Experimental Section

General Procedures

All experimental manipulations were carried out under a dry nitrogen or argon atmosphere, using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. The precursor $[(\mu\text{-N}^t\text{Bu})\text{PCl}]_2$ was prepared according to the published procedure.[1] All pyridyl derivatives and CuI were purchased from Aldrich and used without further purification.

Spectroscopy

The ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were obtained on a Varian VXR 400 spectrometer operating at frequencies of 400 and 162 MHz respectively. The tetramethylsilane and 85% H_3PO_4 were used as an internal and external standards for ^{1}H and ^{31}P{^{1}H} NMR respectively. Positive shifts lie downfield of the standard in all the cases. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected.

Synthesis of *cis*-$[(\mu\text{-N}^t\text{BuP})_2(\text{NC}_4\text{H}_8\text{NMe})_2]$ (1)

A solution of *N*-methyl piperazine (2.04 g, 20.35 mmol) in diethyl ether (15 mL) was added dropwise to a stirred solution of $[(\mu\text{-N}^t\text{Bu})\text{PCl}]_2$ (1.40 g, 5.09 mmol) in diethylether (30 mL) at 0 °C over the course of 10 minutes. The reaction mixture was allowed to attain room temperature and the stirring was continued for further 20 h. The hydrochloride salts formed were filtered off through a frit containing celite. All the

volatiles were removed from the filtrate under vacuum leaving an oily liquid which was dissolved in acetonitrile and kept at –25 °C for 10 h to give **1** as a colorless crystalline compound. Yield: 83% (1.70 g, 4.23 mmol). Mp: 92-94 °C. Anal. Cal. for $C_{18}H_{40}N_6P_2$: C, 53.71; H, 10.01; N, 20.88%. Found: C. 53.62; H, 9.82; N, 20.53%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.12 (br s, *CH*$_2$, 8H), 2.21 (s, *NMe*, 6H), 1.14 (s, ^{t}*Bu*, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 91.4 (s).

Synthesis of *cis*-[(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$] (2)

A solution of morpholine (2.41 g, 27.64 mmol) in diethyl ether (15 mL) was added dropwise to a stirred solution of [(μ-N^{t}Bu)PCl]$_2$ (1.90 g, 6.91 mmol) in diethylether (30 mL) at 0 °C over the course of 15 minutes. The reaction mixture was allowed to attain room temperature and stirring was continued for 16 h. The hydrochloride salts formed were filtered off through a frit containing celite. The solvent was removed from the filtrate under vacuum and the white residue was dissolved in toluene and stored at –25 °C for a day to get compound **2** as a colorless crystalline compound. Yield: 90% (2.34 g, 6.22 mmol). Mp: 138-140 °C. Anal. Cal. for $C_{16}H_{34}N_4O_2P_2$: C, 51.05; H, 9.10; N, 14.88%. Found: C. 51.25; H, 9.15; N, 14.75%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.59 (t, J_{HH} = 9.2 Hz, *CH*$_2$, 8H), 3.15 (br s, *CH*$_2$, 8H), 1.24 (s, ^{t}*Bu*, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 92.8 (s).

Synthesis of [Cu$_8$(μ-I)$_8$(CH$_3$CN)$_4$(μ-N^{t}BuP)$_8$(NC$_4$H$_8$NMe)$_8$] (3)

A solution of CuI (0.03 g, 0.158 mmol) in acetnonitrlie (5 mL) was added dropwise to a well stirred solution of *cis*-[(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$] (0.032 g, 0.079 mmol) in 5 mL of dichloromethane. The reaction mixture was stirred for a further 6 h at room temperature. The solution was filtered through a frit and concentrated to 5 mL under reduced pressure. The concentrated solution was stored at room temperature for 48 h to afford **3** as colorless crystals. Yield: 78% (0.051 g, 0.062 mmol). Mp: 228-230 °C (dec). Anal. Cal. for $C_{80}H_{172}N_{28}P_8Cu_8I_8$: C, 29.13; H, 5.25; N, 11.89%. Found: C. 29.46; H, 5.42; N, 11.53%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.58 (br s, *CH$_2$*, 8H), 3.24 (br s, CH_2 8H), 2.30 (br s, *NMe*, 6H), 2.01 (s, *CH$_3$*, 3H), 1.48 (s, ^{t}*Bu*, 18H). ^{31}P {^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 69.2 (br, s).

Synthesis of [Cu$_8$(μ-I)$_8$(CH$_3$CN)$_4$(μ-N^{t}BuP)$_8$(NC$_4$H$_8$O)$_8$] (4)

This was synthesized by a procedure similar to that of **3**, using *cis*-[(μ N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$] (0.052 mg, 0.138 mmol) and CuI (0.053 mg, 0.276 mmol). Yield: 83% (0.086 g, 0.113 mmol). Mp: 208-210 °C (dec). Anal. Cal. for $C_{72}H_{148}N_{20}P_8O_8Cu_8I_8$: C, 27.07; H, 4.67; N, 8.78%. Found: C, 27.25; H, 4.62; N, 8.53%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.47 (br s, *CH$_2$*, 8H), 3.21 (br s, *CH$_2$*, 8H), 2.02 (s, *CH$_3$*, 3H), 1.46 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 69.8 (br, s).

Synthesis of [(C$_5$H$_5$N)$_4$Cu$_2$(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$(I)$_2$] (5)

A solution of pyridine (2 mL) in dichloromethane (5 mL) was added dropwise to **3** (0.039 g, 0.051 mmol) also in dichloromethane (8 mL) at room temperature and the reaction mixture was allowed to stir for 3 h. All the volatiles were removed under

vacuum and the residue was dissolved in dichloromethane, layered with petroleum ether and stored at -30 °C to give yellow crystals of **5**. Yield: 72% (0.041 g, 0.037 mmol). Mp: 140-142 °C (dec). Anal. Cal. for $C_{38}H_{60}N_{10}P_2Cu_2I_2$: C, 41.50; H, 5.50; N, 12.74%. Found: C. 41.62; H, 5.38; N, 12.65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72-7.69 (m, *Py*, 20H), 3.58 (br s, CH_2, 8H), 3.27 (br s, CH_2 8H), 2.34 (br s, *NMe*, 6H), 1.43 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 71.4 (s)

Synthesis of [$(C_5H_5N)_4Cu_2(\mu$-N^{t}BuP$)_2(NC_4H_8O)_2(I)_2$] (6)

This was synthesized by a procedure similar to that of **5**, using **4** (0.040 g, 0.051 mmol) and pyridine (2 mL). Yield: 70% (0.038 g, 0.036 mmol). Mp: 166-170 °C (dec). Anal. Cal. for $C_{36}H_{54}N_8O_2P_2Cu_2I_2$: C, 40.27; H, 5.07; N, 10.44%. Found: C. 40.43; H, 5.15; N, 10.37%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72-7.33 (m, *Py*, 20H), 3.66 (br s, CH_2, 16H), 1.45(s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 71.3 (br s).

Synthesis of [$(2,2'$-bpy$)_2Cu_2(\mu$-N^{t}BuP$)_2(NC_4H_8NMe)_2(I)_2$] (7)

To a solution of **3** (0.039 g, 0.051 mmol) in dichloromethane (5 mL) was added dropwise a solution of 2,2′-bipyridine (0.016 g, 0.102 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was allowed to stir for a further 6 h, concentrated to 4 mL and layered with petroleum ether (2 mL). The clear yellow solution was stored at room temperature for 48 h to obtain **7** as yellow orange crystals. Yield: 65% (0.036 g, 0.033 mmol). Mp: 178-182 °C (dec). Anal. Cal. for $C_{38}H_{56}N_{10}P_2Cu_2I_2$: C, 41.65; H, 5.15; N, 12.78%. Found: C. 41.69; H, 5.10; N, 12.57%. ^{1}H NMR (400 MHz,

$CDCl_3$, δ): 7.96-7.36 (m, *bpy*, 16H), 3.49 (br s, CH_2, 16H), 2.24 (br s, *NMe*, 6H), 1.54 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 75.2 (s).

Synthesis of $[(2,2'\text{-bpy})_2Cu_2(\mu\text{-}N^tBuP)_2(NC_4H_8O)_2(I)_2]$ (8)

This was synthesized by a procedure similar to that of **7**, using **4** (0.040 g, 0.051 mmol) and 2,2′-bipyridine (0.016 g, 0.102 mmol). Yield: 72% (0.039 g, 0.037 mmol). Mp: 156-158 °C (dec). Anal. Cal. for $C_{36}H_{50}Cu_2I_2N_8O_2P_2$: C, 40.42; H, 4.71; N, 10.48%. Found: C. 40.35; H, 4.55; N, 10.33%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.96-7.36 (m, *bpy*, 16H), 3.58 (br s, CH_2, 16H), 1.56 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 71.3 (s).

Synthesis of $[(1,10\text{-phen})_2Cu_2(\mu\text{-}N^tBuP)_2(NC_4H_8NMe)_2(I)_2]$ (9)

This was synthesized by a procedure similar to that of **7**, using **3** (0.039 g, 0.051 mmol) and 1,10-phenanthroline (0.018 mg, 0.102 mmol). Yield: 73% (0.043 g, 0.037 mmol). Mp: 172-174 °C (dec). Anal. Cal. for $C_{42}H_{56}N_{10}P_2Cu_2I_2$: C, 44.10; H, 4.93; N, 12.25%. Found: C. 44.22; H, 4.85; N, 12.36%. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.45-7.81 (m, *phen*, 16H), 3.31 (br s, CH_2, 16H), 2.24 (br s, *NMe*, 6H), 1.62 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 77.7 (s).

Synthesis of $[(1,10\text{-phen})_2Cu_2(\mu\text{-}N^tBuP)_2(NC_4H_8O)_2(I)_2]$ (10)

This was synthesized by a procedure similar to that of **7**, using **4** (0.040 g, 0.051 mmol) and 1,10-phenanthroline (0.018 mg, 0.102 mmol). Yield: 79% (0.049 g, 0.041 mmol). Mp: 162-164 °C (dec). Anal. Cal. for $C_{40}H_{50}Cu_2I_2N_8O_2P_2$: C, 42.98; H, 4.51; N,

10.03%. Found: C. 42.82; H, 4.59; N, 10.17%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.65-7.79 (m, *phen*, 16H), 3.61 (br s, CH_2, 16H), 1.42 (s, ^{t}Bu, 18H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 74.7 (s).

Synthesis of [{[(4,4′-bpy)$_2$Cu$_2$(μ-I)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$][Cu$_2$(μ-I)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$(I)$_2$]}$_\infty$] (11)

To a solution of **3** (0.039 g, 0.051 mmol) in dichloromethane/acetonitrile (8 mL) was added dropwise a solution of 4,4′-bipyridine (0.016 g, 0.102 mmol) in dichloromethane (5 mL). The resulting yellow solution was kept as such at room temperature for 1 day to give analytically pure yellow crystals of **11**. Yield: 68% (0.035 g, 0.035 mmol). Mp: > 250 °C (dec). Anal. Cal. for $C_{56}H_{96}Cu_4I_4N_{16}P_4$: C, 35.79; H, 5.15; N, 11.92%. Found: C. 35.62; H, 5.28; N, 11.88%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.82 (br s, 4H), 7.92 (br s, 4H), 3.52 (br s, CH_2, 8H), 3.31 (br s, CH_2 8H), 2.22 (br s, *NMe*, 6H), 1.38 (s, ^{t}Bu, 18H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, DMSO-d_6, δ): 74.3 (br s).

Synthesis of [{[(4,4′-bpy)$_2$Cu$_2$(μ-I)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$][Cu$_2$(μ-I)(μ-N^{t}BuP)$_2$-(NC$_4$H$_8$O)$_2$(I)$_2$]}$_\infty$] (12)

This was synthesized by a procedure similar to that of **11**, using **4** (0.040 g, 0.051 mmol) and 4,4′-bipyridine (0.016 g, 0.102 mmol). Yield: 60% (0.033 g, 0.031 mmol). Mp: > 250 °C (dec). Anal. Cal. for $C_{52}H_{84}Cu_4I_4N_{12}O_4P_4$: C, 34.19; H, 4.63; N, 9.19%. Found: C. 34.26; H, 4.53; N, 9.30%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.74 (br s, 4H), 8.06 (br s, 4H), 3.17 (br s, CH_2, 8H), 2.86 (br s, CH_2, 8H), 1.46 (s, ^{t}Bu, 18H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, DMSO-d_6, δ): 77.1 (br s).

X-ray Crystallography

A crystal of each of the compounds **3** and **12** suitable for X-ray crystal analysis was mounted in a Cryoloop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. Full spheres of data were collected using a combination of three sets of 400 scans in ω (0.5º per scan) at φ = 0, 90 and 180º plus two sets of 800 scans in φ (0.45º per scan) at ω = -30 and 210º (**3**) or 606 scans in ω (0.3º per scan) at ϕ = 0, 120 and 240º (**12**), all under the control of the APEX2 software package.[2] For **3**, an inspection of a reciprocal space plot prepared from 2404 reflections harvested from the full data set it was evident that the crystal contained two components. Two orientations of a triclinic unit cell differing by a 5.2° rotation about {1,0,0.45} were obtained from CELL_NOW[3] and these orientation matrices were used in the multicomponent version of SAINT+ to integrate the reflections from the two domains. The raw data were reduced to F^2 values using the SAINT+ software[4] and global refinements of unit cell parameters using 3010 (for **3**) and 9630 (for **12**) reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (TWINABS for **3** and SADABS for **12**).[5] All the structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL portion of the APEX2 program package.[2] Final refinement of the model for **3** employed the two-component reflection file produced by TWINABS. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of

the attached non-hydrogen atoms. Pertinent crystallographic data and other experimental details are summarized in Table 1.

Table 1 Crystallographic Data for **3** and **12**

	3.CH_2Cl_2	**12**.$2CH_3CN$
formula	$C_{41}H_{88}Cu_4I_4N_{14}P_4Cl_2$	$C_{56}H_{90}Cu_4I_4N_{14}O_4P_4$
fw	1733.79	1909.06
crystal system	Triclinic	Orthorhombic
space group	P-1, (No. 2)	Pccn, (No. 56)
a, Å	10.261(1)	22.928(1)
b, Å	18.556(1)	14.818(1)
c, Å	18.541(1)	21.085(1)
α, deg	68.787(1)	90
β, deg	80.755(1)	90
γ, deg	81.243(1)	90
V, Å^3	3231.2(4)	7163.8(6)
Z	1	4
ρ_{calc}, g cm^{-3}	1.782	1.770
μ (Mo Kα), mm^{-1}	3.431	3.037
F (000)	1708	3776
crystal size, mm	$0.09 \times 0.17 \times 0.20$	$0.06 \times 0.08 \times 0.10$
T, K	100	100
2θ range, deg	2.0, 28.4	1.6, 28.7
Total no. reflns	35593	61113
No. of indep. reflns	31619 [$R_{(int)} = 0.050$]	8837 [$R_{(int)} = 0.039$]
R1[a]	0.0355	0.0281
wR_2[b]	0.0843	0.0623
GOF (F^2)	0.935	1.043

[a] $R = \Sigma||F_o|-|Fc||/\Sigma|F_o|$

[b] $wR_2 = \{[\Sigma w(F_o^2-F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(xP)^2]$ where $P = (F_o^2+2F_c^2)/3$

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