SOME PENTAFLUOROPHENYL DERIVATIVES OF SELENIUM

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ABSTRACT

The preparations of a number of pentafluorophenyl derivatives of selenium are described. Reactions of transition metal ions with excess of the anion $C_6F_5Se^-$ in aqueous solution generally give complex ions of the type $[M(SeC_6F_5)_x]^{y-}$ but sometimes only simple salts of the type $M(SeC_6F_5)_2$ are obtained. The electronic spectra of these compounds are discussed. The ligand C_6F_5Se has been incorporated into transition metal organometallic compounds giving the derivatives $(\pi\text{-}C_5H_5)Fe(CO)_2SeC_6F_5$, $\{(\pi\text{-}C_5H_5)NiSeC_6F_5\}_n$, $(\pi\text{-}C_5H_5)Ni(PPh_3)SeC_6F_5$, $C_6F_5SeMn(CO)_5$ and $C_6F_5SeRe(CO)_5$. Unsymmetrical selenides, C_6F_5SeR, where the substituents, R, are various alkyl and aryl groups, are prepared by a variety of methods. Preparations of the compounds $C_6F_5SeN(CH_3)_2$, $C_6F_5SeN(C_2H_5)_2$, $(C_6F_5Se)_2NH$ and $C_6F_5SeOCH_3$ are also described. The preparations of various pentafluorophenyl derivatives of higher valent selenium are attempted resulting in the formation of the compounds $C_6F_5SeCl_2CH_3$, $C_6F_5SeCl_2C_6H_5$, $C_6F_5Se(O)C_6H_5$, $(C_6F_5SeO)_2O$ and $C_6F_5Se(O)Cl$. No pentafluorophenyl derivatives of six valent selenium are obtained. Vibrational spectra of the compounds prepared are briefly discussed and SeO stretching mode assignments made. ^{19}F n.m.r. spectra are also discussed.

The properties of pentafluorophenyl derivatives of selenium are compared with those of organoselenium compounds, particularly perfluoroalkyl derivatives of selenium, and with pentafluorophenyl derivatives of sulphur.

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R.T. Poole

FOREWORD

The work presented in this thesis was carried out in the chemistry laboratories of Memorial University of Newfoundland. The apparatus used comprised Pyrex glassware with standard taper sockets and cones; a vacuum line with a mercury diffusion pump, and fitted with connected fractionating traps and a number of standard socket inlets; a glove box, for operations carried out under dry nitrogen; and various other useful pieces of equipment. A number of instruments were available for recording spectra and these are described when encountered in the text.

Analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Western Germany, but mercury (Chapter II) and chlorine (Chapter V) were estimated gravimetrically as $Cu.en_2HgI_4$ and AgCl by the author.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

In 1958 the chemical properties of perfluoroalkyl derivatives of selenium were described in the literature for the first time.[1] It was observed that the properties of trifluoromethyl selenium compounds were in some ways markedly different from those of alkyl and aryl selenium compounds. These differences were ascribed to delocalization of lone pair electrons on the selenium atom by the highly electronegative CF_3- groups. There is now an extensive chemistry of perfluoroalkyl derivatives of selenium and the area was reviewed in 1970 by Cohen and Peacock.[2] The unusual properties of perfluoroalkyl selenium derivatives and the availability of polyfluorobenzenes suggested that an investigation of the properties of perfluoroaryl selenium derivatives would be both interesting and useful in further understanding organoselenium and perfluoroaryl chemistry. When the investigation was started in 1968 the preparations of a few simple perfluoroaryl selenium compounds had been described,[3,4] but no chemical properties had been reported. The investigation paralleled that of perfluoroalkyl selenium derivatives and showed similar unusual properties of pentafluorophenyl selenium derivatives.[5]

The work presented in this thesis was started in 1970. In view of the above considerations it was felt that, while the preliminary investigation indicated a strong similarity between the properties of perfluoroaryl and perfluoroalkyl selenium derivatives, it would be useful to expand this field to determine how far the similarity extends. This should also allow interesting and productive comparisons with the wide field of organoselenium chemistry and with the expanding field of perfluoroaryl sulphur chemistry. As the expansion of this field takes place in several directions various other aspects will also be considered as they are encountered. Further, while it has been the custom to classify the chemistry of compounds containing selenium bonded to carbon as "The Organic Chemistry Of Selenium",[6] "Carbon Compounds" of selenium[7] or "Organic Selenium Chemistry"[8] in the titles of review articles, it is intended here to approach the problem from an inorganic chemist's view point. Perhaps, one day, organoselenium chemistry will become not only a branch of organic chemistry but also a branch of organometallic chemistry, having its own section in the "Annual Reviews Of Organometallic Chemistry".

To provide the background necessary for the work proposed, sections on 'Organoselenium Chemistry' and

'Perfluoroaryl Chemistry' are presented below. These two very extensive fields are covered briefly and by a general treatment, but more detailed information will be presented in the text wherever it is considered useful for understanding the chemistry encountered. The mating of these two fields results in perfluoroaryl selenium chemistry which is reviewed up to the present time. In the literature there are a few inconsistencies in the nomenclature of some closely related compounds. It is felt necessary, therefore, to include first a brief account of the nomenclature rules adopted herein.

Nomenclature

Fluorocarbons

Banks suggests that for the purposes of nomenclature fluorocarbons and their derivatives are treated as hydrocarbon derivatives.[9] The number of fluorine atoms may be indicated in the names of the compounds, e.g. octafluoropropane (C_3F_8), but since this may often be cumbersome and may not immediately reveal the fluorocarbon nature of the compounds the prefix 'perfluoro' in conjunction with basic hydrocarbon nomenclature[10] is often preferred. The term 'perfluoro' denotes substitution of all hydrogen atoms attached to carbon except those whose substitution would affect the nature of the functional groups present; for example, perfluorobutyraldehyde is is C_3F_7.CHO and not C_3F_7.CFO. However, the naming of $C_6F_5SeCF_3$ as perfluoromethylphenyl selenide is somewhat inconsistent with the naming of $C_6F_5SeCH_3$ as methylperfluorophenyl selenide. Therefore, to avoid confusion and because it is not cumbersome, the prefix pentafluoro- before phenyl or benzene to denote C_6F_5- will be used in this work. Thus $C_6F_5SeCF_3$ becomes pentafluorophenyltrifluoromethyl selenide and $C_6F_5SeCH_3$ is written methylpentafluorophenyl selenide. This is also consistent with the nomenclature currently used by most authors (e.g. see reference [2]) in connection with C_6F_5 derivatives. The term 'perfluoro' will be used for perfluorinated aliphatics and aromatics of a more general nature.

Organoselenium

Bagnall[7] recommends that the nomenclature used by Chemical Abstracts be used for organoselenium compounds. The Chemical Abstracts system is based on the latest I.U.P.A.C. rules at any particular time. The rules pertaining to selenium as an organic substituent were only recently laid down by I.U.P.A.C. in 1969[10] and have not yet been adopted by Chemical Abstracts. Before 1969 and especially in the older literature, there were many inconsistencies in organoselenium nomenclature. Thus seleninic acids RSeO.OH were often reported as selenonic acids (the term used for compounds of the type $RSeO_2OH$) e.g. see Chemical Abstracts 29:5812[1]. Even in the more recent literature (1958) trifluoromethyl hydrogen selenide was used to describe trifluoromethaneselenol.[1] The compound C_6F_5SH has variously been called pentafluorothiophenol[11] and pentafluorobenzenethiol.[12] The latter is preferred since it is consistent with I.U.P.A.C. rules and denotes that it has the properties of a thiol -SH rather than properties analogous to a phenol -OH. For the same reason pentafluorobenzeneselenol for C_6F_5SeH is used here.

Representative examples consistent with the above rules are given in Table 1.1.

Organoselenium Chemistry

Organoselenium chemistry is an important part of the chemistry of selenium. It is not quite as extensive as organosulphur chemistry but this is mainly due to the lesser availability of selenium, the somewhat lower stability of the Se-C bond and the notorious properties of organoselenium compounds: foul smell and toxicity.[8] These properties reduced the likelihood of technological applications of organoselenium chemistry and no doubt deterred many researchers from entering the field. However, recent interest has been shown in organoselenium compounds

TABLE 1.1

Some Examples Of The Nomenclature Of Pentafluorophenyl Derivatives Of Selenium

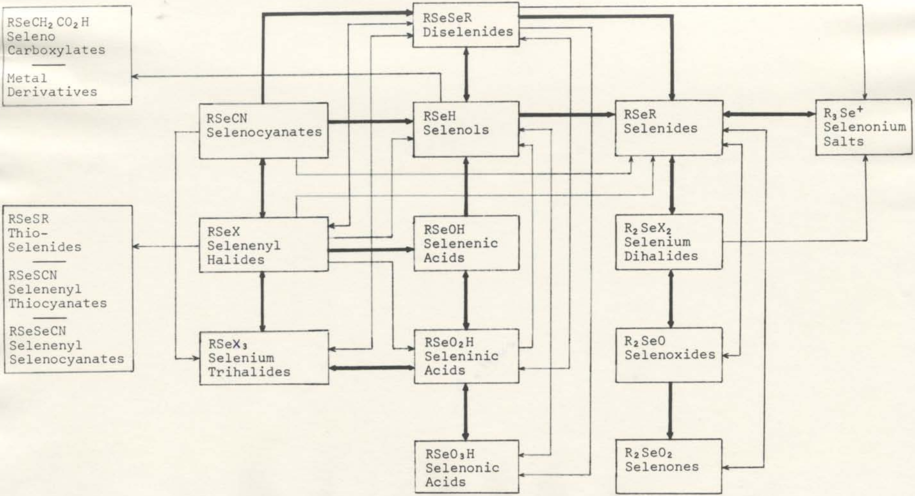
Compound Formula	I.U.P.A.C. Name
$(C_6F_5)_2Se$	bis(pentafluorophenyl) selenide
$(C_6F_5)_2Se_2$	bis(pentafluorophenyl) diselenide
C_6F_5SeH	pentafluorobenzeneselenol
$[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$	tetramethylammonium tetrakis(pentafluorobenzeneselenolato)cadmate(II)
C_6F_5SeBr	pentafluorobenzeneselenenyl bromide
$C_6F_5SeCl_3$	pentafluorophenylselenium trichloride
$C_6F_5SeC_2H_5$	ethyl pentafluorophenyl selenide
$C_6F_5SeCl_2CH_3$	methylpentafluorophenylselenium dichloride
$C_6F_5Se(O)C_6H_5$	pentafluorophenyl phenyl selenoxide
$C_6F_5SeO.OH$	pentafluorobenzeneseleninic acid

because of their potential applications as oil additives, vulcanization enhancers in natural rubber and in photoconducting polymers.[13] In the life sciences there is interest, not only in the toxicity of selenium, but also in its beneficial effects in trace quantities.[14] Selenium isologues of naturally occurring organosulphur compounds are used as probes in biochemical systems.[15]

The literature on organoselenium chemistry is spread widely and until 1952 there were few reviews on the subject and none printed in English. It was at this time that Campbell, Walker and Coppinger presented a comprehensive review of "The Organic Chemistry Of Selenium".[6] In this review are considered the preparations and properties of what may be described as the common organoselenium derivatives shown in Figure 1.1. In more recent times reviews of a less comprehensive nature have been presented by Gosselck in 1963 and Bagnall in 1966. Their approach, however, is important. Gosselck considered some new aspects in this field, particularly in relation to the oxygen and sulphur isologues,[16] while Bagnall compared organoselenium compounds with those of tellurium and polonium.[7] The field of perfluoro-organoselenium chemistry was comprehensively reviewed by Cohen and Peacock in 1970.[2] The most recent development of a review nature

FIGURE 1.1

The More Important Organoselenium Compounds



occurred in March 1971 when a number of leading organoselenium chemists met at a conference in New York. A complete volume, Volume 192, of the Annals of the New York Academy of Sciences was dedicated to this conference.[8]

Some important general aspects of organoselenium chemistry will now be considered together with some detail of more recent developments not covered in the reviews and material that is particularly relevant to this work. Reference to Figure 1.1 shows that the oxidation states of selenium are generally +2, +4 and +6 in organoselenium compounds although formally the oxidation states of selenium in diselenides, RSeSeR (+1) and metal derivatives of the type RSe-M (0) are inconsistent with this statement. The predominant oxidation states are +2 and +4 unlike sulphur where +2 and +6 are more common. One or two organic groups bonded to selenium are commonly observed, together with three groups in selenonium salts. Four organic groups bonded to sulphur, in $(C_6F_5)_4S$[17] and tellurium, in $(C_6F_5)_4Te$ [18] and $(C_6H_5)_4Te$[19] are known but the only tetraorganyl derivative of selenium known is the chelate stabilized bis-2, 2'-biphenylyleneselenium reported recently by Hellwinkel.[20]

Selenium in the +6 oxidation state is found only when bonded to oxygen atoms in such compounds as the selenonic acids and selenones, while the +2 oxidation state when selenium is bonded to oxygen is rare, only being observed in a few selenenic acids where the electronegativity of the organic group is low, e.g. $o\text{-}O_2NC_6H_4SeOH$.[21]

Three types of halogen derivatives, the selenenyl halides or monohalides RSeX, the diorganoselenium dihalides R_2SeX_2 and the organoselenium trihalides $RSeX_3$ are known. Of each type the chlorides and bromides are well known, but of the iodo derivatives only the rather unstable diorganoselenium diiodides have been reported. It is surprising that the first fluorine derivative, dimethylselenium difluoride, was reported as recently as 1968.[22] This preparation, by Wynne *et al.*, using the reaction of silver difluoride and a selenide has been applied to several other organic selenides and appears to be general.[23] In a systematic study of organochalcogen halides, Wynne has found that organoselenium(IV) halides act as halide ion donors with Lewis acids, e.g.

$$CH_3SeCl_3 + SbCl_5 \longrightarrow [CH_3SeCl_2^+][SbCl_6^-]$$

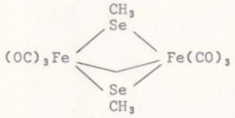
Similarly there is some evidence that the unstable adduct

$(C_6H_5)_2SeCl_2.BCl_3$ decomposes via the species $[(C_6H_5)_2SeCl^+]$.[24] Halide ion acceptor properties have been observed in organoselenium(II) halides, resulting in salt formation.[25]

$$C_6H_5SeBr + [Et_4\overset{+}{N}]\overset{-}{Br} \longrightarrow [Et_4\overset{+}{N}][C_6H_5SeBr_2^-]$$

In the older literature more emphasis was placed on the donor properties of organoselenium(II) derivatives, observed by the formation of selenonium salts, $[CH_3(C_2H_5)_2Se]I$, and adducts with e.g. mercuric halides, $(C_2H_5)_2Se \longrightarrow HgCl_2$;[26] which were easily rationalized by the presence of selenium lone pair electrons.

Presumably because of the "organic" emphasis placed on organoselenium chemistry, metal derivatives have received scant attention in the reviews. However, there has been increasing interest in selenium containing ligands in transition metal complexes, particularly of metal carbonyls.[27,28] Two general types of compounds are encountered, derivatives of selenides, e.g. $Mn(CO)_3[Se(C_6H_5)_2]_2Br$[29] and derivatives of selenols, e.g.[30]



Compounds of transition metal ions have also been prepared by Andra, from the reaction of aluminium benzeneselenolate and 1-naphthaleneselenolate with metal salts giving the corresponding transition metal selenolates,[31] e.g.

$$CrCl_3 + Al(SeC_6H_5)_3 \longrightarrow Cr(SeC_6H_5)_3 + AlCl_3$$

Apart from selenocyanate $SeCN^-$ complexes,[28] however, no transition metal complexes of the type $[M(SeR)_n]^{x-}$ appear to have been reported.

A study of trifluoromethyl derivatives of selenium yielded some interesting and unusual observations.[1] Bis(trifluoromethyl)selenide $(CF_3)_2Se$ forms neither a selenonium salt with methyl iodide, nor an adduct with mercuric chloride, suggesting that selenium exhibits no basic properties arising from the presence of the highly electronegative trifluoromethyl groups which delocalise the lone pairs on the selenium atom. There is also a resistance to oxidation. No dichloride $(CF_3)_2SeCl_2$ is obtained when $(CF_3)_2Se$ is treated with chlorine and when only one trifluoromethyl group is present the tribromide CF_3SeBr_3 cannot be obtained, nor is six valent selenium attained even under conditions where formation of the selenonic acid CF_3SeO_2OH might be expected. These observations are in contrast to the known properties of organoselenium derivatives. Following this study there has been a rapid expansion of the field, including replacing CF_3- groups by C_2F_5- and C_3F_7- groups, and also increasing the types of compounds investigated, including some metal derivatives. This work has been reviewed.[2] More recent developments have been the determination of molecular parameters of several trifluoromethyl derivatives of selenium by X-ray diffraction, $[CF_3SeMn(CO)_4]$,[32] and by electron diffraction, $(CF_3)_2Se$,[33] CF_3SeCN[34] and $(CF_3)_2Se_2$.[35] Studies of the vibrational spectra of some trifluoromethyl derivatives of selenium have also been carried out.[36,37]

Perfluoroaryl Chemistry

Following the commercial availability of highly fluorinated benzene derivatives in the sixties there has been a surge of interest in organometallic compounds having polyfluoroaromatic groups either bonded directly to various elements or incorporated in ligand molecules which are themselves forming complexes with metals. Polyfluoroaromatic derivatives of the elements, including nearly all of the more common elements and many of the less common elements, are known. This field has recently (1970) been covered in a very comprehensive review by Cohen and Massey on "Polyfluoroaromatic Derivatives Of Metals and Metalloids",[38] in which the chemistry of these derivatives is considered in detail. It is intended in this section to look at polyfluoroaromatic chemistry in a more general way, to compare polyfluoroaryl groups with other organic groups and to look at the effects of polyfluoroaromatic groups on the elements to which they are bonded.

Generally the scope of perfluoroaryl derivatives is no more limited than the scope of hydrocarbon or perfluoroalkyl derivatives of the elements but there are some significant exceptions to this generalization. These and other differences arise from the unusual influence of perfluoroaryl groups on the metal or metalloid atom which is manifested in such differences as increased stability, increased acceptor strength of the metal and various other properties that may enhance or inhibit the preparation and stability of different analogous compounds.

It has been observed that acceptor properties of an element are increased when bonded to a perfluoroaryl group. Thus bis(pentafluorophenyl)mercury forms a neutral coordination complex with bipyridyl whereas dimethylmercury, diphenylmercury and other organomercurials do not.[39] As acceptor properties are increased so donor properties are decreased. Bis(pentafluorophenyl) selenide forms no selenonium salt with methyl iodide, nor an adduct with mercuric chloride[5] in precise analogy to bis(trifluoromethyl) selenide.[1]

Similarly tris(pentafluorophenyl)phosphine forms no phosphonium salt with methyl iodide.[40] These observations may be explained by electron withdrawal by the pentafluorophenyl groups making the metal or metalloid more acidic (in the Lewis sense). This is compatible with a classical study on pentafluorobiphenyl derivatives (meta- and para- substituted) $C_6F_5C_6H_4X$ by Sheppard in which it was shown that the pentafluorophenyl group is inductively electron withdrawing, intermediate between phenyl and trifluoromethyl.[41] It should be noted, however, that, whereas lone pair donation is minimal, adduct formation may still take place when back donation occurs. Thus tris(pentafluorophenyl)phosphine forms adducts with transition metals, the low donor ability being enhanced by a synergic π interaction between the metal *d* orbitals and empty *d* orbitals on phosphorus:[42]

$$(C_6F_5)_3P \underset{\sigma}{\overset{\overset{\pi(d\text{-}d)}{\longleftarrow}}{\longrightarrow}} M$$

Another property of pentafluorophenyl metal derivatives is their resistance to oxidation. The formation of tris(pentafluorophenyl)phosphine oxide from $(C_6F_5)_3P$ required a stronger oxidation procedure than that used for the conversion of triphenylphosphine to triphenylphosphine oxide.[40]

Similarly, oxidation of bis(pentafluorophenyl) selenide has not been achieved using a variety of oxidising agents.[5] No reasonable or accepted explanation may as yet be given for this resistance to oxidation but Wall *et. al.*[40] feel that it may have something to do with π interaction between the C_6F_5 group and the lone pairs on the substituent atom.

Stability is an often quoted property of pentafluorophenyl derivatives and many examples are known where pentafluorophenyl derivatives of the elements are more stable than their alkyl, aryl or perfluoroalkyl counterparts.[38] Consideration of a few examples in detail and of some exceptions to that rule may throw some light on the reasons for this stability.

In a study of the thermal stabilities of some pentafluorophenyl phosphorus and silicon derivatives relative to their phenyl analogues,[40] tris(pentafluorophenyl)phosphine, which has a lone pair of electrons, was found to be more stable than triphenylphosphine but for the silanes, with no lone pairs, the reverse is found, $(C_6F_5)_4Si$ being less stable than $(C_6H_5)_4Si$. Similarly in the case of the phosphine oxides, where the phosphorus lone pair is involved in bonding to oxygen, $(C_6F_5)_3PO$ is less stable than $(C_6H_5)_3PO$. In another study it was noted that the thermal stability of tris(pentafluorophenyl)boron probably arises from π interaction with the vacant boron p_z orbital.[43] In a study of the ^{19}F nuclear magnetic resonance spectra of a large number and variety of pentafluorophenyl derivatives of the elements,[44,45] Graham *et.al.* have shown that generally there can be π interaction between the C_6F_5 ring π system and *p* and *d* orbitals on the element concerned. It is likely, therefore, that thermal stability is the result of greater C_6F_5-M bond strength arising from increased bond order by some degree of π bond formation. The Ni-C bond lengths revealed in the crystal structures of $(\pi\text{-}C_5H_5)(Ph_3P)Ni\text{-}C_6F_5$[46] 1.914 (σ 0.014)A and $(\pi\text{-}C_5H_5)(Ph_3P)Ni\text{-}C_6H_5$[47] 1.904 (σ 0.007)A are not significantly different. Their relative stabilities have not been reported, however.

Apart from thermal stability *in vacuo* pentafluorophenyl derivatives are generally stable in air. An example of this is $(C_6F_5)_3B$ which is not attacked by oxygen[48] while $(C_6H_5)_3B$ rapidly decomposes in air at room temperature.[49] With metal vacant orbitals or lone pairs interacting with the C_6F_5 ring π system, routes to decomposition by valency expansion or oxidation are less favourable in pentafluorophenyl derivatives.

Occasionally the properties of C_6F_5 enhance a particular form of decomposition. Slow hydrolysis, not usually observed with organoboron derivatives, is found with $(C_6F_5)_3B$.[43] Presumably this arises from the polarity of the $\overset{\delta-}{C_6F_5}—\overset{\delta+}{B}$ bond due to the highly electronegative nature of the C_6F_5- group.

Relative to perfluoroalkyl derivatives of the elements perfluoroaryl derivatives are more stable to the extent that sometimes C_6F_5 derivatives exist e.g. $(C_6F_5)_3B$ where their CF_3 analogues are unknown e.g. $(CF_3)_3B$.[50] It is not certain whether a weaker C-X bond is formed, since it has been postulated that with CF_3, too, π interactions with substituent orbitals may occur via π acceptance by the σ^* antibonding orbitals of the C-F bonds which are presumably lowered in energy by the highly electronegative fluorine atoms.[51] It would appear, however, that loss of fluorine as fluoride ion, or migration of fluorine to the metal atom, from a perfluoroalkyl group is easier than from a perfluoroaryl group. An important consequence of this is that while perfluoroaryl lithium and Grignard reagents provide extremely useful routes to further derivatives of the elements attempts to prepare analogous perfluoroalkyl reagents result in decomposition giving LiF and MgF_2/MgFX.

Perfluoroalkyl derivatives are prepared almost exclusively by reaction of the perfluoroalkyl halides.[9]

It is, however, not unknown for perfluoroaryl derivatives of the elements to decompose giving the metal fluoride, as in the case of some pentafluorophenyl aluminium derivatives which decompose explosively.[38] It is noteworthy that pentafluorophenyllithium has been reported to explode occasionally.[53] In this laboratory ether was accidently allowed to evaporate from an ether solution of the Grignard reagent, pentafluorophenylmagnesium bromide. This resulted in a violent explosion.[54]

While the perfluoroaryl-metal bond appears to be strong, when working with these derivatives one must bear in mind that nucleophilic attack resulting in displacement of a fluoride of the aromatic ring is common. Most often, in the case of pentafluorophenyl compounds, it is the para position that suffers attack.[9]

The chemical effects noted above can generally be understood in terms of electron withdrawal by the perfluoroaryl group and by π interactions between the perfluoroaryl ring π system and the orbitals of the bonded atom. Although the inductive effect of the C_6F_5 group is known and is positioned between CF_3 and C_6H_5, π interactions may result in π donation or π acceptance depending on the electronic nature of the element X according to the following scheme:[45]

$$\mathrm{C_6F_5}\underset{\underset{\pi(p-p)}{\curvearrowleft}}{\overset{\overset{\pi(p-d)}{\curvearrowright}}{\text{——}}}\mathrm{X}$$

The total electron withdrawing (inductive and resonance) effect on C_6F_5 varies from substituent to substituent and naturally the effective electronegativity of the C_6F_5 group will depend on the way it can interact with the rest of the molecule. This is demonstrated by the electronegativity values that have been reported for the pentafluorophenyl group, Table 1.2, obtained by different methods and from different series of derivatives. It can be seen that the pentafluorophenyl group exhibits a diversity of electronegativity values depending on its environment and perhaps on the method used. This diversity is seen even when C_6F_5 is bonded only to tin. Evidently the perfluoroaryl groups exert an influence on the properties of the elements to which they are bonded but they are also influenced by these elements and their environments.

In general, the differences in properties between the pentafluorophenyl derivatives and their hydrocarbon analogues are of a similar nature to, but not as marked as with the perfluoroalkyl compounds.

TABLE 1.2

Reported Electronegativity Values Of The Pentafluorophenyl C_6F_5 Group

Compound Type Or Series	Method Of Estimation	Reported Value	Reference
$(C_6H_5)_nX_{3-n}SnMn(CO)_5$ X = Cl, C_6F_5, Br	Linear relation between ν(C=O) and electronegativity	2.4	55
$XMn(CO)_5$ X = Cl, Br, C_6F_5, I	ν(C=O) frequency shift	Br(2.8)>C_6F_5>I(2.5)	55
X_4Sn	Mossbauer chemical shift	2.68 ±0.05	56
$(C_2H_5)_2SnX_2$	Chemical shift in ^1H n.m.r.	Cl(3.0)>C_6F_5>Br(2.8)	57
$(C_6F_5)_nX_{3-n}PO$ X = CH_3, C_2H_5, C_6H_5, H	ν(P=O) frequency shift	2.6	58

Perfluoroaryl Derivatives Of Selenium

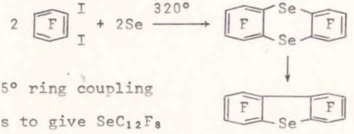
The first perfluoroaryl derivative of selenium was reported in 1965 by Burdon *et.al.* when bis(pentafluorophenyl) selenide was prepared by the reaction of elemental selenium on bis(pentafluorophenyl)mercury.[3]

$$Se + (C_6F_5)_2Hg \rightarrow (C_6F_5)_2Se + Hg$$

Since then Massey *et.al.* have investigated other methods of forming the carbon-selenium bond. The reaction of selenium with iodopentafluorobenzene[4] and the reaction of pentafluorophenyllithium with selenium halides[18] lead to mixtures of bis(pentafluorophenyl) mono- and diselenide.

$$\left.\begin{array}{l} C_6F_5I + Se \xrightarrow{230^\circ} \\ C_6F_5Li + \begin{array}{l} Se_2Cl_2 \\ \text{or } SeCl_4 \end{array} \longrightarrow \end{array}\right\} (C_6F_5)_2Se + (C_6F_5)_2Se_2$$

Variations of these methods using difunctional perfluoroarenes lead to the formation of the perfluoroaromatic selenium heterocycles, octafluorodibenzoselenanthrene (I) and octafluorodibenzoselenophene (II). Selenium with 1,2-di-iodotetrafluorobenzene reacts[4,18] at 320°.



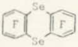
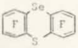
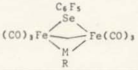
I

II

At 375° ring coupling occurs to give $SeC_{12}F_8$

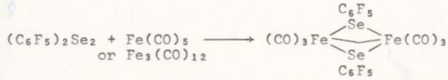
TABLE 1.3

Physical Properties Of Perfluoroaryl Selenium Compounds

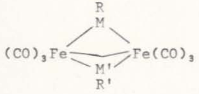
Formula	Odour	Appearance	mp.	Reference
$(C_6F_5)_2Se$	Sweet	Colourless crystals	71-72	3
$(C_6F_5)_2Se_2$	Mildly unpleasant	Yellow needles	46-48	18
C_6F_5SeH	Foul	Colourless liquid	(157-159 b.p.)	5
			118.5-120.5	18
			117-120	18
		Off-white solid	102-103	60
C_6F_5SeCl	Halogen	Dark red viscous involatile liquid		5
C_6F_5SeBr	Halogen	Dark brown viscous involatile liquid		5
$C_6F_5SeCl_3$	Halogen	Pale yellow crystals	78	5
$C_6F_5SeO_2H$	Odourless	Colourless plates	120	5
C_6F_5SeCN	Foul	Colourless crystals	40.5	5
C_6F_5SSeCN		White solid		61
$C_6F_5SeSC_6F_5$			43-45	59
$C_6F_5SeCH_2CH_2Cl$	Lachrymating	Colourless crystals	30	5
$C_6F_5SeCH_2CH_2Br$	Lachrymating	Colourless crystals	47	5
$(C_6F_5Se)_2Hg$	Mildly unpleasant	Off white plates	171-173	59
$(C_6F_5Se)_2Hg.PPh_3$	Odourless	Off white needles	130-131	5
$C_6F_5SeHgSC_6F_5$			168-170	59
 RM = SeC_6F_5		Red solid		59
= SeC_6H_5		Red solid		59
= SC_6F_5		Red solid		59

This material can also be prepared from Se and $2,2'\text{-}I_2C_{12}F_8$, or $SeCl_4$ and $2,2'\text{-}Li_2C_{12}F_8$. There was little investigation into the chemical properties of these new pentafluorophenyl selenium derivatives but two metal derivatives were prepared, bis(pentafluorophenylseleno)mercury and di-μ-pentafluorobenzeneselenatohexacarbonyldiiron.[59]

$$(C_6F_5)_2Se_2 + Hg \xrightarrow{180°} (C_6F_5Se)_2Hg$$



Also the mixed compound bis(pentafluorophenyl) thioselenide and other mixed iron carbonyl derivatives of the type:



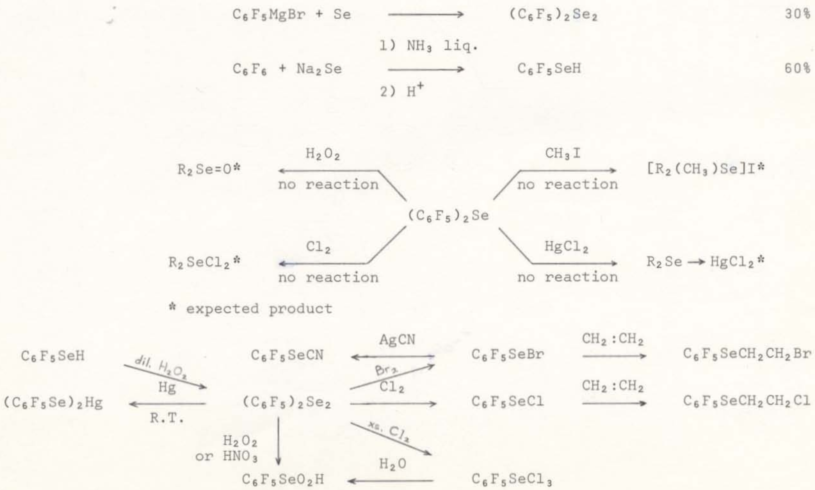
$R,R' = C_6H_5,\ C_6F_5$

$M,M' = S,\ Se,\ Te$

were prepared. At this point it was felt that some interesting properties might be observed in pentafluorophenyl selenium chemistry in light of the unusual properties of trifluoromethyl derivatives of selenium.[1] The following is an account of that investigation[5] and is summarized in Figure 1.2.

FIGURE 1.2

Reactions Of Pentafluorophenyl Derivatives Of Selenium



Whereas preparation of starting material generally gives a mixture of bis(pentafluorophenyl) mono- and diselenide, which are difficult to separate physically, two new methods have been developed giving clean yields of just one pentafluorophenyl selenium derivative. The reaction of pentafluorophenylmagnesium bromide with elemental selenium gives a 33% yield of the diselenide[59] while the nucleophilic attack by sodium selenide on hexafluorobenzene in liquid ammonia followed by acidification of the resulting selenolate gives a 62% yield of pentafluorobenzeneselenol.

Bis(pentafluorophenyl) selenide is unreactive towards oxidation and shows no basic character toward mercuric chloride, where adduct formation is expected, nor in the formation of a selenonium salt with methyl iodide. These observations are analogous to the properties of bis(trifluoromethyl) selenide and the same explanation is offered; selenium shows hardly any basic character owing to the delocalization of lone pairs by the electronegative C_6F_5 groups. Resistance to oxidation is undoubtedly due to the influence of the C_6F_5 groups on selenium but the reason is not entirely clear. When one C_6F_5 group is bonded to selenium oxidation is still restricted unless oxidation results in the formation of selenium bonds to the highly electronegative atoms oxygen or chlorine. Thus there is no evidence for the formation of pentafluorophenylselenium tribromide in contrast to the formation of organic selenium tribromides. While organic derivatives of selenium(VI) are known in the form of selenones, R_2SeO_2 and selenonic acids $RSeO_2OH$ no such derivatives are found here.

Having observed unusual properties of the pentafluorophenyl selenium system it became evident that further work would be useful both in expanding this field and in attempting to obtain a deeper understanding of the factors affecting the properties of this system. The analogous fields, perfluoroalkyl selenium derivatives and perfluoroaryl sulphur derivatives might also yield interesting comparisons. Further, the properties of the C_6F_5- group are still not well understood and vary when bonded to different elements. If the interactions of C_6F_5 with selenium can be understood, then the general properties of perfluoroaryl groups are still better defined.

CHAPTER II

METAL COMPLEXES OF PENTAFLUOROBENZENESELENOLATE

Introduction

Previous work on the pentafluorophenyl derivatives of selenium indicates that the C_6F_5Se- group has properties that may be ascribed to a pseudohalogen.[5] These properties include the formation of "interhalogen compounds", C_6F_5SeBr, C_6F_5SeCl, $C_6F_5SeCl_3$, C_6F_5SeCN, together with an "acid" C_6F_5SeH, the "free halogen" $(C_6F_5Se)_2$ and a "mercury salt", $(C_6F_5Se)_2Hg$ which is insoluble in water and which shows some tendency to form mixed mercury salts with mercuric halides. Monocovalent derivatives of the C_6F_5Se- group are known, e.g. $C_6F_5SeCH_2CH_2Cl$, but the existence of the anion, $C_6F_5Se^-$, would provide extra evidence of pseudohalogen character, particularly if its reactions are typical of halogens. A classical method of studying halogenides and pseudohalogenides is to look at their complexes with a number of metal ions. Ligand field parameters from transition metal complexes place F, Cl, Br, I, and pseudohalogens, together with other ligands, in well defined positions in the spectrochemical and nephelauxetic series, while charge transfer bands provide an indication of the electronegativity of ligands from the concept of optical electronegativity.

This type of study should also provide some useful material for comparison with analogous ligands, particularly $C_6F_5S^-$, which has been investigated in a similar way. This should also provide some insight into the properties of the CF_3Se- group which appears to have properties[1] very similar to those of the C_6F_5Se- group in its covalent chemistry. Various complexes of CF_3Se with mercury have been investigated by several physical methods which show that the CF_3Se- group displays pseudohalogen character.[62] An investigation of complexes with other metal ions has not been carried out because of the instability of the CF_3Se^- anion in water. Since the CF_3Se^- anion decomposes in water giving fluoride ion as one of the products, it is likely that the mechanism of decomposition is similar to that of CF_3S^-.[63]

$$CF_3S^- \xrightarrow{H_2O} F^- + F_2CS \qquad (2.1)$$

The pentafluorobenzeneselenolate $C_6F_5Se^-$ anion, however, is quite stable in water

Reactions Of Pentafluorobenzeneselenolate With Aqueous Transition Metal Ions.

Pentafluorobenzeneselenol, which has a disgusting odour and is readily oxidised by atmospheric oxygen, is conveniently handled in aqueous alkaline solution as 1 molar Na[SeC_6F_5]. The white anhydrous salt is not isolated because of rapid decomposition, even in a sealed vial.

Solutions of the divalent group IIB metal ions are treated with the selenolate solution in the expectation that the four coordinate complexes $[M^{II}(SeC_6F_5)_4]^{2-}$ would be formed. Therefore, a slight excess of the selenolate ion is used in the ratio 5:1 (selenolate:metal). With zinc(II) this gives a four coordinate complex which is isolated as the tetramethylammonium salt $[(CH_3)_4N]_2[Zn(SeC_6F_5)_4]$ on addition of tetramethylammonium chloride solution. However, with cadmium(II) some white precipitate is formed on addition of pentafluorobenzeneselenolate solution and it is necessary to increase the ratio to 6:1 ($C_6F_5Se^-:Cd^{2+}$) in order to effect complete solution. The four coordinate complex anion is isolated as the tetramethylammonium salt; $[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$. Similarly, with mercury(II), it is necessary to add even more selenolate solution, making the ratio 7.5:1 ($C_6F_5Se^-:Hg^{2+}$), to effect complete solution. Presumably, in this case, the intermediate precipitate is $Hg(SeC_6F_5)_2$ which is known to be insoluble in water.[5]

Addition of tetramethylammonium chloride to the solution gives a salt containing the complex anion of stoichiometry $[Hg(SeC_6F_5)_3]^-$.

The same stoichiometry is observed when the complex is precipitated out with cesium. This seems to be a preferred structure of the pentafluorobenzeneselenolate mercury(II) system. It has been observed that the mercury salt, $Hg(SeC_6F_5)_2$, only forms a 1:1 complex with triphenylphosphine even when an excess of triphenylphosphine is present.[5] It should be noted that both mercury(II) pentafluorobenzenethiolate[64] and mercury(II) trifluoromethaneselenolate[65] give 1:2 complexes with triphenylphosphine, and the four coordinate complex, $[Hg(SC_6F_5)_4]^{2-}$, is formed from the reaction of mercury(II) with excess pentafluorobenzenethiolate.[66] Steric hindrance has been invoked to explain the unexpectedly low coordination found with triphenylphosphinemercury(II) pentafluorobenzeneselenolate,[5] but in view of the fact that the smaller ions, zinc(II) and cadmium(II) form four coordinate complexes with pentafluorobenzeneselenolate this cannot be the case. The ^{19}F n.m.r. spectra of acetone solutions of $[Hg(SeC_6F_5)_3]^-$ salts indicate that the anion is monomeric (see Chapter VII). The zinc complex is extremely unstable in air and precaution must be taken to "work up" the material under dry nitrogen. The white solid slowly turns orange even in a well stoppered vial. The sulphur analogue, tetraethylammonium tetrakis(pentafluorobenzenethiolato)zincate(II), also decomposes to an orange material.[66] The cadmium and mercury complexes are air stable.

Since it is anticipated that silver(I) would give a two coordinate complex a ratio of 2.5:1 ($C_6F_5Se^-:Ag^+$) is chosen. This results in a voluminous yellow precipitate. However, when more pentafluorobenzeneselenolate is added, making the ratio 1:5 the precipitate, undoubtedly silver pentafluorobenzeneselenolate, redissolves giving a clear colourless solution.

$$C_6F_5Se^- + Ag^+ \longrightarrow C_6F_5SeAg \xrightarrow{C_6F_5Se^-} [Ag(SeC_6F_5)_2]^- \quad (2.2)$$

The two coordinate silver complex is isolated as the colourless tetramethylammonium salt.

With other group 1b metals redox reactions are observed. Copper(II) is reduced by pentafluorobenzeneselenolate giving bis(pentafluorophenyl)diselenide and a copper(I) complex.

$$8C_6F_5Se^- + 2Cu^{2+} \longrightarrow (C_6F_5)_2Se_2 + 2[Cu(SeC_6F_5)_3]^{2-} \quad (2.3)$$

The three coordinate copper(I) complex is isolated as the tetramethylammonium salt. Gold(III) gives a water insoluble square planar four coordinate complex with potassium pentafluorobenzeneselenolate solution.

$$4K[C_6F_5Se] + Au^{3+} \longrightarrow K[Au(SeC_6F_5)_4] + 3K^+ \quad (2.4)$$

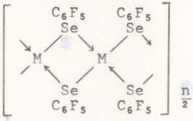
The complex is soluble in oxygen containing solvents but is insoluble in non-polar solvents. Addition of hexane to the red solution of the gold(III) complex in ether results in disproportionation to give bis(pentafluorophenyl) diselenide and the two coordinate gold(I) complex which is isolated as a light sensitive, white solid from this solution.

$$\underset{\text{red}}{K[Au(SeC_6F_5)_4]} \underset{\text{ether}}{\overset{\text{hexane}}{\rightleftharpoons}} \underset{\text{white}}{K[Au(SeC_6F_5)_2]} + (C_6F_5)_2Se_2 \qquad (2.5)$$

Addition of the diselenide dissolved in ether to a colourless solution of the gold(I) complex results in the formation of the original red colour of the gold(III) complex in ether, indicating the reversibility of equation (2.5). The nature of the solvent influence on the equilibrium is unclear.

Silver halides are white or yellow and insoluble in water but dissolve slightly in excess halide solutions. Although chloro- and bromocuprate(II) complex anions may be isolated from aqueous solutions containing halide and Cu^{2+} ions,[67,68] copper(II) gives iodocuprate(I) complex anions and iodine[69] in the presence of iodide. Similarly $KAuBr_4$ may be isolated from a solution of gold(III) and potassium bromide, but the product isolated from a solution of gold(III) and potassium iodide contains I_3^-.[70] The pentafluorobenzeneselenolate ion is similar in properties to a halide ion. It is similar to iodide in its interaction with copper(II) but is more specifically between bromide and iodide in its interactions with gold(III) since the $[Au(SeC_6F_5)_4]^-$/ $[Au(SeC_6F_5)_2]^-$ system is borderline between the gold/bromide and gold/iodide systems, the equilibrium (2.5) being only shifted by solvent effects.

While the metal ions, nickel(II), palladium(II) and platinum(II) form tetrahalometallate(II) complexes in excess halide solutions only platinum(II) gives a four coordinate complex anion with pentafluorobenzeneselenolate. The platinum complex $K_2[Pt(SeC_6F_5)_4]$ is prepared in aqueous solution from potassium pentafluorobenzeneselenolate and potassium tetrachloroplatinate(II). It is necessary to warm the solution to effect reaction of the square planar $[PtCl_4]^{2-}$ complex ion. Nickel(II) and palladium(II) give only the salts, $M(SeC_6F_5)_2$. These salts are insoluble in water and organic solvents which suggests that they are probably polymeric.



M = Ni, Pd.

The palladium salt is diamagnetic (Table 2.1) indicating a square planar arrangement of selenium atoms about the

TABLE 2.1

Magnetic Measurements Of Some Complexes

Complex	T°K	$\chi_g \cdot 10^6$	$\chi_M \cdot 10^6$	$\chi_M^P \cdot 10^6$	μ_{eff}
$[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$	299	6.342	7556	501	4.38
$Ni(SeC_6F_5)_2$	296	4.519	2489	192	2.53
$Pd(SeC_6F_5)_2$	296	-0.303	-181	208	
$K_2[Pt(SeC_6F_5)_4].H_2O$	296	-0.301	-378	393	
$K[Au(SeC_6F_5)_4]$	296	-0.221	-270	365	

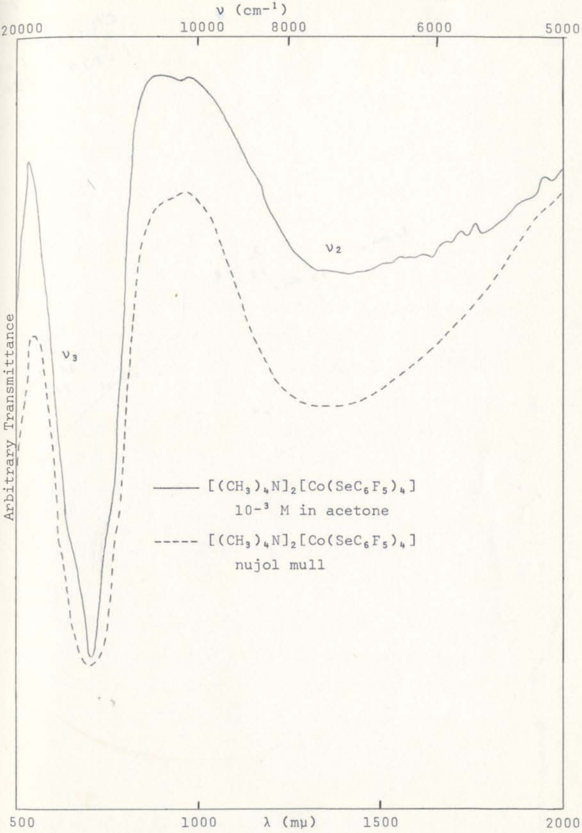
palladium atom. High spin d^8 nickel(II) compounds generally have magnetic moments in the range 2.80 - 3.50 B.M., while low spin square planar complexes have a zero magnetic moment.[71] The nickel salt has a magnetic moment of 2.53 B.M. and, therefore, cannot be low spin. The high spin assignment indicates a tetrahedral arrangement of selenium atoms about the nickel atom. The low magnetic moment may arise from "direct interaction" between adjacent nickel atoms or from "super-exchange interaction" through a π pathway set up using $3d$ orbitals of the nickel atom and a $4p$ orbital on the bridging selenium atom. Such interactions are believed to account for subnormal magnetic moments in some copper(II) complexes.[72]

The reaction of nickel(II) with pentafluorobenzeneselenolate is similar to that of nickel(II) with pentafluorobenzenethiolate,[66,11] both reactions giving the polymeric salt $\{NiX_2\}_n$. While pentafluorobenzenethiolate reacts with a stoichiometric quantity of palladium(II) to give the polymeric palladium salt $\{PdX_2\}n$,[66,11] excess pentafluorobenzenethiolate leads to the formation of the four coordinate complex anion $[Pd(SC_6F_5)_4]^{2-}$.[66] With excess pentafluorobenzeneselenolate only the polymeric salt $\{Pd(SeC_6F_5)_2\}_n$ is formed.

With excess (5:1) pentafluorobenzeneselenolate, cobalt(II) gives a green solution, from which a four coordinate complex anion may be isolated as the tetramethylammonium salt. The green crystalline solid decomposes rapidly in air and must be "worked up" under dry nitrogen. It is stable in a vial sealed under dry nitrogen, but decomposes after several months even under these conditions. The electronic spectrum of the cobalt complex (Figure 2.1) is similar to the spectra obtained from tetrahedral cobalt(II) complexes.[73] The solid is paramagnetic, having a magnetic moment of 4.38 B.M. This falls within the range 4.30-5.20 B.M. observed for high spin tetrahedral and octahedral d^7 cobalt(II) complexes[71] and provides further evidence that the structure of $[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$ consists of the cobalt atom at the centre of a tetrahedral arrangement of selenium atoms.

It has been suggested that aqueous solutions of cobalt(II) and excess halide, X^-, contain species of the type $[CoX_4]^{2-}$ and $[CoX_3H_2O]^-$ in agreement with the fact that the energies of the absorptions, in the visible region, in these aqueous systems are always higher than those associated with the species $[CoX_4]^{2-}$ since H_2O is a stronger ligand than halide.[73] Since the energies of the absorptions of an aqueous solution containing

FIGURE 2.1 Visible And Near Infrared Spectrum Of $[Co(SeC_6F_5)_4]^{2-}$ Complex Anion



Co^{2+} and excess $C_6F_5Se^-$ ions are higher than those of an acetone solution of $[(CH_3)_4N][Co(SeC_6F_5)_4]$ (Table 2.2) it would appear that some hydrolysis occurs in aqueous solution.

While most of the complexes are stable to atmospheric conditions the complexes of zinc(II) and cobalt(II) are relatively unstable. This is not an unexpected observation if the concept of class A and class B acceptors and donors is considered.[74] Of the metals encountered here, only zinc(II) and cobalt(II) are class A acceptors, the rest being class B. It is well known that selenium is a B type donor and it would appear that selenium in pentafluorobenzeneselenolate is no exception. Donors and acceptors of the same class form stable complexes together, whereas complexes containing donors and acceptors of a different class are unstable. Thus, complexes of the class B donor $C_6F_5Se^-$ with the class A acceptors, zinc(II) and cobalt(II) are unstable.

Ligand Field Parameters

Of the complexes studied, only that of cobalt(II) provides sufficient information for meaningful discussion in the light of Ligand Field Theory. Cotton, Goodgame and Goodgame have made a through spectral and magnetic study of tetrahedral cobalt(II) species, $[CoL_4]^{2-}$, with a number of ligands.[73]

TABLE 2.2

Electronic Spectra

Complex	Solvent	[cm^{-1}]	ϵ_{max}	Description
$[(CH_3)_4N]_2[Zn(SeC_6F_5)_4]$	Methanol	37700	34200	C.T.[a]
		46000	33700	C.T.
$[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$	Methanol	37900	37900	C.T.
$[(CH_3)_4N][Hg(SeC_6F_5)_3]$	Methanol	36000	34000	C.T.
		46500	29800	C.T.
$Cs[Hg(SeC_6F_5)_3]$	Methanol	∿36500(sh)	28100	C.T.
		39500	30300	C.T.
$[(CH_3)_4N]_2[Cu(SeC_6F_5)_3]$	Methanol	36200	25300	C.T.
		46700	23500	C.T.
$[(CH_3)_4N][Ag(SeC_6F_5)_2]$	Methanol	37700	21900	C.T.
		47400	18100	C.T.
$K[Au(SeC_6F_5)_4]$	Methanol	20000	568	*d-d*[b]
		40000	25800	C.T.
		44000	27700	C.T.
	Nujol	20400		*d-d*
$Ni(SeC_6F_5)_2$	Nujol	19200		*d-d*
$Pd(SeC_6F_5)_2$	Nujol	23900		*d-d*
$K_2[Pt(SeC_6F_5)_4]$	Methanol	21900	1120	*d-d*
		34700	32700	C.T.
		43000	31300	C.T.
		46000	30000	C.T.
	Nujol	21400		*d-d*
$[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$	Acetone	7050 ν_2	122	*d-d*
		14100 ν_3	511	*d-d*
	Methanol	39000	27000	C.T.
	Nujol	7200 ν_2		*d-d*
		14300 ν_3		*d-d*
$Co^{2+}:SeC_6F_5^-::1:5$	Water	7300 ν_2		*d-d*
		14500 ν_3		*d-d*

---

a) Electron transfer transition b) *d-d* transition

The *d-d* bands of $[Co(SeC_6F_5)_4]^{2-}$ were obtained under three different conditions and are presented in Table 2.2 and diagrammatically in Figure 2.1. The spectrum of the crystalline solid, $[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$, dispersed in nujol is similar to that of the acetone solution, indicating that solvolysis has not occurred. The solution spectrum is most reliable since lattice effects in the crystalline solid can cause distortions of the tetrahedral symmetry of the $[Co(SeC_6F_5)_4]^{2-}$ ion. The spectrum of the aqueous solution, although close to that of the acetone solution, shows some deviation and cannot be relied upon, as it has been shown that solvolysis occurs in aqueous solutions of tetrahalocobaltate(II) ions.[73]

The low intensities of ν_2 ($\varepsilon = 122$) and ν_3 ($\varepsilon = 522$) are similar to the intensities of ν_2 ($\varepsilon = 78$) and ν_3 ($\varepsilon = 750$) observed in the spectrum of $[Bu^n{}_4N]_2[CoCl_4]$,[73] indicating that these bands are correctly assigned as *d-d* transitions. They may be understood more clearly by considering the Tanabe-Sugano plot, Figure 2.2. Since *d-d* transitions are Laporte forbidden the intensity of the bands is weak, but the transitions observed are spin allowed (i.e. quartet ⟶ quartet). Transitions from the quartet ground state to levels of different spin are forbidden and therefore not observed since they are

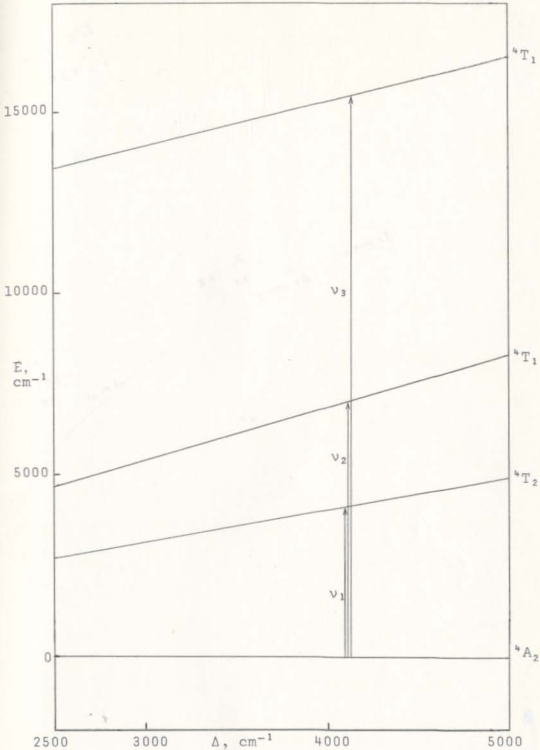


FIGURE 2.2 *Energy Levels For Tetrahedrally Coordinated Co(II) As Obtained From Tanabe And Sugano's*[75] *Secular Equations. Only The Quartet Levels Are Shown.*

extremely weak. Thus only the transitions $^4T_2 \leftarrow {}^4A_2$ (ν_1), $^4T_1(F) \leftarrow {}^4A_2$ (ν_2) and $^4T_1(P) \leftarrow {}^4A_2$ (ν_3) are expected to be observed. In practice (ν_1) is found in the region of near infrared, generally obscured by vibrational transitions as is found in this instance. However, (ν_1) is obtained from ν_2 and ν_3 from Cotton's derivation[76] of Tanabe and Sugano's results:[75]

$$\begin{aligned} \nu_1 &= \Delta \\ \nu_2 &= 1.5\Delta + 7.5B' - Q \\ \nu_3 &= 1.5\Delta + 7.5B' + Q \\ Q &= \tfrac{1}{2}[(0.6\Delta - 15B')^2 + 0.64\Delta^2]^{\frac{1}{2}} \end{aligned} \tag{2.6}$$

Equations (2.6) give Δ, the ligand field strength and B', the effective value of the Racah interelectronic repulsion integral.

Knowing Δ, it is now possible to calculate λ', the effective value of the spin orbit coupling constant using equation (2.7),[76] in which μ_{obs} is the observed magnetic

$$\mu_{obs} = \mu_{so} - \frac{15.59\lambda'}{\Delta} = 3.89 - \frac{15.59\lambda'}{\Delta} \tag{2.7}$$

moment and μ_{so} = 3.89 B.M. is the spin only moment. These results, together with those of other tetrahedral cobalt(II) complexes, are presented in Table 2.3. By comparison of the data it is possible to estimate some

TABLE 2.3

Ligand Field Parameters Of $[Co(SeC_6F_5)_4]^{2-}$ And Other Tetrahedral Cobalt(II) Complexes

Experimental datum or parameter	Ligand, X, in $[CoX_4]^{2-}$								
	$SeC_6F_5^-$	$SC_6F_5^-$ [77]	I^- [73]	Br^- [73]	Cl^- [73]	OH^- [73]	N_3^- [76]	NCO^- [76]	NCS^- [78]
ν_2, cm^{-1}	7050	7300	4500-4700	4880- 5080	5220- 5700	7300	6750	7150	7780
ν_3, cm^{-1}	14100	15000	13000-13500	13800-14200	14600-14800	16600	14900	16100	16250
Δ, cm^{-1}	4150	4250	2590- 2700	2790- 2910	2985- 3275	4230	3920	4150	4550
B', cm$^-$	582	635	640- 690	670- 720	690- 730	747	658	720	691
$\beta(=B'/B^a)$	0.61	0.66	0.66-0.71	0.70-0.74	0.72-0.75	0.773	0.680	0.745	0.715
μ, B.M.	4.38	4.45	4.77	4.69	4.59		4.47	4.44	4.40
λ', cm^{-1} b	131	153	140- 170	145- 160	130- 160		146	145	149

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a. B (free ion) = 967 cm^{-1}, b. λ (free ion) = 178 cm^{-1}

properties of the ligand, $C_6F_5Se^-$ relative to other ligands.

The parameter Δ gives the position of C_6F_5Se in the spectrochemical series:

$$I^- < Br^- < \mathit{S}CN^- \sim Cl^- << N_3^- < \mathit{N}CO^- \sim \mathit{Se}C_6F_5^- < OH^- \sim \mathit{S}C_6F_5^- < \mathit{N}CS^- \qquad (2.8)$$

This series is fairly invariant for ligands in complexes with different metal ions in different geometries. It reflects the strength of the field generated by these ligands around central metal ions. The increasing field strength with diminishing ligand size for a particular type of ligand, as indicated by the halides, is also found with the C_6F_5M series, where the sulphur atom is smaller than the selenium atom and thus gives rise to a stronger field. The π electron donors lie at the lower end of the scale. The halide ions, after forming a σ bond to the metal, still have three lone pairs available for π donation, while the $C_6F_5M^-$ ions under the same conditions only have two lone pairs. Thus the $C_6F_5M^-$ ions exert a weaker field than the halide ions. The parameter β (= B'/B) is a measure of the interelectronic repulsion in the metal *d* orbitals in complexes, B', relative to that in the free ion, B. Both orbital overlap resulting in delocalization of the *d* electrons and interpenetration of metal and ligand charge clouds resulting in increased screening of the *d* electrons, which in turn increases their mean orbital radii, give rise to a lowering of electron-electron repulsion.[79] These are probably best considered as alternative descriptions of the same physical process, which is in effect a measure of covalency of the metal-ligand bond. Thus β gives the position of $C_6F_5Se^-$ in the nephelauxetic (cloud expanding) series reflecting decreasing covalence of the ligands.

$$C_6F_5\mathit{Se}^- > C_6F_5\mathit{S}^- \sim I^- \sim N_3^- > \mathit{N}CS^- \sim Br^- \sim Cl^- > OH^- \qquad (2.9)$$

Like B the spin orbit coupling constant λ for the free ion is reduced to λ' in complexes for similar reasons, but although β values and λ'/λ ratios are both thought to be related to the degree of orbital overlap in metal-ligand bonding no good correlation between them was found by Cotton *et.al.*[73] This is not significant since the uncertainties of λ' values are high. However, it should be noted that the value of λ' (= 131 cm^{-1}) obtained is considerably lower than the free ion value, λ = 178 cm^{-1}, indicating a large degree of orbital overlap.

Optical Electronegativity

It has been observed[80] that in a variety of different metal halide complexes the absorption bands of the first charge transfer transitions shift to lower wave numbers as a function of the halide, X, in a very regular way. The shift from F to Cl is 28,000 cm^{-1}, from Cl to Br 6,000 cm^{-1}, and from Br to I 10,000 cm^{-1}. These shifts are proportional to differences between electronegativity values of X on the Pauling scale

$$\text{F } 3.9 \quad \text{Cl } 3.0 \quad \text{Br } 2.8 \quad \text{I } 2.5 \tag{2.10}$$

if one unit of this scale is made equivalent to 30,000 cm^{-1}. This is the reason why Jorgensen[80] introduces an optical electronegativity, χ_{opt}, of both ligand, X, and central metal atom, M, defined by

$$\nu_{corr} = [\chi_{opt}(X) - \chi_{opt}(M)].30{,}000 \text{ cm}^{-1} \tag{2.11}$$

where ν_{corr} is the energy of the first Laporte-allowed electron transfer transition corrected for interelectronic repulsions and χ_{opt} is the electronegativity for the halide ligands described by the Pauling scale (2.10). Using the relationship eq.(2.11) it is possible to obtain the optical electronegativities of metal ions from the electron transfer spectra of halo- complexes of various metals. It is possible then to define the optical electronegativities of other ligands compared to the four halogens of scale (2.10).

While there may be some theoretical basis for this concept,[80] electron transfer transitions are still not well understood[81] and the relationship eq.(2.11) should be considered empirical.

For most complexes considered here the transition involves a d^{10} metal ion. The electron transfer is from a ligand orbital to a metal orbital other than a *d* orbital, since the *d* orbitals are filled (see Figure 2.3a). Because there is no information on the nature of the orbitals involved no correction is made for interelectronic repulsions.[80] In the case of the cobalt(II) complex, the only complex considered with unfilled *d* orbitals, it is necessary to correct for ligand field and spin pairing energy, Figure 2.3b. The first Laporte allowed transition is the hypothetical transition $L^n e^4 t_2{}^3 \rightarrow L^{n-1} e^5 t_2{}^3$. However, this cannot occur since the *e* orbitals are filled and the observed transition is $L^n e^4 t_2{}^3 \rightarrow L^{n-1} e^4 t_2{}^4$. It is therefore necessary to correct for ligand field strength, Δ, and spin pairing energy, P, according to $\nu_{corr} = \nu_{obs} - \Delta - P$. The corrections are taken as $\Delta = 4150\ cm^{-1}$, $P = 5440\ cm^{-1}$, $(P = \frac{28}{3}B')$.[81]

The optical electronegativity values for the C_6F_5Se- group, presented in Table 2.4 were estimated using equation (2.11), from the charge transfer spectra of the appropriate complexes and from published data of the optical electronegativities of the metal ions,[80]

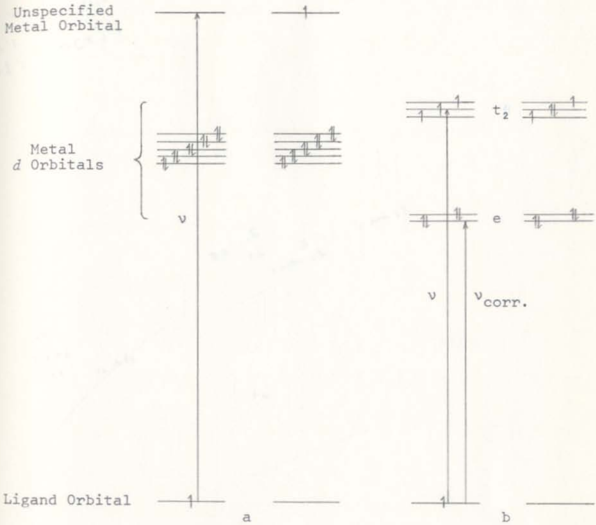


FIGURE 2.3 (a) Electron Transfer Transition From Ligand Orbital To d^{10} Metal Orbital

(b) Electron Transfer Transition From Ligand Orbital To d^7 Metal Orbital In A Tetrahedral Geometry, $L^n e^4 t_2{}^3 \rightarrow L^{n-1} e^4 t_2{}^4$

TABLE 2.4

Optical Electronegativity Of The C_6F_5Se- Ligand

Complex	First C.T. Band [cm^{-1}]	χ_{opt}
$[(CH_3)_4N]_2[Zn(SeC_6F_5)_4]$	37700	2.77
$[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$	37900	2.7-2.8
$[(CH_3)_4N][Hg(SeC_6F_5)_3]$	36000	2.70
$[(CH_3)_4N]_2[Cu(SeC_6F_5)_3]$	36200	2.8-2.9
$[(CH_3)_4N][Ag(SeC_6F_5)_2]$	37700	2.8-2.9
$[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$	39000	2.87

or from estimated optical electronegativities of the metal ions in azido[82] or pentafluorothiophenolato[77] complexes. Since various estimations are involved it is not surprising that there is quite a large spread of results, 2.7-2.9, and that the mean result 2.8 may only be quoted to one decimal place.[81] Solvent effects and the broad bands observed also add to the uncertainty of the meaning of these results. However, it is clear that the electronegativity of the selenium atom normally regarded as 2.4 is raised by the influence of the highly electron withdrawing C_6F_5- group to a value close to that of bromine. This effect has been noted before for S, Se bonded thiocyanate (χ_{opt} = 2.9) and selenocyanate (χ_{opt} = 2.8) where delocalization leads to an increased electronegativity of the sulphur or selenium atom.[83] It is strange that the electronegativity of sulphur, normally 2.5, is almost unchanged in the ligand C_6F_5S-, χ_{opt} 2.5-2.6. Chemical evidence supports the observed optical electronegativities of C_6F_5S- and C_6F_5Se-. Generally the lower the electronegativity of a species, the greater is its tendency to reduce, or be oxidised. Both $C_6F_5S^-$ and $C_6F_5Se^-$ reduce copper(II) to copper(I) whereas the bromide ion leaves copper(II) unchanged. This indicates that the electronegativities of $C_6F_5S^-$ and $C_6F_5Se^-$ are below that of bromide, (χ = 2.8). Iodide and $C_6F_5S^-$ reduce gold(III) to gold(I) but the $C_6F_5Se^-$ ion leaves the gold(III) ion unchanged placing the electronegativity of C_6F_5Se- above that of C_6F_5S-. These results are compatible with the optical electronegativity values determined.

$$I \sim C_6F_5S^-\ 2.5\text{-}2.6 < C_6F_5Se\ 2.8 \pm 0.1 < Br\ 2.8$$

Chemically the behaviour of the pentafluorobenzeneselenolate anion in its interactions with the transition metal ions is similar to that of halide ions and quantitatively it may be placed between bromide and iodide in its properties. Optical electronegativity places it closer to bromine. The position of $C_6F_5Se^-$ in the spectrochemical and nephelauxetic series is somewhat outside the range for halides, being a weaker π donor than chloride and more polarizable than iodide. These differences are by no means sufficiently large to preclude pentafluorobenzeneselenolate from the classification of pseudohalide.

TABLE 2.5

Products and Analyses

Compound	Appearance	M.P.	Yield %	Elemental Analysis							
				Found				Calculated			
				C	H	F	M	C	H	F	M
$[(CH_3)_4N]_2[Zn(SeC_6F_5)_4]$	White crystals	290	66	32.2	2.1	31.6	5.6	32.1	2.0	31.8	5.5
$[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$	White needles	164d	74	30.7	1.9	30.5	9.1	30.9	1.9	30.6	9.0
$[(CH_3)_4N][Hg(SeC_6F_5)_3]$	Off white needles	170	82	26.1	1.2	28.3	19.5	26.1	1.2	28.1	19.8
$Cs[Hg(SeC_6F_5)_3]$	Yellow needles	175	44	20.3	<0.2	26.2	18.6	20.2	0.0	26.6	18.7
$[(CH_3)_4N]_2[Cu(SeC_6F_5)_3]$	Yellow crystals	138	31	32.5	2.7	30.0	7.2	32.9	2.5	30.0	6.7
$(CH_3)_4N[Ag(SeC_6F_5)_2]$	White needles	187	24	28.7	1.9	28.2	16.1	28.5	1.8	28.2	16.2
$K[Au(SeC_6F_5)_4]$	Brown solid	185d	75	25.0	<0.2	31.0		23.6	0.0	31.2	
$K[Au(SeC_6F_5)_2].2H_2O$	White needles	160d	40	18.1	0.5	23.8		18.6	0.5	24.6	
$\{Ni(SeC_6F_5)_2\}_n$	Dark brown powder	>300	92	23.7	0.2	31.7	12.2	26.2	0.0	34.5	10.7
$\{Pd(SeC_6F_5)_2\}_n$	Brown powder	>300	52	24.1	0.2	31.4	18.2	24.1	0.0	31.7	17.8
$K_2[Pt(SeC_6F_5)_4].H_2O$	Orange crystals	229	55	22.9	0.2	30.1		22.6	0.2	29.8	
$[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$	Green needles	120d	37	32.2	2.2	31.4	4.8	32.3	2.0	31.9	4.9

Experimental

Preparation Of Pentafluorobenzeneselenol

This previously reported method[5] has been modified to give a higher yield.

A 3-neck flask (1 litre) set up for mechanical stirring and passage of dry nitrogen was cooled in a solid carbon dioxide-methanol slush bath. Liquid ammonia (700 ml.) was introduced. A suspension of sodium selenide was prepared *in situ* by adding selenium powder (79.0 g. : 1 mole) in 1 g. portions to a stirred blue solution of sodium (46.0 g. : 2 moles) in the liquid ammonia. The blue solution decolourised to a white suspension and was stirred for one hour. Hexafluorobenzene (186.0 g. : 1 mole) was added and the ammonia allowed to evaporate off over-night. The reaction mixture was extracted with water (300 ml.) and acidified with concentrated hydrochloric acid until the initial red colour became white and the selenol separated out as a heavy black oil. The aqueous layer was washed with chloroform and this was combined with the selenol. The organic solution was dried over anhydrous sodium sulphate and distilled under dry nitrogen. The fraction boiling at 156°, pentafluorobenzeneselenol, was collected (151.9 g.) in 62% yield.

Various residues from the above reaction were collected together and allowed to stand open to the atmosphere for one week. After this time solvents were removed to leave brown tar. The tar was dissolved in benzene, poured onto a column of neutral alumina, and eluted with benzene. The yellow band was collected. Solvent was removed, leaving an orange oil which was recrystallised from aqueous methanol giving yellow needles (29.1 g.) of bis(pentafluorophenyl) diselenide (m.p. 47°, lit. 46-48°).[4] This gave a total yield of pentafluorophenyl-selenium products of 72%.

General Method Of Preparation Of Complexes

Stock solutions of pentafluorobenzeneselenol were made up with a slight excess of alkali such that the solutions were 1.00 molar with respect to sodium or potassium and 0.98 molar with respect to selenol. This was achieved by weighing pentafluorobenzeneselenol (24.20 g. : 98 mmoles) into a volumetric flask (100 ml.). To this was added the contents of an ampoule of sodium hydroxide (0.1 M./ 1,000 ml.). The cooled solution was made up to the mark.

Removal of water by vacuum transfer from a 10.0 ml. aliquot of this solution gave a white solid. This material was recrystallised from acetone to give a white crystalline solid (2.6 g.). The material rapidly decomposed to a dark brown solid even in a well stoppered vial.

Aqueous solutions of a salt of the desired metal were added dropwise with stirring to an excess of selenol solution and the resulting metal oxides and hydroxides filtered off. Solutions of tetramethylammonium chloride were added to precipitate the complex metal anions which were filtered off, dried and recrystallised from organic solvents. Since there were several deviations from this procedure, each preparation is given in detail.

Residues were collected together and treated with iodine dissolved in methanol. The bis(pentafluorophenyl) diselenide produced was purified as described above.

Preparation Of Tetramethylammonium Tetrakis(pentafluorobenzeneselenolato)zincate(II)

Zinc sulphate, $ZnSO_4.7H_2O$ (0.575 g. : 2 mmoles) dissolved in water (5 ml.) was added dropwise with stirring to the sodium selenolate solution (10.0 ml. 10 mmoles). The solution was filtered and tetramethylammonium chloride solution added to the filtrate. The resulting precipitate was dried *in vacuo* and recrystallised from methanol under an atmosphere of dry nitrogen to give colourless crystals (1.57 g.). The white crystals became orange tinged after three months in a stoppered vial.

Preparation Of Tetramethylammonium Tetrakis(pentafluorobenzeneselenolato)cadmate(II)

Cadmium sulphate, $CdSO_4.8/3H_2O$ (0.513 g. : 2 mmoles) dissolved in water (10 ml.) was added dropwise with stirring to sodium selenolate solution (10 ml.). It was necessary to add more selenolate solution (2 ml.) to redissolve some material making a total of 12 ml. (12 mmoles). The solution was filtered and tetramethylammonium chloride solution added. The precipitate was filtered off, dried *in vacuo* and recrystallised from ethanol to give colourless needles (1.85 g.).

Preparation Of Tetramethylammonium Tris(pentafluorobenzeneselenolato)mercurate(II)

Mercuric chloride (0.543 g. : 2 mmoles) dissolved in water (15 ml.) was added dropwise with stirring to the sodium selenolate solution (10 ml.). It was necessary to add more selenolate (5 ml.) to redissolve some material, making a total of 15 ml. (15 mmoles). The solution was filtered and tetramethylammonium chloride solution added to the filtrate. The precipitate was filtered off and dried *in vacuo* and recrystallised from ethanol to give off-white needles (1.66 g.).

Preparation Of Cesium Tris(pentafluorobenzeneselenolato)-mercurate(II)

Mercuric chloride (0.543 g. : 2 mmoles) dissolved in water (15 ml.) was added dropwise with stirring to the sodium selenolate solution (15 ml. : 15 mmoles). The solution was filtered and cesium chloride solution added to the filtrate. The precipitate was filtered off, dried and recrystallised from aqueous ethanol to give pale yellow needles (0.93 g.).

Preparation Of Tetramethylammonium Tris(pentafluorobenzeneselenolato)cuprate(I)

Copper sulphate, $CuSO_4.5H_2O$ (1.00 g. : 4 mmoles) dissolved in water (5 ml.) was added dropwise with stirring to the selenolate solution (20 ml. : 20 mmoles) to give a voluminous dark grey solid which was filtered off. The solid was extracted with petroleum ether 40/60 and recrystallised from aqueous methanol to give yellow needles (1.70 g.) of bis(pentafluorophenyl) diselenide (m.p. 47°, lit. 46-48°).[4] Tetramethylammonium chloride solution was added to the filtrate and the resulting yellow precipitate filtered off and dried *in vacuo*. The solid was reprecipitated twice from acetone by addition of ether to give pale yellow crystals (0.389 g.).

Preparation Of Tetramethylammonium Bis(pentafluorobenzeneselenolato)argentate(I)

Silver nitrate (0.340 g. : 2 mmoles) dissolved in water was added dropwise with stirring to the sodium selenolate solution (5 ml.). It was necessary to add more selenolate solution (5 ml.) to redissolve some material making a total of 10 ml. (10 mmoles). The solution was filtered and tetramethylammonium chloride solution was added to the filtrate. The precipitate was dried *in vacuo* and recrystallised from ethanol to give colourless needles (0.159 g.).

Preparation Of Potassium Tetrakis(pentafluorobenzeneselenolato)aurate(III)

Potassium tetrachloroaurate(III) $KAuCl_4$ (0.378 g. : 1 mmole) dissolved in water (2 ml.) was added dropwise with stirring to the potassium selenolate solution (5 ml. : 5 mmoles) to give a skin-pink solid which was filtered off and dried *in vacuo*. The solid was extracted with ether and the solvent then removed by vacuum transfer to yield a brown solid (0.917 g.).

Preparation Of Potassium Bis(pentafluorobenzeneselenolato)aurate(I)

Potassium tetrakis(pentafluorobenzeneselenolato)aurate(III) (0.610 g. : 0.5 mmoles) was dissolved in ether to give a red solution. Hexane was added to this solution until the colour faded to orange. Solvent (mainly ether) was removed by boiling the solution until white crystals began to separate out. On cooling to room temperature a mass of white needles separated out.

The product (0.153 g.) was filtered off and washed with hexane. The solvent was removed from the filtrate leaving a brown solid residue. This was dissolved in hexane. The solution was filtered and solvent removed leaving a yellow solid which was recrystallised from aqueous methanol giving yellow needles (0.294 g.) of bis(pentafluorophenyl) diselenide (m.p. 46°, lit. 46-48°).[4]

The white solid product, potassium bis(pentafluorobenzeneselenolato)aurate(I) decomposed after one month in a sealed vial in the dark, but decomposed after three hours on exposure to light.

Addition of bis(pentafluorophenyl) diselenide to a colourless ether solution of the gold(I) complex gave the red colour of the original gold(III) solution.

Preparation Of Nickel Pentafluorobenzeneselenolate

Nickel chloride, $NiCl_2.6H_2O$ (0.475 g. : 2 mmoles) in water (3 ml.) was added dropwise with stirring to the sodium selenolate solution (10 ml. : 10 mmoles) to give a dark brown precipitate which was filtered off and dried *in vacuo*. The filtrate was colourless and gave no precipitate on addition of tetramethylammonium chloride solution. The dried dark brown solid (1.013 g.) was insoluble in organic solvents.

Preparation Of Palladium Pentafluorobenzeneselenolate

Palladium nitrate, $Pd(NO_3)_2.2H_2O$ (0.583 g. : 2 mmoles) in water (5 ml.) was added dropwise with stirring to the sodium selenolate solution (10 ml. : 10 mmoles). The dark brown precipitate was filtered off and dried *in vacuo*. The filtrate was colourless and gave no precipitate on addition of tetramethylammonium chloride solution. The brown solid, insoluble in most organic solvents, was partially soluble in acetone. It was recrystallised from hot acetone/petroleum ether 40/60 to give a brown powder (0.626 g.).

Preparation Of Potassium Tetrakis(pentafluorobenzeneselenolato)platinate(II)

Potassium tetrachloroplatinate, K_2PtCl_4 (0.830 g. : 2 mmoles) dissolved in water (10 ml.) was added to the potassium selenolate solution (10 ml. : 10 mmoles). Initially there appeared to be no reaction, but on warming (60°) the solution an orange precipitate formed. This was filtered off and dried *in vacuo*. The solid was recrystallised twice from ether/petroleum ether 40/60 to give orange crystals (1.38 g.).

Preparation Of Tetramethylammonium Tetrakis(pentafluorobenzeneselenolato)cobaltate(II)

Cobalt sulphate (0.562 g. : 2 mmoles) in water (5 ml.) was added dropwise with stirring to the sodium selenolate solution (10 ml. : 10 mmoles). The green solution was filtered and tetramethylammonium chloride solution added. The precipitate was filtered off and dried *in vacuo*. The green powder was recrystallised from hot, sodium dried tetrahydrofuran/hexane under an atmosphere of dry nitrogen to give green needles (0.882 g.). The product decomposed rapidly in air to give a brown powder. Decomposition even occurred, when the sample was stored under dry nitrogen in a wax sealed vial, after six months.

CHAPTER III

METAL CARBONYL DERIVATIVES

Introduction

While many examples are known of metal carbonyl complexes which contain organosulphur ligands there are few carbonyl complexes known with organoselenium ligands.[27] Five general methods have been employed to synthesise organoselenium derivatives of the metal carbonyls.

1. Metal carbonyl hydrides are reactive compounds and have been shown to react with diselenides to give organoselenium metal carbonyl derivatives.

$$HM(CO)_n + R_2Se_2 \longrightarrow RSeM(CO)_n \qquad (3.1)$$

Diselenides react with both hydridopentacarbonylmanganese[84] and hydrido(π-cyclopentadienyl)tricarbonylmolybdenum[85] to give selenium bridged compounds.

$$HMn(CO)_5 + R_2Se_2 \rightarrow [RSeMn(CO)_4]_2 \qquad (3.2)$$

$$(R = CH_3,\ C_2H_5,\ C_3H_7,\ CF_3,\ C_2F_5,\ C_3F_7)$$

$$cpMo(CO)_3H + R_2Se_2 \rightarrow [cpMo(CO)_2SeR]_2 \qquad (3.3)$$

$$(R = CH_3,\ C_2H_5,\ CF_3,\ C_2F_5)$$

2. Metal carbonyl halides are also useful reagents and are easier to handle than the corresponding hydrides. They react with metal derivatives of selenols, resulting in nucleophilic displacement of the halide by the corresponding selenolate.

$$XM(CO)_n + RSeM' \rightarrow RSeM(CO)_n + M'X \qquad (3.4)$$

Examples of this are the reactions of organotin selenium compounds with halopentacarbonylmanganese and -rhenium,[86]

$$XM(CO)_5 + R'_3SnSeR \rightarrow [RSeM(CO)_4]_2 \qquad (3.5)$$

$(X = Cl, Br. \quad M = Mn, Re. \quad R' = CH_3, C_6H_5.$
$R = CH_3, C_2H_5, C_6H_5)$

and the reaction of $Mn_2(CO)_8P(CF_3)_2I$ with a mercury selenolate.[87]

$$Mn_2(CO)_8P(CF_3)_2I + (CF_3Se)_2Hg \rightarrow Mn_2(CO)_8P(CF_3)_2SeCF_3 + HgI_2 \qquad (3.6)$$

All of the above contain selenium bridges.

3. Metal carbonyl dimers and trimers are easier to handle than the hydrides but are generally less reactive. Those polymers containing bridging carbonyls are usually the most reactive of this class and are found to react with diselenides

$$[M(CO)_n]_x + R_2Se_2 \rightarrow RSeM(CO)_n \qquad (3.7)$$

Examples of this are the reactions of diselenides with nonacarbonyltriiron,[30,59] and with (π-cyclopentadienyl)dicarbonyliron dimer.[30]

$$Fe_3(CO)_9 + R_2Se_2 \rightarrow [RSeFe(CO)_3]_2 \qquad (3.8)$$

$(R = CH_3,\ C_2H_5,\ C_3H_7,\ CF_3,\ C_2F_5,\ C_6F_5,\ C_6H_5)$

$$[cpFe(CO)_2]_2 + R_2Se_2 \rightarrow [cpFe(CO)SeR]_2 \qquad (3.9)$$

$(R = C_2H_5,\ C_3H_7)$

$$[cpFe(CO)_2]_2 + R_2Se_2 \rightarrow 2cpFe(CO)_2SeR \qquad (3.10)$$

$(R = CF_3,\ C_2F_5,\ C_3F_7)$

4. Pyrolysis of organoselenium derivatives of metal carbonyls may result in the loss of carbon monoxide giving further derivatives.

$$2[RSeM(CO)_4]_2 \rightarrow [RSeM(CO)_3]_4 + 4CO \qquad (3.11)$$

$(R = CH_3,\ C_6H_5.\quad M = Mn,\ Re)$

The structure of these compounds is uncertain but probably involves increased bridging by each selenium from two to three metal atoms.[86]

5. Organic selenides have lone pairs suitable for donation and are known to displace carbon monoxide from metal carbonyls.[29]

$Mn(CO)_5Br + 2(C_6H_5)_2Se \rightarrow Mn(CO)_3[Se(C_6H_5)_2]_2Br + 2CO$ (3.12)

This type of reaction can result in halogen bridge splitting.[88]

$[Re(CO)_4Cl]_2 + (C_2H_5)_2Se \rightarrow Re(CO)_4[Se(C_2H_5)_2]Cl$ (3.13)
and $Re(CO)_3[Se(C_2H_5)_2]_2Cl$

Many pentafluorophenyl sulphur derivatives of metal carbonyls have been reported and examples will be given where necessary in the discussion. The small number of organoselenium derivatives of metal carbonyls known makes a study of some pentafluorophenyl selenium derivatives an important contribution to this field. Also a comparison of these compounds with other organoselenium and pentafluorophenyl sulphur derivatives should provide some useful insight into the properties of the C_6F_5Se- group.

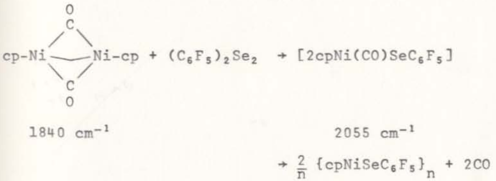
Present Work

The reaction between (π-cyclopentadienyl)dicarbonyliron dimer and bis(pentafluorophenyl) diselenide in refluxing benzene affords the mononuclear complex

$(C_6F_5)_2Se_2 + [cpFe(CO)_2]_2 \rightarrow 2cpFe(CO)_2SeC_6F_5$ (3.14)

in good yield.

Reaction between (π-cyclopentadienyl)carbonylnickel dimer and bis(pentafluorophenyl) diselenide in benzene at room temperature gives as the final product a black solid, insoluble in organic solvents, and exhibiting no carbonyl stretching bands in the infrared spectrum. Monitoring the reaction by infrared spectroscopy shows a diminishing bridging carbonyl and the formation of a terminal carbonyl, which disappears slowly.



$$\underset{1840\ \mathrm{cm^{-1}}}{\text{cp-Ni}(\mu\text{-CO})_2\text{Ni-cp}} + (C_6F_5)_2Se_2 \rightarrow \underset{2055\ \mathrm{cm^{-1}}}{[2\mathrm{cpNi(CO)SeC_6F_5}]} \rightarrow \frac{2}{n}\{\mathrm{cpNiSeC_6F_5}\}_n + 2\mathrm{CO} \qquad (3.15)$$

Although the proposed mononuclear complex is identified spectroscopically it decomposes during the total reaction time: the black solid is the only product isolated. Its insolubility suggests a polymeric structure and this probably involves selenium bridging.

π-cyclopentadienyl-catenadi-μ-pentafluorobenzeneselenolatonickel dissolves readily and completely in a solution of triphenylphosphine in benzene from which a monomeric triphenylphosphine adduct may be isolated in high yield.

$$\frac{1}{n}\{cpNiSeC_6F_5\}_n + Ph_3P \rightarrow cpNi(PPh_3)SeC_6F_5 \qquad (3.16)$$

The isologous sulphur polymer, prepared from nickelocene and pentafluorobenzenethiol, is depolymerised in the same way.[89]

Neat pentafluorobenzeneselenol, acting as reactant and solvent, and decacarbonyldimanganese or decacarbonyldirhenium react at room temperature on irradiation with ultra violet light. Reaction is clean giving good yields of the air stable monomeric derivatives.

$$2C_6F_5SeH + M_2(CO)_{10} \xrightarrow{U.V.} 2C_6F_5SeM(CO)_5 + H_2 \qquad (3.17)$$

$(M = Mn, Re)$

There is no reaction between $Mn_2(CO)_{10}$ and the selenol in the absence of U.V. irradiation even after three months.

Structural Considerations

Apart from the insoluble $\{cpNiSeC_6F_5\}_n$ which is probably polymeric, the proposed mononuclear structures of the other new pentafluorobenzeneselenol derivatives are confirmed by osmometrically determined molecular weights.

The number of carbonyl stretching frequencies observed in the infrared spectra (Table 3.1a) provides an indication of the geometries of the compounds studied.

TABLE 3.1a

Carbonyl Stretching Frequencies In C_6F_5Se And Other Derivatives Of Metal Carbonyls

Compound R=	C_6F_5Se	C_6F_5S	I	Br
$RFe(CO)_2(\pi-C_5H_5)$	2037	2040[89]	2042[90]	2049[90]
	1995	1997	1982	1995
$RMn(CO)_5$	2114	2120[12]	2125[91]	2133[91]
	2078	2085		
	2037	2050	2044	2050
	2024	2038	2016*	2019*
	2002	2015	2003	2001
$RRe(CO)_5$	2142	2146[12]	2145[91]	2150[91]
		2077		
	2043	2046	2042	2045
	2031	2036	2013*	2016*
	1991	1994	1987	1984

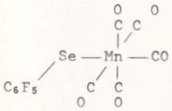
* unexplained, but probably $\nu(^{13}C{=}O)$

TABLE 3.1b

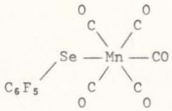
Carbonyl Stretching Frequencies In C_6F_5Se And Other Derivatives Of Iron Carbonyls

Compound R=	CF_3Se[30]	C_6F_5Se[59]	C_6H_5Se[59]	CH_3Se[30]	$[C_6F_5S]$[59]
$[RFe(CO)_3]_2$	2095	2080	2066	2060	2087
	2055	2051	2029	2010	2058
	2010	2016	2000	1955	2023
		2004	1988		2010

The two bands observed for $cpFe(CO)_2SeC_6F_5$ are consistent with the C_s symmetry expected for this type of compound. The five absorptions exhibited by the pentacarbonylmanganese derivative show that it has symmetry (C_s), lower than that of the pentacarbonylmanganese halides, which show three infrared active carbonyl stretches ($2A_1 + E$) in accord with C_{4v} symmetry.[92] The lower symmetry of this compound is to be expected because the C_6F_5SeMn group will not be axially symmetric. It is not possible to distinguish between an eclipsed ($4A' + A''$) and a staggered ($3A' + 2A''$) conformation.



eclipsed



staggered

While only four bands are shown by the pentacarbonylrhenium derivative the pattern is very similar to that of the pentacarbonylmanganese derivative and it is the weakest band (expected at around 2070 cm^{-1}) that is not observed. It is reasonable, therefore, to assume

C_s symmetry for $C_6F_5SeRe(CO)_5$.

Bands arising from C_6F_5Se- group vibrations are observed in all infrared spectra (Appendix A).

The π-cyclopentadienyl signals in the ^1H n.m.r. spectra (Appendix C) confirm the presence of this group in $cpFe(CO)_2SeC_6F_5$ and $cpNi(PPh_3)SeC_6F_5$. Phenyl protons are also indicated for the latter compound.

Discussion

It should be noted from the examples given in the introduction that selenium exhibits a strong tendency toward bridging with the result that most organoselenium metal carbonyl derivatives are isolated, not as the unbridged monomers, but as selenium bridged dimers and even tetramers. This may be understood by the fact that compounds of the type $RSeM(CO)_n$ are similar to organic selenides, R_2Se, since the selenium atom still has lone pairs suitable for donation in each case. It has been postulated that there is initial formation of the monomer, e.g.

$$[cpFe(CO)_2]_2 + R_2Se_2 \rightarrow 2cpFe(CO)_2SeR \qquad (3.18)$$

followed by displacement of carbon monoxide from another monomeric species by the lone pair on the selenium atom acting as a Lewis base.[93]

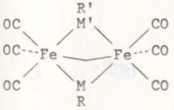
$$2cpFe(CO)_2SeR \rightarrow [cpFe(CO)SeR]_2 + 2CO \qquad (3.19)$$

Indeed, the monomer is isolated when the selenium atom is bonded to a perfluoroalkyl group[93] or a pentafluorophenyl group but not when bonded to an alkyl group.[93] The pentafluorophenyl sulphur derivative $cpFe(CO)_2SC_6F_5$ is also monomeric.[89] It has been suggested that when the organic group is highly electron withdrawing the lone pair electrons on the sulphur or selenium atoms are delocalised. This results in reduced donor ability so that bonding to another metal atom to form a bridged structure is not favoured.[30,89,12]

Organoselenium derivatives of iron carbonyl are selenium bridged dimers, $[RSeFe(CO)_3]_2$, even when selenium is bonded to the highly electron withdrawing perfluoroalkyl[93] and pentafluorophenyl[59] groups, in contrast to the organoselenium derivatives of decacarbonyldimanganese. The effect of replacing two carbonyl groups with the electron withdrawing cyclopentadienyl group is to reduce the "back-donation" power of the central iron atom. Weakening of this "back-donation" stabilises the monomers making bridge formation less favourable. The metal ligand bond cannot be viewed as derived solely from the electron pairs from the ligand to the metal. Back coordination via a π interaction between filled metal *d* orbitals and empty selenium *d* orbitals also contributes to the stability of these complexes.

$$C_6F_5Se \overset{\overset{\pi d\text{-}d}{\curvearrowleft}}{\longrightarrow} M(CO)_n$$

Massey *et.al.* prepared and studied a series of compounds of the type:[59]



$R,R' = C_6H_5,\ C_6F_5.$
$M,M' = S,\ Se,\ Te.$
where $M = M',\ M \neq M'$
$R = R',\ R \neq R'$

Comparison of the Mössbauer and infrared spectra (C=O stretching frequencies) of this series of compounds indicated respectively a decreased σ-donor ability and decreased π-bonding of C_6F_5Se relative to C_6F_5S. Similarly it was deduced that σ-donor ability was decreased but compensated by a π bonding increase in C_6F_5 relative to C_6H_5.[59,94]

Irradiation of iodine and decacarbonyldirhenium by ultraviolet light results in the formation of the monomer, $IRe(CO)_5$, at room temperature or a dimer,

$[IRe(CO)_4]_2$, at 100°.[95] Although the reactions are different similar conditions are employed in the U.V. irradiation of pentafluorobenzeneselenol and decacarbonyldimanganese or decacarbonyldirhenium. The monomeric products, $C_6F_5SeMn(CO)_5$ or $C_6F_5SeRe(CO)_5$, are obtained in good yield. The sulphur isologues of these pentacarbonyl derivatives have been prepared in low yields by reaction of pentafluorobenzenethiol with the appropriate metal carbonyl hydride.

$$C_6F_5SH + HM(CO)_5 \rightarrow C_6F_5SM(CO)_5 + [C_6F_5SM(CO)_4]_2 \qquad (3.20)$$

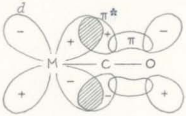
$$(M = Mn, Re)$$

Generally, but depending on conditions, the major product is the dimer.[12] Although the reactions of the thiol and selenol are different, and do not allow valid comparison, it would appear that the sulphur monomers have a greater tendency to dimerise than the selenium monomers. This is also supported by the observation that the sulphur monomers slowly dimerise in solution at room temperature while no such dimerisation was observed when the infrared solution spectra of the selenium monomers were being recorded.

Again it must be noted that alkyl and aryl selenium derivatives of both manganese and rhenium carbonyl are known and that these are dimeric $[RSeM(CO)_4]_2$ and tetrameric $[RSeM(CO)_3]_4$ compounds.[86] Even perfluoroalkyl selenium derivatives of manganese carbonyl are dimers.[84]

The reaction between bis(pentafluorophenyl) diselenide and (π-cyclopentadienyl)carbonylnickel dimer (eq. 3.15) illustrates clearly the mechanism postulated;[30,12] that there is initial formation of an unbridged monomer followed by displacement of a carbonyl group of another monomer by the selenium lone pair. It does not indicate what happens in the second step; loss of carbonyl followed by lone pair attack or lone pair attack followed by loss of carbonyl. The latter involves an intermediate that violates the 16 and 18 electron rule, a violation that Tolman, in his review of a large number of metal carbonyl reaction mechanisms, feels is very unlikely.[96] There is, however, insufficient information to distinguish between the two mechanisms.

The carbonyl stretching frequencies observed in metal carbonyls are thought to be related to π bonding between metal *d* orbitals and pπ* antibonding orbitals on the carbonyl group, which reduces the bond order of the C-O bond.



The extent of metal carbon π bonding depends on the properties of other ligands and appears to be influenced by metal-ligand π bonding (competing for metal *d* electrons) and electron donation or withdrawal by the ligand. In a general way this may be related to the electronegativity of the ligand.[97]

Comparison of the carbonyl stretching frequencies in Table 3.1a shows a trend,

$$Br > I > C_6F_5S > C_6F_5Se \qquad (3.21)$$

Because several factors influence the ν(C-O) shifts it is not possible to provide an unambiguous explanation for this order. It does show, however, that the overall electronic properties of C_6F_5Se are similar to those of a halogen. The relative position of C_6F_5Se to C_6F_5S is as expected in analogy with iodine and bromine.

In Table 3.1b the effect of changing the organic group on selenium is illustrated.

$$CF_3 > C_6F_5 > C_6H_5 > CH_3 \qquad (3.22)$$

This is compatible with current ideas on the inductive effects[41,98] of these organic groups and presumably reflects their electron withdrawing properties, transmitted through selenium.

The idea that a perfluorinated organic group bonded to selenium delocalizes the lone pairs relative to hydrocarbon derivatives, reducing the donor properties of selenium and hence the tendency to dimerise, appears to be valid. The contribution to the metal-selenium bond of back coordination of filled metal *d* orbitals to vacant selenium *d* orbitals is also important.

Relative to its sulphur isologue, pentafluorobenzeneselenolate seems to be a poorer bridging ligand, in agreement with the observations of Massey *et.al.*[59]

Experimental

Preparation Of Bis(pentafluorophenyl) Diselenide

Pentafluorobenzeneselenol (24.7 g. : 0.1 mole) was dissolved in water (100 ml.) containing sodium hydroxide (4.0 g. : 0.1 mole). To this solution, cooled in ice, was added iodine (12.7 g. : 0.1 mole) dissolved in methanol (400 ml.). This gave clumps of bis(pentafluorophenyl) diselenide. Water was added slowly, with stirring until no more diselenide precipitated. The solid was filtered off and recrystallised from methanol-

TABLE 3.2

Products and Analyses

Compound	Appearance	M.P. °C	Yield %	Elemental Analysis								MW†	
				Found				Calculated				Found	Calculated
				C	H	F	M	C	H	F	M		
$C_6F_5SeFe(CO)_2(\pi\text{-}C_5H_5)$	Dark red needles	77	51	37.0	1.3	22.7	13.3	36.9	1.2	22.5	13.2	387	423
$\{C_6F_5SeNi(\pi\text{-}C_5H_5)\}_n$	Black powder	>300	100									insoluble	
$C_6F_5SeNi(PPh_3)(\pi\text{-}C_5H_5)$	Red-brown crystals	137	87	55.0	3.2	15.0		55.1	3.2	15.0		648	632
$C_6F_5SeMn(CO)_5$	Orange crystals	80	51	30.1	<0.2	21.3		30.0	0.0	21.6		338	441
$C_6F_5SeRe(CO)_5$	Pale yellow crystals	105	49	23.3	<0.2	16.2		23.1	0.0	16.6		477	572

† Determined osmometrically in benzene

water to give yellow needles (24.0 g.) of bis(pentafluorophenyl) diselenide (m.p. 48°, lit. 46-48°)[4] in 98% yield.

Preparation Of π-cyclopentadienyl(pentafluorobenzeneselenolato)dicarbonyliron

Bis(pentafluorophenyl) diselenide (2.54 g. : 5.15 mmoles) and dicarbonyl-(π-cyclopentadienyl)iron dimer (2.08 g. : 5.9 mmoles) were refluxed in benzene (50 ml.) under an atmosphere of dry nitrogen for twenty-four hours. The benzene was removed by vacuum transfer and the resulting brown solid recrystallised from hexane (175 ml.) between 25° and -78° to give dark red needles (2.14 g.).

Preparation Of π-cyclopentadienyl-catenadi-μ-pentafluorobenzeneselenolatonickel

π-cyclopentadienyl nickel carbonyl dimer (1.50 g. : 5 mmoles) dissolved in benzene (40 ml.) was added to a stirred solution of bis(pentafluorophenyl) diselenide (2.5 g. : 5 mmoles) in benzene (10 ml.). The mixture was stirred at room temperature under an atmosphere of dry nitrogen for one hour. Infrared spectra of samples of the solution showed a strong peak at 2055 cm^{-1}; together with a diminishing peak at 1840 cm^{-1}

(C=O bridging). The benzene was removed by vacuum transfer to leave a black solid (3.7 g.) which was washed with hexane. Because of its insolubility in organic solvents the material was not recrystallised.

Preparation Of π-cyclopentadienyl(pentafluorobenzeneselenolato)triphenylphosphinenickel

Triphenylphosphine (1.10 g. : 4.2 mmoles) dissolved in benzene (10 ml.) was stirred with π-cyclopentadienyl-catenadi-μ-pentafluorobenzeneselenolatonickel (1.23 g. : 3.3 mmoles) for ten minutes to give a dark brown solution. The solution was filtered, but only a negligible quantity of insoluble material was retained on the filter pad. Solvent was removed by vacuum transfer. The residue, a red-brown oil, was scratched with a glass rod under hexane to give red-brown crystals (1.82 g.) which were washed with hexane.

Preparation Of Pentafluorobenzeneselenolatopentacarbonyl manganese

Using standard vacuum line techniques pentafluorobenzeneselenol (0.666 g. : 2.7 mmoles) was condensed onto decacarbonyldimanganese (0.381 g. : 1.0 mmoles) in a pyrex tube which was evacuated and sealed. There was no apparent reaction after three months at room temperature. The tube was subjected to ultra-violet radiation from a water cooled Hanovia 450 watt medium pressure mercury arc lamp at 10 cm. distance. After six hours some orange crystals were deposited on the walls of the tube. The deposit was removed by shaking manually every eight hours. Irradiation was continued for a total of twenty-four hours. The tube was opened (after cooling to -196°). Excess selenol was washed out with hexane (5 ml.). The remaining solid was dissolved in benzene. Removal of solvent by vacuum transfer gave a mass of orange crystals (0.437 g.) which were washed with a small quantity of hexane.

Preparation Of Pentafluorobenzeneselenolatopentacarbonylrhenium.

Pentafluorobenzeneselenol (1.973 g. : 8.0 mmoles) was condensed onto decacarbonyldirhenium (0.648 g. : 1.0 mmoles) in a pyrex tube which was evacuated and sealed. There was no apparent reaction after two weeks at room temperature. The tube was subjected to ultra-violet radiation from a water cooled Hanovia 450 watt medium pressure mercury arc lamp at 10 cm. distance, for forty-eight hours with manual shaking every eight hours to remove an opaque deposit on the tube walls. The tube was opened and washed with hexane (5 ml.) to remove excess selenol. The remaining solid was extracted with benzene.

Removal of solvent gave pale yellow crystals (0.559 g.) which were washed with a little hexane.

CHAPTER IV

SELENIUM(II) DERIVATIVES

Introduction

Organic selenides are the best known organoselenium compounds. The simplest of these compounds are the symmetrical selenides, the preparation of which usually involves the introduction of the two organic groups simultaneously. Thus the simplest compound in this series is bis(pentafluorophenyl) selenide. Several methods have been used to prepare this material, all of which involved bonding both pentafluorophenyl groups in a one stage synthesis. It was first prepared by the reaction between selenium and bis(pentafluorophenyl)mercury.[3] Other methods of preparation are the reactions of selenium with iodopentafluorobenzene[4] and of pentafluorophenyllithium with selenium halides.[18]

The preparation of unsymmetrical selenides is at least a two stage process involving the preparation of an organoselenium derivative which then combines with a reactive organic compound to give an unsymmetrical selenide.

$$RSeA + R'Z \rightarrow RSeR' + AZ \qquad (4.1)$$

Several promising pentafluorophenyl selenium derivatives have already been prepared in preliminary work[5] and their use will be discussed as they are encountered in this chapter. Using these derivatives it should also be possible to prepare unsymmetrical selenides containing selenium-nitrogen and selenium-oxygen bonds, of the type $C_6F_5SeNR_2$ and C_6F_5SeOR, by extending the method outlined above.

In order for reaction (4.1) to give good yields of the desired product there should be a high affinity of A for Z. This is generally so when the electronegativity difference between A and Z is large. There are two methods by which this may occur.

(i) $\chi_A < \chi_Z$ Here, as an extreme example A is an alkali metal and Z a halogen as in the well known reaction of alkali selenolates with haloacetic acids to give organoselenoacetic acids.[99]

$$\mathrm{ArSeNa + ClCH_2CO_2H \rightarrow ArSeCH_2CO_2H + NaCl} \qquad (4.2)$$

(ii) $\chi_A > \chi_Z$ In this instance A is electronegative and Z electropositive. A typical reaction of this type is the reaction of a selenenyl halide with a Grignard reagent:[100]

$$\mathrm{RSeCl + R'MgBr \rightarrow RSeR' + MgBrCl} \qquad (4.3)$$

In this type of reaction it is necessary that in selenenyl halides the bond polarity is $\overset{\delta+}{\text{RSe}}-\overset{\delta-}{\text{X}}$. In Chapter II it was found that the pentafluorophenyl group had a surprisingly large effect on the selenium atom in the species C_6F_5Se- in that it effectively increased the optical electronegativity of selenium to a value (~2.8) close to that of bromine (=2.8). Reactions of pentafluorobenzeneselenenyl bromide will, therefore, indicate the position of C_6F_5Se- relative to bromine on the electronegativity scale.

Discussion

Several unsymmetrical selenides of the type RfSeR (where Rf = CF_3, C_3F_7; R = CH_3, C_2H_5, ½CH_2) have been prepared by the reaction of mercuric perfluoroalkaneselenolates with an alkyl iodide.[101]

$$(CF_3Se)_2Hg + 2CH_3I \rightarrow 2CF_3SeCH_3 + HgI_2 \qquad (4.4)$$

This route, a type (i) reaction, is employed here to prepare alkylpentafluorophenyl selenides from mercuric pentafluorobenzeneselenolate and alkyl iodides.

$$(C_6F_5Se)_2Hg + 2RI \rightarrow 2C_6F_5SeR + HgI_2 \qquad (4.5)$$

This method gives a good yield of product and has the advantage that progress of the reaction may be followed by observing the formation of red mercuric iodide from the almost colourless reactants. While the electronegativity difference between mercury and iodine is not very large there is a high affinity of mercury towards iodine, resulting from the high lattice energy of mercuric iodide.

It is interesting to note that while methyl iodide and the mercurial react smoothly at room temperature, ethyl iodide and trifluoromethyl iodide require more vigorous conditions; refluxing and ultra-violet irradiation. This, presumably, reflects the increasing strength of the carbon-iodine bond in the alkyl iodides: $CH_3\text{-}I < C_2H_5\text{-}I < CF_3I$.

Alkali metal selenolate salts are more often used for reaction with organic halides. Sodium pentafluorobenzeneselenolate reacts with chloroacetic acid in aqueous alkali to give a good clean yield of pentafluorophenylselenoacetic acid.

$$C_6F_5SeNa + ClCH_2CO_2Na \rightarrow C_6F_5SeCH_2CO_2Na + NaCl \qquad (4.6)$$

It is necessary to warm the reactants but reaction is fast relative to that of the mercurial with the alkyl iodides.

Pentafluorobenzeneselenenyl halides have been employed in the synthesis of unsymmetrical selenides of the type C_6F_5SeR (where $R = CH_2CH_2Cl, CH_2CH_2Br, CN$).[5] With ethylene the selenenyl halides give 2-haloethyl pentafluorophenyl selenides.

$$C_6F_5SeX + CH_2{=}CH_2 \rightarrow C_6F_5SeCH_2CH_2X \qquad (4.7)$$

This type of reaction may be considered as an insertion of ethylene into the selenium-halogen bond or, more traditionally, as addition across the double bond of ethylene in analogy to halogenation of alkenes. This type of reaction has been reported in the reaction of ethylene with selenium monochloride to give the selenium analogue of mustard gas,[102]

$$Se_2Cl_2 + 2CH_2{=}CH_2 \rightarrow (ClCH_2CH_2)_2Se + Se \qquad (4.8)$$

and with trifluoromethaneselenenyl chloride.[103]

$$CF_3SeCl + CH_2{=}CH_2 \rightarrow CF_3SeCH_2CH_2Cl \qquad (4.9)$$

With silver cyanide, pentafluorobenzeneselenenyl bromide reacts to give pentafluorobenzeneselenocyanate.[5]

$$C_6F_5SeBr + AgCN \rightarrow C_6F_5SeCN + AgBr \qquad (4.10)$$

Although, strictly, this should be termed an exchange reaction since the pseudohalogenide, cyanide, is replacing bromide, it is convenient to consider this as the first example of a type (ii) reaction as it effectively concerns the formation of a second selenium-carbon bond.

It would be useful to investigate the possibility of extending this type of reaction as a route to further unsymmetrical selenides.

Grignard reagents are useful intermediates in organic chemistry. Many selenides have been prepared using these reactive intermediates with selenenyl halides.[100] Pentafluorobenzeneselenenyl chloride reacts with phenylmagnesium bromide to give a good yield of phenylpentafluorophenyl selenide.

$$C_6F_5SeCl + C_6H_5MgBr \rightarrow C_6F_5SeC_6H_5 + MgClBr \qquad (4.11)$$

Halogenation occurs when an organic compound containing an active hydrogen is exposed to the free halogen. An example of this is the reaction of acetone with bromine.

$$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr \qquad (4.12)$$

It is found that pentafluorobenzeneselenenyl chloride reacts with acetone to give 1-(pentafluorophenylseleno)propan-2-one.

$$CH_3COCH_3 + C_6F_5SeCl \rightarrow CH_3COCH_2SeC_6F_5 + HCl \qquad (4.13)$$

Trifluoromethaneselenenyl chloride behaves similarly with acetone.[103]

Perfluoroalkaneselenenyl chlorides have been shown to react with amines to form perfluoroalkaneselenenamides,[101] e.g.

$$CF_3SeCl + 2(CH_3)_2NH \rightarrow CF_3SeN(CH_3)_2 + (CH_3)_2NH_2Cl \qquad (4.14)$$

Pentafluorobenzeneselenenyl chloride and bromide react with dimethylamine and diethylamine respectively to give the corresponding selenenamides:

$$C_6F_5SeX + 2R_2NH \rightarrow C_6F_5SeNR_2 + R_2NH_2X \qquad (4.15)$$

$$(X = Cl,\ Br;\quad R = CH_3,\ C_2H_5)$$

With ammonia pentafluorobenzeneselenenyl halides give bis(pentafluorobenzeneselenen)imide:

$$2C_6F_5SeX + 2NH_3 \rightarrow (C_6F_5Se)_2NH + NH_4X \qquad (4.16)$$

This type of reaction has been observed in the reaction of trifluoromethaneselenenyl chloride[104] and pentafluorobenzenesulphenyl chloride[105] giving the analogous products $(CF_3Se)_2NH$ and $(C_6F_5S)_2NH$.

It is evident from the reactions of pentafluorobenzeneselenenyl chloride and bromide that the bond polarity is $C_6F_5\overset{+}{Se}\text{-}\overset{-}{Cl}$ and $C_6F_5\overset{+}{Se}\text{-}\overset{-}{Br}$.

While aliphatic amines give a selenium-nitrogen bond it is found that the aromatic amine, aniline, gives a selenium-carbon bond with the formation of a ring substituted aniline *p*-(pentafluorophenylseleno)-aniline:

$$C_6F_5SeCl + 2C_6H_5NH_2 \rightarrow p\text{-}(C_6F_5Se)C_6H_4NH_2 + C_6H_5NH_3Cl \qquad (4.17)$$

Trifluoromethaneselenenyl chloride gives an analogous product, p-$(CF_3Se)C_6H_4NH_2$, with aniline[106] but trifluoromethanesulphenyl chloride reacts with aniline to give *N*-(trifluoromethylthio)aniline, $C_6H_5NHSCF_3$, a stable N-S bonded compound.[107] It has been postulated that there is initial formation of a selenium-nitrogen bond giving *N*-(trifluoromethylseleno)aniline, but as a result of the lower stability of the N-Se bond (as compared with N-S) this is converted to *p*-(trifluoromethylseleno)aniline by electrophilic aromatic rearrangement.[106] *N*,*N*-dimethylaniline also reacts with trifluoromethaneselenenyl chloride [106] and trifluoromethanesulphenyl chloride[108] to give the para substituted *N*,*N*-dimethylanilines.

N-Chloroanilines have been postulated as intermediates in the chlorination of anilines[109] and indeed *N*-chloroanilines have recently been isolated[110] and shown to undergo thermal rearrangement to *o*- and *p*-chloroanilines.

Even *N,N*-dialkylanilines are thought to be chlorinated via an intermediate N-Cl species.[111] Bromination is thought to proceed by a similar mechanism[111] but no *N*-bromoanilines have been reported in the literature.

It must be pointed out at this stage that *N,N*-diphenyl pentafluorobenzenesulphenamide, $C_6F_5SN(C_6H_5)_2$, has been reported as the product of the reaction of diphenylamine and pentafluorobenzenesulphenyl chloride.[61] However, the infrared spectrum of this compound exhibits a strong peak at 3400 cm^{-1}, in the N-H stretching region.[112] This suggests that the reported structure is erroneous and that ring substitution occurs giving $(C_6F_5S)C_6H_4NHC_6H_5$, substitution probably being in the para position.

Another route to sulphenamides is the reaction of disulphides with silver nitrate and an amine, which is reported to give better yields than the reaction of sulphenyl chlorides with amines.[113] This reaction, using bis(pentafluorophenyl) diselenide, silver nitrate and aniline, gives the same product, *p*-(pentafluorophenylseleno)aniline.

$$\begin{aligned} AgNO_3 + (C_6F_5)_2Se_2 + 2C_6H_5NH_2 \rightarrow {} & C_6F_5SeAg + C_6H_5NH_3NO_3 \\ & + p\text{-}(C_6F_5Se)C_6H_4NH_2 \end{aligned} \qquad (4.18)$$

Since two dissimilar routes, which "should" lead to the formation of a Se-N bond, give the same para substituted aniline, it is reasonable to accept the idea that there is initial formation of a Se-N bond which rearranges to give a Se-C bond.

Similarly, reaction of pentafluorobenzeneselenenyl bromide with sodium phenoxide leads to substitution of the phenyl ring. However, in this instance the similarity stops here. Trisubstitution of the ring occurs giving 2,4,6-tris(pentafluorophenylseleno)phenol.

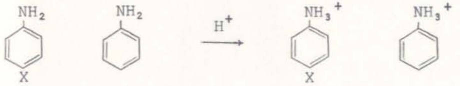
$$3C_6F_5SeBr + 3C_6H_5ONa \rightarrow 3NaBr + 2,4,6\text{-}(C_6F_5Se)_3C_6H_2OH + 2C_6H_5OH \tag{4.19}$$

Consider the first step in this process:

$$C_6F_5SeCl + C_6H_5O^- \rightarrow p\text{-}C_6F_5SeC_6H_4OH + Cl^- \tag{4.20}$$

Since C_6F_5Se- in the para position is electron withdrawing and delocalising this initial product is more easily ionized than phenol and is thus more amenable to electrophilic attack; that is monosubstitution activates further substitution in the ortho position. Further, disubstitution activates the phenol to further attack at the last ortho position. These observations are in line with those of halogenation.[114] However, by comparison with halogenation of aniline it would appear that trisubstitution of aniline should also occur.

The reasoning is similar to that of phenol. Monosubstitution of aniline gives a less basic amine, therefore, of the two species now present:



(4.21)

the nonsubstituted anilinium cation is favoured. The substituted aniline exists almost completely as the neutral compound and is more susceptible to electrophilic attack than the unsubstituted aniline, which has a greater concentration of the cation form. Similarly, disubstitution activates trisubstitution. Since with phenols it is the phenoxide anion that is attacked electrophilically, reaction is expected to be faster than attack on the neutral aniline molecule. Perhaps this driving force gives rise to a relatively more stable Se-N species than Se-O species so that during the addition time the Se-N species is present in a large concentration, whereas the Se-O species decays rapidly, affording further activated substitution. It is possible that some trisubstituted aniline occurs in small quantities.

This is not to say that all Se^{II}-O bonded compounds are unstable. Reaction of pentafluorobenzeneselenenyl chloride with sodium methoxide gives rise to methyl pentafluorobenzeneselenenate.

$$C_6F_5SeCl + NaOCH_3 \rightarrow NaCl + C_6F_5SeOCH_3 \qquad (4.22)$$

The infrared spectrum gives one band in the Se-O stretching region consistent with a single selenium-oxygen single bond. This derivative is the methyl ester of pentafluorobenzene selenenic acid. Few selenenic acids are known since controlled hydrolysis of selenenyl halides results in disproportionation to give the seleninic acid and the diselenide.

$$3RSeX + 2H_2O \rightarrow RSeO_2H + R_2Se_2 + 3HX \qquad (4.23)$$

The only selenenic acids known are those aromatic selenenic acids in which the electronegativity of the aryl group is low, e.g. *o*-nitrophenyl selenenic acid.[21] Therefore, the existence of pentafluorobenzene selenenic acid is not expected. It appears that while the divalent selenium-oxygen bond is stable in pentafluorophenyl selenium compounds, as demonstrated by the formation of $C_6F_5SeOCH_3$, other, more stable compounds are produced whenever there is a suitable alternative. In this investigation the alternatives have been the preferred formation of the selenium-carbon bond ($2,4,6\text{-}(C_6F_5Se)_3C_6H_2OH$) or disproportionation ($C_6F_5SeO_2H + (C_6F_5)_2Se_2$).

There seems to be no trouble in the preparation of pentafluorophenyl selenium(II) compounds containing the $(C_6F_5)Se{-}C$ bond and indeed the selenium-carbon bond is formed where it is naively expected that selenium-nitrogen or selenium-oxygen bonds should be formed. Amines react readily with pentafluorobenzeneselenenyl halides and simple tests show that even tertiary amines, triethylamine and pyridine, react with the selenenyl halides. The consequences of this are that reactions of the type:

$$C_6F_5SeX + HY \xrightarrow{\text{amine}} C_6F_5SeY + \text{amine}\ \overset{+}{H}\overset{-}{X} \qquad (4.24)$$

cannot be carried out since unwanted byproducts from the reaction of the selenenyl halides and amines will result, to the detriment of the desired product, C_6F_5SeY. This is unfortunate since reaction (4.24) is a potentially useful route to pentafluorophenyl selenium derivatives of, say, the main group elements. Using reaction (4.24) without the amine may be useful in some cases but the hydrogen halide formed may cause decomposition of products or reactants. Absorbing the hydrogen halide into water has been used in the reaction of pentafluorobenzeneselenenyl chloride with acetone but this technique is only valid if the products are stable to hydrolysis.

The products obtained from the above reactions are generally as expected by comparison with organoselenium chemistry and to a large extent with organosulphur chemistry. The reactions of the pentafluorobenzeneselenenyl halides are very similar to those of the halogens, bearing in mind the polarity $C_6F_5\overset{\delta+}{Se}-\overset{\delta-}{X}$ where X is chlorine or bromine, whereas in reactions of the free halogens X_2 polarity is induced.

While the optical electronegativity of the group C_6F_5Se- has been shown (Chapter II) to be close to that of bromine, the reactions of pentafluorobenzeneselenenyl bromide more precisely place the electronegativity of C_6F_5Se- lower than that of bromine.

Infrared spectra (Appendix A), ^1H n.m.r. spectra (Appendix C) and elemental analyses (Table 4.1) are consistent with the structures of the new compounds encountered in the above discussion.

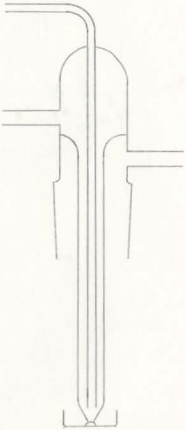
Experimental

Most of the compounds containing alkyl groups were involatile liquids. Although several different methods were employed in their preparation these compounds required purification by vacuum distillation above room temperature. The apparatus chosen for this purpose consisted of a cold finger with a bucket attachment, which

Products and Analyses

Compound	Appearance	M.P. (B.P.) °C	Yield %	Elemental Analysis					
				Found			Calculated		
				C	H	F	C	H	F
$C_6F_5SeCH_3$	Colourless liquid	(184)	91	32.1	1.2	36.6	32.2	1.2	36.4
$C_6F_5SeC_2H_5$	Pale amber liquid	(193)	63	35.1	1.9	34.4	34.9	1.8	34.5
$C_6F_5SeCF_3$	Colourless liquid	(152)	77	26.7	<0.1	47.9	26.7	0.0	48.3
$C_6F_5SeCH_2COCH_3$	Colourless liquid	15	84	35.6	1.7	31.5	35.7	1.7	31.2
$C_6F_5SeC_6H_5$	White crystals	35	65	44.5	1.6	29.6	44.6	1.6	29.4
$C_6F_5SeCH_2CO_2H$	White crystals	55	85	31.7	1.1	30.8	31.5	1.0	31.2
$C_6F_5SeN(C_2H_5)_2$	Yellow liquid	(219)	77	37.8	3.2	30.1	37.6	3.2	29.8
$C_6F_5SeN(CH_3)_2$	Yellow liquid	(197)	83	33.3	2.1	32.4	33.1	2.1	32.8
$(C_6F_5Se)_2NH$	Yellow crystals	112	55	28.5	0.2	2.7 (N)	28.4	0.2	2.8 (N
p-$(C_6F_5Se)C_6H_4NH_2$	Pale yellow needles	91	58	42.7	1.9	28.5	42.6	1.8	28.1
2,4,6-$(C_6F_5Se)_3C_6H_2OH$	White crystals	125	54	34.8	0.4	34.3	34.7	0.4	34.2
$C_6F_5SeOCH_3$	Amber liquid		48	30.4	0.9	34.7	30.4	1.1	34.3

could be inserted into a flask containing a B24 ground glass socket. The apparatus was made up as described by Maruca.[115]



Vacuum
Microdistillation
Apparatus

Preparation Of Methyl Pentafluorophenyl Selenide

Mercury(II) pentafluorobenzeneselenolate[5] (1.61 g.) was stirred with methyl iodide (3 ml. - sufficient to dissolve mercurial) at room temperature. After twelve hours red crystals (mercuric iodide) appeared but stirring was continued for a total of four days after which time the solution was filtered into a flask. Volatile methyl iodide was removed by heating on a steam bath. The residue was vacuum microdistilled at 60° to give a colourless liquid (1.10 g.).

Preparation Of Ethyl Pentafluorophenyl Selenide

Mercury(II) pentafluorobenzeneselenolate (2.02 g.) was stirred with ethyl iodide (6 ml.) at room temperature for forty-eight hours. No red crystals appeared. The mixture was then refluxed for twenty-four hours and the resulting red crystals filtered off. Excess ethyl iodide was removed by heating the solution on a steam bath. The resulting dark amber liquid was vacuum microdistilled at 60° to give a pale amber liquid (1.00 g.).

Preparation Of Pentafluorophenyl Trifluoromethyl Selenide

Mercury(II) pentafluorobenzeneselenolate (2.13 g.) and trifluoromethyl iodide (5.16 g.), which was condensed from the vacuum line, were sealed in a pyrex tube.

There was no noticeable reaction after one week at room temperature. Rather than heat the tube, which might not withstand the increased pressure of trifluoromethyl iodide vapour, the tube was subjected to ultra-violet radiation from a water cooled Hanovia 450 watt medium pressure mercury arc lamp at 10 cm. distance. The tube was shaken every eight hours to remove an opaque deposit of red crystals on the walls of the tube. After four days reaction appeared to be complete. The tube was opened to the vacuum line and the colourless liquid product (1.49 g.) collected in a trap at -78°.

The Pentafluorobenzeneselenenyl Halides

Since the selenenyl halides are viscous involatile liquids, no method has been developed for their purification. For this reason, in order to obtain a good product, it is necessary to react a stoichiometric quantity of the halogen with a stoichiometric quantity of bis(pentafluorophenyl) diselenide. Their preparations have previously been described.[5]

Preparation Of Pentafluorobenzeneselenenyl Bromide

Using a vacuum line, bromine was condensed into a weighed tap-ampoule and reweighed. In this way bromine (2.996 g.) was weighed out.

This was condensed onto the diselenide (9.220 g.) in a flask connected to the vacuum line and cooled to -78°. The reactants were allowed to warm to room temperature. The bromine melted and reacted with some splashing to give a dark brown liquid (12.214 g.) close to the expected weight (12.216 g.) for pentafluorobenzeneselenenyl bromide. There were no bromine vapours in the vacuum above the product.

Preparation Of Pentafluorobenzeneselenenyl Chloride

Chloride was dried by admitting it to the vacuum line, pumping from a trap at -78° and collecting it in a trap at -196°. The chlorine was then condensed into a weighed Carius tube which was sealed and reweighed. By this method chlorine (0.951 g.) was weighed out and condensed onto the diselenide (6.620 g.) in a flask at -196°. The reactants were allowed to warm to room temperature. On melting the chlorine reacted with the diselenide with some splattering, resulting in an unavoidable small loss of product to connecting tube walls, to give a red-brown liquid (7.533 g.) in 99.4% yield for pentafluorobenzeneselenenyl chloride.

Preparation Of Acetonyl Pentafluorophenyl Selenide

A large excess of acetone (5 ml.) was added to a flask containing pentafluorobenzeneselenenyl chloride (2.0 g.).

After stirring for one minute, the dark red-brown colour of the selenenyl chloride had faded to pale yellow. Water (15 ml.) was added and the mixture shaken. This settled into two layers. The heavy pale yellow liquid was drawn off by pipet and vacuum microdistilled at 80°. The product condensed on the cold finger as a white crystalline solid, but passing warm water through the finger caused it to melt. Thus it was possible to collect the product (1.8 g.) which is a colourless liquid at room temperature.

Preparation Of Phenyl Pentafluorophenyl Selenide

The Grignard reagent, phenylmagnesium bromide, was prepared in the usual way[116] from bromobenzene (6.3 g. : 40 mmoles) and magnesium (1.0 g. : 40 mmoles) in ether (40 ml.). The solution was slowly syphoned under nitrogen onto a solution of pentafluorobenzeneselenenyl chloride (7.4 g. : 26 mmoles) in ether (20 ml.) cooled to 0°. After the vigorous reaction the solution was filtered and washed with dilute hydrochloric acid (30 ml.) followed by water (2 x 15 ml.). The ether solution was dried over anhydrous magnesium sulphate and filtered. Ether was removed by vacuum transfer to leave a pale yellow oil. The oil was dissolved in methanol at room temperature. On cooling this solution to -78° a mass of white crystals (5.5 g.) separated out and were filtered off.

Preparation Of Pentafluorophenylselenoacetic Acid

Chloroacetic acid (1.0 g. : 10.6 mmoles) was dissolved in water and neutralised (litmus) with dilute sodium hydroxide solution. This was added to 1 M. sodium pentafluorophenylselenolate solution (for preparation see p.55) (10.0 ml.). The solution was heated to boiling. Dilute sulphuric acid was added to the cooled solution until no more colourless oil separated out. The mixture, now of 30 ml. volume, was extracted with ether (30 ml.). The ether layer was washed with water (2 x 15 ml.). The solvent was removed by vacuum transfer to give a white crystalline product (2.6 g.).

Preparation Of N,N-Diethylpentafluorobenzeneselenenamide

Pentafluorobenzeneselenenyl bromide (2.0 g.) dissolved in ether (10 ml.) was added dropwise with stirring to excess diethylamine (2 ml.) cooled to 0°. The brown colour of the selenenyl bromide faded immediately on contact with the amine. The resulting white suspension was filtered to give a pale yellow solution.

Solvent was removed by vacuum transfer to give a yellow oil which was vacuum microdistilled at 60° giving a pale yellow liquid (1.5 g.).

Preparation Of N,N-Dimethyl Pentafluorobenzeneselenenamide

Pentafluorobenzeneselenenyl chloride (2.0 g.) dissolved in ether (15 ml.) was added dropwise with stirring to an excess of dimethylamine (3 ml.) condensed in a vacuum at -78°. Reaction was vigorous. The resulting suspension was filtered to give a pale yellow solution. Solvent was removed by vacuum transfer and the oil vacuum microdistilled at 80° to give a pale yellow liquid (1.7 g.).

Preparation Of Bispentafluorobenzeneselenenimide

Ammonia gas was bubbled through a solution of pentafluorobenzeneselenenyl bromide (4.8 g.) in hexane (10 ml.) until the brown colour had faded to yellow. The suspension was filtered and the clear solution cooled to -78°. The resulting yellow crystals (2.1 g., 56% yield) were filtered off.

A similar reaction using pentafluorobenzeneselenenyl chloride gave the same product in 32% yield.

Preparation Of p-Pentafluorophenylselenoaniline

Pentafluorobenzeneselenenyl chloride (1.41 g. : 5 mmoles) in ether (10 ml.) was added dropwise with stirring to a solution of aniline (0.93 g. : 10 mmoles) in ether (10 ml.). The suspension was filtered and solvent removed from the filtrate by vacuum transfer. An infrared spectrum of the resulting crude pale yellow solid exhibited two peaks in the N-H stretching region at 3465 cm^{-1} and 3355 cm^{-1}. The material was purified by recrystallisation from aqueous methanol, discarding the oil which separated out on cooling, to give off-white needles (0.57 g.) in 34% yield.

Bis(pentafluorophenyl) diselenide (2.0 g. : 4 mmoles), silver nitrate (0.7 g. : 4 mmoles) and aniline (0.75 g. : 8 mmoles) were stirred together in methanol (50 ml.) in the dark for fifteen hours. The mixture was filtered and solvent removed from the filtrate to give a brown residue. Two peaks were observed in the N-H stretching region at 3465 cm^{-1} and 3355 cm^{-1} in the infrared spectrum. The residue was dissolved in ether (30 ml.) and washed with water (2 x 10 ml.). Ether was removed by vacuum transfer to give a yellow brown solid which was recrystallised twice from aqueous methanol to give pale yellow needles (0.80 g.) in 58% yield.

Reactions Of Pentafluorobenzeneselenenyl Halides With Other Amines

In a simple test the brown colour of pentafluorobenzeneselenenyl bromide faded on addition of pyridine.

Similarly the red-brown colour of pentafluorobenzeneselenenyl chloride faded on addition of triethylamine.

Preparation Of 2,4,6-Tris(pentafluorophenylseleno)phenol

Pentafluorobenzeneselenenyl bromide (3.3 g. : 10 mmoles) in ether (20 ml.) was added dropwise with stirring to a suspension of sodium phenoxide (1.2 g.) in ether (10 ml.) cooled to 0°. The brown colour of the selenenyl bromide faded immediately. The suspension was filtered and solvent removed by vacuum transfer to give an off-white crystalline solid. The infrared spectrum of this material showed one peak at 3380 cm^{-1} in the O-H stretching region. Recrystallisation from aqueous ethanol between 50° and 10° gave a mass of white needles (1.5 g.) which were dried in a vacuum desiccator.

Preparation Of Methyl Pentafluorobenzeneselenenate

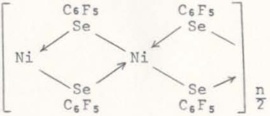
1 Molar sodium methoxide solution (5.0 ml. : 5.0 mmoles) was added dropwise, with stirring to a solution of pentafluorobenzeneselenenyl chloride (1.4 g. : 5 mmoles) in carbon tetrachloride (10 ml.). The suspension was filtered to give a pale yellow filtrate. Solvent was removed by vacuum transfer and the resulting liquid vacuum microdistilled at 60° to give an amber liquid (0.7 g.).

CHAPTER V

Selenium Derivatives Of Higher Valency

Introduction

In this chapter the influence of the pentafluorophenyl group on the ability of selenium to expand its valency will be considered. Valency may refer to the coordination number of an atom or ion or to the oxidation state of an atom or ion. So far in this work the pentafluorophenyl derivatives of selenium encountered have been derivatives of divalent selenium in one sense of valency or the other. Most compounds have been of the type RR'Se where selenium is two coordinate and generally in the oxidation state of +2 although bis(pentafluorophenyl) diselenide, $C_6F_5SeSeC_6F_5$, and pentafluorobenzeneselenol derivatives of metals, C_6F_5SeM, have respectively selenium in the formal oxidation states of +1 and 0. A few compounds contain three coordinate selenium in the +2 oxidation state, e.g.



Preliminary studies[5] indicate that the influence of pentafluorophenyl groups bonded to selenium is to restrict valency expansion of selenium both by coordination expansion and by oxidation, relative to hydrocarbon derivatives of selenium. It will be interesting to further investigate this field to extend the range of higher valent pentafluorophenyl selenium derivatives in an attempt to find their limits in relation to other organoselenium compounds.

Discussion

Organic derivatives of selenium in the oxidation state of +2 are known to possess lone pair electrons by which the coordination number of selenium may be increased. Thus diethyl selenide forms an adduct with mercuric chloride, $(C_2H_5)_2Se{\rightarrow}HgCl_2$, and forms a selenonium salt $[CH_3(C_2H_5)_2Se]I$ with methyl iodide.[26] However, dimethylphenylselenonium iodide is only formed in very low yield from methyl phenyl selenide and methyl iodide.[117] The reason for this is that since aryl groups are more delocalising than alkyl groups the selenium lone pair electrons are more delocalised, and therefore, less available for bonding in aryl selenides. Bis(trifluoromethyl) selenide with two highly electron delocalising CF_3- groups bonded to selenium exhibits no basic properties, forming no adduct with mercuric chloride, nor a selenonium salt with methyl iodide.[1]

The electronegativity of the pentafluorophenyl group depends on its environment, but is generally intermediate between iodine and bromine (see Table 1.2) while that of the trifluoromethyl group is about the same as chlorine.[118] It has recently been shown that the pentafluorophenyl group inductively withdraws electrons more strongly than a phenyl group, but much less strongly than the trifluoromethyl group, so that the relative inductive effects are $CF_3>C_6F_5>C_6H_5$.[41] However, it has been observed that bis(pentafluorophenyl) selenide, like its trifluoromethyl analogue, exhibits no basic properties, forming no adduct with mercuric chloride nor a selenonium salt with methyl iodide.[5]

It is to be expected that selenides containing one hydrocarbon group and one perfluorocarbon group should have properties intermediate between those of hydrocarbon selenides and perfluorocarbon selenides. Neither methyl pentafluorophenyl selenide nor phenyl pentafluorophenyl selenide forms adducts with mercuric chloride or selenonium salts with methyl iodide using standard methods that give these types of derivatives with diethyl selenide.[26] The preparations of methyl trifluoromethyl selenide[101] and phenyl trifluoromethyl selenide[119] have been reported. It would be interesting to investigate the basic properties of the unsymmetrical trifluoromethyl selenides in a similar way.

It has been demonstrated that the influence of two pentafluorophenyl groups manifests itself in another way to again reduce the valency of selenium in the sense that raising the oxidation state from +2 to +4 is restricted. Whereas dialkyl[26] and diaryl[120] selenides are readily oxidised by chlorine or bromine to diorganyl selenium dihalides, e.g.

$$(C_6H_5)_2Se + Cl_2 \rightarrow (C_6H_5)_2SeCl_2 \qquad (5.1)$$

it is found that bis(trifluoromethyl) selenide[1] and bis(pentafluorophenyl) selenide[5] resist oxidation even by elemental chlorine. The reaction between organic selenides and silver difluoride has recently been shown to give diorganoselenium difluorides[23] e.g.

$$(C_6H_5)_2Se + 2AgF_2 \rightarrow (C_6H_5)_2SeF_2 + 2AgF \qquad (5.2)$$

However, there is no reaction between $(C_6F_5)_2Se$ and silver difluoride. Similarly no selenoxide resulted from ozonolysis of bis(pentafluorophenyl) selenide. Bis(pentafluorophenyl) sulphide is oxidised by hydrogen peroxide to the corresponding sulphone:[121]

$$(C_6F_5)_2S + H_2O_2 \rightarrow (C_6F_5)_2SO_2 \qquad (5.3)$$

Again, the properties of mixed fluorocarbon hydrocarbon selenides should be of an intermediate nature. The only reported reactions of this type are the chlorination of aryl trifluoromethyl selenides to give aryl trifluoromethylselenium dichlorides[119]

$$ArSeCF_3 + Cl_2 \rightarrow ArSeCl_2CF_3 \qquad (5.4)$$

and the reaction of methyl trifluoromethyl selenide with chlorine to give a white unstable solid, presumably $CF_3SeCl_2CH_3$ which rapidly decomposes to give

$$CH_3SeCF_3 + Cl_2 \rightarrow CH_3SeCl_2CF_3 \qquad (5.5)$$

trifluoromethane selenenyl chloride and methyl chloride.[122]

$$CH_3SeCl_2CF_3 \rightarrow CF_3SeCl + CH_3Cl \qquad (5.6)$$

Unsymmetrical pentafluorophenyl selenides behave similarly. Phenyl pentafluorophenyl selenide and methyl pentafluorophenyl selenide are oxidised by chlorine in non polar solvents to give phenyl or methyl pentafluorophenyl selenium dichloride.

$$RSeC_6F_5 + Cl_2 \rightarrow RSeCl_2C_6F_5 \qquad (5.7)$$

Neither of these compounds is particularly stable; $C_6H_5SeCl_2C_6F_5$ appears to lose chlorine (reverse of reaction 5.7), while $CH_3SeCl_2C_6F_5$ decomposes in a more complex fashion giving a red liquid. This is in line with the decomposition of diorganoselenium dihalides containing alkyl groups, e.g.

$$C_6H_5SeBr_2CH_2C_6H_5 \rightarrow C_6H_5SeBr + CH_2BrC_6H_5 \qquad (5.8)$$

where the red or brown selenenyl halide is formed, together with the alkyl halide.[123]

The diorganoselenium dichlorides are readily hydrolysed by water. Phenyl pentafluorophenyl selenium dichloride gives the expected product phenyl pentafluorophenyl selenoxide.

$$C_6H_5SeCl_2C_6F_5 + H_2O \rightarrow C_6H_5Se(O)C_6F_5 + 2HCl \qquad (5.9)$$

Hydrobromic acid is oxidised to bromine by this selenoxide indicating that although diorganoselenium dibromides are known[26] the presence of one perfluoroaryl group still restricts oxidation of the selenium atom by bromine. Unexpectedly there is no reaction between pentafluorophenyl phenyl selenide or methyl pentafluorophenyl selenide and hydrogen peroxide. Alkyl and aryl selenides are generally oxidised to selenoxides by hydrogen peroxide.[124]

$$R_2Se + H_2O_2 \rightarrow R_2Se{=}O + H_2O \qquad (5.10)$$

Methyl pentafluorophenylselenium dichloride, however, hydrolyses in a different manner giving, as one of the products, pentafluorobenzeneseleninic acid, indicating that cleavage of the Se-CH_3 bond takes place.

When only one organic group is attached to selenium a large range of organoselenium derivatives are known with selenium in a higher valency. Included in this class are organoselenium tribromides and trichlorides, together with seleninic acids and even derivatives of six valent selenium, the selenonic acids. It has been shown that when one perfluoroalkyl group is attached to selenium the range is more limited. Thus, while trifluoromethylselenium trichloride may be prepared, no tribromide exists[1] whereas alkyl selenium tribromides[123] and aryl selenium tribromides[125] are readily formed from the reaction of excess bromine on the corresponding selenenyl bromide. Trifluoromethaneseleninic acid is formed even by reactions that are expected to give selenonic acids.[1] Preliminary studies indicate that the same situation occurs with pentafluorophenyl selenium derivatives; the only four valent selenium derivatives so far prepared are $C_6F_5SeCl_3$ and $C_6F_5SeO_2H$.[5]

It would be useful, therefore, to extend the range of four valent pentafluorophenyl selenium derivatives in an attempt to find their limits in relation to other organoselenium(IV) compounds.

An attempt to prepare the anhydride of pentafluorobenzeneseleninic acid by dehydration of the acid with anhydrous phosphorus pentoxide led to the formation of bis(pentafluorophenyl) selenide and probably an oxide of selenium.

$$2C_6F_5SeO_2H \xrightarrow{P_2O_5} H_2O + (C_6F_5)_2Se + SeO_3 \text{ (or } SeO_2 + \tfrac{1}{2}O_2) \qquad (5.11)$$

It is, however, possible to prepare the anhydride by oxidation of bis(pentafluorophenyl) diselenide with ozone with the rigorous exclusion of atmospheric moisture.

$$(C_6F_5)_2Se_2 + 3O_2 \rightarrow (C_6F_5SeO)_2O \qquad (5.12)$$

Similarly, it is found that pentafluorobenzeneselenenyl chloride is oxidised by ozone to pentafluorophenyl selenoxychloride.

$$C_6F_5SeCl + O_3 \rightarrow C_6F_5Se(O)Cl \qquad (5.13)$$

It is reported that the trifluoromethyl selenium analogues, $(CF_3SeO)_2O$ and $CF_3Se(O)Cl$, are prepared in a similar way.[126]

It is known that diaryl disulphides are oxidised by silver difluoride to give arylsulphur tri-[127] and pentafluorides.[128]

$$\begin{tikzcd} Ph_2S_2 + AgF_2 \arrow[r] \arrow[rr, bend right] & PhSF_3 \arrow[r, "AgF_2"] & PhSF_5 \end{tikzcd} \qquad (5.14)$$

However, the reaction of bis(pentafluorophenyl) diselenide with silver difluoride in Freon solvent gives bis(pentafluorophenyl) selenide. No other Freon soluble materials could be isolated. The production of bis(pentafluorophenyl) selenide suggests that this reaction may be analogous to the attempted dehydration of pentafluorobenzeneseleninic acid by warming with phosphorus pentoxide. Perhaps initially formed pentafluorophenylselenium trifluoride disproportionates or decomposes giving the monoselenide. Under milder conditions, in Freon 113 at room temperature, there is no reaction between bis(pentafluorophenyl) diselenide and silver difluoride. It has been reported, however, that bis(pentafluorophenyl) disulphide reacts with silver difluoride to give pentafluorophenyl sulphur trifluoride.[17]

$$(C_6F_5)_2S_2 + 6AgF_2 \rightarrow 2C_6F_5SF_3 + 6AgF \qquad (5.15)$$

Pentafluorobenzeneseleninic acid has been prepared by the oxidation of bis(pentafluorophenyl) diselenide with nitric acid or hydrogen peroxide, and by the hydrolysis of pentafluorophenylselenium trichloride.[5] Careful neutralisation of this acid with sodium hydroxide results in the formation of the sodium salt, which is characterised by its quantitative conversion to the insoluble silver salt. However, an excess of alkali causes decomposition to give pentafluorobenzene, evidently resulting from cleavage of the C-Se bond.

Pentafluorobenzeneseleninic acid is only sparingly soluble in cold water but dissolves readily in hydrochloric acid. This increased solubility leads to the belief that some complex formation takes place. A solution of selenium dioxide in hydrochloric acid contains hexachloroselenium(IV) anions.[129] Hexachloroselenium(IV) salts may be isolated from this solution using suitable cations,[130] but attempts to isolate such a complex (perhaps $[C_6F_5SeCl_5]^{2-}$) using a variety of cations do not result in precipitate formation. Pentafluorobenzeneseleninic acid oxidises hydrobromic acid resulting in the formation of a heavy red-brown liquid, a mixture of pentafluorobenzeneselenenyl bromide and bromine.

$$C_6F_5SeO_2H + 3HBr \rightarrow C_6F_5SeBr + Br_2 + 2H_2O \qquad (5.16)$$

Under similar conditions benzeneseleninic acid gives phenylselenium tribromide, a red solid.[125]

It is known that seleninic acids are oxidised to selenonic acids by permanganate.[26] Potassium permanganate solution is decolourised by a neutral solution of pentafluorobenzeneseleninic acid. Acidification of this solution results in the formation of a deliquescent material, insoluble in organic solvents and exhibiting no C_6F_5 vibrations in its infrared spectrum. Its properties indicate that it is hydrated selenic acid $H_2SeO_4.4H_2O$. Again cleavage of the C-Se bond occurs. There is no reaction when ozone is passed through an acidified aqueous suspension of pentafluorobenzeneseleninic acid or through a neutral solution of sodium pentafluorobenzeneseleninate. A six valent sulphur acid chloride, pentafluorophenyl sulphonyl chloride is known. It is prepared by the action of chlorine, in the presence of hydrogen peroxide on pentafluorobenzenethiol:[131]

$$C_6F_5SH + Cl_2 \xrightarrow{H_2O_2} C_6F_5SO_2Cl \qquad (5.17)$$

Relative to hydrocarbon derivatives of selenium, valency expansion of selenium is restricted by the presence of one pentafluorophenyl group and is non-existent in the presence of two pentafluorophenyl groups. Perfluoroalkyl groups have a similar influence on selenium.

Se-C bond cleavage occurs frequently in the presence of oxidising agents and when selenium is in higher (greater than +2) oxidation states.

Pentafluorophenyl derivatives of sulphur in higher oxidation states are more easily attained.

Experimental

Reactions Of Pentafluorophenyl Phenyl Selenide

(a) With Mercuric Chloride Pentafluorophenyl phenyl selenide (0.646 g. : 2 mmoles) dissolved in benzene (5 ml.) was added to a solution of mercuric chloride (0.544 g. : 2 mmoles) in hot benzene (50 ml.). There was no precipitate from the hot solution although crystals (probably mercuric chloride) appeared on cooling to room temperature. Solvent was removed by vacuum transfer leaving a white solid. Petroleum ether was added and the resulting solution decanted from the insoluble mercuric chloride (0.537 g) (no C_6F_5 peaks in

TABLE 5.1

Products and Analyses

Compound	Appearance	M.P.	Yield %	Analysis					
				Found %			Calculated %		
$C_6F_5SeCl_2C_6H_5$	White crystals	81	84		18.3 (Cl)			18.0 (Cl)	
$C_6F_5SeCl_2CH_3$	White crystals	81	92		20.9 (Cl)			21.4 (Cl)	
$G_6F_5Se(O)C_6H_5$	White crystals	127	48	42.6 (C)	1.6 (H)	28.3 (F)	42.5 (C)	1.5 (H)	28.0 (F)
$(C_6F_5SeO)_2O$	White crystals	45	91	26.7 (C)	<0.2 (H)		26.7 (C)	0.0 (H)	
$C_6F_5Se(O)Cl$	White crystals	61	89		11.8 (Cl)			11.9 (Cl)	
$C_6F_5SeO_2Na$	White crystals	>300	60	Almost quantitative conversion of $C_6F_5SeO_2Na$ into $C_6F_5SeO_2Ag$ on semi-micro scale					
$C_6F_5SeO_2Ag$	White powder	>300	94						

the infrared spectrum). Removal of petroleum ether from the solution left white crystals (0.520 g.) identified (infrared spectrum and m.p. 35°) as unchanged pentafluorophenyl phenyl selenide.

(b) With Methyl Iodide Pentafluorophenyl phenyl selenide (0.95 g.) was dissolved in methyl iodide (2 ml.) and left overnight at room temperature. Removal of solvent by vacuum transfer left an off-white solid (0.94 g.) identified (infrared spectrum and m.p. 35°) as pentafluorophenyl phenyl selenide.

Reactions Of Methyl Pentafluorophenyl Selenide

(a) With Mercuric Chloride Methyl pentafluorophenyl selenide (0.5 g.) was added to a solution of mercuric chloride (0.5 g.) in ethanol (50 ml.). The solution was boiled for five minutes and allowed to cool. No solid separated out on cooling to room temperature. Solvent was removed by vacuum transfer to leave a mixture of white crystals (infrared spectrum showed no C_6F_5 peaks) and colourless liquid identified as unchanged methyl pentafluorophenyl selenide (infrared spectrum).

(b) With Methyl Iodide Methyl pentafluorophenyl selenide (1.0 g.) was dissolved in methyl iodide (2 ml.) and left overnight at room temperature. Removal

of volatiles by vacuum transfer left a colourless liquid (1.0 g.) identified (infrared spectrum) as unchanged methyl pentafluorophenyl selenide.

Reactions Of Bis(pentafluorophenyl) Selenide

The preparation of bis(pentafluorophenyl) selenide has previously been described.[5]

(a) With Silver Difluoride A solution of bis(pentafluorophenyl) selenide (2.8 g.) in freon 113 (CCl_2FCClF_2) (20 ml.) was added to a suspension of silver difluoride (2.5 g.) in Freon 113 (10 ml.) in a three neck flask (100 ml.) set up for reflux, passage of dry nitrogen and stirring. Stirring pulverised the coarse silver difluoride to a fine suspension. The mixture was refluxed for twenty-four hours, then filtered hot. No crystallization occurred until most of the solvent was removed. The resulting white solid (2.6 g.) was identified (infrared spectrum and m.p. 74°, lit. 71-72°)[3] as unchanged bis(pentafluorophenyl) selenide.

(b) With Ozone Bis(pentafluorophenyl) selenide (1.1 g.) dissolved in ethanol (25 ml.) was acidified with syrupy phosphoric acid (2 ml.). Ozone (produced from oxygen, dried at -78°, in a Welsbach Laboratory Ozonator, Model T-816) was bubbled through this solution cooled to 0° for one hour. The solution was reduced in volume,

water added and the resulting colourless crystals (1.0 g.) filtered off. The product was identified (infrared spectrum and m.p. 74°, lit. 71-72°)[3] as unchanged bis(pentafluorophenyl) selenide.

Preparation Of Phenylpentafluorophenylselenium Dichloride

Chlorine gas was bubbled through a solution of phenyl pentafluorophenyl selenide (1.0 g.) in hexane (10 ml.) cooled to 0°. When no more solid appeared to form, passage of chlorine was stopped. The hexane was drawn off and discarded leaving a white crystalline solid (1.04 g.) which was freed from hexane by vacuum transfer. The sample was stored in a vial with a plastic cap. After three weeks the cap was corroded.

Preparation Of Methylpentafluorophenylselenium Dichloride

Chlorine gas was bubbled through a solution of methyl pentafluorophenyl selenide (1.56 g.) in hexane (10 ml.) cooled to 0°. When no more solid appeared to form, passage of chlorine was stopped. The hexane was drawn off and discarded leaving a white crystalline solid (1.82 g.) which was freed of hexane by vacuum transfer. After storing for one week in a well sealed vial the white solid had decomposed to a red-brown liquid.

Hydrolysis Of Phenylpentafluorophenylselenium Dichloride

Phenylpentafluorophenylselenium dichloride (1.34 g.) was dissolved in methanol (20 ml.) and heated. Water was added carefully to the boiling solution until a white cloudiness appeared. On cooling a white crystalline solid, pentafluorophenylphenylselenoxide, separated out. The solid (0.79 g.) was filtered off and dried *in vacuo.*

Addition of concentrated hydrobromic acid to a suspension of pentafluorophenylphenylselenoxide in water resulted in the immediate formation of bromine.

Hydrolysis Of Methylpentafluorophenylselenium Dichloride

Methylpentafluorophenylselenium dichloride (1.68 g.) was dissolved in methanol (10 ml.) to give a yellow solution. On addition of water a yellow oil separated out. The solution was decanted off and more water added (a total of 10 ml. water added). The solution was boiled down to 10 ml. and allowed to cool. This resulted in the formation of white crystals (0.63 g.) which were filtered off and dried *in vacuo* over phosphorus pentoxide. The white product was identified as pentafluorobenzeneseleninic acid by its melting point (120°; lit. 120°)[5] and infrared spectrum.

Reaction Of Pentafluorophenyl Phenyl Selenide With Hydrogen Peroxide

30% Hydrogen peroxide solution (2 ml.) was added to a solution of pentafluorophenyl phenyl selenide (0.95 g.) in ethanol (20 ml.). The solution was refluxed for one hour. Water was added slowly, with stirring, to the cooled solution. This resulted in the formation of colourless flakes (0.89 g.) of unreacted pentafluorophenyl phenyl selenide (m.p. 35°).

Reaction Of Methyl Pentafluorophenyl Selenide With Hydrogen Peroxide

30% Hydrogen peroxide solution (2 ml.) was added to a solution of methyl pentafluorophenyl selenide (1.0 g.) in ethanol (20 ml.). The solution was refluxed for one hour. Water was added slowly, with stirring, to the cooled solution to give a colourless heavy oil. Some of this was drawn off by pipet and identified by its infrared spectrum as unchanged methyl pentafluorophenyl selenide.

Preparation Of Pentafluorobenzeneseleninic Acid

This method has been previously reported[5] but is slightly modified here by using methanol as solvent rather than using the reagents neat.

30% Hydrogen peroxide (50 ml.) was added to a solution of bis(pentafluorophenyl) diselenide (10.0 g.) in methanol (200 ml.). The solution was stirred overnight, after which time the yellow solution had changed to a white suspension. Most of the solvent was removed on a rotory evaporator leaving a white slurry which was filtered. The white insoluble solid was washed with ether and dried in a vacuum desiccator over phosphorus pentoxide to give pentafluorobenzeneseleninic acid (9.4 g.) (m.p. 120°, lit. 120°).[5]

The product, pentafluorobenzeneseleninic acid, is sparingly soluble in water but dissolves readily in hydrochloric acid.

Reaction Of Pentafluorobenzeneseleninic Acid With Phosphorus Pentoxide

Pentafluorobenzeneseleninic acid (1.0 g.) and phosphorus pentoxide (3.0 g.) were mixed together and placed in a cold finger sublimation apparatus. The apparatus was evacuated and heated to 100° for five days. A small quantity of colourless crystals (0.06 g.) were deposited on the cold finger. The involatile material was yellow coloured. Infrared spectrum and melting point (73°, lit. 71-72°)[3] indicated that the colourless crystals were bis(pentafluorophenyl) selenide.

Preparation Of Pentafluorobenzeneseleninic Acid Anhydride

Ozone (prepared from oxygen, dried at -78°, in a Welsbach Laboratory Ozonator, Model T-816) was bubbled gently through a solution of bis(pentafluorophenyl) diselenide (5.0 g.) in carbon tetrachloride (30 ml.) until the solution was colourless. The carbon tetrachloride was removed by pumping to give a colourless glass. Prolonged (12 hours) pumping under high vacuum gave a white solid (5.0 g.).

Preparation Of Pentafluorophenylselenium Oxychloride

Dry ozone (prepared as above) was bubbled through a solution of pentafluorobenzeneselenenyl chloride (5.0 g.) in carbon tetrachloride until the solution was colourless. Removal of the solvent by prolonged (12 hours) pumping gave a colourless oil. Anhydrous ether (10 ml.) was condensed by vacuum transfer onto the material to give a solution. Removal of solvent by pumping gave a white crystalline solid (4.7 g.).

Reaction Of Bis(pentafluorophenyl) Diselenide With Silver Difluoride

Bis(pentafluorophenyl) diselenide (2.76 g. : 6.7 mmoles) and powdered silver difluoride (2.52 g.: 17 mmoles) were stirred in refluxing Freon 113 (30 ml.) for twenty hours under an atmosphere of dry nitrogen. The warm solution was filtered. Solvent was removed by vacuum transfer to leave a white crystalline solid identified by its infrared spectrum and melting point (75° cf. lit. 71-72°)[3] to be bis(pentafluorophenyl) selenide.

In another experiment, bis(pentafluorophenyl) diselenide (2.5 g. : 5 mmoles) and silver difluoride (5.0 g. : 34.5 mmoles) were stirred together in Freon 113 (25 ml.) for seven days at room temperature. After this time the solution was filtered. Solvent was removed from the filtrate by vacuum transfer, giving yellow needles (2.1 g.) of bis(pentafluorophenyl) diselenide (m.p. 46°, lit. 46-48°).[4]

Reaction Of Pentafluorobenzeneseleninic Acid With Excess Alkali

Excess sodium hydroxide solution (20 ml. 1 M.: 20 mmoles) was added to pentafluorobenzeneseleninic acid (2.8 g. : 10 mmoles) and the mixture stirred. The resulting white suspension settled to give a clear solution and a heavy white precipitate. The mixture had a "musty" odour characteristic of polyfluoroaromatics. The mixture appeared to contain white solid and liquid droplets. The clear solution was decanted off and the flask containing the precipitate attached to the vacuum line. Volatiles were dried by condensing onto phosphorus pentoxide and collected to give a colourless liquid (0.32 g.). The infrared spectrum showed the material to be pentafluorobenzene.

Neutralisation Of Pentafluorobenzeneseleninic Acid

1 M. Sodium hydroxide solution was added slowly to a stirred suspension of pentafluorobenzeneseleninic acid (2.8 g. : 10 mmoles). Monitoring the neutralization with a pH meter the solution was kept below pH 7 at all times. At neutralization (pH = 7) addition of alkali was stopped and the fine white suspension filtered. Water was removed from the filtrate on a rotary evaporator to give a white crystalline solid, sodium pentafluorobenzeneseleninate, (1.8 g.) which was washed with ethanol.

Preparation Of Silver Pentafluorobenzeneseleninate

Silver nitrate (0.6 g.) dissolved in water (2 ml.) was added to a solution of sodium pentafluorobenzeneseleninate (0.903 g.) in water to give a white precipitate. The precipitate was filtered, washed with water and dried in a vacuum desiccator to give a white powder (1.089 g.). No attempt was made at quantitative transfer of the product since it formed a layer on the surface of water and crept up the sides of glass vessels used.

On a smaller (quantitative analysis) scale sodium pentafluorobenzeneseleninate (0.09953 g.) was converted to silver pentafluorobenzeneseleninate (0.12573 g. :

calculated 0.1275 g.) representing a 98.6% conversion. Again difficulty was experienced with the poor wetting nature of the silver salt precipitate.

Pentafluorobenzeneseleninic Acid And Hydrochloric Acid

Pentafluorobenzeneseleninic acid (1.6 g. : 5.8 mmoles) and tetramethylammonium chloride (1.3 g. : 12 mmoles) were dissolved in concentrated hydrochloric acid (10 ml.) in a flask (50 ml.) fitted with inlet and outlet tubes to allow passage of gas over the solution. Hydrogen chloride gas was passed over the stirred solution, cooled to 0° until no more hydrogen chloride was absorbed (indicated by the appearance of white fumes at the outlet tube). Although the colour changed from colourless to yellow as reaction proceeded no crystalline precipitate was obtained.

Similarly ammonium, potassium or cesium chlorides, substituted for tetramethylammonium chloride, gave no precipitates. Tetraphenylarsonium chloride was not sufficiently soluble in hydrochloric acid to be useful.

Pentafluorobenzeneseleninic Acid And Hydrobromic Acid

Concentrated hydrobromic acid was added to a slurry of pentafluorobenzeneseleninic acid in water. This immediately resulted in the formation of a heavy red-brown liquid, presumably pentafluorobenzeneselenenyl bromide and bromine.

Reaction Of Pentafluorobenzeneseleninic Acid With Potassium Permanganate

Potassium permanganate (1.1 g. : 7 mmoles) dissolved in water (40 ml.) was stirred with a solution of pentafluorobenzeneseleninic acid (2.8 g. : 10 mmoles), just neutralised with potassium hydroxide, in water (40 ml.). After three hours the resulting dark brown mixture was filtered to give a pale pink solution. Boiling removed the colour and the solution was again filtered. Excess potassium hydrogen sulphate (2.0 g.) was added and the solution reduced to near dryness by boiling. Ethanol (50 ml.) was added and the mixture boiled. The cooled solution was filtered to remove insoluble inorganic material. Solvent was removed from the filtrate by vacuum transfer to give a colourless viscous oil. To induce crystallization benzene (20 ml.) was added and the insoluble oil scratched with a glass rod. This gave fine white needles (2.3 g.) which were filtered off under dry nitrogen. The infrared spectrum of the solid showed no C_6F_5 peaks and was identified as $H_2SeO_4.4H_2O$ from its melting point 51° (lit. 51.7°).[132]

Ozone With Pentafluorobenzeneseleninic Acid

Ozone was bubbled through a suspension of pentafluorobenzeneseleninic acid (1.0 g.) in 1 molar sulphuric acid (20 ml.) at 0° for three hours. There was no apparent change. The white insoluble material was filtered off, washed with water (2 x 5 ml.) and dried in a vacuum desiccator over phosphorus pentoxide. The solid (0.8 g.) was identified (infrared spectrum and m.p. 120°)[5] as unchanged pentafluorobenzeneseleninic acid.

Ozone With Sodium Pentafluorobenzeneseleninate

Ozone was bubbled through a solution of sodium pentafluorobenzeneseleninate (0.9 g.) in water (10 ml.) for two hours. After this time water was removed by vacuum transfer to give a white solid (0.9 g.) identified by its infrared spectrum as unchanged sodium pentafluorobenzeneseleninate.

CHAPTER VI

VIBRATIONAL SPECTRA

Results and Discussion

If the C_6F_5Se- group is assumed to be planar, then it has C_{2v} symmetry and the vibrations are classified as follows: $11a_1 + 10b_2$ (in-plane) and $3a_2 + 6b_2$ (out-of-plane). The in-plane frequencies have been calculated for C_6F_5X molecules where the mass of X is taken successively as 35.5, 80 and 127.[133] The calculated vibrations were shown to be quite insensitive to changes in the mass of X and no vibrational mode could be adequately described as simply arising from one bond but all arose from vibrations of the whole molecule. Presumably this is caused by the large mass of fluorine, compared with that of hydrogen in the phenyl group, where vibrations, to a good approximation may often be described as arising between two adjacent atoms. These calculations agree well with the observed spectra of C_6F_5Cl, C_6F_5Br and C_6F_5I.[134] The remaining out-of-plane assignments ($3a_2 + 6b_2$) have also been reported.[135]

Since the C_6F_5X vibrations do not change appreciably with the large mass changes in X it is reasonable to expect that the effect of substituents bonded to selenium in C_6F_5Se- compounds is very small. Indeed only small changes are observed in the range of compounds reported (see Appendix A: Infrared Spectra; and Appendix B: Raman Spectra). The similarity of infrared spectra with one another and of Raman spectra with one another is a striking feature of these compounds. Typical spectra are shown in Figure 6.1.

The infrared spectra show two very intense absorptions at approximately 1510 and 1480 cm^{-1}, and strong absorptions at approximately 1630, 1080, 970 and 820 cm^{-1} together with many more of lower intensity which are found in all C_6F_5 compounds.[135]

The Raman spectra show two very intense peaks at approximately 580 and 490 cm^{-1} and strong peaks at approximately 1630, 1400 and 820 cm^{-1} together with many more of lower intensity.

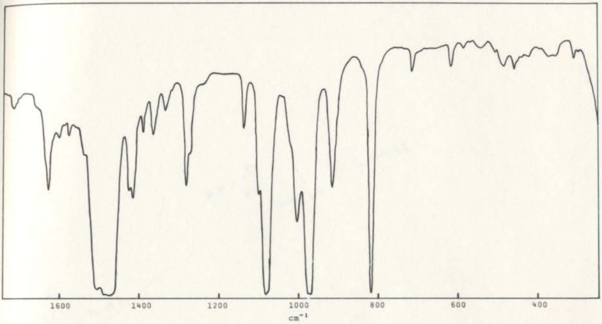
The spectra are similar to those reported of C_6F_5Cl, C_6F_5Br and C_6F_5I and are particularly similar to those of C_6F_5Br. This is expected since the masses of bromine (80) and selenium (79) are very close in value.

By analogy with the reported assignments of bands in the spectra of C_6F_5Cl, C_6F_5Br and C_6F_5I the major characteristic bands are assigned as follows:

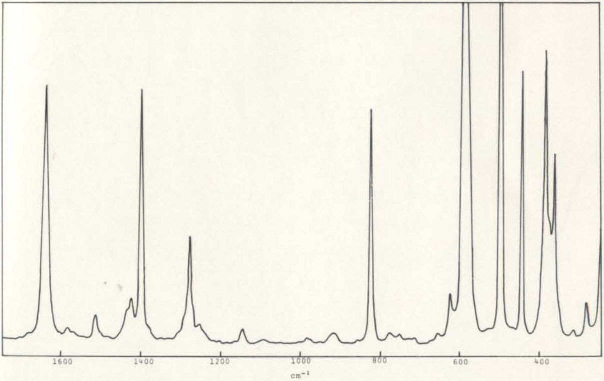
FIGURE 6.1

Vibrational Spectra Of A Typical Pentafluorophenyl Derivative Of Selenium In The Region 1750-250 cm^{-1}

Infrared Spectrum Of $C_6F_5SeCH_3$ (Liquid Film)



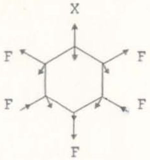
Raman Spectrum Of $C_6F_5SeCH_3$ (Liquid In Capillary Tube)



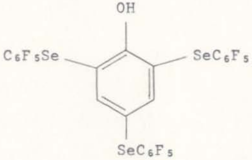
Frequency of vibration (cm^{-1})	Assignment
1630	ring stretching mode
1510	ring stretching mode
1480	combination band
1400	symmetric C-F stretching mode
1080	C-F stretching mode
970	combination band
820	C-Se stretching mode
580	ring deformation mode
490	ring stretching mode

Most of these vibrations are found to be quite insensitive to changes in halogen from Cl through Br to I. The band observed at 820 cm^{-1} in the C_6F_5Se compounds is fairly sensitive to mass changes and is observed at 885 cm^{-1} in C_6F_5Cl, at 836 cm^{-1} in C_6F_5Br and at 808 cm^{-1} in C_6F_5I in their infrared spectra.[134]

These bands are assigned to the C-X stretching modes[134] and by analogy the band at 820 cm^{-1} in the spectra of the pentafluorophenyl selenium compounds is assigned to the C-Se stretching mode although C-Se stretching is usually observed at much lower frequency, e.g. 575 cm^{-1} in $(CH_3)_2Se_2$[136] and 578 cm^{-1} in $(CH_3)_2SeO$.[137] The higher frequency arises from mixing with vibrations from other parts of the molecule as illustrated.



Nevertheless, it is the band most suitably assigned to this mode and, being the most sensitive to the mass of the atom substituent to the C_6F_5- group, is the most characteristic band for the compounds C_6F_5X for different atoms X. It is perhaps better described as the (C_6F_5)-Se stretching mode in these compounds. Further, this band is very sharp. The consequences of the sensitivity to changes in X and the sharpness of the band at 820 cm^{-1} are that it can distinguish between two or more different C_6F_5Se environments. Thus in the compound



where there are two C_6F_5Se environments a doublet is observed in the 820 cm^{-1} region in the infrared spectrum (see Appendix A) whereas no splitting of any other bands was resolved. This is also valuable in synthetic chemistry to determine if more than one C_6F_5Se compound is present in a reaction mixture.

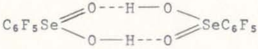
Because the spectra are so similar, comparison of the spectra allows several non-C_6F_5Se- vibrations to be isolated by "subtraction". Some of these vibrations appear above 2000 cm^{-1}, where no C_6F_5Se peaks are observed, and are easily picked out. Others, in the "main body" of the spectrum are not so easily isolated and it is likely several have been obscured. Some selenium-substituent atom vibrations have been assigned: Se-H stretching mode at 2333 cm^{-1} in C_6F_5SeH, Se-Se stretching mode at 280 cm^{-1} in $(C_6F_5)_2Se_2$, Se-Hg stretching mode at 174 cm^{-1} in $(C_6F_5Se)_2Hg$ and Se-O and Se=O stretching modes at 683 cm^{-1} and 857 cm^{-1} in $C_6F_5SeO_2H$.[5]

Bands assigned to Se-O stretching modes are readily identified by inspection and comparison of the spectra of compounds containing selenium bonded to oxygen (see Table 6.1). The observed bands in the infrared spectrum of $C_6F_5SeO_2H$ at 857 cm^{-1} and 683 cm^{-1}

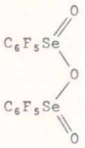
SeO Vibrational Frequencies And Assignments

$C_6F_5SeOCH_3$ (I.R.)	$C_6F_5Se(O)Cl$ (I.R.)	$C_6F_5Se(O)C_6H_5$ (I.R.)	$C_6F_5SeC_6H_5$ (I.R.)	$(C_6F_5SeO)_2O$ (I.R.)	$C_6F_5SeO_2H$ (I.R.)	$C_6F_5SeO_2H$ (R.)	$C_6F_5SeO_2Na$ (I.R.)	$C_6F_5SeO_2Ag$ (I.R.)	Assignments
	899 vs	850 vs		887 vs	857 vs	860 vs			ν(Se=O)
819 vs	800 m	830 vs	819 vs	790 vs	833 s	809 vs	811 vs	802 s	ν($[C_6F_5]$-Se
	753 w	798 m		758 m					
		738 vs	738 vs						
							781 vs	774 s	ν(Se==O)
								731 vs	
723 m,	721 m	720 m	719 m	723 m	721 w		722 m	721 m	
					683 s	684 s			ν(Se-O)
	647 w	687 vs	686 s						
			663 m						
628 w	619 m	620 s	622 m	631 m	619 w	626 w	622 m	621 m	
	590 w	590 w	612 w			587 vs	595 w	597 w	
598 vs				602 vs					ν(Se-O)

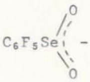
have been assigned to Se=O and Se-O stretching modes and other data are consistent with a hydrogen bonded structure[5]:



The Raman spectrum exhibits these peaks at similar frequencies 860 cm^{-1} and 684 cm^{-1}. A similar pattern is observed in the Raman spectrum of CF_3SeO_2H with peaks at 880 cm^{-1} and 680 cm^{-1} assigned to SeO stretching modes.[138] In the Raman spectrum of $CF_3SeO.OCH_3$ where there is no hydrogen bonding a peak at 573 cm^{-1} is assigned to the Se-O(CH_3) stretching mode.[138] In the infrared spectrum of $C_6F_5Se.OCH_3$ the intense peak at 598 cm^{-1} is assigned to a Se-O stretching mode. Similarly the intense peak at 602 cm^{-1} in the infrared spectrum of $(C_6F_5SeO)_2O$ is assigned to a Se-O stretching mode. The intense peak at 887 cm^{-1} is assigned to an Se=O stretching mode. In the infrared spectrum of $(C_6H_5SeO)_2O$ a band at 859 cm^{-1} is assigned to the Se=O stretching mode.[138] The spectrum of $(C_6F_5SeO)_2O$, therefore, is consistent with the structure:



for which the peak at 602 cm^{-1} is more adequately assigned as ν_{asym} (Se-O-Se). The high frequency bands in the infrared spectra of $C_6F_5Se(O)Cl$ and $C_6F_5Se(O)C_6H_5$ at 899 cm^{-1} and 850 cm^{-1} are assigned to Se=O stretching modes. The strong bands observed in the infrared spectra of the pentafluorobenzeneseleninic acid salts of sodium at 781 cm^{-1} and of silver at 774 cm^{-1} and 731 cm^{-1} are intermediate in frequency between ν(Se=O) and ν(Se-O) suggesting the ionic structure:



Two bands are expected, ν_{sym} (Se$\overset{\cdots}{-}$O) and ν_{asym} (Se$\overset{\cdots}{-}$O), and are observed in the spectrum of $C_6F_5SeO_2Ag$ but it appears that they are coincident in $C_6F_5SeO_2Na$.

The range of the frequencies of the SeO stretching modes is indicative of multiple bonding between selenium and oxygen. This presumably arises from π interactions involving donation of electrons from filled *p* orbitals on oxygen to empty *d* orbitals on selenium.

It had been anticipated that other selenium-substituent atom vibrations might be observed in the vibrational spectra of other compounds prepared, but inspection of the spectra failed to reveal Se-C stretching modes, expected in the region 550-600 cm^{-1}, in unsymmetrical selenides even when Raman spectroscopy was employed. The reason for this is unclear. In the infrared spectra this region is unobscured but it may be that, like C-S stretching modes which are reported to be weak,[139] the absorptions associated with C-Se stretching modes are weak. In the Raman spectra, where C-S bands are strong,[139] there are intense bands in the region 500-600 cm^{-1} that may be obscuring strong bands associated with C-Se stretching modes. Similarly no Se-N stretching modes could be identified from the infrared spectra of the selenenamides. The intense peak at 174 cm^{-1} observed in the Raman spectrum of $(C_6F_5Se)_2Hg$ has been assigned to the Se-Hg stretching mode.[5] It is to be expected other selenium-metal stretching modes should appear in this region although those of the lighter metals should be of somewhat higher frequency. Since infrared spectra could only be recorded down to 250 cm^{-1} on the instrument used no selenium-metal stretching modes were observed for the metal derivatives. No Raman spectra of these compounds were recorded.

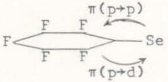
CHAPTER VII

FLUORINE-19 NUCLEAR MAGNETIC RESONANCE

Introduction

Chemical reactivities are related to the charge density at the reacting region of the molecule. The effect of changing substituents on a nonreacting part of the molecule is to alter the charge density distribution in the molecule and hence the charge density at the reacting region. When substitution occurs on a saturated carbon atom, the charge density changes are transmitted via an inductive effect and a parameter σ_I, called the inductive effect parameter, is defined for different substituent groups. When substitution occurs at an unsaturated carbon atom, the inductive effect does not sufficiently account for reactivity changes. This arises because of delocalization of electrons via π interactions or a resonance effect and a parameter σ^o_R, the resonance effect parameter, is defined for different substituents to account for this effect. The parameters σ_I and σ^o_R are obtained experimentally from chemical reactivities of organic molecules, e.g. acidity constants for substituted benzoic acids.[98]

Taft has related the ^{19}F n.m.r. chemical shifts in para- and meta- substituted monofluorobenzene derivatives to the reactivity parameters, σ_I and σ_R^o, of the substituent showing that the chemical shift is a measure of the charge density around the fluorine nucleus. Lawrenson noted that in the ^{19}F n.m.r. spectra of pentafluorophenyl derivatives the chemical shifts of the fluorines para and meta to the substituent show a considerable resemblance to the fluorine chemical shifts in para- and meta-substituted monofluorobenzenes, and he was indeed able to show that there are relationships between the para and meta chemical shifts and σ_R^o and σ_I.[140] Further, it has been concluded that the para chemical shift ϕ_p in pentafluorophenyl derivatives is determined largely by σ_R^o alone, so that, to a first approximation, ϕ_p is a measure of π interaction between the pentafluorophenyl ring and its substituent.[141] Since it has been found that the ortho-para coupling constant J_{24} is related linearly to ϕ_p, this coupling constant is also a measure of π interaction. Furthermore, it is suggested that the relation of J_{24} to ϕ_p distinguishes between π electron donation to the ring and π electron withdrawal from the ring by the substituent group.[141] Up to this point only a limited variety of different pentafluorophenyl derivatives had been considered; until Hogben, Graham *et.al.* recorded and interpreted the spectra of a large number of pentafluorophenyl derivatives of different elements and groups.[44,45] Initially they found a number of good empirical linear relationships between various chemical shifts ϕ and coupling constants J and related some of these to σ_R^o and σ_I. Similarly they were able to show that a fair straight line relationship exists between ϕ_o, the ortho fluorine chemical shift and ϵ, the electronegativity of the substituent atom bonded directly to the pentafluorophenyl ring. The best simple relationship was that between ϕ_p and J_{24} and it was demonstrated that within this relationship, the positions of common organic substituents are such that π- acceptor groups occur at low ϕ_p values and high J_{24} values, whereas π-donor groups occur at high ϕ_p values and large negative J_{24} values.[141] In a study of various series selected from a large number of pentafluorophenyl derivatives of the elements it has been shown that atoms with empty ***d*** orbitals suitable for π acceptance are net π electron acceptors even when filled *p* orbitals are available for π donation. Many observations and tests support the idea that $\pi(p \rightarrow p)$ donation to the ring is more than compensated by $\pi(p \rightarrow d)$ acceptance from the ring by the substituent atom[45] in the following way:



Having presented the background and justification for using ^{19}F n.m.r. parameters in interpreting π electron interactions between the pentafluorophenyl ring and substituents, the n.m.r. spectra of pentafluorophenyl selenium derivatives will be interpreted in a similar way.

Results and Discussion

The chemical shifts and coupling constants of the compounds studied are presented in Table 7.1. Although, strictly, the π withdrawal effects should be inferred from the para-fluorine chemical shift, ϕ_p, the compounds are listed in decreasing value of J_{24} since the coupling constant is less affected by solvent effects[44] (several solvents are used) and there is a very good correlation between J_{24} and ϕ_p. The table thus reflects

TABLE 7.1

^{19}F Chemical Shifts And Coupling Constants Of Pentafluorophenyl Selenium Compounds

	Compound	Solvent	Chemical Shifts ppm[a]			Coupling Constants cps					
			ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$
1.	$C_6F_5SeCl_3$[b]	C_6F_6	131.3	144.8	157.4	6.3	19.0	29.0	11.0	0.0	0.0
2.	$C_6F_5SeCl_3$	CCl_4	132.4	145.5	157.7	5.9	20.7	29.4	10.1	0.0	0.0
3.	$C_6F_5SeCl_2C_6H_5$	CCl_4	126.2	147.3	158.2	5.8	20.0	21.6	5.5	0.0	0.0
4.	C_6F_5SeCl[b]	C_6H_6	123.2	146.7	159.9	5.3	21.0	25.6	8.5	1.1	5.2
5.	$C_6F_5SeCl_2Me$	CCl_4		146.9	157.8	5.1	20.8	21.5	5.8	0.0	0.0
6.	C_6F_5SeBr[b]	C_6H_6	120.9	147.6	160.2	5.1	21.0	25.6	8.4	1.3	5.1
7.	$C_6F_5Se(O)Cl$	CCl_4	138.6	145.7	158.9	5.0	20.1	23.5	8.2	0.0	0.0
8.	$C_6F_5SeCF_3$	C_6H_6	124.2	147.2	159.7	4.8	20.6	24.1	8.4	0.0	0.0
9.	C_6F_5SeCN[b]	C_6H_6	125.5	147.8	158.9	4.5	21.0	24.7	7.9	0.0	6.6
10.	$C_6F_5Se(O)C_6H_5$	C_6H_6	127.8	149.0	159.5	3.9	20.7	25.2	9.0	0.0	0.0
11.	$(C_6F_5)_2Se_2$[b]	C_6H_6	125.9	149.6	160.3	3.7	20.7	24.4	7.0	1.2	4.3
12.	$(C_6F_5)_2Se$[b]	C_6H_6	126.9	150.6	160.2	3.4	20.7	25.1	8.4	0.0	3.5
13.	$C_6F_5SeNMe_2$	C_6H_6	123.1	149.7	160.5	3.4	21.3	28.3	9.4	1.9	3.9
14.	$C_6F_5SeNEt_2$	C_6H_6	123.2	150.2	160.6	3.0	20.3	28.0	9.2	1.7	4.5
15.	$[C_6F_5SeFe(CO)_3]_2$[c]	$CFCl_3$	127.0	150.5	160.2						
16.	$C_6F_5SeCH_2CO_2H$	C_6H_6	126.9	151.6	160.9	3.0	20.9	25.5	8.4	1.8	3.7
17.	$C_6F_5SeCH_2COCH_3$	C_6H_6	127.0	153.4	161.2	2.9	20.6	25.4	8.2	1.5	3.6
18.	$C_6F_5SeC_6H_5$	C_6H_6	127.0	152.3	160.8	2.9	20.9	25.1	8.3	1.4	2.9
19.	$C_6F_5Se(CH_2)_2Br$[b]	C_6H_6	126.9	152.2	160.6	2.7	21.1	25.9	8.4	1.3	3.1
20.	$C_6F_5Se(CH_2)_2Cl$[b]	C_6H_6	127.0	152.4	160.7	2.7	20.9	25.7	8.3	1.3	3.1
21.	$C_6F_5SeO_2H$	$(CH_3)_2CO$	126.4	153.1	161.6	2.7	20.2	24.8	8.2	1.4	3.0
22.	$p(C_6F_5Se)C_6H_4NH_2$	C_6H_6	128.0	153.8	161.4	2.6	20.4	26.4	8.8	1.6	2.0
23.	$C_6F_5SeC_2H_5$	C_6H_6	127.6	154.0	162.1	2.1	20.8	25.7	8.6	1.7	2.7
24.	$C_6F_5SeCH_3$	C_6H_6	128.6	154.7	161.3	1.9	20.1	25.0	8.3	1.6	2.9
25.	$C_6F_5SeHgCl$[b]	$(CH_3)_2CO$	123.8	157.0	162.3	1.3	20.1	24.9	7.1	1.0	1.0
26.	C_6F_5SeHgI[b]	$(CH_3)_2CO$	123.0	157.1	162.3	1.2	20.1	26.0	7.7	1.4	1.4
27.	$(C_6F_5Se)_2Hg$[b]	C_6H_6	125.6	155.8	161.0	1.1	20.9	25.9	7.7	1.5	1.5
28.	$C_6F_5SeMn(CO)_5$	C_6H_6	123.8	154.9	163.0	0.0	20.5	26.6	8.9	0.0	0.0
29.	$C_6F_5SeRe(CO)_5$	C_6H_6	124.4	156.6	162.3	0.0	20.7	27.4	8.4	0.0	0.0
30.	$C_6F_5SeFe(CO)_2cp$	C_6H_6	124.1	156.9	163.0	0.0	20.7	28.2	8.7	0.0	0.0
31.	C_6F_5SeH	C_6H_6	130.4	157.4	161.6	0.0	20.7	25.3	8.8	1.1	3.8
32.	$C_6F_5SeNi(PPh_3)cp$	C_6H_6	124.2	160.2	163.0	0.0	21.0	28.4	8.3	0.0	0.0
33.	$K[Au(SeC_6F_5)_4]$	$(CH_3)_2CO$	125.1	[163.0]	163.6						
34.	$Cs[Hg(SeC_6F_5)_3]$	$(CH_3)_2CO$	123.8	[163.0]	163.9	0.0	19.5	27.5	8.0	2.4	2.4
35.	$[Me_4N][Hg(SeC_6F_5)_3]$	$(CH_3)_2CO$	123.9	[163.0]	163.9	0.0	19.2	27.2	8.0	2.3	2.3
36.	$K[Au(SeC_6F_5)_2]$	$(CH_3)_2CO$	124.4	[163.0]	164.8	0.0	19.7	27.8	8.1	3.0	3.0
37.	$[Me_4N]_2[Cd(SeC_6F_5)_4]$	$(CH_3)_2CO$	123.2	165.1	165.6						
38.	$[Me_4N][Ag(SeC_6F_5)_2]$	$(CH_3)_2CO$	124.0	165.4	165.6						
39.	$[Me_4N]_2[Zn(SeC_6F_5)_4]$	$(CH_3)_2CO$	123.6	165.6	166.1						
40.	$[Me_4N]_2[Cu(SeC_6F_5)_3]$	$(CH_3)_2CO$	125.2	[166.4]	166.4						

a) The ϕ scale is based on C_6F_6 (internal reference) = 163.0 ppm upfield from $CFCl_3$.

b) Based on data from reference 5.

c) Reference 38.

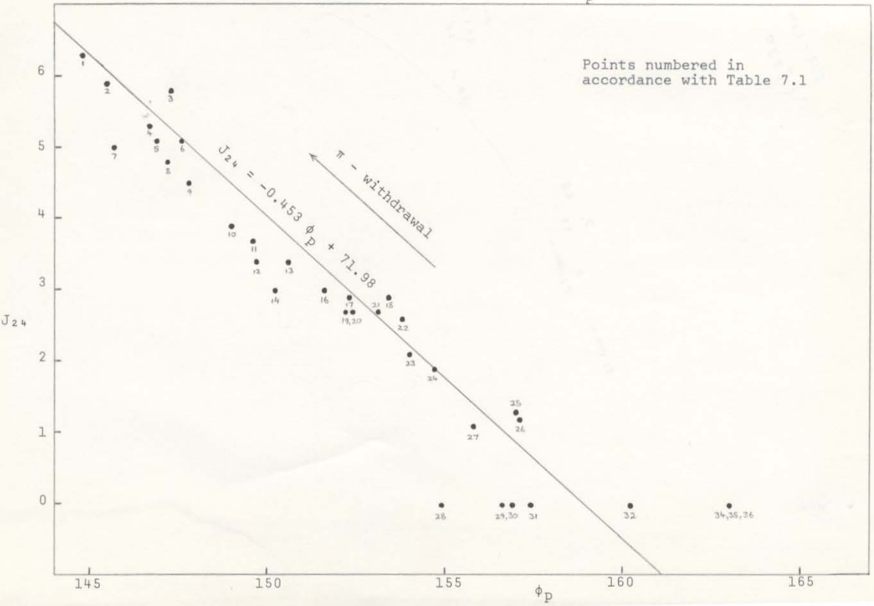
decreasing π withdrawal by selenium. Where the coupling constant is unavailable the value of ϕ_p is used and similarly for equal J_{24}, ϕ_p is used to determine the extent of π withdrawal. The good correlation between J_{24} and ϕ_p is illustrated for the selenium compounds in Figure 7.1.

Simple inspection of Table 7.1 and Figure 7.1 shows that generally selenium is a π electron acceptor indicating that $\pi(p\rightarrow d)$ withdrawal more than offsets $\pi(p\rightarrow p)$ donation by selenium as expected. It is also clear that substituents on selenium have quite a large effect on π electron density on the pentafluorophenyl ring; and that generally electron withdrawing substituents increase π electron withdrawal by selenium from the ring. To obtain a deeper understanding of substituent effects it is necessary to discuss the data in more detail.

In the divalent, 2-coordinate selenium situation π electron withdrawal by selenium is influenced by the substituent atoms in the following way

$$\mathrm{Cl}>\mathrm{Br}>\mathrm{SeC_6F_5}>\mathrm{NR_2}>\mathrm{CH_3}>\text{metal(covalent type)}\sim\mathrm{H}>\text{metal (ionic type)} \qquad (7.1)$$

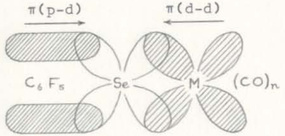
FIGURE 7.1 Plot Of J_{24} vs. ϕ_p



The most electron withdrawing elements withdraw electrons from selenium which in turn withdraws electrons from the pentafluorophenyl ring π system. While electron withdrawal and electronegativity are related this does not seem to explain completely the series since the highly electronegative nitrogen substituent is low in the series. It is likely that the lone pair electrons on nitrogen are involved in a π donor interaction with selenium and thence to the ring system. Carbon, in the methyl group, has no filled or empty orbitals suitable for π interaction with selenium, nor is there a significant polarity of the C-Se bond. It is likely, therefore, that the electron distribution in the compound $C_6F_5SeCH_3$ is the closest representation of the "true" nature of the interaction of selenium with the pentafluorophenyl group. It would thus appear that π interactions between selenium and substituent elements are important, but this does not rule out some electron withdrawal based on the electronegativity argument.

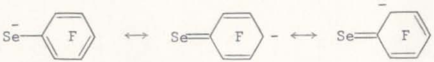
In terms of the generally accepted picture of the bonding in metal carbonyls[97] as represented schematically in A, the *d* electrons of the metal and the π electrons

A.



of the C_6F_5 ring compete for access to the vacant *d* orbitals of selenium. A similar π interaction has been shown to occur between phosphorus and molybdenum in pentafluorophenylphosphine derivatives of molybdenum carbonyl.[141]

In the complex metal anions, $M(SeC_6F_5)_n^{y-}$ the Se-M bond has some ionic character (60% in the cobalt complex - see Chapter II) and the observed low withdrawing nature is compatible with this. The negative charge is transferred from the selenium to the



pentafluorophenyl ring, resulting in increased π donation as indicated by the high (higher or similar to C_6F_6) value of ϕ_p.

Another interesting series appears when the atom, in this case carbon, substituent to selenium is unchanged and groups on the carbon atom are changed, $C_6F_5SeC\equiv$.

$$CF_3>CN>C_6F_5>CH_2CO_2H>CH_2COCH_3>C_6H_5>CH_2CH_2X>{}_{p}C_6H_4NH_2>CH_2CH_3>CH_3 \quad (7.2)$$

In this series the highly electron withdrawing groups influence the selenium atom to π electron withdrawal. The trends may be better understood by looking at various sub-series.

The series containing a CH_2 group bonded to

$$CH_2CO_2H>CH_2COCH_3>CH_2CH_2X>CH_2CH_3>CH_2H \quad (7.3)$$

selenium, where π effects are minimal, shows that electron withdrawing properties are transmitted inductively to selenium.

A similar aromatic series is explained by the fact that amino benzenes are electron rich in the para

$$C_6H_5>p\text{-}C_6H_4NH_2 \quad (7.4)$$

position relative to benzene. Thus the para-aminophenyl group donates charge to selenium probably by $\pi(p\text{-}d)$ interaction.

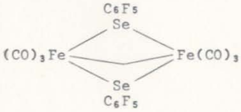
It is well known[142] that CN is highly electron withdrawing primarily by π interaction via vacant anti-bonding π* orbitals. Interaction with selenium *p* and *d* orbitals would tend to diminish π donation to and enhance π withdrawal from the pentafluorophenyl group. It has been postulated that the σ* anti-bonding orbitals of the CF_3 group are lowered in energy[51] and it is likely that here too a π withdrawal effect similar to that of the cyanide group is transmitted through the selenium atom. Undoubtedly inductive electron withdrawal by the three fluorine atoms is important also.

The trend

$$CF_3 > C_6F_5 > C_6H_5 > CH_3 \qquad (7.5)$$

seems to reflect what is known chemically of the electron withdrawing properties of these four fundamental organic groups.[41,98]

Up to this point both *p* and *d* orbital interactions have been considered. In the pentafluorophenyl selenium derivative of iron carbonyl, one of the lone pairs



B

of the divalent selenium is involved in bonding. The n.m.r. spectrum of the analogous sulphur compound shows the presence of two C_6F_5 environments suggesting *anti* and *syn* isomers.[59] This type of isomerism requires sp^3 hybridisation on sulphur which is unsuitable for good overlap with the C_6F_5 ring π system. It is likely that bonding in the selenium analogue is similar. This is supported by the n.m.r. spectrum which shows that relative to π-cyclopentadienyl-(pentafluorobenzeneselenolato)dicarbonyliron (a monomer) B is considerably more π electron withdrawing indicating poor π(*p*-*p*) donation by selenium. This is compatible with the properties of pentafluorophenylphosphines where the lone pair is removed by coordination to boron trihalides or metal carbonyls.[44]

It is unexpected that addition of two highly electron withdrawing chlorine atoms to $C_6F_5Se^{II}Cl$ (J_{24} = 5.3) giving $C_6F_5Se^{IV}Cl_3$ (J_{24} = 5.9) should result in such a small increase in π electron withdrawal by selenium. It is even more surprising to find that π electron withdrawal should follow the contradicting trends

$$\begin{array}{ll} & C_6F_5SeCl > C_6F_5Se(O)Cl \\ \text{while} & C_6F_5SePh < C_6F_5Se(O)Ph \end{array} \qquad (7.6)$$

It is evident that expansion of the valency of selenium does not allow valid comparison of π interactions of selenium(II) and selenium(IV) *p* and *d* orbitals and the ring π system. This may be understood by the fact that the result of changing the oxidation state of an element is a change in the energy, shape and size of orbitals.

Trends within the selenium(IV) compounds appear to be similar to those within the selenium(II) series, as illustrated by the following decreasing series of π withdrawal by selenium:

$$\begin{array}{lll} C_6F_5SeCl_2Cl > & C_6F_5SeCl_2Ph > & C_6F_5SeCl_2CH_3 \\ C_6F_5SeCl > & C_6F_5SePh > & C_6F_5SeCH_3 \end{array} \quad (7.7)$$

A similar series occurs with selenium double bonded to oxygen.

$$C_6F_5Se(O)Cl > C_6F_5Se(O)Ph > C_6F_5Se(O)OH \quad (7.8)$$

Here it is observed that bonding to oxygen (OH) results in a very low π withdrawal influence on selenium. Although oxygen is highly electronegative and would be expected to cause a strong electron withdrawal by selenium it is evident that the presence of filled oxygen *p* orbitals markedly offsets π withdrawal by a strong π donor effect.

Inspection of the fluorine n.m.r. data for the pentafluorophenyl selenium derivatives (Table 7.1) and comparison with the data from other elements[44,45] indicates that the general range for selenium is from a fair π electron acceptor to a poor electron acceptor and is perhaps even a net donor in the case of the metal complex anions where the C_6F_5Se group may be considered to hold a negative charge to some degree. This type of range is not unexpected for an element with filled *p* orbitals and vacant, low energy *d* orbitals where net π withdrawal by the element is observed.[45]

It is informative to look more specifically at the pentafluorophenyl derivatives of the group VI elements where the properties of isologues may be usefully compared (Table 7.2). The most striking feature of this comparison is that the oxygen isologues are π donors to the ring while the sulphur, selenium and tellurium derivatives are π acceptors. This is expected since oxygen has filled *p* orbitals for donation but, being a first row element, has no vacant *d* orbitals for π acceptance. Unfortunately there is insufficient data on tellurium analogues but it would appear that tellurium is a net π acceptor of the same order as sulphur and selenium.

TABLE 7.2

Chemical Shifts Of Some Group VI C_6F_5 Derivatives

Compound	ϕ_o	ϕ_p	ϕ_m	Solvent	Ref.
$(C_6F_5)_2O$	156.2	159.4	162.0	Acetone	121
$(C_6F_5)_2S$	132.4	150.5	160.5	CCl_4	38
$(C_6F_5)_2Se$	126.9	150.6	160.2	C_6H_6	5
$(C_6F_5)_2Te$	138.0	151.1	161.4	CCl_4	38
C_6F_5OH	164.1	170.9	165.6	CCl_4	143
C_6F_5SH	137.5	159.1	162.3	C_6H_6	61
C_6F_5SeH	130.4	157.4	161.6	C_6H_6	This work
$C_6F_5OCH_3$	158.5	164.6	164.9	Neat	140
$C_6F_5SCH_3$	134.2	155.2	162.5	C_6H_6	61
$C_6F_5SeCH_3$	128.6	154.7	161.3	C_6H_6	This work
C_6F_5SCl	128.0	145.0	160.1	C_6H_6	61
C_6F_5SeCl	123.2	146.7	159.9	C_6H_6	5
$[Cd(SC_6F_5)_4]^{2-}$	134.3	172.1	169.8	Acetone	66
$[Cd(SeC_6F_5)_4]^{2-}$	123.2	165.1	165.6	Acetone	This work

Comparison of the sulphur and selenium isologues shows that when the substituent is CH_3, which has low inductive and resonance interactions, the moderate withdrawing effect is nearly equal (as measured by ϕ_p). When the substituent, e.g. Cl, influences sulphur or selenium to strong π withdrawal sulphur is more π withdrawing than selenium. Conversely when the substituent influences weak withdrawal, e.g. H, or even donation, e.g. the metal complex anions, sulphur is the poorer withdrawer or the better donor. Thus the sulphur derivatives seem to be more susceptible to π effects than their selenium isologues and this suggests better interaction between sulphur *p* and *d* orbitals and substituent orbitals and the pentafluorophenyl ring π system. There is, however, insufficient data to determine the exact nature of these interactions or to distinguish between *p* and *d* orbital interaction or substituent and pentafluorophenyl interaction. The higher position of the pentafluorobenzeneselenolate "anion" relative to the pentafluorobenzenethiolate "anion" in the nephelauxetic series (see Chapter II) indicates a greater orbital interaction between selenium and transition metals (actually inferred from cobalt) than between sulphur and transition metals. This lends weight to the idea of good interaction of the sulphur orbitals with the ring π system rather than with substituents.

The π interaction between the pentafluorophenyl ring π system and the selenium *p* and *d* orbitals, as measured by ^{19}F n.m.r. may be understood in terms of the following considerations.

(i) $\pi(p \rightarrow p)$ donation from filled *p* orbitals on the selenium atom to the ring π system.

(ii) $\pi(p \rightarrow d)$ acceptance by the vacant selenium *d* orbitals.

(iii) Generally $\pi(p \rightarrow d)$ acceptance is greater than $\pi(p \rightarrow p)$ donation so that selenium is a net π electron acceptor.

(iv) In comparison with the data for pentafluorophenyl derivatives of many other elements, selenium may be rated as a fair π electron acceptor.

(v) Relative to other group VI elements selenium is a similar acceptor to sulphur and tellurium. Oxygen is a net donor since it has no suitable *d* orbitals for π acceptance.

(vi) Sulphur is more susceptible to substituent effects probably indicating a better π interaction between the ring π system and sulphur orbitals rather than selenium orbitals.

(vii) The effects of substituents on selenium can be understood in terms of σ bond and π bond interactions. Coordination of lone pair electrons reduces $\pi(p \rightarrow p)$ donation.

(viii) π interactions between the ring π system and orbitals of selenium in different oxidation states are different. Therefore comparisons are not valid between compounds containing selenium in different oxidation states.

Experimental

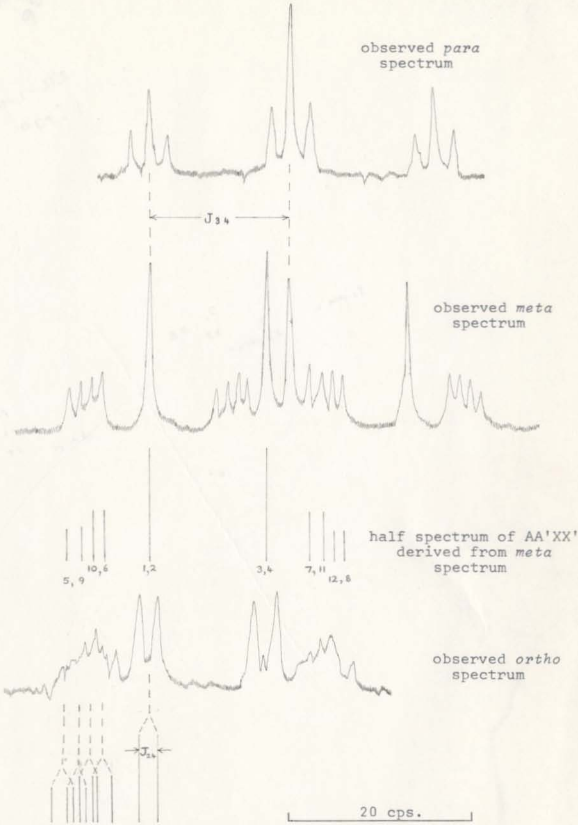
^{19}F N.M.R. Measurements

The ^{19}F n.m.r. spectra were recorded at 94.08 MHz on a Varian HA 100 instrument. Hexafluorobenzene was used as internal reference and the chemical shifts presented relative to $CFCl_3$ (a more universal reference) by adding 163.0 ppm. to the chemical shifts from C_6F_6. Where possible, spectra were obtained from 20-30% solutions in benzene containing 5% hexafluorobenzene since benzene has been shown to be a good solvent for these systems.[44] However, because of solubility and reactivity problems acetone and carbon tetrachloride were also used as solvents.

Occasionally only two fluorine signals were observed. The signal shapes are distinctive (Figure 7.2) so that it was easy to decide which fluorine signal was missing. In one instance, that of $C_6F_5SeCl_2CH_3$, the ortho signal was missing. Spectra of the similar compounds $C_6F_5SeCl_2C_6H_5$ and $C_6F_5SeCl_3$ showed considerable broadening of the ortho fluorine signal, perhaps due to rapid exchange, and it is thought that in the case of $C_6F_5SeCl_2CH_3$ broadening of the ortho signal was so extreme as to make observation impossible. With some of the metal derivatives, again only two signals were observed. In some cases it was thought that the para fluorine signals occurred at the same chemical shift as the lock signal and were thus obscured while in other cases overlap of the meta and para fluorines made separation difficult. However, inspection of Figure 7.3 shows that the smoothness of trends is unbroken and that the chemical shifts were chosen correctly.

^{19}*F N.M.R. Analysis*

The pentafluorophenyl system is treated as an AA'KXX' system in which there are five magnetically



<u>*FIGURE 7.2*</u> *Typical ^{19}F N.M.R. Spectra Showing Detailed Structure of Para, Meta and Ortho Fluorine Signals*

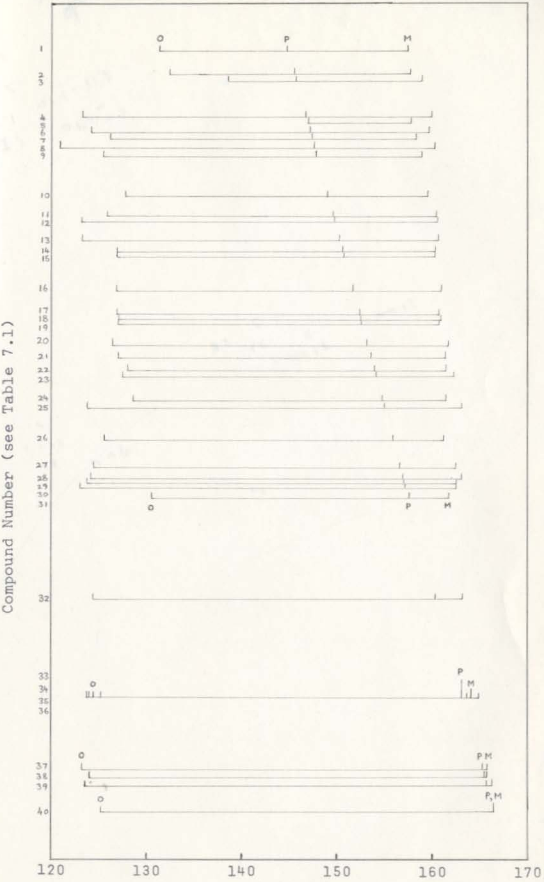
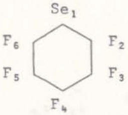


FIGURE 7.3 *The Chemical Shifts of the o-, p-, and m-Fluorines For The Pentafluorophenyl Selenium Derivatives*

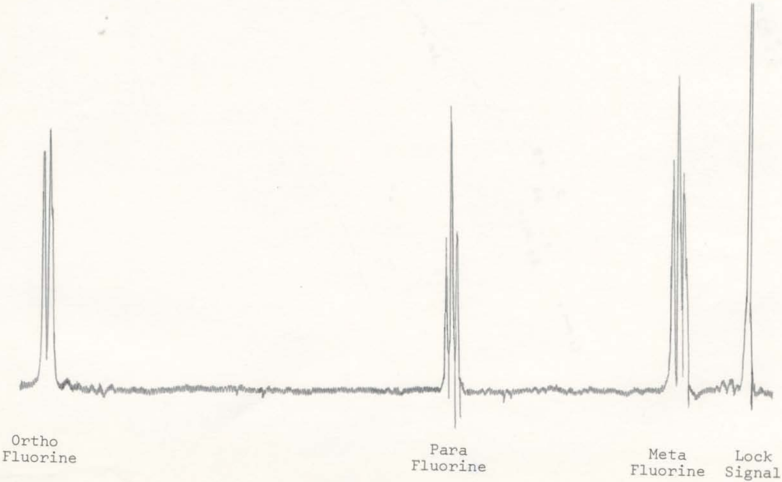
non-equivalent nuclei and two pairs of chemically equivalent nuclei. Since the chemical shifts are much greater than any coupling constants (Figure 7.4) a first order (weak coupling) spectrum is obtained.



The coupling constants J_{24} and J_{34} are obtained directly from the spectrum of the para fluorine (Figure 7.2) The value of J_{34} is then used to separate the two overlapping parts of the meta fluorine spectrum, the result being the upfield half of an AA'XX' system which is analysed after the manner of Grant *et.al.*[144] yielding J_{23}, J_{25}, J_{35} and J_{26}. Similarly the value of J_{24} may be used to separate the two halves of the ortho fluorine spectrum giving the low field half of the AA'XX' system, but the small value of J_{24} as compared to J_{34} does not give sufficient separation to be useful. Also the ortho spectrum is generally less well resolved than the meta spectrum because the proximity of the ortho fluorines to the selenium atom and other substituents gives rise to various interactions. For these reasons the meta spectrum is used exclusively to supply

FIGURE 7.4

Typical ^{19}F N.M.R. Spectrum Of C_6F_5Se- Compound



the coupling constants. Although analysis of the ortho fluorine spectra of pentafluorophenyl phosphorus derivatives has given ^{31}P coupling constants[44] no ^{77}Se ($I = \frac{1}{2}$) splitting is observed here probably because the 7.5% ^{77}Se satellites are obscured by the complex and much larger ortho fluorine signals.

Chemical shifts are correct to ±0.5 ppm.; coupling constants are correct to ±0.2 cps. Due to line overlap the resolution limit for J_{24} is approximately 1 cps.

CHAPTER VIII

CONCLUSION

Introduction

Several different aspects of the chemistry of pentafluorophenyl derivatives of selenium have been investigated in this work. The investigations have yielded some interesting general results but some of these conclusions are unconnected from one section to another. It is intended, therefore, to attempt to correlate the results to give a general picture of the chemistry of these derivatives.

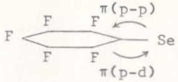
Discussion

A number of different methods has been employed to synthesize a variety of compounds. The range of synthetic methods used and of compounds prepared is broad. This is probably due in part to the stability of the C_6F_5Se- group under the various reaction conditions employed. The range of derivatives prepared is similar in scope to the range of organoselenium derivatives but, like the analogous perfluoroalkyl selenium derivatives, the attainment of higher valent selenium compounds is more restricted. This is offset, however, by the stability of the $C_6F_5Se^-$ anion particularly in water, which opens up a new region, virtually unexplored in perfluoroalkyl selenium chemistry, of aqueous ionic reactions. This made possible the study of interactions of the pentafluorobenzeneselenolate anion with transition metal ions.

Generally in the reactions employed the C_6F_5Se- group remains intact, reaction occurring at the selenium atom without any attack on the rest of the molecule. With higher oxidation states or in the presence of oxidising agents the C-Se bond is sometimes broken, however. Peach, in a study of the reactions of pentafluorobenzenethiol with aqueous metal ions[145] noted the lability of the para fluorine in C_6F_5S- species which often resulted in the formation of polymers of the type $C_6F_5SC_6F_4S$-- probably by nucleophilic attack on C_6F_5S- species by the $C_6F_5S^-$ anion produced in some of these reactions. While, admittedly, no deliberate attempt was made to influence this sort of side reaction no such polymer formation or other nucleophilic attack on the ring was noted here, either in the reactions of $C_6F_5Se^-$ with metal ions or in other types of reaction. Such a reaction may occur in the decomposition of C_6F_5SeNa but this was not examined in detail.

The stability of the C_6F_5Se- group must be due in part to the strength of the C-Se bond. The alkyl C-Se bond is broken in preference to the pentafluorophenyl C-Se bond when such an alternative arises. The ^{19}F n.m.r. data and other evidence strongly suggests a certain amount of π interaction between selenium *d* and *p* orbitals and the pentafluorophenyl ring π system and this no doubt gives rise to some multiple bonding in the C-Se bond with its attendant increase in bond strength.

The influence of pentafluorophenyl groups on selenium is to make selenium less basic by effectively delocalising the lone pair electrons. In an attempt to ascertain the relative effects of different groups on the selenium atom the reactions of unsymmetrical selenides were studied but, as far as the study went, the relative delocalising effects of C_6F_5 and CF_3 could not be distinguished even though the CF_3 group is more inductively electron withdrawing than the C_6F_5 group.[41] Delocalisation via a π interaction cannot be invoked since the ^{19}F n.m.r. study shows that in C_6F_5Se compounds the selenium atom is a net π electron acceptor. The interaction proposed to account for the ^{19}F n.m.r. spectra effectively depopulates



the directional selenium *p* orbitals by promoting electrons to the *d* orbitals. This explanation is highly speculative but until some difference in the base properties of perfluoroaryl and perfluoroalkyl selenium analogues is observed no other explanation can be offered.

The other influence of pentafluorophenyl groups on selenium, in precise analogy with perfluoroalkyl groups, is to lower the tendency of selenium to attain higher oxidation states relative to hydrocarbon derivatives of selenium. Also cleavage of the Se-C bond, not observed with pentafluorophenyl selenium(II) derivatives, sometimes occurs in reactions of pentafluorophenyl derivatives of higher valent selenium or in attempts to prepare them, suggesting a weakening of the C-Se bond. The reasons for these properties of higher valent selenium derivatives are not clear and no explanations are offered. It is not even clear if these observations are connected.

The properties and reactions of compounds containing the C_6F_5Se- group certainly characterise the group as a pseudohalide. It is more akin to a halide than some of the more common pseudohalides, e.g. CN, since the orbitals of the coordinating selenium atom in the C_6F_5Se species are similar in nature to those of its neighbour, the halogen bromine. Further, the effect of the C_6F_5- group is to increase the electronegativity of selenium, as determined by optical electronegativity, to a value close to that of bromine. The uncertainty of this value is high but the polarity of the $C_6F_5\overset{\delta+}{Se}-\overset{\delta-}{Br}$ bond, as deduced from the reactions of C_6F_5SeBr places the electronegativity of C_6F_5Se more precisely below that of bromine. The interactions of the $C_6F_5Se^-$ anion with transition metal ions shows that it has properties intermediate between bromide and iodide, and yet it is oxidised by iodine giving $C_6F_5SeSeC_6F_5$ and iodide

$$2C_6F_5Se^- + I_2 \rightarrow (C_6F_5)_2Se_2 + 2I^-$$

The carbonyl stretching frequencies in metal carbonyl derivatives suggest that the electronegativity of C_6F_5Se is lower than that of iodine, but here π

interactions are of prime importance. What is shown above is that while C_6F_5Se exhibits pseudohalogen properties and has the electronic structure of a halogen it cannot be precisely placed in the halogen series.

Several general observations have been made in various parts of this thesis and some have been related together in this last chapter. They may be summarised as follows.

(i) A wide range of pentafluorophenyl derivatives of selenium may be prepared using a variety of methods.
(ii) The C_6F_5Se group is generally stable.
(iii) C-Se bond cleavage sometimes occurs in oxidising media, or when selenium is in a high oxidation state.
(iv) C_6F_5Se may be classed as a pseudohalide. In this light its properties are variable but on average are similar to those of iodine.
(v) Unlike hydrocarbon derivatives pentafluorophenyl derivatives of selenium are not basic.
(vi) Oxidation of selenium bonded to pentafluorophenyl groups is restricted relative to hydrocarbon derivatives.

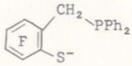
(vii) Properties (v) and (vi) of pentafluorophenyl derivatives of selenium are precisely analogous to those of perfluoroalkyl derivatives of selenium. Indeed, apart from the extensive aqueous chemistry of the pentafluorobenzeneselenolate anion, while CF_3Se^- decomposes in water, the chemistries of C_6F_5Se and CF_3Se are indistinguishable.

(viii) The properties of pentafluorophenyl derivatives of selenium and pentafluorophenyl derivatives of sulphur are similar, but sulphur isologues are more readily oxidised. Derivatives of six-valent sulphur are common, whereas four is the highest valency achieved by selenium in these compounds.

Recommendations For Further Work

An attempt has been made to cover a fairly broad range of chemistry of pentafluorophenyl derivatives of selenium. Metal derivatives and organo derivatives have been investigated, and to complete this study it would be interesting to prepare compounds with selenium bonded to main group elements. Work along these lines is currently underway in this laboratory.[54]

Nyholm, in commenting on the $C_6F_5S^-$ anion as a ligand,[146] has speculated that work in this field could be extended to chelate ligands, such as



to simulate, say, a tertiary phosphine and a Cl^- ion in a chelate group. Certainly, such groups with selenium replacing sulphur would also be interesting, but likening the -Se^- moiety too closely to Br^- is not valid. Indeed, neither should the sulphur isologue be so closely compared to Cl^-.

The stubborn similarity of the chemistries of pentafluorophenyl and perfluoroalkyl derivatives of selenium could perhaps be distinguished by investigating reactions of $CF_3SeSeC_6F_5$ with, for example, amines. A similar investigation of reactions of $C_6F_5SeSC_6F_5$ would also be interesting.

Extending the range of higher valent derivatives of selenium would be useful and it is likely that $C_6F_5SeF_3$ could be prepared by the choice of a suitable fluorinating agent. The elusive six valent selenium derivative,and four valent derivative of selenium bonded to two pentafluorophenyl groups, might also be obtained in the forms of $C_6F_5SeF_5$ and $(C_6F_5)_2SeF_2$.

The species present in a solution of $C_6F_5SeO_2H$ in hydrochloric acid might be identified by Raman spectroscopy and such a study could be extended to the hydrofluoric acid system. A more detailed study of the vibrational spectra of other pentafluorophenyl selenium compounds would be useful and might reveal the C_6F_5Se-C stretching frequencies in the unsymmetrical selenides.

The crystal structures of $(C_6F_5)_2Se$ and $(C_6F_5)_2Se_2$ should be determined. The C-Se bond lengths would give an idea of the extent of multiple bonding and comparison with those of $(CF_3)_2Se$[33] and $(CF_3)_2Se_2$[35] might also be interesting.

It is hoped that the work presented in this thesis will stimulate further research along these and other lines.

APPENDIX A

Infrared Spectra

Infrared spectra were recorded in the region 4000 cm^{-1} - 250 cm^{-1} on a Perkin Elmer 457 Grating Infrared Spectrophotometer. Solid samples were presented as potassium bromide disks or as mulls in nujol, and hexachlorobutadiene between KRS-5 plates. Liquids were recorded as films between KRS-5 plates. Spectra were calibrated with standard polystyrene film. Metal carbonyl derivatives were also presented as solutions in cyclohexane in the carbonyl stretching region (2200 cm^{-1} - 1800 cm^{-1}) and were calibrated with DCl gas.

Absorptions, not considered to arise from C_6F_5Se- vibrations, are in italic type.

$(C_6F_5)_2Se$ (KBr disc)[5]

1721 w, 1627 m, 1602 w, 1508 vs, 1482 vs, 1392 m, 1368 m, 1349 w, 1335 w, 1280 m, 1150 w, 1083 s, 1044 w, 1001 w, 970 vs, 825 m, 815 s, 719 w, 630 w, 617 w, 483 w, 390 w, 352 w, 309 w, 301 w.

$(C_6F_5)_2Se_2$ (KBr disc)[5]

1724 w, 1631 m, 1612 w, 1580 w, 1546 w, 1504 vs, 1479 vs, 1389 s, 1372 m, 1346 m, 1341 m, 1279 m, 1249 w, 1143 m, 1101 s, 1082 vs, 1028 w, 1011 m, 970 vs, 818 s, 720 m, 630 w, 622 m, 543 w, 487 m, 375 m, 309 m.

C_6F_5SeH (liquid film)[5]

1722 m, 1661 w, 1632 s, 1607 m, 1583 m, 1507 vs, 1488 vs, 1417 w, 1390 s, 1373 w, 1357 m, 1321 m, 1282 m, 1254 w, 1178 m, 1142 m, 1098 s, 1080 vs, 1058 m, 1001 vs, 977 vs, 838 s, 818 vs, 721 m, 622 w, 543 w, 491 m, 424 w, 346 m, 308 m.

C_6F_5SeCl (liquid film)[5]

1749 w, 1727 w, 1658 w, 1628 s, 1603 w, 1588 w, 1506 vs, 1476 vs, 1418 w, 1389 s, 1373 m, 1344 m, 1283 s, 1250 w, 1231 w, 1144 m, 1083 vs, 1027 m, 1008 s, 973 vs, 879 m, 817 s, 720 m, 622 m, 542 w, 489 m, 394 m, 376 m, 350 w, 309 w.

C_6F_5SeBr (liquid film)[5]

1728 w, 1668 w, 1628 s, 1603 w, 1587 w, 1509 vs, 1480 vs, 1418 w, 1391 s, 1373 m, 1346 m, 1284 s, 1250 w, 1232 w, 1147 m, 1102 s, 1087 vs, 1030 m, 1009 m, 976 vs, 820 s, 720 m, 623 m, 543 w, 490 m, 376 m, 357 w, 309 w, 270 m.

$C_6F_5SeCl_3$ (mull)[5]

1627 m, 1601 w, 1583 w, 1504 vs, 1485 vs, 1419 w, 1391 m, 1372 w, 1344 w, 1282 m, 1144 w, 1099 m, 1083 vs, 1026 w, 1008 m, 976 vs, 818 s, 720 w, 621 w, 543 w, 489 w, 372 w, 355 w, 310 w.

C_6F_5SeCN (KBr disc)[5]

2160 m, 1729 w, 1629 m, 1509 s, 1488 vs, 1401 m, 1372 m, 1346 w, 1286 m, 1251 w, 1175 w, 1147 w, 1087 s, 977 s, 819 s, 719 m, 624 w, 542 m, 517 m, 480 w, 420 w, 342 w, 309 w, 299 w, 278 w.

$C_6F_5SeCH_3$ (liquid film)

2943 s, 1744 w, 1633 s, 1607 w, 1583 w, 1544 m, 1504 vs, 1483 vs, 1431 s, 1422 s, 1395 w, 1371 m, 1342 w, 1287 s, 1246 w, 1143 m, 1106 s, 1084 vs, 1009 s, 974 vs, 922 s, 823 vs, 722 w, 624 w, 547 w, 490 w, 429 w, 376 w, 360 w, 315 w.

$C_6F_5SeC_2H_5$ (liquid film)

2958 s, 2917 s, 2862 s, 1716 m, 1656 w, 1623 s, 1599 w, 1578 m, 1502 vs, 1458 vs, 1433 m, 1390 m, 1374 s, 1340 m, 1280 s, *1229 vs,* 1170 w, 1139 s, 1073 vs, 1043 w, 1009 vs, 970 vs, 910 w, 861 w, 818 vs, *755 m, 746 m,* 720 m, 625 m, *576 w,* 557 m, 490 w, 382 m, 361 w, 315 w, 283 w.

$C_6F_5SeCF_3$ (liquid film)

1719 w, 1661 w, 1623 s, 1598 w, 1502 vs, 1478 vs, 1415 w, 1398 m, 1377 m, 1349 m, 1321 w, 1285 s, 1268 w, 1250 w, *1144 vs,* 1098 vs, *1065 vs,* 1013 s, 988 vs, 910 w, 827 vs, 807 w, 742 s, 725 m, 711 w, 630 m, 538 w, 496 w, 393 m, 365 w, 310 w, 289 w, 261 w.

$C_6F_5SeCH_2CH_2Cl$ (KBr disc)[5]

2975 w, 1721 w, 1629 m, 1601 w, 1580 w, 1503 s, 1480 s, 1433 m, 1420 m, 1391 m, 1367 m, 1339 w, 1280 m, 1251 m, 1186 m, 1139 w, 1100 m, 1082 s, 1037 w, 1007 m, 972 s, 819 s, 714 m, *657 w,* 619 m, 542 w, 487 w, 355 w, 310 w, 280 w.

$C_6F_5SeCH_2CH_2Br$ (KBr disc)[5]

3012 w, 2994 w, 1718 w, 1628 m, 1602 w, 1508 s, 1497 s, 1427 m, 1417 w, 1385 m, 1370 m, 1343 w, 1284 w, 1244 m, 1176 s, 1132 w, 1103 m, 1083 s, 1038 w, 1013 m, 969 s, 819 s, 730 m, *638 w,* 622 m, *570 s,* 482 w, 367 w, 308 w, 277 w.

$C_6F_5SeCH_2COCH_3$ (liquid film)

3000 m, 2920 m, 1701 vs, 1631 s, 1606 w, 1584 w, 1541 m, 1509 vs, 1474 vs, 1411 m, 1391 s, 1359 s, 1284 m, 1260 s, *1229 vs,* 1140 s, 1104 s, 1082 vs, 1029 m, 1009 vs, 857 w, 823 vs, 724 w, 624 w, 546 s, 483 w, 381 w, 357 w, 315 w, 286 w.

$C_6F_5SeCH_2CO_2H$ (KBr disc)

2900 s.br, 1685 vs, 1620 s, 1500 vs, 1461 vs, 1419 s, 1382 m, 1373 w, 1341 w, 1272 vs, 1165 m, 1137 w, 1101 m, 1076 vs, 1037 w, 1009 m, 970 vs, 913 m, 857 w, 820 vs, 765 m, 721 m, *644 s,* 627 m, 520 w, *464 s,* 384 m, 311 m.

$C_6F_5SeC_6H_5$ (KBr disc)

3072 w, 1719 w, 1639 s, 1630 s, 1576 s, 1545 w, 1509 vs, 1481 vs, 1448 s, 1390 m, 1369 m, 1341 w, 1329 w, 1301 w, 1277 m, 1179 w, 1158 w, 1139 w, 1100 s, 1083 vs, 1021 m, 1010 m, 974 vs, 819 vs, *738 vs*, 719 m, *686 s*, *663 m*, 622 m, *612 w*, 547 w, 489 w, *468 s*, 379 m, 360 w, 343 w, 310 m, 284 w.

p-$(C_6F_5Se)C_6H_4NH_2$ (KBr disc)

3465 m, *3355 m*, *3010 w*, 1611 s, 1583 s, 1504 vs, 1477 vs, 1418 w, 1386 m, 1367 w, 1339 w, 1294 m, 1281 s, 1174 m, 1136 w, 1120 w, 1079 vs, 1069 m, 1039 w, 1012 m, 976 vs, 820 vs, *753 w*, *747 w*, 720 m, 624 m, 512 s, 497 w, 391 m, 358 w, 314 w, 282 w.

2,4,6-$(C_6F_5Se)_3C_6H_2OH$ (KBr disc)

3380 s, *3040 w*, *2910 w*, 1718 w, 1630 s, 1573 m, 1508 vs, 1474 vs, 1423 s, 1384 m, 1374 m, 1299 s, 1268 w, *1224 s*, 1139 vs, 1090 vs, 1012 m, 970 vs, 871 m, 841 w, 823 s, 816 s, 752 w, 721 m, 664 m, 630 m, 568 w, 554 m, 511 m, 490 m, 400 w, 360 w, 315 m, 282 w, 272 w.

$C_6F_5SeN(CH_3)_2$ (liquid film)

2970 m, *2920 s*, *2850 m*, *2815 m*, *2775 m*, 1614 s, 1504 vs, 1463 vs, 1432 m, 1398 w, 1380 m, 1275 w, 1224 s, 1178 m, 1137 w, 1067 vs, 1028 w, 972 vs, 961 vs, 939 s, 803 m, *789 w*, *751 w*, 722 w, 645 w, 625 w, 553 m, 490 w, 475 w, 432 w, 410 w, 349 w, 290 w.

$C_6F_5SeN(C_2H_5)$ (liquid film)

2970 vs, *2930 s*, *2865 m*, *2830 s*, 1718 w, 1628 s, 1580 w, 1543 w, 1504 vs, 1469 vs, 1375 vs, 1357 s, 1334 m, 1277 s, 1251 w, 1172 w, 1153 m, 1140 w, 1080 vs, 1030 w, 1015 m, 972 vs, 879 m, 803 vs, 725 m, 626 m, 585 m, 528 m, 495 m, 457 w, 432 m, 396 w, 315 w, 287 w.

$(C_6F_5Se)_2NH$ (KBr disc)

3285 vs, 1721 w, 1631 s, 1576 w, 1507 vs, 1472 vs, 1380 s, 1350 w, 1285 m, 1229 w, 1134 w, 1085 vs, 1011 m, 969 vs, 910 w, 819 vs, 721 m, 700 m, 629 m, 544 w, 488 w, 390 w, 353 m, 312 w, 280 w, 269 w.

$C_6F_5SeOCH_3$ (liquid film)

2925 s, *2815 m*, 1626 s, 1599 w, 1570 w, 1556 w, 1502 vs, 1477 vs, 1425 w, 1388 s, 1378 m, 1347 w, 1280 s, 1251 w, 1160 w, 1142 m, 1083 vs, 975 vs, 819 vs, 723 m, 628 w, *598 vs*, 501 m, 429 s, 393 m, 357 s, 314 w, 284 w.

$C_6F_5Se(O)Cl$ (mull)

1726 w, 1663 w, 1628 s, 1586 w, 1506 vs, 1281 s, 1235 w, 1190 w, 1149 m, 1077 vs, 1035 w, 1007 m, 978 vs, *899 vs,* 800 m, 753 w, 721 m, 647 w, 619 m, 590 w, 497 m, 447 w, 384 s, 360 s, 320 vs, 289 s, 252 w.

$C_6F_5Se(O)C_6H_5$ (KBr disc)

3055 m, 1629 s, 1571 m, 1545 w, 1509 vs, 1477 vs, 1442 s, 1387 vs, 1369 w, 1336 w, 1324 w, 1301 m, 1280 s, 1246 w, 1181 w, 1172 w, 1164 m, 1141 m, 1082 vs, 1059 m, 1019 w, 1008 m, 972 vs, 914 m, *850 vs,* 830 vs, 798 m, *738 vs,* 720 m, *687 vs,* 620 s, 590 w, 549 w, 496 s, *471 vs,* 429 m, 378 m, 349 s, 314 m, 294 s, 273 w, 264 w.

$(C_6F_5SeO)_2O$ (mull)

1722 w, 1631 s, 1582 w, 1508 vs, 1480 vs, 1437 w, 1386 s, 1340 w, 1288 s, 1194 w, 1149 m, 1084 vs, 1035 w, 1007 m, 979 vs, *887 vs,* 790 s, 758 m, 723 m, 631 m, *602 vs,* 530 m, 499 m, 428 w, 387 w, 357 w.

$C_6F_5SeO_2H$ (KBr disc)[5]

2770 s.br, 2355 s.br, 1633 m, 1507 s, 1481 vs, 1383 m, 1373 m, 1340 w, 1282 m, 1250 m, 1141 w, 1087 s, 1038 w, 1003 m, 973 vs, *857 s,* 833 s, 721 w, *683 s,* 619 w, 546 w, 489 w, 424 w, 396 w, 382 m, 347 w, 313 w, 291 w.

$C_6F_5SeO_2Na$ (KBr disc)

1719 w, 1637 s, 1551 w, 1516 vs, 1482 vs, 1458 s, 1370 s, 1290 m, 1279 w, 1128 w, 1105 m, 1089 vs, 1035 m, 1016 m, 967 vs, 811 vs, *781 vs,* 722 m, 622 m, 595 w, 502 m, 416 s, 391 m, 375 s, 347 s, 316 m, 286 w, 262 m.

$C_6F_5SeO_2Ag$ (KBr disc)

1633 s, 1512 vs, 1472 vs, 1459 vs, 1372 s, 1289 m, 1279 w, 1179 w, 1090 vs, 1034 w, 1012 m, 969 vs, 802 s, *774 s, 731 vs,* 721 m, 621 m, 597 w, 502 w, 490 m, 414 s, 365 s, 338 s, 311 m, 266 w.

$C_6F_5SeCl_2CH_3$ (mull)

2940 w, 1629 s, 1541 w, 1509 vs, 1486 vs, 1391 m, 1372 w, 1343 w, 1283 m, 1147 m, 1104 m, 1087 vs, 1025 w, 1009 m, 978 vs, 821 s, 767 w, 719 w, 621 w, 544 w, 492 m, 380 m, 352 m, 281 m.

$C_6F_5SeCl_2C_6H_5$ (mull)

3065 m, 1636 s, 1575 m, 1541 w, 1508 vs, 1481 vs, 1438 s, 1393 m, 1362 w, 1330 w, 1301 w, 1283 m, 1181 w, 1144 m, 1082 vs, 1020 w, 999 w, 974 vs, 910 w, 818 vs, *737 vs,* 720 m, *688 s,* 620 m, 540 w, 488 w, *471 s,* 389 w, 350 m, 306 w, 283 w, 259 w.

$[(CH_3)_4N]_2[Zn(SeC_6F_5)_4]$ (KBr disc)
3015 m, 1607 m, 1509 vs, 1478 vs, 1381 w, 1352 m, 1323 m, 1281 w, 1268 m, 1245 w, 1127 m, 1072 vs, 998 s, 964 vs, 946 s, 812 vs, 709 w, 612 m, 583 w, 538 w, 474 w, 351 w, 312 w.

$[(CH_3)_4N]_2[Cd(SeC_6F_5)_4]$ (KBr disc)
3020 m, 1603 m, 1541 w, 1498 vs, 1476 vs, 1382 w, 1351 m, 1321 m, 1282 w, 1268 m, 1127 m, 1094 w, 1072 vs, 998 s, 962 vs, 948 vs, 813 vs, 709 w, 612 m, 582 w, 538 w, 480 m, 352 w, 304 w, 291 w, 282 w.

$[(CH_3)_4N]Hg(SeC_6F_5)_3$ (KBr disc)
1634 w, 1608 m, 1550 w, 1503 s, 1463 vs, 1386 w, 1360 m, 1329 w, 1272 m, 1131 m, 1083 s, 1077 s, 1007 m, 966 vs, 951 s, 815 vs, 715 w, 616 w, 586 w, 543 w, 477 m, 356 w, 307 w, 294 w, 286 w.

$CsHg(SeC_6F_5)_3$ (KBr disc)
1633 m, 1603 m, 1567 w, 1542 w, 1498 vs, 1474 vs, 1389 w, 1379 w, 1362 w, 1344 w, 1332 w, 1311 w, 1268 m, 1127 s, 1078 vs, 1070 vs, 1000 s, 964 vs, 906 w, 812 vs, 707 m, 608 m, 584 w, 541 w, 485 m, 357 m, 312 w, 281 w.

$Hg(SeC_6F_5)_2$ (KBr disc)[5]
1721 w, 1627 m, 1602 w, 1508 vs, 1389 m, 1363 m, 1347 w, 1288 w, 1138 m, 1089 s, 1081 s, 1011 m, 969 vs, 818 s, 717 w, 620 w, 484 w, 349 w, 277 w.

$(C_6H_5)_3P.Hg(SeC_6F_5)_2$ (KBr disc)[5]
3056 m, *3004 w*, 1632 w, 1609 w, *1569 w*, 1537 w, 1497 vs, 1471 vs, *1430 s*, 1381 m, 1352 w, *1324 w*, *1310 m*, *1267 w*, 1189 w, *1158 m*, 1128 m, 1095 s, 1079 s, *1024 w*, *997 m*, 966 vs, *849 w*, 615 w, 583 w, 540 w, *518 s*, *500 s*, *442 w*, *425 w*, *346 w*, 310 w, 278 w.

$[(CH_3)_4N]_2[Cu(SeC_6F_5)_3]$ (KBr disc)
3005 m, 1628 w, 1605 m, 1497 vs, 1463 vs, 1349 m, 1318 m, 1284 w, 1265 s, 1124 m, 1067 vs, 1027 w, 996 s, 960 vs, 810 vs, 708 m, 610 m, 583 m, 539 w, 478 m, 350 m, 309 w.

$(CH_3)_4N[Ag(SeC_6F_5)_2]$ (KBr disc)
3000 w, 1601 m, 1562 w, 1543 w, 1498 vs, 1460 vs, 1408 m, 1374 m, 1348 m, 1317 m, 1267 s, 1244 w, 1120 m, 1079 vs, 993 s, 959 vs, 944 vs, 810 vs, 708 m, 608 m, 581 m, 540 w, 473 m, 341 m, 311 w.

$K[Au(SeC_6F_5)_2].2H_2O$ (KBr disc)
3630 s, 3450 s, 1643 m, 1610 s, 1574 w, 1542 w, 1507 vs, 1470 vs, 1381 m, 1356 m, 1327 w, 1281 w, 1269 m, 1124 m, 1082 vs, 1074 vs, 1009 s, 964 vs, 904 w, 811 vs, 712 w, 618 m, 539 w, 485 m, 340 m, 284 w.

$K[Au(SeC_6F_5)_4]$ (KBr disc)
1720 w, 1658 w, 1627 s, 1602 w, 1578 w, 1542 w, 1506 vs, 1470 vs, 1380 s, 1363 m, 1332 w, 1280 m, 1138 m, 1099 s, 1077 vs, 1028 w, 1011 m, 970 vs, 907 w, 818 vs, 747 w, 718 m, 621 m, 589 w, 541 w, 488 m, 446 w, 383 m, 356 w, 313 m, 281 w.

$\{Ni(SeC_6F_5)_2\}_n$ (KBr disc)
1629 s, 1508 vs, 1480 vs, 1389 s, 1374 w, 1343 w, 1281 m, 1143 m, 1080 vs, 1025 w, 1011 m, 973 vs, 817 s, 719 w, 620 w, 550 w, 489 m, 374 m, 358 w, 307 w.

$\{Pd(SeC_6F_5)_2\}_n$ (KBr disc)
1706 m, 1631 s, 1614 m, 1545 w, 1500 vs, 1477 vs, 1384 s, 1364 w, 1343 w, 1282 m, 1232 w, 1143 s, 1076 vs, 1007 s, 972 vs, 815 vs, 720 m, 680 w, 621 m, 583 w, 542 w, 491 m, 372 m, 314 w, 290 w, 263 w.

$K_2[Pt(SeC_6F_5)_4].H_2O$ (KBr disc)
3615 s, 3390 s, 1631 m, 1606 m, 1581 s, 1544 w, 1507 vs, 1465 vs, 1377 s, 1358 m, 1328 w, 1279 w, 1270 w, 1230 w, 1129 m, 1071 vs, 1007 s, 962 vs, 903 w, 809 vs, 745 w, 713 m, 619 s, 540 w, 483 w, 448 w, 379 s, 314 w, 281 w.

$[(CH_3)_4N]_2[Co(SeC_6F_5)_4]$ (KBr disc)
3015 m, 1630 w, 1607 m, 1568 w, 1497 vs, 1469 vs, 1379 w, 1351 m, 1322 m, 1280 w, 1268 m, 1127 m, 1071 vs, 997 s, 963 vs, 948 s, 812 vs, 710 w, 612 m, 587 m, 539 w, 480 m, 352 m, 313 m, 282 w

$\{\pi C_5H_5NiSeC_6F_5\}_n$ (KBr disc)
3105 w, 1631 s, 1607 w, 1572 w, 1543 w, 1502 vs, 1468 vs, 1391 s, 1378 s, 1359 w, 1344 s, 1329 w, 1271 m, 1229 w, 1129 m, 1080 vs, 1071 vs, 1046 s, 1007 s, 962 vs, 901 w, *864 m, 833 s,* 803 vs, *787 vs,* 714 w, 677 w, 617 m, 587 w, 540 w, 507 w, 486 m, 436 w, 362 s, 313 w, 281 w.

$\pi C_5H_5Ni(SeC_6F_5)P(C_6H_5)_3$ (KBr disc)
3055 m, 1628 w, 1607 w, 1581 w, 1569 w, 1497 vs, 1467 vs, *1431 vs,* 1393 m, 1379 w, 1355 w, 1329 w, 1310 m, 1267 m, *1180 s, 1159 w,* 1128 w, 1093 vs, 1067 vs, 1044 w, 1018 w, 999 m, 967 vs, 898 w, *850 w, 833 m,* 809 vs, *785 vs, 751 vs, 744 vs,* 705 w, *693 vs,* 617 m, 587 w, 538 vs, *513 vs,* 496 s, 459 m, 442 m, 433 m, 353 s, 312 w, 280 w.

$\pi C_5H_5Fe(CO)_2SeC_6F_5$ (cyclohexane solution)

2037 s, 1995 vs.

(KBr disc)

3110 m, 1630 w, 1602 w, 1577 w, 1544 w, 1504 vs, 1471 vs, 1432 s, 1381 m, 1361 w, 1333 w, 1271 w, 1132 m, 1071 s, 1009 m, 966 vs, *879 m, 841 s,* 810 vs, 716 w, 611 s, 570 vs, 556 vs, 500 s, 444 m, 428 w, 354 m, 308 w, 280 w.

$C_6F_5SeMn(CO)_5$ (cyclohexane solution)

2114 s, 2078 w, 2037 sh, 2024 vs, 2002 vs.

(KBr disc)

1624 m, 1609 w, 1571 w, 1538 w, 1502 vs, 1473 vs, 1384 m, 1367 w, 1337 w, 1273 w, 1240 w, 1185 w, 1135 s, 1096 s, 1077 s, 1027 w, 1010 w, 971 vs, 902 w, 818 vs, 721 m, 639 vs, 547 w, 494 m, 434 s, 412 w, 317 m.

$C_6F_5SeRe(CO)_5$ (cyclohexane solution)

2142 s, 2043 sh, 2031 vs, 1991 vs.

(KBr disc)

1630 m, 1578 w, 1544 w, 1500 vs, 1476 vs, 1389 m, 1368 m, 1341 w, 1274 w, 1249 w, 1137 s, 1096 m, 1077 vs, 1011 m, 971 vs, 910 w, 819 vs, 721 m, 627 m, 594 vs. 532 w, 490 w, 472 w, 445 m, 347 vs, 303 w, 283 m, 257 w.

APPENDIX B

Raman Spectra

Raman spectra were recorded on a Coderg CPH 100 instrument. Samples were presented in capillary tubes, the solids as small crystals, and the liquids neat.

The exciting wavelength was the 4880 Å argon line from a Coherent Radiation Model 52 Argon/Krypton Ion Laser.

Previously reported spectra of some C_6F_5Se-derivatives are also included here.

$(C_6F_5)_2Se$ (solid)
1643 s, 1589 w, 1519 w, 1448 w, 1426 w, 1408 s, 1309 w, 1291 w, 1280 m, 1260 w, 1146 w, 1095 w, 831 s, 821 m, 774 w, 757 w, 725 w, 657 w, 635 m, 590 vs, 537 w, 502 vs, 449 vs, 386 s, 364 s, 315 w, 287 m, 255 m, 247 w, 229 m, 180 w, 163 w.

$(C_6F_5)_2Se_2$ (solid)[5]
1628 m, 1391 s, 1277 w, 820 s, 625 w, 587 s, 497 s, 444 m, 389 m, 378 w, 374 w, 360 w, *280 vs*, 241 s, 224 m, 177 w, 162 s, 127 w.

C_6F_5SeH (liquid)
2530 w, *2333 s.br*, 1687 vw, 1639 s, 1584 w, 1513 w, 1425 w, 1407 s, 1390 w, 1288 m, 1275 w, 1260 w, 1225 w, 1146 w, 1086 w, 843 w, 822 s, 780 w, 725 m, 700 w, 647 vw, 612 m, 583 vs, 522 w, 495 vs, 443 s, 389 s, 361 m, 349 s, 283 m, 236 s, 215 w, 146 m.

$C_6F_5SeCH_3$ (liquid)
3025 m, 2946 s, 2829 w, 2544 w, 2528 w, 1645 m (sh), 1637 s, 1585 w, 1514 w, 1424 w, 1398 s, 1305 w, 1278 m, 1255 w, 1143 w, 1089 vw, 979 w, 913 w, 852 vw, 823 s, 773 w, 750 w, 713 w, 652 w, 623 m, 584 vs, 496 vs, 445 s, 388 s, 364 m, 315 w, 285 m, 246 s, 227 s, 198 m, 151 m.

$C_6F_5SeC_2H_5$ (liquid)
2970 m (sh), 2933 s, 2900 vw, 2877 m, 2843 w, 2741 w, 2543 w, 2527 w, 1636 s, 1583 vw, 1513 w, 1452 m, 1442 w, 1431 m, 1398 s, 1382 w, 1305 w, 1286 m, 1272 w, 1237 m, 1143 w, 1088 vw, 1051 m, 1012 w, 1000 w, 966 m, 852 w, 824 s, 774 w, 722 vw, 703 vw, 654 w, 625 m, 586 vs, 571 s, 552 vs, 497 vs, 446 s, 388 s, 363 m, 316 w, 299 m, 285 m, 240 m, 225 s, 185 m, 159 m, 134 w.

$C_6F_5SeCF_3$ (liquid)
2532 vw, 1657 w, 1638 s, 1518 w, 1445 w, 1427 w, 1408 s, 1388 w, 1318 vw, 1296 w, 1265 vw, 1170 vw, 1153 w, 1100 m, 1095 w, 1073 w, 1060 vw, 1047 vw, 986 vw, 858 vw, 829 s, 812 vw, 774 w, 746 vs, 716 vw, 660 vw, 634 w, 589 vs, 544 w, 534 vw, 499 vs, 388 s, 364 m, 333 vs, 302 s, 283 m, 224 vs, 208 vw, 180 vw, 152 m, 121 vw.

$(C_6F_5Se)_2Hg$ (solid)[5]
1635 m, 1394 m, 1288 w, 823 s, 622 m, 585 s, 497 s, 443 m, 394 m, 371 w, 361 w, 283 w, 241 s, 226 w, 200 vs, *174 s,* 149 s.

$C_6F_5SeO_2H$ (solid)
2655 w.br, 2560 w.br, 1642 m, 1391 w, 1141 w, 1114 w, 1104 m, *860 vs,* 809 m, *684 s,* 626 w, 587 vs, 495 vs, 444 s, 393 vs, 358 m, 324 w, 302 m, 280 m, 204 s, 187 m, 150 vs, 121 s.

APPENDIX C

^1H Nuclear Magnetic Resonance Spectra

The spectra were recorded at 60 MHz on a Varian A60 instrument. Tetramethylsilane was used as internal reference. In some spectra coupling with the 7.5% abundant ^{77}Se isotope ($I = \frac{1}{2}$) was observed as satellites appearing as doublets (a doublet of triplets in the spectrum of C_6F_5SeH[5]). For completeness previously reported spectra of C_6F_5Se derivatives are also included.

$C_6F_5SeCH_3$ (neat liquid)
7.45τ (singlet with $^{1}H-^{77}Se$ satellites, J = 13 cps.)

$C_6F_5SeCH_2CH_3$ (neat liquid)
6.88τ (quartet, J = 7.5 cps, 2H), 8.49τ (triplet, J = 7.5 cps, 3H)

$C_6F_5SeCH_2CH_2Br$ (solution in $CDCl_3$)[5]
6.48τ (multiplet, 2H), 6.76τ (multiplet, 2H)

$C_6F_5SeCH_2CH_2Cl$ (solution in $CDCl_3$)[5]
6.40τ (multiplet, 2H), 6.80τ (multiplet, 2H)

$C_6F_5SeCH_2COCH_3$ (neat liquid)
6.10τ (singlet with $^{1}H-^{77}Se$ satellites, J = 13 cps, 2H), 7.62τ (singlet, 3H)

$C_6F_5SeCH_2CO_2H$ (solution in $CDCl_3$)
6.42τ (singlet with $^{1}H-^{77}Se$ satellites, J = 16 cps, 2H), -1.35τ (singlet, 1H)

C_6F_5SeH (neat liquid)[5]
8.08τ (triplet $J[^{1}H-^{9}F_{ortho}]$ = 2.2 cps, with $^{1}H-^{77}Se$ satellites, J = 60 cps)

$C_6F_5SeN(CH_3)_2$ (neat liquid)
7.11τ (singlet)

$C_6F_5SeN(CH_2CH_3)_2$ (solution in CCl_4)
7.15τ (quartet, J = 7.0 cps, 2H), 8.80τ (triplet, J = 7.0 cps, 3H)

$(C_6F_5Se)_2NH$ (solution in $CDCl_3$)
5.4τ (singlet)

$C_6F_5SeCl_2CH_3$ (solution in CCl_4)
5.77τ (singlet)

$C_6F_5SeC_6H_5$ (solution in $CDCl_3$)
2.47τ (multiplet, 2H), 2.70τ (multiplet, 3H)

$C_6F_5Se(O)C_6H_5$ (solution in $CDCl_3$)
2.20τ (multiplet, 2H), 2.38τ (multiplet, 3H)

$C_6F_5SeCl_2C_6H_5$ (solution in CCl)
1.73τ (multiplet, 2H) 2.49τ (multiplet, 3H)

p-$(C_6F_5Se)C_6H_4NH_2$ (solution in $CDCl_3$)
2.53τ (doublet, J = 8.5 cps, 2H), 3.46τ (doublet, J = 8.5 cps, 2H), 6.22τ (singlet, 2H)

$2,4,6\text{-}(C_6F_5Se)_3C_6H_2OH$ (solution in $CDCl_3$)
2.33τ (singlet, 2H), 2.97τ (singlet, 1H)

$(\pi\text{-}C_5H_5)Fe(CO)_2SeC_6F_5$ (solution in $CDCl_3$)
4.95τ (singlet)

$(\pi\text{-}C_5H_5)Ni[P(C_6H_5)_3]SeC_6F_5$ (solution in $CDCl_3$)
2.38τ (multiplet, 18H), 4.86τ (singlet, 5H)

REFERENCES

1. Dale, J.W., Emeléus, H.J., Haszeldine, R.N. *J. Chem. Soc.* 2939 (1958)

2. Cohen, B., Peacock, R.D. *Advances Fluorine Chem.* 6, 343 (1970)

3. Burdon, J., Coe, P.L., Fulton, M. *J. Chem. Soc.* 2094 (1965)

4. Cohen, S.C., Reddy, M.L.N., Massey, A.G. *Chem. Comm.* 451 (1967)

5. Poole, R.T. M.Sc. Thesis. Memorial, Canada. (1970)

6. Campbell, T.W., Walker, H.G., Coppinger, G.M. *Chem. Rev.* 50, 279 (1952)

7. Bagnall, K.W. *The Chemistry of Selenium, Tellurium and Polonium.* Elsevier, Amsterdam. (1966), Chapter 7.

8. Fredga, A. *Annals New York Academy of Sciences.* 192, 1 (1972)

9. Banks, R.E. *Fluorocarbons and their Derivatives.* Ed. 2, Oldbourne Press, London, (1970), p.4.

10. International Union of Pure and Applied Chemistry. *Nomenclature of Organic Chemistry.* Butterworth, London (1970).

11. Nyholm, R.S., Skinner, J.F., Stiddard, M.H.B. *J. Chem. Soc., A.* 38 (1968)

12. Osborne, A.G., Stone, F.G.A. *J. Chem. Soc., A.* 1143 (1966)

13. Okamoto, Y., Yano, T., Homsany, R. *Annals New York Academy of Sciences.* 192, 60 (1972)

14. Walter, R., Schwartz, I.L., Roy, J. *Annals New York Academy of Sciences.* 192, 175 (1972)

15. Mautner, H.G. *Annals New York Academy of Sciences.* 192, 167 (1972)

16. Gosselck, J. *Angew. Chem. Internat. Edit.* 2, 660 (1963)

17. Sheppard, W.A. *J. Amer. Chem. Soc.* 93, 5597 (1971)
Sheppard, W.A., Foster, S.S. *J. Fluorine Chem.* 2, 53 (1973)

18. Cohen, S.C., Reddy, M.L.N., Massey, A.G. *J. Organometal. Chem.* 11, 563 (1968)

19. Wittig, G., Fritz, H. *Liebigs Ann. Chem.* 577, 39 (1952)

20. Hellwinkel, D. *Annals New York Academy of Sciences.* 192, 158 (1972)

21. Behagel, O., Muller, W. *Ber.* 68, 1540 (1935)

22. Wynne, K.J., Puckett, J. *Chem. Commun.* 1532 (1968)

23. Wynne, K.J. *Inorg. Chem.* 9, 299 (1970)

24. Wynne, K.J. *Annals New York Academy of Sciences.* 192, 107 (1972)

25. Wynne, K.J., Pearson, P.S. *Inorg. Chem.* 11, 1196 (1972)

26. Bird, M.L., Challenger, F. *J. Chem. Soc.* 570 (1942)

27. Livingstone, S.E. *Quart. Rev.* 19, 386 (1965)

28. George, J.W. *M.T.P. International Review of Science. Inorganic Chemistry, Series One.* Vol. 2, London, Butterworth, (1971)

29. Hieber, W., Stanner, F. *Chem. Ber.* 102, 2930 (1969)

30. Rosenbuch, P., Welcman, N. *J.C.S. Dalton.* 1963 (1972)

31. Andra, V.K. *Z. Anorg. Chem.* 373, 209 (1970)

32. Marsden, C.J., Sheldrick, G.M. *J. Organometal. Chem.* 40, 175 (1972)

33. Marsden, C.J., Sheldrick, G.M. *J. Mol. Structure.* 10, 405 (1971)

34. Marsden, C.J., Sheldrick, G.M. *J. Mol. Structure.* 10, 413 (1971)

35. Marsden, C.J., Sheldrick, G.M. *J. Mol. Structure.* 10, 419 (1971)

36. Bomford, D.R.L. M.Sc. Thesis. Sussex, England. (1968)

37. Wahi, P.K. M.Sc. Thesis. Memorial, Canada. (1973)

38. Cohen, S.C., Massey, A.G. *Adv. Fluorine Chem.* 6, 83 (1970)

39. Chambers, R.D., Coates, G.E., Livingstone, J.G., Musgrave, W.K.R. *J. Chem. Soc.* 4367 (1962)

40. Wall, L.A., Donadio, R.E., Plummer, W.J. *J. Amer. Chem. Soc.* 82, 4846 (1960)

41. Sheppard, W.A. *J. Amer. Chem. Soc.* 92, 5419 (1970)

42. Kemmitt, R.D.W., Nichols, D.I., Peacock, R.D. *J. Chem. Soc., A.* 2149 (1968)

43. Massey, A.G., Park, A.J. *J. Organometal. Chem.* 2, 245 (1964)

44. Hogben, M.G., Graham, W.A.G. *J. Amer. Chem. Soc.* 91, 283 (1969)

45. Hogben, M.G., Gay, R.S., Oliver, A.J. Thompson, J.A.J., Graham, W.A.G. *J. Amer. Chem. Soc.* 91, 291 (1969)

46. Churchill, M.R., O'Brien, T.A. *J. Chem. Soc., A.* 2970 (1968)

47. Churchill, M.R., O'Brien, T.A. *J. Chem. Soc., A.* 266 (1969)

48. Massey, A.G., Park, A.J. *J. Organometal. Chem.* 5, 218 (1966)

49. Krause, E., Nitsche, R. *Ber.* 55B, 1261 (1922)

50. Massey, A.G., Park, A.J., Stone, F.G.A.
Proc. Chem. Soc. 212 (1963)

51. Churchill, M.R., Fennessey, J.P.
Inorg. Chem. 6, 1213 (1967)

52. Banks, R.E. *Fluorocarbons and their Derivatives.*
Ed. 2, Oldbourne Press, London, (1970)

53. Kinsella, E., Massey, A.G. *Chem. Brit.*
7, 457 (1971)

54. Toope, K. Personal Communication.

55. Thompson, J.A.J., Graham, W.A.G.
Inorg. Chem. 6, 1875 (1967)

56. Cordey-Hayes, M. *J. Inorg. Nucl. Chem.*
26, 915 (1964)

57. Massey, A.G., Randall, E.W., Shaw, D.
Chem. Ind. London, 1244 (1963)

58. Fild, M., Hollenberg, I., Glemser, O.
Z. Naturf. 22B, 248 (1967)

59. Kostiner, E., Reddy, M.L.N., Urch, D.S., Massey, A.G.
J. Organometal. Chem. 15, 383 (1968)

60. Cohen, S.C., Massey, A.G. *J. Organometal. Chem.* 12, 341 (1968)

61. Neil, R.J., Peach, M.E. *J. Fluorine Chem.*
1, 257 (1971-2)

62. Clase, H.J. Ph.D. Thesis. Cambridge, England, (1963)

63. Jellinek, F. *Proc. Chem. Soc.* 319 (1959)

64. Beck, W., Tadros, S. *Z. Anorg. Chem.*
375, 231 (1970)

65. Clase, H.J., Ebsworth, E.A.V. *J. Chem. Soc.*
940 (1965)

66. Beck, W., Stetter, K.H., Tadros, S., Schwarzhans, K.E.
Chem. Ber. 100, 3944 (1967)

67. Moeller, T. *J. Phys. Chem.* 48, 111 (1944)

68. Kosower, E.M., Martin, R.L., Meloche, V.W. *J. Amer. Chem. Soc.* 79, 1509 (1957)

69. Cotton, F.A., Wilkinson, G. *Advanced Inorganic Chemistry.* Ed. 3, New York, Interscience Publishers, (1972), p.905.

70. Gangopadhayay, A.K., Chakravorty, A. *J. Chem. Phys.* 35, 2206 (1961)

71. Figgis, B.N., Lewis, J. *Modern Coordination Chemistry.* Ed. Lewis, J., Wilkins, R.G., New York, Interscience Publishers, (1964), Ch. 6.

72. Kato, M., Jonassen, H.B., Fanning, J.C. *Chem. Rev.* 64, 99 (1964)

73. Cotton, F.A., Goodgame, D.M.L., Goodgame, M. *J. Amer. Chem. Soc.* 83, 4690 (1961)

74. Ahrland, S., Chatt, J., Davies, N.R. *Quart. Rev.* 12, 265 (1958)

75. Tanabe, Y., Sugano, S. *J. Phys. Soc. Japan.* 9, 753 (1954)

76. Cotton, F.A., Goodgame, M. *J. Amer. Chem. Soc.* 83, 1777 (1961)

77. Beck, W., Fehlhammer, W.P., Stetter, K.H., Tadros, S. *Chem. Ber.* 100, 3955 (1967)

78. Cotton, F.A., Goodgame, D.M.L., Goodgame, M., Sacco, A. *J. Amer. Chem. Soc.* 83, 4157 (1961)

79 Phillips, C.S.G., Williams, R.J.P. *Inorganic Chemistry.* Vol. II, New York, Oxford University Press, (1966), p.397.

80. Jorgensen, C.K. *Oxidation Numbers and Oxidation States.* New York, Springer, (1969), Ch. 7.

81. Lever, A.B.P. *Inorganic Electronic Spectroscopy.* Elsevier, Amsterdam, (1968), Ch. 8.

82. Beck, W., Fehlhammer, W.P., Pollmann, P., Schuierer, E., Feldl, K. *Chem. Ber.* 100, 2335 (1967)

83. Schmidtke, H.H. *Ber. Bunsenges. Physik. Chem.* 71, 1138 (1967)

84. Welcman, N., Rot, I. *J. Chem. Soc.* 7515 (1965)

85. Welcman, N., Josef, A. *Israel J. Chem.* 6, (Proc.) 33 (1968)

86. Abel, E.W., Cross, B.C., Hutson, G.V. *J. Chem. Soc., A.* 2014 (1967)

87. Grobe, J. *Z. Anorg. Chem.* 331, 63 (1964)

88. Faraone, F., Sergi, S., Pietropaolo, R. *J. Organometal. Chem.* 24, 453 (1970)

89. Cooke, J., Green, M., Stone, F.G.A. *J. Chem. Soc., A.* 170 (1968)

90. Hagihara, N., Kumada, M., Okawara, R. *Handbook of Organometallic Compounds.* New York, Benjamin, (1968), p.867.

91. Hileman, J.C., Huggins, D.K., Kaesz, H.D. *Inorg. Chem.* 1, 933 (1962)

92. Orgel, L.E. *Inorg. Chem.* 1, 25 (1962)

93. Welcman, N. Private Communication, (1972)

94. Kostiner, E., Massey, A.G. *J. Organometal. Chem.* 19, 233 (1969)

95. Moedritzer, K. *Synthesis Inorg. Metal-org. Chem.* 1, 63 (1971)

96. Tolman, C.A. *Chem. Soc. Reviews.* 1, 337 (1972)

97. Abel, E.W. *Quart. Rev.* 17, 133 (1963)

98. Hammet, L.P. *Physical Organic Chemistry.* Ed. 2, New York, McGraw-Hill, (1970), Ch.11.

99. Porrit, W.H. *J. Chem. Soc.* 27 (1927)

100. Behagel, O., Hofmann, K. *Ber.* 72, 697 (1939)

101. Emeléus, H.J., Welcman, N. *J. Chem. Soc.* 1268 (1963)

102. Bauser, H.W., Gibson, C.S., Pope, W.J. *Trans. Chem. Soc.* 117, 1453 (1920)

103. Yarovenka, N.N., Shemanina, V.N., Gazieva, G.B. *Zhur. Obshchei. Khim.* 29, 942 (1959)

104. Welcman, N., Regev, H. *J. Chem. Soc.* 7511 (1965)

105. Peach, M.E., Spinney, H.G. *Can. J. Chem.* 49, 644 (1971)

106. Yagupol'skii, L.M., Voloshchuk, V.G. *Zhur. Obshchei. Khim.* 36, 165 (1966)

107. Emeléus, H.J., Nabi, S.N. *J. Chem. Soc.* 1103 (1960)

108. Andreades, S., Harris, Jr., J.F., Sheppard, W.A. *J. Org. Chem.* 29, 898 (1964)

109. Neal, R.S., Schepers, R.G., Walsh, M.R. *J. Org. Chem.* 29, 3390 (1964)

110. Gassman, P.G., Campbell, G.A., Frederick, R.C. *J. Amer. Chem. Soc.* 94, 3884 (1972)

111. Gassman, P.G., Campbell, G.A. *J. Amer. Chem. Soc.* 94, 3891 (1972)

112. Neil, R.J. M.Sc. Thesis. Acadia University, Canada. (1971)

113. Bentley, M.D., Douglas, I.B., Lacadie, J.A., Weaver, D.C. *Chem. Comm.* 1625 (1971)

114. Noller, C.R. *Text Book of Organic Chemistry.* Ed. 3, (1966), pp.420, 439.

115. Maruca, R. *J. Chem. Ed.* 47, 301 (1970)

116. Vogel, A.I. *Practical Organic Chemistry.* Ed. 3, London, Longmans, (1962), p.756.

117. Baker, J.W., Moffitt, W.G. *J. Chem. Soc.* 1722 (1930)

118. Lagowski, J.J. *Quart. Rev.* 13, 233 (1959)

119. Yagupol'skii, L.M., Voloshchuk, V.G. *J. Gen. Chem. U.S.S.R.* 37, 1463 (1967)

120. Foster, D.G., Brown, S.F. *J. Amer. Chem. Soc.* 50, 1182 (1928)

121. Chambers, R.D., Cunningham, J.A., Spring, D.J. *J. Chem. Soc., C.* 1560 (1968)

122. Wahi, P.K. Private Communication.

123. Behagel, O., Hofmann, K. *Ber.* 72, 697 (1939)

124. Rheinboldt, H., Giesbrecht, E. *J. Amer. Chem. Soc.* 69, 644 (1947)

125. Foster, D.G. *J. Amer. Chem. Soc.* 55, 822 (1933)

126. Paetzold, R., Wolfram, E. *Z. Anorg. Chem.* 353, 167 (1967)

127. Sheppard, W.A. *J. Amer. Chem. Soc.* 84, 3058 (1962)

128. Sheppard, W.A. *J. Amer. Chem. Soc.* 84, 3064 (1962)

129. Katsaros, N., George, J.W. *J. Inorg. Nucl. Chem.* 31, 3503 (1969)

130. Feher, F. *Handbook of Preparative Inorganic Chemistry*. Ed. Brauer, G., ed.2, vol.1, New York, Academic Press, (1963), p.425.

131. Robson, P., Smith, T.A., Stephens, R., Tatlow, J.C. *J. Chem. Soc.* 3692 (1963)

132. Bagnall, K.W. *The Chemistry of Selenium, Tellurium and Polonium.* Elsevier, Amsterdam, (1966), p.63.

133. Long, D.A., Steele, D. *Spectrochim. Acta.* 19, 1947 (1963)

134. Long, D.A., Steele, D. *Spectrochim. Acta.* 19, 1955 (1963)

135. Hyams, I.J., Lippincott, E.R., Bailey, R.T. *Spectrochim. Acta.* 22, 695 (1966)

136. Frankiss, S.G. *J. Mol. Structure.* 3, 89 (1969)

137. Hopf, G., Paetzold, R. *J. Mol. Structure.* 13, 361 (1972)

138. Paetzold, R., Borek, S., Wolfram, E. *Z. Anorg. Chem.* 353, 53 (1967)

139. Sheppard, N. *Trans. Faraday Soc.* 46, 429 (1950)

140. Lawrenson, I.J. *J. Chem. Soc.* 1117 (1965)

141. Hogben, M.G., Gay, R.S., Graham, W.A.G. *J. Amer. Chem. Soc.* 88, 3457 (1966)

142. Cotton, F.A., Wilkinson, G. *Advanced Inorganic Chemistry.* Ed. 3, New York, Interscience Publishers, (1972), p.722.

143. Boden, N., Emsley, J.W., Feeney, J., Sutcliffe, L.H. *Mol. Phys.* 8, 133 (1964)

144. Grant, D.M., Hirst, R.C., Gutowsky, H.S. *J. Chem. Phys.* 38, 470 (1963)

145. Peach, M.E. *Can. J. Chem.* 46, 2699 (1968)

146. Nyholm, R. *Quart. Rev.* 24, 1 (1970)