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AN ORGANOMETALLIC JOURNEY FROM FLUORINE TO PLATINUM

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Introduction

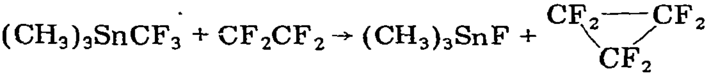
As in most universities, the chemistry curriculum at a New Zealand university, in the late 1940's and early 1950's contained little, if any, organometallic chemistry other than a brief mention of Grignard reagents and related species. My interest in organometallic compounds was first stimulated during a two-year period in 1955—1957 in the laboratory of Professor H.J. Emeléus at Cambridge. Although my research was on the chemistry of vanadium, niobium and tantalum pentafluorides, the extensive research [1] in the Emeléus group over the preceding ten years on perfluoroalkyl compounds of main group metals attracted my interest. Numerous derivatives of non-metals such as phosphorus, arsenic, antimony, sulphur and selenium had been prepared and it was clear that the presence of the fluorinated alkyl group, especially CF_3, brought about substantial changes in properties. Thus, $P(CF_3)_3$ shows [2] little or no basic character, in contrast to $P(CH_3)_3$. The prospect of extending this effect into the organometallic chemistry of both main group and transition metals was intriguing, and so after taking up an appointment at the University of British Columbia in 1957, I commenced a research program into two aspects of fluorine chemistry, one involving the further study of volatile transition metal fluorides such as chromium(IV) fluoride, and chromium(V) fluoride [3], the other being concerned with the synthesis and study of perfluoroalkyl derivatives of main group metals, particularly those of Groups III and IV.

Fluorocarbon chemistry

The earlier work in Emeléus's group and later work by Haszeldine [4] and West [5] and others had shown the difficulty of applying the more common synthetic methods, such as lithium or Grignard reagents, to the preparation of perfluoroalkyl compounds, Particularly for CF_3 derivatives, this meant that a specific synthetic route was necessary for each desired compound. Our attention was turned initially to tin, for which an extensive organic chemistry was well-known, and after a number of unsuccessful attempts to bring about redistribution reactions between organotin halides and perfluoroalkyl iodides, we found that a smooth reaction occurred between hexamethylditin and CF_3I [6].

$$(CH_3)_3Sn{-}Sn(CH_3)_3 + CF_3I \rightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI \tag{1}$$

We very quickly also found that the thermal decomposition of this first trifluoromethyl-tin compound occurred by the elimination of difluorocarbene, since decomposition in the presence of tetrafluoroethylene gave the difluorocarbene addition product, perfluorocyclopropane.



$$(CH_3)_3SnCF_3 + CF_2CF_2 \rightarrow (CH_3)_3SnF + \begin{array}{c} CF_2 - CF_2 \\ \diagdown \quad \diagup \\ CF_2 \end{array} \tag{2}$$

This ability to characterize perfluoroalkyltin compounds, as well as their interesting chemistry, appeared to us to be sufficiently novel to warrant publication as a Communication in a reputable North American journal, but while the referees reported that the work was sound, in their opinion it might best appear as a full paper. Unfortunately, while this paper was in press, a short communication [7] by F.G.A. Stone and his co-workers at Harvard heralded their extensive work, which rapidly uncovered much [8] of the fluoroalkyl chemistry of the transition metals as well as of tin and lead, including their own use of reaction 1.

Our own continued work, however, raised questions concerning the mechanisms by which reaction 1, occurred. We had initially proposed a four centre type of intermediate, but revisions were necessary when we found that, on attempting to repeat reaction 1 with a different, although apparently pure sample of hexamethylditin, no reaction occurred! Subsequent investigation [9] established the involvement of a radical process which could be initiated by ultra-violet light or by radical initiators. This was our first encounter with free radical processes of organometal compounds, but it played a major part in developing an interest in organometallic reaction mechanisms, a theme which has become increasingly important in our more recent work.

Because of Stone's published work [7] we did not delve into lead chemistry, but rather attempted to prepare perfluoroalkyl compounds of germanium. Again, since general methods were not available, and since the higher Ge—Ge bond strength [10] makes the germanium analogue of reaction 1 unattractive, it was necessary to find a specific synthetic route. This was found [11] in the reaction of germanium(II) iodide with trifluoroiodomethane (reaction 3).

$$CF_3I + GeI_2 \rightarrow CF_3GeI_3 \tag{3}$$

Although this can be an essentially quantitative process, it is also unpredictable depending on the particular sample of GeI_2 used, and again may suggest that a radical process is involved. Although our further work [12] developed some of the chemistry of this trifluoromethylgermanium compound, including its conversion to the analogous fluoride CF_3GeF_3 which itself participates in complex formation to species such as $K_2[CF_3GeF_5]$, there remains much interesting research to be done on perfluoroalkyl derivatives of germanium.

From trimethyltrifluoromethyltin, prepared as described above, it also was possible to prepare [13] the first perfluoroalkylboron derivatives in the form of salts containing the remarkably stable $CF_3BF_3^-$ ion.

The synthesis, employing the pseudo-halogen character of the highly electronegative CF_3 group [14], involves the reaction of the tin compound with boron trifluoride in carbon tetrachloride.

$$(CH_3)_3SnCF_3 + BF_3 \xrightarrow{CH_4} (CH_3)_3Sn^+(CF_3BF_3)^- \qquad (4)$$

The product is freely soluble in water, giving a stable solution from which quite stable salts MCF_3BF_3, ($M = K^+$, NH_4^+ etc) could be readily isolated. The remarkable stability of this $CF_3BF_3^-$ anion is demonstrated by the fact that a temperature of 450° C was necessary for pyrolysis, with decomposition again occurring through elimination of CF_2 and formation of BF_4^-.

While these investigations helped to open up perfluoroalkyl chemistry of Group III and IV elements, further development has been hampered by the lack of more general synthetic routes. We did, subsequently, make some improvements [15] to the preparation of n-perfluoropropyllithium and used it to prepare some C_3F_7-silicon derivatives [16], but even here there are substantial synthetic difficulties, not the least being the tendency towards decomposition to lithium fluoride and fluorocarbon polymer, as well as reactions between C_3F_7-Li and solvent. However, these early studies in organo-tin, -germanium and -boron chemistry helped to set the balance, reflected in our later research, between synthetic and chemical studies and the wide use of spectroscopic techniques. In particular, the considerable amount of useful information to be extracted from NMR spectra of organometallic compounds was apparent from a study [17] of $CF_3BF_3^-$. This was possible because at that time there was a remarkably strong group of young chemists at the University of British Columbia amongst whom there was strong competition in terms of research productivity, but amongst whom there was also considerable collaboration. This led, in my own case, to joint work with L.W. Reeves, and later to a lesser extent with J. Trotter, as well as the sharing of much equipment and chemicals with N. Bartlett and W.R. Cullen, both of whom were also at that time working on aspects of fluorine chemistry. It is amusing now (but was not then!) to recall the occasion when both Neil Bartlett and I, having had previous experience only with electrolytic fluorine generators, attempted to open and close our first cylinder of compressed fluorine and managed to release quite a burst of the gas across the university campus!

Studies with organotin compounds

The work with hexamethylditin and trimethyltrifluoromethyltin had brought me into contact with the rapidly growing organometallic chemistry of tin and this then dominated the organometallic research undertaken in my laboratory over the next few years. Three main themes developed. The first arose because of some interesting aspects of the reaction described by equation 4.

The resulting trimethyltin product was, somewhat unexpectedly, very hygroscopic although its aqueous solution was quite stable. Moreover, its infrared spectrum showed [13] some interesting features, particularly the low $\nu(C—F)$ frequencies observed, presumably because of the negative ionic charge. Wishing to confirm these infrared assignments, we attempted to prepare $(CH_3)Sn^+$-

$(CF_3BF_3)^-$, the analogous $(CH_3)_3SnBF_4$ and also $(CH_3)_3SnClO_4$ under completely anhydrous conditions and then to examine their infrared spectra. For the latter two compounds we were surprised to observe [18] the ν_3 mode (triply degenerate) of the tetrahedral anionic group, not as the usual broad band at 1000—1150 cm^{-1} but as three-well-resolved strong absorptions. Moreover, the ν_1 mode, usually seem as a weak "forbidden" transition at ca. 775 cm^{-1} was seen as a strong sharp absorption. Such data imposed C_{2v} symmetry on the anion. At the same time, the non-observance of ν(Sn—C, symmetric) suggested a planar geometry for the $(CH_3)_3Sn$ group. We, therefore, concluded that a sufficiently strong interaction occurred between $(CH_3)_3Sn$ and the anionic group to be equivalent to coordination, thus rendering the tin atom effectively five-coordinate. Simultaneously, essentially the same results were published [19,20] by Okawara and Hathaway. Further work [21] then showed that octahedral anions, MF_6^- (M = P, As, or Sb) apparently suffered a similar lowering of symmetry through interaction with $(CH_3)_3Sn$, to the extent that for M = P, extraction of fluoride occurred to generate trimethyltin fluoride as product.

During these studies, we became impressed with the fact that, according to infrared data, the trimethyltin group in $(CH_3)_3SnF$ must be planar, in contrast to the trigonal geometry in the other halides. Such a structural differentiation also parallels the considerable differences in physical properties, trialkyltin fluorides being white, insoluble solids and the corresponding chlorides being much lower melting, generally soluble compounds. Accordingly, we determined [22] the single crystal structure of trimethyltin fluoride, and although some ambiguities of interpretation arise because of disorder problems, the structure is indeed polymeric, with bent Sn—F—Sn bridges, probably with planar $(CH_3)_3$-Sn groups, and perhaps most importantly five-coordinate tin. The general conclusion that free R_3Sn^+ ions do not exist in the solid state then had to be extended to the analogous R_2Sn species by investigations [23,24] of dimethyltin derivatives. Again, in the compounds $(CH_3)_2SnX_2$, X = NO_3, BF_4, PF_6, and X_2 = SO_4, CO_3, infrared spectroscopic data always indicated a linear geometry of the $(CH_3)_2Sn$ group, and an interaction between cationic and anionic groupings strong enough to lower the symmetry of the anion. Indeed, attempts to obtain pure $(CH_3)_2Sn(BF_4)_2$ or $(CH_3)_2SnSiF_6$ caused partial or complete decomposition to $(CH_3)_2SnF_2$, indicating considerable strength for this interaction.

If free organotin cations cannot exist in the solid state and instead always attain five- or six-coordination through interaction with the anion, then it was reasonable to ask whether analogous species of other main group metals behaved similarly. The preparation and infrared study [25] of a range of trimethylantimony derivatives $(CH_3)_3SbX_2$ showed that strong coordinative interactions occurred between $(CH_3)_3Sb$ and X leading to non-ionic five-coordinate structures, and in some cases to breakdown of the anionic group. Our work in this area, along with that of others such as Tobias [26], Schlemper [27], and Okawara [28], has thus demonstrated that free organometallic cations of many main group metals do not exist in either solid state or solution. To define the nature of the coordinative interaction between such organometallic and anionic group is more difficult but certainly the results cannot be attributed just to the combined effect of low crystal site symmetry of the anion with the high polarizing effect of, say, the $(CH_3)_3Sn^+$ cation. This was evident from the observation that concentrated solutions of $(CH_3)_3SnClO_4$ in methanol show [29] the same splittings of infrared bands. This, and other arguments combine to offer a strong case for the occurrence [30] of a genuine coordinative interaction.

The second area of organotin chemistry which we pursued in the 1960—65 period at the University of British Columbia sprang from the recognition that the high reactivity of the Sn—H bond in organotin hydrides, first reported by Van der Kerk [31], might provide a synthetic route to fluoroalkyltin compounds, through reaction with fluoro-olefins. Moreover, the fact that the resulting organo(fluoroalkyl)tin derivatives would contain four magnetically active nuclei, ^1H, ^{19}F, ^{117}Sn and ^{119}Sn suggested that their NMR spectra would be interesting. We first [32] explored the decomposition of organotin hydrides, particularly dimethyltin dihydride, and found that this decomposition is accelerated by ultraviolet light with $(CH_3)_3SnH$, Sn and H_2 being the initial products and after longer reaction times, $(CH_3)_6Sn_2$, $(CH_3)_4Sn$ being formed. We then showed [32] that such a dihydride reacts with tetrafluoroethylene in a stepwise fashion giving first the mono(fluoroethyl) product, $(CH_3)_2SnH(CF_2CF_2H)$, and subsequently the bis product, $(CH_3)_2Sn(CF_2CF_2H)_2$. With other fluoro-olefins, such as CF_2CFH and CF_2CH_2, unstable mono-addition products appeared to be formed but decomposed via halogen—hydrogen exchange to the organotin fluoride and olefin. Although we did not conduct kinetic studies, qualitative data suggested [33] strongly that these addition reactions between organotin dihydrides and fluoro-olefins proceed via a radical mechanism in which the generation of radicals from the tin hydride may be the rate determining step. Further evidence to this effect came from an examination [34] of the addition reactions of dimethyltin dihydride with simple olefins such as ethylene, butadiene and *cis*- and *trans*-butene. We also found considerable interest [35—36] in the NMR spectra of some of the products, the complexity of some of which is illustrated by the fact [35] that the ^1H resonance for the hydride proton of $(CH_3)_2SnH(CF_2CF_2H)$ consists of 126 components, many of which could be at least partially resolved!

Subsequently, we extended this type of work further by investigating [37] the reactions of dimethyltin dihydride with perfluorovinyltin compounds. While theoretically these might yield substituted 1,4-distannacyclohexane derivatives [38], we found again that the considerable stability of trimethyltin fluoride, presumably because of its polymer-type structure, always drives the reactions to its formation together with substituted (fluorovinyl) organotin products. Again, qualitative observations suggest that free radical processes are occurring. Later we carried out similar reactions using the related fluorovinyl derivatives of silicon [39] and germanium [40]. While the chemistry involved in these systems is relatively simple, they were interesting to us because of the elegant way in which NMR spectra could be used to identify products and to distinguish between isomeric possibilities. This background, particularly as it relates to the geometry of vinyl groups attached to a metal, has been most valuable in our more recent work, since knowledge of the vinylic geometry has allowed mechanistic conclusions to be drawn.

The third theme coming out of our first foray into organotin chemistry developed because of my interest in the obviously high reactivity of the Sn—Sn bond in compounds such as hexamethylditin. We had already used this in the preparation of $(CH_3)_3SnCF_3$, and it appeared to be a useful starting material for the preparation of other fluorinated organotin derivatives. Moreover, the characterization of cyclic and linear oligomers of $[(CH_3)_2Sn]_x$ and $[(C_6H_5)_2Sn]_x$ by Neumann [41], Rundle [42], and Brown [43] suggested their possible use to prepare organometallic polymers based on a repeating [Sn—C—C—] unit. We therefore studied the behaviour of hexamethylditin with C_2F_4, ethylene and several fluoro-olefins under conditions which favour the formation of $(CH_3)_3Sn$ radicals. Two types of products could be isolated with C_2F_4 or C_3F_6, namely (polyfluoroalkyl)trimethyltin compounds e.g. $(CH_3)_3SnCF_2CF(R)H$ and insertion products of the type $(CH_3)_3SnCF_2CF(R)Sn(CH_3)_3$ where R = F or CF_3. The results were consistent with the formation of intermediate radicals such as $(CH_3)_3SnCF_2C(R)F^{\cdot}$ which then participated either in hydrogen abstraction or in the formation of insertion products. Unfortunately, tetrafluoroethylene with the cyclic hexamers of diphenyltin and dimethyltin gave products of indeterminate composition. This was typical of much of our subsequent work in this area; the metal—metal bonded compounds themselves, when sufficiently reactive with interesting substrates, were often fairly difficult to handle and tended to give products whose identity could not easily be determined. Again, however, we were able to make good use of NMR facilitaties in collaboration [44] with L.W. Reeves and E.J. Wells, by observing both the ^1H and ^{119}Sn resonances for hexamethylditin.

Metal—metal bonds and other extensions

In our next choice of a metal—metal bonded compound, we were lucky to choose the one compound with the almost ideal degree of metal—metal reactivity, namely $(CH_3)_3SnMn(CO)_3$. We did not realize the extent of our luck until we attempted subsequently, and with some frustation, to extend this work later to quite closely related derivatives, e.g. $(C_6H_5)_3SnMn(CO)_5$ which is remarkably unreactive! The first compound, however, $(CH_3)_3SnMn(CO)_5$ reacted quite beautifully with C_2F_4, to give (equations 5 and 6) the simple insertion products and also subsequent decomposition products [45,46].

$$(CH_3)_3SnMn(CO)_5 + C_2F_4 \rightarrow (CH_3)_3SnCF_2CF_2Mn(CO)_5 \qquad (5)$$

$$(CH_3)_3SnCF_2CF_2Mn(CO)_5 \rightarrow 2(CH_3)_3SnF + [(CO)_4MnCF{=}CF_2]_2 + 2\ CO \qquad (6)$$

With other fluoro-olefins, the Sn—Mn compound gave trimethyltin halides and interesting fluorovinylmanganese pentacarbonyl derivatives whose vinylic geometry could be deduced from ^1H and ^{19}F NMR parameters. As far as we could tell from qualitative observations, the reaction of equation 5 occurred via an ionic or four-centre type of mechanism and our later work also seemed consistent with this.

It seemed easy to predict very similar behaviour for $(CH_3)_3MMn(CO)_5$ where M = Sn or Ge, but this we did not find. Trimethylgermyl(pentacarbonyl)manganese certainly gave [47], even more cleanly that its tin analogue, the simple tetrafluoroethylene addition product, $(CH_3)_3GeCF_2CF_2Mn(CO)_5$, but with other fluoro-olefins either fluorovinyl-germane or fluorovinyl(pentacarbonyl)-manganese derivatives were formed in reactions whose course could not be predicted from either the nature of the olefin or our previous results. We made several studies of other covalent Sn—metal bonded compounds, the first [48] involving Sn—Co species. Here, the nature of the products was even more dependent on the reaction conditions; under UV irradiation in non-polar solvents both $Co_2(CO)_8$ and $R_3SnCo(CO)_4$ ($R = CH_3C_6H_5$) with C_2F_4 gave simple insertion compounds (e.g. $R_3SnCF_2CF_2Co(CO)_4$) as major products, but under thermal conditions in acetone, fluorination by the olefin is extensive yielding cobalt fluorides, triorganotin fluorides, and significant amounts of tricobalt nonacarbonyl derivatives, principally $Co_3(CO)_9CCF_3$. We then moved to the related iron compounds and compared [49] the reactivities of Si—Fe, Ge—Fe bonds, as a series, and also against Sn—Mn as a reference, looking at reactions with both fluoro-olefins and fluoroacetylenes. Although we were able to prepare a number of interesting new fluorocarbon derivatives [50], the M—Fe compounds were generally unreactive and their study, therefore, disappointing. Subsequently, we examined [51] simple cleavage reactions, of halogens, hydrogen halides and related compounds with $(CH_3)_3SnMn(CO)_5$ and also explored [52,53] the reactions of sulphur dioxide with compounds containing Sn—Sn, Sn—Mn, Si—Fe, Ge—Fe and Sn—Fe bonds although precise structural characterization of the products was difficult. In general, though, the chemical studies with metal—metal bonded compounds turned out to be less productive than we had hoped, in large part because we found it impossible to predict, in going from one metal—metal species to another, just what the change in reactivity would be. Also, the processes were often complicated by the occurrence of secondary reactions such as fluorination by the olefin, or the elimination of a triorganotin fluoride, or the formation of a metal cluster. Two quite worthwhile side-lines did emerge, however; we were among the first to use low frequency infrared spectroscopy to study [54,55] metal—metal vibrations although unfortunately at the time we did not have facilities readily available to make the parallel Raman spectroscopic studies. We also, through the preparation and crystal structure determination of some of the fluorovinylmanganese pentacarbonyl derivatives described above, were able to participate [56] in the debate on the nature of the bonding between transition metals and fluoroalkyl or fluoroalkenyl groups. Thus, in *cis*-$CFH{=}CFMn(CO)_5$ we observed lengthening of the C—F distances (to 1.50 Å for C_B—F), lowering of the ν(C—F) frequencies, anomalous features in the ^{19}F NMR spectrum, and unique molecular dimensions, all of which provide excellent evidence for the π-bonding interaction between transition metals and fluorinated σ-organic groups.

Finally, also arising from previous interests in the nature of organometallic ions, e.g. R_3Sn^+, we ventured into indium chemistry. Our observations, outlined above, of the non-ionic and frequently polymeric nature of compounds of the types R_3SnX, R_2SnX_2 and R_3SbX_2, were in considerable contrast to similar studies of organothallium derivatives, which indicate high stability and wide occurrence of R_2Tl^+ ions. A better comparison to our mind, was that between R_2InX and R_3SnX, but this required some development of organoindium chemistry. We developed [57] a simple one-step synthesis of trimethylindium, or dimethylindium chloride, from $InCl_3$ and methyllithium, the final product depending on the length of time for which the reaction is allowed to run. We then used these two compounds to prepare and characterize a number of dimethylindium and methylindium derivatives [58] of the types Me_2InX, $Me_2InX \cdot L$ (L = neutral ligand e.g. pyridine), $Me_2InX \cdot L_2$ (L_2 = bidentate ligand e.g. *o*-phenanthroline), $MeInX_2$ and $MeInX_2 \cdot L_2$ [L = pyridine or 1/2 (2,2-bipyridine)]. The stereochemistry was examined, primarily by infrared methods, leading to the conclusion that the dimethylindium halides and their 1 : 1 complexes with Lewis bases have a distorted tetrahedral geometry about indium, while the 1 : 1 complexes of Me_2InX with bidentate ligands probably contain five coordinate indium. There was certainly no evidence for the existence in the solid state of free $(CH_3)_2In^+$ ions.

An introduction to platinum

One objective of this article is to show what was, I hope, a logical train of thought, running through from perfluoroalkyl chemistry of main group metals to the organic chemistry of platinum to which really all of our attention has been devoted for 10 years. This move to platinum chemistry happened, also, to roughly coincide with my move from British Columbia to the University of Western Ontario in 1965.

These themes came together first in 1964—1966 when from my previous interest in fluorinated organometallic compounds and our recent work with organotin hydrides, the thought occurred to me that the reactions of fluoroolefins with platinum(II) hydrides [59] should provide an easy route to fluorinated platinum derivatives. Somewhat to our surprise, the products of such reactions were found to be fluorovinyl rather than fluoroalkyl compounds [60,61] with silicon tetrafluoride being the final product from the accompanying hydrogen fluoride (equation).

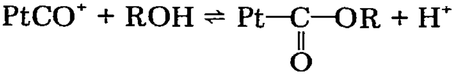
e.g. $trans\text{-}(PEt_3)_2PtHCl + CF_2{=}CFH \rightarrow trans\text{-}(PEt_3)_2PtCl(CF{=}CFH) + HF$ (7)

The most puzzling reaction was that with tetrafluoroethylene in which the vinylic derivative, $trans\text{-}(PEt_3)PtCl(CF{=}CF_2)$ was accompanied by two other products one of which was identified as $trans\text{-}(PEt_3)_2PtCl[C(CF_2H){=}CF_2]$ and the other we tentatively identified as a five coordinate $\pi\text{-}C_2F_4$ complex. Just before we published these results, I presented a paper on them at a EUCHEM Conference on Metal Hydrides in Bristol in 1966. Although I expressed some reservation as to whether we had indeed characterized a five coordinate platinum-olefin complex, discussions with F.G.A. Stone and others encouraged us to publish these results. At the same time, I gave a crystalline sample of the products to J.A. Ibers for crystal structure determination. On almost the same day as our paper [60] was published, Ibers phoned me in some irritations to say that our product was neither five coordinate nor an olefin complex, but rather a platinum(II) carbonyl salt! This was confirmed by further chemical work and the full crystal structure [62]. It was apparent then that a most remarkable chemical reaction had occurred; although both the platinum(II) hydride and C_2F_4 are, separately, completely stable and unreactive in benzene at 120°C, together they react through initial formation [63] of the $Pt{-}C_2F_4H$

group. This then eliminates HF and generates the $Pt{-}CF{=}CF_2$ product, while from the further reaction of the HF with the glass container in the presence of the Pt^{II} compounds, both the $Pt[C(CF_2H){=}CF_2]$ derivative as well as the cation $(PEt_3)_2PtCl(CO)^+$ are formed! An additional but quite exciting discovery was that while the anion accompanying the carbonyl cation was in large part the expected BF_4^-, it was accompanied by the previously unknown SiF_5^- ion. It was truly a remarkable reaction and one which convinced us of the scope and fascination of organoplatinum chemistry.

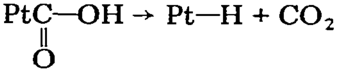
The carbonyl cation *trans*-$(PEt_3)_2PtCl(CO)^+$ was itself of considerable interest since it is isoelectronic with Vaska's compound [64], $IrCl(CO)(R_3P)_2$. Although we quickly found that it was much less reactive than those Ir or Rh analogues, we were able to find simple synthetic routes [65,66] to it, and to the related cations $MX(CO)(R_3P)_2^+$ and $MX(R_3P)_3^+$, M = Pt or Pd, some of which involved the cleavage of halogen-bridged dimeric complexes by neutral ligands such as CO or R_3P, or the removal of Cl by silver or thallium from a neutral metal complex followed by replacement with CO or R_3P. We were also able to prepare [67] a number of simple pentafluorosilicates by the remarkably simple reaction of, say a quaternary ammonium chloride with silica in the presence of aqueous hydrofluoric acid, and from an examination of the infrared and Raman spectra of SiF_5^-, deduced that it probably has the expected trigonal bipyramidal geometry.

We then very quickly discovered [68] an interesting relationship between the platinum-carbonyl cation and the neutral Pt^{II} hydride, in that the latter can be formed by reaction of the carbonyl cation with water. With ethanol or methanol, rather than water, alkoxycarbonyl derivatives are formed and kinetic data indicated that these processes occurred by nucleophilic attack on the carbonyl carbon to generate, through H^+ dissociation, alkoxycarbonyl species. These decompose to hydride and carbon dioxide. The overall sequence of reactions, therefore, involves transition metal hydride formation from water and oxidation of carbon monoxide to carbon dioxide.



$$PtCO^+ + ROH \rightleftharpoons Pt{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OR + H^+ \qquad (8)$$

R = H or alkyl



$$Pt\underset{\underset{\displaystyle O}{\|}}{C}{-}OH \rightarrow Pt{-}H + CO_2 \qquad (9)$$

The final element in the future framework of our organoplatinum research came in work done with J.D. Ruddick. We had already made and characterized cationic Pt^{II} species containing hydridic hydrogen or carbon monoxide; since neutral methylplatinum(II) species were known, it seemed useful to prepare and study principally by ^1H NMR spectroscopy a wide range of cationic methylplatinum(II) complexes. This was readily done [69] and added substantially to our expertise in preparing cationic Pt^{II} species and also provided a considerable amount of useful NMR data.

Organoplatinum chemistry

It was now increasing clear to me that these platinum(II) systems possessed a unique combination of properties, although the importance of some of them has only become fully apparent more recently. These properties, summarized below, suggested in turn that organoplatinum chemistry was likely to be a remarkably productive field not only because new and unexpected types of organic derivatives might be identified, but more importantly because so many of them modelled other metal derivatives thought to be key intermediates in important catalytic processes. Among such useful characteristics are:

(a) The stability of platinum(II) hydrides, alkyls and other organic derivatives. Simple experimental techniques can therefore be used generally, and decomposition during a reaction is usually not a problem.

(b) Their reactivity is far greater than might be intuitively expected from their overall stability, so that many varieties of reaction are observed. Moreover, reaction rates tend to be sufficiently slow that kinetics can be determined by simple techniques.

(c) Reactions frequently tend to be quantitive, so that products, which can usually be crystallized readily, are obtained in excellent yield and high purity.

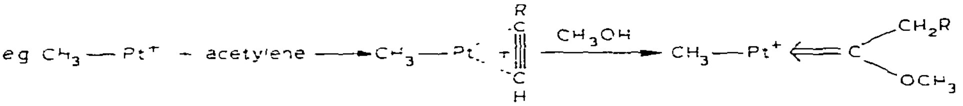
(d) The presence of ^{195}Pt, approximately 33% abundant, $I = 1/2$, provides a wealth of NMR data, particularly if phosphines are present as ligands. From J(P—H), J(Pt—H), and more recently in our case, from J(Pt—P) values, there is now such an enormous body of data for Pt^{II} compounds that one can now determine, almost unambiguously, the geometry at platinum, and for vinylic derivatives the geometry of that group, for any Pt^{II} compound. Moreover, for hydride and carbonyl species, such information can be usefully supplemented by infrared data. Nearly all of our work, therefore, since 1970 has been concentrated on platinum chemistry, and has increasingly attempted to use their valuable characteristics to understand key processes relevant to catalysis.

With R.J. Puddephatt, in 1969—1970, we began to compare Pt—CH_3 and Pt—H bonds. We knew that insertion of olefins and acetylenes into Pt—H could be induced fairly easily and we attempted to extend such behaviour to methylplatinum compounds. While we found that, under thermal conditions (70°C), both C_2F_4 and $CF_3C{\equiv}CCF_3$ readily inserted [70] into the Pt—CH_3 bond to give fluoroalkyl and fluoroalkenyl compounds, the same reactions at room temperature gave [71] reasonably stable π-olefinic or π-acetylenic complexes. These on prolonged standing underwent rearrangement to the insertion products formed under thermal conditions and were found [72] to have a trigonal bipyramidal geometry.

Again, we were fascinated, as with the platinum(II) hydrides, by the ease with which under very mild conditions an extensive molecular rearrangement occurred and we began to give increasing attention to mechanistic aspects.

$$\mathrm{Pt{-}R + C = C \rightarrow Pt{-}C{-}C{-}R} \qquad (10)$$

At this stage, since we now had stable five-coordinate Pt^{II}-acetylene complexes, it seemed useful to try to prepare four-coordinate, cationic acetylene complexes, similar to the carbonyl cations; in other words to broaden the variety of cations *trans*-$[PtClL_2L']^+$ with L′ = olefin or acetylene. This was undertaken by M.H. Chisholm and was initially frustrating until in discussion late one afternoon, we both suddenly realized [73] that the ^{1}H NMR spectrum of a sample which we had expected to an acetylene complex, was in fact that of a platinum carbene complex. Very quickly then we were able to prepare and characterize a number of cationic Pt^{II}-carbene complexes [74], as well as a smaller number of cationic acetylenic [75] and olefin [76] complexes. Although we initially proposed that the formation of Pt^{II} alkoxycarbene cations from methylplatinum cations and terminal acetylenes in methanol takes place via intermediate vinyl ether complexes, we were later able to present, I think very convincingly, arguments that these and many other reactions can best be described in terms of the chemistry of metal-stabilized carbonium ions [77,78].



(11)

(Other ligands omitted)

The importance of regarding cationic organometallic species as metal stabilized carbonium ions has not yet, I think, been fully appreciated or utilized. Certainly, in the case of platinum, it explains elegantly a variety of reactions of methylplatinum cations leading to alkoxycarbenes, alkoxyvinyl, and cyclobutadiene [79] derivatives, etc., and also provides a mechanistic route for acetylene polymerization and other processes.

While I had previously benefitted from having many able graduate students and post-doctoral fellows, the particular group members over the 1970—1973 period were not only remarkably productive individually but perhaps more importantly stimulated vigorous discussion from which many fruitful ideas were generated. Alongside Chisholm at that time were L.E. Manzer, T.G. Appleton, and K. Itoh followed later by others such as H. Kurosawa, A.G. Shaver, T. Yasufuku and C.S. Wong. The enthusiasm for platinum chemistry was remarkably strong, as demonstrated by Manzer's impressive preparation of a considerable series of cationic organometallic complexes with unsaturated systems. These included methylplatinum(II)-nitrile and -imino ether complexes [80], platinum(II)-isocyanide and -carbene complexes [81], as well as the related nickel and palladium isocyanide derivatives [82]. Further work by Manzer delved into the chemistry of dimethylplatinum(IV) cations [83], and oxidative addition and reductive elimination between methylplatinum(II) and methylplatinum(IV) species [84,85].

A particularly interesting development, since it extended in an important way our knowledge of five coordinate Pt^{II} complexes, was Manzer's preparation and characterization of trigonal bipyramidal acetylene, allene and olefin complexes of Pt^{II} containing polypyrazolylborate ligands [86,87]. Not only did some of these products show interesting NMR spectroscopic features [88], but their geometry and stability were notable. These complexes obviously were entirely analogous to those phosphine- or arsine-stabilized complexes prepared by Puddephatt [71], but they did not undergo insertion and from NMR evidence, the bound acetylene or olefin did not rotate out of the equatorial plane even at high temperature. These properties posed further questions to us concerning the various factors which might determine the actual mechanism for insertion of olefins or acetylenes into the Pt—C bond.

Some other interesting work, undertaken with Manzer and Appleton, made use of our earlier experiences with the trifluoromethyl group, and after we had prepared [89] some new perfluoro-alkylplatinum complexes, a comparison was made of their spectroscopic properties, particularly NMR coupling constants, with those of analogous alkyl compounds. This stimulated much discussion in the group on the nature of the *trans* influence, and as we result we found ourselves compiling a useful review [90] on the *trans* influence in which a variety of types of experimental data were compiled, largely for square planar complexes, and then discussed in light of the extent to which they reflected the *trans* influence as a genuine and measurable phenomenon.

We were, at the same time, continuing with studies of olefin insertions into the Pt—H bond. Indeed, increasingly we were able to tie together our work with Pt—CH_3 and Pt—H compounds to give a reasonable understanding of insertion processes. Kurosawa, at this stage, contrasted [92,93] the slow insertion of ethylene into the Pt—H bond of the neutral hydride *trans*-$(PEt_3)_2PHCl$, observed by Chatt and Shaw [94], with the rapid insertion which he observed into cationic *trans*-$(PR_3)_2PtHL^+$ (L = solvent or displaceable ligand) We thus concluded contrary to other reports, that the olefin insertion process involved four-coordinate and not five-coordinate intermediates and occurred readily when the ligand *trans* to hydride could be easily displaced by olefin. Kurosawa also applied this understanding of insertion to some work [95] on the mechanism of double bond migration in allyl derivatives and hence examined [96] some insertion and isomerization reactions of allyl compounds with cationic Pt^{II} hydrides.

With Pt^0 chemistry, there has been only a limited but interesting involvement. With K. Itoh, we looked [97] at several new tertiary phosphine complexes at Pt^0 as well as one analogue of Pd^0 and studied by variable temperature NMR the phosphine dissociation processes. Somewhat later we looked [98] in more detail at the low temperature (^1H and ^{19}F) NMR spectra of tris(diphenyltrifluoromethylphosphine)platinum(0), observing evidence for an unidentified new species at low temperature. These and related systems deserve more study since the identity and geometry of species which may be stable only at low temperatures have yet to be explored.

The following generation of students and post-doctoral fellows in my laboratory brought some new interests to the work. Ward, with others in the group, made use of the extensive series of platinum compounds we had accumulated to carry out some comprehensive work [99,100] on the ^{13}C NMR spectra of organoplatinum compounds. This had been commenced originally with Chisholm and Manzer [101], in collaboration with Stothers, well-known for his work on ^{13}C NMR of organic compounds, and allowed some considerable discussion of *cis* and *trans* influences in square-planar Pt^{II} complexes in terms of the hybridization on platinum and surrounding ligand atoms as expressed through NMR parameters.

With A.G. Shaver, we prepared [102] and studied some Pt^{II}-methyl compounds with cyclopentadienyl as another ligand, finding some fascinating examples of σ to π-interconversion of the C_5H_5 ligand, as well as some quite remarkable cases [103] where Diels-Alder addition of an acetylene to the cyclopentadienyl ligand occurs in preference to insertion into the Pt—CH_3 bond. With Yasufuku we examined aminolysis reactions of Pt^{II}-alkoxycarbene complexes [104], as well as some reactions of Pt—CH_3 complexes with acetylenes which occur by a radical process but which also involve participation by the solvent [105].

But increasingly, our work concentrated on gaining as complete an understanding as possible of all the factors which influence olefin insertion into Pt—H (and also Pt—C) bonds, and hence a full description of the mechanism. We looked with Christian [106], at the way in which neutral and also cationic Pt^{II} hydrides undergo insertion with other types of multiply bonded substrates, in this case particularly isocyanides. Some attempts were also made, with limited success, to look at comparable reactions of iridium hydrides with acetylenes [107], and to describe some new chemistry of cationic rhodium and iridium complexes [108]. We came to some appreciation of the role which steric factors play in the insertion process, expecially the bulk of the tertiary phosphine ligands, through work with Attig [109] and Shaver [110], studying nickel and platinum hydrides containing tricyclohexylphosphine. Interestingly, this led to some consideration of what actually defines the bulk of steric requirements of a ligand such as a tertiary phosphine and I discussed some thoughts on this in a 1977 paper [111]. Very recently, we have been able to use stabilizing properties of bulky phosphines to prepare a number of Pt^{II} dihydrides [112].

Mechanism of insertion

However, perhaps the most important recent work was that largely with C.S. Wong, in which we studied the kinetics of olefin insertion into Pt—H bonds. This work was based on much of our previous platinum research and drew heavily on the experience gained therefrom. Building on the studies which Kurosawa had completed [92,93]. Jablonski first investigated the kinetics of ethylene insertion into a cationic hydrido(acetone)platinum(II) complex. Although much of our previous work [92,93] had stressed the importance of four-coordinate intermediates in such a process, in contrast to the prevailing wisdom which favoured five-coordinate species, the kinetics in Jablonski's case did not allow an unambiguous distinction to be made between these two possible mechanisms. However, by choosing an olefin such as methyl acrylate whose concentration could be easily monitored, and by using a platinum-nitrate complex so that the rate dependence on anion concentration could also be followed, Wong [114] was able to determine the kinetics in a system in which insertion unquestionably occurred through a sequence of four-coordinate intermediates. Simultaneously, Halpern [115] investigated ethylene insertion into Pt—H under catalysis by $SnCl_2$ and showed that, in that system, five-coordinate intermediates were involved. We were thus able to describe a generalized mechanism [116,117] for olefin insertion into square-planar Pt complexes, in which the lability of the ligand *trans* to hydridic hydrogen is the dominant factor in determining whether four- or five-coordinate intermediates are more important.

Conclusion

These is no need for me to describe work which is being published in the current literature. The intent has been to trace a journey in organometallic chemistry which began with an interest in the unusual properties of perfluoroalkyl and particularly the CF_3 group and which has evolved to a detailed mechanistic investigation of the insertion reaction, using both platinum hydrides and platinum alkyls as model systems, and to the application of the results of those studies to further work in catalysis. In particular, I have wanted to show how some apparently unrelated themes were, in fact, tied together, and perhaps more importantly, how experience with one class of compound can be used to address problems in other organometallic areas. Our use of previous knowledge of the CF_3 group to study *trans* influences in platinum chemistry is one example, and the way in which our early work with ^{119}Sn NMR of simple organotin compounds can now be applied to our studies of tin-platinum catalyst systems is another.

But the most rewarding aspect of my involvement in organometallic chemistry has been to collaborate with, and hopefully assist, many fine co-workers. It is a pleasure to recall both those times of considerable frustration when predicted reactions just did not occur, as well as those very exciting periods of rapid accomplishment. I recall particularly the astonishingly clean reaction, performed by C. Willis [11] of GeI_2 with CF_3I which allowed us to do the reaction itself one day, characterize the products the next, and write up a paper describing the first $Ge—CF_3$ compounds the next! The astonishment with which we greeted Ibers' identification of the platinum-carbonyl cation together with BF_4^- and SiF_5^- is worth recalling, as is the satisfaction we felt in identifying, with Chisholm, that a cationic Pt^{II}-acetylene complex in methanol had generated a carbene complex. The sense of accomplishment we have had in knowing that, based on some years of work, we really understood the principal features of the mechanism of the insertion reaction is also rewarding. I have not been able in this short article to mention by name all those who have worked with me but to each of them I express my gratitude. The human side of chemistry is, in the long run, at least as important as the scientific progress we make, and for me the former has been an especially warm experience.

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