CADMIUM

ANNUAL SURVEY COVERING THE YEAR 1971

Jan G. Noltes
Organisch Chemisch Instituut TNO, Utrecht (The Netherlands)

I. PREPARATION AND REACTIONS OF ORGANOCADMIUM COMPOUNDS

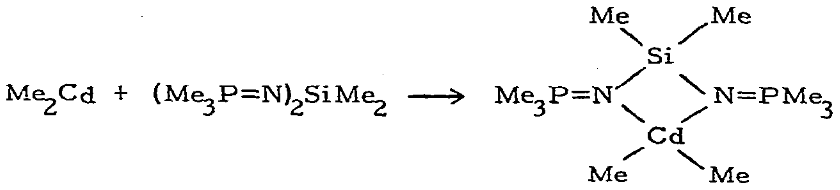
Diazoalkane derivatives of Group II B metals among which cadmium have been synthesized by Lorberth via acidolysis of very reactive bis(trimethylsilylamino) derivatives with diazoacetic ester or diazomethane [1]:

$$\mathrm{Cd[N(SiMe_3)_2]_2} + \mathrm{CH_2N_2} \xrightarrow{\mathrm{Et_2O}} \mathrm{[CdCN_2]_2} + 2\,\mathrm{HN(SiMe_3)_2}$$

$$\mathrm{Cd[N(SiMe_3)_2]_2} + \mathrm{HC(N_2)COOEt} \xrightarrow{\mathrm{Et_2O}} \mathrm{Cd[C(N_2)COOEt]_2} + 2\,\mathrm{HN(SiMe_3)_2}$$

Dyatkin et al. have demonstrated the presence of methyltrifluoromethylcadmium and bis-trifluoromethylcadmium in solution, but these compounds were not actually isolated [2].

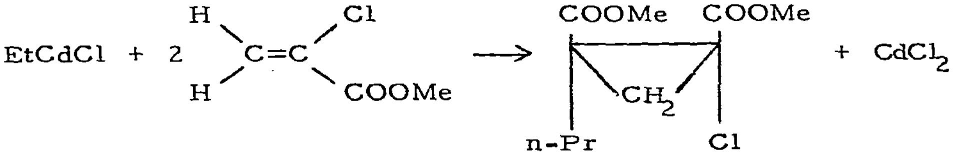
A crystalline 1/1 complex of dimethylcadmium with bis-trimethyl phosphinimino-dimethylsilane which acts as a 1,3-bidentate ligand has been reported by Schmidbaur and Wolfsberger [3]:



Anionic cadmium complexes of the dodecahydro-*nido*-decaborate(2-) ion have been isolated by Greenwood et al. The compound previously formulated as $CdB_{10}H_{12}.2\,Et_2O$ is, as shown by single crystal X-ray studies, in fact a dimer in which each cadmium is bound to two $B_{10}H_{12}$ cages. In water ionization occurs with formation of Cd^{2+} and $Cd(B_{10}H_{12})_2^{\,2-}$ the latter anion having been isolated as the tetramethylammonium or methyltriphenylphosphonium salt [4].

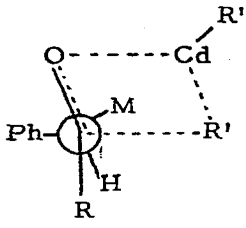
The reactivity of diethylcadmium towards carbon tetrachloride differs from that of diethylzinc in that formation of cadmium chloride is not observed. Reaction with CCl_4 in the presence of cyclohexene yielded EtCdCl, but no dichloronorcarane of C_2-hydrocarbons [5].

The reaction of ethylcadmium chloride with methyl α-chloroacrylate in benzene at 80° results in the formation of *cis*-dimethyl 1-propyl-2-chloro-1,2-cyclopropanedicarboxylate (I) in 7% yield [6]:



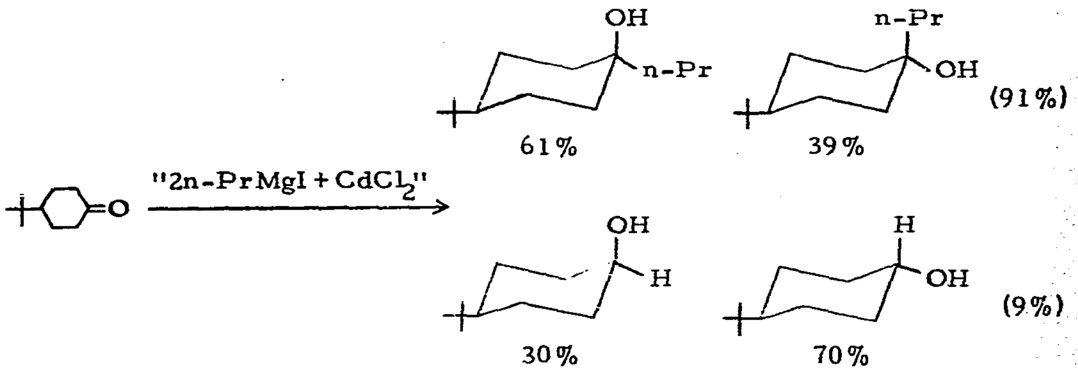
(I)

Jones et al. have made a detailed investigation of the stereochemistry of addition of dimethylzinc and dimethylcadmium towards 2-phenylpropanal, 2-phenylbutanal and 2-phenyl-3-methylbutanal. The lower stereoselectivity observed for the cadmium and the zinc reagent as compared with Grignard reagents has been rationalized as resulting from a tight four-centre transition state (II) for such reactions [7].



(II)

The product composition and stereochemistry of the reaction of *in situ* n-propylzinc and n-propylcadmium reagents with 4-tert-butylcyclohexanone (AS 69; 284) has been compared with that observed for the corresponding reaction of the n-propyl Grignard reagent. The cadmium reagent exhibits the greatest preference for addition (equatorial attack predominates) over reduction (axial reduction predominates for the cadmium reagent), e.g. [8]:



II. SPECTROSCOPIC, STRUCTURAL AND PHYSICAL STUDIES OF ORGANOCADMIUM COMPOUNDS

Several reports have dealt with the study of exchange reactions of organocadmium species.

Alkyl group exchange between dimethylcadmium and bis(trifluoromethyl)mercury has been studied by Dyatkin et al. using ^1H and ^{19}F NMR spectroscopy. The results were discussed in terms of the following equilibria:

$$\text{(a)}\quad (CF_3)_2Hg + (CH_3)_2Cd \rightleftarrows CH_3HgCF_3 + CH_3CdCF_3$$

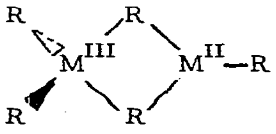
$$\text{(b)}\quad (CF_3)_2Hg + CH_3CdCF_3 \rightleftarrows CH_3HgCF_3 + (CF_3)_2Cd$$

$$\text{(c)}\quad (CH_3)_2Cd + CH_3HgCF_3 \rightleftarrows (CH_3)_2Hg + CH_3CdCF_3$$

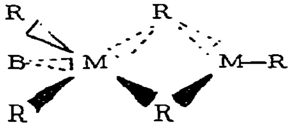
$$\text{(d)}\quad (CH_3)_2Cd + (CF_3)_2Cd \rightleftarrows 2\,CH_3CdCF_3$$

The reactivity of the CH_3–Cd bond towards exchange in CH_3CdCF_3 is essentially lower than in $(CH_3)_2Cd$. Spin-spin coupling constants for the new compounds CH_3CdCF_3 $[J\,^{111(113)}Cd—C—^1H = 64(67)$ Hz and $J\,^{111(113)}Cd—C—^{19}F = 309(323)$ Hz$]$ and $(CF_3)_2Cd$ $[J\,^{111(113)}Cd—C—^{19}F = 359(376)$ Hz$]$ were reported [2].

A PMR study of the self-exchange of $Cd(CH_3)_2$ in diethylether and the exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$ in cyclopentane and in toluene has been reported [9]. In going to strongly basic solvents the activation energy for the self-exchange reaction drops dramatically, e.g. $E_a = 16$ Kcal / mole in toluene and 6.8 Kcal/mole in THF. Activation energies and kinetic parameters are reported for various exchange systems $Cd(CH_3)_2/Ga(CH_3)_3$, $Cd(CH_3)_2/Zn(CH_3)_2$ and $Cd(CH_3)_2/Zn(CH_3)_2$ revealing the following order of reaction rates in non-coordinating solvents: $Zn + Ga > In + Zn > Ga + Cd \sim In + Cd > Zn + Cd \gg Cd + Cd$. The most likely transition state for a Group II - Group III exchange is thought to be (III), but in a strong donor solvent the Group III metal is more probably five-coordinate in the transition state (IV) [9].



(III)



(IV)

No case has been observed in which the dissociation step is rate-controlling, all of the reactions being second order [9].

Röder and Dehnicke have presented ^{1}H—NMR evidence for the occurrence of the following exchange equilibria occurring in the reaction mixture obtained on dissolution of tetramethylammonium cyanate and thiocyanate in dimethylcadmium (X = OCN, SCN) [10]:

$$[(^*CH_3)_2{}^*CdX]^- + (CH_3)_2Cd \rightleftarrows [(CH_3)_2{}^*CdX]^- + (^*CH_3)_2Cd$$

$$[(CH_3)_2CdX]^- + (CH_3)_2Cd^* \rightleftarrows [(CH_3)_2Cd^*X]^- + (CH_3)_2Cd$$

The anionic complexes are not sufficiently stable to allow their isolation.

In the IR spectrum the antisymmetric and symmetric Cd—C_2 stretching frequency for the $Cd(CH_3)_2OCN^-$ species is observed at 509 and 499 cm^{-1} as compared with 528 and 460 cm^{-1} for $(CH_3)_2Cd$ [10].

The 28.87 MHz and 80.53 MHz ^{11}B-NMR spectra of $CdB_{10}H_{12}\cdot 2\,Et_2O$ and of $[Me_4N]_2[Cd(B_{10}H_{12})_2]$ ($B_{10}H_{12}$ = dodecahydro-nido-decaborate(-) ion) have been presented. The results for the latter anionic complex have been correlated with the known structure in the solid state [4].

t-Butoxy radicals generated thermally from di-t-butyl hyponitrite in the presence of dimethylcadmium induce an S_H2 reaction at the metal centre. If the reaction is carried out in an E.S.R. cavity the E.S.R. spectrum of the methyl radical can be observed [11]:

$$\text{t-BuO}\cdot + \text{Me}_2\text{Cd} \longrightarrow \text{MeCdO-t-Bu} + \text{Me}\cdot$$

A single crystal X-ray study has shown that the anionic cadmium-borane complex $[Ph_3MeP]_2[Cd(B_{10}H_{12})_2]$ is isostructural with the zinc and mercury analogs indicating a structure comprising two bidentate $B_{10}H_{12}^{2-}$ ligands coordinated tetrahedrally to the cadmium dinegative ion [12].

Dimethylcadmium has been photolyzed at very low pressures with polarized light (anisotropic photodissociation). The results have been interpreted in terms of the transition movement being perpendicular to the axis of the molecule and the fragments separating along the molecular axis [13].

REFERENCES

1. J. Lorberth, J. Organometal. Chem., 27 (1971) 303
2. B. L. Dyatkin, B. I. Martynov, I. L. Knunyants, S. R. Sterlin, L. A. Fedorov and Z. A. Strumbrevichute, Tetrahedron Lett., 1971, 1345
3. H. Schmidbaur and W. Wolfsberger, Syn. Inorg. Metal-Organ. Chem., 1 (1971) 111
4. N. N. Greenwood and N. F. Travers, J. Chem. Soc. (A), 1971, 3257

5. V. I. Shcherbakov, R. F. Galiulina, Yu. N. Krasnov and V. N. Pankratova, Zh. Obshch. Khim., 41 (1971) 2043; Chem. Abstr., 76 (1972) 34372 g

6. Y. Kawakami and T. Tsuruta, Tetrahedron Lett., 1971, 1173

7. P. R. Jones, E. J. Goller and W. J. Kauffman, J. Org. Chem., 36 (1971) 3311

8. P. R. Jones, E. J. Goller and W. J. Kauffman, J. Org. Chem., 36 (1971) 186

9. J. Soulati, K. L. Henold and J. P. Oliver, J. Am. Chem. Soc., 93 (1971) 5694

10. N. Röder and K. Dehnicke, J. Organometal. Chem., 33 (1971) 281

11. A. G. Davies, D. Griller and B. P. Roberts, J. Chem. Soc. (B), 1971, 1823

12. N. N. Greenwood, J. A. McGinnety and J. D. Owen, J. Chem. Soc. (A), 1971, 809

13. C. Jonah, P. Chandra and R. Bersohn, J. Chem. Phys., 55 (1971) 1903