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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XXV*. THE REACTION OF TETRAFLUOROBENZYNE WITH SOME TRANSITION METAL COMPLEXES

D. M. ROE AND A. G. MASSEY
Department of Chemistry, Queen Mary College, London E.1. (Great Britain)

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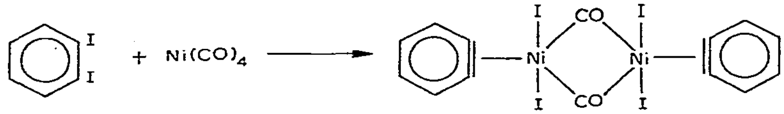
SUMMARY

Decomposing "(pentafluorophenyl)magnesium bromide" in dioxane provides a convenient system for generating tetrafluorobenzyne in the presence of transition metal complexes. Four benzyne "adducts", $C_5H_5NiC_5H_5C_6F_4$ (two isomers), $Co_4(CO)_{10}C_6F_4$ and $Fe_2(CO)_8C_6F_4$, have been isolated during the initial survey of this highly promising synthetic technique.

INTRODUCTION

In recent years there have been a number of attempts to generate benzyne in the presence of transition metal complexes, with a view to stabilizing the highly reactive C_6H_4, by complexing it with the metal; essentially, two different ways of generating the benzyne intermediate have been employed. In the first a 1,2-dihalobenzene is stripped of halogen[2,3] using, for example an excess of the transition metal complex under study; in the second method the benzyne is formed in the presence of a transition metal complex by the thermal decomposition of an *ortho* diazonium carboxylate or similar compound[4,5]. In the latter method complications arise from complex formation between the transition metal and the benzyne precursor and thus far only one definite benzyne–transition metal π-complex has been claimed[3]:



RESULTS AND DISCUSSION

It is well known[6] that pentafluorophenyl derivatives of lithium and magnesium are very useful reagents for the production of tetrafluorobenzyne which can be trapped in very high yield by suitable organic reagents. It seemed to us that these organometallic derivatives (which are extremely simple to synthesise from commercially available materials) could provide a more effective means of studying the reaction of substituted arynes with transition metal derivatives. For our model transition

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[*] For Part XXIV see ref. 1.

metal system we chose nickelocene because it has at least a two-fold chance of reacting with C_6F_4, either by forming a direct Ni–C_6F_4 complex or by trapping the tetrafluorobenzyne with the relatively reactive cyclopentadienyl ring systems. (Nickelocene is known to add olefins and acetylenes to one of the π-C_5H_5 rings[7,8]). It was soon evident that pentafluorophenyllithium decomposed at too low a temperature to react with the nickelocene and we therefore concentrated on the production of tetrafluorobenzyne from (pentafluorophenyl)magnesium bromide. In refluxing diethyl ether a mixture of decomposing C_6F_5MgBr and nickelocene always failed to produce any products containing both Ni and C_6F_4; changing the solvent to tetrahydrofuran produced a 0.1% yield of what was later discovered to be $C_5H_5NiC_5H_5$-C_6F_4. In diglyme (diethyleneglycol dimethyl ether) the yield was still tantalisingly small, being only about 1% based on bromopentafluorobenzene. However, in well-dried dioxane the addition of tetrafluorobenzyne to nickelocene occurred smoothly to give a 20% yield of $C_5H_5NiC_5H_5C_6F_4$ (this product is in fact an approximately 50/50 mixture of two isomers formed by either 1,2- or 1,3-addition of C_6F_4 to one of the cyclopentadienyl rings[1]).

We are not yet sure why the addition of tetrafluorobenzyne to the nickelocene is so solvent-dependent. It is not simply due to the fact that in dioxane "C_6F_5MgBr" disporportionates into $(C_6F_5)_2Mg$ and $MgBr_2$, because Evans has shown[9] that bis(pentafluorophenyl)magnesium makes up a substantial proportion of this Grignard reagent even in the weakly coordinating solvent, diethylether; furthermore, we have shown that the decomposition of bis(pentafluorophenyl)magnesium in tetrahydrofuran gives only 0.6% yield of the $C_5H_5NiC_5H_5C_6F_4$ isomers. However, the system is a very useful one for studying the reaction of tetrafluorobenzyne with transition metal derivatives and we have carried out a limited survey on a representative selection of such compounds.

Tetrafluorobenzyne adds readily to benzene giving the 1,4-addition product tetrafluorobenzobicyclo[2.2.2]octatriene[6]. As might be expected when the benzene is already forming part of a π-complex, as in benzenechromium tricarbonyl, we have been unable to add tetrafluorobenzyne to it.

Attempts to add tetrafluorobenzyne to the free double bonds in cyclooctatetraeneiron tricarbonyl also failed but, rather inexplicably, the major iron-containing product of the reaction was the diiron complex of cyclooctatetraene, $C_8H_8Fe_2(CO)_6$, 25% (m.p. 190° decompn., lit. value[10], 190° decompn.). (Found: C, 43.63; H, 2.11. $C_{14}H_8Fe_2O_6$ calcd.: C, 43.6; H, 2.1%.) This is in contrast to tetracyanoethylene which adds to $C_8H_8Fe(CO)_3$[11].

Cobalt carbonyl and decomposing "C_6F_5MgBr" react in refluxing dioxane to give a crystalline, air-sensitive compound shown by mass spectroscopy to be $Co_4(CO)_{10}C_6F_4$ (Found: Co, 35.6; C, 28.7; H, 0.2; F, 11.8; $C_{16}F_4O_{10}Co_4$ calcd.: Co, 35.6; C, 28.9; H, 0.0; F, 11.4%). The IR spectrum of these very dark green crystals shows a complex group of peaks both around 2000 cm^{-1} (terminal carbon monoxide ligands) and around 1850 cm^{-1} (bridging carbon monoxide groups). The mass spectrum of the complex contains all the ions of the $Co_4(CO)_nC_6F_4^+$ series for $n = 0$–10, strongly indicating that the C_6F_4 moiety is not bonded in any way to one or more of the carbon monoxide ligands. The complex reacts with dilute hydrochloric acid forming 1,2,3,4-tetrafluorobenzene and decomposes on heating *in vacuo* to give mainly cobalt, carbon monoxide and octafluorofluorenone[12], 45%. (Found: mol.wt. from mass spectrum, 324; $C_{13}F_8O$ calcd.: mol.wt., 324.) The UV spectrum was also identical to that published for octafluorofluorenone[12]. We were unable to detect, using mass spectroscopy or gas–liquid chromatography, the presence of any perfluorotriphenylene or higher polyphenylenes among the decomposition products; a strong meta-stable peak in the mass spectrum of the octafluorofluorenone showed that most, if not all, of the $C_{12}F_8^+$ ion arose via the extrusion of carbon monoxide from octafluorofluorenone and not from perfluorobiphenylene impurity:

$$C_{12}F_8CO^+ \rightarrow CO + C_{12}F_8^+$$
$$m^* \text{ at } m/e \text{ 270.4; calcd.: 270.5}$$

A small amount of a carbonyl derivative having the empirical formula $C_6F_5C_6F_4$-COC_6F_5 was detected in the mass spectrum of the octafluorofluorenone showing that the C_6F_4 "entity" which is formed on disruption of the cobalt complex is capable of abstracting fluorine from neighbouring fluoroaromatic groups.

The cobalt carbonyl compound has an identical stoichiometry and a very similar IR spectrum in the carbonyl stretching region to the acetylene complex[13], $Co_4(CO)_{10}C_2(C_2H_5)_2$. This suggests that both derivatives have the same basic molecular shape and that the C_6F_4 group is σ-bonded to two cobalt atoms, but we consider an X-ray structure determination to be necessary before any discussion as to the exact mode of bonding of the C_6F_4 entity can be given; we plan to carry out such a structural determination in the near future.

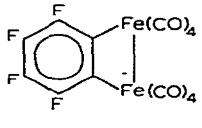
Triiron dodecacarbonyl and tetrafluorobenzyne produce a 10% yield of an air-stable, yellowish complex having the composition $Fe_2(CO)_8C_6F_4$. (Found: C, 34.30; H, 0.0; F, 15.34; $C_{14}F_4Fe_2O_8$ calcd.: C, 34.75; H, 0.0; F, 15.71%.) The IR spectrum of the complex shows that all the carbon monoxide groups are in terminal positions around the iron atoms and, in the C–F region, the spectrum closely resembles that of the cobalt carbonyl complex discussed above. No identifiable products other than carbon monoxide could be detected among the polymeric material formed by heating $Fe_2(CO)_8C_6F_4$ in a sealed tube. In the mass spectrum, peaks are present for all the ions in the $Fe_2C_6F_4(CO)_n$ series where $n = 0$–8 and at least seven metastable transitions of the type:

$$Fe_2C_6F_4(CO)_n^+ \rightarrow CO + Fe_2C_6F_4(CO)_{n-1}^+$$

are present; the ion responsible for the base peak, $Fe_2C_6F_4^+$, mainly fragments by the loss of iron difluoride:

$$Fe_2C_6F_4^+ \rightarrow FeF_2 + FeC_6F_2^+$$
$$m^* \text{ (obs.) 106.2, } m^* \text{ (calcd.) 106.1}$$

but we could detect no significant formation of $C_6F_4^+$. The IR and mass spectral data together with the complex's high general stability towards heat and air suggest that a suitable structure would be that of a diiron heterocycle in which the C_6F_4 group forms a σ-bond to each of the iron atoms:



Attempts to form the same complex by simply heating together iron pentacarbonyl (or triiron dodecacarbonyl) and 1,2-diiodotetrafluorobenzene, failed.

Cyclopentadienyliron dicarbonyl dimer appeared only to react with the (pentafluorophenyl)magnesium reagent and not with any tetrafluorobenzyne intermediate because the only iron derivative which could be isolated was the known[14] cyclopentadienyl(pentafluorophenyl)iron dicarbonyl, π-$C_5H_5(C_6F_5)Fe(CO)_2$ (m.p., 143–145°; lit.[14] 142–143°). (Found: C, 45.26; H, 1.53; mol.wt. osmometric, 336. $C_{13}H_5F_5FeO_2$ calcd.: C, 45.23; H, 1.45%; mol.wt., 344.)

Tetrakis(triphenylphosphine)platinum gave no isolable products on being treated with decomposing (pentafluorophenyl)magnesium bromide in dioxane.

These results suggest that the hope of stabilising arynes by complexing them with transition metals is rather remote especially under the conditions we employed. Tetrafluorobenzyne should, theoretically, be one of the best arynes with which to attempt π-type stabilization because back-bonding from the transition metal to antibonding orbitals on the aryne will be strongest when highly electronegative groups are present on the π-ligand. However, the system we have described for generating the tetrafluorobenzyne in the presence of transition metal complexes should provide a convenient synthesis to some interesting and highly novel derivatives.

EXPERIMENTAL

(Pentafluorophenyl)magnesium bromide was prepared from bromopentafluorobenzene (12 g, 50 mmoles) and magnesium turnings (1.2 g, 50 mmoles) in diethyl ether (20 ml). The transition metal organometallic reagent was dissolved in freshly dried dioxane and added to the Grignard with stirring; the diethyl ether was then distilled off and the remaining solution refluxed for 1 h. Removal of dioxane, extraction of the solid with dry hexane followed by either crystallization or sublimation yielded the products discussed in the Introduction.

All manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen; analyses were performed by the microanalytical department at Queen Mary College.

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