Preliminary Note

Chemistry of the metal carbonyls

XXIII. Pentafluorophenyl derivatives of transition metals*

The recent preparation of pentafluorophenylmagnesium iodide and bromide[2], as well as pentafluorophenyllithium[3] suggests the use of these reagents in the synthesis of pentafluorophenyl–transition metal complexes. Besides representing a new class of organometallic compound, these latter substances would increase the range of known compounds possessing transition metal–carbon σ-bonds[4], and would add to our knowledge of aromatic fluorine chemistry[5], both subjects of current interest.

Manganese pentacarbonyl bromide (2.1 g, 7.6 mmoles) and dry diethyl ether (500 cc) were placed in a 1-l three-necked flask fitted with stirrer, condenser, dropping funnel and nitrogen inlet. After cooling the flask to 0°, a solution of pentafluorophenyllithium [prepared at —78° from 2.0 g (8.1 mmoles) of pentafluorophenyl bromide and 3.15 g of a 15% solution of *n*-butyllithium (7.4 mmoles) in hexane] was added. The mixture was stirred for 6 h at 0°, then for 16 h at room temperature.

After filtration of precipitated lithium bromide, the filtrate was evaporated to dryness on a water pump, and the residue was subjected to fractional sublimation. White crystalline pentafluorophenylmanganese pentacarbonyl (m.p. 118–120°) was obtained (0.8 g, 29% yield); this was further purified by recrystallisation from benzene.

[Found: C, 36.4; H, 0.0; F, 25.9; mol. wt. (vapour pressure osmometer), 378. $C_{11}F_5MnO_5$ calcd.: C, 36.5; H, 0.0; F, 26.2%; mol. wt., 362.]

The high resolution infrared spectrum of pentafluorophenylmanganese pentacarbonyl (cyclohexane solution) shows carbonyl stretching frequencies at 2135 (m), 2068 (w), 2040 (vs), 2012 (s) and 1968 (w) cm^{-1}. These bands are rather similar in position and relative intensity to those observed with perfluoroalkylmanganese pentacarbonyl compounds[6]. Other bands in the infrared spectrum of pentafluorophenylmanganese pentacarbonyl (carbon disulphide solution, sodium chloride optics) appear at 1061 (m), 1045 (w), 1012 (w), 967 (s), 760 (s) and 746 (w) cm^{-1}.

Treatment of iron tetracarbonyl diiodide with pentafluorophenyllithium affords pentafluorophenyliron tetracarbonyl iodide (2% yield), as a dark red air-stable solid (m.p. 74–76°) which sublimes at 30° (10^{-3} mm). The infrared spectrum (carbon disulphide solution) shows bands characteristic of the pentafluorophenyl group at 1060 (w), 1008 (w), 965 (m), 838 (m), 775 (w) cm^{-1} and carbonyl stretching frequencies at 2141 (w), 2079 (vs), 2049 (w) cm^{-1}.

From reactions between bis(cyclopentadienyl)titanium dichloride and penta-

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* For Part XXII of this series, see ref. 1.

fluorophenyllithium, it has been possible to isolate the first fluorocarbon derivatives of titanium: $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ (orange needles, m.p. 228–230°, 44% yield) and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ (pale orange, m.p. 201–203°, 29% yield).

The new pentafluorophenyl–transition metal complexes are chemically extraordinarily robust for compounds containing organic groups bound to the metal by carbon–metal σ-bonds.

A sample (316 mg, 0.874 mmoles) of pentafluorophenylmanganese pentacarbonyl was undecomposed after heating *in vacuo* at 138° for 72 h. Subsequent pyrolysis at 162° for 72 h, caused some darkening in colour, but on opening the Pyrex reaction vessel the quantity (0.58 mmoles) of carbon monoxide removed was only 13% of that expected for complete decomposition. Moreover, although some pentafluorophenylmanganese pentacarbonyl was lost in working up the product, 161 mg (51% of that taken for pyrolysis) of pure $C_6F_5Mn(CO)_5$ was recovered. Pentafluorophenylmanganese pentacarbonyl is, therefore, not only thermally more stable than phenylmanganese pentacarbonyl, which decomposes at 100°, but is also more stable than pentafluoroethylmanganese pentacarbonyl which is largely decomposed on heating at 150°.[6b]

Bis(cyclopentadienyl)bis(pentafluorophenyl)titanium is thermally stable *in vacuo* at 110°, but pyrolysis at 150° yields small quantities of the new compound $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$, a yellow solid which sublimes *in vacuo*, and decomposes without melting at 240°.

Treatment of perfluoroalkyl–manganese and –iron compounds with aqueous base at room temperature, or with hydrogen chloride gas in Pyrex bulbs at 100° yields, respectively, fluoride ion or silicon tetrafluoride[6b]. The behaviour of the new pentafluorophenyl–transition metal compounds towards these reagents is different. Aqueous base at room temperature has no apparent effect, and although hydrogen chloride gas does react with the pentafluorophenyl compounds, pentafluorobenzene is produced rather than silicon tetrafluoride, and temperatures required for detectable reaction appear to be higher. Thus a sample (402 mg, 0.785 mmoles) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ on treatment with hydrogen chloride (5.0 mmoles) in a Pyrex bulb at 110° for 2 days was unaffected. However, further heating at 150° for 24 h yielded 1.2 mmoles of pentafluorobenzene (identified by its infrared spectrum). After the bulb had been resealed with the remaining HCl (3.5 mmoles) and heated at 150° (1 day) there was a further uptake of 0.6 mmoles of HCl and formation of an additional 0.15 mmoles of C_6F_5H. The total amount of pentafluorobenzene recovered was thus 86% of the available C_6F_5 groups. Recrystallisation of the solid residue in the bulb from toluene gave 45 mg of bis(cyclopentadienyl)titanium dichloride.

From the reaction between boron trichloride and bis(cyclopentadienyl)bis(pentafluorophenyl)titanium at 160° it is possible to isolate pentafluorophenylboron dichloride, a liquid stable *in vacuo*. This suggest that the new pentafluorophenyl–transition metal compounds will be useful intermediates in the synthesis of pentafluorophenyl derivatives of other elements.

Examination of the ^{19}F NMR spectra of pentafluorophenylmanganese pentacarbonyl shows bands centred at 104.3, 157.5 and 161.2 p.p.m. relative to CCl_3F (0.0 p.p.m.) increasing to high field. These bands are assignable to the *ortho-*, *para-*, and *meta-*fluorine atoms of the C_6F_5–Mn group respectively[7].

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Book Review

Industrial Applications of the Organometallic Compounds. A Literature Survey, by G. J. H. HARWOOD. Chapman and Hall, London, 1963, xi + 451 pages, £ 3/-/-

This book is primarily for the industrial chemist, who can, according to the author's preface, use it to assess rapidly whether any organometallic compounds are likely to provide a solution of a particular problem.

The term "organometallic compounds" in this book covers organic derivatives of all the elements with the exception of the permanent gases, boron, carbon, silicon, phosphorus, and the halogens; it includes not only compounds with carbon–metal bonds, but also those with alkoxy– and aryloxy–metal bonds, and chelate compounds in which organic groups are coordinated to metals through oxygen or nitrogen. The book is essentially a compilation of references to proposed industrial applications of such compounds, and very little critical evaluation has been attempted. There are references in the main survey to patents and papers up to 1960, and an appendix, listing some later references, includes some 1961 papers. There is a very good index, and an appendix giving addresses of chemical manufacturers referred to in the text.

This book will serve adequately the limited purpose for which it was produced, namely, to provide the industrial chemist with references to the technical and patent literature. More general readers will find it interesting if somewhat frustrating to glance at the many and varied claims made for applications of organometallic compounds; this reviewer is left curious to know, for example, whether tetraethylgermane really is used to activate aluminium to be employed in preparation of alkylaluminiums, what quantities of cyclopentadienylniobium chlorides are used as polymerization catalysts for drying oils, alkyd resins and curable silicones, and how many of the very large number of suggested anti-knock additives find their way into commercial motor fuels.

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