Supplementary Information

Transition metal complexes of the pyridylphopshine ligand *o*-$C_6H_4(CH_2PPy_2)_2$

Teresa F. Vaughan and John L. Spencer

School of Chemical and Physicial Sciences, Victoria University of Wellington, Wellington, New Zealand

Email: john.spencer@vuw.ac.nz

Phone: +64 4 463 5119

X-ray diffraction

X-ray diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer using Mo Kα radiation or an Agilent SuperNova (Dual Source) CCD diffractometer using Cu Kα radiation. Data were reduced using Bruker SAINT or Agilent CrysAlisPro software. Absorption correction was performed using the SADABS or SCALE3 ABSPACK programs. OLEX2 (Version 1.2.5)[1] was used as a front-end for SHELX[2] or Superflip[3] executables during structure solution and refinement. The positions of all hydrogen atoms were calculated during refinement.

The three isomorphous crystals all showed evidence of disordered solvent molecules in the lattice. Attempts to define the solvent molecule positions were partly successful in the case of complex **3** ($CHCl_3$), but not for complexes **7** and **9** (CH_2Cl_2). It was therefore decided to account for the solvent electron density using the SQUEEZE[4] routine. In each case this identified approximately 320 electrons/unit cell, corresponding to six $CHCl_3$ (**3**) or eight CH_2Cl_2 (**7** and **9**) molecules of solvent of crystallization.

Platinum(II) and Palladium(II) Complexes

Crystals of the [$PtCl_2$(PP)] complex **3** suitable for single crystal X-ray diffraction were grown from a solution of the complex in $CDCl_3$, whereas crystals of the [$PdCl_2$(PP)] complex **7** were grown by inwards diffusion of *n*-hexane into a dichloromethane solution of the complex at 4°C. The X-ray structures confirmed that the [MCl_2(PP)] complexes **3** and **7** were simple diphosphine complexes and that the nitrogens were not coordinated to the metal as indicated by the NMR and IR data. Crystallographic data is given in Supplementary Table 1 and selected bond lengths and angles are given in Supplementary Table 2.

Supplementary Table 1: Crystallographic data of [MCl_2(PP)] complexes (M = Pt **3**, Pd **7**), [PtClMe(PP)] complex **9** and [Ir(1-*κ*-4,5,6-*η*^{3}-C_8H_{12})(PPN)]BPh_4 compound [**21**]BPh_4.

Complex	**3**	**7**	**9**	[**21**]BPh_4
Empirical Formula	$C_{28}H_{24}N_4P_2Cl_2Pt\cdot1.5CHCl_3$	$C_{28}H_{24}N_4P_2Cl_2Pd\cdot2CH_2Cl_2$	$C_{29}H_{24}N_4P_2ClPt\cdot2CH_2Cl_2$	$C_{60}H_{56}BIrN_4P_2$
Formula Weight	863.82	655.75	724.04	1098.13
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	14.5058(5)	14.43316(19)	14.4790(4)	9.38338(15)

b/Å	10.2019(5)	10.2502(2)	10.3594(4)	14.6521(4)
c/Å	22.9424(8)	22.5901(5)	22.7769(8)	17.9389(5)
α/°	90	90	90	84.324(2)
β/°	91.017(3)	90.1316(15)	89.905(3)	88.2410(17
γ/°	90	90	90	79.2307(17)
V/ Å^3	3394.7(2)	3342.02(22)	3426.4(2)	2410.85(10)
Z	4	4	4	2
D_{calc}/g cm^{-3}	1.459	1.303	1.408	1.513
μ/mm^{-1}	4.646	0.886	4.300	6.332
Temperature/K	120(1)	121(1)	120(1)	120(1)
Radiation type	MoKα	MoKα	MoKα	CuKα
Radiation (λ)/Å	0.71073	0.71073	0.71073	1.54184
$R_1[I > 2\sigma(I)]$	0.025	0.054	0.051	0.031
wR_2 [$I > 2\sigma(I)$]	0.057	0.150	0.107	0.080
R_1 [all data]	0.031	0.062	0.064	0.032
wR_2 [all data]	0.060	0.157	0.115	0.081

Unsurprisingly the two structures were very similar, with P–M–P bite angles of 100.91(4)° and 100.04(3)° for the platinum and palladium complexes respectively. This was similar to that reported for other [$PtCl_2$(PP)] complexes of diphosphines with the *o*-xylene backbone (PP = *o*-$C_6H_4(CH_2PBu^t_2)(CH_2PPh_2)$ 100.51(3)°,[5] *o*-$C_6H_4(CH_2PBu^t_2)_2$ 104.06(10)°[6]).

Supplementary Table 2: Selected bond distances and angles of [MCl_2(PP)] complexes (M = Pt **3**, Pd **7**).

Bond distances (Å)			Bond angles (°)		
	3	**7**		**3**	**7**
M1-P1	2.2321(9)	2.2451(10)	P1-M1-P2	100.91(4)	100.04(3)
M1-P2	2.2274(10)	2.2513(10)	Cl1-M1-Cl2	89.65(4)	91.56(3)
M1-Cl1	2.3549(9)	2.4093(8)	P1-M1-Cl1	84.87(4)	84.41(3)
M1-Cl2	2.3517(9)	2.3836(8)	P2-M1-Cl2	84.59(4)	84.01(2)
P1-C1	1.823(4)	1.835(4)	P1-M1-Cl2	174.25(4)	175.81(3)
P1-C11	1.831(4)	1.822(3)	P2-M1-Cl1	174.21(4)	175.11(2)
P1-C21	1.834(4)	1.821(4)	C1-P1-M1	121.9(1)	122.51(13)
P2-C8	1.838(4)	1.821(4)	C8-P2-M1	122.2(1)	122.18(13)
P2-C31	1.825(4)	1.829(4)	P1-C1-C2	113.3(2)	110.3(2)
P2-C41	1.830(4)	1.827(4)	P2-C8-C7	111.7(2)	112.1(2)

While the analogous dppox complex of palladium had an almost identical bite angle (100.04(6)°),[7] the bite angle in the analogous palladium dbpx complex was slightly larger (101.88(1)°).[8]

The Pt–P bond lengths of 2.2321(9) and 2.2274(10) Å in the [$PtCl_2$(PP)] complex **3** were slightly shorter than those observed in the structures of *cis*-[$PtCl_2(PPh_3)_2$], 2.2515(8) and 2.2713(9) Å,[9] and *cis*-[$PtCl_2$(dppp)], 2.239(2) Å.[10] The Pd–P bond lengths in the [$PdCl_2$(PP)] complex **7** were very similar to those in the analogous dppox complex [$PdCl_2$(PP)] (PP = *o*-$C_6H_4(CH_2PPh_2)_2$), 2.2451(10) and 2.2513(10) Å compared to 2.2572(5) Å.[7]

When complex **9** was synthesised on a macroscale yellow crystals of sufficient quality for single crystal X-ray diffraction analysis were grown by the diffusion of *n*-hexane into a dichloromethane solution of complex **9** at 4°C. The X-ray structure confirmed that in the solid state complex **9** had the formulation [PtClMe(PP)]. Crystallographic data is given in Supplementary Table 1 and selected bond lengths and angles are given in Supplementary Table 3.

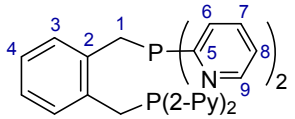
Supplementary Table 3: Selected bond distances and angles of [PtClMe(PP)] complex **9**.

Bond distances (Å)		Bond angles (°)	
Pt1-P1	2.2118(18)	P1-Pt1-P2	101.36(5)
Pt1-P2	2.2952(17)	Cl2-Pt1-C51	87.23(14)
Pt1-C51	2.178(5)	P1-Pt1-C51	86.05(14)
Pt1-Cl2	2.355(2)	P2-Pt1-Cl2	85.41(5)
P1-C11	1.832(7)	P1-Pt1-Cl2	173.24(5)
P1-C1	1.827(6)	P2-Pt1-C51	172.41(16)
P1-C21	1.820(5)	C1-P1-Pt1	121.7(2)
P2-C8	1.816(7)	C8-P2-Pt1	122.0(2)
P2-C41	1.828(6)	P1-C1-C2	110.9(4)
P2-C31	1.829(7)	P2-C8-C7	112.1(4)

The structure of the [PtClMe(PP)] complex **9** was very similar to that of the dichloride complexes [MCl_2(PP)] (M = Pt **3**, Pd **7**) discussed previously. The bite angle of the ligand in this complex was 101.36(5)°, which was very slightly larger than that observed in the structures of the [MCl_2(PP)] complexes **3** and **7**. The difference in the Pt–P bond lengths was due to the difference in the *trans* influences of the methyl and chloride ligands, with the longer bond, Pt1–P2, being *trans* to the methyl ligand which is higher in *trans* influence.[11] The Pt–Cl and Pt–C bond lengths were similar to the 2.323(5) and 2.17(1) Å observed in the structure of [PtClMe(PP)] (PP = (+)-2S,3S-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane).[12]

Experimental and characterisation data

Ligand 1



^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.66 (d, J = 4.5 Hz, 4H, H9), 7.54 (t, J = 7.5 Hz, 4H, H7), 7.45 (d, J = 7.5 Hz, 4H, H6), 7.15 (t, J = 6.0 Hz, 4H, H8), 6.90 (d, J = 4.5 Hz, 2H, H3), 6.84 (d, J = 3.5 Hz, 2H, H4), 3.97 (s, 4H, H1). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 162.95 (d, $^1J_{PC}$ = 5.2 Hz, C5), 150.41 (vt, $^3J_{PC}$ + $^8J_{PC}$ = 3.9 Hz, C9), 136.50 (vt, $^2J_{PC}$ + $^3J_{PC}$ = 6.0 Hz, C2), 135.49 (vt, $^3J_{PC}$ + $^8J_{PC}$ = 3.2 Hz, C7), 130.57 (vt, $^3J_{PC}$ + $^4J_{PC}$ = 2.9 Hz, C3), 129.58 (d, $^2J_{PC}$ = 28.8 Hz, C6), 125.98 (s, C4), 123.81 (s, C8), 31.00 (d, $^1J_{PC}$ = 9.1 Hz, C1). ^{15}N NMR (60 MHz, CDCl3): δ/ppm −56.1 (s). ^{31}P NMR (121 MHz, CDCl3): δ/ppm −6.81 (s). IR (film from CH_2Cl_2): ν_{max}/cm^{-1} 3043 (sp^{2}C–H stretch), 2960 (sp^{3}C–H stretch), 1573, 1560 (C=N stretch). HRMS calcd for $C_{28}H_{25}N_4O_2P_2$ [M+2O+H]$^+$: m/z = 511.1453, found = 511.1452. HRMS calcd for $C_{28}H_{24}N_4NaO_2P_2$ [M+2O+Na]$^+$: m/z = 533.1272, found = 533.1277.

Phosphine selenide 2

^{1}H NMR (500 MHz, CDCl3): δ/ppm 8.71 (d, J = 4.0 Hz, 4H, H9), 8.16 (t, J = 7.5 Hz, 4H, H6), 7.71 (m, 4H, H7), 7.31 (m, 4H, H8), 6.85 (m, 2H, H4), 6.81 (m, 2H, H3), 4.67 (d, $^2J_{PH}$ = 14.0 Hz, 4H, H1). ^{13}C NMR (125 MHz, CDCl3): δ/ppm 154.76 (d, $^1J_{PC}$ = 97.4 Hz, C5), 149.69 (d, $^3J_{PC}$ = 18.2 Hz, C9), 136.45 (d, $^3J_{PC}$ = 9.6 Hz, C7), 136.13 (m, C2), 131.51 (s, C3), 129.23 (d, $^2J_{PC}$ = 25.9 Hz, C6), 126.76 (s, C4), 125.05 (s, C8),

33.71 (d, $^{1}J_{PC}$ = 44.1 Hz, C1). ^{31}P NMR (121 MHz, CDCl3): δ/ppm 34.19 (s, $^{1}J_{PSe}$ = 737.6, $^{5}J_{PP}$ = 6.6 Hz). ^{77}Se NMR (95 MHz, CDCl3) : δ/ppm −352.46 (d, $^{1}J_{PSe}$ = 737.6 Hz). HRMS calcd for $C_{28}H_{25}N_4P_2Se_2$ $[M+H]^+$: m/z = 638.9885; found = 638.9873.

Platinum(II) complexes

Synthesis of [$PtCl_2$(PP)] (**3**)

Dichloro(hexa-1,5-diene)platinum (17 mg, 0.05 mmol) was added to a solution of ligand **1** (23mg, 0.05mmol) in $CDCl_3$ (0.5mL) in an NMR tube. The ^{31}P and ^{1}H NMR spectra recorded after 15 minutes showed that the reaction had gone to completion (quantitative conversion).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.82 (d, *J* = 4.8 Hz, 4H, H9), 8.14 (br s, 4H, H6), 7.70 (m, 4H, H7), 7.38 (m, 4H, H8), 6.71 (m, 2H, H4), 6.10 (m, 2H, H3), 4.54 (br s, 4H, H1). ^{13}C NMR (125MHz, $CDCl_3$): δ/ppm 153.56 (d, $^{1}J_{PC}$ = 90.9 Hz, C5), 149.65 (vt, $^{3}J_{PC}$ + $^{8}J_{PC}$ = 8.1 Hz, C9), 135.74 (s, C7), 133.56 (br s, C6), 132.00 (s, C2), 130.30 (s, C3), 127.19 (s, C4), 125.15 (s, C8), 32.11 (d, $^{1}J_{PC}$ = 37.9 Hz, C1). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm 0.64 (s, $^{1}J_{PtP}$ = 3500.0 Hz). IR (film from CH_2Cl_2): ν_{max}/cm^{-1} 1573, 1562 (C=N stretch). HRMS calcd for $C_{28}H_{24}ClN_4P_2Pt$ $[M-Cl]^+$: m/z = 707.0792; found = 707.0793. HRMS calcd for $C_{28}H_{25}Cl_2N_4P_2Pt$ $[M+H]^+$: m/z = 743.0558; found = 743.0556. Elemental Analysis: C, 43.2; H, 3.5; N, 7.4% ($C_{28}H_{24}Cl_2N_4P_2Pt \cdot ½CH_2Cl_2$ requires C, 43.5; H, 3.2; N, 7.1%).

[$PtMe_2$(PP)] (**4**)

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.86 (d, *J* = 4.5 Hz, 4H, H9), 7.75 (br s, 4H, H6), 7.64 (t, *J* = 7.1 Hz, 4H, H7), 7.29 (t, *J* = 6.0 Hz, 4H, H8), 6.58 (m, 2H, H4), 6.11 (m, 2H, H3), 4.56 (br s, 4H, H1), 0.30 (q, $^{3}J_{PH}$ = 5.9, $^{2}J_{PtH}$ = 68.7 Hz, 6H, Pt–CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 157.13 (d, $^{1}J_{PC}$ = 69.3 Hz, C5), 150.22 (s, C9), 135.30 (s, C7), 134.35 (s, C2), 131.78 (s, C6), 130.48 (s, C3), 125.99 (s, C4), 124.02 (s, C8), 34.01 (d, $^{1}J_{PC}$ = 23.2 Hz, C1), 5.40 (dd, $^{2}J_{PC}$ = 97.0, 9.6, $^{1}J_{PtC}$ = 598.8 Hz, Pt–CH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm 10.50 (s, $^{1}J_{PtP}$ = 1839.9 Hz). IR (film from CH_2Cl_2): ν_{max}/cm^{-1} 1574, 1562 (C=N stretch). HRMS calcd for $C_{29}H_{27}N_4P_2Pt$ $[M-CH_3]^+$: m/z = 687.1338; found = 687.1332. Elemental Analysis: C, 48.9; H, 4.3; N, 7.5% ($C_{30}H_{30}N_4P_2Pt \cdot ½CH_2Cl_2$ requires C, 49.1; H, 4.2; N, 7.5%).

Synthesis of [PtI_2(PP)] (**5**)

A solution of diiodo(hexa-1,5-diene)platinum (26 mg, 0.05 mmol) in $CDCl_3$ (0.3 mL) was combined with a solution of ligand **1** (23 mg, 0.05 mmol) in $CDCl_3$ (0.3 mL) in an NMR tube. ^{31}P and ^{1}H NMR spectra recorded after 10 minutes showed that the reaction had gone to completion (quantitative conversion).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.83 (d, *J* = 4.5 Hz, 4H, H9), 8.16 (m, 4H, H6), 7.69 (m, 4H, H7), 7.38 (m, 4H, H8), 6.64 (m, 2H, H4), 6.01 (m, 2H, H3), 4.55 (d, $^{2}J_{PH}$ = 10.6 Hz, 4H, H1). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 155.75 (d, $^{1}J_{PC}$ = 91.7 Hz, C5), 149.46 (m, C9), 135.26 (s, C7), 133.78 (m, C6), 132.20 (s, C2), 130.10 (s, C3), 126.97 (s, C4), 124.93 (s, C8), 33.65 (d, $^{1}J_{PC}$ = 32.1 Hz, C1). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm −13.0 (s, $^{1}J_{PtP}$ = 3303.5 Hz). HRMS calcd for $C_{28}H_{25}I_2N_4P_2Pt$ $[M+H]^+$: m/z = 926.9271; found = 926.9279. HRMS calcd for $C_{28}H_{24}I_2N_4NaP_2Pt$ $[M+Na]^+$: m/z = 948.9090; found = 948.9089.

Synthesis of [$PtEt_2$(PP)] (**6**)

Diethyl(cycloocta-1,5-diene)platinum (15 mg, 0.04 mmol) was added to a solution of ligand **1** (20 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL) in a NMR tube. ^{31}P and ^{1}H NMR spectra recorded after 10 minutes showed that the reaction had gone to completion (quantitative conversion).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.85 (d, J = 4.8 Hz, 4H, H9), 7.76 (br s, 4H, H6), 7.62 (d, J = 5.9 Hz, 4H, H7), 7.27 (d, J = 6.1 Hz, 4H, H8), 6.60 (br s, 2H, H4), 6.23 (s, 2H, H3), 4.43 (br s, 4H, H1), 0.92 (q, $^{3}J_{HH}$ = 6.6, $^{2}J_{PtH}$ = 104.3 Hz, Pt–CH_2CH$_3$), 0.61 (t, $^{3}J_{HH}$ = 7.0, $^{3}J_{PtH}$ = 70.4 Hz, Pt–CH$_2$CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 157.08 (d, $^{1}J_{PC}$ = 65.1 Hz, C5), 149.96 (s, C9), 135.14 (s, C7), 134.39 (s, C2), 131.71 (s, C6), 130.64 (s, C3), 125.84 (s, C4), 123.82 (s, C8), 34.58 (d, $^{1}J_{PC}$ = 21.1 Hz, C1), 15.38 (m, Pt–CH$_2$CH$_3$), 13.72 (m, Pt–CH$_2$$CH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm 9.47 (s, $^{1}J_{PtP}$ = 1687.1 Hz). HRMS calcd for $C_{30}H_{29}N_4P_2Pt$ $[M-C_2H_5]^+$: m/z = 701.1494; found = 701.1495.

Palladium(II) complexes

Synthesis of [$PdCl_2$(PP)] (**7**)

Dichloro(cycloocta-1,5-diene)palladium (175 mg, 0.6 mmol) was added to a solution of ligand **1** (294mg, 0.6mmol) in CH_2Cl_2 (5 mL) in a schlenk tube and stirred for 15minutes. The solvent was removed under reduced pressure and the resulting yellow solid washed with hexane (2×5 mL). The solid was dissolved in CH_2Cl_2, filtered and hexane was added. After 4 days at −20°C the product had crystallised out (122 mg, 31%). While these crystals were found to be unsuitable for single crystal X-ray structure determination, X-ray quality crystals were grown from inwards diffusion of hexane into CH_2Cl_2 at 4°C.

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.80 (d, J = 4.5 Hz, 4H, H9), 8.15 (br s, 4H, H6), 7.70 (m, 4H, H7), 7.38 (m, 4H, H8), 6.70 (m, 2H, H4), 6.08 (br s, 2H, H3), 4.35 (d, $^{2}J_{PH}$ = 8.0Hz, 4H, H1). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 156.29 (d, $^{1}J_{PC}$ = 23.6Hz, C5), 149.54 (s, C9), 135.85 (s, C7), 134.05 (br s, C6), 131.78 (s, C2), 130.39 (s, C3), 127.28 (s, C4), 125.19 (s, C8), 32.15 (d, $^{1}J_{PC}$ = 32.0 Hz, C1). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm 17.56 (s). HRMS calcd for $C_{28}H_{24}ClN_4P_2Pd$ $[M-Cl]^+$: m/z = 617.0205; found = 617.0209. Elemental Analysis: C, 48.8; H, 3.5; N, 8.2% ($C_{28}H_{24}Cl_2N_4P_2Pd \cdot ½CH_2Cl_2$ requires C, 49.0; H, 3.6; N, 8.0%).

Synthesis of [$PdMe_2$(PP)] (**8**)

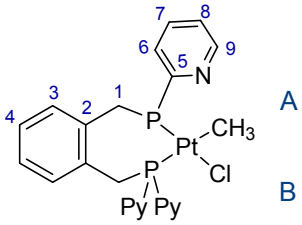
Dimethyl(N,N,N′,N′-tetramethylethylenediamine)palladium (10 mg, 0.04 mmol) was added to a solution of ligand **1** (20 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube. The ^{31}P and ^{1}H NMR spectra recorded after 10 minutes showed that the reaction was complete (quantitative conversion).

^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.83 (d, J = 4.2 Hz, 4H, H9), 7.80 (m, 4H, H6), 7.60 (m, 4H, H7), 7.27 (m, 4H, H8), 6.69 (m, 2H, H4), 6.13 (t, J = 4.1 Hz, 2H, H3), 4.36 (br s, 4H, H1), 0.40 (s, Pd–CH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm 14.71 (s). HRMS calcd for $C_{29}H_{27}N_4P_2Pd$ $[M-CH_3]^+$: m/z = 598.0762; found = 598.766.

Unsymmetric platinum(II) complexes

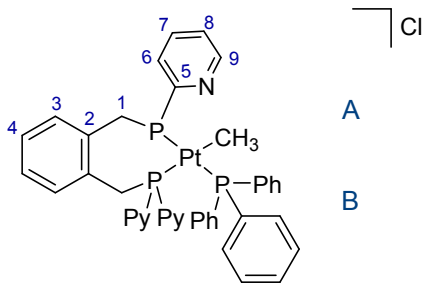
Synthesis of [PtClMe(PP)] (**9**)

A solution of ligand **1** (100 mg, 0.21 mmol) in CH_2Cl_2 (2 mL) was added to chloromethyl(hexa-1,5-diene)platinum (68 mg, 0.21 mmol). An immediate colour change was observed. After five minutes of stirring the solvent was removed under reduced pressure. The resulting brown oil was washed with hexane (2 × 2 mL) to give a brown solid. Yellow crystals of the product were grown via inward diffusion of hexane into a concentrated solution of the product in CH_2Cl_2 (129 mg, 85%).



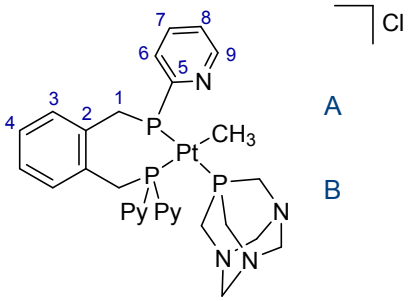
^{1}H NMR (600 MHz, CD_2Cl_2): δ/ppm 8.88 (d, J = 4.5 Hz, 2H, H9a), 8.81 (d, J = 4.5 Hz, 2H, H9b), 7.94 (br s, 2H, H6a), 7.84 (m, 2H, H6b), 7.73 (m, 2H, H7a), 7.67 (m, 2H, H7b), 7.40 (m, 2H, H8a), 7.35 (m, 2H, H8b), 6.64 (m, 2H, H4a+H4b), 6.18 (d, J = 6.5 Hz, 1H, H3b), 6.12 (d, J = 6.5 Hz, 1H, H3a), 4.52 (br s, 2H, H1a), 4.41 (br s, 2H, H1b), 0.39 (dd, $^3J_{PH}$ = 6.9, 4.5, $^2J_{PtH}$ = 52.8 Hz, 3H, Pt–CH_3). ^{13}C NMR (150 MHz, CD_2Cl_2): δ/ppm 157.20 (m, C5b), 154.34 (m, C5a), 150.34 (m, C9a), 150.20 (m, C9b), 136.00 (d, $^3J_{PC}$ = 8.6 Hz, C7a), 135.36 (d, $^3J_{PC}$ = 8.6 Hz, C7b), 134.01 (s, C2a), 132.96 (s, C2b), 130.89 (br s, C3b), 130.69 (s, C3a) 126.85 (s, C4a), 126.65 (s, C4b), 125.14 (s, C8a), 124.62 (s, C8b), 33.87 (d, $^1J_{PC}$ = 35.0 Hz, C1a), 32.69 (d, $^1J_{PC}$ = 23.0 Hz, C1b), 9.64 (dd, $^2J_{PC}$ = 92.1, 7.6 Hz, Pt–CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ/ppm 11.31 (d, $^2J_{PP}$ = 14.0, $^1J_{PtP}$ = 1724.6 Hz, *trans* CH_3), 10.04 (d, $^2J_{PP}$ = 13.9, $^1J_{PtP}$ = 4210.6 Hz, *trans* Cl). HRMS calcd for $C_{29}H_{27}N_4P_2Pt$ $[M-Cl]^+$: m/z = 688.1356; found = 688.1370. Elemental Analysis: C, 46.5; H, 3.6; N, 7.5% ($C_{29}H_{27}ClN_4P_2Pt \cdot ½CH_2Cl_2$ requires C, 46.2; H, 3.3; N, 7.3%).

[PtMe(PP)PPh$_3$]Cl (**10**)



^{1}H NMR (300 MHz, CD_2Cl_2): δ/ppm 8.98 (d, J = 3.6 Hz, 2H, H9a), 8.72 (m, 2H, H9b), 8.35 (m, 2H, H6a), 8.10 (m, 2H, H7a), 7.90 (m, 2H, H7b), 7.72 (m, 5H, H6b+3Ar-H), 7.43 (m, 16H, H8a+H8b+12Ar-H), 6.71 (m, 2H, H4a+H4b), 6.11 (d, J = 5.7 Hz, 1H, H3b), 5.94 (d, J = 6.9 Hz, 1H, H3a), 4.36 (dd, J = 12.6, 4.8 Hz, 2H, H1a), 4.03 (d, J = 11.1 Hz, 2H, H1b), 0.40 (m, $^2J_{PtH}$ = 52.5 Hz, 3H, Pt–CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ/ppm 26.57 (dd, $^2J_{PP}$ = 376.0, 23.6, $^1J_{PtP}$ = 2904.2 Hz, PPh_3), 8.44 (dd, $^2J_{PP}$ = 376.0, 25.5, $^1J_{PtP}$ = 2871.4 Hz, P *trans* PPh_3), −0.61 (t, $^2J_{PP}$ = 24.8, $^1J_{PtP}$ = 2076.3 Hz, P *trans* CH_3). HRMS calcd for $C_{47}H_{42}N_4P_3Pt$ $[M-Cl]^+$: m/z = 950.2268; found = 950.2232.

[PtMe(PP)PTA]Cl (**11**)



^{1}H NMR (600 MHz, CD_2Cl_2): *δ*/ppm 8.92 (d, *J* = 4.4 Hz, 2H, H9a), 8.86 (d, *J* = 4.4 Hz, 2H, H9b), 8.30 (m, 2H, H6a), 8.01 (m, 2H, H7a), 7.81 (m, 2H, H7b), 7.75 (m, 2H, H6b), 7.58 (br s, 2H, H8a), 7.48 (br s, 2H, H8b), 6.76 (m, 2H, H4a+H4b), 6.18 (d, *J* = 5.4 Hz, 1H, H3b), 6.13 (d, *J* = 5.6 Hz, 1H, H3a), 4.45 (d, *J* = 9.0 Hz, 2H, H1a), 4.41 (m, 3H, CH_2), 4.30 (d, $^{2}J_{PH}$ = 11.5 Hz, 2H, H1b), 4.12 (d, J_{PH} = 13.4 Hz, 3H, CH_2), 3.76 (s, 3H, CH_2), 3.56 (s, 3H, CH_2), 0.37 (t, *J* = 6.0, $^{2}J_{PtH}$ = 52.5 Hz, 3H, Pt–CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): *δ*/ppm 8.77 (d, $^{2}J_{PP}$ = 348.0, $^{1}J_{PtP}$ = 2803.7 Hz, P *trans* PTA), −0.68 (s, $^{1}J_{PtP}$ = 1962.2 Hz, P *trans* CH_3), −70.16 (d, $^{2}J_{PP}$ = 362.0, $^{1}J_{PtP}$ = 2495.5 Hz, PTA). HRMS calcd for $C_{35}H_{39}N_7P_3Pt$ $[M-Cl]^+$: m/z = 845.2125; found = 845.2091. HRMS calcd for $C_{29}H_{27}N_4P_2Pt$ $[M-Cl-C_6H_{12}N_3P]^+$: m/z = 688.1356; found = 688.1326.

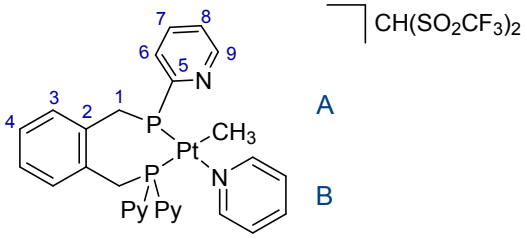
***trans*-[PtClMe(PPh_3)$_2$]** (**12**)

^{1}H NMR (500 MHz, $(CD_3)_2CO$): *δ*/ppm 7.76 (m, 12H, Ph), 7.48–7.39 (m, 18H, Ph), −0.11 (t, $^{3}J_{PH}$ = 6.2, $^{2}J_{PtH}$ = 78.1 Hz, 3H, Pt–CH_3). ^{31}P NMR (121MHz, $(CD_3)_2CO$): *d*/ppm 29.42 (s, $^{1}J_{PtP}$ = 3146.5 Hz).

***trans*-[PtClMe(PTA)$_2$]** (**13**)

^{1}H NMR (500 MHz, D_2O): *δ*/ppm 4.50 (br s, 12H, CH2), 4.20 (br s, 12H, CH2), 0.42 (t, $^{3}J_{PH}$ = 7.2, $^{2}J_{PtH}$ = 82.2 Hz, 3H, Pt–CH_3). ^{31}P NMR (121MHz, D_2O): *δ*/ppm −55.8 (s, $^{1}J_{PtP}$ = 2812.0 Hz).

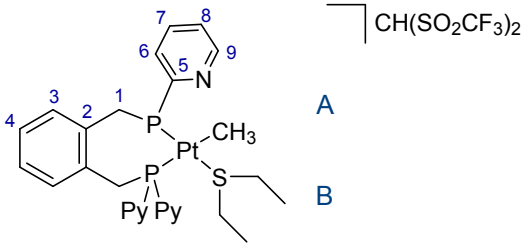
[PtMe(PP)Py]CH(SO_2CF_3)$_2$ (**14**)



^{1}H NMR (500 MHz, CD_2Cl_2): *δ*/ppm 8.89 (s, 2H, Py), 8.77 (br s, 2H, Py), 8.65 (br s, 2H, Py), 8.08 (s, 1H, Py), 7.93 (br s, 2H, Py), 7.84 (br s, 2H, Py), 7.60 (br s, 2H, Py), 7.48 (br s, 2H, Py), 7.40 (br s, 2H, Py), 7.35 (br s, 2H, Py), 7.14 (m, 2H, Py), 6.82 (m, 1H, H4a), 6.72 (m, 1H, H4b), 6.57 (d, *J* = 6.5 Hz, 1H, H3b), 6.34 (d, *J* = 6.5 Hz, 1H, H3a), 4.47 (d, $^{2}J_{PH}$ = 13.9 Hz, 2H, H1a), 4.41 (d, $^{2}J_{PH}$ = 11.7 Hz, 2H, H1b), 3.92 (s, 1H, $CH(SO_2CF_3)_2$), 0.26 (br s, $^{2}J_{PtH}$ = 50.8 Hz, 3H, Pt–CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): *δ*/ppm 155.03 (d, J_{PC} = 65.8 Hz, Py), 153.57 (m, Py), 151.18 (d, J_{PC} = 14.9 Hz, Py), 150.72 (d, J_{PC} = 15.3 Hz, Py), 150.68 (s, Py), 136.59 (s, Py), 136.53 (s, Py), 132.87 (br s, C2a), 132.05 (br s, C2b), 131.95 (br s, Py), 131.57 (br s, C3b), 131.37 (br s, C3a), 130.56 (br s, Py), 130.39 (br s, Py), 127.56 (br s, C4a), 127.44

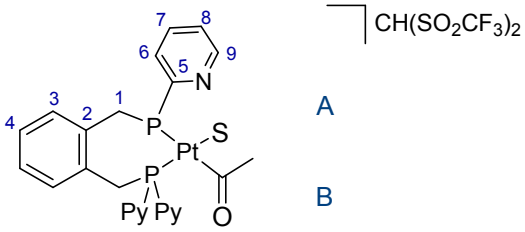
(br s, C4b), 126.83 (s, Py), 125.81 (s, Py), 125.39 (s, Py), 121.58 (q, $^{1}J_{CF}$ = 325.6 Hz, CH(SO$_2$*C*F$_3$)$_2$), 54.46 (s, *C*H(SO$_2$CF$_3$)$_2$), 33.66 (d, $^{1}J_{PC}$ = 37.3 Hz, C1a), 33.33 (d, $^{1}J_{PC}$ = 25.4 Hz, C1b), 9.62 (dd, J_{PC} = 80.5, 5.3 Hz, Pt–CH$_3$). ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): *δ*/ppm −81.48 (s, CH(SO$_2$CF$_3$)$_2$). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): *δ*/ppm 7.71 (d, $^{2}J_{PP}$ = 16.1, $^{1}J_{PtP}$ = 1720.8 Hz, P *trans* CH3), 3.88 (d, $^{2}J_{PP}$ = 16.7, $^{1}J_{PtP}$ = 3743.5 Hz, P *trans* pyridine).

Synthesis of [PtMe(PP)SEt2]CH(SO2CF3)2 (15)



^{1}H NMR (500 MHz, CD$_2$Cl$_2$): *δ*/ppm 8.91 (d, *J* = 4.5 Hz, 2H, H9a), 8.88 (d, *J* = 4.5 Hz, 2H, H9b), 7.85 (m, 8H, H6+H7), 7.50 (m, 4H, H8), 6.75 (m, 2H, H4), 6.26 (d, *J* = 6.0 Hz, 1H, H3b), 6.20 (d, *J* = 6.0 Hz, 1H, H3a), 4.52 (d, $^{2}J_{PH}$ = 14.0, $^{3}J_{PtH}$ = 51.0 Hz, 2H, H1a), 4.41 (d, $^{2}J_{PH}$ = 12.5 Hz, 2H, H1b), 3.85 (s, 1H, CH(SO$_2$CF$_3$)$_2$), 2.66 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H, SC*H*$_2$CH$_3$), 2.63 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H, SC*H*$_2$CH$_3$), 1.28 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, SCH$_2$C*H*$_3$), 1.27 (br s, 3H, SCH$_2$C*H*$_3$), 0.37 (vt, $^{3}J_{PH}$ + $^{3}J_{PH}$ = 5.0, $^{2}J_{PtH}$ = 53.5 Hz, 3H, Pt–CH$_3$). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): *δ*/ppm 154.70 (d, $^{1}J_{PC}$ = 67.4 Hz, C5), 151.21 (d, $^{3}J_{PC}$ = 15.3 Hz, C9b), 150.90 (d, $^{3}J_{PC}$ = 16.6 Hz, C9a), 136.65 (d, $^{3}J_{PC}$ = 9.1 Hz, C7a), 136.46 (d, $^{3}J_{PC}$ = 7.1 Hz, C7b), 132.34 (m, C2a+C2b), 131.79 (m, C6a+C6b), 131.02 (br s, C3a+C3b), 127.71 (m, C4a+C4b), 125.93 (s, C8a+C8b), 121.51 (q, $^{1}J_{CF}$ = 325.6 Hz, CH(SO$_2$*C*F$_3$)$_2$), 54.11 (s, *C*H(SO$_2$CF$_3$)$_2$), 34.15 (d, $^{1}J_{PC}$ = 33.5 Hz, C1a), 33.92 (d, $^{1}J_{PC}$ = 24.3 Hz, C1b), 45.29 (s, S*C*H$_2$CH$_3$), 6.89 (s, SCH$_2$*C*H$_3$), 4.99 (dd, $^{2}J_{PC}$ = 79.2, 7.0 Hz, Pt–CH$_3$). ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): *δ*/ppm −81.57 (s, CH(SO$_2$CF$_3$)$_2$). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$): *δ*/ppm 9.88 (d, $^{2}J_{PP}$ = 19.0, $^{1}J_{PtP}$ = 3690.0 Hz, P *trans* SEt$_2$), 5.51 (d, $^{2}J_{PP}$ = 19.0, $^{1}J_{PtP}$ = 1793.7 Hz, P *trans* CH$_3$).

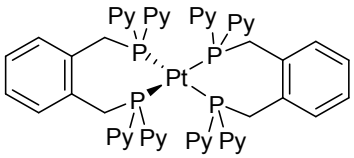
[Pt(COMe)(PP)(S)]CH(SO$_2$CF$_3$)$_2$ (16)



^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): *δ*/ppm 8.86 (br s, 4H, H9), 7.85 (br m, 4H, H6), 7.74 (m, 4H, H7), 7.45 (m, 4H, H8), 6.64 (m, 2H, H4), 6.31 (d, *J* = 6.5 Hz, 1H, H3b), 6.26 (d, *J* = 6.5 Hz, 1H, H3a), 4.33 (m, 4H, H1), 3.89 (s, 1H, CH(SO$_2$CF$_3$)$_2$), 1.54 (s, 3H, COCH$_3$). ^{19}F NMR (282 MHz, (CD$_3$)$_2$CO): *δ*/ppm −81.59 (s, CH(SO$_2$CF$_3$)$_2$). ^{31}P NMR (121 MHz, (CD$_3$)$_2$CO): *δ*/ppm 3.22 (d, $^{2}J_{PP}$ = 23.0, $^{1}J_{PtP}$ = 1389.9 Hz, P *trans* COCH$_3$), 1.67 (d, $^{2}J_{PP}$ = 23.0, $^{1}J_{PtP}$ = 4500.7 Hz, P *trans* solvent).

Platinum(0) complexes

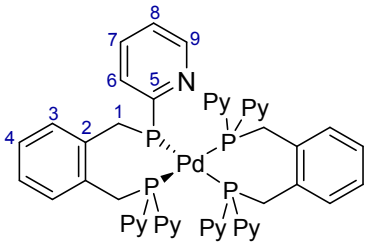
[Pt(PP)$_2$] (**17**)



^{1}H NMR (500 MHz, C_6D_6): δ/ppm 8.54 (br s, 2H, Ar-H), 8.48 (br s, 2H, Ar-H), 8.44 (br s, 2H, Ar-H), 8.37 (br s, 2H, Ar-H), 7.77 (d, J = 7.50 Hz, 2H, Ar-H), 7.23 (d, J = 7.00 Hz, 2H, Ar-H), 7.19 (br s, 2H, Ar-H), 7.03 (m, 4H, Ar-H), 6.90 (m, 4H, Ar-H), 6.69 (br s, 4H, Ar-H), 6.61 (br s, 4H, Ar-H), 6.53 (m, 2H, Ar-H), 6.41 (m, 2H, Ar-H), 6.39 (m, 2H, Ar-H), 6.21 (br s, 2H, Ar-H), 5.54 (s, 2H, Ar-H), 5.21 (m, 2H, CH_2), 4.79 (br s, 2H, CH_2), 4.76 (br s, 2H, CH_2), 4.58 (br s, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ/ppm 169.39 (m, Ar-C), 166.87 (m, Ar-C), 160.47 (m, Ar-C), 158.23 (m, Ar-C), 148.90 (m, Ar-C), 148.80 (m, Ar-C), 147.73 (m, Ar-C), 147.39 (m, Ar-C), 139.34 (m, Ar-C), 139.23 (m, Ar-C), 134.21 (m, Ar-C), 132.10 (m, Ar-C), 131.80 (m, Ar-C), 131.39 (m, Ar-C), 131.07 (m, Ar-C), 125.29 (br s, Ar-C), 125.15 (br s, Ar-C), 124.18 (s, Ar-C), 121.78 (br s, Ar-C), 121.54 (m, Ar-C), 120.43 (m, Ar-C), 120.43 (m, Ar-C), 35.89 (m, CH_2), 33.62 (m, CH_2). ^{31}P NMR (121 MHz, C_6D_6): δ/ppm 6.69 (t, $^2J_{PP}$ = 40.7, $^1J_{PtP}$ = 3815.8 Hz), 3.16 (t, $^2J_{PP}$ = 40.7, $^1J_{PtP}$ = 3548.2 Hz). HRMS calcd for $C_{56}H_{49}N_8P_4Pt$ $[M+H]^+$: m/z = 1151.2658; found = 1151.2649. Elemental Analysis: C, 50.4; H, 3.7; N, 8.4% ($C_{56}H_{48}N_8P_4Pt \cdot 2CHCl_3$ requires C, 50.1; H, 3.6; N, 8.1%).

Palladium(0) complexes

[Pd(PP)$_2$] (**18**)

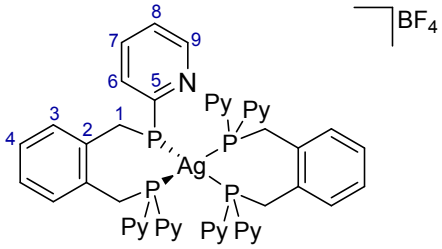


^{1}H NMR (500 MHz, C_6D_6): δ/ppm 8.82 (d, J = 4.5 Hz, 8H, H9), 8.17 (br s, 8H, H6), 7.71 (m, 8H, H7), 7.39 (m, 8H, H8), 6.70 (m, 4H, H4), 6.04 (m, 4H, H3), 4.40 (br s, 8H, H1). ^{31}P NMR (121 MHz, C_6D_6): δ/ppm 19.54 (s), 16.97 (s).

Silver(I) complexes

Reaction of 1 with silver tetrafluoroborate (synthesis of [19]BF_4)

A solution of the ligand **1** (35 mg, 0.073 mmol) in CD_2Cl_2 (0.4 mL) was added to $AgBF_4$ (7 mg, 0.037 mmol) in an NMR tube. As the speed of the reaction was limited by the solubility of the $AgBF_4$ in CD_2Cl_2, the reaction mixture was heated gently to dissolve the silver tetrafluoroborate. ^{31}P, ^{1}H and ^{19}F NMR spectra recorded after 20 minutes showed the reaction had gone to completion (quantitative conversion).



[**19**]BF_4 ^{1}H NMR (500 MHz, CD_2Cl_2): δ/ppm 8.54 (br s, 8H, H9), 7.12 (br s, 16H, H6+H7), 6.99 (m, 8H, H8), 6.37 (br s, 8H, H3+H4), 4.47 (br s, 8H, H1). ^{19}FNMR (282MHz, CD_2Cl_2): δ/ppm −152.97 (s, BF_4). ^{31}P NMR (121 MHz, CD_2Cl_2): δ/ppm 4.06 (dd, $^1J_{107AgP}$ = 224.1, $^1J_{109AgP}$ = 258.0 Hz). IR (film from CH_2Cl_2): ν_{max}/cm^{-1} 1573, 1561 (C=N stretch). HRMS calcd for $C_{56}H_{48}AgN_8P_4$ $[M-BF_4]^+$: m/z = 1065.2006; found = 1065.2045. HRMS calcd for $C_{28}H_{24}AgN_4P_2$ $[M-BF_4-C_{28}H_{24}N_4P_2]^+$: m/z = 585.0522; found = 585.0522.

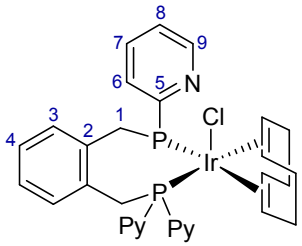
Reaction of 1 with silver nitrate (synthesis of [19]NO_3)

A solution of the ligand **1** (35 mg, 0.073 mmol) in $CDCl_3$ (0.3 mL) was added to $AgNO_3$ (6 mg, 0.037 mmol) in $(CD_3)_2CO$ (0.3 mL) in an NMR tube. The speed of the reaction was once again limited by the solubility of the $AgNO_3$ in the solvent mixture. ^{31}P and ^{1}H NMR spectra recorded after one hour showed the reaction mixture was comprised of 70% **1** and 30%$[Ag(PP)_2]NO_3$ ([**19**]NO_3). The reaction mixture was then heated in a water bath at 35°C. ^{31}P and ^{1}H NMR spectra recorded after 48 hours of heating showed the reaction had gone to completion (quantitative conversion).

[**19**]NO_3: ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ/ppm 8.52 (br s, 8H, H9), 7.12 (br s, 16H, H6+H7), 6.97 (m, 8H, H8), 6.32 (br s, 8H, H3+H4), 4.56 (br s, 8H, H1). ^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ/ppm 160.3 (br m, C5), 150.30 (br s, C9), 135.98 (br s, C7), 132.2 (br m, C2+C3), 131.86 (br s, C6), 127.02 (s, C8), 124.2 (brm, C4), 37.5 (m, C1). ^{31}P NMR (121MHz, $(CD_3)_2CO$): d/ppm 4.02 (dd, $^1J_{107AgP}$ = 224.2, $^1J_{109AgP}$ = 257.0 Hz). IR (film from CH_2Cl_2): ν_{max}/cm^{-1} 1573, 1561 (C=N stretch). HRMS calcd for $C_{56}H_{48}AgN_8P_4$ $[M-NO_3]^+$: m/z = 1065.2006; found = 1065.2043.

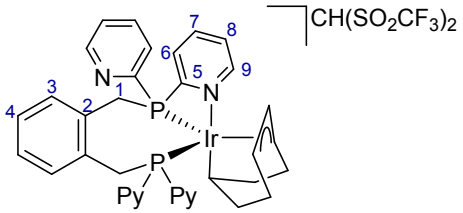
Iridium complexes

Synthesis of [IrCl(PP)(COD)] (20)



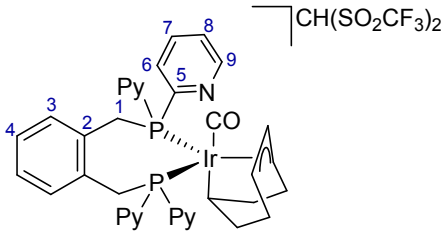
^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.53 (br s, 4H, H9), 8.23 (br s, 4H, H6), 7.70 (br s, 4H, H7), 7.18 (m, 4H, H8), 6.52 (m, 2H, H3), 6.50 (m, 2H, H4), 5.06 (br m, 4H, COD =CH), 4.30 (br s, 4H, H1), 2.21 (d, $^2J_{HH}$ = 8.5 Hz, 4H, COD CH_2), 1.75 (d, $^2J_{HH}$ = 8.5 Hz, 4H, COD CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 155.61 (br m, C5), 148.61 (br m, C9), 135.20 (br m, C7), 134.01 (s, C2), 131.82 (s, C3), 125.54 (s, C4), 123.58 (br s C8), 33.09 (d, $^1J_{PC}$ = 13.4 Hz, C1), 32.85 (s, COD CH_2). ^{31}P NMR (121 MHz, $CDCl_3$): δ/ppm −13.62 (s). IR (film from $CHCl_3$): ν_{max}/cm^{-1} 1573 (C=N stretch). HRMS calcd for $C_{28}H_{25}ClIrN_4P_2$ $[M-C_8H_{12}+H]^+$: m/z = 707.0859; found = 707.0870.

Synthesis of [Ir(1-*κ*-4,5,6-*η*^{3}-C_8H_{12})(PPN)]CH(SO_2CF_3)$_2$ ([21]CH(SO_2CF_3)$_2$)



^{1}H NMR (500 MHz, $CDCl_3$): *δ*/ppm 8.89 (d, *J* = 4.5 Hz, 2H, H9a), 7.93 (br s, 2H, H6a), 7.89 (m, 2H, H7a), 7.73 (br s, 2H, H9b), 7.70 (tm, *J* = 7.8 Hz, 2H, H7b), 7.56 (br s, 2H, H3), 7.50 (dd, *J* = 8.0, 3.5 Hz, 2H, H6b), 7.44 (m, 2H, H8a), 7.13 (br s, 2H, H4), 7.05 (t, *J* = 5.5 Hz, 2H, H8b), 5.29 (m, 2H, allyl CH), 5.17 (t, $^2J_{PH}$ = 14.0 Hz, 2H, H1), 4.69 (dd, $^2J_{PH}$ = 13.0, 11.5 Hz, 2H, H1), 4.45 (t, *J* = 8.0 Hz, 1H, allyl CH), 3.96 (s, 1H, $CH(SO2CF_3)_2$), 1.29 (m, 3H, CH_2 + CH), 0.89 (m, 2H, CH_2), 0.54 (m, 2H, CH_2), 0.38 (m, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): *δ*/ppm 162.25 (d, $^1J_{PC}$ = 63.4 Hz, C5b), 155.72 (d, $^1J_{PC}$ = 71.0 Hz, C5a), 150.29 (d, $^3J_{PC}$ = 14.8 Hz, C9a), 149.18 (d, $^3J_{PC}$ = 15.8 Hz, C9b), 136.95 (d, $^3J_{PC}$ = 5.8 Hz, C7b), 136.62 (d, $^3J_{PC}$ = 8.1 Hz, C7a), 134.76 (m, C2), 131.79 (dd, J_{PC} = 6.3, 3.9 Hz, C3), 128.10 (s, C6a), 127.91 (s, C6b), 127.63 (vt, $^4J_{PC}$ + $^5J_{PC}$ = 3.4 Hz, C4), 125.82 (br s, C8b), 125.09 (d, $^4J_{PC}$ = 2.5 Hz, C8a), 121.30 (q, $^1J_{CF}$ = 325.6 Hz, $CH(SO_2CF_3)_2$), 97.88 (s, allyl CH), 77.92 (d, $^2J_{PC}$ = 27.8 Hz, allyl CH), 53.85 (br s, $CH(SO_2CF_3)_2$), 50.73 (m, CH2), 30.52 (dm, $^1J_{PC}$ = 28.4 Hz, C1), 29.79 (s, CH), 23.18 (d, J_{PC} = 2.8 Hz, CH_2). ^{19}F NMR (282 MHz, $CDCl_3$): *δ*/ppm −80.88 (s, $CH(SO_2CF_3)_2$). ^{31}P NMR (121 MHz, $CDCl_3$): *δ*/ppm −27.36 (br s). IR (film from $CHCl_3$): ν_{max}/cm^{-1} 1587, 1573 (C=N stretch). HRMS calcd for $C_{36}H_{36}IrN_4P_2$ [M−$CH(SO_2CF_3)_2$]$^+$: m/z = 779.2041; found = 779.2055. Elemental Analysis: C, 44.1; H, 3.6; N, 5.6% ($C_{39}H_{37}F_6IrN_4O_4P_2S_2$ requires C, 44.3; H, 3.5; N, 5.3%).

Reaction of complex 21 with carbon monoxide (synthesis of complex 22)



^{1}H NMR (600 MHz, $CDCl_3$): *δ*/ppm 8.91 (d, *J* = 4.5Hz, 2H, H9a), 8.75 (d, *J* = 4.5Hz, 2H, H9b), 8.31 (dd, *J* = 7.7, 3.0 Hz, 2H, H6a), 8.00 (m, 4H, H6b+H7b), 7.94 (m, 2H, H7a), 7.51 (m, 4H, H8a+H8b), 6.91 (m, 2H, H4), 6.52 (m, 2H, H3), 5.23 (br s, 2H, allyl CH), 5.03 (t, *J* = 7.8 Hz, 1H, allyl CH), 4.81 (dd, *J* = 14.1, 8.4 Hz, 2H, H1a), 4.44 (t, $^2J_{PH}$ = 14.6 Hz, 2H, H1b), 3.94 (s, 1H, $CH(SO_2CF_3)_2$), 1.70 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.25 (m, 3H, CH_2 + CH), 0.85 (m, 2H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): *δ*/ppm 155.14 (d, $^1J_{PC}$ = 39.2 Hz, C5b), 154.37 (d, $^1J_{PC}$ = 38.0 Hz, C5a), 150.22 (d, $^3J_{PC}$ = 16.7 Hz, C9a), 149.75 (d, $^3J_{PC}$ = 18.3 Hz, C9b), 136.80 (m, C7a+C7b), 133.02 (br s, C2), 131.21 (br s, C3), 129.44 (s, C6a), 128.82 (s, C6b), 128.33 (s, C4), 125.78 (s, C8a+C8b), 121.26 (q, $^1J_{CF}$ = 324.3 Hz, $CH(SO_2CF_3)_2$), 94.93 (s, allyl CH), 86.18 (d, $^2J_{PC}$ = 28.1 Hz, allyl CH), 53.81 (br s, $CH(SO_2CF_3)_2$), 51.32 (m, CH2), 39.09 (d, $^1J_{PC}$ = 30.0 Hz, C1), 22.84 (s, CH_2). ^{19}F NMR (282 MHz, $CDCl_3$): *d*/ppm −80.94 (s, $CH(SO_2CF_3)_2$). ^{31}P NMR (121 MHz, $CDCl_3$): *δ*/ppm −1.64 (br s).

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