# Supporting Information

# Coordination of $NO_2^-$ ligand to Cu(I) ion in an *O,O*-bidentate fashion that evolves NO gas upon protonation: a model reaction relevant to denitrification process

Chi-Shian Chen and Wen-Yann Yeh*

*Department of Chemistry and Center for Nanoscience and Nanotechnology*

*National Sun Yat-Sen University, Kaohsiung 804, Taiwan*

## Experimental procedures

### General remarks

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. $[Cu(MeCN)_4]BF_4$ was prepared as described in the literature (Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90). 2,6-pyridinediamine, *o*-(diphenylphophino)benzaldehyde, $[(Ph_3P)_2N]NO_2$ ($[PPN]NO_2$), and glacial acetic acid were purchased from Aldrich and were used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Infrared spectra were recorded on a Jasco FT/IR-4100 IR spectrometer. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Fast-atom-bombardment (FAB) and electrospray ionization (ESI) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer and a Waters ZQ-4000 mass spectrometer, respectively. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan. Gas chromatography experiments were performed by using a Varian CP-3800, with a Porpak Q column (6 ft, 20 mL/min flow rate, 30° C, dinitrogen carrier gas) and a TCD detector. Nitric oxide (NO) quantitation was performed by calibrating detector response with known concentrations of NO mixed with $N_2$; molar quantities were calculated using the ideal gas equation.

**Preparation of 1**

Under a dinitrogen atmosphere, 2,6-pyridinediamine (109 mg, 1 mmol), *o*-(diphenylphophino)benzaldehyde (600 mg, 2.06 mmol), NaOH (83 mg, 2.08 mmol), and benzene (30 mL) were placed in an oven-dried 250 mL Schlenk flask, equipped with a magnetic stir bar and a reflux condenser. The reaction mixture was refluxed for 8 h, yielding a yellow solution. The solution was filtrated and concentrated to *ca.* 15mL under dinitrogen and layered with *n*-hexane (50 mL) overnight. A yellow solid was obtained, characterized as 2,6-($Ph_2P$(*o*-$C_6H_4$)CH═N$)_2C_5H_3N$ (**1**; 520 mg, 80%). Mass (FAB): *m*/*z* 653 ($M^+$). $^1H$ NMR ($CD_2Cl_2$, 24° C): $\delta$ 9.77 (d, $J_{P–H}$ = 5 Hz, 2H, N=CH), 8.22 (m, 2H, $C_6H_4$), 7.65 (t, 1H, $J_{H–H}$ = 8 Hz, Py), 7.51 (t, $J_{H–H}$ = 8 Hz, 2H, $C_6H_4$), 7.40 (t, $J_{H–H}$ = 8 Hz, 2H, $C_6H_4$), 7.38–7.30 (m, 20H, Ph), 7.04 (m, 2H, $C_6H_4$), 6.90 (d, 2H, $J_{H–H}$ = 8 Hz, Py). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 24 °C): $\delta$ –12.85 (s).

**Preparation of 2**

[$Cu(NCMe)_4$][$BF_4$] (102 mg, 0.324 mmol), acetonitrile (1 mL) and dichloromethane (10 mL) were placed in an oven-dried 50 mL Schlenk flask, equipped with a magnetic stir bar. Compound **1** (212 mg, 0.325 mmol) in dichloromethane solvent (5 mL) was then introduced into the flask and the mixture was stirred at room temperature for 24 h, yielding an orange-red solution. The solution was filtrated under dinitrogen and carefully layered with diethyl ether (30 mL). The air-stable, red crystals of [(2,6-($Ph_2P$(*o*-$C_6H_4$)CH═N$)_2C_5H_3N)_2Cu_2$]$(BF_4)_2$ (**2**; 182 mg, 70% based on the Cu atoms) were obtained. Anal. Calcd for $C_{86}H_{66}N_6P_4B_2F_8Cu_2{\cdot}CH_2Cl_2$: C, 61.72; H, 4.05; N, 4.96. Found: C, 61.59; H, 4.25; N, 5.21. Mass (ESI): *m*/*z* 1519 ($^{63}$Cu, $^{11}$B; [M – $BF_4^-$]$^+$). $^1H$ NMR ($CD_2Cl_2$, 24° C): $\delta$ 7.98 (br, 4H, N=CH), 7.59 (t, $J_{H–H}$ = 8 Hz, 4H, $C_6H_4$), 7.55 (t, $J_{H–H}$ = 8 Hz, 4H, $C_6H_4$), 7.47 (br, 2H, Py), 7.38 (br, 4H, $C_6H_4$), 7.27 (br, 8H, Ph), 7.14 (m, 4H, $C_6H_4$), 6.99 (br, 16H, Ph), 6.54 (br, 16H, Ph), 6.48 (d, 4H, $^3J_{H-H}$ = 8 Hz, Py). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 24 °C): $\delta$ –7.72 (br).

**Preparation of 3**

Compound **2** (75 mg, 0.047 mmol) and acetonitrile (5mL) were placed in an oven-dried 50 mL Schlenk flask, equipped with a magnetic stir bar. [PPN]$NO_2$ (58 mg, 0.100 mmol) in acetonitrile solvent (5 mL) was then introduced into the flask and the mixture was stirred at room temperature for 8 h, yielding a yellow solution. The solution was filtrated under dinitrogen and carefully layered with diethyl ether (20 mL). The slightly air-sensitive, canary yellow crystals of (2,6-($Ph_2P$(*o*-$C_6H_4$)CH=N$)_2C_5H_3N$)Cu($NO_2$) (**3**; 60 mg, 85% based on the Cu atoms) were afforded. Anal. Calcd for $C_{43}H_{33}N_4P_2O_2Cu{\cdot}H_2O$: C, 66.10; H, 4.51; N, 7.17. Found: C, 66.07; H, 4.66; N, 6.97. Mass (FAB): *m*/*z* 716 ($^{63}$Cu ; $[M–NO_2^-]^+$). $^1$H NMR ($CD_2Cl_2$, 24° C): $\delta$ 10.62 (s, 2H, N=CH), 8.46 (d, $J_{H–H}$ = 8 Hz, 2H, $C_6H_4$), 7.76 (t, $J_{H-H}$ = 8 Hz, 1H, Py), 7.62 (t, $J_{H–H}$ = 8 Hz, 2H, $C_6H_4$), 7.44 (t, $J_{H–H}$ = 8 Hz, 2H, $C_6H_4$), 7.37 (t, $J_{H–H}$ = 7 Hz, 4H, Ph), 7.25–7.18 (m, 18H, Ph, Py), 6.92 (m, 2H, $C_6H_4$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 24 °C): $\delta$ –7.43 (br).

**Protonation of 3**

A solution of compound **3** (10 mg, 0.013 mmol) in $CH_2Cl_2$ (0.5 mL) was prepared in a small vial capped with a rubber septum. A degassed solution of $CH_3COOH$ (2 μL) in $CH_2Cl_2$ (0.05 mL) was then introduced with a syringe at room temperature. The solution color changed immediately from yellow to brown. Analysis of the head-space gas by GC indicated that nitric oxide (NO) was generated (0.124 mmol, 95%). Diethyl ether (5mL) was then added to the solution to precipitate a yellow-brown solid, characterized as **1**·Cu$^{II}$(OAc)$_2$ (10 mg, 92%). IR (KBr): 3055, 1695, 1602, 1589, 1576, 1559, 1457, 1436, 1402, 1267, 1164, 1117, 1095, 1027, 998, 794, 747, 725, 696 cm$^{-1}$.

**Structure determination for 2 and 3**

The crystals of **2** and **3** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The data were collected at 200K. The $\theta$ range for data collection is 2.08–25.38º for **2** and 1.36–25.02º for **3**. Of the 52637 and 6361 reflections collected for **2** and **3**, 15746 and 6361 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package. The data collection and refinement parameters are presented in Table 1-S.

**Table 1-S. Crystal data and refinement details for 2 and 3**

| | **2** | **3** |
|---|---|---|
| chem formula | $C_{86}H_{66}B_2Cu_2F_8N_6P_4$ | $C_{43}H_{33}CuN_4O_2P_2$ |
| crystal system | triclinic | triclinic |
| crystal solvent | $CH_2Cl_2$ | — |
| formula weight | 1692.95 | 763.21 |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| unit cell dimensions | | |
| *a*, Å | 12.8700(2) | 9.882(2) |
| *b*, Å | 15.1448(2) | 13.036(3) |
| *c*, Å | 23.0511(3) | 15.533(3) |
| α, deg | 98.7830(10) | 81.005(5) |
| β, deg | 93.5300(10) | 76.103(7) |
| γ, deg | 101.6710(10) | 83.054(5) |
| $V$, Å$^3$ | 4328.59(10) | 1911.3(7) |
| $Z$ | 2 | 2 |
| $D_{\mathrm{calcd}}$, Mg/m$^{-3}$ | 1.299 | 1.326 |
| $F$(000) | 1732 | 788 |
| absorption coefficient (mm$^{-1}$) | 0.690 | 0.697 |
| $\theta$ range (°) | 2.08 to 25.38 | 1.36 to 25.02 |
| $R_1$ | 0.0899 | 0.0545 |
| $wR_2$ | 0.2385 | 0.1273 |
| GOF on $F^2$ | 1.240 | 1.001 |