Supporting Information for *Dalton Trans*. B902314N

Versatile coordination modes of novel hemilabile *S*-NHC ligands.

Christophe Fliedel, Gilles Schnee and Pierre Braunstein*

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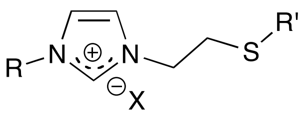
Laboratoire de Chimie de Coordination, Institut de Chimie, UMR 7177 CNRS,
Université de Strasbourg, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France.
E-mail: braunstein@chimie.u-strasbg.fr ; Fax: +33 390 241 322.

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 (^1H, 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 (^1H) or solvent (^{13}C) resonance. Assignments are based on ^1H, ^1H-COSY, ^1H, ^{13}C-HMQC and ^1H, ^{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 $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$[S2] were prepared according to literature methods. All other reagents were used as received from commercial suppliers.



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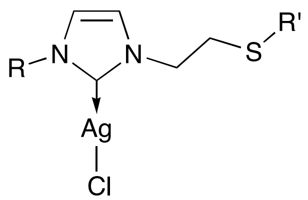

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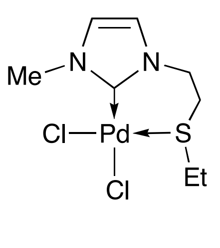

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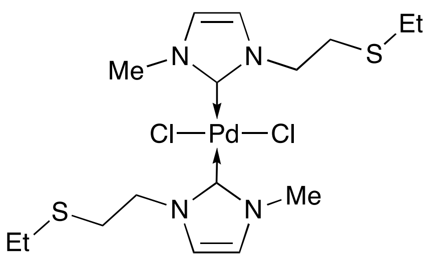

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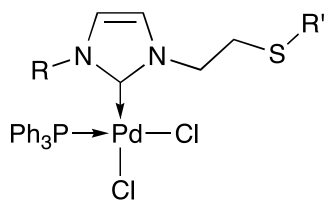

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Formula of imidazolium salts and complexes described in this paper.

S1 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publishers, London, 1973.

S2 M. Noskowska, E. Sliwinska and W. Duczmal, *Trans. Met. Chem.*, 2003, **28**, 756-759.

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 equiped 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 $C_8H_{15}ClN_2S$ (206.74): 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. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 1.20 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 2.60 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 3.04 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 4.03 (3H, s, NCH_3), 4.57 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.41 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, C*H*=CH), 7.56 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*), 10.41 (1H, br s, NCHN). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 14.53 (SCH_2CH_3), 25.85 (SCH_2CH_3), 31.73 (NCH_2CH_2S), 36.50 (NCH_3), 49.11 (NCH_2CH_2S), 122.38, 122.93 (*C*H=*C*H), 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 $C_{11}H_{21}ClN_2S$ (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, 3040m, 2956vs, 2929s, 2869m, 1561s, 1452m, 1374w, 1332w, 1266w, 1159vs, 1062w, 1022w, 972w, 949w, 869w, 752m. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.91 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.18 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 1.33 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.85 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.58 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 3.04 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 4.27 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 4.57 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.46 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, C*H*=CH), 7.73 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*), 10.45 (1H, br s, NCHN). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 13.21 (CH_3 butyl), 14.54 (SCH_2CH_3), 19.35 ($NCH_2CH_2CH_2CH_3$), 25.75 (SCH_2CH_3), 31.75 (NCH_2CH_2S), 32.00 ($NCH_2CH_2CH_2CH_3$), 48.97 ($NCH_2CH_2CH_2CH_3$), 49.64 (NCH_2CH_2S), 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 $C_{12}H_{15}ClN_2S$ (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. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 3.52 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 3.93 (3H, s, NCH_3), 4.53 (2H, pseudo t, ^3J = 6.3 Hz, NCH_2CH_2S), 7.20-7.41 (6H, m, H arom + C*H*=CH), 7.55 (1H, t, ^3J = ^4J = 2.1 Hz, CH=C*H*), 10.36 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 34.10 (NCH_2CH_2S), 36.38 (NCH_3), 49.17 (NCH_2CH_2S), 122.79, 122.97 (CH=CH), 126.96 (C_{para}), 129.26 (C_{meta}), 130.10 (C_{ortho}), 133.80 (C_{ipso}), 138.12 (NCN). MS (ESI): *m/z* 219.1 $[M-Cl]^+$.

4·HCl: R = *n*-butyl ; R' = phenyl:

The same procedure was used with 1-*n*-butylimidazole (5.29 ml, 5.00 g, 40.26 mmol) and 2-chloroethyl phenylsulfide (5.92 ml, 6.95 g, 40.26 mmol). Yield: 96%. Anal. Calc. for $C_{15}H_{21}ClN_2S$ (296.86): C, 60.69; H, 7.13; N, 9.44. Found: C, 59.7; H, 7.4; N, 8.6. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1}: 3374br, 3137w, 3056w, 2958m, 2871w, 1627m, 1561s, 1438s, 1333w, 1304w, 1157s, 1087w, 1023m, 871w, 741vs, 692vs. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.93 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.33 (2H, m, CH_2CH_3), 1.82 (2H, m, $CH_2CH_2CH_3$), 3.54 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 4.21 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2$), 4.56 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 7.18-7.40 (6H, m, H arom + C*H*=CH), 7.50 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*), 10.51 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 13.22 (CH_3), 19.41 (CH_2CH_3), 31.92 (NCH_2CH_2S), 34.14 ($NCH_2CH_2CH_2$), 49.12 ($NCH_2CH_2CH_2$), 49.73 (NCH_2CH_2S), 121.29, 122.93 (CH=CH), 126.98 (C_{para}), 129.30 (C_{meta}), 130.02 (C_{ortho}), 133.79 (C_{ipso}), 137.78 (NCN). MS (ESI): *m/z* 261.1 $[M-Cl]^+$.

General procedure for the anion exchange:

1·HPF_6: R = methyl ; R' = ethyl:

The imidazolium chloride **1**·HCl (1.96 g, 9.53 mmol) and solid KPF_6 (8.77 g, 47.64 mmol) were dissolved in a CH_2Cl_2/H_2O (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 $C_8H_{15}F_6N_2PS$ (316.25): C, 30.38; H, 4.78; N, 8.86. Found: C, 28.9; H, 5.2; N, 7.7. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1}: 3169w, 3123w, 2964w, 2931w, 2872w, 1564m, 1536m, 1507m, 1456w, 1380w, 1360w, 1207m, 1162s, 1025m, 824vs, 740s, 703m. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 1.23 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.56 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 2.96 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 3.91 (3H, s, NCH_3), 4.33 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.34 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, C*H*=CH), 7.42 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*), 8.49 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 14.40 (SCH_2CH_3), 25.70 (SCH_2CH_3), 31.26 (NCH_2CH_2S), 36.22 (NCH_3), 49.26 (NCH_2CH_2S), 122.56, 123.56 (CH=CH), 136.00 (NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz) δ: - 143.1 (sept., $^1J_{P,F}$ = 711 Hz, PF_6). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.4 MHz) δ: - 72.4 (d, $^1J_{P,F}$ = 711 Hz, PF_6). MS (ESI): *m/z* 171.1 $[M-PF_6]^+$.

2·HBF_4: R = *n*-butyl ; R' = ethyl:

The same procedure was used with **2**·HCl (1.93 g, 7.83 mmol) and $NaBF_4$ (4.77 g, 43.48 mmol). Yield: 98%. Anal. Calc. for $C_{11}H_{21}BF_4ClN_2S$ (300.17): C, 44.01; H, 7.05; N, 9.33. Found: C, 42.7; H, 7.2; N, 8.3. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1}: 3152w, 3115w, 2962w, 2931w, 2874w, 1564m, 1507m, 1456m, 1378w, 1359w, 1209m, 1159s, 1033vs, 825m, 751s, 704m. ^1H NMR (CD_2Cl_2, 300 MHz) δ: 0.91 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.19 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 1.30 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.85 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.53 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 2.97 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 4.20 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 4.38 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.46 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, C*H*=CH), 7.53 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*), 8.78 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 12.38 (CH_3 butyl), 13.72 (SCH_2CH_3), 18.55 ($NCH_2CH_2CH_2CH_3$), 24.87 (SCH_2CH_3), 30.72 (NCH_2CH_2S), 31.11 ($NCH_2CH_2CH_2CH_3$), 48.38 ($NCH_2CH_2CH_2CH_3$), 49.08 (NCH_2CH_2S), 121.60, 122.01 (CH=CH), 135.14 (NCN). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.4 MHz) δ: - 150.7 (BF_4). MS (ESI): *m/z* 213.1 $[M-BF_4]^+$.

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 CH_2Cl_2 and solid Ag_2O (0.340 g, 1.47 mmol) 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 and the solvent was evaporated under reduced pressure to give a light sensitive white solid. Yield: 82%. Anal. Calc. for $C_8H_{14}AgClN_2S$ (313.60): C, 30.64; H, 4.50; N, 8.93. Found: C, 29.9; H, 4.7; N, 8.5. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1} 3421br, 3094w, 2959w, 2922m, 2868w, 1652w, 1565w, 1457s, 1441s, 1404s, 1375w, 1351w, 1263m, 1222s, 1158w, 1117w, 1097w, 972w, 874w, 729vs, 698sh, 663w. ^1H NMR (CD_2Cl_2, 300 MHz) δ: 1.28 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 2.57 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 2.96 (2H, t, ^3J = 6.7 Hz, NCH_2CH_2S), 3.86 (3H, s, NCH_3), 4.31 (2H, t, ^3J = 6.7 Hz, NCH_2CH_2S), 7.03 and 7.11 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 14.60 (SCH_2CH_3), 26.34 (SCH_2CH_3), 33.09 (NCH_2CH_2S), 38.85 (NCH_3), 51.50 (NCH_2CH_2S), 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 Ag_2O (0.280 g, 1.21 mmol). Yield: 78%. Anal. Calc. for $C_{11}H_{20}AgClN_2S$ (355.68): C, 37.15; H, 5.67; N, 7.88. Found: C, 36.5; H, 5.7; N, 7.1. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1} 3438br, 3090w, 2956s, 2926s, 2869m, 1635w, 1563w, 1454s, 1417s, 1375w, 1261m, 1229s, 1202w, 1156w, 1105w, 1060w, 973w, 874w, 750s, 666w. ^1H NMR (CD_2Cl_2, 300 MHz) δ: 0.97 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.25 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 1.37 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.82 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.54 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 2.96 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 4.13 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 4.32

(2H, t, ^3J = 6.6 Hz, NCH_2CH$_2$S), 7.07 and 7.15 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 13.44 (CH_3 butyl), 14.59 (SCH$_2$$CH_3$), 19.69 (NCH$_2CH_2$$CH_2CH_3$), 26.34 (S$CH_2CH_3$), 33.08 (NCH$_2$$CH_2$S), 33.44 (NCH$_2$$CH_2CH_2CH_3$), 51.66 (N$CH_2CH_2CH_2CH_3$), 51.90 (N$CH_2CH_2$S), 120.86, 121.45 (CH=CH), 179.44 (NCN). MS (ESI): *m/z* 319.0 [M-Cl]$^+$.

3·AgCl: R = methyl ; R' = phenyl:
The same procedure was used with **3**·HCl (0.300 g, 1.01 mmol) and Ag_2O (0.230 g, 1.01 mmol). Yield: 81%. Anal. Calc. for $C_{12}H_{14}AgClN_2S$ (361.64): C, 39.85; H, 3.90; N, 7.75. Found: C, 39.0; H, 3.9; N, 6.9. FTIR: ν_{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_2Cl_2, 300 MHz) δ: 3.36 (2H, t, ^3J = 6.6 Hz, NCH$_2$CH_2S), 3.74 (3H, s, NCH$_3$), 4.31 (2H, t, ^3J = 6.6 Hz, NCH_2CH$_2$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_2Cl_2, 75.5 MHz) δ: 35.05 (NCH$_2$$CH_2$S), 38.81 (NCH$_3$), 51.03 (N$CH_2CH_2$S), 121.72, 122.38 (CH=CH), 126.59 (*C* para), 129.28 (C_{meta}), 128.50 (C_{ortho}), 134.54 (C_{ipso}), 180.41 (NCN). MS (ESI): *m/z* 545.1 [Ag(**3**)$_2$]$^+$.

4·AgCl: R = *n*-butyl ; R' = phenyl:
The same procedure was used with **4**·HCl (0.320 g, 1.07 mmol) and Ag_2O (0.250 g, 1.07 mmol). Yield: 80%. Anal. Calc. for $C_{15}H_{20}AgClN_2S$ (403.72): C, 44.63; H, 4.99; N, 6.94. Found: C, 43.8; H, 5.7; N, 6.2. FTIR: ν_{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_2Cl_2, 300 MHz) δ: 0.94 (3H, t, ^3J = 7.5 Hz, CH$_3$ butyl), 1.32 (2H, m, CH_2CH$_3$), 1.75 (2H, m, CH_2CH$_2$CH$_3$), 3.37 (2H, t, ^3J = 6.7 Hz, NCH$_2$CH_2S), 4.05 (2H, t, ^3J = 7.2 Hz, NCH_2CH$_2$CH$_2$), 4.32 (2H, t, ^3J = 6.7 Hz, NCH_2CH$_2$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_2Cl_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_2CH_2CH_3$), 51.12 (N$CH_2CH_2CH_2$), 51.84 (N$CH_2CH_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_2Cl_2 and solid Ag_2O 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), Ag_2O (0.213 g, 0.92 mmol) and $[PdCl_2(NCPh)_2]$ (0.352 g, 0.92 mmol). Yield: 72%. This complex is poorly soluble in CH_2Cl_2 and in DMSO. Anal. Calc. for $C_8H_{14}Cl_2N_2PdS$ (347.60): C, 27.64; H, 4.06; N, 8.06. Found: C, 27.8; H, 4.2; N, 7.6. FTIR: ν_{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 (ν_{Pd-Cl}), 298vs (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 1.40 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.61 (2H, m br, SCH_2CH_3), 3.03 (2H, m br, NCH_2CH_2S), 4.09 (3H, s, NCH_3), 4.45 (2H, t br, NCH_2CH_2S), 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), Ag_2O (0.211 g, 0.91 mmol) and $[PdCl_2(NCPh)_2]$ (0.175 g, 0.46 mmol). Yield: 65%. This complex is poorly soluble in CH_2Cl_2 or $CHCl_3$. Anal. Calc. for $C_{16}H_{28}Cl_2N_4PdS_2$ (517.88): C, 37.11; H, 5.45; N, 10.82. Found: C, 37.0; H, 5.7; N, 10.2. FTIR: ν_{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 (CD_2Cl_2, 300 MHz) δ: 1.26 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.59 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 3.21 (2H, m br, NCH_2CH_2S), 4.07 (3H, s, NCH_3), 4.63 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 6.96 (1H, br, *CH*=CH), 7.12 (1H, br, CH=*CH*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 14.64 (SCH_2CH_3), 22.32 (SCH_2CH_3), 32.54 (NCH_2CH_2S), 37.74 (NCH_3), 50.72 (NCH_2CH_2S), 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), Ag_2O (0.452 g, 1.93 mmol) and $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ (0.851 g, 0.97 mmol). Yield: 69%. This complex is soluble in CH_2Cl_2, $CHCl_3$ or THF, but insoluble in toluene or pentane. Anal. Calc. for $C_{26}H_{29}Cl_2N_2PPdS$ (609.89): C, 51.20; H, 4.79; N, 4.59. Found: C, 50.6; H, 4.8; N, 4.3. FTIR: ν_{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 (CD_2Cl_2, 300 MHz) δ: 1.24 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.49 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 2.86 (1H, m, NCH_2CHHS), 3.08 (1H, m, $NCHHCH_2S$), 3.59 (3H, s, NCH_3), 3.72 (1H, m, NCH_2CHHS), 4.42 (1H, m, $NCHHCH_2S$), 6.64 and 6.77 (2H, AB spin system, ^3J = 2.1 Hz, CH=CH), 7.35-7.60 (15H, m, H arom). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 14.81 (SCH_2CH_3), 26.24 (SCH_2CH_3), 31.21 (NCH_2CH_2S), 37.53 (NCH_3), 50.62 (NCH_2CH_2S), 122.16, 122.84 (CH=CH), 128.55 (d, $J_{P\text{-}C}$ = 11.0 Hz, CH arom), 129.83 (d, $J_{P\text{-}C}$ = 54.1 Hz, C_{ipso}), 131.23 (d, J_{P-C} = 2.4 Hz, CH arom), 134.03 (d, $J_{P\text{-}C}$ = 11.1 Hz, CH arom), 161.01 (NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 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), Ag_2O (0.279 g, 1.21 mmol) and $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ (0.530 g, 0.60 mmol). Yield: 73%. This complex is soluble in CH_2Cl_2, $CHCl_3$ or THF, but insoluble in toluene or pentane. Anal. Calc. for $C_{29}H_{35}Cl_2N_2PPdS$ (651.97): C, 53.42; H, 5.41; N, 4.30. Found: C, 53.1; H, 5.8; N, 4.3. FTIR: ν_{max}(pure, diamond orbit)/cm^{-1} 3394br, 3151w, 3115w, 3096w, 3073w, 3052w, 2957m, 2928m, 2871m, 1566w, 1480w, 1463m, 1432s, 1374w, 1353w, 1331w, 1311w, 1267m, 1242m, 1228s, 1202w, 1183w, 1157m, 1131w, 1096vs, 1028w, 998w, 973w, 874w, 844w, 798w, 754s, 749s, 741s, 707s, 692vs, 684vs, 533vs, 513vs, 494vs, 453m, 441m, 429m, 305vs ($\nu_{Pd\text{-}Cl}$), 284vs ($\nu_{Pd\text{-}Cl}$). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 0.88 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.23 (3H, t, ^3J = 7.2 Hz, SCH_2CH_3), 1.30 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.48 (1H, m, $NCH_2CHHCH_2CH_3$), 1.81 (1H, m, $NCH_2CHHCH_2CH_3$), 2.49 (2H, q, ^3J = 7.2 Hz, SCH_2CH_3), 2.85 (1H, m, NCH_2CHHS), 3.08 (1H, m, $NCHHCH_2S$), 3.71 (2H, m, $NCHHCH_2CH_2CH_3$ and NCH_2CHHS), 4.17 (1H, m, $NCHHCH_2CH_2CH_3$), 4.44 (1H, m, $NCHHCH_2S$), 6.67 and 6.81 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH), 7.34-7.58 (15H, m, H arom). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 13.38 (CH_3 butyl), 14.81 (SCH_2CH_3), 19.92 ($NCH_2CH_2CH_2CH_3$), 26.25 (SCH_2CH_3), 31.10 (NCH_2CH_2S), 31.69 ($NCH_2CH_2CH_2CH_3$), 50.72 ($NCH_2CH_2CH_2CH_3$), 50.81 (NCH_2CH_2S), 121.04, 122.18 (CH=CH), 128.51 (d, $J_{P\text{-}C}$ = 11.0 Hz, CH arom), 129.87 (d, $J_{P\text{-}C}$ = 53.8 Hz, C_{ipso}), 131.18 (d, $J_{P\text{-}C}$ = 2.4 Hz, CH arom), 134.10 (d, $J_{P\text{-}C}$ = 11.0 Hz, CH arom), 160.32 (NCN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz) δ: 28.5. MS (ESI): *m/z* 617.1 $[M\text{-}Cl]^+$.

Formation of **9** (R = methyl ; R' = phenyl): **3**·HCl (0.283 g, 1.11 mmol), Ag_2O (0.257.4 g, 1.11 mmol) and $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ (0.488 g, 0.56 mmol). Yield: 72%. This complex is soluble in CH_2Cl_2, $CHCl_3$ or THF, but insoluble in toluene or pentane. Anal. Calc. for $C_{30}H_{29}Cl_2N_2PPdS$ (657.93): (9·0.75CH_2Cl_2) C, 51.17; H, 4.27; N, 3.88. Found: C, 51.1; H, 4.4; N, 3.7. ^1H NMR (CD_2Cl_2, 300 MHz) δ: 3.07 (1H, m, NCH_2CHHS), 3.58 (1H, m, NCH_2CHHS), 3.63 (3H, s, NCH_3), 3.78 (1H, m, $NCHHCH_2S$), 4.51 (1H, m, $NCHHCH_2S$), 6.63 and 6.67 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH) 7.26-7.59 (20H, m, H arom). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz) δ: 31.63 (NCH_2CH_2S), 37.56 (NCH_3), 49.72 (NCH_2CH_2S), 121.87, 123.10 (CH=CH), 126.14 (C_{para} SPh), 128.23 (C_{meta} SPh), 128.49 (d, $J_{P\text{-}C}$ = 11.1 Hz, CH arom PPh_3), 129.71 (C_{ortho} SPh), 129.73 (d, $J_{P\text{-}C}$ = 54.2 Hz, C_{ipso} PPh_3), 131.12 (d, $J_{P\text{-}C}$ = 2.4 Hz, CH arom PPh_3), 133.95 (d, $J_{P\text{-}C}$ = 11.2 Hz, CH arom PPh_3), 134.27 (C_{ipso} SPh), (NCN) not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz) δ: 28.6. MS (ESI): *m/z* 623.0 $[M\text{-}Cl]^+$.

Formation of **10** (R = *n*-butyl; R' = phenyl): **4**·HCl (0.288 g, 0.97 mmol), Ag_2O (0.225 g, 0.97 mmol) and $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ (0.427 g, 0.49 mmol). Yield: 55%. This complex is soluble in CH_2Cl_2, $CHCl_3$ or THF, but insoluble in toluene or pentane. Anal. Calc. for $C_{33}H_{35}Cl_2N_2PPdS$ (700.01): C, 56.62; H, 5.04; N, 4.00. Found: C, 56.3; H, 5.6; N, 3.4. FTIR: ν_{max}(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, 873w, 799s, 736vs, 728vs, 704s, 689vs, 533vs, 512s, 494s, 475vs, 350vs, 307s (Pd-Cl), 287s ($\nu_{Pd\text{-}Cl}$). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.88 (3H, t, ^3J = 7.2 Hz, CH_3 butyl), 1.30 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.46 (1H, m, $NCH_2CHHCH_2CH_3$), 1.81 (1H, m, $NCH_2CHHCH_2CH_3$), 3.07 (1H, m, NCH_2CHHS), 3.57 (1H, m, NCH_2CHHS), 3.76 (2H, m, $NCHHCH_2CH_2CH_3$ and $NCHHCH_2S$), 4.20 (1H, m, $NCHHCH_2CH_2CH_3$), 4.54 (1H, m, $NCHHCH_2S$), 6.67 and 6.71 (2H, AB spin system, ^3J = 2.1 Hz, CH=CH), 7.26-7.58 (20H, m, H arom). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 13.39 (CH_3), 19.93 ($NCH_2CH_2CH_2CH_3$), 31.50 (NCH_2CH_2S), 31.63 ($NCH_2CH_2CH_2CH_3$), 49.88 ($NCH_2CH_2CH_2CH_3$), 50.85 (NCH_2CH_2S), 121.36, 121.98 (CH=CH), 126.06 (C_{para} SPh), 128.16 (C_{meta} SPh), 128.46 (d, $J_{P\text{-}C}$ = 11.0 Hz, CH arom PPh_3), 129.67 (C_{ortho} SPh), 129.72 (d, $J_{P\text{-}C}$ = 54.1 Hz, C_{ipso} PPh_3), 131.09 (d, $J_{P\text{-}C}$ = 2.5 Hz, CH arom PPh_3), 134.00 (d, $J_{P\text{-}C}$ = 11.0 Hz, CH arom PPh_3), 134.36 (C_{ipso} SPh), 160.84 (NCN). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz) δ: 28.6. MS (ESI): *m/z* 665.1 $[M\text{-}Cl]^+$.

Procedure for the ligand displacement reactions:

Formation of **7** starting from **5**: Complex **5** (0.070 g, 0.201 mmol) and solid PPh_3 (0.053 g, 0.201 mmol) were placed in a Schlenk tube and dry CH_2Cl_2 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 CH_2Cl_2 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(PPh_3)] 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 Cs_2CO_3 (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 Cs_2CO_3 (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, λ = 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**·0.75CH_2Cl_2 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).

[S3] Bruker-Nonius, *Kappa CCD Reference Manual*, Nonius BV, The Netherlands, **1998**.

[S4] M. Sheldrick, *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.

S2.1 Crystallographic data of compound 5:

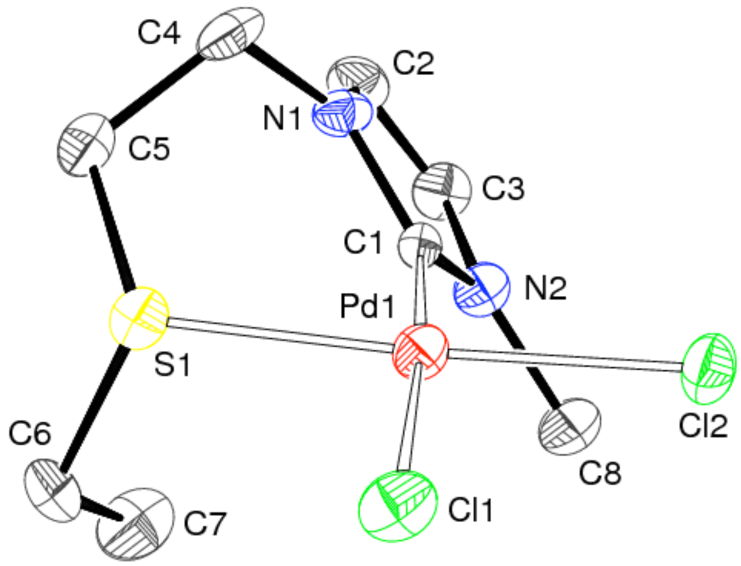

Figure S-1. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **5** in dichloromethane. ORTEP plot of the molecular structure of **5** (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (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 $C_8H_{14}Cl_2N_2PdS$, M = 347.57, monoclinic, space group $P2_1/c$, a = 10.9199(6), b = 8.3242(4), c = 14.8290(9) Å, β = 118.849(4), V = 1180.66(11) Å^3, Z = 4, crystal size = 0.05 x 0.05 x 0.03 mm^3, D_c = 1.955 g·cm^{-3}, μ = 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 2θ = 53) and 129 refined parameters, ρ_{max} and ρ_{min} = 1.844 and -1.012 e/Å^3.

S2.2 Crystallographic data of compound 6:

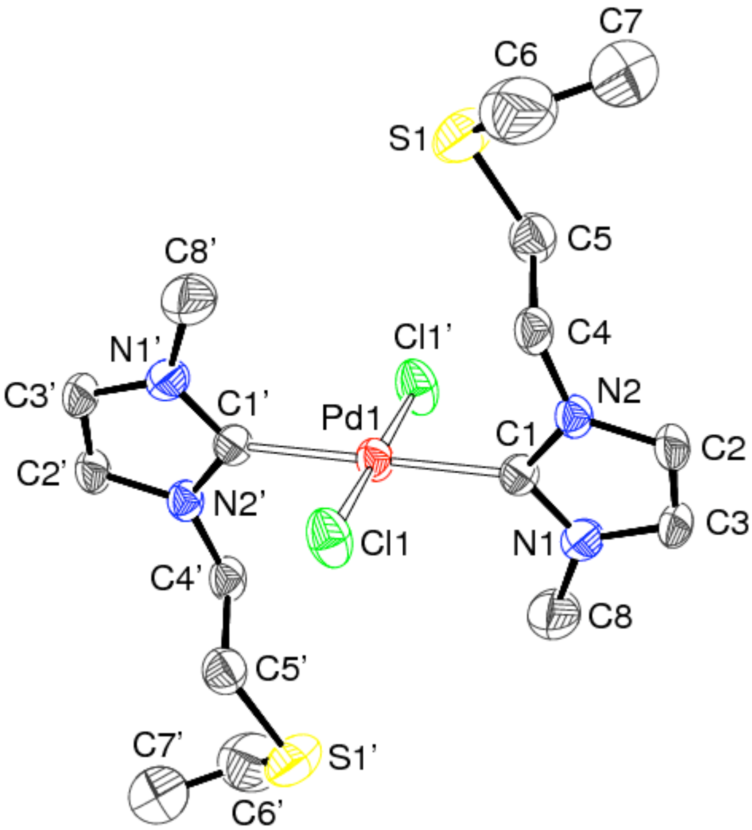

Figure S-2. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **6** in dichloromethane. ORTEP plot of the molecular structure of **6** (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (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 $C_{16}H_{28}Cl_2N_4PdS_2$, M = 517.84, triclinic, space group P-1, a = 7.8872(8), b = 7.9205(9), c = 9.8308(7) Å, α = 96.521(6), β = 91.623(6), γ = 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}, μ = 1.275 mm^{-1} (Mo-Kα), 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 2θ = 52) and 115 refined parameters, ρ_{max} and ρ_{min} = 0.933 and -1.122 e/Å^3.

S2.3 Crystallographic data of compound 8:

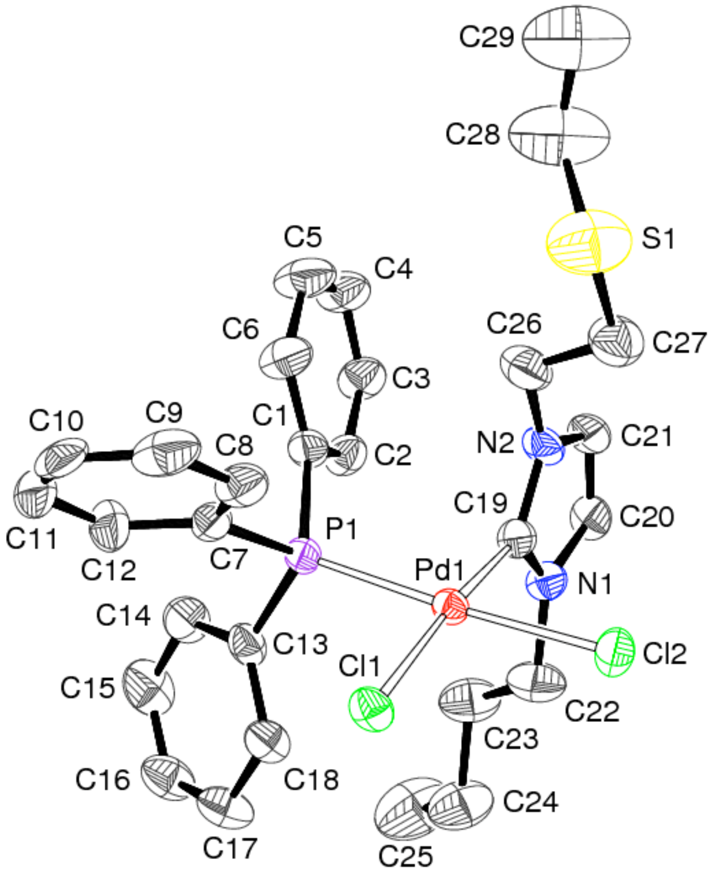

Figure S-3. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **8** in dichloromethane. ORTEP plot of the molecular structure of **8** (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (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), P(1)-Pd(1)-Cl(1) 90.74(5), C(19)-Pd(1)-Cl(2) 85.33(15), Cl(1)-Pd(1)-Cl(2) 92.44(5), N(1)-C(19)-N(2) 105.2(4).

Data collection and refinement parameters: formula $C_{29}H_{35}Cl_2N_2PPdS$, M = 651.92, monoclinic, space group $P2_1/c$, a = 12.8722(6), b = 17.6615(5), c = 18.3472(6) Å, β = 133.128(2), V = 3044.18(22) Å^3, Z = 4, crystal size = 0.07 x 0.06 x 0.06 mm^3, D_c = 1.422 g·cm^{-3}, μ = 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_{int} = 0.0575, max 2θ = 51) and 329 refined parameters, ρ_{max} and ρ_{min} = 2.245 and -1.11 e/Å^3.

S2.4 Crystallographic data of compound 9·0.75CH$_2$Cl$_2$:

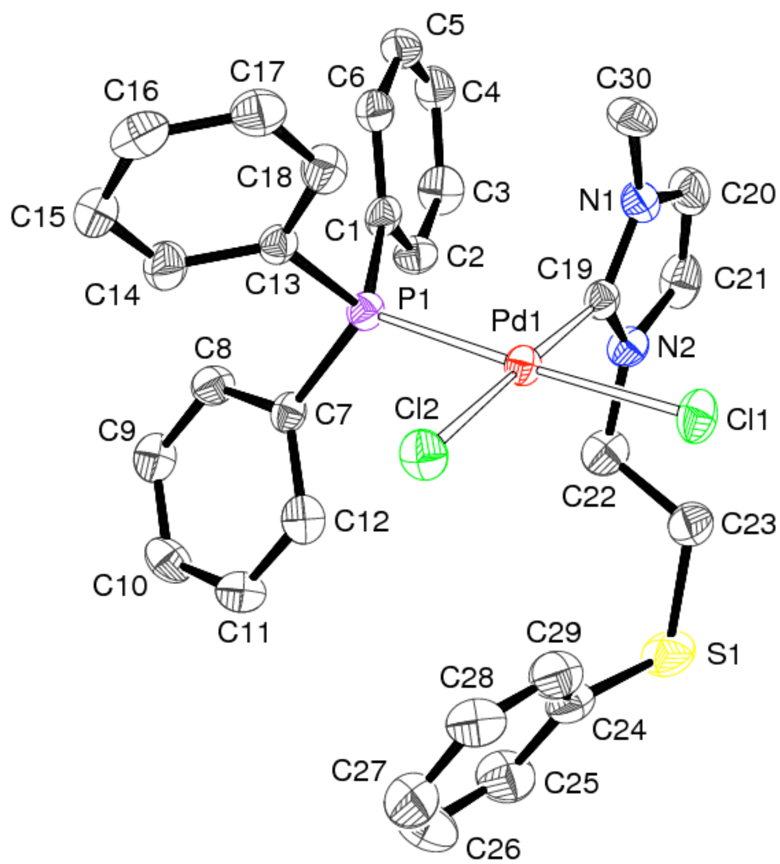

Figure S-4. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **9** in dichloromethane. ORTEP plot of the molecular structure of **9**·0.75CH$_2$Cl$_2$ (independent molecule A (molecule B is very similar), 50% probability level chosen for 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] 176.93(5) [B], P(1)-Pd(1)-Cl(1) 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 $C_{30.75}H_{30.50}Cl_{3.50}N_2PPdS$, 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) Å^3, Z = 4, crystal size = 0.07 x 0.06 x 0.06 mm^3, D_c = 1.540 g·cm^{-3}, μ = 1.039 mm^{-1} (Mo-Kα), T = 173(2), $R(I>2\sigma(I))$ = 0.0539, $wR(I>2\sigma(I))$ = 0.1388, S = 1.036 for all 12890 unique data (31306 meas., R_{int} = 0.0557, max 2θ = 53) and 711 refined parameters, ρ_{max} and ρ_{min} = 2.079 and -1.653 e/Å^3.

S2.5 Crystallographic data of compound 10:

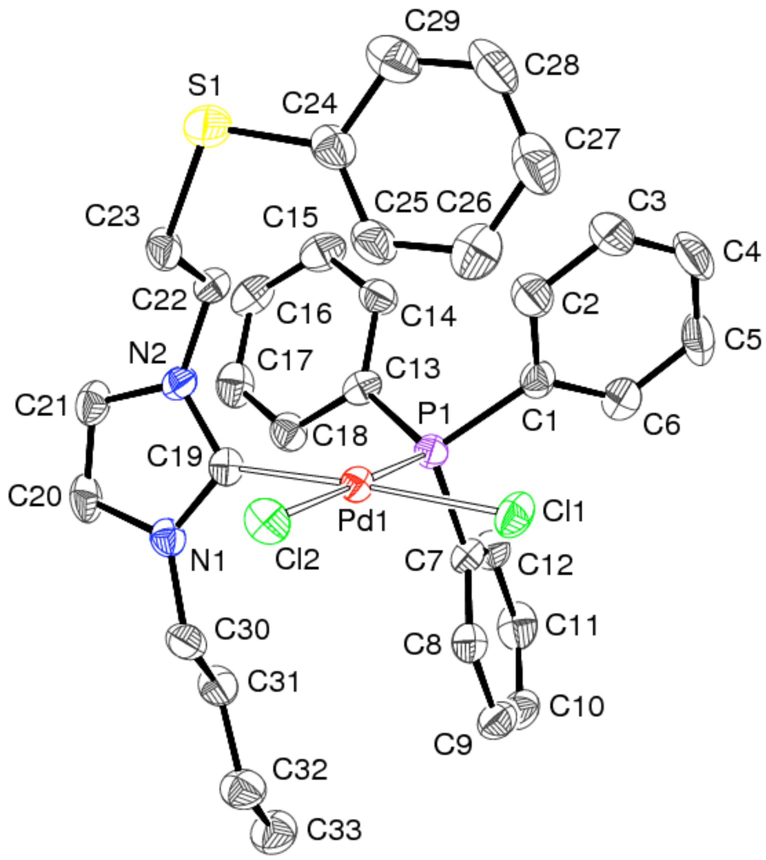

Figure S-5. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **10** in dichloromethane. ORTEP plot of the molecular structure of **10** (50% probability level chosen for the ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (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 $C_{33}H_{35}Cl_2N_2PPdS$, M = 699.96, monoclinic, space group $P2_1/c$, a = 19.5332(10), b = 9.1372(5), c = 20.1256(8) Å, β = 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}, μ = 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 2θ = 52) and 362 refined parameters, ρ_{max} and ρ_{min} = 1.244 and -1.481 e/Å^3.