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Synthesis, characterisation and catalytic activity of metal complexes of neutral, unsymmetrical P/S ferrocenediyl ligands

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Two asymmetric 1,1′-disubstituted ferrocenediyl ligands, 1-(diphenylphosphino)-1′-(methylthio)ferrocene (**1**) and 1-(diphenylphosphino)-1′-(mesitylthio)ferrocene (**2**) featuring phosphine and thioether substituents have been conveniently synthesised and the coordination chemistry of **1** probed by reaction with transition metal reagents. With Group 10 metal and Rh(I) species, chelating complexes are formed in high yield and a monodentate *bis* ligand complex with *trans* phosphorus ligation can also be synthesised using a Pd(II) species and three equivalents of **1**. With [M(CO)$_5$thf] (M = Cr, Mo or W), **1** forms a mixture of monodentate, P-bound pentacarbonyl and P/S-chelating tetracarbonyl products. The monodentate pentacarbonyl product can be converted into the chelating tetracarbonyl species *via* prolonged reflux in toluene. Preliminary studies show that **1**, in combination with Pd(0) precursors, can act as a catalyst for the Suzuki coupling reaction.

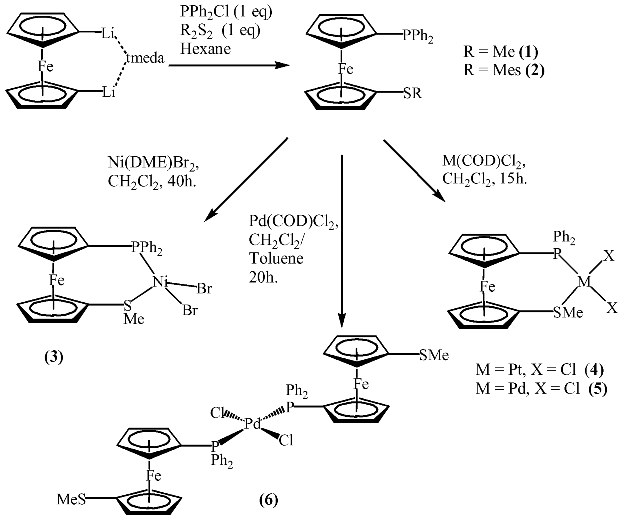
Introduction

The formation of asymmetric, multidentate ligands, focussing on aspects of hemilability,[1] has been of great interest. In particular, ferrocenyl and ferrocenediyl ligands are sought after due to their extensive coordination chemistry and applications within catalysis.[2,3] Whilst hemilabile P/S$^-$,[4] P/S,[5] P/O[6,7] and N/O$^-$ [8] ligand systems are well-known and important in catalysis, examples of analogous asymmetric 1,1′-disubstituted *ferrocenes*[9,10] are rare. The first 1-(PR$_2$), 1′-(SR)ferrocenediyl species (R = Ph) was published in 1992[11] followed by an alternative five-step synthesis of the same ligand reported by Dong and co-workers in 1998.[12] Butler *et al.*[13] have formed [{η^5-C$_5$H$_4$SMe}Fe{η^5-C$_5$H$_3$(PPh$_2$)(SMe)-1,2}] *via* the ortho-lithiation of dibromoferrocene and recently, a chiral phosphine–thioether ferrocene ligand has been utilised to facilitate the copper-catalysed asymmetric addition of diethylzinc to alkylidene malonates.[14] Our group first reported the mixed phosphine–thioether ligand **1** in 1999,[15] but herein the synthesis has been improved and the synthetic methodology extended to include the bulky mesityl substituent (ligand **2**). To explore the formation of new ferrocenophanes (species that feature linking of the cyclopentadienyl rings by the introduction of a heteroannular bridge or bridges) and to probe the hemilability of asymmetric, 1,1′-disubstituted ligands, **1** has been treated with a range of transition metal reagents and the coordination chemistry, spectroscopic, crystallographic and electrochemical characterisation and preliminary catalytic studies are reported.

Results and discussion

Synthesis and characterisation of the ligands 1 and 2

The ligands 1-(diphenylphosphino)-1′-(methylthio)ferrocene (**1**) and 1-(diphenylphosphino)-1′-(mesitylthio)ferrocene (**2**) were synthesised using a one step route from ferrocene (Scheme 1). Initial work on the formation of **1** and preliminary coordination chemistry with Cu^I and Ag^I metal centres has been published previously.[15] However, **1** can now be synthesised in improved yields (*ca.* 40 %) *via* the reaction of 1,1′-dilithioferrocene with a 1 : 1 mixture of dimethyl disulfide and chlorodiphenylphosphine at room temperature in hexane. The reaction gives both the symmetrically and asymmetrically disubstituted products, 1,1′-bis(methylthio)ferrocene, 1-(diphenylphosphino)-1′-(methylthio)ferrocene (**1**) and 1,1′-bis(diphenylphosphino)ferrocene in a 1 : 2 : 1 ratio. **1** can be separated from the other products by careful column chromatography (neutral grade II alumina, diethyl ether–hexane, 1 : 4) in 40% yield compared to 21% obtained previously.[15] The difference in yields is attributed to the preparation and purification of the 1,1′-dilithioferrocene precursor; distilled TMEDA and oxygen-free hexane were used to maximise the yield of 1,1′-dilithioferrocene and minimise the yield of lithioferrocene and the former was also washed thoroughly with oxygen-free hexane, which enabled separation of any unreacted materials before further reaction.



Scheme 1 The syntheses of compounds **1**–**6**.

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Ligand **2** was synthesised in an analogous manner to **1** *i.e.* a mixture of dimesityl disulfide and chlorodiphenylphosphine were added to 1,1′-dilithioferrocene and the resulting suspension stirred for 15 h. After an aqueous work up, column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, 3 : 7) enabled isolation of the pure ligand in 10% yield. Higher proportions of monosubstituted products are isolated than during the synthesis of **1**, which could be due to the increased steric hindrance of the mesityl groups. The ligands were characterised by microanalysis, ^1H NMR, $^{31}P\{^1H\}$ NMR (a singlet is observed at *ca.* −16.5 ppm for both ligands) and FAB mass spectroscopy (with molecular ions and the expected fragmentation patterns observed).

Synthesis and characterisation of Group 10 metal complexes of 1

As a guide to the coordinating properties of the ligands, Group 10 metal precursors were reacted with **1** (the small amount of **2** obtained precluded coordination studies).

The Ni(II) complex (**3**) was synthesised in good yield (Scheme 1) *via* the reaction of (1,2-dimethoxyethane)dibromonickel(II) and **1** in CH_2Cl_2. There was an immediate colour change from pale pink to dark green, and after 40 h the green solution was separated from the unreacted starting material and decomposition products and evaporated to dryness to leave a green powder. This was washed with heptane to remove any unreacted ligand, and recrystallisation by layering a CH_2Cl_2 solution of the complex with pentane yielded the air-sensitive, green needle-like **3** in 75% yield. **3** did not display any distinct signals in ^1H NMR and showed a very broad peak around 42 ppm in the $^{31}P\{^1H\}$ NMR spectrum indicating a paramagnetic nature and tetrahedral geometry. The positive ion FAB mass spectrum shows the molecular ion (635 amu) and fragmentation peaks due to loss of methylthio (588 amu), bromide (555 and 475 amu) and diphenylphosphino (450 amu) groups. The X-ray analysis of **3** shows the complex (Fig. 1) to crystallise with two independent molecules in the asymmetric unit for which the only major difference is in the relative orientations of the phenyl substituents. The geometry at nickel is distorted tetrahedral with angles in the range 96.77(6)–125.03(5)° [99.69(7)–128.14(5)°], the most obtuse angle being associated with the two bromide ligands (the values in square brackets refer to the second independent molecule). A noticeable departure of the nickel centre from tetrahedral geometry is a small square planar-type distortion with the $NiBr_2$ and NiSP planes being twisted by *ca.* 11° [6°] from an orthogonal relationship. The Ni–P bond is *ca.* 0.02 Å [0.03 Å] shorter than that to sulfur (Table 1). Distortions from tetrahedral geometry at phosphorus are quite large with angles ranging from 100.7(3) to 118.9(2)° [105.2(2) to 115.0(2)°] whilst those at sulfur range between 101.5(4) and 109.2(2)° [102.3(4) and 111.9(2)°]. The cyclopentadienyl rings are essentially eclipsed (less than 1° [4°] stagger) the rings being inclined by *ca.* 3° [6°]—the phosphorus and sulfur atoms effectively overlay each other. The pseudo six-membered chelate ring formed by Ni/P/C(10)/Fe/C(5)/S has a steeply folded geometry with an out-of-plane bend of *ca.* 56° about the P···S vector. The non-bonded S···P and Ni···Fe distances are 3.46 Å [3.52 Å] and 4.00 Å [4.04 Å] respectively. There are no intermolecular packing interactions of note. The most closely related literature structure[11] is that of 1-diphenylphosphino-1′-phenylthioferrocenetricarbonyliron(0) which has non-bonded S···P and Fe···Fe separations of 3.16 and 4.12 Å respectively, the ferrocenyl ring systems having a slightly increased degree of stagger at *ca.* 13°.

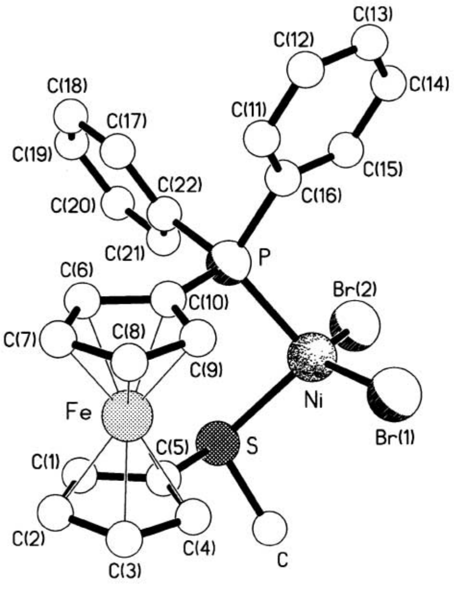


Fig. 1 Molecular structure of **3**.

Dichloro[1-(diphenylphosphino)-1′-(methylthio)ferrocene]-platinum(II) (**4**) was formed by the dissolution of **1** in toluene followed by the addition of dichloro(1,5-cyclooctadiene)-platinum(II) dissolved in CH_2Cl_2. The solution was stirred for 15 h at room temperature and the crude product was filtered off and washed with hexane to remove any unreacted starting materials. **4** was isolated as a yellow powder in 91% yield. In the NMR spectra, the peaks are all shifted to lower field compared to the free ligand due to the usual inductive effect of the platinum centre. In the ^1H NMR spectrum, the methyl group exhibits a singlet at 2.86 ppm with platinum satellites, the ferrocenyl protons give only two broad peaks shifted to lower field at 4.39 and 4.83 ppm and the phenyl ring protons display a multiplet at 7.43 ppm, shifted slightly compared to the free ligand. In the $^{31}P\{^1H\}$NMR spectrum, a peak at 8.64 ppm is observed with platinum satellites ($^1J_{Pt-P}$ = 3737 Hz), which is in close agreement with the analogous dppf–$PtCl_2$ species.[16] The mass spectrum shows a molecular ion peak (682 amu) and fragmentation signals due to loss of chloride groups (647, 611 amu). The X-ray analysis of crystals of **4** shows (Fig. 2) it to have a ligand structure very similar to that of **3** with an eclipsed geometry for the ferrocenyl unit (less than 1° stagger, rings inclined by *ca.* 2°) and non-bonded S···P and Pt···Fe distances of 3.15 and 3.88 Å respectively, the noticeable reduced S···P distance *cf.* that in **3** reflecting an inclining of the P–C_5H_4 and S–C_5H_4 vectors towards the platinum centre in **4** *cf.* away from the nickel atom in **3**. The departures from tetrahedral

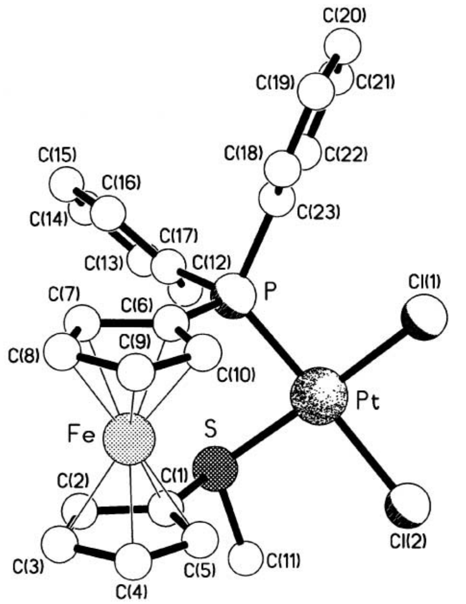


Fig. 2 Molecular structure of **4**.

Table 1 Selected bond lengths (Å) and angles (°) for **3**

	Molecule A	Molecule B		Molecule A	Molecule B
Ni–P	2.298(2)	2.281(2)	Ni–S	2.319(2)	2.310(2)
Ni–Br(1)	2.3408(13)	2.3380(12)	Ni–Br(2)	2.3497(13)	2.3298(13)
S–C(5)	1.764(7)	1.750(8)	P–C(10)	1.796(7)	1.801(7)
P–Ni–S	97.22(7)	100.20(7)	P–Ni–Br(1)	104.30(6)	105.12(6)
S–Ni–Br(1)	117.74(6)	108.74(7)	P–Ni–Br(2)	112.66(6)	111.45(6)
S–Ni–Br(2)	96.77(6)	99.69(7)	Br(1)–Ni–Br(2)	125.03(5)	128.14(5)
C(5)–S–C	101.5(4)	102.3(4)	C(5)–S–Ni	109.2(2)	111.9(2)
C–S–Ni	104.9(3)	102.5(3)	C(10)–P–C(16)	105.4(3)	105.9(3)
C(10)–P–C(22)	106.9(4)	106.0(3)	C(16)–P–C(22)	100.7(3)	105.2(2)
C(10)–P–Ni	112.2(2)	112.9(2)	C(16)–P–Ni	111.5(2)	111.2(2)
C(22)–P–Ni	118.9(2)	115.0(2)			

Table 2 Selected bond lengths (Å) and angles (°) for **4**

Pt–Cl(1)	2.300(2)	Pt–Cl(2)	2.364(2)
Pt–S	2.293(2)	Pt–P	2.241(2)
S–C(1)	1.761(6)	P–C(6)	1.807(7)
P–Pt–S	88.04(5)	P–Pt–Cl(1)	90.29(6)
S–Pt–Cl(1)	177.81(6)	P–Pt–Cl(2)	169.64(7)
S–Pt–Cl(2)	93.82(6)	Cl(1)–Pt–Cl(2)	88.08(7)
C(1)–S–C(11)	99.8(3)	C(1)–S–Pt	105.6(2)
C(11)–S–Pt	112.9(3)	C(6)–P–C(17)	107.8(3)
C(6)–P–C(23)	104.4(3)	C(17)–P–C(23)	100.6(2)
C(6)–P–Pt	107.2(2)	C(17)–P–Pt	119.37(14)
C(23)–P–Pt	116.3(2)		

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Pd–Cl	2.3373(13)	Pd–P	2.3500(14)
S–C(10)	1.746(7)	P–C(5)	1.805(6)
Cl–Pd–Cl′	180	Cl–Pd–P′	92.62(5)
Cl′–Pd–P′	87.38(5)	Cl–Pd–P	87.38(5)
Cl′–Pd–P	92.62(5)	P–Pd–P′	180
C(10)–S–C(11)	102.4(4)	C(5)–P–C(17)	105.8(2)
C(5)–P–C(23)	102.1(3)	C(17)–P–C(23)	102.4(2)
C(5)–P–Pd	115.3(2)	C(17)–P–Pd	108.88(14)
C(23)–P–Pd	120.69(14)		

geometry at phosphorus and sulfur are again quite large with angles ranging from 100.6(2) to 119.37(14)°, and from 99.8(3) to 112.9(3)° respectively (Table 2). The six-membered chelate ring fold angle (*vide supra*) is here 69°. The platinum adopts an only slightly distorted square planar geometry with *cis* angles in the range 88.04(5)–93.82(6)°, the most noticeable deformation being an out-of-plane deviation of *ca.* 0.43 Å of the phosphorus atom from the $PtCl_2S$ plane. The Pt–P distance is *ca.* 0.05 Å shorter than that to sulfur. There are no particularly short intermolecular contacts, though it is interesting to note that the coordination planes of C_2 related complexes have a non-bonded Pt···Pt separation of only 4.15 Å.

The palladium(II) complex (**5**) can be synthesised in the same way as the platinum(II) analogue **4** (Scheme 1) to give an orange powder in 81% yield. In the ^1H NMR spectrum, as with **4**, all the ligand peaks are shifted to lower field on coordination to the metal. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 31.82 ppm and the FAB mass spectrum does not show the molecular ion but rather a peak due to loss of a chloride group at 558 amu.

During attempts to synthesise the chelating complex (**5**), a palladium complex with two monodentate ligands bound through their phosphorus atoms was noted (Scheme 1). This complex (**6**) arose when there was an excess of ligand, leading to the observation that in order to synthesise the chelating complex in high yield an excess of palladium precursor should be used. **6** can be synthesised as an orange-red powder in 80% yield when an excess of the ligand **1** (*ca.* 3 : 1 ratio) in toluene is reacted with $Pd(COD)Cl_2$ in CH_2Cl_2. Clearly, the better donating properties of phosphorus compared to sulfur are utilised here, leading to the bonding with palladium being exclusively through phosphorus. The *trans* isomer is the only one observed, presumably due to the steric bulk of the ligand precluding formation of the *cis* species. The ^1H NMR spectrum of **6** shows a singlet at 2.25 ppm due to the methylthio protons but these are not shifted compared to the free ligand, indicating that the sulfur atoms are not bound to the metal and illustrating the mono-dentate binding mode. The $^{31}P\{^1H\}$ NMR shows one peak only at 15.57 ppm, which indicates that the P atom is metal bound (there is a large downfield shift from the equivalent signal in the free ligand) and that there is only a single isomer formed – presumably the *trans* species, as shown by X-ray diffraction. The mass spectrum does not show the molecular ion, but rather fragmentation peaks due to loss of chloride (974 and 938 amu), methylthio (891 amu) and diphenylphosphino (754 amu) groups. The failure to achieve *P,S* chelation is illustrated by the X-ray crystallographic determination of the centrosymmetric complex L_2PdCl_2 **6** (Fig. 3). The palladium is square planar with *cis* angles of 87.38(5) and 92.62(5)°, and Pd–P and Pd–Cl distances of 2.350(1) and 2.337(1) Å respectively; the non-bonded Pd···Fe separation is 4.40 Å (Table 3). Departures from tetrahedral geometry at phosphorus are comparable with those seen in **3** and **4**, with angles in the range 102.1(3)–120.69(14)°; the angle at sulfur is 102.4(4)°. The two cyclopentadienyl rings are essentially eclipsed (*ca.* 3° stagger) but the P–C_5H_4 and S–C_5H_4 vectors are here rotated by *ca.* 74° with respect to each other. There are no noteworthy intermolecular packing interactions.

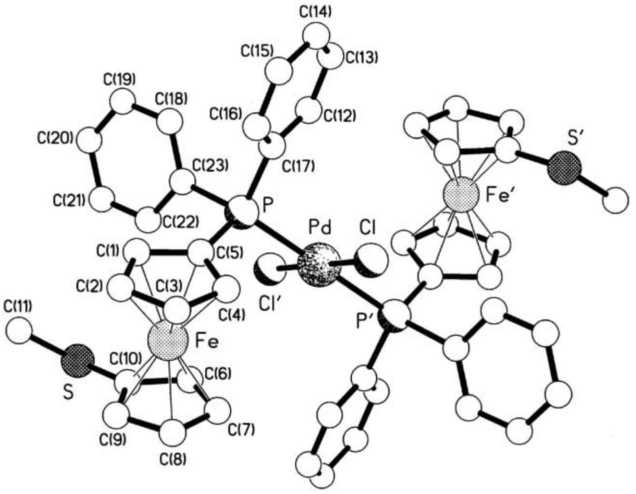
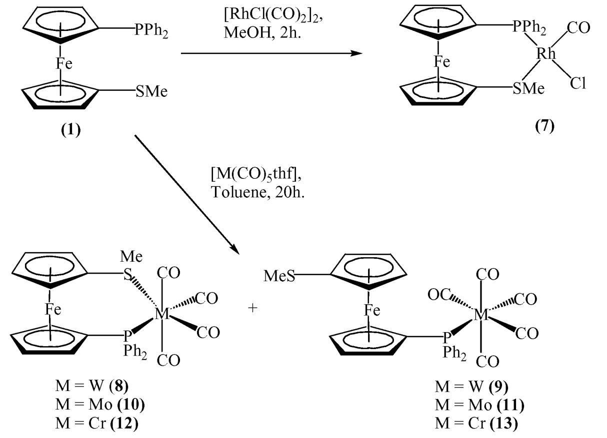


Fig. 3 Molecular structure of **6**.

Synthesis and characterisation of Rh(I) complex of 1

Two new classes of methanol carbonylation catalysts, featuring P/S-substituted ligands and Rh(I) metal centre(s), which show significant improvements in absolute rates, under industrial conditions, over those obtained with $[RhI_2(CO)_2]^-$ have been recently reported.[17] An analogous Rh(I) complex (**7**) was formed by dissolving two equivalents of **1** in the minimum amount of toluene and adding this to a solution of tetracarbonyldichlorodirhodium(I) dissolved in methanol (Scheme 2). An orange precipitate formed immediately, which was filtered off after 2 h and washed with diethyl ether and methanol. Carbonylchloro[1-(diphenylphosphino)-1′-(methylthio)ferrocene]rhodium(I) (**7**) was isolated in 79% yield. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 37.42 ppm due to coupling with the Rh nucleus, the coupling constant $^1J_{Rh–P}$ being 168 Hz, which is in good agreement with other rhodium ferrocenediyl phosphine chelating complexes.[18] A single metal carbonyl IR stretching frequency is observed at 2006 cm^{-1} and the positive ion FAB mass spectrum shows the molecular ion (583 amu) and fragmentation peaks due to loss of carbonyl (555 amu) and chloride (547 amu) groups.



Scheme 2 The syntheses of compounds **7**–**13**.

Synthesis and characterisation of Group 6 metal complexes of 1

The reactivity of **1** with Group 6 metal carbonyl species was explored *via* the addition of $[M(CO)_5thf]$ to a solution of the ligand under inert atmospheres with the reactions being monitored *via* IR spectroscopy. The $[M(CO)_5thf]$ starting material (M = W, Mo, Cr) was prepared by photolysis of $M(CO)_6$ in dry, degassed thf for an appropriate period of time using a 400 W UV lamp. The irradiation time varied for each of the metal carbonyls employed (Cr, 35 min, W, 14 min, Mo, 6 min) and the formation of the $[M(CO)_5thf]$ intermediate was monitored by IR spectroscopy [the diagnostic peaks being ν(CO) (in thf) $M(CO)_6$ = *ca.* 1978 cm^{-1}, $M(CO)_5(thf)$ = *ca.* 2075, 1924, 1889 cm^{-1}].

Tungsten complexes. The compounds **8** and **9** were synthesised as shown in Scheme 2. An excess of pentacarbonyl(tetrahydrofuran)tungsten(0) was added to a solution of **1** in toluene. The yellow solution was stirred at room temperature for 20 h after which time the IR spectrum remained the same and indicated the formation of a mixture of penta- and tetracarbonyl species. The crude reaction mixture was purified by column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, starting with 1 : 9 and increasing the polarity to 1 : 5 to remove **9** and 1 : 3 to remove **8**) enabling isolation of tungsten hexacarbonyl, **9** in 39% yield and **8** in 50% yield. The reason for the isolation of both penta- and tetra-carbonyl products rather than the expected compound **8** could be due to the relative proportions of pentacarbonyl(tetrahydrofuran)tungsten and tetracarbonyl(tetrahydrofuran)tungsten in the starting mixture and an indication of the poorer donating ability of the thioether group compared to the phosphine.

In the ^1H NMR spectrum of **8**, the chelating coordination mode can be seen by the shifting to lower field of both the methylthio and the phenyl group resonances. The methylthio protons exhibit a singlet at 2.90 ppm and the ferrocenyl region shows three peaks: a multiplet, with an integral value of four, at 4.22 ppm due to the β and β′ protons and two pseudo triplets, each integrating to two, at 4.40 and 4.58 ppm due to the α and α′ protons. The phenyl groups show two multiplets at 7.38 and 7.54 ppm. The $^{31}P\{^1H\}$ NMR spectrum also indicates that a chelating complex has been formed as only one peak is seen at 19.53 ppm with tungsten satellites ($^1J_{W–P}$ = 234 Hz).[19] The positive ion FAB mass spectrum shows a molecular ion (712 amu) and a fragmentation pattern due to loss of carbonyl groups (684, 656, 628 and 600 amu). The carbonyl region of the IR spectrum shows four peaks at 2016, 1905, 1890 and 1875 cm^{-1}, this being the expected pattern for a *cis* chelate metal tetracarbonyl complex.[19,20] The ^1H NMR of **9** provides good evidence for the monodentate nature of the ligand in this complex, with the phosphorus atom bonding to tungsten and the sulfur atom not coordinating. The signal for the methylthio protons at 2.15 ppm is hardly shifted from that of the free ligand. The ferrocenyl region of the spectrum shows four pseudo triplets and the phenyl groups exhibit one resonance at 7.42 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, there is one peak in the spectrum at 11.15 ppm ($^1J_{W–P}$ = 245 Hz) which is not as downfield shifted as for **8**. The positive ion FAB mass spectrum shows a peak for the molecular ion (740 amu) and peaks due to loss of four and five carbonyl groups respectively (628, 600 amu). The carbonyl region of the IR spectrum shows three peaks at 2070, 1980 and 1934 cm^{-1}, the expected number and position of peaks for a pentacarbonyl complex.[19]

The X-ray structure of the tungsten complex **8** again reveals (Fig. 4) a *P*,*S* ligand structure essentially unchanged from that seen in **3** and **4** with eclipsed cyclopentadienyl ring systems (less than 1° stagger, rings inclined by *ca.* 2°). The non-bonded S· · ·P and W· · ·Fe separations are 3.48 and 4.36 Å respectively, the P–C_5H_4 and S–C_5H_4 vectors being tilted slightly away from the tungsten centre. The fold of the six-membered chelate ring (*vide supra*) is *ca.* 52°. The angles at phosphorus and sulfur are in the ranges 102.2(2)–118.47(13)° and 101.0(3)–114.2(2)° respectively (Table 4). The geometry at tungsten is slightly distorted octahedral with *cis* angles in the range 85.4(3) to 97.7(2)°. The W–P bond length is *ca.* 0.02 Å shorter than that to

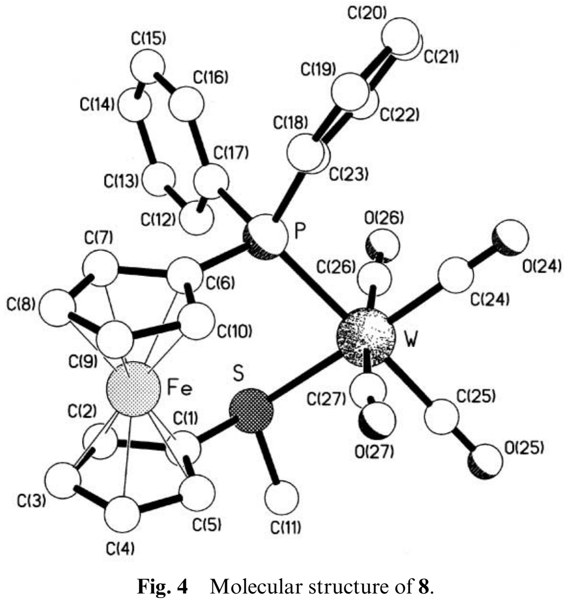


Fig. 4 Molecular structure of **8**.

Table 4 Selected bond lengths (Å) and angles (°) for **8**

W–S	2.555(2)	W–P	2.5378(14)
W–C(24)	1.952(7)	W–C(25)	1.986(6)
W–C(27)	2.008(7)	W–C(26)	2.050(7)
S–C(1)	1.760(6)	P–C(6)	1.820(6)
C(24)–W–C(25)	88.1(3)	C(24)–W–C(27)	85.4(3)
C(25)–W–C(27)	89.4(3)	C(24)–W–C(26)	88.0(3)
C(25)–W–C(26)	90.6(3)	C(27)–W–C(26)	173.4(3)
C(24)–W–P	92.8(2)	C(25)–W–P	178.3(2)
C(27)–W–P	89.2(2)	C(26)–W–P	90.9(2)
C(24)–W–S	176.6(2)	C(25)–W–S	93.0(2)
C(27)–W–S	97.7(2)	C(26)–W–S	88.8(2)
P–W–S	86.17(5)	C(1)–S–C(11)	101.0(3)
C(1)–S–W	114.2(2)	C(11)–S–W	111.5(3)
C(6)–P–C(17)	102.2(2)	C(6)–P–C(23)	103.3(2)
C(17)–P–C(23)	103.3(2)	C(6)–P–W	116.1(2)
C(17)–P–W	118.47(13)	C(23)–P–W	111.5(2)

sulfur, and the W–C bond *trans* to phosphorus is longer than that *trans* to sulfur. There are no intermolecular contacts of note.

Molybdenum and chromium complexes. The molybdenum complexes **10** (tetracarbonyl, 22%) and **11** (pentacarbonyl, 47%) and chromium complexes **12** (tetracarbonyl, 61%) and **13** (pentacarbonyl, 10%) were synthesised in an analogous manner to the tungsten species (Scheme 2) with crude reaction mixtures being purified by column chromatography (neutral grade II alumina, under nitrogen, CH_2Cl_2–hexane). All the species are air-sensitive and similar shifts in NMR signals are observed as for **8** and **9**.

Conversion of 11 to 10. A toluene solution of **11** was refluxed and the reaction monitored by IR and $^{31}P\{^1H\}$ NMR spectroscopy, which indicated that complete conversion of **11** into **10** had occurred after 20 h. The solvent was removed *in vacuo* to yield analytically pure **10** in virtually quantitative yield. This reaction provides evidence that **11** is the kinetic product of the reaction and **10** is the thermodynamic product and that the formation of penta- and tetra-carbonyl metal complexes is also a function of (i) the purity of the starting materials ($[M(CO)_5thf]$ or $[M(CO)_4(thf)_2]$) and (ii) the reaction conditions *i.e.* at higher temperatures, greater quantities of tetracarbonyl complexes are formed.

Electrochemistry

It has been reported previously that the ferrocene ligand **1** exhibits a one-electron oxidation in dichloromethane solution, which appears to be chemically reversible on the cyclic voltammetric time scale.[15] As expected, the related ligand **2** displays very similar voltammetric behaviour. Nevertheless, the two derivatives differ in the stability of the respective monocations, in that exhaustive electrolysis shows that $[\mathbf{1}]^+$ tends to reorganize to a new compound (probably a dimer, in that it affords two slightly separated reversible oxidations at $E^{\circ\prime} = +0.62$ V and +0.78 V, respectively (attempts to determine its nature are under study), whereas $[\mathbf{2}]^+$ proves to be stable. The redox ability of some of the metal complexes of ligand **1** was also investigated. Fig. 5 shows the cyclic voltammetric behaviour of complex **4** with respect to that of the free ligand **1**. The insertion of a $PtCl_2$ bridge causes the ferrocene oxidation to shift towards more positive potential values by about 0.6 V, thus indicating that the platinum fragment exerts a rather strong electron withdrawing effect with respect to the ferrocendiyl unit. Despite the apparent chemical reversibility of the ferrocenophane oxidation on the cyclic voltammetric time scale (the i_{pc}/i_{pa} ratio approaches unity even at the low scan rate of 0.02 V s^{-1}), exhaustive one-electron oxidation reveals that $[\mathbf{4}]^+$ is unstable *i.e.* cyclic voltammetric tests on the resulting solution only detect traces of the original peak system. As shown in Fig. 5, **4** also affords an irreversible reduction, which is confidently attributed to the Pt(II)/Pt(0) process. As far as **3** is concerned, the presence of the redox-active Ni(II) fragment complicates the redox path, in that a first irreversible oxidation ($E_p = +0.89$ V) almost overlaps a partially chemically reversible second oxidation ($E^{\circ\prime} = +1.00$ V). For simplicity, we assign such a process to the Ni(II)/Ni(III) oxidation, the irreversibility of which destabilises the subsequent ferrocene-centred oxidation. It cannot however, be ruled out that the process may arise from the oxidation of the bromide ligand.[21] An irreversible reduction is also detected ($E_p = -0.51$ V).

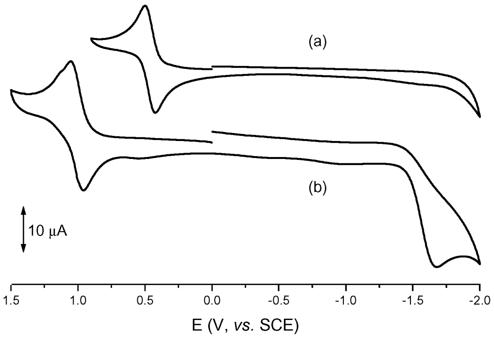


Fig. 5 Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4]PF_6$ (0.2 mol dm^{-3}) and: (a) **1** (1.6×10^{-3} mol dm^{-3}); (b) **4** (1.6×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

A more subtle redox pattern is exhibited by the Pd(II) analogue **5**, in that it also exhibits a one-electron oxidation that appears to be chemically reversible at very low scan rates (i_{pc}/i_{pa} ratio close to unity at 0.02 V s^{-1}), but the increase of the scan rate results in a decrease of the current ratio. Such behaviour is diagnostic of a first-order reversible chemical reaction following a reversible electron transfer, in which the chemical complication is neither too slow nor too fast.[22] In fact, exhaustive electrolysis once again confirms the instability of $[\mathbf{5}]^+$. On this basis, we assume that the oxidation of **4** might also be complicated by a first-order reversible chemical reaction, but that the rate of the chemical complication is so fast that the cyclic voltammogram apparently looks like a non-complicated reversible electron transfer.[22]

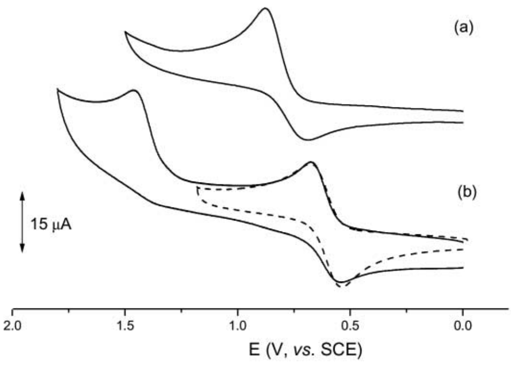


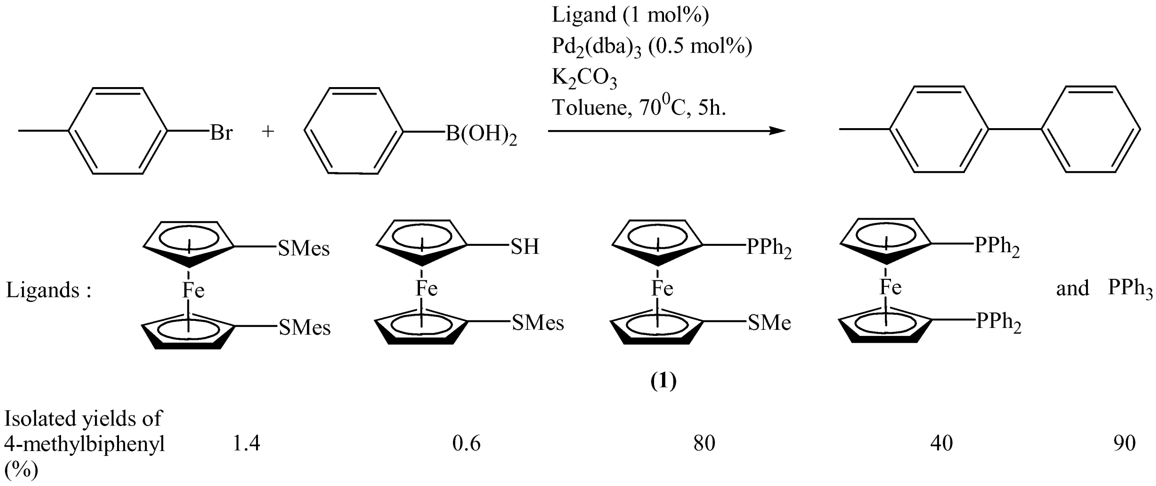
Fig. 6 Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4]PF_6$ (0.2 mol dm^{-3}) and: (a) **10** (0.8×10^{-3} mol dm^{-3}); (b) **11** (0.8×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

Complexes **7**, **8** and **10** display an anodic pattern similar to that of **5** (in fact, the i_{pc}/i_{pa} ratio for the ferrocene oxidation is close to unity at low scan rate and decreases at high scan rates). Comparison of the oxidation paths of **10** and **11** (Fig. 6) is worthwhile as the molybdoferrocenophane **10** displays a partially chemically reversible one-electron oxidation, whereas the molybdoferrocene **11** undergoes a (coulometrically-tested) chemically reversible one-electron oxidation followed by an irreversible (molybdenum-centred) oxidation at high potential values. This could account for the instability of the above-

Table 5 Electrochemical characteristics for the oxidation processes exhibited by compounds **1**–**12** in CH_2Cl_2 solution

Complex	$E^{\circ\prime}_{\mathrm{Fe(II)/Fe(III)}}$/V	ΔE_p[a]/mV	i_{pc}/i_{pa}[a]	$E^{\circ\prime}_{\mathrm{M(II)/M(III)}}$/V	$E^{\circ\prime}_{\mathrm{M(0)/M(I)}}$/V
1	+0.46	69	1.0		
2	+0.43	90	1.0		
3	+1.00	140	[b]	+0.89[a,c]	
4	+1.04	74	1.0		
5	+0.92	140	0.8		
7	+0.88	130	0.8		
8	+0.79	170	0.7		
10	+0.79	140	0.6		
11	+0.63	70	1.0		+1.46[a,c]
12	+0.65	90	1.0		+1.17[d]

[a] Measured at 0.1 V s^{-1}. [b] Measurement not possible. [c] Peak-potential value. [d] Measured at 5.12 V s^{-1}.



Scheme 3 Suzuki coupling reaction used to carry out preliminary studies into the catalytic capabilities of the ligands.

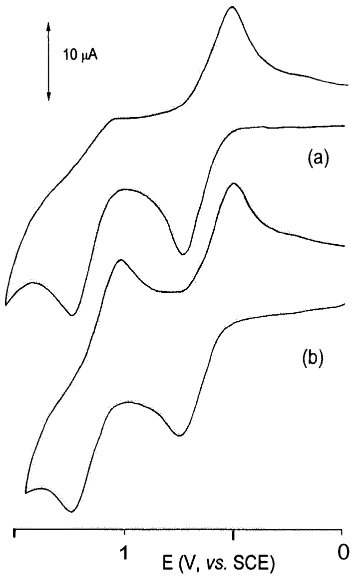


Fig. 7 Cyclic voltammetric responses recorded at a platinum electrode on a CH_2Cl_2 solution of **12** (0.9×10^{-3} mol dm^{-3}). $[NBu_4]PF_6$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rates: (a) 0.2 Vs^{-1}; (b) 5.12 V s^{-1}.

mentioned ferrocenium congeners. It is plausible that the structural constraints imposed by such ferrocenophane assemblies are not sufficiently flexible to support the expected elongation of the Fe–cyclopentadienyl ring distances consequent to the Fe(II)/Fe(III) process.[23] Despite the fact that most metalloferrocenophanes exhibit ferrocene-centred oxidations displaying features of chemical reversibility on the cyclic voltammetric time scale (see for example[24–27]), they are commonly unstable in the oxidised ferrocenium state,[23–25] or at least in most cases their stability during the long times of exhaustive electrolysis has not been tested. Obviously this is not a general rule, in that, as illustrated in Fig. 7, the chromoferrocenophane **12** not only is stable in the Fe(III)–Cr(0) oxidation state (the exhaustive one-electron oxidation at +0.8 V proves that $[\mathbf{12}]^+$ is quite stable), but also the subsequent Cr(0)/Cr(I) oxidation manifests some degree of chemical reversibility, thus indicating that the Fe(III)–Cr(I) oxidation state is not totally unaccessible. Table 5 summarizes the electrode potentials of the above discussed redox changes.

Catalysis studies

The Suzuki reaction. The ligands 1,1′-bis(mesitylthio)-ferrocene,[28] 1′-(mesitylthio)ferrocene-1-thiol[10] and **1** were investigated with Pd(0) reagents as possible systems for the Suzuki C–C bond forming reaction.[29] The studies are preliminary but do give an indication into their catalytic activities. 1,1′-bis(diphenylphosphino)ferrocene and triphenylphosphine were chosen as suitable ligands to benchmark any activity for the Suzuki reaction.[30] The reaction studied is shown in Scheme 3, along with the catalytic species tested and the yields of product obtained.

The reactants were mixed with two equivalents of base and suspended in toluene. To this solution, a one mole percent solution of the ligands and palladium(0) precursor were added. It is assumed that the ligands form 1 : 1 complexes with the palladium(0) precursor, although this still needs to be proven. The solutions were heated at 70 °C for 5 h and the work up carried out as described later. The isolated yields of 4-methylbiphenyl are shown in Scheme 3. The results are reproducible (the experiment was carried out three times), and these preliminary studies show that there is encouraging catalysis with ligand **1** in the synthesis of biaryls *via* the Suzuki coupling reaction. The ligand gives double the yield obtained with

1,1′-bis(diphenylphosphino)ferrocene and close to the value obtained with triphenylphosphine, under these experimental conditions. Ligands 1,1′-bis(mesitylthio)ferrocene and 1′-(mesitylthio)ferrocene-1-thiol are not useful for this coupling reaction, in the case of the latter this is presumably due to its charge and that it would almost certainly oxidise the palladium(0) centre prior to any reaction with the substrates, thus hindering the reductive elimination step in the catalytic cycle.

Conclusions

The improved synthesis of **1** and also a new route to 1-(diphenylphosphino)-1′-(mesitylthio)ferrocene **2** have been reported. The coordination chemistry of **1** has been explored with Group 10 metal and Rh(I) halides and the ligand forms chelating complexes in high yield. A monodentate bis ligand complex can be formed using Pd(II) and three equivalents of **1** and the complex shows exclusively *trans* phosphorus ligation. The coordination chemistry of **1** with M(CO)$_5$THF (M is Cr, Mo and W) shows that the ligand forms a mixture of monodentate, P-bound pentacarbonyl and P/S-chelating tetracarbonyl products. The monodentate pentacarbonyl product can be converted into the chelating tetracarbonyl *via* prolonged reflux in toluene and this is thought to be the kinetic product of the complexation reaction, whilst the tetracarbonyl is the thermodynamic product. Preliminary studies into the efficacy of ligands synthesised recently in the Long group, including **1**, in combination with Pd(0) precursors as catalysts for the Suzuki coupling reaction show that **1** is a good ligand for this reaction and future studies will focus on this.

Experimental

All preparations were carried out using standard Schlenk techniques.[31] All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral – grade II) was used for chromatographic separations unless specified otherwise.

All NMR spectra were recorded using a Delta upgrade on a Jeol EX270 MHz spectrometer operating at 250.1 MHz (^{1}H) and 101.3 MHz (^{31}P{^{1}H}) respectively. Chemical shifts are reported in δ using CDCl$_3$ (^{1}H, δ 7.25) as the reference for ^{1}H spectra, while the ^{31}P{^{1}H} spectra were referenced to H_3PO_4. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2 or thf) on a Mattson Polaris Fourier Transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out by SACS, University of North London. Material and apparatus for electrochemistry have been described elsewhere.[32]

1-(Diphenylphosphino)-1′-(methylthio)ferrocene (1)

1,1′-Dilithioferrocene (generated from 5 g of ferrocene) was suspended in dry hexane (70 mL). To the dropping funnel was added dimethyl disulfide (1.93 mL, 21.5 mmol, 0.8 equiv.), chlorodiphenylphosphine (3.85 g, 21.5 mL, 0.8 equiv.) and dry hexane (10 mL). This solution was added dropwise over *ca.* 10 min to the suspension of 1,1′-dilithioferrocene causing warming and darkening of the mixture and this was stirred for 15 h. Water (20 mL) was added and the suspension stirred for further 1 h. A solid was formed which was filtered off and the supernatant layers were separated and the aqueous layer washed with dry hexane (2 × 10 mL). The combined organic extracts were dried (MgSO$_4$) and solvent removed *in vacuo* to give a foul-smelling orange oil. Column chromatography (neutral grade II alumina, diethyl ether–hexane, 1 : 4) enabled separation of 1-(diphenylphosphino)-1′-(methylthio)ferrocene (4.48 g, 10.77 mmol, 40% from ferrocene, *cf.* 21% from ferrocene.[15]) Found: C 66.38, H 5.09%; Anal. calc. for $C_{23}H_{21}FePS$: C 66.35, H 5.05 %. ^{1}H NMR δ (CDCl$_3$): 2.23 (s, 3H, SCH_3), 4.04 (q, 2H, C$_5H_4$), 4.11 (q, 2H, C$_5H_4$), 4.19 (t, 2H, C$_5H_4$), 4.38 (t, 2H, C$_5H_4$), 7.31 (m, 10 H, C$_6H_5$); ^{31}P{^{1}H} NMR δ (CDCl$_3$): −16.78; *m/z*: 416 (M)$^+$, 401 (M − Me)$^+$, 369 (M − SMe)$^+$, 339 (M − Ph)$^+$, 232 (M − PPh$_2$)$^+$.

1-(Diphenylphosphino)-1′-(mesitylthio)ferrocene (2)

1,1′-Dilithioferrocene (generated from 5 g of ferrocene) was suspended in dry hexane (100 mL). To the dropping funnel was added dimesityl disulfide (6.50 g, 21.5 mmol, 0.8 equiv.), chlorodiphenylphosphine (3.85 g, 21.5 mL, 0.8 equiv.) and dry toluene (50 mL). This solution was added dropwise over around 10 min to the suspension of 1,1′-dilithioferrocene causing warming and darkening of the mixture which was stirred for 15 h. Water (20 mL) was added and the suspension stirred for a further 1 h. A solid was formed which was filtered off and the supernatant layers were separated and the aqueous layer washed with dry hexane (2 × 10 mL). The combined organic extracts were dried (MgSO$_4$) and solvent was removed *in vacuo* to give an orange oil. Column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, 3 : 7) enabled separation of 1-(diphenylphosphino)-1′-(mesitylthio)ferrocene (1.40 g, 2.70 mmol, 10% from ferrocene). Found: C 71.44, H 5.82 %; Anal. calc. for $C_{31}H_{29}FePS$: C 71.54, H 5.58%. ^{1}H NMR δ (CDCl$_3$): 2.30 (s, 3H, CH_3), 2.55 (s, 6H, CH_3), 4.05 (t, 2H, C$_5H_4$), 4.25 (m, 4H, C$_5H_4$), 4.53 (t, 2H, C$_5H_4$), 7.33 (m, 6 H, C$_6H_5$), 7.50 (m, 6 H, C$_6H_5$); ^{31}P{^{1}H} NMR δ (CDCl$_3$): −16.50 ppm; *m/z*: 520 (M)$^+$, 401 (M − Mes)$^+$, 370 (M − SMes)$^+$, 336 (M − PPh$_2$)$^+$.

Dibromo[1-(diphenylphosphino)-1′-(methylthio)ferrocene]nickel(II) (3)

(1,2-Dimethoxyethane)dibromonickel(II) (0.12 g, 0.4 mmol, 1 equiv.) was added to a dry Schlenk tube containing 1-(diphenylphosphino)-1′-(methylthio)ferrocene (0.20 g, 0.5 mmol, 1.25 equiv.). Dry, deoxygenated CH_2Cl_2 (50 mL) was injected into the Schlenk tube, under nitrogen, causing the solution to turn green within a few minutes. The reaction was stirred for 40 h at room temperature. A brown precipitate was visible in the green solution; the solution was removed by cannula and evaporated to dryness, then washed (20 mL heptane) to remove any unreacted ligand. Analysis of the brown precipitate showed it to be insoluble in all solvents tested, microanalysis showed it to be mostly inorganic in composition. The green powder isolated from the filtrate was the required product (0.18 g, 0.3 mmol, 75%). Crystals suitable for X-ray studies were grown by layering a CH_2Cl_2 solution of the complex with pentane. Found: C 44.09, H 3.05%; Anal. calc. for $C_{23}H_{21}Br_2FeNiPS$: C 43.46 H 3.31%. *m/z*: 635 (M)$^+$, 588 (M − SMe)$^+$, 555 (M − Br)$^+$, 475 (M − 2Br)$^+$, 450 (M − PPh$_2$)$^+$.

Dichloro[1-(diphenylphosphino)-1′-(methylthio)ferrocene]platinum(II) (4)

1-(Diphenylphosphino)-1′-(methylthio)ferrocene (0.25 g, 0.6 mmol) was dissolved in dry toluene (3 mL) and added *via* cannula to dichloro(1,5-cyclooctadiene)platinum(II) (0.20 g, 0.53 mmol) dissolved in dry CH_2Cl_2 (7 mL). The colour of the solution changed from pale yellow to orange on completion of the addition and a precipitate formed and the reaction mixture was stirred for 15 h. The yellow precipitate was filtered off and washed with dry hexane (10 mL) and dry CH_2Cl_2 (2 mL). Recrystallisation of the precipitate was achieved by dissolution in CH_2Cl_2 and layering with hexane enabling isolation of the product as yellow needles (0.33 g, 0.48 mmol, 91%). Found: C 39.93, H 2.95%; Anal.calc. for $C_{23}H_{21}Cl_2FePPtS$: C 40.47, H 3.08%. ^{1}H NMR δ (CDCl$_3$): 2.86 (s, 3H, SCH_3, $^2J_{\text{Pt–H}}$ 23.25Hz), 4.39 (br, 4H, C$_5H_4$), 4.83 (br, 4H, C$_5H_4$), 7.43 (br m, 10H, C$_6H_5$); ^{31}P{^{1}H} NMR δ (CDCl$_3$): 8.64 (s, $^1J_{\text{Pt–P}}$ 3737 Hz); *m/z*: 682 (M)$^+$, 647(M − Cl)$^+$, 611 (M − 2Cl)$^+$.

Dichloro[1-(diphenylphosphino)-1′-(methylthio)ferrocene]-palladium(II) (5)

1-(Diphenylphosphino)-1′-(methylthio)ferrocene (0.25 g, 0.6 mmol) was dissolved in dry toluene (7 mL) and added *via* cannula to dichloro(1,5-cyclooctadiene)palladium(II) (0.15 g, 0.53 mmol) dissolved in dry chloroform (18 mL). The colour of the solution changed from yellow to red on completion of the addition and the reaction was stirred for 15 h. The red solution was concentrated slightly leading to precipitation of a red solid which was filtered off and washed with dry hexane (10 mL). Recrystallisation of the precipitate was attempted by dissolution in CH_2Cl_2 and layering with hexane. However, despite repeated attempts an orange microcrystalline powder was always obtained (0.26 g, 0.43 mmol, 81%). Found: C 46.40, H 3.57%; Anal. calc. for $C_{23}H_{21}Cl_2FePPdS$: C 46.46, H 3.54%; ^1H NMR δ ($CDCl_3$): 2.80 (s, 3H, SCH_3), 4.37 (t, 2H, C_5H_4), 4.60 (t, 2H, C_5H_4), 4.82 (t, 2H, C_5H_4), 5.03 (t, 2H, C_5H_4), 7.42 (m, 6H, C_6H_5), 7.70 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 31.82 (s); *m*/*z*: 558 $(M - Cl)^+$, 523 $(M - 2Cl)^+$, 416 $(PSF)^+$.

Bis[1-(diphenylphosphino)-1′-(methylthio)ferrocene]dichloro-palladium(II) (6)

1-(Diphenylphosphino)-1′-(methylthio)ferrocene (0.10 g, 0.24 mmol, 2.5 equiv.) was dissolved in toluene (10 mL) and added to a solution of dichloro(1,5-cyclooctadiene)palladium(II) (0.03 g, 0.095 mmol, 1 equiv.) dissolved in CH_2Cl_2 (5 mL). The solution instantly changed colour from yellow to red, and was stirred for 20 h at room temperature. The solvent was removed and the red residue washed with hexane (3 × 10 mL) yielding **6** as an orange–red powder (0.08 g, 0.076 mmol, 80%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a hexane–toluene solution of the complex. Found: C 54.67, H 4.93%; Anal. calc. for $C_{46}H_{42}Cl_2Fe_2P_2PdS_2$: C 54.81, H 5.00%. ^1H NMR δ ($CDCl_3$): 2.25 (s, 3H, SCH_3), 4.39 (m, 2H, C_5H_4), 4.43 (m, 2H, C_5H_4), 4.59 (m, 2H, C_5H_4), 4.63 (m, 2H, C_5H_4), 7.39 (m, 6H, C_6H_5), 7.62 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 15.57 (s); *m*/*z*: 974 $(M - Cl)^+$, 938 $(M - 2Cl)^+$, 891 $(M - 2Cl - SMe)^+$, 754 $(M - 2Cl - PPh_2)^+$, 522 $(M - 2Cl - PSF)^+$.

Carbonylchloro[1-(diphenylphosphino)-1′-(methylthio)-ferrocene]rhodium(I) (7)

1-(Diphenylphosphino)-1′-(methylthio)ferrocene (0.16 g, 0.39 mmol, 2 equiv.) was dissolved in a minimum amount of toluene (10 mL) and added to a solution of tetracarbonyldichlorodirhodium(I) (0.08 g, 0.19 mmol, 1 equiv.) in methanol (10 mL). An orange precipitate formed immediately, which was filtered off after 2 h. The precipitate was washed with diethyl ether (20 mL) and methanol (20 mL), enabling isolation of **7** (0.09 g, 0.15 mmol, 79%). Found: C 49.46, H 3.42%; Anal. calc. for $C_{24}H_{21}ClFeOPRhS$: C 49.40, H 3.60%. ^1H NMR δ ($CDCl_3$): 2.63 (s, 3H, SCH_3), 4.21 (t, 2H, C_5H_4), 4.51 (t, 2H, C_5H_4), 4.55 (t, 2H, C_5H_4), 4.73 (t, 2H, C_5H_4), 7.37 (m, 6H, C_6H_5), 7.68 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 37.42 (d, $^1J_{Rh-P}$ 168 Hz); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 24.03 (s, SCH_3), 71.04 (s, C_5H_4), 72.59 (d, C_5H_4), 75.22 (d, C_5H_4), 75.43 (s, C_5H_4), 77.99 (s, C_5H_4), 81.91 (s, C_5H_4), 128.23 (d, *o*-C_6H_5, $^2J_{P-C}$ 10.38 Hz), 130.55 (s, *m*-C_6H_5), 131.42 (s, *p*-C_6H_5), 133.63 (d, *ipso*-C_6H_5, $^1J_{P-C}$ 12.46 Hz), 135.47 (d, *C*O, $^1J_{Rh-C}$ 52 Hz); IR (CH_2Cl_2): υ(CO) 2006 cm^{-1}; *m*/*z*: 583 $(M)^+$, 555 $(M - CO)^+$, 547 $(M - Cl)^+$, 519 $(M - CO - Cl)^+$.

[1-(Diphenylphosphino)-1′-(methylthio)ferrocene]tetracarbonyl-tungsten(0) (8) and [1-(diphenylphosphino)-1′-(methylthio)-ferrocene]pentacarbonyltungsten(0) (9)

Pentacarbonyl(tetrahydrofuran)tungsten(0) (53 mL of a 0.01 M solution in thf, 0.53 mmol, 1.5 equiv.), prepared by UV photolysis, was injected into a solution of 1-(diphenylphosphino)-1′-(methylthio)ferrocene (0.15 g, 0.36 mmol, 1 equiv.) dissolved in toluene (50 mL). The yellow solution was stirred at room temperature for 20 h and then evaporated to dryness. The crude product was purified by column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, 1 : 9 to remove hexacarbonyl, 1 : 5 to remove **9** and 1 : 3 to remove **8**) which enabled isolation of compounds **9** (0.10 g, 0.14 mmol, 39%) and **8** (0.13 g, 0.18 mmol, 50%). Crystals of **8** suitable for X-ray crystallography were grown by layering a CH_2Cl_2 solution with hexane. **8** Found: C 45.12, H 2.64%; Anal. calc. for $C_{27}H_{21}FeO_4PSW$: C 45.50, H 2.95%. ^1H NMR δ ($CDCl_3$): 2.90 (s, 3H, SCH_3), 4.22 (m, 4H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.58 (t, 2H, C_5H_4), 7.38 (m, 6H, C_6H_5), 7.54 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 19.53 (d, $^1J_{W-P}$ 234 Hz); IR (THF): υ(CO) 2016, 1905, 1890, 1875 cm^{-1}; *m*/*z*: 712 $(M)^+$, 684 $(M - CO)^+$, 656 $(M - 2CO)^+$, 628 $(M - 3CO)^+$, 600 $(M - 4CO)^+$. **9** Found: C 45.33, H 2.76%; Anal. calc. for $C_{28}H_{21}FeO_5SPW$: C 45.41, H 2.84%. ^1H NMR δ($CDCl_3$): 2.15 (s, 3H, SCH_3), 3.97 (t, 2H, C_5H_4), 4.05 (t, 2H, C_5H_4), 4.31 (t, 2H, C_5H_4), 4.51 (t, 2H, C_5H_4), 7.42 (m, 10H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 11.15 (d, $^1J_{W-P}$ 245 Hz); IR (thf): υ(CO) 2070, 1980, 1934 cm^{-1}; *m*/*z*: 740 $(M)^+$, 628 $(M - 4CO)^+$, 600 $(M - 5CO)^+$.

[1-(Diphenylphosphino)-1′-(methylthio)ferrocene]tetracarbonyl-molybdenum(0) (10) and [1-(diphenylphosphino)-1′-(methylthio)-ferrocene]pentacarbonylmolybdenum(0) (11)

Pentacarbonyl(tetrahydxrofuran)molybdenum(0) (53 mL of a 0.01 M solution in thf, 0.53 mmol, 1.5 equiv.), prepared by UV photolysis, was injected into a solution of 1-(diphenylphosphino)-1′-(methylthio)ferrocene (0.15 g, 0.36 mmol, 1 equiv.) dissolved in toluene (50 mL). The yellow solution was stirred at room temperature for 20 h and then evaporated to dryness. The crude product was purified by column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, 1 : 9 to remove hexacarbonyl, 1 : 5 to remove **11** and 1 : 3 to remove **10**) which enabled isolation of compounds **11** (0.11 g, 0.17 mmol, 47%) and **10** (0.05 g, 0.08 mmol, 22%). **10** Found: C 51.82, H 3.43%; Anal. calc. for $C_{27}H_{21}FeMoO_4SP$: C 51.84, H 3.36%. ^1H NMR δ ($CDCl_3$): 2.70 (s, 3H, SCH_3), 4.22 (m, 4H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.57 (t, 2H, C_5H_4), 7.38 (m, 6H, C_6H_5), 7.55 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 30.07 (s); IR (thf): υ(CO) 2020, 1902, 1877 cm^{-1}; *m*/*z*: 625 $(M)^+$, 597 $(M - CO)^+$, 541 $(M - 3CO)^+$, 513 $(M - 4CO)^+$. **11** Found: C 51.72, H 3.19%; Anal. calc. for $C_{28}H_{21}FeMoO_5SP$: C 51.53, H 3.2 %. ^1H NMR δ ($CDCl_3$): 2.15 (s, 3H, SCH_3), 3.96 (t, 2H, C_5H_4), 4.05 (t, 2H, C_5H_4), 4.31 (t, 2H, C_5H_4), 4.48 (t, 2H, C_5H_4), 7.42 (m, 10H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 28.26 (s); IR (thf): υ(CO) 2071, 1988, 1944 cm^{-1}; *m*/*z*: 652 $(M)^+$, 540 $(M - 4CO)^+$, 512 $(M - 5CO)^+$.

Chromium(0)[1-(diphenylphosphino)-1′-(methylthio)ferrocene]-tetracarbonyl (12) and chromium(0)[1-(diphenylphosphino)-1′-(methylthio)ferrocene]pentacarbonyl (13)

Chromium(0)pentacarbonyl(tetrahydrofuran) (53 mL of a 0.01 M solution in thf, 0.53 mmol, 1.5 equiv.), prepared by UV photolysis, was injected into a solution of 1-(diphenylphosphino)-1′-(methylthio)ferrocene (0.15 g, 0.36 mmol, 1 equiv.) dissolved in toluene (50 mL). The yellow solution was stirred at room temperature for 20 h and then evaporated to dryness. The crude product was purified by column chromatography (neutral grade II alumina, CH_2Cl_2–hexane, 1 : 9 to remove hexacarbonyl, 1 : 5 to remove **13** and 1 : 3 to remove **12**) enabled isolation of compounds **13** (0.02 g, 0.036 mmol, 10%) and **12** (0.13 g, 0.22 mmol, 61%). **12** Found: C 55.79, H 3.74%; Anal. calc. for $C_{27}H_{21}CrFeO_4PS$: C 55.86, H 3.62%. ^1H NMR δ ($CDCl_3$): 2.65 (s, 3H, SCH_3), 4.20 (t, 2H, C_5H_4), 4.27 (t, 2H, C_5H_4), 4.38 (t, 2H, C_5H_4), 4.56 (t, 2H, C_5H_4), 7.38 (m, 6H, C_6H_5), 7.58 (m, 4H, C_6H_5); $^{31}P\{^1H\}$ NMR δ ($CDCl_3$): 46.22 (s);

Table 6 Crystal data, data collection and refinement parameters for compounds **3**, **4**, **6** and **8**[a]

	3	**4**	**6**	**8**
Formula	$C_{23}H_{21}PSBr_2FeNi$	$C_{23}H_{21}PSCl_2FePt$	$C_{46}H_{42}P_2S_2Cl_2Fe_2Pd$	$C_{27}H_{21}O_4PSFeW$
Formula weight	634.8	682.3	1009.9	712.2
Colour, habit	Dark olive green blocks	Yellow prisms	Orange prisms	Orange rhombs
Crystal size/mm	0.70 × 0.57 × 0.19	0.17 × 0.13 × 0.13	0.32 × 0.13 × 0.07	0.57 × 0.47 × 0.23
Temperature/K	293	293	293	293
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.928(1)	11.450(1)	9.434(1)	11.502(2)
b/Å	15.880(3)	22.142(3)	11.605(1)	17.863(2)
c/Å	17.155(2)	18.201(2)	18.583(1)	12.446(1)
α/°	64.82(1)	—	—	—
β/°	78.56(1)	108.07(1)	94.32(1)	95.60(1)
γ/°	87.62(1)	—	—	—
V/Å^3	2396.4(5)	4386.9(8)	2028.7(2)	2545.0(6)
Z	4[b]	8	2[c]	4
D_c/g cm^{-3}	1.760	2.066	1.653	1.859
μ/mm^{-1}	4.89	7.45	12.38	5.26
Radiation used	Mo-Kα	Mo-Kα	Cu-Kα	Mo-Kα
θ range/°	2.1–25.0	1.8–25.0	4.5–60.0	2.0–25.0
No. of unique reflections				
measured	8109	3874	3017	4375
observed, $\|F_o\| > 4\sigma(\|F_o\|)$	5159	3145	2389	3683
Absorption correction	Gaussian	Ellipsoidal	Ellipsoidal	Empirical
Max., min. transmission	0.43, 0.08	0.47, 0.35	0.34, 0.18	0.78, 0.36
No. of variables	488	239	227	293
R_1, wR_2[d]	0.049, 0.095	0.031, 0.060	0.048, 0.114	0.032, 0.071

[a] Details in common: graphite monochromated radiation, refinement based on F^2. [b] There are two crystallographically independent molecules in the asymmetric unit. [c] The complex has crystallographic C_i symmetry. [d] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

IR (thf): υ(CO) 2010, 1908, 1891, 1876 cm^{-1}; m/z: 580 (M)$^+$, 468 (M − 4CO)$^+$. **13** Found: C 55.34, H 3.44%; Anal. calc. for $C_{28}H_{21}CrFeO_5PS$: C 55.26, H 3.45%. ^{1}H NMR δ ($CDCl_3$): 2.16 (s, 3H, SCH_3), 3.94 (t, 2H, C_5H_4), 4.05 (t, 2H, C_5H_4), 4.31 (t, 2H, C_5H_4), 4.47 (t, 2H, C_5H_4), 7.43 (m, 10H, C_6H_5); ^{31}P{^{1}H} NMR δ ($CDCl_3$): 47.22 (s); IR (thf): υ(CO) 2061, 1988, 1939 cm^{-1}; m/z: 608 (M)$^+$, 468 (M − 5CO)$^+$.

Suzuki coupling reactions

The experimental procedure used to test the ligands as catalysts in the Suzuki coupling reaction: 4-bromotoluene (1.71 g, 10 mmol, 1 equiv.), phenyl boronic acid (1.34 g, 11 mmol, 1.1.equiv.) and potassium carbonate (2.76 g, 20 mmol, 2 equiv.) were placed in a dry two-necked round bottomed flask fitted with a reflux condenser and under nitrogen. The starting materials were suspended in dry, deoxygenated toluene (30 mL). To the suspension was added a solution of Pd_2dba_3 (0.046 g, 0.05 mmol, 0.005 equiv.) and the ligand (0.12 mmol, 0.012 mmol) in toluene (20 mL). The reaction was heated to 70 °C and maintained at this temperature for 5 h. The solvent was removed and the residue suspended in diethyl ether (40 mL), washed with brine (3 × 30 mL) and evaporated to dryness. The crude product was purified by column chromatography (silica gel, hexane) and the solvent evaporated to give a white powder (the yield of which is quoted for each of the ligand systems in Scheme 3 and used to assess their catalytic activities). The purity of the product was determined by GC.

Crystallography

Table 6 provides a summary of the crystallographic data for compounds **3**, **4**, **6** and **8**. Data were collected on Siemens P4/PC diffractometers using ω-scans. The structures were solved by direct methods and they were refined based on F^2 using the SHELXTL program system.[33]

CCDC reference numbers 187540–187543.

See http://www.rsc.org/suppdata/dt/b2/b205653d/ for crystallographic data in CIF or other electronic format.

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