CADMIUM

LITERATURE SURVEY COVERING THE YEARS 1972 AND 1973

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I. PREPARATION AND REACTIONS OF ORGANOCADMIUM COMPOUNDS

Cadmium metal reacts with pentafluoroiodobenzene in a variety of coordinating solvents such as TMF, DMF and DMSO to give almost quantitative yields of pentafluorophenylcadmium iodide [1]:

The reversible formation of a complex of diethylcadmium with two molecules of oxygen has been established by a kinetic method. This complex may subsequently be transformed into bis(ethylperoxo)cadmium [2]:

The 2/1 reaction of triphenylgermane and triphenyltin hydride with coordinatively saturated organocadmium compounds affords the corresponding bis(triphenylgermyl)- and bis(triphenyltin)cadmium complexes [3]:

L = TMED, Bipy

L = THF, DME, TMED, Bipy

Unsolvated bis(triethylgermyl)cadmium reacts with organic halides such as trityl chloride, benzyl bromide and allyl iodide in a 1/1 ratio with selective cleavage of one Ge-Cd bond. Evidence has been presented that the first step of this reaction involves one electron-transfer from the organometal compound to the organic halide and indeed in the reaction with trityl chloride trityl radicals may be detected by ESR spectroscopy [4].

A four-centre mechanism is proposed for the exothermal 1/1 reaction of bis(triethylgermyl)cadmium with 1,2-dibromoethane which runs selectively according to [4]:

Dimethylcadmium, diethylcadmium and methylcadmium ethoxide react with chlorine azide with formation of the corresponding azide derivatives which according to their properties and IR spectra are coordination polymers [5].

The 1/1 reaction of a di-Grignard reagent with cadmium halides affords reagents containing two Cd-C bonds as evidenced by the products formed in reactions with carbonyl compounds and acid halides. The monomeric cadmium heterocycle (I) has been isolated by distillation and has been characterized [6]:

The reaction with acyl halides affords diketones as the main product, but in reactions with aldehydes and ketones the yield of monocarbinol generally surpasses that of the dicarbinol [6]:

The 1/2 reaction of di-Grignard reagents with cadmium halides affords an organodicadmium compound of the type $\text{XCd}-(\text{CH}_2)_n-\text{CdX}$ the reactivity of which differs from that of $[\text{-Cd}(\text{CH}_2)_n\text{-}]$ formed in the 1/1 reaction in that the relative yield of di-functional products formed in the reaction with acyl halides and carbonyl compounds is generally higher [7].

Dibutylcadmium reacts rapidly with cyclohexanone and acetophenone in HMPT solution at room temperature with the formation of enoxycadmium derivatives [8], e. g.:

Soussan et al. have made an extensive study of the reaction of organocadmium compounds with α, β -unsaturated carbonyl compounds. In general, 1,4-addition takes place with α, β -unsaturated ketones, the 1,4-enolate (II) formed being capable of undergoing a secondary 1,4-addition

with the carbonyl compound to afford after hydrolysis δ -diketones (III) [9, 10]:

However, mesityl oxide and fluorenone undergo 1,2-addition. These reactions require the presence of magnesium halides, but tetraphenylcyclopentadienone reacts quantitatively in the absence of magnesium halides [10]. Like organomagnesium compounds organocadmium compounds as a rule react in a 1,2-fashion with α, β -unsaturated aldehydes, but in some cases 1,4-addition has been observed as well [11], e.g.:

The presence of magnesium halides is required. The addition of copper(I) chloride in some cases leads to enhanced 1,4-addition [11]. In the reaction of acroleine with diphenylcadmium a secondary 1,2-addition of the primary 1,4-adduct takes place leading to the formation of an adduct (IV) containing an aldehyde function which undergoes condensation with the organocadmium compound, the final product isolated being an unsaturated 1,3-diol (VII) [9]:

The reactivity of diethylcadmium towards Schiff bases is strongly enhanced in the presence of magnesium bromide, the yield of amine isolated from the reaction with benzalaniline increasing from 3 to 92 %, if the amount of MgBr_2 present during the reaction is increased from 10 to 200 mole % [12]:

The reaction of dialkylcadmium compounds with aromatic nitro compounds leads to the formation of substituted amines, but this reaction is often followed by substitution of the aromatic nucleus [13], e. g.:

The mechanism of the displacement of halogen from a saturated carbon atom by phenylcadmium chloride has been studied by Jones and Costanzo. The intermediacy of a free-radical intermediate is consistent with the observation of a strong ESR signal upon mixing of the reactants and with the fact that the displacement proceeds with racemization, which was established by the formation of (+)-methyl hydratropate from (R)-(+)-bromopropionate under conditions when the starting ester was optically stable [14]:

The synthetic scope of this type of displacement reaction has been investigated [14].

II. SPECTROSCOPIC, STRUCTURAL AND OTHER MISCELLANEOUS STUDIES OF ORGANOCADMIUM COMPOUNDS

The 60 MHz ^1H NMR spectral parameters for divinyl cadmium have been reported by Visser and Oliver. The change in the chemical shifts and coupling constants for the series of compounds $(\text{H}_2\text{C}=\text{CH})_2\text{M}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) has been discussed as a function of the central metal atom [15]. Evans and Phillips have studied the occurrence of exchange of pentafluorophenyl groups in solutions of pentafluorophenylcadmium iodide using ^{19}F NMR spectroscopy (p-fluorine region). The calculated value for the equilibrium constant K for the Schlenk equilibrium

at -40° in DMF is 3.2 ± 0.7 and at 15° in DMSO is 3.2 ± 0.2 [1].

The UV spectrum of the complex $\text{Et}_2\text{Cd} \cdot 2 \text{O}_2$ contains an intense absorption at 276 nm [2]. The 2,2'-bipyridyl complex of bis(triphenyl-

germyl)cadmium and of bis(triphenylstannyl)cadmium display charge-transfer absorptions in the visible spectrum, $\lambda_{\max}$ of which decreases with increasing polarity of the solvent [3]. The consistently lower metal-metal stretching frequency ($\nu_{\text{as}} \text{ MCdM}$) in $(\text{Ph}_3\text{M})_2\text{Cd}\cdot\text{Bipy}$ as compared with in $(\text{Ph}_3\text{M})_2\text{Cd}\cdot\text{TMED}$ ($\text{M} = \text{Ge}, \text{Sn}$) has been explained in terms of $\text{Cd} \rightarrow \text{Bipy}$ charge-transfer [3].

The UV absorption spectrum has been recorded for the transient monomethylcadmium radical produced in the flash photolysis of dimethylcadmium. Two absorption systems are observed at 4000–4450 Å and 2640–2870 Å [16].

A molecular structure study of dimethylcadmium and its perdeuterated analog has been carried out assuming a free rotation model. A normal coordinate analysis is presented and the normal frequencies and eigenvectors have been calculated [17].

The full details of the X-ray crystal structure of bis(pentacarbonylmanganese)-2, 2':6', 2''-terpyridylcadmium $\text{C}_{15}\text{H}_{11}\text{N}_3\text{Cd}[\text{Mn}(\text{CO})_5]_2$ have been published. The coordination of cadmium is very distorted trigonal bipyramidal and there is considerable distortion of the octa-

Fig. 1 Structure of $[(\text{Et}_2\text{O})_2\text{Cd}(\text{B}_{10}\text{H}_{12})]_2$ showing positions of boron, cadmium and oxygen atoms (from N.N.Greenwood et al., J. C. S. Dalton, 1972, 989).

bedral manganese coordination [18, 19]. The X-ray crystal structure of the diethylether complex of (dodecahydro-nido-decaborato)cadmium with empirical formula $(\text{Et}_2\text{O})_2\text{Cd}(\text{B}_{10}\text{H}_{12})$ has revealed a dimeric molecule with each cadmium atom being bonded (via three-centre bonds) to two icosahedral $\text{B}_{10}\text{H}_{12}$ units [20] (Fig. 1)

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