Synthesis and characterisation of benzyl phosphino-thioether and -thiolato Pd(II) complexes and their applications in Suzuki coupling reactions

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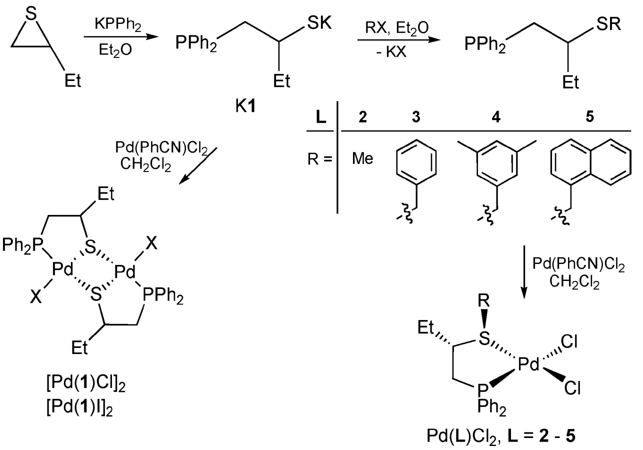
The synthesis of the benzyl phosphinothioether derivatives $Ph_2PCH_2CH(Et)SR$ and their corresponding palladium complexes are reported, where R = CH_2Ph (**3**), R = CH_2-3,5-Me-C_6H_3 (**4**) and R = 1-$CH_2C_{10}H_7$ (**5**). Crystallographic data obtained for the complexes Pd(**3**)Cl_2 and Pd(**4**)Cl_2 show intra- and inter-molecular π–π interactions between the aromatic rings on the P and S substituents, and NOE experiments for Pd(**4**)Cl_2 show that these interactions persist in solution. The performance of the phosphinothioether palladium complexes in aryl–aryl cross-coupling reactions is compared with that of the corresponding complex of the parent phosphinothiolato ligand $Ph_2PCH_2CH(Et)S^-$ (**1**). High turnover numbers up to 2000000 are reported for the coupling of bromobenzene, using the palladium dimer [Pd(**1**)I]$_2$ as the catalyst precursor. Kinetic studies show a linear dependence of the reaction on catalyst loading. The effect of other variables on the cross-coupling reaction, such as temperature, solvent and base, is also reported.

Introduction

Complexes of chelating diphosphine ligands continue to find wide applications as auxiliaries in a variety of organic transformations. In particular, diphosphines have been shown to be effective in catalytic reactions such as C–C and C–N coupling reactions, allylic substitutions, hydrogenations, hydroformylations and carbonylations.[1] More recently, there has been great interest in the development of non-symmetrically substituted bidentate systems where only one of the donor atoms is phosphorus. Such chelating ligands break the electronic and steric symmetry of the more classical C_2-symmetric P,P ligands. Electronic differences between the two donors may control the activity and selectivity of a reaction *via* operation of their differing *trans* influence. Further, steric differences between the two co-ordination sites of the chelate can control the catalyst regioselectivity by accommodation of the more bulky side of the participating ligand adjacent to the least hindered side of the chelate. Accordingly, mixed P,O-[2] and P,N-donor[3] ligands have been extensively applied in catalysis and there is a growing interest with respect to potential applications of P,S ligands.[4] Sulfur containing compounds, often regarded as catalyst poisons,[5] have become versatile auxiliaries in transition metal chemistry. Thioether-phosphite and phosphine ligands have found applications in a number of catalytic reactions, such as allylic alkylations,[6] hydroformylations,[7] hydrogenations[8] and aminations. Catalytic applications of phosphinothiolate ligands however, have been studied to a much lesser extend, with reports so far mainly focusing on olefin and methanol carbonylation reactions.[4i,9] Indeed, there is sparse information on the performance of P,S catalytic systems on C–C and C-heteroatom cross-coupling reactions.[4f] Palladium-catalysed coupling reactions, such as the Heck and Suzuki reactions, provide highly versatile and mild methods for the creation of new carbon–carbon bonds that tolerate many functional groups.[10]

Our work in this area has focused on the study of P,S systems and their catalytic applications. Previously, we have reported the synthesis of the P,S ligands **1** and **2** (Scheme 1) and their corresponding group 10 metal complexes.[11] Here, we report the synthesis of benzyl phosphinothioether derivatives of **1** and a new catalytic Suzuki system based on ligand **1** derivatives which display exceptional reactivity and stability that are simple to use.



Scheme 1 Synthesis of P,S ligands and their corresponding palladium complexes.

Results and discussion

Synthesis and properties of the Pd(L)Cl_2 complexes, L = 3–5

The benzyl phosphinothioether ligands **3–5**, shown in Scheme 1, were prepared in a one pot reaction from 2-ethylthiirane. Addition

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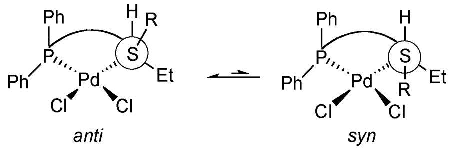
of potassium diphenylphosphide to an ether solution of the thiirane, followed by the appropriate alkyl halide afforded in quantitative yields the corresponding P,S ligand. According to this protocol, phosphinothioether ligands with methyl, benzyl, 3,5-dimethylbenzyl and 1-methylnaphthalene sulfur substituents were prepared. The corresponding Pd(L)Cl$_2$ complexes were obtained from the simple addition of the P,S ligand to a dichloromethane solution of Pd(PhCN)$_2$Cl$_2$. All complexes were air and moisture stable, and after their formation all manipulations were carried out under aerobic conditions. The free P,S ligands revealed a singlet close to δ_P −20 ppm. However, upon coordination to the metal a large change in the chemical shift was observed, with the Pd(L)Cl$_2$ complexes resonating within the range of δ_P 50–54 ppm. The main feature in the ^{1}H NMR spectra of the benzylic complexes was the large change in the δ_H of the diastereotopic benzylic protons, from the free to the coordinated ligand. For example, the benzylic protons of ligand **3** resonate at 3.53 and 3.58 ppm with $J = 13.3$ Hz, whereas upon coordination, a downfield shift was observed to 3.95 and 4.90 ppm, respectively. It is worth noting that coordination of the phosphinothioether ligand to the metal centre renders the sulfur donor a stereogenic centre thus, in principle, it is possible to form both *syn* and *anti* diastereomers (eqn (1)). However, due to unfavourable steric interactions between substituents on the sulfur and the *α* substituted carbon, the *anti* diastereomers were expected to be more stable. Indeed, the ^{1}H and ^{31}P NMR spectra of the Pd(L)Cl$_2$ complexes, L = **3**–**5**, showed only one set of resonances that did not change upon cooling.



(1)

Further evidence supporting an *anti* conformation adopted in solution was observed in the 2D-NOESY NMR spectrum of the Pd(**4**)Cl$_2$ complex, where interactions between the substituents of the xylene group (methyl and *ortho* protons) and the aromatic protons of the PPh$_2$ unit were observed. In addition, the absence of any interactions between the pendant ethyl group and the phenyl rings on the phosphorus confirmed that the ethyl substituent remains in a pseudoequatorial position in solution. For the related Pd(**3**)Cl$_2$ and Pd(**5**)Cl$_2$ complexes, NOESY experiments did not allow us to propose the spatial arrangement of the sulfur substituents, although they did confirm the pseudoequatorial conformation of the ethyl substituent.

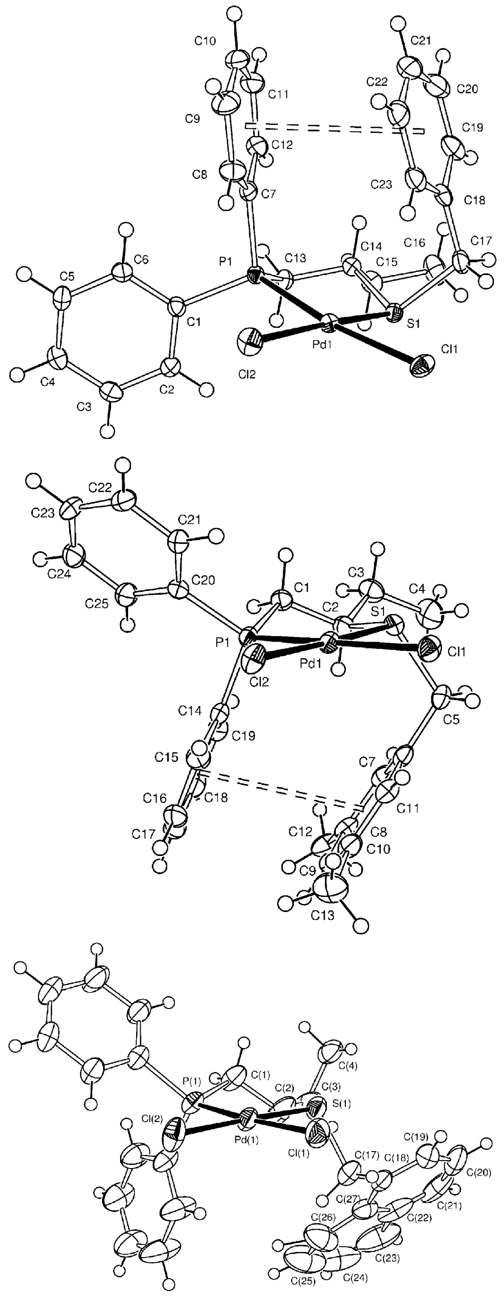


Fig. 1 Structural representations of complexes Pd(**3**)Cl$_2$, Pd(**4**)Cl$_2$ and Pd(**5**)Cl$_2$.

Crystal structures of the Pd(L)Cl$_2$ complexes, L = 3–5

In agreement with the NMR data, the crystal structures of the Pd(**3**)Cl$_2$, Pd(**4**)Cl$_2$ and Pd(**5**)Cl$_2$ complexes show only the sterically preferred *anti* enantiomers, Fig. 1. The five-membered chelate in these benzylic complexes adopts a λ conformation for the C$_R$/S$_S$ isomer (shown in Fig. 1 for Pd(**3**)Cl$_2$) and a δ conformation for the C$_S$/S$_R$ isomer (shown in Fig. 1 for Pd(**4**)Cl$_2$ and Pd(**5**)Cl$_2$), thus placing the ethyl substituent in the favourable pseudoequatorial position. The sulfur benzylic substituent of the Pd(**3**)Cl$_2$ complex occupies a pseudoaxial position, as suggested by the dihedral angle between the C(14)–S–C(17) and H(14)–C(14)–S planes at 26.53°. The corresponding dihedral angle for Pd(**4**)Cl$_2$ is 26.56°.† Interestingly, in all cases the sulfur pendant group is on the same side of the plane as the axial P-phenyl. This preference for axial disposition of the sulfur substituent has been observed for the majority of palladium thioether complexes and is attributed to the unfavourable interaction between the sulfur lone pair and the metal centre.[8b,6b] Selected bond lengths and angles for the palladium complexes are given in Table 1. In the case of the Pd(**5**)Cl$_2$ complex the crystal structure has disorder involving the P,S ligand, but it only concerns the orientation of the

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† Due to the distortion in the structure of Pd(**5**)Cl$_2$ the dihedral angle could not be determined.

Table 1 Selected bond lengths (Å) and angles (°) in the Pd(**L**)Cl$_2$ complexes

	Pd(**3**)Cl$_2$	Pd(**4**)Cl$_2$	Pd(**5**)Cl$_2$
P(1)–Pd(1)	2.2141(6)	2.2185(8)	2.2187(7)
S(1)–Pd(1)	2.2916(6)	2.2825(8)	2.265(2)
Cl(1)–Pd(1)	2.4082(6)	2.3991(7)	2.3660(7)
Cl(2)–Pd(1)	2.3163(6)	2.3304(7)	2.2986(7)
P(1)–Pd(1)–S(1)	87.36(2)	86.95(3)	90.14(6)
P(1)–Pd(1)–Cl(2)	89.86(2)	90.99(3)	91.45(2)
S(1)–Pd(1)–Cl(2)	174.01(2)	177.47(3)	177.85(6)
P(1)–Pd(1)–Cl(1)	172.61(2)	174.88(3)	174.78(3)
S(1)–Pd(1)–Cl(1)	90.40(2)	88.00(3)	85.31(6)
Cl(2)–Pd(1)–Cl(1)	93.00(2)	94.08(3)	93.16(3)

methylnaphthyl and ethyl groups and does not affect the primary coordination sphere.

Small tetrahedral distortions are observed for the Pd(**4**)Cl$_2$ and Pd(**5**)Cl$_2$, however a more noticeable departure from the square planar geometry is observed for the Pd(**3**)Cl$_2$ complex, with a dihedral angle of 8.62° between the PdPS and the PdCl$_2$ planes. The molecular structures of Pd(**3**)Cl$_2$ and Pd(**4**)Cl$_2$ in Fig. 2 also reveal a face-to-face π–π stacking intramolecular interaction between the benzylic groups and the axial phosphorus benzene ring. In contrast, the methylnaphthalene group of the Pd(**5**)Cl$_2$ complex points away from the coordination plane. The centroid–centroid distances for Pd(**3**)Cl$_2$ and Pd(**4**)Cl$_2$ are 3.831 Å and 3.727 Å, respectively; with the closest contact distances at 3.483 Å for complex Pd(**3**)Cl$_2$ [carbons C(9) and C(22)] and 3.453 Å for Pd(**4**)Cl$_2$ [carbons C(9) and C(17)]. The dihedral angle between the two mean aromatic planes is 16.64° for Pd(**3**)Cl$_2$ and 12.65° for Pd(**4**)Cl$_2$.

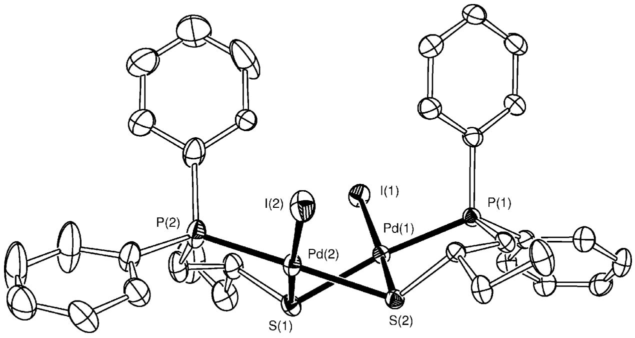


Fig. 2 ORTEP-3 representation of complex [Pd(**1**)I]$_2$. The hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°) for [Pd(**1**)I]$_2$: I(1)–Pd(1) 2.6349(4), I(2)–Pd(2) 2.6179(4), P(1)–Pd(1) 2.2436(9), P(2)–Pd(2) 2.2570(10), Pd(1)–S(2) 2.2947(9), Pd(1)–S(1) 2.3719(9), Pd(1)–Pd(2) 3.0273(4), Pd(2)–S(1) 2.3016(10), Pd(2)–S(2) 2.3679(9), P(1)–Pd(1)–S(2) 86.76(3), P(1)–Pd(1)–S(1) 166.71(3), S(2)–Pd(1)–S(1) 79.98(3), P(1)–Pd(1)–I(1) 94.20(2), S(1)–Pd(1)–I(1) 99.04(2), P(2)–Pd(2)–S(1) 86.28(4), S(1)–Pd(2)–S(2) 79.92(3), P(2)–Pd(2)–I(2) 96.05(3), S(2)–Pd(2)–I(2) 97.23(2).

Synthesis and properties of the [Pd(1)I]$_2$ dimer

The potassium salt of ligand **1** and corresponding palladium dimer, [Pd(**1**)Cl]$_2$, were prepared as previously described.[11] Thiolato ligands are well known in forming sulfur-bridged species, such as the [Pd(**1**)Cl]$_2$ dimer in Scheme 1, in the absence of other coordinating ligands.[7,8] The iodide derivative [Pd(**1**)I]$_2$ was prepared in order to compare their activity in various catalytic reactions. [Pd(L^1)I]$_2$ was obtained from the reaction of the chloride dimer with a ten-fold excess of potassium iodide. In converting [Pd(**1**)Cl]$_2$ to [Pd(**1**)I]$_2$ a small downfield shift from δ_P 40.9 to 43.5 ppm was observed in the NMR spectrum of the iodide dimer. The *rac* and *meso* diastereomers of the [Pd(**1**)I]$_2$ were indistinguishable by NMR spectroscopy, probably due to the long distance between the two stereogenic carbon centres.

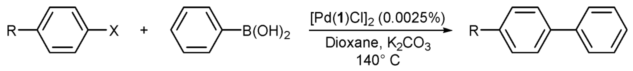
Crystal structure of the [Pd(1)I]$_2$ dimer

Crystallographic data obtained for the *rac* isomer of [Pd(**1**)I]$_2$ confirmed its dimeric structure, as shown in Fig. 2. The geometry around the two metal atoms is distorted square planar and the molecule is bent about the S–S axis adopting the usual hinged core structure and *syn* orientation of the sulfur substituents observed for palladium P,S dimeric complexes.[8–11] This ligand arrangement around the metal centres leaves the *exo* face of the two coordination planes, where the sulfur lone pairs reside, relatively unhindered. Both *syn* and *anti* orientations of the sulfur substituents have been observed in bridging thiolate complexes; an *anti* orientation usually results in a planar M$_2$S$_2$ core.[12] The dihedral angle defined by the two MS$_2$ planes is 115.57° for complex **2**, close to the value reported for the chloride analogue at 116.02°. The hinged structure of the palladium dimer **2** brings the two metal atoms in close proximity [3.0273(4) Å] but no bonding interactions are observed. The S–Pd–S angles, 79.92(3)° and 79.98(3)°, are at the lower end of the literature range of 80–88°.[4i,7]

Suzuki cross-coupling reactions

As part of a study regarding catalytic applications of the 1,2-butane-based P,S ligands, their palladium complexes were tested in the Suzuki coupling of aromatic substrates. There are sparse reports in the literature where phosphinothioether ligands are used in Suzuki coupling reactions and, to our knowledge, no reports regarding phosphinothiolate systems. A phosphinothioether ligand with a binaphthyl backbone[13] reported by Zhang and Shi gave very low yields of the cross-coupling products. More promising results though were obtained by Gibson *et al.* with a ferrocenyl based P,S system[14] at 1 mol% catalyst loadings. The performance of the palladium complexes [Pd(**1**)Cl]$_2$, [Pd(**1**)I]$_2$, Pd(**2**)Cl$_2$ and Pd(**4**)Cl$_2$ was evaluated in the Suzuki cross-coupling reaction and results are listed in Table 2. In a typical reaction, 5 mmol of arylhalide were reacted with 7 mmol of phenylboronic acid and K$_2$CO$_3$ in dioxane at 140 °C in a sealed pressure tube. Representative catalysts' loadings were 0.0025 mol%, although the P,S complexes were active at loadings as low as 10^{-5} mol%. Due to the air and water stability of the P,S systems, catalytic reactions were carried out under aerobic conditions, using undistilled reagents and solvents. At the end of the reaction no catalyst decomposition was visible and if an additional load of reagents was added catalytic activity was maintained. From the substrates tested, best results were obtained with bromobenzene, where high turnover numbers (ton) up to two million were obtained (run 1, Table 2). High ton were also obtained for 4-bromoacetophenone, although with a lower catalyst activity than that of bromobenzene (run 4).

Table 2 Suzuki couplings of haloarenes with phenylboronic acid[a]



Run	R, X	Complex (mol%)	Time/h	Ton (10^3)	Yield[b] (%)
1	H, Br	[Pd(**1**)I]$_2$ (0.00005)	1	2000	>99
2	MeCO, Br	[Pd(**1**)I]$_2$ (0.001)	6	91	91
3	MeCO, Br	[Pd(**1**)I]$_2$ (0.0005)	6	116	58
4	MeCO, Br	[Pd(**1**)I]$_2$ (0.00005)	6	860	43
5	Me, Br	[Pd(**1**)I]$_2$ (0.0025)	3	40	>99
6	MeCO, Cl	[Pd(**1**)I]$_2$ (1)	24	0.01	10[c]
7	MeCO, Cl	[Pd(**1**)I]$_2$ (1)	24	0.1	>99[b,d]
8	MeCO, Cl	[Pd(**1**)I]$_2$ (0.5)	24	0.2	>99[b,d]
9	H, Cl	[Pd(**1**)I]$_2$ (1)	24	0.003	3[d]
10	Me, Br	[Pd(**1**)Cl]$_2$ (0.0025)	6	33.6	84
11	Me, Br	Pd(**2**)Cl$_2$ (0.0025)	6	36.4	91
12	Me, Br	Pd(**4**)Cl$_2$ (0.0025)	6	40.0	>99
13	Me, Br	Pd(**4**)Cl$_2$ (0.0025)[e]	6	40.0	>99
14	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[f]	3	26.8	67
15	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[g]	3	34.8	87
16	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[h]	3	38.4	96
17	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[i]	3	39.2	98
18	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[j]	6	38.0	95
19	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[k]	6	26.8	67
20	Me, Br	[Pd(**1**)I]$_2$ (0.0025)[l]	6	6.8	17

[a] Reaction conditions: unless otherwise noted, ArX (5 mmol), PhB(OH)$_2$ (7 mmol), K$_2$CO$_3$ (7 mmol), dioxane (5 mL) at 140 °C. [b] Determined by GC-MS. [c] Small amounts (<5 mol%) of the homocoupling product Ph–Ph were also observed. [d] NBu$_4$Br (5 mmol) added. [e] KI (5 mmol) added. [f] $T = 110$ °C. [g] $T = 120$ °C. [h] $T = 130$ °C. [i] $T = 150$ °C. [j] Solvent = di(ethylene glycol)diethyl ether. [k] Solvent = DME. [l] Solvent = DMA.

With the weakly deactivated substrate bromotoluene low catalysts' loadings were also used, although the activity was *ca.* twenty times lower than that observed for bromoacetophenone. Best results were obtained at 0.0025 mol% catalyst loadings (run 5). Although excellent results were obtained in the Suzuki coupling with aromatic bromides, the reaction of chloroacetophenone with phenylboronic acid at 1 mol% catalyst loading resulted in only a 10% yield after 24 h (run 6). However, with the addition of one equivalent of tetrabutylammonium bromide (TBAB) in the reaction quantitative results were obtained after a day (runs 7 and 8) at 0.5 mol% catalyst loadings. Unfortunately, even with the addition of TBAB in the Suzuki coupling of chlorobenzene, negligible activity was observed (run 9). Low yields in the coupling of arylchlorides have also been observed with a related phosphine adduct of a thioether palladacycle. In this case, a significantly lower activity of the P,S catalyst was observed when compared to analogous P,N and P,P systems.[15]

In order to establish the relative reactivities and identify any differences in the catalytic behaviour of the thiolato and thioether palladium complexes in the Suzuki reaction, the P,S complexes were tested in the catalytic coupling of 4-bromotoluene and phenylboronic (Table 2, runs 10–20). In these investigations 4-bromotoluene was used as a substrate, since its cross-coupling reaction proceeded at convenient to follow rates. The effect of temperature, solvents and bases on the reaction was also studied.

Runs 5 and 10–13 show the catalytic results obtained with the [Pd(**1**)I]$_2$, [Pd(**1**)Cl]$_2$, Pd(**2**)Cl$_2$ and Pd(**4**)Cl$_2$ complexes. According to these results, the iodide dimer formed the most active catalyst, with the reaction completed within 3 h. The corresponding chloride dimer however, after twice the reaction time reached only an 84% yield. The methyl and xylyl phosphinothioether complexes, Pd(**2**)Cl$_2$ and Pd(**4**)Cl$_2$, reached a corresponding yield of 91 and 99+% after 6 h. The relative activity of these complexes is more clearly seen when comparing their turnover frequencies (tof) after 1 h. For the [Pd(**1**)Cl]$_2$ a tof of 15600 h^{-1} was obtained, compared to 34800 h^{-1} for the [Pd(**1**)I]$_2$ and 24400 h^{-1} for complexes Pd(**2**)Cl$_2$ and Pd(**4**)Cl$_2$. From these results a large dependence of the reaction rate on the halide ligand in the [Pd(**1**)Cl]$_2$ and [Pd(**1**)I]$_2$ dimers can be seen. However, the same effect was not observed in the case of the monomeric phosphinothioether complexes. Addition of an iodide source to the reaction with precatalyst Pd(**4**)Cl$_2$ had a negligible effect on the reaction profile, as shown by comparing runs 12 and 13 in Table 2 and their corresponding tof after an hour at 24400 and 26000. The relatively large difference in the activity of palladium dimers is not clearly understood at present.

The role of temperature on the catalyst activity was examined using the [Pd(**1**)I]$_2$ dimer as the precatalyst. Runs 5 and 14–17 show the catalyst performance within the temperature range of 110 to 150°. A marked difference in activity can be observed for the reaction at 110 °C and at temperatures above that. After 1 h, the run at 110 °C has a turnover frequency of 5200 h^{-1}, compared to a nearly five-fold increase in rate at 120 °C with a tof of 24400 h^{-1}. The corresponding tof at 130°, 140° and 150 °C are 25600, 34800 and 27600 h^{-1}, with best results obtained at 140 °C. From our experience with these P,S systems in C–C coupling reactions, a sharp increase in catalyst activity is observed with increasing temperature; at temperatures below 100 °C they are usually catalytically inert. This behaviour is in agreement with other related anionic chelating systems such as phosphino- and amino-based palladacycles.[16]

A comparison between run 5 and runs 18–20 shows that reactions in dioxane gave the best results, within the range of solvents used. In general, reactions in solvents of medium polarity, such as dioxane and di(ethylene glycol)diethyl ether proceeded at significantly higher rates than in polar solvents, such as DMA (run 20). This behaviour may be attributed to the coordinating properties of polar solvents that may block the catalyst's active sites. Different bases were also tested. In preliminary experiments organic bases, such as di-and tri-ethylamine, gave inferior results to inorganic bases, such as carbonate salts. Caesium carbonate gave comparable results with that of potassium carbonate. This is in accordance with previous observations in Suzuki reactions where inorganic bases led to higher yields than organic bases, such as triethylamine,[17] and has been attributed to the formation of base-borane adducts with the organic bases.

Having established the optimum reaction conditions in terms of catalyst, temperature, solvent and base we then proceeded to investigate the effect of catalyst loading on the rate of the Suzuki coupling. In Fig. 3 a plot of the tof at 50% conversion *versus* the catalyst's concentration shows that first order kinetics are followed within the 0.01–0.025 mM range of [Pd] using the [Pd(**1**)I]$_2$ dimer as the catalyst precursor, which suggests a homogeneous catalytic system in operation.

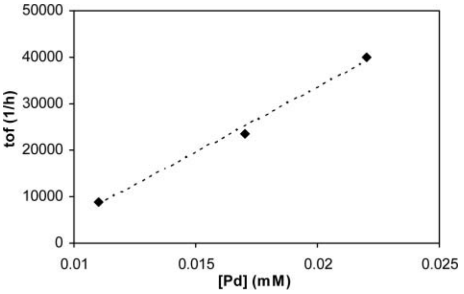
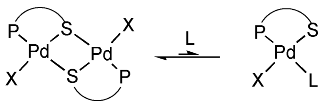


Fig. 3 Reaction rate (at 50% conversion) as a function of catalyst concentration. Conditions: 4-bromotoluene (1.0 M), PhB(OH)$_2$ (1.4 M), K$_2$CO$_3$ (1.4 M), dioxane, using [Pd(**1**)I]$_2$ at 140 °C.

The above results are in contrast with reports on the related Heck coupling reaction with dimeric catalysts, where an inverse rate dependence on the catalyst concentration is usually observed. This type of rate dependence has been attributed to either a large dimerisation constant between the dimer–monomer equilibria of the catalytic species (eqn (2)) or the existence of soluble colloidal palladium species.[18]



(2)

We also have observed an inverse rate dependence in the Heck coupling of iodobenzene with styrene using the palladium dimer [Pd(**1**)Cl]$_2$ as the precatalyst.[19] These results were further supported by NMR experiments, where the only process observed by ^{31}P NMR during catalysis was the clean conversion of [Pd(**1**)Cl]$_2$ to [Pd(**1**)I]$_2$ *via* a mixed chloride–iodide intermediate. In this case we concluded that the palladium dimers were the resting state of the catalyst, present at high concentrations during the catalytic reaction relative to the active catalytic species (colloidal or otherwise). However, attempts to identify the phosphorus containing species during a Suzuki reaction by ^{31}P NMR were unsuccessful.

Conclusions

The results presented show that the P,S complexes in Scheme 1 form highly active Suzuki catalysts for the coupling of aryl bromide substrates,[20] although significantly higher catalysts' loadings are required for the coupling of aryl chlorides.[21] Desirable features of the 1,2-butane-based P,S complexes include their ease of synthesis, facile modification, air and water stability. In general, short reaction times were observed with the Suzuki reactions, and in the case of arylbromides the majority of the reactions reached completion within the first hour. From the P,S precatalysts tested the phosphinothiolate dimer [Pd(**1**)I]$_2$ was the most active, although the phosphinothioether based systems [Pd(**2**)Cl$_2$ and Pd(**4**)Cl$_2$] did reach completion after longer reaction times. Given the shorter synthetic path leading to the parent ligand **K1** there is a clear advantage in using phosphinothiolate catalysts over the corresponding phosphinothioether ones in this type of transformations.

Experimental

General remarks

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All palladium complexes after their formation were treated under aerobic conditions. Solvents of analytical grade and deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N$_2$ immediately prior to use following standard literature methods.[22] Literature methods were employed for the synthesis of 2-ethylthiirane,[23] [Pd(L^1)Cl]$_2$ and Pd(L^{1}Me)Cl$_2$.[11] All other reagents were used as received.

NMR spectra were obtained on Bruker Avance AMX 400, 500 or Jeol Eclipse 300 spectrometers and referenced to external TMS. GC-MS results were obtained from an Agilent GC-MS detector equipped with an HP-5SM capillary column (30 m). Mass spectra and high-resolution mass spectra were obtained in electrospray (ES) mode unless otherwise reported, on a Waters Q-Tof micromass spectrometer.

Ligand 3. 2-Ethylthiirane (0.44 g, 5.0 mmol) was dissolved in dry diethyl ether (20 mL) and added drop-wise to a tetrahydrofuran solution of potassium diphenylphosphide (10.0 mL, 0.5M) at 0 °C whilst stirring under argon. After 1 h, benzylbromide (0.60 mL, 5.0 mmol) was slowly added to the solution and the reaction was left stirring overnight. Subsequently the precipitated KBr was filtered over Celite and a clear colourless solution was obtained. Evaporation of the solvent afforded **3** as an opaque oil, which was suitable to use without further purification. Yield 1.56 g (85.4%). δ_P (CDCl$_3$, 121 MHz) −20.3; δ_H (CDCl$_3$, 300 MHz 0.83 (3H, t, $^3J_{HH} = 7.3$, CH$_2$CH_3), 1.57 (1H, m, CH_2CH$_3$), 1.72 (1H, m, CH_2CH$_3$), 2.23 (1H, m, $^2J_{HH} = 13.5$, $^3J_{HH} = 8.5$, PCH_2), 2.33 (1H, m, $^2J_{HH} = 13.5$, $^3J_{HH} = 6.5$, PCH_2), 2.43 (1H, m, CHEt), 3.53 (1H, d, $^2J_{HH} = 13.3$, CH_2Ph), 3.58 (1H, d, $^2J_{HH} = 13.3$, CH_2Ph), 7.05–7.35 (15H, m, Ar); δ_C (CDCl$_3$, 100 MHz) 9.9 (1C, s, CH$_3$), 24.8 (1C, s, CH$_2$), 27.1 (1C, d, $^1J_{CP} = 8.1$ Hz, CH$_2$), 34.3 (1C, d, $^2J_{CP} = 15.1$, CH), 43.1 (1C, d, $^4J_{CP} = 15.1$, CH$_2$), 126.0 (1C, s), 127.5–128.1 (6C, m), 132.0 (2C, d, $J_{CP} = 16.0$), 132.2 (2C, d, $J_{CP} = 16.2$), 137.7 (2C, m), 137.8 (1C, m); *m*/*z* (ES) 365.1499 (MH$^+$. C$_{23}$H$_{25}$PS requires 365.1493), 293 (100%).

Ligands **4** and **5** were prepared according to the same procedure followed for **3**.

Data for 4. 3,5-Dimethylbenzylbromide (1.0 g, 5.0 mmol) was used. Yield 1.41 g (72%). δ_P (CH_2Cl_2–D_2O insert, 121 MHz) −20.8; δ_H ($CDCl_3$, 400 MHz) 0.84 (3H, t, $^3J_{HH} = 7.3$, $\mathrm{CH_2C}H_3$), 1.59 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.71 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.16 (6H, s, $\mathrm{C}H_3$), 2.24 (1H, m, $^2J_{HH} = 13.6$, $^3J_{HH} = 8.5$, $\mathrm{PC}H_2$), 2.33 (1H, m, $^2J_{HH} = 13.6$, $^3J_{HH} = 6.2$, $\mathrm{PC}H_2$), 2.47 (1H, m, $\mathrm{C}H\mathrm{Et}$), 3.47 (1H, d, $^2J_{HH} = 13.0$, $\mathrm{C}H_2\mathrm{Xyl}$), 3.52 (1H, d, $^2J_{HH} = 13.0$, $\mathrm{C}H_2\mathrm{Xyl}$), 6.73 (1H, s, Xyl), 7.2–7.7 (12H, m, Ar); δ_C ($CDCl_3$, 75 MHz) 12.3 (1C, s, $C\mathrm{H_3}$), 21.4 (2C, s, $C\mathrm{H_3}$), 26.2 (1C, d, $^1J_{CP} = 16.2$ Hz, $C\mathrm{H_2}$), 29.8 (1C, s, $C\mathrm{H_2}$), 37.5 (1C, d, $^2J_{CP} = 34.0$, $C\mathrm{H}$), 41.4 (1C, br, $C\mathrm{H_2}$), 128.1 (2C, s), 128.9 (2C, d, $J_{CP} = 16.9$), 129.1 (2C, d, $J_{CP} = 15.4$), 130.6 (2C, s), 132.2 (2C, m), 133.2 (2C, d, $J_{CP} = 13.8$), 138.7 (2C, s); *m/z* (ES) 393.1793 (MH^+. $C_{25}H_{30}PS$ requires 393.1806), 287 (65%).

Data for 5. 1-Chloromethylnapthalene (0.38 mL, 2.5 mmol) was used. Yield 0.65 g (63%). δ_P (CH_2Cl_2–D_2O insert, 121 MHz) −20.5; δ_H ($CDCl_3$, 400 MHz) 0.81 (3H, t, $^3J_{HH} = 7.3$, $\mathrm{CH_2C}H_3$), 1.62 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.75 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.28 (1H, m, $^2J_{HH} = 13.8$, $^3J_{HH} = 8.5$, $\mathrm{PC}H_2$), 2.38 (1H, m, $^2J_{HH} = 13.8$, $^3J_{HH} = 6.3$, $\mathrm{PC}H_2$), 2.51 (1H, m, $\mathrm{C}H\mathrm{Et}$), 3.95 (1H, d, $^2J_{HH} = 13.0$, $\mathrm{C}H_2\mathrm{Ph}$), 4.05 (1H, d, $^2J_{HH} = 13.0$, $\mathrm{C}H_2\mathrm{Ph}$), 7.05 (1H, d, $^3J_{HH} = 8.1$), 7.17 (1H, d, $^3J_{HH} = 8.3$), 7.2–7.5 (12H, m, Ar), 7.62 (1H, d, $^3J_{HH} = 8.3$), 7.74 (1H, m), 8.04 (1H, d, $^3J_{HH} = 8.4$); δ_C ($CDCl_3$, 100 MHz) 9.7 (1C, s, $C\mathrm{H_3}$), 27.0 (1C, d, $^1J_{CP} = 9.1$, $C\mathrm{H_2}$), 33.5 (1C, s, $C\mathrm{H_2}$), 34.3 (1C, d, $^2J_{CP} = 10.1$, $C\mathrm{H}$), 43.8 (1C, d, $^4J = 15.1$, $C\mathrm{H_2}$), 123.2 (1C, s), 124.1 (1C, s), 124.7 (1C, s), 125.0 (1C, s), 126.8 (1C, s), 127.2–127.7 (6C, m), 130.2 (1C, d, $J_{CP} = 9.2$), 130.4 (1C, s), 130.8 (1C, m), 131.7 (2C, d, $J_{CP} = 13.3$), 131.9 (2C, d, $J_{CP} = 10.6$), 132.9 (1C, d, $J_{CP} = 11.7$), 137.4 (1C, d, $J_{CP} = 13.8$), 137.5 (1C, d, $J_{CP} = 13.9$); *m/z* (ES) 415.1647 (MH^+. $C_{27}H_{28}PS$ requires 415.1649).

[Pd(1)I]$_2$. To a 20 mL ethanol solution of [Pd(**1**)Cl]$_2$ (0.42 g, 0.5 mmol) a methanol solution (1M) of potassium iodide (0.83 g, 5.0 mmol) was added and stirred overnight. As the reaction progressed the colour of the solution changed from yellow to orange and a precipitate was formed. Evaporation of the solvents left an orange solid, which was subsequently extracted with dichloromethane (2 × 10 mL) and filtered. The filtrate was evaporated to dryness to afford the iodide dimer as a red solid. Crystals of the complex were obtained after slow diffusion of ether to a dichloromethane solution of [Pd(**1**)I]$_2$. Yield 0.42 g (83%). Found: C, 37.54; H, 3.56. $C_{32}H_{36}I_2P_2Pd_2S_2$ requires C, 37.93; H, 3.58%. δ_P ($CDCl_3$, 300 MHz) 43.5; δ_H ($CDCl_3$, 400MHz) 0.97 (3H, t, $^3J_{HH} = 7.4$, $\mathrm{CH_2C}H_3$), 1.69 (1H, m, $^2J_{HH} \cong {}^3J_{HH} = 7.5$, $\mathrm{C}H_2\mathrm{CH_3}$), 1.94 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.70 (1H, ddd, $^2J_{HH} \cong {}^3J_{HH} = 6.54$, $^2J_{HP} = 13.48$, $\mathrm{PC}H_2$), 2.99 (1H, ddd, $^2J_{HH} \cong {}^2J_{HP} = 11.59$, $^3J_{HH} = 3.93$, $\mathrm{PC}H_2$), 3.89 (1H, br m, $\mathrm{C}H\mathrm{Et}$), 7.30 (2H, m, ArH), 7.42 (4H, m, ArH), 7.83 (4H, m, ArH); δ_C ($CDCl_3$, 100 MHz) 11.48 (1C, s, C^1), 28.58 (1C, m, C^2), 46.15 (1C, m), 46.39 (1C, s), 127.84 (1C, m), 127.97 (1C, m), 130.51 (1C, s), 132.63 (1C, m); *m/z* (ES) 1012.8002 (MH^+. $C_{32}H_{37}I_2P_2Pd_2S_2$ requires 1012.7981), 1015 (8%), 887 ($M^+ - I$, 15).

Pd(3)Cl$_2$. $Pd(PhCN)_2Cl_2$ (0.31 g, 0.8 mmol) was added to a dichloromethane solution (10 mL) of **3** (0.29 g, 0.8 mmol). The resulting orange solution was left stirring overnight. Subsequently, the solvents were evaporated to afford an oil, which was triturated with diethyl ether (2 × 10 mL) and dried. Crystals of the complex were obtained after the diffusion of petroleum ether into a chloroform solution of Pd(**3**)Cl$_2$. Yield 0.36 g (83%). Found: C, 50.36; H, 4.59. $C_{23}H_{25}Cl_2PPdS$ requires C, 50.99; H, 4.65%. δ_P ($CDCl_3$, 300 MHz) 50.7; δ_H ($CDCl_3$, 400 MHz) 0.94 (3H, t, $^3J_{HH} = 7.3$, $\mathrm{CH_2C}H_3$), 1.73 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.82 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.34 (1H, m), 2.56 (2H, m), 3.95 (1H, d, $^2J_{HH} = 13.6$, $\mathrm{C}H_2\mathrm{Ph}$), 4.90 (1H, d, $^2J_{HH} = 13.6$, $\mathrm{C}H_2\mathrm{Ph}$), 7.05–7.70 (15H, m, Ar); δ_C ($CDCl_3$, 100 MHz) 9.9 (1C, s, $C\mathrm{H_3}$), 24.7 (1C, s, $C\mathrm{H_2}$), 27.0 (1C, d, $^1J_{CP} = 8.0$ Hz, $C\mathrm{H_2}$), 34.1 (1C, d, $^2J_{CP} = 15.0$, $C\mathrm{H}$), 43.1 (1C, d, $^4J_{CP} = 15.0$, $C\mathrm{H_2}$), 127.1 (1C, s), 128.3–128.9 (6C, m), 132.0 (2C, m), 132.2 (2C, m), 138.0 (2C, m), 138.3 (1C, m); *m/z* (ES) 505.0132 ($M - Cl^+$. $C_{23}H_{25}ClPPdS$ requires 505.0129), 439 (14%).

Pd(4)Cl$_2$. $Pd(PhCN)_2Cl_2$ (1.15 g, 3.0 mmol) was added to a dichloromethane solution (10 mL) of **4** (1.18 g, 3.0 mmol) and the reaction was left to stir overnight. Subsequently, the solvents were removed *in vacuo* and the yellow solid formed was washed with diethyl ether (20 mL) and dried. The pure compound was obtained after slow diffusion of petroleum ether into a chloroform solution of Pd(**4**)Cl$_2$. Yield 1.50 g (87%). Found: C, 52.33; H, 5.10. $C_{25}H_{29}Cl_2PPdS$ requires C, 52.69; H, 5.13%. δ_H ($CDCl_3$, 500 MHz) 0.95 (3H, t, $^3J_{HH} = 7.3$, $\mathrm{CH_2C}H_3$), 1.65 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 1.79 (1H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.14 (6H, s, CH_3), 2.28 (1H, m), 2.66 (2H, m), 3.88 (1H, d, $^2J_{HH} = 13.5$, $\mathrm{C}H_2\mathrm{Xyl}$), 4.70 (1H, d, $^2J_{HH} = 13.5$, $\mathrm{C}H_2\mathrm{Xyl}$), 6.69 (1H, s, Xyl), 7.17 (2H, s, Xyl), 7.3–7.6 (10H, m, ArH); δ_C ($CDCl_3$, 100 MHz) 12.3 (1C, s, $C\mathrm{H_3}$), 21.3 (2C, s, $C\mathrm{H_3}$), 26.1 (1C, d, $^1J_{CP} = 16.1$, $C\mathrm{H_2}$), 31.0 (1C, s), 37.3 (1C, d, $^2J_{CP} = 34.2$, $C\mathrm{H}$), 41.3 (1C, s, $C\mathrm{H_2}$), 128.0 (2C, s), 128.9 (2C, d, $J_{CP} = 12.0$), 129.1 (2C, d, $J_{CP} = 11.3$), 130.6 (2C, s), 132.1(2C, m), 133.1 (2C, d, $J_{CP} = 10.1$), 138.6 (2C, s); δ_P ($CDCl_3$, 121 MHz) 52.4; *m/z* (ES) 533.0445 ($M - {}^{35}Cl^+$. $C_{25}H_{29}ClPPdS$ requires 533.0445), 588 ($M + NH_4^+$, 20%).

Pd(5)Cl$_2$. To a solution of $Pd(PhCN)_2Cl_2$ (0.32 g, 0.83 mmol) in 20 mL of dichloromethane **5** (0.83 mmol) was added. The orange solution was allowed to stir overnight. Subsequently the volume of the solution was reduced to *ca.* 10 mL and diethyl ether (20 mL) was added to precipitate the product as an orange solid. Yield 0.34 g (69%). Found: C, 53.93; H, 4.55. $C_{27}H_{27}Cl_2PPdS$ requires C, 54.79; H, 4.60%. δ_P (D_2O insert, 121 MHz) 54.2; δ_H ($CDCl_3$, 400 MHz) 0.58 (3H, t, $^3J_{HH} = 7.3$, $\mathrm{CH_2C}H_3$), 1.24 (2H, m, $\mathrm{C}H_2\mathrm{CH_3}$), 2.32 (1H, m, $\mathrm{PC}H_2$), 2.55 (2H, m, $\mathrm{PC}H_2/\mathrm{C}H\mathrm{Et}$), 4.77 (1H, d, $^2J_{HH} = 13.8$, $\mathrm{C}H_2\mathrm{Ph}$), 5.14 (1H, d, $^2J_{HH} = 13.8$, $\mathrm{C}H_2\mathrm{Ph}$), 7.2–7.7 (14H, m, Ar), 7.71 (1H, d, $^3J_{HH} = 8.0$), 7.76 (1H, d, $^3J_{HH} = 8.0$), 8.43 (1H, d, $^3J_{HH} = 8.3$); δ_C ($CDCl_3$, 75 MHz) 12.3 (1C, s, $C\mathrm{H_3}$), 27.3 (1C, m, $C\mathrm{H_2}$), 38.8 (1C, m, $C\mathrm{H}$), 41.9 (1C, s, $C\mathrm{H}$), 49.5 (1C, m, $C\mathrm{H_2}$), 124.3 (1C, s), 125.0 (1C, s), 126.8 (1C, s), 127.7 (1C, s), 128.9–129.1 (6C, m), 130.2 (1C, br), 131.1 (1C, br), 132.4 (2C, m), 133.1 (4C, m), 133.9 (1C, m); *m/z* (ES) 555.0279 ($M - Cl^+$. $C_{27}H_{27}ClPPdS$ requires 555.0294).

General procedure for the Suzuki reaction

A 1,4-dioxane (5 mL) solution containing 4-bromotoluene (5 mmol), benzene boronic acid (7 mmol), base (7 mmol), naphthalene (2.5 mmol, used as GC standard) and catalyst was introduced into an ACE® glass pressure tube which was subsequently sealed, stirred and heated at the stated temperature. The course of the reaction was monitored by GC-MS; samples

(0.1 mL) were taken at set time intervals, separated with 0.1 mL water and extracted with 0.1 mL dichloromethane.

X-Ray crystallography

Crystal structure determination of [Pd(1)I]$_2$, Pd(3)Cl$_2$·CHCl$_3$ and Pd(4)Cl$_2$. Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation. The instrument was equipped with an Oxford Cryosystems cooling apparatus The structure was solved *via* Patterson methods (Dirdif 99.2)[24] and refined on $F_o{}^2$[24] by full matrix least squares[25] using all unique data corrected for Lorentz and polarisation factors and for absorption using SORTAV.[26] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with U_{iso} set at 1.2 or 1.5 times the U_{eq} of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached.

Crystal data for the [Pd(1)I]$_2$ complex. $C_{32}H_{36}I_2P_2Pd_2S_2$, M = 1013.27, orthorhombic, a = 14.50820(10), b = 16.0768(2), c = 29.9895(2) Å, U = 6994.91(11) Å^3, T = 150(2) K, space group *Pbca*, Z = 8, absorption coefficient 3.026 mm^{-1}, reflections collected 76617, independent reflections 10173 (R_{int} = 0.1120). The final $R_1(F^2)$ was 0.0367 and $wR(F^2)$ 0.0776.

Crystal data for the Pd(3)Cl$_2$·CHCl$_3$ complex. $C_{24}H_{26}Cl_5PPdS$, M = 661.13, monoclinic, a = 14.7145(2), b = 13.2355(2), c = 14.8381(2) Å, β = 112.770(1)°, U = 2664.56(6) Å^3, T = 150(2) K, space group $P2_1/c$, Z = 4, absorption coefficient 1.349 mm^{-1}, reflections collected 39701, independent reflections 7770 (R_{int} = 0.0873). The final $R_1(F^2)$ was 0.0350 and $wR(F^2)$ 0.0761.

Crystal data for the Pd(4)Cl$_2$ complex. $C_{25}H_{29}Cl_2PPdS$, M = 569.81, monoclinic, a = 14.029(2), b = 12.600(2), c = 14.870(3) Å, β = 109.835(1)°, U = 2472.56(7) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4, absorption coefficient 1.127 mm^{-1}, reflections collected 40943, independent reflections 5613 (R_{int} = 0.0784). The final $R_1(F^2)$ was 0.0355 and $wR(F^2)$ 0.0802.

Crystal structure determination and crystal data for the Pd(5)Cl$_2$ complex. Suitable crystals were selected and data collected on a Bruker Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å) driven by COLLECT[27] and DENZO[28] software at 120 K. Structures were determined in SHELXS-97[29] and refined using SHELXL-97.[30] $C_{27}H_{27}Cl_2PPdS$, M = 591.82, triclinic, a = 9.9134(3), b = 11.6302(5), c = 11.7817(4) Å, α = 102.154(2), β = 99.477(2), γ = 103.735(2)°, U = 1256.57(8) Å^3, T = 120(2) K, space group $P\bar{1}$, Z = 2, absorption coefficient 1.112 mm^{-1}, reflections collected 24762, independent reflections 5748 (R_{int} = 0.0408). The final $R_1(F^2)$ was 0.0341 and $wR(F^2)$ 0.0745.

CCDC reference numbers 602963, 602964, 602965 and 602966.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609607g

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