CADMIUM

LITERATURE SURVEY COVERING THE YEARS 1972 AND 1973

Jan G. Noltes

Organisch Chemisch Instituut TNO, Utrecht (The Netherlands)

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]:

$$Cd + IC_6F_5 \longrightarrow C_6F_5CdI$$

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]:

$$Et_2Cd + 2O_2 \rightleftarrows Et_2Cd \cdot 2O_2$$

$$Et_2Cd \cdot 2O_2 \longrightarrow (EtOO)_2Cd$$

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]:

$$2Ph_3GeH + Me_2Cd \cdot L \longrightarrow (Ph_3Ge)_2Cd \cdot L + 2MeH$$

L = TMED, Bipy

$$2Ph_3SnH + Me_2Cd.L \longrightarrow (Ph_3Sn)_2Cd \cdot L + 2MeH$$

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].

$$Et_3GeCdGeEt_3 + Ph_3CCl \longrightarrow \left[\begin{array}{c} Et_3GeCd^{+}\cdot\ GeEt_3 \\ Cl^{-}\cdot\ CPh_3 \end{array}\right] \longrightarrow$$

$$\begin{array}{ccc} Et_3GeCdCl & + & \underbrace{Ph_3C\cdot\ +\ Et_3Ge\cdot} \\ \downarrow & & \downarrow \\ Et_3GeCl + Cd & & Ph_3CCPh_3 + Et_3GeCPh_3 + Et_3GeGeEt_3 \end{array}$$

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]:

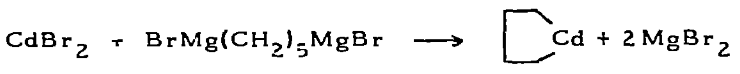
$$\begin{array}{lcl} Et_3GeCd{-}{-}{-}GeEt_3 & \longrightarrow & Et_3GeCdBr + Et_3GeCH_2CH_2Br \\ \quad\ \vdots \qquad\ \ \vdots & & \qquad\qquad\qquad \downarrow \\ \quad Br{-}{-}{-}CH_2CH_2Br & & \qquad Et_3GeBr + CH_2{=}CH_2 \end{array}$$

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].

$$R_2Cd + ClN_3 \longrightarrow RCdN_3 + RCl$$
$$(R = Me,\ Et)$$

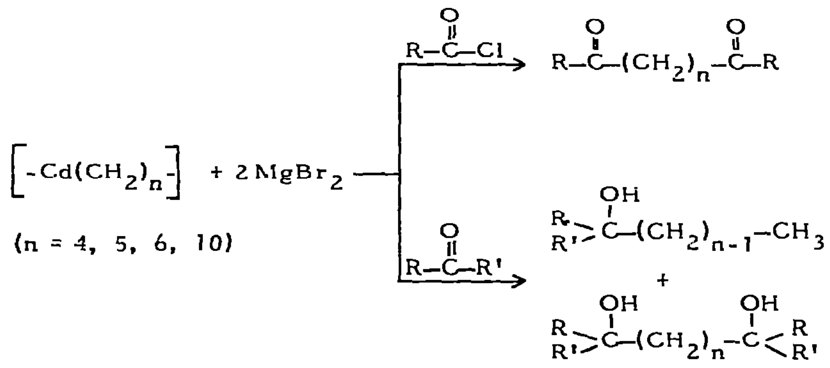
$$MeCdOEt + ClN_3 \longrightarrow EtOCdN_3 + MeCl$$

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]:



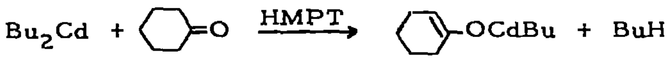
(I)

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]:

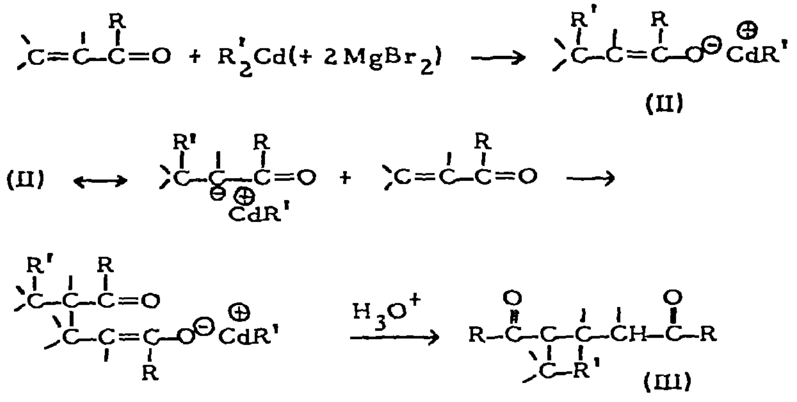


The 1/2 reaction of di-Grignard reagents with cadmium halides affords an organodicadmium compound of the type $XCd{-}(CH_2)_n{-}CdX$ the reactivity of which differs from that of $[-Cd(CH_2)_n-]$ formed in the 1/1 reaction in that the relative yield of di-functional products formed in the reaction with acyl halides and carbonyl compounds is generally higher [7].

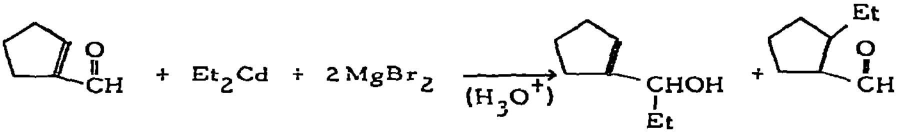
Dibutylcadmium reacts rapidly with cyclohexanone and acetophenone in HMPT solution at room temperature with the formation of enoxycadmium derivatives [8], e.g.:



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]:

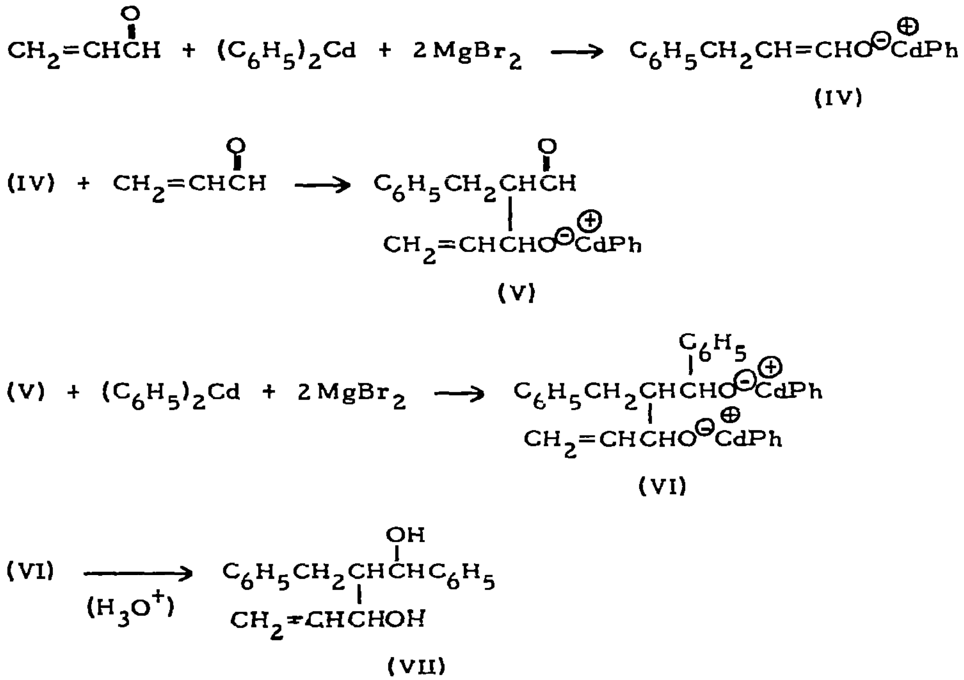


However, mesityl oxide and fluorenon undergo 1, 2-addition. These reactions require the presence of magnesium halides, but tetraphenylcyclopentadienone reacts quantitatively in the absence of magnesium halides [10]. Like organomagnesium compounds organocadmium compounds as a rule react in a 1, 2-fashion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



(51 %) (49 %)

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]:



$$CH_2{=}CH\overset{O}{\overset{\|}{C}}H + (C_6H_5)_2Cd + 2\,MgBr_2 \longrightarrow C_6H_5CH_2CH{=}CHO^{\ominus}\overset{\oplus}{Cd}Ph$$

(IV)

$$(IV) + CH_2{=}CH\overset{O}{\overset{\|}{C}}H \longrightarrow C_6H_5CH_2\underset{\underset{CH_2=CHCHO^{\ominus}\overset{\oplus}{Cd}Ph}{|}}{C}H\overset{O}{\overset{\|}{C}}H$$

(V)

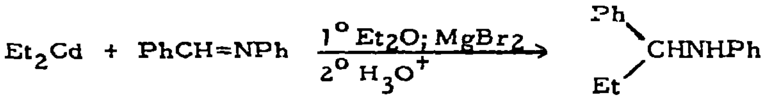
$$(V) + (C_6H_5)_2Cd + 2\,MgBr_2 \longrightarrow C_6H_5CH_2\underset{\underset{CH_2=CHCHO^{\ominus}\overset{\oplus}{Cd}Ph}{|}}{C}H\overset{\overset{C_6H_5}{|}}{C}HO^{\ominus}\overset{\oplus}{Cd}Ph$$

(VI)

$$(VI) \xrightarrow[(H_3O^+)]{} C_6H_5CH_2\underset{\underset{CH_2=CHCHOH}{|}}{C}H\overset{\overset{OH}{|}}{C}HC_6H_5$$

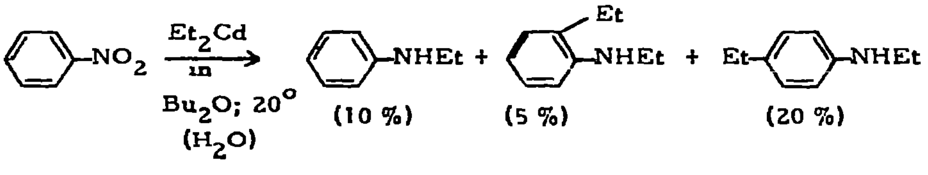
(VII)

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]:



$$Et_2Cd + PhCH{=}NPh \xrightarrow[2^{\circ}\ H_3O^+]{1^{\circ}\ Et_2O;\ MgBr_2} \begin{matrix}Ph\\ \\Et\end{matrix}\!\!>\!CHNHPh$$

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]:

$$\text{(R)-(+)-}CH_3CHBrCOOCH_3 + PhCdCl \xrightarrow[Et_2O]{60\ \%} (\pm)\text{-}CH_3CH(Ph)COOCH_3$$

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 $(H_2C{=}CH)_2M$ (M = Zn, Cd, 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

$$(C_6F_5)_2Cd + CdI_2 \rightleftarrows 2\ C_6F_5CdI$$

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 $Et_2Cd \cdot 2\,O_2$ contains an intense absorption at 276 nm [2]. The 2,2'-bipyridyl complex of bis(triphenylgermyl)cadmium and of bis(triphenylstannyl)cadmium display charge-transfer absorptions in the visible spectrum, λ_{max} of which decreases with increasing polarity of the solvent [3]. The consistently lower metal-metal stretching frequency (ν_{as} MCdM) in $(Ph_3M)_2Cd\cdot Bipy$ as compared with in $(Ph_3M)_2Cd\cdot TMED$ (M = Ge, Sn) has been explained in terms of Cd ⟶ 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 $C_{15}H_{11}N_3Cd[Mn(CO)_5]_2$ have been published. The coordination of cadmium is very distorted trigonal bipyramidal and there is considerable distortion of the octa-

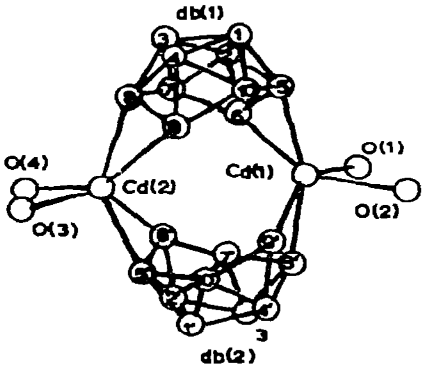


Fig. 1 Structure of $[(Et_2O)_2Cd(B_{10}H_{12})]_2$ showing positions of boron, cadmium and oxygen atoms (from N. N. Greenwood et al., J. C. S. Dalton, 1972, 989).

hedral manganese coordination [18, 19]. The X-ray crystal structure of the diethylether complex of (dodecahydro-nido-decaborato)cadmium with empirical formula $(Et_2O)_2Cd(B_{10}H_{12})$ has revealed a dimeric molecule with each cadmium atom being bonded (via three-centre bonds) to two icosahedral $B_{10}H_{12}$ units [20] (Fig. 1)

REFERENCES

1. D. F. Evans and R. F. Phillips, J. C. S. Dalton, 1973, 978
2. U. A. Alexandrov, G. N. Figurova and G. A. Razuvaev, J. Organometal. Chem., 57 (1973) 71
3. F. A. J. Des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers, N. A. D. Carey and J. G. Noltes, J. Organometal. Chem., 44 (1972) 247
4. N. S. Vyazankin, V. T. Bychkov, O. V. Linzina, L. V. Aleksandrova and G. A. Razuvaev, J. Organometal. Chem., 31 (1971) 311
5. H. Müller and K. Dehnicke, Bol. Soc. Chil. Quim., 19 (1972) 17; Chem. Abstr., 78 (1973) 84507s
6. G. Soussan and P. Fréon, Bull. Soc. Chim. France, 1972, 4228
7. G. Soussan and P. Fréon, Bull. Soc. Chim. France, 1972, 4233
8. Yu. A. Veits, V. L. Foss and I. F. Lutsenko, Vestn. Mosk. Univ., Khim., 13 (1972) 10; Chem. Abstr., 76 (1972) 153880f
9. M. Gocmen and G. Soussan, J. Organometal. Chem., 61 (1973) 19
10. M. Gocmen, G. Soussan and P. Fréon, Bull. Soc. Chim. France, 1973, 562
11. M. Gocmen, G. Soussan and P. Fréon, Bull. Soc. Chim. France, 1973, 1310
12. J. Thomas, Bull. Soc. Chim. France, 1973, 1300
13. L. Le Guilly, R. Setton and F. Tatibouët, J. Organometal. Chem., 40 (1972) C5

14. P. R. Jones and S. J. Constanzo, J. Org. Chem., 38 (1973) 3189

15. H. D. Visser and J. P. Oliver, J. Organometal. Chem., 40 (1972) 7

16. P. J. Young, R. K. Gosavi, J. Connor, O. P. Strausz and H. E. Gunning, J. Chem. Phys., 58 (1973) 5280

17. A. M. W. Bakke, J. Mol. Spectrosc., 42 (1972) 1

18. W. Clegg and P. J. Wheatley, J. C. S. Chem. Comm., 1972, 760

19. W. Clegg and P. J. Wheatley, J. C. S. Dalton, 1973, 90

20. N. N. Greenwood, J. A. McGinnety and J. D. Owen, J. C. S. Dalton, 1972, 989