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Review

Fluoroarylphosphines as ligands

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Abstract

This short review concentrates on important aspects of fluoroarylphosphines, in particular their synthesis, ligand properties and chemical and catalytic properties of their complexes. Although the electronic, steric and chemical properties of fluoroarylphosphines have been known for 30 years, their use as ligands for homogeneous catalysis and in the synthesis of elaborate multidentate ligands has occurred more recently. The number of recent reports suggests that their importance is growing.

Keywords: Fluoroaryl; Phosphines; Ligands; Transition metal complexes; Catalysis

Contents

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1. Introduction

Since the first report of tris(pentafluorophenyl)phosphine in 1960 [1], many phosphines bearing fluoroaryl substituents have been synthesized and their coordination chemistry studied. Table 1 lists important examples showing the range of fluoroarylphosphines that have been reported. The earliest reference is given for each phosphine and those for which the structure has been determined by single-crystal X-ray diffraction are marked (†) and the reference detailing the structure is also given if different from the earliest reference. (The positions of the aryl substituents are numbered sequentially from a phosphorus atom (position 1) and such that the positions of further phosphorus atoms, if present, are the lowest possible.)

This short review is concerned with the use of phosphines bearing fluoroaromatic substituents as ligands, and so focuses on their synthesis, ligand properties, and the reactions and catalytic properties of their complexes. It is not intended to be comprehensive, but rather to highlight important aspects of these ligands. For the purposes of this review fluoroarylphosphines are defined as compounds of trivalent phosphorus bonded only to carbon or hydrogen (PR_xH_{3-x}), and bearing at least one aromatic substituent to which at least one fluorine atom is bonded (ArF). Phosphites ($P(OR)_3$), phosphonites ($PR'(OR)_2$), phosphinites ($PR'_2(OR)$) and their nitrogen analogues ($PR'_x(NR_2)_{3-x}$), and metal phosphides (MPR_2) will not be discussed. Neither will phosphines bearing aromatic substituents to which fluorine is not directly bonded be discussed, excepting appropriate comparisons with (trifluoromethylphenyl)phosphines, $PR_x\{C_6H_{5-y}(CF_3)_y\}_{3-x}$. Discussion of reactions involving non-coordinated or coordinated fluoroarylphosphines will focus on those in which the fluorine plays an essential role in determining the product, for example nucleophilic attack at the fluoroaryl substituents, rather than general reactions of phosphines, such as oxidation to phosphine oxide.

Section 2 details the synthetic strategies for the preparation of fluoroarylphosphines. Along with the most commonly adopted methods, which involve nucleophilic attack at or by a phosphorus(III) reagent, other reactions that produce fluoroarylphosphines are given. Section 3 describes the ligand properties of fluoroarylphosphines, and Section 4 highlights the effects exerted on metal complexes, including complex stability and reactivity. Although the chemical properties conferred on phosphines by fluorine have been well known for many years, it is only relatively recently that there has been interest in their exploitation in, for example, the functionalization of coordinated phosphines to synthesize elaborate ligands (Section 5) and homogeneous catalysis (Section 6).

2. Synthesis

2.1. Electrophilic phosphorus

The most commonly used method for preparing polyfluoroaryl phosphines is that shown in Scheme 1.

Fluoroaryl Grignard reagents are readily generated from fluorobromoarenes. Lithium reagents can be generated from fluorobromoarenes by transmetallation or less conveniently by deprotonation of polyfluoroarenes. These reagents are nucleophilic and readily react with electrophilic phosphorus reagents, in particular phosphorus mono-, di- and tri-halides. Typically diethyl ether or THF is used as solvent, and low temperatures

Table 1
Examples of fluoroarylphosphines[a]

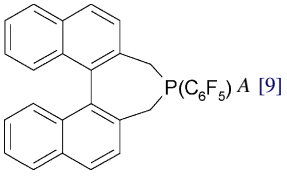
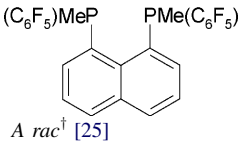
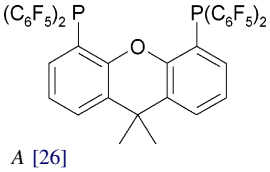
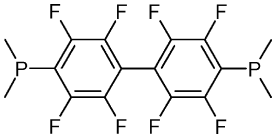
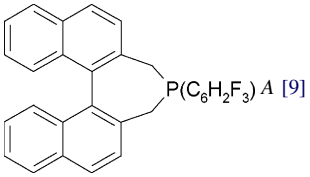
R_2PArF	$RP(ArF)_2$	$P(ArF)_3$	Polyphosphines
Pentafluorophenyl			
$R_2P(C_6F_5)$: R = H *A* [2], Me, Ph† *A* [3,4], $C_6F_5C{\equiv}C$ *A* [5] $PhP(C_6F_5)C_6H_4SMe$-2 *A* [6] $Ph_2P(\eta^6\text{-}C_6F_5)Cr(\eta^6\text{-}C_6H_6)$ *A* [7,8]  $P(C_6F_5)$ *A* [9]	$RP(C_6F_5)_2$: R = H *A* [2], Me, Ph *A* [3], *cyclo*-C_5Me_5 *A* [10], $MeC{\equiv}C$, $PhC{\equiv}C$ *A* [11], $C_6F_5C{\equiv}C$ *A* [12], $MeOC{\equiv}C$ *A* [13], C_6H_4SMe-2 *A* [14], $CH_2C(CF_3)_2OH$ *A* [15]	$P(C_6F_5)_3$† *A* [1,16]	$(C_6F_5)_2PCH_2P(C_6F_5)_2$ (dfppm)† *A* [17,18] $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe)† *A* [19,20] $(C_6F_5)PhPCH_2CH_2PPh(C_6F_5)$ *A* [21] $(C_6F_5)_2PC{\equiv}CPPh_2$ *A* [11] $\{(C_6F_5)_2P\}_2C{=}C{=}O$ *A* [22] $\{(C_6F_5)_2PC_6H_4\text{-}2\}_2O$ *A* [23] $C_6H_4\{CH_2P(C_6F_5)_2\}_2$-1,3 *A* [24]  *A rac*† [25]  *A* [26]
2,3,4,5-Tetrafluorophenyl			
$Ph_2P(C_6F_4Br\text{-}2)$ *A* [27] $Ph_2P(C_6F_4SMe\text{-}2)$ *A* [27]	$PhP(C_6F_4SMe\text{-}2)_2$ *A* [27]	$P(C_6F_4Br\text{-}2)_3$ *A* [28] $P(C_6F_4)_3E$ E = As, Sb *A* [28]	$(C_6HF_4)_2PCH_2CH_2P(C_6HF_4)_2$ *A* [29] $C_6F_4(PR_2)_2$ R = Me *A* [30], Ph *A* [27] $PhP(C_6F_4PPh_2)_2$ *A* [27] $PhP(C_6F_4)_2PPh$ *A* [31] $P(C_6F_4)_3P$ (see Section 2.7) [32]
2,3,5,6-Tetrafluorophenyl			
$Me_2P(C_6F_4Y\text{-}4)$ Y = H, CF_3, Cl *B* [33] $Ph_2P(C_6F_4Y\text{-}4)$ Y = OMe, NMeH *F* [34], $\{CF_2CF(CF_3)O\}_nC_3F_7$ *n* = 1,2, 4 *A* [35]	$PhP(C_6F_4SiMe_3\text{-}4)_2$ *A* [36]	$P(C_6F_4Y\text{-}4)_3$ Y = NH_2, NMe_2, $NHNH_2$, OMe *F* [37], CF_3, $C_6F_4CF_3$ *A* [38], OC_6F_5-4 *A* [39] $OC_6F_4CF_3$ *A* [38], $CF_2CF(CF_3)OC_3F_7$, $(CF_2CF(CF_3)O)_5C_3F_7$ *A* [35]	$C_6F_4(PMe_2)_2$ *B* [33]  *B* [33] $C_6F_4\{P(C_6H_2Me_3\text{-}1,3,5)_2\}_2$† *A* [40]
2,3,5,6-Tetrafluoropyridyl			
$R_2P(C_5F_4N)$ R = Me *B* [33], Pr^i, Ph *B* [41] $PRBu^t(C_5F_4N)$ R = H, Me, Pr^i *B* [41]	$PR(C_5F_4N)_2$ R = Bu^t, Ph *B* [41]	$P(C_5F_4N)_3$ *B* [41]	$Ph_2PCH_2CH_2PPh(C_5F_4N)$ *B* [42]
2,3,4,5-Tetrafluoropyridyl			
$Bu^t{}_2P(C_5F_4N)$ *B* [41]			
2,4,6-Trifluorophenyl			$Ph_2PCH_2CH_2CH_2P(C_6H_2F_3)_2$ *A* [43]
2,3,6-Trifluorophenyl		$P(C_6H_2F_3)_3$ *A* [44]	
2,4,5-Trifluorophenyl			$(C_6H_2F_3)_2PCH_2CH_2P(C_6H_2F_3)_2$ *A* [45]
3,4,5-Trifluorophenyl  $P(C_6H_2F_3)$ *A* [9]	$(MeO\text{-}4\text{-}C_6H_4)P(C_6H_2F_3)_2$ *A* [46]	$P(C_6H_2F_3)_3$ *A* [47]	$(C_6H_2F_3)_2PCH_2CH_2P(C_6H_2F_3)_2$ *A* [48] $Ph_2PCH_2CH_2P(C_6H_2F_3)_2$ *A* [49]

Table 1 (*Continued*)

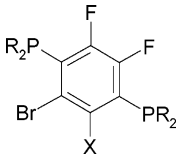
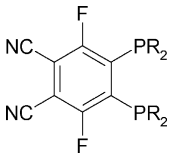
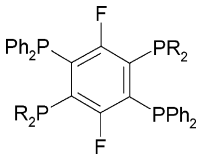
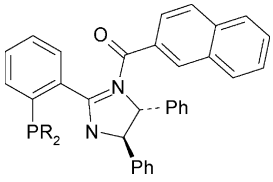
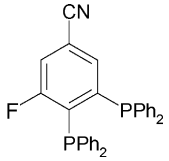
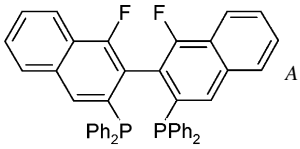
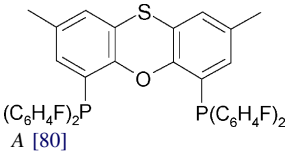
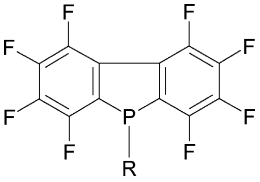
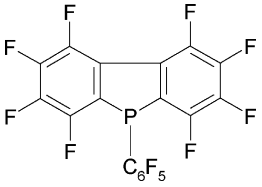
R_2PArF	$RP(ArF)_2$	$P(ArF)_3$	Polyphosphines
2,3-Difluorophenyl			
$Me_2P(C_6F_2H_3)$ *B* [50]			
$Ph_2PC_6F_2Br_2H$-4 *A* [51]			X = Br, R = Pr^i, Ph†; X = Cl, Ph† *A* [51]
2,4-Difluorophenyl			$(C_6H_3F_2)_2PCH_2CH_2P(C_6H_3F_2)_2$ *A* [45]
2,5-Difluorophenyl		$P(C_6H_3F_2)_3$ *A* [44]	
			R = Et *B* [52], Ph† *B* [53]
			$C_6H_2F_2(PPh_2)_2$-1,4† *B* [54,55]
			
			R = Et†, Pr^{i}†, Ph† *A* [56]
			$C_6R_2F_2\{P(C_6H_2Me_3$-1,3,5$)Ph_2\}_2$-1, 4 R = Ph, Bu^n *B* [40]
2,6-Difluorophenyl			
$PMe_2(C_6H_3F_2)$† *B* [50]	$PPh(C_6H_3F_2)_2$† *A* [57]	$P(C_6H_3F_2)_3$† *A* [58,57]	$(C_6H_3F_2)_2PCH_2CH_2P(C_6H_3F_2)_2$† *A* [59]
$PPh_2(C_6H_3F_2)$† *A* [57]			
3,4-Difluorophenyl			
	$(MeO$-4-$C_6H_4)P(C_6H_3F_2)_2$ *A* [46]	$P(C_6H_3F_2)_3$ *A* [60]	
3,5-Difluorophenyl			
	$HP(C_6H_3F_2)_2$ *E* [61]	$P(C_6H_3F_2)_3$ *A* [63]	$(C_6H_3F_2)_2PCH_2P(C_6H_3F_2)_2$ *A* [64]
	$HP(C_6H_2F_2OMe$-4$)_2$ *E* [61]		$(C_6H_3F_2)_2PCH_2CH_2PPh(C_6H_3F_2)$ *A* [65]
			$Ph_2PCH_2CH_2P(C_6H_3F_2)_2$ *A* [49]
			
	(*R,R*) R = $C_6H_2F_3$-3,5 *C* [62]		$Ph_2PCH_2CH_2CH_2P(C_6H_3F_2)_2$ *A* [43]
2-Fluorophenyl			
$Ph_2P(C_6H_4F)$ *A* [66]	$PhP(C_6H_4F)_2$ *A* [67]	$P(C_6H_4F)_3$ *A* [67]	$(C_6H_4F)_2PCH_2CH_2P(C_6H_4F)_2$ [68]
			 *B* [53]

Table 1 (*Continued*)

R_2PArF	$RP(ArF)_2$	$P(ArF)_3$	Polyphosphines
3-Fluorophenyl			
$R_2P(C_6H_4F)$ R = Me, CF_3, Ph *A* [69] $PhP(C_6H_4F)CH_2OH$ [70]	$RP(C_6H_4F)_2$ R = H [71], CF_3 *A* [69], Ph *A* [72], CH_2Ph *A* [73]	$P(C_6H_4F)_3$ [74] $P(C_6H_4F\text{-}3)_{3-x}(C_6H_4F\text{-}4)_x$ x = 1, 2 [72]	$(C_6H_4F)_2PCH_2CH_2P(C_6H_4F)_2$ *A* [75] $Ph_2PCH_2CH_2P(C_6H_4F)_2$ *D* [71]  *A* [76]
4-Fluorophenyl			
$R_2P(C_6H_4F)$ R = H, Me, Ph *A* [77], CF_3 *A* [69]	$RP(C_6H_4F)_2$ R = CF_3 *A* [69], Ph [72], CH_2Ph *A* [73]	$P(C_6H_4F)_3$† *A* [77,78]	$(C_6H_4F)_2P(CH_2)_nP(C_6H_4F)_2$ n = 2 *A* [75], n = 4 *A* [79] $Ph_2PCH_2CH_2P(C_6H_4F)_2$ *D* [71]  *A* [80]
Dibenzophosphole			
	 R = Ph *A* [81], Bu^t *A* [82]	 *A* [82]	

[a] For each phosphine the earliest reference is given. Phosphines for which the structure has been determined by single-crystal X-ray diffraction are marked (†) and the reference detailing the structure is also given if different from the earliest reference. The method of preparation is denoted by: *A* using electrophilic phosphorus reagents (see Section 2.1), *B* using nucleophilic phosphorus reagents (see Section 2.2), *C* using palladium-mediated phosphorus–carbon coupling (see Section 2.3), *D* by hydrophosphination (see Section 2.4), *E* by reduction of phosphorus(V) (see Section 2.5), and *F* functionalization of fluoroarylphophines (see Section 2.6). Other fluoroarylphosphines are mentioned in the text. 2,3,4,6-Tetrafluorophenylphosphines, 2,3,4,6-tetrafluoropyridylphosphines, 2,3,4-trifluorophenylphosphines and 2,3,5-trifluorophenylphosphines have not been reported.

are used for reactions involving lithium reagents. A polymer-supported halodiphosphine, prepared by treating Merrifield's resin with *tert*-butylamine and 1,2-bis(dichlorophosphino)ethane, has allowed the synthesis of asymmetrically substituted diphosphines, such as $(C_6H_3F_2)_2PCH_2CH_2PPh(C_6H_3F_2)$, in moderate to high yields (Scheme 2) [65].

The cleavage of P–C(ArF) bonds of non-coordinated phosphines by nucleophilic metal reagents has been reported (Scheme 3) [83]. However, an attempt to prepare $(C_6F_5)_2PC_6H_4SMe\text{-}2$ by the treatment of $P(C_6F_5)_3$ with $LiC_6H_4SMe\text{-}2$ yielded a mixture of $P(C_6F_5)_3$, $(C_6F_5)P(C_6H_4SMe\text{-}2)_2$ and the desired product, but this was isolated in only 4% yield [84].

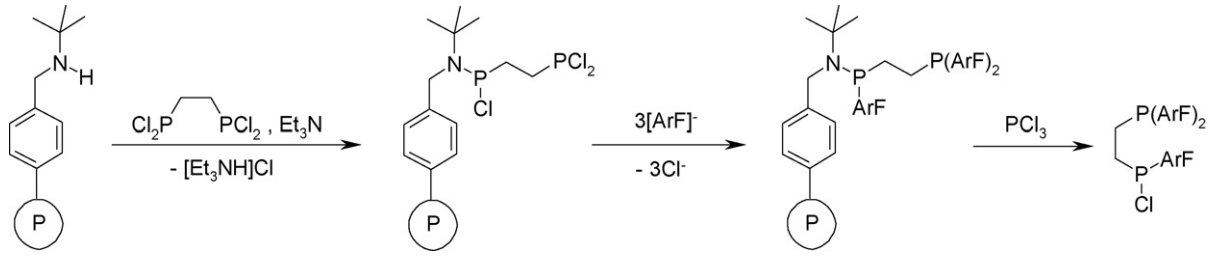
Pentafluorophenylphosphines have also been prepared from pentafluorophenyltrimethylsilane (Scheme 4), although the yields were moderate [85].

Scheme 1.

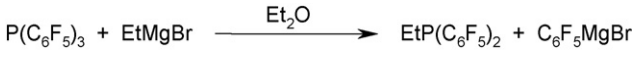
2.2. Nucleophilic phosphorus

The electronegativity of fluorine renders polyfluoroarylphosphides, $[(ArF)_2P]^-$ or $[(ArF)RP]^-$, only weakly nucleophilic [86]. The lack of reaction with most electrophiles precludes the syntheses of phosphines by a route which is extremely convenient for non-fluorinated phosphines, such as dppe, which is prepared by the reaction between diphenylphosphide and 1,2-dichloroethane [87]. However, since fluoroaromatic compounds undergo S_NAr reactions [88], phosphines bearing only one fluoroaromatic substituent may be synthesized readily by the reaction between a polyfluoroaromatic compound and a nucleophilic phosphide, secondary phosphine or equivalent. The success of the synthesis is highly dependent on the nucleophilicity of the phosphorus reagent, the nature of the substrate and the temperature. Typically substitution occurs *para* to substituents [88], and this can be used to direct the positions of di- and poly-substitution, for example in the syntheses of chelating *ortho*-fluorophenylene bridged diphosphines [53].

Phosphides have been used to synthesize phosphines from polyfluorobenzenes. For example, $C_6F_4\{P(C_6H_2Me_3\text{-}2,4,6)_2\}_2\text{-}1,4$ was synthesized by the reaction between



Scheme 2.



Scheme 3.

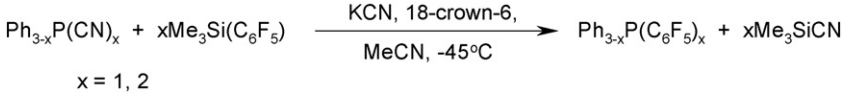
$NaP(C_6H_2Me_3\text{-}2,4,6)_2$ and hexafluorobenzene in THF at 0 °C [40], $C_6H_2F_2$-2,5-$(PPh_2)_2$-1,4 was synthesized by the reaction between 1,2,4,5-tetrafluorobenzene and two equivalents of $LiPPh_2$ in THF [54], and the phosphine enolate $Bu^tP{=}C(OLi)Bu^t$, underwent reaction with pentafluoropyridine at ambient temperature to give a quantitative yield of $Bu^tP\{C(=O)Bu^t\}(C_5F_4N\text{-}4)$ [41]. In reactions involving phosphides care must be taken to control both stoichiometry, to avoid complete substitution of fluorine [89], and temperature, since the reactions involving highly fluorinated aromatic groups or those bearing strongly electron-withdrawing groups are strongly exothermic leading to undesirable reactions and decomposition. For example, the reaction between diphenylphosphide and tetrafluorophthalonitrile in THF at 0 °C produced intractable tars [53]. The latter problem can be overcome by the use of secondary phosphines or trimethylsilyl- or trimethylstannyl-phosphines.

Although much less nucleophilic than phosphides, secondary phosphines react smoothly with some highly fluorinated aromatic compounds bearing strongly electron-withdrawing groups. For example tetrafluorophthalonitrile underwent nucleophilic attack by diphenylphosphine at 100 °C in acetonitrile to give $C_6F_2(CN)_2$-4,5-$(PPh_2)_2$-1,2 in 60% yield [53]. The secondary phosphine $HPPh(C_6F_5)$ underwent reaction with hexafluoroacetone to form $PhP(C_6F_5)C(CF_3)_2OH$, although this readily decomposed to the starting materials amongst other compounds, but the phosphine $HP(C_6F_5)_2$, which is less nucleophilic, failed to react with hexafluoroacetone [90].

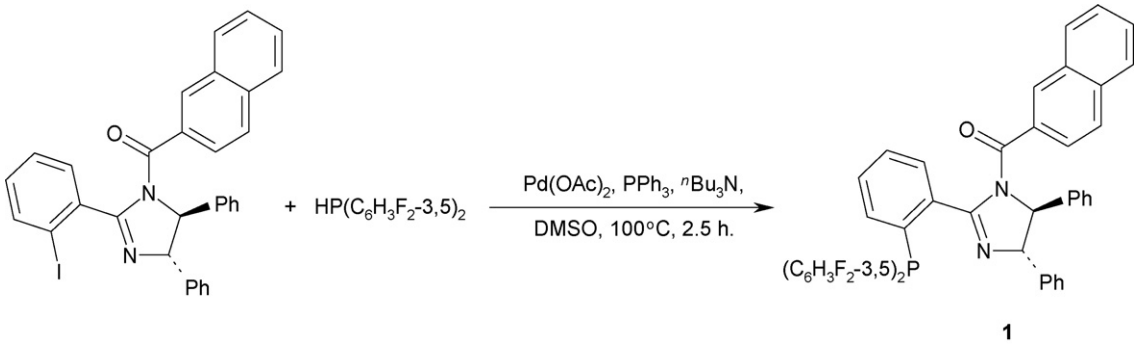
Trimethylsilylphosphines [33,41,42,50] and trimethylstannylphosphines [33] have been reported to react with polyfluoroarenes giving products in high yields. The driving force for the reaction is the strength of the $Me_3Si–F$ and $Me_3Sn–F$ bonds. The reactions are usually performed at elevated temperature and are complete after a few hours, although some, for example that between $Me_3SiPHBu^t$ and pentafluoropyridine, can be performed at ambient temperature but require longer times (days) to reach completion [41]. Phosphines with more than one polyfluoroaryl substituent have also been synthesized by this method; the pentafluoropyridylphosphines $R_xP(C_5F_4N\text{-}4)_{3-x}$ ($x = 0$, 1, R = Ph, Bu^t) were synthesized in high yields by the reaction between the trimethylsilylphosphines $R_xP(SiMe_3)_{3-x}$ and pentafluoropyridine [41].

2.3. Palladium-mediated phosphorus-carbon coupling

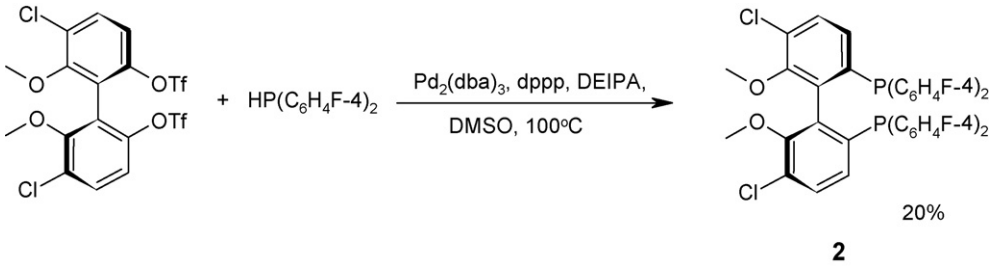
In contrast to the non-fluorinated analogues, the synthesis of the phosphinoimidazoline **1** cannot be carried out using a S_NAr reaction due to the low nucleophilicity of fluoroarylphosphides.



Scheme 4.



Scheme 5.



Scheme 6.

However, **1** was synthesized in 32% yield by a palladium-catalysed coupling reaction (Scheme 5) [62].

A similar palladium-catalysed coupling was used to prepare $HPBu^t(C_6H_4F\text{-}4)$ from $IC_6H_4F\text{-}4$ and $Me_3SiPHBu^t$ [91]. Palladium-catalysed substitution of triflate has also been used in the synthesis of the chiral diphosphine **2** (Scheme 6) [92].

2.4. Hydrophosphination

$Ph_2PCH_2CH_2P(C_6H_4F\text{-}3)_2$ and $Ph_2PCH_2CH_2P(C_6H_4F\text{-}4)_2$ were prepared in 78% and 73% yields, respectively, by base catalyzed addition of $(ArF)_2PH$ across the vinyl bond of $Ph_2PCH{=}CH_2$ [71]. ($Ph_2PCH_2CH_2P(C_6H_4F\text{-}3)_2$ has also been synthesized by addition of $[C_6H_4F]^-$ to $Ph_2PCH_2CH_2PCl_2$ [49].)

2.5. Reduction of phopshorus(V)

Phosphine oxides ($R_3P{=}O$) are typically prepared by oxidation of the phosphine. However, they may also be prepared by the treatment of phosphoryl halides with fluoroaryl metal reagents in high yields, *e.g.* $Ph_2PO(C_6H_3F_2\text{-}2,4)$ [93]. The reduction of phosphine oxides provides another route to fluoroarylphosphines. For example, the reduction of difluoroaryl-substituted secondary phosphine oxides by di-*iso*-butylaluminium hydride (DIBAL-H) has been accomplished in high yields: $HP(C_6H_2F_2\text{-}3,5\text{-}R\text{-}4)_2$ were prepared in 80% (R = H) and 90% (R = OMe) yield from $HPO(C_6H_2F_2\text{-}3,5\text{-}R\text{-}4)_2$ [60]. The synthesis of enantiopure (−)-bis(phosphino)-1,1′-binaphthyl **3** involved reduction of the dioxide, which was necessary for resolution (Scheme 7) [94].

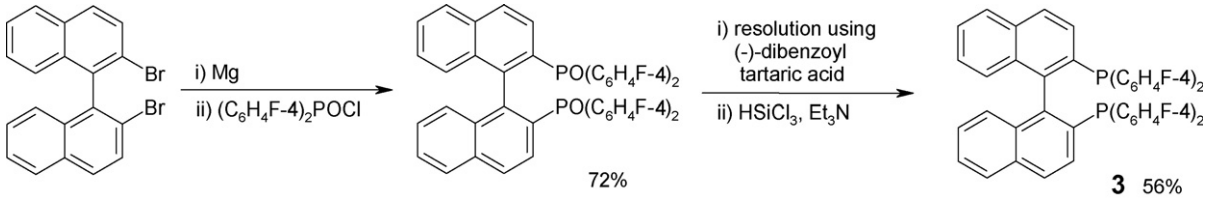
2.6. Functionalization

The susceptibility of fluoroarenes to nucleophilic attack [88] offers an attractive route to their functionalization. However, the susceptibility of the P–C(ArF) bond to cleavage by nucleophiles can be problematic to the synthesis of the desired product.

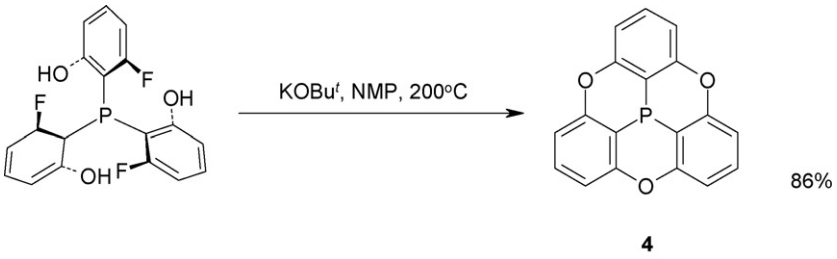
A number of phosphines have been prepared by treatment of pentafluorophenylphosphines with oxygen and nitrogen nucleophiles. $Ph_2P(C_6F_4Y\text{-}4)$ Y = OMe, NMeH [34] and $P(C_6F_4Y\text{-}4)_3$ Y = NH_2, NHPh, NMe_2, NEt_2, $NHNH_2$, $NHNMe_2$, NHNHPh, OMe [37] were obtained from $Ph_2P(C_6F_5)$ and $P(C_6F_5)_3$. The reaction between $P(C_6F_5)_3$ and $OP(NMe_2)_3$, yielding $P(C_6F_4NMe_2\text{-}4)_3$, was particularly rapid, reaching completion in 10 min. The reactions between $P(C_6F_5)_3$ and, respectively, $PhNH_2$, $PhNHNH_2$ and R_2NCOH were slower and the mono- and bis-substituted products were also observed. Of note is that treatment of the phosphine oxide $OPPh_2(C_6F_5)$ with $MeNH_2$ in benzene gave predominantly the *ortho*-substituted product $OPPh_2(C_6F_4NHMe\text{-}2)$, which is presumed to arise from a NH···O interaction [34]. Treatment of $P(C_6F_5)_3$ with thiolates lead to P–C bond cleavage [37]. Evidently the nature of the nucleophile is important in determining whether nucleophilic attack occurs at carbon or phosphorus.

The reaction between $P(C_6F_5)_3$ and C_6F_5Li yielded a mixture of $P(C_6F_5)_{3-x}(C_6F_4C_6F_5\text{-}4)_x$ (x = 1–3). The phosphines were not separated but identified by GC/MS analysis [95]. The reaction may occur by either or both of nucleophilic attack of C_6F_5Li on the carbon atoms *para* to phosphorus and nucleophilic attack at phosphorus by $C_6F_5C_6F_4Li\text{-}4$, the formation of which was evidenced by the production of $C_{6n}F_{4n}H_2$ (n = 2, 3) and $C_{6n}F_{4n+1}H$ (n = 1–4). The latter mechanism is supported by the observations that $P(C_6F_5)_{3-x}(C_6F_4C_6F_5\text{-}4)_x$ (x = 1–3) and similar polyfluorinated polyphenylphosphines, although expected as by-products, have not been isolated in more than small yields from the reaction between PX_3 and an excess of C_6F_5MgBr, the yields of $P(C_6F_5)_3$ being high, and that Grignard and lithium hydrocarbyls have been reported to cleave P–C(ArF) bonds [83,84].

5-Phenyl-octafluorodiphenzophosphole, $PhP(C_6F_4)_2$, underwent nucleophilic attack by dimethylamine and methoxide at



Scheme 7.



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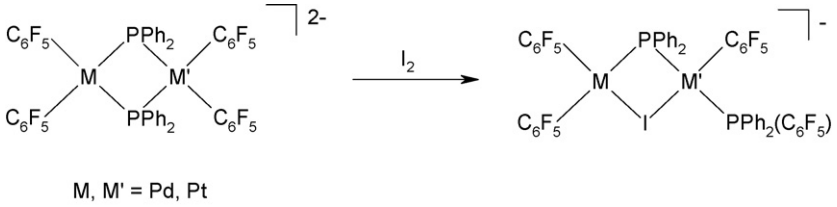
Scheme 8.



M, M' = Pd, Pt

Scheme 9.

the 3 position giving $PhP(C_6F_3Y\text{-}3)_2$ (Y = NMe_2, OMe) [81]. In contrast nucleophilic attack occurred at the 4-position of the phosphole oxide $PhPO(C_6F_4)_2$. Reduction of this product by trichlorosilane gave $PhP(C_6F_3NMe_2\text{-}4)_2$.

Nucleophilic substitution of fluorine can also be important for the synthesis of phosphines with non-fluorinated substituents, for example the preparation of **4** (Scheme 8) [96].

2.7. Other methods

Other reactions have produced fluoroarylphosphines, although these have been synthesized more conveniently and in higher yields by the routes described in the previous sections. For example, the phosphines $P(C_6F_5)_3$ and $P(C_6F_5)_2(C_6F_4C_6F_5\text{-}4)$ were detected in the reaction between PPh_3 and C_6F_5Li prepared from C_6F_5H and n-BuLi, although not in the reaction between PPh_3 and C_6F_5Li prepared from C_6F_5Br and n-BuLi [95]. The diphosphine $P(C_6F_4)_3P$ was first prepared in 15% yield by heating red phosphorus and 1,2-diiodotetrafluorobenzene in a sealed tube at 250 °C for 3 days [32], but has since been prepared by the reaction between $P(C_6F_4Li\text{-}2)_3$ and PCl_3 [28]. Coupling of coordinated diphenylphosphide and pentafluorophenyl ligands has been observed on oxidation of platinum and palladium complexes, as in Scheme 9 [97].

3. Ligand parameters

When considering ligand properties, the most important effects of fluorination of arylphosphines are those that impact on the phosphorus atom, since in the overwhelming majority of complexes the phosphorus atom is coordinated to the metal. In only a very few examples, such as $[(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_6F_5)PPh_2]$ [7,8] and $[Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2]$ [98], are substituents bound to a metal whilst phosphorus is not. The two most obvious effects of fluorination are the lowering of phosphine basicity and the increase in bulk, although other factors, such as ligand flexibility and the bite angle for bidentate ligands, are also important. These factors are not independent and often display non-linear relationships [99].

3.1. Electronic properties

Fluorine is strongly σ-withdrawing, but also acts as a π-donor. These properties are reflected in the Hammett constants σ_m and σ_p for the substituent in the *meta* and *para* positions, respectively, and the Swain-Lupton constants F and R, which are measures of the field and inductive effects, and resonance effects, respectively, [100]. These are given in Table 2 with those of other electron-withdrawing groups for comparison. The strongly σ-withdrawing nature is indicated by the value of F of 0.45 and the π-donor ability by the value of R of −0.39. As a consequence fluoroaryl substituents decrease the basicity of phosphines relative to their perprotio analogues. In general basicity decreases with the degree of fluorination, but since the electron-withdrawing effect of fluorine is much stronger when it occupies a *meta* position, for which resonance effects are minimal, than the *para* position; the pattern of fluorination is

Table 2
Hammett and modified Swain-Lupton constants [100]

	σ_m [a]	σ_p [a]	F [b]	R [b]
Fluorine	0.34	0.06	0.45	−0.39
Chlorine	0.37	0.23	0.42	−0.19
Bromine	0.39	0.23	0.45	−0.22
Trifluoromethyl	0.43	0.08	0.38	0.16
Pentafluorophenyl	0.32	0.03	0.27	0.00
Nitrile	0.56	0.66	0.51	0.15
Nitro	0.71	0.78	0.65	0.13

[a] σ_m and σ_p are the Hammett constants for the substituent in the *meta* and *para* positions, respectively.

[b] F and R are Swain-Lupton constants, which are measures of the field and inductive effects, and resonance effects, respectively.

Table 3
Electronic parameters of substituents [101]

Substituent	χ (cm^{-1})[a]	Substituent	χ (cm^{-1})[a]
Me	2.6	C_6H_4F-4	5.0
Et	1.8	C_6H_4F-3	6.0
Ph	4.3	C_6F_5	11.2

[a] ν(C≡O) for $(R^1R^2R^3P)Ni(CO)_3 = 2056.1 + \chi(R^1) + \chi(R^2) + \chi(R^3)$ cm^{-1}.

Table 4
Cone angles [101,102]

Phosphine	Cone angle (°)	Phosphine	Cone angle (°)
PH_3	87	$MePPh(C_6F_5)$	149
PMe_3	118	$PPh_2(C_6F_5)$	158
PEt_3	132	$MeP(C_6F_5)_2$	162
PPh_3	145	$EtP(C_6F_5)_2$	167
$H_2P(C_6F_5)$	119	$PPh(C_6F_5)_2$	171
$Me_2P(C_6F_5)$	140	$P(C_6F_5)_3$	184
$Et_2P(C_6F_5)$	148	$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$	151

also important. For example, $P(C_6H_4F\text{-}3)_3$ is less basic than $P(C_6H_4F\text{-}4)_3$ (Table 3).

The effect of fluorination is manifested in the IR spectroscopic properties of complexes containing one or more carbonyl ligands (see Section 4.3). The value of ν(C≡O) for $LNi(CO)_3$ has been used to obtain an electronic parameter χ for substituents (Table 3) [101]. Lowering the basicity of the phosphine leads to less back-donation into the carbonyl π^* orbital and a higher value of ν(C≡O).

Although quantifying the electronic effects of phosphines from these data is not always appropriate since other factors, such as complex geometry and steric factors, cannot be ignored, the data do provide an indication of the effect of fluorination on phosphines and their complexes. More sophisticated ligand parameters, typically derived from X-ray structural data, kinetic data and equilibrium constants as well as infrared spectroscopic studies of carbonyl complexes, have been proposed as a means to quantify the electronic effects of ligands on the properties of complexes [102].

3.2. Steric properties

The fluorine atom is larger than the hydrogen atom (covalent radii 0.68 Å *versus* 0.32 Å [103], van der Waals' radii 1.47 Å *versus* 1.20 Å [104]) and aryl C–F bonds are longer than analogous C–H bonds (1.34 Å *versus* 1.08 Å [105]). As a consequence C–F is isosteric with C–OH or C=O not C–H [106] and polyfluorinated organic molecules are much bulkier than their perprotio analogues. The increased bulk leads to increased steric pressure when fluorine occupies the *ortho* positions of the aryl substituents of phosphines. The concept of cone angle, θ, which is determined from structural data determined by single-crystal X-ray diffraction, is an attempt to quantify this [101], and, although simplistic, it is generally accepted as a guide to the steric impact of phosphine ligands. Table 4 presents the cone angles of some important fluoroarylphosphines and other phosphines for comparison.

3.3. Other properties

The high electronegativity of fluorine polarizes the C–F bond such that the fluorine is negatively charged, whereas the C–H bond is polarized conversely. Therefore, in salts of cationic complexes of fluoroarylphosphines the anions are expected to be closer to the non-fluorinated ligands, with which an attractive interaction is expected. This has been found in the solid state structures of the salts $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]BF_4$ [107] and $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)(dfppe)]PF_4$ [108] (dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$). In addition to the difference in polarity, C–F bonds are stronger than analogous C–H bonds (D°_{298}: C_6H_5–F 525 ± 8.4 kJ mol^{-1} *versus* C_6H_5–H 472 ± 2.2 kJ mol^{-1} [109]). As a consequence fluoroaryl substituents have to date been found to be inert to the reactions that occur with other phosphine aryl substituents, with the notable exception of nucleophilic attack (see Sections 2.4 and 5.1). The P–C(ArF) bond, unlike the P–C(Ar) bond, is susceptible to nucleophilic displacement (see Section 2.1) [83,84].

4. Effects on transition metal complexes

The effect of fluorination of arylphosphines may have dramatic consequences for a variety of properties of their metal complexes, such as coordination number, Lewis acidity, geometry, reactivity and catalytic properties. This section will briefly highlight complex stability, reactivity and IR spectroscopic properties to illustrate the range of effects that can arise from fluorination. Effects on catalytic properties and stoichiometric reactions are discussed in more detail in Sections 6 and 7.

4.1. Complex stability

The lower basicity of fluoroarylphosphines compared with perprotio analogues is expected to lead to weaker M–P bonds. This has been confirmed for rhodium(I) complexes in an investigation of substitution enthalpies, determined by calorimetry of the reaction between $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and phosphines of similar cone angles, which show a dependence on electronic properties: $P(C_6H_4CF_3\text{-}4)_3$ (−183.4(0.9) kJ mol^{-1}) > $P(C_6H_4F\text{-}4)_3$ (−209.8(1.3) kJ mol^{-1}) > PPh_3 (−216.5(1.3) kJ mol^{-1}) > $P(C_6H_4Me\text{-}4)_3$ (−234.9(0.9) kJ mol^{-1}) [110]. The greater bulk of fluoroarylphosphines is also expected to affect adversely complex stability by increasing steric congestion, and in some cases can prevent complex formation, for example $[(\eta^5\text{-}C_5Me_5)RhCl_2\{PPh_{3-x}(ArF)_x\}]$, ArF = C_6F_5, $C_6H_3F_2$-2,6, have been prepared for $x = 0$ and 1, but the attempted syntheses of the complexes with $x = 2$ and 3 were unsuccessful [57,111]. The combination of electronic and steric properties typically renders fluoroarylphosphines, especially those that are highly fluorinated and possess large cone angles, poorer and more labile ligands than their perprotio analogues. This has been demonstrated by a study of displacement reactions of rhodium, palladium and

platinum complexes which revealed that ligand lability decreased in the order $Me_2S > P(C_6F_5)_3 > PhP(C_6F_5)_2 > P(C_6H_3F_2\text{-}2,6)_3 >$ cycloocta-1,5-diene $> Ph_2P(C_6F_5) > PPh_3$ [58]. Lability is significantly lower for chelating fluoroarylphosphines, even those with large cone angles and that are highly fluorinated, such as dfppe [19].

4.2. Reactivity

It is expected that the greater bulk and lower basicity of fluoroarylphosphines compared with their perprotio analogues affects the reactivity of their complexes. Although in the majority of cases this is a small change of rate and selectivity, in some cases, especially those involving the bulkiest and most electron-poor phosphines, the effects are dramatic leading to starkly contrasting reactivity. Reactions may be turned on or off by fluorination, as illustrated by the following examples (see also Sections 5 and 6). Thermally induced reductive elimination of biphenyl from $[Pt(Ar)_2(dfppe)]$ occurs readily, but has not been reported from $[Pt(C_6H_5)_2(dppe)]$ [112]. (The syntheses of some $[Pt(Ar)_2(dppe)]$ complexes are performed at elevated temperature [113].) The reaction between singlet oxygen and Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, leads to both quenching to give triplet oxygen and oxidative addition to form a peroxo complex at a much faster rate than with triplet oxygen [114]. In contrast *trans*-$[IrCl(CO)\{P(C_6F_5)_3\}_2]$ neither undergoes oxidative addition nor quenches singlet oxygen. It is likely that this lack of reactivity arises from the electron-poor phosphine increasing the electrophilic nature of the iridium and stabilizing the lower oxidation state, thereby disfavouring oxidative addition, and the steric congestion around iridium. Treatment of the coordinatively unsaturated rhodium(III) complex $[Rh(C_6H_5)Cl_2(PPh_3)_2]$ with dppe led to the displacement of one phosphine ligand and formation of the six-coordinate rhodium(III) complex $[Rh(C_6H_5)Cl_2(PPh_3)(dppe)]$ [115], whereas treatment with dfppe led to reductive elimination of chlorobenzene and formation of the four-coordinate rhodium(I) complex $[RhCl(PPh_3)(dfppe)]$ [20]. The difference in reactivity is presumed to arise from the greater bulk of dfppe favouring the lower coordination number and the electron-poor character which favours the lower oxidation state.

4.3. IR spectroscopic properties

IR spectral data of a complex can give valuable information regarding the electronic character of the metal centre. Particularly useful are those functional groups that give strong bands outside regions of C–H stretching and bending vibrations and whose frequencies are susceptible to subtle changes in electronic character. For those groups with multiple-bonding and low-lying π^* orbitals, such as carbonyl and isonitrile, an electron-rich metal will give more π back-donation than an electron-poor metal, and the multiple bond will be weakened more and the frequency of its stretching vibration will be reduced more. Therefore, for analogous complexes the stretching frequencies can be related to the Lewis acidity of the metal centre, with frequency increasing with Lewis acidity. For example, in a study of $[PtCl(C{\equiv}NC_6H_3Me_2\text{-}2,6)(R_2PCH_2CH_2PR_2)]BF_4$ the values of $\nu(C{\equiv}N)$ confirmed Lewis acidity increased with the degree of fluorination: R = Ph 2207 cm^{-1}, $C_6H_3F_2$-2,4 2211 cm^{-1}, $C_6H_2F_3$-2,4,5 2213 cm^{-1}, C_6HF_4-2,3,4,5 2215 cm^{-1}, C_6F_5 2221 cm^{-1} [29]. A more useful indicator of metal electronic character is $\nu(C{\equiv}O)$, since this shows a greater range of frequency and the carbonyl ligand is a common spectator ligand in organometallic chemistry. The values of $\nu(C{\equiv}O)$ for a range of *trans*-[RhCl(CO)(phosphine)$_2$] (Table 5) reveal the effect of fluorination on the electronic character of the metal. However, steric factors also affect $\nu(C{\equiv}O)$ [102], and valid comparisons can be made only between complexes of ligands of similar cone angle. Similar variations of $\nu(C{\equiv}O)$ are observed for *trans*-[IrCl(CO)(phosphine)$_2$] and many other transition metal complexes.

The effect of fluorination of diphosphines is evident from $\nu(C{\equiv}O)$ of complexes such as [Mo(CO)$_4$(diphosphine)]. $[Mo(CO)_4(dppe)]$ exhibits the two A_1, B_1 and B_2 bands at 2020, 1919, 1907 and 1881 cm^{-1} [121], $[Mo(CO)_4\{(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2\}]$ at 2030, 1945, 1924 and 1885 cm^{-1} [57], and $[Mo(CO)_4(dfppe)]$ at 2041, 1965, 1935 and 1912 cm^{-1} [122].

Table 5
$\nu(C{\equiv}O)$ of *trans*-[RhCl(CO)(phosphine)$_2$]

	$\nu(C{\equiv}O)$ (cm^{-1})		$\nu(C{\equiv}O)$ (cm^{-1})
Cone angle ≈ 145°		Cone angle ≈ 158°	
PPh_3 [116]	1961	$[(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_6F_5)PPh_2]$ [8]	1955
$PPh_2(C_6H_4Bu^t\text{-}4)$ [117]	1964	$PPh_2(C_6H_3F_2\text{-}2,6)$ [57]	1967
$PPh(C_6H_4Bu^t\text{-}4)_2$ [117]	1964	$PPh_2(C_6F_5)$ [20]	1982
$PPh_2(C_5H_4N\text{-}2)$ [118]	1969	$PPh_2(C_6F_4C{\equiv}N\text{-}4)$ [120]	1987
$P(C_6H_4SO_3Na\text{-}3)_3$ [119]	1973	$PPh_2(C_5F_4N\text{-}4)$ [42]	1993
$P(C_6H_4F\text{-}4)_3$ [110]	1982	$P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ [47]	2000
$P(C_6H_4Cl\text{-}4)_3$ [110]	1984	Cone angle ≈ 171°	
$P(C_6H_4CF_3\text{-}4)_3$ [110]	1990	$PPh(C_6H_3F_2\text{-}2,6)_2$ [57]	1961
		$PPh(C_6F_5)_2$ [20]	2002
		Cone angle ≈ 184°	
		$P(C_6H_3F_2\text{-}2,6)_3$ [57]	1965
		$P(C_6F_5)_3$ [20]	2008

4.4. M···F–C interactions

Although intramolecular M···F–C interactions have been observed in complexes of ligands other than phosphines, for example $[IrH_2(PPh_3)_2(8\text{-fluoroquinoline})]SbF_6$ [123], and many M···X interactions with the other halogens have been reported, M···F–C interactions strong enough to be observed in solution are unknown for fluoroarylphosphine complexes. For example, multinuclear NMR spectroscopic studies revealed that $[(\eta^5\text{-}C_5H_5)Ru(CO)\{PPh_2(C_6H_4X\text{-}2)\}]^+$ (X = Cl, Br), formed by silver(I)-mediated chloride abstraction from $[(\eta^5\text{-}C_5H_5)RuCl(CO)\{PPh_2(C_6H_4X\text{-}2)\}]$, possessed an intramolecular Ru···X interaction, whereas no Ru···F interaction was observed on chloride abstraction from $[(\eta^5\text{-}C_5H_5)RuCl(CO)\{PPh_2(C_6H_4F\text{-}2)\}]$ [124]. These observations were supported by calculations that revealed that there is no stabilization gained by a Ru···F interaction in the cation $[(\eta^5\text{-}C_5H_5)Ru(CO)\{PPh_2(C_6H_4F\text{-}2)\}]^+$, although considerable stabilization arose for the chloride and bromide analogues [125]. Similarly Ir···Cl and Ir···Br interactions, but not an Ir···F interaction, are found in $[(COD)Ir\{PPh_2(C_6H_4X\text{-}2)\}]^+$ (COD = η^2,η'^2-cycloocta-1,5-diene) [126]. Short M···F–C distances can be present in solid state structures, for example that of *trans*-$[IrBr(CO)\{P(C_6F_5)_3\}_2]$ includes two Ir···F distances of 3.13 and 3.16 Å, which are slightly shorter than the sum of the van der Waals' radii, 3.25 Å [127], however it is more likely that these arise from geometric constraints and steric congestion than from attraction between the metal and the fluorine atom.

5. Reactions of coordinated fluoroarylphosphines

5.1. Reactions involving C–F bond cleavage

Fluoroarylphosphines are susceptible to nucleophilic attack [88], with substitution of the *para*-fluorine atoms observed in most cases. The susceptibility of polyfluoroaryl substituents to nucleophilic attack can be enhanced by coordination to metals, especially in cases where the resulting complex is cationic [128].

5.1.1. Intermolecular C–F bond cleavage

Reports of intermolecular nucleophilic attack at coordinated polyfluoroarylphosphines are rare. The nucleophilic substitution of fluoride by methoxide and thiomethoxide at the *para* positions of coordinated tris(pentafluorophenyl)phosphine of a cationic rhenium complex was accomplished at low temperatures with high and moderate yields, respectively, (Scheme 10) [129].

5.1.2. Intramolecular C–F bond cleavage

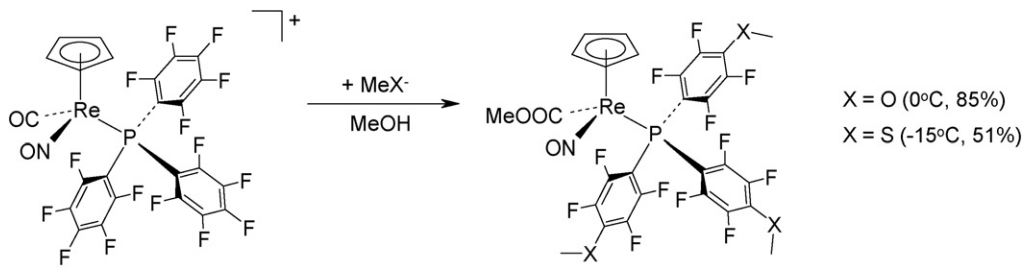
Reports of intramolecular nucleophilic attack at coordinated polyfluoroarylphosphines are more common than the intermolecular reactions.

Treatment of *trans*-$[PtMe(THF)\{PPh_2(C_6F_5)\}_2]X$ (**5**) with aqueous KOH rapidly afforded the metallacyclic complex $[PtMe(\kappa P,\kappa O\text{-}Ph_2PC_6F_4O\text{-}2)\{PPh_2(C_6F_5)\}]$, the identity of which was confirmed by a structure determination by single-crystal X-ray diffraction, in 68% yield [130,131]. A similar reaction was observed with $NaNH_2$ [131]. All four *ortho* fluorine atoms were substituted by treatment of the salt **5** (X = ClO_4^- or $CF_3SO_3^-$) with five equivalents of NaOMe. The reaction was rapid and afforded *trans*-$[Pt(OMe)Me(PPh_2\{C_6F_3(OMe)_2\text{-}2,6\})_2]$ in quantitative yield. Although the intramolecular nature of the reaction was not confirmed *ortho* substitution strongly suggests an intramolecular nucleophilic reaction for which the mechanism depicted in Scheme 11 has been proposed [131].

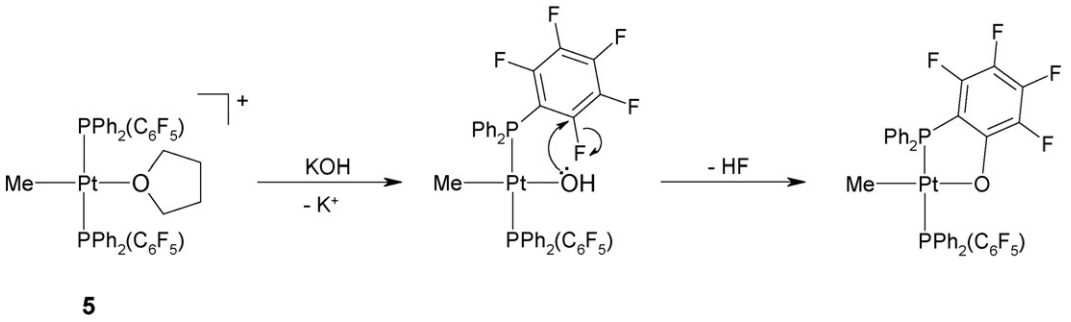
Nucleophilic substitution of *ortho* fluorine atoms of $PPh(C_6F_5)_2$ and $PPh_2(C_6F_5)$ coordinated to platinum by thiolate has also been reported [132]. Reaction of *trans*-$[PtCl_2\{PPh_x(C_6F_5)_{3-x}\}_2]$ ($x = 1, 2$) with $Pb(SC_6F_4H\text{-}4)_2$ in acetone at ambient temperature yielded a mixture of *cis* and *trans* isomers of $[Pt(SC_6F_4H\text{-}4)_2\{PPh_x(C_6F_5)_{3-x}\}_2]$, the bimetallic complexes $[Pt(SC_6F_4H\text{-}4)(\mu\text{-}SC_6F_4H\text{-}4)\{PPh_x(C_6F_5)_{3-x}\}]_2$ and the complexes $[Pt(SC_6F_4H\text{-}4)_2\{\kappa P,\kappa S\text{-}Ph_xP(C_6F_5)_{2-x}(C_6F_4\text{-}2\text{-}SC_6F_4H\text{-}4)\}]$, which were structurally characterized by single-crystal X-ray diffraction. The mechanism of the reaction was not determined, but, as with the previous reactions, the position of the substitution strongly suggests intramolecular nucleophilic attack by a coordinated thiolate.

The intramolecular nucleophilic substitution of *ortho* fluorine atoms of polyfluoroarylphosphines in cationic complexes has been used to link the phosphines to η^5-cyclopentadienyl, η^6-arene, imidazolidin-2-ylidene and primary phosphine ligands. This method generates complexes of chelating multidentate ligands which are difficult to prepare by other routes, and because the reactions are intramolecular, they are typically rapid, high yielding and highly regioselective.

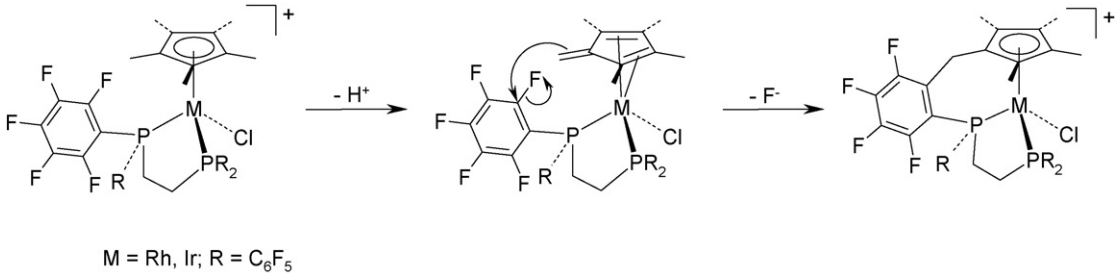
The rhodium and iridium complexes of a chelating trifunctional $\eta^5,\kappa P,\kappa P$-cyclopentadienyl-diphosphine ligand, $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_3[CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)CH_2]_2\text{-}1,3\}MCl]^+$, M



Scheme 10.



Scheme 11.

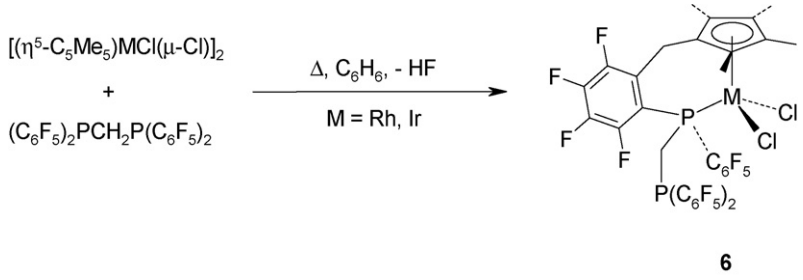


Scheme 12.

= Rh and Ir, were synthesized in almost quantitative yield by heating a solution of $[(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)]_2$ and dfppe [107]. It was found that the coupling occurred in a stepwise fashion via the intermediates $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+$ and the singly-linked complex $[(\eta^5\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P\text{-}(C_6F_5)_2\}RhCl]^+$. Subsequently it was found that the same products were obtained rapidly at ambient temperature by addition of a strong, non-nucleophilic base, such as 1,8-bis(dimethylamino)naphthalene (Proton Sponge), to $[(\eta^5\text{-}C_5Me_5)MCl(dfppe)]BF_4$ [6]. On the basis of this and similar observations [133], it was proposed that the reaction occurs by loss of a proton from the η^5-pentamethylcyclopentadienyl forming an η^4-fulvene ligand, the nucleophilic methylene carbon of which attacks an *ortho* carbon atom of the dfppe ligand (Scheme 12). Less than the stoichiometric amount of base is required, presumably because the fluoride by-product is sufficiently basic to facilitate the reaction.

This reaction provides a convenient access to rhodium and iridium complexes of trifunctional $\eta^5,\kappa P,\kappa L$-cyclopentadienyl-phosphine ligands, and a range of complexes has been prepared in high yield using this method [6,21,42,84,111,134]. The same method has been used to link the η^5-cyclopentadienyl ligand and monodentate phosphines of $[(\eta^5\text{-}C_5Me_5)MCl\{R_2P(C_6F_5)\}(CNR')]^+$, affording $[(\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_4PR_2)MCl(CNR')]^+$, but the yields were lower, reaction times were longer and more by-products were formed [6,84]. The complexes **6**, M = Rh and Ir, in which one phosphine moiety of the trifunctional ligand is not coordinated to the metal, were also formed by this method. (Scheme 13) [17,18]. NMR spectroscopic data suggest that the reaction proceeds via the intermediates $[(\eta^5\text{-}C_5Me_5)MCl\{\kappa P,\kappa P\text{-}(C_6F_5)_2PCH_2P(C_6F_5)_2\}]^+$ and that geometric changes that occur on coupling force dissociation of the $P(C_6F_5)_2$ moiety.

η^6-Arene complexes of ruthenium have also been found to undergo similar dehydrofluorinative couplings. Treatment of $[(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)RuCl\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}]BF_4$ with proton sponge gave $[\{\eta^6,\kappa P,\kappa P\text{-}C_6H_3Me\text{-}5\text{-}[CH_2\text{-}C_6F_4P\text{-}(C_6F_5)CH_2]_2\text{-}1,3\}RuCl]BF_4$ in 87% yield via $[\{\eta^6,\kappa P,\kappa P\text{-}C_6H_3Me_2\text{-}3,5\text{-}CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RuCl]BF_4$ [135]. In contrast to the reactions of η^5-pentamethylcyclopentadienyl rhodium and iridium complexes, the reaction required the stoichiometric quantity of base, and the product could not be



Scheme 13.

formed by heating $[(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)RuCl(\mu\text{-}Cl)]_2$ and dfppe.

The linking of imidazolidin-2-ylidene and diphosphine ligands was achieved by treating salt **7** with two equivalents of $KOBu^t$ (Scheme 14). The product **8**, which contains a meridionally coordinated cyclic diphosphino-imidazolidin-2-ylidene ligand, was obtained in 91% yield [136].

The coupling of the phosphine ligands of $[(\eta^5\text{-}C_5H_5)Fe\{\kappa P,\kappa P\text{-}(C_6H_4F\text{-}2)_2PCH_2CH_2P(C_6H_4F\text{-}2)_2\}(PH_2Ph)]PF_6$ (**9**) was achieved by addition of base (Scheme 15) [68]. Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)]PF_6$ in the presence of $(C_6H_4F\text{-}2)_2PCH_2CH_2P(C_6H_4F\text{-}2)_2$ in acetonitrile, followed by treatment with $PhPH_2$ at elevated temperature gave the salt **9**, which on treatment with two equivalents of $KOBu^t$ in THF gave salt **10** in an overall yield of 75% (with respect to $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)]PF_6$). The reaction is postulated to occur by deprotonation of the primary phosphine ligand giving a phosphide, which attacks a fluorinated carbon atom forming a P–C bond. The process is repeated to generate the triphosphacyclononane.

5.2. Reactions involving P–C bond cleavage

In contrast to the cleavage of P–C bonds of non-fluorinated phosphines [137], there are only three reports of the transition metal mediated cleavage of P–C(ArF) bonds. Treatment of $Pd_2(dba)_3$ (dba = dibenzylideneacetone, $(PhCH{=}CH)_2CO$) with an equimolar quantity of dfppe in THF produced a mixture of $[Pd(dba)_2]$, [Pd(dfppe)(THF)] and [Pd(dba)(dfppe)], which on prolonged heating yielded the phosphine-phosphide complex $[Pd(C_6F_5)\{\mu\text{-}(C_6F_5)PCH_2CH_2P(C_6F_5)_2\}]_2$ [138]. The complex *trans*-$Ir(C_6F_5)(CO)\{PPh_2(C_6F_5)\}_2$, which was structurally characterized by single-crystal X-ray diffraction, was formed from *mer*-$[IrF_3(CO)\{PPh_2(C_6F_5)\}_2]$ on standing in CD_2Cl_2 for several weeks [139]. The reaction between $[Os_3H(CO)_{11}]^-$ with $(C_6F_5)_2PH$ resulted in the formation of $[Os_3(\mu\text{-}H)\{\mu\text{-}PH(C_6F_5)\}(CO)_{10}]$ [140].

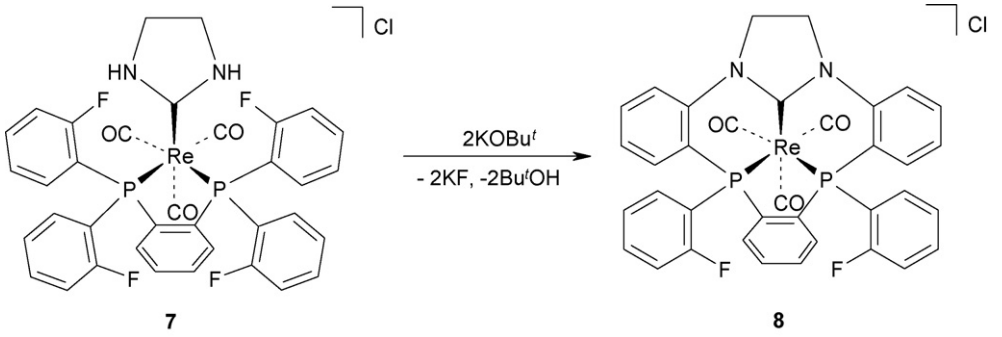
5.3. Orthometallation

Although orthometallation involving cleavage of a C–F bond of a polyfluoroaryl-substituent has been reported for ligands such as imine [141] and azine [142], it is yet to be observed for phosphines. However, orthometallation of $R_2P(C_6F_4Br\text{-}2)$ with oxidative addition of the C–Br bond across rhodium or iridium or two metal atoms has been reported. A number of complexes of $\kappa P,\kappa C\text{-}R_2P(C_6F_4\text{-}2)$ have been prepared by this reaction [143], for example that in Scheme 16 [144].

The reactions are similar to those that occur with non-fluorinated analogue, $Ph_2P(C_6H_4Cl\text{-}2)$ [145].

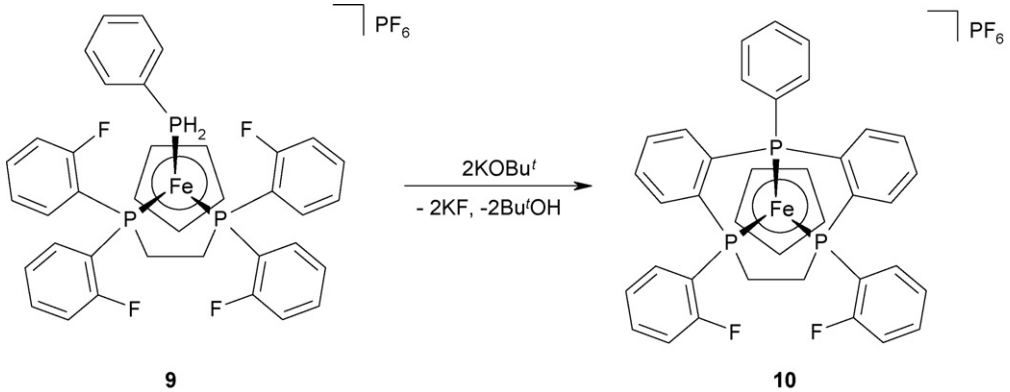
6. Fluoroarylphosphines as ligands for catalysis

The electronic and steric properties of fluoroarylphosphines (see Section 3) impact on the chemical properties of metal complexes (see Section 4) and consequently it is expected that these will effect their catalytic properties. For



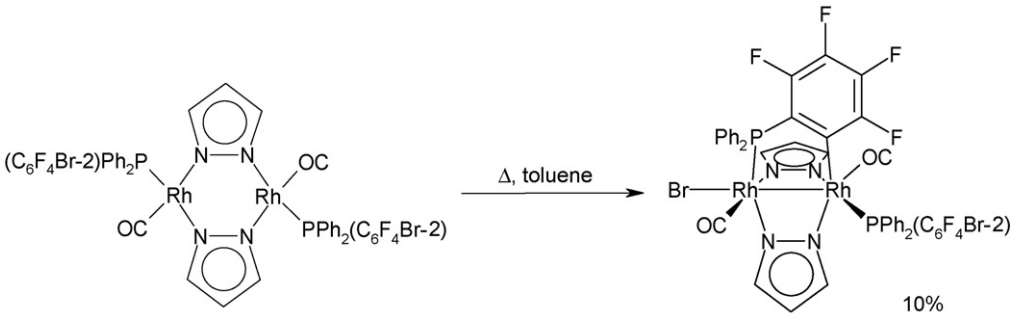
7 **8**

Scheme 14.



9 **10**

Scheme 15.



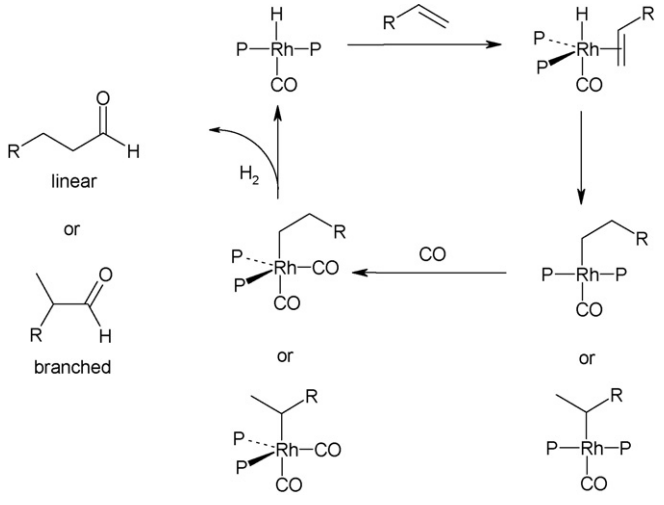
Scheme 16.

example, fluoroarylphosphines stabilize lower oxidation states which may be beneficial for reductive elimination reactions, and enhance metal Lewis acidity which is advantageous for catalytic activity in reactions such as Baeyer-Villiger oxidation. The greater bulk of fluoroarylphosphines may enhance catalytic activity by favouring lower coordination numbers and is also expected to be important to selectivity. The increased lability of the highly fluorinated phosphines may also have some important consequences, although these are likely to be detrimental since catalyst decomposition is a likely outcome. Fluoroarylphosphines are inert to most reactions, nucleophilic attack being a notable exception, and can be used in conditions where electron-withdrawing aryl substituents such as nitrile and nitro undergo reactions. As well as the potential to provide highly active and selective catalysts, fluoroaryl phosphines can be used as a tool for observing how changes in electronic or steric bulk affect the activity and selectivity of a catalytic system. This is especially important since the mechanisms of catalysis of many reactions are not fully understood. It is only over the past decade that there has been much interest in the effects of fluorination on the catalytic properties of metal phosphine complexes. Although in most of the studies a systematic variation of the degree and pattern of fluorination has not been performed, it is evident that for some reactions fluorination has a positive effect on activity or selectivity and can provide the best catalyst.

6.1. Hydroformylation

Rhodium-catalysed hydroformylation is industrially important for the production of desirable linear aldehydes from terminal alkenes. A simplified depiction of the commonly accepted mechanism is shown in Scheme 17. It has been found that the rate is inversely related to phosphine basicity, which is ascribed to lower phosphine basicity giving weaker Rh–CO bonds due to less Rh–CO back-donation, which facilitates CO dissociation [146]. For this reason, fluoroarylphosphines are expected to provide catalysts with good activity. The electronic nature of the phosphines has also been found to exert an influence on selectivity. When both phosphine ligands occupied equatorial positions less basic phosphines favoured formation of the linear product, but when one was axial and other equatorial the selectivity for linear products decreased [146]. The position of the phosphine ligands can be controlled by the use of a chelating diphosphine with an appropriate bite angle. It is also expected that steric properties of fluoroarylphosphines would affect selectivity.

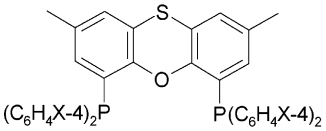
An early study on the hydroformylation of 1-hexene at 70 °C and 1.38 MPa catalysed by $[RhH(CO)_2\{P(C_6H_4X\text{-}4)_3\}_2]$ reported that rate and selectivity decreased in the order X: $CF_3 > Cl > F > H > OMe > NMe_2$ [147]. $[RhH(CO)_2\{P(C_6H_4F\text{-}4)_3\}_2]$ gave a selectivity for the linear product (78%) identical to that of $[RhH(CO)_2(PPh_3)_2]$. A subsequent study investigated the effect of electron-withdrawing phosphine substituents on the hydroformylation of acrolein acetal at 100 °C and 1 MPa using catalysts formed *in situ* from $[Rh(CO)_2(acac)]$ (acac = $[MeCOCHCOMe]^-$) and a large excess of monophosphine [60]. The selectivity displayed an almost linear relationship to $\Sigma\sigma$, the sum of the Hammett constants for the phosphine, ranging from 57% with $P(C_6H_4Me\text{-}3)_3$ to 85% with $P(C_6H_3F_2\text{-}3,5)_3$. However, activity did not show a simple relationship to electronic properties. Under the conditions of the experiment, after 4 h $P(C_6H_3F_2\text{-}3,5)_3$, $P(C_6H_3F_2\text{-}3,4)_3$ and PPh_3 gave conversions of only 33%, 23% and 24% respectively, whereas $P(C_6H_4F\text{-}3)_3$ gave a conversion of 73%. *Ortho*-substituted phenylphosphines gave very low conversions, which was ascribed to



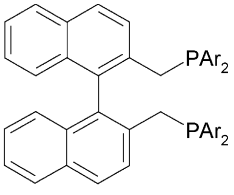
Scheme 17.

steric congestion destabilizing the catalysts, although triaryl phosphines bearing fluorine in the *ortho* positions were not tested. In another study, the activity and selectivity of catalysts containing $P(C_6F_5)_3$, $P(C_6H_2F_3\text{-}3,4,5)_3$, $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$, $P(C_6H_4CF_3\text{-}2)_3$, PPh_3 and $P(OPh)_3$ were compared for the hydroformylation of 1-hexene at 60 °C and 20 bar [47]. The activities of the catalysts with the bulkiest phosphines, $P(C_6F_5)_3$ and $P(C_6H_4CF_3\text{-}2)_3$, were very low, possibly due to incomplete coordination of these poor ligands, whereas the activities, and selectivities, of the catalysts containing $P(C_6H_2F_3\text{-}3,4,5)_3$ and $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ were similar to those of the catalyst containing PPh_3 (linear: branched ratios of 2.5:1, 3:1 and 2.9:1, respectively). The phosphite gave the most active catalyst, which gave a similar selectivity (linear: branched 2.6:1). The catalyst containing $P(C_6H_2F_3\text{-}3,4,5)_3$ was also assessed for the hydroformylation of 4-methoxystyrene, but was found to be less active than catalysts containing $P\{C_6H_3(CF_3)_2\text{-}3,5\}_3$ and PPh_3.

A study of the effect of chelating ligands **11** (X = H, F, Cl, CF_3, Me, OMe, NMe_2) on the hydroformylation of styrene at 120 °C and 10 bar showed a general increase in both rate and selectivity for the linear aldehyde with decreasing phosphine basicity [80]. However, the activity of the ligand X = F was slightly lower than that with X = H and the selectivities were the same (56%). The effect of the substituents on the selectivity of the hydroformylation of 1-octene at 80 °C and 20 bar was minimal; all ligands gave *ca.* 92% linear product, but the rate increased with decreasing phosphine basicity, with the exception of the ligands X = F and Cl, which gave similar rates to X = Me, which was presumed to be due to incomplete catalyst formation or deactivation. The lack of a difference in selectivity between the ligands was a result of β-hydrogen elimination from the branched alkyl intermediate, the rate of which also increases with increasing electrophilicity of the rhodium. The product of β-hydrogen elimination is 2-octene, which is much less reactive to hydroformylation. The product of β-hydrogen elimination from the styrene analogue regenerates the substrate, and so β-hydrogen elimination has no effect on the selectivity of the hydroformylation of styrene.



11



12

Rhodium complexes of the diphosphines **12** (Ar = $C_6H_3(CF_3)_2$-3,5, $C_6H_3F_2$-3,5, $C_6H_2F_3$-3,4,5, $C_6H_3Me_2$-3,5) have been shown to catalyse the hydroformylation of internal alkenes, in particular 2-octene, to linear aldehydes with good selectivities at 120 °C and 10 bar [148]. The trends in activity follow that of the electron-withdrawing nature of the phosphine substituents, Ar = $C_6H_3(CF_3)_2$-3,5 > $C_6H_2F_3$-3,4,5 > $C_6H_3F_2$-3,5 > $C_6H_3Me_2$-3,5, but the selectivities for Ar = $C_6H_3F_2$-3,5 (93% linear) and $C_6H_2F_3$-3,4,5 (94% linear) were slightly higher than that for Ar = $C_6H_3(CF_3)_2$-3,5 (91% linear), all of which were higher than for Ar = $C_6H_3Me_2$-3,5 (78% linear).

A study comparing $[Rh(dfppe)(nbd)]BF_4$ and $[Rh(dppe)(nbd)]BF_4$ (nbd = norbornadiene) as pre-catalysts for the hydroformylation of vinylarenes, $H_2C{=}CHC_6H_4X$-4 (X = H, Me, Cl, NO_2), in benzene at 200 psi and 55 °C using 5 mol% of catalyst has been reported [149]. 100% conversion was obtained for all substrates with both catalysts after 24 h. The catalyst containing dfppe consistently gave better selectivity (>90%) for the branched aldehyde, and with $H_2C{=}CHC_6H_4NO_2$-4 gave exclusively branched product. In contrast, the catalyst containing dppe gave branched:linear ratios of 3.2:1 to 4:1 for X = H, Me and Cl and 24:1 for X = NO_2. It was argued that since the bulk of dfppe would favour a linear product, a powerful electronic effect is exerted.

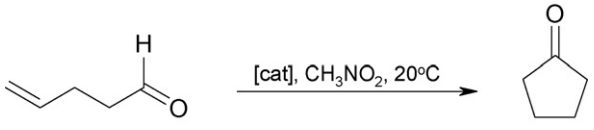
The catalytic activities of the trinuclear ruthenium(0) complexes $[(\mu_2\text{-dfppe})Ru_3(CO)_{10}]$ and $[(\mu_2\text{-dfppe})\{Ru(CO)_3\}_2Ru(dfppe)(CO)_2]$ towards hydroformylation of ethene and propene have been assessed [150]. $[(\mu_2\text{-dfppe})Ru_3(CO)_{10}]$ was found to be more active for ethene hydroformylation than the non-fluorinated analogues $[(\mu_2\text{-dppe})Ru_3(CO)_{10}]$ and $[\{\mu_2\text{-}(C_6H_{11})_2PCH_2P(C_6H_{11})_2\}Ru_3(CO)_{10}]$. The activity of $[(\mu_2\text{-dfppe})Ru_2(CO)_6Ru(dfppe)(CO)_2]$ was found to be much lower and similar to that of $Ru_3(CO)_{12}$. These five complexes showed similar activity for propene hydroformylation, but the complexes of the fluorinated ligands displayed almost no selectivity for linear over branched propionaldehyde.

6.2. Hydroacylation

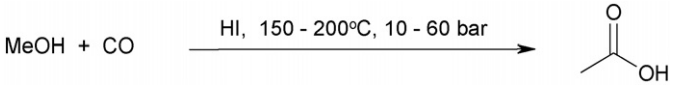
Dfppe has been used to confirm the hypothesis that decreasing the basicity of the chelate decreases the rate of the hydroacylation of pent-4-enal catalysed by $[(diphosphine)Rh(OCMe_2)_2]^+$ in nitromethane (Scheme 18) [151]. Although $[(dfppe)Rh]^+$, which was formed by addition of hydrogen to $[(dfppe)Rh(nbd)]ClO_4$, was found to be an active catalyst for the hydroacylation, it was considerably less active than $[\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}Rh]^+$ and $[(\mu\text{-dppe})_2Rh_2]^{2+}$. These species also catalysed the decarbonylation of pentenal under the same conditions. The ratio of rates of hydroacylation and decarbonylation were found to be the same for $[(dfppe)Rh]^+$ and $[(\mu\text{-dppe})_2Rh_2]^{2+}$, indicating the lower activity of the former for decarbonylation.

6.3. Methanol carbonylation

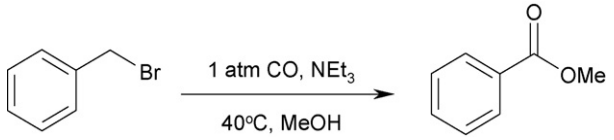
The synthesis of acetic acid by carbonylation of methanol (Scheme 19) is of immense industrial importance and carried



Scheme 18.



Scheme 19.



Scheme 21.

out on a scale of several million tonnes each year [152]. A number of rhodium complexes formed *in situ* from $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and analogues of dppe, including the fluorophenyl-substituted phosphines $Ph_2PCH_2CH_2P(ArF)_2$ (ArF = C_6H_4F-3, $C_6H_3F_2$-3,5 and $C_6H_3F_2$-3,4,5) and $(C_6H_4F\text{-}3)_2PCH_2CH_2P(C_6H_4F\text{-}3)_2$, have been assessed as catalysts for methanol carbonylation [49]. All showed good activity, although not approaching that of $[RhI_2(CO)_2]^-$, and the selectivity for acetic acid was >99%, with lower formation of propionic acid than with $[RhI_2(CO)_2]^-$. Catalysts formed by the unsymmetrical diphosphines were more active than those formed by the symmetrical diphosphines. The activity increased with increasing electron-withdrawing nature (fluorination) of the aryl substituents, reaching a maximum with $Ph_2PCH_2CH_2P(C_6H_3F_2\text{-}3,5)_2$, but then decreased as the electron-withdrawing nature increased. It was suggested that the maximum could derive from a balance between the σ-donor and π-acceptor abilities of the phosphines being necessary for optimum rate. Addition of the iodide-abstracting $[RuI_2(CO)_4]$, a promoter in the industrial *Cativa* process, to the catalyst formed by $Ph_2PCH_2CH_2P(C_6H_4F\text{-}3)_2$ more than doubled the rate, but led to the production of more propionic acid.

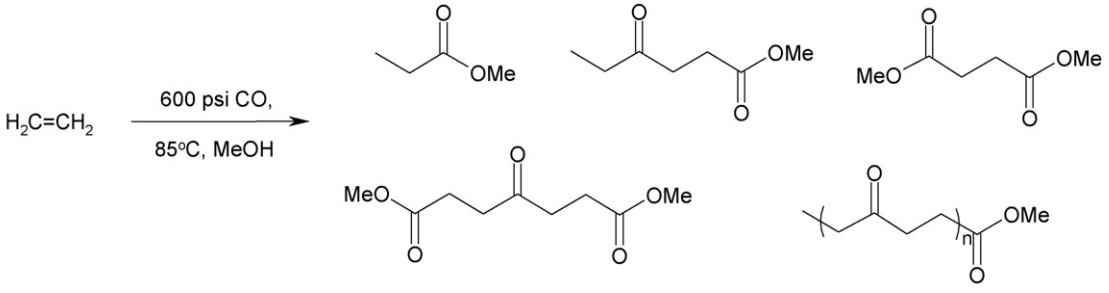
6.4. Methoxycarbonylation

Cationic palladium(II) complexes, especially those of 1,1′-bis(phosphino)ferrocene, $[Fe(\eta^5\text{-}C_5H_4PR_2)_2]$, have been found to be efficient catalysts for the methoxycarbonylation of alkenes (Scheme 20), with the product distribution highly dependent on the nature of the phosphine substituent R [153]. A comparative study showed that $[\kappa P,\kappa P\text{-}Fe(\eta^5\text{-}C_5H_4PR_2)_2Pd(NCMe)(OTf)]OTf$, R = Ph, C_6H_4OMe-2 and C_6H_4Me-2, were active catalysts, giving a mixture of methoxycarbonylated products (R = Ph), polyketone (R = C_6H_4OMe-2) and methyl propanoate [154]. In contrast $[\kappa P,\kappa P\text{-}Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2Pd(NCMe)(OTf)]OTf$ was almost inactive. This was ascribed to the destabilization of the palladium(II) cation due to the electron-withdrawing effect of the pentafluorophenyl groups, and reduction to inactive species under the reaction conditions ($E = -0.31$ V *cf.* R = C_6H_4OMe-2 −0.78 V).

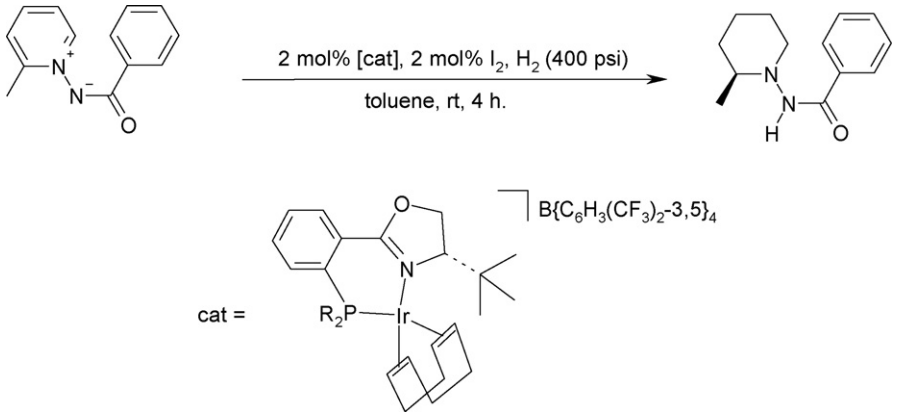
The catalysis of the methoxycarbonylation of benzyl bromide (Scheme 21) by bis{phosphorus(III)} palladium complexes has been studied [155]. Activity, as assessed by yield after 2 h, showed an inverse relationship to cone angle with the highest and lowest activities for the catalysts derived from trimethylphosphite and tricyclohexylphosphine, respectively. The catalyst derived from $P(C_6F_5)_3$ displayed the highest activity of any phosphine studied, equal to that derived from $P(OCH_2CF_3)_3$. The activities of catalysts formed by $Ph_2P(C_6F_5)$ and $PhP(C_6F_5)_2$ showed activities close to that of the catalyst formed by PPh_3. For the fluoroarylphosphines, electronic factors dominated over the steric factors; the active catalyst is a palladium(0) complex, the formation of which is favoured by electron-poor phosphines.

6.5. Alkene polymerization

The catalytic activity of group 10 metal complexes $[(R_2PCH_2CH_2PR_2)MCl_2]$ activated by methylaluminoxane towards the polymerization of 2-norbornene has been assessed [45]. The polymerization of alkenes catalysed by late transition metal complexes is often compromised by competition with β-hydride elimination [156], but this reaction is thermodynamically disfavoured for 2-norbornene. The palladium complexes $[(R_2PCH_2CH_2PR_2)PdCl_2]$, R = $C_6H_3F_2$-2,4 and C_6F_5, displayed much higher activity then the non-fluorinated complexes $[(dppe)PdCl_2]$ and $[(dppp)MCl_2]$ (M = Ni, Pd), but lower activity than $[\{(C_6H_3(CF_3)_2\text{-}3,5)_2PCH_2CH_2P(C_6H_3(CF_3)_2\text{-}3,5)_2\}PdCl_2]$. It was concluded that high activity was provided by electron-withdrawing phosphine substituents, but there was no clear relationship between the degree of fluorination and activity. It was presumed that steric factors are also important. β-Hydride elimination can be suppressed by the use of bulky chelating ligands [157], and it is suggested that suitably fluorinated bulky diphosphines may provide active



Scheme 20.



Scheme 22.

catalysts for the polymerization of alkenes for which β-hydride elimination is not inherently disfavoured.

6.6. Alkene/CO copolymerization

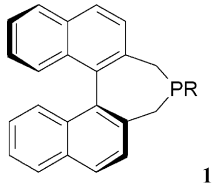
The catalytic activity of palladium complexes of fluorinated diphosphine ligands, $[(Ph_2PCH_2CH_2CH_2PR_2)Pd(NCMe)_2][BF_4]_2$, towards the copolymerization of propene and carbon monoxide [158] has been assessed by comparison with that of $[(dppp)Pd(NCMe)_2][BF_4]_2$ [43]. The activities of the complexes $[\{Ph_2PCH_2CH_2CH_2PR_2\}Pd(NCMe)_2][BF_4]_2$ followed the order R = $C_6H_4CF_3$-2 < R = $C_6H_2F_3$-2,4,6 < R = Ph < R = $C_6H_3Me_2$-3,5 < R = $C_6H_3F_2$-3,5 < R = $C_6H_3(CF_3)_2$-3,5. No conclusions were drawn regarding the effect of fluorination on activity, although the adverse effect of *ortho* substitution was ascribed to increased steric demand. The molecular weight of the product polyketone showed a similar variation with R as activity. The regio-regularity of the polyketone increased with the bulk of the substituents in the 3 and 5 positions. Those for R = $C_6H_4CF_3$-2 and $C_6H_2F_3$-2,4,6 were similar to that of R = $C_6H_3Me_2$-3,5.

6.7. Baeyer-Villiger oxidation

Homogeneous Baeyer-Villager oxidation catalysts act as Lewis acids which are postulated to undergo nucleophilic attack by the peroxidic oxidant [159]. The presence of electron-withdrawing phosphine substituents in the cationic platinum complexes $[Pt(\mu\text{-}OH)(R_2PCH_2CH_2PR_2)]_2^{2+}$ was expected to increase Lewis acidity and therefore catalytic activity [29]. This was confirmed by a study of the Baeyer-Villager oxidation of 2-methylcyclohexanone, which showed that activity followed the order: R = Ph < $C_6H_3F_2$-2,4 < $C_6H_2F_3$-2,4,5 < C_6HF_4-2,3,4,5 < C_6F_5. However, decomposition of the catalysts, yielding phosphine oxides, occurred, which severely limited their lifetimes and productivities.

6.8. Hydrogenation

Hydrogenation of *N*-iminopyridinium ylides catalysed by iridium complexes of phosphinooxazolines (Scheme 22) has been accomplished recently [160]. Of a range of catalysts, that with the ligand R = C_6H_4F-4 gave the best results for the substrate $PhCON(NC_5H_3Me\text{-}2)$, giving good selectivity for full hydrogenation of the pyridine ring and 90% ee. Although the ligands with R = Ph, $C_6H_4CF_3$-4 and C_6H_4OMe-4 showed similar activity, the selectivities were lower. The activity of the catalyst with R = C_6F_5 was much lower, but was higher than that with R = C_6H_4Me-2. The catalyst with R = C_6H_4F-4 gave good yields and moderate to good enantioselectivities (50–97% ee) for the hydrogenation of a range of *N*-benzoyliminopyridinium ylides.



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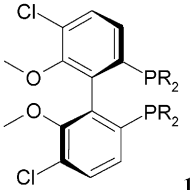

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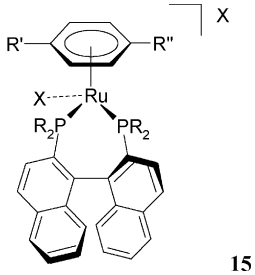

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Chiral monodentate binaphthophosphepines **13** have been assessed as ligands for the rhodium-catalysed hydrogenation of vinyl amides and esters [161] and the ruthenium catalysed hydrogenation of β-ketoesters [9]. Although catalysts generated *in situ* from $[Rh(COD)_2]BF_4$ and two equivalents of the binaphthophosphepines **13** R = C_6H_4F-2 and R = C_6H_4F-4 were active for the hydrogenation of $H_2C{=}C(NHAc)COOMe$, $PhCH{=}C(NHAc)COOMe$ and $H_2C{=}C(COOMe)CH_2COOMe$ under mild conditions, 25 °C and 1 atm H_2, the enantioselec-

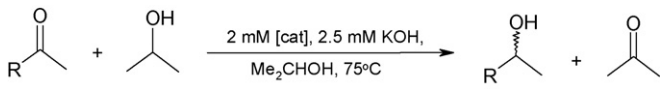
tivites were moderate in comparison to other aryl substituents such as R = $C_6H_3Bu^t_2$-3,5 (for the amides) and R = C_6H_4OMe-3 (for the diester) [161]. Of the range of catalysts tested, that generated *in situ* from [Ru(COD)(η^3-MeCHCHCH$_2$)$_2$] and two equivalents of the binaphthophosphepine R = C_6H_4F-4 gave the best enantioselectivity (95% ee *R*) and high activity for the hydrogenation of methyl acetoacetate at 120 °C in methanol at 60 bar [9]. It was found that substituents in only the *para* position, whether electron-releasing or electron-withdrawing, gave good enantioselectivities. The fluoroaryl substituents C_6F_5, C_6H_4F-2 and $C_6H_2F_3$-3,4,5 gave lower activity and selectivity. However, activity and enantioselectivity were highly substrate dependent; with $ClCH_2COCH_2COOMe$, **13** R = C_6H_4F-4 gave the *S* enantiomer in only 6% ee.

The effect of fluorination of the *para* positions of phenyl substituents of ligand **14** has been assessed in the hydrogenation of dimethyl itaconate catalysed by [Ru(O$_2$CCF$_3$)$_2$(**14**)] [92]. After 1 h at 22 °C under 1 bar of H_2, 70% conversion of 2 mmol of dimethyl itaconate was obtained using 0.02 mmol of catalyst (R = C_6H_4F-4) in 5 cm^3 of methanol. In comparison R = Ph, C_6H_3OMe-2,4 and xylyl gave 100% conversions. Good enantioselectivity was observed for these catalysts: 95% ee R = C_6H_4F-4 and xylyl, 92% R = Ph, C_6H_3OMe-2,4. At 50 °C the catalysts gave 100% conversion after 30 min with similarly high enantioselectivities.

The catalysis of the hydrogenation of a range of α- and β-functionalized ketones by ruthenium BINAP complexes **15**, including R = C_6H_4F-4, has been investigated [94]. The complex R = C_6H_4F-4, R′ = Me, R″ = CHMe, X = I showed good enantioselectivity and activity for the hydrogenation of methyl acetoacetate (97% ee), similar to the complex R = C_6H_4Me-4, R′ = Me, R″ = CHMe. However, the activity and selectivity were substrate dependent, and although the complex R = C_6H_4F-4, R′ = Me, R″ = CHMe, X = I gave good enantioselectivity for the hydrogenation of methyl-2-(benzamidomethyl)-3-oxobutanoate, $PhCONHCH_2CH(COMe)COOMe$ (94% ee), it gave poor diastereoselectivity (39% de) and was less active than complexes such as R = C_6H_4Me-3, R′ = Me, R″ = CHMe, X = I. Studies of other complexes revealed that activity and selectivity were also dependent on the halide, anion, and η^6-arene. The complex R = C_6H_4F-4, R′ = R″ = H, X = Cl showed reasonable enantioselectivity for the hydrogenation of PhCOCOOMe to PhCHOHCOOMe (80% ee), but was inferior to the complex R = C_6H_4Me-4, R′ = R″ = H, X = Cl.

6.9. Hydrogen transfer

Complexes of fluoroarylphosphine ligands have recently been assessed for the catalysis of hydrogen transfer (Scheme 23) by piano stool complexes [18].



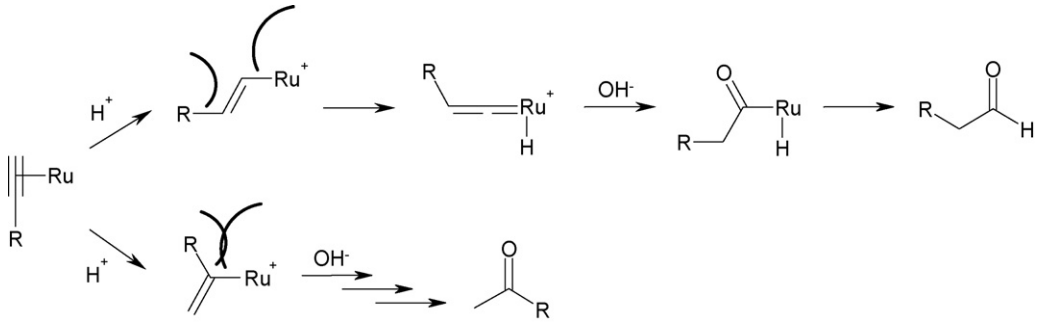
Scheme 23.

[(η^6-MeC$_6$H$_4$CHMe$_2$-4)RuCl(dfppm)]BF$_4$ (dfppm = $(C_6F_5)_2PCH_2P(C_6F_5)_2$), [($\eta^5$,κP,κP-$C_5Me_4CH_2$-2-$C_5F_3$N-4-$PPhCH_2CH_2PPh_2$)RhCl]BF$_4$ and [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_6F_4-$P(C_6F_5)CH_2P(C_6F_5)_2$}RhCl$_2$] gave conversions of acetophenone (0.2 M) of 85%, 94% and 81% respectively after 2 h, which are comparable to those with [(η^6-$C_6H_3Me_3$-1,3,5)RuCl(μ-Cl)]$_2$/DPEN and [(η^5-C_5Me_5)RhCl(μ-Cl)]$_2$/DPEN (DPEN = 1,2-diphenylethylenediamine) (90%), which are commonly used systems for catalysing hydrogen transfer. However, after 30 min the conversions with [(η^6-MeC$_6$H$_4$CHMe$_2$-4)RuCl(dfppm)]BF$_4$ (69%) and [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_5F_3N-4-$PPhCH_2CH_2PPh_2$)RhCl]BF$_4$ (94%) were significantly higher than that with [(η^6-$C_6H_3Me_3$-1,3,5)RuCl(μ-Cl)]$_2$/DPEN (48%). Other ruthenium, rhodium and iridium complexes of fluoroarylphophines were less active: [(η^6-$C_6H_3Me_3$-1,3,5)RuCl(dfppm)]BF$_4$ 21% conversion, [(η^6-$C_6H_3Me_3$-1,3,5)Ru(μ-Cl)$_3$RuCl(dfppm)] 67% conversion, [(η^5-C_5Me_5)RhCl(dfppm)]BF$_4$ 49% conversion, [(η^5-C_5Me_5)RhCl(dfppe)]BF$_4$ 29% conversion, [(η^5-C_5Me_5)IrCl(dfppm)]BF$_4$ 5% conversion, [(η^5-C_5Me_5)IrCl(dfppe)]BF$_4$ 1% conversion. Although high activity is important, enantioselectivity is equally desirable for catalysis of hydrogen transfer reactions. The enantioselectivity of the hydrogen transfer reactions catalysed by the chiral complexes [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_5F_3N-4-$PPhCH_2CH_2PPh_2$)RhCl]BF$_4$ and [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_6F_4-$P(C_6F_5)CH_2P(C_6F_5)_2$}RhCl$_2$] has not yet been assessed.

Although [(η^6-MeC$_6$H$_4$CHMe$_2$-4)RuCl(dfppm)]BF$_4$ and [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_5F_3N-4-$PPhCH_2CH_2PPh_2$)RhCl]BF$_4$ showed high activity for transfer hydrogenation in isopropanol, their activity for the reverse reaction, Oppenauer oxidation, in acetone was disappointing [18]. Under the conditions of the study [(η^6-MeC$_6$H$_4$CHMe$_2$-4)RuCl(dfppm)]BF$_4$ and [(η^5,κP,κP-$C_5Me_4CH_2$-2-C_5F_4N-4-$PPhCH_2CH_2PPh_2$)RhCl]BF$_4$ gave turnover frequencies for oxidation of *rac*-phenylethanol to acetophenone of 24 and 8 h^{-1}, respectively, which were lower than with [(η^5-C_5Me_5)MCl(μ-Cl)]$_2$ (M = Rh 29 h^{-1}) and (M = Ir 37 h^{-1}).

6.10. Alkyne hydration

A ruthenium(II) complex of $PPh_2(C_6F_5)$ has been found to be an efficient catalyst for the anti-Markovnikov hydration of alkynes [162]. In the presence of three equivalents of $PPh_2(C_6F_5)$, 10 mol% of [(η^6-C_6H_6)RuCl$_2${$PPh_2(C_6F_5)$}] catalysed the hydration of a range of alkynes in isopropanol at elevated temperature. The best results were achieved with 1-hexyne and 1-octyne, which gave upwards of 70% yields of, respectively, hexanal and octanal with high selectivtity (<5% ketone) after 12 h at 65 °C. [(η^6-C_6H_6)RuCl$_2${$PPh_2(C_6F_5)$}] alone yielded 18% octanal and 22% 2-octanone. NMR spectroscopic studies revealed that $PPh_2(C_6F_5)$ displaced benzene from [(η^6-C_6H_6)RuCl$_2${$PPh_2(C_6F_5)$}] leading to the suggestion that [RuCl$_2${$PPh_2(C_6F_5)$}$_3$] is the resting state of the catalyst. In comparison [(η^6-C_6H_6)RuCl$_2${$P(C_6H_4SO_3Na$-3)$_3$}]/8 $P(C_6H_4SO_3Na$-3)$_3$ gave a 45% yield of octanal after 40 h at 100 °C in 2-methoxyethanol, with 4.5% 2-octanone and 8.8% octanal. Extensive mechanistic studies of reactions



Scheme 24.

catalysed by $[(\eta^6\text{-}C_6H_6)RuCl_2\{PPh_2(C_6F_5)\}]/3PPh_2(C_6F_5)$ and the complex $[(\eta^5\text{-}C_5H_5)RuCl(PPhMe_2)]$, supported by DFT calculations, has allowed a mechanism involving protonation of an η^2-coordinated alkyne, nucleophilic attack by hydroxide on a ruthenium(IV) hydride vinylidene complex and reductive elimination from a ruthenium hydride acyl complex to be proposed (Scheme 24) [163]. It was suggested that the bulk of the ligands favours the vinyl intermediate in which the alkyl group is β, which leads to the aldehyde, rather than α, which leads to the ketone.

6.11. Methanol dehydrogenation

A study of the dehydrogenation of methanol by ruthenium tris(triarylphosphine) complexes $[RuCl_2\{P(C_6H_4X\text{-}4)_3\}_3]$ at 64 °C found that the activity increased with σ_p: F > H > Me > OMe [164]. The product selectivity also showed a dependence on σ_p. $[RuCl_2\{P(C_6H_4F\text{-}4)_3\}_3]$ produced only formaldehyde and dimethoxymethane, whereas the complexes of the tolyl- and methoxyphenyl-phosphines formed only dimethoxymethane and methyl formate, and $[RuCl_2(PPh_3)_3]$ gave all three products.

6.12. Amination

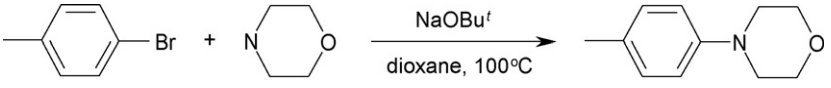
Metallocene-bridged diphosphines have been screened as ligands for palladium(II) catalysts for the amination of 4-bromotoluene and 4-bromobiphenyl by morpholine. It was found that ligands bearing electron-withdrawing aryl substituents showed poor activity [98]. For the amination of 4-bromotoluene (Scheme 25) in dioxane at 100 °C, $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ gave 63% conversion in 20 min, whereas $Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2$ gave only 13% conversion. For the amination of the more reactive 4-bromobiphenyl $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ gave 60% conversion in 10 min, whereas $Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2$ gave only 12% conversion. The diphosphine ligands bearing bulky electron-donating substituents, $Fe\{\eta^5\text{-}C_5H_4P(C_6H_4Pr^i\text{-}2)_2\}_2$ and $Fe\{\eta^5\text{-}C_5H_4P(C_6H_4OMe\text{-}2)_2\}_2$, showed the highest activities for both aminations giving almost quantitative conversions. It was concluded from the data that activity increases with the bulk and electron-donating ability of the phosphine substituents. It is the electron-withdrawing nature of pentafluorophenyl that leads to the low activity of the catalyst derived from $Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2$.

6.13. Suzuki coupling

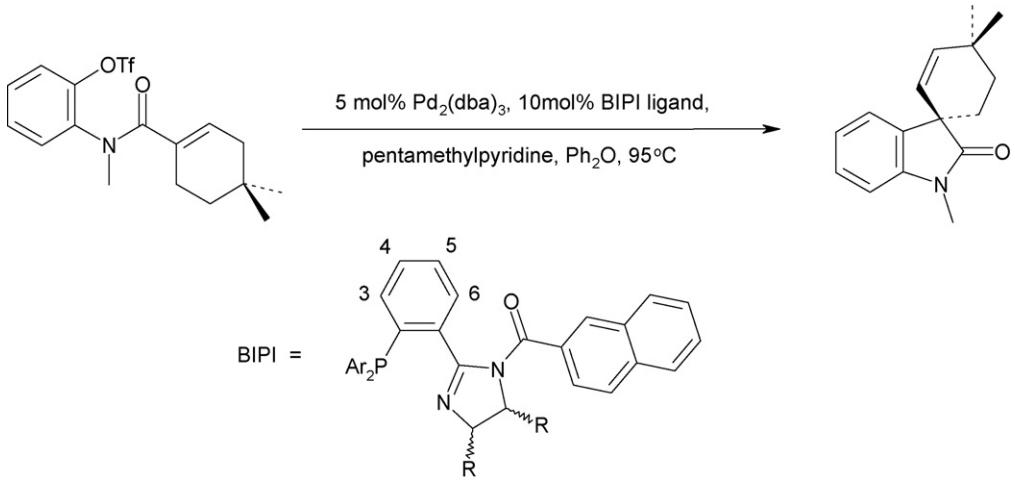
$Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2$ was assessed as a ligand for palladium(II) catalysts for the Suzuki coupling of 4-bromotoluene and 4-methoxyphenylboronic acid in dioxane at 100 °C [98]. Under the conditions of the study the catalyst derived from $Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2$ gave a yield of the product 4-methyl-4′-methoxybiphenyl of 52% after 10 min, which was similar to that given by $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$ (60%), but lower than the quantitative yields obtained with $[Fe\{\eta^5\text{-}C_5H_4P(C_6H_4Pr^i\text{-}2)_2\}_2]$ and $[Fe\{\eta^5\text{-}C_5H_4P(C_6H_4OMe\text{-}2)_2\}_2]$. As for amination (see Section 6.12) high activity is associated with bulky, electron-donating phosphine substituents.

6.14. Heck coupling

A series of BIPI ligands (Scheme 26) has been assessed as ligands for the palladium(II) catalyzed intramolecular Heck reaction [62,165]. For the reaction in Scheme 26 after 18 h the ligand Ar = $C_6H_3F_2$-3,5, R = *S*-Ph yielded 39% of product with 78.1% ee, and Ar = $C_6H_3F_2$-3,5, R = *R*-$C_6H_3F_2$-3,5 yielded 38% of product with 87.6% ee. In contrast the ligand Ar = Ph, R = *S*-Ph yielded 68% of product with 44.6% ee and Ar = C_6H_4Cl-4, R = *R*-$C_6H_3F_2$-3,5 yielded 25% of product with 80.6% ee. Similar results were obtained for the Heck coupling of similar substrates. The data clearly indicated that electron-withdrawing susbtituents, especially fluoroaryl groups, had a positive influence on the stereoselectivity, but reduced catalytic activity. It was concluded that electronic properties played a more important role than steric factors in determining the stereoselectivity of the reaction. Although the



Scheme 25.



Scheme 26.

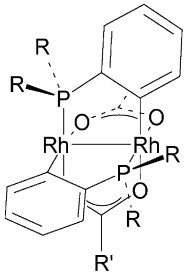
reason was not elucidated, it was suggested that this may arise from stabilization of a trigonal bipyramidal transition state. Fluorination of the phenylene group of the BIPI ligand Ar = Ph, R = *S*-Ph was found to decrease yield, enantioselectivity or both compared to the non-fluorinated ligand: 3-F 73% yield, 26.3% ee, 4-F 46% yield, 52.8% ee, 5-F 15% yield, 52.8% ee, 6-F 15% yield, 27.3% ee.

6.15. Reductive coupling

The reductive coupling of acid chlorides by disilanes is catalysed by palladium(II) phosphine complexes. $[PdCl_2\{P(C_6H_4F\text{-}4)_3\}_2]$ and $[PdCl_2(dfppe)]$ were assessed as catalysts for the coupling depicted in Scheme 27 [166]. $[PdCl_2\{P(C_6H_4F\text{-}4)_3\}_2]$ was found to be less active than $[PdCl_2(PPh_3)_2]$ (83% conversion *cf.* 100% conversion), but produced a similar proportion of the side-product $Me_2SiCl\{C_6H_4(CO)_2O\}$ (*ca.* 25%). $[PdCl_2(dfppe)]$ was found to be much less active than $[PdCl_2(dppe)]$ (38% conversion *cf.* 95% conversion), and produced a much greater proportion of $Me_2SiCl\{C_6H_4(CO)_2O\}$ (*ca.* 95%).

6.16. Cyclopropanation and C–H insertion of diazo compounds

Dirhodium(II) carboxylate complexes containing bridging orthometallated phosphines **16** catalyse intramoleclar C–C bond forming reactions of diazo compounds via a mechanism proposed to involve a rhodium carbene intermediate [167]. It has been found that activity increases with the electron-withdrawing nature of the carboxylate substituents, and to a lesser extent the phosphine. It was expected that the electronic and steric properties of the phosphine would be important in controlling the selectivity, and a number of studies have been undertaken.



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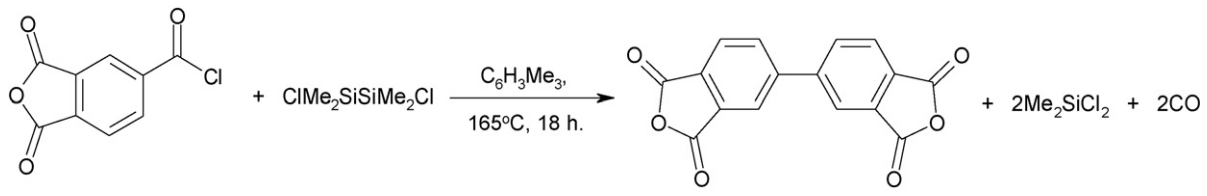
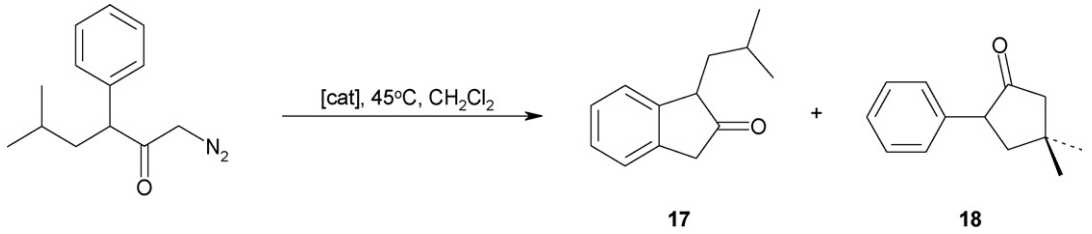
Rhodium acetate catalysts synthesized from $P(C_6H_4F\text{-}3)_3$, $P(C_6H_4F\text{-}4)_3$ and $PPh_2(C_6F_5)$ displayed good activity, specificity for cyclopropanation over C–H insertion and aromatic substitution, and moderate to good selectivities for C–H insertion over aromatic substitution [168]. The results were comparable to those of catalysts prepared from other phosphines, such as PPh_3 and $P(C_6H_4Me\text{-}3)_3$. Electron-withdrawing carboxylate and phosphine substituents were found to increase selectivity for aromatic substitution, but steric affects were also important since the catalyst prepared from $[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PPh(C_6F_4Br\text{-}2)(C_6H_4)\}_2]$ favoured aromatic substitution (**17**:**18** 7:3) whereas $[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}_2]$ favoured C–H insertion (**17**:**18** 2:8) for the reaction in Scheme 28.



Scheme 27.



Scheme 28.

The selectivity for tertiary over secondary aliphatic C–H insertion was investigated for a range of complexes, including $[Rh_2(\mu\text{-}O_2CR)_2\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}_2]$ R = Me, C_3F_7, and $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}]$. In general these three complexes showed similar activities and selectivities to their non-fluorinated analogues, but the results varied with substrate [169]. The doubly metallated complexes showed greater selectivity.

$[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}_2]$ and $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}]$ were also assessed as catalysts for the cyclization in Scheme 29 [170]. *Endo*,*endo*-$[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}_2]$ and *endo*,*exo*-$[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}_2]$ gave 26% and 20% de, respectively. A mixture of the two isomers gave 30% de. In contrast $[Rh_2(\mu\text{-}O_2CMe)_3\{\mu\text{-}PPh(C_6F_5)(C_6H_4)\}]$ gave only 14% de.

In comparison to chiral $[Rh_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}PR_2\text{-}(C_6H_3R')\}_2]$ catalysts prepared from non-fluorinated triarylphosphines, such as PPh_3 and $P(C_6H_4Me\text{-}3)_3$, the catalyst prepared from $P(C_6H_4F\text{-}4)_3$ showed moderate to good enantioselectivity for a variety of C–H insertion reactions [171].

6.17. Silane alcoholysis

The electron-withdrawing effect of fluorine has been found to have a positive effect on the diastereoslectivity of the reaction depicted in Scheme 30 [172]. The diastereomeric ratio increased in the order Ar = C_6H_4Me-4 (89:11) < Ph (90:10) < C_6H_4F-4 (93:7) < $C_6H_3F_2$-3,5 (97:3).

6.18. Photoisomerization

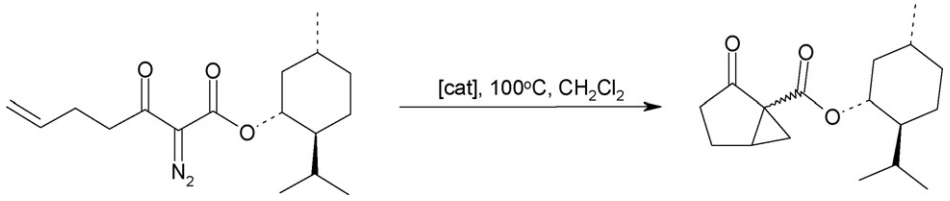
$[CuCl\{PPh_2(C_6F_5)\}]$ has been assessed as a catalyst for the photoisomerization of norbornadiene to quadricyclene and *trans*-stilbene to *cis*-stilbene, but was found to show very little activity in comparison to $[CuCl(PEt_3)]$ and $[CuCl\{P(C_6H_4Me\text{-}4)\}]$ [173]. It was suggested that the bulk of the ligand disfavoured coordination of the alkene, which was supported by the minimal activity of $[CuCl\{P(C_6H_4Me\text{-}2)\}]$.

6.19. Diene cycloisomerization

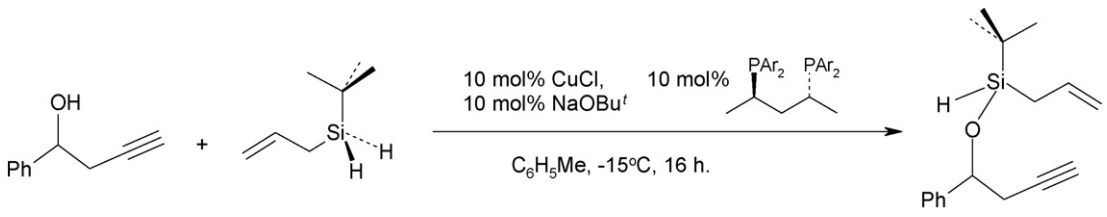
The dication $[Pt(dppm)\{P(C_6F_5)_3\}]^{2+}$, formed *in situ* by addition of silver tetrafluoroborate and $P(C_6F_5)_3$ to $[Pt(dppm)Cl_2]$ in nitromethane, showed a low activity for the catalysis of the cycloisomerization shown in Scheme 31 [174]. After 3 h the yield was 53% with a diastereomeric ratio of 24:1. In comparison the catalysts formed by PMe_3 and PEt_3 gave yields of 94% and 87%, respectively and diastereomeric ratios of 12:1 and 20:1, respectively, and the catalyst formed by PPh_3 gave a yield of 64% with a diasereomeric ratio of 24:1 after only 48 min.

6.20. Alkyne cyclotrimerization

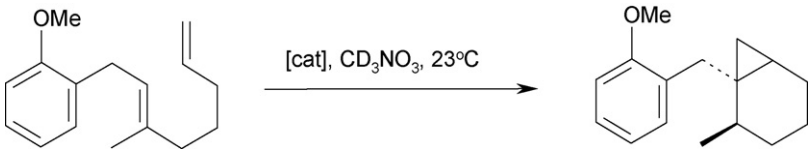
Although [Ir(OMe)(COD)(dfppe)] was found to display catalytic activity for the trimerization of phenylacetylene, its activity was much lower than that of the similar complexes $[IrH(\eta^2,\eta'^2\text{-}C_8H_{12})(dppm)]$ and [IrH(COD)(dppe)] [175]. Furthermore, in contrast to [IrH(COD)(dppm)] and



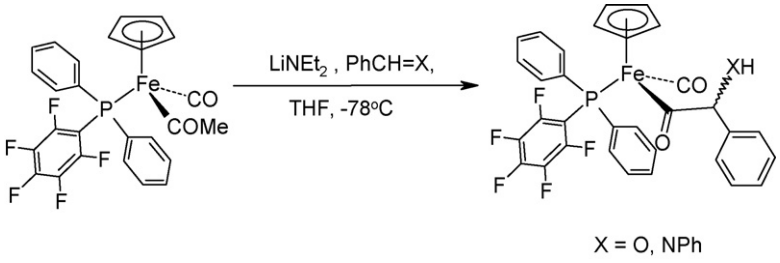
Scheme 29.



Scheme 30.



Scheme 31.



Scheme 32.

[IrH(COD)(dppe)] which gave almost exclusively 1,2,4-triphenylbenzene, [Ir(OMe)(COD)(dfppe)] produced predominantly polyphenylacetylene, similar to that obtained with [IrH(COD)(PR_3)$_2$] [176].

7. Fluoroarylphosphines as ligands for stoichiometric reactions

Aldol and imine condensation reactions of the chiral complex [(η^5-C_5H_5)Fe(CO){$PPh_2(C_6F_5)$}(COMe)] (PFCHIRAC) (Scheme 32) have been studied [177] and the stereoselectivities found to be better than those of the non-fluorinated analogue, [(η^5-C_5H_5)Fe(CO)(PPh_3)(COMe)] (CHIRAC), which is a well-established reagent for asymmetric induction in aldol and imine condensations and Michael type additions [178]. In aldol condensations with benzaldehyde PFCHIRAC formed preferentially the R_{Fe}*,S_c* stereoisomer of [(η^5-C_5H_5)Fe(CO){$PPh_2(C_6F_5)$}{$COCH_2CH(OH)Ph$}] over the R_{Fe}*,R_c* stereoisomer with ratios ranging from 8:1 to 80:1 depending on the metal of the enolate and the presence of a Lewis acid. In contrast, the stereoselectivities of the analogous reaction with CHIRAC were much lower, and for some enolates the R_{Fe}*,R_c* stereoisomer was favoured. PFCHIRAC also showed good stereoselectivity in its imine condensation with benzylideneaniline, with the R_{Fe}*,S_c* stereoisomer of [(η^5-C_5H_5)Fe(CO){$PPh_2(C_6F_5)$}{$COCH_2CH(NPh)Ph$}] preferred over the R_{Fe}*,R_c* stereoisomer in ratios of 8:1 to 50:1. The R_{Fe}*,R_c* stereoisomer is preferred for CHIRAC, but with lower selectivity. On the basis of IR spectral data an attractive electron donor–acceptor interaction between the carbonyl oxygen and pentafluorophenyl substituent was proposed to account for the differences between the reactions of PFCHIRAC and CHIRAC. This was supported by the apparent slow rotation about the P–C_6F_5 bond observed by dynamic NMR spectroscopy [177]. However, extensive dynamic NMR studies of CHIRAC, PFCHIRAC and [(η^5-C_5H_5)Fe(CO){$P(C_6H_3F_2$-3,5)$_3$}(COMe)] revealed that rotation about the P–C bonds of all three complexes is rapid on the NMR timescale (at a spectrometer frequency of 235 MHz) even at −90 °C, and the process previously observed in PFCHIRAC is rotation about the Fe–P bond with a calculated upper limit of the energy barrier of 66.9 kcal mol^{-1} [63]. It was concluded that the C=O···C_6F_5 interaction is insignificant at ambient temperature, and does not account for the difference in reaction diastereoselectivity between PFCHIRAC and its non-fluorinated analogue.

8. Final comments

This research described in this review demonstrates that arylfluorophosphines can confer desirable properties on metal complexes. Their steric and electronic properties have been found to enhance the activity and selectivity of some homogeneous catalysts and the stoichiometric reagent PFCHIRAC. The susceptibility of fluoroaryl substituents to nucleophilic attack has allowed the functionalization of coordinated phosphines and the synthesis of complexes of multidentate phosphine ligands. Although the properties of fluoroarylphosphines were determined 30 years ago, it is only relatively recently that their potential is being investigated and their benefits exploited. Recent results suggest that fluoroarylphosphines still have a lot to offer, especially for the synthesis and catalytic properties of complexes of elaborate multidentate ligands.

Acknowledgements

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