Supplementary Information

Oxidative Addition of Tetrathiocins to Palladium(0) and Platinum(0): A Route to Dithiolate Coordination Complexes.

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I. Synthesis

Unless otherwise states all chemicals were purchased from Sigma-Aldrich, Strem or Alfa Aesar. Tetrathiocins **1a** – **1d** were prepared according to a modified procedure and their analytical data matched the literature report.[17] N,N'-dimethylbenzimidazole, $Pd_2dba_3{\cdot}CHCl_3$ and $Pt_2dba_3{\cdot}CH_2Cl_2$ were prepared according to the literature methods.[25,26,27] $Pt_2dba_3{\cdot}CH_2Cl_2$ is known[27] to be sub-stoichiometric in Pt and micro-analytical data were recorded on each batch prepared before use. In our hands the quantity of Pt persistently fell close (x = 1.9 – 2.0) to the stoichiometric value and the experimental desciption refers to the composition as Pt_2dba_3 although there is some minor variation between samples. Standard solvents were dried and deoxygenated using an Innovative Technology Solvent Purification System and manipulation of air-sensitive materials carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and a dry-nitrogen glove box (Braun Labmaster). Microwave reactions were carried out in sealed vessels using a Biotage *Initiator 1* microwave.

2',3',8',9'-bisdioxepinyldibenzo-1,2,5,6-tetrathiocin, 1e
3,4-dihydro-2*H*-1,5-benzodioxepin (1.9 mL, 14.3 mmol) was added to 30 mL of degassed glacial acetic acid in an inert nitrogen atmosphere. S_2Cl_2 (1.15 mL, 14.3 mmol) was added dropwise to the rapidly stirring solution under a nitrogen atmosphere. The solution was stirred for 7 days, after which the yellow and brown solid was isolated by cannula filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo. Once thoroughly dried, the solid was suspended in 60 mL of MeOH and treated with $SnCl_2$ (0.5 g) and left to stir for 7 days to afford a homogenous yellow solid with no trace of brown material. The solid was isolated by filtration using a cannula and washed with MeOH (2 × 60 mL) before being dried *in vacuo* to afford a yellow powder (2.83 g, 78% yield).
HRMS (ASAP) *m/z*: $[M+H]^+$ calc. for $C_{18}H_{17}O_4S_4^+$ 425.0010; found 425.0011. **Elemental analysis** calc. for $C_{18}H_{16}O_4S_4{\cdot}\frac{1}{6}CHCl_3$: C 49.09, H 3.67%; found: C 49.18, H 3.76%. **IR** (ν_{max}, cm^{-1}): 2955(w), 1541(m), 1448(s), 1383(m), 1299(s), 1247(vs), 1156(m), 1040(s), 981(s), 881(m), 839(m), 674(m), 447(w).

2',3',8',9'-*bis*-N,N'-dimethylbenzimidazolo-1,2,5,6-tetrathiocin, 1f
N,N'-dimethylbenzimidazole (0.500 g, 3.08 mmol) was added to 15 mL of degassed glacial acetic acid. S_2Cl_2 (0.25 mL, 3.08 mmol) was added dropwise to the rapidly stirred solution, which turned bright yellow. After 24 h, a bright yellow solid began to form and the mixture continued to stir at room temperature for a further 2 days. The yellow solid was isolated by cannula filtration and washed with Et_2O (2 × 10 mL), then dried *in vacuo* (0.497 g, 71% yield).
HRMS (ASAP) *m/z*: $[M+H]^+$ calc. for $C_{18}H_{17}O_2N_4S_4^+$ 449.0234; found 449.0234. **Elemental analysis** calc. for $C_{18}H_{16}O_2N_4S_4$: C 44.97, H 3.35, N 11.45%; found: C 44.54, H 3.63, N 10.29%. **IR** (ν_{max}, cm^{-1}): 3051(w), 2933(w), 1703(vs), 1699(vs), 1651(m), 1486(s), 1399(m), 1353(w), 1262(m), 1242(m), 1135(m), 1092(m), 873(m), 862(m), 743(s), 618(s), 580(s), 457(s).

Diethoxybenzenedithiolate complex, (deobdt)Pd(dppe), 2b
Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1b** (0.050 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant pink solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.133 g, 83% yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce red needles suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, $CDCl_3$) δ_H = 7.88–7.81 (8H, m, phosphine *m*-H), 7.51–7.44 (12H, m, phosphine *o*,*p*-H), 6.93 (2H, s, benzo C–H), 3.97 (4H, q, J = 6.9 Hz, OCH_2), 2.51 (4H, d, $^2J_{PH}$ = 20.7 Hz, PCH_2), 1.36 (6H, t, J = 6.9 Hz CH_3). **^{31}P NMR** (121 MHz, ppm, $CDCl_3$) $\delta_P\{^1H\}$ = 51.73. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calc. for $C_{36}H_{37}O_2P_2S_2Pd^+$ 733.0757; found 733.0767. **Elemental Analysis** calc. for $C_{36}H_{36}O_2P_2S_2Pd$: C 58.98, H 4.95%; found: C 58.92, H 4.87%. **IR** (ν_{max}, cm^{-1}): 3050(w), 2974(m), 2901(w), 1583(w), 1463(s), 1434(vs), 1389(m), 1337(m), 1235(vs), 1148(s), 1101(s), 1046(s), 998(w), 877(m), 820(m), 745(m), 690(vs), 528(vs), 483(m).

Dioxolobenzenedithiolate complex (doxlbdt)Pd(dppe), 2c
Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1c** (0.040 g 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant dark red solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.125 g, 83% yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce red-orange needles suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, $CDCl_3$) δ_H = 7.87–7.81 (8H, m, phosphine *m*-H), 7.51–7.44 (12H, m, phosphine *o*,*p*-H), 6.85 (2H, s, benzo C–H), 5.82 (2H, s, O–CH_2–O), 2.51 (4H, d, $^2J_{P-H}$ = 20.7 Hz, P–CH_2). **^{31}P NMR** (121 MHz, ppm, $CDCl_3$) $\delta_P\{^1H\}$ = 51.52. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calc. for $C_{33}H_{29}O_2P_2S_2Pd^+$ 689.0131; found 689.0153. **Elemental Analysis** calc. for $C_{33}H_{28}O_2P_2S_2Pd{\cdot}\frac{1}{8}CH_2Cl_2$: C 56.87, H 4.05%; found: C 57.07, H 3.82%. **IR** (ν_{max}, cm^{-1}): 3052(w), 2888(w), 1498(w), 1454(vs), 1435(s), 1309(w), 1216(vs), 1102(m), 1036(m), 998(w), 928(m), 819(m), 745(m), 690(s), 662(m), 527(s), 480(m).

Dioxanobenzenedithiolate complex (doxbdt)Pd(dppe), 2d
Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1d** (0.043 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant red-orange solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.137 g, 89% yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce red-orange needles suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, $CDCl_3$): δ_H = 7.87–7.81 (8H, m, phosphine *m*-H), 7.49–7.43 (12H, m, phosphine *o*,*p*-H), 6.89 (2H, s, benzo C–H), 4.13 (4H, s, O-CH_2-CH_2-O), 2.50 (4H, d, $^2J_{PH}$ = 20.7 Hz, PCH_2). **^{31}P NMR** (121 MHz, ppm, $CDCl_3$) $\delta_P\{^1H\}$ = 51.63. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calc. for $C_{34}H_{31}O_2P_2S_2Pd^+$ 703.0287; found 703.0265. **Elemental Analysis** calc. for $C_{34}H_{30}O_2P_2S_2Pd{\cdot}\frac{1}{5}CH_2Cl_2$: C 57.05, H 4.26%; found: C 57.07, H 4.13%. **IR** (ν_{max}, cm^{-1}): 3052(w), 2972(w), 2917(w), 2869(w), 1556(m), 1458(vs), 1435(vs),1289(vs), 1246(vs), 1093(s), 1067(s), 894(m), 749(m), 690(vs), 529(vs), 483(m).

Dioxepinobenzenedithiolate complex (doxebdt)Pd(dppe), 2e
Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1e** (0.046 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant dark red-brown solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.122 g, 78% yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce orange needles suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, $CDCl_3$): δ_H = 7.86–7.80 (8H, m, phosphine *m*-H), 7.50–7.45 (12H, m, phosphine *o*,*p*-H), 7.03 (2H, s, benzo C–H), 3.99 (4H, t, *J* = 5.1 Hz, O-C**H$_2$**-CH_2-C**H$_2$**-O) , 2.50 (4H, d, $^2J_{P-H}$ = 21.0 Hz, P–CH_2), 2.06 (2H, t, *J* = 5.1 Hz, O-CH_2-C**H$_2$**-CH_2-O). **^{31}P NMR** (121 MHz, ppm, $CDCl_3$) $\delta_P\{^1H\}$ = 51.96. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calc. for $C_{35}H_{33}O_2P_2S_2Pd^+$ 717.0444; found 717.0462. **Elemental Analysis** calc. for $C_{35}H_{32}O_2P_2S_2Pd{\cdot}\frac{1}{4}CH_2Cl_2$: C 57.34, H 4.44%; found: C 57.17, H 4.30%. **IR** (ν_{max}, cm^{-1}): 3072(w), 2953(w), 2865(w), 1467(vs), 1450(vs), 1435(vs), 1382(m), 1296(m), 1264(vs), 1250(s), 1096(s), 1046(s), 874(m), 690(vs), 528(vs), 482(m).

N,N-dimethylimidazolone-benzenedithiolate complex (dmbimdt)Pd(dppe), 2f
Pd_2dba_3 (0.100 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1f** (0.049 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant dark purple solid was isolated from a pale solution by filtration. The precipitate was washed with hexanes and dried in air (0.104 g, 65% yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce red needles suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, $CDCl_3$): 7.90-7.80 (8H, m, phosphine *m*-H), 7.48-7.45 (12H, m, phosphine *o,p*-H), 7.00 (2H, s, benzo C–H), 3.28 (6H, s, NCH_3), 2.52 (4H, d, $^2J_{PH}$ = 20.7 Hz, PCH_2). **^{31}P NMR** (121 MHz, ppm, $CDCl_3$) $\delta_P\{^1H\}$ = 51.66. **HRMS** (ASAP) *m/z*: $[M+H]^+$ calc. for $C_{35}H_{33}N_2OP_2S_2Pd^+$ 729.0556; found

729.0561. **Elemental Analysis** calc. for $C_{35}H_{32}N_2O_2P_2S_2Pd$: C 57.65, H 4.42, N 3.84%; found: C 57.62, H 4.38, N 3.47%. **IR** (ν_{max}, cm^{-1}): 3048(w), 2960(w), 2915(w), 1690(C=O, vs), 1580(m), 1496(m), 1483(m), 1435(s), 1398(m), 1378(m), 1319(w), 1261(s), 1187(w), 1101(s), 1081(m), 1027(m), 998(m), 941(w), 876(w), 820(m), 730(s), 691(s), 650(s), 617(m), 582(m), 530(s), 482(m).

Diethoxybenzenedithiolate complex, (deobdt)Pt(dppe), 3b

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.133 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1b** (0.050 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a yellow-brown solid was isolated from a pale orange solution by filtration. The precipitate was washed with hexanes and dried in air (0.103 g, 57 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction. **^{1}H NMR (ppm)** (300 MHz, ppm, $CDCl_3$): δ_H 7.825 (8H, 7.84-7.81, m, *m*-H), 7.46 (12H, 7.51-7.40, m, *o,p*-H), 7.09 (2H, s, benzo C-H), 3.97 (4H, q, J = 8.4 Hz, CH_2), 2.47 (4H, d, $^2J_{PH}$ = 20.4 Hz, PCH_2), 1.36 (6H, t, J = 6.3 Hz, CH_3); $\delta P\{^1H\}$ = 44.05. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ calcd for $C_{36}H_{37}O_2P_2S_2Pt^+$ 822.1358; found 822.1306. **Elemental Analysis** calc. for $C_{36}H_{36}O_2P_2S_2Pt$: C 52.61; H 4.42%; found: C 52.47; H 4.37%. **IR** (ν_{max}, cm^{-1})**:** 3049 (w), 2969 (w), 2954 (w), 2915 (w), 2848 (w), 1585 (w), 1572 (m), 1463 (m), 1433 (s), 1402 (m), 1388 (m), 1338 (m), 1237 (s), 1182 (m) 1156 (m), 1152 (m), 1099 (s), 1043 (m), 998 (m), 917 (m), 877 (m), 847 (m), 815 (m), 746 (s), 714 (s), 693 (vs), 654 (s), 532 (vs), 792 (s), 463 (m), 438 (m)

Dioxolobenzenedithiolate complex (doxlbdt)Pt(dppe), 3c

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.128 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1c** (0.040 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a yellow-brown solid was isolated from a pale orange solution by filtration. The precipitate was washed with hexanes and dried in air (0.064 g, 38 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction. **NMR (ppm)** ($CDCl_3$): δH = 7.845 (8H, 7.87-7.82, m, m-H), 7.47 (12H, 7.51-7.44, m, o,p-H), 6.99 (2H, s, benzo C-H), 5.84 (2H, s, O-CH2-O), 2.45 (4H, d, $2J_{PH}$ = 17.4 Hz, PCH_2); $\delta P\{^1H\}$ = 44.99. **HRMS (ESI-TOF) *m/z*:** $[M + H]^+$ calcd for $C_{33}H_{29}O_2P_2S_2Pt^+$ 778.0732; found 778.0695. **Elemental Analysis** calc. for $C_{33}H_{28}O_2P_2S_2Pt \cdot 1/2\ CH_2Cl_2$: C 48.33; H 3.44%; found: C 48.11; H 3.60%. **IR** (ν_{max}, cm^{-1}): 3050 (w), 2860 (w), 1494 (w), 1472(m), 1455(s), 1435 (s), 1405(m), 1350(w), 1310 (w), 1220 (s), 1102 (m), 1064 (m), 1035 (m), 998 (w), 949 (w), 933 (m), 877 (m),842 (m), 820 (m), 745 (m), 688 (s), 655 (m), 527 (s), 485 (m), 439 (m).

Dioxanobenzenedithiolate complex (doxbdt)Pt(dppe), 3d

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.138 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1d** (0.043 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a brown-orange solid was isolated from a pale yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.0632 g, 37 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction. **NMR (ppm)** ($CDCl_3$)**:** δH = 7.82 (8H, 7.83-7.81, m, *m*-H), 7.45 (12H, 7.46-7.44, m, *o,p*-H), 7.04 (2H, s, benzo C-H), 4.13 (4H, s, O-CH_2-CH_2-O), 2.45 (4H, d, $^2J_{PH}$ = 18.3 Hz, PCH_2); $\delta P\{^1H\}$ = 44.21. **HRMS (ESI-TOF) *m/z***: $[M + H]^+$ calcd for $C_{34}H_{31}O_2P_2S_2Pt^+$ 703.0287; found 703.0265. **Elemental Analysis** calc. for $C_{34}H_{30}O_2P_2S_2Pt \cdot 1/4\ CH_2Cl_2$: C 50.23; H 3.72 %; found: C 50.50; H 3.49%. **IR** (ν_{max}, cm^{-1}): 3045(w), 2912(w), 2865(w), 1554(m), 1458(m), 1449(m), 1433 (s), 1376 (w), 1349 (w), 1287(s), 1245 (s), 1186 (w), 1169 (w), 1101 (m), 1091 (s), 1062(s), 1027 (m), 998 (m), 910 (m), 893(m), 880 (m), 854 (m), 749(m), 742 (m), 714 (s), 703 (s), 688(vs), 528(vs), 483(s).

Dioxepinobenzenedithiolate complex (doxebdt)Pt(dppe), 3e

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.128 g, 0.056 mmol), dppe (0.087 g, 0.104 mmol) and tetrathiocin **1e** (0.024 g, 0.056 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a yellow-brown solid was isolated from a pale orange solution by filtration. The precipitate was washed with hexanes and dried in air (0.079 g, 86 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction. NMR (ppm) ($CDCl_3$)**:** δ_H = 7.845 (8H, 7.88-7.81, m, *m*-H), 7.455 (12H, 7.47-7.44, m, *o,p*-H), 7.12 (2H, s, benzo C-H), 4.00 (4H, 4.02-3.98, t, J = 5.4 Hz, OCH_2), 2.46 (4H, d, $^2J_{PH}$ = 18.3 Hz, PCH_2), 2.07 (2H, 2.087-2.053, t, J = 5.1 Hz, CH_2)); $\delta_P\{^1H\}$ = 45.30. **HRMS (ESI-TOF)** ***m/z***: $[M + H]^+$ calcd for $C_{34}H_{31}O_2P_2S_2Pt^+$ 806.1045; found 806.1049. **Elemental Analysis** calc. for $C_{34}H_{30}O_2P_2S_2Pt \cdot 1\ 1/2\ CH_2Cl_2$: C45.05; H 3.46%; found: C 44.93; H 3.56%. **IR** (ν_{max}, cm^{-1}): 3048 (w), 2953 (w) , 2860 (w), 1585 (vw), 1572 (vw), 1537 (vw), 1483 (m), 1468 (m), 1449 (s), 1409 (m), 1381 (m), 1335 (w), 1296 (m), 1252 (s), 1184 (m) 1160 (w), 1097 (s), 1043 (s), 983 (m), 948 (w), 878 (m), 820 (w), 746 (m), 688 (vs), 654 (s), 634 (m), 528 (vs) 489 (m), 480 (m), 447 (m)

N,N-dimethylimidazolone-benzenedithiolate complex (dmbimdt)Pt(dppe), 3f

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.138 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1f** (0.046 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a yellow-brown solid was isolated from a yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.121 g, 68 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction. NMR (ppm) ($CDCl_3$)**:** δ_H = 7.85 (8H, 7.887-7.802, m, *m*-H), 7.48 (12H, 7.52-7.45, m, *o,p*-H), 7.14 (2H, s, benzo C-H), 3.285 (6H, s, NCH_3), 2.49 (4H, d, 2.524-2.462, $^2J_{PH}$ = 18.6 Hz, PCH_2) $\delta_P\{^1H\}$ = 45.05. **HRMS (ESI-TOF)** ***m/z***: $[M + H]^+$ calcd for $C_{35}H_{33}N_2OP_2S_2Pt^+$ 729.0556; found 729.0561. **Elemental Analysis** calc. for $C_{35}H_{32}O_2P_2S_2Pt \cdot ½\ CH_2Cl_2$: C 48.87; H 3.75%; N 3.26%; found: C 48.22; H 3.61% N 3.26%. **IR** (ν_{max}, cm^{-1}): 3056 (w), 3048 (w), 2978 (w), 2943 (w), 2904 (w), 1695 (vs), 1582 (w), 1504 (s), 1481 (m), 1435 (s), 1398 (m), 1357 (w), 1320 (w), 1293 (w), 1262 (m), 1243 (m), 1137 (m), 1098 (s), 1079 (m), 1027 (m), 897 (m), 851 (m), 741 (s), 703 (s), 690 (vs), 649 (m), 618 (s), 581 (s), 531 (vs), 486 (s), 476 (s), 455 (s)

15-crown-5-benzodithiolate complex (b-15-c-5-dt)Pt(dppe), 3g:

$Pt_2dba_3{\cdot}CH_2Cl_2$ (0.138 g, 0.109 mmol), dppe (0.087 g, 0.218 mmol) and tetrathiocin **1g** (0.066 g, 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 60 min at 150 °C. The resultant solution was stirred overnight and a yellow-brown solid was isolated from a yellow solution by filtration. The precipitate was washed with hexanes and dried in air (0.061 g, 30 % yield). The solid was recrystallized from a saturated CH_2Cl_2 solution layered with hexanes to produce clear yellow plate-shaped crystals suitable for X-ray diffraction.). **^{1}H NMR** (<u>300 MHz, ppm, $CDCl_3$</u>):δ_H = 7.81 (8H, 7.82–7.80, m, *m*-H), 7.45 (12H, 7.48–7.44, m, *o,p*- H), 6.93 (2H, s, benzo C–H), 2.51 (4H, 2.54–2.48, d, PCH_2); $\delta_P\{^1H\}$ = 51.89. **HRMS (ESI-TOF)** ***m/z*:** $[M + H]^+$ calcd for $C_{40}H_{42}O_5P_2S_2Pt^+$ 923.1597; found 923.1588. **Elemental Analysis** calc. for $C_{40}H_{42}O_5P_2S_2Pt{\cdot}\ ½\ CH_2Cl_2$: C 48.65; H 4.29 %; found: C 49.08; H 4.11%. **IR** (ν_{max}, cm^{-1}): 3048 (w), 2908 (w), 2862 (w), 1584 (w), 1483 (m), 1449 (m), 1434 (s), 1405 (m), 1356 (m), 1346 (m), 1308 (s), 1246 (m), 1193 (m), 1132 (vs), 1099 (s), 1064 (m), 1028 (m), 996 (m), 942 (m), 928 (m), 878 (m), 846 (m), 821 (m), 750 (m), 712 (vs), 692 (vs), 683 (vs), 651 (m), 526 (vs), 473 (s)

[(b-15-c-5-Na-dt)Pt(dppe)][BPh4], [Na(3g)][BPh_4]

Complex **3g** (0.020 g, 0.0218 mmol) and $NaBPh_4$ (0.010 g, 0.0218 mmol) were combined in a small 10 mL vial with a 1:1 mixture of CH_2Cl_2 and MeOH (8 mL) and left to stir for 1 hour under ambient conditions. Crystallization occurred by layering hexanes on a concentrated CH_2Cl_2:MeOH mixture to afford yellow crystals suitable for X-ray diffraction (0.022g, 79% yield). **^{1}H NMR** (<u>300 MHz, ppm, d^6-DMSO</u>): δ_H = 7.82-7.74 (8H, m, phosphine *m*-H), 7.55-7.48 (12H, m, phosphine *o,p*-H), 7.18-7.11 (8H, m, borate C–H), 6.94-6.83 (8H, m, borate

C−H), 6.81-6.76 (4H, m, borate *p*-C−H), 6.74 (2H, s, benzo C−H), 3.95-3.89 (4H, m, crown C−H), 3.71 (4H, m, crown C−H), 3.64 (8H, br s, crown C−H), 2.63 (4H, d, $^2J_{PH}$ = 19.6 Hz, PCH_2); (300 MHz, *d*^{3}-MeCN) δ_H = 7.86 – 7.77 (8H, m, *m*-H), 7.59-747 (12H, m, *o,p*-H), 7.31-7.24 (8H, m, borate C−H), 7.06-6.96 (8H, m, borate C−H), 6.88-6.82 (4H, m, borate C−H), 5.47 (2H, s, benzo C−H), 4.08 (4H, s, crown C−H), 3.80 (4H, s, crown C−H), 3.68 (8H, s, crown C−H), 2.60 (4H, d, $^2J_{PH}$ = 18.9 Hz, PCH_2). **^{31}P NMR** (121 MHz, ppm, *d*^{6}-DMSO) $\delta_P\{^1H\}$ = 46.14 with satellites at 57.519.94 and 34.80 ($^1J_{Pt\text{-}P}$ = 2748 Hz); (121 MHz, ppm, *d*^{3}-MeCN) $\delta_P\{^1H\}$ = 46.23 with satellites at 57.57 and 34.85 ($^1J_{Pt\text{-}P}$ = 2749 Hz). **HRMS** (ESI(+)) *m/z*: $[M+H]^+$ calc. for $C_{40}H_{42}O_5P_2S_2PtNa^+$ 946.1494; found: 946.1492. **Elemental Analysis** calc. for $C_{64}H_{62}BO_5NaP_2S_2Pt\cdot$½MeOH: C 59.71, H 4.85 %; found: C 59.70, H 4.94%. **IR** (ν_{max}, cm^{-1}): 3052(w), 2980(w), 2917(w), 2873(w), 1684(w), 1654(w),1602(w), 1579(w), 1535(w),1513(w), 1482(m), 1452(m), 1435(s), 1384(w), 1350(m), 1290(w), 1245(m), 1177(m), 1120(m), 1100(vs), 1087(s), 1047(m), 1029(m), 975(w), 938(m), 923(m), 909(m), 878(m), 847(m), 825(m), 798(w), 782(w), 747(m), 733(s), 704(vs), 689(vs), 658(m), 611(s), 533(vs), 484(s), 432(w)

15-crown-5-benzodithiolate complex (b-15-c-5-dt)Pd(dppf), 4g

Pd_2dba_3 (0.100 g, 0.109 mmol), dppf (0.121 g, 0.218 mmol) and tetrathiocin **1g** (0.072 g 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the suspension was heated in the microwave for 20 min at 150 °C. The resultant dark solution was filtered off leaving behind a small amount of dark red solid. The filtrate was evaporated *in vacuo* to afford dark solid (0.062 g, 57% yield). Recrystallization of the solid was achieved by layering hexanes on a concentrated CH_2Cl_2:MeOH mixture affording yellow crystals suitable for X-ray diffraction.
^{1}H NMR (300 MHz, ppm, *d*^{6}-DMSO): δ_H = 7.73-7.67 (8H, m, phosphine *m*-H), 7.46-7.41 (12H, m, phosphine *o,p*-H), 6.38 (2H, s, benzo C−H), 4.55 (4H, s, *Fc* C−H), 4.16 (4H, s, *Fc* C−H), 3.84-3.82 (4H, m, crown C−H), 3.65 (4H, m, crown C−H), 3.59 (8H, s, crown C−H); (300 MHz, ppm, *d*^{3}-MeCN) δ_H = 7.75-7.73 (8H, m, phosphine *m*-H), 7.44-39 (12H, m, phosphine *o,p*-H), 6.42 (2H, s, benzo C−H), 4.26 (4H, s, *Fc* C−H), 4.20 (4H, s, *Fc* C−H), 3.88-3.86 (4H, m, crown C−H), 3.71-3.69 (4H, m, crown C−H), 3.60 (8H, br s, crown C−H). **^{31}P NMR** (121 MHz, ppm, *d*^{6}-DMSO) $\delta_P\{^1H\}$ = 24.97; (121 MHz, ppm, *d*^{3}-MeCN) $\delta_P\{^1H\}$ = 25.10. **HRMS** (ESI(+)) *m/z*: $[M+H]^+$ calc. for $C_{48}H_{47}FeO_5P_2S_2Pd^+$ 991.0743; found: 991.0726. **Elemental Analysis** calc. for $C_{48}H_{46}FeO_5P_2S_2Pd\cdot$¼$CH_2Cl_2$: C 57.24, H 4.64 %; found: C 57.42, H 5.06 %. **IR** (cm^{-1}): $\tilde{\nu}$ = 3053(w), 2911(m), 2865(m), 1480(s), 1450(s), 1435(vs), 1306(w), 1247(s), 1133(m), 1096(s), 1063(m), 931(w), 847(w), 824(w), 746(m), 732(m), 695(vs), 635(w), 546(s), 491(s), 466(m).

[(b-15-c-5-Na-dt)Pd(dppf)][BPh_4], [Na(4g)][BPh_4]

Complex **2g** (0.089 g, 0.089 mmol) and $NaBPh_4$ (0.031 g, 0.089 mmol) were combined in a small 10 mL vial with a 1:1 mixture of CH_2Cl_2 and MeOH and left to stir for 1 hour under ambient conditions. Crystallization occurred by layering hexanes on a concentrated CH_2Cl_2:MeOH mixture to afford orange crystals suitable for X-ray diffraction. The yield for this reaction was invariably low, yielding only a few crystals per reaction attempt.
^{1}H NMR (300 MHz, ppm, *d*^{6}-DMSO): δ_H = 7.54 (8H, m, *m*-H), 7.43 (12H, m, phosphine *o,p*-H), 6.92 (12H, m, borate C−H), 6.78 (8H, m, borate C−H), 6.41 (2H, s, benzo C−H), 4.54 (4H, s, *Fc* C−H), 4.16 (4H, s, *Fc* C−H), 3.85 (4H, m, crown C−H), 3.65 (4H, m, crown C−H), 3.58 (12H, m, crown C−H); (300 MHz, ppm, *d*^{3}-MeCN) δ_H = 7.53 (8H, m, phosphine *m*-H), 7.27 (12H, m, phosphine *o,p*-H), 6.99 (12H, m, borate C−H), 6.84 (8H, m, borate C−H), 6.52 (2H, s, benzo C−H), 4.47 (4H, s, *Fc* C−H), 4.19 (4H, s, *Fc* C−H), 3.97 (4H, m, crown C−H), 3.64 (4H, m, crown C−H), 3.58 (12H, s, crown C−H). **^{31}P NMR** (121 MHz, ppm, *d*^{6}-DMSO) $\delta_P\{^1H\}$ = 25.49; (121 MHz, ppm, *d*^{3}-MeCN) $\delta_P\{^1H\}$ = 25.78. **HRMS** (MALDI-MS) *m/z*: $[M]^+$ calc. for $C_{48}H_{46}FeO_5P_2S_2PdNa^+$ 1013.0562; found 1013.0568. **Elemental Analysis** calc. for $C_{72}H_{66}BFeO_5NaP_2S_2Pd$ C 64.85, H 4.99%; found: C 64.50, H 4.95%. **IR** (ν_{max}, cm^{-1}): 3049(w), 2153(w), 1982(w), 1579(w), 1480(m), 1454(m), 1433(m), 1385(w), 1351(w), 1242(m), 1179(m), 1126(m), 1095(s), 1058(m), 1031(m), 998(w), 938(w), 927(w), 910(w), 846(m), 823(m), 744(s), 732(s), 704(vs), 693(vs), 631(w), 611(s), 544(m), 527(m), 520(s), 491(vs), 464(vs), 430(s).

15-crown-5-benzodithiolate complex (b-15-c-5-dt)Pt(dppf), 5g

Pt_2dba_3 (0.119 g, 0.109 mmol), dppf (0.121 g, 0.218 mmol) and tetrathiocin **1g** (0.072 g 0.109 mmol) were combined in an oven-dried 5 mL microwave vial in the glove box. Dry toluene (5 mL) was added and the

suspension was heated in the microwave for 60 min at 150 °C. The resultant dark solution was filtered off leaving behind a small amount of dark brown solid. The filtrate was evaporate in vacuo to afford dark solid (0.062 g, 57% yield). The solid was recrystallized from DCM layered with hexanes to produce yellow plates suitable for X-ray diffraction.

^{1}H NMR (300 MHz, ppm, d^6-DMSO): δ_H = 7.69-7.66 (8H, m, phosphine *m*-H), 7.55-7.40 (12H, m, phosphine *o*,*p*-H), 6.54 (2H, s, benzo C−H), 4.52 (4H, s, *Fc* C−H), 4.15 (4H, s, *Fc* C−H), 3.862-3.830 (4H, m, crown C−H), 3.65 (4H, m, crown C−H), 3.59 (8H, s, crown C−H); (300 MHz, ppm, d^3-MeCN) δ_H = 7.77-7.71 (8H, m, phosphine *m*-H), 7.52-7.49 (12H, m, phosphine *o,p*-H), 6.59 (2H, s, benzo C−H), 4.44 (4H, s, *Fc* C−H), 4.21 (4H, s, *Fc* C−H), 3.91-3.88 (4H, m, crown C−H), 3.72-3.69 (4H, m, crown C−H), 3.60 (8H, br s, crown C−H). **^{31}P NMR** (121 MHz, ppm, d^6-DMSO) $\delta_P\{^1H\}$ = 17.72 with satellites at 29.94 and 5.59 ($^1J_{Pt\text{-}P}$ = 2946 Hz); (121 MHz, ppm, d^3-MeCN) $\delta_P\{^1H\}$ = 17.49 with satellites at 29.70 and 5.33 ($^1J_{Pt\text{-}P}$ = 2949 Hz). **HRMS** (ESI(+)) *m/z*: $[M+H]^+$ calc. for $C_{48}H_{47}O_5P_2S_2PtFe^+$ 1080.1338; found: 1080.1306. **Elemental Analysis** calc. for $C_{48}H_{46}FeO_5P_2S_2Pt$: C 52.39, H 4.29 %; found: C 53.70, H 4.58 %. **IR** (ν_{max}, cm^{-1}): 3071(w), 3046(w), 2920(w), 2860(w), 1647(w), 1622(w), 1579(w), 1547(w), 1472(m), 1453(m), 1433(m), 1393(w), 1344(w), 1301(m), 1251(m), 1170(m), 1131(s), 1094(m), 1061(m), 1028(m), 982(w), 868(w), 832(w), 748(s), 693(vs), 636(m), 550(m), 530(m) 511(m), 490(s), 464(vs), 436(m)

[(b-15-c-5-Na-dt)Pt(dppe)][BPh4], [Na(5g)][BPh$_4$]

Complex **5g** (0.020 g, 0.0218 mmol) and $NaBPh_4$ (0.010 g, 0.0218 mmol) were combined in a small 10 mL vial with a 1:1 mixture of CH_2Cl_2 and MeOH (8 mL) and left to stir for 1 hour under ambient conditions. Crystallization occurred by layering hexanes on a concentrated CH_2Cl_2:MeOH mixture to afford yellow crystals suitable for X-ray diffraction (0.022g, 79% yield). **^{1}H NMR** (300 MHz, ppm, d^6-DMSO): δ_H = 7.73-7.64 (8H, m, phosphine m H), 7.55-7.38 (12H, m, phosphine *o*,*p*-H), 7.18-7.11 (8H, m, borate C−H), 6.94-6.86 (8H, m, borate C−H), 6.81-6.75 (4H, m, borate *p*-C−H), 6.54 (2H, s, benzo C−H), 4.53-4.45 (4H, s, *Fc* C−H), 4.16-4.12 (4H, s, *Fc* C−H), 3.85-3.81 (4H, m, crown C−H), 3.66-3.58 (12H, m, crown C−H); (300 MHz, d^3-MeCN) δ_H = 7.78-7.66 (8H, m, phosphine m H), 7.55-7.31 (12H, m, phosphine *o*,*p*-H), 7.30-7.18 (8H, m, borate C−H), 7.03-6.90 (8H, m, borate C−H), 6.88-6.77 (4H, m, borate *p*-C−H), 6.70 (2H, s, benzo C−H), 4.45-4.33 (4H, s, *Fc* C−H), 4.22-4.12 (4H, s, *Fc* C−H), 4.02-3.92 (4H, m, crown C−H), 3.68-3.53 (12H, m, crown C−H) **^{31}P NMR** (121 MHz, ppm, d^6-DMSO) $\delta_P\{^1H\}$ = 17.47 with satellites at 29.58 and 5.26 ($^1J_{Pt\text{-}P}$ = 2943 Hz); (121 MHz, ppm, d^3-MeCN) $\delta_P\{^1H\}$ = 17.80 with satellites at 30.05 and 5.64 ($^1J_{Pt\text{-}P}$ = 2954 Hz). **HRMS** (ESI(+)) *m/z*: $[M+H]^+$ calc. for $C_{48}H_{46}O_5P_2S_2PtNaFe^+$ 1103.1171; found: 1103.1172. **Elemental Analysis** calc. $C_{72}H_{66}BFeO_5NaP_2S_2Pt$·: C 60.81, H 4.68 %; found: C 60.50, H 4.54%. **IR** (ν_{max}, cm^{-1}): 3053(w), 2036(w), 3003(w), 2902(w), 2864(w), 1578(w), 1475(m), 1451(m), 1431(m), 1381(w), 1353(w), 1293(w), 1239(m), 1166(m), 1115(m), 1093(s), 1036(m), 997(w), 975(w), 940(w), 919(m), 846(m), 822(m), 735(s), 696(vs), 636(m), 610(m), 550(s), 516(m), 490(vs), 466(vs), 436(m)

II. UV-Vis Studies

UV-Vis titration experiments were performed on an Agilent 8453 Spectrophotometer, using quartz cuvettes (1 cm optical path length) at 25 °C. Solutions of **2g** in a 1:1 CH_2Cl_2:MeCN mixture were prepared with a concentration of 0.002mol L^{-1} and aliquots of a 0.0001 mol L^{-1} $NaBPh_4$ solution in the same solvent mixture were added. The resultant UV/vis data are presented in Figure S-II-1. The position of λ_{max} shifts with increasing equivalents of Na^+ is shown in Figure S-II-2.

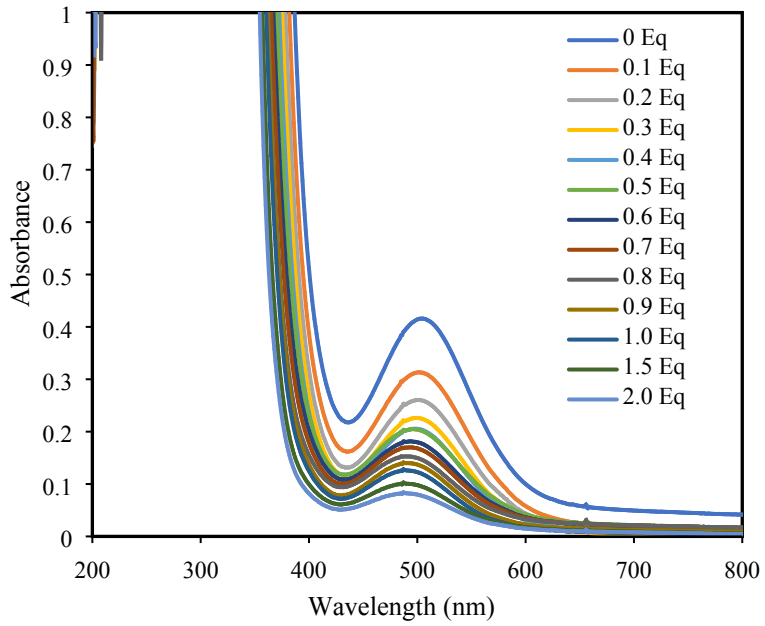

Figure S-II-1: Solution UV-vis data for **2g** in the presence of increasing numbers of equivalents of Na^+ ions.

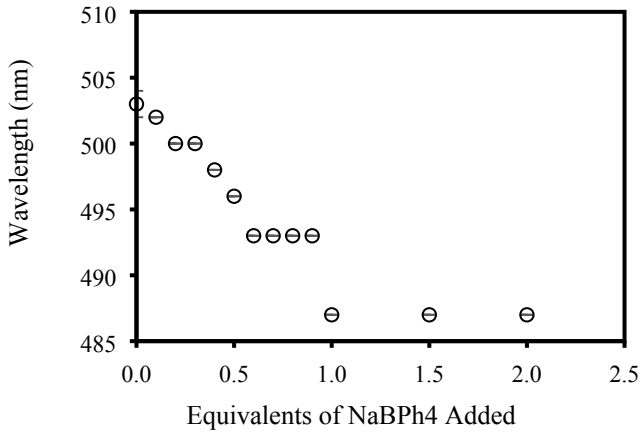

Figure S-II-2: Change in λ_{max} for **2g** with equivalents of $NaBPh_4$ added (solvent = 1:1 CH_2Cl_2:MeCN).

III. Single Crystal X-Ray Diffraction

Crystals were mounted on a cryoloop with paratone oil and examined on either a Bruker D8 Venture diffractometer equipped with Photon 100 CCD area detector or a Bruker APEX-II diffractometer with CCD detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). An Oxford Cryostream cooler was used to maintain cryogenic temperatures for these studies. Data were collected using the APEX-II software,[1] integrated using SAINT[2] and corrected for absorption using a multi-scan approach (SADABS).[3] Final cell constants were determined from full least squares refinement of all observed reflections. The structures of **2c-2f** were solved by direct methods (SHELXS),[4] **[Na(2g)][BPh$_4$]** was solved using charge flipping methods (olex2.solve),[5] while all other structures were solved using intrinsic phasing (SHELXT).[6] All structures were refined with full least squares refinement on F^2 using either SHELXL[7] or Olex2 software.[5] In structures **2b**, **2g**, **3b**, and **4g** there were regions of poorly resolved electron density located in voids indicative of residual lattice solvent that could not be modelled sensibly and was then removed using PLATON SQUEEZE.[8] All hydrogen atoms were added at calculated positions and refined isotropically with a riding model. A summary of key crystallographic data for the complexes is presented in Tables III.1 – III.6. The structures have been deposited with the Cambridge Structural Data Centre (1972236–1972253). Thermal ellipsoid plots for each metal dithiolate complex with selected atom labelling are presented in Figures III.1 – III.18.

References:

1 APEX II, Bruker AXS, Madison, WI, USA.
2 SAINT, Bruker AXS, Madison, WI, USA.
3 SADABS, Bruker AXS, Madison, WI, USA.
4 G. M.Sheldrick, SHELXS-97, A Program for Automatic Solution of Crystal Structures, University of Göttingen, 1997.
5 O. V. Dolomanov, L. J. Bourhis, R. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339-341.
6 G. M. Sheldrick *Acta Crystallog.. Sect. A: Found. Adv.*, 2015, **71**, 3-8.
7 SHELXTL, Bruker AXS, Madison, WI, USA, 2015.
8 A. L. Spek, *Acta Crystallogr. Sect. C: Struct. Chem.,* 2015, **71**, 9-18.

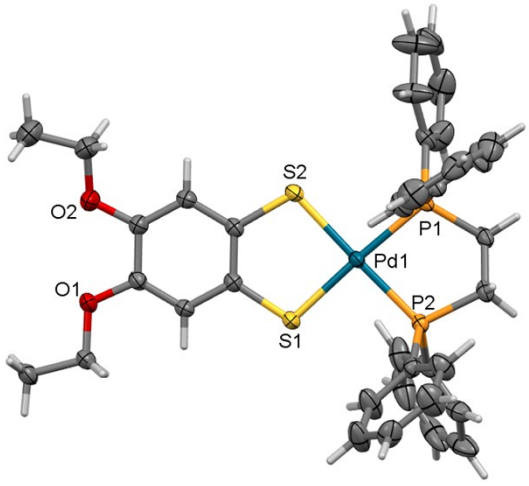

Figure III.1: Crystal structure of **2b** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

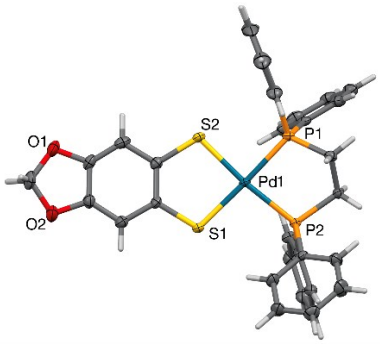

Figure III.2: Crystal structure of **2c** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

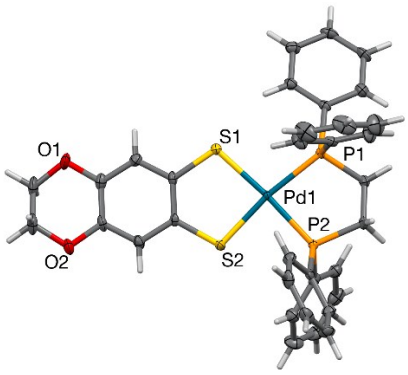

Figure III.3: Crystal structure of **2d** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Solvent molecules omitted for clarity.

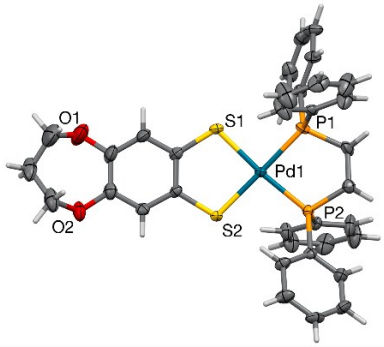

Figure III.4: Crystal structure of **2e** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Minor component of disorder omitted for clarity.

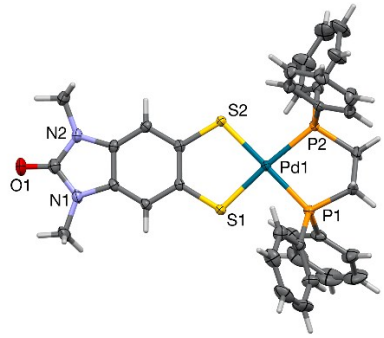

Figure III.5: Crystal structure of **2f** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Lattice solvent omitted for clarity.

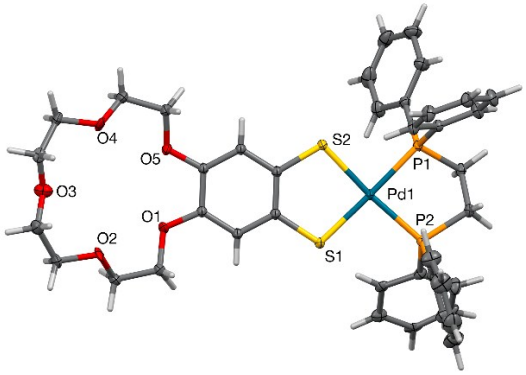

Figure III.6: Crystal structure of **2g** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Minor component of disorder omitted for clarity.

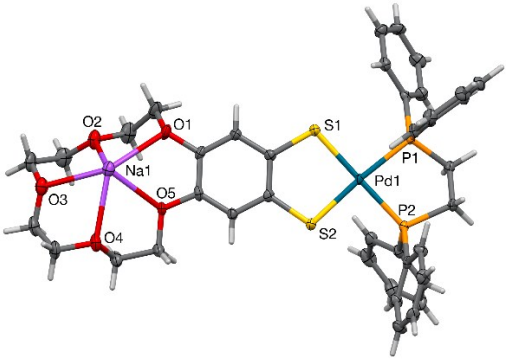

Figure III.7: Crystal structure of [Na(**2g**)]$^+$ with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. The BPh_4^- counterion and lattice solvent molecules are omitted for clarity.

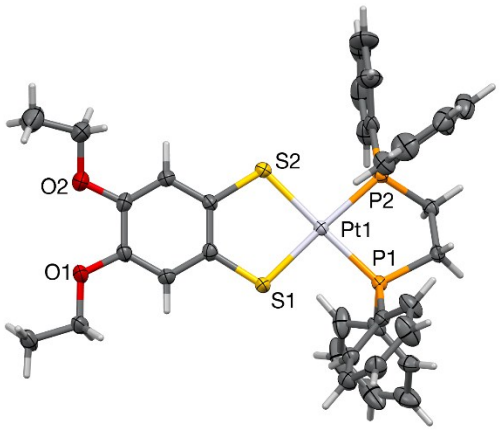

Figure III.8: Crystal structure of **3b** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

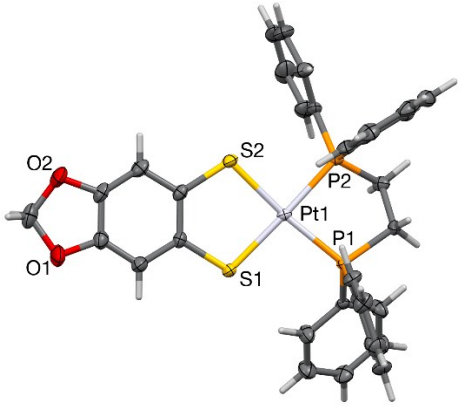

Figure III.9: Crystal structure of **3c** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

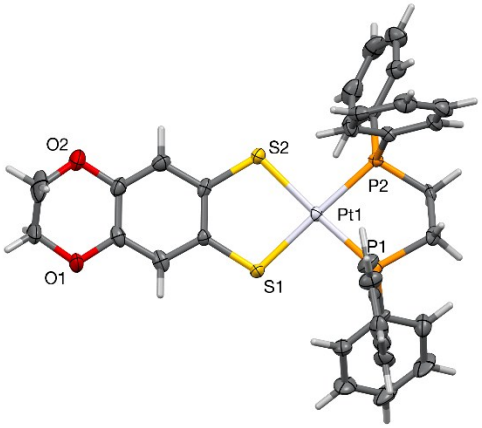

Figure III.10: Crystal structure of **3d** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Lattice solvent molecules omitted for clarity.

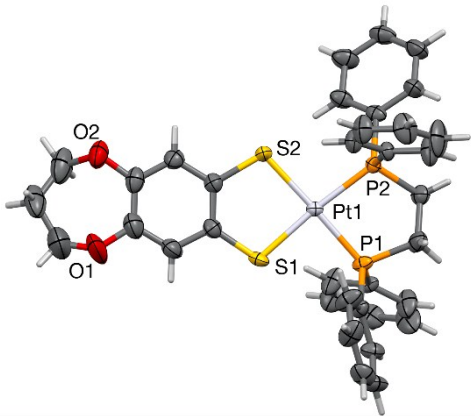

Figure III.11: Crystal structure of **3e** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Minor component of disorder omitted for clarity.

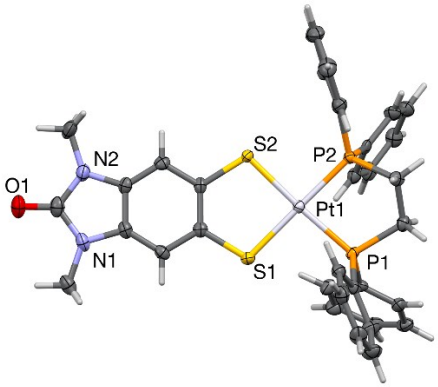

Figure III.12: Crystal structure of **3f** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

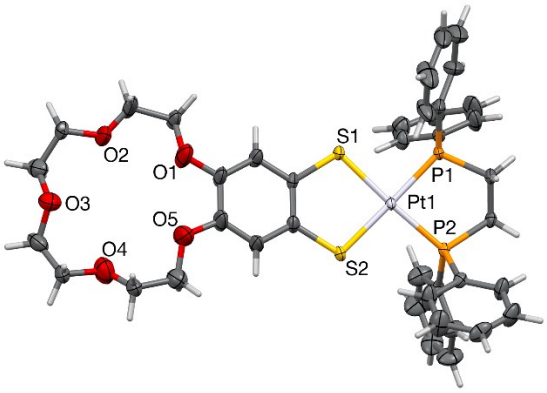

Figure III.13: Crystal structure of **3g** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level.

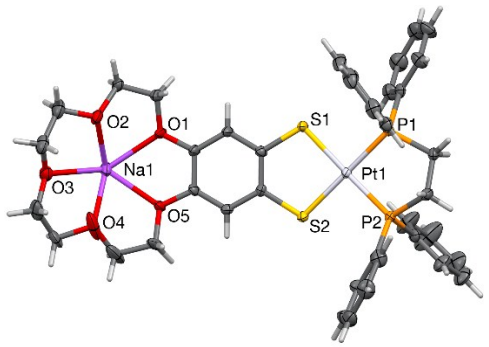

Figure III.14: Crystal structure of [Na(**3g**)]$^+$ with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Minor components of disorder, BPh_4^- counterion and residual solvent molecules omitted for clarity.

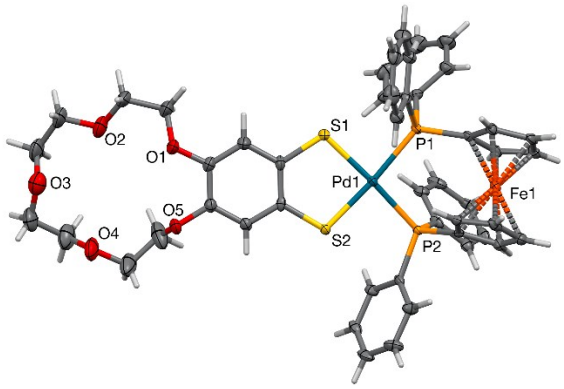

Figure III.15: Crystal structure of **4g** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Lattice solvent molecules omitted for clarity.

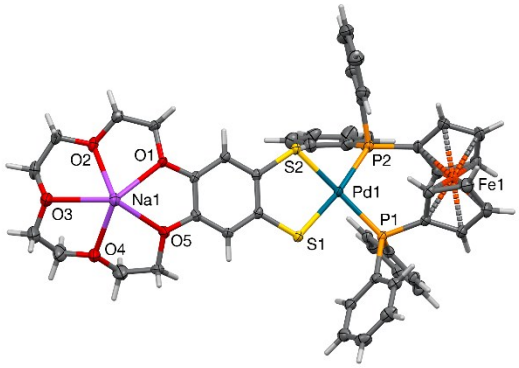

Figure III.16: Crystal structure of [Na(**4g**)]$^+$ with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Lattice solvent and BPh_4^- counterion omitted for clarity.

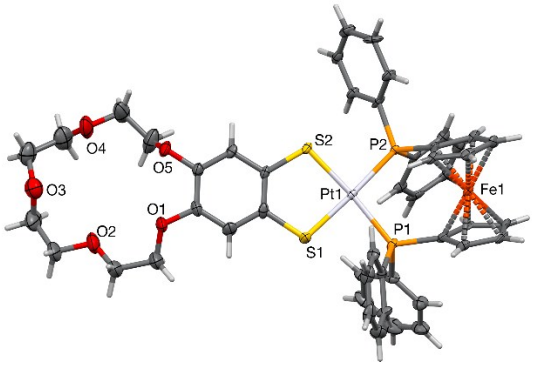

Figure III.17: Crystal structure of **5g** with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Lattice solvent molecules omitted for clarity.

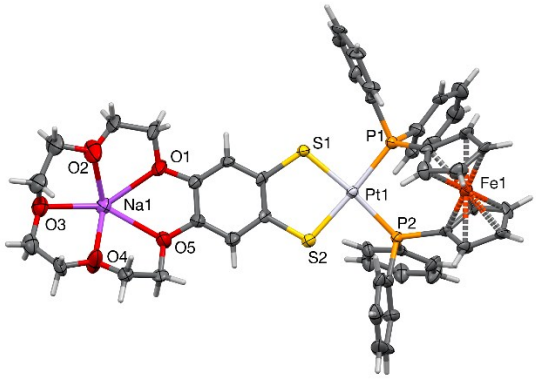

Figure III.18: Crystal structure of [Na(**5g**)]$^+$ with selected atom labelling, thermal ellipsoids for non-H atoms drawn at 50% probability level. Minor components of disorder and BPh_4^- counterion omitted for clarity.

Table III.1 Crystal data for compounds **2b**, **2c** and **2d**·0.5CH_2Cl_2

Compound	**2b**	**2c**	**2d·0.5CH_2Cl_2**
Empirical formula	$C_{36}H_{36}O_2P_2PdS_2$	$C_{33}H_{28}O_2P_2PdS_2$	$C_{34.5}H_{31}ClO_2P_2PdS_2$
Formula weight	733.11	689.01	745.50
Temperature/K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	12.247(3)	11.053(5)	17.797(7)
b/Å	13.509(4)	12.788(6)	20.004(7)
c/Å	23.332(7)	20.727(9)	17.816(7)
$\alpha/°$	90	90	90
$\beta/°$	91.730(3)	97.308(6)	92.047(4)
$\gamma/°$	90	90	90
Volume/Å^3	3858.5(19)	2906(2)	6338(4)
Z	4	4	8
ρ_{calc} g/cm^3	1.262	1.575	1.562
μ/mm^{-1}	0.699	0.923	0.934
F(000)	1504	1400	3032
Crystal size/mm^3	0.160 × 0.090 × 0.070	0.180 × 0.040 × 0.040	0.160 × 0.090 × 0.070
θrange for data collection/°	2.25 to 27.57	1.981 to 27.697	1.018 to 26.714
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -29 ≤ l ≤ 30	-14 ≤ h ≤ 14 -16 ≤ k ≤ 16 -27 ≤ l ≤ 26	-22 ≤ h ≤ 22, -25 ≤ k ≤ 25, -22 ≤ l ≤ 22
Reflections collected	8830	32920	70375
Independent reflections	8830 [R(int) = 0.0290]	6654 [R(int) = 0.0718]	13391 [R(int) = 0.0470]
Data/restraints/parameters	8830 / 0 / 391	6654 / 0 / 361	13391 / 0 / 767
Goodness-of-fit on F^2	1.129	1.086	1.106
Final R indices [I>=2σ (I)]	R_1=0.0298, wR_2= 0.0861	R_1=0.0439, wR_2= 0.0849	R_1=0.0304, wR_2= 0.0689
Final R indices [all data]	R_1=0.0341, wR_2=0.0939	R_1=0.0621, wR_2= 0.0918	R_1=0.0321, wR_2= 0.0698
Largest diff. peak/hole /e Å^3	0.741 and -0.326	0.679 and -0.704	1.189 and -0.448
CSD Deposition No.	1972253	1972245	1972248

Table III.2 Crystal data for compounds **2e**, **2f**·CH_2Cl_2 and **2g**

Compound	**2e**	**2f·CH_2Cl_2**	**2g**
Empirical formula	$C_{35}H_{32}O_2P_2PdS_2$	$C_{36}H_{34}Cl_2N_2OP_2PdS_2$	$C_{40}H_{42}O_5P_2PdS_2$
Formula weight	717.06	814.01	835.19
Temperature/K	150(2)	173(2)	150(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P 2_1 2_1 2_1	$P2_1/c$	$P2_1/c$
a/Å	11.4906(12)	14.1330(5)	11.8434(12)
b/Å	12.9099(14)	24.2766(10)	13.561(3)
c/Å	21.333(2)	22.0469(9)	24.616(7)
$\alpha/°$	90	90	90
$\beta/°$	90	106.2705(15)	101.568(14)
$\gamma/°$	90	90	90
Volume/Å^3	3164.6(6)	7261.4(5)	3873.2(15)
Z	4	8	4
ρ_{calc} g/cm^3	1.505	1.489	1.432
μ/mm^{-1}	0.851	0.893	0.712
F(000)	1464	3312	1720
Crystal size/mm^3	0.160 × 0.060 × 0.050	0.511 × 0.200 × 0.062	0.340 × 0.160 × 0.140
θrange for data collection/°	1.844 to 27.500	2.931 to 28.312	1.755 to 28.631
Index ranges	-14 ≤ h ≤ 14 -16 ≤ k ≤ 16 -27 ≤ l ≤ 27	-18 ≤ h ≤ 18 -32 ≤ k ≤ 32 -29 ≤ l ≤ 29	-15 ≤ h ≤ 15 -17 ≤ k ≤ 18 -31 ≤ l ≤ 32
Reflections collected	36543	135287	9295
Independent reflections	7243 [R(int) = 0.0465]	18020 [R(int) = 0.0641]	9295 [R(int) = 0.0222]
Data/restraints/parameters	7243 / 68/ 435	18020 / 19 / 845	9295 / 44 / 461
Goodness-of-fit on F^2	1.056	1.054	1.052
Final R indices [I>=2σ (I)]	R_1=0.0337, wR_2= 0.0728	R_1=0.0408, wR_2=0.0837	R_1=0.0235, wR_2 = 0.0609
Final R indices [all data]	R_1=0.0389, wR_2= 0.0756	R_1=0.0661, wR_2=0.1001	R_1=0.0261, wR_2 =0.0624
Largest diff. peak/hole /e Å^{-3}	1.016 and -0.636	1.293 and -1.505	0.543 and -0.266
CSD Deposition No.	1972249	1972252	1972246

Table III.3 Crystal data for [Na(**2g**)$(MeOH)_2$][BPh_4]·MeOH·CH_2Cl_2, **3b** and **3c**

Compound	**[Na(2g)$(CH_3OH)_2$][BPh_4]·CH_3OH·CH_2Cl_2**	**3b**	**3c**
Empirical formula	$C_{68}H_{76}BCl_2NaO_8P_2PdS_2$	$C_{36}H_{36}O_2P_2PtS_2$	$C_{33}H_{28}O_2P_2PtS_2$
Formula weight	1358.45	821.80	777.70
Temperature/K	150(2)K	170(2)	170(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	9.565(7)	12.1612(5)	11.1176(4)
b/Å	17.558(12)	13.3852(5)	12.7701(5)
c/Å	20.088(14)	23.7430(10)	20.8750(9)
α/°	95.318(9)	90	90
β/°	98.525(9)	94.925(2)	97.1010(10)
γ/°	100.269(9)	90	90
Volume/Å^3	3258(4)	3850.6(3)	2941.0(2)
Z	2	4	4
ρ_{calc} g/cm^3	1.385	1.418	1.756
μ/mm^{-1}	0.541	3.863	5.052
F(000)	1412	1632	1528
Crystal size/mm^3	0.270 × 0.120 × 0.050	0.363 × 0.159 × 0.134	0.387 × 0.086 × 0.016
θrange for data collection/°	2.066 to 27.601	2.934 to 26.447	2.987 to 25.433
Index ranges	-12 ≤ h ≤ 12 -22 ≤ k ≤ 22 -25 ≤ l ≤ 26	-15 ≤ h ≤ 15 -16 ≤ k ≤ 16 -29 ≤ l ≤ 29	-13 ≤ h ≤ 12 -15 ≤ k ≤ 15 -25 ≤ l ≤ 25
Reflections collected	36253	85346	49441
Independent reflections	14503 [R(int) = 0.0410]	7914 [R(int) = 0.0368]	5420 [R(int) = 0.0650]
Data/restraints/parameters	14503 / 3 / 779	7914 / 0 / 390	5420 / 0 / 361
Goodness-of-fit on F^2	1.054	1.029	1.116
Final R indexes [I>=2σ (I)]	R_1=0.0489, wR_2=0.1122	R_1=0.0200, wR_2=0.0424	R_1=0.0268, wR_2=0.0478
Final R indexes [all data]	R_1=0.0642, wR_2=0.1215	R_1=0.0268, wR_2=0.0450	R_1=0.0392, wR_2=0.0519
Largest diff. peak/hole /e Å^{-3}	1.315 and -0.719	0.801 and -0.527	1.227 and -0.869
CSD Deposition No.	1972247	1972237	1972244

Table III.4 Crystal data for compounds **3d**·0.5CH_2Cl_2, **3e** and **3f**

Compound	**3d·0.5CH_2Cl_2**	**3e**	**3f**
Empirical formula	$C_{34.5}H_{31}ClO_2P_2PtS_2$	$C_{35}H_{32}O_2P_2PtS_2$	$C_{35}H_{32}O_2N_2P_2PtS_2$
Formula weight	834.19	805.75	817.77
Temperature/K	170(2)	170(2)	170(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P\ 2_1\ 2_1\ 2_1$	$P2_1/n$
a/Å	17.8196(7)	11.4938(4)	10.2809(5)
b/Å	20.1432(10)	12.8694(4)	16.2519(7)
c/Å	17.8701(9)	21.4788(6)	18.8916(9)
α/°	90	90	90
β/°	92.049(2)	90	95.946(2)
γ/°	90	90	90
Volume/Å^3	6410.3(5)	3177.11(17)	3139.5(3)
Z	8	4	4
ρ_{calc} g/cm^3	1.729	1.685	1.730
μ/mm^{-1}	4.723	4.680	4.737
F(000)	3288	1592	1616
Crystal size/mm^3	0.508 × 0.278 × 0.088	0.420 × 0.252 × 0.241	0.269 × 0.227 × 0.138
θrange for data collection/°	3.049 to 26.25	3.040 to 27.544	3.057 to 27.578
Index ranges	-19 ≤ h ≤ 22 -24 ≤ k ≤ 25 -21 ≤ l ≤ 22	-14 ≤ h ≤ 14 -13 ≤ k ≤ 16 -27 ≤ l ≤ 27	-13 ≤ h ≤ 13 -20 ≤ k ≤ 21 -24 ≤ l ≤ 24
Reflections collected	96564	36129	108432
Independent reflections	12897 [R(int) = 0.1349]	7216 [R(int) = 0.0276]	7241 [R(int) = 0.0901]
Data/restraints/parameters	12897 / 0 / 766	7216 / 60 / 409	7241 / 0 / 390
Goodness-of-fit on F^2	1.040	1.018	1.130
Final R indexes [I>=2σ (I)]	R_1=0.0501, wR_2=0.0863	R_1=0.0233, wR_2=0.0511	R_1=0.0383, wR_2=0.0629
Final R indexes [all data]	R_1=0.0897, wR_2=0.1009	R_1=0.0263, wR_2=0.0524	R_1=0.0619, wR_2=0.0712
Largest diff. peak/hole /e Å^{-3}	2.409 and -1.733	0.692 and -0.767	1.502 and -0.993
CSD Deposition No.	1972238	1972236	1972242

Table III.5 Crystal data for compounds **3g**, [Na(**3g**)][BPh_4]·$2CH_2Cl_2$ and **4g**·$2CH_2Cl_2$

Compound	**3g**	**[Na(3g)][BPh_4]·$2CH_2Cl_2$**	**4g·$2CH_2Cl_2$**
Empirical formula	$C_{40}H_{42}O_5P_2PtS_2$	$C_{66}H_{66}BCl_4NaO_5P_2PtS_2$	$C_{50}H_{50}Cl_4FeO_5P_2PdS_2$
Formula weight	923.88	1435.93	1161.01
Temperature/K	170(2)	150(2)	173(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	11.6904(5)	13.0406(8)	18.363(4)
b/Å	13.5792(6)	16.0671(16)	19.821(4)
c/Å	24.8680(12)	16.7995(11)	15.185(3)
α/°	90	80.747(4)	90
β/°	101.911(2)	78.054(2)	101.90(3)
γ/°	90	66.431(3)	90
Volume/Å^3	3862.7(3)	3144.4(4)	5408.0(2)
Z	4	2	4
ρ_{calc} g/cm^3	1.589	1.517	1.426
μ/mm^{-1}	3.866	2.575	0.977
F(000)	1848	1452	2368
Crystal size/mm^3	0.216 × 0.137 × 0.129	0.237 × 0.228 × 0.118	0.200 × 0.150 × 0.100
θrange for data collection/°	2.925 to 29.206	2.941 to 27.530	2.834 to 24.998
Index ranges	-14 ≤ h ≤ 16 -18 ≤ k ≤ 18, -34 ≤ l ≤ 34	-12 ≤ h ≤ 16 -20 ≤ k ≤ 20 -21 ≤ l ≤ 21	-21 ≤ h ≤ 21 -23 ≤ k ≤ 23 -18 ≤ l ≤ 17
Reflections collected	158228	37422	9499
Independent reflections	10455 [R(int) = 0.0819]	14041[R(int) = 0.0250]	9499 [R(int) = 0.0632]
Data/restraints/parameters	10455 / 0 / 451	14041 / 29 / 762	9499 / 0 / 586
Goodness-of-fit on F^2	1.051	1.133	1.163
Final R indexes [I>=2σ (I)]	R_1=0.0478, wR_2=0.1012	R_1=0.0319 wR_2=0.0658	R_1=0.0438, wR_2=0.0949
Final R indexes [all data]	R_1=0.0693, wR_2=0.1117	R_1=0.0416, wR_2=0.0712	R_1=0.0657, wR_2=0.1197
Largest diff. peak/hole / e Å^{-3}	3.365 and -1.828	2.209 and -1.181	0.974 and -0.865
CSD Deposition No.	1072240	1972243	1972250

Table III.6 Crystal data for compounds [Na(**4g**)][BPh_4]·3CH_2Cl_2, **5g**·2.75CH_2Cl_2 and [Na(**5g**)][BPh_4]

Compound	**[Na(4g)][BPh_4]·3CH_2Cl_2**	**5g·2.75CH_2Cl_2**	**[Na(5g)][BPh_4]**
Empirical formula	$C_{75}H_{72}BCl_6FeNaO_5P_2PdS_2$	$C_{50.75}H_{51.50}Cl_{5.50}FeO_5P_2PtS_2$	$C_{72}H_{66}BFeNaO_5P_2PtS_2$
Formula weight	1588.13	1313.39	1422.04
Temperature/K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	18.640(7)	18.343(2)	10.8886(6)
b/Å	17.432(7)	19.8358(19)	33.2871(17)
c/Å	22.044(9)	15.1897(17)	17.9102(9)
α/°	90	90	90
β/°	97.523(5)	102.082(4)	106.0570(10)
γ/°	90	90	90
Volume/Å^3	7101(5)	5404.4(10)	6238.3(6)
Z	4	4	4
ρ_{calc} g/cm^3	1.485	1.614	1.514
μ/mm^{-1}	0.845	3.307	7.587
F(000)	3256	2622	2880
Crystal size/mm^3	0.160 × 0.130 × 0.070	0.388 × 0.274 × 0.149	0.176 × 0.153 × 0.109
θrange for data collection/°	1.783 to 26.348	2.836 to 26.434	3.984 to 50.358
Index ranges	-23 ≤ h ≤ 23, -21 ≤ k ≤ 21, -27 ≤ l ≤ 27	-22 ≤ h ≤ 22 -24 ≤ k ≤ 24 -18 ≤ l ≤ 19	-10 ≤ h ≤ 10 -33 ≤ k ≤ 33 -17 ≤ l ≤ 17
Reflections collected	75252	170329	59803
Independent reflections	14432 [R(int) = 0.0524]	11090 [R(int) = 0.0965]	6471 [R(int) = 0.0834]
Data/restraints/parameters	14432 / 864 / 62	11090 / 26 / 631	6471 / 365 / 787
Goodness-of-fit on F^2	1.069	1.103	1.271
Final R indexes [I>=2σ (I)]	R_1=0.0541, wR_2=0.1319	R_1=0.0736, wR_2=0.1667	R_1=0.0961, wR_2=0.1992
Final R indexes [all data]	R_1=0.0675, wR_2=0.1418	R_1=0.0980, wR_2=0.1822	R_1=0.1125, wR_2=0.2065
Largest diff. peak/hole / e Å^{-3}	1.558 and -1.517	4.480 and -2.389	1.120 and -3.703
CSD Deposition No.	1972251	1972241	1972239

IV. Electrochemistry Studies: Cyclic Voltammetry

Electrochemical studies were undertaken using a BAS electrochemical instrument controlled through BAS epsilon software using scan rates between 100 and 500 mV/s. Samples were measured using a degassed CH_2Cl_2 solution of 0.10 M [TBA][PF_6] supporting electrolyte and a 3.0 M NaCl reference electrode at room temperature.

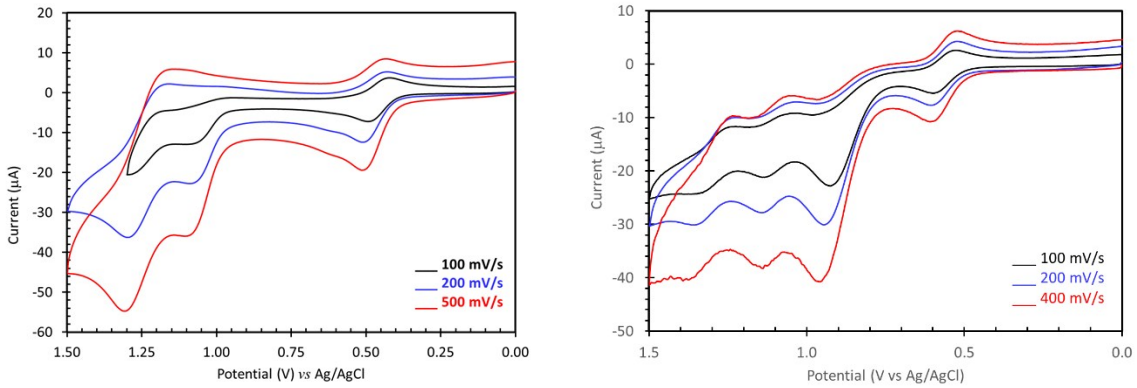

Figure IV-1: Cyclic voltammetry studies on (left) **4g** (right) [Na(**4g**)][BPh_4]

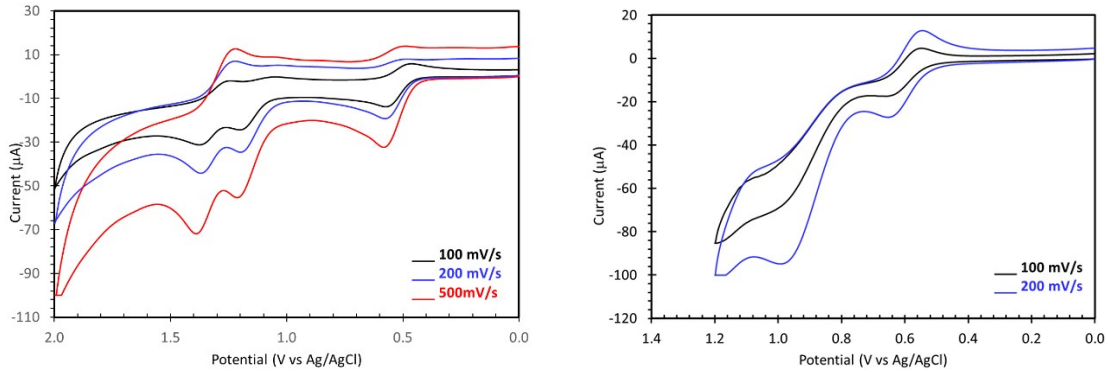

Figure IV-2: Cyclic voltammetry studies on (left) **5g** (right) [Na(**5g**)][BPh_4]

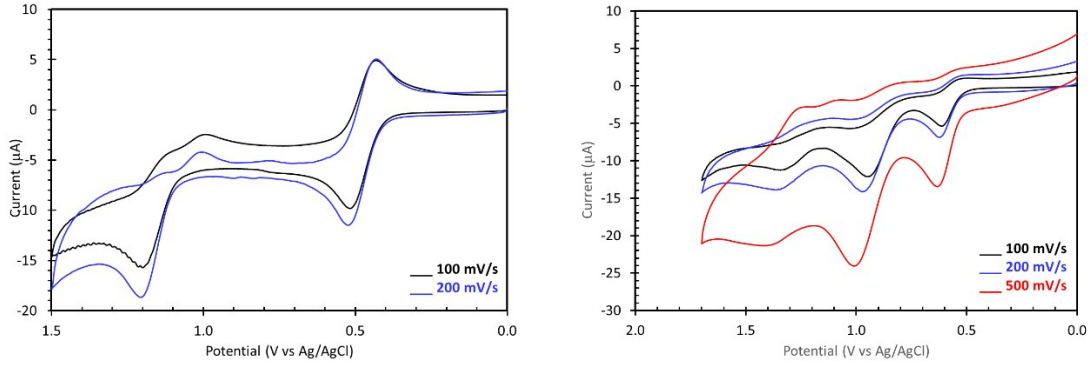

Figure IV-3: Cyclic voltammetry studies on (left) **2g** (right) [Na(**2g**)$(MeOH)_2$][BPh_4]

V. Computational Studies

Geometry-optimized DFT calculations on **2g**, **2g**$^+$ and [Na(**2g**)]$^+$ as well as **4g** and [Na(**4g**)]$^+$ were made within Jaguar and visualized using the Maestro GUI.[1] Geometry optimization used the B3LYP functional and 6-31G* basis set for all non-metals and the LACV3P* basis set for Na, Pd and Fe. The crystallographic geometry was implemented as an initial starting point for these calculations. The extent of solvation of the Na^+ ion in [Na(**2g**)]$^+$ and [Na(**4g**)]$^+$ in solution is unknown and likely solvent dependent. For these qualitative studies the methanol solvate molecules in the cation [Na(**2g**)$(MeOH)_2]^+$ were omitted and the donor S-atom making up the coordination environment of the sodium ion in [Na(**4g**)]$^+$ was similarly omitted. For the paramagnetic species **2g**$^+$ and **4g**$^+$ an unrestricted Hartree Fock approach was implemented while RHF formulisms were implemented for closed shell complexes. Refined atomic coordinates are provided in Tables V.1 – V.5.

References:

1. Jaguar, version 9.8, Schrodinger, Inc., New York, NY, 2017; A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang, and R. A. Friesner, *Int. J. Quantum Chem.*, 2013, **113**, 2110-2142.

Table V.1 Z-matrix for 2g

Pd1	0.6941350217	5.3570948584	-4.3050676257
S1	0.9055002891	3.6225595357	-2.7424753119
S2	-0.9286899563	4.0851741393	-5.4121884536
P1	0.3850567504	7.2121180555	-5.7303570562
P2	2.4203023290	6.6271398537	-3.3183471402
C11	0.2864624170	7.0227131820	-7.5554821244
C12	-0.2027003798	8.0478247762	-8.3807936183
H12	-0.5961755203	8.9612503257	-7.9433012617
C13	-0.2022165016	7.8942781268	-9.7664342174
H13	-0.5855984996	8.6929074228	-10.3964912264
C14	0.2801003374	6.7160155615	-10.3423339332
H14	0.2746507527	6.5967685972	-11.4226473273
C15	0.7553969078	5.6890529963	-9.5262355412
H15	1.1153777663	4.7631306034	-9.9666918255
C16	0.7559718622	5.8360456911	-8.1375133739
H16	1.0944750004	5.0230185455	-7.5015956254
C21	-1.0545366321	8.2530992440	-5.2451953712
C22	-2.2295821670	7.5978382237	-4.8402424275
H22	-2.2567041625	6.5107541597	-4.8165333605
C23	-3.3510280422	8.3348016603	-4.4604054373
H23	-4.2529210322	7.8136840949	-4.1502478999
C24	-3.3137872349	9.7300487065	-4.4656810126
H24	-4.1861192865	10.3014235285	-4.1586945934
C25	-2.1494837773	10.3899630579	-4.8595304972
H25	-2.1104578063	11.4764571425	-4.8619081944
C26	-1.0271986843	9.6574521347	-5.2497265518
H26	-0.1337604144	10.1953981505	-5.5535328125
C31	4.1082714224	6.1040500139	-3.8344647131
C32	5.1486815613	7.0095599216	-4.0982427831
H32	4.9922569734	8.0800070040	-3.9998985556
C33	6.4048228830	6.5483845275	-4.4939555202
H33	7.1995801094	7.2608400344	-4.7002593234
C34	6.6374473218	5.1789434524	-4.6262699069
H34	7.6152962257	4.8207794985	-4.9380133992
C35	5.6094814072	4.2719180486	-4.3640262966
H35	5.7828980352	3.2042189945	-4.4691918212
C36	4.3497707039	4.7276297425	-3.9763476623
H36	3.5458922123	4.0194047337	-3.7882108511
C41	2.4836297648	6.8661735554	-1.4990008819
C42	3.6459691736	7.3007526358	-0.8423925081
H42	4.5677817765	7.4437970493	-1.3993831680
C43	3.6302063986	7.5367404653	0.5319400059
H43	4.5367051264	7.8698235032	1.0310775622
C44	2.4579431973	7.3380806846	1.2657910682
H44	2.4494197929	7.5186810106	2.3375686670
C45	1.3032158876	6.8941295851	0.6204408254
H45	0.3926767371	6.7196730498	1.1873631388
C46	1.3136521695	6.6526484682	-0.7545899401
H46	0.4246996155	6.2720400185	-1.2491567007
C51	1.8762519666	8.3093414142	-5.4765390459
H51A	2.6906390794	7.8492825941	-6.0488102817
H51B	1.7214069421	9.3104474643	-5.8936675559
C52	2.2279653271	8.3639728668	-3.9837788610
H52A	1.4105907443	8.8174139566	-3.4106763865
H52B	3.1207064708	8.9714951803	-3.7996700756
O11	-1.5579726066	-0.9292971592	-2.2636928158
C61	-1.0416561307	-1.0744318255	-0.9539820653
H61A	-1.2854418219	-0.1942290296	-0.3426350285
H61B	0.0538503194	-1.1908690708	-0.9703686371
C62	-1.6685593591	-2.3162992589	-0.3452347324
H62A	-1.1460165320	-2.5568033774	0.5985860452
H62B	-1.5325388859	-3.1664426898	-1.0327257570
O12	-3.0387320128	-2.0671836920	-0.1246461107
C63	-3.7963071907	-3.1987046148	0.2450056506
H63A	-3.6693468132	-3.4275941060	1.3183140517
H63B	-3.4849451899	-4.0865126672	-0.3278277267
C64	-5.2601044488	-2.9165047392	-0.0514714258
H64A	-5.8937756663	-3.6575010123	0.4691396508
H64B	-5.5214585457	-1.9181927616	0.3345657218
O13	-5.4441211515	-2.9825120980	-1.4482124668
C65	-6.6786138860	-2.4833687952	-1.9127728187
H65A	-6.8904284257	-1.4914958005	-1.4821847116
H65B	-7.5104722346	-3.1570188338	-1.6370982480
C66	-6.5985447141	-2.3654844291	-3.4259919619
H66A	-6.1819680711	-3.3012579444	-3.8307666245
H66B	-7.6124279113	-2.2377885165	-3.8456589895
O14	-5.7755726324	-1.2651165785	-3.7472601697
C67	-5.2110922353	-1.3033997550	-5.0388218825
H67A	-5.9824027765	-1.1697161107	-5.8192156916
H67B	-4.7132410097	-2.2697079999	-5.2182270454
C68	-4.1930344917	-0.1834443048	-5.1584014671
H68A	-3.8767292031	-0.0921474498	-6.2098513185
H68B	-4.6480744073	0.7688946142	-4.8520868196
O15	-3.0954670557	-0.5014288568	-4.3223796028
C71	-0.2760188970	2.4082499409	-3.2906789519
C72	-0.4143419267	1.2107505200	-2.5587775790
H72	0.2229966935	1.0498963022	-1.6954086282
C73	-1.3551288306	0.2538898411	-2.9183034966
C74	-2.1893707111	0.4837514661	-4.0407868882
C75	-2.0417771100	1.6560951273	-4.7698311960
H75	-2.6674990886	1.8410238898	-5.6368040232
C76	-1.0840061096	2.6241740205	-4.4065775972

Table V.2 Z-matrix for $2g^{+}$

Pd1	0.6640305284	5.4176540953	-4.2704089258
S1	0.8360926373	3.6690565585	-2.6792980220
S2	-1.0293971832	4.1467325112	-5.3317336375
P1	0.4101605955	7.2476896827	-5.7358198323
P2	2.4396309443	6.6571062746	-3.3308917935
C11	0.2741229719	6.9215161600	-7.5278658051
C12	-0.5880334767	7.6511477289	-8.3603318118
H12	-1.2353367148	8.4168979909	-7.9442522619
C13	-0.6200038116	7.3914974697	-9.7311328992
H13	-1.2916288248	7.9600034852	-10.3683876223
C14	0.2006019870	6.4054428799	-10.2809144562
H14	0.1706994005	6.2054229080	-11.3481868811
C15	1.0523659369	5.6685427391	-9.4542727162
H15	1.6835868089	4.8909558111	-9.8751119000
C16	1.0855644893	5.9176050322	-8.0834896792
H16	1.7314478658	5.3219345880	-7.4428385945
C21	-0.9802954068	8.3319821840	-5.2446563068
C22	-2.0989763211	7.7617348103	-4.6148743860
H22	-2.1280115015	6.6921248498	-4.4278877163
C23	-3.1738070150	8.5627289346	-4.2293215274
H23	-4.0337108257	8.1093470949	-3.7441591967
C24	-3.1435376451	9.9382515707	-4.4613500620
H24	-3.9796791054	10.5610710126	-4.1557173281
C25	-2.0356942087	10.5143613313	-5.0860209318
H25	-2.0073315034	11.5847116869	-5.2701347976
C26	-0.9597761142	9.7183985228	-5.4776742730
H26	-0.1130187308	10.1880978344	-5.9695734810
C31	4.0807622179	6.0566018222	-3.8760013732
C32	5.2017303433	6.9050944134	-3.9013516985
H32	5.1230365539	7.9392450612	-3.5775167475
C33	6.4370038978	6.4247159867	-4.3328843990
H33	7.2965545257	7.0889274066	-4.3495603984
C34	6.5682453879	5.0954681875	-4.7408478874
H34	7.5318512570	4.7244613159	-5.0788478566
C35	5.4623442218	4.2456140926	-4.7135987196
H35	5.5611318384	3.2103285887	-5.0277548610
C36	4.2225040954	4.7210743991	-4.2850824156
H36	3.3638768095	4.0558871112	-4.2657224449
C41	2.4817173878	6.8766695583	-1.5176258817
C42	3.6442194451	6.6738778643	-0.7598307937
H42	4.5638515346	6.3553477135	-1.2401933562
C43	3.6228472642	6.8805996147	0.6207545750
H43	4.5280592126	6.7206516223	1.1998066000
C44	2.4479659899	7.2862646990	1.2548047362
H44	2.4356699311	7.4452551452	2.3293148880
C45	1.2838178590	7.4778725977	0.5054516081
H45	0.3630036338	7.7819623008	0.9953240278
C46	1.2957085433	7.2676792340	-0.8716964630
H46	0.3783511144	7.3956053629	-1.4420142688
C51	1.9427089580	8.2884729925	-5.5258424243
H51A	2.7409859074	7.7904984931	-6.0883449211
H51B	1.8089070451	9.2800114473	-5.9701110923
C52	2.2970625208	8.3788180717	-4.0373132981
H52A	1.5064593858	8.8910347783	-3.4769697787
H52B	3.2224531536	8.9416035658	-3.8779899883
O11	-1.6425320747	-0.8003930844	-2.1937079820
C61	-1.0168226035	-1.0649393005	-0.9296435077
H61A	-1.2193854915	-0.2340975153	-0.2434557231
H61B	0.0676298908	-1.1707353662	-1.0643642838
C62	-1.6130784660	-2.3521802580	-0.3925158624
H62A	-1.0512586698	-2.6441957371	0.5124117512
H62B	-1.4876911646	-3.1531951688	-1.1383911126
O12	-2.9721862972	-2.1201746939	-0.1207161883
C63	-3.7282468740	-3.2805205927	0.1882752395
H63A	-3.6283170516	-3.5363250082	1.2556067400
H63B	-3.3800647159	-4.1402013116	-0.4035754893
C64	-5.1844722374	-3.0133211286	-0.1495223609
H64A	-5.8144655237	-3.8024931954	0.2968909407
H64B	-5.4929075977	-2.0490464591	0.2857242797
O13	-5.3082349275	-2.9976380909	-1.5556633302
C65	-6.5814043181	-2.6136982759	-2.0291680555
H65A	-6.8859731742	-1.6440203578	-1.6031776247
H65B	-7.3494902240	-3.3586117430	-1.7567317984
C66	-6.5029854823	-2.5028843539	-3.5417112370
H66A	-6.0233353518	-3.4103458707	-3.9375815128
H66B	-7.5165279689	-2.4366688823	-3.9692004460
O14	-5.7448068291	-1.3499118346	-3.8735542586
C67	-5.0991560928	-1.4027810298	-5.1206335122
H67A	-5.8127531459	-1.3474809987	-5.9618300649
H67B	-4.5223971316	-2.3348442497	-5.2307446266
C68	-4.1611389006	-0.2144911444	-5.2143489889
H68A	-3.7096418920	-0.1602567011	-6.2136173293
H68B	-4.7022167828	0.7166058853	-5.0082104720
O15	-3.1373879946	-0.3974907356	-4.2251832728
C71	-0.3475887881	2.5072063142	-3.1921511438
C72	-0.4952126253	1.3166603500	-2.4489822919
H72	0.1372672376	1.1633180774	-1.5825605086
C73	-1.4223073485	0.3572944896	-2.8180253267
C74	-2.2696967277	0.5838765352	-3.9761263938
C75	-2.1353070942	1.7530142364	-4.7046829241
H75	-2.7604681525	1.9344417860	-5.5710009711
C76	-1.1796325092	2.7259059760	-4.3447917255

Table V.3 Z-matrix for $[Na(2g)]^+$

Pd1	0.0826061194	5.4518791192	2.8780865974
S1	-1.5965329177	3.8497252799	2.5222702910
Na1	-2.6575142333	0.7033377990	-3.8830606756
O1	-3.2217039891	1.3755276292	-1.7125054885
P1	-0.2492883648	5.4513321521	5.2094651091
S2	0.5960468436	5.3495228893	0.5837614095
O2	-5.0034793573	1.0141835935	-3.7923920717
P2	1.5907946015	7.2184442292	3.2753101273
O3	-3.6296556521	0.1184391948	-6.0241924227
O4	-1.0803536857	1.2335069808	-5.6035198926
O5	-1.5741866457	2.7270342804	-3.3480666766
C11	-1.9457405922	5.4528196779	5.8994336651
C12	-2.9651276850	6.0761230284	5.1617488547
H12	-2.7492774989	6.4767441836	4.1750611700
C13	-4.2574347436	6.1567443543	5.6810869010
H13	-5.0399467217	6.6399195096	5.1022439911
C14	-4.5483133830	5.6049761026	6.9304157969
H14	-5.5570038352	5.6620468545	7.3303757343
C15	-3.5417213346	4.9690052249	7.6602691330
H15	-3.7650231108	4.5281937900	8.6281502955
C16	-2.2456697240	4.8905168124	7.1499417185
H16	-1.4735100745	4.3855436540	7.7227914244
C21	0.6689987447	4.0973511234	6.0407883508
C22	1.2954095311	4.2578413329	7.2880783520
H22	1.2482126058	5.2052528915	7.8169288286
C23	1.9896018433	3.1976978348	7.8718958724
H23	2.4734638076	3.3373063292	8.8348666239
C24	2.0626622387	1.9653678990	7.2211514741
H24	2.6066018057	1.1419190318	7.6761430943
C25	1.4395001548	1.7957741667	5.9838012498
H25	1.4945616647	0.8387790232	5.4718878439
C26	0.7504357433	2.8538245273	5.3918523571
H26	0.2772430988	2.7210080461	4.4223681201
C31	0.8718702262	8.8554492742	2.8539983211
C32	0.0623620149	8.9518902019	1.7097298213
H32	-0.1237309425	8.0667572704	1.1070102486
C33	-0.5053386102	10.1739259459	1.3505210200
H33	-1.1287143152	10.2345503628	0.4623703746
C34	-0.2834353163	11.3104904818	2.1294255159
H34	-0.7342598490	12.2595558963	1.8519585576
C35	0.5164499844	11.2241955825	3.2694149402
H35	0.6929458620	12.1045109462	3.8816331380
C36	1.0934228505	10.0058778306	3.6298207919
H36	1.7166805020	9.9669500089	4.5182075795
C41	3.2776941158	7.1739075071	2.5624118917
C42	4.0061937636	8.3426127922	2.2907620718
H42	3.5551243451	9.3180205131	2.4476537216
C43	5.3122458283	8.2577453457	1.8080985281
H43	5.8674106665	9.1681883282	1.5985743791
C44	5.9023219377	7.0109683429	1.5901050739
H44	6.9192584097	6.9490758967	1.2124500846
C45	5.1783624339	5.8453608056	1.8483690437
H45	5.6270972198	4.8724356097	1.6673810485
C46	3.8695951643	5.9229922155	2.3253124760
H46	3.2981407355	5.0145472181	2.4955784164
C47	1.8585661676	7.2641330016	5.1225427921
H47A	2.5682693810	6.4596010676	5.3486083531
H47B	2.3297053007	8.2009062913	5.4377694397
C48	0.5236752536	7.0286614347	5.8411232477
H48A	-0.1882490178	7.8309135603	5.6141430728
H48B	0.6459313925	7.0091815929	6.9291822834
C51	-1.5036984342	3.5326327023	0.7840483796
C52	-2.3809290486	2.5921335940	0.2200060821
H52	-3.0589537636	2.0399817228	0.8654776482
C53	-2.3857139567	2.3440250109	-1.1454715426
C54	-4.6390797105	1.4998306694	-1.4967103824
H54A	-4.8427008716	2.2049664508	-0.6860115702
H54B	-5.0067360874	0.5095157699	-1.2090237391
C55	-5.3283561750	1.9598594044	-2.7718414458
H55A	-6.4166058054	1.9978622457	-2.6161471309
H55B	-4.9798013744	2.9626074176	-3.0618905502
C56	-5.5536533945	1.2851924893	-5.0767125332
H56A	-5.2313753652	2.2793937278	-5.4257510825
H56B	-6.6531275774	1.2774856367	-5.0406655252
C57	-5.0614127117	0.1840056557	-6.0073199495
H57A	-5.4064215412	-0.7869308730	-5.6388462742
H57B	-5.4570481164	0.3313700280	-7.0199091000
C58	-2.9909949704	0.8329340379	-7.0830892173
H58A	-3.3037632563	1.8877564802	-7.0844902069
H58B	-3.2622084802	0.3971345852	-8.0555362942
C59	-1.4878882704	0.7071403959	-6.8708767008
H59A	-1.2080816886	-0.3505789166	-6.8613838736
H59B	-0.9472469438	1.2014919506	-7.6887108218
C60	-0.8102410573	2.6380550039	-5.5945381443
H60A	-1.6861137391	3.2032201839	-5.9449319433
H60B	0.0354470903	2.8633009787	-6.2593092971
C61	-0.4632657942	3.0600299780	-4.1799840812
H61A	0.4388717948	2.5467761240	-3.8216845381
H61B	-0.2784363910	4.1412784491	-4.1754580012
C62	-1.4849602273	3.0182204181	-1.9853495507
C63	-0.5876146315	3.9267676334	-1.4360205963
H63	0.1230363999	4.4533649968	-2.0640593629
C64	-0.5845512202	4.1960479747	-0.0538750916

Table V.4 Z-matrix for 4g

Pd1	6.3029455838	5.1675366917	4.7976753109
Fe2	8.9622800112	1.7168841398	5.0658303327
S3	6.3497068809	7.4649477717	5.2774110405
P4	8.3270648431	4.9564679009	6.0516366594
P5	5.7418510513	2.8419030601	4.5059782130
S6	4.4694252416	5.6282776491	3.3860268980
O7	1.1190512331	9.6031251473	3.3778065752
O8	-1.6098991927	10.2195849604	3.1430571519
O9	-2.0176024279	12.9899030335	4.1084397782
O10	0.4306488341	13.0997649084	5.8444360057
O11	2.6778239205	11.0619155382	5.0414556322
C12	3.9594962370	7.2564835249	3.8788524774
C13	2.7237750487	7.7509673821	3.4211839672
H14	2.1076054471	7.1122630117	2.7974521376
C15	2.2948061800	9.0273336944	3.7770963455
C16	3.1021574791	9.8141724884	4.6288994648
C17	4.3285186338	9.3288285979	5.0603383564
H18	4.9310702664	9.9585829765	5.7094755311
C19	4.7751318283	8.0488373371	4.6922981692
C20	0.2631925920	8.8692128800	2.5219772245
H21	-0.1671437548	8.0067100209	3.0526433394
H22	0.8129767738	8.4952764589	1.6453523039
C23	-0.8352144445	9.7980998410	2.0416587898
H24	-0.3848262769	10.6655507976	1.5340878271
H25	-1.4512275874	9.2539002282	1.3030682235
C26	-2.6585034967	11.1060200713	2.8006126065
H27	-3.5520544972	10.5420696078	2.4810181621
H28	-2.3629028365	11.7686641101	1.9732759573
C29	-2.9865938664	11.9628483092	4.0105115674
H30	-3.9958460682	12.3972623186	3.9015301244
H31	-2.9930318640	11.3187672645	4.9026454531
C32	-1.8754713459	13.5518092156	5.4010747438
H33	-2.8484410236	13.6056306947	5.9163538737
H34	-1.5095095326	14.5745349205	5.2599829792
C35	-0.8805846121	12.7983417879	6.2774141399
H36	-1.0142375099	13.1114534734	7.3300593502
H37	-1.0852086768	11.7168481340	6.2273269198
C38	1.4399618859	12.4345011912	6.5848637587
H39	1.1718596687	12.4159993211	7.6551867683
H40	2.3527720507	13.0294731887	6.4740692763
C41	1.7383469847	11.0108751804	6.1202598000
H42	2.1778650969	10.4391161075	6.9528910912
H43	0.8200851968	10.5029320724	5.7980868334
C44	4.2585849604	2.3400576482	5.4984902158
C45	4.0652475774	1.0082616011	5.9070433230
H46	4.7990603242	0.2482131220	5.6576355589
C47	2.9346785252	0.6458935897	6.6407595519
H48	2.8030872118	-0.3894321612	6.9458622484
C49	1.9802805823	1.6059168269	6.9828954162
H50	1.1016130008	1.3231938956	7.5570869868
C51	2.1651162423	2.9301455368	6.5832954723
H52	1.4292432595	3.6870943914	6.8424751864
C53	3.2931833300	3.2981094259	5.8469268010
H54	3.4207238063	4.3270711787	5.5261372248
C55	5.3367577856	2.4049326530	2.7606076087
C56	4.4282857027	1.3868964321	2.4358077946
H57	3.8895828773	0.8652021503	3.2209052089
C58	4.2020758006	1.0443128720	1.1032053425
H59	3.4902413825	0.2584318606	0.8630781321
C60	4.8801836321	1.7119823270	0.0810265441
H61	4.6992881861	1.4453648877	-0.9572789770
C62	5.7794219474	2.7310477273	0.3956062299
H63	6.2964609663	3.2683385742	-0.3951478645
C64	6.0028913162	3.0813351166	1.7281877953
H65	6.6738442956	3.9014132567	1.9672190804
C66	8.0485143272	4.5318467206	7.8208435052
C67	9.0964481294	4.5154717694	8.7569627717
H68	10.1025967539	4.7902223039	8.4527390616
C69	8.8498134599	4.1723158523	10.0856200084
H70	9.6688663430	4.1614803040	10.8004423322
C71	7.5533883369	3.8563068224	10.5002547782
H72	7.3631443205	3.5937768811	11.5378883749
C73	6.5027512389	3.8954948596	9.5838241615
H74	5.4884699680	3.6705385617	9.9031400322
C75	6.7477052052	4.2358242448	8.2513323959
H76	5.9257178798	4.2892290924	7.5422551468
C77	9.4318093445	6.4295693963	6.1557941646
C78	10.5107726891	6.5881579537	5.2724879202
H79	10.7303431907	5.8224951271	4.5348393230
C80	11.3179816320	7.7240664399	5.3375665609
H81	12.1532535267	7.8272505797	4.6495554505
C82	11.0580285511	8.7199055342	6.2807268554
H83	11.6877611747	9.6041927691	6.3301403832
C84	9.9815029710	8.5738525407	7.1566695165
H85	9.7649619146	9.3463973955	7.8897413888
C86	9.1706741029	7.4401671709	7.0956335475
H87	8.3337113175	7.3454702084	7.7796244869
C88	6.9197516437	1.5004707505	4.9316906756
C89	7.5634484091	0.6000760751	4.0168009369
H90	7.4471553158	0.6118562789	2.9424798695
C91	8.4032378792	-0.2744618490	4.7629367614

H92	9.0465827713	-1.0395048606	4.3485121968
C93	8.2825867842	0.0653494548	6.1420674157
H94	8.8194275830	-0.3947446519	6.9612743119
C95	7.3762325508	1.1579683024	6.2521751221
H96	7.0949035469	1.6591394244	7.1676906306
C97	9.4570538986	3.6721194555	5.4150362047
C98	9.6004342654	3.3701450231	4.0151860949
H99	9.0339992420	3.8310204946	3.2169038819
C100	10.5677957249	2.3355043662	3.8762336894
H101	10.8615282914	1.8640989431	2.9476919251
C102	11.0339298954	1.9877297197	5.1777859780
H103	11.7411764478	1.2022966311	5.4118157640
C104	10.3596404705	2.8084654590	6.1257288668
H105	10.4652641951	2.7523720877	7.1993192411

Table V.5 Z-matrix for optimized structure of **4g⁺**

Pd1	6.0610908428	5.0524469579	5.0301987564
Fe2	9.1961914045	2.0363987982	4.6722443806
S3	5.8894269341	7.3324765563	5.6442712912
P4	8.2137716061	4.9954723114	6.0894426847
P5	5.8242310665	2.6861212292	4.5836912135
S6	4.0269931079	5.3913701087	3.8228847153
O7	0.7132935141	9.3167974944	3.6805812668
O8	-1.8690039966	10.2288932479	3.0100521603
O9	-0.6062852980	12.7610993316	3.4561342713
O10	1.1202303174	13.4483862745	5.9917917163
O11	2.1794824666	10.7319940600	5.5310691380
C12	3.5017720987	6.9782368261	4.2802606491
C13	2.2689577894	7.4637428061	3.7967318295
H14	1.6833638260	6.8378909023	3.1326200783
C15	1.8148400011	8.7230672387	4.1554080814
C16	2.5710576343	9.5236283602	5.1007913870
C17	3.8067442477	9.0664557008	5.5281150685
H18	4.3792251656	9.6961446839	6.2011023127
C19	4.3081675016	7.8176723266	5.1224652857
C20	-0.0399044369	8.7571731536	2.5970505498
H21	-0.6547306423	7.9281471125	2.9680478628
H22	0.6407860918	8.3879527031	1.8200136469
C23	-0.9010144068	9.8745404257	2.0405327062
H24	-0.2587459551	10.7284112199	1.7911419545
H25	-1.3809041072	9.5155417559	1.1144554424
C26	-2.5123651943	11.4774816950	2.7742328255
H27	-3.5842978116	11.3383106019	2.9630943157
H28	-2.3899926970	11.7878797834	1.7279033384
C29	-1.9913831715	12.5707439052	3.6991470729
H30	-2.5541125935	13.4989966874	3.5042284085
H31	-2.1731487835	12.2806389905	4.7454591876
C32	-0.0714208670	14.0059107137	3.8907434144
H33	-0.6867951714	14.8321655967	3.4961123889
H34	0.9224272234	14.0719403451	3.4374044539
C35	0.0678549183	14.1985095211	5.4036103757
H36	0.3114657920	15.2566889332	5.5691515777
H37	-0.8858549828	14.0013251916	5.9167392831
C38	0.7716921501	12.2745652498	6.6979736285
H39	-0.2301712447	12.3670270677	7.1480726935
H40	1.4977769182	12.1705802127	7.5124566507
C41	0.7884311658	11.0177462147	5.8430243923
H42	0.3740233676	10.1727211415	6.4079158914
H43	0.2247484420	11.1611404894	4.9236073723
C44	4.5494616742	1.9195508166	5.6713131868
C45	4.5532945581	0.5337838210	5.9131536701
H46	5.3239972153	-0.0955303951	5.4792108431
C47	3.5705733892	-0.0468074432	6.7151822920
H48	3.5864568174	-1.1193791804	6.8891151066
C49	2.5753356192	0.7439691395	7.2935795802
H50	1.8133910991	0.2897313440	7.9207951344
C51	2.5680519468	2.1205809042	7.0636374449
H52	1.7993875826	2.7446642645	7.5113112554
C53	3.5461318475	2.7070662961	6.2584178430
H54	3.5245418056	3.7777743367	6.0816719254
C55	5.2787696912	2.4078302016	2.8500138420
C56	4.3890960260	1.3787779123	2.5086737887
H57	3.9480638733	0.7563847788	3.2809695102
C58	4.0625162626	1.1504696091	1.1716790134
H59	3.3695733478	0.3531176531	0.9170319889
C60	4.6196564318	1.9420453754	0.1659055408
H61	4.3631219212	1.7604079086	-0.8742471891
C62	5.4988351030	2.9737815487	0.4992755792
H63	5.9252760142	3.6018186141	-0.2781385668
C64	5.8218166685	3.2112026315	1.8352023714
H65	6.4847879433	4.0335817036	2.0906150293
C66	8.1471100391	4.3459520171	7.8010751994
C67	9.2752249647	4.3897899539	8.6393058636
H68	10.1973465471	4.8475175206	8.2928037180
C69	9.2117261050	3.8663051443	9.9295299524
H70	10.0902932798	3.9015706608	10.5680396059
C71	8.0213709712	3.3089527852	10.4042194746
H72	7.9747682495	2.9052621631	11.4120148793
C73	6.8903367642	3.2854257529	9.5882585550
H74	5.9571636297	2.8689958018	9.9576752791
C75	6.9510721251	3.8039392801	8.2929389353
H76	6.0636251597	3.7937085350	7.6660787245
C77	9.0642640743	6.6171058277	6.2611793247
C78	9.9582968405	7.0613567935	5.2735257297
H79	10.1761727197	6.4397817716	4.4106481139
C80	10.5917136512	8.2973735533	5.4011751229
H81	11.2893198368	8.6228927004	4.6344069226
C82	10.3396386445	9.1072082258	6.5105255704
H83	10.8384697547	10.0669895120	6.6101751124
C84	9.4450947242	8.6760475913	7.4915313504
H85	9.2425566470	9.2992546241	8.3581125325
C86	8.8060214329	7.4418843090	7.3687859372
H87	8.1169258753	7.1195980131	8.1432921643
C88	7.2186332980	1.5183351447	4.7281133619
C89	7.8640251993	0.8266187614	3.6444299235
H90	7.6185046822	0.9311379028	2.5973995544
C91	8.8974362071	0.0157069701	4.1884682235

H92	9.5848838860	-0.5957236187	3.6192268261
C93	8.8995569850	0.1855155067	5.6031034343
H94	9.5902759319	-0.2737460670	6.2977578436
C95	7.8727756287	1.1091535111	5.9440343857
H96	7.6359672205	1.4552977265	6.9400951171
C97	9.4291663987	3.9890206788	5.1881919620
C98	9.4709232969	3.8563407745	3.7543385216
H99	8.7696298481	4.2997265493	3.0603391113
C100	10.5653359041	3.0126486104	3.4170937260
H101	10.8306481450	2.6896878681	2.4192791569
C102	11.2127541046	2.6206209249	4.6238481258
H103	12.0532745848	1.9435306878	4.7037644855
C104	10.5253021046	3.2200436579	5.7153981996
H105	10.7530046085	3.0760313608	6.7613340001