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Synthesis of a new tetradentate bis(imino-phosphine) ligand and its complexation with copper(I) ions

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ABSTRACT

Schiff base condensation of *m*-phenylenediamine with two equivalents of *o*-(diphenylphophino)benzaldehyde products the potentially tetradentate molecule $1,3-(Ph_2P(o-C_6H_4)CH=N)_2C_6H_4$ (1) in high yield. The reaction of 1 and [Cu(NCMe)_4]BF₄ affords the dinuclear complex [(1,3-(Ph_2P(o-C_6H_4)CH=N)_2C_6H_4)_2-Cu_2](BF_4)_2 (2) through coordination of the imino-phosphine groups. The structure of 2 has been determined by an X-ray diffraction study.

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1. Introduction

The multifunctional, hemilabile ligands [1–4], which contain both soft (such as P, S) and hard (such as N, O) donor atoms, have attracted considerable interest for their unusual coordination chemistry and their increasing importance in catalysis [5–8], with the reactivity being controlled by the differential donor properties of the ligands [9]. One of the early notable successes associated with complexes of P^O-ligands was their application in the Shell higher olefin process which utilizes a nickel-catalyzed oligomerization of ethylene [10]. In addition, the hemilabile property of pyridyl group has made the complexes [Pd(allyl)(Ph₂P($o-C_6H_4$)-CH=NC₂H₄($o-C_5H_4N$))]⁺ very active in allylic alkylation reactions [11]. As part of our interest in the design and coordination chemistry of multifunctional ligands [12–16], herein we present the synthesis of a new tetradentate P₂N₂ ligand and its coordination to copper(I) ions.

2. Results and discussion

Schiff base condensation reaction of *m*-phenylenediamine with two equivalents of *o*-(diphenylphophino)benzaldehyde (PPh₂(*o*-C₆H₄)C(=O)H) in refluxing benzene produces the potentially tetradentate molecule 1,3-(Ph₂P(*o*-C₆H₄)CH=N)₂C₆H₄ (1) in 90% yield (Scheme 1), as an air-stable yellow solid. The FAB mass spectrum of **1** gives the molecular ion at *m*/*z* 652, corresponding to combina-

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tion of *m*-phenylenediamine with two PPh₂(o-C₆H₄)C(=O)H molecules and loss of two H₂O. The starting compound PPh₂(o-C₆H₄)-C(=O)H presents a ³¹P resonance at -11.4 ppm for the phosphorus atom and an ¹H resonance at 10.50 ppm for the formyl proton. The ³¹P{¹H} NMR spectrum of **1** displays a slightly downfield signal at -13.18 ppm for the phosphine ligands, and the ¹H NMR spectrum (Fig. 1) shows missing of the formyl proton resonance and a new 2H doublet signal ($J_{P-H} = 5$ Hz) appearing at 9.01 ppm, assigned to the imine protons.

Compound **1** contains two imino-phosphine moieties connected to the 1,3-positions of a benzene ring. Due to rigidity of the arene spacer, the two N^P groups are restricted to bind separate metal atoms (or ions) instead of acting as a tetradentate chelating agent to coordinate one metal center. Such that, treatment of **1** with equimolar [Cu(NCMe)₄]BF₄ in dichloromethane at ambient temperature produces an orange-red solution, from which airstable, red crystals of the dimetallic complex [(1,3-(Ph₂P($o-C_{6}H_4$)CH=N)₂C₆H₄)₂Cu₂](BF₄)₂ (**2**) were obtained in 80% yield by adding diethyl ether. The ESI mass spectrum displays the ion peak at *m*/*z* 1517 corresponding to the [M – BF₄⁻⁻]⁺ fragment. A related N₂P₂ ligand, 1,2-(Ph₂P($o-C_{6}H_4$)CH=N)₂C₂H₄, forms a mononuclear copper(1) complex with a tetraligate coordination at the Cu center from the four donor atoms [17].

Single crystals of **2** were grown by slow diffusion of diethyl ether into a dichloromethane solution at ambient temperature. The ORTEP drawing for the cation of **2** is illustrated in Fig. 2, where a crystallographic center of symmetry is imposed on the molecule. The complex consists of a dimeric $[Cu_2^l \cdot 1_2]$ structure with each copper ion bonded to two phosphorus and two nitrogen atoms from different molecule of **1**. The coordination about the Cu⁺ ion can be described as an irregular tetrahedral, such that the angles





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Scheme 1. Preparation of 1 and 2.



Fig. 1. ¹H NMR spectra of 1 and 2 in CD₂Cl₂ at 24 °C.

around the copper atom range from $90.1(1)^{\circ}$ for P1–Cu1–N1 to 133.1(1)° for P1–Cu1–N2. The two imino-phosphine links are coordinated to the copper ion asymmetrically with the bond distances Cu1–N1 2.107(4), Cu1–N2 2.068(4), Cu1–P1 2.275(2) and Cu1–P2 2.231(1) Å, and the bite angles P1–Cu1–N1 90.1(1)° and P2–Cu1–N2 97.7(1)°. The bond distances N1–C19 1.271(6) and N2–C26 1.285(7) Å retain a N=C double bond character for the imine moieties. It is interesting that the two benzene spacers are in the anti-position and parallel to each other with the interplane distance of 3.18 Å (Fig. 3), and the two Cu(I) ions are separated by 7.44 Å.

The ³¹P{¹H} NMR spetrum of **2** presents a sharp singlet at -9.39 ppm. The ¹H NMR spectrum (Fig. 1) shows that the imine proton resonance (H^{a'}) and one arene proton resonance (H^{b'}) are shifted upfield to 8.06 and 5.60 ppm, respectively, in comparion with the free ligand **1**. Shielding of the imine protons is likely due to back-donation of electrons from the d^{10} Cu(I) ion to the

 π * orbital of the N=C double bond, while shielding of H^{b'} might be attributed to ring-current from the opposite arene species.

We recently prepared the molecule $2,6-(Ph_2P(o-C_6H_4)CH=N)_2-C_5H_3N$ (**3**) and showed its reaction with Cu⁺ ions to give [(2,6-(Ph_2P(o-C_6H_4)CH=N)_2C_5H_3N)_2Cu_2](BF_4)_2 (**4**) (Eq. (1)), in which the two pentadentate ligands wrap the Cu(I) ions in a double-helical fashion [18]. Furthermore, complex **4** reacted with NO₂⁻ ions with the activity mimicking the biological denitrification process [19]. The Cu(I) ions in **2** are each coordinated by two "soft" phosphorus and two 'hard' nitrogen atoms, and are also expected to carry out similar ligand substitution reactions. However, attempts to react **2** with [Ph₃PNPPh₃]NO₂, KN₃, O₂ or CNC₆H₄NC were unsuccessful. This is likely due to the kinetic reasons that the two close benzene spacers of **2** block the incoming ligands to attack the copper ions. In addition, steric constraints of the P₂N₂ ligands might hinder dissociation of the imine groups for undergoing substitution reactions.



Fig. 2. Molecular structure of **2** with 30% probability ellipsoids. The BF_4^- counter ions and hydrogen atoms have been artificially omitted. Selected bond distances (Å) and angles (°): Cu1–N1 2.107(4), Cu1–N2 2.068(4), Cu1–P1 2.275(2), Cu1–P2 2.231(1), N1–C19 1.271(6), N2–C26 1.285(7) and P1–Cu1–P2 120.67(5), P1–Cu1–N1 90.1(1), P1–Cu1–N2 133.1(1), P2–Cu1–N1 113.2(1), P2–Cu1–N2 97.7(1), N1–Cu1–N2 99.0(2), C19–N1–C20 115.0(4), C24–N2–C26 115.7(4).



Fig. 3. Skeleton of 2 showing parallel of the two arene spacers.

In conclusion, we have prepared a new polyfunctional molecule 1 and shown its coordination with Cu^+ ions to generate a dimetallic complex 2, which displays a quite different geometry and reactivity comparing with 4. We are currently investigating the viability of 1 as a bridging ligand to assemble supramolecules or coordination polymers.

3. Experimental

3.1. General remarks

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. [Cu(-MeCN)₄]BF₄ was prepared as described in the literature [20]. *m*-Phenylenediamine and *o*-(diphenylphophino)benzaldehyde (Al-drich) were used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. ¹H and ³¹P{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.

3.2. Preparation of 1

Under a dinitrogen atmosphere, *m*-phenylenediamine (109 mg, 1 mmol), *o*-(diphenylphophino)benzaldehyde (600 mg, 2.06 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. 15 ml under dinitrogen and layered with *n*-hexane (50 ml) overnight. A yellow solid was obtained, characterized as $2,6-(Ph_2P(o-C_6H_4)CH=$



(1)

Table 1 Crystallographic data for compound 2.

Formula	$C_{88}H_{68}B_2Cu_2F_8N_4P_4\cdot 2CH_2Cl_2$
Formula weight	1775.90
Crystal system	triclinic
Space group	ΡĪ
a (Å)	12.3888(3)
b (Å)	12.9899(3)
c (Å)	13.9411(4)
α (°)	96.275(2)
β (°)	99.964(2)
γ(°)	110.410(1)
V (Å ³)	2035.70(9)
T (K)	200(2)
Ζ	1
μ (mm ⁻¹)	0.800
Final R_1/wR_2	0.0766, 0.1879
Goodness-of-fit	1.100

N)₂C₆H₄ (**1**; 586 mg, 90%). Anal. Calc. for C₄₄H₃₄N₂P₂: C, 80.97; H, 5.25; N, 4.29. Found: C, 81.20; H, 5.54; N, 4.13%. Mass (FAB): m/z 652 (M⁺). ¹H NMR (CD₂Cl₂, 24° C): 9.01 (d, J_{P-H} = 5 Hz, 2H, N=CH), 8.18 (m, 2H, C_6H_4) 7.52–6.72 (m, 29H, Ph, C_6H_4), 6.70 (d, $J_{H-H} = 8 \text{ Hz}, 2H, C_6H_4$, 6.46 (s, 1H, C_6H_4) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 24 °C): -13.18 (s) ppm.

3.3. 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. vielding an orange-red solution. The solution was filtrated under dinitrogen and carefully lavered with diethyl ether (30 ml). The air-stable, red crystals of [(2,6-(Ph₂P(o-C₆H₄)CH=N)₂C₆H₄)₂Cu₂](BF₄)₂ (2; 208 mg, 80% based on the Cu atoms) were obtained. Anal. Calc. for C₈₈H₆₈N₄P₄B₂F₈Cu₂: C, 65.81; H, 4.27; N, 3.49. Found: C, 64.96; H, 4.81; N, 3.21%. Mass (ESI): m/z 1517 (⁶³Cu, ¹¹B; $[M - BF_4^-]^+$). ¹H NMR (CD₃CN, 24 °C): 8.06 (br, 4H, N=CH), 7.75–6.90 (m, 56H, Ph, C₆H₄), 6.71 (t, J_H-_H = 8 Hz, 2H, C₆H₄), 6.46 (d, J_{H-H} = 7 Hz, 4H, C₆H₄), 5.60 (s, 2H, C₆H₄) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 24 °C): -9.39 ppm.

3.4. Structure determination for 2

A crystal of 2 found suitable for X-ray analysis was mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The data were collected at 200 K. The θ range for data collection is 2.06–25.37°. Of the 25 806 reflections collected. 7365 reflections were independent. 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 leastsquare cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [21]. The data collection and refinement parameters are presented in Table 1.

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Appendix A. Supplementary material

CCDC 804438 for compound 2 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.015.

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