

Presidential Address

Transition-metal Complexes of Some Perfluoro-ligands

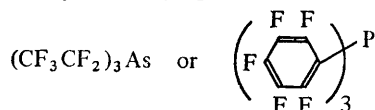
By Sir Ronald Nyholm, F.R.S.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE LONDON,
GOWER ST., LONDON, W.C.1

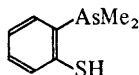
(Delivered at Nottingham, 16th April, 1969)

Introduction

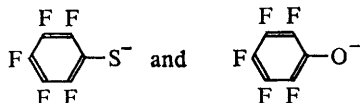
The past two decades have seen a rapid development in organic fluorine chemistry. This has resulted in the availability of suitable intermediates from which fluoro- and perfluoro-ligands can now be synthesised readily and those interested need not be specially skilled in synthetic organo-fluorine chemistry as such. This has led to the preparation and use of many new fluorinated ligands and the range of these is now quite extensive. We use the term 'fluoro-ligand' to mean one in which *some* of the hydrogen atoms have been replaced by fluorine, *e.g.* $(\text{CF}_3\text{CH}_2)_3\text{As}$; a 'perfluoro-ligand' is one in which *all* hydrogen atoms have been replaced by fluorine, *e.g.*



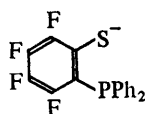
The complexes obtained between these fluorinated ligands and transition metals in particular have often been found to display marked stability and to possess unusual properties. Our interest in fluoro-ligands was derived initially from a desire to incorporate in a chelate molecule the equivalent of a Cl^- ion. Thus the compound



is *formally* the equivalent of one mole of PhAsMe_2 , and one mole of a weak acid. Ligands such as



have therefore been investigated as the equivalent Cl^- , *i.e.* anions of strong acids. The properties of chelate ligands such as



which combine a strong acid and a neutral donor should prove of considerable interest.

We discuss here the following aspects of this subject:

1. Relevant properties of fluorine.
2. Classification of perfluoro-ligands.
3. Survey of complexes of PF_3 and other ligands in which F is attached to the donor atom.
4. Synthesis and properties of perfluoro-alkyl and perfluoro-aryl complexes.
5. The nature of the metal-carbon bond in perfluoro-alkyl and -aryl metal complexes.
6. Complexes of ligands in which fluorine is substituted on atoms distant from the donor atom.

Particular attention is paid to perfluoro-ligands, but some reference will be made to partially substituted ligands (*e.g.* tetrafluorodiarisine).

1 Relevant Properties of Fluorine

The properties of fluorine are dependent partly upon its strong electron attracting power, expressed by the highest electronegativity of all elements, partly upon the presence of lone pairs of electrons potentially available for π bonding to other atoms, and partly upon its size. It is useful to summarise in advance certain properties of fluorine in relation to the other halogens and hydrogen in Table I.

Table 1 *Properties of the halogens and hydrogen*

<i>Element</i>	<i>H</i>	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Ionisation potential (eV)	13.595	17.42	13.01	11.84	10.45
Electron affinity (eV)	0.7	3.48	3.69	3.45	3.15
Pauling electronegativity	2.20	3.98	3.16	2.96	2.66
Dissociation of X_2^1 (kcal/mole)	103.3	37.0	57.1	45.4	35.6
Covalent radius (Å)	0.30	0.64	0.99	1.14	1.33
Bond energy of $\text{H}-\text{X}^1$ (kcal/mole)	103.3	134.9	102.2	86.5	70.5

The high electronegativity of fluorine explains the strong inductive effect which leads to an increase in the acid strength of compounds such as perfluorophenol as compared with phenol. Also, since the strength of a covalent bond, for bonds of the same type, is roughly proportional to the product of the electronegativities of the bonded atoms, covalent bonds to fluorine are specially strong (*cf* the hydrogen halides in Table 1). The inductive effect of the fluorine atoms diminishes

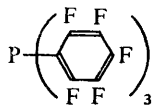
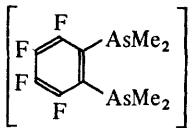
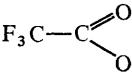
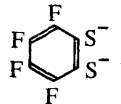
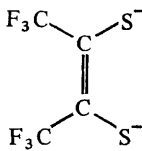
¹ A. G. Gaydon, 'Dissociation Energies', Chapman and Hall, London, 3rd edn., 1968.

as the position of substitution from the donor atom increases, as discussed below. The lone pairs on fluorine atoms, combined with the small covalent radius of fluorine, can increase or decrease the strength of the bond to the atom to which fluorine is attached depending upon whether there are vacant orbitals of the correct symmetry on the second atom (as in PF_3), or lone pairs thereon (as in F_2) respectively. The higher inter-electron repulsion in the $2s2p^3$ shell of the fluorine atom as compared with that in the $3s3p^3$ shell of chlorine is generally assumed to explain why the electron affinity of fluorine is lower than chlorine. On the other hand, the proximity of the lone pairs on the two adjacent fluorine atoms in F_2 explains its low bond energy compared with that of Cl_2 , even though the electronegativity product of fluorine is larger than that of chlorine.

2 Classification of Fluorine-substituted Ligands

It is convenient to classify these with three features in mind. First, the position of the fluorine substituent with respect to the donor atom; secondly, whether the donor atom carries a charge; and thirdly, the extent to which π delocalisation occurs in the ligand. Table 2 shows how such a classification enables ligands

Table 2 Types of perfluoro-ligands

	<i>Examples</i>
1. Fluoride Ion	{ Uncharged $\text{R}-\text{F}$, $\text{H}-\text{F}$ (H Bonding only) Charged F^- (Class A Ligand)
2. F on Donor Atom	{ Uncharged NF_3 , PF_3 , SF_4 Charged $-\text{CF}_3^-$, $-\text{PF}_2^-$
3. F on Atom ONE Removed from Donor	{ Uncharged $\text{N}(\text{CF}_3)_3$, $\text{P}(\text{CF}_3)_3$ -----* Charged† C_6F_5^-
4. F on Atom TWO Removed from Donor	{ Uncharged $\text{P}(\text{C}_6\text{F}_4)_3$  $\left[\text{C}_6\text{F}_4(\text{AsMe}_2)_2 \right]$  Charged $\text{F}_3\text{C}-\text{C}(\text{O})_2^-$,  ,  ,  $\text{C}_6\text{F}_5\text{O}^-$, $\text{C}_6\text{F}_5\text{S}^-$

* Ligands shown below this line have delocalised π systems.

† The (unstable) CF_3S^- anion derived from MeSH is also in this category.

to be subdivided in this way. In this survey we consider σ bonded perfluoro-ligands only. Only a few π -type perfluoro-complexes, *e.g.* of C_2F_4 , are known.²

3 Survey of Complexes of PF_3 and Other Ligands in which F is Attached to the Donor Atom

(i) Direct attachment of the fluoride ion occurs in covalent metallic fluorides. The fluoride ion behaves as a good ligand towards Class A metals (*e.g.* Mg^{2+} , Al^{3+} , Th^{4+}) even in aqueous solution; for these metals stability constant data indicate that the halide ions are attached in the order $F^- > Cl^- > Br^- > I^-$. However, F^- can also form strong bonds to Class B metals in the absence of water, and similar solvents, as evidenced by the stabilisation of Pt^{VI} in PtF_6 . It should be borne in mind that if a Class B metal ion forms a covalent $M-F$ bond, this will usually be stronger than an $M-Cl$, an $M-Br$ or an $M-I$ bond but, in the presence of water, the highest solvation energy of the F^- ion often leads to a lower stability constant in solution as compared with the other halide ions. Except for hydrogen bonding between the fluorine atom and a proton in the $[HF_2]^-$ ion, fluorine in alkyl or aryl halides and in hydrogen fluorides shows virtually no tendency to donate its lone pairs to metal atoms.

(ii) When fluorine is attached to the donor atom, its effect is to decrease the donor capacity of the lone pair in σ bond formation but, when there are vacant orbitals on the donor atom, it can enhance the acceptor capacity of that atom provided that the acceptor vacant orbital is of the appropriate size and symmetry to overlap with a filled d orbital of the metal. Considering first uncharged ligands, the Group V and VI fluorides only need concern us. Substitution of hydrogen by fluorine in ammonia or water greatly diminishes σ donor capacity to metals and of course there are no vacant d orbitals to receive electrons in $d\pi$ bond formation. (The effect of antibonding p orbitals on the N or O appears to be negligible in saturated compounds but they may be important in complexes of pentafluoropyridine.) Of the later Group V elements, the fluorides of PF_3 only appear to have been investigated in detail, although AsF_3 , SbF_3 , and BiF_3 may behave similarly unless they act as fluorinating agents. Group VI fluorides of the type SF_4 with one lone pair might be expected to behave like PF_3 but so far SF_4 has been found to behave mainly as a reactive fluorinating agent.³

Following the first preparation of $Ni(PF_3)_4$ by Wilkinson,⁴ we are indebted to Kruck for most of the detailed investigation of the chemistry of PF_3 complexes, summarised in his review.⁴ This ligand is capable of stabilising transition metals in low oxidation states, and derivatives corresponding to complete replacement of carbon monoxide from the equivalent metal carbonyl can be prepared as shown in Table 3. It is noteworthy, however, that PF_3 forms derivatives such as $Pd(PF_3)_4$ and $Pt(PF_3)_4$ for which the corresponding metal tetracarbonyls are unstable or unknown, at least at room temperatures.

² G. Parshall and R. Cramer, *J. Amer. Chem. Soc.*, 1965, **87**, 392.

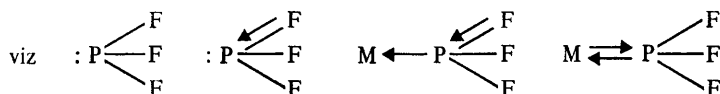
³ W. Sheppard, E. I. du Pont de Nemours and Co., 1969, personal communication.

⁴ G. Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501.

Table 3 Trifluorophosphine metal (O) compounds

VI	VII	VIIIA	VIIIB	VIIIC
Cr(PF ₃) ₆ m.p. 193°	—	Fe(PF ₃) ₅ m.p. 45°	[Co(PF ₃) ₄] _x	Ni(PF ₃) ₄ m.p. -55° b.p. 70.5°
(-CO, Sublimes)	(-CO, m.p. 154°)	(-CO, m.p. -20°)	(-CO, m.p. 51°)	(-CO, m.p. -25°) b.p. 43°)
Mo(PF ₃) ₆ m.p. 196°	—	Ru(PF ₃) ₅ m.p. 30°	[Rh ₂ (PF ₃) ₆]	Pd(PF ₃) ₄ m.p. -41° decomp. -20°
(-CO, Sublimes)	(-CO, m.p. 160°)	(-CO, m.p. -22°)	(-CO, m.p. 76°)	(-CO, unknown)
W(PF ₃) ₆ m.p. 214°	[Re ₂ (PF ₃) ₁₀] m.p. 182°	Os(PF ₃) ₅ m.p. ?	—	Pt(PF ₃) ₄ m.p. -15° b.p. 86°
(-CO, Sublimes)	(-CO, m.p. 177°)	(-CO, m.p. -15°)	(-CO, m.p. ?)	(-CO, unknown)

A study of the P—F stretching frequency of PF₃ complexes⁵ enables one to infer much about the nature of the metal—P bond, in the same way that the C—O stretching frequency in metal carbonyls has been used. However, interpretation of the results is made more difficult because F \rightleftharpoons P or M \rightleftharpoons P double bonding or both types may take place. If we assume that there is some P \rightleftharpoons F



double bonding in free PF₃, then an increase in P—F stretching frequency in a complex, such as Ni(PF₃)₄, is expected simply because donation of the 'non-bonding' lone pair of the P atom to the metal should increase the capacity of the P atom to attract electron pairs from the fluorine atoms. This is presumed to occur in the first group of compounds shown in Table 4; these consist of monomeric PF₃ complexes of the Cr, Mo, and W congeners and the hydrometal PF₃ derivatives of Co, Rh, and Ir because P—F stretching frequencies higher than in PF₃ are observed. When, however, one places a negative charge on the complex anion, as in [Co(PF₃)₄]⁻, the maximum P—F stretching frequency is observed at a lower frequency. The formal negative charge on the metal apparently increases the size of the non-bonding *d* orbitals thus enhancing metal \rightarrow phosphorus π bonding as in metal carbonyl anions; this in turn decreases the P—F bond order as is observed. Force constant calculations indicate that the

⁵ Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, 6, 53.

Ni—P bond in Ni(PF₃)₄ (2.71 mdyne/Å) is little different from that of Ni—C in Ni(CO)₄ (2.52 mdyne/Å). The powerful electron withdrawing power of PF₃ is also indicated by the fact that the Re—Cl stretching frequency in Re(PF₃)₅Cl is 37 cm⁻¹ higher than in Re(CO)₅Cl⁶. It will be noted that when one replaces one or more PF₃ groups in a neutral complex [*e.g.* Ni(PF₃)₄] by a weaker π -bonding ligand, *e.g.* Ph₃P, there is a decrease in the P—F stretching frequency as compared with free PF₃. As with the [Co(PF₃)₄]⁻ anion this suggests that greater metal—PF₃ double bonding has decreased the donation of lone pairs from fluorine to phosphorus.

Table 4 Phosphorus–fluorine stretching frequencies of PF₃ and its complexes

Compound	P–F Frequency (cm ⁻¹)
PF ₃	892, 848
HCo(PF ₃) ₄	961, 917, 907, 867
HRh(PF ₃) ₄	949, 912, 904, 863
HIr(PF ₃) ₄	965, 925, 910, 877
Cr(PF ₃) ₆	916, 851
Mo(PF ₃) ₆	911, 853
W(PF ₃) ₆	914, 852
Fe(PF ₃) ₅	915, 901, 873, 864, 851
Ru(PF ₃) ₅	926, 906, 876, 856
Ni(PF ₃) ₄	904, 864
Pd(PF ₃) ₄	910, 860
Pt(PF ₃) ₄	906, 867
[Co(PF ₃) ₄] ⁻	820, 804
[Rh(PF ₃) ₄] ⁻	814, 794
[Ir(PF ₃) ₄] ⁻	830, 811
Ni(PF ₃) ₃ (PPh ₃)	856, 824
Ni(PF ₃) ₂ (PPh ₃) ₂	815, 800
[Co(PF ₃) ₃ (PPh ₃)] ⁻	873, 821, 788, 775, 749

4 Synthesis and Properties of Perfluoroalkyl and Perfluoroaryl Complexes

A considerable number of perfluoro-metal complexes involving charged ligands of carbon (CF₃⁻, CF₃CH₂⁻, CF₂=CF⁻) and of phosphorus (PF₂⁻), *e.g.* [(PF₃)₃CoPF₂]₂, are now known⁷ but the perfluoro-carbon derivatives of the transition metals have been prepared only during the past few years. Indeed, Lagowski⁸ in his review of perfluoroalkyl derivatives of metals and non-metals

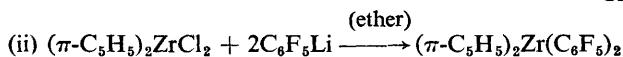
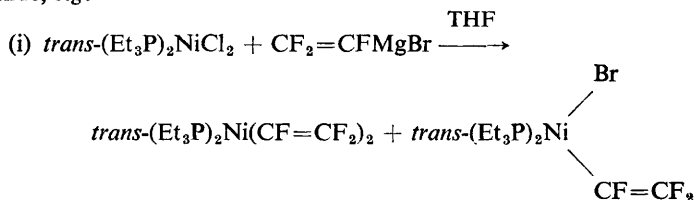
⁶ Th. Kruck, A. Engelmann, and W. Lang, *Chem. Ber.*, 1966, **99**, 2473.

⁷ Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1967, **6**, 454.

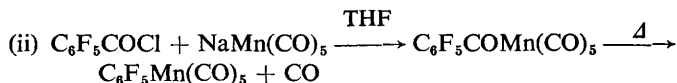
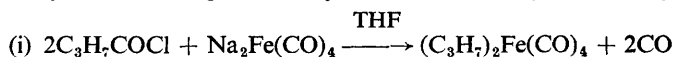
⁸ J. J. Lagowski, *Quart. Rev.*, 1959, **13**, 233.

in 1959 did not mention any transition-metal compounds. More recently in 1963 H. C. Clark⁹ states that 'there have been only a few brief reports of the preparation of such (*i.e.* transition metal) derivatives and full details have yet to be published. . . . Obviously this field of perfluoro-alkyl chemistry is, as yet, virtually untouched.' The main reason for the absence of these compounds was undoubtedly the lack of suitable preparative methods. This deficiency has been remedied in recent years using Grignard and other techniques; these have been summarised by Stone and Treichel¹⁰ and by Stone¹¹ in reviews of the subject. These methods are summarised below for both perfluoro-alkyl and perfluoroaryl (C₆F₅-) derivatives. (See also appendix, p. 19.)

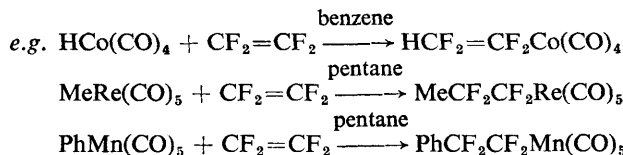
(1) Reaction of a Grignard or organo-lithium reagent with a complex metal halide, *e.g.*



(2) Double decomposition *via* the reaction of an alkali-metal salt of a metal carbonylanion with a perfluoroacyl halide followed by loss of CO, *e.g.*



(3) Insertion of a perfluoro-olefin in an M—H bond of a carbonyl metal hydride or a metal-alkyl or -aryl bond of a metal carbonyl alkyl or aryl. Strictly speaking this does not yield a perfluoro-alkyl derivative but the carbon atom attached to the metal is fully fluorinated,



⁹ H. C. Clark, *Adv. Fluorine Chem.*, 1963, 3, 19.

¹⁰ P. M. Treichel and F. G. A. Stone, *Advances in Organometallic Chemistry*, 1964, 1, 143.

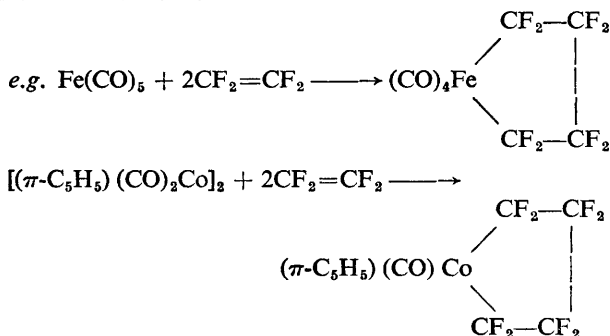
^{10a} See also F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1966, 1326.

^{10b} M. G. Hogben and W. G. A. Graham, *J. Amer. Chem. Soc.*, 1969, 91, 283; M. G. Hogben, A. S. Gray, A. J. Oliver, J. A. J. Thompson, and W. G. A. Graham, *J. Amer. Chem. Soc.*, 1969, 91, 291.

¹¹ F. G. A. Stone, *Endeavour*, 1966, 25, 33; M. I. Bruce and F. G. A. Stone, *Angew. Chem. Internat. Edn.*, 1968, 7, 747; see also references therein.

Transition-metal Complexes of Some Perfluoro-ligands

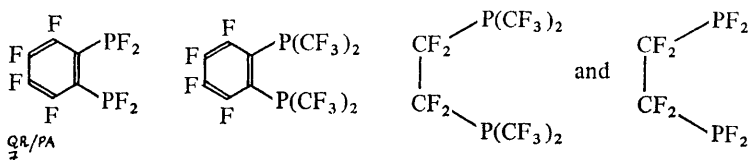
- (4) Direct reaction of a perfluoro-olefin with a metal carbonyl, in effect an oxidation of the metal:



- (5) Oxidation of a metal carbonyl compound with a perfluoro-alkyl iodide,
e.g. $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2 + \text{CF}_3\text{I} \xrightarrow{\text{benzene}} (\pi\text{-C}_5\text{H}_5)(\text{CO})\text{ICoCF}_3$

The effective electronegativity of the perfluoroalkyl group and the stability of perfluoroalkyl compounds generally will be discussed below.

(iii) Next we consider perfluoro-complexes in which the fluorine atom is attached to the atom(s) one removed from the donor. Uncharged ligands of this type include $\text{N}(\text{CF}_3)_3$ and $\text{P}(\text{CF}_3)_3$. The former is expected to be a very poor σ donor and, like NF_3 , unable to accept π electrons from the metal atom (except *via* anti-bonding p_{π}^* orbitals). No derivatives of $\text{N}(\text{CF}_3)_3$ appear to have been reported. Metal complexes of $\text{P}(\text{CF}_3)_3$ has been studied by Emeléus¹² and others. It behaves as a poor σ donor and a reasonably good π acceptor but few complexes have been investigated in detail. In general it forms less stable complexes than those of PF_3 . In view of the enhancement of stability arising from chelation, bidentate groups such as



should yield complexes of much greater stability but the ligands have not yet been reported. Charged fluoro-ligands such as CF_3CH_2^- in which the fluorine atom exerts its effect through a CH_2 group appear not to have been studied but presumably ligands such as this will be intermediate in behaviour between the ethyl and perfluoro-ethyl group, probably resembling more the ethyl group.

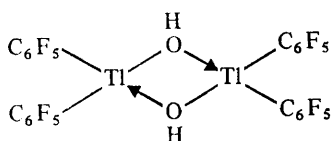
The charged ligand C_6F_5^- is of special interest because it combines two unique features. Although the nearest fluorine atom is on an atom one removed from the donor carbon atom, there are five fluorine atoms around the ring exerting

¹² H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 1958, 527.

an inductive effect. Also, there exists here the π delocalisation effect which ensures that the effect of the fluorine atoms at the donor carbon is greater than in, say, the CF_3CH_2^- group. As shown by Stone¹⁰ and his collaborators perfluorophenyl bromide or iodide, conveniently prepared from hexafluorobenzene, can be used to prepare a Grignard or a lithio-compound; these react with covalent metal halide bonds such as in *trans*- $[\text{Et}_3\text{P}]_2\text{PtCl}_2$ to yield derivatives such as *trans*- $[\text{Et}_3\text{P}]_2\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}$ and *cis*- $[\text{Et}_3\text{P}]_2\text{Pt}(\text{C}_6\text{F}_5)_2$. This type of reaction has yielded a considerable number of transition-metal and post transition-metal complexes.

Another general method has recently been reported¹³ from our laboratories which involves the use of bis(pentafluorophenyl)thallium(III) bromide as an oxidising agent for the transfer of C_6F_5 -groups to a transition metal in a 'low' oxidation state. A simple example is the oxidation of triphenylphosphine gold(I) chloride, *viz.* $2\text{Ph}_3\text{P} \rightarrow \text{AuCl} + [(\text{C}_6\text{F}_5)_2\text{TlBr}]_2 \rightarrow 2\text{Ph}_3\text{P} \rightarrow \text{Au}(\text{C}_6\text{F}_5)_2\text{Cl} + \text{TlBr}$. The reaction is carried out in benzene solution and on warming, or in some cases, under reflux a nearly quantitative transfer of the C_6F_5 -groups occurs with the precipitation of thallium(I) bromide. In the square complex $\text{Au}(\text{PPh}_3)(\text{C}_6\text{F}_5)_2\text{Cl}$ the two C_6F_5 -groups are *cis*.^{13a}

This work arose out of an investigation¹⁴ of the reduction of thallium(III) compounds in an attempt to prepare derivatives with a Tl—Tl bond. Simple alkyl and aryl derivatives of thallium(III) are usually salt-like derivatives of 2-co-ordinate thallium, *e.g.* $[\text{Et—Tl—Et}]^+\text{Cl}^-$. In order to obtain a 4-co-ordinate thallium(III) complex a more electronegative ligand than C_2H_5 is needed; the dimeric C_6F_5 compound $[(\text{C}_6\text{F}_5)_2\text{TlBr}]_2$ was prepared for this purpose. The structure is unknown but is presumably similar to that of the 2-co-ordinate bridged thallium(III) hydroxide obtained by treatment with alkali;



the crystal structure of this has been determined by Bright and Truter.¹⁵ Earlier Nesmeyanov¹⁶ had shown that $(\text{C}_6\text{H}_5)_2\text{TlBr}$ is reduced by stannous chloride to yield $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$; but similar reactions have not been reported with other metallic reducing agents.

We have now been able to prepare C_6F_5 -derivatives of the metals shown in Table 5 in the oxidation states indicated either by oxidation with $[(\text{C}_6\text{F}_5)_2\text{TlBr}]_2$ or by oxidation with this reagent followed by reduction with hydrazine or other

¹³ R. S. Nyholm and P. Royo, *Chem. Comm.*, 1969, 421.

^{13a} R. Baker and P. Pauling, *Chem. Comm.*, 1969, 745.

¹⁴ G. B. Deacon, J. H. S. Green, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 4367.

¹⁵ D. Bright and M. R. Truter, *Chem. Comm.*, 1969, in the press.

¹⁶ A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izvest. Akad. Nauk S.S.S.R. Otdel Khim. Nauk.*, 1959, 644.

reducing agents. This process preferentially removes one halide ion and one C_6F_5 -group rather than two C_6F_5 -groups, *e.g.*

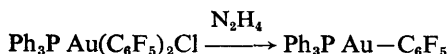


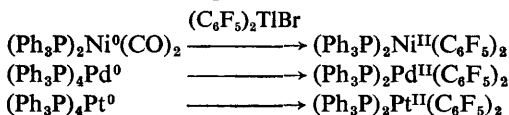
Table 5 Metals and oxidation states (underlined) yielding C_6F_5 -complexes by $[(C_6F_5)_2TiBr]_2$ oxidation

Fe	<u>Co^{III}</u>	<u>Ni^{II}</u> and IV	Cu
Co	<u>Rh^I</u> and III	<u>Pd^{II}</u> and IV	Ag
Ni	<u>Ir^I</u> and III	<u>Pt^{II}</u> and IV	<u>Au^I</u> and III

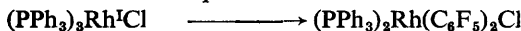
Oxidation of mercury(I) chloride to $Hg(C_6F_5)_2$ and $SnCl_2$ to $SnCl_2(C_6F_5)_2$ by this general reaction has also been achieved. Deacon and co-workers¹⁷ have extended the reaction for the oxidation of the elements in the free state for Groups IIB, IIIB, IVB, VB, VIB, and VIIB to form derivatives such as $Zn(C_6F_5)_2$, $(C_6F_5)_3In(PPh_3)$, $(C_6F_5)_4Sn$, $(C_6F_5)_3As$, $(C_6F_5)_2Se$, and C_6F_5Br . All elements from Zn, Cd, and Hg to Cl, Br, and I have been shown to react except Ga, Si, Pb, and Bi.

So far we have not observed reactions of the elements of Group VIII and IB with $(C_6F_5)_2TiBr$ but the following oxidations have been carried out with $(C_6F_5)_2TiBr$. The properties of the complexes are shown in Table 6.

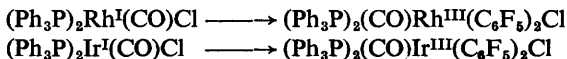
(a) Zerovalent Metal Complexes



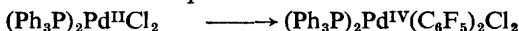
(b) Univalent Metal Complexes



The formation of a 5-co-ordinate rhodium(III) complex is noteworthy. This is presumably due to the bulky nature of the Ph_3P group. Indeed, Wilkinson¹⁸ has suggested that dissociation of a Ph_3P group takes place even from 4-co-ordinate $(Ph_3P)_3RhCl$ when the latter behaves as a hydrogenation catalyst with olefins. The rhodium(I) analogue of Vaska's compound reacts similarly:



(c) Bivalent Metal Complexes

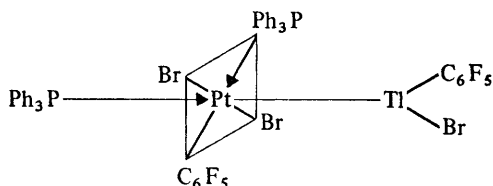


$(Ph_3P)_2Pt^{II}Cl_2$ reacts with $(C_6F_5)_2TiBr$ without deposition of thallium(I)

¹⁷ G. B. Deacon, 1969, personal communication.

¹⁸ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

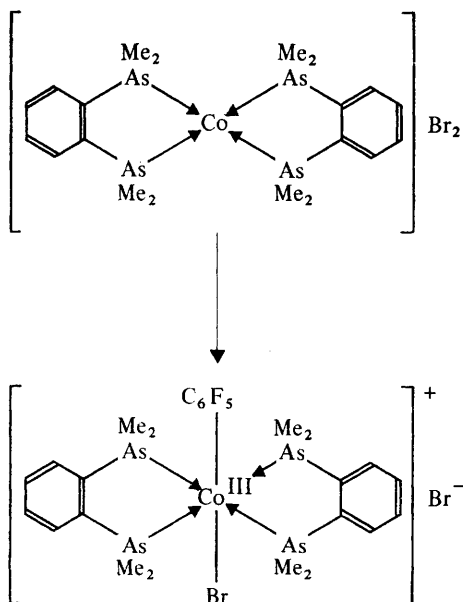
bromide to yield a more deeply coloured compound. The structure of this is uncertain but the products of its reactions with bromine, yielding $(\text{Ph}_3\text{P})_2\text{Pt}^{\text{IV}}\text{-(C}_6\text{F}_5)_2\text{Br}_2$, and on reduction, which gives $(\text{Ph}_3\text{P})_2\text{Pt(C}_6\text{F}_5)_2\text{Br}$, suggest the following possible structure:



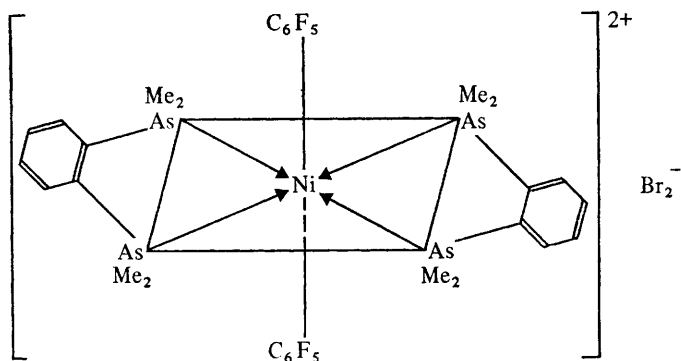
This possible structure is based on the products obtained by halogen oxidation and hydrazine reduction and on the observed molecular weight and molecular conductivity.

The compound is monomeric and a non-electrolyte; the crystal structure is at present being investigated by Professor H. M. Powell.

Oxidation of Co^{II} and Ni^{II} complexes can be effected also:

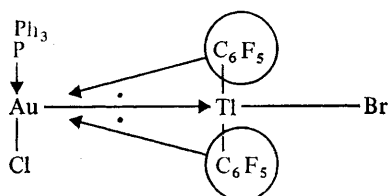


This Co^{III} complex is green and hence presumably the C_6F_5^- and the Br -groups are in *trans*-positions. The corresponding *bis*-diarsine nickel(II) dibromide is oxidised by $(\text{C}_6\text{F}_5)_2\text{TlBr}$ to the following nickel(IV) complex:



This derivative is thus similar to the corresponding di-chloro- and di-bromonickel(IV) cations described some years ago.¹⁹ As pointed out below the $C_6F_5^-$ group has an electronegativity about the same as that of bromine, and the preparation of metal complexes involving $C_6F_5^-$ in place of bromine or chlorine is thus in principle feasible, given a similar reaction path to facilitate the mechanism of $C_6F_5^-$ -addition. Attempts to synthesise an $Fe^{III}-C_6F_5$ complex by oxidising $[Fe^{II}(\text{diarsine})_2Cl_2]$ ⁰ were unsuccessful.

With one or two exceptions, *e.g.* $(Ph_3P)_2Ni(CO)_2$, addition of $C_6F_5^-$ takes place most readily when the metal ion being oxidised is co-ordinatively unsaturated.* This seems to throw some light on the mechanism of the reaction. It is possible that a weak metal-thallium bond is first formed as the reaction intermediate; formation of this is then followed by transfer (presumably stepwise) of the two $C_6F_5^-$ groups. The process for the oxidation of $Ph_3P \rightarrow AuCl$ would then involve the following intermediate:



The alternate free radical mechanism is not favoured because if $[(C_6F_5)_2TlBr]_2$ in benzene is heated to the temperatures used for oxidation no $C_6F_5-C_6F_5$ is isolated; this would be expected if $\cdot C_6F_5$ free radicals were formed.

The reduction of these perfluorophenyl metal complexes, for example with hydrazine, gives rise to products containing $C_6F_5^-$ attached to the metal atom in the lower oxidation state. There is preferential loss of halogen rather than of the two C_6F_5 groups. Thus, reduction of $Ph_3P \rightarrow Au(C_6F_5)_2Cl$ yields $Ph_3P \rightarrow Au-C_6F_5$. $(Ph_3P)_2Pd^{IV}(C_6F_5)_2Cl_2$ forms $(Ph_3P)_2Pd^{III}(C_6F_5)Cl$ which, incident-

¹⁹ R. S. Nyholm, *J. Chem. Soc.*, 1951, 2602.

* Even with $(Ph_3P)_2Ni(CO)_2$ three-co-ordination may arise owing to the loss of a CO group.

ally, may be re-oxidised with chlorine to form a Pd^{IV} complex with only one C₆F₅-group attached, *i.e.* (Ph₃P)₂Pd^{IV}(C₆F₅)Cl₃. As mentioned above, reduction of the adduct between (Ph₃P)₂Pt^{II}Cl₂ and (C₆F₅)₂TiBr yields (Ph₃P)₂Pt^{II}(C₆F₅)Cl which can, like the Pd^{II} compound be re-oxidised with chlorine to yield the -C₆F₅ complex (Ph₃P)₂Pt^{IV}(C₆F₅)Cl₃. Table 6 summarises the properties of these compounds.

Table 6 Properties of perfluorophenyl transition-metal complexes prepared using [(C₆F₅)₂TiBr]₂ as oxidant

Compound	Starting material	Colour	m.p. (°C)	
[Co(diars) ₂ (C ₆ F ₅)Br]Br	Co(diars) ₂ Br ₂	Green	194	
Ni(PPh ₃) ₂ (C ₆ F ₅) ₂ ^b	Ni(PPh ₃) ₂ (CO) ₂	Yellow	203	
[Ni(diars) ₂ (C ₆ F ₅) ₂]Br ₂	Ni(diars) ₂ Br ₂	Green-black	dec. 185	
Rh(PPh ₃) ₂ (C ₆ F ₅) ₂ Cl	Rh(PPh ₃) ₃ Cl	Yellow-red	115	
<i>trans</i> -Rh(PPh ₃) ₂ (C ₆ F ₅) ₂ (CO)Cl	<i>trans</i> -Rh(PPh ₃) ₂ (CO)Cl	Yellow	189	
<i>trans</i> -Ir(PPh ₃) ₂ (C ₆ F ₅) ₂ (CO)Cl	<i>trans</i> -Ir(PPh ₃) ₂ (CO)Cl	Yellow	196	
<i>cis</i> -Pd(PPh ₃) ₂ (C ₆ F ₅) ₂	Pd(PPh ₃) ₄	White	235	
<i>cis</i> -Pt(PPh ₃) ₂ (C ₆ F ₅) ₂ ^c	Pt(PPh ₃) ₄	White	245	
<i>trans</i> -Pd(PPh ₃) ₂ (C ₆ F ₅) ₂ Cl ₂	<i>trans</i> -Pd(PPh ₃) ₂ Cl ₂	Pale yellow	250	
'PtTi(C ₆ F ₅) ₂ Cl ₂ Br(PPh ₃) ₂ '	<i>cis</i> -Pt(PPh ₃) ₂ Cl ₂	White	276	
<i>cis</i> -Au(PPh ₃)(C ₆ F ₅) ₂ Cl	Au(PPh ₃)Cl	White	160	
A {	Au(PPh ₃)C ₆ F ₅ ^d	<i>cis</i> -Au(PPh ₃)(C ₆ F ₅) ₂ Cl	White	171
	Pd(PPh ₃) ₂ (C ₆ F ₅)Cl	<i>trans</i> -Pd(PPh ₃) ₂ (C ₆ F ₅) ₂ Cl ₂	White	230
	Pt(PPh ₃) ₂ (C ₆ F ₅)Cl ^e	'PtTi(C ₆ F ₅) ₂ Cl ₂ Br(PPh ₃) ₂ '	White	286
B {	Pt(PPh ₃) ₂ (C ₆ F ₅)Cl ₃	Pt(PPh ₃) ₂ (C ₆ F ₅)Cl	Yellow	180
		or PtTi(C ₆ F ₅) ₂ Cl ₂ Br(PPh ₃) ₂		

^a Diarsine is *o*-phenylenebisdimethylarsine.

^b First reported by J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, 2, 455.

^c First reported by D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5275.

^d Also reported by L. G. Vaughan and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1969, 91, in the press, who have also prepared (Ph₃P)Au(C₆F₅)₃ (a) by N₂H₄ reduction and (b) by Cl₂ oxidation.

The reactivity towards various small molecules of these perfluoro-compounds of metals in higher oxidation states has been relatively little studied and offers an interesting area for research. The behaviour of carbon monoxide with some derivatives has, however, been investigated. Thus when (PPh₃)₂Rh(C₆F₅)₂Cl is treated with carbon monoxide one obtains the perfluoro-ketone (C₆F₅)₂CO according to the reaction (PPh₃)₂Rh(C₆F₅)₂Cl + 2CO → (PPh₃)₂Rh(CO)Cl + (C₆F₅)₂CO. The extension of this reaction to the study of perfluoro-alkyl complexes is being followed up.

The preparation of a wide range of C₆F₅-complexes of metals in various oxida-

tion states has provided a unique opportunity for the study of the behaviour of the C_6F_5 -group in different environments. In general one observes that as the oxidation state of the metal to which the C_6F_5 -group is attached rises the stretching frequency of the C—F band of highest intensity (*ca.* 1050 cm^{-1}) increases significantly. A similar increase in stretching frequency occurs as one passes along the series C_6F_5 —I, C_6F_5 —Br, C_6F_5 —Cl to C_6F_5 —F. Presumably metals of high oxidation state or groups of high electronegativity increase the positive charge on the C_6F_5 -group thereby enhancing the strength of attachment of the fluorine to the individual carbon atoms.

The ^{19}F n.m.r. spectra of pentafluorophenyl metal complexes have been studied by Stone and co-workers^{10a}, by Vaughan and Sheppard (see footnote *d* to Table 6) and by Graham and collaborators.^{10b} Taking the chemical shift of the ^{19}F in hexafluorobenzene as 163.0 p.p.m. upfield from CFCl_3 as the basis then, in general, the *meta* fluorine atoms in a C_6F_5 -transition metal complex are the same or a shade smaller, the *para* fluorine shifts are about 2 p.p.m. lower and the *ortho* shifts are about 40 p.p.m. lower. In complexes such as $(C_6F_5)_3\text{Au}(\text{PPh}_3)$, there are small differences between the *ortho* fluorine atoms according as to whether one is concerned with a C_6F_5 -group *cis* or *trans* to the PPh_3 group, the chemical shift of the *ortho*-fluorine in the *cis*- C_6F_5 being slightly less (2 p.p.m.) than in the *trans*-isomer. In general, the more electronegative the group attached to the C_6F_5 —the larger is the chemical shift of the *ortho*-fluorine; the n.m.r. spectra of C_6F_5 -complexes of Au(I) and Au(III) are in agreement with this generalisation. However, whilst good qualitative correlations such as the above are available a quantitative separation of the diamagnetic and paramagnetic terms in the chemical shift is not yet possible. Also the proximity of the *ortho*-fluorine atoms to the metal atom undoubtedly leads to field effects which cannot be assessed quantitatively at present.

A wealth of chemistry remains for investigation among compounds of the earlier transition elements. We are currently extending our studies to the lower oxidation states of complexes ranging from the Ti, Zr, and Hf triad across to Fe, Ru, and Os.

5 The Nature of the Metal–Carbon Bond in Perfluoro-alkyl and -aryl Metal Complexes

The greater 'stability' of perfluoro-alkyl and -aryl transition-metal complexes as compared with the unsubstituted alkyl and aryl derivatives calls for comment. The word 'stability' is used here in the rather loose sense that the compound can be prepared and does not readily decompose spontaneously or in the presence of air and moisture. This use of the word 'stability' implies a combination of thermodynamic factors (free energy of formation, *i.e.* a strong M—C bond) and a relatively large energy of activation for reaction with reagents such as air, moisture, solvents, *etc.* The main factors which lead to this 'stability' are:

(i) A high M—C bond energy. Other factors being equal, this is dependent on the product of the electronegativities of the bonded atoms. Lagowski²⁰ has

²⁰ H. B. Powell and J. J. Lagowski, *J. Chem. Soc.*, 1965, 1392.

estimated effective electronegativity values for various perfluoro-alkyl groups using pK values of the perfluoro-alkyl and -aryl mercury(II) hydroxides and i.r. stretching frequencies of the Hg—Cl bond in substituted mercury(II) chlorides. Stone²¹ has estimated values of electronegativity by studying the C—O stretching frequencies of compounds of the type X—Mn(CO)₅ where X = a halogen C₆F₅-, Me, etc. Stone has noted the variation in electronegativities depending on whether one studies R₇SnR₃ or R₇Mn(CO)₅ compounds. The following sequence of electronegativities is then obtained as a mean of the various estimates: F(4.0) > Cl(3.2) ~ CF₃(3.2) ~ C₂F₅(3.2) > C₃F₇(3.1) > C₆F₅(3.0) ~ Br(3.0) > Ph-(2.8) > I(2.7) > Me(2.6) (no useful purpose is served by attempting to give values to more than one decimal place). In terms of electronegativity product alone one would expect that perfluoroalkyl bonds will be stronger than perfluoro-aryl bonds; both in turn are stronger than unsubstituted metal-alkyls and -aryls. As a simple illustration, CF₃Co(CO)₄ distills without decomposition at 91° but MeCo(CO)₄ is stable only below -30°. The effect of possible double bonding is discussed in (ii) below. For a particular carbon ligand, the metal-carbon bond strength should also increase with increasing electronegativity of the transition metal. This arises with increasing oxidation state of the metal (e.g. Pt^{IV} > Pt^{II}) and in general as one moves vertically down the periodic table, especially to the third transition series (Pt^{IV} > Ni^{IV} and Pd^{IV}) and as one passes to the right in any transition series. It is understandable, therefore, that very stable metal-carbon σ bonds are commonly found with Pt^{IV} and Au^{III}.

(ii) Double bond character. Unfortunately there are not many data available yet to permit a comparison of perfluoro- and unsubstituted alkyl and aryl transition metal bonds but a survey of these data by Churchill and Mason²² indicates the following:

(a) There is a shortening of the M—C bond of ca. 0.1 Å in a perfluoroalkyl transition-metal bond as compared with an unsubstituted alkyl-metal bond.

(b) There is less difference between perfluoroalkyl-metal bonds and unsubstituted alkyl metal bonds but both appear to be 0.05–0.1 Å shorter than the bond between a metal and an unsubstituted alkyl-metal bond. Churchill and O'Brien²³ have summarised recent data on simple aryl compounds. These data suggest that some double bonding occurs between the transition metal and a perfluoroalkyl group; this probably involves the overlap of a filled t_{2g} orbital of the metal with a vacant antibonding C—F orbital of suitable symmetry. As pointed out by Mason²⁴ use of an antibonding orbital of the carbon atom alone is unlikely because of the way in which the C—F stretching frequency in the —CF₃ group changes on co-ordination to a metal. Cotton²⁵ has shown that in (CO)₅MnCF₃ the C—F stretching frequency is lowered by

²¹ J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 1212.

²² M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1968, **5**, 125.

²³ M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. (A)*, 1969, 266.

²⁴ R. Mason, 1969, personal communication.

²⁵ F. A. Cotton and J. A. McCleverty, *J. Organometallic Chemistry*, 1965, **5**, 490.

ca. 100 cm^{-1} as compared with CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). This is consistent with a weaker C—F bond and a stronger and shorter M—C bond.

Comparing the normal aryl and perfluoroaryl groups it seems that the double bonding, which apparently occurs in both cases, is little enhanced by the substitution of all five hydrogen atoms by fluorine. However, this substitution presumably increases the strength of the σ M—C bond.

(iii) A large energy separation between the σ bonding orbital and the lowest empty anti-bonding orbital is desirable to minimise bond breaking by electron promotion from the bond.²⁶ In general, the separation between these molecular orbitals increases as the separation between atomic orbitals increases in the free atom and this in turn depends upon the effective nuclear charge on the metal—or its effective electronegativity. Hence the effect of this should be most apparent with metals such as Pt and Au.

(iv) Minimum M—C polarity will help to enhance stability in the kinetic sense, since a highly polar $\text{Ti}^{\delta+}\text{—C}^{\delta-}$ bond for example, is more likely to be attacked by a nucleophilic reagent than a less polar Pt—C bond.

(v) The absence of vacant d orbitals on the metal (or indeed donor atom) will inhibit nucleophilic reagent attack. This favours stability of $\text{Pt}^{\text{IV}}\text{—C}$ bonds as compared say with $\text{Ti}^{\text{IV}}\text{—C}$ bonds.

(vi) The absence of lone pairs on the metal or ligand will increase stability by minimising attack by an electrophilic reagent. These conditions are satisfied ideally in bonds between Pt^{IV} and a saturated carbon atom.

(vii) Finally reference should be made to intramolecular reactivity. It has been noted that $\text{F}_3\text{C}\text{—metal}$ complexes are less stable than the corresponding $\text{C}_6\text{F}_5\text{—metal}$ derivatives. Here the proximity of the fluorine atoms to metal in the case of the —CF_3 derivatives assists the formation of M—F and $:\text{CF}_2$ radicals; alternatively if there are reactive groups on the metal these can react with a nearby fluorine atom of a —CF_3 group in a *cis*-position. Such a reaction is, of course, much less likely with the *ortho*-fluorine atoms of a co-ordinated C_6F_5 -group.

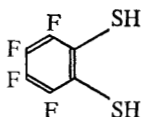
6 Complexes of Ligands in which Fluorine is Attached to an Atom Two Removed from the Donor Atom

In the cases of both charged and uncharged ligands we need to consider perfluoroaryl types only, because it is reasonable to assume that in ligands such as $\text{CF}_3\text{CH}_2\text{CH}_2^-$, or $(\text{CF}_3\text{CH}_2)_3\text{As}$, the inductive effect of the fluorine atoms would be largely neutralised by the intervening CH_2 group.

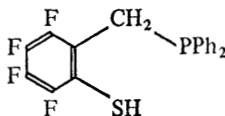
Examples of charged ligands of the aryl type include pentafluorophenol and pentafluorothiophenol. These ligands and the corresponding pentachloro-derivatives have been studied to obtain ligands which are the organic equivalent of halide ions. For this purpose one needs a relatively polarisable ligand (*e.g.*

²⁶ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1960, 1718.

$C_6F_5-S^-$) which forms a strong acid. From these pseudo-halide ligands it is possible to prepare the equivalent of tetrahalogenometallate(II) anions from a range of bivalent metals of the first transition series by the following type of reaction.²⁷ The silver or thallium salt of the pseudo-halide ligand is prepared and allowed to react with $[Ph_4As]_2MCl_4$ in a suitable non-aqueous solvent. Thus with $[Ph_4As]_2CoCl_4$ metathesis occurs with precipitation of silver or thallium(I) chloride and the $[Ph_4As]_2[Co(ligand)_4]$ can be isolated by concentration of the solvent. The complexes are deep blue and have spectra and magnetic moments characteristic of tetrahedrally co-ordinated Co^{II} complexes. The corresponding reactions take place with Ni^{II} , Cu^{II} , and Zn^{II} . Table 7 shows the properties of a selection of these complexes. The values of $10Dq$ and β (Jorgensen's nephelauxetic covalency parameter) are similar to those of the halogens. For the usual halides, and the ligands studied, values of $10Dq$ decrease in the order $-NCO > -NCS > \text{pentafluorophenol} > \text{pentachlorophenol} > \text{thiophenol} > \text{pentafluorothiophenol} > Cl^- > Br^- > I^-$. The β value in the nephelauxetic series decreases in the order $\text{pentafluorophenol} > Cl^- > -NCO > \text{pentachlorophenol} > -NCS > Br^- > I^- > \text{pentafluorothiophenol}$.²⁸ A study of the bidentate group

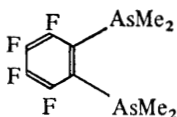


shows²⁹ that it behaves like other thiolene type ligands, much of the negative charge residing on the ring. This chelate group dissolves readily each of the first transition metals if they are finely divided. However, to simulate say a tertiary phosphine and a Cl^- ion in a chelate group, ligands such as



should prove of considerable interest.

Finally we refer to uncharged ligands with fluorine substitution β to the donor atom. These include ligands of the type $(C_6F_5)_3As$. These are known to co-



²⁷ B. Hollebne and R. S. Nyholm, 1969, unpublished observations.

²⁸ A. Kemmit, A. Nicholas, and R. D. Peacock, *Chem. Comm.*, 1967, 599.

²⁹ A. Callaghan, A. J. Layton, and R. S. Nyholm, *Chem. Comm.*, 1969, 399.

Transition-metal Complexes of Some Perfluoro-ligands

Table 7 Spectral and magnetic properties of tetrahalide and pseudohalide metal-late(II) complexes

	$10Dq$ (cm^{-1})	β (cm^{-1})	μ_{eff} (B.M.)
* $\left[\text{Co} - \left(\text{O} - \text{C}_6\text{F}_4 \right)_4 \right]^{2-}$	3920	770	4.75
$\left[\text{Co} - \left(\text{O} - \text{C}_6\text{Cl}_4 \right)_4 \right]^{2-}$	3850	715	4.76
$\left[\text{Co} - \left(\text{S} - \text{C}_6\text{F}_4 \right)_4 \right]^{2-}$	3660	631	4.69
$\left[\text{Co} - \left(\text{S} - \text{C}_6\text{H}_4 \right)_4 \right]^{2-}$	3870	600	4.42
$\left[\text{Ni} - \left(\text{O} - \text{C}_6\text{Cl}_4 \right)_4 \right]^{2-}$	4300	695	3.65
$\left[\text{Ni} - \left(\text{S} - \text{C}_6\text{F}_4 \right)_4 \right]^{2-}$	—	—	Diamag.

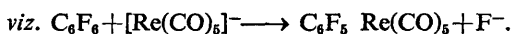
* The Ni^{II} derivative, $\text{Ni}(\text{ligand})_6$, is octahedrally co-ordinated.

ordinate to transition metals less strongly than the corresponding $(\text{C}_6\text{H}_5)_3\text{As}$ derivatives, but detailed studies are lacking. The tetrafluorodiarisine ligand, in which the aromatic ring only has been fully substituted with fluorine has been studied in some detail.³⁰ In general it differs from the unsubstituted diarsine in two main ways. Overall it is a weaker donor. With the d^8 metals Ni^{II} , Pd^{II} ,

³⁰ N. V. Duffey, A. J. Layton, R. S. Nyholm, D. Powell, and M. L. Tobe, *Nature*, 1966, **212**, 177.

and Pt^{II} it forms derivatives of the type $\text{M}(\text{F-diarsine})_2\text{Hal}_2$. The Pd^{II} and Pt^{II} derivatives display the usual diamagnetic behaviour; but whereas the di-iodide of Ni^{II} is brown and diamagnetic in the solid state, the chloride and bromide are green and paramagnetic. Secondly it shows a greater tendency than diarsine to attach itself by *one* donor arsenic atom only, *e.g.* in complexes of the type $\text{RhCl}_3(\text{F-diarsine})_2$. This can be isolated as a non-electrolyte in which one ligand is chelated and the other attached as a unidentate group. The presence of one unco-ordinated $-\text{AsMe}_2$ group is shown by the reaction of CH_3I with the complex. A 1:1 electrolyte is formed. It is clear from these studies that even when as far removed from the donor atom as the β atom the fluorine exerts a marked effect in co-ordination provided that it is attached to an aryl group.

Appendix. In the discussion on p. 7 we inadvertently omitted the method for synthesising fluorocarbon-metal complexes which involves the attack of a metal carbonyl anion on a fluorocarbon, although it is implicit in method 2 (p. 7). Thus, hexafluorobenzene reacts with the $[\text{Re}(\text{CO})_5]^-$ anion (but not the corresponding $[\text{Mn}(\text{CO})_5^-]$ ion) to yield $\text{C}_6\text{F}_5 \text{Re}(\text{CO})_5$,



The procedures have been summarised by Bruce and Stone³². Finally, a useful review of the preparation and properties of fluorocarbon-metal complexes has been published by Bland.³³

Acknowledgements. The author is indebted to his collaborators for much of the work referred to before publication. Thanks are due also to Professors F. G. A. Stone and R. Mason and Dr. W. A. Sheppard³¹ for valuable discussions.

³¹ W. A. Sheppard and C. M. Sharto, 'Organic Fluorine Chemistry', W. A. Benjamin, New York, 1969.

³² M. I. Bruce and F. G. A. Stone, 'Preparative Inorganic Reactions', ed. W. L. Jolly, Interscience, 1968, 4, 177.

³³ W. J. Bland, *Leicester Chem. Rev.*, 1967, 8, 15.