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A Rapid General Synthesis and the Spectroscopic Data of 2,2′-Bis-(Di-Isopropylphosphino)-1,1′-Dibromoferrocene, (*bpdbf*), 1,1′, 2,2′-Tetrakis-(Di-Isopropylphosphino) Ferrocene, (*tdipf*) and Related Ligands. Taking *dppf* into the Future

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A Rapid General Synthesis and the Spectroscopic Data of 2,2′-Bis-(di-isopropylphosphino)-1,1′-dibromoferrocene, (*bpdbf*), 1,1´,2,2´-Tetrakis-(di-isopropylphosphino) ferrocene, (*tdipf*) and Related Ligands. Taking *dppf* into the Future

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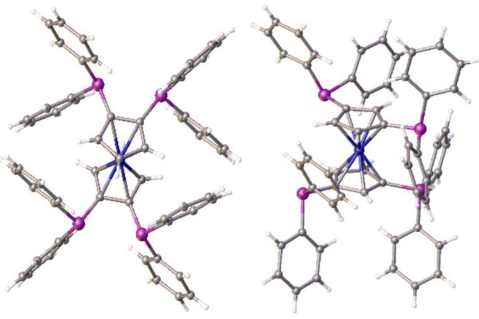
Abstract: The clean high yielding, synthesis and structure of the tetraphosphine ligand, 1,1´,2,2´-tetrakis-(di-isopropyl-phosphino)ferrocene, (*tdipf*), is described. In addition, an improved synthesis of the 1,1´,2,2´-tetrakis(diphenylphosphino)ferrocene, (*tppf*) and 2,2´-bis-(diphenylphosphino)-1,1´-dibromoferrocene are also reported and the synthetic method is generalised to include the synthesis of 3,3'-bis-(diphenylphosphino)-1,1´,2,2´-tetrabromoferrocene. The related ligands 2,2´-bis-(iso-propylphosphino)-1,1´-bis-diphenylphosphinoferrocene (*diprdppf*) and 2,2´-bis-(di-isopropylphosphino)-dibromoferrocene have also been prepared and characterised. The crystal structure of the square planar bimetallic nickel (II) dichloride of *tdipf* is also described, together with a brief NMR study investigating the synthesis of this and related metal complexes. The crystal structures of the palladium and platinum dichloride complexes of 2,2'-bis-(di-isopropylphosphino)-1,1'-dibromoferrocene, *bpdbf*, are also discussed in the context of comparison with previously known crystal structures in the same general family. A general discussion on the synthetic methodology is given and pointers to future research other researchers might explore.

Keywords: phosphine; ligand; complex; ferrocene; nickel; palladium; synthesis; coordination.

1. Introduction

Ferrocene ligands are ubiquitous in organic synthesis primarily being used as chiral and achiral ligands in catalysis. [1–40] These fluctuate popularity, but they have maintained their prominence as utilitarian ligands in synthesis since their initial development. Of the achiral ligands *dppf* **1**, [41–43] scheme 1, is the most used probably because of its ready availability and stability even although it is not necessarily the optimum ligand of choice in many metal-catalysed applications. Related to this are the arsine derivatives [44,45] and the more basic and soluble ligands *dippf* [46] **2** and *bdbf* [47,48] **3** which were first described in the early 1980´s. The library of ligands has expanded since then but essentially most of these ligands are similar in design to the original ligands and simply use different R groups on the phosphorus. This is also true of the ferrocene-based chiral ligands such as compound **7**, Figure 1, which derive from the early work of Ugi, [49–52] Hayashi and Kumada [3,53–57] and Cullen [58,59] and the later adaptation to chiral ferrocenyl-bis-phosphines by Togni and co-workers.[4,60–66] Permethylated ligands, such as ligand **4,** Figure 1, have also been prepared for use in methoxycarbonylation. [67–71]

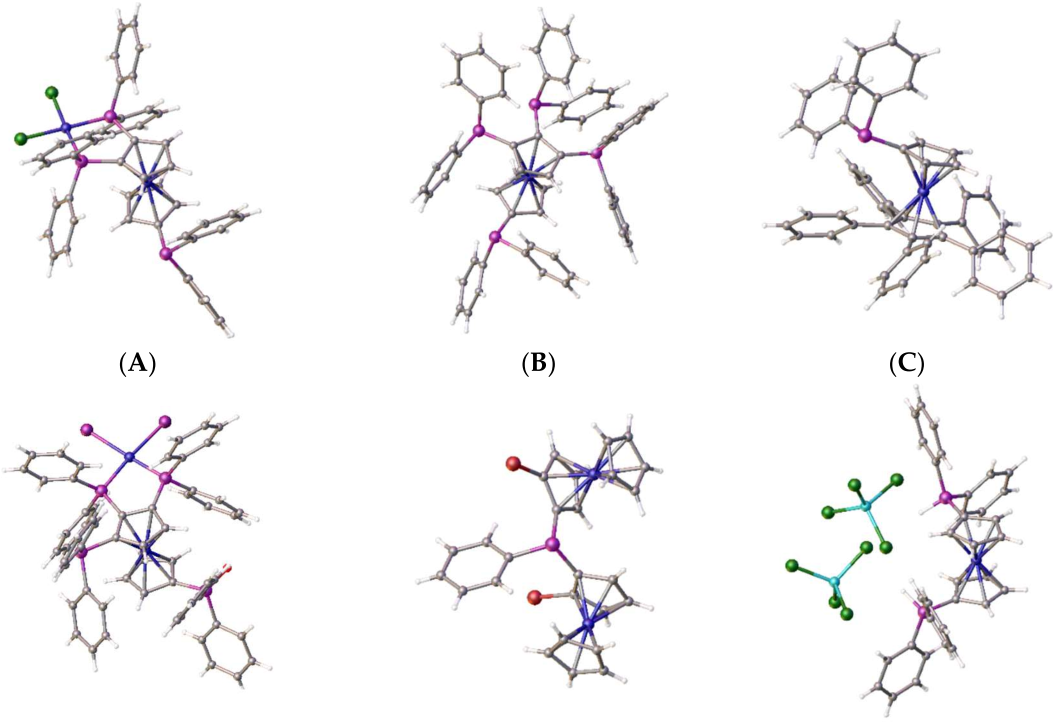


(**a**) (**b**)

Figure 1. a) Some important ligand designs of multiply substituted phosphinoferrocenes, **b)** showing compounds such as 1,1′,2,2′-tetrakis-(diphenylphosphino)ferrocene, **8**,* 1,1′,3,3′-tetrakis-(diphenylphosphino)ferrocene as examples. (* taken from Pd complex with Pd removed).

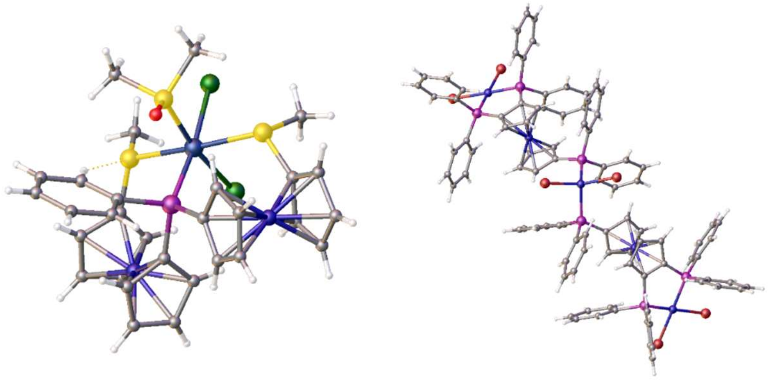
1.1. Ligand Diversity

To pictorially illustrate the structural diversity of ferrocenylphosphine ligands and their metal complexes some representative structures are shown in Figure **2** (aryl-substituted phosphines) and Figure **3** (isopropyl-substituted phosphines) which are taken from our own archives. It should be noted however that there are literally thousands of known ferrocenylphosphine metal complexes with prominent researchers in the field each having large own ligand portfolios and that these are simply a few of our own chosen to illustrate the structural diversity.



(**A**) (**B**) (**C**)

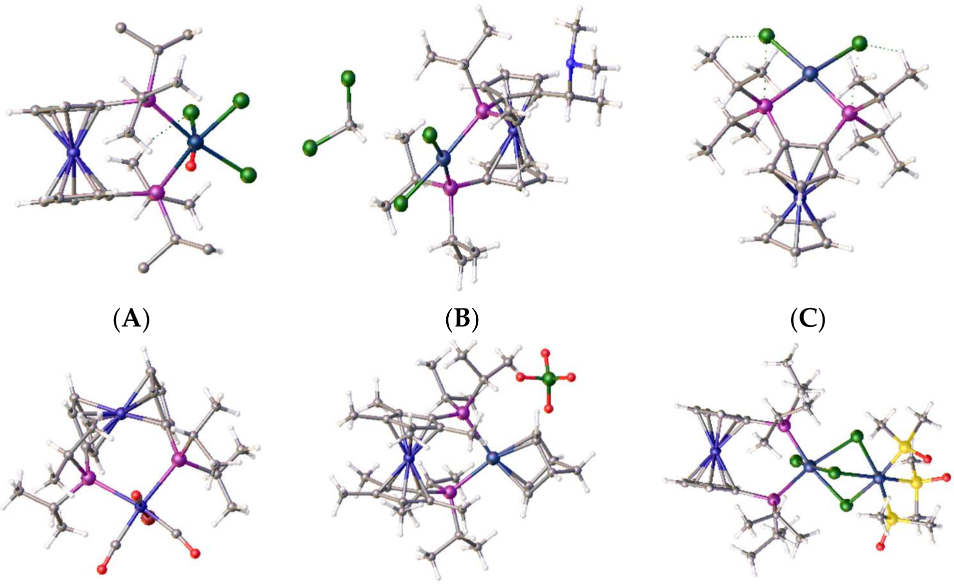
(**D**) (**E**) (**F**)



(**G**) (**H**)

Figure 2. Examples of some ferrocenylarylphosphines to show structural diversity. **A**: Nickel dichloride complex of 1,2,1′-tris-diphenylphoshinoferrocene. **B**: 1,2,3,1′-tetrakis-diphenylphosphinoferrocene ligand. **C**: 1-diphenylphosphino-1′,2′,3′,4′,5,′-pentaphenylferrocene. **D**: nickel dichloride complex of ligand **B**. **E**: bis-(1′-bromoferrocenyl)-phenylphosphine, **F**: 1,1′-bis-diphenyl(oxo)phosphinoferrocenes (CCl_4 solvate). **G**: Ruthenium (DMSO) dichloride complex of the ligand bis-(1′-*S*-methyl-1-ferrocenyl)phenylphosphine. **H**: Bis-1-[(1′,2′-diphenylphosphino)nickel(II)dibromide]phenylphosphino-nickel(II)dibromide. Further details of these compounds may be found in the S.I..

It can be noted that in structures **A**, **D**, and **H** in Figure 2 the metal complexes have square planar geometry which contrasts with the tetrahedral coordination observed in the parent *dppf* nickel dihalides. Thus, by examination of typical structures, initially, it becomes clear that nickel halide complexes exhibit a square planar metal coordination mode with two *homo*-annular phosphines and a tetrahedral coordination mode with *hetero*-annular phosphines. In Figure 3 isopropyl-substituted phosphines, **A-F**, exhibit a broad range of coordination modes with different metals and again the nickel complex in structure **C,** the homo-annular diphosphinoferrocene, is square planar. More interestingly perhaps is that in the methylamine substituted complex B, which has *hetero*-diphosphines, the metal coordination geometry is also square planar. Therefore, *a priori*, it is difficult to make general rules. Complexes **A, D, E** and **F** the metal (Mn, Re, Ru) are examples where the geometries are *puesdo* octahedral -there are many examples of this coordination mode particularly in metal carbonyl complexes.



(**A**) (**B**) (**C**)

(**D**) (**E**) (**F**)

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Figure 3. Crystal structures of some iso-propylphosphinoferrocenes to show their diversity. **A**: [(*dippf*)Re(=O)Cl_3], **B**: [(2-N,N-Dimethylaminomethyl-1,1′-bis-diisopropylphosphinoferrocene)$NiCl_2$], **C**: [(*1,2-dippf*)$PdCl_2$], **D**: [(*1,1′-dippf*)Mn$(CO)_3$Br], **E**: [(*1,1′-pmdippf*)Rh(1,5-*nbd*)], ClO_4, *pmdippf* is the permethylated *dippf* ligand and *nbd* = 1,5-norbornadiene **F**: [(*1,1′-dippf*)Ru$(\mu^{2}$-$Cl)_3$Ru(*S*-$DMSO)_3$.

1.2. Tetra-Dialkylphosphinoferrocenes or Tetra-Diarylphosphinoferrocenes.

Tetra-substituted phosphinoferrocenes have been the subject of many research articles and some of these ligands are commercially available. There are 2 routes to this family of ligands either from the phosphine-substituted cyclopentadiene or directly from ferrocene. The first route uses the chemistry of cyclopentadiene which was developed by Broussier [73–75] and carried forward, by Meunier and Hierso. [76–80] This research has become one of the best widely adopted areas of ferrocene ligand chemistry and some elegant coordination chemistry and catalysis with these ligands has been reported. [81–84]. The second route uses alpha-metalation of haloferrocenes, [85–90] which was developed in our research group and since has seen fruitful development from several high-profile research groups. [91–100]. The adapted methodology has enabled the synthesis of fully substituted ferrocenes such as *deca*-bromoferrocene [101]and *deca*-(trimethylsilyl)ferrocene. [102] The synthetic method is clearly suitable to use to prepare a range of other P4-ligands such as the known tetra phosphine ligand, *tppf*, **8, (**scheme 1) which may be considered the tetradentate version of *dppf*, however as noted earlier, based on the coordination chemistry of compound **8** it may be more reasonably be considered the tetradentate version of the ligand 1,2-bis-diphenylphosphine ligand, **5,** as bidentate coordination of nickel, palladium and platinum is favored between phosphines on the same cp-ring rather than inter-annular coordination.[85] Hierso has championed this ligand type especially the di t-butyl substituted ligand 4,4'-bis(t-butyl)-1,1',2,2'-tetrakis(diphenylphosphino)ferrocene,**10** (see Figure 1) in which the t-butyl groups give the ligand increased solubility in organic solvents. The compound 4,4'-bis(t-butyl)-1,1',2,2'-tetrakis(diphenylphosphino)ferrocene, *HiersoPHOS-5,* is commercially available. This family of ligands can bind two metals in a bidentate mode, but the resultant complexes can be poorly soluble in common organic solvents. Of the tetradentate ligands the ligands 1,1′,2,2′-tetrakis-(di-isopropylphosphino)ferrocene, *tippf,* **9,** has always been the principal target for us: this had been prepared previously by us using the *ortho*-metalation method but its synthesis was not optimum and hence was never published. The present paper presents a reliable synthesis of this ligand in high yield together with a brief *in-situ* NMR investigation into its coordination chemistry. This ligand is of special interest because of the success of the related ligand *dippf*, **2,** in catalytic applications [103] and it also has added basicity and should be able to bind to different metals or form homo-dimetallic complexes which should improve the catalyst activity and performance. In comparison with the related arylphosphines *dppf,* **1,** and *tppf,* **8** it will have the added non-polar solution solubility and the enhanced activity associated with *dippf.* In this work we seek to develop a synthetic route which avoids the use of column chromatography, where possible.

2. Results and Discussion

The general synthetic route diagram used in this work is shown in Figure 4.

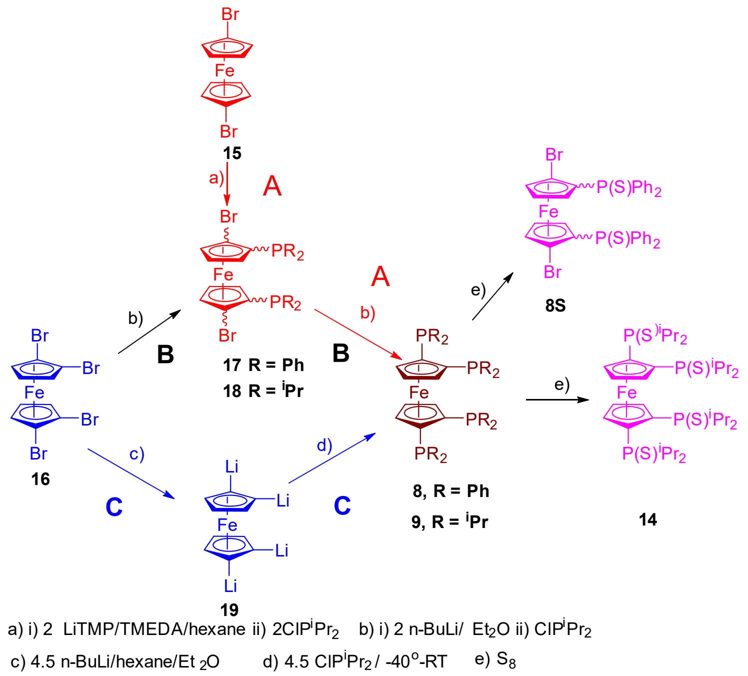


Figure 4. Generalised synthetic routes **A**, **B**, and **C** to 1,1′,2,2′-tetrakis-(di-isopropylphosphino)ferrocene, *tippf*, **9**, **A** from 1,1′-dibromoferrocene; **B** and **C** from 1,1′, 2,2′-tetrabromoferrocene . The method is also adaptable to the improved synthesis its phenyl analogue **8**.

We had attempted the synthesis of compound **9** from 1,1'-dibromoferrocene, **15** via the dibromide **18,** without its isolation, previously but we were unable to obtain **9** by a reproducible method. The yields are low caused by the presence of many by-products (isomers formed because of the isomerisation of the lithium intermediates). Here we used a new modified route **A**, Figure 4, which is identical except for the addition of TMEDA to stop the isomerisation (the halogen dance) and we carry out the reaction at room temperature. This results in a much-improved synthetic method and compound **18** can be isolated and crystallised as red/orange nodules following flash chromatography in high yields (80%+). Both diastereomers are formed in slightly differing ratios. The crystal structure of *rac*-**18** is shown in Figure 5, together with that of *rac*-2,2′-bis-(di-isopropylphosphino)-1,1′-dichloroferrocene, **30**, for comparison. The phosphorus chemical shifts for these compounds are observed at -4.90 (**18**) and -4.98 ppm (**30**). Pertinent NMR spectra of compounds **18** are shown in Figure 6.

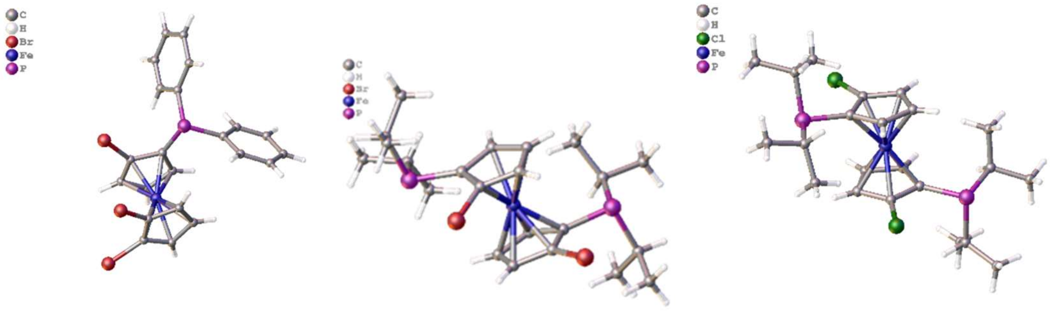


Figure 5. Crystal structures of ligands of 2′-diphenylphosphino-tribromoferrocene, **21**, 2,2′-bis-(di-isopropylphosphino)-dibromoferrocene, *rac*-**18** (and 2,2′-bis-di-isopropylphosphino-1,1′-dichloroferrocene, **30,** *meso*, added for comparison).

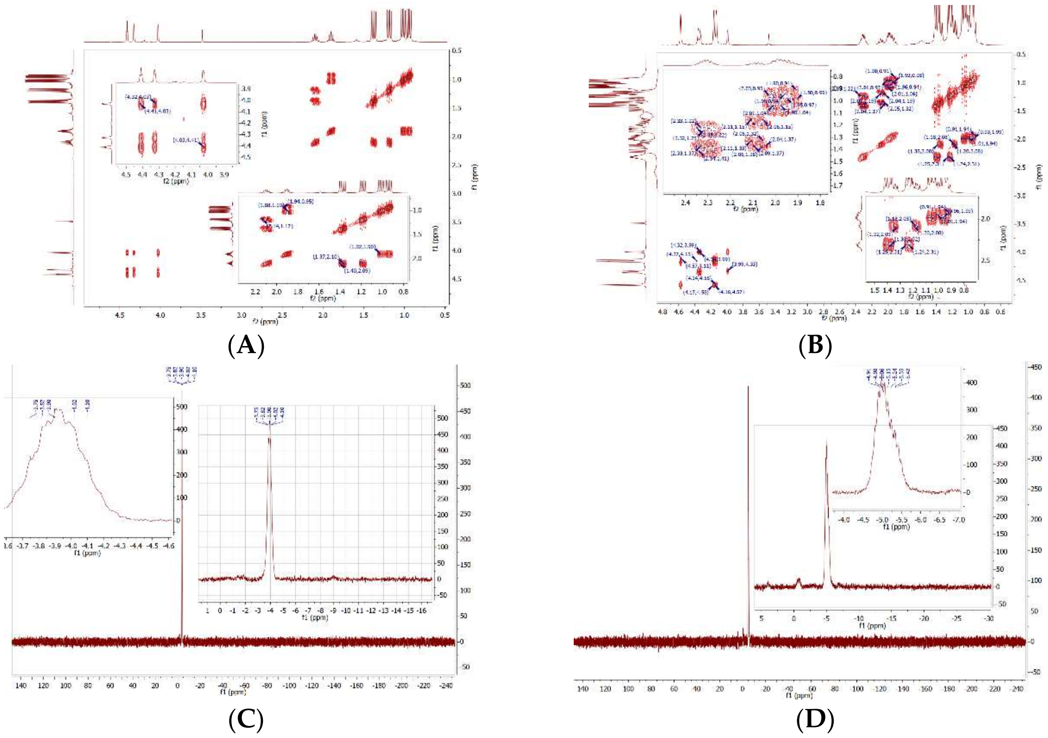

(A) (B) (C) (D)

Figure 6. ^{1}H Correlation spectrum of 2,2’-bis-di-isopropylphosphino-1,1’-dibromoferrocene,**18**, **A**, and ^{31}P NMR spectrum, one isomer and **B**, **D** both isomers (approx. 2:1 ratio). Note that both phosphorus resonances overlap in the mixed isomer sample. .

Compound **18** (as an isomer mixture) is then dilithiated and quenched with chlorodi-isopropylphosphine a second time to give compound **9,** again in reasonable yields, 70-80%., overall, 56-64%. Mid-way through this project 1,1′,2,2′-tetrabromoferrocene, **16,** became available in multi-gram quantities in our lab, [104,105], and thus was used as an ideal starting material, Figure 4, routes **B** and **C**. Again, in route **B** diastereomers of **18** are formed thus these are best reacted as a mixture to give **9**. However, the preferred synthetic route is following route **C** which is a one-step method. 1,1′,2,2′-Tetralithioferrocene, **19,** is generated in either hexane/ether or in neat diethyl ether and chlorodi-isopropylphosphine is added to the chilled solution. The yield obtained after workup is >90%. Ligand **9** is obtained as red nodules from methanol. It is readily soluble in hexane, diethyl ether and chloroform but it is poorly soluble in DMF and DMSO as was observed when attempting complexation reactions in these solvents. Its proton NMR spectrum is essentially as anticipated by direct comparison with that of **6**; the ferrocene resonances are observed as the characteristic pseudo doublet (4.33 ppm) and pseudo triplet (4.55 ppm), Figure 8. The chemical shift of the phosphorus resonance which is observed at -1.27 ppm, is a similar value to that of 1,1’- and 1,2- bis-(di-isopropylphosphino)ferrocene, **2** and **6,** (in Figure 1) The crystal structure of compound *tippf*, **9** is shown in Figure 7.

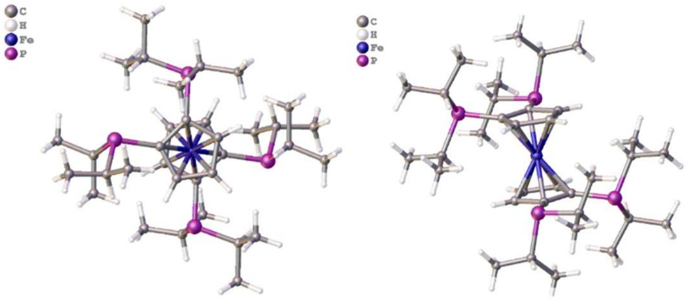


Figure 7. Top and side view of the crystal structure of compound **9**, *tippf*.

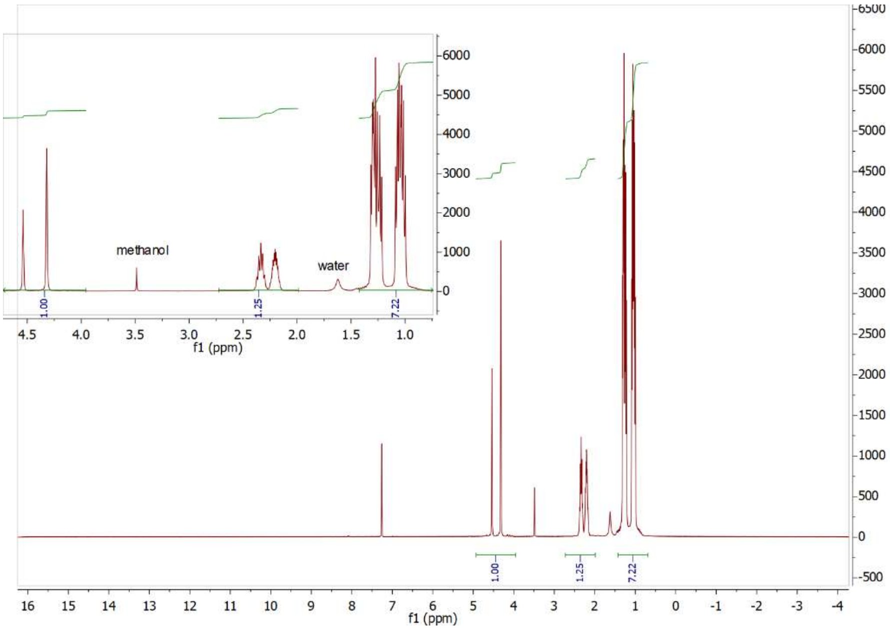
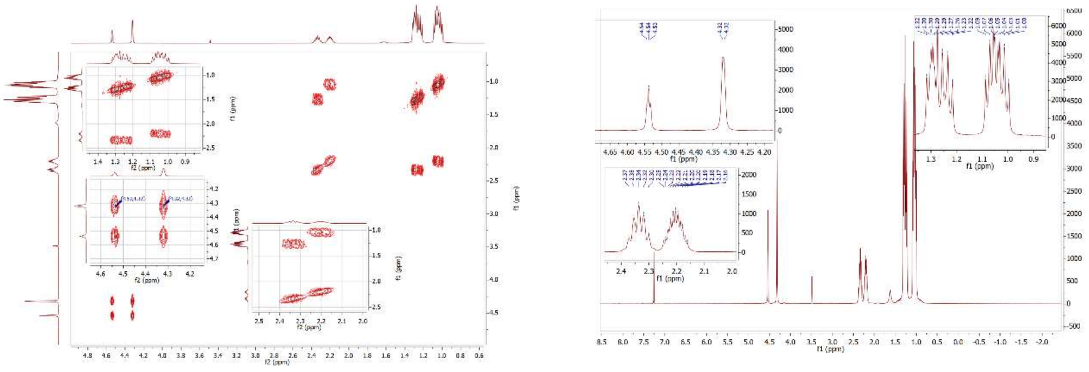


Figure 8. ¹H NMR spectrum of 1,1′,2,2′-tetrakis(di-isopropylphosphino)ferrocene, **9**. (crystallised from reagent grade methanol.

As shown in Figure 9, the methyl proton presents as a pair of doublets of doublets of doublets, while the methylene protons present as a broad pseudo pentet and a sharper 11-line resonance.



(**A**) (**B**)

Figure 9. ¹H NMR spectra A (with correlations) of compound **9** and B, showing the detailed multiplicity of the methyl and methylene resonances.

Treatment of ligand **9** with elemental sulfur (nmr tube) gives the tetrasulfide **14** in which the two ferrocenyl proton resonances exchange positions and move downfield to 4.90 ppm and 5.22 ppm, respectively, see Figure 10.

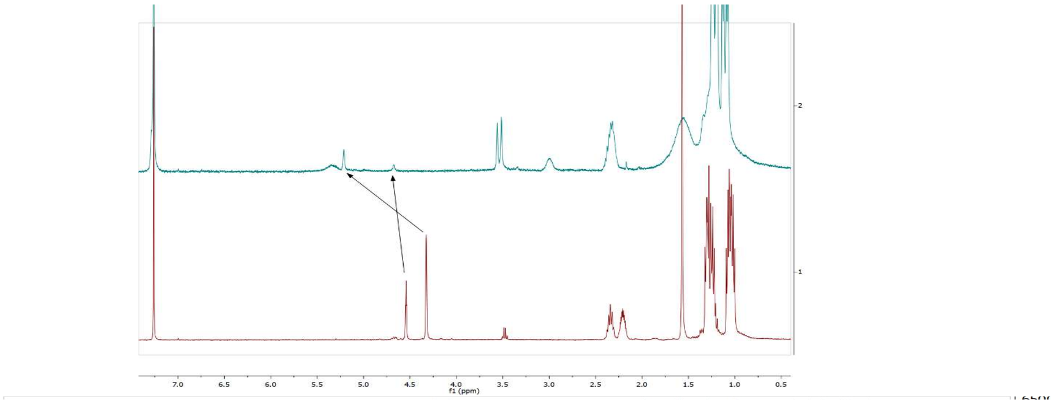


Figure 10. ^{1}H NMR tube experiment to illustrate that the ferrocenyl resonance change positions when the phosphine sulfide is formed. Bottom spectrum, compound **9**, top spectrum with addition of elemental sulfur. The appearance of other broad resonances indicates this is not a clean process.

The new procedure used here also allowed for a much improved synthesis of the previously reported compound, 1,1′,2,2′-tetrakis-(diphenylphosphino)ferrocene, **8**. This compound was obtained as orange crystals on a 5g scale. This preparation is straightforward although removal of trace impurities of tris-1´,2,2´-tris-(diphenylphosphino)bromoferrocenes and traces of phosphine oxides caused by using commercial chlorodiphenylphosphine proved a little difficult, (see supplementary section). For this reason, it is recommended to use freshly opened or distilled samples of chlorodiphenylphosphine. Nevertheless, this synthetic method is an excellent one with improved yields compared to existing methodology which again had the problem of the formation of isomers. Spectral data is given in supporting information which shows the presence of 2,1′,2′-tris-(diphenylphosphino)bromoferrocenes which is occasionally observed as an impurity. This compound complements the 1,1′,3,3′-tetrakis-(diphenylphosphino) ferrocene, **11,** see Figure 1, inset, which we prepared in the early 2000′s.

It was thought that the synthetic method would be suitable for the preparation of the related 1,1′,2,2′-tetrakis-(di-*tert*-butylphosphino)ferrocene, essentially by changing the quenching reagent to chlorodi-*tert*-butylphosphine, however when we attempted the reaction, we were unsuccessful in obtaining the anticipated product, probably because of the steric congestion of having adjacent bulky phosphines is too much. Highly air sensitive product mixtures resulted. If we were to add THF in this synthesis it is likely that the 1,3-disubstituted products would result following a *halogen dance* mechanism. However, 1,1´,2,2´-tetrabromoferrocene, **16,** may be used as a precursor for the synthesis of 2ˈ-diphenylphosphino-1,1ˈ,2-tribromoferrocene, **21**. (See Figure 11 for general synthetic scheme) This was obtained in one step by lithium exchange of one bromine and quenching with chlorodiphenylphosphine. The correlation NMR spectrum of this compound (*rac*-) is shown in Figure 12. The reaction yield is greater than 80% (not optimised). Clearly compound **21** will be a useful precursor compound for the synthesis of other many other phosphines and this will allow the future synthesis of ferrocenes with 4 *different* phosphine substituents. In this case there are six distinct ferrocenyl-proton resonances.

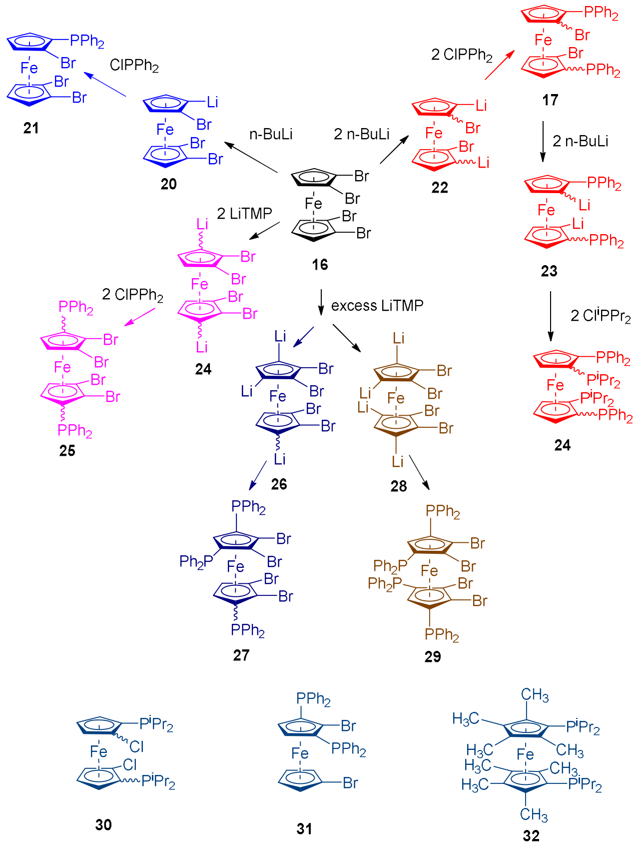


Figure 11. Schematic showing the ferrocenylphosphines which may be obtained from 1,1′,2,2′-tetrabromoferrocene, **16**, and structural drawings of compounds **30-32**.

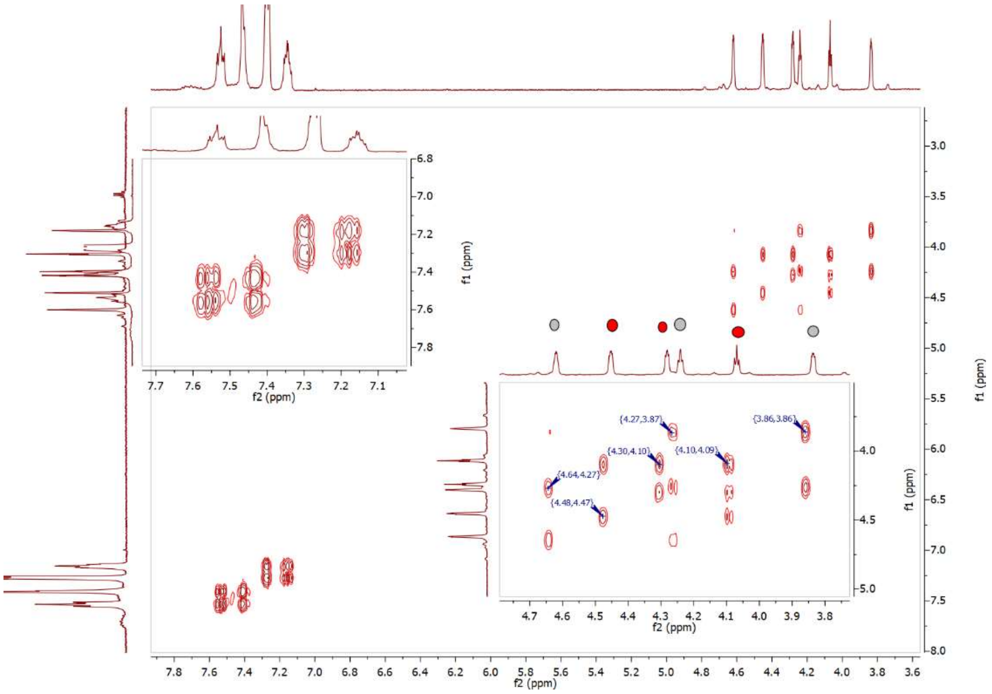
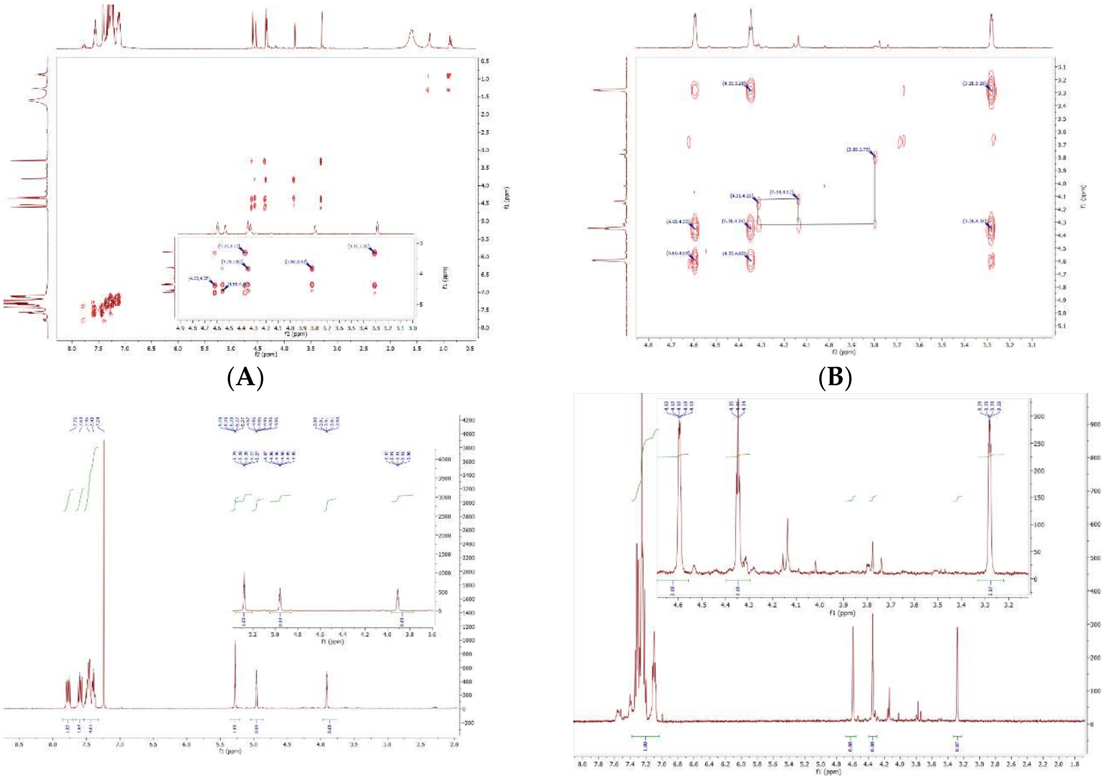


Figure 12. Correlation NMR spectrum of 2'-diphenylphosphino-1,1',2-tribromoferrocene, **21.** In the Figure the grey circles are the ferrocenyl protons on the phosphine-substituted ring while the red circles represent resonances on the dibrominated ring.

The reaction of the 1,1′,2,2′-tetrabromoferrocene, **16,** with two equivalents of n-butyllithium followed by the same quenching reagent gave the known 2,2′-bis-(diphenylphosphino)-1,1′-dibromoferrocene **17** in good, isolated yields (Figure 4, route **A**), however the recommended route to this compound is from 1,1′-dibromoferrocene **15,** (Figure 4, route **B**). This compound may now be obtained free from the other isomers such as 2,4-bis-(diphenylphosphino)-1,1′-dibromoferrocene, **31**, which plagued the earlier reported synthesis. [88] There is no need for chromatography. It is possible to conduct this reaction in multi-gram quantities. Detailed (in addition to those spectra shown below) NMR spectra of this compound are given in supporting information section. From this the mixed phosphine compound bis-2,2′-di-isopropylphosphino-1,1′-bis-(diphenylphosphino)ferrocene, **24** (see Figure 11) was also obtained following the lithiation and quench method as an orange/red crystalline solid. The ^{1}H/^{1}H COSY NMR spectrum of this compound is shown in Figure 13. On crystallisation from methanol the product obtained was an approximately 2:1 mixture of meso and racemic isomers. Despite its highly crystalline appearance we were unable to obtain a crystal structure.



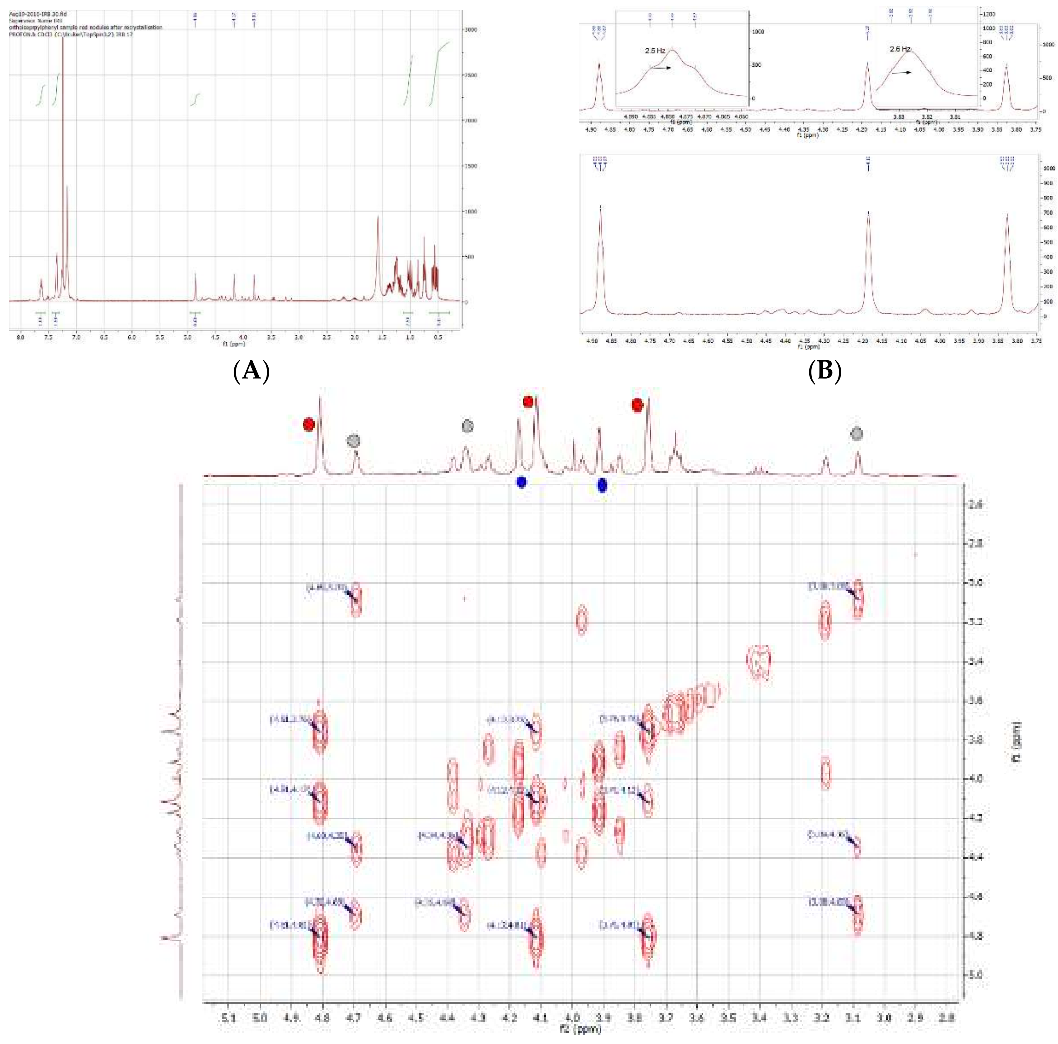
(**A**) (**B**)

(**C**) (**D**)

Figure 13. ^{1}H NMR correlation spectra, 2,2′-bis-diphenylphosphine-1,1′-dibromoferrocene, **17**, (A, both isomers) and B, D predominantly one isomer (ferrocenyl expansion only) from crystallization. Treatment of single isomer with sulfur gives the sulfide, 2,2′-bis-(diphenylphosphinesulfido)-1,1′-dibromoferrocene, shown in C, cleanly with the ^{31}P resonance moving from to ca -22.0 ppm (in D) to +41.2 ppm.

A point that should be emphasized here is that the lithiated intermediate compound **23** (see Figure 10) is best precipitated from solution as reactions of the lithium with the phosphine can cause isolation problems.

The phosphorus chemical shifts in **24** are observed at -26.46 (d, $J_{P,P}$ = 89 Hz), and -5.73 ppm respectively for the isomer obtained from a sample of compound **13** with mainly one isomer.


(**A**) (**B**)

(**C**)

Figure 14. A, **B**: NMR spectrum of compound **24** (prepared from one isomer of compound **13**) and the expansion of the ferrocenyl region, and **C**: $^1H/^1H$ COSY NMR spectrum of impure solid **24**, (*rac* and *meso* 2:1 ratio produced by a second crystallisation of residual solid).

As discussed earlier, the proton NMR of a crystallised sample indicates that both diastereomers are present and the small quantity of the second isomer may have thwarted our attempted crystallographic characterisation. However, we do have a structural report of the palladium complex of compound **24** which is available in the S.I. Further pertinent NMR spectra are also shown in the S.I. section. In theory the general synthetic method should be extendable to the preparation of more highly substituted ferrocenes, therefore a test reaction was carried out on the alpha dilithiation of 1,1ʹ,2,2ʹ-tetrabromoferrocene, **16**, to give the 3,3ʹ-bis-diphenylphosphino-1,1ʹ,2,2ʹ-tetrabromoferrocene **25**, directly via the dilithium compound **24**, (see Figure 11 for drawing).

Compound **25** was indeed the major product obtained from this reaction; however, it was only isolated following a chromatographic separation because of the significant number of by-products present. This was because *thf* had to be added to enhance the reagent solubility in the synthesis when quenching with the phosphine. This causes isomerisation of the lithiated intermediate resulting in several byproducts. The ferrocene protons in the NMR spectrum (Figure 15) of this compound are observed as two doublets, (3.22, 4.62 ppm, isomer 1), and 3.23, 4.67 ppm, isomer 2)). The protons adjacent to the bromines are the low field resonances and the high field resonance are assigned as the protons next to the phosphines. The phosphorus resonances are observed at -26.11 ppm for both isomers indicating a progression of chemical shifts as more bromines are added to *dppf*: *dppf*, (-16.7ppm), dibromo-*dppf*, (-21.9), tetrabromo-*dppf* (-26.1). As discussed above multiple lithiations (more than dilithiation) can occur in this synthesis and when even a small an excess of the

LiTMP/TMEDA reagent was used the tris-phosphine, **27**, (scheme 3) and small quantities of the tetraphosphine, **29**, were also observed by NMR. The three phosphorus resonances of compound **27** are observed at -25.01, -28.41 and -30.37 ppm and for the tetra phosphine, **29** a singlet at -32.1ppm.

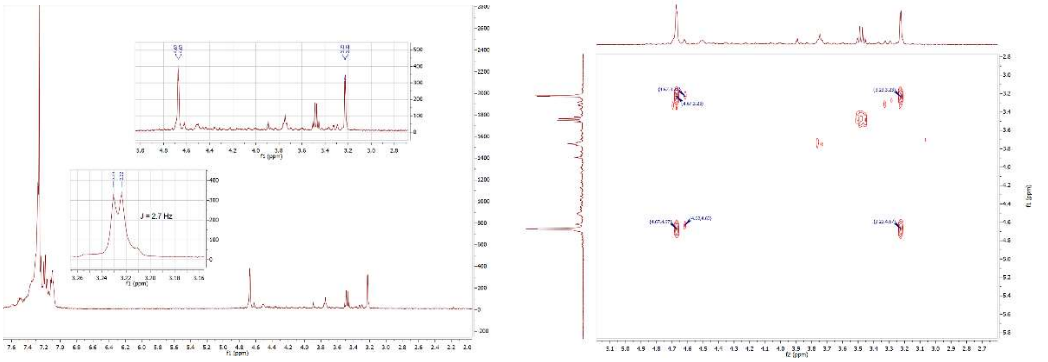
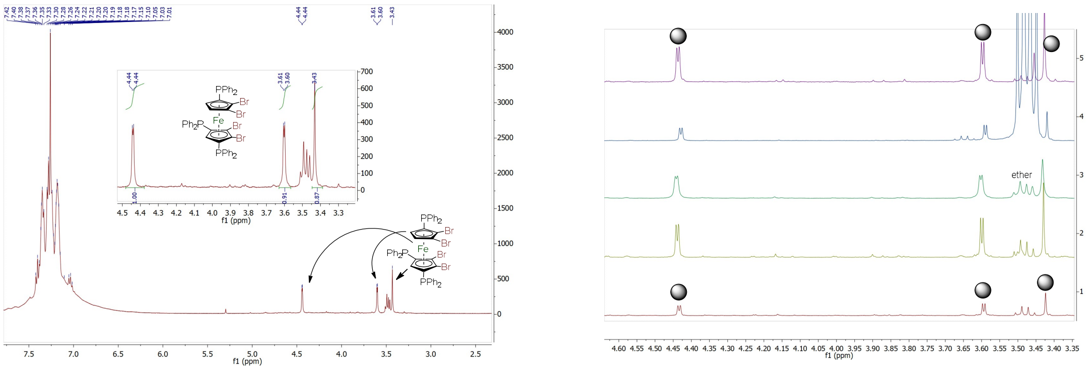


Figure 15. Band 1: chromatographic fraction showing major product, 3,3ˈ-bis-diphenylphosphino-1,1ˈ,2,2ˈ-tetrabromoferrocene **25**, from the dilithiation and quench with $ClPPh_2$. A: full spectrum, B, COSY of ferrocenyl proton resonances. The second isomer of this compound could only be identified in product mixtures using COSY NMR.



(**A**) (**B**)

Figure 16. A, ¹H NMR spectrum showing the presence of the 3,5,3ˈ-tris-diphenylphosphino-1,1ˈ,2,2ˈ-tetrabromoferrocene, **27. B**, expansion of stacked ferrocenyl-region.

This poly lithiation is not unexpected and may be a useful adaptation of the synthetic methodology. Indeed, when we used excess lithiation reagents in early syntheses of **17** from 1,1′-dibromoferrocene we also observed the presence of more highly substituted phosphinoferrocenes in the product mixtures. As we now have access to multi-gram quantities of 1,1′,2,2′,3,3′-hexabromoferrocene, [104] it was hoped it would be possible to exploit the same reaction chemistry to prepare even more highly substituted ferrocenes as well as examining the preparation of other phosphines with different phosphorus substituents. Unfortunately, this will require the use of more polar solvents in the case of the preparation of ferrocenylarylphosphines. On two attempted dilithiation reactions of 1,1′,2,2′,3,3′-hexabromoferrocene and quenching with chlorodiphenylphosphine in thf, we observed that extensive lithium scrambling led to too many products to separate easily. Of course, this synthesis should be relatively easy for alkylphosphine synthesis since they are soluble in hexane/ether and we hope to see others pioneer this area of work. As mentioned earlier the *per*-methylated *dippf* ligand, 2,3,4,5,7,8,9,10-octamethyl-1,6-*bis*-di-isopropyl-phosphino-ferrocene, *omdippf*, **32**, (shown in Figure 10) had been used by us in previous ligand tests in the Lucite alpha process,[106] however the synthetic data has not been published. The synthetic methodology is thus given in the supporting information. NMR data for ligand **32** is included in the supporting information section as it makes a useful NMR comparison with both *dippf*, **2**, and **9**, *tippf*.

The phosphorus resonance of **32** is thus observed at 1.04 ppm. Its structure can be seen when coordinated to palladium is shown in S.I.

2.1:. In Situ NMR-Based Coordination Studies of 2,2´-Bis-(diphenylphosphino)-1,1′-dibromoferrocene, 17 with Palladium and Platinum.

Detailed coordination studies on related diphosphine and tetraphosphines and more highly phosphinated ferrocene ligands have been carried out by Hierso and co-workers therefore the reader is directed to these reports. [76–84] No bulk coordination complexes were possible here with precious metals simply because we had limited resources. However, some basic coordination chemistries of nickel, palladium and platinum (II) were examined using NMR spectroscopy by incremental addition of a metal precursor complex to a solution of the ligand in a deuterated solvent. This method is useful to enhance selectivity where complex product mixtures are possible due to a range of different coordination modes for polyphosphine ligands. For nickel compounds, the nickel complex [Ni(DME)Cl_2)], (DME = 1,2-dimethoxyethane) was used as a precursor. In the case of palladium, the precursor complexes [Pd(1,5-COD)Cl_2] or [Pd(CH_3CN)$_2$$Cl_2$] were used and for platinum [Pt(DMSO)$_2$$Cl_2$ was used. Typical NMR spectra are given in the supporting information section. In the case of palladium and platinum we were able to isolate crystalline samples of the meso isomer which were structurally characterised. These are both square planar as expected and are shown in Figure 17.

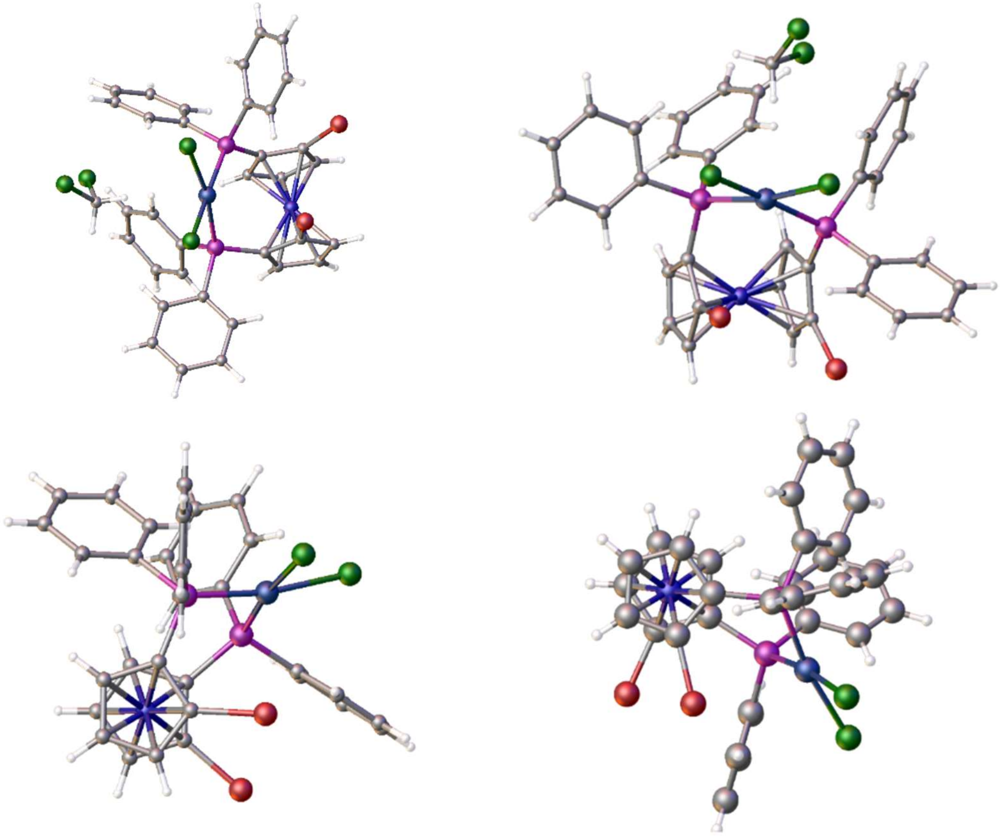


Figure 17. Side and top views of the crystal structure of platinum dichloride complex of 2,2′-bis-diphenylphospino-1,1′-dibromoferrocene, **17**. (*meso*) and side and top views of the palladium dichloride complex of **17**. Full details are given in S.I. section.

2.11. Coordination of 1,1´,2,2´-Tetrakis-(di-isopropyl-phosphino)ferrocene, (Tdipf), 9.

It is noted that both the yellow trigonal nickel(I)- and the green tetrahedral nickel (II)-complexes of *dippf* have been structurally characterised previously. [107] On addition of nickel to a solution of ligand **9** (*tiiprf)* in chloroform the monometallic complex is formed initially- this confirms it is square planar as tetrahedral complexes are paramagnetic. This mono metallic complex forms from two phosphorus atoms on one cyclopentadienyl ring– thus both free and coordinated phosphorus are observed- the free phosphine is observed at -2.59 ppm whereas the co-ordinated phosphine is observed at +60.17 ppm. In the case of the ferrocene protons the initial simplicity of the ligand resonances makes complex assignment easy as the initial doublet and triplet pattern acts as a marker and two new sets of resonances designated coordinated and unligated cyclopentadienyl rings. Both resonances move downfield- the uncoordinated cyclopentadienyl ring moves to 4.41 ppm (4.32) and 5.06 (4.55) ppm whereas the coordinated ring protons move to 4.51 and 4.87ppm. (Figures in brackets are for the free ligand). Further additions of nickel result in the formation of the bimetallic complex, however the solubility of this was extremely low in the chlorinated solvents we had available for NMR experiments.

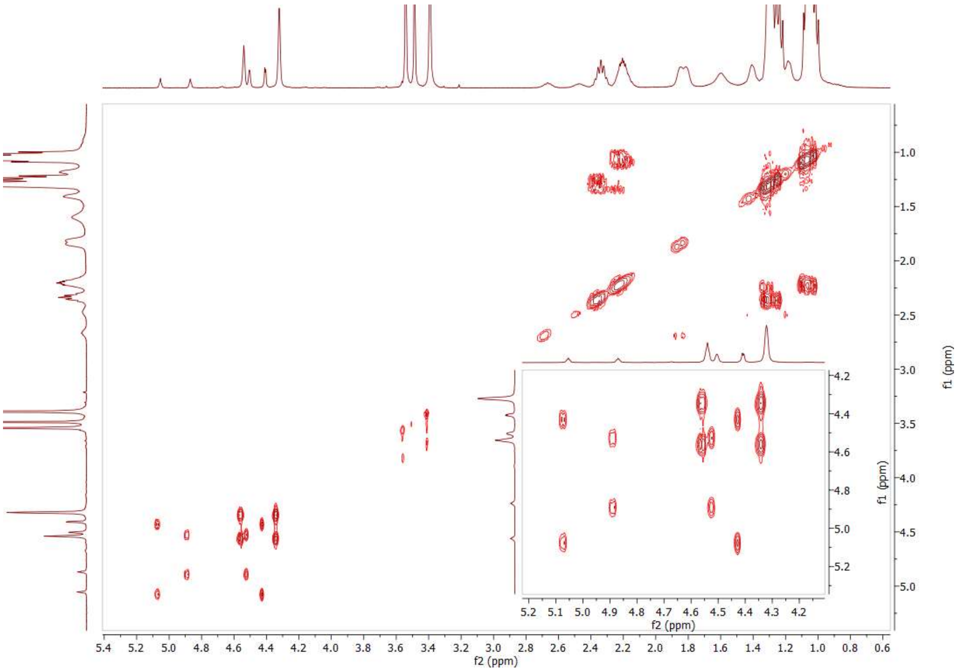
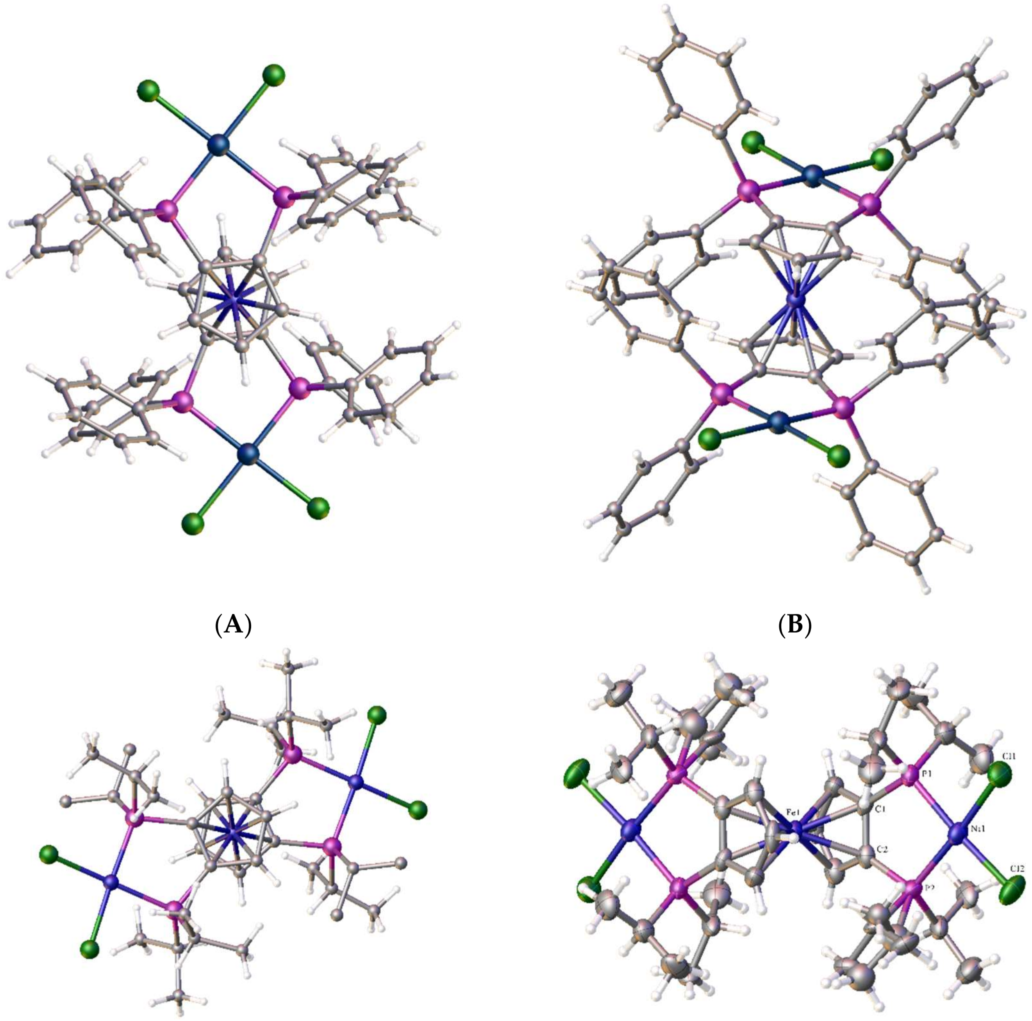


Figure 18. Formation of monometallic nickel dichloride complex of compound **9** (NMR experiment) – see inset Both ferrocenyl resonances move downfield- the uncoordinated cyclopentadienyl ring proton resonance moves to 4.41 ppm (from 4.32) and 5.06 (from 4.55) ppm whereas the coordinated ring protons move to 4.51 and 4.87ppm.

Because of this no phosphorus resonance was identified for the bimetallic complex (which had precipitated) and only one very low resolution ferrocenyl proton resonance was observed at 4.67ppm. Despite these problems the nickel complex could be isolated as a crystalline compound on a larger scale by slow solvent diffusion and its crystal structure is shown in Figure 18. In the case of palladium, a preparative scale the addition of an excess of palladium bis acetonitrile dichloride to the ligand results in a deep red solution from which a red brown precipitate is immediately formed. If the precipitate is ether washed dried, then washed with chloroform-*d* a sparingly soluble red complex is observed with a phosphorus singlet resonance at +72 ppm due to the bimetallic complex. Unfortunately, at that time we had not obtained crystals suitable for single crystal analysis. Similar results were observed on carrying out palladium addition to ligand **8**. (see S.I.)

Lastly, the coordination chemistry with platinum is as expected and fits the pattern with those of the other group 16 metals. In the NMR experiments with platinum, [Pt(DMSO)$_2$Cl$_2$] was used as the precursor even although it is poorly soluble in chloroform. On coordination with *tiipf* case two complexes in significant concentration were observed by NMR with phosphorus chemical shifts observed at +22.22 ppm (major) and +21.66 (minor) with ^{195}Pt-^{31}P coupling constants of 3651 and 3616 Hz respectively. Analogous results are observed by NMR in that the mono platinum complex forms first with the ligand proton resonance adjacent to phosphorus shifting from 4.35 ppm to [4.43 and 4.52ppm (bound ring)] and 4.56 ppm (on Pt bound ring) to 4.89 and 5.07 ppm. The major product complex which precipitates is assigned as the bidentate complex with the structure analogous to that of the nickel complex, (see Figure 19). In a preparative scale reaction, an orange complex was formed which immediately precipitated from solution. Here again redissolution in the solvents used for NMR experiments was difficult. Despite the difficulty involved in these NMR scale experiments we were able to isolate some crystalline compounds and their structures are shown in Figure 19. These new complexes are thus ready to use in catalytic applications in powder form.



(**A**) (**B**)

(**C**) (**D**)

Figure 19. Crystal structures of the nickel dichloride complexes of ligands **8** and **9**.

2.3. Extension of Methodology.

Finally, one last frontier in ligand chemistry is now possible which is the easy preparation of poly-ligands or polymers made of ligands. Polyligands are scaffolds for multi-metal catalysis. In the simplest case the dilithium compounds may be simply reacted with one half equivalent (w.r.t. Li) of dichlorophosphines, instead of an equivalent of monochlophophines with the potential examples shown in Figure 20. We have briefly examined some reactions of this kind and isolated some poly-brominated precursors which are pale yellow/cream in color. In the case of dichlorophenylphosphine the limitation is the solubility of the polymer, as oligomers tend to precipitate from solution. Thus, to achieve the desired scaffolds it will be necessary to isolate the dilithium compounds and redissolve the in THF and add the solution to a to a solution of the dichlorophosphines in THF. During the preparation of compound **35** the intermediate compound **34** appears briefly at low temperature as the solution turned deep red before returning the customary yellow orange colour. This area of work clearly requires exploration as it will be possible to host an array of different metals on these ligands which should allow for very detailed, if complex, catalytic experiments to be performed. This bodes well for future research.

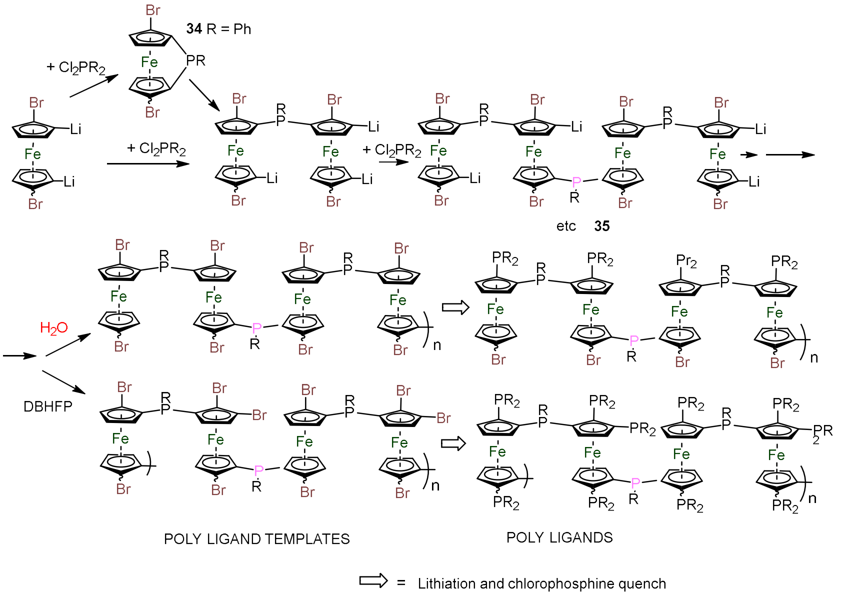


Figure 20. Schematic showing synthetic routes to polyphosphine ligands. (R = alkyl, aryl).

Clearly the future work in this area should focus on the use of alkylphosphines to obtain soluble polyphosphinoferrocene ligands. Where required and if a solid ligand support is required, it is important to ensure the solvents used in the synthesis are highly polar and have no acidic protons. It should be relatively easy to obtain more highly substituted phosphinoferrocenes such as the fully phosphoryated decakis-(diphenylphosphino)ferrocene if its poor solubility does not become the limiting factor. However, this aside we now have derivatives of *dppf* which can be easily substituted, Figure 20.

3. Summary

In summary, the alpha lithiation method has been used to establish an easy synthetic route to more highly substituted *dppf* and *diipf* ligands. This will make it possible to vary the methods in which these two commercially important ligands are used. It is now possible to predict whether nickel (II) will bind in a square planar or tetrahedral mode based on the ligand structure. The metal complexes of these poly-phosphine ligands reported here primarily exhibit square planar coordination- these should be excellent ligands for use in alkoxy carbonylation and related industrial catalytic processes. The coordination studies reported here have examined the stepwise room temperature metal complex formation. This paves the way for the bulk synthesis of the product complexes for commercial exploitation. At the outset we stated that the experimental work described here was carried out several years ago, finishing in 2017 and thus some time has passed and consequentially there have been some progress, not in this area specifically but in areas relating to starting material synthesis. We always welcome contact which researchers who would like to take this work forward and will be happy to help any research group doing so.

4. Materials and Methods

All materials used, including lithiation reagent, phosphines and solvents were commercially sourced and used without repurification. Diethyl ether and tetrahydrofuran were dried using a commercial solvent drying instrument. ^{1}H NMR data were obtained on a Bruker WM400 instrument operating at 400 MHz for proton. All crystallography work was carried out at the National Crystallography Centre based at the University of Southampton. Mass spectroscopic data was carried out in house and at the EPSRC National Mass Spectrometry Centre based at Swansea University. We thank the staff of both these institutions for their excellent and painstaking work.

4.1. General Experimental Details.

All reactions were carried out under a nitrogen atmosphere however all workups were performed under normal laboratory conditions. All reaction solvents were pre-dried using a commercial solvent drying instrument and other solvents used for work ups were standard reagent grade. NMR experiments were conducted in $CDCl_3$ using a 400 MHz instrument for proton unless otherwise indicated. 1,1′-Dibromoferrocene and 1,1′,2,2′-Tetrabromoferrocene were prepared according to the literature method. [104] Other regents were all obtained from commercial suppliers and were used as received. Bromoferrocene solutions in hexane(s) were prepared by vigorously shaking the bromoferrocene in a large vial until fully dissolved. TMEDA = tetramethylethylenediamine; TMP = tetramethylpiperidine. It is important that the bromoferrocene(s) are fully dissolved before commencing work.

4.2. Lithiation of 1,1′-Dibromoferrocene. [104]

4.2.1. Preparation of 2,2′-Dilithio-1,1′-dibromoferrocene, General Method.

The method used follows the experimental work reported recently by Butler [104] except that the scales of reaction used here are somewhat lower. A mixture of LiTMP and TMEDA (*Alphalith*) was prepared in hexane or hexanes by addition of n-BuLi to TMP and then adding half an equivalent of TMEDA. To this solution was added a solution of 1,1′-dibromoferrocene in the minimum quantity of hexane required to fully dissolve it. Typically, a scale of 10 mmol was used. Reagent quantities: 1,1′-dibromoferrocene (3.44g); TMEDA (1.20g), TMP (2.90g) in hexane (200mL). After stirring for 20-30 minutes a slurry of the 2,2′-dilithio-1,1′-dibromoferrocene.TMEDA reagent was obtained ready for quenching with the appropriate electrophile.

4.3. Lithiation of 1,1′,2,2′-Tetrabromoferrocene: Preparation of 3,3′-Dilithio-1,1′,2,2′-tetrabromoferrocene. General Method. [104]

The reaction was carried out in an identical manner to the previous experiment except that because of the lower solubility of 1,1′,2,2′-tetrabromoferrocene in hexane(s) larger volumes of hexane are required to fully dissolve the precursor ferrocene. A mixture of LiTMP and TMEDA (*Alphalith*) was prepared in hexane or hexanes by addition of n-BuLi to TMP the adding half an equivalent of TMEDA. To this solution was added a solution of 1,1′,2,2′-tetrabromoferrocene in the minimum quantity of hexane required to fully dissolve it. Typically, a scale of 5 mmol was used- 1,1′,2,2′-tetabromferrocene (2.6 g), TMEDA (0.60g), TMP (1.45g) in hexane (200mL). After stirring for 20-30 minutes a slurry of the 3,3′-dilithio-1,1′,2,2′-tetrabromoferrocene.TMEDA reagent was obtained ready for quenching with the appropriate electrophile.

4.4. Tetra-Lithiation of 1,1′,2,2′-Tetrabromoferrocene. [108]

4.4.1. A Solution of 1,1′,2,2′-Tetrabromoferrocene (2.5g, 5 mmol) in Diethyl Ether Maintained at -40-50^{o}C Was Treated with a Slight Excess of t-Butyllithium and the Deep Red Solution Was Used After 5-10 Minutes.

4.4.2. A Slurry of 1,1′,2,2′-Tetralithioferrocene Was Prepared at Room Temperature by Stirring a Solution of 1,1′,2,2′-Tetrabromoferrocene in Hexane with n-BuLi or t-BuLi. Addition of a Few mL of Diethyl Ether Facilitates the Production of 1,1′,2,2′-Tetralithioferrocene Which Gradually Precipitates. The Slurry Was Used After 1h.

Quenching Reagents Used: a) chlorodiphenylphosphine; b) chlorodi-isopropylphosphine; c) dichloroisopropylphosphine d) dichlorodphenylphosphine.

4.5. Quench Methodology

Generally, the quench reagent may be added dropwise to the well stirred solution of the lithiated reagent and stirring was continued for 1-2hr. In the case of the less soluble reagents such as chlorodiphenylphosphine the reaction solution was warmed by immersion of the reaction flask (with a reflux condenser added to the reaction flask) in an oil bath for a further 2h. after the initial stirring period.

4.5.1. Work-Up: Isopropylphosphine Quench Reagents.

The reactions were quenched with an aqueous solution of sodium carbonate and diethyl ether was added to facilitate product extraction. The product contained in the organic layer was separated in a filter funnel and this organic solution was dried over anhydrous magnesium sulfate. The solution was then suction filtered gently using a Buchner funnel through a small plug (2-3cm depth) of silica gel. The gel was washed with ether to ensure any trapped product is removed. The volatiles were removed from the combined organic phases on a rotary evaporator. The resultant oil was resolved in methanol and the product solution was left to stand in a sealed container or cooled in a freezer until crystallisation occurred. The products generally crystallise as nodules which are orange red or red.

4.5.2. Work-Up: Phenylphosphine Quench Reagents.

The reactions were quenched with an aqueous solution of sodium carbonate and diethyl ether and dichloromethane was added to facilitate product extraction. The product contained in the organic layer was separated in a filter funnel and this organic solution was dried over anhydrous magnesium sulfate. The solution was then suction filtered gently using a Buchner funnel through a small plug (2-3cm depth) of silica gel. The volatiles were removed on a rotary evaporator. The resultant oil was resolved in dichloromethane and the solution was triturated with diethyl ether until the first signs of clouding appeared then the solution was allowed to stand or cooled to -20^{0}C to facilitate crystallisation. In methanol the product solution was left to stand in a sealed container or cooled in a freezer until crystallisation occurred. The products generally crystallise as crystals or microcrystals which are yellow-orange or orange.

4.6. Compound Preparations

4.6.1. Preparation of the 1,1′,2,2′-Tetrakis-(diphenylphosphino)ferrocene, Tdppf, 8. [5g Scale]

1,1′,2,2′-Tetrabromoferrocene 5.0 g (10 mml) was suspended in a mixture of diethyl ether 50 ml and hexane 150ml at room temperature. A solution of n-BuLi in hexane (17 mL, 42.5 mmol) was added slowly and after a few minutes turbidity is observed which quickly results in the formation of the characteristic precipitate of 1,1′,2,2′-tetralithioferrocene. After 90 minutes the solution was cooled to *ca* -50°C and chlorodiphenylphosphine (9.4g, 43 mmol) in diethyl ether (100mL) was added with rapid stirring (this is to avoid the phosphine freezing as droplets on addition). On warming the colour changes through orange to a red brown final colour. The solution was gently warmed to ensure complete reaction after it attains room temperature. The solution was the hydrolysed with an excess of an aqueous saturated potassium bicarbonate solution (100 ml) and the two phases were thoroughly mixed for 15 minutes. Following this the red solution was filtered through a glass frit and the precipitate was washed with excess diethyl ether until the washing were clear. The aqueous fraction was discarded, and the combined ether solution were combined and dried over magnesium sulfate. The solution was then passed through a short silica plug (use excess ether to remove the colour) and the red filtrate was reduced in volume- at the point where the last few mls of ether is removed the product precipitates as a red/orange solid. The is redissolved in the minimum volume of ether and is recrystallised at low temperature. (N.B. this reaction has been carried out numerous times and each time the work up method has been varied dependent on how the product precipitates. To obtain a highly pure sample the product can be chromatographed on deactivated neutral alumina or celite using hexane and ether eluents- this results in a red microcrystalline sample).

* (^{t}BuLi can also be used in the series of experiments, but the solution is cooled (min -30°C) prior to addition)

1,1′,2,2′-Tetrakis-(diphenylphosphino)ferrocene, **8**: ^{1}H NMR.: 3.83 (br dd, 4H, J = 1.0, 2.2Hz), 4.72 (pt, J = 2.2Hz), 6.85-7.30 (m’s, 40H). ^{13}C NMR: 74.30 (2C), 77.53 (4C) (fc C’s),127.52(t, J = 3.5Hz), 127.80, 128.14 (t, J = 3.7Hz), 128.74, 133.24 (t, J = 8.2Hz), 134.55 (t, J = 9.5Hz), (non quat. C’s) 137.35 (t, J = 3.3Hz), 138.18 (t, J = 4.3Hz), (quat C’s). ^{31}P -23.37. Mass spectrum: m/z, 923.1975, (theoretical), 923.1979 (observed). (see S.I for additional spectra).

4.6.2. Preparation of 1,1′,2,2′-Tetrakis-Diisopropylphosphinoferrocene, 9. Method 1.

A solution of 2,2′-bis-di-isopropylphosphino)-1,1′-dibromoferrocene (1.44g, 2.5mmol) dissolved in diethyl ether (100mL) maintained at -40°C was treated with a solution of n-butyllithium (2.2mL of a 2.5M solution in hexanes, 5.5 mmol) and was stirred for 30 min. Chlorodiisopropylphosphine, (0.9mL, 5.6mmol) was added dropwise using an airtight syringe and the solution was subsequently warmed to room temperature. Following hydrolysis with water, drying and filtration following the method outlined above the product was crystallised from methanol at -20°C. Crystallisation in this case took several days where the product was obtained as waxy red nodules. (0.74g, 52%). N.B. the residual solution may be retained to obtain metal complexes.

4.6.3. Preparation of 1,1′,2,2′-Tetrakis-Diisopropylphosphinoferrocene, 9. Method 2.

1,1′,2,2′-Tetralithioferrocene was prepared as a red suspension by addition of n-butyllithium (8.0 ml of a 2.5M solution) to a solution of 1,1′,2,2′-tetra-bromoferrocene (2.5g, 5mmol) dissolved in diethyl ether (50mL) at room temperature. The solution was cooled to ca -50° C before chloro-di-isopropylphosphine was added. The solution was then warmed slowly to room temperature before being hydrolysed with a solution of potassium bicarbonate in water. The reaction mixture was poured into a separating funnel and the organic fraction was collected using small further increments of ether to extract any residual product (using the colour as an indication). This solution was flash filtered through a plug consisting of separate layers of silica and magnesium sulfate the plug was further ether washed. The total filtrate was reduced in volume to leave an oil which was redissolved in the minimum volume of methanol for complete solution. The solution was cooled to -20^{o}C in a flask under nitrogen for 3 days whereupon it crystallised to give the product as red-pink nodules, (91%). The residual solution which still contained some ligand, 9, was used directly to form metal complex with nickel by addition of [Ni(DME)Cl$_2$] to the solution.

1,1′,2,2′-Tetrakis-(diisopropylphosphino)ferrocene, 9: ^{1}H NMR. 1.02 (ddd, 24H), 1.26 (ddd, 24H), 2.19 (m, 4H), 2.32 (m, 4H), 4.30 (m, 4H,), 4.52 (pt, 4H, J = 2.1Hz). ^{13}C NMR: 20.29 (pt), 20.23 (pt), 21.86 (pt), 23.06 (pt), 24.96 (dd), 25.89 (pt), 73.62, 75.90, 85.33 (quat.). ^{31}P NMR: -1.29 (s). pt = pseudo triplet. Mass spectrum: M$^+$+1, m/z 651.3598 (observed); 651.3223, (theor.). See S.I. for actual spectra.

4.6.4. Preparation of Compounds 2.2′-Bis-diphenylphosphino-1,1′-dibromoferrocene, 17 and 2,2′-Bis-diisopropylphosphino-1,1′-dibromoferrocene. 18.

A solution of 2,2′-dilithio-1,1′-dibromoferrocene.TMEDA was prepared as follows: a solution of LiTMP in hexanes (300ml) was prepared by slow addition (2-3 minutes) addition of n-BuLi (8.5 mL of a 2.5M sol., 21.3 mmol) to a solution of TMP (3.10g, 22.0 mmol) in hexanes (20mL). To this TMEDA (1.25g, 10.8 mmol) was added. A saturated solution of 1,1′-dibromoferrocene (3.44g, 10 mmol) in hexanes (prepared separately by shaking 1,1′-dibromoferrocene in the minimum volume of hexanes needed to dissolve it) was added dropwise over 10 min. This was subsequently left to stir for 30 minutes. The solution/slurry was cooled to -40^{o}C and chlorodi-isopropylphosphine (3.25 g, 21.3mmol) or chlorodiphenylphosphine (5.13g, 21.3 mmol).

2,2′-Bis-diphenylphosphino-1,1′-dibromoferrocene, **17**. (major): Isomer 1: *meso* from 4 equiv. prep. 3.80 (dd, 2H, J = 1.2, 2.5 Hz), 4.33 (pt, 2H, J = 2.5Hz), 4.55(dd, 2H, J = 1.2, 2.5 Hz), 7.14 (m, 4H), 7.26 (m, 6H), 7,41 (m, 6H), 7.56 (m, 4H). ^{13}CNMR: 74.55, 75.26, 76.25, 128.40, 128.93, 132.32, 135.34. (*ipso* C's not reported). ^{31}P: - 21.6 (pt, J$_{P-H}$ = 7.4Hz). Isomer 2, rac.: 3.33(dd,2H, J = 1.5, 2.5 Hz), 4.38 (bt,2H, J = 2.5Hz), 4.62 (dd, J = 1.5,2.5), 7.07-7.66 M's, H). C 71.63 (J = 3.7Hz), 72.95 (J = 4.5Hz), 80.70 (d, J = 1.9Hz) 78.72 (ipso), 78.80 (ipso) 128.30 (2d, J = 3.5, 8.5Hz),132.14 (d, J = 19Hz), 134. 81 (d, J = 20Hz) 136.27, (*ipso*), 136.37, (ipso). ^{31}P: -21.9. (NMR spectra of both isomers together are included in S.I.)

Mass Spectral data: Mass spec 712.9257, [M+H], 711(56), 712(24) 713(100), 714 (39), 715(50), 716(19), M+H ion profile, 708.9334, (theor.) 708.9345, (obs.)

Compound **18** crystallised as a mixture of two isomers labelled as major and minor (see previous NMR spectra, major = higher concentration).

2,2′-Bis-diisopropylphosphino-1,1′-dibromoferrocene, **18**. (*meso*): ^{1}H NMR(CDCl$_3$): 0.94 (6H, dd, 7.5, 13.0), 1.03 (6H, dd, 6.9, 14.3), 1.21 (6H, dd, 6.9, 10.7), 1.37 (6H, dd, 6.9,16.3), 1.93 (2H, m), 2.29 (2H, m), 4.11(2H, bs) 4.14(2H, br s), 4.55 (2H, br s). ^{13}C NMR: 19.89(d, 8.8), 20.17 (d, 11.2), 20.46 (d, 16.7), 22.59 (d, 21.7), 22.96 (d, 10.5), 24.88(d, 13.8),72.16, 73.08 (d, 1.2Hz), 73.32, 98.48, 97.69. ^{31}P: -3.99. (*rac*): ^{1}H NMR(CDCl$_3$): 0.92 (6H, dd, overlapped), 1.00 (6H, dd, overlapped), 1.15 (6H, dd,6.9,13.2), 1.33 (6H, dd,7.6 overlapped), 1.98 (2H, m), 2.07 (2H, m), 3.97(2H, br. s), 4.32(2H, br. s) 4.34 (2H, br s). ^{13}C NMR: (minor): 19.60 (d, 9.2), 20.01 (d, 7.9), 20.16 (d, 7.1), 21.94 (d, 18.2), 22.61 (d,18.9), 25.23 (d,13.8), 68.99, 71.80 (d, J = 2.9), 78.73. (quat. not observed). ^{31}P: -4.98 ppm, (*meso*), - 5.15 ppm (*rac*). Mass spec. C$_{22}$H$_{34}$Br$_2$FeP$_2$H; m/z 572.9981 (obs.), 572.9971 (theoretical). Mass spec.: m/z, 576.9882, [M+ H], theoretical (obs.), 575(58), 576(16), 577(100), 578(30), 579(51), 580(16), 580(16).

4.6.5. Compound **24**, 2,2′-Bis-(Di-isopropylphosphino)-bis-1,1′-(diphenylphosphino)ferrocene.

This compound was prepared according to method in section 4.2.1 quenching with one equivalent (w.r.t. Li) of chlorodi-isopropylphosphine. Product crystallisation was from methanol/ether.

2,2′-Bis-(di-isopropylphosphino)-bis-1,1′-(diphenylphosphino)ferrocene, **24**: (note this was prepared from compound **17** , predominantly one isomer of compound **17**, maj. Data for maj. isomer reported here) ^{1}H NMR.: 0.53 (dd, 6H), 0.59 (dd, 6H), 0.75 (p pt, 6h), 1.01 (dd, 6H), 1.10-1.45 (m's, 4H), 3.81 (bs, 2H), 4.17 (bs, 2H), 4.86 (bs, 2H), 7.12-7.25 (m's, 10H), 7.33 (bs, 6H), 7.64 (pt, 4H). ^{31}P: -26.46

doi:10.20944/preprints202412.1243.v1

(d, J = 89 Hz), -5.73 (m). ^{13}C (DEPT) 127.9, 128.4, 132.72, 132.92, 135.63, 136.86, 138.02 (incomplete weak res.). Mass spec. m/e 786 parent ion; 784 (5.8), 785 (3.1) 786 (100%), 787 (51.9) 788 (4.1), 789 (2.4).

4.9. Preparation of 2′-Diphenylphosphino-1,1′,2-tribromoferrocene, compound 21.

This compound was prepared from 1,1′,2,2′-tetrabromoferrocene by addition of one equivalent of n-BuLi to a solution of 1,1′,2,2′-tetrabromoferrocene in dry THF at -70°C (10 min) followed by quenching with one equivalent of chlorodiphenylphosphine. Following the normal workup (addition of dilute sodium carbonate solution and separation of the organic layer, drying ($MgSO_4$) and volatile removal) the product oil was crystallised from a mixture of dichloromethane and diethyl ether.

2′-Diphenylphosphino-1,1′,2-tribromoferrocene, **21**: ^{1}H NMR: 3.82(dd, 1H, J = 1.46, 2.74 Hz), 4.05 (t, 1H, J = 2.75, 2.75 Hz), 4.22 (pt, J = 1.44 Hz), 4.27(m), 4.43(dd, 1H, J = 1.48, 2.76 Hz), 4.60 (1H, m, J = 1.44, 1.44 Hz). (note, coupling constants are as read) -blue is P-substituted Cp ring; 7.15(m, 2H), 7.26 (m, 2H), 7.39 (m, 3H) 7.51.(pt, 3H). ^{31}P, t, -22-66, ^{13}C NMR: 70.42, 71.21, 73.66. 73.70, 74.23, 76.01, 138.33, 128.58, 132.25, 135,12. (quaternaries not included). Mass spec. parent ion isotopic pattern, m/e 604-613, prominent ions at m/e 608(30%), 610(28), 612 (10).

4.10. Preparation of 3,3′-Bis-(diphenylphosphino)-1,1′,2,2′-tetrabromoferrocene, 25, (maj)

2,2′-bis(diphenylphosphino)-1,1′,2,2′-tetrabromoferrocene: ^{1}H NMR: 3.24 (d, 2H, J =2.6Hz), 4.69 (d, 2H, J = 2.6Hz), 7.00-7.50 (m′s, 20H) ^{31}P {H}NMR: -26.10 (s). ^{31}P NMR: -26.10 (pt, J = 7.8 Hz). ^{13} C NMR: 70.12, 75.08 phenyl resonances are overlapped. Minor isomer: 3.55 (2H), 4.68 (2H), 7.00-7.60 (m′s). (N.B. no integration reported on minor isomer). (see S.I. for spectrum)

Compound **27**; observed as a byproduct, 3,5,3′-tris-(diphenylphosphino),1,1′,2,2′-tetrabromoferrocene, : ^{1}H NMR: 3.42 (s, 1H), 3.59 (d, 1H, J = 2.7Hz), 4.43 (d, 1H, J = 2.7Hz), 7.08-7.45 (m′s, 30 H) ^{31}P -25.04, -25.09, -28.48.

Additional Synthetic Information, (compounds prepared for spectroscopic comparisons)

2,2′-Bis-diisopropylphosphino-1,1′-dichloroferrocene, **30**.

A sample of 2,2′-bis-diisopropylphosphino-1,1′-dichloroferrocene, **30**, (both isomers) was prepared directly in diethyl ether by direct lithiation (2 equivs) of 1,1′-dichloroferrocene in the presence of TMEDA (0.5 equiv.), followed by quenching with 2 equivalents of chlorodi-isopropylphosphine. In this case there is no need for special reactions conditions and no product isomerisation occurs. A comparison of chemical shifts with those of 2,2′-bis-di-isopropylphosphino-1,1′-dibromoferrocene is shown in S.I.

Synthesis: 2,3,4,5,7,8,9,10-octamethyl-1,6-*bis*-di-isopropylphosphinoferrocene, *omdippf*, **32**.

At the outset it was mentioned that the *per*-methylated *dppf* ligand, *dppomf* 18, had been used in previous ligand tests in the Lucite process and we decided it would be useful to have access to this ligand and its di-isopropyl analogue, 2,3,4,5,7,8,9,10-octamethyl-1,6-*bis*-di-isopropylphosphinoferrocene, *omdippf*, **32**, available for comparative tests. This new ligand was prepared using a simple modification of literature methods used for the preparation of compound **18**. Full synthetic details are again presented in the S.I. section.

Preparation of oligomeric 2,2′-phenylphosphino-1,1′-dibromoferrocene. **35**

A sample of of 2,2′-dilithio-1,1′-dibromoferrocene was prepared as described above from a 3.46g sample of 1,1′-dibromoferrocene in hexane (200ml) The slurry was cooled to -60°C and -0.5 equivalent of dichlorophenylphosphine was added. Diethyl ether (200mL) was then added and the solution was allowed to warm to room temperature. On warming the soltion briefly turned deep red which indicated the presence of the ferrocenophane compound **34**, which disappeared on further warming to room temperature. The sample was left to stir for 4hr and was gently warmed in a water bath. Flowing this, the work up was idential to that of other samples hydrolysis with dil. sodium carbonate solution. Following these steps the oligomeric product was obtained as a cream coloured solid which was removed by filtration before being washed with water and hexane /ether. The solid was the vacuum dried. This compound was stored under a nitrogen atmosphere as it darkens in air after several days. This polymeric compound has a complex broad NMR spectrum with broad resonance between 2.1-6.0 ppm and 6.8-7.8 ppm. Mass spectroscopy showed it to be oligomeric rather than polymeric m/e range to from m/e 400-1800.

The conclusion which can be drawn is that to make polymer of these ligands it will be necessary to use alkylphophines (proposed in Figure 21 above) or alkyated derivatives of the phenylphosphines to increase the solubily of the precursors themselves.

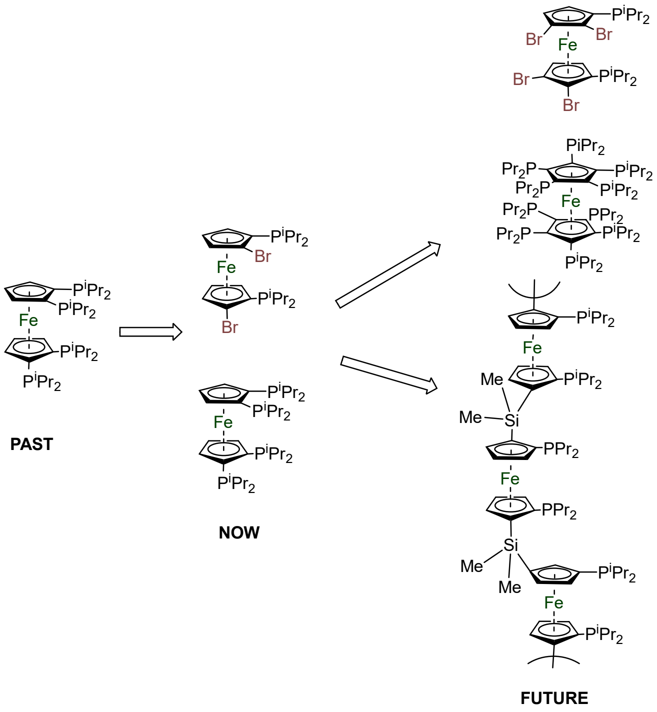


Figure 21. Scheme showing applications for the chemistry developed in this work; fully phosphine substituted ferrocenes, poly-brominated phosphines and polymers which may be used as ligands to bind multiple metals. .

5. Overall Conclusions

A new method for the synthesis of bulky ferrocenylphosphine ligands and their metal complexes has been established. In general, the coordination of 1,2-bis-phosphines give square planar complexes with nickel, palladium and platinum, whereas the 1,1'-bis-phosphine ligands can give either tetrahedral or square planar depending on the presence of adjacent substituents (Ni) or square planar complexes (Pd, Pt). This variation in coordination is important as these and related metal complexes are useful in catalysis in a wide range of reactions. These new nickel and palladium complexes have the perfect design for use in alkoxycarbonylation reactions. In this work all the new metal complexes have been prepared at room temperature with a view to the examination of the binding mechanism. There is a large area of research which may now be explored from the bulk synthesis of these complexes to the preparation of ferrocenes which are fully substituted with 10 alkyphosphines. Finally, since this work was completed there have been several reports published which use the lithiation protocols reported here. [109–111].

6. Supplementary Materials:

The following are available online at www.mdpi.com/xxx/s1, Additional NMR and general spectroscopic data, CIF files and checkCIF output files for compounds, **9, 21, 18, 30**, $PdCl_2$ complexes of compound **17**, $PtCl_2$ complex of **8**, $NiCl_2$ complex of **9**, palladium complex of **24**. Total 126 pages.

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Data Availability Statement: In this section, please provide details regarding where data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study. Please refer to suggested Data Availability Statements in section "MDPI Research Data Policies" at https://www.mdpi.com/ethics. You might choose to exclude this statement if the study did not report any data.

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