Inorg. Chem. **2005**, *44*, 6122–6128

Inorganic Chemistry
Article

Mononuclear and Dinuclear Copper(I) Complexes of Bis(3,5-dimethylpyrazol-1-yl)methane: Synthesis, Structure, and Reactivity

Chang-Chuan Chou,[†,‡] Chan-Cheng Su,*[,†] and Andrew Yeh[§]

Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan,
Center for General Education, Chang Gung Institute of Technology, Tao-Yuan 333, Taiwan, and
Department of Chemistry, Tunghai Christian University, Taichung 407, Taiwan

Received April 12, 2005

The synthesis and structures of a mononuclear copper(I) carbonyl complex $[Cu(OClO_3)(CO)(H_2CPz'_2)]$ (**3**) and a dinuclear copper(I) carbonyl complex $[\{Cu(CO)(H_2CPz'_2)\}_2(\mu\text{-pyrazine})](ClO_4)_2$ (**4**), where $H_2CPz'_2$ = bis(3,5-dimethylpyrazol-1-yl)methane, are described. These two compounds were generated by the carbonylation of the corresponding copper(I)-acetonitrile complexes, $[Cu(H_2CPz'_2)(MeCN)](ClO_4)$ (**1**) and $[\{Cu(H_2CPz'_2)(MeCN)\}_2(\mu\text{-pyrazine})](ClO_4)_2$ (**2**). Alternatively, treatment of mononuclear **1** and **3**, respectively, with pyrazine in a molar ratio of 2:1 produces the pyrazine-bridged dinuclear Cu^I complexes **2** and **4**. Each of the complexes **1**–**4** can react with PPh_3 to generate a common three-coordinated copper(I) complex $[Cu(PPh_3)(H_2CPz'_2)](ClO_4)$ (**5**). The structures of complexes **1**–**5** were all confirmed by X-ray crystallography. Comparison of the Cu^I–C(CO) bond distances and the CO stretching frequencies of **3** and **4** indicates the back-donating properties of $d\pi(Cu)$–π^*(pyrazine) bonds in **4**, and accordingly, stabilizes the mixed-valence species generated from **2**. Complex **3**, stabilized by the strong interaction between copper(I) ion and perchlorate counteranion (Cu^I–$O(ClO_4)$ = 2.240(3) Å), is a potential precursor for polynuclear copper(I) carbonyl complexes.

Introduction

Copper(I) carbonyl complexes have been extensively studied because of their importance in bioinorganic chemistry[1] and their potential use in catalysis.[2] Since the structural characterization of the neutral copper(I) carbonyl complex $[Cu(HB(pz)_3(CO))]$ in 1975,[3] where $HB(pz)_3^-$ = hydrotris(1-pyrazolyl)borate, the ensuing copper(I) carbonyl complexes containing tris(3,5-disubstituted pyrazolyl) tripodal ligands, in which tunable steric and/or electronic effects are evident at the 3 and/or 5 positions of the pyrazole ring, have been reported. Typical examples include $[Cu(HB(3,5\text{-}(CF_3)_2\text{-}pz)_3)(CO)]$,[4] $[Cu(HB(3,5\text{-}(i\text{-}Pr)_2pz)_3)(CO)]$,[5] and $[Cu(CO)(HC(3\text{-}(t\text{-}Bu)pz)_3)]PF_6$.[6] The structures of these complexes have been determined by X-ray diffraction analyses. However, Cu(I) carbonyl complexes that have been structurally confirmed to contain bis(3,5-disubstituted pyrazolyl) bidentate ligands have not been reported. The lowering of the ligand dentisity from three to two may result in opening a potential coordination site on the central copper and therefore increase the reactivity of the Cu(I) complexes with bidentate pyrazolyl derivatives.[7] Structural information on such complexes would be worthy of further pursuit in order to better understand their chemical and electronic properties.

In our previous studies[8] of the reactions of bis(1-pyrazolyl)methane (H_2CPz_2) with $[Cu(CH_3CN)_4]^+$, an intriguing air-stable bisacetonitrile Cu(I) complex, $[Cu(H_2CPz_2)(MeCN)_2]$-

---

* To whom correspondence should be addressed. E-mail: chefv003@scc.ntnu.edu.tw.

[†] National Taiwan Normal University.

[‡] Chang Gung Institute of Technology.

[§] Tunghai Christian University.

(1) Kretzer, R. M.; Ghiladi, R. A.; Lebeau, E. L.; Liang, H.-C.; Karlin, K. D. *Inorg. Chem.* **2003**, *42*, 3016, and the references therein.

(2) Solomon, E. I.; Jones, P. M.; Maj, J. A. *Chem. Rev.* **1993**, *93*, 2623.

(3) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051.

(4) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **1995**, *34*, 5380.

(5) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

(6) Reger, D. L.; Collins, J. E. *Organometallics* **1996**, *15*, 2029.

(7) (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191. (b) Pasquali, M.; Marini, G.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 2525.

(8) Chou, C.-C.; Su, C.-C.; Tsai, H.-L.; Lii, K.-H. *Inorg. Chem.* **2005**, *44*, 628.

10.1021/ic050568e CCC: $30.25

(ClO$_4$), and an air-sensitive Y-shaped monoacetonitrile Cu(I) complex, [Cu(H$_2$CPz$_2$)(MeCN)](ClO$_4$), were prepared. This finding prompted us to attempt the preparation of a related monoacetonitrile Y-shaped Cu(I) complex, [Cu(H$_2$CPz$'_2$)(MeCN)](ClO$_4$) (**1**), and investigate its reactivity with respect to small molecules such as pyrazine, carbon monoxide, triphenylphosphine, and dioxygen.[9] Herein we present the synthesis, characterization, molecular structures, and reactions of some of the aforementioned complexes.

Experimental Section

Materials and Methods. All operations were carried out under N$_2$ by means of standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures and distilled under N$_2$ before use. Triphenylphosphine, pyrazine, and CO gas were purchased and used as received. The ligand, H$_2$CPz$'_2$,[10] and the copper(I) starting material, [Cu(MeCN)$_4$](ClO$_4$),[11] were prepared according to literature procedures. **Warning:** *Perchlorate compounds are potentially explosive! Extreme care must be taken when working with perchlorate complexes, and only small quantities should be handled.*

Physical Measurements. IR spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer. NMR spectra were obtained on Bruker Avance 400 (^{1}H, 400; ^{13}C, 100 MHz) and Bruker Avance 500 (^{1}H, 500; ^{13}C, 126 MHz) FT NMR spectrometers using CD$_2$Cl$_2$ (δ 5.32 ppm for ^{1}H NMR and δ 54.00 ppm for ^{13}C NMR) or CD$_3$CN (δ 1.94 ppm for ^{1}H NMR and δ 1.39 ppm for ^{13}C NMR) as the lock solvent and internal standard. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Cyclic voltammetric measurements were carried out on a potentiostat (EG&G Potentiostat/Galvan Model 273) at room temperature in acetonitrile solutions (10^{-3} M). The supporting electrolyte was tetra-*n*-butylammonium perchlorate (0.1 M). A three-electrode assembly comprised of a glassy-carbon working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode was used. All of the measurements were referenced externally to Cp$_2$Fe. Elemental analyses were performed on a Heraeus CHN−OS Rapid Elemental Analyzer by the microanalysis laboratories of National Chung Hsin University.

[Cu(H$_2$CPz$'_2$)(MeCN)](ClO$_4$) (1). A 5 mL CH$_2$Cl$_2$ solution of [Cu(MeCN)$_4$]ClO$_4$ (0.164 g, 0.50 mmol) and H$_2$CPz$'_2$ (0.102 g, 0.50 mmol) was stirred at room temperature for 30 min under N$_2$. The white precipitates formed were filtered and washed with Et$_2$O to yield 0.18 g (88%) of product. Single crystals suitable for X-ray structure determination were grown from CH$_2$Cl$_2$/hexane. IR (Nujol): ν_{CN} 2275 cm^{-1}; $\nu_{\mathrm{ClO_4^-}}$ 1097, 623 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 6.07 (s, 2H, C*H*), 6.01 (s, 2H, C*H*$_2$), 2.42 (s, 6H, C*H*$_3$), 2.33 (s, 3H, NCC*H*$_3$), 2.27 (s, 6H, C*H*$_3$) ppm. Positive ESI-MS: 307.9 (M$^+$, 100%), 267.4(M$^+$ − NCMe, 8%). Anal. Calcd for C$_{13}$H$_{19}$ClCuN$_5$O$_4$ (**1**): C, 38.24; H, 4.83; N, 17.15. Found: C, 38.07; H, 4.69; N, 16.88.

[{Cu(H$_2$CPz$'_2$)(MeCN)}$_2$(μ-pyrazine)](ClO$_4$)$_2$ (2). To a stirred solution of complex **1** (0.163 g, 0.40 mmol) in 10 mL CH$_2$Cl$_2$ was added, dropwise, a solution of pyrazine (0.017 g, 0.21 mmol) in 5 mL CH$_2$Cl$_2$ at room temperature. After reaction for 1 h, the resulting orange-yellow precipitates were filtered and washed with *n*-hexane to give 0.16 g (89%) of product. Single crystals suitable for X-ray structure determination were grown from CH$_3$CN/Et$_2$O. IR (Nujol): ν_{CN} 2274 cm^{-1}; $\nu_{\mathrm{ClO_4^-}}$ 1092, 623 cm^{-1}. ^{1}H NMR (CD$_3$CN, 500.13 MHz): δ 8.59 (s, 4H, pyrazine), 6.01 (s, 4H, C*H*), 5.97 (s, 4H, C*H*$_2$), 2.38 (s, 12H, C*H*$_3$), 2.13 (s, 12H, C*H*$_3$), 1.96 (s, 6H, NCC*H*$_3$) ppm. ^{13}C NMR (CD$_3$CN, 125.8 MHz): δ 150.9 (C of pyrazolyl), 146.3 (C of pyrazine), 142.0 (C of pyrazolyl), 107.2 (*C*H of pyrazolyl), 58.3 (*C*H$_2$), 13.7 (*C*H$_3$), 11.2 (*C*H$_3$) ppm. Anal. Calcd for C$_{30}$H$_{42}$Cl$_2$Cu$_2$N$_{12}$O$_8$ (**2**): C, 40.18; H, 4.72; N, 18.74. Found: C, 40.52; H, 4.74; N, 18.45.

[Cu(OClO$_3$)(CO)(H$_2$CPz$'_2$)] (3). A suspension of complex **1** (0.204 g, 0.50 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred for ~10 min while CO is bubbled in at room temperature. The resulting transparent solution was layered with Et$_2$O (saturated with CO) to yield 0.18 g (91%) of white crystals. IR (Nujol): ν_{CO} 2108 cm^{-1}, $\nu_{\mathrm{ClO_4^-}}$ 1115, 1052 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400.13 MHz): δ 6.03 (s, 2H, C*H*), 6.00 (s, 2H, C*H*$_2$), 2.39 (s, 6H, C*H*$_3$), 2.35 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz): δ 173.9 (*C*O), 152.4 (C of pyrazolyl), 142.1 (C of pyrazolyl), 107.3 (*C*H of pyrazolyl), 56.8 (*C*H$_2$), 14.3 (*C*H$_3$), 11.3 (*C*H$_3$) ppm. Anal. Calcd for C$_{12}$H$_{16}$ClCuN$_4$O$_5$ (**3**): C, 36.24; H, 4.08; N, 16.17. Found: C, 36.22; H, 3.95; N, 16.24.

[{Cu(CO)(H$_2$CPz$'_2$)}$_2$(μ-pyrazine)](ClO$_4$)$_2$ (4). Method 1. A suspension of complex **2** (0.204 g, 0.50 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred while CO is bubbled in at room temperature. The CO bubbling was continued until the solvent was removed completely.

Method 2. To a CH$_2$Cl$_2$ (5 mL) solution of complex **3** (0.160 g, 0.40 mmol) was added, dropwise, a solution of pyrazine (0.017 g, 0.21 mmol) in 5 mL of CH$_2$Cl$_2$ at room temperature for ca. 20 min under a CO atmosphere. The resulting solution was layered with Et$_2$O saturated with CO to yield 0.15 g (86%) of pale-yellow crystals. IR (Nujol): ν_{CO} 2119 cm^{-1}, $\nu_{\mathrm{ClO_4^-}}$ 1098, 625 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 8.66 (s, 4H, pyrazine), δ 6.03 (s, 4H, C*H*), 5.89 (s, 4H, C*H*$_2$), 2.40 (s, 12H, C*H*$_3$), 2.32 (s, 12H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 125.8 MHz): δ 173.7 (*C*O), 152.0 (C of pyrazolyl), 146.6 (C of pyrazine), 142.4 (C of pyrazolyl), 107.3 (*C*H of pyrazolyl), 57.2 (*C*H$_2$), 14.3 (*C*H$_3$), 11.3 (*C*H$_3$) ppm. Anal. Calcd for C$_{28}$H$_{36}$Cl$_2$Cu$_2$N$_{10}$O$_{10}$ (**4**): C, 38.63; H, 4.17. Found: C, 38.55; H, 4.11.

[Cu(PPh$_3$)(H$_2$CPz$'_2$)](ClO$_4$) (5). Method 1. To a CH$_2$Cl$_2$ (10 mL) solution of complex **1** or **3** (0.30 mmol) was added PPh$_3$ (0.08 g, 0.31 mmol) followed by stirring for 30 min at room temperature. The resulting solution was concentrated and layered with Et$_2$O to yield 0.18 g (95%) of white crystals.

Method 2. To a CH$_2$Cl$_2$ (10 mL) solution of complex **2** or **4** (0.20 mmol) was added PPh$_3$ (0.11 g, 0.42 mmol) followed by stirring for 30 min at room temperature. The resulting solution was concentrated and layered with Et$_2$O to yield 0.22 g (87%) of white crystals. IR (Nujol): $\nu_{\mathrm{ClO_4^-}}$ 1096, 623 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 7.54−7.45 (m, 15H, phenyl), 6.32 (s, 2H, C*H*), 5.99 (s, 2H, C*H*$_2$), 2.49 (s, 6H, C*H*$_3$), 1.89 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 125.8 MHz): δ 152.26 (C of pyrazolyl), 142.93 (C of pyrazolyl), 134.30 (C of phenyl), 134.18 (C of phenyl), 131.73 (C of phenyl), 131.63 (C of phenyl), 131.40 (C of phenyl), 129.92 (C of phenyl), 129.83 (C of phenyl), 107.54 (*C*H of pyrazolyl), 57.99 (*C*H$_2$) 14.19 (*C*H$_3$), 11.39 (*C*H$_3$) ppm. Anal. Calcd for C$_{29}$H$_{31}$ClCuN$_4$O$_4$P (**5**): C, 55.33; H, 4.93; N, 8.90. Found: C, 55.12; H, 4.86; N, 8.75.

X-ray Crystallography. Crystal data and collection parameters are listed in Table 1. The selected bond lengths and angles are given in Table 2. Data collection was carried out on a Bruker SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods using SHELXL-97,[12] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All of the non-hydrogen atoms were refined with anisotropic temperature factors.

---

(9) Chou, C.-C.; Su, C.-C. To be published.

(10) Julia, S.; Mazo, J. del; Sancho, M.; Ochoa, C.; Elguero, J.; Fayet J.-P.; Vertut, M.-C. *J. Heterocycl. Chem.* **1982**, *19*, 1141.

(11) Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

Table 1. Crystal Structure and Refinement Data for **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{13}H_{19}ClCuN_5O_4$	$C_{30}H_{42}Cl_2Cu_2N_{12}O_8$	$C_{12}H_{16}ClCuN_4O_5$	$C_{28}H_{36}Cl_2Cu_2N_{10}O_{10}$	$C_{29}H_{31}ClCuN_4O_4P$
fw	408.32	896.74	395.28	870.65	629.54
temp (K)	100(2)	200(2)	100(2)	200(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.6670(2)	7.60200(10)	7.7670(3)	7.7460(7)	8.3966(5)
b (Å)	13.0930(2)	11.3620(2)	9.7260(4)	10.5840(9)	10.3157(7)
c (Å)	14.6660(4)	12.1490(3)	12.1940(5)	11.0030(12)	18.923(1)
α (deg)	90	83.9930(10)	112.1980(10)	83.844(3)	102.178 (1)
β (deg)	95.1150(10)	75.5730(10)	97.5550(10)	83.124(4)	96.048 (1)
γ (deg)	90	73.3260(10)	103.242(2)	84.848(4)	106.382 (1)
V ($Å^3$)	1659.54(6)	972.91(3)	805.55(6)	887.71(15)	1513.2(2)
Z	4	1	2	1	2
D_{calcd} (Mg/m^3)	1.634	1.531	1.630	1.629	1.382
abs coeff (mm^{-1})	1.506	1.293	1.551	1.417	0.903
θ range (deg)	2.09−25.02	2.50−25.00	2.32−25.02	2.56−25.29	1.12−28.25
no. of reflns collected	17739	13990	9001	10158	16104
no. of independent reflns	2928	3402	2797	3122	7184
R(int)	0.0596	0.0487	0.0705	0.1189	0.0687
no. of data/restraints/ params	2928/0/218	3402/0/244	2797/0/208	3122/0/235	7184/0/361
GOF on F^2	1.094	1.079	1.139	1.022	0.826
$R1^{a,b}$	0.0475	0.0430	0.0449	0.0702	0.0623
$wR2^{a,c}$	0.1390	0.1251	0.1230	0.1527	0.1471
max, min peaks (e $Å^{-3}$)	0.886, −0.732	0.693, −0.489	0.885, −0.519	0.547, −0.591	0.564, −0.441

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$. [c] $wR2 = \{\Sigma[w(F_o - F_c)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

	bond lengths		bond angles	
1	Cu1−N1	1.988(3)	N1−Cu1−N5	136.0(1)
	Cu1−N4	2.006(3)	N4−Cu1−N5	128.3(1)
	Cu1−N5	1.879(4)	N1−Cu1−N4	95.2(1)
2	Cu1−N1	2.037(3)	N1−Cu1−N4	94.2(1)
	Cu1−N4	2.042(3)	N1−Cu1−N5	111.9(1)
	Cu1−N5	2.040(3)	N1−Cu1−N6	118.3(1)
	Cu1−N6	1.972(3)	N4−Cu1−N5	113.5(1)
	N5−C12	1.338(4)	N4−Cu1−N6	114.6(1)
	N5−C13	1.339(4)	N5−Cu1−N6	104.6(1)
	C12−C13A	1.372(5)		
3	Cu1−N1	2.007(3)	N1−Cu1−N4	95.3(1)
	Cu1−N4	2.001(3)	N4−Cu1−C12	129.7(2)
	Cu1−C12	1.806(5)	N1−Cu1−O2	103.5(1)
	Cu1−O2	2.240(3)	O2−Cu1−C12	102.4(2)
	C12−O1	1.124(6)	N1−Cu1−C12	126.3(2)
			N4−Cu1−O2	92.4(1)
			Cu1−C12−O1	176.8(4)
4	Cu1−N1	2.043(6)	N1−Cu1−N4	93.7(2)
	Cu1−N4	2.046(6)	N1−Cu1−N5	107.3(2)
	Cu1−N5	2.056(5)	N1−Cu1−C14	113.2(3)
	Cu1−C14	1.835(8)	N4−Cu1−N5	107.1(2)
	C14−O1	1.121(8)	N4−Cu1−C14	118.4(3)
	N5−C12	1.334(8)	N5−Cu1−C14	114.8(3)
	N5−C13	1.329(8)	Cu1−C14−O1	171.9(7)
	C12−C13A	1.38(1)		
5	Cu1−N1	2.020(6)	N1−Cu1−N4	95.0(2)
	Cu1−N4	2.018(6)	P1−Cu1−N1	132.1(2)
	Cu1−P1	2.171(2)	P1−Cu1−N4	130.3(2)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figures 1 and 2.

All hydrogen atoms were located geometrically and refined in the riding mode. Additional crystallographic data as CIF files are available as Supporting Information.

Results and Discussion

The white complex **1** was generated in high yield by the reaction of $[Cu(MeCN)_4](ClO_4)$ with an equimolar amount of $H_2CPz'_2$ at room temperature for ca. 30 min under N_2. After treatment of **1** with 0.5 equiv of pyrazine in CH_2Cl_2, complex **2** was formed as an orange-yellow precipitate in 30 min. The addition of CO to a suspension of **1** or **2** in CH_2Cl_2 gave the colorless soluble mononuclear Cu^I-carbonyl **3** or light yellow dinuclear biscarbonyl **4**, respectively. The uptake of CO was rapid for **1** or **2**, as evidenced by the instantaneous solubilization of the suspension of **1** or **2** upon the addition of CO. The reverse reactions took place readily by bubbling N_2 into a CH_2Cl_2 solution of **3** or **4**, allowing the starting **1** or **2** to be recovered. Complex **4** was also isolated from the reaction of **3** with 0.5 equiv of pyrazine. When PPh_3 was added to **1**, no ν_{CN} was detected for **5**, consistent with the replacement of MeCN by PPh_3. While PPh_3 was added to **3**, CO gas was released instantaneously and no ν_{CO} was detected for **5**, indicative of the replacement of CO by PPh_3. Similar reactions were observed for **2** and **4**. The overall reactions are depicted in Scheme 1.

The molecular structure of $[Cu(H_2CPz'_2)(MeCN)](ClO_4)$ (**1**) is shown in Figure 1a. The complex cation adopts a Y-shaped trigonal planar structure with the copper ion slightly deviated (0.0779 Å) from the N1−N4−N5 best plane toward the discrete ClO_4^- at a distance of 3.181 Å. The Cu^I−N(MeCN) bond distance of 1.879(4) Å is close to those previously reported for Y-shaped Cu(I) complexes.[13] The mean Cu^I−N(Pz′) bond distance of 1.997 ± 0.009 Å is significantly longer than those of Sorrell's pyrazole-derived three-coordinate Cu(I) complexes (1.874−1.895 Å),[14] which

---

(12) Sheldrick, G. M. SHELXL97, version 97-2; University of Gottingen, Gottingen, Germany, 1997.

(13) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307.

(14) (a) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250. (b) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883.

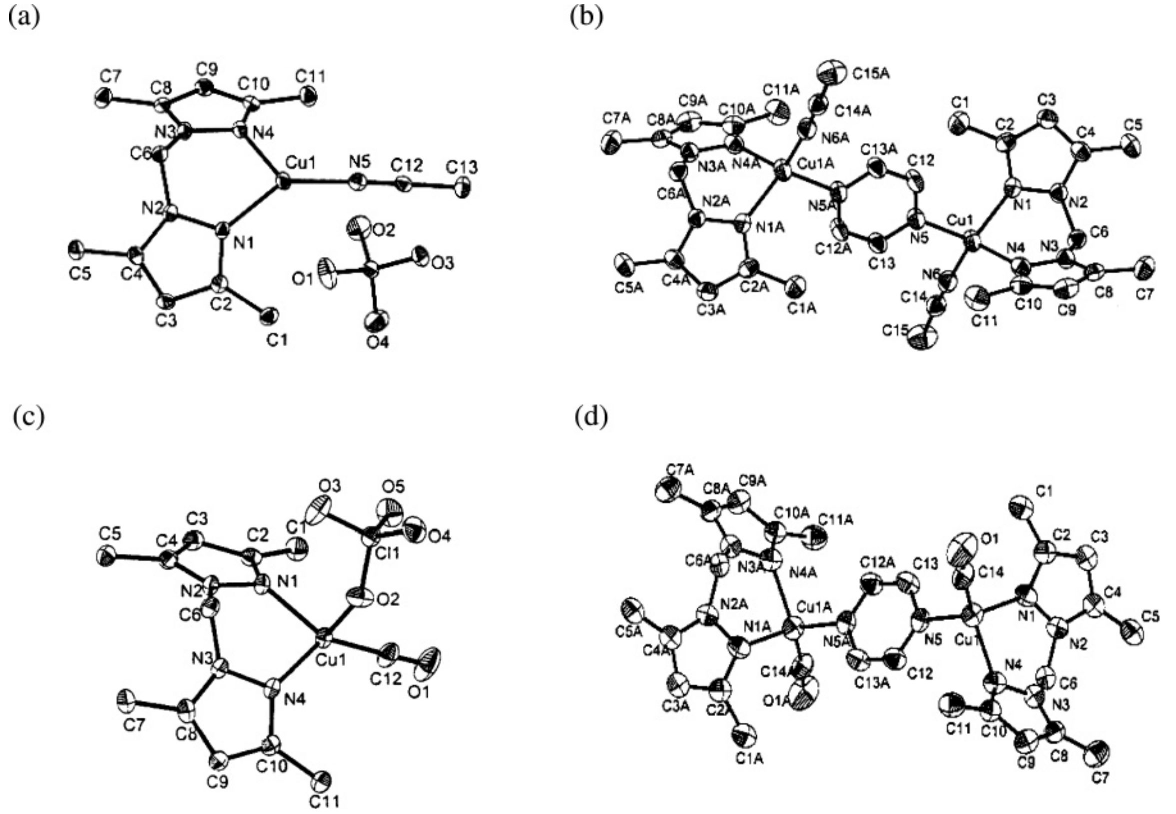
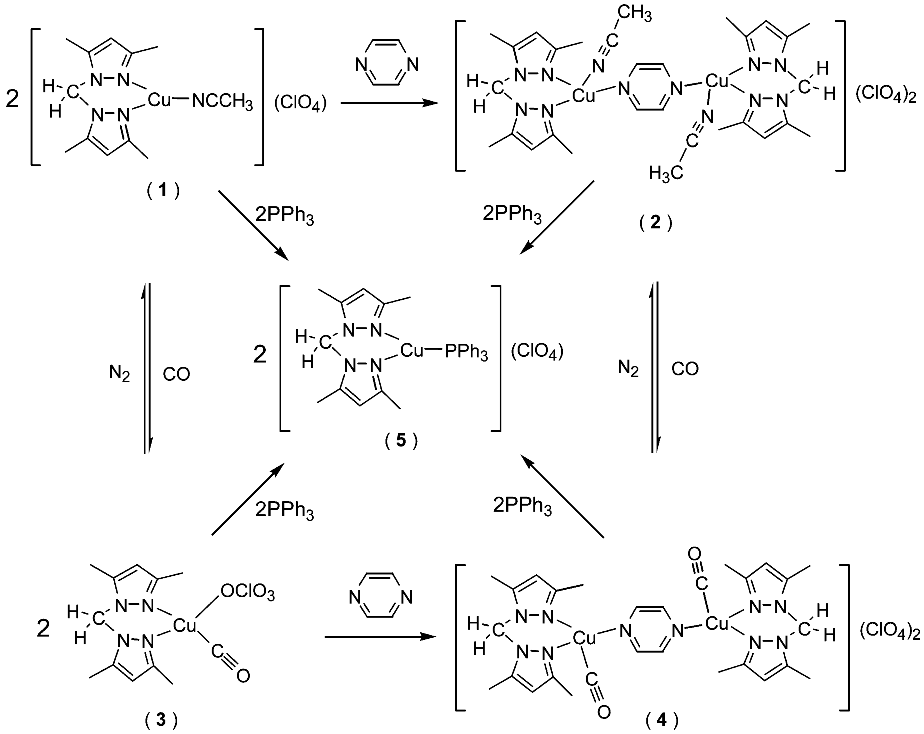


Figure 1. ORTEP diagrams of copper(I) complexes (a) **1**, (b) cation of **2**, (c) **3**, and (d) cation of **4** showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Scheme 1. Reactions of Copper(I) Complexes **1**−**5** in CH_2Cl_2



can be attributed to the different coordination geometry adopted by Sorrell's complexes (T-shaped, ∠N(Pz′)−Cu−N(Pz′) = 156°). Accordingly, the Cu^I−N(Pz′) bonds in **1** tend to become weakened. Compound **1** was also characterized by means of ESI-MS (+) spectrometry. The *m*/*z* (%) at 308 (M^+, 100) and 267 (M^+−MeCN, 8) indicates the presence of one-coordinated MeCN. The ν_{CN} at 2275 cm^{-1} (IR, Nujol mull) observed for **1** also suggests the presence of a coordinated MeCN, consistent with the X-ray structure of **1**. After treatment of **1** with pyrazine, a ν_{CN} band at 2274 cm^{-1} was observed for **2**, consistent with the coordinated MeCN, as evidenced by the X-ray structure of **2** (vide infra).

Table 3. Selected CO Vibrational and Cu−C Structural Data for Copper(I) Carbonyl Complexes with Pyrazole-Derived Polydentate Ligands

complexes	ν_{CO}, cm^{-1}	Cu−C (Å)	ref
$[Cu\{HB(Pz)_3\}(CO)]$	2083	1.765(14)	3, 19
$[Cu\{HB(3,5\text{-}(CF_3)_2Pz)_3\}(CO)]$	2137	1.808(4)	4
$[Cu\{HB(3,5\text{-}(CH_3)_2Pz)_3\}(CO)]$	2066		20
$[Cu(CO)\{HC(3,5\text{-}(CH_3)_2Pz)_3\}]PF_6$	2113		6
$[Cu(CO)\{HC(3,5\text{-}(t\text{-}Bu)_2Pz)_3\}]PF_6$	2100	1.778(10)	6
$[Cu(OClO_3)(CO)\{H_2C(3,5\text{-}(CH_3)_2Pz)_2\}]$ (**3**)	2108	1.806(5)	this work

The X-ray structure of the centrosymmetric complex cation of $[\{Cu(H_2CPz'_2)(MeCN)\}_2(\mu\text{-pyrazine})](ClO_4)_2$ (**2**) is shown in Figure 1b. Each Cu(I) is coordinated to four N donor atoms in a distorted tetrahedral geometry. The Cu^I−N(Pz′) bonds are slightly elongated by 0.043 Å, compared with the corresponding mean bond distance of **1**. The Cu^I−N(MeCN) bond distance of 1.978(3) Å is significantly elongated by 0.1 Å, compared with that of **1**, but is nearly identical to those of the Cu−N in $[Cu(MeCN)_4]^+$ (1.98 ± 0.01 Å).[15] The Cu^I−N(μ-pyrazine) bond distance of 2.042(3) Å is close to the literature values for Cu^{II}−N(μ-pyrazine) (2.02−2.06 Å).[16] Note that the pyrazine is bonded equatorially to the imposed boat conformation of the $Cu(N{-}N)_2C$ ring, while the acetonitrile is bound axially. The intramolecular and nearest intermolecular Cu−Cu distances are 6.872(1) and 6.831(2) Å, respectively.

The molecular structure of $[Cu(OClO_3)(CO)(H_2CPz'_2)]$ (**3**), as shown in Figure 1c, is best described as a trigonally distorted tetrahedron with two nitrogen atoms of the boat fragment $Cu(N{-}N)_2C$, an equatorial carbonyl group, and an axial oxygen atom from the perchlorate anion bound to the central Cu^I. Owing to the strong interaction between the Cu^I cation and the perchlorate anion, the copper ion deviates 0.3219 Å from the N1−N4−C12 best plane toward the ClO_4^- anion at a distance of 2.240(3) Å, which is very close to the upper limit of Cu(I)−O single bonds (2.23 Å).[14b] Similar to the perchlorate-coordinated Cu(I) complex $[Cu(OClO_3)(CO)(NH(py)_2)]$ [py = 2-pyridyl, $\nu_{CO} = 2110$ cm^{-1}, Cu−C(CO) = 1.808(2) Å],[17] the splitting perchlorate IR bands of **3** appeared at 1052 and 1115 cm^{-1}, suggesting a unidentate coordination mode, in agreement with the X-ray data. The CO stretching frequency at 2108 is in agreement with a terminal carbonyl in **3**. It is noteworthy that the $NH(py)_2$ (pK_a = 5.3 for Hpy)[18] would be expected to be a better σ-donor than $H_2CPz'_2$ (pK_a = 2.5 for HPz),[18] and therefore, the Cu^I−O(ClO_4) bond distance in **3** would be expected to be shorter than that in $[Cu(OClO_3)(CO)(NH(py)_2)]$ (2.429(1) Å).[17] The perchlorate anion plays a key role in a subtle electronic balance required for the central Cu^I upon binding the carbonyl molecules. Accordingly, the bond distance of Cu−C(CO) and stretching frequencies observed for these two complexes are nearly equal. Evaluation of the N-donor ability of the bidentate ligand $H_2CPz'_2$ through the CO stretching frequency is perturbed by the coordinated perchlorate anion. As shown in Table 3, the value of ν_{CO} for **3** is unexpectedly lower than that of the related tris(3,5-dimethylpyrazolyl)methane copper(I) carbonyl complex, $[Cu(CO)\{HC(3,5\text{-}(CH_3)_2Pz)_3\}]PF_6$.

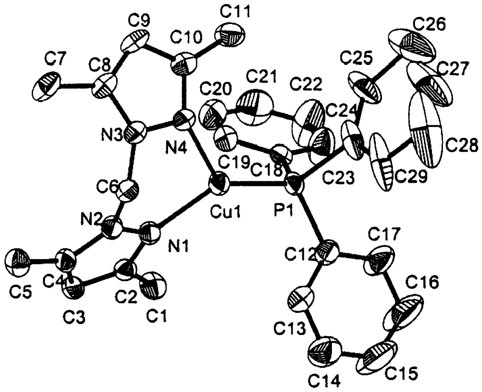


Figure 2. ORTEP diagram of the complex cation of **5** showing 30% probability thermal ellipsoids for all non-hydrogen atoms.

The X-ray structure of the centrosymmetric complex cation of $[\{Cu(CO)(H_2CPz'_2)\}_2(\mu\text{-pyrazine})](ClO_4)_2$ (**4**), as shown in Figure 1d, is quite different from that of **2**. The bridging pyrazine binds to the boat fragments in **4** in an axial orientation. Similar to complex **3**, the carbonyl groups are situated at equatorial sites. However, the grossly longer Cu^I−C(CO) bond distance of 1.835(8) Å and the considerably high CO stretching frequency at 2119 cm^{-1} suggest a poorer back π-bonding from Cu to CO in **4**. Evidently, this is caused by dπ(Cu) to pπ*(pyrazine) back π-bonding. Moreover, compared with complex **2**, the Cu^I−N(pyrazine) bonds in **4** are slightly elongated by 0.016 Å and the average bond distance among the pyrazine ring is virtually unaffected, suggesting that the dπ(Cu) to pπ*(pyrazine) back π-bonding in **4** is somewhat lessened. This can be attributed the difference in bonding properties of MeCN and CO, i.e., MeCN is a moderately strong σ-donor and a very weak π-acceptor, whereas CO is a weak σ-donor and strong π-acceptor.[6]

The molecular structure of the complex cation of $[Cu(PPh_3)(H_2CPz'_2)](ClO_4)$ (**5**) is shown in Figure 2. The complex cation adopts a Y-shaped trigonal planar structure with the copper ion slightly deviated (0.186 Å) from the N1−N4−P1 best plane toward the discrete ClO_4^- at a distance of 2.574 Å.[21] The coordination sphere of the central copper(I) is similar to that of the related three-coordinate copper(I) complex $[Cu((mpz)_2B(mpz)_2)(P(cy)_3)]$.[22] (mpz = 3-me-

---

(15) Csoregh, I.; Kierkegaard, P.; Norrestam, R. *Acta Crystallogr.* **1975**, *B31*, 314.

(16) Oshio, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2985.

(17) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813.

(18) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3.

(19) Bruce, M. I.; Ostazewski, A. P. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

(20) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

(21) (a) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1998**, *110*, 1196. (b) Patch, M. G.; Choi, H.; Chapman, D. R.; Bau, R.; McKee, V.; Reed, C. A. *Inorg. Chem.* **1990**, *29*, 110.

Table 4. CV Data and Comproportionation Constants for MeCN−Dicopper(I) Complexes

complex	$E_{1/2}$[a]	K_{com}	solvent	ref
$[Cu_2(L^2)(MeCN)_2](ClO_4)_2$[b]	+140 +568	2×10^7	MeCN	28
$[Cu_2(Ph_4bdptz)(MeCN)_2](OTf)_2$[c]	+41 +516	1×10^8	MeCN	29
$[Cu_2(H_2CPz'_2)_2(MeCN)_2(\mu\text{-pyrazine})](ClO_4)_2$ (**2**)	+164 +548	3×10^6	MeCN	this work

[a] mV (vs Cp_2Fe^+/Cp_2Fe). [b] L^2 = 5,5,16,16-tetramethyl-23,24-dioxa-3,7,14,18-tetraazatricyclo[18.2.1.1^{9,12}]tetracosa-1(22),2,7,9,11,13,18,20-octaene. [c] Ph_4bdptz = 1,4-bis[bis(6-phenyl-2-pyridyl)methyl]phthalazine. OTf = triflate.

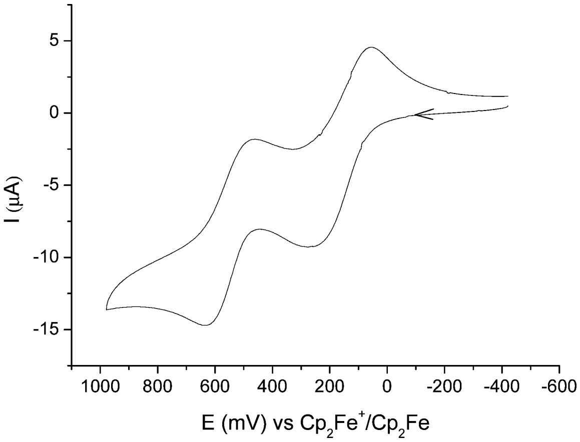


Figure 3. Cyclic voltammogram of **2** in MeCN (1×10^{-3} M). Scan rate = 20 mV/s, electrolyte = $(Bu_4N)(ClO_4)$ (0.1 M).

thylpyrazol-1-yl; cy = cyclohexyl) The low basicity of the neutral bidentate $H_2CPz'_2$ ligand results in a large bite angle of $H_2CPz'_2$ [95.0(2)°] and a short Cu−P bond distance (2.171 Å) for complex **5**, to comply with the electronic and geometrical requirements of the nearly planar three-coordinate geometry. The formation of the three-coordinated complex stems mainly from the good σ-donating and π-accepting properties of the PPh_3. The steric repulsion between the methyl groups of the $H_2CPz'_2$ ligand and the bulky PPh_3 leads to the slight lengthening of the average Cu−N bond distances (2.019 Å) and, consequently, the suppressing of the bite angle of **5** as compared with those of the other two mononuclear copper(I) complexes, **1** [95.2(1)°] and **3** [95.3(1)°].

The redox properties of **1**, **2**, and **5** were examined by cyclic voltammetry in MeCN. Compounds **1** and **5** exhibited a quasireversible wave (cf. Figures S1 and S2) with $E_{1/2}$ potentials of +187 mV (ΔE_p = 202 mV) and +224 mV (ΔE_p = 276 mV), respectively. Compared to other Y-shaped Cu^I−N(MeCN) complexes with the strong electron-donating β-diketiminate ligands (−122 to −242 mV versus Fc/Fc$^+$),[13] the $E_{1/2}$ potential of compound **1** is apparently more positive and closer to that of the three-coordinate Cu^I−N(MeCN) complex with a neutral N-donor ligand, $[Cu_2(L^2)(MeCN)_2](ClO_4)_2$, as shown in Table 4. Evidently, the redox potentials of Cu(I) complexes are greatly influenced by the coordinated bidentate ligand and the coligands as well. While the anionic coligands of β-diketiminate-copper complexes depress the $E_{1/2}$ potentials,[13] the neutral coligand PPh_3 of compound **5** raises the $E_{1/2}$ value.

Two well-separated quasireversible waves (Figure 3) with $E_{1/2}$ potentials of +164 mV (ΔE_p = 174 mV) and +548 mV (ΔE_p = 226 mV) for complex **2** suggest that no significant structural reorganization occurs during the redox process on the electrochemical time scale. These waves are believed to be associated with the Cu^ICu^I to Cu^ICu^{II} and Cu^ICu^{II} to $Cu^{II}Cu^{II}$ processes. The high redox potentials comparable with the compounds listed in Table 4 are probably due to the weak N-donor bidentate ligand, its "environment effect",[23] and the stabilization effect of the MeCN solvent toward Cu(I),[29] making the oxidation to Cu(II) more difficult.

$$Cu^ICu^IL^{2+} + Cu^{II}Cu^{II}L^{4+} \overset{K_{com}}{\rightleftharpoons} 2Cu^ICu^{II}L^{3+} \qquad (1)$$

The comproportionation constant for eq 1,[24] as calculated from the appropriate reduction potentials, is $K_{com} = 3.1 \times 10^6$. This corresponds to an additional stability for the mixed valence ion of 4.4 kcal mol^{-1}, with respect to its isovalent species. The contributions to the stability of the mixed valence compounds have been discussed previously on the basis of the interaction between metal centers, MLCT back-bonding stabilization, and the energy difference between the mixed valence and isovalent states due to electrostatics.[25,26] In the present system, the electrostatic factor is rather small because the binuclear complexes are made up of moieties of like charges. The electrostatic contribution, as calculated from the appropriate ion pair formation constants,[27] is 0.18 kcal mol^{-1}. Apparently, the stabilization of the mixed valence ion arises predominantly from electronic delocalization and $d\pi-\pi^*$ back-bonding. Unfortunately, the mixed-valence species could not be obtained as of this writing. In fact, such a situation is similar to those reported for the bis-MeCN dicopper(I) compounds listed in Table 4. Their K_{com} values are even larger than the present one.

In summary, we report herein on a novel three-coordinate Cu(I)-NCMe complex, $[Cu(H_2CPz'_2)(MeCN)](ClO_4)$ (**1**), and a perchlorate coordinated Cu(I)-carbonyl complex, $[Cu(OClO_3)(CO)(H_2CPz'_2)]$ (**3**), which were first explored in

---

(22) Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B. W.; Somers, N.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 3416.

(23) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014.

(24) The value of K_{com} was obtained from $\Delta E_{1/2}$ (0.384 V) via the equation: $\Delta E_{1/2} = 0.0591 \log K_{com}$. Gagne, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571.

(25) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(26) Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *107*, 369.

(27) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

(28) Yates, P. C.; Drew, M. G. B.; Trocha-Grimshaw, J.; McKillop, K. P.; Nelson, S. M.; Ndifon, P. T.; McAuliffe, C. A.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1991**, 1973.

(29) Kuzelka, J.; Mukhopadhyay, S.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 1751.

the synthesis of the symmetric dicopper(I) complexes [{Cu($H_2CPz'_2$)(MeCN)}$_2$(μ-pyrazine)](ClO_4)$_2$ (**2**) and [{Cu(CO)($H_2CPz'_2$)}$_2$(μ-pyrazine)](ClO_4)$_2$ (**4**), although binucleating ligands[30] or macrocyclic polydentate ligands[31] are commonly employed in the preparation of dicopper(I) complexes. In fact, complex **3** is a promising precursor, namely a source of $[Cu(CO)]^+$, for the preparation of biscarbonyl dicopper(I) species, for example, [{Cu(CO)($H_2CPz'_2$)}$_2$(μ-4,4′-bpy)](ClO_4)$_2$(CH_2Cl_2)$_2$.[32] An exploration of different types of dinuclear and polynuclear copper(I) carbonyl complexes for potential applications in catalysis is currently in progress.

Acknowledgment. Financial support of the National Science Council of the Republic of China is highly appreciated. We thank Prof. Dr. W. -Z. Lee for valuable discussion and assistance on standard Schlenk line manipulations and Mr. T.-S. Kuo for collecting X-ray data. Our gratitude also goes to the Academic Paper Edition Clinic, NTNU.

Supporting Information Available: X-ray crystallographic data in CIF format for compounds **1**−**5** and CV diagrams of **1** (Figure S1) and **5** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050568E

---

(30) (a) Karlin, K. D.; Tykelár, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436. (b) Lee, D.-H.; Wei, N.; Tykelár, Z.; Murthy, N. N.; Zubieta, J.; Karlin, K. D.; Kaderli, S.; Jung, B.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1995**, *117*, 12498. (c) Kodera, M.; Katayama, K.; Tachi, Y.; Kano, K.; Hirota, S.; Fujinami, S.; Suzuki, M. *J. Am. Chem. Soc.* **1999**, *121*, 11006.

(31) (a) Rockcliffe, D. A.; Martell, A. E. *Inorg. Chem.* **1993**, *32*, 3143. (b) Utz, D.; Heinemann, F. W.; Hampel, F.; Richens, D. T.; Schindler, S. *Inorg. Chem.* **2003**, *42*, 1430. (c) Costa, M.; Xifra, R.; Llobet, A.; Solà, M.; Robles, J.; Parella, T.; Stoeckli-Evans, H.; Neuburger, M. *Inorg. Chem.* **2003**, *42*, 4456.

(32) Chou, C.-C.; Su, C.-C. Unpublished results.