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Phosphorus(III) ligands in fluorous biphase catalysis

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Abstract

The synthesis, coordination chemistry and catalytic applications of a series of perfluoroalkyl-substituted phosphorus(III) ligands is illustrated. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Following the disclosure of the fluorous biphase approach to the heterogenisation of homogeneous catalysts in 1994 [1], the catalysis community has been polarised; they are either staunchly in favour or strongly opposed to developments based upon the fluorous biphase concept. In essence, this approach relies upon the unique physical and chemical properties of perfluorinated fluids which are immiscible with many conventional organic solvents at ambient temperatures, but which dissolve other highly fluorinated molecules. Hence, by derivatising conventional homogeneous catalysts with long perfluoroalkyl sidechains (called fluorous pony*tails*, Fig. 1) it is possible to anchor the metal catalysts in the perfluorinated solvent. In addition, however, with an appropriate choice of fluorous and organic solvents (containing the substrate), on warming or under pressure the fluorous and organic solvents become miscible and catalysis occurs homogeneously (Fig. 2). On cooling (or pressure release) the biphase is re-established and, hence, catalyst/product separation simplifies to the separation of two, immiscible, fluids. Although research into the development of this approach has been reported across a broad spectrum of catalytic reactions (oxidation [2-6], C-C bond formation [7,8], polymerisation [9], hydrogenation [10,11], hydroboration [12], hydroformylation [1,13,14,15,16],) using a wide variety of perfluoroalkyl-derivatised ligand systems, phos-

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phorus(III) ligands have been used more widely than any other single class of ligand, and here we outline the synthesis, properties and catalytic applications of phosphorus(III) ligands prepared within our laboratory.

2. Ligand synthesis

The first phosphorus(III) ligand prepared specifically for its application in the fluorous biphase was $P(C_2H_4C_6F_{13})_3$ (Fig. 1). This molecule, prepared in 1994 [1] by the radicalinduced reaction of C₆F₁₃CH=CH₂ with PH₃, illustrates the two key components for a fluorous biphase-compatible ligand system: (i) long, linear, perfluoroalkyl substituents and (ii) a hydrocarbon spacer unit to insulate the donor atom from the extremely electron-withdrawing fluorous ponytails. Although there have been subsequent improvements in the procedure and yield in this reaction [17,18], we [19] and others [20] have found that reaction of the Grignard reagent $\{C_6F_{13}C_2H_4MgI\}$ with phosphorus chloride reagents (e.g. PCl₃, PPhCl₂, PPh₂Cl) offers a more general route into ligands with perfluoroalkyl substituents without the need to use the highly toxic phosphine, PH₃; a similar route via organo-zinc reagents has also been described [21]. However, in our hands, we were unable to extend this Grignard route to derivatives with longer perfluoroalkyl substituents [22]. Unfortunately, coordination chemistry studies (see below) and theoretical calculations [14] indicate that the C2H4 unit is not a particularly good electronic insulator, and although these latter calculations suggest that a C₃H₆ group will be a better spacer unit $\{P(C_3H_6C_6F_{13})_3$ has subsequently been

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Fig. 1. Tris(1H,1H,2H,2H-perfluorooctyl)phosphine.



Fig. 2. Catalysis within a fluorous biphase system (FBS).

prepared [18]}, we turned our attention to the synthesis and application of ligands containing aryl groups as electronic insulators.

The copper-mediated cross-coupling reaction of a perfluoroalkyl iodide with an aryl halide offers a convenient, general, route to a comprehensive series of perfluoroalkylated aryl intermediates (Figs. 3 and 4) [19]. In the reactions with 2-, 3- and 4-C₆H₄BrI, the principle by-product is the bis-substituted arene which is readily separated on distillation. Yields are generally good, except in the coupling reaction with 2-C₆H₄BrI which is probably because of steric interactions. For the perfluoroalkylated aryl bromides, lithiation at low temperature followed by reaction with a range of phosphorus chloride reagents offers a widely applicable route to a comprehensive series of ligands with fluorous ponytails. The steric congestion associated with the ortho-C₆F₁₃ unit is reflected in the reaction of 2-LiC₆H₄C₆F₁₃ with PCl₃ which does not lead to complete substitution but rather affords $PCl(2-C_6H_4C_6F_{13})_2$ as an unusual air- and moisture-stable phosphorus(III) chloride [22]. A structural determination (Fig. 5) confirms the steric congestion and indicates short intramolecular interactions between phosphorus and various fluorine atoms on the

perfluoroalkyl units which presumably "protect" the phosphorus atom from attack by incoming nucleophilic reagents. In this structure, the perfluoroalkyl groups radiate, linearly, away from the aryl rings and line-up with other perfluoroalkyl groups from adjacent molecules to generate fluorous domains within the crystal lattice. This appears to be a common observation in the structural determinations of molecules with perfluoroalkyl substituents to date. Unfortunately, we have been unable to structurally characterise any of our ligand systems, however, we have obtained single crystals of $O=P(3-C_6H_4C_6F_{13})_3$ from a chloroform solution of the free ligand left to stand for several weeks (Fig. 6). Although the crystals were of relatively poor quality and the ends of the perfluoroalkyl groups showed considerable disorder, the $O=P(C_6H_4)_3$ core of the molecule is well defined and offers an insight into the influence of the perfluoroalkyl substituents by comparison with data for triphenylphosphine oxide (Table 1) [23]. The slight lengthening of the P=O and P-C bond lengths and compression of the C-P-C bond angles indicate that the perfluoroalkyl groups have some influence on the electron density at the phosphorus atom. A crystal packing diagram for this structure illustrates how the perfluoroalkyl units align within the



Reaction Conditions: i, $C_6F_{13}I$, Cu, bipy, DMSO, C_6F_6 ; ii, Bu^nLi , Et_2O ; iii, $Cl_2PCH_2CH_2PCl_2$, Et_2O ; iv, PPh_xCl_{3-x} , Et_2O ; v, $PCl_2(NEt_2)$, Et_2O ; vi, HCl(g); vii, $LiCF=CF_2$, Et_2O , -100 °C; viii, PCl_3 , Et_2O ; ix, 48% HBr(aq), reflux; x, 3% NaOH(aq); xi, CH_3CO_2H ; xii, $F_{15}C_7CH_2OTf$, K_2CO_3 , DMF, 65 °C.

Fig. 3. Synthetic routes to perfluoroalkyl-derivatised phosphine ligands.

crystal and the formation of the fluorous domains within the structure (Fig. 7).

The residual electronic influence of the perfluoroalkyl units on the phosphorus atom is reflected in our coordination chemistry studies (see below), and consequently, we have investigated the incorporation of additional hydrocarbon spacer units. The reaction of $F_{15}C_7CH_2OTf$ with P(4-C₆H₄OH)₃ allows the insertion of an additional OCH₂ unit

(Fig. 3) [24] whilst the synthesis of perfluoroalkyl-substituted phenols (Fig. 4) allows the generation of a series of phosphinite, phosphonite and phosphite ligands [19]. Here, the additional oxygen atom alleviates any steric constraints associated with the *ortho*-substituents.

Throughout this work, our primary goal has been the application of these derivatised ligand systems in fluorous biphase catalysis. Hence, preferential solubility of the



Reaction Conditions: i, $C_6F_{13}I$, Cu, bipy, DMSO, C_6F_6 ; ii, $Cl_2PCH_2CH_2PCl_2$, NEt_3 , Et_2O ; iii, $PPh_xCl_{3,x}$, NEt_3 , Et_2O ; iv, PCl_3 , NEt_3 , Et_2O ;

Fig. 4. Synthetic routes to perfluoroalkyl-derivatised phosphonite, phosphinite and phosphite ligands.



Fig. 5. Molecular structure of PCl(2-C_6H_4C_6F_{13})_2. Displacement ellipsoids are shown at the 30% probability level.

ligand in a perfluorocarbon/organic solvent biphase is essential and we have undertaken qualitative assessments of fluorous phase compatability using ³¹P NMR spectroscopy. These experiments indicate that, for these ligand systems, at



Fig. 6. Molecular structure of $O{=}P(3{-}C_6H_4C_6F_{13})_3.$ Displacement ellipsoids are shown at the 30% probability level.

Table 1 Selected bond length (Å) and bond angle (\degree) data for O=PPh₃ and O=P(3-C₆H₄C₆F₁₃₎₃^a

	O=PPh ₃ ^b	$O=P(3-C_6H_4C_6F_{13})_3$
Р-О	1.46(1)	1.49(2)
P–C	1.75(1)	1.77(2)
P–C	1.77(1)	1.84(2)
P–C	1.77(1)	1.84(2)
C-P-C	106.5(7)	105.0(10)
C-P-C	107.2(7)	106.0(10)
C-P-C	107.6(6)	106.7(10)

^aStandard deviations in parentheses.

^bData taken from [23].



Fig. 7. Crystal packing diagram for $O=P(3-C_6H_4C_6F_{13})_3$ illustrating short intermolecular interactions and fluorous domains.

Table 2		
The variation in	${}^{1}J_{\text{PtP}}$ (Hz) with L in <i>cis</i> -[PtCl ₂ L ₂]	

L	$^{1}J_{\mathrm{PtP}}$
PPh ₃	3672
$PPh_2(4-C_6H_4C_6F_{13})$	3653
$PPh(4-C_6H_4C_6F_{13})_2$	3635
$P(4-C_6H_4C_6F_{13})_3^a$	3631
$PPh_2(3-C_6H_4C_6F_{13})^a$	3633
$PPh(3-C_6H_4C_6F_{13})_2^a$	3602
$P(3-C_6H_4C_6F_{13})_3$	b
P(2-C ₆ H ₄ C ₆ F ₁₃)(4-C ₆ H ₄ C ₆ F ₁₃) ₂	b
PEtPh ₂	3640
$P(C_2H_4C_6F_{13})Ph_2$	3630
$PEt(4-C_6H_4C_6F_{13})_2$	3617
$P(4-C_6H_4OCH_3)_3$	3703
$P(4-C_6H_4OCH_2C_7F_{15})_3$	3680

^aFormed as a mixture of *cis*- and *trans*-isomers.

^bAll attempts to form *cis*-[PtCl₂L₂] failed, *trans*-[PtCl₂L₂] isolated exclusively.

least three C_6F_{13} units are required to confer preferential fluorous phase solubility, which is in line with the recently reported >60% (w/w) fluorine requirement indicated by quantitative solubility measurements [25]. Consequently, only ligands which satisfy this criteria have been evaluated in our preliminary catalytic studies (see below).

3. Coordination chemistry

At the outset of this work, the influence of the perfluoroalkyl substituents on the donor properties of phosphorus(III) ligands, and consequently, the catalytic activity of derivatised metal complexes was unknown. Since many transition metal catalysts are generated in situ from the free ligand and metal-containing precursors, the successful development of the fluorous biphase approach to catalysis depended upon the reactivities of these ligands mirroring conventional phosphorus(III) ligands. We have investigated the reactions of the ligands prepared in this study with a broad spectrum of platinum-metal reagents (Figs. 8 and 9) [26-28]. These investigations indicate that, for the mostpart, the perfluoroalkyl substituents do not have a significant influence on the donor properties of the phosphorus atoms wherein the displacement of weakly coordinated ligands and the cleavage of halide-bridged dimers occur in good yields.

Spectroscopic investigations on these metal complexes offer an insight into the electronic effects of the perfluoroalkyl substituents. Table 2 compares the ${}^{1}J_{PtP}$ coupling constants of the *cis*-[PtCl₂L₂] of the fluorous-derivatised phosphines with the protio-parent ligands and shows how the number and position of the perfluoroalkyl groups affects the ${}^{1}J_{PtP}$ values. These values can be correlated with the σ donor strength or Hammett constant (σ_{P}) of the ligands [29] whilst Table 3 { ν (CO) for *trans*-[MCl(CO)L₂] (M = Rh, Ir)} indicates the π -bonding characteristics of these ligands. These data confirm that:



Fig. 8. Coordination chemistry of monodentate perfluoroalkyl-derivatised phosphorus(III) ligands.



Fig. 9. Coordination chemistry of bidentate perfluoroalkyl-derivatised phosphorus(III) ligands.

Table 3 Variation in ν (CO) (cm⁻¹) in *trans*-[MCl(CO)L₂] (M = Rh, Ir) with L

L	Rh	Ir
PPh ₃	1965	1953
$PPh_2(4-C_6H_4C_6F_{13})$	1982	1959
$PPh(4-C_6H_4C_6F_{13})_2$	1983	1972
$P(4-C_6H_4C_6F_{13})_3$	1993	1979
$PPh_2(3-C_6H_4C_6F_{13})$	1980	-
$PPh(3-C_6H_4C_6F_{13})_2$	1984	-
$P(3-C_6H_4C_6F_{13})_3$	1992	-
$P(4-C_6H_4OCH_3)_3$	1958	1961
$P(4-C_6H_4OCH_2C_7F_{15})_3$	1977	1967
PEt ₃	1953	1929
$P(C_2H_4C_6F_{13})_3$	1992	1977

- 1. The aryl unit is a better electronic insulator than the C_2H_4 unit, but that it is not perfect; even the $C_6H_4OCH_2$ unit does not completely insulate the phosphorus atom.
- 2. The electronic influence through the aryl ring is purely inductive whereby a *meta*-substituent has a greater effect than a *para*-substituent.
- 3. Ortho- and meta-substitution can generate steric interactions whereby the thermodynamically less favoured

trans-[PtCl₂L₂] can be formed in preference to the *cis*-isomer.

Further information on the donor properties of these ligands can be obtained, in selected cases, from a comparison of the data from single crystal structure determinations with that from similar protio-ligand metal complexes; Tables 4 and 5 illustrate two such comparisons. The most important conclusion from these comparisons is that, for both pairs of complexes, the perfluoroalkyl substituents have very little influence on the first coordination spheres about the metal centres. For the trans-[RhCl(CO)L₂] complexes [26,30] the Rh-P, Rh-Cl and C-O distances are unperturbed on substitution and only the variation in length in Rh-C offers any suggestion of the electronic influence of the fluorous ponytails. This might have a slight knock-on effect in the configuration around the metal centre whereby, although the rhodium, phosphorus, chlorine and carbonyl carbon atoms are coplanar, the P-Rh-P axis is bent towards the chlorine atom. Further structural studies, using Rh Kedge EXAFS in the solid state and in perfluorocarbon solution indicate that, within the accuracy of this technique, the metal first coordination sphere is unperturbed on disTable 4 Selected bond length (Å) and bond angle (°) data for *trans*- $[RhCl(CO)L_2]^a$

	$L = P(CH_3)_3^{b}$	$L = P(C_2H_4C_6F_{13})_3^c$		
Rh–P	2.307(1)	2.300(2)		
Rh–P	2.309(1)	2.304(2)		
Rh–C	1.770(4)	1.807(5)		
RhCl	2.354(1)	2.356(2)		
C–O	1.146(4)	1.152(6)		
C–Rh–P	91.0(1)	94.2(2)		
C-Rh-P	91.6(1)	93.7(2)		
Cl-Rh-P	89.3(1)	85.5(1)		
Cl-Rh-P	88.1(1)	86.5(1)		
P–Rh–P	177.2(1)	172.1(1)		

^aStandard deviations in parentheses.

^bData taken from Ref. [30].

^cData taken from Ref. [26].

Table 5

Selected bond length (Å) and bond angle ($^{\circ}$) data for *cis*-[PtCl₂L₂]^a

$L = PPh_3^{b}$		$L = P(4-C_6H_4C_6F_{13})_3^{c}$	
Pt–P	2.251(2)	2.254(3)	
Pt–P	2.265(2)	2.271(3)	
Pt-Cl	2.356(2)	2.349(3)	
Pt-Cl	2.333(2)	2.328(2)	
P-Pt-P	97.8(1)	97.73(9)	
P-Pt-Cl	89.8(1)	89.97(9)	
P-Pt-Cl	87.1(1)	86.36(9)	
Cl-P-Cl	85.3(1)	86.30(9)	

^aStandard deviations in parentheses.

^bData taken from Ref. [33].

^cData taken from Ref. [27].

solution [26]. The packing diagram for the fluorous-derivatised metal complex again shows short intermolecular distances and fluorous domains as reported for the isostructural iridium complex [31,32]. For the *cis*-[PtCl₂L₂] complexes [27,33] {when $L = P(4-C_6H_4C_6F_{13})_3$ the *cis*-complex co-crystallizes with its *trans*-isomer [27]} there are slight asymmetries in the Pt–P and Pt–Cl bond lengths and the coordination geometries around the metal centres in the two complexes are virtually identical.

Our qualitative solubility assessments for these metal complexes indicate that, in addition to requiring three perfluoroalkyl units per ligand, two monodentate ligands per metal centre are essential to confer preferential solubility and that, even having satisfied these criteria, the other ligands at the metal centre can be important, i.e. although *trans*-[RhCl(CO){P(4-C₆H₄C₆F₁₃)₂] is preferentially fluorous-phase soluble *trans*-[PdCl₂{P(4-C₆H₄C₆F₁₃)₂] is not.

4. Catalytic studies

Although homogeneous catalysts can provide very high activities and selectivities towards industrially desirable products, their commercialisation can be thwarted by an inability to separate them from the products. A number of approaches directed towards the heterogenisation of established homogeneous catalysts, which would facilitate such separations, (e.g. ship-in-a-bottle, attachment to insoluble supports, supercritical solvents) are under investigation [34] and the fluorous biphase offers an interesting and potentially valuable alternative strategy. However, a number of important criteria would have to be satisfied before a system using perfluorocarbon solvents could possibly be used on an industrial scale:

- 1. The solvent and catalyst must be stable under process conditions and both must be recoverable with 100% efficiency.
- The system should offer efficiency and/or selectivity gains over established processes.

In our initial studies we have concentrated on two catalytic processes; (a) the extensively studied *hydrogenation of styrene* to allow a direct comparison between perfluoroalkyl-derivatised catalysts and their protio-congeners and (b) the *hydroformylation of long chain alkenes*, an important industrial process where, currently, a relatively unreactive and unselective cobalt-based catalyst has to be employed because the more reactive and selective rhodium-based catalysts cannot be separated from the long chain aldehyde products without decomposition [34].

In the hydrogenation of styrene using Wilkinson's catalyst analogues (Table 6), although quantitative recovery of

Table 6				
Hydrogenation o	f styrene	catalysed	by rhodium	complexes ^a

Ligand	Rate (mmol dm ^{-3} h ^{-1})		
PPh ₃	155		
PPh ₃ ^b	211		
PPh ₃ ^c	160		
PPh ₃ ^d	276		
PEt ₃	177		
$P(4-C_6H_4CF_3)_3$	139		
$P(3-C_6H_4CF_3)_3$	100		
$P(4-C_6H_4OCH_3)_3$	218		
$P(4-C_6H_4OCH_2C_7F_{15})_3$	201		
$P(C_2H_4C_6F_{13})_3$	79		
$P(4-C_6H_4C_6F_{13})_3$	128		
$P(3-C_6H_4C_6F_{13})_3$	117		
$P(4-C_6H_4C_6F_{13})_3^{c}$	146		
$P(4-C_6H_4C_6F_{13})_3^d$	86		
$P(4-C_6H_4C_6F_{13})_3^{e}$	115		

^aConditions: the ligand $(1.257 \times 10^{-4} \text{ mol dm}^{-3})$ (except where stated) was dissolved in a degassed mixture of hexane (6 cm³), PP3 (10 cm³) and styrene (1.8 cm³; 15.7 mmol), pressurised to 1 bar with H₂ and equilibriated with stirring at 63.5°C (unless otherwise stated). A solution of [RhCl(C₂H₄)₂]₂ (6.1 mg, 1.571 × 10⁻⁵ mol) in toluene (2 cm³) was added and the mixture was stirred for 1 h. Analyses by glc. Rates $\pm 4 \text{ mmol dm}^{-3} \text{ h}^{-1}$.

^bSolvent system toluene (18 cm³).

 $^{\circ}$ Catalytic runs at 75 $^{\circ}$ C and solvent system fluorobenzene (8 cm³)/PP3 (10 cm³).

^dSolvent system toluene (8 cm³)/PP3 (10 cm³).

 $^{\rm e}$ Solvent system PP3 (18 cm³)(product extracted at the end of the catalytic runs with toluene).

Ligand	Conversion (%)	Selectivity (%)	n/i	Rate constant (s^{-1})	Initial rate (mol dm ^{-3} s ^{-1})
PPh ₃ ^b	99.6	96.1	2.5	c	2.3×10^{-3}
PPh ₃	99.0	98.2	3.1	с	$3.2 imes 10^{-3}$
$P(4-C_6H_4C_6F_{13})_3$	98.3	89.2	3.8	$6.3 imes 10^{-3}$	$1.3 imes 10^{-2}$
P(OPh) ₃	99.6	92.0	2.9	с	$4.75 imes 10^{-2}$
$P(OC_6H_4-4-C_6F_{13})_3$	99.7	82.3	6.4	6.2×10^{-3}	1.2×10^{-2}
$P(OC_6H_4-4-C_6F_{13})_3^d$	99.7	89.3	6.6	$3.2 imes 10^{-3}$	6.4×10^{-3}

Table 7 Hydroformylation of 1-hexene catalysed by rhodium complexes^a

^aReaction conditions: $[Rh(acac)(CO)_2] = 0.01 \text{ mol dm}^{-3}$, ligand $= 0.03 \text{ mol dm}^{-3}$, 1-hexene $= 1 \text{ cm}^3$ in a mixture of toluene (2 cm^3) and PP3 (2 cm^3) , 70°C, 20 bar, 1 h, (unless otherwise stated), product analysis by GC.

^bIn toluene (4 cm³).

^cZero order throughout most of the reaction.

^dPressure = 8 bar.

the rhodium catalyst could be established by atomic absorption spectroscopy, the electronic influence of the perfluoroalkyl substituents (identified in the spectroscopic studies) is clearly evident; the best electronic insulator, as indicated by the least reduction in rate between the derivatised and underivatised ligands, is the $C_6H_4OCH_2$ unit. Of greater importance, however, is the significant reduction in rate solely on the introduction of the perfluorinated solvent which warrants further investigation. Similarly poor reactivities have been reported in related work on the hydrogenation of linear alkenes [10,11].

In contrast, in the hydroformylation of 1-hexene under 20 atm H_2/CO 1 : 1 (Table 7), the introduction of perfluoro-1,3-dimethylcyclohexane solvent does not have a deleterious effect upon the rate of reaction using a catalyst generated in situ using PPh₃ and the introduction of the fluorous ponytails is accompanied by a slight improvement in both rate of reaction and selectivity. Further improvements in rate and selectivity are obtained using a catalyst prepared from P(O-4-C₆H₄C₆F₁₃)₃ which is also active for the hydroformylation of internal alkenes and is the subject of further detailed investigations [15,16].

5. Conclusions

A broad range of phosphorus(III) ligands which are compatible with the fluorous biphase approach to homogeneous catalysis have been prepared. Coordination chemistry and preliminary catalytic studies illustrate the electronic influence of the perfluoroalkyl substituents in these ligands, which have not been eliminated completely but which may offer advantages in some catalytic applications. Further work in this area is underway.

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