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Fluorocarbon metal compounds—role models in organotransition metal chemistry

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Abstract

Early studies on organo-transition metal complexes with fluorocarbon ligands are reviewed in a historical context in relation to the renaissance of organometallic chemistry which followed the discovery of ferrocene. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organo-transition metal; Fluorocarbons; Pentafluorophenyl

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1. Introduction

Some 20 years have elapsed since studies on metal complexes having fluorinated organic groups as ligands ceased to be a dominant theme for research in my laboratory. I therefore greeted with some trepidation the Editor's invitation to contribute to this special issue of *Journal of Fluorine Chemistry*, because it is difficult to recall the essence of work done so long ago. However, since I believe there is merit in works that document the history of the sub-areas of our science, I am glad to have been given the opportunity to write this paper.

In 1952, the sandwich structure of the molecule ferrocene $[Fe(\eta^5\text{-}C_5H_5)_2]$ was established [1,2]. Characterization of this complex initiated a renaissance in organometallic chemistry, followed as it was by the preparation of cyclopentadienyl compounds of most of the transition elements, and by the synthesis of several π-arene complexes of these metals, e.g. $[Cr(\eta^6\text{-}C_6H_6)_2]$ [3,4]. By the early 1950s, however, few metal complexes had been authenticated with alkyl or aryl moieties attached to the metal by conventional two-center, two-electron σ bonds [5]. This situation began to change with the discovery of species such as $[TiPh_2(\eta^5\text{-}C_5H_5)_2]$ [6], $[WMe(CO)_3(\eta^5\text{-}C_5H_5)]$ [7,8] and $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ [8]. A further pivotal result was the synthesis of $[MnMe(CO)_5]$ [9][1], which came after the development at the Ethyl Corporation, of a convenient route to its precursor $[Mn_2(CO)_{10}]$ [11]. The successful isolation of compounds such as $[FeMe(CO)_2(\eta^5\text{-}C_5H_5)]$ or $[MnMe(CO)_5]$ led to the belief that carbon–metal σ bonds would be stable only if there were also present in the same molecule ligands like CO or $\eta^5\text{-}C_5H_5$, groups possessing both donor and acceptor properties. This idea at the time was seemingly reinforced with the characterization of a plethora of alkyl and aryl platinum complexes, of which $[PtI(Me)(PPh_3)_2]$, $[PtPh_2(PEt_3)_2]$, and $[PtI_2(Me)_2(PEt_3)_2]$ are representative [12,13]. These complexes contained phosphine ligands considered to have both σ-donor and π-acceptor properties. A combination of either carbonyl, cyclopentadienyl, or phosphine ligands with alkyl or aryl groups was considered to favor a synergism between the various bonding modes, thereby enhancing stability. These early ideas, at the time they were advanced, greatly stimulated further research. However, the preparation in much more recent times of isoleptic metal–alkyl and metal–aryl compounds has shown that it is not essential that π bonding groups be present for metal–alkyl or –aryl bonds to exist.[2]

2. Results and discussion

2.1. Fluorocarbon metal compounds—early days

It was my good fortune to commence work on organotransition metal chemistry in 1958, when, as I have

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[1] Methyl(pentacarbonyl)manganese was prepared independently at about the same time by Walter Hieber and his coworkers at the Technischen Hochschule, München. Walter Hieber is generally regarded as the father of metal carbonyl chemistry, and he has given a valuable personal account of his work in [10].

[2] The much later isolation of molecules such as $[WMe_6]$ or $[Mo_2(CH_2SiMe_3)_6]$ by Wilkinson and his coworkers [14,15] demonstrated that the facile decomposition of carbon–metal σ-bonds, when this occurs, is due to kinetic rather than thermodynamic factors. Strategies for the synthesis of 'stable' species must, therefore, block decomposition pathways.

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described elsewhere [16], there was no shortage in this field of interesting problems to address. Moreover, NMR spectroscopy (then at 40 or 60 MHz!) had recently been added to the tools available to gain information on the structure of molecules. The routine use of single-crystal X-ray diffraction for structure determination was to occur some years later. The paucity of compounds of the d-block metals, at that time known to have alkyl or aryl groups σ-bonded to the metals, was an enigma seeking a solution. Earlier (1948–1951), I had carried out my postgraduate research with Harry Emeléus at Cambridge. I believe, Norman Greenwood and I were the only persons in his group in this period who were not working with fluorine compounds. I was encouraged to work with diborane as a consequence of contacts Professor Emeléus had with scientists working for the Admiralty. He had been asked to initiate studies with boranes,[3] and I was, therefore, guided into this area. Nevertheless, I was acutely aware that the main thrust of the group was on fluorine chemistry, one consequence of which had been the discovery of the then very novel mercurial compound $Hg(CF_3)_2$ [17].

In my early years of independent research at Harvard, in 1958, I recalled that the properties of $Hg(CF_3)_2$ were very unlike those of $HgMe_2$. Whereas the latter was a highly toxic liquid with the well-known ability to transfer Me groups to other metals via reactions with their halides, the former was a white crystalline solid which did not engage in ligand-exchange reactions.[4] The property that sets the two molecules apart is the high electronegativity of the CF_3 group, which is comparable with that of a Cl atom. Hence, the properties of $Hg(CF_3)_2$ may be qualitatively related to those of $HgCl_2$. I reasoned that a similar situation would exist with the transition elements, with fluoroalkyl–metal derivatives existing with stabilities similar to those of well-established metal complex halides. Hence, since $[MnCl(CO)_5]$ was stable, surely $[Mn(CF_3)(CO)_5]$ would also be. Accordingly, we prepared perfluoroalkylmanganese and -rhenium pentacarbonyls through the intermediacy of their acyl derivatives [19]:[5]

$$Na[M(CO)_5] + R_FCOCl \xrightarrow{THF} [M(COR_F)(CO)_5] + NaCl$$

$$[M(COR_F)(CO)_5] \xrightarrow{heat} [MR_F(CO)_5] + CO$$

where M is Mn or Re, and R_F is CF_3, C_2F_5, or n-C_3F_7.

As we had anticipated, these species proved to be more robust towards thermal or oxidative decomposition than their alkyl analogs.[6]

Emeléus and Haszeldine had shown that CF_3I would oxidize Hg to CF_3HgI, and much of the chemistry they developed, reflected the pseudo halide characteristics of perfluoroalkyl groups [22,23]. This property suggested to me that perfluoroalkyl iodides would similarly oxidize transition metal complexes when the metal was in a low oxidation state, an idea which led to the discovery of the important reactions [24–26]:

$$\begin{array}{ll} {[Fe(CO)_5]} + C_3F_7I \rightarrow & {[FeI(C_3F_7)(CO_4)]} + CO \\ Fe^0(d^8) & Fe^{II}(d^6) \end{array}$$

$$\begin{array}{ll} {[Co(CO)_2(\eta^5-C_5H_5)]} + C_2F_5I & \\ Co^I(d^8) & \rightarrow {[CoI(C_2F_5)(CO)(\eta^5\text{-}C_5H_5)]} + CO \\ & Co^{III}(d^6) \end{array}$$

These syntheses are now known to be examples of a widespread class of reactions in which the metal's oxidation state and coordination number are both increased as a result of interaction with a substrate molecule. Moreover, the reaction between perfluoroalkyl iodides and iron pentacarbonyl to give $[FeI(R_F)(CO)_4]$ is formally similar to the reaction between the carbonyl complex and I_2 which gives $[FeI_2(CO)_4]$. This similarity in behavior between R_FI and I_2 reflects the pseudo interhalogen-like properties of the former [22,23].

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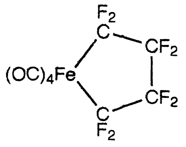
[3] Towards the end of World War II, the American Navy, through its Office of Naval Research, had sponsored in Herman Schlesinger's group, at Chicago, extensive studies on metal borohydrides and related species. It was thought that, upon hydrolysis, these compounds might be convenient solid sources of hydrogen for use in weather balloons. Subsequently, the value of both $NaBH_4$ and $LiAlH_4$ as reducing agents in organic chemistry and the possibility of using borane compounds as propellants became apparent. This gave a huge boost to research in boron chemistry in the USA and former Soviet Union that lasted for many years. Scientists at the Admiralty had learned of the work on boron chemistry in the USA and wished to encourage studies in this area in Britain. Unfortunately, when I set out to make B_2H_6, neither of the precursors used at that time (BCl_3 and $LiAlH_4$) were commercially available. These had to be made; a character-forming experience for a new research student.

[4] Much later, perfluoromethyl cadmium compounds were shown to be CF_3 donors and sources of difluorocarbene. For a review, see [18].

[5] Unknown to us, workers at the Ethyl Corporation had earlier reported (First International Conference on Coordination Chemistry, held in London in April 1959) the compound $[Mn(CF_3)(CO)_5]$. Abstracts of this meeting were not available to us prior to the completion of our study. At this first and relatively informally held ICCC meeting, distribution of abstracts of the papers presented was not on the scale of later conferences. In a paper submitted one month later than ref. [19], W.R. McClellan [20], of DuPont, also independently reported the synthesis of several cobalt and manganese fluoroalkyl complexes $[CoR_F(CO)_4]$ and $[MnR_F(CO)_5]$ These reports illustrate the increasingly competitive nature of research on organotransition metal compounds which followed the seminal work of Fischer and Wilkinson on the metallocenes.

[6] Following our discoveries, and the subsequent work of others who also made fluoroalkyl metal compounds, the cause of the enhanced stability of these complexes over their hydrocarbon analogs became a matter for controversy revolving around relative bond strengths, back bonding possibilities and electrostatic effects. These arguments have been reviewed by Hughes [21]. It is important to stress that our initial work was intuitive, being based on the known pseudo halogen behavior of CF_3 and other fluoroalkyl groups.

We also observed that $[Fe(CO)_5]$ and $[Co(CO)_2(\eta^5\text{-}C_5H_5)]$ reacted with $CF_2{=}CF_2$ to yield the metallacycles **1** and **2**, respectively [24,27]. These metallacycles have been described correctly as the first examples of metallacyclopentanes reported in the literature [28]. Metallacycles are now recognized as key intermediates in many syntheses involving transition metals. Similarly, the synthesis of the complexes $[FeI(C_3F_7)(CO)_4]$ and $[CoI(C_2F_5)(CO)(\eta^5\text{-}C_5H_5)]$ demonstrated in these early times the ability of transition metals in low oxidation states to insert into carbon–iodine bonds. Reactions of this type were later widely developed, as in the commercial synthesis of acetic acid from methanol using rhodium or iridium complexes as catalysts, with HI as a co-catalyst.



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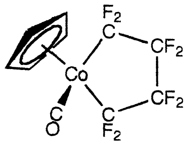

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Reactions between alkenes, hydrogen and CO to yield aldehydes, with cobalt species as catalysts (hydroformylation), had been known for many years. It had been conjectured that the addition of metal–hydrogen bonds to C=C bonds took place along the reaction pathway. However, well-authenticated examples of the addition of metal–hydrogen bonds to C=C or C≡C linkages were not known. The characterization of $[Mn(CF_2CF_2H)(CO)_5]$ and $[Mo(CF_2CF_2H)(CO)_3(\eta^5\text{-}C_5H_5)]$ from reactions between $CF_2{=}CF_2$ and $[MnH(CO)_5]$ and $[MoH(CO)_3(\eta^5\text{-}C_5H_5)]$, respectively [29,30], as well as the formation of $[Mn\{C(CF_3){=}C(H)CF_3\}(CO)_5]$ from $CF_3C{\equiv}CCF_3$ and $[MnH(CO)_5]$ [30,31] provided well-defined examples of metal–hydride additions to C=C and C≡C bonds.[7] Thus, a significant amount of the fluorocarbon–metal chemistry served as a role model for a vast array of hydrocarbon–metal chemistry that later came to light.

The above mentioned similar reactivity patterns shown by $[Fe(CO)_5]$ and $[Co(CO)_2(\eta^5\text{-}C_5H_5)]$ towards certain fluorocarbon substrates led to our drawing attention to other pairs of molecules that behaved similarly in their chemistry [25], e.g., $[Mn_2(CO)_{10}]$ and $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$, or $[Co_2(CO)_8]$ and $[Ni_2(CO)_2(\eta^5\text{-}C_5H_5)_2]$. This was an early appreciation of isolobal mapping between molecules, a concept subsequently given a theoretical basis and elegantly developed by Hoffmann [33] to build bridges between inorganic and organic chemistry.

During the period in which the work described in this section was accomplished, I trained my coworkers in the use of the high-vacuum techniques I had learned initially with Harry Emeléus when working with diborane and had developed to a much more sophisticated level when studying with Anton Burg as my postdoctoral mentor. This was important as it allowed us to manipulate compounds in the absence of air and moisture and often to analyze the products we had made without recourse to microanalytical laboratories. A good example of this involved the metallacycle **1**. We established that it contained four carbonyl ligands, rather than three, by treating the complex with iodine and measuring the CO gas released from weighed samples. In this manner, we avoided the error of formulating **1** as a bis(alkene) complex $[Fe(CO)_3(\eta^2\text{-}CF_2{=}CF_2)_2]$.

A further factor in the good progress made in this period was the enthusiasm displayed by the graduate students for research in this new field. Interaction between each and everyone was very close to the point where they would join with each other to bring laboratory experiments to a rapid conclusion. An example of this was the synthesis of the important cobaltacycle **2**, which was the fruit of work by several collaborators [27].

2.2. Pentafluorophenyl metal complexes

Success in preparing perfluoroalkyl metal compounds and the timely coincidence that perfluoroaromatic compounds had become commercially available, led naturally to our synthesizing pentafluorophenyl metal species upon my arrival at Queen Mary College in late 1962 [34,35]. Disruptions associated with moving the research programme were alleviated to a degree by Paul Treichel, one of my Harvard students, who came with me to Queen Mary College as a National Science Foundation postdoctoral fellow. Fortunately, his experiences in dealing with the primitive facilities available to us, together with the onset of the last of the London smogs, did not impede his subsequently having a distinguished career as a professor at the University of Wisconsin. Our preparation of molecules like $[Zr(C_6F_5)_2(\eta^5\text{-}C_5H_5)_2]$, $[Re(C_6F_5)(CO)_5]$, and $[Pt(C_6F_5)_2(PEt_3)_2]$ initiated a further sub-area of fluorocarbon metal chemistry,[8] activity in which has continued to this day. In recent years, important contributions have been made by Usón and Forniés and their coworkers [38,39], especially in the area of pentafluorophenyl complexes of palladium and platinum. Novel discoveries from the Zaragoza group include anionic complexes such as $[Pt(C_6F_5)_4]^{2-}$, donor (Pt) acceptor (Ag or Au) molecules like $[PtAg(C_6F_5)_3(SC_4H_8)(PPh_3)]$, and polynuclear metal species such as $[Pt_2Pd_2(C_6F_5)_3(\mu\text{-}PPh_2)_3(CO)(PPh_2C_6F_5)]$ [40].

While studying pentafluorophenyl metal complexes, my long-time interest in boron compounds, including an earlier

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[7] At about the same time, in another demonstration of the addition of metal–hydride to C=C bonds, Chatt and Shaw [32] reported a reversible reaction between $[Pt(H)Cl(PEt_3)_2]$ and $CH_2{=}CH_2$, yielding $[PtCl(C_2H_5)(PEt_2)_2]$.

[8] After the article first mentioning C_6F_5 metal derivatives appeared [34,35], it became apparent that others [36,37] had independently focused on this area, probably as a result of the demonstrated existence of the perfluoroalkyl compounds.

preparation of $B(CF{=}CF_2)_3$ [41], led to our synthesizing $B(C_6F_5)_3$ and demonstrating the strong Lewis acidity of this compound [42,43].[9] After being ignored for some 30 years, tris(pentafluorophenyl)boron has re-emerged into the literature as a very important activator component in homogeneous metallocene Ziegler catalyst formation [44–46]. The discovery of $B(C_6F_5)_3$ followed by the very long period before its usefulness became recognized in a different area of chemistry well illustrates the benefit of conducting unfettered research in chemical synthesis.

2.3. A new environment

In 1963, I was rescued from the smog and commuting problems associated with living in London by my appointment to a newly created chair of inorganic chemistry at Bristol. Since I had been born in the West Country, this was a very welcome move. The studies on fluorocarbon metal compounds were carried over to the new location. Initially, I was greatly assisted by Peter Jolly, who accompanied me from Queen Mary College. In the syntheses of new metal complexes, Peter exploited the susceptibility of highly fluorinated olefinic hydrocarbons to nucleophilic attack by using metal carbonyl anions as nucleophiles [47], e.g.

$$[Re(CO)_5]^- + CF_2{=}CF_2 \longrightarrow [Re(CF{=}CF_2)(CO)_5] + F^-$$

$$[Mn(CO)_5]^- + \textit{cyclo}\text{-}C_4F_6 \longrightarrow [Mn(\overline{C{=}CFCF_2C}F_2)(CO)_5] + F^-$$

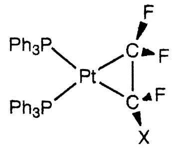
This methodology was based on the earlier observations that the anionic complexes $[Mn(CO)_5]^-$ and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ react with $CF_2{=}CFCF_2Cl$ to afford $[Mn(CF{=}CFCF_3)(CO)_5]$ [19] and $[Fe(CF{=}CFCF_3)(CO)_2(\eta^5\text{-}C_5H_5)]$ [29], respectively. These reactions involve migration of F^-. That between $CF_2{=}CFCF_2Cl$ and $[Mn(CO)_5]^-$ was independently reported by McClellan [20].

Michael Bruce, a new student who joined my group, showed that [Na][[Re(CO)$_5$] in tetrahydrofuran with C_6F_6 afforded $[Re(C_6F_5)(CO)_5]$ and NaF [48]. My former student Bruce King and one of his coworkers [37] had found that a similar reaction occurred between $[Na][Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ and C_6F_6 to give $[Fe(C_6F_5)(CO)_2(\eta^5\text{-}C_5H_5)]$. In collaboration with Michael Bruce and various students, it was subsequently shown that many fluoroaromatic metal complexes could be prepared by reacting carbonyl metal anions with fluoroaromatic compounds [49].

2.4. Metallacyclopropanes and metallacycles

My move to Bristol coincided with a substantial expansion of the British University system following adoption by the U.K. government of the recommendations of an independent report (Robbins). It was thus possible to make several new appointments to the inorganic chemistry staff to teach the increasing numbers of students. One of those appointed was Michael Green, who came from the University of Manchester Institute of Science and Technology. Michael became actively involved in research with me on the fluorocarbon metal compounds in addition to setting up his own independent research group. He contributed many new ideas, particularly on mechanistic aspects of the chemistry.

In the 1960s, tetrafluoroethylene was being used by workers at the Central Research Department of the DuPont Company [50,51] and by us [52,53] to probe the ability of d^8 and d^{10} metal complexes to activate small molecules. Recognition of the metallacyclic nature of the product **1**, obtained from the reaction between $[Fe(CO)_5]$ and C_2F_4 [24], had led me to appreciate the potential for using fluoroalkene and other unsaturated fluorocarbons as synthons for preparing new metal complexes. For the early work leading to compounds **1** and **2**, we had obtained C_2F_4 by pyrolysis of Teflon powder, given to us by DuPont, and had purified the gas by vacuum-system techniques. At Bristol, we required a steady source of C_2F_4 for our work, and in this regard the ICI laboratory at Runcorn (Cheshire) was very helpful in sending us supplies of the gas at low pressures in balloons shipped by rail in large, thick-walled cardboard containers. (It was well known that transporting C_2F_4 under pressure in steel cylinders was hazardous.) These cardboard containers later proved useful for shipping household goods when I moved homes.



	X
3a	F
3b	Cl
3c	Br
3d	CF_3

At Bristol, we focused initially on the reaction of Malatesta's complex $[Pt(PPh_3)_4]$ with $CF_2{=}CF_2$, which afforded the very stable compound $[Pt(C_2F_4)(PPh_3)_2]$ (**3a**) [52,53]. Similar products were obtained from $CF_2{=}CFX$ (X=Cl (**3b**), Br (**3c**), or CF_3 (**3d**)). Variable temperature ^{19}F NMR studies conducted by Tony Rest revealed that in solution at ambient temperatures, the fluoroalkene ligands in these complexes do not rotate about an axis through the metal atom and midpoint of the C=C bond, as do hydrocarbon alkenes in the compounds $[Pt(alkene)(PR_3)_2]$. Moreover, ^{19}F NMR measurements showed that J_{FFgem} values for the CF_2 groups in the fluoroalkene–platinum compounds were similar in value to those for fluorocyclopropanes. These coupling constants were much higher (ca. 190 Hz) than expected (ca. 60 Hz) for $=CF_2$ groups associated with sp^2 hybridized carbon atoms, a result implying that the complexes are best formulated as metallacyclopropanes with σ bonds between the platinum and the carbon atoms. On the basis of the Dewar–Chatt–Duncanson [54–56] model for metal–alkene bonding, there is an extreme form of back bonding between the filled d

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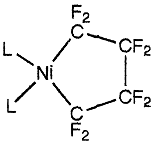
[9] The discovery of $B(C_6F_5)_3$ occurred a few months before I left Queen Mary College. Unfortunately, I was unable to take my co-discovers of the compound with me and so left them to bring the study to completion, as they have described in [43].

orbitals of platinum and the π^* orbitals of the fluoroalkene ligands in the complexes **3**. This is brought about through the highly electronegative fluorine atoms lowering the energy of the these orbitals. A pivotal study in this area was made by John D. Roberts, of the California Institute of Technology, in collaboration with workers at DuPont [57]. It was shown by variable temperature NMR measurements that whereas the C_2H_4 ligand in the complex $[Rh(C_2H_4)(C_2F_4)(\eta^5\text{-}C_5H_5)]$ underwent rotation about an axis through the rhodium atom and the midpoint of the $H_2C{=}CH_2$ bond, the $F_2C{=}CF_2$ molecule remained rigid, behaving in accordance with that expected for a rigid rhodacyclopropane structure $\overline{\text{Rh–CF}_2\text{–CF}_2}$. Indeed, George Parshall and colleagues at DuPont [50,51] had earlier prepared the complex $[IrCl(CO)(C_2F_4)(PPh_3)_2]$ and had proposed that it was formally an Ir^{III} compound containing a $[C_2F_4]^{2-}$ ligand. Similarly, the complexes **3** are best regarded as Pt^{II} species, rather than Pt^0 complexes like $[Pt(C_2H_4)_3]$ [16].

As discussed elsewhere [58,59], the metallacyclopropane nature of molecules like **3b** and **3c** is probably responsible for their facile rearrangement in polar solvents to yield σ-vinylplatinum compounds $[PtX(CF{=}CF_2)(PPh_3)_2]$ (X is Cl or Br), a process accelerated by the presence of silver salts. Corresponding reactions with nickel and palladium occur even more readily. Thus, treatment of $[Ni(AsMe_2Ph)_4]$ with $CF_2{=}CFBr$ in suitable solvents yields $[NiBr(CF{=}CF_2)(AsMe_2Ph)_2]$, and $[Pd(CNBu^t)_n]$ reacts with $CF_2{=}CFCl$ to give $[PdCl(CF{=}CF_2)(CNBu^t)_2]$; the intermediate fluoroalkene complexes $[M(C_2F_3X)(L)_2]$ are not isolated [60,61]. These reactions provide a good route to perfluorovinyl complexes of Ni, Pd, and Pt.

We were able to widen the scope of our work to probe the reactivity of zerovalent complexes of Ni, Pd and Pt by using $(CF_3)_2C{=}O$ and $(CF_3)_2C{=}NH$ as substrate molecules. In this, we were much assisted by the advent of new metal reagents, notably $[Ni(CNBu^t)_4]$ [62], $[Ni(cod)_2]$ (cod is cyclo-octa-1,5-diene) [63,64], and $[Pt(cod)_2]$ [65,66].[10] The synthons $[M(cod)_2]$ (M=Ni or Pt) proved especially useful, as they could be used to form in situ other complexes where the metal is ligated by a variety of phosphines or isocyanide groups. Thus, the nucleophilicity of the metal center could be adjusted so as to change its reactivity towards electrophilic fluorocarbon substrate molecules.

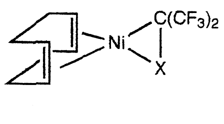
Tetrafluoroethylene and the various nickel reagents generally afforded the metallacyclopentanes $[\overline{Ni(CF_2CF_2CF_2CF_2)}(L_2)]$ (**4**) [68] Only when [Ni(cdt)] (cdt is *t,t,t*-cyclododeca-1,5,9-triene) was treated with $CF_2{=}CF_2$, was a three-membered ring complex $[Ni(C_2F_4)(cdt)]$ obtained.



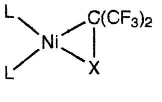
	L
4a	PPh_3
4b	$PMePh_2$
4c	PEt_3
4d	PBu^n_3
4e	$P(OMe)_3$

The latter reacted with PPh_3 to give $[Ni(C_2F_4)(PPh_3)_2]$, which then, in turn, with $CF_2{=}CF_2$ very rapidly yielded the nickelacyclopentane **4a** [69]. This observation implicated metallacyclopropanes as intermediates in the formation of metallacyclopentane ring systems. The resistance of $[Ni(C_2F_4)(cdt)]$ towards further ring expansion with $CF_2{=}CF_2$ is probably due to the cdt ligand blocking access to a coordination site on the metal by another molecule of the fluoroalkene.

Further examples of the expansion of three- to five-membered rings came with studies of reactions of Ni^0 complexes with the molecules $(CF_3)_2C{=}X$ (X is O or NH) [70–72].

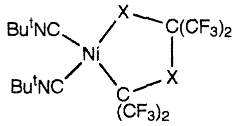


	X
5a	O
5b	NH



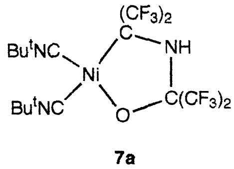
	L	X
5c	PPh_3	O
5d	PPh_3	NH
5e	$PMePh_2$	O
5f	$P(OPh)_3$	O
5g	$CNBu^t$	O
5h	$CNBu^t$	NH
5i	CNPh	O

A series of 1 : 1 adducts **5a–f** were isolated when cyclo-octa-1,5-diene, tertiary phosphines or phosphites were ligating the nickel. However, when $[Ni(CNBu^t)_4]$ was used

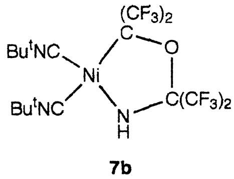


	X
6a	O
6b	NH

as the precursor, the five-membered ring metallacycles **6** were obtained. These compounds were also obtained from reactions between **5g** or **5h** and $(CF_3)_2C{=}O$ or $(CF_3)_2C{=}NH$, respectively. Compounds **5g** and **5h**, required as starting points for these ring-expansion reactions, were prepared by displacement of cod ligands from **5a** and **5b** with $CNBu^t$. Interestingly, ring expansion of **5g** with $(CF_3)_2C{=}NH$



7a



7b

yields exclusively complex **7a**; its isomer **7b** is not formed [72]. Formation of **7a** thus occurs by opening of the carbon–nickel bond in **5g**. Determination of the molecular structure of **7a** by X-ray diffraction by Penfold and Countryman [73], was of pivotal importance. At the time, we did not have sufficient capacity at Bristol for X-ray diffraction studies of all the unusual metal complexes being made by the several different groups, and so we were helped in this situation by Professor Penfold in Christchurch, New Zealand. In a

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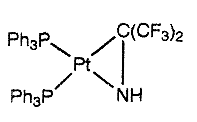
[10] We were not the first to prepare $[Pt(cod)_2]$ [67]. However, Dr. (now Professor) J.L. Spencer in my group was the first to devise a synthesis of the compound that made useful quantities available for its use as a precursor [16].

reaction related to the synthesis of **7a**, the platinum complex **8** reacts with $(CF_3)_2C{=}O$ to give the heterocyclic compound **9**.



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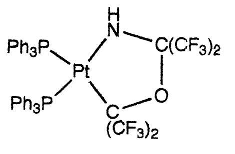
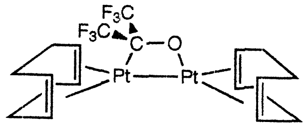


9

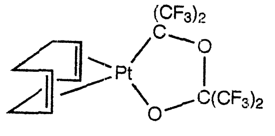
It became evident from these and other observations [74] that the formation of three-versus five-membered rings is delicately controlled by the metal involved (Ni, Pd or Pt), the relative σ-donor and π-acceptor properties of the ligands on the metals, and the nature of the fluorocarbon substrate molecules. Many features of the chemistry remain unresolved to be solved by others who come later. Thus, neither the perfluoropropene–platinum complex **3d** [53] nor, more surprisingly, the nickel compound $[Ni\{CF_2CF(CF_3)\}(cod)]$ [68] react further with $CF_2{=}CFCF_3$ to afford a five-membered ring heterocycle. Also, metallacycles with ring sizes larger than five were not found when employing $CF_2{=}CF_2$. Further studies with this fluoroalkene and M^0 compounds in the presence of cocatalysts are merited to determine if conditions for oligomerization or polymerization can be observed.

Interesting differences between the behavior of analogous Ni^0 and Pt^0 complexes towards the same fluorocarbon substrates $(CF_3)_2C{=}O$, $CF_2{=}CF_2$, and $CF_2{=}CFCF_3$ became apparent during our work. Thus, $[Ni(cod)_2]$ reacts with $(CF_3)_2C{=}O$ to give the three-membered ring complex **5a** as the only product [70].



10

In contrast, the main product obtained from reactions between $[Pt(cod)_2]$ and $(CF_3)_2C{=}O$ employing a 1 : 1 ratio of these reagents is the diplatinum complex **10**, with the species **11** and **12** also being formed as minor products [75]. When $(CF_3)_2C{=}O$ is used in excess with $[Pt(cod)_2]$, compounds **11** and **12** are the only products, with the former predominating. Compound **13**, the platinum analog of the nickel complex **5a**, was prepared as part of our program by treating $[Pt(C_2H_4)_3]$ with cod, followed by addition of $(CF_3)_2C{=}O$.



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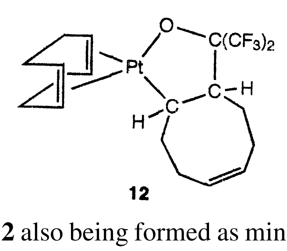
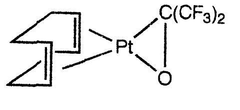
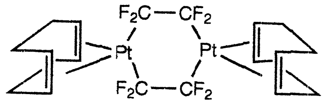


12

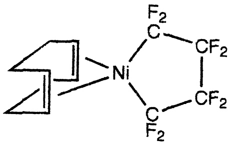


13

Interestingly, whereas Ni^0 complexes form octafluoronickelacyclopentane structures very readily, e.g., complexes **4**, the Pt^0 precursors do not form the corresponding octafluoroplatinacyclopentanes. Thus, platinum complexes $[Pt(PR_3)_4]$ or $[Pt(C_2H_4)(PR_3)_2]$ (R = alkyl or aryl) react with $CF_2{=}CF_2$ to afford very stable molecules with platinacyclopropane structures like **3a**. The reagent $[Pt(cod)_2]$ reacts with excess $CF_2{=}CF_2$ to yield the diplatinum complex **14** [76], whereas under the same conditions, $[Ni(cod)_2]$ affords a very unstable species possibly $[Ni(C_2F_4)(cod)]$ [68]. If $PMePh_2$ is added to solutions of the latter, before deposition of nickel metal occurs, the nickelacyclopentane complex **4b** is obtained. The cycloocta-1,5-diene nickel complex **15** was prepared by an indirect route involving treatment of **4d** with cod in the presence of $ZnBr_2$ as a scavenger for the removal of the $PBu^n{}_3$ ligands.

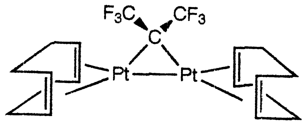


14



15

Mention was made earlier of the perfluoropropene complex $[Ni\{CF_2CF(CF_3)\}(cod)]$. This labile species forms in the reaction between $[Ni(cod)_2]$ and $CF_2{=}CFCF_3$, and with PPh_3, gives the very stable derivative $[Ni\{CF_2CF(CF_3)\}(PPh_3)_2]$, akin to the platinum complex **3d** [68].



16

In contrast, $[Pt(cod)_2]$ reacts with $CF_2{=}CFCF_3$ to produce a diplatinum complex **16** [76]. Evidently, a fluorine migration reaction occurs in the synthesis of this interesting product, and the intermediacy of a fluoroalkylidene species $[Pt\{{=}C(CF_3)_2\}(cod)]$, derived from $[Pt\{CF_2CF(CF_3)\}(cod)]$ by F migration, was proposed. Formation of **16** could then result through a combination of the species [Pt{=C(CF$_3$)$_2$(cod)] and Pt(cod).

3. Conclusion

During two decades (1958–1977), the study of fluorocarbon derivatives of the transition elements formed the main focus of my research. However, from 1963 onwards, studies in other areas gathered momentum. These were organoruthenium chemistry, following Michael Bruce's discovery of a convenient low-pressure synthesis of the carbonyl [Ru$_3$(CO)$_{12}$] [77], and metallacarboranes [78], through John Spencer's interests in employing Pt^0 complexes for new syntheses of the cage compounds. Work with the fluorocarbon metal compounds seemed less exciting at the time and was therefore terminated. This was especially so following our synthesis of naked platinum complexes where alkenes are the only ligands, e.g., [Pt(C$_2$H$_4$)$_3$] [16,79]. The very successful application of isolobal mapping to the synthesis of organometallic compounds [80] diverted us still further from the fluorocarbon studies. Nevertheless, even with the later work, the strong bonding properties of CF$_2$=CF$_2$ as a ligand were used to probe the structures and dynamic behavior of some molecules, e.g., [Pt(C$_2$H$_4$)$_2$(C$_2$F$_4$)] [81,82] and [Pt(C$_2$H$_4$)(C$_2$F$_4$){P(C$_6$H$_{11}$)$_3$}] [83]. With hindsight, I have had some regrets at abandoning studies on fluorocarbon metal compounds, as it is easy to envisage much new chemistry that could be developed. Further research in the area would certainly be profitable.

The above work became possible through the aid of many coworkers, whom I thank, and list approximately in order in which they studied with me, together with their present titles: Professors H.D. Kaesz, R.B. King, Emily Pitcher (Mrs. E.O. Dudek), P.M. Treichel, Drs. T.D. Coyle, T.A. Manuel, S.L. Stafford, J. Morris, and Professor P.M. Maitlis, of the Harvard group. These were followed in the UK by Drs. P.W. Jolly, D.T. Rosevear, J.B. Wilford, Professor M.I. Bruce, Drs. A.J. Rest, C.S. Cundy, J. Ashley-Smith, Professors J.A.K. Howard, J.L. Spencer, A.J.Mukhedkar, Drs. P.K. Maples, Jane Browning (Mrs. D. Berry), H.D. Empsall, A. Greco, Professors A. Laguna and J. Forniés. It is particularly gratifying to me that Antonio Laguna and Juan Forniés in recent years have published so much novel metal complex chemistry involving fluoroaromatic ligands attached to gold and platinum, respectively. The chemistry they have developed could not possibly be envisaged when we began our work in the late 1950s. Finally, it should be mentioned that within the confines of this article, it was not possible to mention all of our own work with unsaturated fluorocarbons. Many interesting reactions between CF$_3$C≡CCF$_3$ and low valent metal complexes were discovered by Professors J.L. Davidson, M.I. Bruce, and Dr B.L. Goodall.

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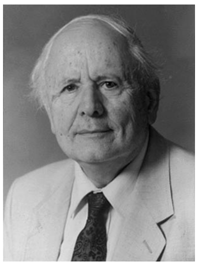

F. Gordon A. Stone was born in Exeter in 1925 and educated at Exeter School. He entered Christ's College, Cambridge, as a student in 1945. After obtaining first class honours in Parts 1 and 2 of the Natural Sciences Tripos, he carried out graduate work with H.J. Emeléus, receiving his Ph.D. in 1951. He, then, spent two years as a postdoctoral fellow under the Fulbright programme with Anton Burg at the University of Southern California. He moved to Harvard in 1954, working initially with Gene Rochow, but within a few months, he was appointed an instructor and subsequently an assistant professor. In 1962, he returned to the UK to head the inorganic chemistry section at Queen Mary College, University of London. In 1963, he became the first professor of inorganic chemistry at Bristol University, remaining there until 1990 when he accepted an invitation to become the Robert A. Welch Foundation Distinguished Professor of Chemistry at Baylor University, in Texas, where he is able to concentrate on research. In recognition of his contributions to the advancement of inorganic chemistry, Gordon Stone has received many major awards. He was elected to the Royal Society in 1976, and for services to chemistry in UK, was appointed CBE in 1990. He is one of very few chemists who have received both the Davy Medal of the Royal Society and the Longstaff Medal of the Royal Society of Chemistry. He has also received the American Chemical Society's award for research in inorganic chemistry, and his RSC awards include the Tilden Lectureship, the Ludwig Mond Medal, and the Frankland Prize Lectureship. He is the author of over eight hundred primary journal articles, was the founding editor of Advances in Organometallic Chemistry, of which 43 volumes have been published, and co-edited with E.W. Abel and G. Wilkinson the well-known series of volumes, Comprehensive Organometallic Chemistry. His scientific autobiography, *Leaving No Stone Unturned*, was commissioned by the American Chemical Society and published in 1993 as part of a series of scientific autobiographies by eminent chemists. Approximately sixty of the 180 persons who have worked in Gordon's laboratory, either as Ph.D. students or postdoctoral assistants, now hold permanent academic positions throughout the world.