the monophenylboron
species as phenylboronic acid after hydrolysis. The relative proportions
of both product types appears to depend markedly on the method of formation
of the phenylcadmium.
The dimethoxyethane complex of bis(trifluoromethyl)cadmium, $(CF_3)_2Cd.DME$,
was found to be by far the most convenient reagent known for the preparation
of trifluoromethyl-substituted metal compounds [23]. E.g. the reaction of
this complex with SnI_4 yields $(CF_3)_4Sn$ in 66% yield at room temperature in
minutes.
Courtois and Miginiac have shown that the addition of di-t-butylzinc to the
triple bond of a conjugated enyne in refluxing THF proceeds regioselectively,
but not stereoselectively [35]. This contrasts with the corresponding reactions
in boiling diethylether, which proceed both regio- and stereoselectively.
The formation of two, three, or all four stereoisomeric dienes is observed.
The authors assume, that initially two stereoisomeric organozinc intermediates
 form which equilibrate via an α-allenic intermediate:
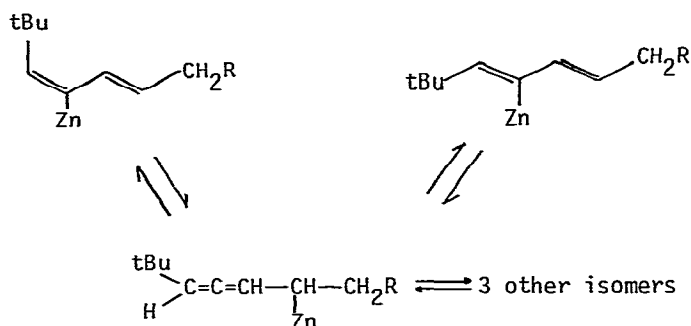
When group R contains a potential donor atom or group, like oxygen or
nitrogen, intramolecular chelation will shift the equilibria, thus
accounting for the preferential formation of certain product isomers
in these cases.

The reactions of ethylene oxide with various ethylzinc and ethylcadmium
alkoxides have ben investigated [36]. Whereas EtZnOSiPh$_3$, EtCdOSiPh$_3$ and
EtCdOCPh$_3$ react via the metal-carbon bond, EtZnOCPh$_3$ reacts both via the
metal-carbon and the metal-oxygen bond.

The protonolysis of diethylzinc with dialkyl- or diarylboric acids in
toluene at room temperature has been found to afford compounds (XX) [37].

$$Et_2Zn + R_2BOH \rightarrow EtZnOBR_2$$

(XX)
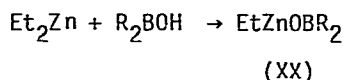
R= Bu, α-naphtyl

Selective mono-alkylation and -arylation of aromatic dihalides containing
the same halogen atoms, has been achieved by the palladium-catalyzed cross-
-coupling reaction with Grignard and organozinc reagents [38].
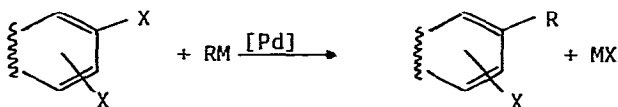

X= Cl, Br; M= MgX, ZnX; R= Ph, PhCH$_2$ (M= ZnX)

In most cases, yields range from 50-75% and di-substituted products are
formed only in small amounts. Although in most cases both magnesium and
zinc reagents gave comparable results, benzylzinc chloride was superior

in the mono-benzylation reaction. Also heterocyclic dihalides undergo
these reactions with fairly good selectivity. The successfull use of a
palladium catalyst has been attributed to the fact that the produced
monoalkylated monohaloaromatics are replaced from the coordination site
faster by another substrate molecule than further oxidative addition
of the former to a catalytically active palladium species.

The palladium-catalyzed cross-coupling reaction of homoallylic or
homopropargylic zinc halides, which was mentioned already in Section II C,
is a new selective route to 1,5 dienes and 1,5 enynes [39]:
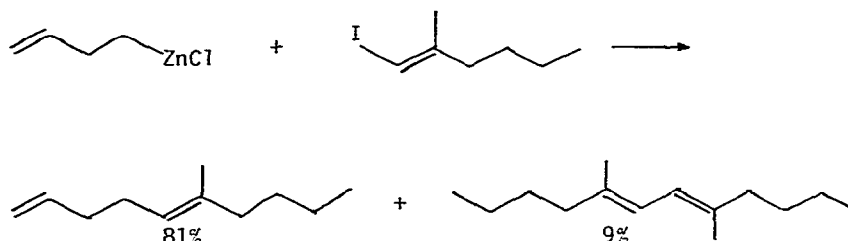
Despite the presence of allylic or propargylic β-hydrogens, the extent of
β-elimination was less than 1-2%. The synthetic utility of this procedure
has been illustrated by the synthesis of (E,E) farnesol and a precursor
of mokupalide.

Lapkin and co-workers have prepared aromatic ketones (XXI) by condensing
aldehydes with organozinc reagents [40]:

$$PhCOCMe_2ZnBr \xrightarrow[2)H_2O]{1)RCHO} PhCHOCMe_2CHROH$$
$$(XXI)$$
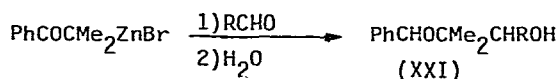
R= Ph, 2,3-, and 4-ClC$_6$H$_4$, 2,4-Cl$_2$C$_6$H$_3$, 3- and 4-BrC$_6$H$_4$, CCl$_3$, 2-thienyl,
2-thienylethyl

Both diethylzinc and diethylcadmium were found to react with bifunctional
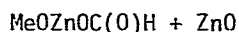phenols to yield ethane and metal alkoxides [41].
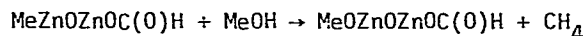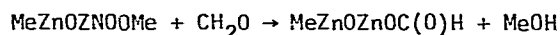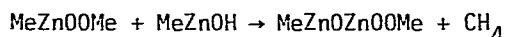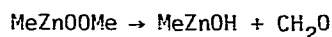
$$Et_2M + R(OH)_2 \rightarrow (RO)_2M + EtH$$
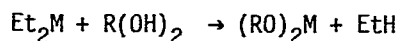
M= Zn,Cd; R(OH)$_2$= O-dihydroxy benzene, 2,2^1-dihydroxybiphenyl, 2,2^1-dihydroxy-
-1,1^1-binaphtyl

The reaction products form complexes with Bipy.

The reaction of 2-(perfluorohexyl)ethyl iodide with zinc/copper couple was found to yield the corresponding organozinc iodide, which reacts with SO_2, followed by hydrolysis, to give the thiosulphonate $CF_3(CF_2)_5CH_2CH_2SO_2SCH_2CH_2(CF_2)_5CF_3$ [42].

Alexandrov and co-authors have made a detailed investigation into the thermal decomposition of the organozinc- and organocadmium peroxides methyl(methylperoxy)zinc (XXII), methyl(tert-butylperoxy)zinc (XXIII), and methyl(tert-butylperoxy)cadmium (XXIV) [43].

The decomposition occurs heterolytically without free-radical formation and in case of (XXII) has been formulated as follows:

$MeZnOOMe \rightarrow MeZnOH + CH_2O$

$MeZnOOMe + MeZnOH \rightarrow MeZnOZnOOMe + CH_4$

$MeZnOZnOOMe + CH_2O \rightarrow MeZnOZnOC(O)H + MeOH$

$MeZnOZnOC(O)H + MeOH \rightarrow MeOZnOZnOC(O)H + CH_4$

$$MeOZnOC(O)H + ZnO$$

The selectivity of these reactions has been explained in terms of decomposition occurring in association complexes via a concerted mechanism (XXII was found to be a tetramer im benzene solution). These results invalidate earlier beliefs that decomposition reactions of this type occur via intramolecular rearrangements or interaction with initial dialkyl-metal compounds.

The same group has found that the autoxidation of diphenylcadmium proceeds via initial formation of a 2:1 diphenylcadmium/oxygen complex [44]. This complex is unstable and decomposes mainly into phenylcadmium phenoxide PhCdOPh.

The oxidation of diethylzinc has been used to grow highly oriented zinc oxide films [45].

III. Organozinc compounds as polymerization catalysts

The group around T. Tsuruta has investigated the mechanism of the stereoselective polymerization of methyloxirane (propylene oxide) in the presence of a single crystal of the enantiomorphic dicubic zinc complex $Zn(OMe)_2 \cdot (EtZnOMe)_6$ [46,47]. The proposed mechanism starts with the loosening

of a zinc-oxygen coordinate bond in the complex, followed by coordination
of an oxirane molecule to the resulting coordinatively unsaturated central
zinc atom. This coordination site is enantiomorphic and will preferentially
accept L- or D-monomer depending on which cube the bond-loosening occurred.
The oxirane ring of the coordinated monomer will then be cleaved by nucleo-
philic attack of an inner methoxy group in the complex. There should be
equal numbers of each enantiomer in the polymer since there are equal chan-
ces of bond loosening in each cube.

Effective catalysts for the copolymerization of methyloxirane with carbon
dioxide have been made by reacting diethylzinc with partially O-methylated
or diisocyanate-crosslinked poly(p-hydroxystyrene) [48]. The most active cata-
lysts had degrees of O-methylation or cross-linking of 30-40%. The cross-
-linking, resulting in high rigidity of the catalyst structure, increased
the yield of polymer by preventing inactivation of the catalyst.

The S-isomer of racemic methylthiirane has been polymerized preferentially
with nearly perfect stereoselectivity in the presence of a catalyst formed
by reacting diethylzinc with S-(-)-2,2'-dihydroxy-1,1-binaphtyl [49]. At
50% conversion, the unreacted monomer had an optical purity of 85%. The
chloroform-soluble product fraction obtained at -33% had the S-configuration.
The toluene-soluble fraction had an optical purity of 85%.

The lewis acidity of catalysts of the type EtZnR (R= Et, MeO, AcO, 2- and
3-MeOC$_6$H$_4$, and MeOCH=COMe) has been shown to influence the monomer distribu-
tion in maleic anhydride-methyloxirane copolymers [50]. An increase in the
acidity of the zinc favours the formation of a copolymer with a low degree
Of alternation, the incorporation of more oxirane units, and a lower average
number-averaged molecular weight.

Contrary to the Et$_3$Al/POCl$_3$ system, the Et$_2$Zn/POCl$_3$ system did not lead to
a stereoregular homopolymer in the cationic polymerization of isobutylvinyl-
ether and N-vinylcarbazate at ambient temperatures or lower [51]. The rate of
catalysis has been shown to be first order in both components up to a molar
ratio of one, and it decreased thereafter. At a fixed Et$_2$Zn/POCl$_3$ ratio, the
polymerization was second order in substrate. A cationic mechanism has been
proposed.

IV Physical and spectroscopic studies

Vibrational frequencies and modes of diethylzinc have been calculated by
means of a modified valence-force field derived from vibrational spectra of

dimethylzinc and perdeuterodimethylzinc [52]. The calculated frequencies were compared with IR and Raman Spectra of diethylzinc.

The IR spectra of the C-H stretch region of $(CHD_2)_{0.5} (CD_3)_{1.5}$ M (M= Zn, Cd, Hg) have been recorded and the isolated C-H stretching frequencies have been derived [53]. These frequencies were used to predict values of r_0 CH and new geometries of these molecules were based on these.

The full paper on the crystal- and molecular structure of tetrameric methylzinc methoxide, which was published in preliminary form in 1966, has appeared [54]. The tetramer consists of two interpenetrating tetrahedra of zinc and oxygen, which are regular within the limits of experimental error. The variations found in the O-Zn-C angles were attributed to short intermolecular contacts. The symmetry of the molecule has been discussed and it was shown that it very closely conforms to $\bar{4}3$ m.

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