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A NEW SYNTHESIS OF PERFLUOROAROMATIC GRIGNARD REAGENTS

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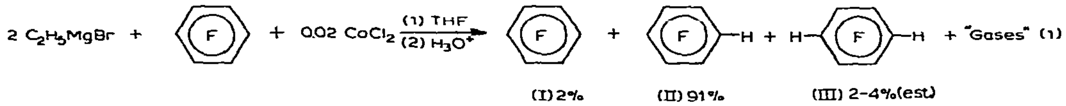
SUMMARY

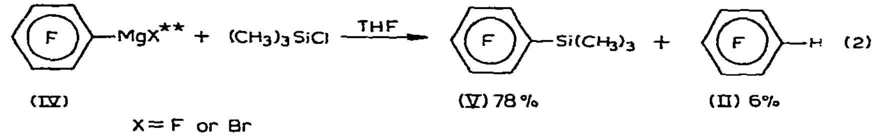
Perfluoroarylmagnesium compounds have been synthesized directly from completely fluorinated aryl compounds (*e.g.*, hexafluorobenzene, decafluorobiphenyl, octafluorotoluene and octafluoronaphthalene) through their reaction with ethylmagnesium bromide and certain transition metal halides ($CoCl_2$, $FeCl_2$, $NiCl_2$, CuI, $TiCl_4$, $PdCl_2$, $RhCl_3$ and AgCl). The yields of the perfluoroarylmagnesium compound vary with the type of perfluoroaryl substrate and metal halide. The perfluoroarylmagnesium compounds thus formed undergo typical Grignard reactions.

Organomagnesium reagents have proven to be very versatile as intermediates in organic syntheses. This has been no less true for the perfluoroaromatic Grignard reagent which has been prepared by a variety of techniques. (Pentafluorophenyl)magnesium halides have been prepared in diethyl ether from chloro-[1], bromo-[2], or iodopentafluorobenzene[3] and magnesium by conventional methods. (Pentafluorophenyl)magnesium bromide has been prepared in tetrahydrofuran from bromopentafluorobenzene and magnesium[4]. We have recently reported its synthesis from bromopentafluorobenzene and ethylmagnesium bromide in tetrahydrofuran (halogen–metal interconversion)[5] and from pentafluorobenzene and ethylmagnesium bromide (acid–base reaction)[6]. Each of these syntheses requires a functionally substituted perfluorinated aromatic starting material. Such compounds are not as widely available as the completely fluorinated analogs (*e.g.*, hexafluorobenzene). These completely fluorinated compounds, then, make attractive candidates for starting materials in the synthesis of the corresponding Grignard reagent. To our knowledge, no one has reported the direct reaction (success or failure) between magnesium and hexafluorobenzene. We have, however, recently reported the metalation of a carbon–fluorine bond as a competing reaction occurring with nucleophilic substitution when ethylmagnesium bromide was allowed to react with decafluorobiphenyl and other fluorinated substrates[6,7]. This was shown not to occur by a halogen–metal interchange[7].

In our studies directed toward new synthetic methods for preparation of perfluoroaromatic Grignard reagents, we have observed a very profound effect upon the course of reaction between completely fluorinated substrates and organomagnesium compounds when catalytic quantities of transition metal salts are present. Thus, addition of a tetrahydrofuran solution of ethylmagnesium bromide (2x moles) to a tetrahydrofuran solution of hexafluorobenzene (I) (x moles) and cobalt(II) chloride ($0.02x$ mole) resulted in a vigorous gas evolution. The reaction mixture, upon hydrolysis, produced pentafluorobenzene (II) in excellent yield (91%). A small amount of what is presumed to be 1,2,4,5-tetrafluorobenzene (III) (2–4%) also was detected by VPC analysis. The evolved gases consisted of ethylene, ethane, and butane in the ratio* 4/3/1.



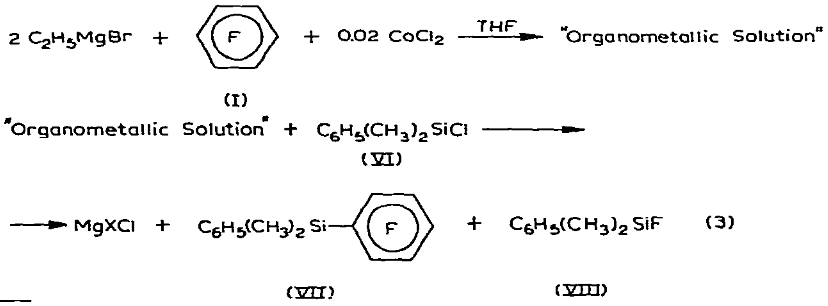
That a (pentafluorophenyl)magnesium compound (IV) was present in solution was demonstrated by allowing trimethylchlorosilane to react with the solution before hydrolysis. In this manner, (pentafluorophenyl)trimethylsilane (V), the expected product, was obtained in 78% yield.



To our knowledge, this represents the first report of a convenient synthesis for a Grignard type reagent from a fluorocarbon. The reagent prepared in this manner decomposes approximately 40% within 5 days. This slow decomposition does not affect the synthetic utility of the Grignard (IV) prepared in this way.

This demonstrated catalytic effect is not limited to cobalt(II) chloride. With the exception of iron(II) chloride (see Table 4), it is however, the most effective inorganic salt used by us.

As indicated in eqn. (1), two equivalents of ethylmagnesium bromide are required to accomplish complete metalation of hexafluorobenzene (I). If only one equivalent of the Grignard reagent was used, pentafluorobenzene (II) was obtained in 49% yield. If the solution containing Grignard reagent (IV) is titrated with HCl, the total base present is just one-half that expected for a solution that would contain one mole of the perfluorophenyl Grignard reagent and one mole of unreacted ethyl-



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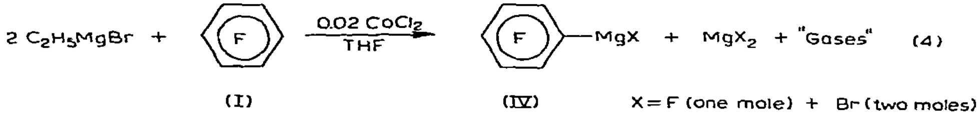
* As no precautions were taken to quantitatively collect the evolved gases, this ratio is not necessarily that actually formed in the reaction, see the *Experimental Section* for details.

** The organometallic formed in this reaction will be expressed by this formula for simplicity without regard for other possible structures allowed by Schlenk equilibria.

magnesium bromide. Treatment of the Grignard reagent IV with phenyldimethylchlorosilane (VI) prior to hydrolysis yielded phenyldimethyl(pentafluorophenyl)-silane (VII). No phenyldimethylethylsilane was obtained. The presence of fluoride ion, suggested in eqn. (2) appears to be confirmed by our observation that the excess chlorosilane (VI) is converted to the fluorosilane (VIII). Collectively, these results imply that two equivalents of ethylmagnesium bromide are consumed in the conversion of one mole of hexafluorobenzene (I) to the Grignard reagent (IV). This conversion is accompanied by the formation of fluoride ion. The overall reaction then becomes:



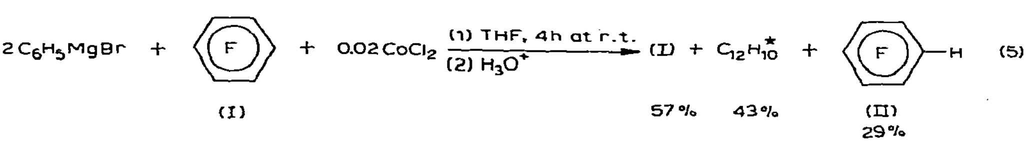
Organomagnesium reagents other than ethylmagnesium bromide are also effective as metalating agents for hexafluorobenzene (I) in the presence of catalytic amounts of cobalt(II) chloride (see Table 1). Thus a reaction using methylmagnesium chloride gave, after hydrolysis, pentafluorobenzene (II) in 86% yield. Phenylmagnesium bromide, however, was not as effective. After complete addition and 4 h additional stirring, pentafluorobenzene (II) was formed in only 29% yield. At this point, 43% of the hexafluorobenzene (I) had been consumed. Interestingly, biphenyl was produced at a rate equal to the loss of hexafluorobenzene (I).

TABLE 1

$$y\,\text{RMgX} + C_6F_6 + 0.02\ \text{CoCl}_2 \xrightarrow[(2)\ H_3O^+]{(1)\ \text{THF}} C_6F_5H$$

y	R	X	C_6F_5H (%)	Time[a]
2	C_2H_5	Br	91	30 min
1	C_2H_5	C_2H_5	91	30 min
2	CH_3	Cl	86	30 min
2	C_6H_5	Br	29	4 h

[a] Time elapsed after complete addition.



When diethylmagnesium was used in the metalation reaction, pentafluorobenzene (II) was produced in 91% yield after hydrolysis. This reaction infers the presence of the very interesting reagent, (pentafluorophenyl)magnesium fluoride (IX) (or at least a solution corresponding to this stoichiometry). Treatment of this organometallic reaction mixture with trimethylchlorosilane produced (pentafluorophenyl)-trimethylsilane (V) in 80% yield.

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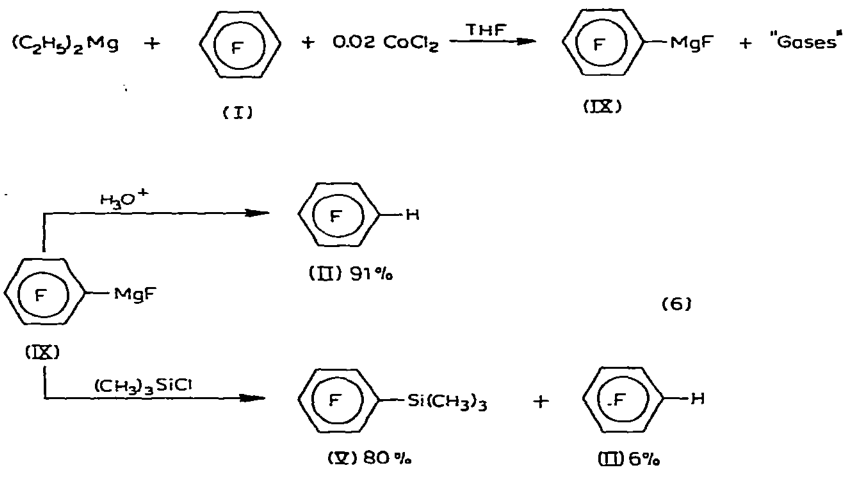
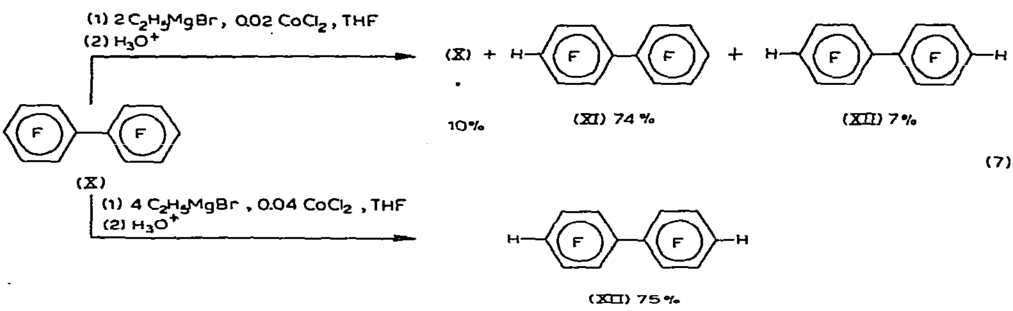
* Yield based on phenylmagnesium bromide added.



(6)

An attempt to metalate two positions of hexafluorobenzene (I) by using four equivalents of ethylmagnesium bromide was not successful. Pentafluorobenzene (II) (68%) and 1,2,4,5-tetrafluorobenzene (III) (6%) were detected by VPC analysis. Apparently, the (pentafluorophenyl)magnesium halide is resistant to further metalation. This view was substantiated by the observation in a separate experiment, that 1,2,4,5-tetrafluorobenzene (III) was produced in only a 5% yield through the reaction between ethylmagnesium bromide (2x mole), pentafluorophenylmagnesium bromide* (x mole) and cobalt(II) chloride (0.02x mole).

We have extended this novel reaction to completely fluorinated substrates other than hexafluorobenzene (I). In the case of decafluorobiphenyl (X) the replacement of one or two nuclear fluorines can be achieved by varying the ratio of the reactants. When ethylmagnesium bromide (2x moles), cobalt(II) chloride (0.02x mole), and decafluorobiphenyl (X) (x moles) were allowed to react in tetrahydrofuran, the major product, after hydrolysis, was 4-hydrononafluorobiphenyl (XI) (74%). When the reactants were ethylmagnesium bromide (4x moles), cobalt(II) chloride (0.04x moles) and decafluorobiphenyl (X) (x moles), 4,4'-dihydrooctafluorobiphenyl (XII) was obtained in 75% yield.



(7)

Aluminum chloride was ineffective as a catalyst for the metalation of decafluorobiphenyl (X) under conditions where cobalt(II) chloride is effective.

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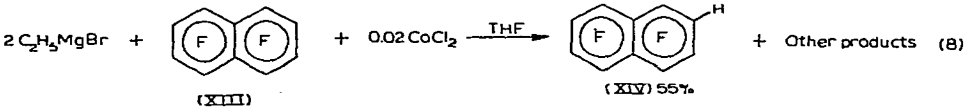
* Prepared by the reaction of ethylmagnesium bromide with pentafluorobenzene.

The metalation of octafluoronaphthalene (XIII) was only moderately successful. After hydrolysis of the reaction mixture, 2-hydroheptafluoronaphthalene (XIV) was found in only 55% yield. A considerable amount of unidentified side products were formed in this reaction.

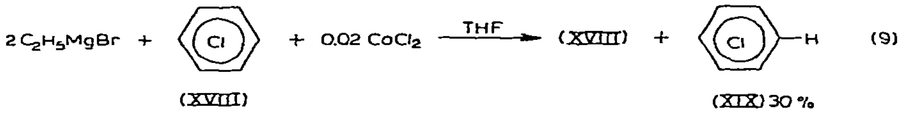


(8)

The replacement of two nuclear fluorines was also attempted. The dihydrohexafluoronaphthalene (presumably 2,6- or 2,8-dihydro) was formed in very low yield.

An attempt to prepare an organomagnesium reagent from octafluorotoluene (XV) was not successful under the conditions (THF solvent) ordinarily used. Instead, a high melting solid (did not melt to 405°), presumably polymeric, was obtained together with a small amount of 4-ethylheptafluorotoluene (XVI). It seems likely that organometallic derivatives were formed but underwent further reaction presumably with the unreacted perfluorotoluene. By varying catalyst concentration and using mixed ether/tetrahydrofuran solvent, some success, as evidenced by the presence of 4-hydroheptafluorotoluene (XVII) (43% maximum yield, see Table 3) after hydrolysis, was achieved.

An attempt was made to extend this reaction to hexachlorobenzene (XVIII). Although pentachlorobenzene (XIX) was formed in the reaction (30%), the amount of metalation this represents presumably is due to halogen–metal interchange* and not to any catalytic effect due to the cobalt(II) chloride.



(9)

During the course of our previous investigations[5,6,7], we have used exclusively totally fluorinated substrates from one source (I.S.C.**). We have since noted a rather marked difference between the properties of hexafluorobenzene (I.S.C.) and that supplied by another source (W.***). When hexafluorobenzene (W.) (*x* moles) was treated with ethylmagnesium bromide (2*x* moles) for 24 h, the major product observed, upon hydrolysis, was pentafluorobenzene (II) (79%)****. In addition, ethylpentafluorobenzene (XX) (9%) was also formed. A gas mixture, very similar to that formed in the cobalt(II) chloride catalyzed reactions, consisting of ethylene, ethane, and butane in the ratio 11/9/1 was evolved from the reaction. We have reported previously the reaction of ethylmagnesium bromide (2*x* moles) with hexafluorobenzene (I.S.C.). After 24 h, the major product was ethylpentafluorobenzene

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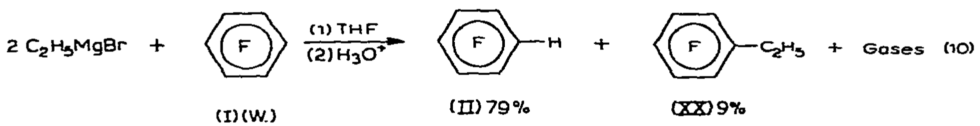
* George J. Moore of our laboratories has observed ca. 35% exchange between ethylmagnesium bromide (1.2*x* moles) and hexachlorobenzene (XVIII) (*x* moles) in tetrahydrofuran solution.

** The source for these compounds was Imperial Smelting Corporation (I.S.C.) Avonmouth, Bristol, Great Britain.

*** Whittaker (W.) Corporation, San Diego, California.

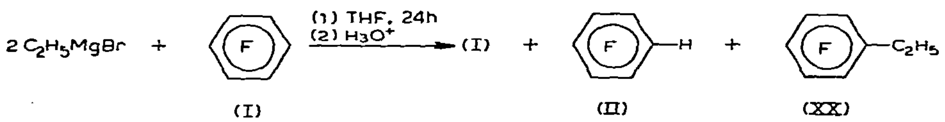
**** Another lot of hexafluorobenzene (W.) gave a similar result. This effect was not a peculiarity of our first lot.



(XX) (69%)^{5,6}. A small amount (6%) of pentafluorobenzene (II) also was present. In view of our results described above, concerning the effect of metal salts on the reaction of ethylmagnesium bromide with hexafluorobenzene (I), it, of course, occurred to us to examine hexafluorobenzene (W.) for such impurities. Analysis of a sample from each source was accomplished by emission spectroscopy, atomic absorption spectroscopy, and colorimetry. The only difference noted was that, by colorimetry, hexafluorobenzene (W.) had 0.06 ppm iron content while hexafluorobenzene (I.S.C.) had 0.03 ppm iron content. In our minds, this low concentration of iron and such small differences between iron concentration in the two samples does not adequately explain these reactivity differences.

A sample of hexafluorobenzene from each source was collected by preparative VPC and their reactions with ethylmagnesium bromide reexamined. In the case of hexafluorobenzene (W.), no change in reactivity could be noted (see Table 2).

TABLE 2



C_6F_6 source	(I) (%)	(II) (%)	(XX) (%)
W.	0	79	9
W.[a]	4	80	10
I.S.C.	19	6	69
I.S.C.[a]	16	19	58

[a] Collected by preparative VPC.

Hexafluorobenzene (I.S.C.), gave after 24 h, more pentafluorobenzene (II) (19%) than was observed previously (see Table 2)^{5,6}.

We are not able to explain these different reactions paths. Because of the effects we have noticed by adding cobalt(II) chloride and other metal salts, we have inferred the presence of some catalytic agent in hexafluorobenzene (W.) which has so far eluded detection by us.

Our results using cobalt(II) chloride and other inorganic salts as catalysts for converting a totally fluorinated substrate such as hexafluorobenzene to an organomagnesium species are quite clear, however. We are continuing our investigations with a view to establishing a mechanism for this unexpected metalation reaction. These results will be published at a later time.

EXPERIMENTAL

All organometallic preparations were carried out under an atmosphere of oxygen-free nitrogen. Tetrahydrofuran (THF) was freshly distilled from calcium hydride prior to use. Nuclear magnetic resonance spectra were carried out using a Varian A56–60 spectrometer. Chemical shifts are reported in ppm from fluorotrichloromethane (^{19}F NMR) or tetramethylsilane (^{1}H NMR) as internal standards. In this study, hexafluorobenzene was used from two sources. The letter W. will designate the source, Whittaker Corporation, San Diego, California and the letters I.S.C. will designate the source Imperial Smelting Corporation Ltd., Avonmouth, Bristol, England. VPC analyses were carried out using an F&M Model 810 or F&M Model 700 gas chromatograph. An 11 ft. column of polyphenyl ether (6 ring), 15% on Chromosorb P, was used for reactions with hexafluorobenzene, pentafluorobenzene, octafluorotoluene, and octafluoronaphthalene. A 6 ft. column of Apiezon L, 10% on Chromosorb W, was used for reactions with decafluorobiphenyl.

Ethylmagnesium bromide was prepared from Grignard grade magnesium and ethyl bromide as a THF or diethyl ether solution. Phenylmagnesium bromide was prepared as a THF solution from Grignard grade magnesium and bromobenzene. Diethylmagnesium was prepared from diethylmercury and magnesium turnings as a THF solution. The concentrations of these solutions, except for diethylmagnesium, were determined by the technique described by Watson and Eastham[8]. A slight modification of this technique, which we have previously described[5], was required for the solution of ethylmagnesium bromide in THF. The concentration of diethylmagnesium was determined by the method of House and Respess[9].

Product yields were determined by VPC analysis using ethylbenzene as an internal standard. All known compounds were characterized by VPC retention time. New compounds in general were characterized by NMR, mass spectral and elemental analysis.

Cobalt(II) chloride catalyzed reactions

C_2H_5MgBr *and* C_6F_6 *(I.S.C.) 2/1 ratio*

(a). Hydrolysis. A THF solution (18 ml) of hexafluorobenzene (4.66 g, 0.025 mole), ethylbenzene (1.81 g as an internal standard) and cobalt(II) chloride (0.077 g, 0.00059 mole) was cooled in an ice-water bath. To this solution, ethylmagnesium bromide (32 ml of a THF solution containing 0.051 mole) was added over 45 min. Vigorous gas evolution occurred and a dark black mixture resulted. After additional stirring for 30 min, the ice-water bath was removed. At this time, an aliquot was removed and hydrolyzed. VPC analyses showed the presence of pentafluorobenzene (II) (91%), hexafluorobenzene (2%), and 1,2,4,5-tetrafluorobenzene (III) (~2% est.). After 5 days stirring at room temperature, a similar analysis showed pentafluorobenzene (II) (55%). A material insoluble in THF was also observed. This material did not melt below 400° and its infrared spectrum (KBr pellet) was similar to that of a known perfluoropolyphenylene polymer.

Mass spectral analysis of the evolved gas indicated ethylene, ethane and butane in a ratio of 4/3/1.

Reaction (*a*) above was repeated using different molar ratios. In a 1/1 mole ratio, hexafluorobenzene (48%) and pentafluorobenzene (II) (49%) were produced. In a 4/1 molar ratio, pentafluorobenzene (II) (68%) and 1,2,4,5-tetrafluorobenzene (III) (6%) were produced.

(*b*). *Treatment with phenyldimethylchlorosilane.* A reaction similar to that described in (*a*) was carried out using hexafluorobenzene (4.66 g, 0.025 mole), cobalt(II) chloride (0.065 g, 0.00050 mole) and ethylmagnesium bromide (0.050 mole). To the resulting mixture was added phenyldimethylchlorosilane (VI) (8.49 g, 0.050 mole) in THF. After 24 h, VPC analysis of an aliquot sample showed the presence of two components in addition to the standard (ethylbenzene). Preparative VPC (F&M 770, SE30 column) separation of the components yielded phenyldimethylfluorosilane (VIII); m. wt. by mass spectroscopy 154, calcd. 154.26. The ^{1}H NMR spectrum was consistent with the structure and exhibited a doublet and 0.99 ppm for $Si(CH_3)_2$ [J(F–Si–CH_3)7.5 Hz] and a complex multiplet at 7.90 ppm (C_6H_5). The other component was identified as phenyldimethyl(pentafluorophenyl)silane (VII); m. wt. by high resolution mass spectroscopy 302.0564, calcd. 302.0550. (Found: C, 55.74; H, 3.72. $C_{14}H_{11}F_5Si$ calcd.: C, 55.62; H, 3.67%.) Its ^{1}H NMR spectrum exhibited a triplet at 0.60 ppm for $Si(CH_3)_2$ [J(*o*-F–C–C–Si–CH_3) 1.5 Hz] and a multiplet at 7.25 ppm (C_6H_5).

(*c*). *Treatment with trimethylchlorosilane.* A reaction similar to that described in (*a*) above was run using hexafluorobenzene (4.66 g, 0.025 mole), cobalt(II) chloride (0.075 g, 0.00057 mole) and ethylmagnesium bromide (0.051 mole). To the resulting mixture was added trimethylchlorosilane (3.07 g, 0.028 mole) in THF (10 ml). The ice-water bath was removed at this time. After 1 h additional stirring, VPC analysis of an aliquot sample showed the presence of hexafluorobenzene (4%), pentafluorobenzene (II) (6%), and (pentafluorophenyl)trimethylsilane (V) (78%).

(*d*). *Determination of base content.* A reaction similar to that described in (*a*) above was run using hexafluorobenzene (4.65 g, 0.025 mole), cobalt(II) chloride (0.070 g, 0.054 mole), and ethylmagnesium bromide (total base 0.057 equiv.). The entire reaction mixture was hydrolyzed using 50.0 ml of aqueous 1.00 *N* HCl (0.050 equiv.). The resulting two phase system was stirred rapidly and neutralized with 21.0 ml of a 1.00 *N* aqueous sodium hydroxide. A pH meter was used to determine the neutralization point. Thus 0.028 equivalents of base was present after the formation of the C_6F_5MgBr. This represents (0.057/0.028) approximately 50% base present presumably in the form of C_6F_5MgBr before hydrolysis of the reaction mixture.

C_2H_5MgBr *and* C_6F_5MgBr

Pentafluorophenylmagnesium bromide was prepared[6] by the addition of ethylmagnesium bromide (21 ml of a THF solution containing 0.025 mole) to pentafluorobenzene (II) (4.21 g, 0.025 mole in 25 ml THF) at 0°. The solution was allowed to stand at room temperature for 1.5 h and then cooled again to 0°. To this mixture was added cobalt(II) chloride (0.065 g, 0.00050 mole) in small portions (vigorous foaming occurred). Ethylmagnesium bromide (42 ml of a THF solution containing 0.050 mole) was then added over a 20 min period. After 1 h additional stirring, VPC analysis of an aliquot sample showed the presence of pentafluorobenzene (II) (80%) and 1,2,4,5-tetrafluorobenzene (III) (5%).

$(C_2H_5)_2Mg$ *and* C_6F_6 *(I.S.C.)*

A reaction similar to that described in (*a*) above was run using diethylmagnesium (30 ml of a THF solution containing 0.025 mole), hexafluorobenzene (4.665 g, 0.025 mole), and cobalt(II) chloride (0.071 g, 0.00055 mole). After 30 min, an aliquot sample was removed and analyzed by VPC showing the presence of hexafluorobenzene (3%) and pentafluorobenzene (91%). To the remainder of the reaction mixture was added trimethylchlorosilane (2.75 g, 0.025 mole) in THF (15 ml). After 4 h, water was added to the reaction mixture, the layers were phase separated, the aqueous layer was extracted with pentane and the combined organic layers were analyzed by VPC, indicating the presence of pentafluorobenzene (II) (6%) and (pentafluorophenyl)-trimethylsilane (V) (80%).

CH_3MgCl and C_6F_6 2/1 ratio

In a manner similar to that described in (*a*) above, methylmagnesium chloride (20 ml of a THF solution containing 0.052 mole) was added to hexafluorobenzene (4.66 g, 0.025 mole) and cobalt(II) chloride (0.072 g, 0.00055 mole) in THF (30 ml). The evolution of gas was noted. After 30 min, an aliquot sample was removed and analyzed by VPC showing the presence of pentafluorobenzene (II) (86%) and hexafluorobenzene (I) (4%).

C_6H_5MgBr and C_6F_6 (I.S.C.) 2/1 ratio

In a manner similar to that described above, phenylmagnesium bromide (35 ml of a THF solution containing 0.050 mole) was added to a mixture of hexafluorobenzene (4.65 g, 0.025 mole) and cobalt(II) chloride (0.069 g, 0.00053 mole) in THF (15 ml). After 4 h, an aliquot sample analyzed by VPC showed the presence of hexafluorobenzene (57%), pentafluorobenzene (II) (29%), and biphenyl (43%).

C_2H_5MgBr and $C_{12}F_{10}$ 2/1 ratio

Ethylmagnesium bromide (32 ml of a THF solution containing 0.050 mole) was added over 25 min to a THF solution (15 ml) containing decafluorobiphenyl (X) (8.35 g, 0.025 mole) and cobalt(II) chloride (0.070 g, 0.00054 mole) which was cooled by an ice-water bath. After 30 min, an aliquot sample was removed, analyzed by VPC the presence of decafluorobiphenyl (X) (10%), 4-hydrononafluorobiphenyl (XI) (74%) and 4,4′-dihydrooctafluorobiphenyl (XII) (7%) was indicated. After 5 h, much polymer formation could be observed. Its infrared spectrum (KBr) was similar to that of a known perfluoropolyphenylene. The material did not melt to 400°.

When the above reaction was repeated using a 4/1 mole ratio (C_2H_5MgBr/$C_{12}F_{10}$), VPC analysis indicated 4,4′-dihydrooctafluorobiphenyl (XII) (75%) and another unidentified product (est. 3–5%).

C_2H_5MgBr and $C_{10}F_8$ 2/1 ratio

Ethylmagnesium bromide (42 ml of a THF solution containing 0.050 mole) was added over a 30 min period to an ice-water cooled THF solution (10 ml) of octafluoronaphthalene (XIII) (6.80 g, 0.025 mole) and cobalt(II) chloride (0.074 g, 0.00057 mole). After 30 min, an aliquot sample was removed and analyzed by VPC indicating 2-hydroheptafluoronaphthalene (55%).

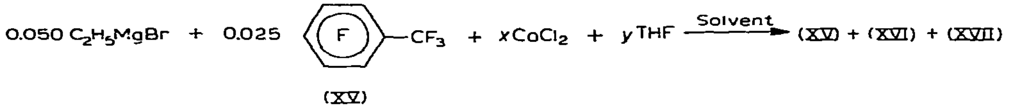
C_2H_5MgBr and $C_6F_5CF_3$ general method

A diethyl ether solution of ethylmagnesium bromide (0.050 mole) (except reaction 1 of Table 3) was added to a diethyl ether solution of octafluorotoluene (0.025 mole) and the additives cobalt(II) chloride and THF over a period of 20–30 min. The volume of diethyl ether used was sufficient to adjust the total reaction volume after addition was completed to about 50 ml. Aliquot samples were withdrawn periodically and analyzed by VPC. See Table 3.

C_2H_5MgBr and C_6Cl_6

Ethylmagnesium bromide (42 ml of a THF solution containing 0.050 mole) was added over a 30 min period to an ice-water cooled THF solution (200 ml) of hexachlorobenzene (XVIII) (7.12 g, 0.025 mole) and cobalt(II) chloride (0.072 g, 0.00055 mole). After 30 min, an aliquot sample was removed and analyzed by VPC. Pentachlorobenzene (XIX) (32%), hexachlorobenzene (31%), and unidentified products were found.

TABLE 3



Run	x	y	Solvent	Time	XV	XVI	XVII (%)
1	0.0005	THF	THF				0
2	0.0005	0	Et_2O	18 h	0	74	11
3	0.0025	0	Et_2O	18 h	4	23	36
4	0.0013	0.05	Et_2O	45 min	30	3	43
5	0.0050	0.05	Et_2O	1 h	30	0	35
6	0.0010	0.10	Et_2O	1 h	23	10	36
7[a]	0.0010	0.10	Et_2O	15 min	40	20	18

[a] In reaction 7, octafluorotoluene was added to a mixture of ethylmagnesium bromide, cobalt(II) chloride and THF in diethyl ether solution.

Reactions of commercial vs. purified hexafluorobenzene

VPC analysis of commercial C_6F_6 (W.) indicated a purity of ~99% with ~1% impurity of C_6F_6Cl. Preparative VPC purification of C_6F_6 (W.) indicated a purity of ~99.9% C_6F_6. VPC analysis of commercial C_6F_6 (I.S.C.) indicated a purity of ~97% with 2–3 minor components of unknown composition. Preparative VPC purification of C_6F_6 (I.S.C.) indicated a purity of >99.9%.

C_2H_5MgBr and C_6F_6 (W.). Commercial hexafluorobenzene (W.) (4.66 g, 0.025 mole) was added to ethylmagnesium bromide (33 ml of a THF solution containing 0.050 mole) at room temperature over a period of 1–2 min. After 24 h, VPC analysis of an aliquot sample indicated pentafluorobenzene (II) (79%) and ethylpentafluorobenzene (XX) (9%). During this 24 h period, the reaction mixture developed a deep blue color.

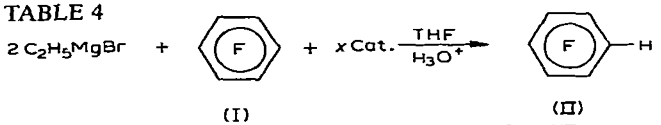
When the above reaction was repeated with purified (~99.9%) C_6F_6 (W.), the yield of products were, pentafluorobenzene (II) (80%), ethylpentafluorobenzene (XX) (10%) and hexafluorobenzene (4%). During the 24 h period, the reaction mixture developed a deep blue color.

C_2H_5MgBr and purified C_6F_6 (I.S.C.) 2/1 ratio. Purified C_6F_6 (I.S.C., >99.9%) (4.65 g, 0.025 mole) was added to ethylmagnesium bromide (33 ml of a THF solution containing 0.050 mole) at room temperature over a period of 1–2 min. After 24 h, an aliquot sample was analyzed by VPC and indicated pentafluorobenzene (II) (19%), ethylpentafluorobenzene (XX) (58%) and hexafluorobenzene (16%). During the 24 h period, the reaction mixture developed a deep blue color.

Other inorganic halide catalyzed reactions of C_2H_5MgBr and C_6F_6 (I.S.C.)

A THF solution of ethylmagnesium bromide (0.050 mole) was added over a period of 20–30 min. to an ice-water cooled mixture of hexafluorobenzene (0.025 mole), ethylbenzene (internal standard) and inorganic salt (see Table 4). After 30 min, the cooling bath was removed and aliquot samples were withdrawn, hydrolyzed and analyzed by VPC. The maximum yields of pentafluorobenzene thus obtained are shown in Table 4. Where metalation was slow, other products (not shown in Table 4) including ethylpentafluorobenzene (XX) and unreacted hexafluorobenzene were observed. In the $TiCl_4$ and $PdCl_2$ catalyzed reactions, ethylnonafluorobiphenyl (identified by retention time only) was formed in 17 to 16% yield respectively.

TABLE 4



Catalyst	x^a	C_6F_5H (%)^b	Time^c
$CoCl_2$	0.02	91	30 min
$FeCl_2$	0.02	96	30 min
$NiCl_2$	0.02	43	1 h
CuI	0.02	25	24 h
$TiCl_4$	0.04	39	5 h
AgCl	0.02	5	5 h
$PdCl_2$	0.04	61	18 h
$RhCl_3$	0.04	58	24 h

[a] x is mole ratio of catalyst. [b] Maximum percent C_6F_5H observed. [c] Elapsed time after addition of C_2H_5-MgBr when maximum percentage C_6F_5H observed.

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