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# Towards the synthesis of perfluoroalkylated derivatives of Xantphos

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**Abstract**—An analogue of Xantphos incorporating four perfluoroalkyl groups has been prepared and successfully used as a ligand in the rhodium-catalysed hydroformylation of 1-octene in toluene. A number of perfluoroalkylated xanthene backbones have also been synthesised, but their conversion into preferentially perfluorocarbon solvent soluble Xantphos-type ligands, suitable for catalysis in fluorocarbon solvents, has not been successful.


## 1. Introduction

The fluorous biphasic approach has been shown to be a useful tool for the efficient separation of catalyst from products in the rhodium-catalysed hydroformylation of long chain alkenes,[1] amongst other catalytic reactions.[2] We have recently shown that $P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$ can be used in the rhodium-catalysed hydroformylation of 1-octene in the fluorous phase resulting in good selectivity to the required linear aldehyde with minimal rhodium leaching (0.05%) into the non-fluorous product phase on phase separation post reaction.[3] With a view to increasing the selectivity further, we investigated the perfluoroalkyl derivatives of analogues of established bidentate phosphines and phosphites that have been shown to offer excellent selectivity in this process.[4] Surprisingly, although a large number of perfluoroalkyl derivatised monodentate phosphorus(III) ligands, prepared by a variety of routes,[4] have been described in the literature, the number of perfluoroalkyl derivatised bidentate phosphorus(III) ligands is still relatively small with only those incorporating the ethyl backbone being perfluorocarbon soluble.[5] Xantphos has been shown to be a remarkable ligand for the rhodium-catalysed hydroformylation of long chain alkenes, giving exceptionally high selectivity to the industrially useful linear aldehyde (linear/branched ratio=50:1).[6] Here, we report our investigations directed towards the synthesis of perfluoroalkylated derivatives of Xantphos.

## 2. Results and discussion

The approach followed in this work draws upon precedents set in earlier Xantphos-[6] and fluorous-based[3] hydroformylation studies. The catalytic data available for Xantphos clearly shows that the bite angle of the bisphosphine is critical for the high selectivities achieved in the hydroformylation of long chain alkenes.[6] Therefore, in order to minimise the steric effects of the perfluoroalkyl groups, linear perfluoroalkyl groups directly attached to the aromatic rings in the *para* positions on the pendant arms ($R_1$ in Fig. 1) or the *meta* positions (for ease of synthesis) on the backbone ($R_2$) are likely to be the most successful. Indeed, water-soluble versions of Xantphos have incorporated sulfonate or dialkylamino groups in these positions.[7] Furthermore, although a wide range of perfluoroalkyl groups have been incorporated into phosphines, many include a so-called spacer group to ameliorate their electron-withdrawing effect. However, in the hydroformylation of alkenes, electron-withdrawing groups are known to lead to catalysts which give greater rates of reaction and higher ratios of linear/branched aldehydes in the final hydroformylation product mixtures than those with

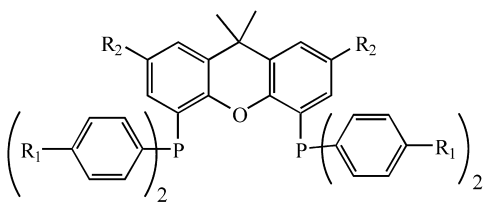


**Figure 1.** Xantphos skeleton, showing the sites where fluorinated side chains may be readily attached ($R_1$ and $R_2$).

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greater electron density.[3] We, therefore, decided to focus solely on ligands with linear perfluoroalkyl groups directly attached to the aromatic rings thereby maximising the electronic advantages of these fluorinated substituents.

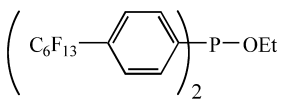



**Figure 2.** Bis(4-tridecafluoro-*n*-hexylphenyl) ethoxy phosphinite.

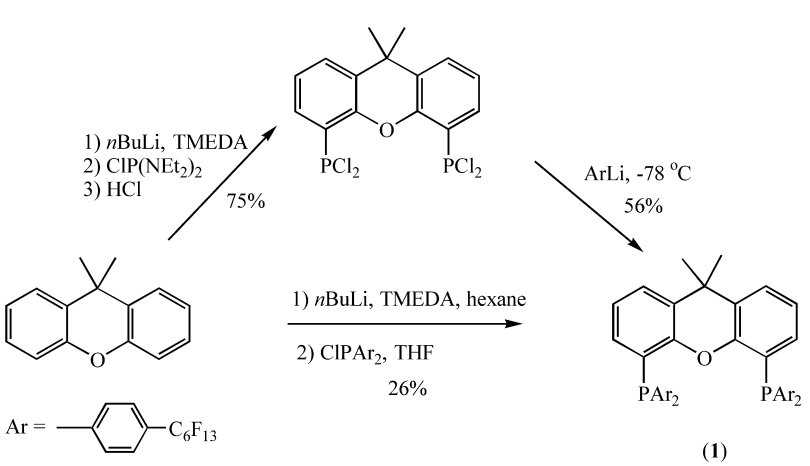
Although quenching the dilithiate of 9,9-dimethylxanthene with $Ph_2PCl$ gives reproducibly high yields of Xantphos, the analogous reaction with $ClP(C_6H_4\text{-}4\text{-}C_6F_{13})_2$[8] in diethyl ether resulted in the isolation of only trace amounts of the desired perfluoroalkylated Xantphos. Instead, bis(4-tridecafluoro-*n*-hexylphenyl) ethoxy phosphinite was isolated, Figure 2. Decomposition of ethereal solvents by organolithiates is a well-known process, giving, in the case of diethyl ether, lithium ethoxide and ethene.[9] Here, therefore, the isolated phosphinite results from the reaction between chlorophosphine and lithium ethoxide. We have detected, by $^{31}P$ NMR spectroscopy, an analogous reaction during the synthesis of Xantphos itself although, in this case, ethoxydiphenyl phosphinite is only formed in trace amounts. This difference in reactivity between the two chlorophosphines is undoubtedly due to the presence of the highly electron-withdrawing perfluoroalkyl groups in $ClP(C_6H_4\text{-}4\text{-}C_6F_{13})_2$. A 17% yield of the perfluoroalkylated Xantphos (**1**) could be achieved by carrying out the reaction in hexane, but the low solubility of the chlorophosphine in this solvent required its addition as a refluxing suspension. By adding the chlorophosphine in THF to the lithiate in hexane, a similar yield could be obtained, which could be increased to 26% by refluxing the solution for 30 min prior to the addition of the chlorophosphine, Scheme 1.

The yield was improved further by following an alternative method. 4,5-Bis[bis(diethylamino)phosphine]-9,9,-dimethylxanthene, prepared via the method of van Leeuwen et al.[10] was converted to 4,5-bis(dichlorophosphino)-9,9-dimethylxanthene by reaction with dry HCl in ether. Reaction of this chlorophosphine with the aryl lithiate derived from 4-(tridecafluoro-*n*-hexyl)bromobenzene gave the perfluoroalkylated Xantphos (**1**) in a 56% yield, Scheme 1.

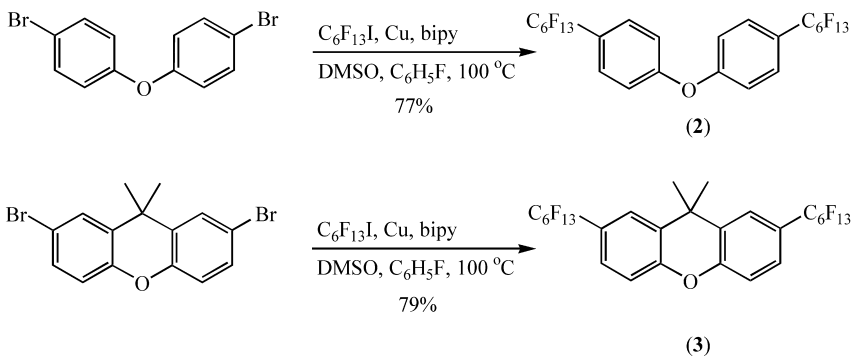
High fluorous phase solubility is required for the successful application of a ligand in a fluorous phase reaction. Previous work has suggested that 60% fluorine (w/w) is generally required for preferential solubility in a perfluorocarbon solvent over an organic solvent.[11] Although a single perfluoroalkyl group per aromatic ring is capable of generating a compound that is preferentially soluble, **1** has only 4 tails for 6 aromatic rings. With only 53.4% fluorine content it is, therefore, unsurprising that the perfluoroalkylated Xantphos (**1**) has a low solubility in perfluoro-1,3-dimethylcyclohexane (PP3). Partition coefficient determinations in a PP3/toluene biphase were complicated further by the low solubility of (**1**) in both phases. This low solubility has been previously noted for other high molecular weight fluorinated compounds. To increase the partition coefficient, the number of perfluoroalkyl groups on the molecule would need to be increased, which could be achieved by increasing the number of tails on the pendant arms. 3,5-Bis-substitution has been used in other ligand systems, but this has a dramatic influence on their steric properties, which would seriously compromise the high selectivity of Xantphos-based hydroformylation catalysts. Alternatively, using a silicon spacer unit, up to three tails per phenyl ring could be introduced. However, as illustrated by van Koten et al.[12] with a molecular weight in excess of 4500 Da, the absolute solubility of such a ligand in any solvent would be so low as to obviate its use in catalysis.

Therefore, to increase the percentage fluorine further, derivatising the xanthene backbone at position $R_2$ (Fig. 1) is likely to be the only viable approach. Perfluoroalkyl groups can be incorporated at position $R_2$ most simply by converting bis(4-bromophenyl)ether to bis(4-tridecafluoro-*n*-hexylphenyl)ether (**2**) by a copper mediated coupling reaction with $C_6F_{13}I$ which affords the desired product in a 77% yield. Similarly, 2,7-dibromo-9,9-dimethylxanthene (prepared by direct bromination of 9,9-dimethylxanthene) was converted to 2,7-bis(tridecafluoro-*n*-hexyl)-9,9-dimethylxanthene (**3**) in a 79% yield, Scheme 2.

Direct lithiation of (**2**) or (**3**) at room temperature (CAUTION! Lithiations of aromatic rings substituted with perfluoroalkyl groups have been reported to lead to explosion)[13] followed by quenching with $ClPPh_2$ in ether




**Scheme 1.**



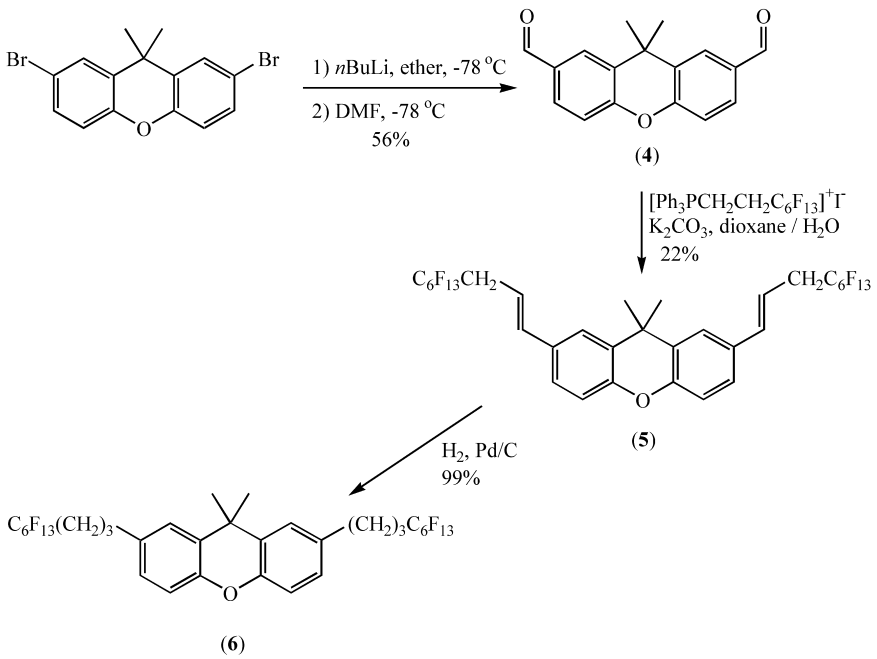

**Scheme 2.**

led to an inseparable mixture of phosphines being formed. The desired bisphosphine could be detected by $^{31}P$ NMR spectroscopy in each case, but could only be isolated in the case of (**2**). Even then, the bisphosphine could only be isolated with a purity of 90%. In each case, in addition to lithiating *ortho* to the oxygen, as occurs with 9,9-dimethylxanthene, lithiation *ortho* to the perfluoroalkyl group also occurs as evidenced by the strong P–F coupling in the $^{31}P$ NMR spectra of the quenched product.[8] It is apparent that the strongly electron-withdrawing perfluoroalkyl groups are having a profound effect on the regioselectivity of the lithiation. The most obvious way to solve this problem is to introduce a spacer between the perfluoroalkyl chain and the aromatic ring and there are numerous suitable groups now available.[12,14] We introduced an alkyl spacer group by conversion of 2,7-dibromo-9,9-dimethylxanthene to 9,9-dimethylxanthene-2,7-dicarbaldehyde (**4**), followed by a Wittig reaction with $[Ph_3PCH_2CH_2C_6F_{13}]^+I^-$ following the known methodology.[15] After hydrogenation with Pd/C in DCM, 2,7-bis(*1H*,*1H*,*2H*,*2H*,*3H*,*3H*-perfluorononanyl)-9,9-dimethylxanthene (**6**) could be isolated in an overall yield of 12% from the dibromoxanthene, Scheme 3.

Unfortunately, repeated attempts at lithiating **6**, followed by quenching with $Ph_2PCl$, failed to yield any of the desired product. Despite a strong colour change upon the addition of *n*-BuLi, the starting xanthene was recovered unchanged after reaction, along with a small amount of a product, the $^{19}F$ NMR spectrum of which suggested attack at or near the perfluoroalkyl groups had occurred. This infers that, rather than deprotonating the aromatic ring, lithiation of the alkyl spacer group had occurred.

## 2.1. Catalysis

The effect of the perfluoroalkyl groups on the donor ability of the phosphorus atoms has been probed previously by examination of the change in $^1J_{PPt}$ of the *cis*-[PtCl-$_2$-L] (L=bidentate or two monodentate phosphines).[5b] As can be seen from Table 1, perfluoroalkylated Xantphos (**1**) shows a similar trend to $(C_6H_4\text{-}4\text{-}C_6F_{13})_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}C_6F_{13})_2$ with a decrease in the magnitude of $^1J_{PPt}$ as expected following the introduction of strongly electron-withdrawing groups.




**Scheme 3.**

**Table 1**. Pt–P coupling constants for platinum complexes containing bidentate ditertiary phosphines

| Complex | $^1J_{PtP}$ (Hz) |
|---|---|
| *cis*-[$PtCl_2$(dppe)][a] | 3594 |
| *cis*-[$PtCl_2${($CH_2P(C_6H_4$-4-$C_6F_{13})_2$}$_2$][a] | 3568 |
| [$PtCl_2$(Xantphos)][b] | 3694 |
| [$PtCl_2$(**1**)][b] | 3662 |

[a] $CD_3COCD_3$, data from Ref. 5b.
[b] $CDCl_3$.

Although **1** does not have sufficiently high perfluorocarbon solubility for use in a fluorous biphasic reaction, it can be successfully used as a ligand in the rhodium catalysed hydroformylation of 1-octene in toluene. We rationalised that the fluoroalkyl groups should have a beneficial effect in this reaction, since electron-withdrawing groups have been shown by others to increase rates of reaction and selectivity in such reactions.[16] Hydroformylation of 1-octene was carried out at 80 °C and 20 bar of 1:1 $CO/H_2$ using 2.2 equiv. of **1** with respect to rhodium. The results are shown in Table 2 and compared to the same reaction carried out with Xantphos. As with Xantphos, the selectivity for the required linear aldehyde is relatively high (linear aldehyde/branched aldehyde=22.9:1 compared to 4.7:1 for P(4-$C_6F_{13}C_6H_4)_3$). However, the isomerisation is greater when **1** is used compared with Xantphos. These findings mirror those found elsewhere for derivatives of thixantphos, where isomerisation to the 2-octene increased as phosphine basicity decreased.[16c] This has been attributed to an increased tendency of the branched alkyl rhodium species to form 2-octene instead of the branched aldehyde. A possible alternative explanation is that the poorer donor ability and larger size of **1** compared with Xantphos may reduce its coordinating power and leave some rhodium uncoordinated to the phosphine. This type of complex is a known alkene isomerisation catalyst, but is poorly selective and rather sluggish in hydroformylation reactions under these conditions. Support for this suggestion comes from the observation that lower loadings of ligand (**1**:Rh=1.7) give much lower linear/branched ratios and significant amounts of aldehydes derived from isomerised alkenes. The rhodium–Xantphos complexes are essentially inactive for the hydroformylation of internal alkenes. This last experiment was carried out in perfluoromethylcyclohexane. This is unlikely to be a medium effect, since our previous work has shown that triphenylphosphine is more selective when the reaction is carried out in a perfluorocarbon solvent as compared to toluene.[3b] At the end of the reaction, both organic and fluorous phases were yellow in colour, confirming that **1** is insufficiently fluorinated to immobilise the catalyst completely within the fluorous phase.

## 3. Conclusion

This work has shown the difficulties in attempting to generate a perfluorocarbon soluble analogue of a known bisphosphine, although a number of new perfluoroalkylated intermediates have been prepared and fully characterised. A derivative of Xantphos has been prepared incorporating four perfluoroalkyl groups. Unfortunately, this is not sufficient to render the bisphosphine preferentially soluble in a perfluorocarbon solvent and attempts at further derivatising this compound have failed. However, the derivatised Xantphos is still an effective ligand for the rhodium catalysed hydroformylation of 1-octene in toluene, offering good selectivity to the desired linear aldehydes but the fluorous groups appear to effect the amount of isomerisation.

## 4. Experimental

### 4.1. General Remarks

$^1H$, $^{19}F$ and $^{31}P$ NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DPX300 spectrometer at 300.14, 282.41 and 121.50 MHz respectively and were referenced to external $SiMe_4$ ($^1H$), external $CFCl_3$ ($^{19}F$) and to external $H_3PO_4$ ($^{31}P$) using the high frequency positive convention. Due to the complicated spectra arising from the extensive coupling to the fluorine atoms, all $^{13}C$ NMR are quoted without the values for the perfluoroalkyl groups (105–120 ppm). Abbreviations for NMR spectral multiplicities are as follows: s=singlet, d=doublet etc., m=multiplet. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. *cis*-[$PtCl_2(MeCN)_2$][17] and 4-(tridecafluoro-*n*-hexyl)bromobenzene[18] were prepared by the literature routes. 4,5-Bis(diethylaminophosphino)-9,9-dimethylxanthene was prepared via the method of Goertz et al.[11] [$Ph_3PCH_2CH_2C_6F_{13}$]$^+I^-$ was prepared via the method of Rocaboy et al.[15]

**4.1.1. 4,5-Bis(dichlorophosphino)-9,9-dimethylxanthene.** 4,5-Bis(diethylaminophosphino)-9,9-dimethylxanthene (0.98 g, 1.76 mmol) was dissolved in ether (30 mL). Concentrated HCl was bubbled through the solution for 15 min. The solution was then flushed with nitrogen for 2 h, filtered through celite and the solvent removed in vacuo to give a white solid (0.54 g, 75%). Anal. calcd for $C_{15}H_{12}OP_2Cl_4$: C, 43.90; H, 2.93. Found: C, 44.02; H,

**Table 2**. Products from the hydroformylation of 1-octene catalysed by rhodium complexes of Xantphos based ligands in toluene at 80 °C and 20 bar $CO/H_2$ (1:1)

| Ligand | Ligand/Rh | 1-Nonanal (%) | 2-Methyloctanal (%) | % Isomer[a] | l:b[b] | $k$ ($s^{-1}$)[c] |
|---|---|---|---|---|---|---|
| Xantphos | 2.2 | 82.1 | 1.9 | 3.4 | 43.5 | $1.2\times10^{-4}$ |
| **1** | 2.2 | 81.0 | 3.5 | 11.5 | 22.9 | $1.2\times10^{-4}$ |
| **1**[d] | 1.7 | 65.6 | 17.7 | 15.5 | 3.7 | $5.0\times10^{-4}$ |

[a] Percentage isomerisation to 2-octene.
[b] Linear over branched ratio.
[c] First order rate constant calculated from gas up take plots at constant pressure.
[d] In perfluoromethylcyclohexane.

2.92. *m/z* (EI): 412 ($MH^+$). $^1H$ NMR ($C_6D_6$) 7.80 (2H, dd, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=1.8 Hz, H3), 6.96 (2H, dd, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=1.8 Hz, H1), 6.79 (2H, t, $^3J_{HH}$=7.6 Hz, H2) 1.07 (6H, s, $CH_3$). $^{31}P\{^1H\}$ NMR ($C_6D_6$) 158.9 (s). $^{13}C$ NMR ($C_6D_6$) 150.8 (t, $J_{PC}$=13.5 Hz), 130.7, 130.4, 129.2, 128.3, 123.4, 34.4, 31.4.

**4.1.2. 4,5-Bis-(bis(4-tridecafluoro-*n*-hexyl-phenyl)phosphino)-9,9-dimethylxanthene (1).** 4-(Tridecafluoro-*n*-hexyl)bromobenzene (1.44 g, 3.03 mmol) was dissolved in diethyl ether (20 mL) under nitrogen and cooled to −78 °C. *n*-BuLi (1.9 mL of a 1.6 M solution in hexane, 3.04 mmol) was added over 1 h and the solution stirred for 4 h at −78 °C. 4,5-Bis(dichlorophosphino)-9,9-dimethylxanthene (0.31 g, 0.76 mmol) in diethyl ether (20 mL) was then added dropwise and the solution allowed to warm to room temperature overnight. Water was then added (30 mL), the organic solution separated and dried. The solvent was removed in vacuo to give a yellow solid. This was washed with perfluoro-1,3-dimethylcyclohexane (3×10 mL) to give a white solid (0.372 g, 27%). By repeatedly cooling the perfluoro-1,3-dimethylcyclohexane solution to −40 °C, a further 0.294 g of 4,6-bis-{bis(4-tridecafluoro-*n*-hexyl-phenyl}phosphino)-9,9-dimethylxanthene was collected (21%). *m/z* (FAB) 1851 ($MH^+$). Anal. calcd for $C_{63}H_{28}OP_2F_{52}$: C, 40.86; H, 1.51. Found: C, 40.76; H, 1.54. $^1H$ NMR ($C_6D_6$) 7.51–7.21 (18H, m, ArH), 6.97 (2H, t, $^3J_{HH}$=7.6 Hz, H2), 6.76 (2H, dd, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=1.6 Hz, H3), 1.62 (6H, s, $CH_3$). $^{19}F\{^1H\}$ NMR ($C_6D_6$) −81.45 (12F, t, $^4J_{FF}$=10.6 Hz, $CF_3$), −110.63 (8F, t, $^4J_{FF}$=14.6 Hz, α-$CF_2$), −121.78 (16F, m, $CF_2$), −123.14 (8F, m, $CF_2$), −126.41 (8F, m, $CF_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$) −18.2.

**4.1.3. 4,4′-Bis(tridecafluoro-*n*-hexyl)phenyl ether (2).** Perfluoro-*n*-hexyl iodide (55.31 g, 124.0 mmol) was added to a stirred solution of *para*-dibromodiphenyl ether (10.03 g, 30.6 mmol), copper bronze (15.75 g, 247.8 mmol) and 2,2′-bipyridine (1.34 g, 9.0 mmol) in DMSO (200 mL) and fluorobenzene (120 mL) under nitrogen at 100 °C. The solution was stirred for 3 days, cooled and poured on to an diethyl ether (300 mL)/water (300 mL) mixture and filtered. The organic layer was separated and washed three times with water, dried and the solvent removed in vacuo. The resulting yellow oil crystallised on standing and was washed with methanol to give a white powder (19.00 g, 77%). Mp 59–61 °C. Anal. calcd for $C_{24}H_8OF_{26}$ C, 35.73; H, 0.99. Found: C, 35.80; H, 0.96. *m/z* (FAB): 806 ($M^+$). $^1H$ NMR ($CDCl_3$) 7.59 (4H, d, $^3J_{HH}$=8.7 Hz, H3), 7.15 (4H, d, $^3J_{HH}$=8.7 Hz, H2); $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.29 (6F, t, $^4J_{FF}$=9.3 Hz, $CF_3$), −110.52 (4F, t, $^4J_{FF}$=14.6 Hz, $CF_2$), −121.89 (4F, m, $CF_2$), −122.27 (4F, m, $CF_2$), −123.25 (4F, m, $CF_2$), −126.59 (4F, m, $CF_2$).

**4.1.4. Bis[(2-diphenylphosphino-4-tridecafluoro-*n*-hexyl)-phenyl]ether.** 4,4′-Bis(tridecafluorohexyl)phenyl ether (0.81 g, 1.0 mmol) was dissolved in diethyl ether (30 mL). TMEDA (0.24 g, 2.1 mmol) was added, followed by *n*-BuLi (1.25 mL of a 1.6 M solution in hexane, 2.0 mmol) dropwise (CAUTION! Lithiations of aromatic rings substituted with perfluoroalkyl groups have been reported to lead to explosions[13]). The resulting red solution was stirred for 3 h and then quenched with chlorodiphenyl phosphine (0.44 g, 2.0 mmol). After stirring overnight, the solution was quenched with water, the organic layer removed, dried with sodium sulfate and the solvent removed in vacuo. The resulting semi-solid was passed down a short silica column to give a yellow solid (87% pure by NMR, 0.36 g, 31%). *m/z* (FAB): 1175 ($MH^+$). $^1H$ NMR ($CDCl_3$) 7.25 (2H, s, H5), 7.17 (8H, m, ArH), 7.05 (2H, d, $^3J_{HH}$=9.0 Hz, H2), 6.91 (12H, m, ArH), 6.29 (2H, dd, $^3J_{HH}$=9.4 Hz, $^4J_{HH}$=3.5 Hz, H3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.39 (6F, t, $^4J_{FF}$=8.5 Hz, $CF_3$), −110.52 (4F, t, $^4J_{FF}$=14.1 Hz, α-$CF_2$), −121.82 (4F, m, $CF_2$), −122.54 (4F, m, $CF_2$), −123.60 (4F, m, $CF_2$), −126.69 (4F, m, $CF_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) −15.5 (s).

**4.1.5. 2,7-Dibromo-9,9-dimethylxanthene.** Bromine (0.51 mL, 10.0 mmol) in glacial acetic acid (1 mL) was added slowly to a stirred solution of 9,9-dimethylxanthene (0.843 g, 4.00 mmol) in acetic anhydride (10 mL) at 0 °C. The solution was then allowed to warm to room temperature and stirred for 2 h. The solution was then poured onto an excess of ice-cold water and the precipitate collected by filtration. The white solid was washed with sodium bisulfate (10% aqueous solution) and water and dried in vacuo (1.33 g, 90%). Anal. calcd for $C_{15}H_{12}OBr_2$: C, 48.95; H, 3.29. Found: C, 49.03; H, 3.19. Mp 113–115 °C. *m/z* (FAB): 368 ($[M]^+$). $^1H$ NMR ($CDCl_3$) 7.59 (2H, d, $^4J_{HH}$=2.3 Hz, H1), 7.40 (2H, dd, $^3J_{HH}$=8.7 Hz, $^4J_{HH}$=2.3 Hz, H3), 7.03 (2H, d, $^3J_{HH}$=8.7 Hz, H4), 1.70 (6H, s, $CH_3$). $^{13}C$ NMR ($CDCl_3$) 149.6, 132.0, 130.9, 129.4, 118.7, 116.1, 34.9, 32.6.

**4.1.6. 2,7-Bis(tridecafluoro-*n*-hexyl)-9,9-dimethylxanthene (3).** Tridecafluoro-*n*-hexyl iodide (4.82 g, 10.8 mmol), 2,7-dibromo-9,9-dimethylxanthene (1.00 g, 2.7 mmol), 2,2′-bipyridine (0.12 g, 0.8 mmol) and copper bronze (1.37 g, 21.6 mmol) were heated to 100 °C in DMSO (40 mL) and fluorobenzene (40 mL) for 4 days. The cooled solution was poured onto a mixture of diethyl ether (100 mL) and water (100 mL), filtered and the organic layer washed three times with water. After drying, the solvent was removed in vacuo and the resulting yellow solid triturated with methanol, giving a white solid, which was recovered by filtration (1.80 g, 79%). Anal. calcd for $C_{27}H_{12}OF_{26}$: C, 38.30; H. 1.42. Found: C, 38.29; H, 1.42. Mp 84–85 °C. *m/z* (FAB): 846 ($M^+$). $^1H$ NMR ($CDCl_3$) 7.55 (2H, bs, H1), 7.38 (2H, dd, $^3J_{HH}$=8.5 Hz, $^4J_{HH}$=1.6 Hz, H3), 7.11 (2H, d, $^3J_{HH}$=8.5 Hz, H4), 1.60 (6H, s, $CH_3$); $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.32 (6F, t, $^4J_{FF}$=10.6 Hz, $CF_3$), −110.58 (4F, t, $^4J_{FF}$=14.6 Hz, $CF_2$), −121.89 (4F, m, $CF_2$), −122.38 (4F, m, $CF_2$), −123.26 (4F, m, $CF_2$), −126.60 (4F, m, $CF_2$). $^{13}C$ NMR ($CDCl_3$) 152.8, 130.4, 127.0, 125.9, 125.0, 124.6, 124.2, 117.4, 34.6, 32.9.

**4.1.7. 9,9-Dimethylxanthene-2,7-dicarbaldehyde (4).** 2,7-Dibromo-9,9-dimethylxanthene (1.40 g, 3.80 mmol) was dissolved in diethyl ether (100 mL) and cooled to −78 °C. *n*-BuLi (5.10 mL of a 1.6 M solution in hexane, 8.16 mmol) was added over 30 min and the solution allowed to warm to room temperature over 90 min. After stirring for 4 h at room temperature, the solution was cooled to −78 °C and *N*,*N*-dimethylformamide (3.00 mL, 38.79 mmol) added. The solution was allowed to warm to room temperature overnight to give a yellow solution with a white precipitate. This was hydrolysed (100 mL), the organic layer separated, dried with sodium sulfate and the solvent removed in vacuo.

The yellow solid was recrystallised from ethanol to give a yellow solid (0.57 g, 56%). Mp 109–110 °C. *m/z* (FAB): 267 ($MH^+$). HRMS (FAB) 267.1022. Calcd for $C_{17}H_{14}O_3$ 267.1021. $^1$H NMR ($CDCl_3$) 9.88 (2H, s, CHO), 7.93 (2H, d, $^4J_{HH}$=1.8 Hz, H1), 7.70 (2H, dd, $^3J_{HH}$=8.3 Hz, $^4J_{HH}$= 1.8 Hz, H3), 7.14 (2H, d, $^3J_{HH}$=8.3 Hz, H4), 1.65 (6H, s, $CH_3$). $^{13}$C NMR ($CDCl_3$) 191.1, 154.6, 133.2, 130.8, 128.9, 117.9, 34.6, 31.4.

**4.1.8. 2,7-Bis(*1H,2H,3H,3H*-perfluorononon-1-enyl)-9,9-dimethylxanthene (5).** 9,9-Dimethylxanthene-2,7-dicarbaldehyde (3.30 g, 12.41 mmol), $[Ph_3PCH_2CH_2C_6F_{13}]^+I^-$ (20.13 g, 27.35 mmol) and potassium carbonate (4.46 g, 32.09 mmol) were heated to 110 °C for 3 days in dioxane (90 mL) and water (3 mL). After cooling, the solvent was removed in vacuo, the solid redissolved in dichloromethane (100 mL) and washed well with water. After drying with magnesium sulphate, the solvent was removed in vacuo and passed through a silica plug with hexane. The solvent was removed in vacuo to give a white glass (2.57 g, 22%). b.p. 202 °C at 0.05 mm Hg. Anal. calcd for $C_{33}H_{20}OF_{26}$: C, 42.77; H, 2.16. Found: C, 42.81; H, 2.17. *m/z* (FAB): 925 (M−H). $^1$H NMR ($CDCl_3$) 7.23 (2H, m, H1), 6.99 (4H, m, H2, H3), 6.75 (2H, d, $^3J_{HH}$=11.4 Hz, C*H*Ar), 5.63 (2H, dt, $^3J_{HH}$=11.4 Hz, $^3J_{HH}$=7.3 Hz, C*H*$CH_2$), 3.02 (td, $^3J_{HF}$= 18.4 Hz, $^3J_{HH}$=7.3 Hz, $CH_2$), 1.55 (6H, s, $CH_3$); $^{19}$F{$^1$H} NMR ($CDCl_3$) −81.27 (6F, t, $^4J_{FF}$=8.5 Hz, $CF_3$), −113.54 (4F, t, $^4J_{FF}$=14.2 Hz, α-$CF_2$), −122.37 (4F, m, $CF_2$), −122.39 (4F, m, $CF_2$), −123.68 (4F, m, $CF_2$), −126.66 (4F, m, $CF_2$). $^{13}$C NMR ($CDCl_3$) 150.0, 135.7, 131.3, 130.2, 128.8, 126.8, 119.5, 118.0, 34.3, 32.6, 30.9 (t, $^2J_{CF}$= 22.2 Hz).

**4.1.9. 2,7-Bis(*1H,1H,2H,2H,3H,3H*-perfluorononanyl)-9,9-dimethylxanthene (6).** 2,7-Bis(*1H,2H,3H,3H*-perfluorononon-1-enyl)-9,9-dimethylxanthene (2.50 g, 2.70 mmol) was dissolved in dichloromethane (75 mL) and palladium on charcoal (0.25 g) added. The mixture was stirred overnight under an atmosphere of hydrogen and then filtered through a celite plug. The solvent was removed to give a white solid (2.49 g, 99%). Mp 101–102 °C. Anal. calcd for $C_{33}H_{24}OF_{26}$: C, 42.58; H, 2.58. Found: C, 42.63; H, 2.51. *m/z* (FAB): 929 (M−H). $^1$H NMR ($CDCl_3$) 7.11 (2H, m, H1), 6.90 (4H, m, H2, H3), 2.61 (2H, t, $^3J_{HH}$= 7.1 Hz, $CH_2$), 1.88 (4H, m, $CH_2CH_2$), 1.54 (6H, s, $CH_3$). $^{19}$F{$^1$H} NMR ($CDCl_3$) −81.40 (6F, t, $^4J_{FF}$=10.0 Hz, $CF_3$), −114.57 (4F, t, $^4J_{FF}$=13.9 Hz, α-$CF_2$), −122.41 (4F, m, $CF_2$), −122.38 (4F, m, $CF_2$), −124.02 (4F, m, $CF_2$), −126.65 (4F, m, $CF_2$). $^{13}$C NMR ($CDCl_3$) 148.1, 134.1, 129.0, 128.1, 126.3, 115.5, 33.6, 33.1, 31.2, 29.2 (t, $^2J_{CF}$= 22.3 Hz), 21.1.

**4.1.10. [{4,5-Bis-(bis(4-tridecafluoro-*n*-hexyl-phenyl)-phosphino)-9,9-dimethylxanthene}$PtCl_2$].** A slurry of *cis*-[$PtCl_2(MeCN)_2$] (0.009 g, 0.027 mmol) and 4,5-bis-(bis(4-tridecafluoro-*n*-hexyl-phenyl)phosphino)-9,9-dimethylxanthene (0.050 g, 0.027 mmol) in dichloromethane (20 mL) was heated to reflux for 15 h in a sealed tube under nitrogen to give a clear solution. After cooling, the solvent was removed in vacuo and the resulting solid was washed well with petroleum ether and dried in vacuo to give a white solid (0.024 g, 42%). Anal. calcd for $C_{63}H_{28}OP_2Cl_2F_{52}Pt$: C, 35.74; H, 1.32. Found: C, 35.69; H, 1.26. *m/z* (FAB): 2081 (M−Cl). $^1$H NMR ($CDCl_3$) 7.66 (2H, d, $^3J_{HH}$=7.1 Hz, H3), 7.49 (8H, m), 7.29 (12H, m), 1.49 (6H, s, $CH_3$). $^{19}$F{$^1$H} NMR ($CDCl_3$) −81.38 (12F, t, $^4J_{FF}$=8.5 Hz, $CF_3$), −112.50 (4F, m, $CF_2$), −112.68 (4F, m, $CF_2$), −122.11 (8F, m, $CF_2$), −122.99 (8F, m, $CF_2$), −123.49 (8F, m, $CF_2$), −126.85 (8F, m, $CF_2$). $^{31}$P{$^1$H} NMR ($CDCl_3$) 7.5 (s, $^1J_{PtP}$=3674 Hz).

**4.1.11. [{Xantphos}$PtCl_2$].** Prepared as above from Xantphos (0.139 g, 0.24 mmol) and *cis*-[$PtCl_2(MeCN)_2$] (0.083 g, 0.24 mmol) giving the product as a white powder (0.183 g, 90%). Anal. calcd for $C_{39}H_{32}OP_2Cl_2Pt$: C, 55.45; H, 3.79. Found: C, 55.39; H, 3.61. *m/z* (FAB): 844 ($M^+$). $^1$H NMR ($CDCl_3$) 7.80 (2H, d, $^3J_{HH}$=7.3 Hz, H3), 7.70–7.10 (24H, m), 2.04 (6H, s, $CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$) 5.90 (s, $^1J_{PtP}$=3694 Hz).

### 4.2. Catalysis

An autoclave, fitted with a substrate injector containing 1-octene (1.0 mL, 6.37 mmol), a mechanical stirrer, a gas delivery system, an injection port and a thermocouple was flushed with $CO/H_2$ (1:1) to remove air. Degassed toluene (4.0 mL) containing dicarbonyl(2,4-pentanedionato)-rhodium(I) ([Rh(acac)$(CO)_2$], 0.01 mmol) and ligand (2 or Xantphos) (0.022 mmol) was added through the injection port against a stream of $CO/H_2$ using a syringe. The autoclave was pressurised with $CO/H_2$ (1:1) to 20 bar and the pressure released. This flushing procedure was repeated twice more. It was repressurised to 16 bar, the stirrer was started (600 rpm) and the autoclave was heated to 80 °C for 45 min. The 1-octene was then added to the autoclave by forcing it in through the substrate injector using a $CO/H_2$ pressure of 20 bar. The data recorder was started and the temperature, pressure in the autoclave and pressure in a ballast vessel, from which gas was fed into the autoclave through a mass flow controller to keep the pressure within the autoclave constant at 20 bar, were monitored and recorded every 5 s. After gas uptake had become very slow (5–8 h), the stirrer was stopped and the autoclave was allowed to cool. The gases were vented and the mixture was syringed into a sample vial for analysis by GC. Kinetic data were obtained from an analysis of the pressure drop in the ballast vessel. A similar reaction was carried out but using 2 (0.017 mmol) in perfluoromethylcyclohexane (4.0 mL). The resulting product consisted of two phases, both of them yellow. GC analysis was carried out on the upper phase.

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