

systems which depend on the validity of an electrical double layer model. Thus for their arachidic acid sols Ottewill and Wilkins¹⁵ found a value of the order of 10^{-14} erg and for aqueous suspensions of solid and liquid paraffinic hydrocarbon Srivastava and Haydon^{16,17} found approximately 10^{-13} erg.

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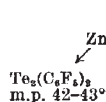
CHEMISTRY

Ligands containing Fluoroaromatic Groups

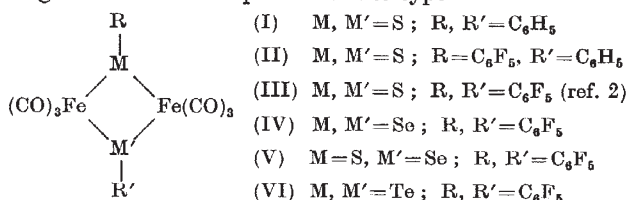
THE relatively high electronegativity of the pentafluorophenyl group, C_6F_5 , is expected to alter the donor characteristics of ligand molecules. We wish to report initial results of studies with three types of fluoroaromatic ligands.

Pentafluorophenyl cyanide, C_6F_5CN , reacts partially with tungsten hexacarbonyl in petrol ether solvent, when the mixture is irradiated with ultraviolet light. Two yellow compounds were separated by column chromatography under a nitrogen atmosphere, but in neither case could analytical samples be obtained, because all attempts at crystallization (under nitrogen) failed because of a facile decomposition. The infrared spectra (in the region close to $2,000\text{ cm}^{-1}$) of the solutions from the column were almost identical to those of $RCNW(CO)_5$ and $(RCN)_2W(CO)_4$ (R, alkyl). Clearly the pentafluorophenyl group is strongly affecting the stability of these complexes. *bis*(Pentafluorophenyl)sulphide and -selenide do not react with either chromium hexacarbonyl or triiron dodecacarbonyl when heated under reflux in 80/100 petrol ether, and palladium dichloride forms no complex with pentafluorophenyl cyanide after 5 days at 110°C in a sealed tube.

Iron pentacarbonyl and triiron dodecacarbonyl react with $S_2(C_6F_5)_2$, $Se_2(C_6F_5)_2$ (ref. 1), $Te_2(C_6F_5)_2$ * and C_6F_5SH

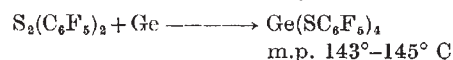
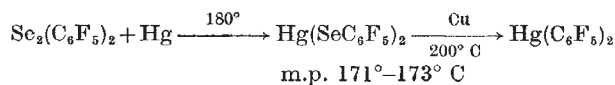
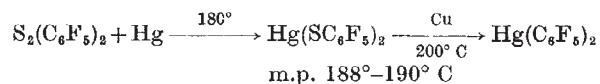


to give air-stable compounds of the type

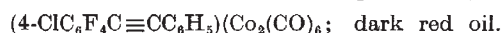


¹⁹F and ¹H nuclear magnetic resonance spectra of these dimers indicate the presence of isomers, but we have, so far, been unable to separate them by chromatographic techniques. A comparison of the stabilities of I and III indicated little difference between them. A competitive reaction carried out using triiron dodecacarbonyl (1 mole) and a mixture of $S_2(C_6H_5)_2$ and $S_2(C_6F_5)_2$ (1 mole each) gave the expected three products (I, II and III) which were readily separated by preparative scale thin-layer chromatography on kieselguhr using petrol ether as eluent. The yields of products were very close to the ratio 1 : 2 : 1 (I : II : III) expected if the bridging ligands were little influenced by the group R; a ready interchange of ligands was also observed if either I or III was treated with S_2R_2 . It is interesting to note that the melting-decomposition points of I, II and III were all $140^\circ-143^\circ\text{C}$; mixed melting points of any two were some $20^\circ-30^\circ\text{C}$ lower.

The thermal decomposition of III in a sealed tube at 160°C gave carbon monoxide and decafluorobiphenyl as the only isolable products. Attempts to remove the sulphur ligand from the iron by heating III with mercury failed, decafluorobiphenyl again being formed; this is in contrast to the free ligand $S_2(C_6F_5)_2$ [and $Se_2(C_6F_5)_2$] which reacts with both mercury and germanium on heating.



Mixed aromatic/fluoroaromatic acetylenes, $\phi_F C \equiv C \phi$, react with cobalt carbonyl in a manner similar to diphenyl acetylene³, the fluoroaromatic group having little influence on the reaction. Typical compounds synthesized are



In the latter case, where two acetylene groups are present, it is possible to isolate a rather unstable solid (decomposes without melting at 156°C) which has two cobalt atoms attached to each acetylenic bond.

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