Tetrahedron Letters No.18, pp. 1345-1348, 1971. Pergamon Press. Printed in Great Britain.

ALKYL EXCHANGE REACTION BETWEEN BIS-TRIFLUOROMETHYL MERCURY AND DIMETHYL CADMIUM

B.L.Dyatkin, B.I.Martynov, I.L.Knunyants, S.R.Sterlin, L.A.Fedorov,
and Z.A.Stumbrevichute
Institute of Organo-Element Compounds, Academy of Sciences of USSR,
Moscow, USSR

(Received in UK 11 March 1971; accepted for publication 25 March 1971)

Alkyl exchange reactions are known to be an important method for preparing compounds of other metals. However, these reactions have not been sufficiently studied for perfluoroalkyl derivatives. Only some examples of alkyl exchange between perfluoroalkyl and alkyl compounds of mercury have been described[1,2]. The alkyl exchange has been investigated for the case of interaction between bis-trifluoromethyl mercury and ethylmagnesium bromide which gave diethyl mercury, but nothing is reported about the fluoroorganic product[3].

We found that bis-trifluoromethyl mercury quite easily exchanges with dimethyl cadmium in such solvents as pyridine or diglyme. According to NMR ^{19}F and ^{1}H spectra four new compounds appeared in the solution just after mixing the reagents at 34°C (the temperature of the NMR spectrometer). These were two organomercurials, $CH_3-Hg-CF_3$ ($J_{^{199}Hg-C-^{1}H}$ = 143.5 Hz) and $(CH_3)_2Hg$ ($J_{^{199}Hg-C-^{1}H}$ = 104.5 Hz), and two organocadmium compounds, $CH_3-Cd-CF_3$ and $(CF_3)_2Cd$ (see the Table). The equilibrium is established rather qiuckly. In NMR ^{19}F spectra the trifluoromethyl derivatives of mercury show a sharp singlet with sharp mercury satellites stipulated by the spin-spin coupling $^{199}Hg-C-^{19}F$. The trifluoromethyl cadmium compounds show a sharp singlet with two sharp pair of satellites stipulated by the spin-spin coupling $^{111(113)}Cd-C-^{19}F$. The constants of spin-spin coupling $J_{M-C-^{19}F}$ for symmetrical compounds $(CF_3)_2M$ (M = Cd or Hg) are greater than for non-symmetrical compounds CH_3-M-CF_3, which may be explained by a considerably greater electronegativity of CF_3. Thus the results obtained clearly indicate the formation of a CF_3-Cd bond and show its relative inactivity in alkyl exchange reactions.

It is known that alkyl exchange reactions between bis-trifluoromethyl mercury and dimethyl mercury[1], as well as those between dimethyl mercury and dimethyl cadmium[4] are so slow to proceed at room temperature that they cannot be detected by NMR method. Therefore the formation of the above-mentioned products of the reaction between $(CF_3)_2Hg$ and $(CH_3)_2Cd$ under conditions studied may be suggested to be the result of the following equilibria:

$$(a)\quad (CF_3)_2Hg + (CH_3)_2Cd \rightleftharpoons CH_3-Hg-CF_3 + CH_3-Cd-CF_3$$

$$(b)\quad (CF_3)_2Hg + CH_3-Cd-CF_3 \rightleftharpoons CH_3-Hg-CF_3 + (CF_3)_2Cd$$

$$(c)\quad (CH_3)_2Cd + CH_3-Hg-CF_3 \rightleftharpoons (CH_3)_2Hg + CH_3-Cd-CF_3$$

$$(d)\quad (CH_3)_2Cd + (CF_3)_2Cd \rightleftharpoons CH_3-Cd-CF_3$$

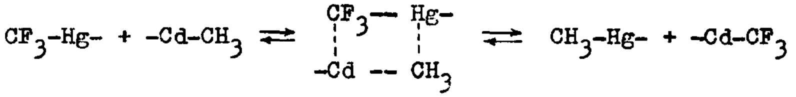
The quantitative ratios between the reaction products depend on those between the initial reagents. When dimethyl cadmium is in excess, we observed only the formation of $(CH_3)_2Hg$ and $CH_3-Cd-CF_3$. The intermediate non-symmetrical compound $CH_3-Hg-CF_3$ probably quickly transforms into dimethyl mercury as a result of the shift of the equilibrium (c) to the right. At an equimolecular ratio of the reagents $CH_3-Hg-CF_3$ is observed as well:

$$(CF_3)_2Hg + (CH_3)_2Cd \dashrightarrow CH_3-Hg-CF_3 + (CH_3)_2Hg + CH_3-Cd-CF_3$$

The absence of $(CF_3)_2Cd$ in the reaction mixture shows that the equilibrium (b) has shifted to the left because of insufficient concentration of $(CF_3)_2Hg$ and equilibrium (d) to the right because of high reactivity of $(CH_3)_2Cd$. This leads to the formation of non-symmetrical $CH_3-Cd-CF_3$ according to the reactions (a) and (c). Finally, we have found that in case of excess of $(CF_3)_2Hg$

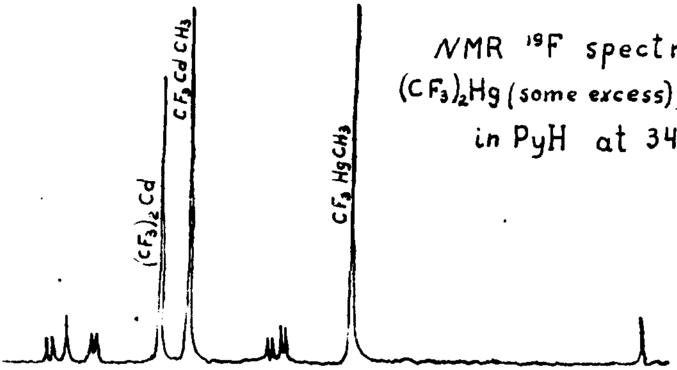
two new compounds, CH_3-Hg-CF_3 and $(CF_3)_2Cd$, and traces of dimethyl mercury have formed. Obviously, in this case the intermediate non-symmetrical product, CH_3-Cd-CF_3, transforms into symmetrical $(CF_3)_2Cd$ according to the reaction (b).

Thus, the Hg-CF_3 bond is more active in alkyl exchange reactions with methyl cadmium compounds than Hg-CH_3 bond.



$$CF_3\text{-}Hg\text{-} + \text{-}Cd\text{-}CH_3 \rightleftarrows \begin{matrix} CF_3 & \text{—} & Hg\text{-} \\ \vdots & & \vdots \\ \text{-}Cd & \text{--} & CH_3 \end{matrix} \rightleftarrows CH_3\text{-}Hg\text{-} + \text{-}Cd\text{-}CF_3$$

The results obtained allow to compare the reactivity of the bonds -Cd-CH_3 and -Cd-CF_3. It is known that $(CH_3)_2Cd$ in pyridine solution exchanges its alkyl groups so quickly that the satellites $^{111(113)}$Cd-C-^{1}H cannot be observed in the NMR ^{1}H spectrum. For the compound CH_3-Cd-CF_3 we could see the summary signal of cadmium satellites in the NMR ^{1}H spectrum at 34°C (in pyridine in the presence of dimethyl cadmium and other compounds that can catalyse alkyl exchange). However, already upon cooling to -15°C the satellites ^{111}Cd and ^{113}Cd become quite distinct. Thus the reactivity of the CH_3-Cd bond in CH_3-Cd-CF_3 is essentially lower than in $(CH_3)_2Cd$. Apparently, this effect may be attributed to the weakening of the nucleophilic character of the methyl group in CH_3-Cd-CF_3 as compared to $(CH_3)_2Cd$ because of pseudohalide properties of the trifluoromethyl group. Therefore this compound can be regarded as a close analogue of CH_3CdX, where X is halogen.



NMR ^{19}F spectrum
$(CF_3)_2Hg$ (some excess) + $(CH_3)_2Cd$
in PyH at 34°C

TABLE

Parameters of NMR ^1H and ^{19}F Spectra of Methyl and Trifluoromethyl Compounds of Hg and Cd (in pyridine)*

Compound Parameter	CH_3-Hg-CF_3	$(CF_3)_2Hg$	CH_3-Cd-CF_3	$(CF_3)_2Cd$
CF_3 p.p.m. (from external CF_3COOH)	-41.2	-44.0	-45.5	-46.7
J Hz (± 1 Hz):				
$^{199}Hg-C-^{19}F$	965	1326		
$^{111(113)}Cd-C-^1H$			64 (67)**	
$^{111(113)}Cd-C-^{19}F$			309 (323)	359 (376)

---

*The NMR ^1H and ^{19}F spectra were obtained on an R-20 "Hitachi-Perkin-Elmer" Spectrometer with the working frequency of 60/56.4 MHz.

**At -15°C.

Taking into account pseudohalide properties of perfluoroalkyl radicals, it can be assumed that the exchange between alkyl or aryl derivatives of various elements and perfluoroalkyl mercurials will proceed similar to their reactions with mercury halides.

References

1.M.D.Rausch and J.R.Van Wazar, Inorg.Chem., 3, 761 (1964).
2.G.F.Reynolds and S.R.Daniel, ibid., 6, 480 (1967).
3.R.N.Sterlin, Lee Wei-ghan, and I.L.Knunyants, ZhVKhO imeni Mendeleeva, 6, 108 (1961) /in Russian/.
4.(a) C.R.McCay and A.L.Allred, J.Am.Chem.Soc., 84, 912 (1962).
(b) R.E.Dessy, F.Kaplan, G.R.Coe, and R.M.Salinger, ibid., 85, 1191 (1965).
5.N.S.Ham and T.Mole, in "Progress in NMR", ed. J.Emsley, J.Feeney, and L.N.Sutcliff, 4, 93 (1969).