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Synthesis, structure and catalytic activity of thioether–phosphane complexes of Pd(II) and Pt(II)

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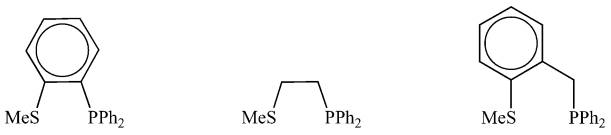
New thioether–phosphanes 2-RSC$_6$H$_4$CH$_2$PPh$_2$ (RS∼PPh$_2$: R = Me, ^{t}Bu, Ph) and the corresponding complexes [PdCl$_2$(MeS∼PPh$_2$)], [PdCl$_2$(^{t}BuS∼PPh$_2$)], [PdCl$_2$(PhS∼PPh$_2$)], [PdClMe(MeS∼PPh$_2$)] and [PtMe$_2$(MeS∼PPh$_2$)] have been prepared, characterized and the X-ray crystal structures of all complexes determined. Whilst Pd(II) complexes of RS∼PPh$_2$ show low activity for CO/ethene copolymerisation, the complexes [PdCl$_2$(RS∼PPh$_2$)] have been found to be very efficient for the Heck arylation of *n*-butylacrylate with bromobenzene under aerobic conditions.

Introduction

The use of transition metal complexes for homogeneous catalysis has been established for a wide variety of phosphorus-, nitrogen- and carbon-based ligands.[1,2] In the quest for ever greater catalyst activity and selectivity, these ligands continue to be the primary focus of academic and industrial research, while other types of ligands are rarely given much attention. Sulfur-based ligands have been less explored in catalysis, possibly due to sulfur's well-known tendency to act as a "catalyst poison",[3–5] however recent results have been very promising.[6,7]

We discovered that certain thioether ligands containing a phosphane "pendant arm" (L_1, L_2, MeS∼PPh$_2$ in Fig. 1) form highly active catalysts for a number of homogeneous reactions. Rhodium(I) thioether–phosphane complexes of the type [RhX(CO)L$_{1,2}$] (X = Cl, I) are three times more active than the Monsanto catalyst [RhI$_2$(CO)$_2$]$^-$ for methanol carbonylation[8] while the palladium(II) complex [PdCl$_2$(MeS∼PPh$_2$)] gives 1.2 × 10^6 turnovers for the Heck arylation of styrene with various aryl bromides and iodides under aerobic conditions.[9]



L_1 **L_2** **MeS~PPh$_2$**

Fig. 1 Thioether–phosphane ligands.

We now wish to report the syntheses and structures of novel Group 10 thioether–phosphane complexes and the catalysis testing in C–C coupling reactions, *i.e.* CO/ethene copolymerisation and Heck arylation. Pd(II) complexes of RS∼PPh$_2$ show low activity towards the copolymerisation of CO and ethene but the complexes [PdCl$_2$(RS∼PPh$_2$)] are all highly active for Heck arylation under aerobic conditions.

Results and discussion

Ligands

The ligands 2-RSC$_6$H$_4$CH$_2$PPh$_2$ (RS∼PPh$_2$: R = Me, ^{t}Bu, Ph) were synthesized by the three-step procedure of Kellner *et al.*[10,11] as shown in Fig. 2 and described in the Experimental section. Intermediates **Ia–c**[12–14] were synthesized using the method of

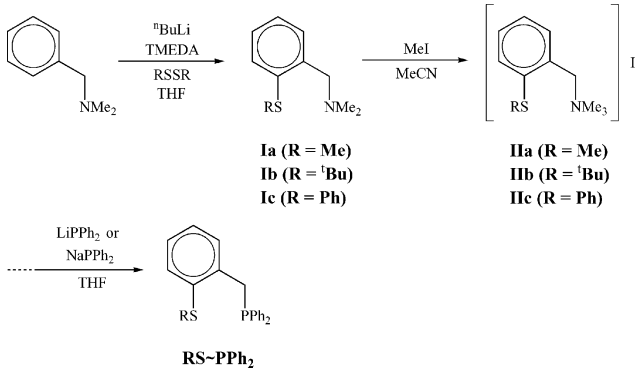


Fig. 2 Synthesis of ligands RS∼PPh$_2$.

Christiaens *et al.*[15] for **Ia** and although **Ia–c**, **IIc** and PhS∼PPh$_2$ were contaminated with traces of starting material, purification was not necessary for the subsequent steps of synthesis.

All RS∼PPh$_2$ ligands were characterized by elemental analysis, mass spectroscopy (EI- or FI-MS), and ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy (See Table 1). All ^{1}H NMR spectra show signals between δ 6.79 and 8.02 ppm due to the aromatic hydrogens. MeS∼PPh$_2$ and ^{t}BuS∼PPh$_2$ additionally show sharp singlets at δ 2.01 and 1.32 ppm corresponding to SCH_3 and SC(CH_3)$_3$, respectively. The CH_2P signals appear as singlets (δ 3.66 ppm for R = Me, δ 3.64 ppm for R = Ph) or finely-split doublets (δ 3.64 ppm, $^2J_{HP}$ = 1.2 Hz for R = ^{t}Bu). Simple doublets are not observed due to free rotation about the CH$_2$–P bond, which averages the H–P scalar couplings to near-zero.[16,17] This has been observed in other benzylphosphanes.[18,19]

The ^{13}C{^{1}H} NMR spectra of ^{t}BuS∼PPh$_2$ and PhS∼PPh$_2$ (MeS∼PPh$_2$ has been described previously[9]) exhibit signals between δ 126.0 and 143.0 ppm due to aromatic carbons. ^{t}BuS∼PPh$_2$ additionally shows signals for SC(CH_3)$_3$ (δ 31.4 ppm) and SC(CH$_3$)$_3$ (δ 47.6 ppm), the latter with long-range scalar coupling to phosphorus. The CH$_2$P signals appear as simple doublets (δ 34.9 ppm, $^1J_{CP}$ = 15.6 Hz for R = ^{t}Bu, δ 34.5 ppm, $^1J_{CP}$ = 16.4 Hz for R = Ph) since free rotation about CH$_2$–P does not "average out" the C–P scalar coupling.

Finally, all ^{31}P{^{1}H} NMR spectra exhibit sharp singlets at δ −12.4 ppm (R = Me), δ −7.4 ppm (R = ^{t}Bu) and δ −9.8 ppm (R = Ph) which are typical for tertiary bis-aryl, mono-alkyl phosphanes.[20,21]

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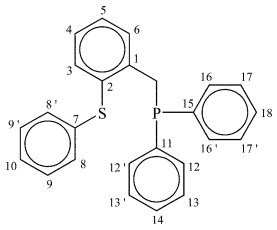
Table 1 Characterizing data of intermediates **Ib–c** and **IIa–c**, ligands RS∼PPh_2 (R= Me, ^{t}Bu, Ph) and complexes [MXY(RS∼PPh_2)] (M = Pd, X = Cl, Y = Cl or Me; M = Pt, X = Y = Me)



Compound		NMR data
Ib	$C_{13}H_{21}NS$ RMM = 223.383 Light-yellow oil Found: C, 69.25; H, 9.29; N, 5.27% Calc.: C, 69.90; H, 9.48; N, 6.27%[a] EI-MS: 223.1 $[M]^+$, 166.1 $[M - {}^t\text{Bu}]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 1.30 [9H, s, SC(CH_3)$_3$], 2.27 [6H, s, N(CH_3)$_2$], 3.77 [2H, s, CH_2N], 7.20 [1H, td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.6, H4 or H5], 7.34 [1H, td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.4, H4 or H5], 7.54 [1H, d, $^3J_{HH}$ = 7.7, H3 or H6], 7.55 [1H, d, $^3J_{HH}$ = 7.7, H3 or H6] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 31.3 [s, SC(CH_3)$_3$], 45.7 [s, N(CH_3)$_2$], 47.3 [s, SC(CH_3)$_3$], 61.9 [s, CH_2N], 126.6 [s, C4 or C5], 128.9 [s, C4 or C5], 129.9 [s, C3 or C6], 132.4 [s, C1 or C2], 138.7 [s, C3 or C6], 144.1 [s, C1 or C2]
Ic	$C_{15}H_{17}NS$ RMM = 243.373 Yellow oil EI-MS: 243.1 $[M]^+$, 242.1 $[M - H]^+$, 197.0 $[M - 2H - NMe_2]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 2.26 [6H, s, N(CH_3)$_2$], 3.56 [2H, s, CH_2N]. Aromatic hydrogens: 7.07–7.54 [br m][b] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 45.5 [s, N(CH_3)$_2$], 62.1 [s, CH_2N]. Aromatic carbons: 126.9 [s], 127.9 [s], 129.2 [s], 130.2 [s], 130.6 [s], 131.1 [s], 132.1 [s], 135.9 [s], 136.3 [s], 139.7 [s]
IIa	$C_{11}H_{18}INS$ RMM = 323.237 Off-white solid Found: C, 41.16; H, 5.66; N, 4.37% Calc.: C, 40.87; H, 5.61; N, 4.33% ES-MS: 196.2 $[M - I]^+$, 137.1 $[M - I - NMe_3]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 2.47 [3H, s, SCH_3], 3.42 [9H, s, N(CH_3)$_3$], 4.97 [2H, s, CH_2N], 7.24 [1H, td, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.3, H4 or H5], 7.36 [1H, dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.2, H3 or H6], 7.43 [1H, td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3, H4 or H5], 7.76 [1H, dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 0.9, H3 or H6] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 17.4 [s, SCH_3], 53.5 [s, N(CH_3)$_3$], 66.4 [s, CH_2N]. Aromatic carbons: 125.8 [s], 126.1 [s], 128.3 [s], 131.6 [s], 134.9 [s], 141.4 [s]
IIb	$C_{14}H_{24}INS$ RMM = 365.318 Off-white solid Found: C, 46.07; H, 6.91; N, 3.60% Calc.: C, 46.03; H, 6.62; N, 3.83% ES-MS: 238.2 $[M - I]^+$, 179.2 $[M - I - NMe_3]^+$, 123.1 $[M - I - NMe_3 - {}^t\text{Bu}]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 1.23 [9H, s, SC(CH_3)$_3$], 3.40 [9H, s, N(CH_3)$_3$], 5.18 [2H, s, CH_2N], 7.47 [2H, m, H4 + H5], 7.69 [1H, dd, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 2.0, H3 or H6], 7.97 [1H, dd, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 2.0, H3 or H6] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 31.1 [s, SC(CH_3)$_3$], 49.3 [s, SC(CH_3)$_3$], 53.4 [s, N(CH_3)$_3$], 66.6 [s, CH_2N], 129.9 [s, C1 or C2], 130.9 [s, C4 or C5], 132.1 [s, C4 or C5], 134.9 [s, C3 or C6], 135.9 [s, C1 or C2], 139.5 [s, C3 or C6]
IIc	$C_{16}H_{20}INS$ RMM = 385.308 Off-white solid Found: C, 50.11; H, 5.93; N, 3.65% Calc.: C, 49.87; H, 5.23; N, 3.64%[b] ES-MS: 258.1 $[M - I]^+$, 227.1 $[M - I - 2Me - H]^+$, 199.0 $[M - I - NMe_3]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 3.50 [9H, s, N(CH_3)$_3$], 5.10 [2H, s, CH_2N], 7.17 [2H, m, H8/8′], 7.29 [br m, H9/9′ + H10], 7.99 [1H, m, H6]. Other aromatic hydrogens: 7.54 [br m][b] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 53.3 [s, N(CH_3)$_3$], 66.2 [s, CH_2N], 127.8 [s, C10], 129.6 [s, C9/9′], 130.6 [s, C8/8′], 133.7 [s, C7], 135.3 [s, C6]. Other aromatic carbons: 127.9 [s], 128.4 [s], 131.8 [s], 133.8 [s], 138.5 [s]
MeS∼PPh_2	$C_{20}H_{19}PS$ RMM = 322.411 White solid	^{1}H NMR (C_6D_6, 300 MHz): 2.01 [3H, s, SCH_3], 3.66 [2H, s, CH_2P], 6.79 [2H, m, 2H of H3–6], 6.94 [1H, m, 1H of H3–6]. Other aromatic hydrogens: 7.05 [7H, m], 7.45 [4H, m] ^{31}P{^{1}H} NMR (C_6D_6, 122 MHz): −12.4 [s, CH_2P]
^{t}BuS∼PPh_2	$C_{23}H_{25}PS$ RMM = 364.492 White solid Found: C, 75.35; H, 7.28% Calc.: C, 75.79; H, 6.91% FI-MS: 364.1 $[M]^+$, 307.1 $[M - {}^t\text{Bu}]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 1.32 [9H, s, SC(CH_3)$_3$], 3.83 [2H, d, $^2J_{HP}$ = 1.2, CH_2P]. Aromatic hydrogens: 6.96 [1H, m], 7.10 [2H, m], 7.32 [5H, m], 7.41 [4H, m], 7.49–7.83 [2H, m] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 31.4 [s, SC(CH_3)$_3$], 34.9 [d, $^1J_{CP}$ = 15.6, CH_2P], 47.6 [d, $^5J_{CP}$ = 1.1, SC(CH_3)$_3$]. Aromatic carbons: 126.0 [d, J_{CP} = 2.6], 128.3 [d, J_{CP} = 6.4], 128.6 [s], 128.6 [s], 130.2 [d, J_{CP} = 9.0], 132.5 [d, J_{CP} = 4.3], 133.1 [d, J_{CP} = 18.4], 138.3 [d, J_{CP} = 15.9], 138.8 [d, J_{CP} = 1.4], 143.0 [d, J_{CP} = 7.2] ^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz): −7.4 [s, CH_2P]
PhS∼PPh_2	$C_{25}H_{21}PS$ RMM = 384.452 Off-white solid Found: C, 76.24; H, 5.41% Calc.: C, 78.10; H, 5.51%[b] EI-MS: 384.1 $[M]^+$, 307.1 $[M - Ph]^+$ Correct isotope pattern	^{1}H NMR ($CDCl_3$, 300 MHz): 3.64 [2H, s, CH_2P], 6.91 [1H, m, 1H of H3–6]. Other aromatic hydrogens: 7.08 [3H, m], 7.15–8.02 [br m][b] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 34.5 [d, $^1J_{CP}$ = 16.4, CH_2P]. Aromatic carbons: 126.5 [s], 127.2 [d, J_{CP} = 3.0], 127.7 [d, J_{CP} = 1.5], 128.5 [d, J_{CP} = 6.5], 128.8 [s], 129.2 [s], 130.0 [s], 130.6 [d, J_{CP} = 8.9], 133.2 [d, J_{CP} = 18.8], 133.7 [d, J_{CP} = 2.0], 134.4 [d, J_{CP} = 4.0], 136.9 [d, J_{CP} = 1.5], 138.2 [d, J_{CP} = 15.9], 139.5 [d, J_{CP} = 8.2] ^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz): −9.9 [s, CH_2P]

Table 1 (*Contd.*)

Compound		NMR data
[$PdCl_2$(MeS∼PPh_2)]	$C_{20}H_{19}Cl_2PPdS$ RMM = 499.737 Yellow–green solid ES-MS: 961.4 [2M − Cl]$^+$, 504.2 [M − Cl + MeCN]$^+$, 463.2 [M − Cl]$^+$ Correct isotope pattern	^{1}H NMR (d_6-DMSO, 300 MHz): 3.08 [3H, s, SCH_3], 4.20 [2H, br d, $^2J_{HP}$ = 12.1, CH_2P], 7.21 [1H, br d, $^3J_{HH}$ = 7.3, H3 or H6], 7.28 [1H, br td, $^3J_{HH}$ = 7.3, J = 0.6, H4 or H5], 7.36 [1H, br tt, $^3J_{HH}$ = 7.7, J = 1.4, H4 or H5], 7.49 [4H, m, (H12/12′ + H16/16′) or (H13/13′ + H17/17′)], 7.57 [2H, m, H14 + H18], 7.63 [1H, br d, $^3J_{HH}$ = 7.7, H3 or H6], 7.81 [4H, br dd, J = 11.9, J = 7.6, (H12/12′ + H16/16′) or (H13/13′ + H17/17′)] ^{31}P{^{1}H} NMR (d_6-DMSO, 122 MHz): 60.9 [br s, CH_2P] ^{1}H NMR (CD_2Cl_2, 300 MHz): 3.13 [3H, s, SCH_3], 3.80 [2H, d, $^2J_{HP}$ = 10.9, CH_2P], 6.80 [1H, d, $^3J_{HH}$ = 7.8, H6], 7.20 [1H, dd, $^3J_{HH}$ = 7.8, H5], 7.30 [6H, m, H3 + H4 + H13/13′ + H17/17′], 7.65 [2H, m, H14 + H18], 7.95 [4H, m, H12/12′ + H16/16′] ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): 18.2 [br s, SCH_3], 32.4 [br s, CH_2P], 125.5 [br s, C5], 127.2 [br s, C4], 128.6 [s, C2], 128.8 [br s, C13/13′ + C17/17′], 129.0 [s, C6], 131.4 [br s, C1], 132.3 [br s, C11 + C15], 132.4 [br s, C14 + C18], 133.4 [br s, C12/12′ + C16/16′] ^{31}P{^{1}H} NMR (CD_2Cl_2, 122 MHz): 63.4 [s, CH_2P]
[$PdCl_2$(^{t}BuS∼PPh_2)]	$C_{23}H_{25}Cl_2PPdS$ RMM = 541.818 Orange solid Found: C, 51.05; H, 5.20% Calc.: C, 50.98; H, 4.65% ES-MS: 546.3 [M − Cl + MeCN]$^+$, 505.3 [M − Cl]$^+$ Correct isotope pattern	^{1}H NMR (d_6-DMSO, 500 MHz): 1.62 [9H, s, SC(CH_3)$_3$], 3.81 [1H, br dd, $^2J_{HH}$ = 14.9, $^2J_{HP}$ = 7.2, 1H of CH_2P], 4.33 [1H, br t, $^2J_{HH}$ = 14.8, $^2J_{HP}$ = 16.7, 1H of CH_2P], 7.37 [1H, br tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.7, $^6J_{HP}$ = 1.4, H4], 7.46 [4H, m, H5 + H6 + H13/13′], 7.56 [3H, m, H14 + H17/17′], 7.63 [1H, m, H18], 7.71 [3H, m, H3 + H16/16′], 7.98 [2H, br t, $^3J_{HH}$ = 6.8, $^3J_{HP}$ = 8.3, H12/12′] ^{13}C{^{1}H} NMR (d_6-DMSO, 126 MHz): 31.9 [d, $^1J_{CP}$ = 29.6, CH_2P], 32.5 [s, SC(CH_3)$_3$], 60.6 [s, SC(CH$_3$)$_3$], 125.0 [d, $^1J_{CP}$ = 53.1, C11 or C15], 129.0 [d, $^5J_{CP}$ = 2.9, C4], 130.9 [d, $^1J_{CP}$ = 58.4, C11 or C15], 131.5 [br s, C18], 134.8 [br d, $^2J_{CP}$ = 10.2, C12/12′], 136.1 [d, $^4J_{CP}$ = 1.8, C3]. Other aromatic carbons: 123.3 [d, J_{CP} = 9.7], 128.6 [m], 132.3 [m], 132.5 [s], 133.1 [d, J_{CP} = 6.2], 137.9 [d, J_{CP} = 3.2] ^{31}P{^{1}H} NMR (d_6-DMSO, 202 MHz): 49.7 [s, CH_2P]
[$PdCl_2$(PhS∼PPh_2)]	$C_{25}H_{21}Cl_2PPdS$ RMM = 561.808 Orange–green solid Found: C, 52.77; H, 4.61% Calc.: C, 53.45; H, 3.77% ES-MS: 566.1 [M − Cl + MeCN]$^+$, 533.1 [M − 2Cl + 2H + MeCN]$^+$ Correct isotope pattern	^{1}H NMR (d_6-DMSO, 60 °C, 500 MHz): 3.63 [2H, d, $^2J_{HP}$ = 12.2, CH_2P], 7.35 [1H, br s, 1H of H3–6], 7.48 [6H, m, 2H of H3–6 + H13/13′ + H17/17′], 7.57 [5H, m, H9/9′ + H10 + H14 + H18], 7.71 [4H, br dd, $^3J_{HH}$ = 7.8, $^3J_{HP}$ = 12.0, H12/12′ + H16/16′], 7.82 [2H, m, H8/8′], 7.93 [1H, br s, 1H of H3–6] ^{13}C{^{1}H} NMR (d_6-DMSO, 60 °C, 126 MHz): 30.1 [d, $^1J_{CP}$ = 26.4, CH_2P], 128.4 [d, $^3J_{CP}$ = 11.3, C13/13′ + 17/17′], 129.3 [d, J_{CP} = 3.3, 1C of C3–6], 129.5 [s, C8/8′], 129.9 [s, C10], 130.1 [s, C9/9′], 131.8 [d, $^4J_{CP}$ = 2.9, C14 + C18], 132.6 [s, 1C of C3–6], 133.1 [m, 1C of C3–6 + C12/12′ + C16/16′], 133.8 [s, 1C of C3–6]. Other aromatic carbon: 136.6 [d, J_{CP} = 3.2] ^{31}P{^{1}H} NMR (d_6-DMSO, 60 °C, 202 MHz): 56.2 [s, CH_2P]
[PdClMe(MeS∼PPh_2)]	$C_{21}H_{22}ClPPdS$ RMM = 479.319 Air- and water-sensitive white solid Found: C, 50.72; H, 3.16% Calc.: C, 52.62; H, 4.63% ES-MS: 921.4 [2M − Cl]$^+$, 443.2 [M − Cl]$^+$, 475.2 [M − Cl + MeOH]$^+$ Correct isotope pattern	^{1}H NMR (CD_2Cl_2, 300 MHz): 0.65 [3H, d, $^3J_{HP}$ = 3.7, PdCH_3], 2.80 [3H, s, SCH_3], 3.58 [2H, d, $^2J_{HP}$ = 9.9, CH_2P], 6.61 [1H, d, $^3J_{HH}$ = 7.5, H6], 6.90 [1H, br d, $^3J_{HH}$ = 7.5, H5], 7.19 [1H, br m, H3], 7.29 [1H, br m, H4], 7.40 [6H, br m, H13/13′ + H14 + H17/17′ + H18], 7.54 [4H, br m, H12/12′ + H16/16′] ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): 3.2 [br s, PdCH_3], 14.9 [br s, SCH_3], 34.5 [d, $^1J_{CP}$ = 22.7, CH_2P], 123.4 [s, C3], 125.5 [s, C5], 127.5 [s, C4], 127.9 [d, $^3J_{CP}$ = 10.6, C13/13′ + C17/17′], 129.0 [s, C2] 130.8 [br s, C1], 131.2 [br d, $^1J_{CP}$ = 53.2, C11 + C15], 131.5 [s, C6], 131.6 [d, $^4J_{CP}$ = 2.9, C14 + C18], 132.5 [d, $^2J_{CP}$ = 11.6, C12/12′ + C16/16′] ^{31}P{^{1}H} NMR (CD_2Cl_2, 122 MHz): 52.5 [s, CH_2P]
[$PtMe_2$(MeS∼PPh_2)]	$C_{22}H_{25}PPtS$ RMM = 547.561 Air- and water-sensitive white solid EI-MS: 553.4 [M + 6H]$^+$	^{1}H NMR (CD_2Cl_2, 300 MHz): 0.39 [3H, d, $^3J_{HP}$ = 7.5, $^2J_{HPt}$ = 69.0, PtCH_3 *trans* to PPh_2], 0.41 [3H, d, $^3J_{HP}$ = 8.1, $^2J_{HPt}$ = 87.6, PtCH_3 *cis* to PPh_2], 2.82 [3H, s, $^3J_{HPt}$ = 29.8, SCH_3], 3.68 [2H, d, $^2J_{HP}$ = 8.4, $^2J_{HPt}$ = 25.8, CH_2P], 6.70 [1H, d, $^3J_{HH}$ = 7.4, H6], 6.85 [1H, br d, $^3J_{HH}$ = 7.5, H5], 7.00 [1H, br m, H3], 7.10 [1H, br m, H4], 7.25 [4H, br m, H12/12′ + H16/16′], 7.50 [6H, br m, H13/13′ + H14 + H17/17′ + H18] ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): 16.8 [br s, SCH_3], 32.4 [br s, CH_2P], 127.6 [br s, C13/13′ + C17/17′], 130.7 [br s, C14 + C18], 132.0 [br s, C12/12′ + C16/16′], 139.6 [s, C2], 135.1 [br s, C1]. Other aromatic carbons: 130.3, 129.5, 128.9. 127.0, 125.2 [br s] ^{31}P{^{1}H} NMR (CD_2Cl_2, 122 MHz): 41.6 [s, CH_2P, $^1J_{PPt}$ = 2072.0]

[a] Traces of $C_6H_5CH_2NMe_2$ and ^{t}BuSS^{t}Bu present. [b] Traces of PhSSPh present.

Metal complexes

The metal complexes [$PdCl_2$(RS∼PPh_2)] (R = Me, ^{t}Bu, Ph), [PdClMe(MeS∼PPh_2)] and [$PtMe_2$(MeS∼PPh_2)] were synthesized from RS∼PPh_2 and one equivalent of [MXY(COD)] (M = Pd, X = Cl, Y = Cl or Me; M = Pt, X = Y = Me) as shown in Fig. 3 and described in the Experimental section.

All complexes were characterized by elemental analysis, mass spectrometry (ES- or EI-MS) and ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy using COSY, HSQC, HMQC, HMBC and NOE difference experiments (see Table 1). The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of all complexes are downfield shifted with respect to the free RS∼PPh_2 ligand, indicative of bidentate coordination to the metal centre. The

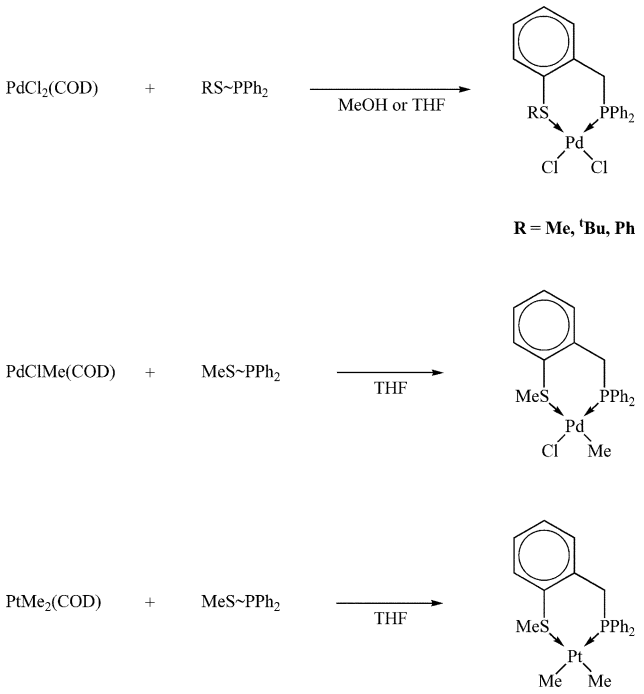


Fig. 3 Synthesis of metal complexes.

chelate complexes are inert and show no hemilability[22,23] or tendency to dissociate in solution.

The most notable feature in the ^{1}H NMR spectra of the [$PdCl_2$(RS~PPh_2)] complexes is the simultaneous variation of the CH_2P and PPh_2 resonances as R changes from Me to ^{t}Bu to Ph. Room temperature d_6-DMSO solutions of the complexes show an A_2X doublet for CH_2P and one resolved set of multiplets for PPh_2 (R = Me), a broad singlet for CH_2P and one broad set of multiplets for PPh_2 (R = Ph) or an ABX octet for CH_2P and two resolved sets of multiplets for PPh_2 (R = ^{t}Bu). This behaviour in solution is due to inversion of the six-membered metal chelate ring which exchanges the chemically-inequivalent AB hydrogens of CH_2P at the same rate as the chemically-inequivalent EF phenyl rings of PPh_2 (Fig. 4). The rate of ring inversion (r.i.) increases with R = Me > Ph > ^{t}Bu. Hence, for R = Me there is fast exchange between conformers I and III (and similarly between conformers II and IV), for R = ^{t}Bu there is slow exchange between conformers I and III (and similarly between conformers II and IV) and for R = Ph there is intermediate (coalescence-type) behaviour. The rate of r.i. is temperature dependent, such that the ^{1}H NMR spectrum of [$PdCl_2$(PhS~PPh_2)] at 60 °C shows an A_2X doublet for CH_2P and one resolved set of multiplets for PPh_2, consistent with faster ring inversion (see Table 1).

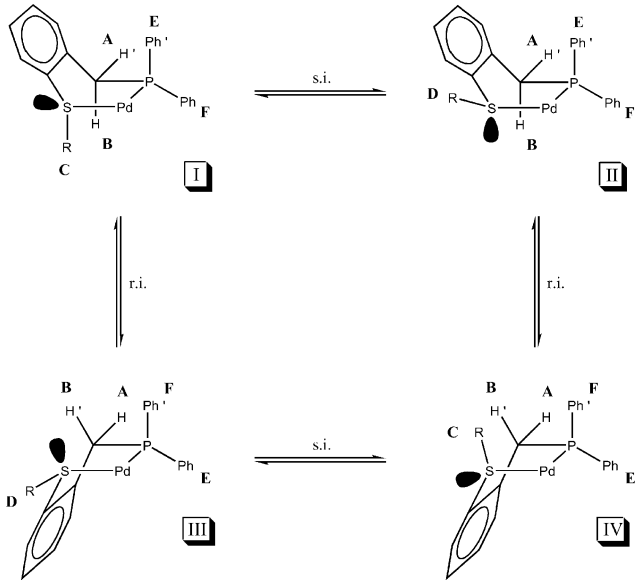


Fig. 4 Ring inversion (r.i.) and sulfur inversion (s.i.) in [$PdCl_2$(RS~PPh_2)] complexes (Cl ligands omitted for clarity).

At room temperature, the ^{1}H NMR resonances of the R group in all [$PdCl_2$(RS~PPh_2)] complexes are very sharp. This is indicative of very fast sulfur inversion (fast exchange between conformers I and II and similarly between conformers III and IV) taking place independently of ring inversion. Related palladium(II) thioether complexes show very fast sulfur inversion at room temperature.[24–26] Further studies of fluxionality by variable-temperature NMR were hampered by the low solubility of the metal complexes at lower temperatures.

We propose a mechanism to describe the fluxional behaviour of the [$PdCl_2$(RS~PPh_2)] complexes in solution (Fig. 4). At room temperature, sulfur inversion (s.i.) is fast for all complexes whilst ring inversion (r.i.) is dependent on the nature of R. When R = Me or Ph, one equilibrium species of all four conformers can be observed by ^{1}H NMR as a result of the two fluxional processes. When R = ^{t}Bu, r.i. is much reduced and two equilibrium species of conformers I and II (and separately conformers III and IV) are present. These two equilibrium species are enantiomeric and indistinguishable by ^{1}H NMR.

The ^{1}H NMR spectra of [PdClMe(MeS~PPh_2)] and [$PtMe_2$(MeS~PPh_2)] are similar to [$PdCl_2$(MeS~PPh_2)], indicating similar states of fluxionality. Additionally, for [PdClMe(MeS~PPh_2)], the PdCH_3 resonance was found at δ 0.65 ppm as a doublet with coupling constant $^3J_{HP}$ = 3.7 Hz. The strong PdCH_3 to H(*ortho*) of PPh_2 NOE indicates that the methyl and phosphorus are coordinated *cis* on the palladium centre. This geometry was further confirmed by X-ray crystallography (*vide infra*). For [$PtMe_2$(MeS~PPh_2)], a centred pair of doublets was observed – assignable by NOE difference experiments to the Pt(CH_3)$_2$ groups – at δ 0.41 ppm (*cis* to PPh_2, $^3J_{HP}$ = 8.1 Hz) and δ 0.39 ppm (*trans* to PPh_2, $^3J_{HP}$ = 7.5 Hz). As expected, the H–Pt coupling is somewhat larger for the $PtCH_3$ *cis* to PPh_2 ($^2J_{HPt}$ = 87.6 Hz) than for the $PtCH_3$ *trans* to PPh_2 ($^2J_{HPt}$ = 69.0 Hz).

X-Ray crystal structures

The solid-state structures of [$PdCl_2$(MeS~PPh_2)], [$PdCl_2$(^{t}BuS~PPh_2)], [$PdCl_2$(PhS~PPh_2)], [PdClMe(MeS~PPh_2)] and [$PtMe_2$(MeS~PPh_2)] were determined by single-crystal X-ray diffraction. Crystals suitable for structural determination were obtained as described in the Experimental section.

We reported that when a mixture of dichloromethane and methanol was used as crystallizing medium, the complex [$PdCl_2$(MeS~PPh_2)] crystallized at room temperature in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit.[9] We were recently surprised when we identified a second polymorph particularly since, when crystals were obtained from a mixture of dichloromethane and pentane by slow cooling to −20 °C, the two polymorphs can be crystallized concomitantly. We now report the structure of the second polymorph (as a dichloromethane solvate) in the triclinic $P\bar{1}$ space group, with two unique metal complex molecules that have similar geometry and conformation in the asymmetric unit. ORTEP representations for [$PdCl_2$(MeS~PPh_2)]·CH_2Cl_2, [$PdCl_2$(^{t}BuS~PPh_2)], [$PdCl_2$(PhS~PPh_2)], [PdClMe(MeS~PPh_2)] and [$PtMe_2$(MeS~PPh_2)] are presented in Figs. 5–9 and their significant molecular parameters in Table 2.

Molecular structure determinations confirm that the studied Pd(II) and Pt(II) complexes are isostructural and their structure is similar in solution and in the solid state. All complexes exhibit pseudo-square-planar geometry at the metal centre. For the MeS~PPh_2 ligand, the S–Pd–P bite angles are 88.51(4) and 88.34(4)° (molecules 1 and 2, respectively) in [$PdCl_2$(MeS~PPh_2)] and 92.09(4)° in [PdClMe(MeS~PPh_2)].

Table 2 Selected bond lengths (Å) and angles (°) for [$PdCl_2$(MeS∼PPh_2)], [$PdCl_2$(^{t}BuS∼PPh_2)], [$PdCl_2$(PhS∼PPh_2)], [PdClMe(MeS∼PPh_2)] and [$PtMe_2$(MeS∼PPh_2)]

[$PdCl_2$(MeS∼PPh_2)]

Molecule 1				Molecule 2			
Pd1–P1	2.2475(10)	S1–C8	1.792(4)	Pd2–P2	2.2540(10)	S2–C28	1.792(4)
Pd1–S1	2.295(1)	P1–C1	1.840(4)	Pd2–S2	2.2873(10)	P2–C21	1.844(4)
Pd1–Cl1	2.3496(10)	P1–C9	1.821(4)	Pd2–Cl3	2.3549(10)	P2–C29	1.801(4)
Pd1–Cl2	2.3166(9)	P1–C15	1.814(4)	Pd2–Cl4	2.3195(9)	P2–C35	1.816(4)
S1–C3	1.771(4)			S2–C23	1.779(4)		
P1–Pd1–S1	88.51(4)	Pd1–P1–C1	111.71(13)	P2–Pd2–S2	88.34(4)	Pd2–P2–C21	111.96(13)
P1–Pd1–Cl1	175.32(4)	Pd1–P1–C15	114.17(12)	P2–Pd2–Cl3	176.18(4)	Pd2–P2–C29	113.18(13)
S1–Pd1–Cl1	93.46(4)	Pd1–P1–C9	117.12(12)	S2–Pd2–Cl3	93.57(4)	Pd2–P2–C35	117.00(12)
P1–Pd1–Cl2	87.48(3)	Pd1–S1–C3	105.38(12)	P2–Pd2–Cl4	87.40(3)	Pd2–S2–C23	106.08(12)
S1–Pd1–Cl2	172.54(4)	Pd1–S1–C8	112.54(15)	S2–Pd2–Cl4	173.09(4)	Pd2–S2–C28	112.45(16)
Cl1–Pd1–Cl2	91.01(4)			Cl3–Pd2–Cl4	91.00(4)		

[$PdCl_2$(^{t}BuS∼PPh_2)]				[$PdCl_2$(PhS∼PPh_2)]			
Pd1–Cl1	2.3686(9)	S1–C8	1.879(3)	Pd1–Cl2	2.3353(9)	P1–C14	1.812(4)
Pd1–Cl2	2.3157(9)	P1–C1	1.830(4)	Pd1–P1	2.2429(10)	P1–C20	1.805(4)
Pd1–S1	2.2979(9)	P1–C12	1.812(4)	Pd1–S1	2.2997(11)	C7–S1	1.773(5)
Pd1–P1	2.2247(9)	P1–C18	1.809(4)	Pd1–Cl1	2.3608(11)	S1–C8	1.798(5)
S1–C7	1.780(4)			P1–C1	1.840(4)		
Cl1–Pd1–Cl2	91.64(3)	Pd1–S1–C7	112.45(12)	Cl2–Pd1–P1	88.49(4)	Pd1–P1–C1	110.57(13)
Cl1–Pd1–S	187.84(3)	Pd1–S1–C8	115.45(12)	Cl2–Pd1–S1	176.64(4)	Pd1–P1–C14	116.89(14)
Cl2–Pd1–S1	173.81(3)	Pd1–P1–C1	113.44(12)	P1–Pd1–S1	94.74(4)	Pd1–P1–C20	114.56(15)
Cl1–Pd1–P1	175.99(3)	Pd1–P1–C12	111.38(12)	Cl2–Pd1–Cl1	92.12(4)	Pd1–S1–C8	106.27(15)
Cl2–Pd1–P1	84.54(3)	Pd1–P1–C18	113.32(13)	P1–Pd1–Cl1	176.50(4)	C7–S1–Pd1	112.40(14)
S1–Pd1–P1	95.83(3)			S1–Pd1–Cl1	84.60(4)		

[PdClMe(MeS∼PPh_2)]				[$PtMe_2$(MeS∼PPh_2)]			
Pd1–Cl1	2.3717(13)	S1–C3	1.781(4)	Pt1–S1	2.3460(6)	S1–C4	1.786(2)
Pd1–S1	2.4331(13)	P1–C9	1.842(5)	Pt1–P1	2.2603(6)	P1–C10	1.852(2)
Pd1–P1	2.2001(12)	P1–C10	1.806(5)	Pt1–C1	2.100(2)	P1–C11	1.821(2)
Pd1–C1	2.069(6)	P1–C16	1.821(5)	Pt1–C2	2.062(2)	P1–C17	1.824(2)
S1–C2	1.797(5)			S1–C3	1.803(4)		
Cl1–Pd1–S1	91.05(5)	Pd1–S1–C2	112.37(19)	S1–Pt1–P1	90.44(2)	Pt1–S1–C3	111.88(11)
Cl1–Pd1–P1	174.74(5)	Pd1–S1–C3	111.61(16)	S1–Pt1–C1	91.25(8)	Pt1–S1–C4	108.11(7)
S1–Pd1–P1	92.09(4)	Pd1–P1–C9	110.48(15)	P1–Pt1–C1	175.84(7)	Pt1–P1–C10	111.11(9)
Cl1–Pd1–C1	89.51(16)	Pd1–P1–C10	115.19(16)	S1–Pt1–C2	178.30(8)	Pt1–P1–C11	119.33(8)
S1–Pd1–C1	176.44(18)	Pd1–P1–C16	116.29(17)	P1–Pt1–C2	90.81(8)	Pt1–P1–C17	114.76(8)
P1–Pd1–C1	87.10(16)			C1–Pt1–C2	87.43(11)		

For the corresponding dichloro complexes of PhS∼PPh_2 and ^{t}BuS∼PPh_2, the S–Pd–P bite angles are significantly larger: 94.74(4) and 95.83(3)° respectively, presumably as a result of increased puckering of the chelate ring induced by bulkiness of the S substituent. The palladium–halogen bond lengths are as expected for Pd(II) complexes,[27] with the longer metal–halogen bond *trans* to the phosphorus atom. In [PdClMe(MeS∼PPh_2)], the Pd–C bond length is 2.069(6) Å with the methyl group located *cis* to the phosphorus atom, as predicted by NMR for the solution species. In general, little variation in the bond lengths and angles of RS∼PPh_2 is observed upon chelation to Pd(II). In the case of [$PtMe_2$(MeS∼PPh_2)], the S–Pt–P bite angle is 90.44(2)°. The Pt–C bond length for the methyl group situated *trans* to phosphorus is 2.100(2) Å. This is somewhat longer than the Pd–C distance *cis* to PPh_2 (2.062(2) Å), which we attribute to the greater *trans*-influence of PPh_2 compared to the SMe donor functionality. The remaining bond lengths and angles are unexceptional and are within the expected limits.

All six-membered metal chelate rings have "boat" geometries, with the methylene group deviated off the best-fit plane [M–P–S–X–Y] at about 0.19 and 0.30 Å (molecule 1 and 2, respectively) in [$PdCl_2$(MeS∼PPh_2)], 0.40 Å in [$PdCl_2$(^{t}BuS∼PPh_2)], 0.43 Å in [$PdCl_2$(PhS∼PPh_2)], 0.49 Å in [PdMeCl(MeS∼PPh_2)] and 0.29 Å in [$PtMe_2$(MeS∼PPh_2)]. We defined the puckering of the rings in terms of the dihedral angle between the best-fit plane [M–P–S–X–Y], and that of the bridging 2-$C_6H_4CH_2$ unit. This angle decreases from 61.2 and 60.5° (molecule 1 and 2 respectively) in [$PdCl_2$(MeS∼PPh_2)] to 55.8° in [$PtMe_2$(MeS∼PPh_2)], 44.5° in [$PdCl_2$(^{t}BuS∼PPh_2)], 43.8° in [$PdCl_2$(PhS∼PPh_2)] and 43.6° in [PdMeCl(MeS∼PPh_2)]. Note that the same angle measures 42° in the earlier reported polymorph of [$PdCl_2$(MeS∼PPh_2)].[9] This data complements the solution studies and indicates that complexes of MeS∼PPh_2 prefer conformers II and III in the solid state whilst complexes of ^{t}BuS∼PPh_2 and PhS∼PPh_2 prefer conformers I and IV in the solid state (Fig. 4).

Finally, in [$PdCl_2$(PhS∼PPh_2)] the distance between Pd(1) and H(91) is 2.80 Å and that between Pd(1) and C(9) is 3.36 Å. The orientation of H(91) is almost perpendicular with respect to the Pd–P–S–Cl–Cl mean plane, *i.e.* the torsion angle between the best-fit [Pd–P–S–Cl–Cl] plane and the [SPh] plane is 87.8°. Similar compounds have been characterized in the solid state[28–31] and the values found by us for *ortho*-H···Pd and *ortho*-C···Pd distances are normal for chelated palladium(II) phenylthioether complexes. The ^{1}H NMR (d_6-DMSO, 60 °C) of [$PdCl_2$(PhS∼PPh_2)] shows no unexpected features in the aromatic region indicative of a potential *ortho*-H···Pd interaction.

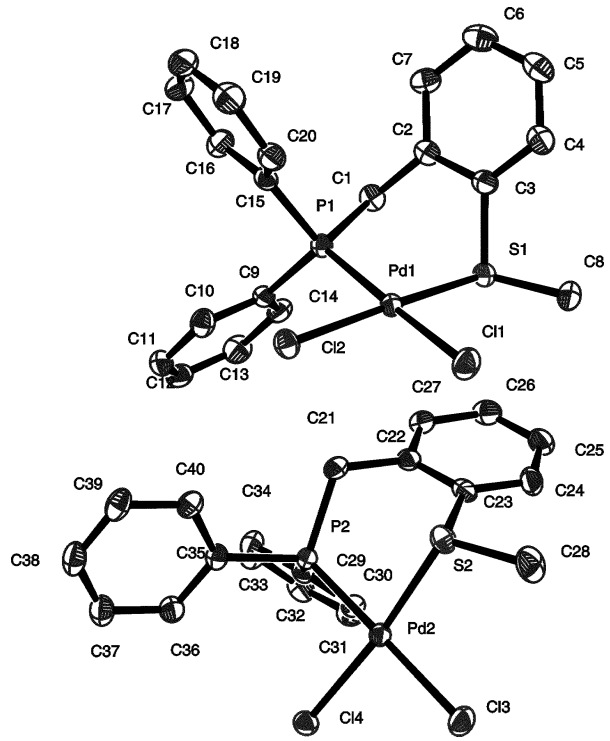


Fig. 5 ORTEP representation of the molecular structure of $[PdCl_2(MeS{\sim}PPh_2)]$. Both complex molecules in the asymmetric unit are shown. Solvent (CH_2Cl_2) excluded.

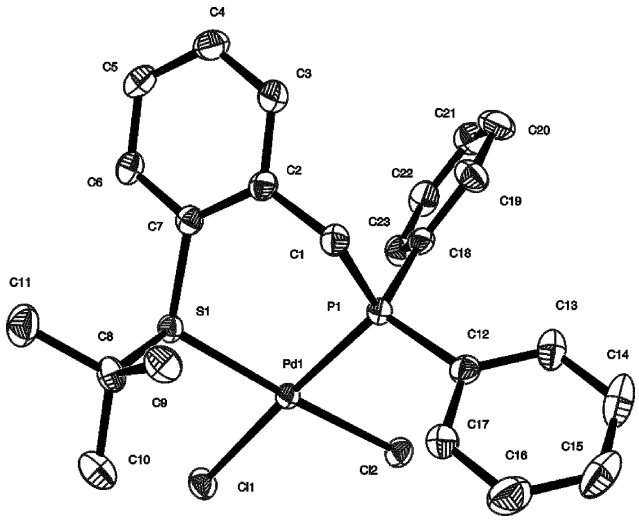


Fig. 6 ORTEP representation of the molecular structure of $[PdCl_2(^tBuS{\sim}PPh_2)]$.

CO/ethene copolymerisation testing

Bidentate phosphane ligands which form six-membered chelate complexes with palladium(II) acetate have been shown to be highly active for the copolymerisation of CO and ethene.[32,33] We were therefore interested in determining the catalytic activity of *in situ* catalysts formed with the $RS{\sim}PPh_2$ ligands.

A mixture of palladium(II) acetate, *p*-toluenesulfonic acid hydrate and $RS{\sim}PPh_2$ in methanol was heated at 80 °C for 2 h under a continuous pressure of 40 bar 1 : 1 CO–ethene. The resultant grey insoluble copolymers were obtained in the following yields: 0.0380 g (activity 1900 ± 90 g mol Pd^{-1}) for R = Me; 0.0003 g (activity 15 ± 10 g mol Pd^{-1}) for R = ^{t}Bu; 0.0014 g (activity 70 ± 10 g mol Pd^{-1}) for R = Ph. Furthermore, a mixture of $[PdClMe(MeS{\sim}PPh_2)]$, silver(I) tetrafluoroborate and acetonitrile in dichloromethane under the same conditions gave a grey insoluble copolymer in a yield of 0.0501 g (activity 2500 ± 60 g mol Pd^{-1}).

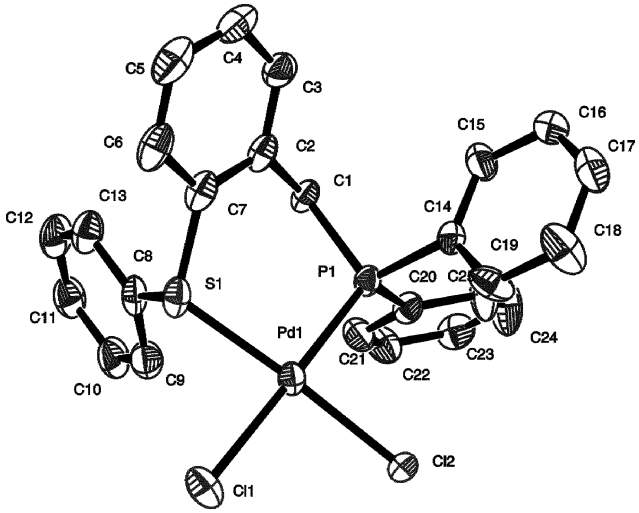


Fig. 7 ORTEP representation of the molecular structure of $[PdCl_2(PhS{\sim}PPh_2)]$.

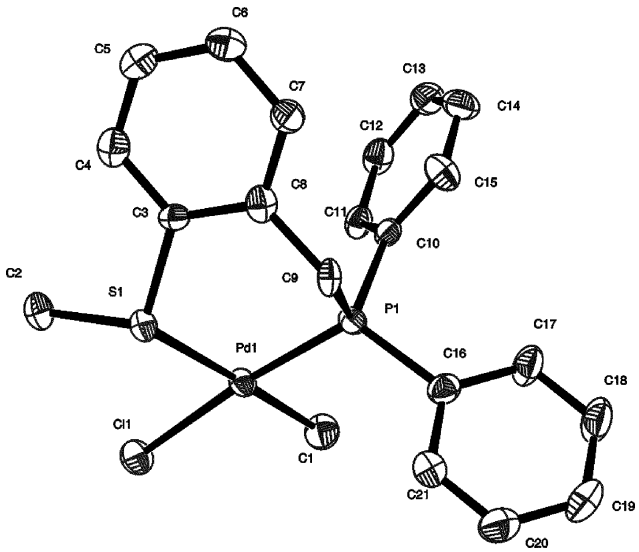


Fig. 8 ORTEP representation of the molecular structure of $[PdClMe(MeS{\sim}PPh_2)]$.

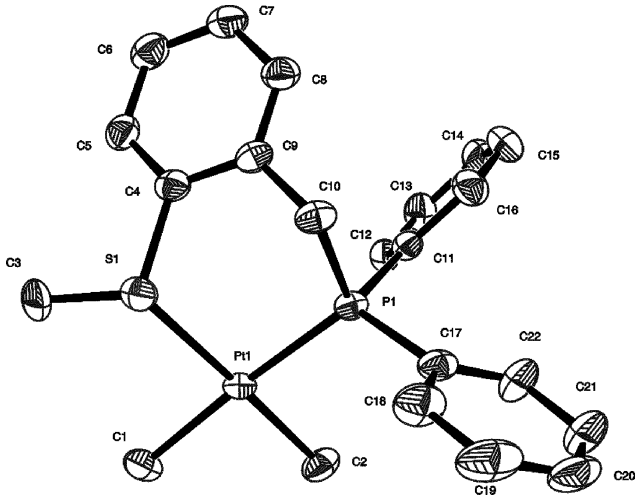


Fig. 9 ORTEP representation of the molecular structure of $[PtMe_2(MeS{\sim}PPh_2)]$.

^{13}C NMR analysis (1,1,1,3,3,3-hexafluoropropan-2-ol–C_6D_6 (9 : 1)) of the copolymers obtained from $MeS{\sim}PPh_2$ catalysts shows that they consist of perfectly alternating CO and C_2H_4 units.[33] GC-MS analysis of the co-oligomers

$X(CH_2CH_2CO)_nY$ ($n = 1$–4) shows a strong dependence on the catalyst system used. For catalyses using palladium(II) acetate, $MeS{\sim}PPh_2$ gives predominantly keto-esters (X = H, Y = OMe), $PhS{\sim}PPh_2$ gives predominantly diesters (X = CO_2Me, Y = OMe) and $^tBuS{\sim}PPh_2$ gives virtually no co-oligomers. Catalysis using $[PdClMe(MeS{\sim}PPh_2)]$ gives no co-oligomers either, which is indicative of a "living" copolymerisation.[34,35]

Comparison to $Ph_2PCH_2CH_2CH_2PPh_2$ (polymer yield 5.3560 g, activity 270000 ± 10000 g mol Pd^{-1} under the same conditions) shows that the $RS{\sim}PPh_2$ ligands give catalytic systems that are over two orders of magnitude less active. The low catalytic activity of thioether–phosphane ligands for CO/ethene copolymerisation has been remarked before.[32]

Heck arylation testing

We have recently shown that $[PdCl_2(MeS{\sim}PPh_2)]$ is an efficient catalyst for the Heck arylation of styrene with various aryl bromides and iodides under aerobic conditions, leading to turnover numbers (TONs) of 10^6.[9] We now report our latest findings on the catalytic activity of $[PdCl_2(RS{\sim}PPh_2)]$ (R = Me, ^{t}Bu, Ph) for the Heck arylation of *n*-butylacrylate with bromobenzene.

A mixture of bromobenzene, 1.2 equivalents *n*-butylacrylate and anhydrous sodium carbonate in 1-methyl-2-pyrrolidinone (NMP) was heated at 130 °C for 72 hours in the presence of $[PdCl_2(RS{\sim}PPh_2)]$ (Fig. 10). All three metal complexes give quantitative yields of *E*-*n*-butylcinnamate with catalyst loadings of 0.001 mol% (TON = 100000). At 0.0001 mol% loading, maximum TONs are obtained for each complex (see Table 3). The activities of $[PdCl_2(RS{\sim}PPh_2)]$ depend on R (Me > ^{t}Bu > Ph) although the differences are small. TONs with *n*-butylacrylate are about one-eighth of those reported with styrene.[9]

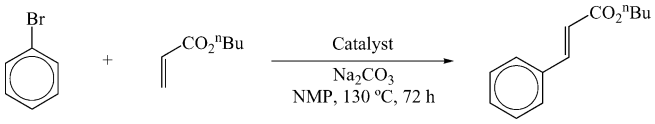


Fig. 10 Conditions of Heck arylation.

The great advantage of the $[PdCl_2(RS{\sim}PPh_2)]$ catalysts is that they are stable to air and water both in solution and the solid state. The Heck arylation with bromobenzene can be performed under aerobic conditions with very high TONs (10^5) unlike most reported high-activity catalysts which give only a few hundred turnovers.[36–41] For comparison, we tested Herrmann's palladacyclic catalyst $[Pd_2(\mu\text{-}OAc)_2\{2\text{-}CH_2C_6H_4P(o\text{-}Tol)_2\}_2]$[36,37] (*o*-Tol = 2-$CH_3C_6H_4$) under aerobic conditions and were surprised to find similar activity to the $[PdCl_2(RS{\sim}PPh_2)]$ systems (See Table 3: $[Pd_2(\mu\text{-}OAc)_2\{2\text{-}CH_2C_6H_4P(o\text{-}Tol)_2\}_2]$ had previously been reported to give only 96 turnovers with *n*-butylacrylate and bromobenzene[36]). The $[PdCl_2(RS{\sim}PPh_2)]$ catalysts therefore show high but not superior activity with respect to this benchmark system. Further testing with a variety of electron-rich and electron-poor aryl bromides and chlorides is underway and will be reported elsewhere.

It is well known that under Heck arylation conditions many palladium(II) catalysts decompose to some palladium(0) or palladium(II) aggregate[36,42–44] and this may well be the case with the $[PdCl_2(RS{\sim}PPh_2)]$ catalysts also. Model studies in d_6-DMSO or d_7-DMF at 130 °C (at concentrations several orders of magnitude higher than those of catalysis) show that $[PdCl_2(MeS{\sim}PPh_2)]$ and $[PdCl_2(^tBuS{\sim}PPh_2)]$ dealkylate[45,46] after only 2 h whilst $[PdCl_2(PhS{\sim}PPh_2)]$ slowly forms free $PhS{\sim}P(O)Ph_2$. Addition of sodium carbonate and prolonged heating gives black, insoluble solids that are slightly active for Heck arylation. Whether discrete $[PdCl_2(RS{\sim}PPh_2)]$ species are mainly responsible for the observed catalytic activity or not, it is clear that sulfur-based ligands can be used in combination with palladium to produce robust and effective Heck arylation catalysis systems.

Conclusions

New Pd(II) and Pt(II) complexes of the thioether–phosphanes 2-$RSC_6H_4CH_2PPh_2$ ($RS{\sim}PPh_2$: R = Me, ^{t}Bu, Ph) have been prepared and fully characterized, showing the ability of the ligand to coordinate in a chelating bidentate fashion. An initial estimation of the catalytic activity of Pd(II) $RS{\sim}PPh_2$ complexes is described: low activity is observed for the copolymerisation of CO and ethene but high activity is observed for the Heck arylation of *n*-butylacrylate with bromobenzene under aerobic conditions.

Experimental

General

All manipulations of air- and/or water-sensitive compounds were performed under an inert atmosphere of pure Ar or N_2 using standard Schlenk line techniques or glove boxes.[47] Inert gases were purified by passage through columns filled with activated 4A molecular sieves and then either manganese(II) oxide suspended on vermiculite (for Schlenk lines) or BASF R-311 catalyst (for glove boxes). Where necessary, solvents were pre-dried over activated 4A molecular sieves and then refluxed and distilled under N_2 from Na/K alloy (light petroleum (bp 40–60 °C), pentane), sodium (toluene), sodium/benzophenone (tetrahydrofuran, diethyl ether), calcium hydride (dichloromethane, acetonitrile) or magnesium(II) methoxide (methanol). CD_2Cl_2 and $CDCl_3$ were stirred over calcium hydride, distilled and degassed prior to use. d_6-DMSO was dried over activated 4A molecular sieves and degassed prior to use. Elemental analyses (Oxidative Digestion/TCD) were performed by the Microanalytical Service of the Inorganic Chemistry Laboratory, University of Oxford. Electrospray (ES,

Table 3 Heck arylation results

Catalyst	mol%	Yield (%)	TON
$[PdCl_2(MeS{\sim}PPh_2)]$	0.001	100.0	100000 ± 8000
	0.0001	15.0	150000 ± 10000
$[PdCl_2(^tBuS{\sim}PPh_2)]$	0.001	100.0	100000 ± 7000
	0.0001	13.0	130000 ± 10000
$[PdCl_2(PhS{\sim}PPh_2)]$	0.001	100.0	100000 ± 7000
	0.0001	4.5	45000 ± 3000
$[Pd_2(\mu\text{-}OAc)_2\{2\text{-}CH_2C_6H_4P(o\text{-}Tol)_2\}_2]$	0.001	100.0	100000 ± 4000
	0.0001	15.5	150000 ± 7000

o-Tol = 2-$CH_3C_6H_4$

methanol–acetonitrile–water (1 : 1 : 1) eluent), electron ionization (EI, 70 eV) and field ionization (FI) mass spectroscopy was performed by the Mass Spectroscopy Service of the Inorganic Chemistry Laboratory, University of Oxford. NMR spectra were acquired on a Varian UNITY*plus* (^{1}H 500 MHz, ^{13}C 126 MHz, ^{31}P 202 MHz) or a Varian Mercury V*x*Works (^{1}H 300 MHz, ^{13}C 76 MHz, ^{31}P 122 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances relative to $SiMe_4$ (^{1}H, ^{13}C, $\delta = 0$) or externally to 85% H_3PO_4 (^{31}P, $\delta = 0$). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz. CO/ethene copolymerisations were performed using a Parr 4561 (300 mL) stainless steel stirred reactor fitted with a glass liner. GC-MS chromatographs and spectra were acquired on an Agilent 6890 Plus instrument fitted with a SGE 15 m × 0.25 mm (i.d.) BPX5 capillary column coupled to a Micromass GCT instrument operating in chemical ionization (CI, NH_3) mode. GC chromatographs were acquired on a Unicam ProGC instrument fitted with a 2 m × 4 mm (i.d.) Carbowax 20 M packed column.

$C_6H_5CH_2NMe_2$, TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), ^{n}BuLi in hexanes (1.6 M), MeSSMe, ^{t}BuSS^{t}Bu, PhSSPh, MeI, HOTs·H_2O, $AgBF_4$, 1-methyl-2-pyrrolidinone (NMP), C_6H_5Br, ^{n}BuO$_2$CCHCH$_2$ (Aldrich), $HPPh_2$ (Strem), $Pd(OAc)_2$ (Alfa-Aesar) and CO : C_2H_4 (1 : 1 by moles) (BOC) were purchased and used as received.

2-$MeSC_6H_4CH_2NMe_2$[15] (**Ia**), $[PdCl_2(COD)]$,[48] [PdClMe(COD)][49] and $[PtMe_2(COD)]$[50] were prepared according to the literature methods.

2-^{t}BuSC$_6$H$_4$CH$_2$NMe$_2$ (Ib). A solution of $C_6H_5CH_2NMe_2$ (0.05 mol, 6.76 g, 7.51 mL) and TMEDA (0.05 mol, 5.81 g, 7.55 mL) in tetrahydrofuran (50 mL) was transferred into a 500 mL three-necked round-bottomed flask equipped with two dropping funnels and a magnetic stirrer. ^{n}BuLi in hexanes (1.6 M, 0.075 mol, 46.88 mL) was added dropwise to the vigorously stirred amine solution at room temperature and the mixture stirred for 24 h. To the orange/red mixture was added a solution of ^{t}BuSS^{t}Bu (0.055 mol, 9.81 g, 10.63 mL) in tetrahydrofuran (50 mL) dropwise at 0 °C. The mixture was stirred at room temperature overnight and was then quenched with ice-water (*ca*. 150 mL). Under air, the tetrahydrofuran phase was separated, the aqueous phase extracted with diethyl ether (3 × 100 mL) and all ethereal solutions combined, dried over Na_2SO_4, filtered and the solvent evaporated off the filtrate under reduced pressure. Fractional distillation under reduced pressure afforded crude **Ib** (73–83 °C/0.13 mbar, 3.64 g) as a light-yellow oil.

2-PhSC$_6$H$_4$CH$_2$NMe$_2$ (Ic). A solution of $C_6H_5CH_2NMe_2$ (0.107 mol, 14.42 g, 16.02 mL) and TMEDA (0.107 mol, 12.39 g, 16.10 mL) in tetrahydrofuran (75 mL) was transferred into a 500 mL three-necked round-bottomed flask equipped with two dropping funnels and a magnetic stirrer. ^{n}BuLi in hexanes (1.6 M, 0.16 mol, 100 mL) was added dropwise to the vigorously stirred amine solution at room temperature and the mixture stirred for 24 h. To the orange/red mixture was added a solution of PhSSPh (0.117 mol, 25.62 g) in tetrahydrofuran (80 mL) dropwise at 0 °C. The mixture was stirred at room temperature overnight and was then quenched with alkaline ice-water (NaOH, pH 10, *ca*. 200 mL). Under air, the tetrahydrofuran phase was separated, the aqueous phase extracted with diethyl ether (3 × 175 mL) and all ethereal solutions combined, dried over Na_2SO_4, filtered and the solvent evaporated off the filtrate under reduced pressure. Fractional distillation under reduced pressure afforded crude **Ic** (124–126 °C/0.13 mbar, 18.12 g) as a yellow oil.

Ic can be purified as follows: To a vigorously stirred solution of crude **Ic** (6.87 g) in methanol (35 mL) was added $HCl_{(aq)}$ (12.9 M, 10.5 mL) dropwise at 0 °C. The brown suspension was stirred for 1 h, filtered and the solvent evaporated off the filtrate under reduced pressure. The resultant brown oil was extracted with deionized water (3 × 75 mL) and filtered. To the vigorously stirred filtrate was added K_2CO_3 (19.52 g) slowly at 0 °C and the mixture then stirred for 2 h. Extraction with diethyl ether (3 × 150 mL), drying over Na_2SO_4, filtration and evaporation of solvent off the filtrate under reduced pressure gave purer **Ic** (3.84 g).

2-MeSC$_6$H$_4$CH$_2$NMe$_3$I (IIa). To a vigorously stirred solution of crude **Ia** (1.21 g) in acetonitrile (7 mL) was added MeI (8.61 mmol, 1.22 g, 0.54 mL) dropwise at room temperature. The mixture was stirred overnight and the resultant off-white suspension then filtered. The residue was washed with diethyl ether (2 × 15 mL), filtered and dried under reduced pressure to afford **IIa** (1.04 g, 3.22 mmol, 23% over two steps).

IIa is soluble in dichloromethane, chloroform, acetonitrile and methanol. It is insoluble in tetrahydrofuran, diethyl ether, toluene and hexane.

2-^{t}BuSC$_6$H$_4$CH$_2$NMe$_3$I (IIb). To a vigorously stirred solution of crude **Ib** (1.51 g) in acetonitrile (8 mL) was added MeI (10.1 mmol, 1.43 g, 0.63 mL) dropwise at room temperature. The mixture was stirred overnight and the solvent then evaporated under reduced pressure. The resultant off-white solid was washed with diethyl ether (2 × 15 mL), filtered and dried under reduced pressure to afford **IIb** (2.27 g, 6.20 mmol, 30% over two steps).

IIb is soluble in dichloromethane, chloroform, acetonitrile and methanol. It is insoluble in tetrahydrofuran, diethyl ether, toluene and hexane.

2-PhSC$_6$H$_4$CH$_2$NMe$_3$I (IIc). To a vigorously stirred solution of crude **Ic** (5.13 g) in acetonitrile (10 mL) was added MeI (21.7 mmol, 3.07 g, 1.35 mL) dropwise at room temperature. The mixture became warm, was stirred overnight and the solvent was then evaporated under reduced pressure. Under air, the resultant off-white solid was washed with diethyl ether (4 × 60 mL), filtered and dried under reduced pressure to afford crude **IIc** (5.67 g).

Crude **IIc** is soluble in dichloromethane, chloroform, acetonitrile and methanol. It is insoluble in tetrahydrofuran, diethyl ether, toluene and hexane.

2-MeSC$_6$H$_4$CH$_2$PPh$_2$ (MeS∼PPh$_2$). To a vigorously stirred suspension of small pieces of sodium (6.0 mmol, 0.138 g) in tetrahydrofuran (20 mL) was added $HPPh_2$ (5.0 mmol, 0.931 g, 0.87 mL) dropwise at room temperature. The red phosphide solution was stirred overnight and then added dropwise to a vigorously stirred suspension of **IIa** (4.0 mmol, 1.30 g) in tetrahydrofuran (20 mL) at room temperature over the course of 0.25 h. The mixture was stirred overnight and a light-brown solution resulted. Evaporation of solvent under reduced pressure gave a solid which was extracted with diethyl ether (3 × 15 mL) and filtered. The light-yellow filtrate was evaporated of solvent under reduced pressure and left to crystallize at room temperature for 2 d. The white solid was washed with methanol (8 mL), filtered and dried under reduced pressure to give MeS∼PPh_2 (0.670 g, 2.1 mmol, 52%).

MeS∼PPh_2 is soluble in dichloromethane, chloroform, acetonitrile, tetrahydrofuran, diethyl ether and toluene. It is insoluble in methanol and light petroleum (bp 40–60 °C).

2-^{t}BuSC$_6$H$_4$CH$_2$PPh$_2$ (^{t}BuS∼PPh$_2$). To a vigorously stirred suspension of small pieces of sodium (8.4 mmol, 0.193 g) in tetrahydrofuran (25 mL) was added $HPPh_2$ (6.2 mmol, 1.15 g, 1.07 mL) dropwise at room temperature. The red phosphide solution was stirred for 9 h and then added dropwise to a vigorously stirred suspension of **IIb** (5.8 mmol, 2.12 g) in tetrahydrofuran (30 mL) at room temperature over the course of 1.5 h. The mixture was stirred overnight and an orange solution resulted. Evaporation of solvent under reduced pressure

gave an orange oil which was extracted with diethyl ether (3 × 20 mL) and filtered. The orange–brown filtrate was evaporated of solvent under reduced pressure, extracted with light petroleum (bp 40–60 °C) (2 × 10 mL) and filtered. The yellow filtrate was evaporated of solvent under reduced pressure and cooled to −78 °C. Addition of methanol (3 × 5 mL) gave a white solid which was filtered through a glass frit and dried under reduced pressure to give ^{t}BuS∼PPh$_2$ (0.839 g, 2.3 mmol, 37%).

^{t}BuS∼PPh$_2$ is soluble in dichloromethane, chloroform, acetonitrile, tetrahydrofuran, diethyl ether and toluene. It is sparingly soluble in methanol and pentane.

2-PhSC$_6$H$_4$CH$_2$PPh$_2$ (PhS∼PPh$_2$). A solution of HPPh$_2$ (5.2 mmol, 0.966 g, 0.90 mL) in tetrahydrofuran (11 mL) was added dropwise into a vigorously stirred solution of ^{n}BuLi in hexanes (1.6 M, 5.2 mmol, 3.24 mL) at −40 °C. The orange solution was stirred at −40 °C for 2 h and then added dropwise into a vigorously stirred suspension of crude **IIc** (2.000 g) in tetrahydrofuran (88 mL) at −78 °C over the course of 0.5 h. The mixture was stirred overnight and an orange solution resulted. Evaporation of solvent under reduced pressure gave an orange oil which was extracted with diethyl ether (3 × 10 mL) and filtered. The light-yellow filtrate was evaporated of solvent under reduced pressure and triturated with methanol (15 mL). The resultant off-white solid was washed with methanol (20 mL), filtered and dried under reduced pressure to give crude PhS∼PPh$_2$ (1.84 g).

PhS∼PPh$_2$ is soluble in dichloromethane, chloroform, tetrahydrofuran and toluene. It is sparingly soluble in acetonitrile and diethyl ether and insoluble in methanol and pentane.

[PdCl$_2$(MeS∼PPh$_2$)]. [PdCl$_2$(COD)] (0.62 mmol, 0.177 g) and MeS∼PPh$_2$ (0.62 mmol, 0.200 g) were suspended in methanol (20 mL) and vigorously stirred at room temperature for 23 h. The resultant yellow-green suspension was filtered and the residue washed with methanol (2 × 7.5 mL), filtered, washed with diethyl ether (7.5 mL), filtered and dried under reduced pressure to give [PdCl$_2$(MeS∼PPh$_2$)] (0.253 g, 0.51 mmol, 82%).

Alternatively, the solids [PdCl$_2$(COD)] (0.31 mmol, 0.089 g) and MeS∼PPh$_2$ (0.31 mmol, 0.100 g) were mixed in a Schlenk tube and cold (−78 °C) tetrahydrofuran was added (50 mL). The reaction mixture was left stirring for 10 h and the solids then removed by filtration. The filtrate was concentrated to 5 mL, layered with pentane and stored at −20 °C. Light-yellow crystals of [PdCl$_2$(MeS∼PPh$_2$)] formed, were isolated by filtration and dried under reduced pressure (0.120 g, 0.24 mmol, 77%). Crystals suitable for X-ray diffraction were grown from a two-phase dichloromethane/pentane liquid diffusion system at −20 °C. X-ray diffraction shows that this is a different polymorph than that reported by us earlier.[9]

[PdCl$_2$(MeS∼PPh$_2$)] is soluble in dichloromethane and hot dimethyl sulfoxide. It is sparingly soluble in chloroform, methanol, tetrahydrofuran and toluene and insoluble in acetonitrile, diethyl ether and hexane.

[PdCl$_2$(^{t}BuS∼PPh$_2$)]. [PdCl$_2$(COD)] (0.53 mmol, 0.150 g) and ^{t}BuS∼PPh$_2$ (0.53 mmol, 0.191 g) were suspended in methanol (20 mL) and vigorously stirred at room temperature for 18 h. The resultant orange suspension was filtered and the residue washed with methanol (2 × 7.5 mL), filtered, washed with diethyl ether (10 mL), filtered and dried under reduced pressure to give [PdCl$_2$(^{t}BuS∼PPh$_2$)] (0.184 g, 0.34 mmol, 65%). Crystals suitable for X-ray diffraction were grown from a two-phase dichloromethane/methanol liquid diffusion system.

[PdCl$_2$(^{t}BuS∼PPh$_2$)] is soluble in dichloromethane, acetonitrile, *N*,*N*-dimethylformamide and warm dimethyl sulfoxide. It is sparingly soluble in chloroform, tetrahydrofuran, benzene and toluene and insoluble in methanol, diethyl ether and hexane.

[PdCl$_2$(PhS∼PPh$_2$)]. [PdCl$_2$(COD)] (0.65 mmol, 0.186 g) and PhS∼PPh$_2$ (0.65 mmol, 0.250 g) were suspended in methanol (20 mL) and vigorously stirred at room temperature for 20 h. The resultant orange–green suspension was filtered and the residue washed with methanol (2 × 10 mL), filtered, washed with diethyl ether (2 × 7.5 mL), filtered and dried under reduced pressure to give [PdCl$_2$(PhS∼PPh$_2$)] (0.292 g, 0.52 mmol, 80%). Crystals suitable for X-ray diffraction were grown from a supersaturated d$_6$-DMSO solution.

[PdCl$_2$(PhS∼PPh$_2$)] is soluble in dichloromethane, *N*,*N*-dimethylformamide and hot dimethyl sulfoxide. It is sparingly soluble in chloroform, acetonitrile, methanol, tetrahydrofuran, benzene and toluene and insoluble in diethyl ether and hexane.

[PdClMe(MeS∼PPh$_2$)]. A cold (−78 °C) solution of MeS∼PPh$_2$ (0.31 mmol, 0.100 g) in tetrahydrofuran (40 mL) was added dropwise to a cold (−78 °C) tetrahydrofuran solution of [PdClMe(COD)] (0.31 mmol, 0.082 g). The complex precipitated out of solution as a white powder after 1 h of stirring. The reaction mixture was left to reach room temperature and the filtrate was removed by filtration. The filtrate was concentrated to 5 mL, layered with pentane and stored at −20 °C to yield a second crop of pure complex (total yield: 0.103 g, 0.21 mmol, 69%). Light-yellow crystals of [PdClMe(MeS∼PPh$_2$)] suitable for X-ray diffraction were grown from a two-phase dichloromethane/pentane liquid diffusion system.

[PdClMe(MeS∼PPh$_2$)] is soluble in dichloromethane, chloroform and tetrahydrofuran. It is sparingly soluble in toluene and insoluble in pentane and hexane.

[PtMe$_2$(MeS∼PPh$_2$)]. A cold (−78 °C) solution of MeS∼PPh$_2$ (0.31 mmol, 0.100 g) in tetrahydrofuran (40 mL) was added dropwise to a cold (−78 °C) tetrahydrofuran solution of [PtMe$_2$(COD)] (0.31 mmol, 0.103 g). The reaction mixture was left to reach room temperature under stirring in darkness for 10 h. The volatiles were removed under reduced pressure to give a white powder, which was washed with pentane and recrystallized from a two-phase tetrahydrofuran/pentane liquid diffusion system. Yellow crystals of [PtMe$_2$(MeS∼PPh$_2$)] suitable for X-ray diffraction were thus formed and isolated by filtration. Yield: 0.087 g, 0.16 mmol, 51%.

[PtMe$_2$(MeS∼PPh$_2$)] is soluble in CH$_2$Cl$_2$, CHCl$_3$ and THF. It is sparingly soluble in toluene and insoluble in pentane and hexane.

CO/ethene copolymerisation testing. Pd(OAc)$_2$ (0.02 mmol, 4.5 mg), RS∼PPh$_2$ (0.022 mmol) and HOTs·H$_2$O (0.04 mmol, 7.6 mg) were placed into a stirred reactor. The reactor was thoroughly purged with N$_2$ and methanol (55 mL) was added. The solution was degassed, all reactor valves closed and the solution then heated up to 80 °C with vigorous stirring (1400 rpm) for 1 h. The reactor was pressurized to 40 bar with CO : C$_2$H$_4$ (1 : 1 by moles) and left for another 2 h. It was then cooled to room temperature, vented and opened. Under air, the grey suspension was filtered and the filtrate immediately analyzed by GC-MS. The residue was washed with methanol (3 × 12 mL), filtered and dried under reduced pressure at 80 °C.

To a solution of [PdClMe(MeS∼PPh$_2$)] (0.02 mmol, 9.6 mg) in dichloromethane : acetonitrile (9 mL : 0.05 mL) was added AgBF$_4$ (0.024 mmol, 4.7 mg) and the mixture stirred for 2 min. The suspension was filtered into a thoroughly N$_2$-purged stirred reactor and dichloromethane (46 mL) was added. The solution was degassed, all reactor valves closed and the solution then heated up to 80 °C with vigorous stirring (1400 rpm) for 0.5 h. The reactor was pressurized to 40 bar with CO : C$_2$H$_4$ (1 : 1 by moles) and left for another 2 h. It was then cooled to room temperature, vented and opened. Under air, the grey suspension was filtered and the filtrate immediately analyzed by GC-MS. The residue was washed with dichloromethane (3 × 15 mL), filtered and dried under reduced pressure at 80 °C.

Heck arylation testing. Under air, a stock solution of [PdCl$_2$(RS∼PPh$_2$)] in 1-methyl-2-pyrrolidinone (NMP) was prepared and 5 mL thereof transferred into a 100 mL ampoule

Table 4 Crystallographic data

	$[PdCl_2(MeS{\sim}PPh_2)]\cdot CH_2Cl_2$	$[PdCl_2(^tBuS{\sim}PPh_2)]$	$[PdCl_2(PhS{\sim}PPh_2)]$	$[PdClMe(MeS{\sim}PPh_2)]$	$[PtMe_2(MeS{\sim}PPh_2)]$
Chemical formula	$C_{42}H_{42}Cl_8P_2Pd_2S_2$	$C_{23}H_{25}Cl_2PPdS$	$C_{25}H_{21}Cl_2PPdS$	$C_{21}H_{22}ClPPdS$	$C_{22}H_{25}PPtS$
Formula weight	1169.30	541.79	561.79	479.30	547.57
T/K	150	150	150	150	150
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	10.3529(2)	12.5554(4)	9.8876(3)	8.7350(10)	8.7885(2)
b/Å	11.5466(2)	15.0824(5)	13.0573(4)	9.2150(10)	15.0806(3)
c/Å	19.6892(4)	12.7084(4)	17.6637(6)	14.7010(10)	16.1036(4)
α/°	86.8988(8)	90	90	101.530(2)	90
β/°	78.5238(8)	109.7231(14)	96.6649(12)	97.460(2)	104.9820(8)
γ/°	87.2643(7)	90	90	116.200(2)	90
V/Å^3	2301.59(8)	2265.35(13)	2265.07(12)	1007.81(18)	2061.75(8)
Z	2	4	4	2	4
D_c/Mg m^{-3}	1.687	1.588	1.647	1.579	1.764
μ/mm^{-1}	1.437	1.225	1.229	1.237	6.986
$F(000)$	1168	1096	1128	484	1064
θ Range for data collection/°	5.0–27.5	5.107–27.496	5.110–27.513	2.679–27.534	5.0–27.5
Reflections measured	19293	9161	8928	8187	7962
Unique reflections	10514	5117	5118	4579	4666
R_{int}	0.03	0.03	0.05	0.02	0.02
Obs. reflections ($I > 3\sigma(I)$)	6679	3429	3808	3219	4256
Parameters refined	505	253	271	226	226
Goodness of fit	1.0776	1.1108	1.0609	1.0815	1.0168
R_1	0.0308	0.0317	0.0500	0.0558	0.0210
wR_2	0.0335	0.0337	0.0534	0.0568	0.0268
$\Delta\rho_{max,\,min}$/e Å^{-3}	−0.68, 0.92	−0.70, 0.59	−1.18, 0.98	−0.80, 3.13	−1.26, 1.11

equipped with a Young's Tap™ and a magnetic stirrer. C_6H_5Br (5 mmol, 0.785 g, 0.527 mL), $^nBuO_2CCHCH_2$ (6 mmol, 0.769 g, 0.860 mL) and anhydrous Na_2CO_3 (6 mmol, 0.636 g) were added and the ampoule closed. The mixture was vigorously stirred at 130 °C for 72 h, cooled to room temperature and immediately analyzed by GC.

X-Ray crystallography

In each case, a single crystal was selected under an inert atmosphere, encased in perfluoro-polyether oil and mounted on the end of a glass fibre. The fibre, secured in a goniometer head, was placed under a cold stream of N_2 maintained at 150 K and diffraction data then collected on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The images were processed with DENZO and SCALEPACK programs[51] and corrections for absorption, Lorentz and polarisation effects performed. The structures were solved by direct methods using the SIR92[54] program and refined by full-matrix least squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters after each cycle of refinement. Three-term Chebychev polynomial weighting schemes were applied. All solution, refinement, and graphical calculations were performed using the CRYSTALS[52] and CAMERON[53] programs. The crystallographic data are summarised in Table 4.

CCDC reference numbers 257327–257331.

See http://www.rsc.org/suppdata/dt/b5/b502195b/ for crystallographic data in CIF or other electronic format.

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