A Rapid Convenient Synthesis of Ferrocene-Based Triphos Analogue Ligands

Ian R. Butler,* Rachel L. Davies
The Department of Chemistry, The University of Wales, Bangor, Gwynedd, LL57 2UW, UK
Fax +44(1248)370528, E-Mail CHS026@BANGOR.AC.UK
Received 19 February 1996; revised 7 May 1996

Dedicated to George Amos, a brilliant chemistry teacher

A rapid synthetic procedure has been developed to prepare diferrrocenyltriphenylphosphine ligands which may be considered as ferrocene based analogues of the important prototype ligand triphos since they mimic triphos in their ligating properties with Rh(I) and Pd(II).

Ferrocenylphosphines form an important subgroup of ligands which have found increasing use in transition metal catalyzed processes. 1-6 The ferrocene may act as an electron reservoir in addition to giving a well defined ligand geometry because of its fixed interannular spacing. The most commonly used bidentate achiral ferrocenylphosphine is 1,1'-bis(diphenylphosphino)ferrocene (dpff2) which may be considered as the ferrocenyl analogue of bis(diphenylphosphino)ethane (dppe). For some time we have been interested in developing the synthesis of a ferrocenyl analogue of the archetypal tridentate ligand bis(diphenylphosphinoethyl)phenylphosphine (triphos').

The method developed here is both simple and cost effective. It makes use of 1,1'-dibromoferrocene as a precursor, which is readily available in multigram quantities. The monolithiation of dibromoferrocene, which has been used by us and others7 for the past five years or so, proceeds smoothly at low temperature (−70 °C) in THF to give 1-bromo-1'-lithioferrocene (I) which can be quenched with a halo- or dihalophosphine according to

Reagents (conditions) A: BuLi (THF, −70 °C),
(B): (−70 °C → r.t.),
(a): A; (b): CIPr3 (B); (c): Cl3P'Br (B); (d): A (ii) Cl3P'Br (B); (e): (i) A (ii) CIPr3; (f, g): (i) A, (ii) CIP(O)PPh3; (h): (i) A (ii) CIPPh3; (i): H2O2(CH2Cl2); (j): (i) A, (ii) DMF; (k): (i) A, (ii) CO2; (m): (i) A, (ii) Cl3P(CH2)2PCL2

Scheme

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>Compound</th>
<th>R</th>
<th>R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ph</td>
<td>-</td>
<td>4a</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>2b</td>
<td>i-Pr</td>
<td>-</td>
<td>4b</td>
<td>Ph</td>
<td>i-Pr</td>
</tr>
<tr>
<td>3a</td>
<td>-</td>
<td>Ph</td>
<td>4c</td>
<td>i-Pr</td>
<td>Ph</td>
</tr>
<tr>
<td>3b</td>
<td>-</td>
<td>i-Pr</td>
<td>4d</td>
<td>i-Pr</td>
<td>i-Pr</td>
</tr>
</tbody>
</table>
the Scheme to give either 1-bromo-1'-dialkyl- or arylphosphinoferrocenes 2 or the bis(1'-bromoferrocenylalky/arylphosphino)ferrocene 3. The latter products are obtained in high yield in both cases and are isolated following flash chromatography on silica gel. The subsequent lithiation of compounds 2 again proceeds smoothly to give in >80 % yield 1-lithio-1'-diphenylphosphinoferrocene or 1-lithio-1'-diospropylphosphinoferrocene. The procedure is developed in a similar manner to those of Wright, Butler and Cullen and Seyforth and Withers, which used alternate precursors. Further reaction of compound 2 followed by the electrophilic quenching with either dichlorophenyl- or dichloroisopropylphosphine yields the useful ligands such as bis(1'-diphenylphosphinoferrocenyl)phenylphosphine (4a, trifer), which is obtained as a pale yellow microcrystalline powder. The other three ligands in the series 4b–d are prepared equally easily, although compound 4d was obtained as an oil. The actual synthesis is rapid because the product isolation is achieved using flash chromatography on either silica gel or alumina. The relevant yields are reported in Table 1.

An alternate, but equally effective, synthetic strategy towards compounds 4a–d involves the dilithiation of the diferrocenes 3a and 3b followed by substitution with dialkyl- or diarylphosphine (Scheme, route e). The yields using this procedure are slightly higher because there is less chance of byproduct formation. The compounds 3 are clearly versatile synthons in their own right and also can be used to generate a range of substituted diferrocenylphosphines, e.g. 9 (R" = CHO), which are obtained

Table 1. Compounds 2–11 Prepared

<table>
<thead>
<tr>
<th>Product*</th>
<th>Yieldb (%)</th>
<th>mp (°C)</th>
<th>1H NMR (CDCl3/TMS)c</th>
<th>δ, J (Hz)</th>
<th>31P NMR (CDCl3/85% H3PO4), δ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FeP</td>
</tr>
<tr>
<td>2a16</td>
<td>83</td>
<td>95–101</td>
<td>3.98 (t, 2 H, J = 1.6), 4.16 (m, 2 H), 4.30 (t, 2 H, J = 1.6), 7.32 (m, 10 H)</td>
<td></td>
<td>18.12</td>
</tr>
<tr>
<td>2b16</td>
<td>84</td>
<td>oil</td>
<td>0.82 (dd, 12 H, J = 16, 7.8), 1.72 (m, 2 H), 3.80 (m, 2 H), 3.93 (m, 2 H), 4.05 (m, 2 H), 4.12 (m, 2 H)</td>
<td></td>
<td>0.63</td>
</tr>
<tr>
<td>3a</td>
<td>76</td>
<td>103–106</td>
<td>1.06 (brm, 12 H, J = 15, 7.7), 2.12 (p sept, 2 H, J = 7.7), 4.05 (brm, 4 H), 4.25 (2 m, 4 H), 4.30 (m, 2 H), 4.32 (m, 2 H), 4.41 (m 2 H), 4.73 (brm, 3 H), 7.44 (m, 2 H)</td>
<td></td>
<td>30.77</td>
</tr>
<tr>
<td>3b</td>
<td>73</td>
<td>92–93</td>
<td>0.97 (dd, 6 H, J = 16), 2.03 ( sept, 2 H, J = 7.4), 3.92 (m, 2 H), 4.03 (m, 2 H), 4.14 (m, 2 H), 4.23 (m, 2 H), 4.36 (m, 2 H), 4.41 (m, 2 H), 7.45 (brm, 20 H)</td>
<td></td>
<td>19.99</td>
</tr>
<tr>
<td>4a</td>
<td>85 (88)</td>
<td>124–126</td>
<td>1.10 (2 dd, 24 H, 1.91 (m, 4 H)), 3.98 (q, 2 H, J = 1.4), 4.06 (q, 2 H, J = 1.4), 4.18 (brm, 4 H), 4.23 (2 m, 4 H), 4.25 (pent, 2 H, J = 1.3), 4.29 (pent, 2 H, J = 1.3), 7.33 (m, 3 H), 7.53 (m, 2 H)</td>
<td></td>
<td>17.63</td>
</tr>
<tr>
<td>4b</td>
<td>83 (87)</td>
<td>53–56</td>
<td>1.06 (2 dd, 30 H, 15.5), 1.92 (2 sept, 5 H, J = 7.8), 4.04 (q, 2 H, J = 1.4), 4.14 (m, 2 H), 4.22 (m, 2 H), 4.27 (2 m, 4 H), 4.30 (m, 4 H), 4.35 (m, 2 H)</td>
<td></td>
<td>17.59</td>
</tr>
<tr>
<td>4c</td>
<td>81 (91)</td>
<td>166–167</td>
<td>1.07 (2 dd, 24 H, 1.91 (m, 4 H)), 3.98 (q, 2 H, J = 1.4), 4.06 (q, 2 H, J = 1.4), 4.18 (brm, 4 H), 4.23 (2 m, 4 H), 4.25 (pent, 2 H, J = 1.3), 4.29 (pent, 2 H, J = 1.3), 7.33 (m, 3 H), 7.53 (m, 2 H)</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>4d</td>
<td>73 (91)</td>
<td>oil</td>
<td>0.97 (dd, 6 H, J = 16), 2.03 ( sept, 2 H, J = 7.4), 3.92 (m, 2 H), 4.03 (m, 2 H), 4.14 (m, 2 H), 4.23 (m, 2 H), 4.36 (m, 2 H), 4.41 (m, 2 H), 7.45 (brm, 20 H)</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>58,15</td>
<td>86</td>
<td>144–146</td>
<td>3.92 (p, 2 H, J = 1.4), 4.40 (br s, 4 H), 4.50 (br s, 2 H), 7.51 (m, 6 H), 7.67 (m, 4 H)</td>
<td></td>
<td>27.65</td>
</tr>
<tr>
<td>6</td>
<td>95 (g)</td>
<td>180–181</td>
<td>1.04 (brs, 2 H, 2.12 (brs, 2 H), 4.37 (brs, 2 H), 4.59 (brs, 2 H), 7.32 (brs, 10 H), 7.31–7.54 (m, 6 H), 7.61–7.70 (m, 4 H)</td>
<td></td>
<td>28.24</td>
</tr>
</tbody>
</table>

Note: All new compounds gave accurate mass values as confirmed by HRMS. The deviation J from calculated values correspond to ±9.6 ppm.

* For compounds 4, the yields given refer to their preparation from precursor 2a or 2b. The yields of 4 given in parenthesis refer to their preparation from 3a or 3b. The letters in parenthesis, denoted in the yields of 5 and 6, refer to the reaction conditions depicted in the Scheme.

pq = pseudo quartet. pt = pseudo triplet.

Lit.8 mp 146–147°C.

Lit.16 dec. 195°C.
in high yield from the reaction of the dilithium salts with DMF/H²O. The dialdehydes are obtained as violet-brown crystalline solids which have a distinctive aroma. These, in turn, should prove to be important synths in their own right because ferrocenyl aldehydes are important precursors to an extremely broad range of more highly functionalised products such as terpyridines, amine macrocycles, alkenes, and polymers. Mixed 1,1'-phosphine/phosphate oxide substituted derivatives, e.g. 6 were prepared either indirectly following routes f, h and i, h (Scheme) or direct from compound 2, route g. Of these methods the latter route was found to be the most effective because prior oxidation of compound 2 to give 5 was relatively low yielding and the product tended to be highly solvated and/or hydrated limiting its direct use in the subsequent lithiation step without prolonged drying.

The product ligands were fully characterised using ¹H and ³¹P NMR and mass spectrometry. In general, the relative position of the ³¹P resonances may be taken as a guide to the relative ligand basicity. The ³¹P NMR data are presented in Table 2. The data show useful trends; in general the different substituted phosphorus nuclei resonate at higher field than those of the phenyl-substituted nuclei which is indicative of their higher basicity. The isopropyl-substituted phosphate derivatives in turn are observed at lower field than their phenyl analogues. The further reaction of four equivalents of 1-lithio-1-diphenylphosphinoferrocene with 1,2-bis(dichlorophosphino)ethane results in the clean formation of the hexaphosphine ligand 10 which was isolated as pale yellow nodules. Characterisation data for this compound is listed in Tables 1 and 2.

The examination of the coordination chemistry of the new tridentate ligands was carried out in order to make a comparison with the coordination chemistry of trisphos. The reaction of [Rh(1,5-COD)]Cl₂, (1,5-COD = 1,5-cyclooctadiene) with ligand 4a was chosen initially as this was considered to be the most important complexation reaction to study. The addition of excess [Rh(1,5-COD)]Cl₂ in CDCl₃ to a solution of compound 4a in the same solvent resulted in a shift of the ³¹P NMR resonances from δ = −17.7 and −32.16 to δ = +13.86 (d) and +22.62 (d), respectively. The isolation of the crystalline product from solution which is identical to the product obtained from a bulk preparation, however, afforded a complex with different spectroscopic features formulated as [P₂-LRhCl], L = 4a which was characterised independently using mass spectrometry, ³¹P and ¹H NMR spectroscopy. Similar results were observed using ligands 4b and 4c with both isolated product complexes exhibiting the signature ³¹P NMR resonances consisting of a doublet of triplets and a doublet of doublets. The identity of the intermediate complexes formed in the NMR solutions is unknown, however, it is likely that these are trinuclear rhodium complexes which would account for the observed spectra. We have observed similar results in in situ experiments with trisphos and [Rh(4,7-COD)]Cl₂. The isolation of the complexes [P₂-LRhCl] is consistent with the ligating behaviour of rhodium(I) and thus the ligands may be considered as true trisphos mimics. In the case of ligand 4d no crystalline products were obtained from the reaction solution. The coordination geometry of the ligands 4a–c with rhodium(I) is as indicated in the Figure (a). This has been verified independently following an X-ray structural determination in the case of the complex [4c]RhCl₃. This data will be published independently together with the electrochemistry of the new ligands and complexes.¹²

The ligands 4a–d react at room temperature with [Pd(1,5-COD)]Cl₂ to afford the cationic complexes [LPdCl]⁺Cl⁻ which again shows a direct analogy with the coordination chemistry of trisphos. The spectroscopic results for these complexes are reported in Table 2 and full characterisation data are listed separately for the complexes of 4a and 4b. The complexes [Pd(trisphos)]Cl⁺, A⁻ (A = Cl, PF₆) were first reported by King et al. in 1971.¹³ The change in chemical shifts observed on coordination in the ³¹P NMR spectra are +125.7 and +70.0 ppm, respectively for triphos (as PF₆⁻ salt), but are only +69 and +47 ppm, respectively for [Pd(4a)]Cl⁺Cl⁻.

The monophosphines ligands 2, 3, 6, 7, 8 and 9 react with [Pd(1,5-COD)]Cl₂ in situ cleanly to form the product complexes [(L)₂PdCl₂], L = 2, 3, 6–9. The relevant ³¹P NMR data are summarised in Table 2.

---

Table 2. ³¹P NMR Data of Ferrocenylphosphine Ligands and Their Palladium (II) and Rhodium (I) Chloride Complexes

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>FeP</th>
<th>Fe₂P</th>
<th>Metal Complex</th>
<th>FeP</th>
<th>Fe₂P</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(4a)PdCl]Cl</td>
<td>+ 29.31</td>
<td>+ 37.90</td>
<td>[(6)₂PdCl]</td>
<td>+ 14.19</td>
<td></td>
</tr>
<tr>
<td>[(4b)PdCl]Cl</td>
<td>+ 28.88</td>
<td>+ 56.02</td>
<td>[(7)PdCl]</td>
<td>+ 13.58</td>
<td></td>
</tr>
<tr>
<td>[(4c)PdCl]Cl</td>
<td>+ 24.43</td>
<td>+ 47.70</td>
<td>[(8)PdCl]</td>
<td>+ 14.61</td>
<td></td>
</tr>
<tr>
<td>[(4d)PdCl]Cl</td>
<td>+ 24.86</td>
<td>+ 43.30</td>
<td>[(3a)PdCl]</td>
<td>+ 7.36</td>
<td></td>
</tr>
<tr>
<td>[(4a)RhCl]</td>
<td>+ 31.48</td>
<td>+ 38.33</td>
<td>[(3b)PdCl]</td>
<td>+ 13.34</td>
<td></td>
</tr>
<tr>
<td>(dd)</td>
<td>(dd)</td>
<td></td>
<td>(dd)</td>
<td>(dd)</td>
<td></td>
</tr>
<tr>
<td>[(4b)RhCl]</td>
<td>+ 27.12</td>
<td>+ 55.86</td>
<td>[(2a)PdCl]</td>
<td>+ 14.14</td>
<td></td>
</tr>
<tr>
<td>(dd)</td>
<td>(dd)</td>
<td></td>
<td>(dd)</td>
<td>(dd)</td>
<td></td>
</tr>
<tr>
<td>[(4c)RhCl]</td>
<td>+ 25.57</td>
<td>+ 28.35</td>
<td>[(2b)PdCl]</td>
<td>+ 24.98</td>
<td></td>
</tr>
</tbody>
</table>

---

* All spectra were measured in CDCl₃/85% H₃PO₄. J values and multiplicity are not included.
* e.g. [(4a)PdCl]Cl = [P₃(µ=P=µ=P)₃(η²-C₅H₅PPh₂)Fe(η²-C₅H₅PPh₂)PPh₃PdCl]⁺Cl⁻.
In conclusion we have demonstrated a rapid viable synthetic procedure for the formation of a new range of ferrocene ligands together with valuable synths for other areas of organic chemistry. The use of the new complexes in organic synthesis is the topic of our continuing research in this area.

All reactions were carried out under N₂ atmosphere.

1-Bromo-1- dialkyl/arylphosphinoferrocenes 2a, b:

1,1'-Dibromoferrocene (2.5 g, 7.3 mmol, 1 equiv), dissolved in anhyd THF (25 mL) was cooled to −70°C. To this rapidly stirred solution BuLi (2.9 mL of a 2.5 M solution in hexane) was added. The solution was stirred at this temperature for 10 min before chloroarylphosphine (1.61 g, 7.3 mmol) or chloroarylphosphine (1.12 g, 7.3 mmol) was added dropwise over a 5 min period. The solution was further stirred at this temperature for a further 15 min and subsequently at 70°C for 90 min. The mixture was then poured carefully into H₂O (30 mL) and the organic layer was separated and isolated by addition of CH₂Cl₂ (20 mL) to facilitate layer separation. Following a H₂O wash (20 mL) of the organic layer and extraction of the aqueous layer with CH₂Cl₂ (20 mL), the combined organic fractions were dried (MgSO₄), filtered and evaporated under reduced pressure to leave an amber oil. This oil was purified by flash chromatography on dry silica eluting initially with petroleum ether (bp 40–60°C)/Et₂O, 10/1. The major yellow product-containing fraction (Rf 0.3, 2a; 0.15, 2b) was concentrated to a pure oil (2a: 2.72 g, 83%; 2b: 2.35 g, 84%). In the case of 2a the oil can be crystallised either on prolonged standing or by redissolution in Et₂O with addition of hexane followed by cooling to −15°C overnight to afford 2.34 g (71.4%) of the orange crystalline product. This procedure has been carried out on scales ranging from 5–100 mmol with yields ranging from 46–87%, the variation in yields caused by the subtle ‘equilibrium’ between the mono- and dilithiated ferrocenes. Compound 2a can be conveniently stored in a normal sample container under aerobic conditions; however, compound 2b should be stored under Ar in the dark.

Bis(1-bromoferrocenyl)diphenylphosphines (3a, b):
The reactions were carried out using 1,1'- dibromoferrocene (10.0 g, 29 mmol) which was monolithiated as described above for compounds 2a and 2b in THF (100 mL) at −70°C, over 10 min. The active chlorophosphine, either dichlorophenylphosphine (2.6 g, 14.5 mmol) or dichlorosorbylphosphine (2.1 g, 14.5 mmol) was then added dropwise. The workup was identical to that described above for compounds 2a and 2b, with the exception that the major product-containing fraction in each case was exited with Et₂O, following an initial elution with petroleum ether: which removed nonpolar byproducts, and a further product-containing fraction was eluted with EtOAc (the latter removes the product which was chemisorbed to the column support). Following the quenching of the mixture with H₂O (100 mL), separation of the organic layer and extraction of the aqueous layer with CH₂Cl₂ (50 mL), the solvent was removed from the combined dried organic fractions to afford yellow microcrystals of the product in each case, 3a: 7.0 g, 76%, 3b: 6.4 g, 73%.

1'-Substituted 1-Dialkyl/arylphosphinoferrocenes; General Procedure:
The 1-bromo-1-dialkyl/arylphosphine 2 or 5 (20 mmol) or the dibromoalkyl/arylphosphine (10 mmol) 3 was dissolved in anhyd THF (80 mL) in a Schlenk tube equipped with a magnetic stirrer. The mixture was cooled in a dry ice-acetone bath to ca. −70°C. BuLi (8.0 mL of a 2.5 M solution in hexane) was added over a period of 2 min. The mixture was stirred for a further 10 min before the appropriate volume of quenching agent (DMF, 2 mL excess), CO₂ (10 g excess), CIP₃-P₃ (4.41 g, 20 mmol), CIP₃-Pr₃ (3.05 g, 20 mmol), CIP₃-P₃ i-Pr₃ (1.79 g, 10 mmol), CIP₃-P₃ t-But₃ (1.45 g, 10 mmol), CIP₃-P₃ (CH₂)₂-P₃ (1.6 g, 5 mmol)) was added. Following the quench, the mixture was allowed to come to r.t. and the solution was subsequently stirred at r.t. for 1 h before hydrolysis performed by addition of H₂O (30 mL) in the case of the DMF and CO₂ quenches dím HCl (1 M) was substituted for H₂O. The organic layer was then separated and reduced in volume to a few mL. This concentrate was then passed through a short silica gel plug contained in a 500 mL separating funnel. Initial elution with hexane removed the reaction byproducts. Subsequent elution with a mixture of Et₂O and EtOAc (70:30, v/v) removed the product containing band in each case which was crystallized (except for compound 4d which was obtained as an oil), following solution concentration under vacuum by slow addition of hexane and cooling to −10°C for 1 d (Table 1).

Rh(I) Complexes of Ligands 4a–c, Complexes ([L]RhCl):

General Procedure:
A solution of the ligand 4a–c (1.0 mmol) in CH₂Cl₂ (5 mL) was combined with a filtered solution containing [Rh(I)-COD]Cl₂ (0.5 mmol in 10 mL). The mixture immediately darkened on addition. After 1 h, the volume was reduced to ca. 4 mL and an equimolar quantity of Et₂O was applied as a top layer. The layers were allowed to mix over a 2 d period and the crystalline product obtained was separated from the supernatant solution by filtration; yield: [(4a)RhCl] 93%, [(4b)RhCl] 92%, [(4c)RhCl] 83% (as CH₂Cl₂ solvates).

[(4a)RhCl]: pale yellow/orange solid.

1H NMR (CDCl₃): δ = 3.95 (m, 2H), 3.98 (2 m, 4H), 4.00 (m, 2H), 4.27 (m, 2H), 4.42 (m, 2H), 5.20 (m, 2H), 5.78 (2 m, 2H), 7.13 (t, 4H, J = 9.3 Hz), 7.20~7.36 (m, 13H), 7.55 (td, 2H, J = ~7 Hz), 7.70~7.90 (m, 6H).

HRMS (FAB): m/z calc for C₅₀H₄₄Fe₂P₂RhCl₃ 983.986351, found 983.98116.

[(4b)RhCl]: orange solid.

1H NMR (CDCl₃): δ = 1.07 (dd, 6H, J = 15.8 Hz), 2.98 (m, 1H), 4.24 (2 m, 4H), 4.35 (m, 2H), 4.36 (m, 2H), 4.53 (m, 2H), 5.48 (m, 2H), 7.20~7.50 (m, 14H), 7.67~7.75 (m, 4H), 7.91~7.99 (m, 2H).

HRMS (FAB): m/z calc for C₄₉H₄₃Fe₂P₂RhCl₃ 915.00826, found 915.01278.

[(4c)RhCl]:

1H NMR (CDCl₃): δ = 1.35 (dd, 6H, J = 14, 7.7 Hz), 1.43 (dd, 6H, J = 15, 7.7 Hz), 2.60 (m, 1H), 2.80 (sept, 1H, J = 7.7 Hz), 4.03 (m, 2H), 4.09 (m, 2H), 4.22 (m, 2H), 4.26 (m, 2H), 4.42 (m, 2H), 4.68
(m, 2 H), 4.90 (br m, 2 H), 4.99 (br m, 2 H), 7.49 (m, 3 H), 8.65 (m, 2 H).

HRMS (FAB): m/z calc. for C₅₈H₄₄Fe₂P₂RhCl 813.1355, found 813.1402.

In Situ NMR Experiments:
The appropriate ligand was dissolved in CDCl₃ and the ³¹P NMR spectrum was recorded. An equal volume of saturated filtered solution of either [Pd(1,5-COD)Cl₂] or [Rh(1,5-COD)Cl₂] was then added and the spectrum was re-recorded.

Complexes formed in situ in NMR experiments:

4a with [Rh(COD)Cl]₂: ³¹P NMR: δ = +22.62 (d, Jₖₜ₋ₚ = 152 Hz), +13.86 (d, Jₖₜ₋ₚ = 152 Hz).

4b with [Rh(COD)Cl]₂: ³¹P NMR: δ = +22.94 (d, Jₖₜ₋ₚ = 151 Hz), +22.28 (d, Jₖₜ₋ₚ = 151 Hz).

4c with [Rh(COD)Cl]₂: +31.11 (bd), +35.64 (bd), Jₖ₋ₚ ≈ not estimated, broad lines.

4d with [Rh(COD)Cl]₂: ³¹P NMR: δ = +32.86 (d, Jₖ₋ₚ = 149 Hz), +21.68 (d, Jₖ₋ₚ = 149 Hz).

Pd(II) Complexes of Ligands 4a – d, Complexes [Pd(P₃-L)Cl]⁺Cl⁻:

General Procedure:
A solution of the ligand 4a – d (1.0 mmol) in CH₂Cl₂ (5 mL) was treated with a filtered solution containing [Pd(1,5-COD)Cl₂] (28.9 mg, 1 mmol) in CH₂Cl₂ (~ 10 mL). The volume was reduced to ca 4 mL in the case of ligands 4c and 4d and the solution was layered with an equal volume of Et₂O. Slow diffusion over 2 d gave the product complexes as red/violet microcrystals. In the cases of 4a and 4b immediate precipitation occurred which was further facilitated by addition of a small volume of Et₂O to give the deep red/violet powdered product complexes. Yields [Pd(L)Cl]⁺Cl⁻: L = 4a, 75%; L = 4b, 75%; L = 4c, 68%; L = 4d, 52% (Addition of NH₄PF₆ facilitated the precipitation of the less soluble PF₅ complexes).

[(4a)PdCl]⁺Cl⁻:

¹H NMR (CDCl₃): 3.77 (m, 2 H), 4.29 (2 m, 4 H), 4.46 (m, 2 H), 4.54 (m, 2 H), 4.61 (m, 2 H), 4.75 (m, 2 H), 4.77 (m, 2 H), 7.26 – 7.80 (overlapping m, 19 H), 7.92 – 8.12 (overlapping m, 6 H).

¹⁹F NMR (CDCl₃): δ = +29.31 (br s), +37.90 (br s).

HRMS (FAB): m/z calc. for C₉₈H₄₄ClFe₂Pd₂⁺ 986.984323, found 986.987503.

[(4b)PdCl]⁺Cl⁻:

¹H NMR (CDCl₃): δ = +1.47 (m, 6 H), 2.68 (m, 1 H), 4.23 (m, 2 H), 4.52 (m, 2 H), 4.58 (m, 2 H), 4.68 (2 m, 4 H), 4.82 (br m, 6 H), 7.18 – 7.70 (m, 17 H), 8.01 – 8.20 (br m, 3 H).

¹⁹F NMR (CDCl₃): δ = +28.88 (br s), +56.02 (br s).

HRMS (FAB): m/z calc. for C₉₈H₄₄ClFe₂Pd₂⁺ 952.9766, found 952.9778.

[(4c)PdCl]⁺Cl⁻: {¹H} ³¹P NMR (CDCl₃): δ = +24.43 (br s), +47.70 (br s).

[(4d)PdCl]⁺Cl⁻: {¹H} ³¹P NMR (CDCl₃): δ = +24.86 (br s), +43.30 (br s).

HRMS: m/z calc. for C₉₈H₄₄ClFe₂Pd 851.04069, found 851.0441.

Peroxide Oxidation Reactions; Formation of 5 and 11:
A solution of the appropriate ligand 2 (2.24 g, 5 mmol) or 3a (3.18 mmol, 5 mmol) in CH₂Cl₂ (10 mL) was treated with an excess of 30% aq H₂O₂ (2 mL). After stirring the solution vigorously for 5 min the aqueous layer was extracted with CH₂Cl₂ (10 mL) and the organic phase was dried (MgSO₄). The filtered solution was then reduced in volume under vacuum to a few mL and was filtered through a Celite plug to give the product phosphine oxides 5 and 11, after solvent evaporation. Characterisations are given in Table 1.

The mass spectral data were obtained at the EPSRC central facility at the University of Wales, Swansea. The ³¹P NMR spectra were recorded by Mr. Eric Lewis to whom the authors are grateful. Funding for the research came directly from a University of Wales grant which is also gratefully acknowledged.

¹ Triphos = bis(diphenylphosphinoethyl)phenylphosphine. This ligand should not be confused with the ligand tris(diphenylphosphino) methane, which is also commonly referred to as triphos.


