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Versatile coordination modes of novel hemilabile S-NHC ligands.

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S1. Synthesis and characterisation of the compounds

**General procedures.** All operations were carried out using standard Schlenk techniques under inert atmosphere. Solvents were purified and dried under nitrogen by conventional methods. d_6-DMSO was degassed and stored over 4 Å molecular sieves. CD_2Cl_2 was dried over 4 Å molecular sieves, degassed by freeze-pump-thaw cycles and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz; ^{31}P, 121.49 MHz and ^{19}F, 282.38 MHz) and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC and ^{1}H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000-100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg and by the “Service Central d’Analyse”, USR-59/CNRS, Solaize. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulising gas and Maldi-TOF analyses were carried out on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1.8.9 trihydroxyanthracene) as a matrix. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 µm film thickness). The complexes [PdCl_2(NCPh)_2]^{S1} and [PdCl(µ-Cl)(PPh_3)]^{S2} were prepared according to literature methods. All other reagents were used as received from commercial suppliers.

![Chemical structures](image)

Formula of imidazolium salts and complexes described in this paper.


Synthesis of N-(R)-N’-ethyl- (R’)-sulfide imidazolium chlorides:

1-HCl: R = methyl; R’ = ethyl:

Pure 1-methylimidazole (4.85 ml, 5.00 g, 60.90 mmol) and 2-chloroethyl ethylsulfide (7.09 ml, 7.59 g, 60.90 mmol) were placed in a Schlenk tube equipped with a magnetic stirrer. The mixture was heated for 2 h at 150 °C and then allowed to cool to room temperature. During heating, the colourless mixture turned brown and became more viscous. After cooling, the brown oil was washed 2 times with 40 ml of dry THF and dried in vacuo. These compounds are known to be very hygroscopic and the elemental analyses performed always afforded carbon and nitrogen percentages lower than theoretical values. Yield: 96%. Anal. Calc. for C₆H₅ClN₂S (220.74): C, 46.48; H, 7.31; N, 13.55. Found: C, 45.5; H, 7.2; N, 12.2. FTIR: ν_max(pure, diamond orbit)/cm⁻¹: 3373br, 3137sh, 3038s, 2958s, 2866m, 1563s, 1450m, 1426m, 1375w, 1334w, 1266w, 1162vs, 869w, 759s, 716w. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 1.20 (3H, t, ³J = 7.4 Hz, SCH₂CH₃), 2.60 (2H, q, ³J = 7.4 Hz, SCH₂CH₃), 3.04 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 4.03 (3H, s, NCH₃), 4.57 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 7.41 (1H, pseudo t, ³J = 4J = 1.8 Hz, CH=CH), 7.56 (1H, pseudo t, ³J = 4J = 1.8 Hz, CH=CH), 10.41 (1H, br s, NCHN). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 14.53 (SCH₂CH₃), 25.85 (SCH₂CH₃), 31.73 (NCH₂CH₂S), 36.50 (NCH₃), 49.11 (NCH₂CH₂S), 122.38, 122.93 (CH=CH), 138.33 (NCN). MS (ESI): m/z 171.1 [M-Cl]⁺.

2-HCl: R = n-butyl; R’ = ethyl:

The same procedure was used with 1-n-butylimidazole (5.29 ml, 5.00 g, 40.26 mmol) and 2-chloroethyl ethylsulfide (4.69 ml, 5.018 g, 40.26 mmol). Yield: 98%. Anal. Calc. for C₁₃H₂₅ClN₂S (248.82): C, 53.10; H, 8.51; N, 11.26. Found: C, 51.9; H, 8.6; N, 9.5. FTIR: ν_max(pure, diamond orbit)/cm⁻¹: 3378br, 3040s, 2929s, 2869m, 1561s, 1452m, 1374w, 1266w, 1159vs, 1062w, 972w, 949w, 869w, 752m. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 0.91 (3H, t, ³J = 7.5 Hz, CH₃ butyl), 1.18 (3H, t, ³J = 7.4 Hz, SCH₂CH₃), 1.33 (2H, m, NCH₂CH₂CH₂CH₃), 1.85 (2H, m, NCH₂CH₂CH₂CH₃), 2.58 (2H, q, ³J = 7.4 Hz, SCH₂CH₃), 3.04 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 4.27 (2H, t, ³J = 7.2 Hz, NCH₂CH₂CH₂CH₃), 4.57 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 7.46 (1H, pseudo t, ³J = 4J = 1.8 Hz, CH=CH), 7.73 (1H, pseudo t, ³J = 4J = 1.8 Hz, CH=CH), 10.45 (1H, br s, NCHN). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 13.21 (CH₃ butyl), 14.54 (SCH₂CH₃), 19.35 (NCH₂CH₂CH₂CH₃), 25.75 (SCH₂CH₃), 31.75 (NCH₂CH₂S), 32.00 (NCH₂CH₂CH₂CH₃), 48.97 (NCH₂CH₂CH₂CH₃), 49.64 (NCH₂CH₂S), 121.67, 122.71 (CH=CH), 137.71 (NCN). MS (ESI): m/z 213.1 [M-Cl]⁺.

3-HCl: R = methyl; R’ = phenyl:

The same procedure was used with 1-methylimidazole (4.85 ml, 5.00 g, 60.90 mmol) and 2-chloroethyl phenylsulfide (8.96 ml, 10.52 g, 60.90 mmol). Yield: 95%. Anal. Calc. for C₁₃H₁₅ClN₂S (254.78): C, 56.57; H, 5.93; N, 11.00. Found: C, 55.3; H, 6.3; N, 9.4. FTIR: ν_max(pure, diamond orbit)/cm⁻¹: 3367br, 3045m, 2958s, 2849w, 1571s, 1473m, 1437s, 1334w, 1301w, 1170vs, 1086m,
1023m, 999w, 872m, 741vs, 691vs. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 3.52 (2H, t, ³J = 6.3 Hz, NCH₂CH₂S), 3.93 (3H, s, NCH₃), 4.53 (2H, pseudo t, ³J = 6.3 Hz, NCH₂CH₂S), 7.20-7.41 (6H, m, H arom + CH=CH), 7.55 (1H, t, ³J = 4 ⁴J = 2.1 Hz, CH=CH), 10.36 (1H, br s, NCHN). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 34.10 (NCH₂S), 54.74 (NCH₂CH₂S), 75.50 (CH₂CH₂S), 116.20, 122.89, 123.58 (CH=CH), 129.40 (C₆H₅S), 130.08 (C₆H₅), 141.87 (CH=CH), 151.24 (CH₃S), 282.40 (NCH₂CH₂S). FTIR (νmax/pure, diamond orbit)/cm⁻¹: 3374br, 3137w, 3056w, 2958m, 2871w, 1627m, 1561s, 1438s, 1333w. Found: C, 28.9; H, 5.2; N, 7.7.

General procedure for the anion exchange:

I·PF₆: R = methyl; R’ = ethyl;

The imidazolium chloride I·HCl (1.96 g, 9.53 mmol) and solid KPF₆ (8.77 g, 47.64 mmol) were dissolved in a CH₂Cl₂/H₂O (1:2) mixture and stirred for 2 days at room temperature. Then the suspension was filtered through a Celite pad and the solvent was evaporated under reduced pressure to give a brown oil. Yield: 98%. Anal. Calc. for C₉H₁₀F₆N₃PS (316.25): C, 30.38; H, 4.78; N, 8.86. Found: C, 28.9; H, 5.2; N, 7.7. FTIR: νmax/pure, diamond orbit)/cm⁻¹: 3169w, 3123w, 2964w, 2931w, 2872w, 1564m, 1536m, 1507m, 1456w, 1380w, 1360w, 1207m, 1162s, 1025m, 824vs, 740s, 703m. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 1.23 (3H, t, ³J = 7.5 Hz, SCH₂CH₃), 2.56 (2H, q, ³J = 7.5 Hz, SCH₂CH₃), 2.96 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 3.91 (3H, s, NCH₃), 4.33 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 7.34 (1H, pseudo t, ³J = 4 ⁴J = 1.8 Hz, CH=CH), 7.42 (1H, pseudo t, ³J = 4 ⁴J = 1.8 Hz, CH=CH), 8.49 (1H, br s, NCHN). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 14.40 (SCH₂CH₃), 25.70 (SCH₂CH₃), 31.26 (NCH₂CH₂S), 36.22 (NCH₃), 49.26 (NCH₂CH₂S), 122.56, 123.56 (CH=CH), 136.00 (NCN). ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz) δ: -143.1 (sept., ¹Jₚ,F = 711 Hz, PF₆). ¹⁹F{¹H} NMR (CD₂Cl₂, 282.4 MHz) δ: -72.4 (d, ¹Jₚ,F = 711 Hz, PF₆). MS (ESI): m/z 171.1 [M-PF₆]⁺.
**General procedure for the synthesis of the silver (I) carbene complexes:**

1·AgCl: R = methyl; R’ = ethyl;

The imidazolium 1·HCl (0.300 g, 1.47 mmol) was dissolved in dry CH₂Cl₂ and solid Ag₂O (0.340 g, 1.47 mmol) was added under nitrogen. The reaction mixture was stirred for 2 h in the dark at room temperature. The suspension was filtered through a Celite pad and the solvent was evaporated under reduced pressure to give a light sensitive white solid. Yield: 82%. Anal. Calc. for C₆H₁₄AgClN₂S (355.68): C, 30.64; H, 4.50; N, 8.93. Found: C, 29.9; H, 4.7; N, 8.5. 

1H NMR (CD₂Cl₂, 300 MHz) δ: 1.28 (3H, t, J = 7.4 Hz, SCH₂CH₃), 2.57 (2H, q, J = 7.4 Hz, SCH₂CH₃), 2.96 (2H, t, J = 6.7 Hz, NCH₂CH₂S), 3.86 (3H, s, NCH₃), 4.31 (2H, t, J = 6.7 Hz, NCH₂CH₂S), 7.03 and 7.11 (2H, AB spin system, J = 1.8 Hz, CH=CH). 13C {¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 14.60 (SCH₂CH₃), 26.34 (SCH₂CH₃), 33.09 (NCH₂CH₂S), 38.85 (NCH₃), 51.50 (NCH₂CH₂S), 121.49, 122.19 (CH=CH), 180.19 (NCN). MS (ESI): m/z 277.0 [M-Cl]⁺.

2·AgCl: R = n-butyl; R’ = ethyl;

The same procedure was used with 2·HCl (0.300 g, 1.21 mmol) and Ag₂O (0.280 g, 1.21 mmol). Yield: 78%. Anal. Calc. for C₁₁H₂₀AgClN₂S (355.68): C, 37.15; H, 5.67; N, 7.88. Found: C, 36.5; H, 5.7; N, 7.1. 

1H NMR (CD₂Cl₂, 300 MHz) δ: 0.97 (3H, t, J = 7.5 Hz, CH₃butyl), 1.25 (3H, t, J = 7.4 Hz, SCH₂CH₃), 1.37 (2H, m, NCH₃CH₂CH₂CH₃), 1.82 (2H, m, NCH₂CH₂CH₂CH₃), 2.54 (2H, q, J = 7.4 Hz, SCH₂CH₃), 2.96 (2H, t, J = 6.6 Hz, NCH₂CH₂S), 4.13 (2H, t, J = 7.2 Hz, NCH₂CH₂CH₂CH₃), 4.32
(2H, t, $^3J = 6.6$ Hz, NCH$_2$CH$_2$S), 7.07 and 7.15 (2H, AB spin system, $^3J = 1.8$ Hz, CH=CH). $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, 75.5 MHz) δ: 13.44 (CH$_3$ butyl), 14.59 (SCH$_2$CH$_2$), 19.69 (NCH$_2$CH$_2$CH$_2$CH$_3$), 26.34 (SCH$_2$CH$_2$), 33.08 (NCH$_2$CH$_2$S), 33.44 (NCH$_2$CH$_2$CH$_2$CH$_3$), 51.66 (NCH$_2$CH$_2$CH$_2$CH$_3$), 51.90 (NCH$_2$CH$_2$S), 120.86, 121.45 (CH=CH), 179.44 (NCN). MS (ESI): m/z 319.0 [M-Cl]$^+$. 

$\textit{3} \cdot \text{AgCl}$: $R = \text{methyl} \ ; R' = \text{phenyl}$:
The same procedure was used with $\textit{3} \cdot \text{HCl}$ (0.300 g, 1.01 mmol) and Ag$_2$O (0.230 g, 1.01 mmol). Yield: 81%. Anal. Calc. for C$_{12}$H$_{14}$AgClN$_2$S (361.64): C, 39.0; H, 3.9; N, 7.75. Found: C, 39.0; H, 3.9; N, 6.8. FTIR: $\nu_{\text{max}}$(pure, diamond orbit)/cm$^{-1}$ 3444br, 3095w, 2942w, 1580m, 1478m, 1458m, 1437m, 1404m, 1350w, 1273w, 1221m, 1155w, 1112w, 1086w, 1023w, 735vs, 690s, 659w. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 3.36 (2H, t, $^3J = 6.6$ Hz, NCH$_2$CH$_2$S), 3.74 (3H, s, NCH$_3$), 4.31 (2H, t, $^3J = 6.6$ Hz, NCH$_2$CH$_2$S), 7.01 (1H, br s, CH=CH), 7.13 (1H, br s, CH=CH), 7.16-7.35 (5H, m, H arom). $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, 75.5 MHz) δ: 35.05 (NCH$_2$CH$_2$S), 38.81 (NCH$_2$), 51.03 (NCH$_2$CH$_2$S), 121.72, 122.38 (CH=CH), 126.59 (C para), 129.28 (C meta), 128.50 (C ortho), 134.54 (C ipso), 180.41 (NCN). MS (ESI): m/z 545.1 [Ag(3)]$^+$. 

$\textit{4} \cdot \text{AgCl}$: $R = \text{n-butyl} \ ; R' = \text{phenyl}$:
The same procedure was used with $\textit{4} \cdot \text{HCl}$ (0.320 g, 1.07 mmol) and Ag$_2$O (0.250 g, 1.07 mmol). Yield: 80%. Anal. Calc. for C$_{15}$H$_{20}$AgClN$_2$S (403.72): C, 44.63; H, 4.99; N, 6.94. Found: C, 43.8; H, 5.7; N, 6.2. FTIR: $\nu_{\text{max}}$(pure, diamond orbit)/cm$^{-1}$ 3456br, 3089w, 2955m, 2928m, 2869w, 1580w, 1478m, 1457m, 1437s, 1416s, 1344w, 1271w, 1227s, 1198m, 1086m, 1023m, 875w, 731vs, 689vs, 667sh. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 0.94 (3H, t, $^3J = 7.5$ Hz, CH$_3$ butyl), 1.32 (2H, m, CH$_2$CH$_3$), 1.75 (2H, m, CH$_2$CH$_2$CH$_3$), 3.37 (2H, t, $^3J = 6.7$ Hz, NCH$_2$CH$_2$S), 4.05 (2H, t, $^3J = 7.2$ Hz, NCH$_2$CH$_2$CH$_3$), 4.32 (2H, t, $^3J = 6.7$ Hz, NCH$_2$CH$_2$S), 7.03 (1H, d, $^3J = 1.8$ Hz, CH=CH), 7.15 (1H, br s, CH=CH), 7.18-7.38 (5H, m, H arom). $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, 75.5 MHz) δ: 13.56 (CH$_3$ butyl), 19.72 (CH$_2$CH$_3$), 33.43 (NCH$_2$CH$_2$S), 35.05 (CH$_2$CH$_2$CH$_3$), 51.12 (NCH$_2$CH$_2$CH$_3$), 51.84 (NCH$_2$CH$_2$S), 121.04, 121.69 (CH=CH), 126.62 (C para), 129.32 (C meta), 129.46 (C ortho), 134.55 (C ipso), 179.44 (NCN). MS (ESI): m/z 369.0 [M-Cl]$^+$. 

General procedure for the transmetallation reaction:
The imidazolium chloride was dissolved in dry CH$_2$Cl$_2$ and solid Ag$_2$O was added under nitrogen. The reaction mixture was stirred for 2 h in the dark at room temperature. Then the suspension was filtered through a Celite pad under nitrogen and the resulting clear solution was slowly added to a suspension of the desired palladium precursor. A white solid precipitated rapidly. The suspension was then filtered through Celite and the solvent was evaporated under reduced pressure. The resulting solid was then washed with pentane (2 x 25 mL) and crystallized from a dichloromethane/pentane solution.
Formation of 5 (R = methyl; R’ = ethyl): 1·HCl (0.190 g, 0.92 mmol), Ag₂O (0.213 g, 0.92 mmol) and [PdCl₂(NCPh₂)] (0.352 g, 0.92 mmol). Yield: 72%. This complex is poorly soluble in CH₂Cl₂ and in DMSO. Anal. Calc. for C₇₄H₇₂Cl₂N₂PdS (347.60): C, 27.64; H, 4.06; N, 8.06. Found: C, 27.8; H, 4.2; N, 7.6. FTIR: v max (pure, diamond orbit)/cm⁻¹ 3472br, 3154w, 3100w, 2954w, 2929w, 2225w, 2160w, 2034w, 1978w, 1566w, 1471s, 1446m, 1407s, 1373w, 1342w, 1284w, 1263w, 1238s, 1206m, 1166w, 1127w, 1089w, 1066w, 1051w, 969w, 883w, 847w, 739vs, 680vs, 310vs (v Pd-Cl), 298vs (v Pd-Cl). ¹H NMR (CD₂Cl₂, 300 MHz) δ: 1.40 (3H, t, ³J = 7.5 Hz, SCH₂CH₃), 2.61 (2H, m br, SCH₂CH₃), 3.03 (2H, m br, NCH₂CH₂S), 4.09 (3H, s, NCH₃), 4.45 (2H, t br, NCH₂CH₂S), 6.95 and 7.02 (2H, AB spin system, ³J = 1.8 Hz, CH=CH). MS (ESI): m/z 313.0 [M·Cl]⁺, 660.9 [2M·Cl]⁺.

Formation of 6 (R = methyl; R’ = ethyl): 1·HCl (0.188 g, 0.91 mmol), Ag₂O (0.211 g, 0.91 mmol) and [PdCl₂(NCPh₂)] (0.175 g, 0.46 mmol). Yield: 65%. This complex is poorly soluble in CH₂Cl₂ or CHCl₃. Anal. Calc. for C₃₆H₃₄Cl₂N₄PdS₂ (517.88): C, 37.11; H, 5.45; N, 10.82. Found: C, 37.0; H, 5.7; N, 10.2. FTIR: v max (pure, diamond orbit)/cm⁻¹ 3499br, 3125w, 3055w, 2991w, 2947w, 1576w, 1540w, 1473s, 1441s, 1407m, 1360w, 1334w, 1284w, 1237m, 1205w, 1106m, 1071sh, 1022w, 999w, 834w, 744vs, 684vs. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 1.26 (3H, t, ³J = 7.5 Hz, SCH₂CH₃), 2.59 (2H, q, ³J = 7.5 Hz, SCH₂CH₃), 3.21 (2H, m br, NCH₂CH₂S), 4.07 (3H, s, NCH₃), 4.63 (2H, t, ³J = 6.6 Hz, NCH₂CH₂S), 6.96 (1H, br, CH=CH), 7.12 (1H, br, CH=CH). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 14.64 (SCH₂CH₃), 22.32 (SCH₂CH₃), 32.54 (NCH₂CH₂S), 37.74 (NCH₃), 50.72 (NCH₂CH₂S), 121.68, 123.96 (CH=CH), (NCN) not observed. MS (ESI): m/z 483.0 [M·Cl]⁺.

Formation of 7 (R = methyl; R’ = ethyl): 1·HCl (0.400 g, 1.93 mmol), Ag₂O (0.452 g, 1.93 mmol) and [PdCl₂(µ-Cl)(PPh₃)]₂ (0.851 g, 0.97 mmol). Yield: 69%. This complex is soluble in CH₂Cl₂, CHCl₃ or THF, but insoluble in toluene or pentane. Anal. Calc. for C₉₀H₈₀Cl₂N₄P₂S₄ (609.89): C, 51.20; H, 4.79; N, 4.59. Found: C, 50.6; H, 4.8; N, 4.3. FTIR: v max (pure, diamond orbit)/cm⁻¹ 3380br, 3147w, 3087w, 3048w, 2960w, 2925w, 1568w, 1480m, 1468m, 1434s, 1404m, 1371w, 1337w, 1268m, 1230m, 1185w, 1169w, 1129w, 1098s, 1092s, 1026w, 997w, 853w, 762m, 750s, 741vs, 706s, 696vs, 685vs. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 1.24 (3H, t, ³J = 7.5 Hz, SCH₂CH₃), 2.49 (2H, q, ³J = 7.5 Hz, SCH₂CH₃), 2.86 (1H, m, NCH₂CHHS), 3.08 (1H, m, NCHHCH₂S), 3.59 (3H, s, NCH₃), 3.72 (1H, m, NCH₂CHHS), 4.42 (1H, m, NCHHCH₂S), 6.64 and 6.77 (2H, AB spin system, ³J = 2.1 Hz, CH=CH), 7.35-7.60 (15H, m, H arom). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 14.81 (SCH₂CH₃), 26.24 (SCH₂CH₃), 31.21 (NCH₂CH₂S), 37.53 (NCH₃), 50.62 (NCH₂CH₂S), 122.16, 122.84 (CH=CH), 128.55 (d, Jₚ-C = 11.0 Hz, CH arom), 129.83 (d, Jₚ-C = 54.1 Hz, Cₐryl), 131.23 (d, Jₚ-C = 2.4 Hz, CH arom), 134.03 (d, Jₚ-C = 11.1 Hz, CH arom), 161.01 (NCN). ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz) δ: 28.6. MS (ESI): m/z 575.0 [M·Cl]⁺.
Formation of 8 (R = n-butyl; R' = ethyl): 2·HCl (0.300 g, 1.21 mmol), Ag₂O (0.279 g, 1.21 mmol) and [PdCl(μ-Cl)(PPh₃)]₂ (0.530 g, 0.60 mmol). Yield: 73%. This complex is soluble in CH₂Cl₂, CHCl₃ or THF, but insoluble in toluene or pentane. Anal. Calc. for C₂₀H₃₅Cl₂N₂PPdS (651.97): C, 53.42; H, 5.41; N, 4.30. Found: C, 53.1; H, 5.8; N, 4.3. FTIR: vₘₐₓ(pure, diamond orbit)/cm⁻¹ 3394br, 3151w, 3315w, 3096w, 3073w, 3052w, 2957m, 2928m, 2871m, 1566w, 1480w, 1463m, 1432s, 1374w, 1353w, 1311w, 1267m, 1242m, 1228s, 1202w, 1183w, 1157m, 1131w, 1106vs, 1028w, 998w, 973w, 874w, 844w, 798w, 754s, 749s, 741s, 707s, 692vs, 684vs, 533vs, 513vs, 494vs, 453m, 441m, 429m, 305vs (νₚd-Cl), 284vs (νₚd-Cl). ¹H NMR (CD₂Cl₂, 300 MHz) δ: 0.88 (3H, t, ³J = 7.5 Hz, CH₃ butyl), 1.23 (3H, t, ³J = 7.2 Hz, SCH₂CH₃), 1.30 (2H, m, NCH₂CH₂CH₂CH₃), 1.48 (1H, m, NCH₂CHHCH₂CH₃), 1.81 (1H, m, NCH₂CHHCH₂CH₃), 2.49 (2H, q, ³J = 7.2 Hz, SCH₂CH₃), 2.85 (1H, m, NCH₂CHHHS), 3.08 (1H, m, NCH₂CHHCH₂CH₃), 3.71 (2H, m, NCH₂CHHCH₂CH₃ and NCH₂CHHHS), 4.17 (1H, m, NCH₂CHHCH₂CH₃), 4.44 (1H, m, NCH₂CHHCH₂CH₃), 6.67 and 6.81 (2H, AB spin system, ³J = 1.8 Hz, CH=CH), 7.34-7.58 (15H, m, H arom). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 13.38 (CH₃ butyl), 14.81 (SCH₂CH₃), 19.92 (NCH₂CH₂CH₂CH₃), 26.25 (SCH₂CH₃), 31.10 (NCH₂CH₂S), 31.69 (NCH₂CH₂CH₂CH₃), 50.72 (NCH₂CH₂CH₂CH₃), 50.81 (NCH₂CH₂S), 121.04, 122.18 (CH=CH), 128.51 (d, Jₚ₋ₓ = 11.0 Hz, CH arom), 129.87 (d, Jₚ₋ₓ = 53.8 Hz, Cᵢₚ₋₀), 131.18 (d, Jₚ₋ₓ = 2.4 Hz, CH arom), 134.10 (d, Jₚ₋ₓ = 11.0 Hz, CH arom), 160.32 (CN). ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz) δ: 28.5. MS (ESI): m/z 617.1 [M-Cl]⁺.

Formation of 9 (R = methyl; R' = phenyl): 3·HCl (0.283 g, 1.11 mmol), Ag₂O (0.257.4 g, 1.11 mmol) and [PdCl(μ-Cl)(PPh₃)]₂ (0.488 g, 0.56 mmol). Yield: 72%. This complex is soluble in CH₂Cl₂, CHCl₃ or THF, but insoluble in toluene or pentane. Anal. Calc. for C₉₀H₇₈Cl₂N₂PPdS (657.93): (9-0.75CH₂Cl₂) C, 51.17; H, 4.27; N, 3.88. Found: C, 51.1; H, 4.4; N, 3.7. ¹H NMR (CD₂Cl₂, 300 MHz) δ: 3.07 (1H, m, NCH₂CHHHS), 3.58 (1H, m, NCH₂CHHHS), 3.63 (3H, s, NCH₃), 3.78 (1H, m, NCH₂CHHCH₂CH₃), 4.51 (1H, m, NCH₂CHHCH₂CH₃), 6.63 and 6.67 (2H, AB spin system, ³J = 1.8 Hz, CH=CH) 7.26-7.59 (20H, m, H arom). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz) δ: 31.63 (NCH₂CH₂S), 37.56 (NCH₃), 49.72 (NCH₂CH₂S), 121.87, 123.10 (CH=CH), 126.14 (Cᵢₚ₋₀ SPh), 128.23 (Cᵢₚ₋₀ SPh), 128.49 (d, Jₚ₋ₓ = 11.1 Hz, CH arom PPh₃), 129.71 (C₀ₚ₋₀ SPh), 129.73 (d, Jₚ₋ₓ = 54.2 Hz, Cᵢₚ₋₀ PPh₃), 131.12 (d, Jₚ₋ₓ = 2.4 Hz, CH arom PPh₃), 133.95 (d, Jₚ₋ₓ = 11.2 Hz, CH arom PPh₃), 134.27 (Cᵢₚ₋₀ SPh), (CN) not observed. ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz) δ: 28.6. MS (ESI): m/z 623.0 [M-Cl]⁺.

Formation of 10 (R = n-butyl; R' = phenyl): 4·HCl (0.288 g, 0.97 mmol), Ag₂O (0.225 g, 0.97 mmol) and [PdCl(μ-Cl)(PPh₃)]₂ (0.427 g, 0.49 mmol). Yield: 55%. This complex is soluble in CH₂Cl₂, CHCl₃ or THF, but insoluble in toluene or pentane. Anal. Calc. for C₃₃H₃₅Cl₂N₂PPdS (700.01): C, 56.62; H, 5.04; N, 4.00. Found: C, 56.3; H, 5.6; N, 3.4. FTIR: vₘₐₓ(pure, diamond orbit)/cm⁻¹ 3386br, 3156w, 3122w, 3095w, 3050w, 2957m, 2929m, 2870m, 1582m, 1571w, 1479m, 1462m, 1437s, 1421s, 1379w, 1356w, 1277w, 1260m, 1231s, 1203w, 1158m, 1088s, 1073sh, 1022s, 949w, 895w, 873m, 799s, 736vs,
Procedure for the ligand displacement reactions:

Formation of 7 starting from 5: Complex 5 (0.070 g, 0.201 mmol) and solid PPh₃ (0.053 g, 0.201 mmol) were placed in a Schlenk tube and dry CH₂Cl₂ was added under nitrogen. The reaction mixture was stirred for 12 h at room temperature. The volume of the yellow solution was reduced to 1/3 under reduced pressure and the product was precipitated by addition of pentane. Yield: 89%.

Formation of 5 starting from 7: Complex 7 (0.070 g, 0.115 mmol) was dissolved in dry CH₂Cl₂ and solid [AuCl(THT)] (0.037 g, 0.115 mmol) was added under nitrogen. The reaction mixture was stirred for 12 h at room temperature. The solvent of the resulting yellow solution was evaporated under reduced pressure. Then the [AuCl(PPh₃)] formed was extracted with THF and the product was crystallized from a dichloromethane/pentane solution. Yield: 84%.

Procedure for the Suzuki–Miyaura cross-coupling reaction with complex 5:
Complex 5 (6.95 mg, 0.02 mmol), phenyl boronic acid (146.3 mg, 1.20 mmol) and Cs₂CO₃ (651.6 mg, 2.00 mmol) were placed in a Schlenk tube and DMSO (3 ml) was added under nitrogen. Then 4-bromotoluene (123.1 µl, 171.0 mg, 1.00 mmol) was added and the reaction mixture was heated for 2 h at 100 °C. The reaction was then quenched by rapid cooling down to room temperature and the suspension was filtered through a Celite pad. The resulting solution was then analysed by gas chromatography and showed 90% conversion.

Following the same procedure in dioxane (3 ml) as solvent gave only 80% conversion.

Procedure for the Suzuki–Miyaura cross-coupling reaction with complex 7:
Complex 7 (12.2 mg, 0.02 mmol), phenyl boronic acid (146.3 mg, 1.20 mmol) and Cs₂CO₃ (651.6 mg, 2.00 mmol) were placed in a Schlenk tube and dioxane (3 ml) was added under nitrogen.
Then 4-bromotoluene (123.1 µl, 171.0 mg, 1.00 mmol) was added and the reaction mixture was heated for 2 h at 100 °C. The reaction was then quenched by rapid cooling down to room temperature and the suspension was filtered through a Celite pad. The resulting solution was then analysed by gas chromatography and showed 78% conversion.

**S2. Crystallographic data**

The intensity data was collected at 173(2) K on a Kappa CCD diffractometer\(^{S3}\) (graphite monochromated MoKα radiation, \(\lambda = 0.71073 \) Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on \(F^2\), SHELXL-97)\(^{S4}\) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. In view of the relatively low absorption coefficient and the small size of the crystals, we have chosen not to apply any absorption correction. The molecular structure of 6 is centrosymmetric, the centre being located on the Pd atom. In 8, the butyl and the ethyl moieties were severely disordered. Attempts to refine a satisfactory model for this disorder failed and the atoms were refined with restrained C-C distances (1.54 Å) and anisotropic thermal parameters restrained to isotropic ones. The asymmetric unit of 9·0.75CH₂Cl₂ consisted in two crystallographically independent molecules of 9 and two dichloromethane molecules, one of which was found disordered in two positions close to the symmetry centre, with an occupancy factor of 0.5. The latter was refined with restrained anisotropic thermal parameters and C-Cl distances (1.74 Å).

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\(^{S4}\) M. Sheldrick, *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, 1997.
S2.1 Crystallographic data of compound 5:

**Figure S-1.** Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of 5 in dichloromethane. ORTEP plot of the molecular structure of 5 (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)-C(1) 1.984(7), Pd(1)-S(1) 2.279(2), Pd(1)-Cl(1) 2.374(2), Pd(1)-Cl(2) 2.3239(19), C(1)-N(1) 1.353(9), C(1)-N(2) 1.339(10); C(1)-Pd(1)-S(1) 90.7(2), C(1)-Pd(1)-Cl(2) 90.6(2), S(1)-Pd(1)-Cl(1) 85.41(7), N(2)-C(1)-N(1) 106.2(6).

Data collection and refinement parameters: formula C₈H₁₄Cl₂N₂PdS, \( M = 347.57 \), monoclinic, space group \( P2_1/c \), \( a = 10.9199(6) \), \( b = 8.3242(4) \), \( c = 14.8290(9) \) Å, \( \beta = 118.849(4) \), \( V = 1180.66(11) \) Å³, \( Z = 4 \), crystal size = 0.05 x 0.05 x 0.03 mm³, \( D_x = 1.955 \) g·cm⁻³, \( \mu = 2.164 \) mm⁻¹ (Mo-Kα), \( T = 173(2) \), \( R(I>2\sigma(I)) = 0.050 \), \( wR(I>2\sigma(I)) = 0.1379 \), \( S = 1.087 \) for all 2443 unique data (4371 meas., \( R_{int} = 0.0442 \), max \( 2\theta = 53 \)) and 129 refined parameters, \( \rho_{max} \) and \( \rho_{min} \) = 1.844 and -1.012 e/Å³.
S2.2 Crystallographic data of compound 6:

**Figure S-2.** Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of 6 in dichloromethane. ORTEP plot of the molecular structure of 6 (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)-C(1) 2.031(6), Pd(1)-Cl(1) 2.3081(16), C(1)-N(1) 1.341(7), C(1)-N(2) 1.344(7); C(1)-Pd(1)-Cl(1) 90.21(16), N(1)-C(1)-N(2) 105.1(5). Symmetry operations generating equivalent atoms (‘): -x, -y, -z.

Data collection and refinement parameters: formula C_{16}H_{28}Cl_{2}N_{4}PdS_{2}, \( M = 517.84 \), triclinic, space group P-1, \( a = 7.8872(8) \), \( b = 7.9205(9) \), \( c = 9.8308(7) \) Å, \( \alpha = 96.521(6) \), \( \beta = 91.623(6) \), \( \gamma = 114.409(4) \), \( V = 553.7(1) \) Å\(^3\), \( Z = 1 \), crystal size = 0.06 x 0.06 x 0.01 mm\(^3\), \( D_c = 1.553 \) g·cm\(^{-3}\), \( \mu = 1.275 \) mm\(^{-1}\) (Mo-K\(\alpha\)), \( T = 173(2) \), \( R(I)>2\sigma(I) = 0.0529 \), \( wR(I)>2\sigma(I) = 0.1156 \), \( S = 1.024 \) for all 2172 unique data (4911 meas., \( R_{int} = 0.0729 \), max \( 2\theta = 52 \)) and 115 refined parameters, \( \rho_{\text{max}} \) and \( \rho_{\text{min}} = 0.933 \) and -1.122 e/Å\(^3\).
S2.3 Crystallographic data of compound 8:

**Figure S-3.** Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of 8 in dichloromethane. ORTEP plot of the molecular structure of 8 (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)-C(19) 1.977(5), Pd(1)-P(1) 2.2547(13), Pd(1)-Cl(1) 2.3549(13), Pd(1)-Cl(2) 2.3585(13), C(19)-N(1) 1.346(6), C(19)-N(2) 1.346(7), P(1)-Pd(1)-C(19) 91.68(15), C(19)-Pd(1)-Cl(1) 90.74(5). C(19)-Pd(1)-Cl(2) 85.33(15), Pd(1)-C(19)-N(1) 105.2(4).

Data collection and refinement parameters: formula C_{29}H_{35}Cl_{2}N_{2}PPdS, $M = 651.92$, monoclinic, space group $P2_1/c$, $a = 12.8722(6)$, $b = 17.6615(5)$, $c = 18.3472(6)$ Å, $\beta = 133.128(2)$, $V = 3044.18(22)$ Å$^3$, $Z = 4$, crystal size = 0.07 x 0.06 x 0.06 mm$^3$, $D_v = 1.422$ g·cm$^{-3}$, $\mu = 0.927$ mm$^{-1}$ (Mo-Kα), $T = 173(2)$, $R(I>2\sigma(I)) = 0.0595$, $wR(I>2\sigma(I)) = 0.1665$, $S = 1.129$ for all 5669 unique data (16443 meas., $R_{\text{int}} = 0.0575$, max $2\theta = 51$) and 329 refined parameters, $\rho_{\text{max}}$ and $\rho_{\text{min}} = 2.245$ and -1.11 e/Å$^3$. 

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S2.4 Crystallographic data of compound 9·0.75CH₂Cl₂:

**Figure S-4.** Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of 9 in dichloromethane. ORTEP plot of the molecular structure of 9·0.75CH₂Cl₂ (independent molecule A (molecule B is very similar), 50% probability level chosen for the ellipsoids, molecules of solvent and hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)-C(19) 1.987(5) [A] 1.973(5) [B], Pd(1)-P(1) 2.2528(12) [A] 2.2559(14) [B], Pd(1)-Cl(1) 2.3583(12) [A] 2.3437(13) [B], Pd(1)-Cl(2) 2.3417(13) [A] 2.3698(13) [B], C(19)-N(1) 1.346(6) [A] 1.345(6) [B], C(19)-N(2) 1.350(6) [A] 1.368(6) [B]; P(1)-Pd(1)-C(19) 92.01(13) [A] 90.77(14) [B], P(1)-Pd(1)-Cl(2) 88.56(5) [A] 177.17(5) [A] 89.26(5) [B], C(19)-Pd(1)-Cl(1) 87.24(13) [A] 177.66(13) [B], C(19)-Pd(1)-Cl(2) 178.32(15) [A] 87.46(14) [B], Cl(1)-Pd(1)-Cl(2) 92.26(5) [A] 92.41(5) [B], N(1)-C(19)-N(2) 105.3(4) [A] 104.6(4) [B].

Data collection and refinement parameters: formula C₃₀H₇₅N₅P₂PdS, M = 721.58, triclinic, space group P-1, a = 10.1476(2), b = 14.9042(5), c = 20.9556(6) Å, α = 97.881(1), β = 90.739(2), γ = 97.207(2), V = 3113.2(1) Å³, Z = 4, crystal size = 0.07 x 0.06 x 0.06 mm³, Dc = 1.540 g·cm⁻³, μ = 1.039 mm⁻¹ (Mo-Kα), T = 173(2), R(I>2σ(I)) = 0.0539, wR(I>2σ(I)) = 0.1388, S = 1.036 for all 12890 unique data (31306 meas., Rₘᵢₙ = 0.0557, max 2θ = 53) and 711 refined parameters, ρ max and ρ min = 2.079 and -1.653 e/Å³.
S2.5 Crystallographic data of compound 10:

Figure S-5. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of 10 in dichloromethane. ORTEP plot of the molecular structure of 10 (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)-C(19) 1.982(6), Pd(1)-P(1) 2.2601(15), Pd(1)-Cl(1) 2.3463(16), Pd(1)-Cl(2) 2.3580(15), C(19)-N(1) 1.340(7), C(19)-N(2) 1.356(7); P(1)-Pd(1)-C(19) 92.48(16), P(1)-Pd(1)-Cl(1) 89.44(6), C(19)-Pd(1)-Cl(2) 85.82(16), Cl(1)-Pd(1)-Cl(2) 92.26(6), N(1)-C(19)-N(2) 106.2(5).

Data collection and refinement parameters: formula C$_{33}$H$_{35}$Cl$_2$N$_2$PdS, $M = 699.96$, monoclinic, space group $P2_1/c$, $a = 19.5332(10)$, $b = 9.1372(5)$, $c = 20.1256(8)$ Å, $\beta = 117.700(2)$, $V = 3180.3(3)$ Å$^3$, $Z = 4$, crystal size = 0.05 x 0.05 x 0.04 mm$^3$, $D_c = 1.462$ g·cm$^{-3}$, $\mu = 0.893$ mm$^{-1}$ (Mo-Kα), $T = 173(2)$, $R(I>2\sigma(I)) = 0.0487$, $wR(I>2\sigma(I)) = 0.1027$, $S = 0.992$ for all 6256 unique data (20288 meas., $R_{int} = 0.0927$, max $2\theta = 52$) and 362 refined parameters, $\rho_{max}$ and $\rho_{min} = 1.244$ and -1.481 e/Å$^3$. 