Reaction of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ $(Ph_2Ppypz = (2\text{-diphenylphosphino-6-pyrazol-1-yl})pyridine)$ with $Fe(CO)_4^{2-}$ and X^- $(X = Cl, I, MeCO_2$ and pyrazolate)

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Abstract

$[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ $(Ph_2Ppypz = (2\text{-diphenylphosphino-6-pyrazol-1-yl})pyridine)$ reacts with $Fe(CO)_4^{2-}$ in tetrahydrofuran to give $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](Fe(CO)_4)$, **1**, and with X^- in acetonitrile or tetrahydrofuran at room temperature to afford $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}X)](ClO_4)$ (X = Cl, **2**; I, **3**; $MeCO_2$, **4**; pyrazolate, **5**). The crystal structures of **1**, **3**·Et_2O, **4**·Et_2O and **5** have been determined by X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Increasing interest in polynuclear copper(I) chemistry is mainly associated with studies related to the reactivity of molecular oxygen, not only in biological systems but also in catalytic oxidation and dioxygen-mediated processes [1]. The major effort in this field is to design binucleating ligands that hold two metal atoms at an appropriate distance apart so as to provide twin-site binding to small molecules and organic functionalities.

Previous works from our laboratories have demonstrated the reactions of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ $(Ph_2Ppypz = (2\text{-diphenylphosphino-6-pyrazol-1-yl})pyridine)$ with $LiC{\equiv}CPh$ to give $[(Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu_2\text{-}\eta^1\text{-}C{\equiv}CPh)](ClO_4)$, with dimethyl acetylenedicarboxylate to yield $[Cu_2(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)(\mu\text{-}Ph_2Ppypz)_2](ClO_4)_2$ [2], and with NaX (X = N_3, SCN) to afford $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}X)](ClO_4)$, which exhibits unusual azide (μ-1, 1-N_3) and

thiocyanate (μ-1, 1-SCN) bridging [3]. We report here the reaction of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ with $Fe(CO)_4^{2-}$ in tetrahydrofuran to give $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](Fe(CO)_4)$, **1** and with X^- in acetonitrile or tetrahydrofuran at room temperature to afford $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}X)](ClO_4)$(X = Cl, **2**; I, **3**; $MeCO_2$, **4**; pyrazolate (pz), **5**). The crystal structures of **1**, **3**·Et_2O, **4**·Et_2O and **5** have been determined by X-ray crystallography.

2. Experimental section

2.1. General procedure, measurement, and materials

All reactions were routinely carried out under nitrogen atmosphere using Schlenk techniques. The solvents were purified by standard methods. IR spectra were measured on a Perkin Elmer 1600 spectrometer. The ^{1}H-NMR spectra were recorded on a Bruker-300 NMR spectrometer using $Si(Me)_4$ as the external standard and

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Table 1
Crystal data for 1, 3 Et$_2$O, 4Et$_2$O and 5

Formula	C$_{48}$H$_{38}$Cu$_2$FeN$_8$O$_4$P$_2$ (1)	C$_{40}$H$_{32}$ClCu$_2$IN$_6$O$_4$P$_2$·Et$_2$O(3·Et$_2$O)	C$_{42}$H$_{35}$ClCu$_2$N$_6$O$_6$P$_2$·Et$_2$O (4·Et$_2$O)	C$_{43}$H$_{35}$ClCu$_2$N$_8$O$_4$P$_2$ (5)
Formula weight	1035.73	108 6.21	1018.35	952.26
Temperature (K)	294	294	294	294
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Sace group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$Pca2_1$ (no. 29)
Unit cell dimensions				
a (Å)	9.865(2)	25.070 (5)	13.607 (3)	19.661 (5)
b (Å)	10.887(2)	12.725 (3)	19.657(3)	9.592 (3)
c (Å)	12.864(3)	15.047 (3)	17.698 (4)	22.913 (3)
α (°)	66.80 (3)	90	90	90
β (°)	88.29 (3)	105.11 (3)	99.01(1)	90
γ (°)	86.41 (3)	90	90	90
V (Å^3)	1267.4 (6)	4634 (2)	4675 (2)	4322 (2)
Z	1	4	4	4
$F(000)$	528	2184	2096	1944
D_{calc} (g cm^{-3})	1.569	1.451	1.448	1.464
λ (Å) (Mo-K$_\alpha$)	0.71073	0.71073	0.71073	0.71073
μ (cm^{-1})	1.515	1.76	1.09	1.17
Two theta range for data collection (°)	4–52	4–52	3–53	4–52
Goodness-of-fit index	1.86	1.34	1.46	1.61
No. of unique reflections	4084 (R_{int} = 0.00%)	6576 (R_{int} = 2.90%)	9670 (R_{int} = 2.90%)	7230 (R_{int} = 3.47%)
No. of observed reflection ($|F| \geq 4\sigma(F)$)	3854	5214	3248	6922
No. of variables, p	334	554	552	541
R_f^a	0.044	0.050	0.071	0.052
RwF_2^b	0.049	0.080	0.195	0.055

^{a} $RF = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
^{b} $RwF_2 = [\{\Sigma w(|F_o| - |F_c|)^2\}/\{\Sigma w|F_o|^2\}]^{1/2}$

CDCl$_3$ as solvent. The ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker-500 NMR spectrometer at 202.45 MHz using 85% H$_3$PO$_4$ as the external standard and CDCl$_3$ as solvent. Ph$_2$Ppypz [2], Na$_2$Fe(CO)$_4$ [4] and [Cu(MeCN)$_4$](ClO$_4$) [5] were prepared from literature procedures.

2.1.1. Reaction of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ with Na$_2$Fe(CO)$_4$

To a solution of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ (0.32 g, 0.3 mmol) in 30ml THF was added solid Na$_2$Fe(CO)$_4$ (0.06 g, 0.30 mmol), and the mixture was stirred at r.t. for 8 h. Filtration followed by vapor diffusion of Et$_2$O into a concentrated solution afforded orange crystals of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$]-(Fe(CO)$_4$), 1 (0.17 g, 67% yield). Anal. Calc. for C$_{48}$H$_{38}$Cu$_2$FeN$_8$O$_4$P$_2$: C, 55.66; H, 3.70; N, 10.82. Found: C, 55.97; H, 3.72, N, 10.49. IR: ν(CO) 2054, 1986, 1882cm^{-1}. ^{1}H-NMR: δ 8.45 (d, J = 0.7Hz, 2H), 7.90 (m, 2H) 7.78 (m, 4H) 7.18 (m, 20H) 6.73 (m, 2H) 6.67 (t, J = 1.0Hz, 2H) 2.28 (s, 6H); ^{31}P{^{1}H}-NMR: δ 8.9 ppm.

2.1.2. Reaction of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ with X$^-$ (X = Cl, I)

To a solution of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ (0.32 g, 0.3 mmol) in 30 ml MeCN was added solid LiCl or KI, (0.30 mmol) and the mixture was stirred at r.t. for 24 h. Filtration followed by vapor diffusion of Et$_2$O into a concentrated solution afforded yellow crystals of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-Cl)](ClO$_4$), 2, (0.21 g, 76%. Anal. Calcd. for C$_{40}$H$_{32}$Cl$_2$Cu$_2$N$_6$O$_4$P$_2$·H$_2$O: C, 51.18; H, 3.65; N, 8.96. Found: C, 51.54; H, 3.48; N, 9.00. ^{1}H-NMR: 8.48 (d, J = 0.7Hz, 2H), 8.20 (m, 2H) 8.06(m, 4H) 7.28 (m, 20H) 7.00 (m, 2H) 6.56 (t, J = 0.90Hz, 2H); ^{31}P{^{1}H}-NMR: δ 3.5 ppm or [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-I)](ClO$_4$)·Et$_2$O, 3·Et$_2$O (0.22 g, 73%. Anal. Calcd. for C$_{40}$H$_{32}$ClCu$_2$IN$_6$O$_4$P$_2$: C, 47.47; H, 3.19; N, 8.31. Found: C, 47.75; H, 3.47; N, 8.22. ^{1}H-NMR: δ 8.65 (d, J = 0.3Hz, 2H) 8.21 (m, 4H) 7.28 (m, 20H) 6.97 (m, 4H) 6.50 (d, J = 0.4Hz) 3.45 (t, J = 0.4 Hz, 2H) 1.21 (t, J = 0.4Hz, 3H). ^{31}P{^{1}H}-NMR: δ 3.5 ppm).

2.1.3. Reaction of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ with MeCO$_{2-}$

A solution of NaO$_2$CMe (25 mg, 0.30 mmol) in 10 ml THF-EtOH(1:1) was added to a solution of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ (0.32 g, 0.3 mmol) in 30 ml THF. The resulting mixture was stirred at r.t. for 8 h. Subsequent diffusion of diethyl ether into the concentrated solution gave yellow crystals of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-O$_2$CMe)](ClO$_4$), 4 (0.24 g, 85%). Anal. Calcd. for C$_{42}$H$_{35}$ClCu$_2$N$_6$O$_6$P$_2$: C, 53.42; H, 3.74; N,

8.90. Found: C, 53.45; H, 3.70; N, 8.79. IR: $\nu(O_2CMe)$ 1558, 1462 cm^{-1}. ^{1}H-NMR: δ 8.48 (s, 2H) 8.05 (m, 4H) 7.10 (m, 20H) 6.67 (m, 4H) 6.50 (t, $J = 0.4$Hz, 2H) 3.45 (t, $J = 0.4$ Hz, 2H) 1.96 (s, 3H) 1.21 (t, $J = 0.4$Hz, 3H). ^{31}P(^{1}H)-NMR: δ 21.2 ppm.

2.1.4. Reaction of [Cu_2(μ-Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2 with pyrazolate (pz)

To a solution of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ (0.32 g, 0.3 mmol) in 30 ml THF was added an equimolar amount of lithium pyrazolate (prepared in situ by the treatment of a THF solution of pyrazole with Li^{n}Bu) at r.t. The resulting mixture was stirred at r.t. for 4 h. Subsequent diffusion of diethyl ether into the concentrated solution gave orange crystals of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-pz)](ClO$_4$), **5** (0.20 g, 63%). Anal. Calcd. for C$_{43}$H$_{35}$ClCu$_2$N$_8$O$_4$P$_2$: C, 54.23; H, 3.70; N, 11.77. Found: C, 54.37; H, 3.49; N, 11.73. ^{1}H-NMR: δ 8.48 (d, $J = 0.6$Hz, 2H) 8.04 (m, 4H) 7.10 (m, 20H) 6.87 (m, 4H) 6.70 (m, 3H) 6.52 (t, $J = 0.4$Hz, 2H). ^{31}P(^{1}H)-NMR: δ −0.5 ppm.

Table 2
Selected bond lengths (Å) and angle (°) in complexes 1, 3·Et$_2$O, 4·Et$_2$O and 5

Complex 1			
Cu(1)···Cu(1a)	3.322(1)	Cu(1)–N(1)	2.121(5)
Cu(1)–N(3)	2.095(5)	Cu(1)–N(4)	2.028(3)
P(1)–Cu(1)–N(1)	104.0(1)	P(1)–Cu(1)–N(3)	136.5(1)
P(1)–Cu(1)–N(4)	116.3(1)	N(1)–Cu(1)–N(3)	78.0(1)
N(1)–Cu(1)–N(4)	105.3(1)	N(3)–Cu(1)–N(4)	104.4(1)
C(24)–Fe(1)–C(25)	105.8(1)	C(25)–Fe(1)–C(26)	116.3(2)
Complex 3·Et$_2$O			
Cu(1)–Cu(2)	2.832(1)		
Cu(1)–N(4)	2.050(1)	Cu(2)–N(1)	2.089(2)
Cu(1)–N(6)	2.154(1)	Cu(2)–N(3)	2.089(1)
Cu(1)–I(1)	2.659(1)	Cu(2)–I(1)	2.675(1)
P(1)–Cu(1)–N(4)	122.6(1)	P(2)–Cu(2)–N(1)	112.5(1)
P(1)–Cu(1)–N(6)	131.5(1)	P(2)–Cu(2)–N(3)	137.2(1)
P(1)–Cu(1)–I(1)	112.3(1)	P(2)–Cu(2)–I(1)	115.2(1)
N(4)–Cu(1)–I(1)	105.2(1)	N(1)–Cu(2)–I(1)	106.9(1)
N(6)–Cu(1)–Cl(1)	98.3(1)	N(3)–Cu(2)–Cl(1)	99.0(1)
N(4)–Cu(1)–N(6)	77.8(1)	N(1)–Cu(2)–N(3)	79.3(1)
Complex 4·Et$_2$O			
Cu(1)–Cu(2)	2.924(2)		
Cu(1)–O(1)	2.020(4)	Cu(2)–O(2)	2.023(5)
Cu(2)–Cu(1)–O(1)	79.3(1)	Cu(1)–Cu(2)–O(2)	80.0(1)
N(1)–Cu(1)–N(3)	76.8(2)	N(4)–Cu(2)–N(6)	77.0(2)
Complex 5			
Cu(1)–Cu(2)	2.930(2)	Cu(1)–N(1)	2.078(2)
Cu(1)–N(3)	2.113(1)	Cu(1)–N(7)	2.016(2)
Cu(2)–N(4)	2.056(2)	Cu(2)–N(6)	2.158(2)
Cu(2)–N(4)	1.998(2)		
Cu(2)–Cu(1)–N(7)	65.7(1)	Cu(1)–Cu(2)–N(8)	66.3(1)
N(1)–Cu(1)–N(3)	77.7(1)	N(4)–Cu(2)–N(6)	78.5(1)

Table 3
Atomic coordinates of complex **1** ($\times 10^5$ for Cu and Fe; $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients (Å$\times 10^4$ for Cu and Fe; Å$\times 10^3$ for other atoms)

Atom	x	y	z	U_{eq}
Cu(1)	38714(3)	55344(3)	40178(3)	501(1)
Fe(1)	88058(5)	115733(5)	22281(5)	679(1)
P(1)	5382(1)	7087(1)	3531(1)	44(1)
O(1)	8551(3)	10723(3)	362(2)	103(1)
O(2)	10690(3)	13676(3)	1242(3)	116(1)
O(3)	10309(3)	9402(3)	3992(3)	115(1)
O(4)	6319(3)	12530(3)	2882(4)	173(1)
N(1)	3171(2)	5596(2)	2422(2)	54(1)
N(2)	3400(2)	4357(2)	2410(2)	50(1)
N(3)	3879(2)	3501(2)	4320(2)	44(1)
N(4)	2178(3)	5870(2)	4823(2)	62(1)
C(1)	3131(3)	6434(3)	1341(2)	61(1)
C(2)	3340(3)	5739(3)	636(3)	73(1)
C(3)	3508(3)	4431(3)	1331(2)	64(1)
C(4)	3494(2)	3242(2)	3448(2)	47(1)
C(5)	3191(3)	1978(3)	3524(2)	55(1)
C(6)	3313(3)	934(3)	4561(3)	63(1)
C(7)	6245(3)	8832(3)	4526(2)	57(1)
C(8)	5979(2)	7537(2)	4658(2)	45(1)
C(9)	5385(3)	9626(3)	1697(3)	68(1)
C(10)	4732(3)	10773(3)	925(3)	80(1)
C(11)	3350(3)	10977(3)	938(3)	70(1)
C(12)	2591(3)	10041(3)	1732(3)	67(1)
C(13)	3235(3)	8898(3)	2536(3)	60(1)
C(14)	4619(3)	8667(2)	2512(2)	48(1)
C(15)	8117(3)	7480(3)	2791(3)	61(1)
C(16)	9231(3)	7315(3)	2168(3)	73(1)
C(17)	9189(3)	6502(3)	1572(3)	70(1)
C(18)	8030(3)	5837(3)	1618(3)	67(1)
C(19)	6916(3)	5990(3)	2239(2)	57(1)
C(20)	6942(3)	6830(2)	2822(2)	48(1)
C(21)	1248(3)	6119(3)	5254(2)	59(1)
C(22)	43(3)	6 426(3)	5817(3)	79(1)
C(26)	7333(3)	12131(3)	2612(3)	79(1)
C(23)	8648(3)	11039(3)	1117(3)	68(1)
C(25)	9693(3)	10280(3)	3292(3)	71(1)
C(24)	9949(3)	12838(3)	1635(3)	68(1)

2.2. X-ray crystallography

The intensity data of **1, 3·Et$_2$O** and **5** were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 KV and 90 mA ($2\theta_{min} = 4°$, $2\theta_{max} = 52°$, 36 5° oscillation frames in the range of 0–180°, exposure 8 min per frame) [6]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the AB-SCOR [7] program. Intensity data of **4·Et$_2$O** were collected in the variable ω-scan mode on a four-circle diffractometer (Simens R3 m/V) using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å, 50 kV, 25 mA) ($2\theta_{min} = 3°$, $2\theta_{max} = 53°$) at 294 K.

Table 4

Atomic coordinates of complex **3**·Et$_2$O ($\times 10^5$ for Cu and I; $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients (Å$\times 10^4$ for Cu and I; Å$\times 10^3$ for other atoms)

Atoms	x	y	z	U_{eq}
Cu(1)	22216(1)	30298(2)	14214(1)	701(1)
Cu(2)	24743(1)	29292(2)	33667(1)	758(1)
I(1)	21234(1)	46956(1)	24334(1)	842(1)
P(1)	3086(1)	2482(1)	1689(1)	70(1)
P(2)	1862(1)	1662(1)	3174(1)	72(1)
Cl(1)	5000	3738(1)	7500	129(1)
Cl(2)	0	1219(1)	7500	72(1)
O(1)	4827(1)	4297(3)	6740(2)	277(2)
O(2)	4555(1)	3115(4)	75 55(2)	289(2)
O(3)	352(1)	598(2)	8177(1)	145(1)
O(4)	294(1)	1885(2)	7070(1)	148(1)
N(1)	2778(1)	3353(2)	4748(1)	82(1)
N(2)	3344(1)	3493(1)	4969(1)	80(1)
N(3)	3317(1)	3073(1)	3456(1)	68(1)
N(4)	1745(1)	3363(1)	124(1)	77(1)
N(5)	1239(1)	2876(1)	−87(1)	70(1)
N(6)	1467(1)	2203(1)	1390(1)	63(1)
C(1)	2647(1)	3540(2)	5534(1)	87(1)
C(2)	3112(1)	3804(2)	6239(1)	97(1)
C(3)	3542(1)	3770(2)	5868(1)	91(1)
C(4)	3619(1)	3425(2)	4266(1)	74(1)
C(5)	4163(1)	3759(2)	4408(2)	92(1)
C(6)	4394(1)	3741(2)	3677(2)	101(1)
C(7)	4079(1)	3380(2)	2828(1)	87(1)
C(8)	3545(1)	3039(2)	2741(1)	72(1)
C(9)	3234(1)	3589(2)	199(1)	88(1)
C(10)	3484(1)	3830(2)	−509(2)	108(1)
C(11)	3929(1)	3312(2)	−592(2)	121(1)
C(12)	4140(1)	2503(2)	−7(2)	112(1)
C(13)	3895(1)	2241(2)	689(2)	95(1)
C(14)	3448(1)	2802(2)	807(1)	73(1)
C(15)	2804(1)	408(2)	1364(2)	101(1)
C(16)	2888(1)	−654(2)	1443(2)	142(1)
C(17)	3341(1)	−1078(2)	2004(2)	153(1)
C(18)	3735(1)	−437(2)	2517(2)	137(1)
C(19)	3676(1)	646(2)	2455(2)	108(1)
C(20)	3204(1)	1083(2)	1876(1)	80(1)
C(21)	1732(1)	3963(2)	−597(1)	94(1)
C(22)	1234(1)	3877(2)	−1271(2)	105(1)
C(23)	924(1)	3188(2)	−927(1)	87(1)
C(24)	1081(1)	2284(1)	589(1)	65(1)
C(25)	566(1)	1834(2)	414(1)	81(1)
C(26)	421(1)	1368(2)	1140(1)	84(1)
C(27)	794(1)	1309(2)	1994(1)	80(1)
C(28)	1318(1)	1723(2)	2090(1)	68(1)
C(29)	1739(1)	−541(2)	2857(2)	108(1)
C(30)	1911(1)	−1551(2)	2978(2)	140(1)
C(31)	2432(1)	−1789(3)	3443(2)	146(1)
C(32)	2773(1)	−985(3)	3871(2)	140(1)
C(33)	2598(1)	44(2)	3748(2)	106(1)
C(34)	2075(1)	281(2)	3252(1)	87(1)
C(35)	1370(1)	1004(2)	4589(1)	113(1)
C(36)	1122(1)	1207(3)	5287(2)	142(1)
C(37)	975(1)	2184(3)	5439(2)	151(1)
C(38)	1060(1)	2972(3)	4903(2)	142(1)
C(39)	1308(1)	2787(2)	4206(2)	110(1)
C(40)	1477(1)	1803(2)	4043(1)	83(1)
O(1W)	0	4706(4)	2500	213(2)
C(1W)	412(2)	4755(5)	1268(3)	171(3)
C(2W)	247(2)	4358(4)	1796(3)	186(2)
O(2W)	5000	−104(18)	5000	510(5)
C(3W)	4321(2)	898(4)	5407(4)	143(2)
C(4W)	4712(2)	520(7)	5615(6)	519(7)

Table 5

Atomic coordinates of complex **4**·Et$_2$O ($\times 10^5$ for Cu; $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients (Å$\times 10^4$ for Cu; Å$\times 10^3$ for other atoms)

Atoms	x	y	z	U_{eq}
Cu(1)	70687(9)	−639(7)	86692(7)	478(1)
Cu(2)	61207(9)	5905(7)	72577(7)	484(1)
P(1)	8385(2)	75(2)	8141(1)	44(1)
P(2)	5835(2)	1380(1)	8053(1)	44(1)
Cl(1)	8072(2)	145(2)	3316(2)	91(1)
O(1)	5951(3)	−724(2)	8325(3)	58(1)
O(2)	5426(3)	−322(2)	7153(3)	63(1)
O(3)	8615(3)	−314(3)	2959(3)	253(1)
O(4)	7382(3)	−163(3)	3675(3)	147(1)
O(5)	7568(3)	450(3)	2630(3)	152(1)
O(6)	8653(3)	581(3)	3738(3)	147(1)
O(7)	9063(3)	2141(3)	5426(3)	214(1)
N(1)	7416(3)	−461(3)	9808(3)	54(1)
N(2)	6898(3)	−132(3)	10298(3)	42(1)
N(3)	6299(3)	613(3)	9326(3)	37(1)
N(4)	5660(3)	833(3)	6087(3)	60(1)
N(5)	6295(3)	582(3)	5638(3)	59(1)
N(6)	7359(3)	279(3)	6736(3)	42(1)
C(1)	7949(3)	−922(3)	10242(3)	66(1)
C(2)	7767(3)	−911(3)	10991(3)	67(1)
C(3)	7111(3)	−407(3)	11005(3)	57(1)
C(4)	6261(3)	410(3)	10036(3)	43(1)
C(5)	5647(3)	695(3)	10496(3)	53(1)
C(6)	5022(3)	1208(3)	10202(3)	59(1)
C(7)	5042(3)	1425(3)	9456(3)	53(1)
C(8)	5725(3)	1121(3)	9045(3)	38(1)
C(9)	6730(3)	2069(3)	8226(3)	48(1)
C(10)	6882(3)	2458(3)	8877(3)	65(1)
C(11)	7479(3)	3031(3)	8921(3)	87(1)
C(12)	7951(3)	3211(3)	8320(3)	81(1)
C(13)	7833(3)	2812(3)	7682(3)	79(1)
C(14)	7236(3)	2243(3)	7612(3)	61(1)
C(15)	4662(3)	1804(3)	7763(3)	48(1)
C(16)	3879(3)	1431(3)	7394(3)	68(1)
C(17)	2935(3)	1730(3)	7198(3)	86(1)
C(18)	2799(3)	2398(3)	7382(3)	96(1)
C(19)	3549(3)	2772(3)	7720(3)	79(1)
C(20)	4479(3)	2484(3)	7921(3)	69(1)
C(21)	4913(3)	1072(3)	5605(3)	84(1)
C(22)	5049(3)	974(3)	4835(3)	97(1)
C(23)	5933(3)	645(3)	4866(3)	83(1)
C(24)	7194(3)	278(3)	5982(3)	47(1)
C(25)	7844(3)	5(3)	5540(3)	61(1)
C(26)	8705(3)	−273(3)	5902(3)	66(1)
C(27)	8896(3)	−284(3)	6695(3)	54(1)
C(28)	8217(3)	−3(3)	7098(3)	44(1)
C(29)	9332(3)	−584(3)	8439(3)	47(1)
C(30)	10320(3)	−480(3)	8586(3)	64(1)
C(31)	10977(3)	−1000(3)	8786(3)	76(1)
C(32)	10617(3)	−1650(3)	8850(3)	75(1)
C(33)	9620(3)	−1764(3)	8705(3)	69(1)
C(34)	8978(3)	−1245(3)	8522(3)	57(1)
C(35)	9058(3)	877(3)	8300(3)	37(1)
C(36)	9070(3)	1209(3)	8982(3)	61(1)
C(37)	9599(3)	1799(3)	9129(3)	74(1)
C(38)	10116(3)	2087(3)	8628(3)	71(1)
C(39)	10114(3)	1764(3)	7935(3)	73(1)
C(40)	9596(3)	1157(3)	7767(3)	58(1)
C(41)	5417(3)	−746(3)	7687(3)	53(1)
C(42)	4645(3)	−1315(3)	7520(3)	76(1)
C(43)	10656(3)	1772(3)	5599(3)	205(1)
C(44)	9745(3)	1653(3)	5410(3)	241(1)
C(45)	7958(3)	2068(3)	4848(3)	308(1)
C(46)	7545(3)	2254(3)	5379(3)	226(1)

Table 6
Atomic coordinates of complex **5** ($\times 10^5$ for Cu; $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients ($\text{Å} \times 10^4$ for Cu; $\text{Å} \times 10^3$ for other atoms)

Atoms	x	y	z	U_{eq}
Cu(1)	18789(3)	31588(6)	34963(6)	567(2)
Cu(2)	18007(3)	29018(7)	22238(6)	578(2)
P(1)	2946(1)	2570(1)	3413(1)	52(1)
P(2)	1722(1)	5187(1)	2290(1)	54(1)
Cl(1)	388(1)	9074(2)	5395(1)	81(1)
O(1)	164(3)	9435(10)	5961(3)	154(2)
O(2)	1084(3)	8769(11)	5340(4)	160(2)
O(3)	47(5)	7993(14)	5195(7)	293(3)
O(4)	275(11)	10137(20)	5069(7)	363(3)
N(1)	1634(3)	3568(5)	4365(2)	73(1)
N(2)	1380(2)	4870(5)	4440(2)	60(1)
N(3)	1472(2)	5194(4)	3449(2)	54(1)
N(4)	1897(3)	2064(6)	1400(2)	72(2)
N(5)	2506(2)	1388(4)	1320(2)	62(1)
N(6)	2812(2)	2029(4)	2260(2)	54(1)
N(7)	1111(2)	1937(5)	3210(2)	64(1)
N(8)	1094(3)	1808(5)	2644(2)	69(1)
C(1)	1693(4)	3040(8)	4896(3)	89(2)
C(2)	1491(4)	4013(8)	5317(3)	93(2)
C(3)	1292(4)	5158(8)	5018(2)	86(2)
C(4)	1241(2)	5702(5)	3949(2)	55(1)
C(5)	862(3)	6909(6)	3998(3)	68(2)
C(6)	744(3)	7672(6)	3502(3)	75(2)
C(7)	992(3)	7189(6)	2970(3)	70(2)
C(8)	1352(2)	5952(5)	2957(2)	55(1)
C(9)	2510(3)	6192(5)	2224(2)	61(1)
C(10)	2727(4)	7194(8)	2595(3)	91(2)
C(11)	3342(4)	7902(9)	2516(4)	100(2)
C(12)	3720(4)	7608(9)	2040(4)	99(2)
C(13)	3528(5)	6579(13)	1663(4)	131(2)
C(14)	2912(4)	5885(11)	1741(4)	119(2)
C(15)	1171(3)	5897(6)	1732(2)	60(1)
C(16)	1279(4)	7183(7)	1452(3)	82(2)
C(17)	814(4)	7620(8)	1027(3)	88(2)
C(18)	284(4)	6853(7)	869(3)	84(2)
C(19)	186(4)	5576(8)	1120(3)	92(2)
C(20)	625(3)	5108(7)	1555(3)	77(2)
C(21)	1519(3)	1704(8)	941(3)	83(2)
C(22)	1884(4)	811(8)	575(3)	88(2)
C(23)	2501(3)	638(6)	829(2)	72(2)
C(24)	3025(3)	1562(5)	1746(2)	55(1)
C(25)	3698(3)	1308(7)	1600(2)	72(2)
C(26)	4179(3)	1515(8)	2016(3)	77(2)
C(27)	3966(3)	1928(7)	2569(2)	68(2)
C(28)	3282(2)	2168(5)	2683(2)	53(1)
C(29)	3085(2)	898(5)	3782(2)	54(1)
C(30)	3727(3)	403(6)	3963(2)	64(1)
C(31)	3793(3)	−877(6)	4213(3)	73(2)
C(32)	3233(4)	−1713(7)	4306(3)	80(2)
C(33)	2598(4)	−1243(7)	4139(3)	84(2)
C(34)	2531(3)	56(6)	3872(3)	74(2)
C(35)	3595(3)	3712(6)	3716(2)	61(1)
C(36)	3722(4)	3707(7)	4 313(3)	85(2)
C(37)	4180(4)	4627(9)	4556(4)	104(2)
C(38)	4525(4)	5554(8)	4211(4)	103(2)
C(39)	4400(4)	5579(8)	3625(4)	101(2)
C(40)	3935(3)	4685(7)	3380(3)	80(2)1
C(41)	538(3)	1423(6)	3437(3)	71(2)
C(42)	139(3)	928(7)	2989(3)	77(2)
C(43)	512(3)	1164(7)	2493(3)	71(2)

centers are bridged by two Ph$_2$Ppypz ligands and an

The crystal structures were determined by the direct method, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement.

Computation was performed on a IBM-compatible 486 PC with the SHELTX/PC program package [8]. Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1. Selected bond distances and angles are given in Table 2. The final atomic parameters are given in Tables 3–6, respectively.

3. Results and discussion

Reaction of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ with Na$_2$Fe(CO)$_4$ in tetrahydrofuran gave [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](Fe(CO)$_4$), **1**, which involves an exchange of anions (Scheme 1).

The reaction of a transition-metal carbonylate anion with an appropriate transition-metal electrophile has proved to be a successful synthetic route to the formation of metal–metal bonds and metal clusters [9]. We intended to utilize this reaction to generate a Cu$_2$Fe cluster with metal–metal bonds, but instead obtained an anion substitution product, [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](Fe(CO)$_4$), which is the first example of a binuclear copper(I) complex with an iron carbonylate anion. We attribute this result to the bulkiness of the Fe(CO)$_4^{2-}$ species which prevents the formation of the Cu$_2$Fe cluster.

The structure of **1** is depicted in Fig. 1. The two highly distorted tetrahedral copper(I) centers are bridged by two Ph$_2$Ppypz ligands. The geometry at the Fe center is slightly distorted tetrahedral with bond angles ranging from 105.8(1) to 116.1(1)°. Compared to [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ in which the Cu$\cdots$Cu distances of two independent cations are 3.625(1) and 3.587(1) Å [2], the Cu$\cdots$Cu separation in **1** is significantly shorter (3.224(1) Å), but no interaction between copper centers and anions exists in both cases.

Treatment of a solution of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ in MeCN at r.t. with an equimolar amount of LiCl or KI gives a solution from which binuclear cationic complexes **2** or **3** can be isolated in high yield. The complexes obtained are stable in the solid state and have been characterized by ^{1}H-NMR and ^{31}P(^{1}H)-NMR spectroscopy. In addition, the structure of **3**·Et$_2$O has been determined by X-ray crystallography.a

Scheme 1.
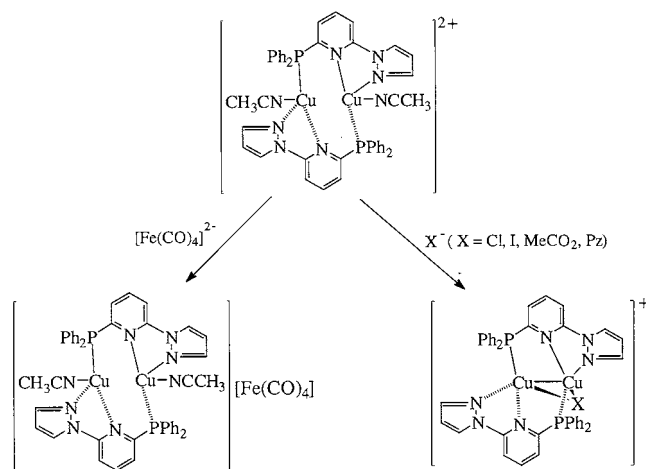
The structure of the cation $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}I)]^+$ in $3 \cdot Et_2O$ is depicted in Fig. 2. The two copper(I) iodine bridge. The geometry at the copper centers is highly distorted but, despite the N(6)–Cu(1)–P(1) and N(3)–Cu(2)–P(2) angles of 131.5(1) and 137.2(1)°, is better described as a distorted square pyramid with the iodo ligand occupying an equatorial position, rather than a trigonal bipyramid. The Cu–Cu distance of 2.832(1) Å is slightly longer than 2.758(1) Å in $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}Cl)](ClO_4) \cdot H_2O$ [2]. The Cu–I–Cu angle of 64.1(1)° is also smaller than 70.2(1)° in $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}Cl)](ClO_4) \cdot H_2O$. The Cu–N bond lengths of 2.154(1), 2.050(1) Å for Cu(1) and 2.089(1), 2.089(2)Å for Cu(2) are typical for a copper(I) center chelated by nitrogen heterocycles [10]. The N–Cu–N

'bite angles' of 77.8(1)° for Cu(1) and 79.3(1)° for Cu(2) for the bidentate pyridylpyrazole fragments are as expected for a relatively rigid bidentate diamine ligand, and the values are very similar to the that (78.9(3)°) found in $[Cu_3L_2(MeCN)_2](PF_6)$ (L = 2, 6-bis(5-methylpyrazol-3-yl)pyridine) [11] and those (78.9(2) and 78.6(2)°) found in $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ [2].

For binuclear copper complexes with a carboxylate bridge, a large number of studies have been devoted to copper(II) complexes, especially the tetracarboxylate-bridged copper(II) dimers [12], but little has been done about copper(I) complexes [13], which is due to the relative instability of binuclear copper(I) systems.

Reaction of NaO_2CMe with $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ in THF afforded $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}O_2CMe)](ClO_4)$, **4**, and similar reaction of Lipz (prepared in situ from Li^nBu and pyrazole) with $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](ClO_4)_2$ gave $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}pz)](ClO_4)$, **5**, in good yield.

The formation of these complexes have been confirmed by IR-, ^1H-NMR and $^{31}P(^1H)$-NMR spectroscopy. For complex **4**, the IR spectrum shows $\nu(O_2CMe)$ at 1558.3 and 1461.5 cm^{-1}, which are typical values for carbonyl stretching in bridging acetate complexes [14].

Fig. 3 shows a perspective drawing of the cation $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}O_2CMe)]^+$ in $4 \cdot Et_2O$ with atomic numbering. The two copper(I) centers with distorted square pyramidal geometry are bridged by two
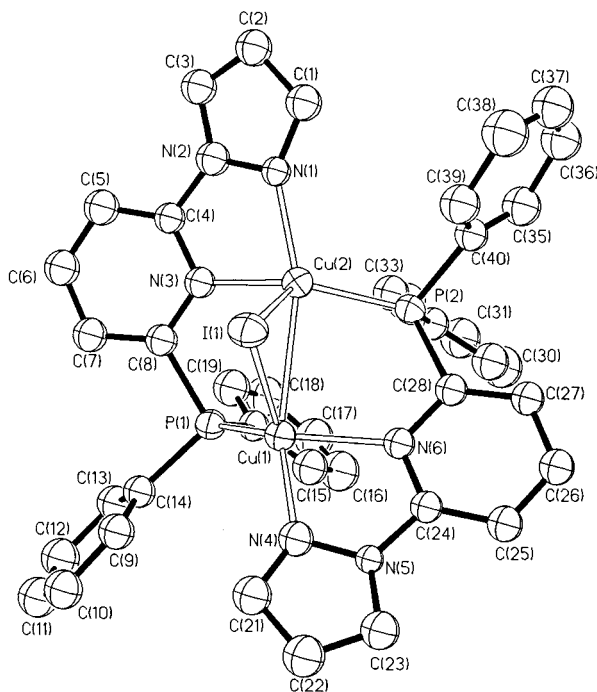

Fig. 1. Perspective view (35% thermal ellipoids) of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(MeCN)_2](Fe(CO)_4)$, **1**.

Fig. 2. Perspective view (35% thermal ellipoids) of the $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}I)]^+$ cation in $3 \cdot Et_2O$.

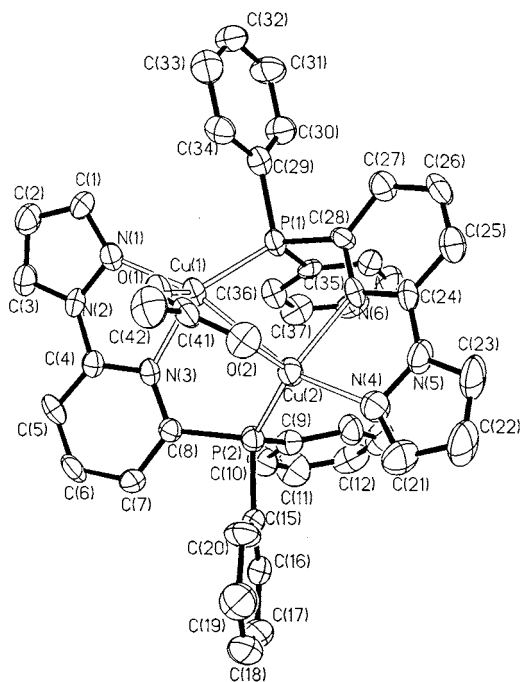Fig. 3. Perspective view (35% thermal ellipoids) of the [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-O$_2$CMe)]$^+$ cation in **4** $\cdot$ Et$_2$O.

Fig. 4. Perspective view (35% thermal ellipoids) of the [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-pz)]$^+$ cation in **5**.

Ph$_2$Ppypz ligands and a acetate bridge. The Cu–Cu distance of 2.924(2) Å is longer than that of complex **3** and 2.750(2) Å in [Cu$_2$(μ-PhCO$_2$)$_2$(p-MeC$_6$H$_4$NC)$_2$], but shorter than that (3.020(3) Å) in [Cu$_2$(μ-PhCO$_2$)$_2$(p-MeC$_6$H$_4$NC)$_3$]$\cdot$THF ([13]a). The Cu–O distances of 2.020(4) Å for Cu(1) and 2.023(5)Å for Cu(2) Å are longer than those (1.998(4), 1.969(5) Å) in [Cu$_2$(μ-PhCO$_2$)$_2$(p-MeC$_6$H$_4$NC)$_2$], but shorter than those (2.061(6), 2.078(5) Å) in [Cu$_2$(μ-PhCO$_2$)$_2$(p-MeC$_6$H$_4$NC)$_3$]$\cdot$THF ([13]a). The torsion angle O(1)–Cu(1)–Cu(2)–O(2) of −11.2° deviates from the ideal value of 0°, which is a consequence of the asymmetry of the phosphine ligand.

The structure of the cation [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(μ-pz)]$^+$ in **5** is depicted in Fig. 4. The molecular structure is very similar to that in **4**$\cdot$Et$_2$O except that the acetate bridge is here replaced by a pyrazolate bridge. The coordination geometry at each copper atom is also highly distorted square pyramidal with the pyrazlote N atom in an equatorial site. The Cu(1)–Cu(2) bond length of 2.930(2) Å is similar to that of complex **4**$\cdot$Et$_2$O. The equatorial Cu–N distances of 2.007(2) Å (average) is markedly shorter than the axial Cu–N distances of 2.101(2) Å (average). The M–{N–N}–C dihedral angle has been used to quantify both tilting and twisting distortions of the pyrazole ring [15]. This is essentially a measure of the displacement of the metal atom from the pyrazole plane and, hence, the effective overlap of a metal orbital with the sp^2 hybridized nitroge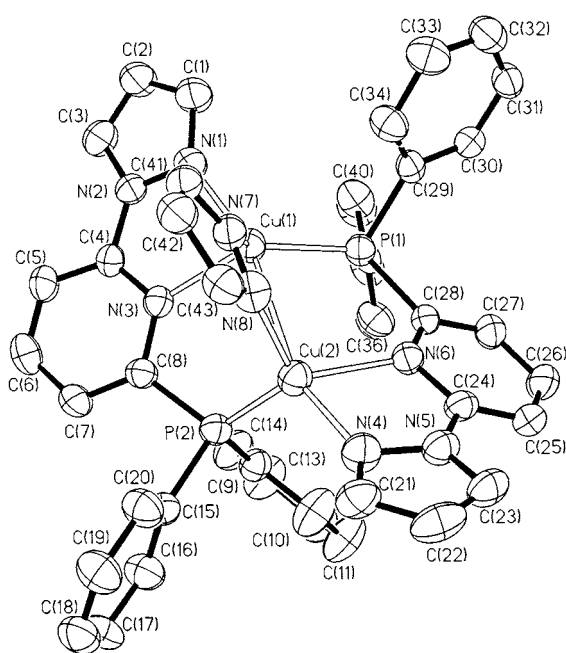n. As such, the M–{N–N}–C dihedral angle should ideally equal to 0°. In complex **5**, the the M–{N–N}–C dihedral angle is −170.5° for Cu(1)–N(7)–N(8)–C(43) and 166.0° for Cu(2)–N(8)–N(7)–C(41), indicating that the metal is not significantly displaced from the pyrazole plane.

In summary, we have investigated the reaction of [Cu$_2$(μ-Ph$_2$Ppypz)$_2$(MeCN)$_2$](ClO$_4$)$_2$ with several kinds of anions to give new binuclear copper(I) complexes that exhibit different structures.

Acknowledgements

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