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Fluorine as a ligand substituent in organometallic chemistry: A second chance and a second research career

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This contribution is dedicated to the memories of my parents, Elliot and Joan Hughes, who always encouraged me to strive for the highest possible education, and my Nain, Edith Profit, who taught me to read when I was very young and thereby enabled everything.

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From an early age as a schoolboy in Wales and England I had a passion for history and yearned to be an archaeologist; the idea of ferreting out hidden secrets and mysteries of the past had a great hold on my mind. But the christmas gift of a chemistry set from my parents in 1958 introduced me to smells, (small) fires, and crystals and I became curious as to cause and effect in chemistry; a less than stellar experience with Latin erased from my mind the idea of detective work on issues involving the ancient world. A career as a research chemist was the chosen path. I did my GCE O- and A-levels at Ecclesfield Grammar School, near Sheffield, and my newfound interest in chemistry was encouraged by a very enthusiastic teacher, Mr. Stanley Spencer.

Fluorine first entered the picture when I visited prospective universities to interview for admission for a chemistry degree. A powerful impression was made during my visit to the Chemistry Department at the Manchester College of Science and Technology; this was then the Faculty of Technology (‘‘Tech’’) at the University of Manchester, later to become UMIST, and recently fully consolidated into the University of Manchester. The whole department seemed to vibrate with excitement about research, particularly in the Haszeldine led effort in organofluorine chemistry. I was fortunate to be taken on a tour of some research labs in the old building on sackville street where I encountered a graduate student who flourished before my eyes with a tube filled with CF_3NO! I was fascinated by its beautiful blue color, and also by the dark mutterings of the student about its rumored toxicity! Immediately I wanted to be part of this great endeavor; my application was approved and I entered ‘‘Tech’’ in the autumn of 1964. The photograph shown in Fig. 1 is the first year class in 1964. The population of the first two rows of faculty represents a veritable who's-who of organic fluorine chemists of the day [1], as well as others who were to find distinction in other areas of chemistry. Robert Haszeldine, Eric Banks, Mike Barlow, Tony Tipping, Mike Birchall, Roy Fields and Brian Booth played roles in my undergraduate education in organic chemistry; Barry Lever taught me some inorganic chemistry and symmetry before he left for Canada. Mike Green, who quickly moved to join the Bristol Chemistry Department, was a person who had a significant impact on my thought processes while I was a postdoc in his group ten years later, but we never met in Manchester. How could I not become a fluorine chemist within this bastion of the field? Easy! Instead of the ‘‘first’’ that would have ensured my choice of research

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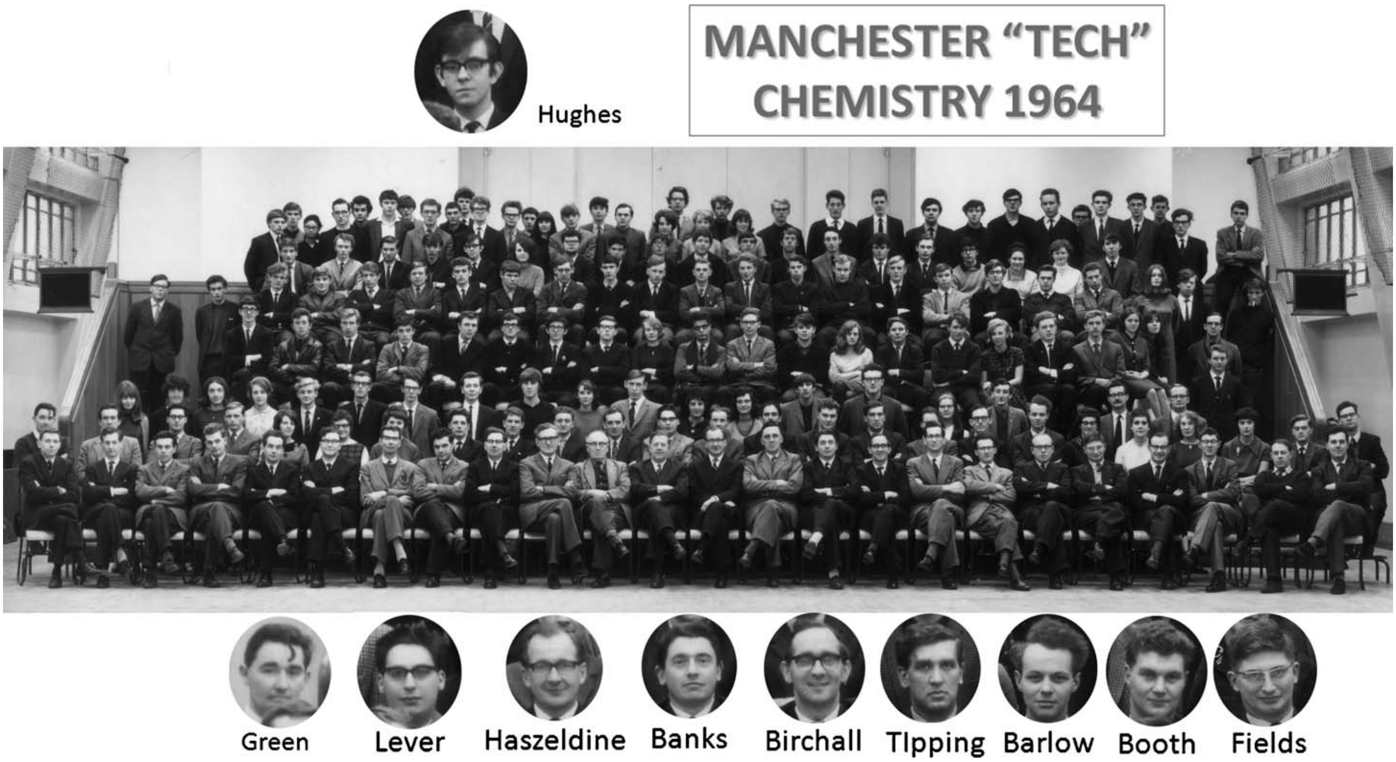


Fig. 1. The chemistry faculty and first year chemistry class at Manchester "Tech" in 1964.

project, I got an upper second class honours degree, good enough to go on for the Ph.D. but low on the pecking order of project choice. When I was summoned to Haszeldine's office to discuss research options, it became frustratingly clear that the project on fluorinated heterocycles for which I yearned had been given to another student. I was given into the care of my new research supervisor, John Powell, a new Assistant Lecturer who had recently obtained his Ph.D. with B.L. Shaw at Leeds University. Our task was to try to make isocyanates from amines and CO using transition metal catalysts under a project sponsored by ICI. All around me were students making fascinating fluorinated molecules, while all I seemed to be able to manage was to make copious quantities of diphenylurea. After a year in Manchester, John Powell moved to the University of Toronto in Canada, and I accompanied him there to work on a very productive project on insertion reactions of allylic complexes of palladium.

When the time came to look for a postdoc I wondered again if fluorine chemistry might be in the cards. Research in organometallic chemistry using fluorinated ligands was dominated at that time by the Bristol group. I wrote to Gordon Stone, inquiring about postdoc opportunities. He had no available funds, but passed my application on to Mike Green, who did. But the timing was wrong and fluorine chemistry at Bristol was on the wane [2]. Fortunately, Mike Green quickly engaged my interest in the organometallic chemistry of small ring compounds, and I had a most productive and enjoyable stay at Bristol. After a subsequent postdoc at McGill University in Montréal with John Harrod, I was lucky enough to get a faculty position at Dartmouth College in the USA, where I met Dave Lemal, who was very active in organofluorine chemistry.

Naturally my main objective at Dartmouth was to get tenure and since I was well grounded in organometallic carbon–carbon activation reactions of small rings, that topic became the main focus of my early independent research work. But one day in late 1978, Dave Lemal and his student Al Barefoot showed me a beautifully crystalline sample of octafluorocyclooctatetraene and the NMR spectrum of its iron tricarbonyl derivative; it was clearly quite different from that of the well known hydrocarbon ligand complex. Based on my knowledge of the organometallic chemistry of cyclooctatetraene (COT) I suggested a structure (discussed below), which was ultimately confirmed crystallographically by Ray Davis at the University of Texas, and my enthusiasm for organofluorine compounds was reawakened. Dave Lemal was kind enough to allow me to take this new ligand and explore its organometallic chemistry. As a well grounded fluorine chemist he wanted to abbreviate it as PFCOT (for perfluorocyclooctatetraene) but I persuaded him that OFCOT tripped from the tongue more smoothly, and besides it might not cause as much amusement when uttered in Australia or England. A second chance at fluorine chemistry had come along and was not going to be wasted!

The study of organometallic complexes with fluorinated ligands was certainly not new. Initial reports of the preparation of $CH_3Mn(CO)_5$ by decarbonylation of the acyl precursor $CH_3COMn(CO)_5$ were communicated by researchers at the Ethyl Corporation in 1957, in two pithy communications that fit on a single journal page [3,4]. These were followed quickly by analogous approaches to the preparation of $CF_3Mn(CO)_5$ almost simultaneously by the group at Ethyl [5], the Stone group at Harvard [6], and by McClellan at DuPont [7], and to $CF_3Co(CO)_4$ and other fluoroalkyl analogues by Hieber [8]. Formation of other perfluoroalkyl–metal compounds via oxidative addition reactions of R_F-I to low-valent metal centers was pioneered by the Stone group [9,10]. The organometallic chemistry of tetrafluoroethylene was initiated by the Wilkinson group [11] and, during a sabbatical leave from DuPont, George Parshall combined with Wilkinson in London to explore the organometallic chemistry of perfluorinated dienes [11,12]. However, the initial fascination with fluorinated ligands in organometallic

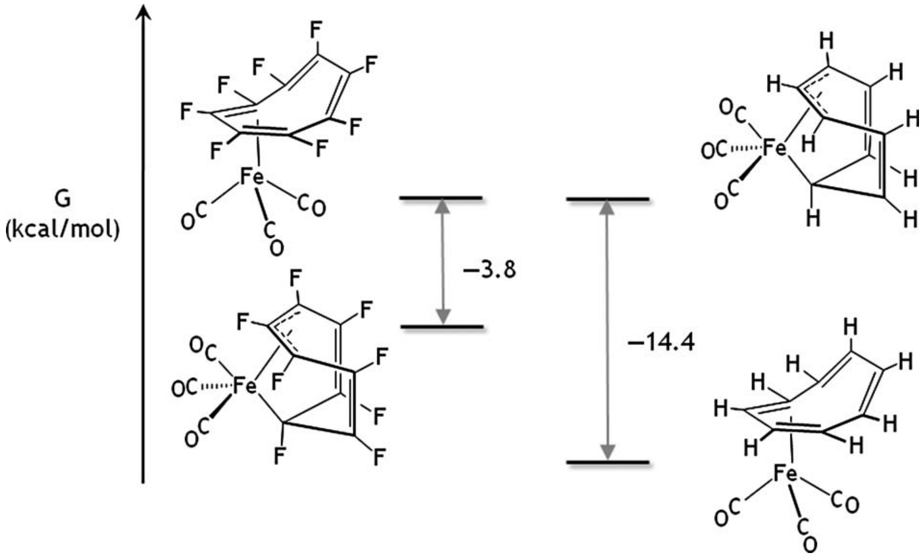
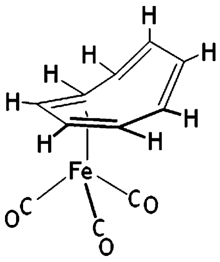


Fig. 2. Relative free energies (gas-phase; ZPE corrected; kcal/mol) calculated using DFT (B3LYP/LACV3P**++) [26].

chemistry, as evidenced by the presence of so many heavy hitters in the initial scramble for new results, seemed to fade, perhaps due to the observations that complexes of fluorinated ligands were almost invariably more stable and much less chemically reactive than their hydrocarbon counterparts. The newly discovered homogeneously catalytic processes that were so facile and important for hydrocarbons [13,14] were not applicable to fluorocarbons, and the organometallic chemistry of hydrocarbon substrates and ligands justifiably dominated the field. In retrospect I also find it interesting that problems with the lengths and strength of C–F bonds in fluorocarbons were being recognized and explored right around this time [15], and also that the foundations of density functional theory that would become so useful later on, were being formulated [16,17].

Nevertheless, with a new route to a ligand like OFCOT available [18–20], I thought that exploration of its coordination chemistry would provide for some interesting undergraduate research projects, and might lead to different bonding modes compared to the already well established chemistry of its hydrocarbon analogue. Contributions to this area were reviewed 20 years ago [21], but a few examples are presented here for the purpose of perspective, and also to introduce some recent illustrative results from DFT calculations. For example, while COT, first reported by Willstätter in 1911 [22], was shown to react with $Fe(CO)_5$ to give **1**, in which the COT is bound as a 1,3-diene, and in which the $Fe(CO)_3$ unit undergoes a facile peripheral perambulation around the ring [23,24], OFCOT forms the previously mentioned complex **2** in which the coordination mode is quite different and the molecule is non-fluxional [25].



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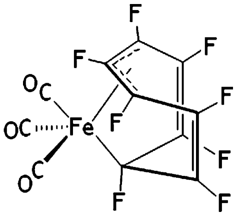

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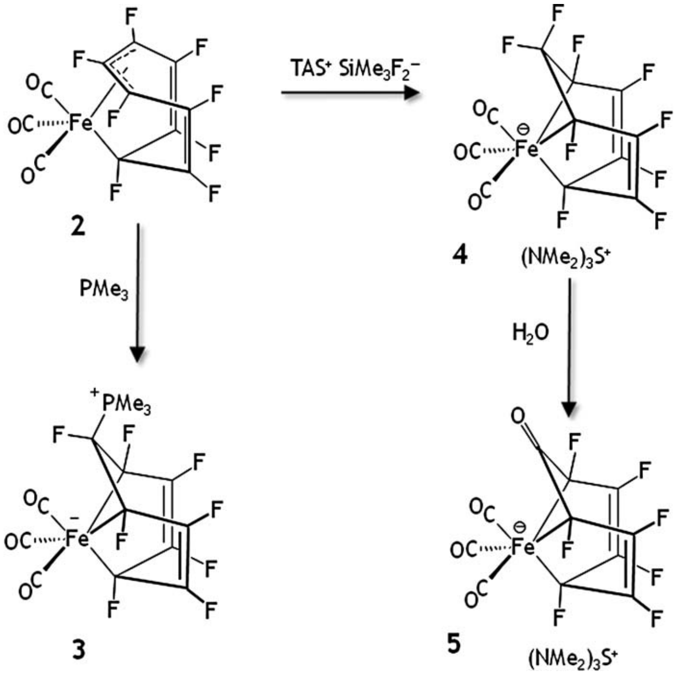
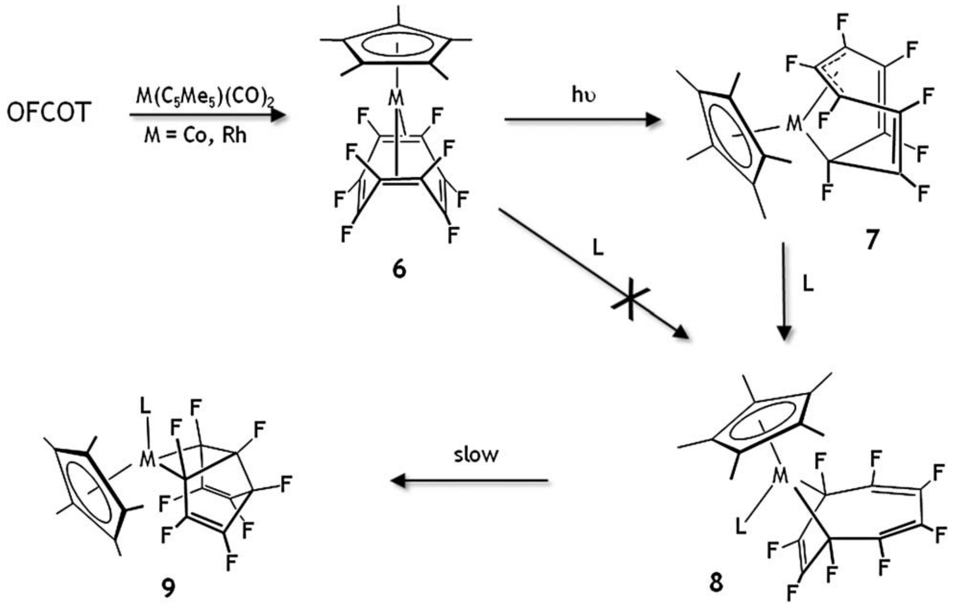
Modern DFT techniques allow the relative energies of isomers to be computed easily and it is now clear that the differences in coordination modes of COT and OFCOT to the $Fe(CO)_3$ unit are truly thermodynamic in nature. Fig. 2 shows the relative free energies of the different coordination isomers of COT and OFCOT calculated by DFT [26]. Preference for isomer **2** for OFCOT probably results from having one F on an sp^3 carbon atom.

The chemistry of the coordinated ligands also proved to be quite different; while **1** reacted with tertiary phosphines to displace COT from the coordination sphere [27], **2** reacted with PMe_3 by exo-selective nucleophilic attack at the internal carbon of the η^3-allylic part of the ligand, to give the zwitterionic complex **3**, providing three fluorines with their preferred locations on sp^3 carbons (Scheme 1) [28]. In analogous fashion a new C–F bond could be formed by reaction of **2** with a source of fluoride anion to give **4** and in a reaction type which was to become important later on, the CF_2 group in **4** underwent rapid hydrolysis to give the ketone functionality in **5** (Scheme 1) [28]. Somewhat ironically, this is



Scheme 1.



Scheme 2.

to my best recollection, the only carbon–fluorine bond that has ever been made in my group. Scheme 2 illustrates some chemistry of OFCOT bound to Co and Rh; initial binding gives compounds **6** in which OFCOT is bound as a 1,5-diene, analogous to the COT analogues prepared earlier by Bennett and Saxby [29]. However, under the influence of ambient light rearrangement to **7** occurs [30,31]. Unlike the iron analogue **2**, compounds **7** do not react with PMe_3 at the ligand but rather at the metal, with an $\eta^3 \rightarrow \eta^1$ rearrangement occurring to give **8** [31,32]. Slow rearrangement of **8** occurs via a transannular ring closure to afford **9**, in which four fluorines have achieved "sp^3 carbon status" [33]. Other metal centers produced this transannular closure product under milder conditions [34], and the stability of these products was quite remarkable; in particular they were frustratingly inert toward reductive elimination of the two M–C bonds to extrude a cyclopropane and produce perfluorosemibullvalene, a molecule long sought after by colleague Lemal.

Once again the relative stabilities of isomers are readily computed by DFT. As shown in Fig. 3 for a Cp(CO) ancillary ligand set, the η^2-alkene isomer is most stable for COT, while for OFCOT it is the transannular closed structure that is lowest in free energy [26].

The striking difference in the air and thermal stability between isostructural COT and OFCOT analogues is perhaps best illustrated

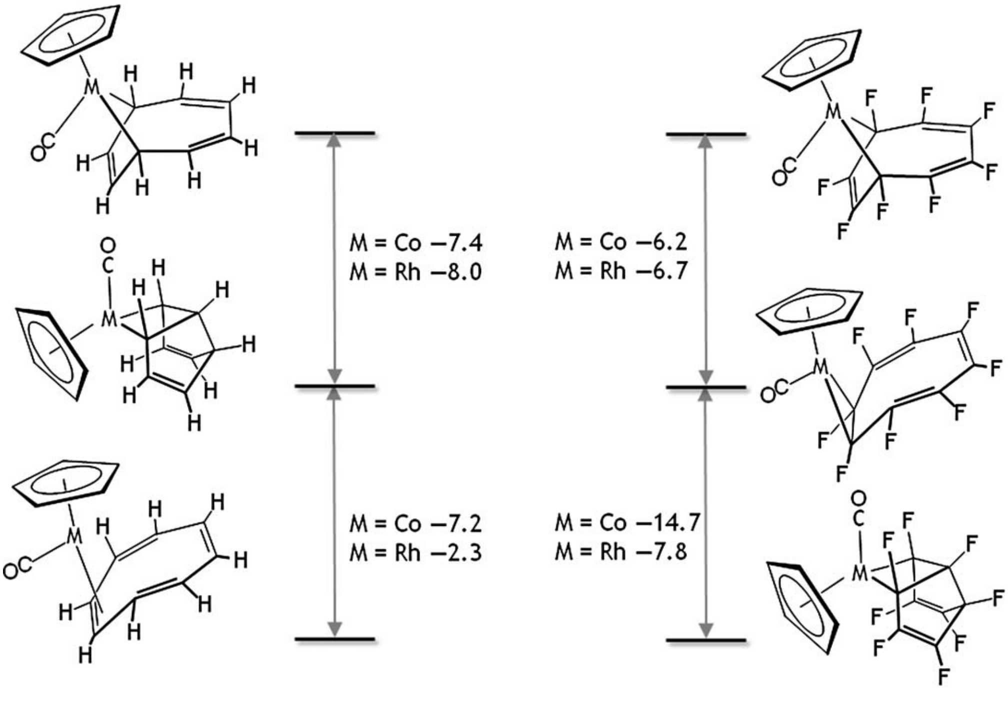
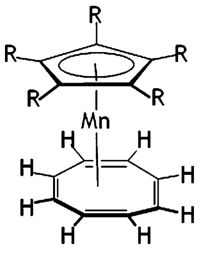


Fig. 3. Relative free energies (gas-phase; ZPE corrected; kcal/mol) calculated using DFT (B3LYP/LACV3P**++) [26].

by the η^6-complexes of manganese. Complex **10** (R=H) was reported to decompose above −78 °C [35], while we found the analogue **10** (R=Me) to be more thermally stable but air-sensitive [36]. In contrast compounds **11** (R=H, Me) were air stable at room temperature. While the COT complex **10** (R=Me) was fluxional with respect to Mn migration around the ring, OFCOT analogues **11** were non-fluxional on the ^{19}NMR timescale [36].



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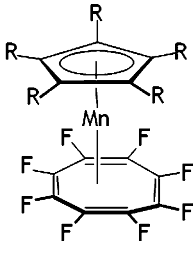

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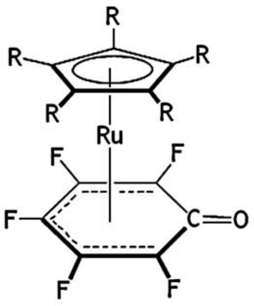
Having confirmed firsthand this remarkable effect of fluorine on the thermal and oxidative stability of organometallic molecules, just as had been observed by the early founders of the field (*vide supra*), we were about to be confronted by some confounding observations from Germany. Reports from the Seppelt group in Berlin describing beautiful synthetic approaches to pentafluoro-5H-cyclopentadiene and its thallium (I) salt [37,38] led us to anticipate the certain advent of the first transition metal complexes containing the pentafluorocyclopentadienyl ligand. To our amazement, and I'm sure to the great disappointment of the Seppelt group, a subsequent paper reported that a variety of standard acid/base or metathesis reactions of these reagents with appropriate inorganic/organometallic precursors were unsuccessful in introducing the η^5-C_5F_5 ligand [39]. This synthetic impasse led to the understandable suggestion that perhaps ring-fluorinated sandwich complexes were unstable in some way [39]. But all our observations on OFCOT chemistry seemed to belie this idea of an intrinsic thermodynamic stability issue associated with multiple fluorinated carbons bound to a transition metal.

Coming up with a different approach to make a η^5-C_5F_5 complex was not a trivial task, and over the years many people have asked me how we arrived at the rather unorthodox method that eventually succeeded. Fortunately I had served on the Ph.D. examination committee of one of Dave Lemal's students, Rick Soelch, who had educated me that hexafluoro-2,4-cyclohexadienone could be persuaded to extrude CO under flash vacuum pyrolysis (FVP) conditions to afford hexafluorocyclopentadiene [40]. My organometallic literature background also equipped me with the knowledge that the Cp*Ru fragment would bind to the π-face of almost any arene [41–43], including phenoxide anions [44,45]. This confluence of information led me to ask Owen Curnow, a postdoc from New Zealand, to do the reaction of $[Cp^*RuCl]_4$ with the thallium salt of pentafluorophenol. As anticipated, the η^5-bound pentafluorophenoxide complex **12** was formed; clearly thermal elimination of CO should afford the desired C_5F_5 ligand. Tentative attempts at FVP of this compound led to recovery of starting material but after I pointed out that the temperature knob on the furnace "went up to eleven" [46], when Curnow finally cranked up the furnace temperature to 770 °C a white crystalline complex **13** (R=Me) emerged from the hot tube. I vividly remember an excited Curnow waving its ^{19}F NMR spectrum, which showed a singlet peak at δ-213.2 ppm [47]. This compound melted in air at $\sim$235 °C, putting to rest any doubts about the thermodynamic stability of the $Ru(C_5F_5)$ moiety. The crystal structure of **13** (R=Me) was irretrievably disordered, but some years later the gas-phase structure was solved by David Rankin's group in Edinburgh using gas-phase electron diffraction [48]. The Cp analogue **13** (R=H) was also prepared by a similar route and its X-ray structure allowed the coordination parameters of C_5H_5 and C_5F_5 to be compared in the same molecule; the fluorinated ring is more tightly bound, as judged by shorter M–C distances [49].



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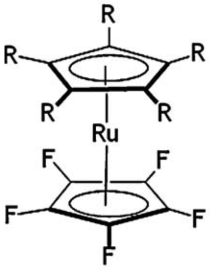

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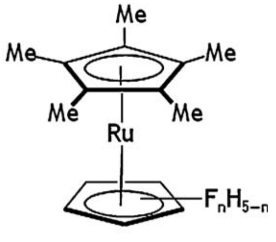

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This approach was used successfully for the synthesis of the whole set of compounds **14** with mono-, di-, tri-, and tetrafluorocyclopentadienyl ligands from the corresponding phenoxide precursors [50]. Collaboration with Dennis Lichtenberger in Arizona allowed measurements of the photoelectron spectra of a series of ruthenocenes [51]. As shown in Fig. 4, fluorination lowers the energies of the top three occupied MOs (basically non-bonding Ru d-orbitals), explaining the increased stability to air oxidation. Studies by the group of Dave Richardson in Florida illustrated this in a different way by measuring ΔG° for electron loss in the gas phase

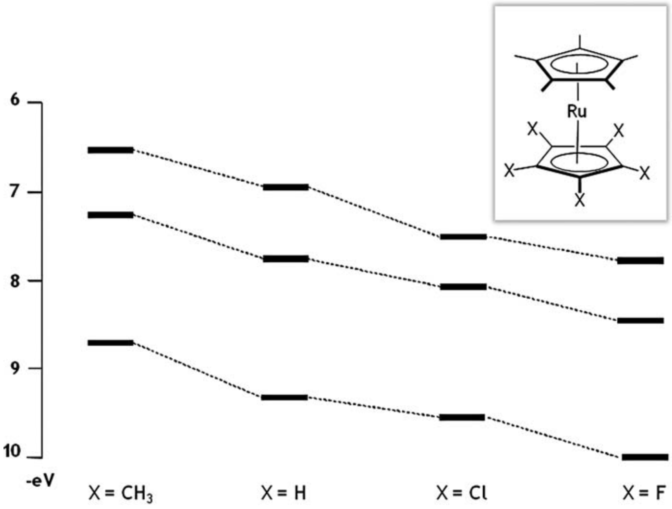
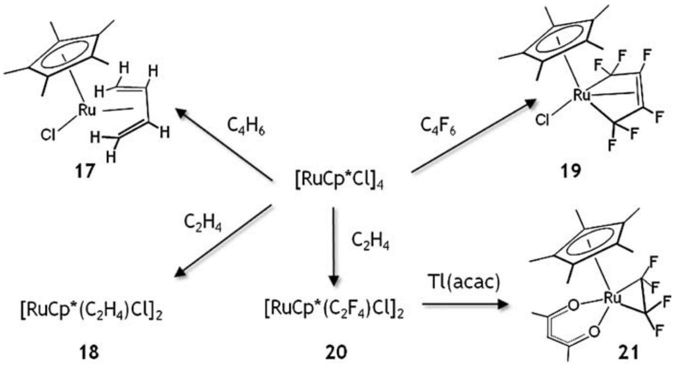


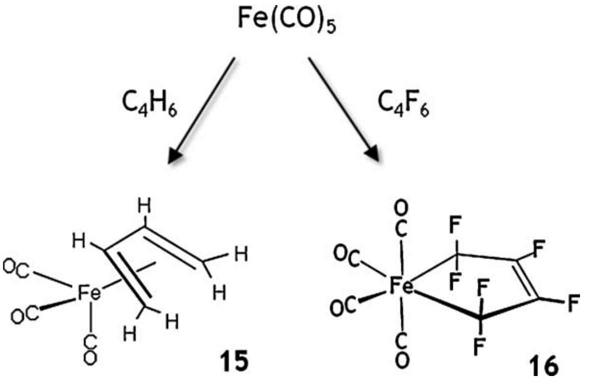
Fig. 4. Energies of the top three occupied MOs of ruthenocenes as measured by gas-phase photoelectron spectroscopy [51].



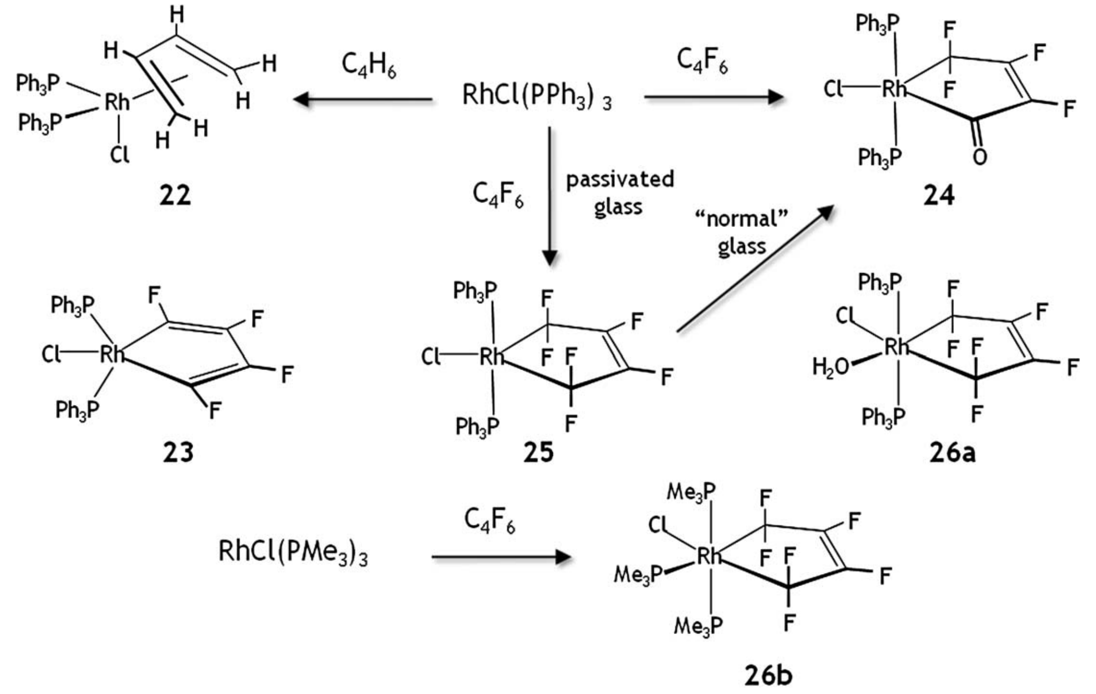
Scheme 3.

[52]. Increasing the number of fluorines on the cyclopentadienyl ring steadily increased the energy required to detach an electron from the ruthenocene; for di- and tri-fluorinated rings the effect was independent of the relative positions of the fluorines [53]. The electrochemistry of **13** demonstrated irreversible oxidation, as observed for other ruthenocenes, but a significantly larger oxidation potential was observed for **13** compared to RuCpCp* [52].

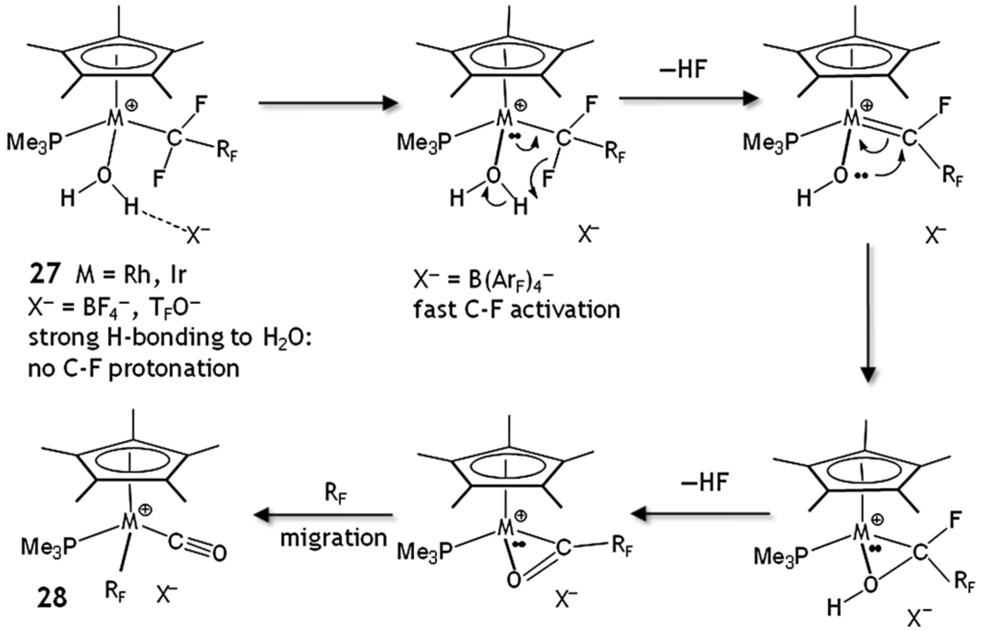
The preference for fluorine to bind to carbon using carbon orbitals of higher p-character has long been known [54–56], and is a nice illustration of Bent's rule [57]. The coordination chemistry of OFCOT, described above [21], provides a number of examples in which fluorine demonstrates a preference for sp^3 over sp^2 carbon, but this was not a new observation. Butadiene binds to $Fe(CO)_3$ in a characteristic η^4-1,3,-diene coordination to give **15**, first made by Reihlen in 1930 [58], but whose structure was correctly formulated much later by Pauson and coworker [59], but hexafluorobutadiene produces metallacycle **16** under the same conditions [60,61]. Fagan had shown that the ruthenium tetramer $[RuCp^*Cl]_4$, so useful to us in making phenoxo precursors to fluorinated cyclopentadienyl ligands (*vide supra*), would also bind butadiene and ethylene to give **17** and **18** respectively [42]; surprisingly, given his DuPont connection, he had not looked at the fluorinated analogues, so we did. Hexafluorobutadiene reacted with $[RuCp^*Cl]_4$ to give **19**, which turned out to be the first example of an η^4–hexafluorobutadiene complex [62], in which the fluorinated diene was bound as shown in Scheme 3, intermediate between the bonding in **17** and a full metallacycle like **16**. Reaction of $[RuCp^*Cl]_4$ with tetrafluoroethylene gave initially the dimeric complex **20**, which could be converted to the monomeric acac analogue **21** [63,64]. The X-ray structures of **20** and **21** both showed metric parameters for the C_2F_4 ligand that were completely consistent with a metallacyclopropane structure [65], as shown in Scheme 3, and as previously observed for other C_2F_4 complexes, exemplified by the structure of $RhCp(C_2H_4)(C_2F_4)$ [66]. However, in contrast to previous examples, the NMR spectra of **20** and **21** showed that they were undergoing propeller rotation on the NMR timescale, with a low activation energy barrier, as predicted by Hoffmann for pseudo-octahedral d^6 metal–alkene complexes [67].



Formation of **21** led us to reinvestigate some earlier chemistry previously reported by the Wilkinson group in which butadiene reacted as expected with $Rh(PPh_3)_3Cl$ to give **22**, while hexafluorobutadiene was reported to undergo a double defluorination to give **23** (Scheme 4) [68]. In our hands, repetition of the latter reaction allowed the characterization of the latter product not as **23** but as **24**, in which the double defluorination appeared to result from a CF_2 hydrolysis reaction with the fate of the two fluorines being HF [69]. The source of the required water reagent was



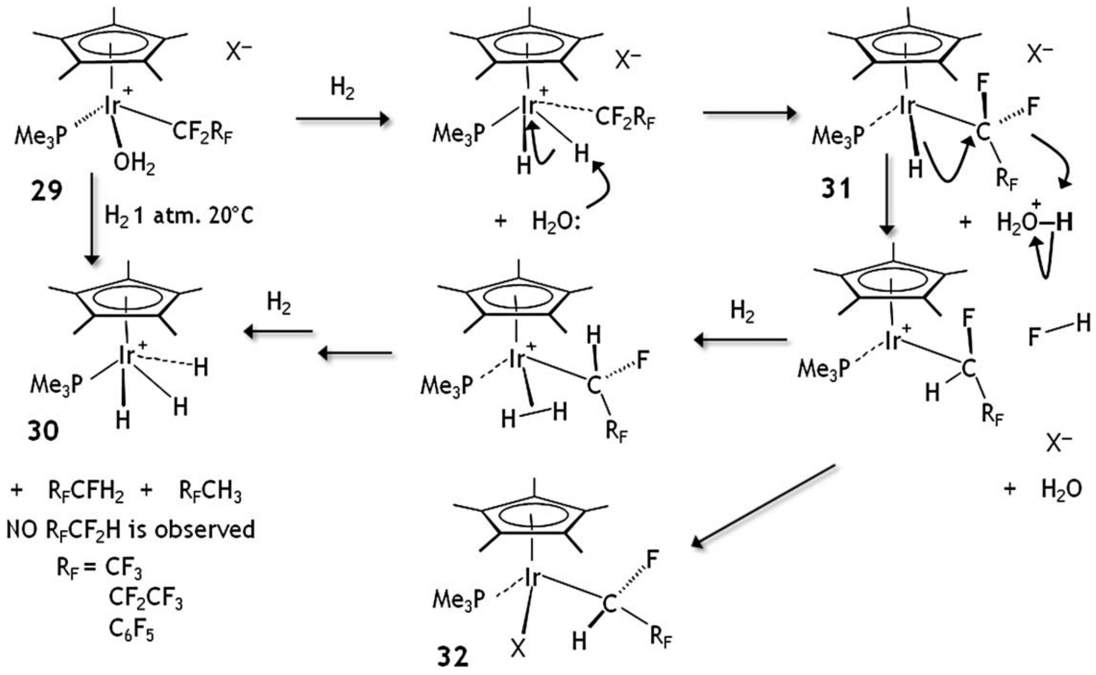
Scheme 4.



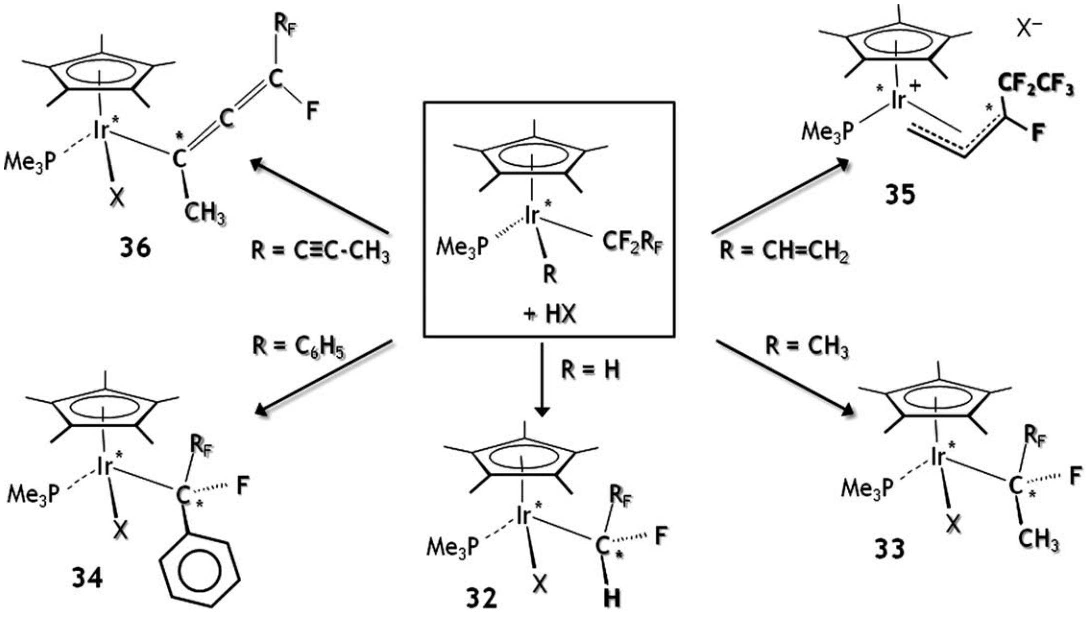
Scheme 5.

identified as the glass surface of the reaction vessel; when this was passivated by silylation the reaction product was identified in solution as metallacycle **25**, and transfer of this solution to unpassivated glass led to rapid hydrolysis of one α-CF_2 group to give a ketone. The vacant coordination site in **25** was suspected to be important, perhaps in binding water to give **26a**; when a smaller cone angle phosphine (PMe_3) was used, metallacycle **26b** was formed and no α-CF_2 hydrolysis was observed [69].

Once again it is important to recognize that hydrolysis of C–F bonds α- to a transition metal was not a new observation; a number of reports of activation of α-CF bonds in M–CF_3 and M–CF_2R groups using exogenous protic and Lewis acids had already appeared in the literature, and often led to overall C–F bond hydrolysis by adventitious moisture [70–77]. But these observations coupled with our own, led us to try to design a system in which we could observe and perhaps control such hydrolysis reactions. We were able to make cations **27** (Scheme 5) containing primary fluoroalkyl ligands and coordinated water molecules, which were isolable provided that the counter-anion (BF_4^-, $CF_3SO_3^-$) was capable of hydrogen-bonding to the water molecule; a number of X-ray structures confirmed this motif [78,79]. But as soon as the counterion was replaced with one incapable of such hydrogen-bonding, such as $B(ArF)_4^-$, a rapid hydrolysis of the α-CF_2 group occurred to give eventually the fluoroalkyl(carbonyl) cation **28**. The mechanism shown in Scheme 5 was suggested, in which the combination of enhanced acidity of coordinated water combined with the ability of the metal d-electrons (lone pairs on the d^6 metal) to stabilize a positive charge on the α-carbon



Scheme 6.



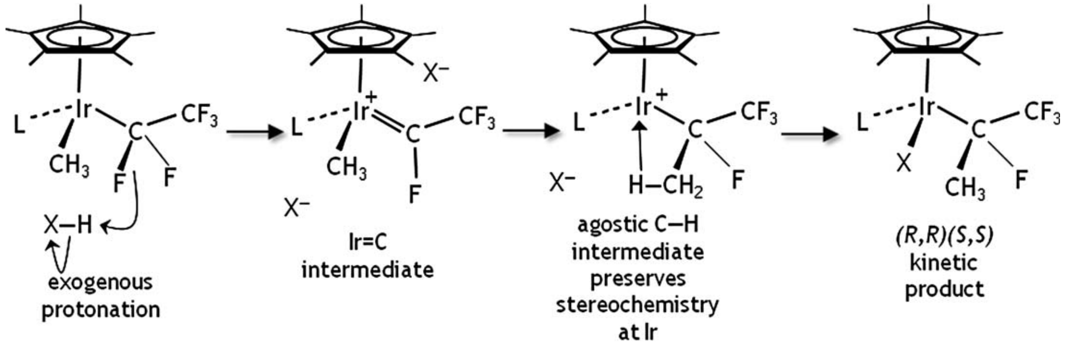
Scheme 7.

combined to afford a facile hydrolysis [78,79]. Secondary fluoroalkyl groups were much less reactive and a conformational rationale for this has been put forth recently [80].

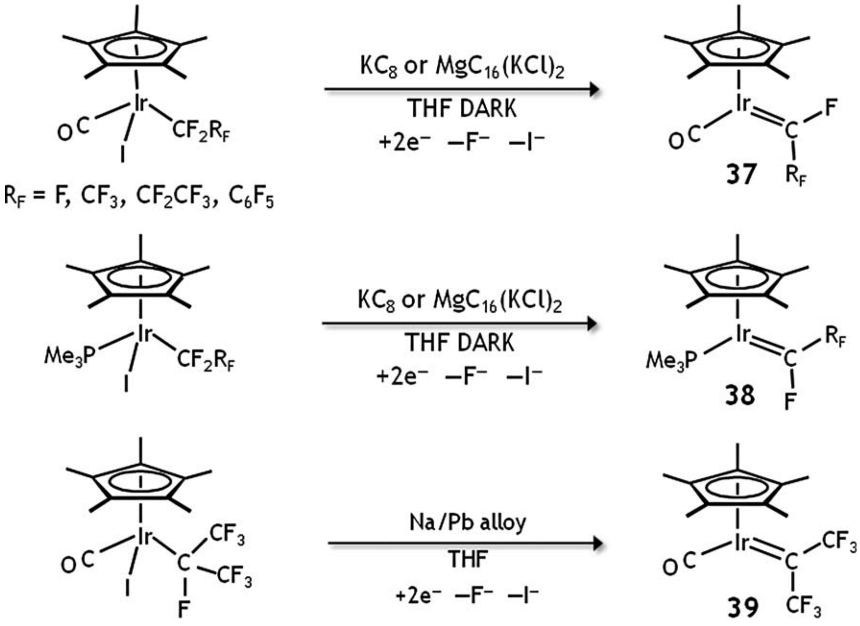
One day in early 1999 Jeremy Smith, a postdoc from South Africa, told me that treatment of the iridium fluoroalkyl(aqua) cations **29** with hydrogen gas under ambient conditions resulted in loss of the entire fluoroalkyl group from the metal and formation of the known trihydride **30** (Scheme 6). I admit to being rather skeptical of this result since no such elimination reactions of perfluoroalkyl groups were known. But more detailed examination showed that Smith was right and that the fluorocarbon products were the result of reductive elimination of a C–H bond, but only after initial hydrogenolysis of one or more of the original α-CF bonds [81]. Detailed mechanistic studies showed that the role of the metal was to activate hydrogen heterolytically and effectively split it into a metal bound hydride and an external proton. The mechanism shown in Scheme 6 was proposed [82]. The reaction manifold could also be entered with greater control of stoichiometry using the hydride precursors **31** and adding a protic source. If the conjugate base X^- trapped irreversibly at the metal complexes **32** were obtained in which the partially hydrogenolyzed ligand was retained in the coordination sphere, and complexes **32** were formed diastereoselectively [83]. If the counterion was a poorly coordinating ligand that could be displaced by H_2, further reaction occurred with more hydrogenolysis and displacement of the original perfluoroalkyl ligand as a hydrofluorocarbon [80].

The mechanism posited in Scheme 6 required that an external protic source be capable of activating an α-C–F bond in **31**, with departure of fluoride as HF, and migration of an internal hydride to carbon to form the new C–H bond, leading eventually to **32**. This should not be restricted to intramolecular hydride migration, and we were able to show that an analogous reaction occurred to give C–F bond activation coupled with migration of a variety of differently hybridized carbon groups, as shown in Scheme 7. Methyl migration occurred to give **33** [84] and phenyl to give **34** [85] in a stereoselective manner to give the (R_C, R_{Ir})(S_C, S_{Ir}) product diastereomer as the kinetic product. Migration of a vinyl group gave the η^3-allylic diastereomer **35** as the kinetic product by internal trapping at the metal by the pendant vinyl group [86]. Similarly alkynyl migration gave the rearranged allenyl diastereomer **36** [87].

A combination of mechanistic investigations [80] and more recent DFT studies [26] point to the pathway shown in Scheme 8 (illustrated using CH_3 as the migrating group) to explain the observed stereochemical results. Selective protonation of one of the α-C–F bonds occurs with stabilization of the developing α-carbocation by a lone pair on the metal, leading to a cationic iridium–carbene intermediate having a specific stereochemistry with the CF_3 group syn to Cp*. Methyl migration affords the new C–C bond and C-stereocenter, while an agostic C–H interaction preserves the stereochemistry at Ir until trapping occurs by the counterion X^- to give the observed relative stereochemistries at C and Ir. For phenyl, vinyl, and alkynyl migration the C–H agostic stabilization is replaced by a donor stabilization using a C=C or



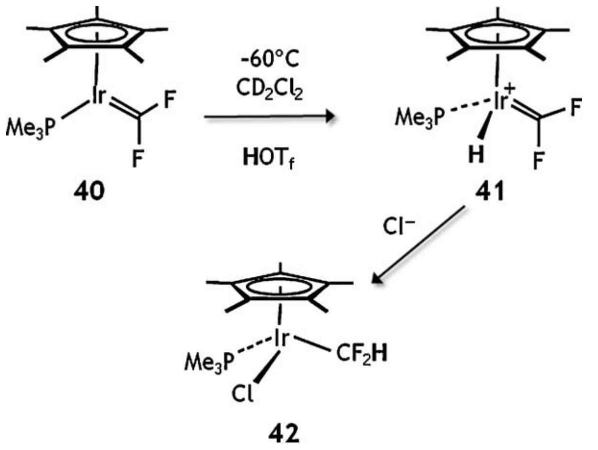
Scheme 8.



Scheme 9.

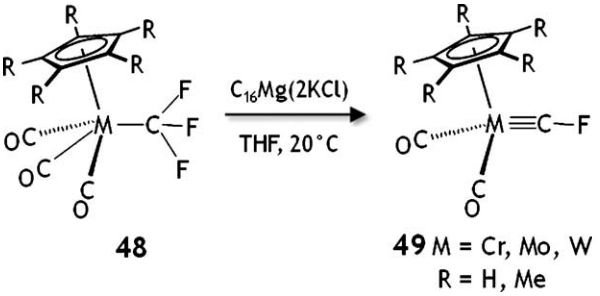
$C{\equiv}C$ multiple bond; in the case of vinyl migration this intermediate (**35**; Scheme 7) is observable [86].

With a view to generating the kind of perfluorinated carbene ligands shown in the intermediate in Scheme 8, we devised a simple reductive route to neutral perfluorocarbene complexes of iridium by the metal templated syntheses shown in Scheme 9 [88–90]. Transition metal complexes containing CF_2 ligands were already well known [71,72,76,91–96], but perfluoroalkylidene analogues were not generally accessible. If these reactions are done in the dark they result in clean formation of **37** and **38**; [97] it should be noted that the stereochemistry of **37** was incorrectly assigned by us in the original publication [89]. A complex **39** containing a carbene ligand bearing two strongly electron-withdrawing CF_3 groups can also be made this way, although judicious choice of reducing agent is important [90]. When the reductions are done under room fluorescent lights, the ratio of E/Z isomers for **37** and **38** varies due to photochemical interconversion of the diastereomers [98]. Addition of HCl to the CF_2 complex **40** affords kinetic protonation at the metal to give **41**, which can be observed at low temperature in the presence of a poorly-coordinating anion; when a strongly coordinating anion is added, hydride migration to carbon occurs to form **42** [88]. In unpublished work, we have shown that addition of HCl to **37–39** follows the identical regiochemistry [98]. This sequence of events is entirely consistent with a pathway analogous to that shown in Scheme 8.

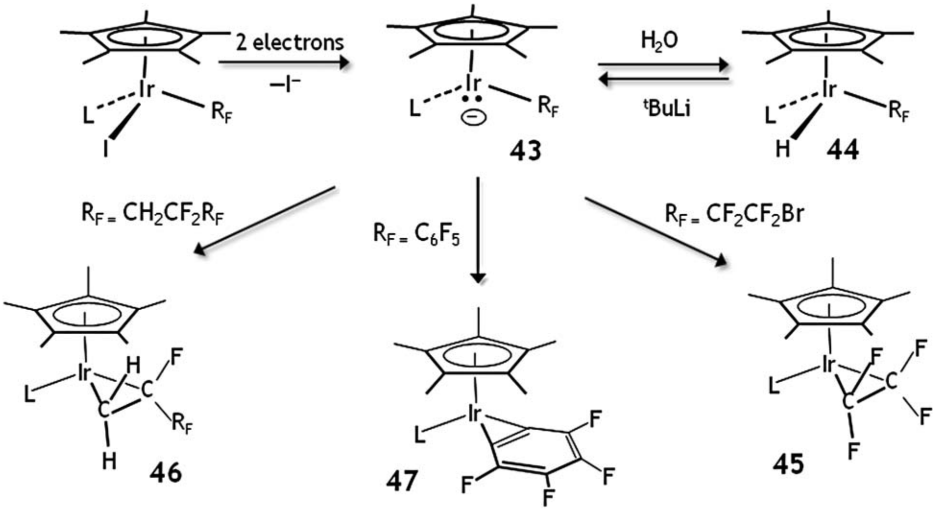


The mechanism of metal templated reduction of coordinated fluoroalkyl ligands to give perfluoroalkylidene ligands is difficult to study as the best reductants are heterogeneous reagents. But a minor unanticipated product provides a clue about the important intermediate. When insufficient care is taken to dry glassware in these reactions, an additional product is the hydride complex **44**, pointing to the intermediacy of anion **43** in the reduction (Scheme 10) [89]. If both α- and β-fluorines are present, **43** undergoes selective α-fluoride elimination to give perfluoroalkylidene ligands, unless a better leaving group like Br is present on the β-carbon in which case β-Br elimination occurs to give **45**; if there are no α-fluorines, β-fluorine elimination will occur to give hydrofluoroalkene complexes **46** [89]. Formation of an anionic intermediate **43** ($R_F{=}C_6F_5$) is also probably responsible for formation of benzyne complexes **47** by initial deprotonation of **44** ($R_F{=}C_6F_5$) with ^{t}BuLi [99–101].

That the extent of reduction of perfluoroalkyl ligands was dependent on the metal–ligand fragment to which the fluoroalkyl group was bound is nicely illustrated by the analogous reduction of the Mo–CF_3 linkage in **48** to give the terminal fluoromethylidyne CF ligand in product **49** [102]. We have now devised syntheses of other group 6 CF_3 complexes [103], and find that formation of CF ligands by this method is quite general [104].

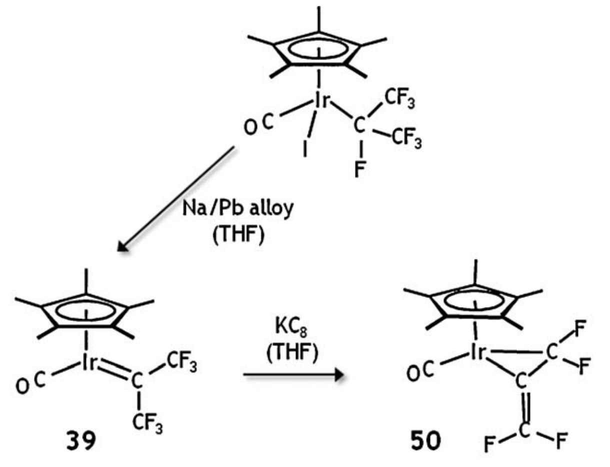


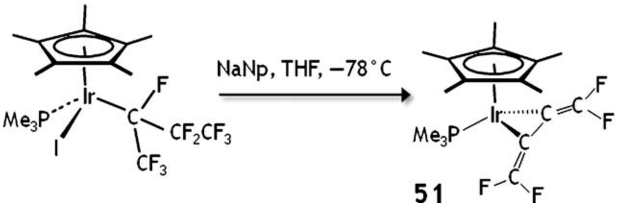
More complex fluoroalkyl ligands undergo more diverse eliminations on reduction. While **39** is formed cleanly on treatment of the perfluoro-iso-propyl precursor with Na/Pb alloy, analogous reduction using KC_8 affords the perfluoroallene complex **50** via the intermediacy of **39** [90]. This inner-sphere construction of the perfluoroallene ligand complements some beautiful earlier work by the Lentz group on coordination chemistry of free



Scheme 10.

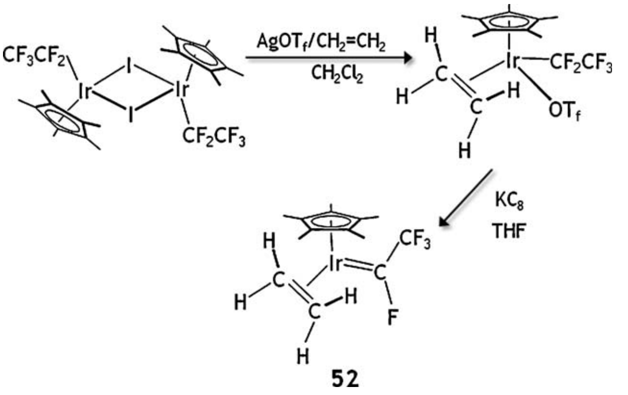
perfluoroallene [105,106]. Similarly we have shown that reduction of the perfluoro-sec-butyl ligand affords an inner-sphere construction of the perfluorobutatriene ligand in **51** [107]. In this case our inner-sphere construction of the ligand preceded a report of coordination of the free perfluorobutatriene [108].





What does the future hold for organometallic compounds containing fluorinated organic ligands?

The development of a synthesis for perfluoroalkylidene and perfluoroalkylidyne ligands should open the door to a great deal of new chemistry. In attempts to generate a system capable of achieving the metathesis of fluorinated alkenes, we have been able to generate the (perfluoroethylidene)(ethylene) complex **52** as shown [109]. Unfortunately the two ligands that are required to interact in any metathesis reaction (to form a metallacyclobutane ring) are conformationally locked in exactly the wrong arrangement for this reaction. DFT studies show that while the required metallacycles are not energetically inaccessible, the strongly non-planar transition states required to interconvert them are very high in energy. We anticipate that DFT will provide a useful design guide as we explore further options in this area.



We are also using DFT to explore systems that may achieve other hitherto unknown reactions of perfluoroalkyl–transition metal complexes; insertion reactions of CO and alkenes are well known catalytically important processes for hydrocarbon alkyls and alkenes, but are essentially unknown for perfluorinated analogues. We hope to provide some future insight into the feasibility of such reactions and design systems capable of achieving them.

The future of organometallic compounds containing fluorinated organic ligands is exceptionally bright, as many new young investigators bring their talent and imagination to the field. Much of this recent activity is driven by the need for synthetic procedures to incorporate fluorine or a CF$_3$ group strategically in the synthesis of pharmaceuticals or PET reagents, leading to the development of new methodology for formation of C–F and C–CF$_3$ bonds [110–122]. Organometallic chemistry involving the chemical functionalization of C–F bonds also continues to be an active field [123–136].

I look forward learning about advances in all these areas in the future, and perhaps participating in a few of them myself.

Acknowledgements

Some personal acknowledgements have been made in the text but I wish to reiterate my deep appreciation to my colleague Dave

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