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**Coordination Chemistry with Phosphine and Phosphine Oxide-Substituted
Hydroxyferrocenes**

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Abstract: New unsymmetrical hydroxyferrocenes were synthesised from dibromoferrocene. The oxygen heteroatom was introduced via lithiation and quenching with bis-trimethylsilylperoxide followed by hydrolysis to unmask the hydroxyl functionality. The coordination chemistry of 1'-(hydroxy)ferrocenediyl diphenylphosphine **2** was explored with palladium and rhodium precursors. A dinuclear palladium methyl complex with bridging ferrocenyloxo groups was obtained from the reaction between **2** and (cyclooctadiene)methylchloropalladium(II). With tetracarbonyldichlorodirrhodium(I), two complexes were isolated. The major product was a bis ligand *cis* phosphine ligated complex with one ligand bound in a chelating mode and one with a pendant hydroxyl group. A minor product was crystallographically characterised as a dinuclear ferrocenyloxo bridged rhodium carbonyl complex. The coordination chemistry of **2** and the corresponding phosphine oxide **3** was examined with group 4 metals and the resulting complexes examined as ethylene polymerisation catalysts. The ligands were found to bind in either a chelating fashion or with pendant phosphine donors. In all cases, low to moderately active ethylene polymerisation catalysts were found. The catalysts seemed to be very unstable and catalyst residues were observed in the isolated polymer indicating a short catalyst lifetime.

Introduction

The synthesis of ferrocenyl ligands featuring one or more donor heteroatoms has received a great deal of attention in recent years and extensive studies into their coordination chemistry and applications within catalysis have been undertaken.^{1,2} As well as providing a rigid ligand framework with a wide bite angle, the electronic (redox) properties of the ferrocene unit provides the possibility of electrochemically controlling the reactivity and binding at a metal centre.³ Planar chiral unsymmetrically 1,2-disubstituted ferrocenes have found wide applications in asymmetric catalysis and symmetrical 1,1'-disubstituted ferrocenes are

common bidentate ligands in coordination chemistry (1,1'-bis{diphenylphosphino}ferrocene being employed most prevalently).^{2,4} Unsymmetrically 1,1'-disubstituted ferrocenes featuring hetero-combinations of N, P, S or O atoms, usually formed *via* bromo,^{5,6} lithio^{7,8} or stannyl⁹ intermediates, have received increasing attention in recent years. Ferrocene compounds containing hydroxyl-substituents and their application in coordination chemistry are rare: their tendency to decompose in air to cyclopentenone species makes their synthesis and handling a challenge.¹⁰ We have recently published the synthesis of novel 1,1'- P/O ferrocenyl ethers (**1**)¹¹ and hydroxyferrocenes (**2**, **3**).¹² The use of bis(trimethylsilyl)peroxide in the preparation of metallocenyl hydroxides^{12,13} and trimethylsilylethers¹⁴ has allowed the convenient preparation of these substituted hydroxyferrocenes. Favourable intermolecular hydrogen-bonding interactions were thought to stabilise these hydroxyferrocenes allowing their structural characterisation and coordination chemistry to be investigated. Despite recent improvements to the synthesis of hydroxyferrocenes, examples of their coordination complexes remain rare. A Pd complex of 1,1'-bis(hydroxy)ferrocene has been reported showing Fe-Pd dative bonding.¹⁵ 1,3-Dioxa-[3]-ferrocenophanes have been synthesised by the reaction of 1,1'-bis(hydroxy)ferrocene with phosphorus, arsenic, antimony and boron dihalides.¹⁶ The only examples of coordination complexes with unsymmetrical hydroxyferrocenes are a square planar Pd complex of 2-[(dimethylamino)methyl]-1-hydroxyferrocene¹⁷ and a nickel(II) complex of **2** reported in a preliminary communication.¹²

Results and discussion

We report an improved procedure for the preparation of 1'-(hydroxy)ferrocenediylidiphenylphosphine oxide **3**. Although the previously reported procedure was reproducible on small scales (to produce up to 0.10 g of **3**), attempts to synthesise larger amounts resulted in failure and only small amounts of **3** could be isolated.

It was found that **3** was not particularly soluble in water and even less so in aqueous potassium hydroxide solution, meaning that it was difficult to isolate large amounts using the aqueous extraction method previously described. **3** may be synthesised more successfully from 1'-(Bromo)ferrocenediyl(diphenylphosphine) oxide.¹⁸ 1'-(Bromo)ferrocenediyl(diphenylphosphine) oxide was lithiated in THF at -78°C before bis(trimethylsilyl)peroxide was added dropwise slowly. The mixture was stirred for one hour before being warmed to room temperature and stirred overnight. The THF was removed and the product purified via column chromatography to give **3** in 40% yield as a yellow powder.

Rh & Pd complexes

The coordination chemistry of **2** was examined with palladium precursors with a view to synthesising a complex that might be suitable for testing as an ethylene polymerisation catalyst. Cationic palladium(II) methyl complexes stabilised by acetonitrile and coordinated by either N/N α -diimine ligands¹⁹ or P/O β -ketophosphine ligands²⁰ have been shown to be competent ethylene polymerisation catalysts by Brookhart and co-workers. Since **2** is an anionic ligand, it was thought that a similar neutral palladium(II) methyl complex stabilised by acetonitrile could be formed by reaction of the sodium salt of **2** with (cyclooctadiene)methylchloropalladium(II) in acetonitrile solvent. The sodium salt of **2** was dissolved in acetonitrile and added to a solution of (1,5-cyclooctadiene)methylchloropalladium(II) in acetonitrile. The reaction mixture was stirred at 35°C for 15 hours after which time a brown pearlescent precipitate was visible. The solvent was removed and the residue extracted with CH₂Cl₂. The solution was then concentrated and the product precipitated by the addition of heptane. Analysis of the product showed that a ferrocenyloxo-bridged dimeric Pd complex $[(C_5H_4PPh_2FeC_5H_4-\mu-O)PdMe]_2$ **4** had been formed in 44% yield as shown in Scheme 1 suggesting that the coordinating strength of

acetonitrile is not strong enough to prevent dimer formation. A similar complex has previously been reported with the corresponding thiol ligand.⁶ The ¹H NMR spectrum of **4** shows a doublet at -0.11 ppm corresponding to the Pd-Me protons. The signal is split into a doublet due to coupling to the phosphorus atom; the ³J_{P-H} coupling constant is 2.22 Hz - a value consistent with the *cis* configuration of the phosphine and methyl groups. The cyclopentadienyl protons show four pseudo-triplets as expected for a 1,1'- unsymmetrically disubstituted ferrocene. The ³¹P{¹H} NMR spectrum shows a single resonance at +34.5 ppm which is similar to the previously reported P/S⁻ complex [(C₅H₄PPh₂FeC₅H₄-μ-S)PdCl]₂ which gives a signal at +27.3 ppm.⁶ The positive ion FAB mass spectrum does not show the molecular ion but shows the expected fragmentation pattern due to cleavage of the dimeric complex into two fragments (506 amu) followed by loss of the methyl group (491 amu). Unfortunately, it was not possible to elucidate the solid state structure of **4** via X-ray crystallography as it was not possible to grow crystals of the complex suitable for X-ray analysis. It is proposed that the complex is a ferrocenyloxo-bridged dimeric complex that is structurally analogous to the previously reported palladium chloride complexes of analogous P/S⁻⁶ and S/S⁻⁷ ferrocenediyl ligands. Elemental analysis is consistent with this formulation and does not show the presence of nitrogen in **4** suggesting that bound acetonitrile is not present. **4** was tested as a precatalyst for ethylene oligomerisation or polymerisation. It was suspected that ethylene would be unable to break up the dimeric complex since acetonitrile had been unable to, so 100 equivalents of methylaluminoxane (MAO) were added to a toluene solution of **4** to aid formation of an active monomeric species and to act as a moisture scavenger. The reaction mixture was subjected to 1 bar ethylene pressure for 1 hour at 70°C. No polymer was observed to form during the experiment and after 1 hour, the reaction mixture was quenched by the addition of concentrated HCl. An aliquot of the organic layer

was filtered through alumina and analysed by GC which showed that no oligomers had been formed.

The reaction between **3** and Pd(COD)MeCl was also attempted following a similar method to that used in the synthesis of **4**. A CH₂Cl₂ solution of the sodium salt of **3** (formed by stirring the ligand with an excess of NaH in a heated THF solution) was added to a CH₂Cl₂ solution of Pd(COD)MeCl. The reaction mixture was stirred for 4 hours at 35°C and then at room temperature overnight after which time the solution had turned dark brown. The mixture was filtered and the filtrate evaporated. This residue was washed with heptane and dried. The ¹H NMR spectrum showed very broad signals but did show four signals for the cyclopentadienyl protons at 3.33, 3.80, 4.17 and 4.40 ppm. The phenyl protons show two multiplets at 7.48 and 7.75 ppm, slightly shifted from the ligand's signals of 7.02 and 7.80 ppm. A tetrahedral Pd complex would be paramagnetic and would lead to the observation of broad signals in the ¹H NMR spectrum. Although tetrahedral Pd(II) complexes are rare, an example has been reported by Hor and co-workers featuring the dppf-O₂ bis(phosphine oxide) ligand which is structurally similar to **3**.²¹ The ³¹P{¹H} NMR showed a singlet at +34.5 ppm, very close to the free ligand (+33.2 ppm). A signal corresponding to the Pd-Me protons could not be observed and the structure of the complex synthesised could not be deduced from the ¹H and ³¹P{¹H} NMR spectra alone. A satisfactory positive FAB mass spectrum or elemental analysis result could not be obtained. The complex was found to be very sensitive and turned to a black insoluble powder over time even when stored in a nitrogen-filled glove box which hampered further attempts to characterise the complex. The O/O' donor combination would be expected to be poorer at stabilising a Pd(II) centre than the strongly σ-donating softer phosphine donor present in **2** explaining the relative instability of the complex formed.

The coordination chemistry of **2** was also investigated with rhodium precursors to provide a comparison with the Rh complexes of **1** previously reported. The methoxy group of **1** was found not to coordinate to the Rh centre and it was thought that the anionic hydroxyl group of **2** would be more likely to bind to the rhodium atom forming a P/O Rh chelate complex. The reaction between **2** and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ proved to be highly interesting and two different products were detected as shown in Scheme 1. The products observed suggest that the oxygen donor group is substitutionally labile allowing the ligand to become hemilabile in any Rh-catalysed process. Although the applications of the new complexes have not been investigated to date, this will be the focus of future work. The synthesis of **5** and **6** was carried out by following the method for the synthesis of the dimeric thiolato equivalent of **6**.⁶ The lithium salt of **2** was formed by adding one equivalent of *n*-butyllithium to a THF solution of **2** and stirring for 30 minutes. The solvent was removed *in vacuo* and the residue was redissolved in THF and added to a solution of tetracarbonyldichlorodirhodium(I) in methanol. The solution turned dark brown and a precipitate was observed after 30 minutes stirring at room temperature. The mixture was stirred for three hours before being concentrated by half and filtered. The residue was a golden yellow solid which was washed with diethyl ether and dried under vacuum. Although the expected product of the reaction was **6**, it was clear from examination of the ^1H NMR spectrum of the yellow solid that this was not the case. The solid was found to be **5** and was formed in 65% yield. The filtrate was left to stand under nitrogen for seven days after which time a small amount of a yellow crystalline solid was visible. The solid was filtered off and recrystallised twice from hot dichloromethane to yield **6** in approximately 10% yield. It is suggested that both products form in the initial reaction as leaving an NMR sample of **5** in CD_2Cl_2 for several days before running the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum did not show a peak corresponding to **6**. The ^1H NMR spectrum of **5** showed seven multiplets corresponding to the cyclopentadienyl protons rather

than the expected four. This indicated that two molecules of **3.3** were present in the complex in inequivalent environments which would form eight separate chemical environments for the cyclopentadienyl protons (these exist as six broadened pseudo-triplets and one multiplet.) In addition to resonances corresponding to the phenyl protons, a sharp singlet corresponding to a single hydrogen atom was observed at 9.64 ppm which was assigned to an OH proton on one of the ligands. It was thought that one ligand was bound in a chelated fashion whereas the other was bound solely through the phosphorus donor leaving the OH group pendant. (Although the OH proton in uncomplexed **2** gives a signal at 3.5 ppm, a secondary hydrogen bonding interaction was suspected to have sharpened the signal and shifted it downfield.) Due to the poor solubility of the complex, not all of the expected peaks in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum could be observed. The cyclopentadienyl carbons showed the expected twelve resonances at 61.49, 62.03, 62.81, 63.05, 63.45, 68.12, 70.78, 70.83, 71.54, 75.24, 75.99 and 76.20 ppm confirming the presence of two inequivalent molecules of **3.3**. The phenyl carbons, however, were not resolved into two separate sets of resonances and the quaternary carbons could not be observed: three peaks were observed at 128.54, 130.55 and 134.20 ppm. No peak corresponding to the carbonyl carbon could be distinguished from the baseline peaks.

The ^{31}P NMR spectrum showed two doublets centred at +21.3 and +21.1 ppm again suggesting that two inequivalent molecules of **2** were present in the complex. Coupling between the phosphorus nuclei and from each phosphorus to the rhodium centre would be expected meaning that two sets of doublets of doublets should be observed. The phosphorus atoms would be expected to have a very similar chemical shift and hence an overlapping splitting pattern would be expected. A ^{31}P - ^{31}P COSY spectrum showed cross peaks within each of the two doublets, but no cross peaks between the two sets of doublets. This suggests that P-P coupling exists with a very low ^2J coupling constant in such a way that the coupling

is not visible. This also suggests a *cis* orientation of the phosphines in **5**. It is not possible to assign the two phosphorus environments exactly, but the two $^1J_{\text{Rh-P}}$ coupling constants are 135.0 and 136.5 Hz respectively. The IR spectrum showed a peak at 1974 cm^{-1} corresponding to the carbonyl stretch. This is very similar to the stretching frequency found for other rhodium carbonyl complexes.[{ref}](#) The positive ion FAB mass spectrum also gave evidence for the formation of **5** as it showed the molecular ion (902 amu) together with the expected fragmentation pattern due to loss of CO (874 amu). Peaks for **2** (386 amu) and **2** + Rh (488 amu) were also visible. The elemental analysis is consistent with the proposed formulation. The ^1H NMR spectrum of **6** showed four pseudo-triplets corresponding to the cyclopentadienyl protons at 3.59, 4.29, 4.34 and 4.57 ppm. The phenyl protons of the diphenylphosphino groups showed two multiplets at 7.43 and 7.85 ppm. It was not possible to obtain a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum due to the insolubility of the complex but the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a doublet at +45.2 ppm due to coupling to the Rh centre with a $^1J_{\text{Rh-P}}$ coupling constant of 180.7 Hz, somewhat larger than that observed in the corresponding thiolato complex (165 Hz) which showed a doublet at +36.6 ppm presumably due to the stronger donor ability of the sulfur atom causing less donation from the phosphine groups in this complex than in **6**. The IR spectrum shows a peak at 1971 cm^{-1} corresponding to the CO stretching frequency. The positive ion FAB mass spectrum does not show the molecular ion but does show a peak corresponding to cleavage of the dimer and loss of CO (488 amu). Crystals of **6** were grown from a saturated CH_2Cl_2 solution and the X-ray crystal structure is shown in Figure 2. [Insert description of crystal structure.](#)

Group 4 complexes of **2 and **3****

Recent work in our group has shown that bis *ortho*-phosphinophenoxy titanium and zirconium complexes are competent ethylene and propylene polymerisation catalysts.[{ref}](#)

Richard Long's work} The coordination chemistry of **2** and **3** has also been investigated with titanium and zirconium precursors and the resulting complexes tested as ethylene polymerisation catalysts. Using $\text{TiCl}_4 \cdot 2\text{THF}$ or $\text{ZrCl}_4 \cdot 2\text{THF}$ as the metal precursor allowed the synthesis of bis ligand metal dichloride complexes. It was found that in contrast to the coordination chemistry of **1** and **2** with softer metals, where the oxygen donor group was often found to be pendant, the phosphine donor group was found to be the more labile group with the harder titanium or zirconium metal centres. The compounds synthesised are summarised in Scheme 2. A titanium dichloride complex of **2** was synthesised by adding two equivalents of the ligand dissolved in CH_2Cl_2 to a solution of $\text{TiCl}_4 \cdot 2\text{THF}$ in CH_2Cl_2 . The solution immediately turned dark blue-green in colour and the reaction mixture was stirred overnight before the solvent was removed *in vacuo*. The residue was washed with heptane and dried to yield **7** as a dark blue-green solid in 56% yield. A zirconium complex was synthesised by adding two equivalents of **2** dissolved in THF to a solution of $\text{ZrCl}_4 \cdot 2\text{THF}$ dissolved in THF (due to the insolubility of the metal precursor in CH_2Cl_2) and the reaction mixture stirred overnight. The solvent was removed *in vacuo* and the residue washed with heptane and dried to yield **8** as an orange solid in 63% yield. The ^1H NMR spectrum of **7** showed two broad signals for the cyclopentadienyl protons at 3.92 and 4.57 ppm together with two signals for the phenyl protons at 7.56 and 7.96 ppm. The phenyl protons are shifted downfield compared to the free ligand and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also shows a downfield shift to -2.6 ppm (compared to -18.0 ppm for **2**) suggesting some interaction with the Ti centre. For this reason, it is suggested that the ligand is chelating and bound through both heteroatoms to an octahedral Ti centre with two ligands and two chlorines bound to it. The positive FAB mass spectrum did not show the molecular ion but did show a peak corresponding to liberated **2** (386 amu). Elemental analysis was consistent with a 2 : 1 titanium dichloride complex. A number of possible geometries exist for **7**: it was not

possible to confirm the exact isomer formed as the complex was found to be extremely air and moisture sensitive and decomposed over time even when stored in a glove box meaning that it was not possible to obtain a $^{13}\text{C}\{^1\text{H}\}$ NMR or grow a crystal suitable for X-ray crystal structure analysis. The ^1H NMR spectrum of **8** was found to be very different from that obtained with **7** which suggested that **2** had a different reactivity with ZrCl_4 than with TiCl_4 . The cyclopentadienyl protons showed four multiplets at 3.84, 4.35, 4.48 and 4.61 ppm. The phenyl protons of the PPh_2 group showed three multiplets centred at 7.61, 7.72 and 8.04 ppm. Unlike **7**, however, a doublet was observed centred at 10.09 ppm with a coupling constant of 565 Hz corresponding to one proton per equivalent of **2** which was thought to correspond to protonated phosphorus atoms due to the HCl liberated in the reaction. This was later confirmed by examining the ^{31}P NMR spectrum which showed a doublet at -2.07 ppm with a coupling constant of 565 Hz whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a single peak. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were also obtained at low temperatures which showed that the signal at -2.07 ppm splits into two signals below room temperature. Although the exact reason for this is not clear, it is possible that at low temperatures, separate signals are observed for the *cis* and *trans* isomers of **8**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed signals corresponding to the cyclopentadienyl and phenyl carbons. An HMQC spectrum showed no correlation between the proton at 10.09 ppm and any carbon atoms as expected for a phosphonium proton.

It is unclear exactly why the reaction to form the P/O chelated complex was successful with titanium but pendant protonated phosphonium salts were obtained with zirconium. The binding affinity of soft phosphine donors to hard transition metals such as those in group IV is rather low in any case and presumably the larger, more electropositive second row elements such as zirconium interact covalently even less favourably with phosphine donors meaning that protonation is preferred. Future work will concentrate on the

reaction between the sodium salt of **2** with $\text{ZrCl}_4 \cdot 2\text{THF}$ in an attempt to synthesise a chelating zirconium dichloride complex.

Due to the differing behaviour of the reactions of **2** with $\text{TiCl}_4 \cdot 2\text{THF}$ and with $\text{ZrCl}_4 \cdot 2\text{THF}$, the reaction between the phosphine oxide **3** and $\text{TiCl}_4 \cdot 2\text{THF}$ was also examined. It was thought that the P(V) species would not be protonated by any liberated HCl and an O/O chelated complex would be formed since the Ti centre should bind much more strongly with the harder oxygen donor than with phosphine donors. A bis ligand titanium dichloride complex was synthesised: two equivalents of **3** were dissolved in CH_2Cl_2 and added to a solution of $\text{TiCl}_4 \cdot 2\text{THF}$ in CH_2Cl_2 . The reaction mixture immediately turned blue-purple in colour and was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue washed with pentane and dried to yield **9** as a purple powder in 46 % yield. The complex was found to be much more stable than **7** and was stable for at least two years in the solid state when stored under an inert atmosphere. The ^1H NMR spectrum of **9** showed two pseudo-triplets at 3.84 and 4.53 ppm and a multiplet consisting of two overlapping pseudo-triplets at 4.75 ppm for the cyclopentadienyl protons. The phenyl protons showed three multiplets centred at 7.30, 7.53 and 8.02 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a single resonance at +41.3 ppm, exhibiting a downfield shift of 8 ppm from **3**. The positive ion FAB mass spectrum does not show the molecular ion, but does show a peak due to **3** (402 amu).

Ethylene polymerisation with 7, 8 and 9

The group 4 metal dichloride complexes **7**, **8** and **9** were tested as pre-catalysts for ethylene polymerisation. The metal complexes were found to be insoluble in toluene which is the solvent of choice for ethylene polymerisation experiments and so 10 μmol of complex was suspended in a small volume of dry toluene and 100 equivalents of methylaluminumoxane

(MAO) was added causing dissolution. The reaction mixture was diluted with toluene to 100 cm³ total volume and the reaction mixture stirred under 1 bar ethylene pressure for 1 hour. The polymerisation was terminated by the addition of concentrated HCl and a known volume of heptane was added as an internal GC standard. An aliquot of the organic layer was removed for GC analysis and methanol was added to precipitate the polymer which was dried *in vacuo* and weighed. The results are shown in Table 1. All the catalysts showed a moderate activity for ethylene polymerisation and it should be noted that the initial traces of polymer to form were seen to contain black residues of the catalyst indicating that the activity may be suppressed by either the instability or insolubility of the catalyst. It is likely that the wide bite angle of **2** and **3** encourages the phosphine or phosphine oxide donor group to dissociate from the metal centre leaving the central metal with little steric protection contributing to the catalyst's instability. The GC analyses of the soluble products formed during the polymerisation showed a trace of oligomer formation in the case of **7** from C₁₀ upwards. Peaks corresponding to several isomers were present.

Conclusions

Work in the Gibson group has shown that bis *ortho*-diphenylphosphinophenoxy ligated titanium and zirconium complexes are highly active ethylene and propylene polymerisation catalysts at least one hundred times more active than catalysts bearing **2** or **3** as ligands. This is likely to be due to the wider bite angle imposed by the 1,1'-ferrocenediyl backbone encouraging the dissociation of the phosphine donor group meaning that the active site is not well protected and prone to decomposition. The ligand is also likely to be considerably more electron rich than a phenol-based ligand which hinders the attainment of an electron poor catalytic metal centre: an essential requirement for a successful ethylene polymerisation catalyst. Alternatively, during activation or at some point during the catalytic cycle, the

potential exists for the formation of iron-metal interactions that may disrupt the catalysis. This phenomenon has been observed in bis(trimethylsilylamido)ferrocene ligated titanium and zirconium ethylene polymerisation catalysts by Arnold and co-workers.²²

The coordination chemistry exhibited by **2** demonstrates the concept of hard and soft donors and their interaction with hard or soft metal centres: with the softer rhodium centre the harder oxygen donor was found to be pendant but with the hard titanium and zirconium metal centres the soft phosphine donor was found to be pendant. The lability of one donor of an unsymmetrical heteroditopic ligand has been intensely investigated in the pursuit of hemilabile catalysts²³ and suggests that applications for **2** and **3** in this area should be investigated.

Experimental

General procedures

All preparations were carried out using standard Schlenk techniques.²⁴ All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Chromatographic separations were carried out on alumina (neutral grade II, 3% H₂O). ¹H NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 MHz (¹H). ¹³C{¹H} NMR spectra were obtained on either a Bruker DRX-400 or AM-500 spectrometer. Chemical shifts (δ) are reported in ppm using the residual proton impurities in the NMR solvent as an internal reference. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out at Department of Health and Human Sciences, London Metropolitan University.

Synthesis of 1'-(hydroxy)ferrocenediyl diphenylphosphine oxide (3)

1'-(Bromo)ferrocenediyl(diphenylphosphino)oxide (0.50 g, 1.08 mmol, 1 eq) was dissolved in dry THF (20 cm³) and cooled to -78°C. To this solution was added *n*-butyllithium (1.6 M solution in hexane, 0.67 cm³, 1.1 mmol, 1 eq) and the solution stirred at -78°C for 10 min. Bis(trimethylsilyl)peroxide (0.18 cm³, 1.6 mmol, 1.5 eq) was added and the solution stirred at -78°C for 1 h before being allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* and the crude product hydrolysed and purified via column chromatography (silica, ethyl acetate / hexane, 2:1) to yield **3** as an orange solid (0.17 g, 0.43 mmol, 40 %). Characterising data as previously described.¹²

Synthesis of [{1-(diphenylphosphino-κP)-1'-(μ-oxo)ferrocene}methyl-palladium(II)]₂ (4**)**
2 (0.080 g, 0.21 mmol, 1 eq) was dissolved in dry THF (10 cm³) and added via cannula to sodium hydride (0.015 g, 0.62 mmol, 3 eq) slurried in dry THF (10 cm³) at room temperature. The mixture was stirred for one hour at room temperature and then heated at 60°C for 15 h, after which time the solution had turned dark brown. The mixture was filtered and the solvent removed *in vacuo*. The residue from this filtrate was redissolved in dry acetonitrile (10 cm³) and added via cannula to a solution of Pd(COD)MeCl (0.041 g, 0.16 mmol, 0.75 eq) in acetonitrile (10 cm³). The solution was stirred at 35°C for fifteen hours. The solvent was removed *in vacuo* and the residue extracted with CH₂Cl₂ (3 x 30 cm³). This solution was concentrated and dry heptane added (50 cm³) causing a brown powder to precipitate. The mixture was filtered and the residue washed with heptane (20 cm³) and refiltered yielding the title compound as a brown powder (0.035 g, 0.034 mmol, 44 %).

Anal. Calc. for C₄₆H₄₂Fe₂O₂P₂Pd₂: C 54.52, H 4.18 %, Found: C 54.32, H 4.00 %; ¹H NMR δ(CD₂Cl₂) ppm: -0.11 (d, 3H, CH₃, ³J_{H-P} = 2.2 Hz), 3.60 (t, 2H, C₅H₄), 4.12 (t, 2H, C₅H₄), 4.28 (t, 2H, C₅H₄), 4.46 (t, 2H, C₅H₄), 7.41 (m, 6H, PC₆H₅), 7.74 (m, 4H, PC₆H₅); ³¹P{¹H} NMR δ(CD₂Cl₂) ppm: 34.5; *m/z*: 506 (M⁺ - PdLMe), 491 (M⁺ - PdLMe₂), 386 (L⁺).

Synthesis of [1-(diphenylphosphino- κ P)-1'-(oxo- κ O)ferrocene][1-(diphenylphosphino- κ P)-1'-(hydroxy)ferrocene]carbonylrhodium(I) (5**) and {[1-(diphenylphosphino- κ P)-1'-(μ -oxo)ferrocene]carbonyl-rhodium(I)}₂ (**6**)**

2 (0.080 g, 0.207 mmol, 1 eq) was dissolved in dry THF (10 cm³) and to this solution was added *n*-butyllithium (1.6 M solution in hexane, 0.13 cm³, 0.21 mmol, 1 eq). The reaction mixture was stirred for 30 min and the solvent was removed *in vacuo*. The residue was redissolved in dry THF (10 cm³) and added via cannula to a solution of tetracarbonyldichlorodirhodium(I) (0.040 g, 0.104 mmol, 0.5 eq) in methanol (20 cm³). The reaction mixture was stirred for three hours and was then concentrated by half and filtered. The residue was washed with diethyl ether (5 cm³) and dried under vacuum to yield **5** as a yellow solid (0.061 g, 0.067 mmol, 65 %). The filtrate was left to stand for seven days after which time a yellow crystalline solid was visible. The solid was filtered off and recrystallised twice from hot CH₂Cl₂ to yield **6** as yellow crystals (0.011 g, 0.010 mmol, 10 %).

5: Anal. Calc. for C₄₅H₃₇Fe₂O₃P₂Rh: C 59.90, H 4.13 %, Found: C 59.81, H 3.99 %; ¹H NMR δ (CD₂Cl₂) ppm: 3.52 (br t, 2H, C₅H₄), 3.64 (br t, 2H, C₅H₄), 3.74 (m, 4H, C₅H₄), 4.28 (t, 2H, C₅H₄), 4.39 (t, 2H, C₅H₄), 4.53 (t, 2H, C₅H₄), 4.72 (t, 2H, C₅H₄), 7.44 (m, 10H, PC₆H₅), 7.74 (m, 5H, PC₆H₅), 7.86 (m, 5H, PC₆H₅), 9.64 (s, 1H, OH); ¹³C{¹H} NMR δ (CD₂Cl₂) ppm: 61.49, 62.03, 62.81, 63.05, 63.45, 68.12, 70.78, 70.83, 71.54, 75.24, 75.99, 76.20 (C₅H₄), 128.54, 130.55, 134.20 (C₆H₅); ³¹P{¹H} NMR δ (CD₂Cl₂) ppm: 21.3 (d, ¹J_{Rh-P} = 135.0 Hz), 21.1 (d, ¹J_{Rh-P} = 136.5 Hz); IR(CH₂Cl₂) ν cm⁻¹: 1974 (CO); *m/z*: 902 (M⁺), 874 (M⁺ - CO), 488 (L⁺ + Rh), 386 (L⁺).

6: ¹H NMR δ (CD₂Cl₂) ppm: 3.59 (t, 2H, C₅H₄), 4.29 (t, 2H, C₅H₄), 4.34 (t, 2H, C₅H₄), 4.57 (t, 2H, C₅H₄), 7.43 (m, 6H, PC₆H₅), 7.85 (m, 4H, PC₆H₅); ³¹P{¹H} NMR δ (CD₂Cl₂) ppm: 45.2 (d, ¹J_{Rh-P} = 180.7 Hz); IR(CH₂Cl₂) ν cm⁻¹: 1971 (CO); *m/z*: 488 (L⁺ + Rh).

Synthesis of bis-[1-(diphenylphosphino- κ P)-1'-(oxo- κ O)ferrocene]-dichlorotitanium(IV)

(7)

2 (0.080 g, 0.207 mmol, 2.1 eq) was dissolved in dry CH_2Cl_2 (10 cm^3) and added via cannula to a solution of $\text{TiCl}_4 \cdot 2\text{THF}$ (0.033 g, 0.099 mmol, 1 eq) dissolved in dry CH_2Cl_2 (10 cm^3) causing the solution to turn dark blue-green. The solution was stirred at room temperature for fifteen hours. The solvent was removed *in vacuo*, the residue washed with dry heptane (20 cm^3) and the mixture filtered. The residue was dried *in vacuo* yielding the title compound as a dark blue-green powder (0.048 g, 0.054 mmol, 54 %).

Anal. Calc. for $\text{C}_{44}\text{H}_{36}\text{Cl}_2\text{Fe}_2\text{O}_2\text{P}_2\text{Ti}$: C 59.43, H 4.08 %, Found: C 59.39, H 4.19 %; ^1H NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: 3.92 (m, 2H, C_5H_4), 4.57 (m, 6H, C_5H_4), 7.56 (m, 6H, PC_6H_5), 7.96 (m, 4H, PC_6H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: -2.6; m/z : 386 (L^+).

Synthesis of bis-[1'-(oxo- κ O)ferrocenediyl]diphenylphosphonium chloride]dichlorozirconium(IV) (8)

2 (0.080 g, 0.207 mmol, 2.1 eq) was dissolved in dry THF (15 cm^3) and added via cannula to a solution of $\text{ZrCl}_4 \cdot 2\text{THF}$ (0.037 g, 0.099 mmol, 1 eq) dissolved in dry THF (40 cm^3) causing the solution to darken. The solution was stirred at room temperature for fifteen hours. The solvent was removed *in vacuo*, the residue washed with dry heptane (20 cm^3) and the mixture filtered. The residue was dried *in vacuo* yielding the title compound as an orange powder (0.059 g, 0.058 mmol, 56 %).

Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{Cl}_4\text{Fe}_2\text{O}_2\text{P}_2\text{Zr}$: C 52.56, H 3.81 %, Calc. for $\text{C}_{44}\text{H}_{36}\text{Cl}_2\text{Fe}_2\text{O}_2\text{P}_2\text{Zr}$: C 56.67, H 3.89 %, Found: C 56.52, H 3.87 %; ^1H NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: 3.84 (m, 2H, C_5H_4), 4.35 (m, 2H, C_5H_4), 4.48 (m, 2H, C_5H_4), 4.61 (m, 2H, C_5H_4), 7.61 (m, 3H, PC_6H_5), 7.72 (m, 3H, PC_6H_5), 8.04 (m, 4H, PC_6H_5), 10.09 (d, 2H, $\text{P}(\text{C}_6\text{H}_5)_2\text{H}^+$, $^1J_{\text{H-P}} = 565$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR

$\delta(\text{CD}_2\text{Cl}_2)$ ppm: 61.8, 63.7, 64.4, 74.2, 74.3, 129.1 (C_5H_4), 120.0, 130.0, 134.1, 134.5 (C_6H_5);
 $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: -2.07; ^{31}P NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: -2.07 (d, $^1J_{\text{H-P}} = 565$ Hz);
 m/z : 386 (L^+).

Synthesis of bis-[1-(diphenylphosphanyloxy- κO)-1'-(oxo- κO)ferrocene]dichlorotitanium(IV) (9)

3 (0.080 g, 0.20 mmol, 2.1 eq) was dissolved in dry CH_2Cl_2 (10 cm^3) and added via cannula to a solution of $\text{TiCl}_4 \cdot 2\text{THF}$ (0.032 g, 0.095 mmol, 1 eq) dissolved in dry CH_2Cl_2 (10 cm^3) causing the solution to turn dark blue. The solution was stirred at room temperature for fifteen hours. The solvent was removed *in vacuo*, the residue washed with dry pentane (30 cm^3) and the mixture filtered. The residue was dried *in vacuo* yielding the title compound as a dark purple powder (0.040 g, 0.043 mmol, 46 %).

Anal. Calc. for $\text{C}_{44}\text{H}_{36}\text{Cl}_2\text{Fe}_2\text{O}_4\text{P}_2\text{Ti}$: C 57.37, H 3.94 %, Found: C 57.30, H 3.87 %; ^1H NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: 3.84 (t, 2H, C_5H_4), 4.53 (t, 2H, C_5H_4), 4.75 (m, 4H, C_5H_4), 7.30 (m, 4H, PC_6H_5), 7.53 (m, 2H, PC_6H_5), 8.02 (m, 4H, PC_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: 61.8, 64.5, 67.4, 74.0, 74.1, 75.0 (C_5H_4), 129.8, 130.1, 131.5, 132.8 (C_6H_5); $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta(\text{CD}_2\text{Cl}_2)$ ppm: 41.3; m/z : 402 (L^+).

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Figure Legends

Table 1 Ethylene polymerisations with group 4 dichloride complexes of **2** and **3**

Figure 1 Literature examples of 1'-substituted hydroxyferrocenes and ferrocenyl ethers

Scheme 1 Syntheses of **4-6**^a

^a Reagents and conditions: (i) NaH, THF, 60°C, 15 h; (ii) Pd(COD)MeCl, MeCN, 35°C, 15 h; (iii) *n*-Butyllithium, THF, rt, 30 min; (iv) Rh₂Cl₂(CO)₄, THF/MeOH, rt, 3 h.

Figure 2 Molecular Structure of **6**

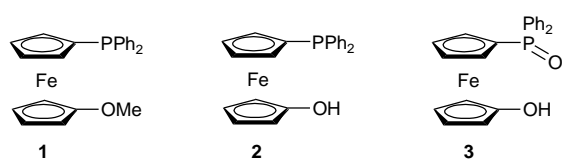
Scheme 2 Syntheses of **7-9**^a

^a Reagents and conditions: (i) TiCl₄.2THF, CH₂Cl₂, rt, 15 h; (ii) ZrCl₄.2THF, THF, rt, 15 h; (iii) TiCl₄.2THF, CH₂Cl₂, rt, 15 h.

Table 1

Complex	Polymer yield (g)	Activity ($\text{gmmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$)
7	0.23	23
8	0.10	10
9 (5 μmol used)	0.08	16

Figure 1



Scheme 1

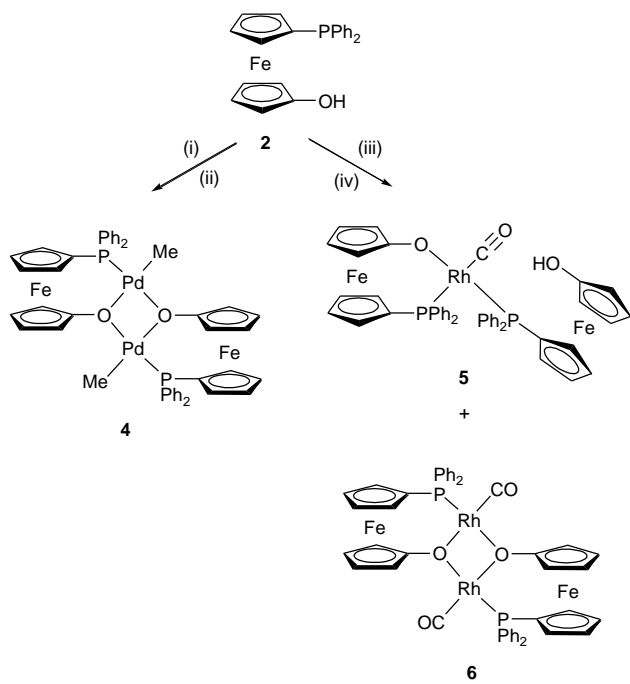
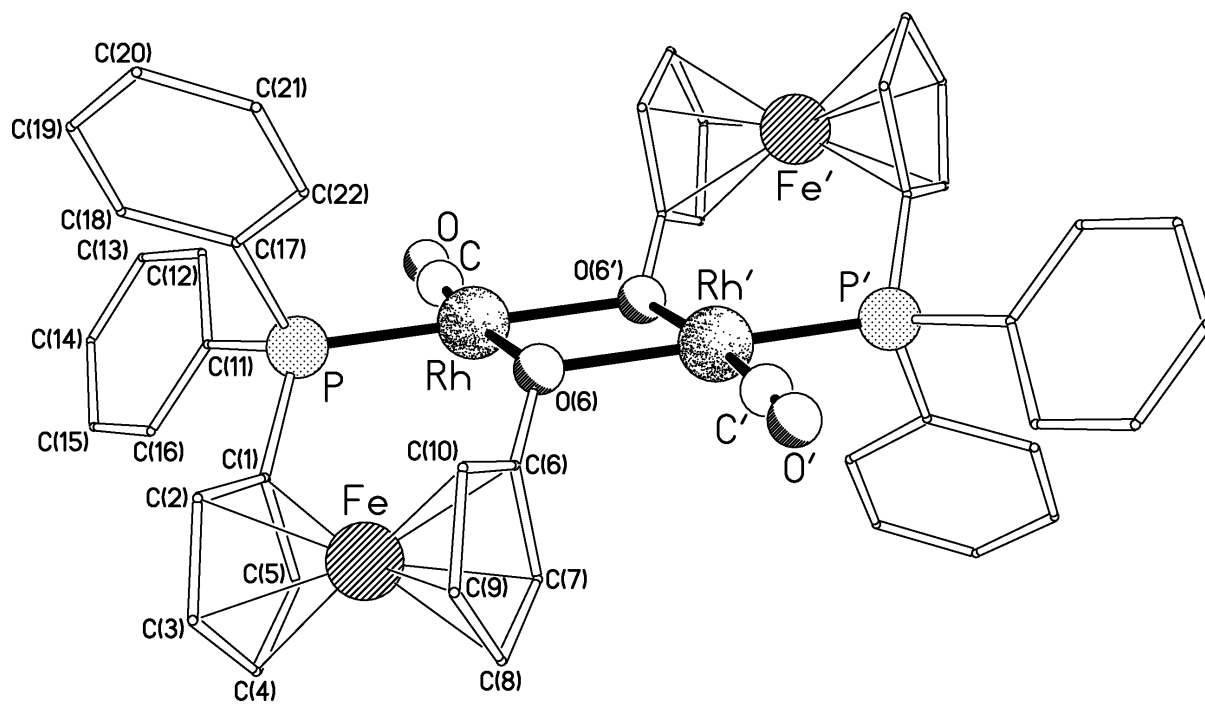
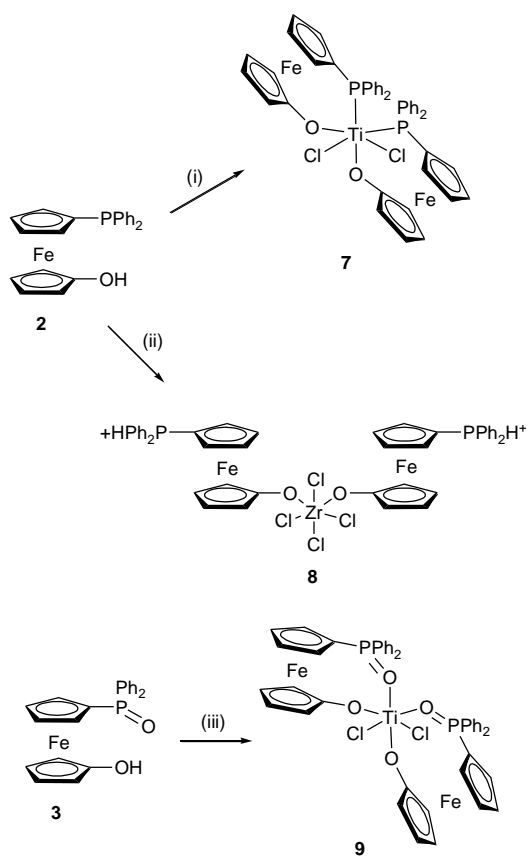


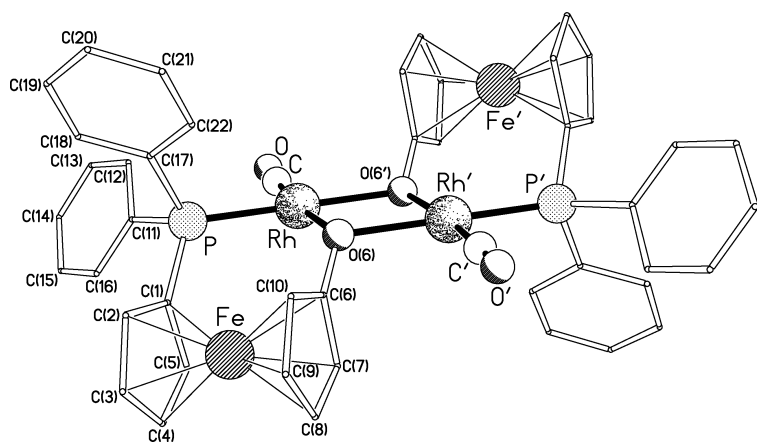
Figure 2



Scheme 2



Graphical Abstract (diagram)



Graphical Abstract (text)

The coordination chemistry of 1'-(diphenylphosphino)hydroxyferrocene and its corresponding phosphine oxide has been investigated with Pd, Rh, Ti and Zr precursors. Chelating, P-pendant or O-pendant complexes were observed depending on the nature of the metal. The group IV complexes catalyse the polymerisation of ethylene with low to moderate activity.