Synthesis, Structure and Reactivity of New Late Transition Metal Complexes Bearing Diphosphane Ligands Derived from Bis(pyrazol-1-yl)methane

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Modification of the multistep synthesis of the previously described bis[5-(diphenylphosphanyl)pyrazol-1-yl)]methane (bppzm, **1**) produces the novel diphosphane (diphenylphosphanyl)-[5-(diphenylphosphanyl)pyrazol-1-yl](pyrazol-1-yl)-methane (p4m, **2**). Treatment of this ligand with $[MCl_2(PhCN)_2]$ (M = Pd, Pt) or $[M(COD)(THF)_2]BF_4$ (M = Rh, Ir) produces $[MCl_2(p4m)]$ (M = Pd **3**, Pt **4**) or $[M(COD)(p4m)]BF_4$ (M = Rh **5**, Ir **6**) complexes, which chelate in a *P*,*P*-bidentate fashion. Sulfidation of bppzm and p4m produces the disulfidophosphanes $bppzmS_2$ (**7**) and $p4mS_2$ (**8**). Treatment of **7** and **8** with $[PdCl_2(PhCN)_2]$ produces $[PdCl_2(bppzmS_2)]$ (**9**) and $[PdCl_2(pmS_2)]$ (**10**), respectively, in which ligands **7** and **8** act in an *N*,*N*-bidentate chelate fashion. In contrast, ligand **8** reacts with $[Rh(COD)(THF)_2]BF_4$ to produce $[Rh(COD)(p4mS_2)]BF_4$, where ligand **7** acts in a dynamic *S*,*S*-chelate fashion. The activity of some of these complexes in the catalytic hydrogenation of olefins is reported and the single-crystal X-ray structures of **4**, **8**, and **9** have been obtained.

Introduction

The synthesis of polydentate phosphanes is a continuously developing field because these ligands are expected to allow greater control over the coordination sphere of a metal.[1] Increasing interest in the use of polyfunctional ligands has focused the attention of researchers on phosphanes with groups bearing nitrogen donors. Phosphorus-nitrogen hemilabile ligands are particularly useful in catalytic processes because one part of the ligand is capable of partially dissociating from the chelate form, thus allowing a substrate to coordinate to the metal centre and undergo some transformation.[2] With these precedents in mind, we have previously prepared and characterized[3] several poly(pyrazol-1-yl)methane derivatives bearing phosphane groups on the pyrazole rings, for example bis[5-(diphenylphosphanyl)-pyrazol-1-yl]methane (bppzm) (**1**). The coordinative capacity of the bppzm ligand was investigated with the metal centres niobium, palladium and platinum. In the first case, *N*,*N*-six-membered metallacyclic species were isolated. However, square-planar species with a *P*,*P*-eight-membered metallacycle were found for the late metals (see Figure 1), confirming the hard-hard, soft-soft acid-base principle.

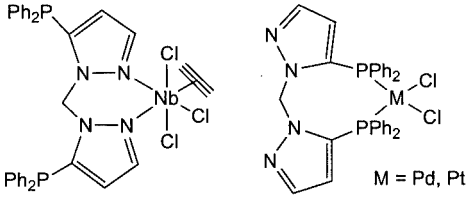

Figure 1. Complexes with the bppzm ligand

Research into the related phosphane sulfide ligands has been much less extensive.[4] Several complexes of late transition metals, namely platinum group metals, have been described with a variety of tertiary phosphane sulfides. The X-ray data suggest that $R_3P{=}S$ groups bind to the metal as simple σ-donors through the *p*-electrons of the sulfur atom, with no evidence of π-bonding between the metal *d* electrons and the empty orbitals of sulfur. This situation gives rise to weaker metal-ligand bonding than with the related phosphane ligands.

In order to extend these studies we sought to develop new functionalised bis(pyrazol-1-yl)methanes and to prepare and characterise new metal complexes formed by these ligands. Furthermore, we present here a modification of the synthesis of **1** to obtain a new chiral diphosphane. The influence of sulfidation of this new diphosphane and the previously described bppzm ligand on their coordination behaviour was also studied. One of the resulting complexes

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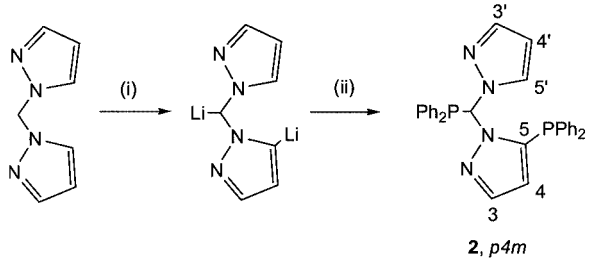
was found to be active in the hydrogenation of simple olefins.

Results and Discussion

We have previously described the synthesis of bis[5-(diphenylphosphanyl)pyrazol-1-yl)]methane (**1**),[3] which was prepared by reaction of bis(pyrazol-1-yl)methane (bpzm) and *n*BuLi at low temperature, followed by the addition of PPh_2Cl and warming. In many cases a minor by-product was observed in these reactions, although this was easily removed by crystallization from CH_2Cl_2/Et_2O.

The minor product has now been isolated and identified as a new asymmetric diphosphane. In an attempt to improve the yield of this new and interesting compound, the previously described synthetic procedure was modified by the addition of a slight excess of first *n*BuLi and then PPh_2Cl at room temperature, followed by recrystallization of the product from CH_2Cl_2 (Scheme 1). Similar behaviour[5] was also observed upon the modification of bis(pyrazol-1-yl)methane with MeI or $PhCH_2Br$.

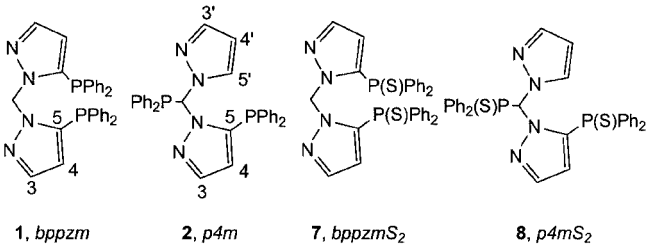


Scheme 1. (i) 2.5 *n*BuLi, THF, room temp., 30 min; (ii) 2 PPh_2Cl, THF, room temp., 16 h

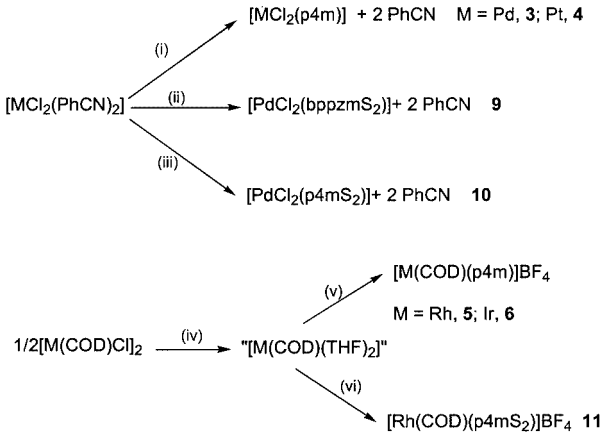
This new ligand, (diphenylphosphanyl)-[5-(diphenylphosphanyl)pyrazol-1-yl](pyrazol-1-yl)methane (**2**) (p4m), can be obtained from the reaction mixture with good purity as a light brown solid (see Exp. Sect.). In this procedure compound **1** is formed as the by-product.

The ^1H NMR spectrum of **2** shows two sets of two doublets assigned to H^3 and H^4 of the two pyrazole rings, with the more shielded peak corresponding to H^4. These data indicate that the two rings are not equivalent. The signal due to the bridging CH group appears as a doublet of doublets due to coupling with the two phosphorus atoms. The $J_{H,P}$ coupling constants are similar to those found for analogous compounds described by us.[3] The ^{13}C NMR spectrum confirms the asymmetry around the CH group, which gives rise to a doublet of doublets due to coupling with phosphorus atoms. Finally, the $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets at $\delta = -30.99$ and -60.94 ppm for the inequivalent phosphorus atoms.

Ligand **2** (Scheme 2) is of considerable interest on two counts; firstly due to its chiral nature and secondly because it can provide different coordination modes than compound **1**. In fact, versatile ligand **2** would form six-membered *P*,*P*-, six-membered *N*,*N*- or seven-membered *N*,*P*-chelating complexes. Chiral chelating ligands that, when complexed to a metal such as rhodium, allow homogeneous hydrogenation to proceed in an enantioselective fashion to yield chiral products are of great interest and have been the focus of many reviews.[6] Compound **2** was used in the complexation of some late transition metal fragments, namely $[MCl_2(PhCN)_2]$ (M = Pd, Pt) and $[M(COD)(THF)_2]BF_4$ (M = Rh, Ir; COD = cyclooctadiene), in order to test its coordination capacity as a chelating agent (Scheme 3).



Scheme 2. Ligands **1**, **2**, **7** and **8**



Scheme 3. (i) p4m, CH_2Cl_2, room temp., 5 h; (ii) $bppzmS_2$, CH_2Cl_2, room temp., 16 h; (iii) $p4mS_2$, CH_2Cl_2, room temp., 16 h; (iv) $AgBF_4$, THF, room temp., 30 min; (v) p4m, THF, 203 K to room temp., 3 h; (vi) $p4mS_2$, THF, 203 K to room temp., 3 h

The complexes were isolated as crystalline solids in good yields (see Exp. Sect.). Complexes **3**, **4** and **5** are very stable under an inert atmosphere but complex **6** slowly decomposes in solution.

The ^1H NMR spectra of **3**, **4**, **5** and **6** show two sets of resonances for the H^3 and H^4 protons of the pyrazolyl rings. In addition, the H^5 proton of the unsubstituted ring appears as a broad singlet. The ^{13}C NMR spectra actually exhibit the signal for the methyne carbon atom and this appears as a doublet due to coupling with the neighbouring phosphorus atom. The asymmetry of these molecules is also reflected in the COD region of the spectra. For example, the diene ligand shows two broad peaks for the =CH carbons. The $^{31}P\{^1H\}$ NMR spectra show two broad peaks for complexes **3** and **6** and these are at significantly lower fields than the corresponding peaks for the free ligand **2**, suggest-

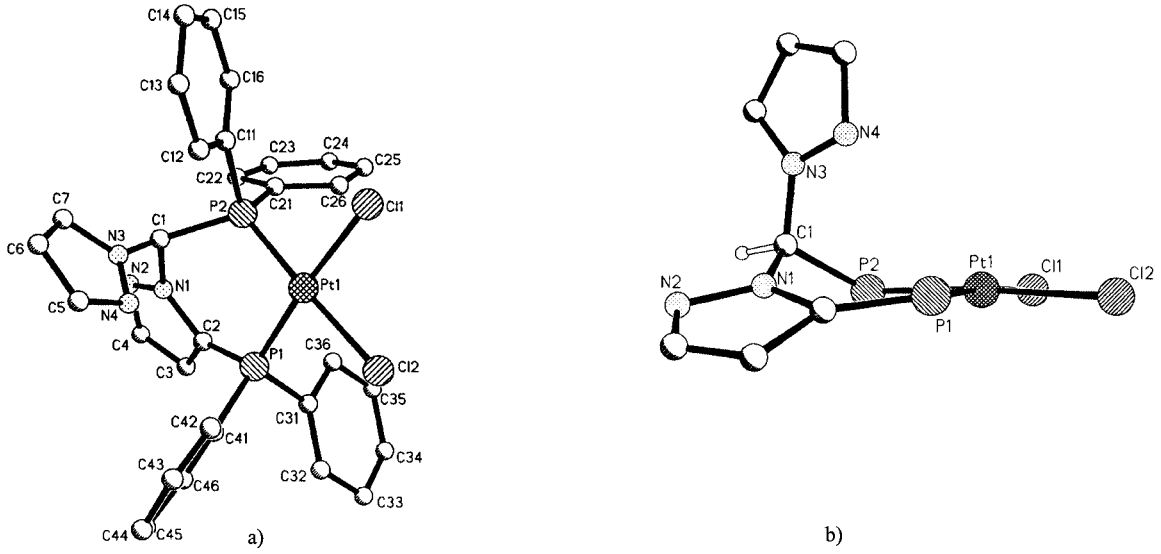


Figure 2. a) Molecular structure and atom-labelling scheme for compound 4; b) conformation of the six-membered chelate ring

ing that in these complexes a coordination of the p4m ligand takes place in a *P,P*-mode. Complex **5** also exhibits lower field signals but, in this case, the peaks appear as two doublets of doublets due to coupling between the two *cis* phosphorus atoms ($^2J_{P,P}$ = 39 Hz), through the metal, and also due to coupling with the rhodium atom ($^1J_{P,Rh}$ = 115 Hz). Complex **4** shows two doublets ($^2J_{P,P}$ = 16 Hz) at lower fields than the corresponding signals in the free ligand and these doublets are flanked by two ^{195}Pt satellites ($^1J_{Pt,P}$ = 1870 and 1791 Hz, respectively).

A crystal structure analysis of complex **4** was carried out in order to confirm the proposed coordination for these complexes. The molecular structure and atomic numbering scheme is shown in Figure 2. Selected bond lengths and angles for **4** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [deg] for **4**

Pt(1)−Cl(1)	2.34(1)
Pt(1)−Cl(2)	2.37(1)
Pt(1)−P(1)	2.23(1)
Pt(1)−P(2)	2.20(1)
P(1)−C(2)	1.66(4)
P(2)−C(1)	1.83(3)
N(1)−C(1)	1.47(5)
N(1)−C(2)	1.41(5)
Cl(1)−Pt(1)−Cl(2)	89.8(4)
Cl(1)−Pt(1)−P(1)	175.5(4)
Cl(1)−Pt(1)−P(2)	89.7(4)
Cl(2)−Pt(1)−P(1)	86.3(4)
Cl(2)−Pt(1)−P(2)	176.7(4)
P(1)−Pt(1)−P(2)	94.0(4)
Pt(1)−P(2)−C(1)	116(1)
Pt(1)−P(1)−C(2)	115(1)

The structure consists of discrete monomeric molecules separated by van der Waals distances. The platinum centre is bound to four atoms (Figure 2b) — the two phosphorus atoms from the p4m group and the two chlorine atoms — in a quasi-planar coordination. The Cl1, Cl2, P1 and P2 atoms are co-planar and Pt1 is displaced from this plane by −0.057(6) Å. The six-membered chelate ring exists in a half-boat conformation with C1 −0.96(4) Å and N1 −0.36(5) Å out of the plane defined by Pt1, P1, P2 and C2. The Pt−P and Pt−Cl distances are in reasonable agreement with the values published for related structures.[3]

In contrast to the well-known use of diphosphanes as chelating ligands, the coordination chemistry of phosphane sulfide derivatives toward platinum group metals is much less extensively studied.[7]

The sulfide derivatives (**7** and **8**) of compounds **1** and **2** (Scheme 2), respectively, were obtained by reaction with an excess of elemental sulfur (see Exp. Sect.).

In the ^{1}H NMR spectrum of **7** the signals due to the methylene protons are shifted to lower field than the precursor ligand **1**. In a similar way to **1**, compound **7** gives rise to a single set of signals for H^3 and H^4 in the ^{1}H NMR spectrum as well as the corresponding C3, C4 and C5 carbon atoms in the ^{13}C NMR spectrum. This observation confirms the equivalence of the two pyrazole rings. Sulfidation of the phosphorus atoms produces a singlet at δ = 3.22 ppm in the ^{31}P{^{1}H} NMR spectrum, at higher field than those found for the more simple diphosphane sulfides such as $dppmS_2$ (δ = 35.4 ppm),[7d] and shifted to lower field than the value found for the original diphosphane ligand **1**. A similar effect was observed in the ^{31}P{^{1}H} NMR spectrum of **8**, which exhibits two singlets at δ = 25.57 and 3.62 ppm. The ^{1}H NMR signal for the proton on the methyne bridge of compound **8** is also shifted to lower field than for **2**. The ^{1}H and ^{13}C NMR spectra of **8** confirm the non-equivalence of the pyrazole rings, with two sets of signals observed for the proton and carbon atoms of the pyrazole rings. The IR spectra of compounds **7** and **8** show characteristic[7d] broad ν(P=S) bands at 658 cm^{-1} and 633 cm^{-1}, respectively.

The molecular structure of **8** was confirmed by X-ray crystallography. The molecular structure and atomic numbering scheme are shown in Figure 3. Selected bond lengths and angles for **8** are given in Table 2.

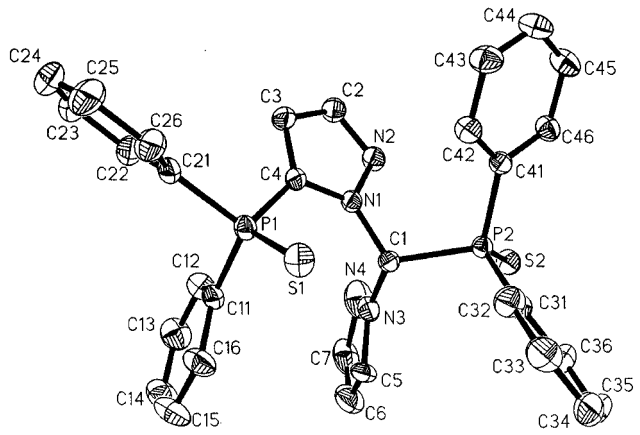


Figure 3. Molecular structure and atom-labelling scheme for compound **8**, with thermal ellipsoids at 30% probability

Table 2. Selected bond lengths [Å] and angles [deg] for **8**

P(1)−S(1)	1.955(1)
P(2)−S(2)	1.939(1)
P(2)−C(1)	1.897(2)
P(1)−C(4)	1.798(2)
N(1)−N(2)	1.354(3)
N(1)−C(1)	1.438(3)
N(1)−C(4)	1.367(3)
N(3)−C(1)	1.438(3)
S(1)−P(1)−C(4)	113.9(1)
S(1)−P(1)−C(11)	113.9(1)
S(1)−P(1)−C(21)	114.6(1)
C(4)−P(1)−C(11)	103.9(1)
C(4)−P(1)−C(21)	103.0(1)
C(11)−P(1)−C(21)	106.3(1)
S(2)−P(2)−C(1)	112.2(1)
S(2)−P(2)−C(31)	113.8(1)
S(2)−P(2)−C(41)	114.2(1)
C(1)−P(2)−C(31)	102.1(1)
C(1)−P(2)−C(41)	106.9(1)
C(31)−P(2)−C(41)	106.6(1)

Each phosphorus atom shows a distorted tetrahedral coordination. The P−S distances of 1.955(1) and 1.939(1) Å indicate a double bond between P and S. The angle between the planes of the pyrazolyl rings is 112.5(1)°.

In order to study the behaviour of these new compounds as ligands in comparison to their phosphorus precursors **1** and **2**, we explored the reactivity of the sulfide derivatives **7** and **8** towards Pd and Rh metal centres. In these cases, we expect the possibility of an *S*,*S*-, *N*,*N*- or *N*,*S*-chelating coordination. Unfortunately, attempts to prepare analogous compounds of Pt or Ir were unsuccessful.

Addition of a stoichiometric amount of **7** to a dichloromethane solution of $[PdCl_2(PhCN)_2]$ led to the formation of complex **9** as a very insoluble solid (Scheme 3). The ^1H NMR spectrum of **9** exhibits two broad singlets for H^3 and H^4, which indicates the equivalence of the two pyrazole rings. A particularly interesting result was found on examining the $^{31}P\{^1H\}$ NMR spectrum of **9**. In this case, a singlet for two equivalent phosphorus atoms appears at δ = 4.80 ppm, which is close to the value of δ = 3.22 ppm found in the free ligand. This result seems to indicate that coordination of the phosphorus atoms to the palladium centre does not take place and hence that the ligand behaves as an *N*,*N*-donor in this complex. The IR spectrum confirms this coordination mode, with a ν(P=S) band at 660 cm^{-1}, similar to the value found in the free ligand. The position of the P=S band in the IR spectrum of previously reported sulfur-coordinated complexes is shifted 20−50 cm^{-1} to lower energy relative to the corresponding band in the uncomplexed ligands.[8]

Similar Pd^{II} complexes incorporating bis(pyrazol-1-yl)methane ligands with *N*,*N*-coordination have been prepared previously[9] with the aim of studying the electronic and steric effects of these ligands on the dynamic structure and reactivity of the corresponding complexes. In some cases, cationic derivatives were used as ethylene polymerization catalysts.

The analogous complex $[PdCl_2(bppzm)]$ shows a dynamic behaviour in solution that involves a boat-to-boat inversion.[3] For this reason, we carried out a variable-temperature NMR study in order to elucidate the possible dynamic behaviour of **9**. In the $^1H\{^{31}P\}$ NMR spectrum, the signal for the CH_2 group appears as a broad singlet at δ = 7.09 ppm at room temperature. At 228 K, however, this peak disappears in the baseline but, unfortunately, a slow exchange limit could not be observed.

The molecular structure of **9** was confirmed by X-ray crystallography. The molecular structure and atomic numbering scheme is shown in Figure 4. Selected bond lengths and angles for **9** are given in Table 3.

The structure consists of discrete monomeric molecules separated by van der Waals distances. There are two molecules per asymmetric unit. The palladium atom is bound to four atoms (Figure 4b) — the two nitrogens from the $bppzmS_2$ group and the two chlorine atoms — in a square-planar coordination. The six-membered chelate ring exists in a boat conformation with C4 and Pd1 out of the plane defined by N1, N2, N3 and N4 [C4: 0.656(7) and −0.638(7) Å for molecules 1 and 2, respectively; Pd1: 0.624(7) and −0.606(7) Å for molecules 1 and 2, respectively]. The Pd−N and Pd−Cl distances are in good agreement with the previously published values.[9] The angle between the planes of the pyrazolyl rings is 47.6(2)° and 47.5(2)° for molecules 1 and 2, respectively. The angles between the N1−N2−N3−N4 and N1−Pd1−N3 planes [154.5(2)° and 155.3(2)° for molecules 1 and 2, respectively] and N1−N2−N3−N4 and N2−C4−N4 planes [128.5(2)° and 129.8(2)° for molecules 1 and 2, respectively] are similar[3] to that in the complex $[PdCl_2(bppzm)]$, in which steric interactions are not appreciable.

It is worth noting that $[PdCl_2(bppzm)]$, which was reported previously by us,[3] shows a *P*,*P*-eight-membered metallacycle in preference to a less-open *N*,*N*-six-membered

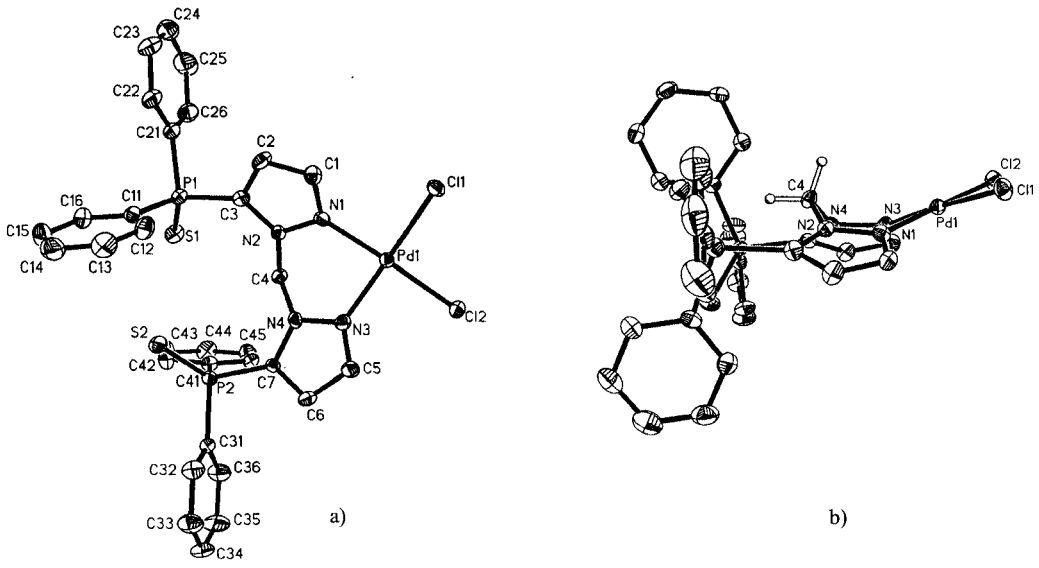


Figure 4. a) Molecular structure and atom-labelling scheme for compound **9** (molecule 1), with thermal ellipsoids at 50% probability; b) conformation of the six-membered chelate ring

Table 3. Selected bond lengths [Å] and angles [deg] for **9**

	Molecule 1	Molecule 2
Pd−Cl(1)	2.283(1)	2.282(1)
Pd−Cl(2)	2.282(1)	2.290(1)
Pd−N(1)	2.024(5)	2.016(5)
Pd−N(3)	2.012(5)	2.027(5)
S(1)−P(1)	1.939(2)	1.934(2)
S(2)−P(2)	1.937(2)	1.941(2)
Cl(1)−Pd−Cl(2)	91.76(5)	91.3(6)
Cl(1)−Pd−N(1)	90.6(1)	89.8(1)
Cl(1)−Pd−N(3)	176.7(1)	177.7(1)
Cl(2)−Pd−N(1)	177.5(1)	176.4(1)
Cl(2)−Pd−N(3)	89.4(1)	90.4(1)
N(1)−Pd−N(3)	88.2(2)	88.4(2)
S(1)−P(1)−C(3)	115.7(2)	111.9(2)
S(2)−P(2)−C(7)	112.0(2)	115.2(2)

system. This behaviour can be explained if one considers the stable soft-soft interactions between Pd^{II} and P atoms. In contrast, in complex **9** a stable *N*,*N*-six-membered chelate is preferred to the soft-soft Pd−S bonds in a ten-membered metallacycle.

The behaviour of sulfur-containing ligand **8** towards $[PdCl_2(PhCN)_2]$ was investigated in order to explore the existence of *N*,*N*-six-membered or *S*,*S*-eight-membered complexation. The reaction of **4** and $[PdCl_2(PhCN)_2]$ was performed in CH_2Cl_2 (see Scheme 3) and afforded $[PdCl_2(p4mS_2)]$ (**10**) as a very insoluble solid.

The ^1H NMR spectrum of **10** shows evidence for the non-equivalence of the pyrazole rings. The signal for the proton of the methyne group appears as a doublet at δ = 9.61 ppm due to coupling with the nearest phosphorus atom. The $^{31}P\{^1H\}$ NMR spectrum of **10** shows two singlets at δ = 26.11 and 5.70 ppm, which are closer to those of the free ligand (δ = 25.57 and 3.62 ppm). The IR spectrum confirms an *N*,*N*-coordination on the basis of the ν(P=S) absorption at 630 cm^{-1} for complex **10** — a value similar to that found in the free ligand.

Finally, reaction of **8** and the solvate moiety $[Rh(COD)(THF)_2]BF_4$ in THF afforded $[Rh(COD)(p4mS_2)]BF_4$ (**11**) as a very insoluble brown solid (see Scheme 3). This complex was prepared in order to study the influence of sulfur on the reactivity of complex **11** in comparison with the analogous complex **5** (see below).

The $^{31}P\{^1H\}$ NMR spectrum of complex **11** contains two peaks near to those of the free ligand **8**. The peak at δ = 20.64 ppm appears as a very broad multiplet, indicating that some interaction with rhodium is present and that the molecule shows a dynamic behaviour in solution. This situation was confirmed by performing a variable temperature $^{31}P\{^1H\}$ NMR study. At low temperature (213 K), the process can be frozen out and the broad peak gives rise to a pseudo-triplet at δ = 18.76 ppm (J = 9 Hz), probably due to coupling with the rhodium and the second phosphorus. On the other hand, a sharp peak at δ = 21.52 ppm was observed at 333 K. A temperature-dependent coordination/decoordination process involving one of the $P(S)Ph_2$ groups was proposed as being responsible for these changes. Additionally, the IR spectrum shows a ν(P=S) absorption at 556 cm^{-1}, which indicates an *S*,*S*-coordination mode.

Hydrogenation of Olefins

Complex **5**, which contains the ligand p4m, is an active hydrogenation catalyst for cyclohexene and 1-heptene (Table 4).

The reactions were conducted under different conditions of pressure, reaction time, solvent, and in the presence/absence of additives. In CH_2Cl_2, a conversion of 26% for cyclohexene was obtained after ca. 20 h. at 10 bar and 353 K. A similar conversion (21%) was obtained in MeOH. In contrast, addition of a small amount of KOH to the

Table 4. Results of the catalysis experiments; reaction conditions: catalyst 0.03 mmol; substrate 3 mmol; solvent 30 mL; KOH 0.04 mmol

Complex	Substrate	Solvent	Additive	Time(h)	Temp.(K)	Pressure(bar)	Conversion (%)
5	cyclohexene	CH_2Cl_2		20	298	1	7.7
5	cyclohexene	CH_2Cl_2		20	353	10	26
5	cyclohexene	MeOH		20	353	10	21
5	cyclohexene	MeOH	KOH	1	353	10	33
5	1-heptene	MeOH	KOH	1	353	10	50

latter reaction mixture produced the highest conversion observed (33%) in only 1 h. The activity is similar to those found for other rhodium derivatives of multidentate heterocyclic ligands, of the type $[Rh(diene)(OPPy_2R)]BF_4$,[2j] under very analogous conditions. As expected, complex **5** is a better catalyst for the hydrogenation of 1-heptene, giving a conversion of 50% in 1 h. The iridium derivative **6**, probably due to its lack of stability in solution, and the rhodium complex **11**, probably due to the presence of sulfur[10] in the coordination sphere and the low solubility of this complex, did not show any catalytic activity at all, in comparison to the analogous phosphane complex **5.**

These results suggest the possibility of testing the activity and enantioselectivity of chiral complex **5** in the hydrogenation of prochiral substrates. Experiments to obtain pure enantiomers of ligand **2** are currently underway.

Conclusion

The preparation of a new chiral functionalised phosphorus-containing bis(pyrazol-1-yl)methane compound, p4m, has been carried out by modification of a previously described procedure. The coordination modes of this compound were studied towards the metal centres palladium, platinum, rhodium and iridium to produce *P*,*P*-six-membered metallacycles. Sulfidation of the previously described bppzm and the new p4m ligands produces the corresponding sulfidodiphosphanes. The compounds $p4mS_2$ and $bppzmS_2$ coordinate a palladium centre in an *N*,*N*-six-membered metallacycle and reaction of $p4mS_2$ with $[Rh(COD)(THF)_2]^+$ produces an *S*,*S*-dynamic coordination of the ligand.

Finally, complex $[Rh(COD)(p4m)]BF_4$ showed a moderate activity in the catalytic hydrogenation of simple olefins.

Experimental Section

All reactions were carried out using Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. ^1H,^{13}C and ^{31}P NMR spectra were obtained on a 300 Unity Varian spectrometer. Assignment of the signals was achieved by means of DEPT, NOE difference and two-dimensional NMR experiments, acquired using standard Varian-FT software. IR spectra were obtained in the region 500−4000 cm^{-1} using a Nicolet Magna FT-IR 550 spectrophotometer. $[MCl_2(PhCN)_2]$ (M = Pd, Pt) and bis(pyrazol-1-yl)-methane were prepared as reported previously.[11,12] $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$ were purchased from Aldrich and used as received

(5-Diphenylphosphanylpyrazol-1-yl)(diphenylphosphanyl)-(pyrazol-1-yl)methane (p4m) (2): A solution of bpzm (3 g, 20 mmol) in dry THF (150 mL) in a 250 mL Schlenk tube was cooled to 203 K. A 1.6 M solution of *n*BuLi (31.3 mL, 50 mmol) in hexane was added and the solution was allowed to reach room temperature slowly. PPh_2Cl (7.27 mL, 41 mmol) was added and the reaction mixture was stirred for 16 h. The suspension was filtered and the solvent removed under vacuum. The resulting red oil was washed with hexane and the residue extracted with CH_2Cl_2. The solvent was removed and the resulting orange oil was washed with Et_2O. A pale-brown solid was obtained and was recrystallized from CH_2Cl_2. Yield 90%. $C_{31}H_{26}N_4P_2$ (516.5): calcd. C 72.08, H 5.07, N 10.85%; found C 72.20, H 5.09, N 10.49. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 7.87 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, H3′), 7.81 (dd, $^2J_{H,P}$ = 6.0, $^4J_{H,P}$ = 3.0 Hz, 1 H, CH), 7.58 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H3), 7.37−7.05 (m, 20 H, Ph), 7.24 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H5′), 6.08 (dd, $^3J_{H,H}$ = 2.0, $^3J_{H,H}$ = 2.5 Hz, 1 H, H4′), 5.87 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 141.05 (d, $^1J_{C,P}$ = 12.0 Hz, C5), 140.83 (d, $^3J_{C,P}$ = 3.5 Hz, C3), 139.53 (d, $^3J_{C,P}$ = 1.5 Hz C5′), 135.20−128.10 (Ph), 128.94 (s, C3′), 114.54 (d, $^2J_{C,P}$ = 2.0 Hz, C4), 107.16 (s, C4′), 73.48 (dd, $^1J_{C,P}$ = 14.0, $^3J_{C,P}$ = 5.0 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = −30.99 (s, PPh_2), −60.94 (s, PPh_2) ppm.

[$PdCl_2$(p4m)] (3): An equimolar quantity of p4m (0.402 g, 0.78 mmol) was added to a CH_2Cl_2 (50 mL) solution of $[PdCl_2(PhCN)_2]$ (0.300 g, 0.78 mmol). The solution was stirred for 5 h at room temperature. The solvent was removed in vacuo and the resulting pale orange solid was washed with cold CH_2Cl_2 and dried in vacuo. Yield 85%. $C_{31}H_{26}Cl_2N_4P_2Pd$ (693.8): calcd. C 53.66, H 3.78, N 8.07; found C 53.89, H 3.79, N 8.01. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 7.67 (d, $^2J_{H,P}$ = 3.0 Hz, 1 H, CH), 7.65−7.26 (m, 20 H, Ph), 7.24 (br. s, 1 H, H5′), 7.13 (br. s, 1 H, H3′), 6.98 (br. s, 1 H, H3), 6.17 (br. s, 1 H, H4′), 5.92 (br. s, 1 H, H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 293 K): δ = 142.21 (s, C3′), 140.08 (d, $^1J_{C,P}$ = 13.1 Hz, C5), 136.00−128.00 (Ph), 130.80 (s, C5′), 129.80 (d, $^3J_{C,P}$ = 11.0 Hz, C3), 118.75 (d, $^2J_{C,P}$ = 7.4 Hz, C4), 107.17 (s, C4′), 68.75 (d, $^1J_{C,P}$ = 48.6 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, H_3PO_4 as reference): δ = −18.36 (s, PPh_2), 15.06 (s, PPh_2) ppm.

[$PtCl_2$(p4m)] (4): The synthetic procedure was the same as for complex 2, using $[PtCl_2(PhCN)_2]$ (0.300 g, 0.64 mmol) and p4m (0.330 g, 0.64 mmol), to give complex **4** as a white solid. Yield 90%. Crystals for X-ray diffraction were grown from a cooled saturated solution in CH_2Cl_2. $C_{31}H_{26}Cl_2N_4P_2Pt{\cdot}4CH_2Cl_2$ (1116.1): calcd. C 37.46, H 3.05, N 4.99; found C 37.50, H 3.06, N 5.02. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 7.82 (d, $^2J_{H,P}$ = 3.0 Hz, 1 H, CH), 7.59−7.26 (m, 20 H, Ph), 7.24 (br. s, 1 H, H5′), 7.06 (br. s, 1 H, H3′), 6.83 (br. s, 1 H, H3), 6.16 (br. s, 1 H, H4′), 5.80 (br. s, 1 H,

H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 293 K): δ = 141.02 (s, C3′), 139.50 (d, $^1J_{C,P}$ = 11.1 Hz, C5), 136.00−128.00 (Ph), 130.71 (s, C5′), 129.65 (d, $^3J_{C,P}$ = 11.0 Hz, C3), 118.48 (d, $^2J_{C,P}$ = 8.0 Hz, C4), 106.71 (s, C4′), 67.28 (d, $^1J_{C,P}$ = 54.3 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, H_3PO_4 as reference): δ = −34.94 (t of d, $^1J_{P,Pt}$ = 1797, $^2J_{P,P}$ = 16.0 Hz, PPh_2), −3.03 (t of d, $^1J_{P,Pt}$ = 1870, $^2J_{P,P}$ = 16.0 Hz, PPh_2) ppm.

[Rh(COD)(p4m)]BF_4 (5): An equimolar quantity of $AgBF_4$ (0.078 g, 0.40 mmol) was added to a THF (10 mL) solution of $[Rh(COD)Cl]_2$ (0.100 g, 0.20 mmol). The solution was stirred for 30 min at room temperature. The precipitated AgCl was filtered off and the filtrate was cooled to 203 K. A cooled solution of p4m (0.103 g, 0.40 mmol) in THF (10 mL) was then added slowly. The reaction was allowed to reach room temperature slowly over 3 h. The solvent was removed in vacuo and the resulting yellow solid was extracted with THF. Concentration of the solution afforded complex 5 as a bright yellow microcrystalline solid. Yield 75%. $C_{39}H_{38}BF_4N_4P_2Rh$ (814.4): calcd. C 57.51, H 4.67, N 6.88; found C 57.60, H 4.80, N 6.76. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 8.25 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H5′), 8.11 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H3′), 7.62−7.20 (m, 20 H, Ph), 7.59 (d, $^2J_{H,P}$ = 3.0 Hz, 1 H, CH), 7.43 (br. s, 1 H, H3), 6.82 (dd, $^3J_{H,H}$ = 2.0, $^3J_{H,H}$ = 2.0 Hz, 1 H, H4′), 5.99 (br. s, 1 H, H4), 4.17, 3.89 (m, 2 H, 2 H, CH, COD), 2.02, 2.33, 2.59, 2.99 (m, 2 H, 2 H, 2 H, 2 H, CH_2, COD) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 144.08 (s, C3′), 140.63 (d, $^3J_{C,P}$ = 10.0 Hz, C3), 138.00−128.00 (Ph), 133.53 (d, $^3J_{C,P}$ = 2.0 Hz, C5′), 132.11 (d, $^1J_{C,P}$ = 15.0 Hz, C5), 116.94 (d, $^2J_{C,P}$ = 6.0 Hz, C4), 112.03 (s, C4′), 86.15 (dd, $^2J_{C,P}$ = 13.0, $^1J_{C,Rh}$ = 14.0 Hz, CH, COD), 84.16 (dd, $^2J_{C,P}$ = 10.0, $^1J_{C,Rh}$ = 10.0 Hz, CH, COD), 72.60 (d, $^1J_{C,P}$ = 60.3 Hz, CH), 35.93 (s, CH_2, COD), 28.54 (s, CH_2, COD) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = 27.40 (dd, $^1J_{P,Rh}$ = 115.0, $^2J_{P,P}$ = 39.0 Hz, PPh_2), 21.10 (dd, $^1J_{P,Rh}$ = 115.0, $^2J_{P,P}$ = 39.0 Hz, PPh_2) ppm.

[Ir(COD)(p4m)]BF_4 (6): The synthetic procedure was the same as for complex **5**, using $[Ir(COD)Cl]_2$ (0.100 g, 0.15 mmol) and p4m (0.077 g, 0.30 mmol), to give complex **6** as a pale orange solid. Yield 55%. $C_{39}H_{38}BF_4IrN_4P_2$ (903.7): calcd. C 51.83, H 4.24, N 6.20; found C 51.95, H 4.30, N 6.26. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 8.43 (br. s, 1 H, H5′), 7.70 (d, $^2J_{H,P}$ = 3.0 Hz, 1 H, CH), 7.60−7.20 (m, 20 H, Ph), 7.40 (d, $^2J_{H,P}$ = 2.0 Hz, 1 H, H3), 7.31 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H3′), 6.45 (br. s, 1 H, H4′), 6.01 (br. s, 1 H, H4), 3.80, 3.42 (m, 2 H, 2 H, CH, COD), 1.42, 2.45 (m, 4 H, 4 H, CH_2, COD) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 142.43 (C3′), 139.59 (d, $^3J_{C,P}$ = 10.0 Hz, C3), 134.48 (d, $^1J_{C,P}$ = 13.0 Hz, C5), 133.10 (C5′), 128−134 (Ph), 117.00 (d, $^2J_{C,P}$ = 4.0 Hz, C4), 111.83 (C4′), 72.90 (d, $^1J_{C,P}$ = 39.2 Hz, CH), 69.12 (d, $^2J_{C,P}$ = 10.0 Hz, CH, COD), 69.09 (d, $^2J_{C,P}$ = 10.0 Hz, CH, COD), 67.45 (d, $^2J_{C,P}$ = 10.0 Hz, CH, COD), 67.43 (d, $^2J_{C,P}$ = 10.0 Hz, CH, COD), 36.22 (CH_2, COD), 36.18 (CH_2, COD), 30.42 (CH_2, COD) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = −44.26 (br. s, PPh_2), 9.36 (br. s, PPh_2) ppm.

Bis(5-diphenylphosphanylpyrazol-1-yl)methane Disulfide (bppzmS_2) (7): An excess of elemental sulfur S_8 (0.640 g, 2.50 mmol) was added to a CH_2Cl_2 (50 mL) solution of bppzm (1.000 g, 2.00 mmol). The reaction mixture was stirred for 48 h at room temperature. The solvent was removed in vacuo and the resultant solid was washed with CS_2 (100 mL). The residue was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O to afford compound 7 as a pale brown solid. Yield 95%. $C_{31}H_{26}N_4P_2S_2$ (580.6): calcd. C 64.13, H 4.48, N 9.65; found C 64.17, H 4.55, N 9.75. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 7.76−7.40 (m, 20 H, Ph), 7.28 (d, $^3J_{H,H}$ = 1.5 Hz, H3), 7.06 (br. s, 2 H, CH_2), 5.91 (d, $^3J_{H,H}$ = 1.5 Hz, H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 138.60 (d, $^3J_{C,P}$ = 14.0 Hz, C3), 138.72 (d, $^1J_{C,P}$ = 38.0 Hz, C5), 132.15−128.42 (Ph), 116.57 (d, $^2J_{C,P}$ = 15.0 Hz, C4), 63.74 (s, CH_2) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = 3.22 [s, $P(S)Ph_2$] ppm. IR (KBr): $\tilde{\nu}$ = 658 cm^{-1} (s) [ν(P=S)].

(5-Diphenylphosphanylpyrazol-1-yl)(diphenylphosphanyl)-(pyrazol-1-yl)methane Disulfide (p4mS_2) (8): The synthetic procedure was the same as for compound **7**, using p4m (1.000 g, 3.88 mmol) and sulfur (1.250 g, 4.85 mmol), to give compound **8** as a pale orange solid. Yield 90%. The crystals for X-ray diffraction were grown from CH_2Cl_2/hexane. $C_{31}H_{26}N_4P_2S_2$ (580.6): calcd. C 64.13, H 4.48, N 9.65; found C 64.02, H 4.62, N 9.45. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 9.35 (d, $^2J_{H,P}$ = 6.8 Hz, 1 H, CH), 8.20−7.15 (m, 20 H, Ph), 7.83 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H3′), 7.45 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H5′), 6.94 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, H3), 5.96 (dd, $^3J_{H,H}$ = 2.3, $^3J_{H,H}$ = 2.0 Hz, 1 H, H4′), 5.84 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 139.58 (d, $^1J_{C,P}$ = 14.0 Hz, C5), 139.59 (s, C5′), 139.37 (d, $^3J_{C,P}$ = 2.0 Hz, C3), 136.60−127.80 (Ph), 130.32 (s, C3′), 116.73 (dd, $^2J_{C,P}$ = 14.4, $^4J_{C,P}$ = 10.0 Hz, C4), 105.96 (d, $^4J_{C,P}$ = 9.0 Hz, C4′), 72.40 (d, $^1J_{C,P}$ = 65.0 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = 25.57 [s, $P(S)Ph_2$], 3.62 [s, $P(S)Ph_2$] ppm. IR (KBr): $\tilde{\nu}$ = 633 cm^{-1} (s) [ν(P=S)].

[$PdCl_2$(bppzmS_2)] (9): An equimolar quantity of bppzmS_2 (0.452 g, 0.78 mmol) was added to a CH_2Cl_2 (50 mL) solution of $[PdCl_2(PhCN)_2]$ (0.300 g, 0.78 mmol). The solution was stirred for 16 h at room temperature. The solvent was removed in vacuo and the residue was washed with Et_2O to give an orange solid. Yield 85%. The crystals for X-ray diffraction were grown from a cooled saturated solution in CH_2Cl_2. $C_{31}H_{26}Cl_2N_4P_2PdS_2{\cdot}3.5CH_2Cl_2$ (1055.2): calcd. C 46.45, H 3.81, N 6.47; found C 46.50, H 3.84, N 6.49. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 8.27 (br. s, H3), 7.70−7.54 (m, 20 H, Ph), 7.09 (br. s, 2 H, CH_2), 5.99 (m, H4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 293 K): δ = 143.62 (d, $^1J_{C,P}$ = 27.0 Hz, C5), 138.85 (d, $^3J_{C,P}$ = 14.0 Hz, C3), 133.35−128.69 (Ph), 117.35 (d, $^2J_{C,P}$ = 14.6 Hz, C4), 63.48 (s, CH_2) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = 4.80 [s, $P(S)Ph_2$] ppm. IR (KBr): $\tilde{\nu}$ = 660 cm^{-1} (s) [ν(P=S)].

[$PdCl_2$(p4mS_2)] (10): The synthetic procedure was the same as for compound **9**, using $[PdCl_2(PhCN)_2]$ (0.300 g, 0.78 mmol) and p4mS_2 (0.452 g, 0.78 mmol), to give compound **10** as an orange solid. Yield 90%. $C_{31}H_{26}Cl_2N_4P_2PdS_2$ (757.9): calcd. C 49.12, H 3.46, N 7.39; found C 49.22, H 3.50, N 7.43. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ = 9.61 (d, $^2J_{H,P}$ = 7.0 Hz, 1 H, CH), 8.35 (m, 1 H, H5′), 8.02 (m, 1 H, H3′), 7.83−7.49 (m, 20 H, Ph), 7.45 (m, 1 H, H3), 6.15 (m, 1 H, H4), 6.13 (m, 1 H, H4′) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, H_3PO_4 as reference): δ = 26.10 [s, $P(S)Ph_2$], 5.70 [s, $P(S)Ph_2$] ppm. IR (KBr): $\tilde{\nu}$ = 630 cm^{-1} (s) [ν(P=S)].

[Rh(COD)(p4mS_2)]BF_4 (11): An equimolar quantity of $AgBF_4$ (0.078 g, 0.40 mmol) was added to a THF (10 mL) solution of $[Rh(COD)Cl]_2$ (0.100 g, 0.20 mmol). The solution was stirred for 30 min at room temperature. The precipitated AgCl was filtered off and the filtrate was cooled to 203 K. A cooled solution of p4mS_2 (0.232 g, 0.40 mmol) in THF (10 mL) was then added slowly. The reaction was allowed to reach room temperature slowly over 3 h. The solvent was removed in vacuo and the resulting brown solid was extracted with THF. The solution was concentrated and cooled to give complex **11** as a brown microcrystalline solid. Yield 65%. $C_{39}H_{38}BF_4N_4P_2RhS_2$ (878.5): calcd. C 53.32, H 4.36, N 6.38; found

C 53.40, H 4.42, N 6.45. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 9.67 (d, $^2J_{H,P}$ = 7.0 Hz, 1 H, CH), 8.42 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H3), 8.20−7.10 (m, 20 H, Ph), 7.24 (d, $^3J_{H,H}$ = 2 Hz, 1 H, H3′), 6.72 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, H5′), 6.51 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, H4), 6.04 (dd, $^3J_{H,H}$ = 2.0, $^3J_{H,H}$ = 2.0 Hz, 1 H, H4′), 4.32−4.17 (m, 4 H, CH, COD), 2.75−2.54 (m, 8 H, CH_2, COD), 2.02−1.82 (m, 8 H, CH_2, COD) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ = 143.25 (d, $^3J_{C,P}$ = 13.0 Hz, C3), 141.19 (s, C3′), 134.00−128.00 (Ph), 134.10 (d, $^1J_{C,P}$ = 12.0 Hz, C5), 133.07 (s, C5′), 118.60 (d, $^2J_{C,P}$ = 13.0 Hz, C4), 107.01 (s, C4′), 79.46 (m, CH, COD), 77.01 (m, CH, COD), 69.00 (d, $^1J_{C,P}$ = 40.1 Hz, CH), 31.35 (m, CH_2, COD), 29.65 (m, CH_2, COD) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, H_3PO_4 as reference): δ = 20.64 [bs, P(S)Ph_2], 4.42 [s, P(S)Ph_2] ppm. IR (KBr): $\tilde{\nu}$ = 556 (s) [ν(P=S)].

X-ray Crystallographic Study: Crystals obtained for complex **4** decomposed quickly with the loss of CH_2Cl_2, even when the data collection was performed at low temperature. We attempted this study with several crystals but data collection could not be completed. Given the importance of this structure, it was solved despite the aforementioned problems. Intensity data for complexes **4**, **8** and **9** were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo-K_α radiation, λ = 0.71073 Å) using the ω/2θ scan technique. The final unit-cell parameters were determined from 25 well-centered reflections and refined by the least-squares method. The space group was determined from the systematic absences and this was vindicated by the success of the subsequent solutions and refinements. Two standard reflections were measured every 60 minutes as an orientation and intensity control; significant intensity decay was not observed for compounds **8** and **9**. However, compound **4** showed an intensity decay of 56% at the end of the process. The structures were solved by direct methods using SHELXS[13] and refined on F^2 by full-matrix least-squares (SHELXL-97).[14] The CH_2Cl_2 solvate molecule could be located in complexes **4** and **9**. All non-hydrogen atoms were refined with anisotropic thermal parameters in complexes **8** and **9**. The hydrogen atoms were included in their calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 5. CCDC-207627 (**4**), -207628 (**8**) and -207629 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Catalytic Activity: Hydrogenation reactions were carried out in a 100 mL stainless steel autoclave (Magnedrive Autoclave Engineers). The autoclave was evacuated for 2 h before a solution containing the catalyst and substrate was introduced by suction. Hydrogen was then introduced and the mixture was warmed to the reaction temperature. The pressure in the autoclave was monitored using a transducer. Samples were analysed by gas chromatography on a Hewlett Packard HP 6890 chromatograph equipped with an FID detector and 30 m × 0.032 mm HP-Innovax column.

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Table 5. Crystal data and structure refinement for **4**, **8** and **9**

	4	**8**	**9**
Formula	$C_{31}H_{26}Cl_2N_4P_2Pt.4CH_2Cl_2$	$C_{31}H_{26}N_4P_2S_2$	$2C_{31}H_{26}Cl_2N_4P_2PdS_2.7CH_2Cl_2$
Mol. wt.	1116.14	580.62	2110.32
T (K)	153(2)	293(2)	153(2)
Cryst syst	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.229(1)	13.697(1)	12.460(1)
b (Å)	15.986(1)	14.795(1)	14.134(1)
c (Å)	29.395(1)	14.913(1)	25.799(1)
α (deg)			86.19(1)
β (deg)	92.12(1)	102.76(2)	84.98(1)
γ (deg)			72.22(1)
V (Å^3)	4333.8(6)	2947.4(4)	4306.1(5)
Z	4	4	1
Dc (g cm^{-3})	1.711	1.308	1.628
μ (mm^{-1})	3.959	0.317	1.193
F(000)	2176	1208	2116
Cryst dimens. (mm)	0.1 × 0.4 × 0.4	0.3 × 0.3 × 0.2	0.2 × 0.3 × 0.3
θ range (deg)	1.39 to 25.11	2.05 to 28.01	2.00 to 28.00
hkl ranges	$-10 \le h \le 10$	$-18 \le h \le 17$	$-16 \le h \le 16$
	$0 \le k \le 18$	$0 \le k \le 19$	$-18 \le k \le 18$
	$0 \le l \le 35$	$0 \le l \le 19$	$0 \le l \le 32$
No. of rflns measd	7756	7676	21062
No. of indep rflns	7595	7083	20607
No. of odsd rflns	3205	4693	13666
Goodness-of-fit on F^2	1.101	0.991	1.034
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1671, wR_2 = 0.3927[a]	R_1 = 0.0497, wR_2 = 0.1221	R_1 = 0.0553, wR_2 = 0.1284
Largest diff. peak (e·Å^{-3})	2.600/−3.862	0.465/−0.513	1.127/−1.094

[a] $R_1 = \Sigma F_o - F_c/\Sigma F_o$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_0^2)^2\}]^{0.5}$.

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