Supplementary Material (ESI) for Chemical Communications


**[Electronic Supplementary Information (ESI)]**

# Bowl–shaped Cu(I) metallamacrocyclic ethylene and carbonyl adducts as structural analogues of organic calixarenes

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## (1) Detailed experimental preparations of complexes **1** – **4**.

(a) *{[Cu(pprd)($C_2H_4$)]$PF_6$}$_n$ (**1**).* [Cu(MeCN)$_4$]$PF_6$ (0.1864 g, 0.50 mmol) and pprd (0.0786 g, 0.50 mmol) were reacted in $Me_2CO$ (10 ml) under Ar. The pure $C_2H_4$ gas was bubbled into dark brown solution to form a pale yellow solution. The reaction solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under $C_2H_4$. The reaction solution was allowed to stand for 2 weeks at –20 °C. The yellowish brown crystals of **1** were collected. Anal. Calcd. for $C_{11}H_{11}CuF_6N_3P$: C, 33.56; H, 2.82; N, 10.67. Found: C, 33.58; H, 2.88; N, 10.75. $^1$H NMR (δ, $(CD_3)_2CO$, 23 °C): {9.75($H^2$), 9.29($H^5$) and 8.75 ($H^6$)} for pyrimidine ring, {8.79($H^{3'}$), 8.38($H^{4'}$), 7.97($H^{5'}$) and 9.15($H^{6'}$)} for pyridine ring, 4.88 for $C_2H_4$. IR (KBr, cm$^{-1}$): 1542 $\nu_{C=C}$($C_2H_4$). Yield. 60mg. The isolated complex **1** is unstable in air. After complex **1** was dried by the flow of $C_2H_4$ gas, complex **1** was immediately used to measure elementary analysis, IR and $^1$H NMR.

(b) *[$Cu_4$(pprd)$_4$($C_2H_4$)$_4$]($PF_6$)$_4$ (**2**).* [Cu(MeCN)$_4$]$PF_6$ (0.0745 g, 0.20 mmol) and pprd (0.0157 g, 0.10 mmol) were reacted in MeOH (10 ml) under Ar. The pure $C_2H_4$ gas was bubbled into the dark brown suspension to produce a clear yellowish brown solution. The reaction solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under $C_2H_4$. The reaction solution was kept to stand for 2 weeks at –5 °C and the yellowish brown crystals of **2** were collected. Anal. Calcd. for $C_{44}H_{44}Cu_4F_{24}N_{12}P_4$: C, 33.56; H, 2.82; N, 10.67. Found: C, 32.26; H, 2.82; N, 10.48. $^1$H NMR (δ, $(CD_3)_2CO$, 23 °C): {9.73($H^2$), 9.30($H^5$) and 8.75($H^6$)} for pyrimidine ring, {8.80($H^{3'}$), 8.39($H^{4'}$), 7.97($H^{5'}$) and 9.13($H^{6'}$)} for pyridine ring, 4.87 for $C_2H_4$. IR (KBr, cm$^{-1}$): 1541 $\nu_{C=C}$($C_2H_4$). Yield. 85mg. The

isolated complex **2** is unstable in air. After complex **2** was dried by the flow of $C_2H_4$ gas, complex **2** was immediately used to measure elementary analysis, IR and $^1$H NMR.

(c) *[Cu$_4$(pprd)$_4$(CO)$_4$](PF$_6$)$_4$ (**3**).* [Cu(MeCN)$_4$]PF$_6$ (0.1864 g, 0.50 mmol) and pprd (0.0393 g, 0.25 mmol) were reacted in $Me_2CO$ (10 ml) under Ar. The pure CO gas was bubbled into the dark brown reaction solution. The resultant yellowish brown solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under CO. The reaction solution was kept to stand for 2 months at –20 °C and the pale yellow crystals of **3** were collected. Anal. Calcd. for $C_{40}H_{28}Cu_4F_{24}N_{12}O_4P_4$: C, 30.51; H, 1.79; N, 10.67. Found: C, 30.28; H, 1.82; N, 10.87. $^1$H NMR (δ, $(CD_3)_2CO$, 23 °C): {9.73(H$^2$), 9.27(H$^5$) and 8.72(H$^6$)} for pyrimidine ring, {8.81(H$^{3'}$), 8.39(H$^{4'}$), 7.96(H$^{5'}$) and 9.16(H$^{6'}$)} for pyridine ring. IR (KBr, cm$^{-1}$): 2124 $\nu_{C\equiv O}$(CO). Yield. 40 mg. The isolated complex **3** is unstable in air. After complex **3** was dried by the flow of CO gas, complex **3** was immediately used to measure elementary analysis, IR and $^1$H NMR.

(d) *{[Cu$_3$(pprd)$_3$(C$_2$H$_4$)$_3$](ClO$_4$)$_3$}$_3$ (**4**).* The precursor Cu(I) $C_2H_4$ complex, $[Cu(C_2H_4)_n]ClO_4$, was prepared by the reductive reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0185 mg, 0.50 mmol) with Cu wire in $Me_2CO$ (5 ml) under $C_2H_4$. A 5 ml $Me_2CO$ solution of pprd (0.0157 mg, 0.10 mmol) was added to the above Cu(I) $C_2H_4$ solution. The pure $C_2H_4$ gas was bubbled for 1 hour. The yellowish brown solution was filtered and the filtrates were sealed in 7 mmϕ glass tubes under $C_2H_4$. The reaction solution was allowed to stand at –20 °C for 1 month and the yellowish brown crystals of **4** were collected. Anal. Calcd. for $C_{99}H_{99}Cl_9Cu_9N_{27}O_{36}$: C, 37.94; H, 3.18; N, 12.07. Found: C, 36.93; H, 3.12; N, 12.06. $^1$H NMR (δ, $(CD_3)_2CO$, 23 °C): {9.77(H$^2$), 9.32(H$^5$) and 8.77(H$^6$)} for pyrimidine ring, {8.82(H$^{3'}$), 8.40(H$^{4'}$), 7.98(H$^{5'}$) and 9.07(H$^{6'}$)} for pyridine ring, 4.96 for $C_2H_4$. IR (KBr, cm$^{-1}$): 1537 $\nu_{C=C}$($C_2H_4$). Yield. 50 mg. The isolated complex **4** is unstable in air. After complex **4** was dried by the flow of $C_2H_4$ gas, complex **4** was immediately used to measure elementary analysis, IR and $^1$H NMR.

*Caution! Perchlorate salts of metal complexes with organic compounds are potentially explosive! Only small amounts of materials should be prepared and handled with great care.*

(2) Detailed crystallographic data of **1** – **4**.

CCDC 659368 – 659371 for complexes **1**–**4**. For crystallographic data in CIF or other electroformat see DOI: 10.1039/b000000x.

(a) *Crystal data for **1***: Formula $C_{11}H_{11}CuF_6N_3P$, $M$=393.74, Monoclinic, $P2_1/c$, $a$=8.520(1), $b$=17.573(2), $c$=9.483(2) Å, $\beta$=102.185(9) °, $V$=1387.9(4) Å$^3$, $Z$=4, $D_c$=1.884 cm$^{-1}$, $\mu$(Mo–K$_\alpha$)=17.56 cm$^{-1}$, $T$=150 K, Measured reflections; 13019 (Total), Observed reflections 3913 (all data); 3022($I$>2σ($I$)), $R$=0.047, $R1$=0.077, $R_w$=0.196. CCDC–659368.

(b) *Crystal data for* ***2***: Formula $C_{44}H_{44}Cu_4F_{24}N_{12}P_4$, $M$=1574.95, Orthormbic, space group *I*ba2, $a$=14.6057(9), $b$=28.370(2), $c$=14.0685(9) Å, $V$=5829(1) Å$^3$, $Z$=4, $D_c$=1.794 cm$^{-1}$, $\mu$(Mo–K$_\alpha$)=16.72 cm$^{-1}$, $T$=150 K, Measured reflections; 22491 (total), Observed reflections 5905 (all data); 5454 ($I$>2σ($I$)), $R$=0.040, $R1$=0.043($I$>2σ($I$)), $R_w$=0.096. CCDC–659369.

(c) *Crystal data for* ***3***: Formula $C_{40}H_{28}Cu_4F_{24}N_{12}O_4P_4$, $M$=1574.78, Tetragonal, space group $P$4/n, $a$=14.8455(8), $c$=12.2984(9) Å, $V$=2710.4(3) Å$^3$, $Z$=2, $D_c$=1.929 cm$^{-1}$, $\mu$(Mo–K$_\alpha$)=18.03 cm$^{-1}$, $T$=150 K, Measured reflections 15811 (total), Observed reflections 3102 (all data); 2732 ($I$>2σ($I$)), $R$=0.042, $R1$=0.051 $R_w$=0.093. CCDC–659370.

(d) *Crystal data for* ***4***: Formula $C_{33}H_{33}Cl_3Cu_3N_9O_{12}$, $M$=1044.67, Orthormbic, space group $P$na2$_1$, $a$=14.4419(7), $b$=38.607(2), $c$=21.448(1) Å, $V$=11958(1) Å$^3$, $Z$=12, $D_c$=1.741 cm$^{-1}$, $\mu$(Mo–K$_\alpha$)=18.60 cm$^{-1}$, $T$=150 K, Measured reflections; 93735 (total), Observed reflections 23226 (all data); 19520 ($I$>2σ($I$)), $R$=0.068, $R1$=0.058($I$>2σ($I$)), $R_w$=0.117. CCDC–659371.