

Fluorous Organometallic Chemistry

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Abstract The synthesis, characterisation and application of organometallic complexes functionalised with fluorous substituents are reviewed.

Keywords Fluorous · Organometallic · Review

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1 Introduction

Organometallic chemistry has made a significant contribution to the developments in fluorous chemistry since its inception in 1994 [1], but this science has never been brought together or reviewed from an organometallic perspective previously. In this article, we attempt to draw together the various strands of fluorous organometallic

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chemistry and present an overview of its contribution to the evolution of fluororous separation methods.

Although originally envisioned by analogy to “aqueous” to embody a third, orthogonal liquid phase that is both lipophobic and hydrophobic, such as a perfluoroalkane or perfluoroether, the scope, meaning and application of the fluororous concept have evolved rapidly, such that it now encompasses solid-phase extraction [2], chromatographic separation [3], solid-supported catalysis [4–8], thermoregulated solubility [9, 10] and release-and-capture concepts [11]. In each of these areas, molecules of interest are adorned with one or more perfluoroalkyl segments in order to generate the desired physical and/or chemical property. These perfluoroalkyl segments are called “ponytails” or “labels” and have traditionally been at least six carbon atoms long (i.e. C₆F₁₃) in order to give a molecule the desired “fluororous” characteristics (solubility or separability). More recently, there has been interest in the development of alternative fluorophilic segments based upon smaller perfluorinated groups, e.g. –OC(CF₃)₃ [12–22], or perfluoropolyethers [23–29] that are designed to reduce the potential environmental impact of the degradation products of organic or organometallic species derivatised with long perfluoroalkyl groups [30–33], but their applications in organometallic systems have been restricted to just a couple of research articles.

In organometallic systems, it is possible to envisage the attachment of the perfluoroalkyl segment either directly within the metal-bound organic ligand, such as an alkyl, cyclopentadienyl or *N*-heterocyclic carbene (NHC), or as part of another donor ligand (phosphine, pyridine, carboxylate, etc.) in the metal coordination sphere. The synthesis, physical properties and applications of these two classes of fluororous organometallic complexes will be considered separately.

2 Organometallic Complexes with Ancillary Fluororous Ligands

Organometallic systems derivatised with perfluoroalkylated ancillary ligands, such as phosphines or carboxylates, have been absolutely fundamental in the development of the fluororous approach to catalysis, whether that catalysis is under classical fluororous biphasic conditions, as part of release-and-capture methodologies or for recycling using solid-phase extraction. However, in many instances, the fluororous organometallic catalysts are only formed *in situ*, e.g. ene catalysts from fluororous rhodium carboxylates [34–36] or fluororous silver trispyrazolylborates [37], and hydrogenation catalysts from fluororous Wilkinson analogues [38–41]. Much of the chemistry in such systems has been very well reviewed elsewhere [42–45] and, since the focus of this article is on the synthesis and characterisation of fluororous

organometallic complexes, these non-isolated fluorous organometallic species will not be discussed further here.

The synthetic approaches to organometallic complexes with fluoroalkylated ligands mirror those applied throughout organometallic chemistry. Cleavage of chloride bridges in $[\text{MCl}(\text{CO})_2]_2$ ($\text{M}=\text{Rh}, \text{Ir}$) or $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M}=\text{Rh}, \text{Ir}$; $\text{Cp}^*=\eta^5\text{-C}_5\text{Me}_5$) with a variety of classes of perfluoroalkylated monodentate phosphorus(III) ligands generates well characterised $[\text{MCl}(\text{CO})\text{L}_2]$ [46–60] and $[\text{Cp}^*\text{MCl}_2\text{L}]$ [50, 52, 55–57, 61] that have been used to establish the impact of the fluorous substituents on the electronic, physical and structural properties of the metal complexes. A number of these systems have been the subject of single crystal X-ray analyses, which generally revealed that the ponytails had little influence on the structural features of the metal centres (bond lengths, bond angles) but dictated the packing of these species in the solid state. Oxidative addition reactions (of H_2 , O_2 , MeI , $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{I}$) on the iridium Vaska's complex analogues $\{\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3$ and $\text{PPh}_n(\text{C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_{3-n}$ ($n=0, 1, 2$) ligands} generate the anticipated octahedral Ir(III) species, but in-depth studies suggest a different mechanism for the addition reactions to these fluorous-functionalised complexes compared to those with protio ligands [46, 47, 50]. The hydroformylation catalyst $[\text{HRh}(\text{CO})\{\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}]$ is formed quantitatively in the reaction of the phosphine with $[\text{Rh}(\text{CO})_2(\text{acac})]$ under Syngas in a closed system [62]. It has been fully identified in solution by spectroscopic studies, but not isolated. The analogous complex with the $\text{P}(\text{C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3$ ligand has also been detected in solution by high-pressure NMR spectroscopy [63]. Carbonyl displacement from tungsten hexacarbonyl with perfluoroalkylated phosphines affords $[\text{W}(\text{CO})_5\text{L}]$ $\{\text{L}=\text{P}(\text{C}_6\text{H}_4\text{-4-C}_2\text{H}_4\text{C}_8\text{F}_{17})_3, \text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}$, the former of which has been structurally characterised [64]. Using the same ligands, this group has also prepared some acetate-bridged ruthenium dimers $[\text{Ru}(\mu\text{-O}_2\text{CCH}_3)(\text{CO})\text{L}]_2$, again using an established organometallic approach, for which the trialkylphosphine complex was the subject of a structural characterisation [65]. The only examples of metal carbonyl clusters derivatised with fluorous ligands were reported in 2010 [66]. $[\text{Os}_3(\text{CO})_{11}\text{L}]$ and $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$ $\{\text{L}=\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}$ were prepared in moderate yields by ligand displacement from the respective acetonitrile adducts. Reaction of the former with triphenylphosphine gave a mixture of $[\text{Os}_3(\text{CO})_{10}\text{L}(\text{PPh}_3)]$ and $[\text{Os}_3(\text{CO})_9\text{L}(\text{PPh}_3)_2]$, which are readily separated by chromatography; the latter has been structurally characterised. Alternatively, reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with either $\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3$ or $\text{P}(\text{C}_6\text{H}_4\text{-4-C}_2\text{H}_4\text{C}_8\text{F}_{17})_3$ gave the hydrido-bridged complex $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{L}]$ [66]. Displacement of tetramethylethylenediamine (tmeda) from $[\text{PdCl}(\text{Me})(\text{tmeda})]$ with 2-[bis(4-{2-(perfluorohexyl)ethyl}dimethylsilyl)phenyl]phosphine]pyridine gave the desired *trans*-square planar $[\text{PdCl}(\text{Me})\text{L}_2]$ [67]. Similar displacement, this time of norbornadiene, using $\text{P}[\text{C}_6\text{H}_4\text{-4-SiMe}_2(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3]$ has been used to access the palladium(0) alkene adduct, $[\text{Pd}(\text{maleic anhydride})\text{L}_2]$ which is a relatively poor pre-catalyst for the methoxycarbonylation of styrene [68]. In an attempt to improve the solubility of [1, 2]-methanofullerene-substituted cyclometalated (C-N) platinum(II)-

based macrostructures, van Koten et al. have displaced DMSO from platinum with $\text{P}[\text{C}_6\text{H}_4\text{-4-SiMe}_{3-n}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_n]_3$ ($n = 1, 2$) (L) to generate highly soluble $[\text{Pt}(\text{C-N})\text{CIL}]$ and $[\{\text{Pt}(\text{C-N})\text{L}\}_2(4,4'\text{-bipy})]$ in which the fluorinated ligand has no electronic impact on the fullerene moieties [69].

In the area of bidentate ligands, coordination of a 2,2'-fluorous-tagged-bipyridine to $[\text{Re}(\text{CH}_3)_3\text{O}_3]$ generates a molecular olefin epoxidation catalyst [70]. Ligand-bridged dinuclear $[\{\text{Cp}^*\text{RhCl}_2\}(\text{L-L})]$ and cationic mononuclear $[\text{Cp}^*\text{RhCl}(\text{L-L})]^+$ complexes are formed in the cleavage of $[\text{Cp}^*\text{RhCl}_2]_2$ with a perfluoroalkylated diphenylphosphinoethane ligand [71]. Displacement of one equivalent of cyclooctadiene (COD) from $[\text{Rh}(\text{COD})_2](\text{BF}_4)$ or $[\text{Rh}(\text{COD})_2](\text{BPh}_4)$ with perfluoroalkylsilyl dppe ligands generates $[\text{Rh}(\text{COD})(\text{L-L})]^+$ cations; $[\text{Rh}(\text{COD})\{\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\}](\text{BPh}_4)$ has been structurally characterised [72]. Alternatively, displacement of acetylacetonate (acac) from $[\text{Rh}(\text{COD})(\text{acac})]$ with fluorous bidentate phosphines, in the presence of fluorous tetraphenyl borate anions, generates highly fluorophilic $[\text{Rh}(\text{COD})(\text{L-L})(\text{BPh}^{\text{Rf}}_4)]$ recyclable hydrogenation catalysts [73]. Ligand displacement is also employed in the reaction of $[\text{CpMX}(\text{PPh}_3)_2]$ ($\text{M}=\text{Ru}$, $\text{X}=\text{Cl}$; $\text{M}=\text{Os}$, $\text{X}=\text{Br}$) with fluorous bidentate phosphines to generate $[\text{CpMX}(\text{L-L})]$ [74]. Displacement of COD from $[\text{MClMe}(\text{COD})]$ ($\text{M}=\text{Pd}$, Pt) or $[\text{PtMe}_2(\text{COD})]$ with the $\text{P}(\text{C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_2$ ligand affords the desired organometallic $[\text{MClMe}(\text{L-L})]$ ($\text{M}=\text{Pd}$, Pt) and $[\text{PtMe}_2(\text{L-L})]$ in modest to good yields; $[\text{PtClMe}(\text{L-L})]$ has been structurally characterised [75].

Recently, organometallic systems have been targeted where the fluorous ligand has been engineered for a specific purpose (Fig. 1). Displacement of pyridine from the Grubbs–Hoveyda catalyst with fluorous trialkyl phosphines (**1**) generates new ring-opening metathesis polymerisation catalysts that offer dramatic rate accelerations in a two-phase organic–fluorous system where “phase transfer activation” following phosphine dissociation is envisaged [76–78]. Cleavage of the chloride bridges in $[(p\text{-cymene})\text{RuCl}_2]_2$ with a perfluoroalkyl-tagged pyridine generates the anticipated mononuclear complexes (**2**) in high yield [79]. These compounds with fluorous tails show greater uptake by tumoral cells than analogues with long alkyl tails and are thermoresponsive, exerting considerable chemotoxicity on mild hyperthermia. Three luminescent rhenium(I) bipyridyl complexes $[\text{Re}(\text{CO})_3(4,4'\text{-dimethylbipy})\text{L}^{\text{Rf}}](\text{PF}_6)$ (**3**) [80] and the closely related $[\text{Re}(\text{CO})_3(\text{phen}^{\text{R}})\text{L}^{\text{Rf}}](\text{PF}_6)$ ($\text{phen}^{\text{R}}=\text{phen}/4,7\text{-diphenylphen}/3,4,7,8\text{-tetramethylphen}$) (**4**) [81], prepared by displacement of acetonitrile from the parent organometallic complexes, have been investigated as trifunctional biological probes that have luminescent properties for detection and a reactive group for bioconjugation and exploit the perfluoroalkyl functionalisation for straightforward isolation using fluorous solid-phase extraction.

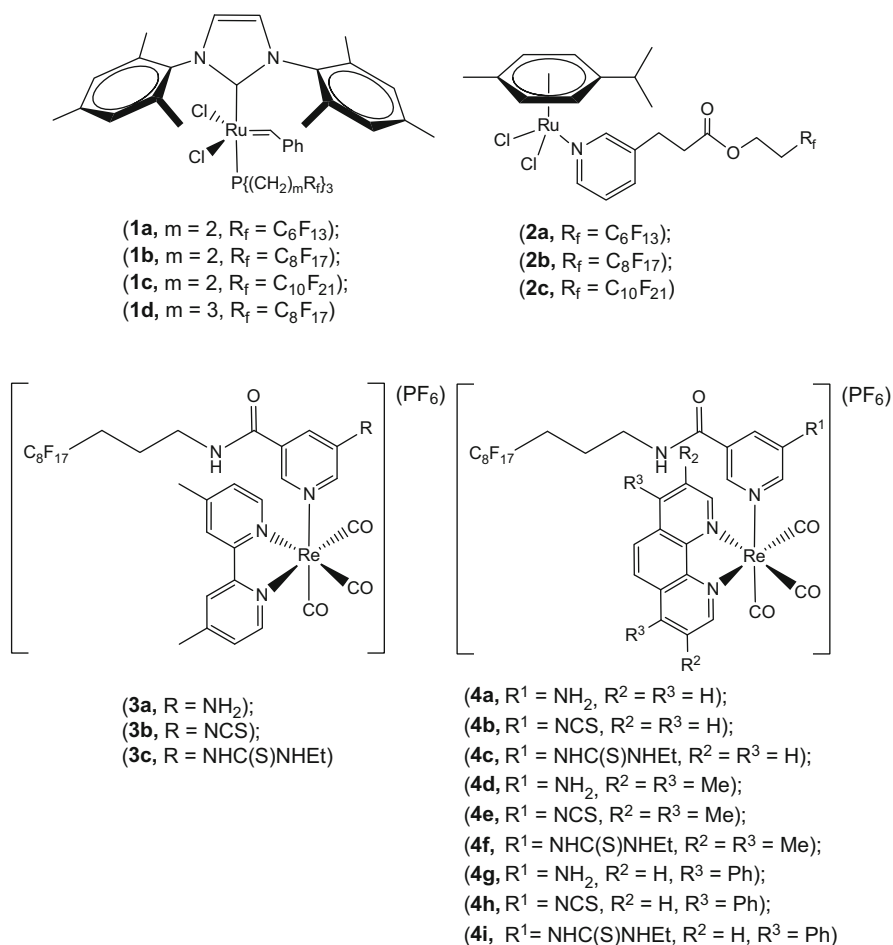


Fig. 1 Designer organometallic complexes incorporating perfluoroalkyl-functionalised ligands

3 Organometallic Complexes with Fluorous Organic Ligands

3.1 Cyclopentadienyl Metal Complexes

Given the ubiquity of the cyclopentadienyl (Cp) and related ligands in organometallic chemistry, it is not surprising that the first perfluoroalkyl-substituted Cp ligand (Cp^{Rf}) was reported relatively soon after Horváth and Rábai's seminal paper, and a number of both early and late transition metal- Cp^{Rf} complexes have been reported. A number of groups found that the usual, direct route to functionalised cyclopentadienes (Fig. 2), the reaction of a metal cyclopentadienide with a

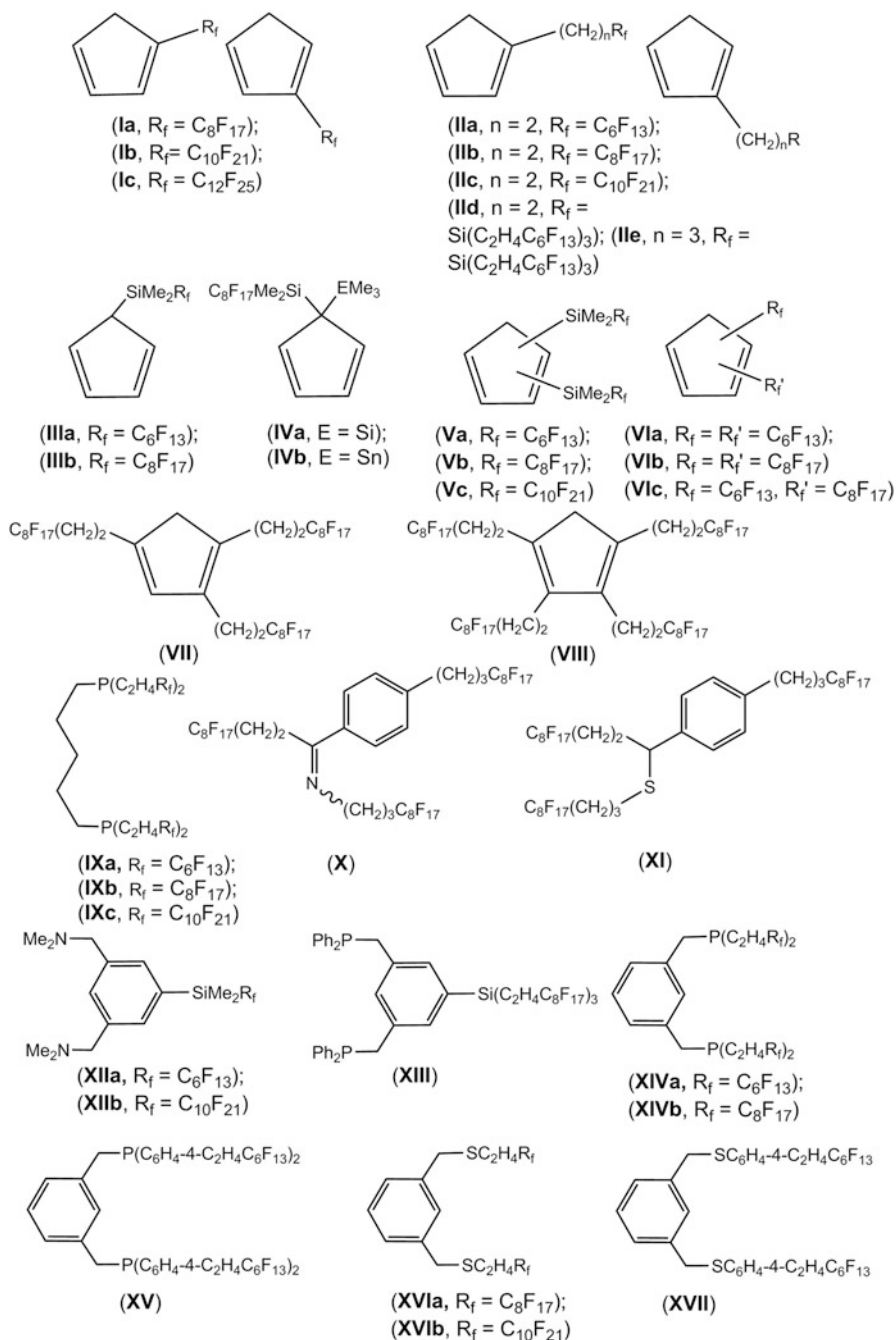


Fig. 2 Perfluoroalkylated pre-ligands and ligands

perfluoroalkyl iodide, gave complicated mixtures of products with the desired perfluoroalkyl cyclopentadienes (**I**) produced in poor yields. In contrast, Hughes and Trujillo [82] adapted Månsson's methodology [83] through the reaction of nickelocene with the appropriate iodide in the presence of triphenylphosphine, to give a series of mixtures of the respective double bond isomers. The dienes with the fluoros ponytail directly attached demonstrated very different properties to those containing the short ethylene spacer unit. Whilst the latter were stable in solution for several days at room temperature and could be deprotonated with butyl lithium to give synthetically useful anions (vide infra), the former dimerise relatively quickly in solution and decomposed on attempted deprotonation. Low-temperature reactions of the more stable lithium cyclopentadienide of (**IIc**) with $[\text{MBr}(\text{CO})_5]$ ($\text{M}=\text{Mn}, \text{Re}$) or of (**IIa**, **IIb**, **IIc**) with $\text{FeCl}_2 \cdot 2\text{THF}$ gave the first light fluoros cyclopentadienyl metal complexes with one or two fluoros substituents, respectively. Alternatively, the reaction of (**Ib**, **Ic** or **IIc**) with $[\text{Co}_2(\text{CO})_8]$ in the presence of 1,3-cyclohexadiene gave the desired $\text{Cp}^{\text{Rf}}\text{Co}(\text{CO})_2$ complexes (Fig. 3; **5a–c**) with and without the ethylene spacer group, although the latter could only be isolated in relatively low yield. As expected, although these light fluoros complexes are soluble in perfluorinated solvents, they are not preferentially soluble in the fluoros phase of a fluoros–organic biphasic system. Later, Horváth and Hughes extended this chemistry to the synthesis of $[\text{Cp}^{\text{Rf}}\text{Rh}(\text{CO})_2]$ (**5d**) and $[\text{Cp}^{\text{Rf}}\text{Rh}(\text{CO})\{\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}]$ by the reaction of the LiCp^{Rf} with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and, subsequently, ligand substitution [84]. Most recently [85], the iridium analogue, $[\text{Cp}^{\text{Rf}}\text{Ir}(\text{CO})_2]$ (**5e**), has been used to study photolytic C–H activation and dehydrogenation processes of alkanes (methane, cyclopentane, cyclohexane) in $\text{CF}_3\text{C}_6\text{F}_{11}$. Here, the light fluoros complex–perfluorinated solvent combination engenders both enhancements in catalyst stability and unprecedented reactivity; for example, methane undergoes photolytic oxidative addition to generate $[\text{Cp}^{\text{Rf}}\text{Ir}(\text{CO})(\text{CH}_3)(\text{H})]$ under 1 bar pressure at room temperature.

There have been three reports on the synthesis of fluoros analogues of the ubiquitous Cp^* ligand. Tetramethylcyclopenta-1,3-dienes with C_6F_{13} , C_8F_{17} or $\text{C}_{10}\text{F}_{21}$ side chains on reaction with rhodium precursors yielded the anticipated $[\text{Cp}^{*\text{Rf}}\text{Rh}(\text{CO})_2]$ (**6a**) and $[\text{Cp}^{*\text{Rf}}\text{RhCl}_2]_2$; exemplars of both have been structurally characterised [86, 87]. Cleavage of the chloride-bridged dimer with PMe_3 or a series of pyridines generated rhodium(III) piano-stool monomers with single C_6F_{13} ponytails [88]. Reduction in the presence of ethylene or various dienes, on the other hand, affords rhodium(I) bisalkene complexes (**6b–e**) [87].

Elsewhere, silicon-based chemistry has been used in order to elaborate cyclopentadienyl ligands with fluoros ponytails. The light fluoros cyclopentadienes with a single fluoros ponytail (**III**, **IV**) were readily prepared by the reaction of RfSiMe_2Cl with LiCp or $\text{LiC}_5\text{H}_4\text{EMe}_3$ ($\text{E}=\text{Si}, \text{Sn}$) [89, 90]. As expected, the monosubstituted species were obtained as mixtures of the 1-, 2- and 5-isomers, of which the 5-isomer was the major species, and the disubstituted species as highly complex mixtures, of which the 5,5-isomer was the major species. The pre-ligand (**Vb**) with two fluoros ponytails was prepared similarly, again as a mixture of isomers, following lithiation of the previously isolated (**IIIb**) and

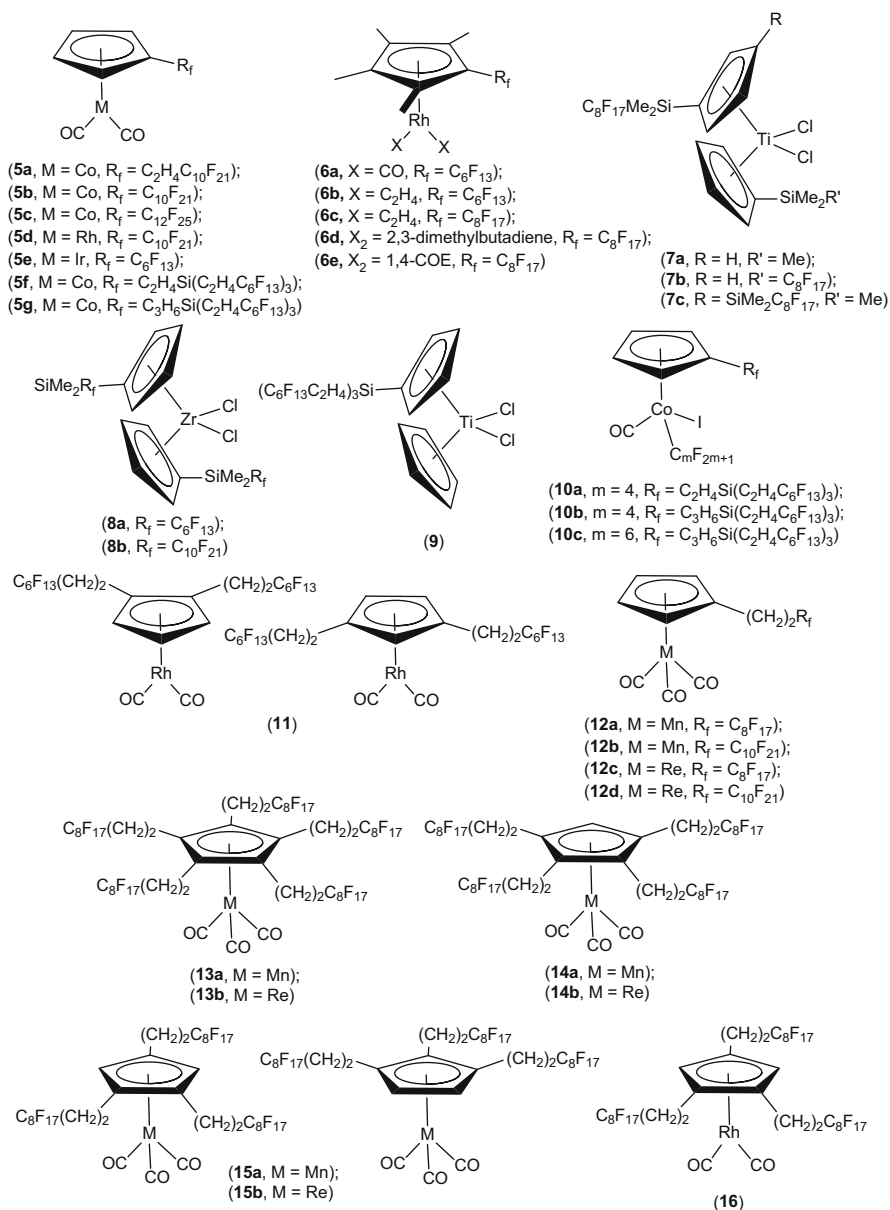


Fig. 3 Perfluoroalkylated cyclopentadienyl metal complexes

reaction with a further equivalent of R_fSiMe₂Cl [89]. On the reaction of **(IVb)** with TiCl₄, loss of trimethyltin gave a good yield of the [Cp^{Rf}TiCl₃] complex with a single ponytail. Alternatively, using well-established protocols from non-fluorous chemistry, LiCp^{Rf} from **(IIIb)** and **(Vb)** on reaction with Cp^{SiMe₃}TiCl₃ gave

asymmetric bis-cyclopentadienyltitaniumdichlorides (**7a**, **7c**) with one or two ponytails, respectively, whilst reaction of LiCp^{Rf} with TiCl_3 , followed by oxidation with PbCl_2 , gave the highly-insoluble symmetrical bis-Cp complex with two ponytails (**7b**), which has been crystallographically characterised [89]. Extending these methodologies has been used to make $[\text{Cp}^{\text{Rf}_2}\text{TiCl}_3]$ with two ponytails and the asymmetric $[\text{Cp}^{\text{Rf}}\text{Cp}^{\text{Rf}_2}\text{TiCl}_2]$ with three ponytails [90]. In closely related chemistry, the symmetrical bis-Cp zirconium dichloride complex (**8a**) was prepared from the reaction of the cyclopentadienyl lithiate with ZrCl_4 and has been structurally characterised [91]. Van Koten has taken this zirconocene derivative further, demonstrating that the dichlorides can be converted into the dimethyl complexes in a stoichiometric reaction with MeLi . The dichloride has also been used, in the presence of methylaluminoxane (MAO), as an ethylene polymerisation catalyst, which interestingly appeared to be more robust than the standard catalyst leading to increased productivity over prolonged polymerisation times [91]. The related zirconocene dichloride (**8b**) with $\text{C}_{10}\text{F}_{21}$ substituents has also been reported [92].

Various attempts to increase the number of perfluoroalkyl substituents on the cyclopentadienyl ring have been made. $[\text{Cp}^{\text{Rf}}\text{CpTiCl}_2]$ (**9**) can be formed via a similar protocol to that described above using $\text{BrSi}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3$ and LiCp , followed by lithiation and reaction with CpTiCl_3 [93]. Recently, cyclopentadienes with the same three-tailed silane unit, but separated from the ring by ethyl or propyl spacer units (**II d**, **II e**), were prepared in three steps from the chloroalkyltrichlorosilanes as mixtures of the 1- and 2-isomers [94]. The subsequent reaction using the $[\text{Co}_2(\text{CO})_8]/1,3\text{-cyclohexadiene}$ approach gave the desired $[\text{Cp}^{\text{Rf}}\text{Co}(\text{CO})_2]$ complexes (**5f**, **5g**) in good yields. Oxidative addition of medium and long perfluoroalkyl iodides to these cobalt(I) derivatives afforded cobalt(III) complexes (**10**) with both functionalised Cp rings and directly metal-bound fluoroalkyl ligands [94]. Reaction of LiCp^{Rf} with 2-(perfluoroalkyl)ethyl triflates afforded inseparable mixtures of four isomers of cyclopentadienes with two fluoruous ponytails (**VI**) [95]. Lithiation and reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gave mixtures of the [1,2- and 1,3- $\{\text{C}_5\text{H}_3(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_2\}\text{Rh}(\text{CO})_2]$ (**11**), whilst reaction with $\text{FeCl}_2 \cdot 2\text{THF}$ gave highly fluorophilic tetrasubstituted ferrocenes as mixtures of the bis-1,2, bis-1,3 and mixed 1,2/1,3 regioisomers [96]. Alternatively, the pre-ligands with two ponytails [**Va**, **Vc**] on lithiation and reaction with ZrCl_4 generate zirconocene dichloride complexes with four perfluoroalkyl substituents, for which the C_6F_{13} complex has been structurally characterised [92].

An alternative approach to fluoruous cyclopentadienes involves the reaction of preformed metal complexes. Acylation of ferrocene with perfluoroalkylated acyl chlorides with C_2H_4 spacers [97] or $\text{C}_{10}\text{H}_{20}$ spacers [98] in the presence of AlCl_3 generates, depending on stoichiometry, mono- or di-acylated ferrocenes. Reduction readily affords complexes with $(\text{CH}_2)_3\text{C}_6\text{F}_{13}$ or $(\text{CH}_2)_{11}\text{C}_6\text{F}_{13}$ ponytails respectively. $[(\eta^5\text{-C}_5\text{H}_4\text{Br})\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mn}, \text{Re}$) undergoes a palladium-catalysed cross-coupling reaction with $\text{IZn}(\text{CH}_2)_2\text{Rf}$ to generate the associated $\text{Cp}^{\text{Rf}}\text{M}(\text{CO})_3$ (**12**) with a single fluoruous ponytail in high yields [99, 100]. This approach can be extended to multiply functionalised Cp metal complexes. $[(\eta^5\text{-C}_5\text{Br}_5)\text{M}(\text{CO})_3]$, $[(\eta^5\text{-C}_5\text{HBr}_4)\text{M}(\text{CO})_3]$ or $[(\eta^5\text{-1,2,3-C}_5\text{H}_2\text{Br}_3)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mn}, \text{Re}$) reacts with

$\text{IZn}(\text{CH}_2)_2\text{Rf}$ to give fairly complex mixtures of products with varying fluorophilicities, which could be readily separated by chromatography on fluorous silica. The pentabromocyclopentadienyl starting materials gave the desired complexes with five perfluoroalkyl substituents (**13**) in poor yields (Mn = 2 %, Re = 15 %) alongside complexes with four perfluoroalkyl substituents (**14**) in which the fifth bromine had been replaced by a hydrogen atom (Mn = 45 %, Re = 30 % yields) and mixtures of the 1,2,4- and 1,2,3-trisubstituted derivatives (**15**) with two hydrogens (Mn = 7 %, Re = 7 %). The tetrasubstituted (**14**) and trisubstituted (**15**) derivatives were similarly isolated following reactions of the parent tetrabromo or tribromo complexes in 50–55 % yields. One of the standard routes for detaching Cp ligands from transition metals involves high-pressure mercury lamp photolysis of manganese tricarbonyl adducts, which has been applied in this study to liberate the parent cyclopentadienes with three and four perfluoroalkyl substituents (**VII**, **VIII**) in reasonable yields. The application of this route to generate other metal complexes of these polyderivatised ligands was amply demonstrated by the subsequent lithiation of 1,2,4- $\text{C}_5\text{H}_2(\text{C}_2\text{H}_4\text{C}_8\text{F}_{17})_3$ (**VII**) and reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to give the desired $[\text{Cp}^{\text{Rf}}\text{Rh}(\text{CO})_2]$ (**16**) [99, 100]. As expected, the fluorophilicities of these multiply functionalised complexes are very high with “no detectable amount of complex remaining in the toluene phase” of a $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene two-phase system.

3.2 Other π -Ligands

In comparison to the studies on functionalised Cp ligands, complexes of other π -donor ligands have received scant attention (Fig. 4). Reaction of the unsymmetrical $\text{F}_{17}\text{C}_8(\text{CH}_2)_3\text{C}\equiv\text{CSi}(\text{CH}_3)_3$ alkyne with dicobalt octacarbonyl at low temperature gave the fluororous-functionalised $[\text{Co}_2(\text{CO})_6\{\eta^2\text{-F}_{17}\text{C}_8(\text{CH}_2)_3\text{CCSi}(\text{CH}_3)_3\}]$ in good yield [101]. Fluorous benzenes with 1, 2 or 3 ponytails [102] and more recently with the shorter $-\text{OC}(\text{CF}_3)_3$ pigtail [103] have been synthesised. Reaction of the former with $\text{Cr}(\text{CO})_6$ under standard conditions affords in moderate to good yields the unremarkable piano-stool $[(\text{arene})\text{Cr}(\text{CO})_3]$ complexes (e.g. **17**) with 1–3 fluororous substituents [101]; the equivalent reactivity of the latter to generate organometallic derivatives has not yet been reported. Alternatively, reaction of the symmetrical $\text{F}_{17}\text{C}_8(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{C}_8\text{F}_{17}$ or unsymmetrical $\text{F}_{17}\text{C}_8(\text{CH}_2)_3\text{C}\equiv\text{CSi}(\text{CH}_3)_3$ alkynes with $[\text{CpCo}(\text{CO})_2]$ gave the well-established mixed sandwich $[\text{CpCo}\{\eta^4\text{-C}_4[(\text{CH}_2)_3\text{C}_8\text{F}_{17}]_2[\text{SiMe}_3]_2\}]$ as a mixture of *cis*- and *trans*-isomers with two ponytails for the latter and the quadruply ponytailed $[\text{CpCo}\{\eta^4\text{-C}_4[(\text{CH}_2)_3\text{C}_8\text{F}_{17}]_4\}]$ (**18**) for the former [101]. The intriguing possibility of combining this dimerisation complexation with the multiple functionalisation of the Cp ring described above to generate a mixed- π -sandwich complex with eight fluororous ponytails has not yet been pursued.

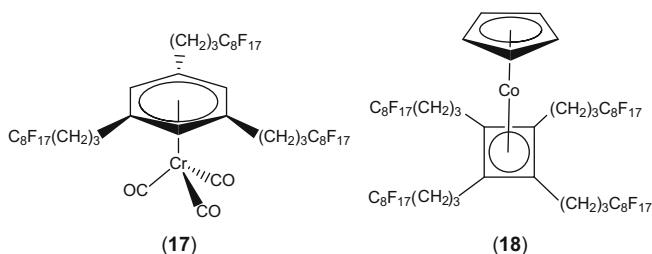


Fig. 4 Perfluoroalkylated arene metal complexes

3.3 Alkyl and Aryl Metal Complexes

The fluorous analogues of classical organometallic reagents (Grignards, organozincs, organocoppers, aryl lithiates, etc.) have been exploited widely throughout the development of fluorous synthetic chemistry, in most cases without isolation or even identification. In contrast, the number of formally isolated and characterised complexes containing a transition metal- sp^3 carbon bond in which the organometallic ligand incorporates a fluorous unit is extremely rare. As outlined above, one of the $\text{Cp}^{\text{Rf}}\text{Co}(\text{CO})\text{Rf}$ complexes (**10c**) contains a directly bound C_6F_{13} ponytail [86], whilst $[\text{IrCl}(\text{C}_2\text{H}_4\text{C}_8\text{F}_{17})(\text{CO})\{\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3\}_2]$ contains a ponytail with a spacer group [47, 49]; both complexes are formed by oxidative addition of the respective alkyl iodides to metal(I) precursors. The reactions of $\text{C}_n\text{F}_{2n+1}\text{I}$ with diethylzinc generate bis(perfluoroalkyl)zinc compounds, $\text{Zn}(\text{C}_n\text{F}_{2n+1})_2 \cdot 2\text{solv}$ ($\text{solv} = \text{MeCN}, \text{THF}, \text{DMSO}$), which have been comprehensively characterised in solution by multinuclear NMR [104, 105]. Reaction of 1,6-diiodododecafluorohexane with ZnEt_2 generates an unusual bisperfluoroalkyl-bridged dizinc species, $[(\text{solv})_2\text{Zn}(\mu^2\text{-C}_6\text{F}_{12})\text{Zn}(\text{solv})_2]$ ($\text{solv} = \text{MeCN}, 1,3\text{-dimethyl-}3,4,5,6\text{-tetrahydro-}1(1H)\text{-pyrimidinone}$); the latter has been used as a transfer reagent for the perfluoroalkyl chain to form perfluoro-bridged diaryls in the presence of CuCl [106]. Some experimental details for the isolation of the highly active Lewis acid scandium and ytterbium(III) tris(perfluoroalkylsulfonyl) methide catalysts have been reported [107–110]. The reaction of fluorous-1,5-diphosphinopentanes (**IX**) with $\text{Pd}(\text{O}_2\text{CCF}_3)_2$ in benzotrifluoride at elevated temperatures afforded a small series of palladium(II) PCP pincers complexes (Fig. 5; **19**) with four perfluoroalkyl substituents in modest yields [111]. Metathesis of (**19b**) gave the chloride complex, which has been crystallographically characterised, and further reaction with MeLi gave the palladium–methyl complex, which has limited stability. The striking exception to this situation arises outside the transition metal series where not only have a wide range of fluorous organotin reagents been widely employed as reagents in organic synthesis but also fluorous tin halides, fluorous tin hydrides and fluorous tin allyl complexes have also been prepared and isolated on large scales [2, 112–116], and even the tetraalkyltin complex, $[\text{Sn}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_4]$, has been described [117].

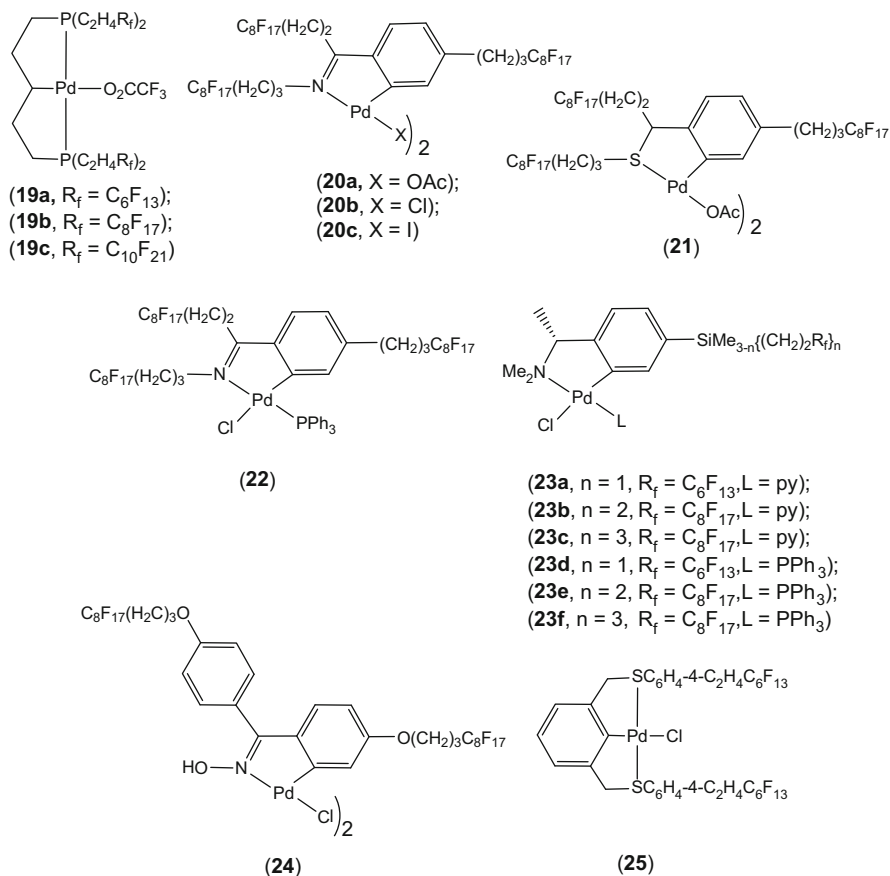


Fig. 5 Perfluoroalkylated cyclometalated and pincer metal complexes

In a similar vein, there are no reports of unsupported fluorine sp^2 hybridised carbon–metal complexes; however, there are a variety of reports of such interactions when they form part of cyclometalated or pincer ligand systems. *Ortho*-C–H activation on the aryl rings in (**X** and **XI**) with palladium acetate readily afforded the cyclopalladated acetate-bridged dimers (**20a** and **21**) with six C_8F_{17} ponytails [118, 119]. These complexes are thermomorphous in that they have little or no solubility in conventional organic solvents at room temperature but have significant solubility at elevated temperatures, but they act mainly as sources of soluble colloidal palladium nanoparticles, rather than as a discrete molecular catalyst, when applied in Heck or Suzuki reactions. The related halide ($X = Cl, I$)-bridged dimers (**20b**, **20c**) are formed readily for the imine palladacycle, and the bridge can be cleaved with triphenylphosphine to give (**22**). A similar C–H activation protocol with $Pd(OAc)_2$, this time in the presence of $LiCl$, affords the related chloride-bridged dimers of chiral NC ligands with two, four or six perfluoroalkyl groups

attached via the silyl linker [120]. Bridge cleavage with pyridine or PPh_3 generates a series of mononuclear complexes (**23**); the complex with one C_6F_{13} unit and $\text{L}=\text{PPh}_3$ (**23d**) has been structurally characterised. In 2011, a series of luminescent iridium(III) biscyclometalated cations $[\text{Ir}(\text{N-C})_2(\text{N-N})](\text{PF}_6)$ with two C_8F_{17} ponytails were reported, in which the fluorine substituents appeared to impact positively on the photophysical and biological properties [121]. The oxime-based palladacycle (**24**), formed in a slow reaction of the free oxime with Li_2PdCl_4 in acetone at reflux, has been shown to be a highly effective pre-catalyst for Suzuki–Miyaura, Sonagashira, Stille, Heck and Kumada reactions, either in aqueous solution or organic solvents, that could be recycled and reused up to five times [122, 123].

The first metal-pincer ligand complex was reported in 1998. Heteroatom-assisted lithiation of the perfluoroalkylsilyl pre-ligands (**XII**) followed by reaction with metal dichloride reagents gave the desired NCN-metal complexes with one ponytail in high yields; one of the nickel complexes was structurally characterised [124]. In a standard Kharasch addition reaction of CCl_4 to methyl methacrylate in dichloromethane, the nickel complexes exhibited almost identical activities to that of the analogous, underivatized pincer complex. Three groups have reported closely related PCP pincer metal complexes; firstly, van Koten et al. described the synthesis of the ruthenium(II) complex with three C_8F_{17} ponytails attached via a silyl spacer to the arene unit in (**XIII**) [125]. Incorporating the fluorine ponytails using the phosphorus donors is an alternative approach: The trialkylphosphine PCP pre-ligands (**XIV**) react readily with $\text{Pd}(\text{O}_2\text{CCF}_3)_2$ or $[\text{IrCl}(\text{COE})_2]_2$ (COE = cyclooctene) to generate square planar palladium(II) or trigonal bipyramidal iridium(III) complexes, each with four perfluoroalkyl groups; the Pd(II) complex with C_8F_{17} groups has been structurally characterised [126]. The triarylphosphine PCP pre-ligand (**XV**) reacts with either $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{PdCl}_2(\text{MeCN})_2$ or $\text{PtCl}_2(\text{COD})$ to generate the anticipated square planar complexes [127]. The palladium(II) complex performed reasonably as a catalyst for the Heck reaction under standard conditions and was recycled four times using a fluorine solid-phase extraction protocol. Analogous alkyl- and aryl-SCS pre-ligands (**XVI** and **XVII**) have also been reported [128, 129]. Coordination of the pre-ligands to palladium(II) is straightforward affording complexes with two fluorine ponytails, and the aryl-SCS-PdCl complex (**25**) has been structurally characterised. These complexes have all been evaluated as catalysts for the Heck reaction and, whilst the S-alkyl catalyst precursors are consumed during the reaction, the S-aryl catalyst could be recycled three times using a fluorine solid-phase extraction approach.

The final area where perfluoroalkyl groups have been incorporated into carbon-based ligands for coordination to a metal centre is in functionalised benzylidenes for the synthesis of Grubbs–Hoveyda-type catalysts (Fig. 6) and their applications in alkene metathesis. In the first of these, a fluorine-soluble acrylate polymer bearing the key isopropoxystyrene unit for coordination was reacted with the Grubbs–Hoveyda catalyst in the presence of CuCl for styrene group exchange [130]. The air-stable catalyst (**26a**) was tested in a series of ring-closing metathesis (RCM) reactions, with a variety of di-, tri- and tetrasubstituted dienes, delivering

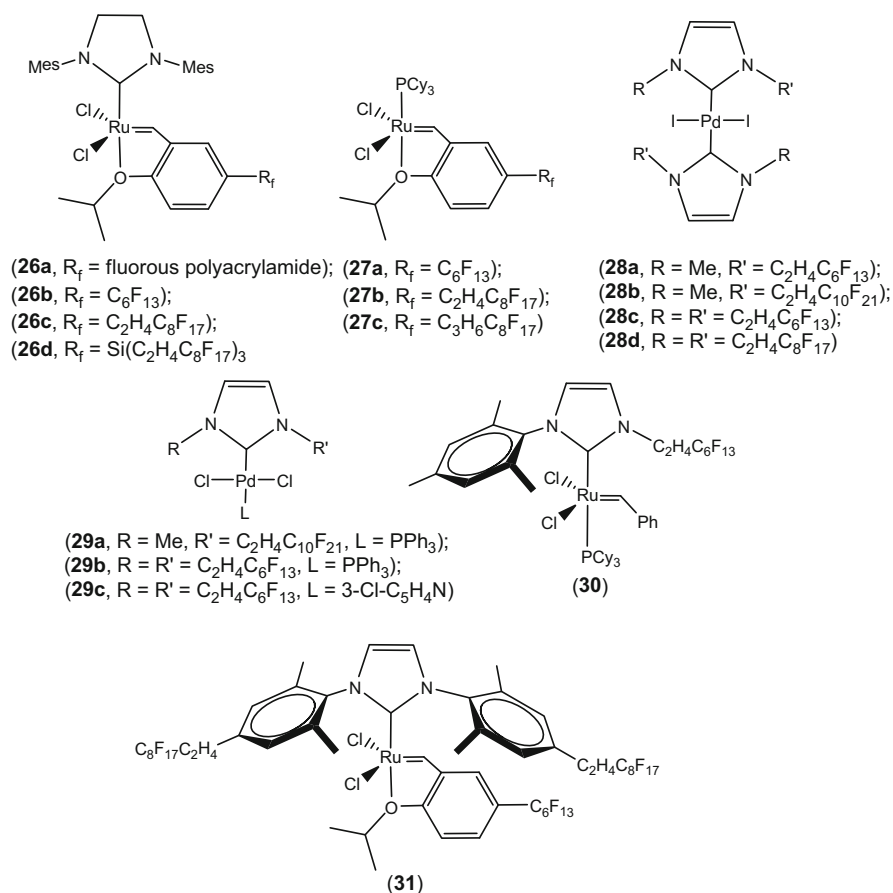


Fig. 6 Perfluoroalkylated benzylidene and *N*-heterocyclic carbene metal complexes

excellent conversions. The catalyst could be readily recovered following extraction with FC-72 and up to 20 catalyst recovery/reuse cycles were demonstrated. More conventional molecular first- and second-generation Grubbs–Hoveyda catalysts have been prepared (**26b–d**; **27a–c**) with a directly attached C_6F_{13} ponytail [131], spacer $(CH_2)_{2/3}C_8F_{13}$ ponytail [132] and a silyl spacer with three $C_2H_4C_8F_{17}$ ponytails [133]. Each of these catalysts shows good activity in model RCM reactions, with recovery/reuse cycles (up to five times) either via a fluorous solid-phase extraction protocol or via noncovalent immobilisation on fluorous silica gel. Most recently, the functionalised benzylidene complexes (**26b**, **27a**) have been converted into their fluorocarboxylate salts to improve their fluorophilicities [134]. Whilst the two complexes with the linear C_6F_{13} carboxylate ligands are modestly fluorophilic, those complexes with the perfluoropolyoxyalkanoate ligands are highly fluorophilic, in line with this group's observations on functionalised silver NHC complexes (vide infra). Whilst those complexes with linear

carboxylates showed reasonable activities in RCM reactions, those with branched carboxylate ligands were virtually inactive, suggesting that steric crowding at the ruthenium centre is an issue for these species.

3.4 NHC Metal Complexes

The versatility and applications of *N*-heterocyclic carbene ligands in catalysis and beyond is now extremely well established. However, the number of reports of fluoroalkylated NHC ligands and their complexes is relatively small (Fig. 6). In 2000, rotationally equilibrated, 1:1 mixtures of the *trans-anti* and *trans-syn* isomers of the palladium(II) complexes (**28a**) with two ponytails were generated readily in the reaction of the parent imidazolium salt with Pd(OAc)₂, for which the *trans-anti* isomer has been structurally characterised [135]. Presumably, a similar isomeric mixture of *trans*-[PdI₂(NHC)₂] (**28b**) with one C₂H₄C₁₀F₂₁ ponytail per NHC ligand (generated in situ but not isolated) and preformed, or generated in situ, *trans*-[PdCl₂(NHC)(PPh₃)] (**29a**) with one C₂H₄C₁₀F₂₁ ponytail have each been used in Mizoroki–Heck arylations of α,β-unsaturated acids in a fluorous ether with similar activities and separation characteristics [136]. In closely related work, *trans*-[PdCl₂(NHC)(PPh₃)] (**29b**) [137] and *trans*-[PdCl₂(NHC)(3-chloropyridine)] (**29c**) [138], both with two C₂H₄C₆F₁₃ ponytails, have been tested as catalysts for Suzuki cross-coupling reactions. Finally in palladium(II) chemistry, the more heavily perfluoroalkylated *trans*-[PdI₂(NHC)₂] complexes with either four C₂H₄C₆F₁₃ (**28c**) [135] or four C₂H₄C₈F₁₇ (**28d**) [139] ponytails have been reported separately, the former being structurally characterised.

Elsewhere, the perfluoroalkylated analogue of the Grubbs-II catalyst with a single C₂H₄C₆F₁₃ ponytail on the carbene (**30**) has been prepared [140], ostensibly to enhance the solubility of such catalysts in scCO₂, but, to date, further work with this complex has not been published. Three perfluoroalkyl units have been attached to a Grubbs–Hoveyda-type catalyst via both the benzylidene and a symmetrically substituted NHC (**31**) [132]. This catalyst showed higher activity in the challenging RCM of a tetrasubstituted diene than the commercially available catalyst, but recycling of the catalyst has not been described. The reactions of perfluoroalkylated imidazolium salts with silver oxide in acetonitrile gave silver NHC complexes, formulated as [Ag(NHC)₂][AgX₂] (X = I, OTf) on the basis of APCI⁺ MS. The analogous complexes formed from imidazolium salts functionalised with perfluoropolyether ponytails exhibit enhanced fluorophilicities, which the authors ascribe to the enhanced flexibility of the perfluoropolyether over the conventional perfluoroalkyl ponytail [28].

4 Conclusions and Future Prospects

In the past 20 years, the synthetic challenges of incorporating long perfluoroalkyl ponytails into organometallic complexes have, for the most part, been overcome through the development and adaptation of existing methodologies. These have generated fluororous analogues of almost every class of organometallic complex that have, almost without fail, been thoroughly characterised analytically and spectroscopically, generating a large amount of new insight into fluororous systems. Studies on the single most extensively studied class of organometallic complex, the Vaska's analogues, have been used to establish the electronic influence of incorporating the fluorinated substituents, but, perhaps, the insight into the role of the fluororous solvent and/or substituents on the kinetics and mechanism of oxidative addition in these systems, mentioned in the work from two groups [47, 50], has been overlooked. Structurally, more than 20 single crystal structure determinations have been reported on fluororous organometallic complexes, and these reveal two significant facts: The perfluoroalkyl groups have little or no impact upon the key structural features in the first metal coordination sphere (M–L bond lengths, L–M–L' bond angles), but they dominate the packing in the solid-state generating fluororous and non-fluororous domains throughout the extended structures. Another aspect that has received considerable attention is the relative partition coefficients of organometallic complexes within organic–fluororous two-phase systems. However, the realisation that the FBS system (as originally conceived) is untenable on an industrial scale, due to the cost of and environmental factors associated with perfluorocarbon solvents, has led to the development of light fluororous and thermomorphic approaches to separation diminishing the importance of relative partition coefficients.

Isolated organometallic compounds, as outlined above, or perfluoroalkylated organometallic catalysts generated in situ, have been evaluated in a diverse range of catalytic processes, with particular emphasis on oxidations, reductions and C–C bond-forming reactions. Generally, these fluororous organometallic systems have performed adequately, some better, some worse, in terms of catalytic activity or selectivity, than other systems reported in the academic literature. The recovery and reuse of the catalysts, combined with the amount of metal leaching to the product phase, have been determined for many systems, but to date none has performed sufficiently better than their non-fluororous counterparts to warrant their development beyond laboratory scale systems.

Where will fluororous organometallic chemistry go in the future?

Firstly, the concerns over the bioaccumulation of the degradation products from organic molecules with the archetypal fluororous ponytails, C₆F₁₃ or C₈F₁₇, are challenging the fluororous community to consider alternative strategies. A number of reports on two of these, the incorporation of perfluoro-*t*-butoxy or perfluoropolyethers, have appeared in the synthetic organic chemistry literature. The recent observation [28] of enhanced fluorophilicity of species functionalised with perfluoropolyether groups over those with perfluoroalkyl groups is a clear signpost of a

direction to be followed in organometallic chemistry. Secondly, insight is provided by the recent work on the engineering of organometallic systems in which the fluorous substituent imparts specific, even unique, biological properties to the organometallic complex [79–81], and this is undoubtedly an area that is going to grow in the next few years. We look forward to the continued evolution of research in fluorous organometallic chemistry.

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