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One ponytail will do: new partially fluorinated phosphines with applications in fluorous biphasic solvent systems

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Abstract

The first 'fluorous soluble' metal complexes derived from a phosphino-amine are reported. Attaching a single perfluorinated 'ponytail' to the $(C_6F_5)_2P$ fragment is sufficient to give rhodium complexes that show high partition co-efficients between perfluoromethylcyclohexane and toluene.

Keywords: Biphasic catalysis; Rhodium complexes; Phosphines; Fluorine chemistry

1. Introduction

In order for catalytic reactions to be viable on a commercial scale, they must be carried out with high efficiency and also utilise catalysts that can be readily separated from the products. Fluorous biphasic catalysis [1] offers an exciting opportunity for generating easily recoverable catalysts. (Fluorous phase catalysts are complexes that are preferentially soluble in highly fluorinated solvents. These solvents are immiscible with organic solvents and products at room temperature, but at elevated temperatures, the organic and fluorous solvents form one phase). This provides a means to separate organic products from catalyst at the end of an otherwise conventional homogeneously catalysed reaction. The catalyst and fluorinated solvent can be reused Fig. 1.

After the key discovery by Horvath and co-workers, intense research effort has realised the application of fluorous biphasic catalysis in a variety of transition metal catalysed reactions [2]. The fluorous soluble ligands known to date are generally simple model ligands (e.g. **1** and **2**), which are not ideal in many processes. A recurring theme in the small range of fluorous phase soluble ligands has been an attempt to 'insulate' the electron-withdrawing properties of the perfluorinated chains from the phosphorus centre. However, there are a variety of catalytic processes that show a preference for electron withdrawing ligands. There is ample evidence that electron poor phosphines show greater reactivity and/or selectivity than triphenylphosphine in rhodium catalysed hydroformylation: one of the most important homogeneously catalysed reactions [3]. We were, therefore, interested in fluorous biphasic ligands that neglect this insulation approach. All of the catalysts that can effectively be recovered into the fluorous phase to date utilise ligands that have three identical substituents at phosphorus. This severely limits the possibilities for fine tuning steric and electronic parameters within the ligand. Appending a fluorous ponytail to the bis(pentafluorophenyl)phosphine fragment should give a ligand of type R_2R^1P that contains $>60\%$ fluorine content: a commonly used rule of

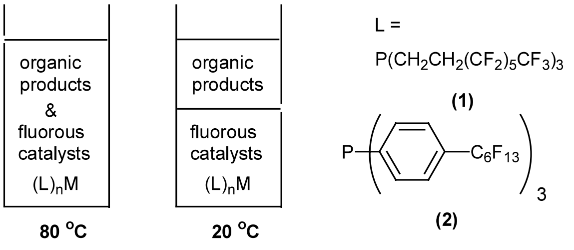

Fig. 1. Effective ligands for fluorous biphasic catalysis.

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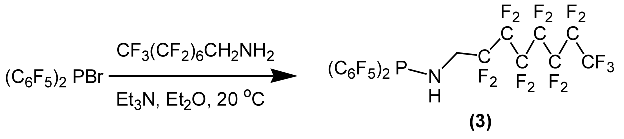
thumb for acceptable fluorous:organic partition co-efficients [4]. In this paper, we report the first metal complexes derived from a ligand with just one ponytail to have preferential solubility in fluorinated solvents.

2. Results and discussion

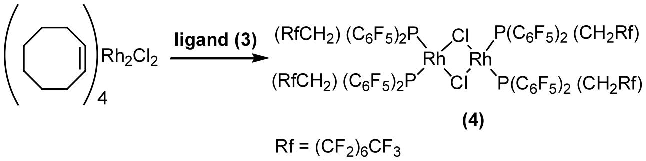
Reaction of 1H, 1H-pentadecafluorooctylamine with readily available bis(pentafluorophenyl)bromophosphine in the presence of pyridine gives phosphine **3** in high purity. The $^{31}P\{^1H\}$-NMR spectrum consists of quintet of triplets splitting pattern ($^3J_{P-F} = 34$; $^4J_{P-F} = 14$ Hz) in which four lines are hidden (Fig. 2, Scheme 1).

We have studied the reaction of this ligand with two organometallic rhodium precursors to help us understand its donor properties and to quantify partition co-efficients between perfluoromethylcyclohexane and toluene. Reaction of four equivalents of **3** with [(cyclooctene)$_2$RhCl]$_2$ gave the chloro-bridged dimer **4** (Scheme 2). The $^{31}P\{^1H\}$-NMR spectrum is a simple broad doublet with a large $^1J_{P-Rh}$ coupling constant (224 Hz). This is indicative of the weak *trans* influence of the bridging chloride ligands, and the simplicity of the spectrum also rules out the formation of a complex of formula [L$_3$RhCl]. Indeed, addition of six equivalents of ligand **3** to [(cyclooctene)$_2$RhCl]$_2$ gave complex **4** contaminated with free ligand. This co-ordination behaviour is in contrast to that seen with Ph$_3$P, which forms Wilkinsons catalyst under these conditions, and tris(pentafluorophenyl)phosphine which forms polymeric structure *trans*-[μ-chloro-bis-(tris-pentafluorophenylphosphine)rhodium]$_n$ when reacted with [(cyclooctene)$_2$RhCl]$_2$ [5].

The perfluoromethylcyclohexane: toluene partition co-efficient was determined in a similar way to that used by van Koten and co-workers for complexes derived from ligand **1** [6,7]. The sample of complex **4** that contained excess ligand was used as this allowed us to also estimate partition co-efficients for the ligand itself.



Scheme 1.



Scheme 2.

The experiment showed that the complex has undetectable solubility in toluene, ($P_{\mathrm{PFMC:toluene}} \geq 99{:}1$) and very high solubility in PFMC. The partition co-efficient of the free ligand between toluene and PFMC is actually low (ca. 1.3:1). Such a marked difference in solubility is surprising, although van Koten et al. have observed a larger proportion of ligand leaching than rhodium leaching under catalytic conditions [7]. This suggests that an excess of free ligand during catalytic experiments would result in products contaminated with phosphines.

To confirm that the solubility of complex **4** was not an exceptional case, we have also prepared complex **5** from [Rh(CO)$_2$Cl]$_2$ and four equivalents of ligand **3** (Scheme 3). The value of ν(CO) in the IR spectrum of this complex serves as a useful probe to evaluate the electronic properties of a ligand, as an extensive literature exists [8]. A value of 2001 cm^{-1} suggests that this ligand behaves much like (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$P, and is a much stronger π-acceptor than triphenylphosphine. This complex is preferentially soluble in PFMC,

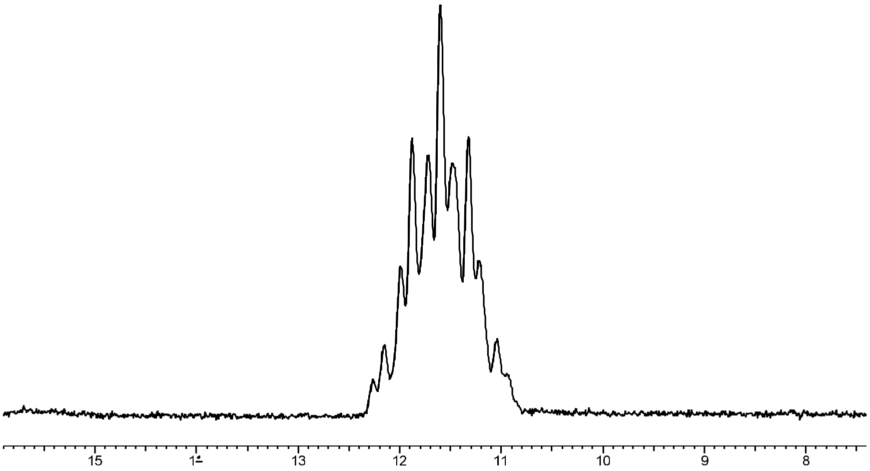
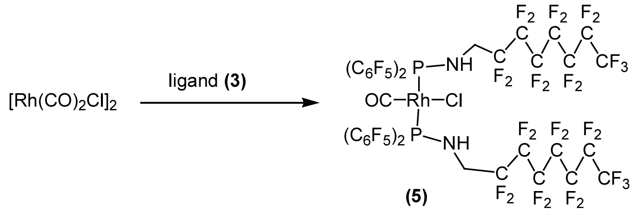


Fig. 2. ^{31}P spectrum of ligand **3**.



Scheme 3.

although the partition co-efficient is only 7:1. This result agrees with observations made by Hope and co-workers who described how complexes that contain broadly similar amounts of fluorine can have radically different fluorous/organic partition co-efficients [9].

The two results taken together show that the pentafluorophenyl groups have a major impact on the solubility of complexes of **3**, as in the past metal complexes of phosphines containing one ponytail have been found to be preferentially soluble in organic solvents (co-efficients <1). The results also suggest that depending on the reaction under investigation, catalysts derived from ligand **3** could be effectively recycled from organic products. Further studies on the factors affecting fluorous phase solubility are clearly required. In summary, we have shown that phosphines containing two fluoro-aryl groups and just one perfluorinated ponytail can be preferentially soluble in perfluorinated solvents. It is envisaged that this observation should allow us to prepare a range of monodentate, bi-dentate and chiral phosphine ligands using this approach, and apply them in fluorous biphasic catalysis. The synthesis of more complex phosphines containing one fluorinated ponytail and their catalytic applications are currently under investigation.

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of nitrogen, using standard Schlenk line techniques, and at room temperature (r.t.) unless otherwise stated. Organic solvents were dried and degassed by elution through an alumina column impregnated with deoxygenating catalysts under nitrogen, and stored under nitrogen. ^{31}P-, ^{1}H- and ^{19}F-NMR spectra were recorded using an Eclipse (ecp) 300 spectrometer. Chemical analyses were performed by the School of Chemistry Microanalytical Laboratory. EI and FAB mass spectra were recorded by the University of Bristol mass spectrometry service using a 'VG Analytical Autospec' mass spectrometer. IR were recorded on NaCl discs as Nujol mulls on a Perkin–Elmer 1600 Series FTIR (samples were rapidly prepared in air). $(C_6F_5)_2PBr$ was prepared from PBr_3 as described in the literature [10]. All other chemicals were obtained commercially (Aldrich, Fluorochem) and used as received. Perfluoro-(methylcyclohexane) was degassed by freeze–thaw cycles before use.

3.2. $(C_6F_5)_2PNHCH_2(CF_2)_6CF_3$ (**3**)

A solution of $(C_6F_5)_2PBr$ (0.509 g, 1.144 mmol) in diethyl ether (10 ml) was added slowly to a solution of 1H, 1H-pentadecafluorooctylamine (0.35 ml, 0.457 g, 1.144 mmol) and pyridine (0.090 g, 1.144 mmol) in diethyl ether (20 ml). After stirring overnight, the suspension was filtered (Schlenk filter stick) to remove Py·HCl and solvent was removed in vacuo to yield an air sensitive colourless powder of ca. 90% purity. The new ligand was purified by extraction with 10 ml PFMC and cannula filtration to remove the fluorous soluble ligand from the $(C_6F_5)_2P(OH)$ by product. Yield: 0.57 g, 0.747 mmol, 65%. Found: C, 32.5; H, 0.49; N, 1.86. $C_{20}H_3F_{25}PN$ req's C, 31.5; H, 0.40; N, 1.83%. IR (ν_{NH} 3444 cm^{-1}). ^{31}P-NMR (121.4 MHz; C_6D_6): δ: 11.4 (11 lines derived from quintet of triplets $^{3}J_{P-F}=34$, $^{4}J_{P-F}=14$ Hz. ^{1}H-NMR (300 MHz; C_6D_6): δ: 3.3 (1H, m, NH), 3.6 (2H, m, CH_2). ^{19}F-NMR (282.7 MHz; C_6D_6): δ: -81.4 (tt, $J=10.5$, 2.3 Hz), -120.1 (q app, $J=14.5$ Hz), -121.9 (m), -122.2 (s, br), -123.0 (m, br), -123.9 (s, br), -126.5 (m, *o*-ArF), -152.1 (tt, $J=20.3$, 3.5 Hz, *p*-ArF), -162 (m, *m*-ArF). EIMS 763 [M^{+}].

3.3. $[(C_6F_5)_2PNHCH_2(CF_2)_6CF_3]_4Rh_2Cl_2$ (**4**)

Tetrahydrofuran (5 ml) was added to a Schlenk tube containing $(C_6F_5)_2PNHCH_2(CF_2)_6CF_3$ (0.152 g, 0.199 mmol) and $[(cyclooctene)_2RhCl]_2$ (0.036 g, 0.05 mmol). The solvent was removed in vacuo after 0.5 h stirring, and the resulting red oil dissolved in PFMC (4 ml) and washed with warm toluene (3×5 ml). Removal of solvents in vacuo gave a red air sensitive powder. Yield: 0.120 g, 0.037 mmol, 75%. We have found that purified authentic samples of ligand **3** and complex **4** do not show repeatability (giving a range of values ca. 1% either side of calculated composition) when analysed. This situation, which persists even when the samples are run with Lead nitrate as an agent to break C–F bonds, is almost certainly due to incomplete combustion of the highly fluorinated compounds. This phenomenon is often observed in perfluorinated compounds. For example, Found: C, 28.5; H, 0.19; N, 2.25. $C_{80}H_{12}F_{100}P_4N_4Rh_2Cl_2$ req's C, 29.8; H, 0.37; N, 1.74. IR (ν_{NH} 3420 cm^{-1}). ^{31}P-NMR (121.4 MHz; C_4D_8O): δ: 56 (d, $^{1}J_{P-Rh}=224$ Hz). ^{1}H-NMR (300 MHz; C_4D_8O): δ: 4.1 (2H, m), 6.1 (1H, dt, $J_{H-P}=18.3$ Hz, $J_{H-H}=7.9$ Hz). ^{19}F-NMR (282.7 MHz; C_4D_8O): δ: -81.4 (t, $J=2.5$ Hz, CF_3), -118.5 (s, br), 122.0 (s, br),

−122.1 (s, br), −123.0 (s), −123.8 (s), −126.5 (s), −130 (s, very broad, *o*-ArF), −150 (t, $J = 5.7$ Hz, *o*-ArF, −162 (t app, $J = 5.0$ Hz, *m*-ArF).

3.4. $[(C_6F_5)_2PNHCH_2(CF_2)_6CF_3]_2RhCl(CO)$ (5)

Tetrahydrofuran (5 ml) was added to a Schlenk tube containing $(C_6F_5)_2PNHCH_2(CF_2)_6CF_3$ (0.122 g, 0.160 mmol) and $[Rh(CO)_2Cl]_2$ (0.016 g, 0.04 mmol). The solvent was removed in vacuo after 0.5 h stirring, and the resulting red oil dissolved in PFMC (4 ml) and washed with warm toluene (1 × 5 ml). The toluene phase was washed with PFMC (4 ml). The fluorous extracts were combined and solvent removed in vacuo to give an air sensitive yellow powder. Yield: 0.078 g, 0.046 mmol, 58%. Found: C, 29.2; H, 0.21; N, 1.80; $C_{80}H_{12}F_{100}P_4N_4Rh_2Cl_2$ req's C, 29.1; H, 0.36; N, 1.65%. IR (ν_{NH} 3424 cm^{-1}, $\nu_{(CO)} = 2001$ cm^{-1}). ^{31}P-NMR (121.4 MHz; C_4D_8O): δ: 47 (d, $^1J_{P-Rh} = 153$ Hz). ^{1}H-NMR (300 MHz; C_4D_8O): δ: 4.6 (2H, octet, ca. CH_2), 5.2 (1H, s, br NH). ^{19}F-NMR (282.7 MHz; C_4D_8O): δ: −77.7 (t, $J =$ 10 Hz, CF_3), −114.9 (t, $J = 13.6$ Hz), −117.2 (s, br), −118.3 (s, br), −118.6 (s, br), −119.3 (s, br), −122. 8 (m), −127.3 (d ca. $J = 19$ Hz), −143.1 (t, $J = 20$ Hz, *p*-ArF), −156.5 (dd, $J = 16.4$, 20.9 Hz, *m*-ArF). FABMS 1715 $[M+Na]^+$, 1692 $[M^+]$, 1680 $[M-Cl+Na]^+$, 1664 $[M-CO]^+$, 1657 $[M-Cl]^+$.

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