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Syntheses, characterization and crystal structures of copper(I) *o*-(diphenylphosphino)benzaldehyde complexes

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Abstract

The complexes $[Cu(PCHO)_2(NCMe)][BF_4]$ (**1**) and $[Cu(PCHO)_3][BF_4]$ (**2**) have been prepared by treating $[Cu(NCMe)_4][BF_4]$ with two and three equivalents of $Ph_2P(o\text{-}C_6H_4)C({=}O)H$ (abbreviated as PCHO) at room temperature, respectively. The reaction of **1** and $(Ph_2PC_5H_4)_2Fe$ (abbreviated as DPPF) affords $[Cu(PCHO)(DPPF)][BF_4]$ (**3**). The molecular structures of **1**–**3** have been determined by an X-ray diffraction study. The aldehyde groups in **1** are pendant, while one of the formyl groups in **2** is weakly coordinated to the copper ion through the oxygen atom. On the other hand, the copper atom in **3** is strongly chelated by both DPPF and PCHO ligands.

Keywords: Cu(I) complex; P–O chelation; PCHO ligand

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1. Introduction

The coordination chemistry of copper(I) and copper(II) ions is well established. While copper(II) is generally considered a borderline hard acid, copper(I) clearly behaves as a soft acid. For instance, with O, S, N and P ligands, the O and N ligands dominate the chemistry of copper(II), while the S and P ligands are more frequent in copper(I) chemistry [1]. Recently, functionalized tertiary phosphines have attracted considerable interest for their unusual coordination chemistry and their increasing importance in catalysis [2]. The *o*-(diphenylphosphino)benzaldehyde molecule (abbreviated as PCHO), which contains a "soft" phosphorus and a "hard" oxygen donor atoms, is one of the simplest bidendate P,O-chelating agents [3]. Usually, the phosphine center is coordinated to a metal in advance of the aldehyde group and can serve as a monodentate η^1-P donor in $W(CO)_5(PCHO)$ [4] and $RhCl(CO)(PCHO)_2$ [5]. Subsequent oxidative addition of the aldehyde C–H bond on a Rh(I) [6], Ir(I) [7], Pt(0) [8], Co(I) [9], Pd(II) [10] or Ru(II) [11] center can generate a phosphine-acyl hydrido complex. On the other hand, the PCHO ligand can act as chelating phosphine-aldehyde with the aldehyde moiety bonded to a metal in a σ-fashion through the oxygen atom in $Re(CO)_3Cl(PCHO)$ [12] and $RuCl_2(PCHO)_2$ [13], or in a π-fashion through the carbon–oxygen double bond in $Cp{*}Co(PCHO)$ [14], $W(CO)_3(PCHO)_2$ and $W(CO)_2(PCHO)_2$ [15]. In this paper, we explore the coordination chemistry of PCHO ligand with Cu(I) ion to give complexes with/without the chelation of the aldehyde groups.

2. Results and dissusion

Reaction of $[Cu(NCMe)_4][BF_4]$ with two equivalents of PCHO in dichloromethane solvent at ambient temperature afforded a yellow solution, from which yellow crystals of $[Cu(PCHO)_2(NCMe)][BF_4]$ (**1**) were obtained

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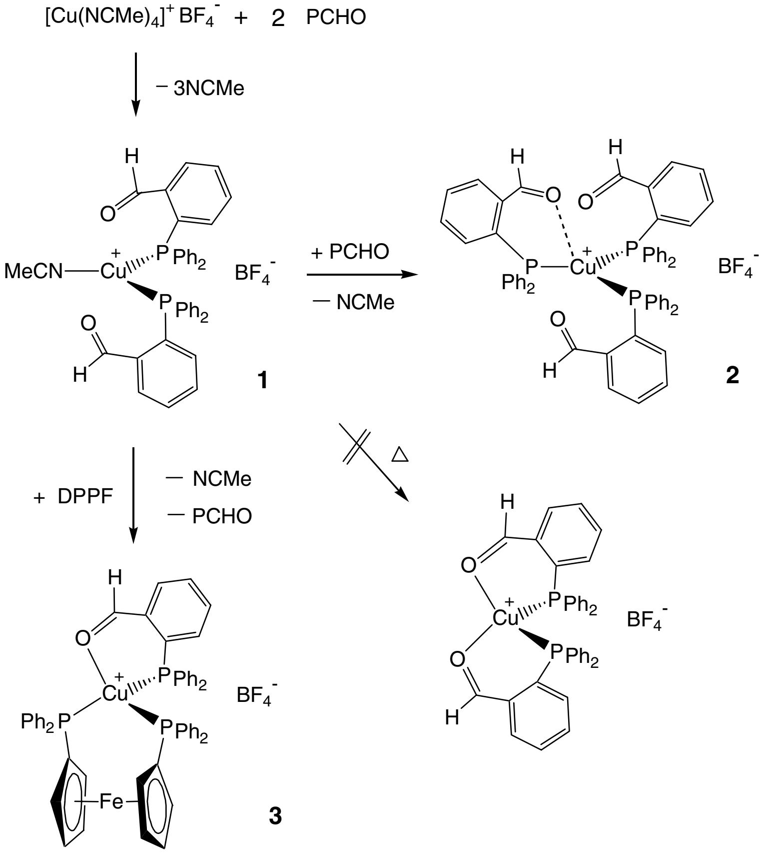
in 89% yield after crystallization from *n*-hexane/dichloromethane. Further reaction of **1** with equimolar amount of PCHO in dichloromethane solvent at ambient temperature produced orange-yellow crystals of $[Cu(PCHO)_3][BF_4]$ (**2**) in 92% yield after crystallization from *n*-hexane/dichloromethane. It was thought that elimination of the acetonitrile ligand from **1** might generate the species, $[Cu(PCHO)_2]^+$, with both PCHO ligands in a P,O-chelating mode. However, heating compound **1** in THF underwent a disproportion reaction to give **2** as the only isolable product. On the other hand, reaction of **1** with the diphosphine molecule $(Ph_2PC_5H_4)_2Fe$ (abbreviated as DPPF) led to dissociation of a PCHO ligand to afford orange crystals of $[Cu(PCHO)(DPPF)][BF_4]$ (**3**) in 56%, in which both DPPF and PCHO act as a chelating ligand. The reactions are summarized in Scheme 1. Previously, the importance of steric constraints in $[Cu(PR_3)_3]^+$ complexes was well established [16], so that the PCHO ligand forming the trigonal complexes **1** and **2** is likely for steric reasons. Nevertheless, the steric properties of the neutral ligands are not the sole determinations and the electronic properties of the ligands can also affect cation stoichiometry. This is well illustrated by Cu(I) complexes formed by pyridine, 2-methylpyridine and 4-methylpyridine [17].

Single crystals of **1**–**3** were grown by diffusion of diethyl ether (for **1**) or *n*-hexane (for **2** and **3**) into a dichloromethane solution of the compound at ambient temperature. The structure of **1** consists of discrete cations $[Cu(PCHO)_2(NCMe)]^+$ and tetrafluoroborate counter anions. The ORTEP drawing for the complex is depicted in Fig. 1. In contrast to the tetrahedron geometry in $[Cu(NCMe)_4]^+$ [18], the copper atom of **1** is nominally three-coordinate with ligation by an acetonitrile and two PCHO ligands. With the N1, P1 and P2 atoms forming the basal trigonal plane, the interligand bond angles surrounding the Cu atom are within 7° of the trigonal expectation of 120° ; the three angles sum to 360°, consistent with the small displacement of the Cu atom from the basal trigonal plane (0.01 Å). The formyl groups are on opposite sides of the CuP_2N plane, with the oxygen atoms oriented toward the copper atom. The two benzaldehyde units are planar, indicating conjugation of C=O π bond with the aromatic system. The benzaldehyde rings are about parallel with a dihedral angle of 4.8° and the mean separation of the planes is 3.41 Å. This value may be compared with 3.35 Å for



Scheme 1.

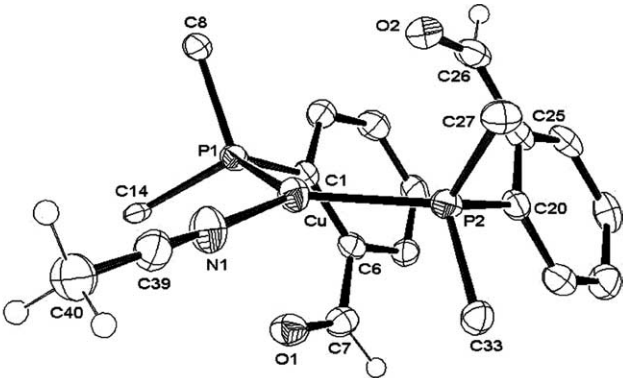


Fig. 1. Molecular structure of **1**. The BF_4^- anion has been artificially omitted. Only the ipso carbons of the C_6H_5 groups are shown for clarity. Selected bond distances (Å) and angles (°): Cu–P1 2.231(1), Cu–P2 2.239(1), Cu–N1 1.954(5), C7–O1 1.218(6), C26–O2 1.217(7), Cu$\cdots$O1 2.74, Cu$\cdots$O2 3.23; P1–Cu–P2 127.12(5), P1–Cu–N1 118.7(1), P2–Cu–N1 114.1(1), Cu–N1–C39 178.2(5), N1–C39–C40 178.5(6), C25–C26–O2 125.7(5), C6–C7–O1 124.1(5).

the interplane distance in graphite and can be described in terms of a van der Waals type interaction [19].

The structure of **2** consists of discrete cations $[Cu(P\text{-}CHO)_3]^+$, tetrafluoroborate counter anions and solvent molecules. The ORTEP drawing for the cation is depicted in Fig. 2. The Cu^+ ion is in a mildly distorted trigonal pyramidal environment with the copper atom lying 0.08 Å above the plane (toward the O3 atom) of the three phosphorous atoms. The Cu–P distances range from 2.297(2) to 2.345(2) Å, with a mean value of 2.324 Å. The mean P–Cu–P bond angle is 119.9°, which is close to the ideal value of 120°. The benzaldehyde groups connected to the P1 and P2 atoms are about parallel, with a mean interplane distance of 3.41 Å. An unusual feature of the copper center is the long, off-normal bond to the apical O3 atom (2.68(7) Å), while the nonbonded Cu$\cdots$O1 and Cu$\cdots$O2 distances are 2.97 and 3.14 Å, respectively. The O1–Cu–P1 angle is very acute, being 68.1(7)°.

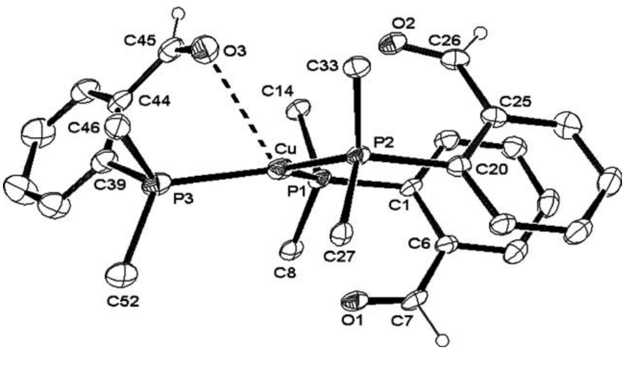


Fig. 2. Molecular structure of **2**. The BF_4^- anion has been artificially omitted. Only the ipso carbons of the C_6H_5 groups are shown for clarity. Selected bond distances (Å) and angles (°): Cu–P1 2.330(2), Cu–P2 2.297(2), Cu–P3 2.345(2), C7–O1 1.204(8), C26–O2 1.210(8), C45–O3 1.202(8), Cu–O3 2.69, Cu$\cdots$O1 2.97, Cu$\cdots$O2 3.14; P1–Cu–P2 123.56(7), P1–Cu–P3 120.47(7), P2–Cu–P3 115.62(7), C25–C26–O2 125.3(6), C6–C7–O1 126.1(6), C44–C45–O3 125.5(6).

The structure of **3** consists of discrete cations $[Cu(P\text{-}CHO)(DPPF)]^+$ and tetrafluoroborate counter anions. The ORTEP drawing for the cation is illustrated in Fig. 3. The coordination about the Cu^+ ion can be described as an irregular tetrahedron. The angles around the copper atom range from 82.90(5)° for P1–Cu–O1 to 127.86(2)° for P1–Cu–P2. Distortion of the CuP_3 configuration is noted with the further displacement of the copper atom to a distance of 0.27 Å above the plane of the three phosphorous atoms. Accompanying the displacement of the copper toward O1 is the decrease of the mean P–Cu–P bond angles from a value of 119.9° in **2** to a value of 118.6° in **3**. The DPPF and PCHO ligands are bidentate, showing a bite angle of 109.31(2)° and 82.90(5)°, respectively. The two Cp rings of DPPF ligand are about parallel, with a dihedral angle of 2.63° and a mean interplane distance of 3.30 Å. The formyl group is coordinated to the copper atom through the oxygen atom with the Cu–O1 length of 2.276(2) Å, which is 0.41 Å shorter than the Cu–O3 length in **2**. The benzaldehyde group is not planar, where the C7–O1 vector is tilted 7.60° away from the ring plane. The Cu$\cdots$Fe distance is 4.12 Å, too large a value to support a significant metal–metal interaction.

Compounds **1**–**3** form stable crystals. The $^{31}\{^1H\}$ NMR of **1** shows one broad signal at δ 0.47. The ^1H NNR spectrum of **1** at 25 °C displays a 2H singlet at δ 9.74 for the formyl protons, a multiplet in the range δ 7.98–7.07 for the phenyl protons, and a 3H singlet at δ 2.12 for the methyl protons. The ^1H and ^{31}P resonance patterns essentially remain unchanged down to −90 °C, in agreement with the structure with a time-averaged C_2 symmetry in solution.

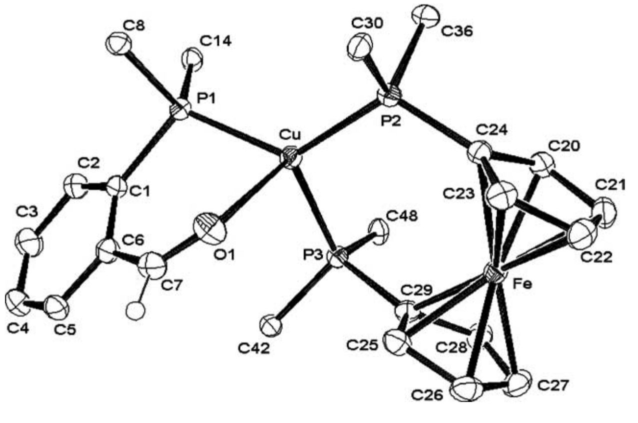


Fig. 3. Molecular structure of **3**. The BF_4^- anion has been artificially omitted. Only the ipso carbons of the C_6H_5 groups are shown for clarity. Selected bond distances (Å) and angles (°): Cu–P1 2.2452(6), Cu–P2 2.2484(6), Cu–P3 2.2586(6), Cu–O1 2.276(2), C7–O1 1.216(3); P1–Cu–P2 127.86(2), P1–Cu–P3 118.52(2), P2–Cu–P3 109.31(2), P1–Cu–O1 82.90(5), P2–Cu–O1 112.04(4), P3–Cu–O1 96.44(5), C6–C7–O1 127.8(2), C7–O1–Cu 126.0(2).

The ^{1}H NNR spectrum of **2** at 25 °C presents a 3H singlet at δ 9.17 for the formyl protons, and a multiplet between δ 7.74 and 6.82 for the phenyl protons. The formyl signal collapses at −30 °C, and at −80 °C splits into three 1H signals at δ 9.18, 8.98, and 8.88 (Fig. 4). The slow-exchange spectrum obtained at −80 °C is consistent with the solid-state structure, where the three aldehyde groups are inequivalent. A dynamic process by exchange of the Cu–aldehyde interaction may account for the spectra observed. The existence of a Cu···O interaction in solution is supported by the IR spectrum in CH_2Cl_2, which displays two C=O stretching bands at 1698 and 1675 cm^{-1} in an approximate 1:2 ratio. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum at 25 °C shows one broad signal at δ5.06, while at −80 °C it becomes a complicate multiplet in the range δ 6.36–3.01, likely due to superimposed coupling between the inequivalent phosphorus nuclei and coupling to the ^{63}Cu (I = 3/2, 69%) and ^{65}Cu (I = 3/2, 31%) nuclei.

The ^{1}H NNR spectrum of **3** at 25 °C displays a 1H singlet at δ 9.65 for the formyl proton, a multiplet between δ 7.70 and 6.99 for the phenyl protons, and two 4H broad signals at δ 4.44 and 4.22 for the Cp protons. The $^{31}P\{^1H\}$ NMR spectrum presents a triplet signal at δ 1.90 and a doublet signal at δ −6.14 ($^2J_{P-P}$ = 81 Hz) in an approximate 1:2 ratio for the PCHO and the DPPF ligands, respectively. The coordinated C=O stretching frequency is recorded at 1663 cm^{-1} in CH_2Cl_2 solvent.

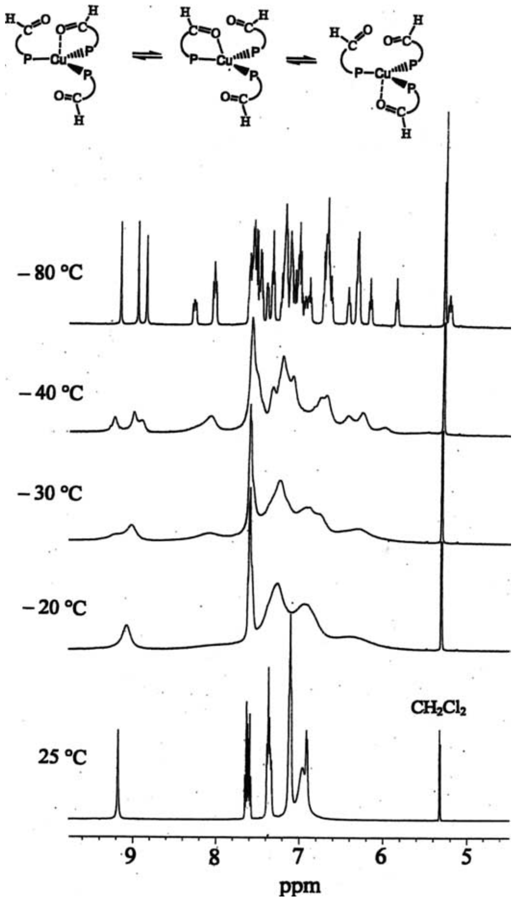
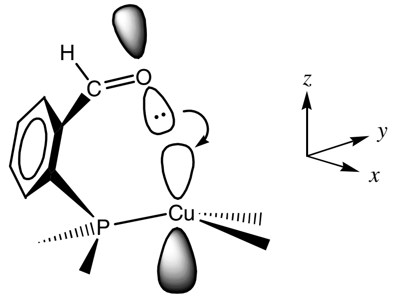


Fig. 4. Variable-temperature 500 MHz ^{1}H NMR spectra of **2** in CD_2Cl_2.

In conclusion, we have prepared three Cu(I)–PCHO complexes with/without the chelation of formyl groups. The Cu–aldehyde interaction presented in **2** is apparently arising from overlap of the carbonyl lone pair with the empty Cu p_z-orbital (see below). One would expect some distortion of the trigonal-planar (sp^2) arrangement of the complex toward a trigonal-pyramidal (sp^3) arrangement in response to this donor–acceptor interaction, as observed for **2**, whereas repulsions between the bulky phosphine groups prevent further distortion toward a tetrahedral arrangement. On the other hand, in **1** the copper atom is essentially lying on the basal trigonal plane, so its short Cu···O contact (2.74 Å) is better described as a consequence of packing constraints instead of bonding. Although complex **3** contains three phosphine ligands as **2**, the confined P–Cu–P bite angle of DPPF ligand (109.3°) likely facilitates chelation of the formyl group to lead to a tetrahedral geometry. Finally, we note that the arrangement of formyl groups in **1** and **2** effectively blocks the access of the BF_4^- counterion to the Cu$^+$ ion, whereas the structures of $[Cu(PPh_3)_3][BF_4]$ [20] and $[Cu(PPh_3)_3][FeCl_4]$ [21] reveal a weak coordination of the anion to the copper atom through one of its terminal halogen atoms.



3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. $[Cu(NCMe)_4][BF_4]$ [22], $Ph_2P(o\text{-}C_6H_4)C(=O)H$ (abbreviated as PCHO) [3b], and $(Ph_2PC_5H_4)_2Fe$ (abbreviated as DPPF) [23] were prepared by the literature methods. 2,2′-bipyridine and 4,4′-bipyridine were purchased from Aldrich and used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. ^{1}H and ^{31}P NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Infrared spectra were recorded with a 0.1 mm path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

3.2. Preparation of **1**

$[Cu(NCMe)_4][BF_4]$ (102 mg, 0.325 mmol), acetonitrile (1 ml) and dichloromethane (10 ml) were placed in an oven-dried 50 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. PCHO (190 mg, 0.65 mmol) in dichloromethane solvent (5 ml) was then introduced into the flask and the mixture was stirred at room temperature for 16 h, yielding a yellow solution. The solution was filtrated under dinitrogen and carefully layered with *n*-hexane (20 ml). The air-stable, yellow crystals of $[Cu(PCHO)_2(NCMe)]$ $[BF_4]$ (**1**) (214 mg, 0.289 mmol) were obtained in 89% yield. *Anal.* Calc. for $C_{40}H_{33}BCuF_4NO_2P_2$: C, 62.23; H, 4.31, N, 1.81. Found: C, 62.70; H, 4.51; N, 1.72%. Mass (FAB): *m*/*z* 643 ($Cu(PCHO)_2{}^+$; ^{63}Cu). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.74 (s, 2H, CHO), 7.97–7.03 (m, 28H, Ph), 2.12 (s, 3H, Me). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ 0.47 (s). IR (CH_2Cl_2, cm^{-1}): 2284 ($C{\equiv}N$), 1670 ($C{=}O$).

3.3. Preparation of **2** *from* **1**

Compound **1** (150 mg, 0.203 mmol) and dichloromethane (5 ml) were placed in an oven-dried 50 ml Schlenk flask. PCHO (59 mg, 0.203 mmol) in dichloromethane solvent (5 ml) was then introduced into the flask and the mixture was stirred at room temperature for 12 h, yielding an orange-yellow solution. The solution was filtrated under dinitrogen and then carefully layered with *n*-hexane (20 ml). $[Cu(PCHO)_3]$ $[BF_4]$ (**2**) (185 mg, 0.187 mmol, 92%) was precipitated as an air-stable, orange-yellow crystalline solid. *Anal.* Calc. for $C_{57}H_{45}BCuF_4O_3P_3$: C, 67.04; H, 4.44. Found: C, 66.65; H, 4.49%. Mass (FAB): *m*/*z* 933 ($Cu(PCHO)_3{}^+$; ^{63}Cu). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.17 (s, 3H, CHO), 7.74–7.56 (m, 6H), 7.42–7.25(m, 9H), 7.11–6.82 (m, 27H, Ph). ^{1}H NMR (CD_2Cl_2, −80 °C): δ 9.18 (s, 1H), 8.98 (s, 1H), 8.88 (s, 1H, CHO), 8.33 (m, 1H), 8.05 (m, 2H), 7.65–6.66 (m, 32H), 6.45 (m, 1H), 6.35 (m, 3H), 6.19 (m, 1H), 5.85 (m, 1H), 5.21 (m, 1H, Ph). $^{31}P\{^{1}H\}$ NMR: (CD_2Cl_2, 25 °C) δ 5.07 (s); (CD_2Cl_2, −80 °C) δ 6.36–3.01 (m). IR (CH_2Cl_2, cm^{-1}): 1698w, 1675m ($C{=}O$).

3.4. Direct synthesis of **2** *from* $[Cu(NCMe)_4][BF_4]$ *and PCHO*

$[Cu(NCMe)_4][BF_4]$ (105 mg, 0.335 mmol), PCHO (310 mg, 1.07 mmol) and THF (5 ml) were placed in an oven-dried 25 ml Schlenk tube. The solution was refluxed for 40 min to afford an orange-yellow precipitate, characterized as compound **2** (298 mg, 90%).

3.5. Preparation of **3**

Compound **1** (37 mg, 0.05 mmol), DPPF (28 mg, 0.05 mmol) and THF (5 ml) were placed in an oven-dried 25 ml Schlenk tube. The solution was refluxed for 40 min, cooled to ambient temperature, and carefully layered with *n*-hexane. $[Cu(PCHO)(DPPF)][BF_4]$ (**3**) (28 mg, 0.028 mmol, 56%) was obtained as air-stable,

Table 1
Crystallographic data for **1**–**3**

	1	**2**	**3**
Formula	$C_{40}H_{33}BCuF_4NO_2P_2$	$C_{57}H_{45}BCuF_4O_3P_3$	$C_{53}H_{43}BCuF_4FeOP_3$
Crystal solvent	0.5 Et_2O	2 CH_2Cl_2	
Crystal system	monoclinic	triclinic	triclinic
Formula weight	809.02	1191.04	994.98
T (K)	150	150	150
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
A (Å)	8.3108(4)	12.496(1)	10.4768(7)
b (Å)	25.293(1)	15.454(1)	14.0088(9)
c (Å)	18.4483(9)	15.693(1)	15.949(1)
α (°)	90	69.724(2)	93.405(1)
β (°)	93.634(1)	88.827(2)	93.115(1)
γ (°)	90	76.487(2)	108.539(1)
V ($Å^3$)	3870.1(3)	2754.5(4)	2208.8(2)
Z	4	2	2
D_{calc} (Mg/m^3)	1.389	1.436	1.496
μ (mm^{-1})	0.705	0.736	0.976
Final *R* indices ($I > 2\sigma(I)$)	0.0746/0.1650	0.0879/0.1997	0.0390/0.0977
Goodness-of-fit on F^2	1.176	1.020	1.057

orange crystals. *Anal.* Calc. for $C_{53}H_{43}BF_4FeOP_3Cu$: C, 63.97; H, 4.36. Found: C, 63.50; H, 4.45%. Mass (FAB): *m/z* 907 $(Cu(PCHO)(DPPF)^+$; ^{63}Cu). ^1H NMR ($CDCl_3$, 25 °C): δ 9.65 (s, 1H, CHO), 7.70–6.99 (m, Ph), 4.44 (br, 4H), 4.22 (br, 4H, C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 1.90 (t, PCHO, $^2J_{P-P} = 81$ Hz), −6.14 (d, DPPF). IR (CH_2Cl_2, cm^{-1}): 1663 (C=O).

3.6. Structure determination for **1–3**

The crystals of **1**, **2** and **3** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Bruker Smart ApexCCD diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.37–25.00° for **1**, 1.39–25.00° for **2**, and 1.28–27.50° for **3**. Of the 30852, 29598 and 28408 reflections collected for **1**, **2** and **3**, 6805, 9704, and 10104 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 [24]. The data collection and refinement parameters are presented in Table 1.

Acknowledgment

We are grateful for support of this work by the National Science Council of Taiwan.

Appendix A. Supplementary material

Crystallographic data for **1–3** have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 249800–249802. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2004.12.049.

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