Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

Catalysis of methyl-group exchange in dimethylcadmium

Some exchange reactions of dimethylcadmium with the Group II and Group III alkyls have already been reported by McCoy and Allred[1] and by Dessy, Kaplan, Coe and Salinger[2]. Here we report on the "homoexchange" of dimethylcadmium which has been studied by proton magnetic resonance (PMR) spectroscopy. Our results indicate a completely novel and hitherto unsuspected mode of catalysis of organometallic exchange and suggest that results previously obtained[1,2] be interpreted with caution.

The PMR spectrum of dimethylcadmium should consist of a strong central peak due to methyl groups attached to spin-zero cadmium nuclei and two smaller satellite peaks due to methyl groups on spin-half nuclei. Such a spectrum is observed for neat dimethylcadmium at room temperature, with $J(\text{CdH}) = 51$ cps, and under optimum conditions each satellite is split into a pair due to the slightly different magnetogyric ratios of ^{111}Cd and ^{113}Cd. When chemical exchange of methyl groups from one cadmium atom to another occurs the spectrum should broaden, collapse and then sharpen again as the rate increases. This behaviour has been observed for dimethylcadmium in toluene and in pyridine over the temperature range -40 to 120° C. For quantitative analysis of this system the exchange-modified Bloch equations[3] have been used to derive computer-simulated spectra. By comparison of these with each experimental spectrum pre-exchange lifetimes have been obtained for the Cd–C bond.

Solutions prepared in a dry-box yielded exchange rates that were irreproducible by a factor of 10. Vacuum-line techniques were then employed, leading to lower and more reproducible rates. The possibility that oxygen was giving rise to an exchange catalyst was considered. Oxygen reacts with excess dimethylcadmium to give methyl(methylperoxy)cadmium and finally methylcadmium methoxide[4], which may equally well be generated by the action of methanol. Small amounts of methanol were therefore added to dimethylcadmium in toluene. Strong catalysis of exchange was observed (see Table 1). Furthermore the order of the exchange with respect to the added methanol was less than unity, so that significant catalysis of exchange will probably arise from contamination by far less than 0.1 mole-percent of methanol or oxygen.

TABLE 1

PRE-EXCHANGE LIFETIMES OF DIMETHYLCADMIUM IN TOLUENE

$[Me_2Cd]^a$	$[MeOH]^a$	τ(sec) at 120° C^b
0.45	0	0.23 ± 0.07
0.58	0.0049	0.014 ± 0.001
0.56	0.010	0.011 ± 0.001
0.48	0.020	0.0072 ± 0.0006

[a] Concentrations in mole/l before reaction. [b] Variation of τ with temperature indicates an average activation energy for catalysed exchange of 16 kcal/mole.

The hypothesis that catalysis arises by exchange of methyl groups between dimethylcadmium and methylcadmium methoxide in its predominant state of association has been disproved by observation of distinct cadmium–methyl resonances for a mixture of the two compounds in toluene at temperatures up to 80° C. The low order in added methanol for homoexchange in dimethylcadmium would be consistent with catalysis by a lower state of aggregation of methylcadmium methoxide in equilibrium with the known tetramer[5].

TABLE 2

PRE-EXCHANGE LIFETIMES OF DIMETHYLCADMIUM IN PYRIDINE

$[Me_2Cd]^a$	$[MeOH]^a$	τ (sec) at 40° C^b
0.57	0	0.030 ± 0.002
0.50	0.0065	0.0082 ± 0.0007
0.48	0.012	0.0025 ± 0.0002
0.50	0.030	0.0012 ± 0.0001

[a] See Table 1. [b] Variation of τ with temperature indicates an average activation energy for catalysed exchange of 13 kcal/mole.

Ethanol has also been found to catalyse the homoexchange of dimethylcadmium in toluene. In exchange reactions rates normally decrease in the order methoxide > ethoxide > isopropoxide > tert-butoxide, and change in this order appears to be indicative of change in state of association of the reacting alkoxide[6]. The cadmium–methyl resonances of a mixture of dimethylcadmium and methylcadmium ethoxide in toluene underwent collapse to a broad average resonance at 70° C. The more facile collapse with the ethoxide as compared with the methoxide supports the hypothesis of a reactive state of low association of the alkoxide.

The observation of Dessy *et al.*[2] that the PMR spectrum of dimethylcadmium showed no satellites in the presence of tetrahydrofuran suggests that complex formation between dimethylcadmium and base leads to faster exchange. We have observed similar catalysis by pyridine (1.1 *M* pyridine accelerated homoexchange of 0.4 *M* dimethylcadmium in toluene by 10^2), but in this case too added methanol accelerated exchange still further.

Catalysis of exchange reactions by Lewis acids[7], hydrides[8], and reactive metal alkyls[8] is already well known. It now appears that bases and metal alkoxides must be added to the list of possible catalysts, and that inadvertant entry of oxygen, even in minute quantities, must be regarded as a potential source of erratic results.

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Received December 13th, 1966; in revised form January 24th, 1967.