ZINC AND CADMIUM

LITERATURE SURVEY COVERING THE YEAR 1977

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Contents

Introduction

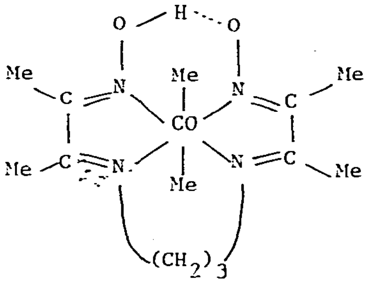
The number of papers dealing with organozinc- and organocadmium chemistry which appeared in 1977 is very nearly the same as that in 1976, confirming the stabilization of research in this area mentioned last year. No significant shifts in interest for the various topics studied can be observed, with the exception of the area of organozinc hydride chemistry where research starts getting fruitful.

Zinc and cadmium, Literature survey covering the year 1976 see J. Organometal. Chem., Vol. 147 (1978) 1-16.

I. Preparation of organozinc and organocadmium compounds

Thiele and co-workers investigated the synthesis and structure of two diorganozinc chelates, i.e., bis-4-methoxybutylzinc, $[MeO(CH_2)_4]_2Zn$, and bis-3-ethylmercaptopropylzinc, $[EtS(CH_2)_3]_2Zn$[1]. Both compounds, which were prepared using the Grignard procedure, are monomeric in benzene. Although some properties of these compounds indicate the presence of intramolecular chelate rings - absence of complexation with ether, mass spectral data - the authors propose open-chain structures containing only minor amounts of chelate rings on the basis of IR spectral data.

Witman and Weber continued their work on the methylation of group IIB metals by the trans-dimethylcobalt complex $Me_2Co(BDM1,3\ pn)$(I)[2].



I

When (I) is reacted in a 2 : 1 ratio with Zn^{2+} and Cd^{2+} ions, a two-step reaction occurs in which an initial fast reaction is followed by a second slower one. In the initial step CH_3M^+ intermediates are formed which in the second step react with a second mole of (I) to give $(CH_3)_2M$ species:

$$(CH_3)_2Co(BDM\ 1{,}3pn) + M^{2+} \xrightarrow{fast} CH_3Co(BDM\ 1{,}3pn)^+ + CH_3M^+$$

$$(CH_3)_2Co(BDM\ 1{,}3pn) + CH_3M^+ \xrightarrow{slow} CH_3Co(BDM\ 1{,}3pn) + (CH_3)_2M$$

In the case of Zn^{2+}, protolysis of CH_3Zn^+ by solvent isopropanol competes with the second reaction and the overall reaction is catalytic in the sense that Zn^{2+} is regenerated to react further with (I).
In the case of Cd^{2+}, $[CH_3Cd(iC_3H_7O)]_4$ was isolated in low yield.
The first stable organozinc hydride, $PhZn_2H_3{\cdot}THF$(II) was obtained by reacting $LiAlH_4$ with Ph_2Zn in 3 : 8 molar ratio in THF[3]:

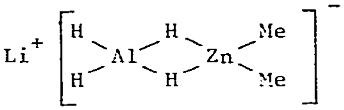
$$3LiAlH_4 + 8\ Ph_2Zn \xrightarrow{THF} 4\ PhZn_2H_3 + 3\ LiAlPh_4$$

(II)

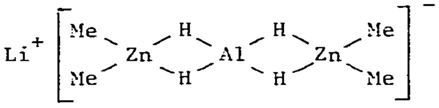
(II) decomposes only at 120° with evolution of hydrogen and benzene. It was characterized by IR spectroscopy and its X-ray powder diffraction pattern.

In a serie of four papers, Ashby and Watkins described the nature of the alkyl-hydrogen exchange reactions involving aluminium and zinc [4,5,6,7].

When AlH_3 is reacted with $LiZn(Me)_2H$ and $LiZn_2(Me)_4H$ in 1 : 1 ratio in THF, $LiZnMe_2AlH_4$(III) and $LiZn_2Me_4AlH_4$(IV) are formed as soluble complexes[4]. The following structures, based on IR spectral data and association measurements, were proposed for (III) and (IV):



III



IV

Reaction schemes for the formation of (III) and (IV) are discussed. It was shown, that (III) and (IV) can also be prepared by reacting $LiAlH_4$ with Me_2Zn in 1 : 1 and 1 : 2 ratio in THF[5].

$$2Me_2Zn + LiAlH_4 \rightleftharpoons LiZn_2Me_4AlH_4$$

$$Me_2Zn + LiAlH_4 \rightleftharpoons LiZnMe_2AlH_4$$

Reversing the order of addition did not change the outcome of these reactions. (III) and (IV) can be converted into each other by the addition of $LiAlH_4$ to (IV) (⟶ (III)) or Me_2Zn to (III) (⟶ (IV)). A mobile equilibrium exists between these two species.

When $LiAlH_4$ and Me_2Zn were reacted in diethylether instead of THF, the course of the reaction was found to be dependent on the order of addition, the ratio, and the concentration of the reactants[6]. When Me_2Zn is added to $LiAlH_4$ in ether, solid ZnH_2 is formed in all cases, no matter which stoichiometry is used. On the other hand, when the order of addition is reversed, the following reactions occur:

2 : 1 ratio: $2Me_2Zn + LiAlH_4 \longrightarrow LiZn_2Me_4AlH_4$

1 : 1 ratio: $Me_2Zn + LiAlH_4 \longrightarrow (LiZnMe_2AlH_4) \longrightarrow LiZnH_3 + ZnH_2$

1 : 2 ratio: $Me_2Zn + 2LiAlH_4 \longrightarrow ZnH_2$

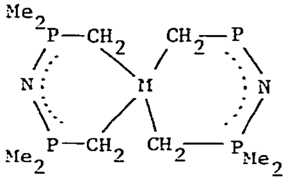
The mechanisms of these reactions are discussed in detail.
In the last paper of this series, similar reactions in which lithium was replaced by sodium or potassium, were described[7].
When AlH_3 is reacted with $NaZnMe_2H$ in THF, ZnH_2 or $NaZn_2H_5$ is obtained, depending on the concentration of the reactants. The corresponding reaction with $NaZn_2Me_4H$ gives the soluble complex $NaZnMe_2AlH_4$, which slowly disproportionates into ZnH_2 or $NaZn_2H_5$, depending on the concentration. The same reaction with KZn_2Me_4H gives KZn_2H_5 directly via intramolecular exchange.
It was established, that in reaction mixtures containing diphenylzinc and cyclopentadienylmolybdenum tricarbonyl hydride, $Cp(CO)_3MoH$, the final equilibrium position of the product cyclopentadienyl NMR resonance is a function of the concentration of unreacted diphenylzinc[8]. This observation is consistent with an initial reaction:

$$Cp(CO)_3MoH + Ph_2Zn \longrightarrow PhZnMo(CO)_3Cp + C_6H_6$$

which yields the unsymmetrical product. This may then undergo a symmetrization reaction:

$$2PhZnMo(CO)_3Cp \rightleftarrows Zn[Mo(CO)_3]_2 + Ph_2Zn$$

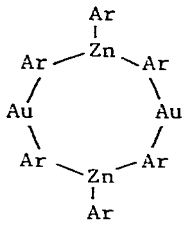
or react further with $Cp(CO)_3MoH$.
No such evidence for the presence of an unsymmetrical product was found in the corresponding reactions of diethylzinc or dimethylcadmium.
Zinc- and cadmiumalkyls react with the ylid $Me_3P{=}N{-}PMe_2{=}CH_2$ to give directly the 1 : 2 complexes (V) and (VI) with alkane evolution[9]:



V: M = Zn
VI: M = Cd

The products were isolated by distillation in vacuo.
Damude and Dean found that ^{13}C-NMR spectra of the systems $Cd(AsF_6)_2$-arene-SO_2 and $Zn(SbF_6)_2$-arene-SO_2 provide evidence for the occurrence

of π-arene complexes of Cd^{2+} and Zn^{2+}[10]. Both types of arene complexes have 1 : 1 stoichiometries and show localized π-interaction between the metal ions and the aromatic rings. The zinc complexes with durene and hexamethylbenzene were sufficiently stable to be isolated. The reactions of diphenylzinc and di-p-tolylzinc with gold(I) and gold(III) salts yield dimeric species of the type $(Ar_3AuZn)_2$[11]. On the basis of spectroscopic data and physical measurements a cyclic structure was proposed which contains both aryl groups exclusively bound to zinc and aryl groups bridging between gold and zinc(VII):



Ar = Ph, p-tolyl

The arylation of carbonylgoldchloride, Au(CO)Cl, with diarylzinc compounds yield either triarylgoldzinc (VII) or diarylgoldzinc chlorides, depending on the reactant ratio and the nature of the aryl group [12]. The same reactions with diphenylcadmium yield exclusively diphenylcadmiumchloride.

II. Reactions of organozinc- and organocadmium compounds

A. The Reformatsky and related reactions

When a zinc-copper couple, prepared in situ by the Le Goff method, is used in the Reformatsky reaction, higher yields are obtained than if zinc alone is used [13]. Even if the less reactive ethyl chloroacetate is used instead of ethyl bromoacetate, yields of about 50% are obtained in boiling benzene solvent.

When the Reformatsky reaction is carried out in the presence of a very large excess of metallic zinc, "abnormal" reactions occur [14].

In this way, ethyl 3,3-diphenylpropionate (VIII) was obtained, along with many other compounds, from ethyl bromoacetate, zinc, and a benzhydrol ester:

$$RCOOCHPh_2 + BrCH_2COOEt + Zn \xrightarrow[2)\ H_2O]{1)\ xylene} RCOOH + Ph_2CHCH_2COOEt$$

VIII

The formation of (VIII) was rationalized by assuming an electron-transfer from the zinc metal to the ester followed by cleavage of the radical anion formed into a carboxylate ion and a radical:

$$RCOOCHPh_2 \xrightarrow{e} [ROOCHPh_2]^{\cdot-} \longrightarrow RCOO^- + Ph_2\dot{C}H$$

This radical may react with the Reformatsky reagent to give (VIII).

The well-known coupling reactions of Grignard reagents with aromatic halides, catalyzed by organometallic complexes of palladium and nickel, can be extended to the Reformatsky reagent. Fauvarque and Jutand found that $BrZnCH_2COOEt$ reacts with phenylpalladium and phenylnickel complexes in a mixture of methylal and HMPT to give benzylic esters (IX)[15]:

$$BrZnCH_2COOEt + PhMX.Ph_3P \longrightarrow PhCH_2COOEt$$

M = Pd,Ni

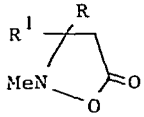
X = Halogen

IX

These reactions could also be carried out using catalytic amounts of metal complexes ML_4 ($M = Ni, Pd; L = Ph_3P$). In that case, the actual reagents $PhMXL_2$ are formed in situ by oxidative addition of the aryl halide to the transition-metal complex.

Isoxazolidinones (X) were prepared by the Reformatsky reaction of ketonitrones with ethyl bromoacetate[16]:

$$RR^1C = N(O)Me + BrZnCH_2COOEt \longrightarrow$$



R = Ph

R^1 = Ph, Me

RR^1 = o-biphenylene

A series of nine α-substituted aromatic β-diketones(XI) was made by reacting α-bromoalkyl phenyl ketones with zinc, followed by reaction with acid chlorides [17]:

$$PhCOCRR^1Br \xrightarrow{Zn} PhCOCRR^1ZnBr \xrightarrow{R^2COCl} PhCOCRR^1COR^2$$

XI

R = H, Me

R^1 = Me, Et

R^2 = Me, Et, Pr, Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$

β-Ketoacid esters XII were prepared by treating α-bromoketones with zinc to give the organozinc reagents which were subsequently reacted with methyl or ethyl chloroformate[18]:

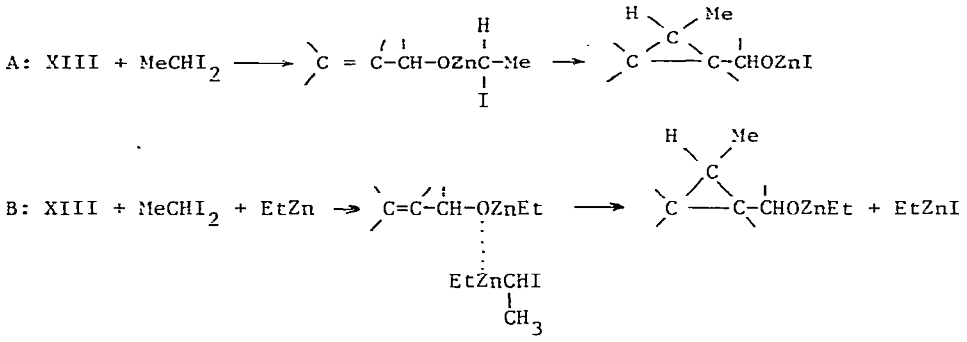
$$RCOCR^1R^2Br \xrightarrow{Zn} RCOCR^1R^2ZnBr \xrightarrow{ClCOOR^3} RCOCR^1R^2COOR^3$$

XII

R = Ph, iPr, Me, cyclohexyl
R^1 = H, Me
R^2, R^3 = Me, Et

B. Carbenoid reactions

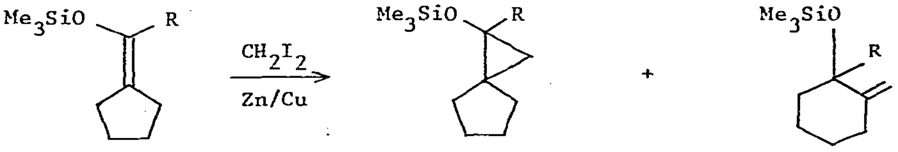
Kawabata and co-workers have investigated the stereochemistry of the cycloaddition of the methylcarbenoid of zinc to cyclic allylic alcohols[19]. Two reaction conditions were used: (A) equimolar amounts of diethylzinc and alcohol, and (B) a diethylzinc: alcohol ratio of 2 : 1. In both cases the authors assumed conversion of the alcohol in a first step into the corresponding ethylzinc alkoxide(XIII). The following reaction schemes are given for conditions A and B:



The steric restraint caused by the hydroxyl group on the configuration of the methyl groups in the products appears to be relatively small in the reactions with the larger cyclic alcohols, in particular when reaction condition B is used.

Three papers have appeared dealing with the synthesis of the synthetically useful trimethylsiloxy cyclopropyl ethers[20,21,22].

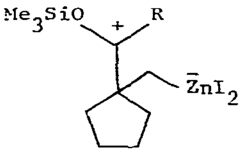
In the Simmons-Smith reaction of the trimethylsilylenol ether(XIV), the expected cyclopropyl ether(XV) was obtained exclusively when the reaction was carried out using low concentrations of reactants[20]:



XIV XV XVI

R = Me, H

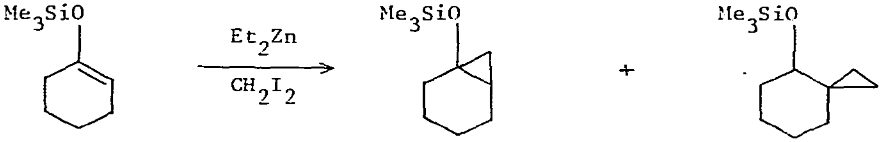
Under more concentrated conditions, also the allylic product(XVI) was formed. In very concentrated reaction mixtures, (XVI) was the major product. The formation of (XVI) was accounted for by assuming the presence of ionic intermediate(XVII), formed by cleavage of the initially formed cyclopropyl ring by zinc iodide:



XVII

In contrast, the Simmons-Smith reaction of trimethylsiloxymethylenecyclohexane gave the expected cyclopropane product under all circumstances, suggesting that strain release may be the driving force in the isomerization of (XV).

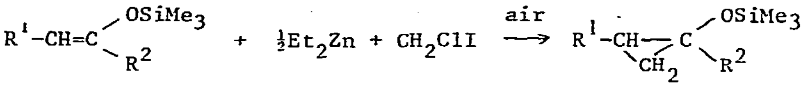
In a later paper[21], the same authors described a one-pot synthesis of spiroethers by reacting silyl enol ethers with diethylzinc and methylene iodide in an aromatic solvent:



XIX XVIII

When the reaction is carried out in diethyl ether or pentane, the intermediate initial cyclopropane derivative(XIX) can be obtained in good yield.

Miyano and co-workers have extended their oxygen-accelerated Simmons-Smith procedure to the synthesis of trimethylsiloxy cyclopropyl ethers (XX)[22]:

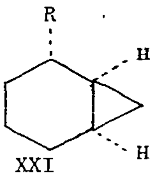


XX

R^1 = H, Me, Et
R^2 = H, Et, Ph
R^1 = cyclohexenyl, cycloheptenyl, benzocyclohexenyl

The authors claim short reaction times and easy work-up as the main advantages of this technique.

The stereochemistry of the Simmons-Smith reaction of some 3-and 4-substituted cyclohexenes has been studied[23]. The yields of trans adducts (XXI) increase in the order R = MeCO < $Me_3COOC{=}CH_2OH$ < CN < CH_2OAc = Me < COOMe < COOEt.

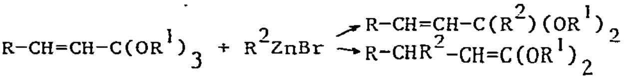


XXI

The stereoselectivity of these reactions is ascribed to steric effects.

C. Reactions of alkenyl- and alkynylzinc compounds.

In a comparative study of the reactivities of saturated, phenylic, and allylic organometallic compounds towards ortho esters, allylzinc bromide reacted to give 1,2- and 1,4-monosubstitution[24]:



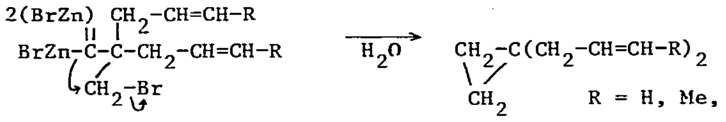
$$R\text{-}CH{=}CH\text{-}C(OR^1)_3 + R^2ZnBr \rightarrow \begin{array}{l} R\text{-}CH{=}CH\text{-}C(R^2)(OR^1)_2 \\ R\text{-}CHR^2\text{-}CH{=}C(OR^1)_2 \end{array}$$

R = H, Me, Ph
R^1 = Et
R^2 = Allyl

The ratio 1,4: 1,2-substitution was always higher for allylzinc bromide than for its magnesium analog.

Bernadou and Miginiac have found that α-, and α,γ-unsaturated organozinc halides do not react with terminal α-acetylenic halides to give the expected Würtz-coupling products, but instead add twice to the triple bond [25]:

$R\text{-}CH{=}CH\text{-}CH_2\text{-}ZnBr + HC{\equiv}C\text{-}CH_2X \longrightarrow$



R = H, Me, $CH_2{=}CH\text{-}CH_2\text{-}$

X = Cl, Br

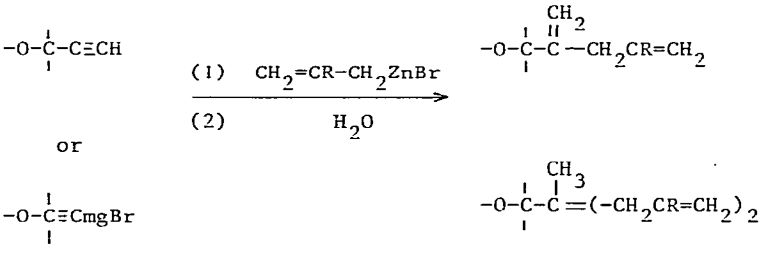
XXII XXIII

The resulting adducts give cyclopropane derivatives by way of a 1,3-elimination. (XXII→XXIII).
Similar results are obtained when the halogen atom in the acetylene is replaced by good leaving groups like phenoxy or trialkylammonium.
Allylzinc bromide reacts with conjugated enynes and conjugates diynes to give products resulting from both mono- and bis-3,4-substitution[26]:

$$C_4H_9CH{=}CH\text{-}C{\equiv}CH + AllZnBr \begin{array}{l} \nearrow C_4H_9CH{=}CH\text{-}CR{=}CH_2 \quad \text{mono } 3,4 \\ \rightarrow C_4H_9CH{=}CH\text{-}C(R)_2\text{-}CH_3 \quad \text{bis } 3,4 \end{array}$$

$$C_4H_9C{\equiv}C\text{-}C{\equiv}CH + AllZnBr \longrightarrow C_4H_9C{\equiv}C\text{-}CR{=}CH_2$$

Similar reactions with α-hydroxy-substituted enynes and diynes proceed only very slowly and give low (25%) yields of products resulting from 1,2-addition to the triple bonds[27].
Frangin and Gaudemar investigated the addition of α-ethylenic organozinc halides to monosubstituted α-acetylenic alcohols, the corresponding ethers and their organomagnesium derivatives [28]. The additions are always regiospecific and result in the corresponding α,γ^1 or γ,γ^1-diethylenic alcohols (XXIV) and ethers (XXV):



$$-O\text{-}\overset{|}{\underset{|}{C}}\text{-}C{\equiv}CH \text{ or } -O\text{-}\overset{|}{\underset{|}{C}}\text{-}C{\equiv}CMgBr \xrightarrow[(2)\ H_2O]{(1)\ CH_2{=}CR\text{-}CH_2ZnBr} -O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{CH_2}{\overset{\|}{C}}\text{-}CH_2CR{=}CH_2 \quad -O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{CH_3}{\overset{|}{C}}{=}({-}CH_2CR{=}CH_2)_2$$

R= H, Me

Plausible reaction mechanisms are given.
Barbot and P. Miginiac have shown that under certain conditions the addition

reaction of an unsubstituted allylzinc compound to a ketone or aldehyde is reversible[29]. When the reaction product of allylzinc bromide and methyl formate is heated in HMPT at 150°, after subsequent hydrolysis both (XXVI) and (XXVII) are obtained:

$$2CH_2{=}CH{-}CH_2ZnBr + HCOOMe \xrightarrow[2)\ H_2O]{1)\ HMPT\ 150^o}$$

$$CH_2{=}CH{-}CH_2{-}CHOH{-}CH_2{-}CH{=}CH_2 + CH_2{=}CH{-}CH_2{-}CHOH{-}CH{=}CH{-}Me$$

XXVI XXVII

The formation of (XXVII) is explained by a reaction of allylzinc bromide formed in the equilibrium, with crotonaldehyde, the latter resulting from isomerization of the aldehyde $CH_2{=}CH{-}CH_2{-}CHO$.

A similar reversibility was observed in the case of the reaction between γ,γ^1-dimethylallylzinc bromide and di-isopropyl ketone[30].

Negishi and co-workers described a stereo-, regio-, and chemo-selective procedure for the synthesis of both terminal and internal conjugated enynes, using the reaction between an alkynylzinc chloride and an alkenyl iodide or bromide in the presence of a Pd-catalyst[31]:

$$RR^1C{=}CR^2X + ClZn{-}C{\equiv}CR^3 \xrightarrow[THF]{Pd\ complex} RR^1C{=}CR^2{-}C{\equiv}CR^3$$

R = H, Bu, COOMe
R^1 = H, Me, Et, Bu
R^2 = H
R^3 = H, Bu, Pent

This procedure has the advantage over routes using other alkynyl-metal derivatives in that no disproportionation occurs so that dienyne-free terminal enynes are obtained.

The generation, and addition of allylzinc halides to aldehydes and ketones can be carried out in alcohols like ethanol and tert. butanol[32]. The yields of addition products are in some cases comparable to those obtained in non-protic solvents. In the absence of reactive carbonyl compounds, coupling reactions and protolysis occur.

D. Miscellaneous reactions of organozinc- and organocadmium compounds

Electrolytically generated diethylcadmium was used to alkylate a lead anode in the synthesis of tetraethyllead[33]. Alkylcadmium compounds are less effective than alkylmagnesium- and alkylzinc compounds for the electrochemical synthesis of tetraethyllead, although cathodically produced diethylcadmium may satisfactorily alkylate a lead anode above room temperature.

Di-tert.butylzinc adds easily to conjugated enynes in a trans-addition reaction involving the acetylenic bond exclusively[34]:

$$3tBu_2Zn + HC\equiv C\text{-}CH{=}CH\text{-}R \xrightarrow{Et_2O} tBu\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2R$$

R = Bu, CH_2OH, CH_2OBu, CH_2NHEt, CH_2NEt_2

In contrast, non-conjugated terminal acetylenes do not react under these conditions[35]. However, when the reaction is carried out in refluxing THF for 48 hrs, a mixture of cis- and trans-addition occurs in varying yields.

The amount of trans product (resulting from cis-addition) appears to depend mainly on the steric crowding around the triple bond.

Phenylmagnesium bromide and diphenylcadmium react with 1-acylpyridinium salts to give addition at the 2- or 6-position of the heterocyclic ring rather than at the 1-acyl carbon[36]. The regioselectivities are very similar. The use of the organo-cadmium reagent is advantageous in the case of 1,3-dibenzoylpyridinium chloride, where the magnesium reagent adds to the carbonyl carbon at the 3-position as well as to the 4- and 6-ring carbons. The cadmium reagent gives good yields of ring-addition only.

Organozinc compounds of the type RZnX readily participate in the Ni- or Pd-catalyzed cross-coupling reaction with aryl halides[37]:

$$RZnX + ArX^1 \xrightarrow{Cat.} R\text{-}Ar$$

R = Aryl, $ArylCH_2$;
X = Br, Cl, Ar;
X^1 = Br, I

The advantage of using zinc in these reactions appears particularly in the synthesis of various diarylmethanes from benzylzinc halides.

The methylation of vanadium with dimethylzinc was studied by Thiele and Lachowicz[38]. Ortho-vanadic esters react with dimethylzinc to give methylvanadiumoxide alkoxides (XVIII):

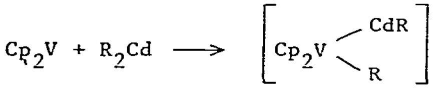
$$VO(OR)_3 + Me_2Zn \longrightarrow \underset{XVIII}{MeVO(OR)_2} + MeZnOR$$

R = Me, Et, iPr, iBu, tBu

Vanadic acid esters with unbranched alkyl groups react already at -50°, whereas those containing tertiairy alkyl groups react only at 30-40°. The thermal stability of compounds (XVIII) increases with the amount of branching.

Vanadium tetraalkoxides also react with dimethylzinc. However, the initially formed methylvanadium trialkoxides are unstable and could not be separated from the accompanying methylzinc alkoxides.

The reactions of dicyclopentadienylvanadium with organocadmium compounds leads to the formation of metallic cadmium and V(IV) compounds[39]. A multi-step reaction is proposed in which the first step is insertion of dicyclopentadienylvanadium into a cadmium-carbon bond:



$$Cp_2V + R_2Cd \longrightarrow \left[Cp_2V \begin{matrix} \diagup CdR \\ \diagdown R \end{matrix} \right]$$

R = Me, Et, Ph, Benzyl

XIX

The intermediate (XIX) is very unstable and decays as follows:

$$XIX \xrightarrow{20^{\circ}} Cd + Cp_2VR_2$$

Stable phenylsilver is formed in quantitative yield when diphenylzinc is reacted with silver salts at 0° in ether[40]:

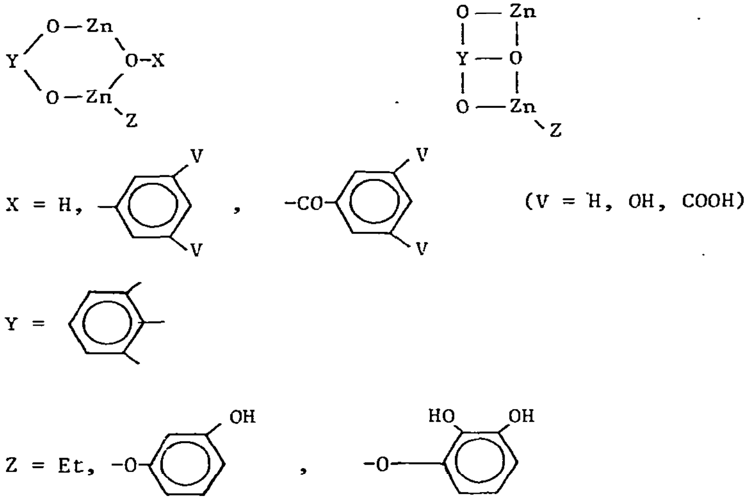
$$Ph_2Zn + AgX \xrightarrow[Et_2O]{0^{\circ}} PhAg + PhZnX$$

X = nitrate, tetrafluoroborate, trifluoromethylsulfonate

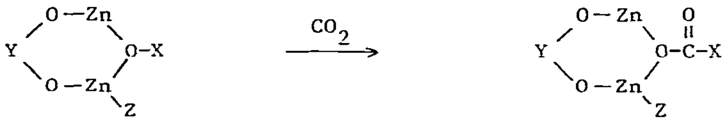
The scale-limitations occurring in the synthesis of phenylsilver from trialkylphenyllead or -tin compounds are absent in this method.

III Organozinc compounds as polymerization catalysts

The structure of the diethylzinc/polyhydric phenol systems, which are active catalysts for the copolymerization of carbon dioxide with propylene oxide, was studied by Pasienkiewicz and co-workers[41]. The presence of an internal Zn←O-Zn coordinate site appears to be essential for high catalytic efficiency. The following structures are proposed for some of these catalysts:



The mechanism of the co-polymerization was investigated by the same authors[42]. The initiation step is insertion of carbon dioxide into a Zn-O bond:



followed by coordination and insertion of propylene oxide. Termination occurs by attack of protons from the OH groups present in the molecule. Propylene oxide was co-polymerized with carbon disulfide using catalysts made up from diethylzinc and electron donors like tertiary amines, tertiary phosphines, and HMPT[43]. The co-polymer had a random distribution containing 30-40% of carbon disulfide units, and was of low molecular weight. A C=O bond was formed during the polymerization.

IV Physical and spectroscopic studies

A method was described for the determination of inpurities in diethylzinc used in semiconductor technology[44]. After destruction of a sample with, consecutively, ethanol and nitric acid, and heating of the residue at 550° to form zinc oxide, the latter was analyzed by emission spectroscopy. Impurities in the 2-10 ppm range were determined with 20-40% standard deviations.

Bancroft and co-workers have determined valence- and core-electron energies in dimethyl- and diethylcadmium by photoelectron spectroscopy [45]. The resolved splitting of the Cd 4d levels was attributed to a ligand-field effect rather than to a bonding effect. This was confirmed by ab initio SCF calculations, which showed that no significant degree of 4 d bonding is present in these compounds.

Similar measurements and calculations were carried out by these authors on dimethylzinc[46]. Also in this case, splitting of the 3 d level was observed and the calculations confirmed the electrostatic rather than bonding origin of these splittings.

The IR, and Raman spectra of gaseous, liquid, and solid dimethylzinc, dimethylcadmium, and dimethylmercury were reinvestigated[47]. The experimental conditions were chosen so that valid spectral comparisons could be made. The effect of cooling on the free rotation of the methyl group was studied in the 15-200 K range. The variable temperature Raman spectra suggested that methyl-group rotation in the solid compounds becomes restricted at very low temperatures.

A ^{13}C-NMR investigation of the olefinic carbon atoms in di-butenyl-, pentenyl-, and hexenylzinc showed no unusual trends which might be due to metal-double bond interactions[48]. The only significant shifts were observed upon complexation of dipentenylzinc with 2,2^{1}-bipyridine. These shifts were attributed to the proximity of the olefinic carbons to the aromatic system of the Bipy with its associated anisotropic magnetic field.

Two papers appeared dealing with Cd-NMR spectroscopy[49,50].

The ^{113}Cd magnetic shielding and Cd-proton coupling constants of a series of simple dialkylcadmium compounds were recorded and compared with those of their mercury analogs[49]. The ^{113}Cd- and ^{199}Hg- chemical shifts show similar changes upon replacing hydrogens by saturated carbon atoms in the alkyl groups.

A ^{113}Cd NMR study of a large series of methylcadmium alkoxides and some alkanethiolates was used to investigate the structures and associations of these compounds[50]. It was shown, that the methylcadmium alkoxides examined are all tetrameric. In the case of alkoxides with smaller substituents in the alkoxygroups, the slow formation of a second species was observed. The similarity of the NMR parameters of the two species was used as an argument for proposing a hexameric structure for the second type.

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