Supporting Information

New Hexaphosphane Ligands 1,3,5-$C_6H_3\{p\text{-}C_6H_4N(PX_2)_2\}_3$ [X = Cl, F, $C_6H_3OMe(C_3H_5)$]: Synthesis, Derivatization and, Palladium(II) and Platinum(II) Complexes

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Experimental Section

General Procedures. All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.[1] The compound 1,3,5-tris(4'-aminophenyl)benzene[2] and $[M(COD)Cl_2]$ (M = Pd, Pt)[3] were prepared according to the published procedures. Phosphorus trichloride was purchased from Spectrochem. Pvt.

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Ltd., India and used as such. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation. The ^{1}H and $^{31}P\{^{1}H\}$ NMR (δ in ppm) spectra were recorded using Varian VXR 400 spectrometer operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield in all the cases. The microanalyses were performed using Carlo Erba Model 1112 elemental analyzer. The melting points were observed in capillary tubes and are uncorrected.

Synthesis of 1,3,5-C_6H_3[*p*-$C_6H_4N(PCl_2)_2$]$_3$ (1)

Triethylamine (14.37 g, 142 mmol) was added dropwise to a mixture of 1,3,5-tris(4'-aminophenyl)benzene (8.33 g, 24 mmol), *N,N*-dimethyl-4-aminopyridine (12 mg) and PCl_3 (102.02 g, 743 mmol) at -78 °C with constant stirring. The resultant suspension was slowly warmed to room temperature, refluxed for 3 days and filtered through a frit. The insoluble residue was extracted with hot PCl_3 (2 × 15 mL). The combined extracts were concentrated to half and kept at room temperature for 24 h to give analytically pure product of **1** as pale yellow crystals. Yield: 59% (9.9 g); mp >140 °C (dec). Anal. Calcd for $C_{24}H_{15}N_3P_6Cl_{12}$: C, 30.13; H, 1.58; N, 4.39. Found: C, 30.02; H, 1.65; N, 4.53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, C_6H_4, 6H, $^{3}J_{HH}$ = 3.1 Hz), 7.83 (d, C_6H_4, 6H), 7.89 (s, C_6H_3, 3H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 153.7 (s).

Synthesis of 1,3,5-C_6H_3[*p*-$C_6H_4N(PF_2)_2$]$_3$ (2)

A mixture of **1** (1.40 g, 1.463 mmol) and SbF_3 (1.05 g, 5.854 mmol) was heated to reflux in toluene (30 mL) for 24 h. It was then cooled to room temperature, filtered, and the solvent was removed under reduced pressure to give a sticky residue. The residue was

extracted with *n*-hexane (3 × 7 mL) and the combined extracts were concentrated and dried under reduced pressure. The residual antimony impurities were removed by subliming the substance at 100 °C under reduced pressure (0.05 mm Hg) to leave compound **2** in an analytically pure form as an unsublimed material. Yield: 72% (0.799 g); mp 225-228 °C (dec). Anal. Calcd for $C_{24}H_{15}N_3P_6F_{12}$: C, 37.97; H, 1.99; N, 5.53. Found: C, 37.72; H, 1.83; N, 5.65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, C_6H_4, 6H, $^{3}J_{HH}$ = 3.2 Hz), 7.81 (d, C_6H_4, 6H), 7.87 (s, C_6H_3, 3H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 130.4 (m, $^{1}J_{PF}$ = 1246 Hz, $^{3}J_{PF}$ = 124 Hz and $^{2}J_{PP}$ = 372 Hz).

Synthesis of 1,3,5-C_6H_3[*p*-$C_6H_4N\{P(OR)_2\}_2$]$_3$ [R = -$C_6H_3OMe(C_3H_5)$] (3)

Method 1: A mixture of eugenol (5.15 g, 31.4 mmol) and Et_3N (3.18 g, 31.6 mmol) in 30 mL of diethyl ether was added dropwise over 1 hour to a well-stirred diethyl ether solution (50 mL) of **1** (2.5 g, 2.6 mmol) at 0 °C. The reaction mixture was further stirred for 12 h at room temperature and then filtered through a frit. The filtrate was concentrated and dried under reduced pressure to afford analytically pure product of **3** as a pale yellow liquid. Yield: 89% (5.8 g).

Method 2: Predried eugenol (4.14 g, 3.9 mL, 25.2 mmol) and sodium (0.58 g, 25.2 mmol) were taken in 50 mL of THF in a two-necked flask topped with a reflux condenser and a dropping funnel. The reaction mixture was refluxed for 6 h and then allowed to cool to room temperature. A solution of **1** (2.00 g, 2.1 mmol) in THF (60 mL) was transferred to the dropping funnel through a cannula and was added dropwise to the reaction mixture at 0 °C. The reaction mixture was further stirred for 12 h at room temperature and then filtered through a frit. The filtrate was concentrated and vacuum dried to give analytically pure product of **3** as a pale yellow liquid. Yield: 78% (4.1 g).

Anal. Calcd for $C_{144}H_{147}N_3O_{24}P_6$: C, 69.47; H, 5.95; N, 1.69. Found: C, 69.21; H, 6.44; N, 1.68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 (d, CH_2, 24H, $^3J_{HH}$ = 6.4 Hz), 3.65 (s, OCH_3, 36H), 5.03 (m, CH_2, 24H), 5.88-5.96 (m, CH, 12H), 6.61 (m, C_6H_3, 12H), 6.67 (s, C_6H_3, 12H), 7.01 (d, C_6H_3, 12H, $^3J_{HH}$ = 7.94 Hz), 7.25 (d, C_6H_4, 6H, $^3J_{HH}$ = 3.2 Hz), 7.67 (d, C_6H_4, 6H), 7.82 (s, C_6H_3, 3H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 128.2 (s).

Synthesis of 1,3,5-C_6H_3[*p*-C_6H_4N{$P(OR)_2$}$_2$($PdCl_2$)]$_3$ [R = -$C_6H_3OMe(C_3H_5)$] (4)

A solution of [Pd(COD)Cl_2] (0.065g, 0.026 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **3** (0.022g, 0.078 mmol) also in CH_2Cl_2 (4 mL). The reaction mixture was allowed to stir at room temperature for 5 h to give a clear pale yellow solution. The solution was then concentrated to 3 mL, layered with 2 mL of *n*-hexane and stored at room temperature to give an analytically pure orange-yellow crystalline precipitate of **4**. Yield: 89% (0.068g); mp 126-128 °C (dec). Anal. Calcd for $C_{144}H_{147}N_3O_{24}P_6Pd_3Cl_6$: C, 57.24; H, 4.90; N, 1.39. Found: C, 57.77; H, 5.00; N, 1.68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.33 (d, CH_2, 24H, $^3J_{HH}$ = 6.2 Hz), 3.88 (s, OCH_3, 36H), 5.07 (m, CH_2, 24H), 5.90-5.99 (m, CH, 12H), 6.69 (m, C_6H_3, 12H), 6.85 (s, C_6H_3, 12H), 7.12 (d, C_6H_3, 12H, $^3J_{HH}$ = 7.9 Hz), 7.14 (d, C_6H_4, 6H, $^3J_{HH}$ = 3.4 Hz), 7.24 (d, C_6H_4, 6H), 7.26 (s, C_6H_3, 3H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 63.2 (s).

Synthesis of 1,3,5-C_6H_3[*p*-C_6H_4N{$P(OR)_2$}$_2$($PtCl_2$)]$_3$ [R = -$C_6H_3OMe(C_3H_5)$] (5)

This was synthesized by a procedure similar to that of **4** using [Pt(COD)Cl_2] (0.016g, 0.043 mmol) and **3** (0.035g, 0.014 mmol). An analytically pure pale yellow crystalline product of **5** was obtained by keeping the saturated CH_2Cl_2/*n*-hexane (1:1 mixture) solution of **5** at room temperature for several days. Yield: 83% (0.038 g); mp >130 °C (dec). Anal. Calcd for $C_{144}H_{147}N_3O_{24}P_6Pt_3Cl_6$: C, 52.61; H, 4.51; N, 1.28.

Found: C, 52.87; H, 4.58; N, 1.66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (d, CH_2, 24H, $^{3}J_{HH}$ = 6.4 Hz), 3.88 (s, OCH_3, 36H), 5.06 (m, CH_2, 24H), 5.92-5.96 (m. CH, 12H), 6.58 (m, C_6H_3, 12H), 6.61 (s, C_6H_3, 12H), 7.01 (d, C_6H_3, 12H, $^{3}J_{HH}$ = 7.9 Hz), 7.26 (d, C_6H_4, 6H, $^{3}J_{HH}$ = 3.2 Hz), 7.43 (d, C_6H_4, 6H), 7.45 (s, C_6H_3, 3H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ57.9 (s, $^{1}J_{PtP}$ = 5913 Hz).

X-ray crystallography. Single crystal X-ray structural study of **1** was performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temprature attachment. Data were collected at 150(2) K using graphite-monochromoated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct method using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[4]

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. Crystal data and the details of the structure determination along with selected bond lengths and bond angles are given in Tables S1 and S2.

Table S1. Crystallographic information for compound **1**.

Empirical formula	$C_{24}H_{15}N_3Cl_{12}P_6$
Fw	956.61
Cryst.system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a, Å	13.162(5)
b, Å	18.095(5)
c, Å	16.316(5)
α, deg	90
β, deg	104.265(5)
γ, deg	90
V, Å^3	3766(2)
Z	4
$\rho_{calcd,}$ g cm^{-3}	1.687
μ (Mo-Kα), mm^{-1}	1.162
F (000)	1896
T (K)	150
2θ range, deg	3.3–25
Total no. reflns	29974
No. of indep reflns	6623 [R_{int} = 0.053]
GOF (F^2)	0.85
R_1	0.0386
wR_2	0.0903

Table S2. Selected bond distances and bond angles for compound **1**

Bond distances (Å)		Bond angles (°)	
N1-P1	1.696(3)	P1-N1-P2	111.28(16)
N1-P2	1.692(3)	P1-N1-C7	124.4(2)
N1-C7	1.444(5)	P2-N1-C7	123.9(2)
P1-Cl1	2.0290(18)	Cl1-P1-Cl2	97.78(7)
P1-Cl2	2.0440(18)	N1-P1-Cl1	101.90(11)
P2-Cl3	2.0331(17)	N1-P1-Cl2	101.52(11)
P2-Cl4	2.0627(17)	Cl3-P2-Cl4	96.87(6)
N2-P3	1.689(3)	N1-P2-C13	100.69(11)
N2-P4	1.694(3)	N1-P2-Cl4	102.62(11)
N2-C16	1.452(4)	P3-N2-P4	112.19(16)
P3-Cl5	2.0254(18)	P3-N2-C16	123.9(2)
P3-Cl6	2.0515(18)	P4-N2-C16	123.5(2)
P4-Cl7	2.0660(17)	Cl5-P3-Cl6	97.93(7)
P4-Cl8	2.0331(16)	N2-P3-Cl5	101.60(11)
N3-P5	1.690(3)	N2-P3-Cl6	101.66(11)
N3-P6	1.690(3)	Cl7-P4-Cl8	96.72(6)
N3-C22	1.457(3)	N2-P4-Cl7	102.72(11)
P5-Cl9	2.0263(18)	N2-P4-Cl8	101.19(11)
P5-Cl10	2.0375(19)	P5-N3-P6	111.41(16)
P6-Cl11	2.0503(18)	P5-N3-C22	124.9(2)
P6-Cl12	2.0284(16)	P6-N3-C22	123.3(2)
		Cl9-P5-Cl10	98.29(7)
		N3-P5-Cl9	100.86(11)
		N3-P5-Cl10	103.29(11)
		Cl11-P6-Cl12	98.62(6)
		N3-P6-Cl11	101.29(11)
		N3-P6-Cl12	100.83(11)

References

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