Fluorine Resonance Spectra of Pentafluorophenyl-zinc and -cadmium Halides

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Zinc reacts quantitatively with bromo- and iodo-pentafluorobenzene in a variety of co-ordinating solvents to give solutions of 'pentafluorophenylzinc halides'. Pentafluorophenyl exchange is normally slow on an n.m.r. time scale at 35°, and equilibrium constants for the Schlenk equilibrium $(C_6F_5)_2Zn + ZnX_2 \rightleftharpoons 2C_6F_5ZnX$ have been obtained from the p-fluorine resonance spectra. Similar results are reported for 'pentafluorophenylcadmium iodide' in very strongly co-ordinating solvents. The Schlenk equilibrium for 'pentafluorophenylzinc chloride' in tetrahydrofuran has been studied by mixing solutions of zinc chloride and bis(pentafluorophenyl)zinc, and is established within 10 s.

It has been shown[1] from the ^{19}F n.m.r. spectra (p-fluorine region) that chemical exchange between pentafluorophenylmagnesium halides and bis(pentafluorophenyl)magnesium is slow on an n.m.r. time scale at room temperature. The present paper reports a similar study of the Schlenk equilibria in pentafluorophenyl-zinc and -cadmium halides. In its general form (neglecting polymeric species) the Schlenk equilibrium[2] for a species RMX in a co-ordinating solvent is:

$$\begin{tikzcd} R_2M,MX_2 \arrow[r, shift left] & R_2M + MX_2 \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & 2RMX \arrow[l, shift left] \arrow[d, shift left] \\ & (MX_2)_2 \arrow[u, shift left] & (RMX)_2 \arrow[u, shift left] \end{tikzcd} \quad (1)$$

The preparations of bis(pentafluorophenyl)zinc and bis(pentafluorophenyl)cadmium have been reported.[3] However, it was found that both zinc and cadmium react directly with pentafluoroiodobenzene in a variety of co-ordinating solvents to give almost quantitative yields of pentafluorophenyl-zinc and -cadmium iodides. Pentafluorophenylzinc bromide could also be prepared in a similar manner from bromopentafluorobenzene.

RESULTS AND DISCUSSION

The Zinc Systems.—The co-ordinating solvents used were tetrahydrofuran (THF), diethyl ether (DEE), 1,2-dimethoxyethane (DME), diethyleneglycol dimethyl ether (DGDM), dimethylformamide (DMF), dimethylacetamide (DMA) and dimethyl sulphoxide (DMSO). Since the THF solutions were the most extensively studied, the results for these will be considered first.

The ^{19}F n.m.r. spectrum of bis(pentafluorophenyl)zinc in tetrahydrofuran shows three regions of absorption ($\delta_o = 54{\cdot}6$ p.p.m., $\delta_p = 95{\cdot}4$ p.p.m., and $\delta_m = 100{\cdot}0$ p.p.m. above benzotrifluoride as an absorption internal reference). The *ortho* and *meta* resonances are complex, but the *para* resonance, as in bis(pentafluorophenyl)magnesium, consisted of a sharp triplet with $J_{34} = 19{\cdot}6$ Hz. (The relationship between J_{24} and δ_p proposed by Hogben and Graham[4] predicts a very small value for J_{24} of 0·3 Hz).

'Pentafluorophenylzinc Iodide.'—The ^{19}F n.m.r. spectrum of a THF solution of pentafluorophenylzinc iodide also shows three regions of absorption. The *para* resonance now consists of two sharp triplets in the intensity ratio low field/high field of 1·3 (35° and 0·85M) at 94·8 and 95·5 p.p.m. Adding zinc iodide solution decreases the relative intensity of the high field triplet, and accordingly this can be assigned to '$(C_6F_5)_2Zn$,' and the low field triplet to 'C_6F_5ZnI'. However, in order to obtain quantitative equilibrium data, it is necessary to know the nature of the species in solution (*i.e.* monomers, dimers, *etc.*).

The Raman spectrum of zinc iodide in THF[5] shows only one Zn–I stretch (polarized) at 155 cm^{-1} which does not shift with change in concentration, indicating that the main species present is monomeric, solvated ZnI_2. It is highly probable that bis(pentafluorophenyl)zinc will also be monomeric, and here the two most likely equilibria are

$$(C_6F_5)_2Zn + ZnI_2 \rightleftharpoons 2C_6F_5ZnI \qquad (2)$$

and

$$(C_5F_5)_2Zn + ZnI_2 \rightleftharpoons (C_6F_5ZnI)_2 \qquad (3)$$

The ratios $\frac{['\,C_6F_5ZnI\,']}{['(C_6F_5)_2Zn\,']}$ were determined for seven solutions over the concentration range 0·15—1·32M, and found to be constant within experimental error. If equilibrium (3) was involved, this ratio would vary by an amount considerably greater than the experimental errors. It can therefore be concluded that the species present in solutions of pentafluorophenylzinc iodide in THF can be represented by a predominantly monomeric Schlenk equilibrium (2). The calculated value for the equilibrium constant $K\left(\frac{[C_6F_5ZnI]^2}{[(C_6F_5)_2Zn][ZnI_2]}\right)$ is $7{\cdot}5 \pm 0{\cdot}9$ at 35°. (Unless otherwise stated all errors quoted are ± two standard deviations.) The chemical shifts of the two triplets changed only very slightly over the same concentration range (by *ca.* 0·1 p.p.m.).

The equilibrium constant K was also measured at 16 other temperatures in the range 188—341 K and found

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[1] D. F. Evans and M. S. Khan, *J. Chem. Soc.* (*A*), 1967, 1643.

[2] B. J. Wakefield, *Organometallic Chem. Rev.*, 1966, **1**, 131.

[3] S. C. Cohen and A. G. Massey, *Adv. Fluorine Chem.*, 1970, **6**, 83.

[4] M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **91**, 283.

[5] K. Cavanagh, Ph.D. Thesis, University of London, 1969.

to vary only slightly (from 10·2 to 7·4). A least squares treatment, gave for reaction (2) ΔH(average) = 0·88 ± 0·30 kJ mol^{-1} and ΔS = 16 J mol^{-1} K^{-1}. The distribution of zinc between pentafluorophenyl and iodide is therefore almost statistical. For a random redistribution $K^* = 4$, $\Delta H^* = 0$, and ΔS^* = 13 J mol^{-1} K^{-1}.

Although the two p-fluorine triplets were quite sharp at 35°, at higher temperatures the line widths increased appreciably due to pentafluorophenyl exchange. From the relationship $\frac{1}{\tau} = \pi(\Delta_{\frac{1}{2}} - \Delta_{\frac{1}{2}}^{\circ})$, where τ is the mean lifetime of a pentafluorophenyl group and $\Delta_{\frac{1}{2}}$ and $\Delta_{\frac{1}{2}}^{\circ}$ are the line widths at half-height in the presence, and absence, of exchange, the activation energy for pentafluorophenyl exchange was found to be *ca.* 70 kJ mol^{-1}. At the highest temperature studied (85°) τ for C_6F_5ZnI was *ca.* 4·5 × 10^{-2} s, and for $(C_6F_5)_2Zn$ was *ca.* 3·6 × 10^{-2} s (0·85M solution of ' C_6F_5ZnI ').

' Pentafluorophenylzinc Bromide.'—The fluorine resonance spectra obtained were very similar to those described above. The Raman spectrum of zinc bromide in THF (Zn–Br stretch at 213 cm^{-1}) [5] suggests that predominantly monomeric species are present. From the observed concentrations of $(C_6F_5)_2Zn$ and C_6F_5ZnBr, the calculated value of K for the monomeric Schlenk equilibrium is 16·0 ± 3·0 at 35°.

' Pentafluorophenylzinc Chloride.'—Chloropentafluorobenzene did not react with zinc in THF, and hence the ' pentafluorozinc chloride ' system was studied by mixing solutions of bis(pentafluorophenyl)zinc and zinc chloride. Precipitation studies on the ethylzinc iodide system suggested that the reaction between diethylzinc and zinc iodide in THF is slow,[6] although in contrast, i.r. measurements [7] indicated that the reaction is essentially complete in less than 5 min. Accordingly the corresponding reaction between bis(pentafluorophenyl)zinc and zinc chloride in THF was monitored closely using the oscilloscope on the n.m.r. spectrometer, and found to reach virtual completion in less than 10 s.

The Raman spectrum of zinc chloride in THF [5] (Zn–Cl stretch at 313 cm^{-1}) again indicates essentially monomeric species, and K for ' C_6F_5ZnCl ' was found to be 18·1 ± 5·4. The two triplets were slightly broad (widths at half-height of the lines were chloride 8 Hz, bromide 4 Hz, and iodide 2·5 Hz at 35°), suggesting that the rate of pentafluorophenyl exchange follows the sequence chloride > bromide > iodide, exactly as found for the corresponding Grignard reagents in ether.[1]

Diethyl ether (DEE) Solutions of ' Pentafluorophenylzinc Iodide '.—In this solvent, pentafluorophenyl exchange was relatively fast on an n.m.r. time scale at 35° but was slowed down below −20°. Addition of zinc iodide showed that the high field triplet again arises from $(C_6F_5)_2Zn$ (Figure 1). Pentafluorophenyl exchange is therefore much faster in the zinc system than in the corresponding pentafluorophenyl Grignard reagent.[1]

Of all the solvents studied, polymerization is most likely to occur in DEE, because of its comparatively weak donor abilities. The Raman spectrum (80—280 cm^{-1}) of a 2M solution of zinc iodide in DEE showed a strong polarized band at 162 cm^{-1} which can be assigned to ν_s(Zn–I), and a very weak and broad band at 238 cm^{-1}, which may be a zinc–oxygen stretch. Diluting the solution to 0·4M did not shift the strong band. It therefore seems likely that zinc iodide in DEE is predominantly monomeric. The ratio $\frac{(C_6F_5)_2Zn}{C_6F_5ZnI}$ in DEE at −40° was within experimental error, independent of concentration, and K for the monomeric Schlenk equilibrium was 6·0 ± 0·6.

Other Solvents.—In all the other solvents studied, pentafluorophenyl exchange was slow on an n.m.r. time scale at 35°. Since these solvents are strongly co-ordinating it seems likely that only monomeric species will be present and the relevant data for these systems are summarized in Table 1. A possible complication arises with DMF, DMA, and DMSO. Because of their high dielectric constants, ionization to give species such as $ZnBr^+$, $ZnBr_3^-$, $C_6F_5Zn^+$, and $C_6F_5ZnBr_2^-$ may occur. Conductivity data and Raman spectra [8] for solutions of zinc bromide and pentafluorophenylzinc bromide indicate that ionic species are, in fact, present. However, in view of the strong solutions (*ca.* 1M) used for the ^{19}F n.m.r. spectra, the equilibrium constants given in Table 1 are probably not greatly affected by ionization.

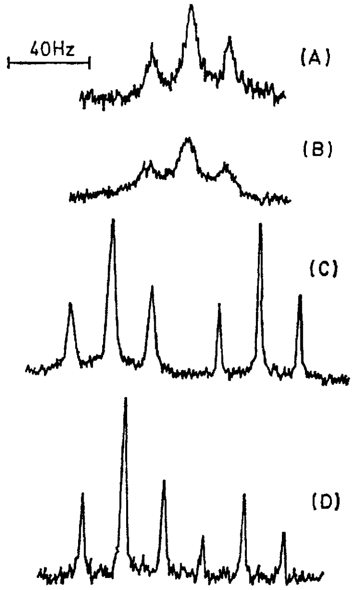

FIGURE 1 p-Fluorine resonance of ' C_6F_5ZnI ' in DEE at (A), 50; (B), 35; (C), −40; and (D), −40 °C, ZnI_2 added (Zn/I ratio 0·7)

Comparison of DMSO and THF as Co-ordinating Solvents.—For both C_6F_5ZnI and $(C_6F_5)_2Zn$ the chemical shifts of the *para*-fluorines are appreciably different in THF and DMSO. Figure 2 shows these fluorine shifts

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[6] M. H. Abraham and P. H. Rolfe, *J. Organometallic Chem.*, 1965, **3**, 222.

[7] D. F. Evans and I. Wharf, *J. Chem. Soc. (A)*, 1968, 783.

[8] R. F. Phillips, Ph.D. Thesis, University of London, 1969.

for the ' pentafluorophenylzinc iodide ' system in mixtures of THF and DMSO.

Table 1

Properties of ' pentafluorophenylzinc halide ' solutions

Solvent	Halide	Chemical shifts (p.p.m.)[a]	K[b]
DEE	I	94·1, 94·9	6·0 ± 0·6 *
THF	I	94·8, 95·45	7·5 ± 0·9
THF	Br	94·8, 95·5	16·0 ± 3·0
THF	Cl	95·1, 95·7	18·1 ± 5·4
DME	I	94·45, 94·9	9·1 ± 0·5
DME	Br	94·4, 94·8	11·4 ± 4·1
DGDM	I	96·0, 96·3	12·6 ± 2·4
DGDM	Br	96·25, 96·5	23·0 ± 5·6
DMA	I	96·8, 97·8	41·0 ± 5·3
DMF	I	96·8, 97·5	21·2 ± 2·7
DMF	Br	96·7, 97·5	19·6 ± 1·8
DMSO	I	96·4, 97·2	30·4 ± 3·9
DMSO	Br	96·6, 97·3	27·0 ± 6·2

[a] To high field of benzotrifluoride as internal reference.
[b] All at 35° except *, which was at −40 °C.

It appears that, as expected, DMSO co-ordinates much more strongly than THF, and also that the predominant species contain one or two moles of co-ordinated DMSO only.

The Cadmium Systems.—It has recently been shown[9] that cadmium reacts under mild conditions with alkyl iodides in the presence of DMSO, DMF, and hexamethylphosphoramide (HMP). It was found in the present work that cadmium also reacts with pentafluoroiodobenzene in THF, DMSO, DMF, and HMP to give brown solutions. (A white precipitate which contains organocadmium species appears with THF, and this system was not studied further.) Figure 3 shows the *para*-fluorine resonance of ' C_6F_5CdI ' in DMSO. Two rather broad overlapping triplets are observed at 35°, which sharpen on cooling the solution to −15°, while at 70° exchange is fast on an n.m.r. time scale and a single triplet is observed. It was shown by varying the Cd/I ratio that, in a similar manner to the zinc system, the low field triplet is due to C_6F_5CdI, and the high field triplet to $(C_6F_5)_2Cd$. In hexamethylphosphoramide the *para*-fluorine resonance at 35° also consists of two rather broad triplets, but in DMF, chemical exchange was much faster. At 35° a single triplet was observed, which collapsed into two overlapping triplets on cooling the solution to −40°. The addition of 1·1 mol of tetraethylethylenediamine (TEED) per mol of cadmium to the DMF solution caused a considerable change in the fluorine resonance spectrum. Two fairly sharp and widely separated triplets were observed at 35° and there was a considerable increase in the relative intensity of the low field C_6F_5CdI triplet. (TEED also slows down chemical exchange in Grignard reagents.[10]) It is clear that in systems of the type ' C_6F_5MI ', the rate of pentafluorophenyl exchange increases in the order Mg < Zn < Cd. The data obtained for the ' C_6F_5CdI ' solutions are summarized in Table 2.

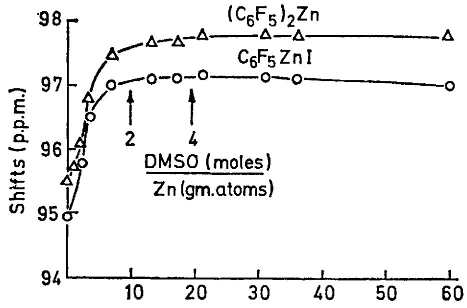

Figure 2 *p*-Fluorine chemical shifts for ' C_6F_5ZnI ' in in THF–DMSO

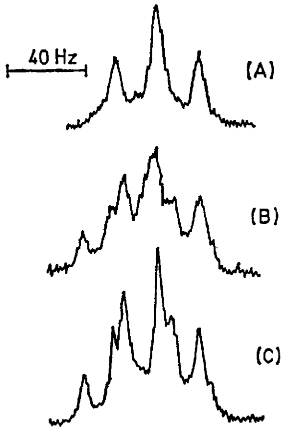

Figure 3 *p*-Fluorine resonance of ' C_6F_5CdI ' in DMSO at (A), 70; (B), 35; and (C), −15 °C

Table 2

Properties of ' pentafluorophenylcadmium iodide ' solutions

Solvent	Chemical shifts, p.p.m.[a]	K	Temp./°C
DMF	96·7, 96·8	3·2 ± 0·7	−40
DMF and TEED	95·2, 96·2	21·0 ± 2·0	35
DMSO	96·3, 96·5	3·2 ± 0·2	15
HMP	97·2, 97·7	2·3 ± 0·3	35

[a] To high field of benzotrifluoride as internal reference.

DISCUSSION

Tables 1 and 2 show that both $(C_6F_5)_2M$ and C_6F_5MX species are present in solutions of pentafluorophenyl-zinc and -cadmium halides. In contrast, in the corresponding alkyl systems only RMX species could be detected[7,11] (thus, for the equilibrium $Et_2Zn + ZnI_2 \rightleftharpoons 2EtZnI$ in THF, K is $\geqslant 100$).[7] This difference can be attributed to the high electronegativity of the pentafluorophenyl group which causes it to behave to some extent as a pseudohalogen. The equilibrium constants K in the pentafluorophenylzinc halide solutions tend to

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[9] J. Chenault and F. Tatibouët, *Compt. rend.* (*C*), 1966, **262**, 499.

[10] D. F. Evans and M. S. Khan, *J. Chem. Soc.* (*A*), 1967, 1648.

[11] D. F. Evans and G. V. Fazakerley, *J. Chem. Soc.* (*A*), 1971, 182.

increase with increasing donor ability of the solvent, although the variations in K are not large.

The p-fluorine chemical shifts in the pentafluorophenylzinc halide systems also shift to higher applied fields as the donor ability of the solvent is increased (Table 1). Two factors which could contribute to this effect are (i) a reduction in p^{π} bonding involving the formally vacant zinc p-orbitals and (ii) an inductive effect transmitted *via* the zinc–carbon bond through the π electrons of the benzene ring.

The pentafluorophenyl exchange observed in several of the systems could occur through a bridged intermediate similar to those suggested to account for alkyl and aryl exchange in Grignard reagents,[12] or *via* ionic intermediates. Thus,

$$C_6F_5{}^*ZnX \rightleftharpoons C_6F_5{}^*Zn^+ + X^-$$
$$2(C_6F_5)_2Zn \rightleftharpoons C_6F_5Zn^+ + (C_6F_5)_3Zn^-$$
$$(C_6F_5)_3Zn^- + C_6F_5{}^*Zn^+ \rightleftharpoons C_6F_5{}^*ZnC_6F_5 + (C_6F_5)_2Zn$$

In pentafluorophenylzinc iodide solutions, pentafluorophenyl exchange is fastest in DEE, which is the poorest ionizing solvent. This would indicate that, for the zinc systems at least, the first mechanism is more likely.

EXPERIMENTAL

Solutions were prepared and handled in oxygen-free nitrogen as described previously.[1] The solvents were purified by standard procedures, and normally stored over Linde 3A Molecular Sieves. The pentafluorophenyl-zinc and -cadmium halides were prepared by adding the halogenopentafluorobenzene to a well stirred suspension of zinc wool or cadmium turnings in the appropriate solvent. Reaction normally occurred almost immediately and sometimes required moderation by cooling in an ice-bath. The metals were cleaned by washing with dilute acetic acid, water, and finally acetone. Bis(pentafluorophenyl)zinc was prepared by decarboxylation of zinc pentafluorobenzoate at *ca.* 210°,[13] and purified by resublimation. The solutions were analysed for zinc or cadmium by titration with ethylenediaminetetra-acetic acid, and for halogen using silver nitrate. In all cases the X : M ratios were in the range 0·96—1·03.

Fluorine resonance spectra were measured on Perkin-Elmer R14 and Varian HA100 spectrometers, and Raman spectra on a Cary 81 instrument with a helium–neon laser source (632·8 nm).

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[12] D. F. Evans and G. V. Fazakerley, *J. Chem. Soc.* (*A*), 1971, 184.

[13] P. Sartori and M. Weidenbruck, *Chem. Ber.*, 1967, **100**, 3016.