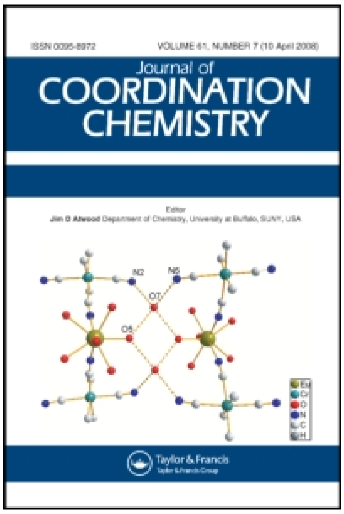

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Cu(I), Ag(I) complexes containing (η^5-cyclopentadienyl) [η^5-1-(diphenylphosphino) cyclopentadienyl] cobaltocenium

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$\{Cu_4Br_5[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]_4\}[PF_6]_3$, $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]^+ = ((\eta^5$-cyclopentadienyl)[$\eta^5$-1-(diphenylphosphino) cyclopentadienyl] cobaltocenium) and $\{Ag(NO_3)(CH_3COCH_3)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]\}_n[PF_6]_n$ have been synthesized and characterized by elemental analyses, infrared spectroscopy, X-ray diffraction techniques, and by cyclic voltammetry. $\{Cu_4Br_5[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]_4\}[PF_6]_3$ contains four coplanar copper atoms bridged by four μ-Br and one central μ_4-Br occupying the apex of a square pyramid, and $\{Ag(NO_3)(CH_3COCH_3)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]\}_n[PF_6]_n$ affording a 1-D coordination zigzag polymer.

Keywords: Phosphine ligand; Cobaltocenium; Copper; Silver; Structure

1. Introduction

Diphenylphosphine ligands containing a ferrocene substituent have been utilized for the development of homogeneous catalysts [1–11]. The ability of this ligand system to alter its steric profile by rotating its phenyl rings or the ferrocene unit allow it to bind to a variety of electron-rich metal centers [12–16]. In comparison to ferrocene-substituted phosphine ligand systems, the coordination chemistry of isoelectronic cobaltocenium phosphine ligands has been less studied [17–23]. In this article we report the synthesis and characterization of two new polynuclear metal complexes that have been isolated from reactions of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ (**1**) with CuBr and $AgNO_3$. The results of X-ray crystallographic analyses and electrochemical properties of these complexes are discussed.

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2. Experimental

2.1. *General methods*

All manipulations were carried out at room temperature under nitrogen using standard Schlenk techniques, unless otherwise stated. Chemicals were supplied from commercial sources and used without purification. All solvents were freshly distilled under nitrogen. The starting material $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ (**1**) was prepared according to literature methods [24]. Elemental analyses (C, H, and N) were performed on a Vario EL III analyzer. ^1H and ^{31}P NMR spectra were collected on a Varian Mercury Plus 400 spectrometer. ^1H NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. IR absorption spectra of the compounds in the range from 400 to 4000 cm^{-1}were recorded on a VECTOR 22 spectrometer.

Cyclic voltammetry measurements were performed using a CHI 660C electrochemical analyzer and carried out in acetonitrile containing 0.1 mol dm^{-3} $n\text{-}Bu_4NPF_6$ using a glassy-carbon working electrode and a platinum-wire counter electrode. All potential values are referred to the saturated calomel electrode (SCE). An argon atmosphere was continuously maintained above the solution while the experiments were in progress. The glassy-carbon working electrode surface was polished with 0.03 mm alumina, sonicated in distilled water, and air-dried immediately before use.

2.2. $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ (1)

Anal. Calcd for $C_{22}H_{19}CoF_6P_2$: C, 50.99; H, 3.70. Found: C, 50.80; H, 3.78. ^1H NMR (400 MHz, CD_3COCD_3): δ 5.51 (s, 2H, C_5H_4), 5.60 (s, 5H, C_5H_5), 5.98 (s, 2H, C_5H_4), 7.36–7.45 (m, 10H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (160 MHz, CD_3COCD_3): δ −144.60 (quintet, $J_{P\text{–}F} = 711.0$ Hz, PF_6), −21.46 ppm. IR (KBr pellet, cm^{-1}): 3120w, 1478w, 1434w, 1419w, 1388w, 1311w, 1095w, 839vs, 697m, and 558m.

2.3. *Synthesis of* $\{(Cu_4Br_5)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]_4\}[PF_6]_3$ (2)

CuBr (7.1 mg, 0.05 mmol) was added to a CH_2Cl_2 solution (15 mL) of **1** (51.8 mg, 0.1 mmol). The mixture was stirred at room temperature overnight. The solvent was evaporated and the residue was purified by column chromatography (silica gel, eluent : dichloromethane/acetone = 10 : 1) to give a red solid (25 mg, 19%). Anal. Calcd for $C_{88}H_{76}Br_5Co_4Cu_4F_{18}P_7$: C, 40.94; H, 2.97. Found: C, 40.69; H, 3.18. ^1H NMR (400 MHz, CD_3COCD_3): δ 5.74 (s, 20H, C_5H_5), 5.96 (s, 8H, C_5H_4), 5.98 (s, 8H, C_5H_4), 7.32–7.74 (m, 40H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (160 MHz, CD_3COCD_3): δ −144.77 (quintet, $J_{P\text{–}F} = 711.0$ Hz, PF_6), −27.28 ppm. IR (KBr pellet, cm^{-1}): 3117w, 1483w, 1437w, 1416w, 1391w, 1312w, 1122w, 837vs, 698m, 559m.

2.4. *Synthesis of* $\{Ag(NO_3)(CH_3COCH_3)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co)]\}_n[PF_6]_n$ (3)

$AgNO_3$ (16.9 mg, 0.1 mmol) in MeOH (5 mL) was added to a CH_2Cl_2 solution (15 mL) of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ (103.6 mg, 0.2 mmol). The mixture was stirred at room temperature for 24 h and yellow precipitate was isolated by filtration. The solid was recrystallized by layering hexane on acetone solution to give yellow $[Ag(NO_3)(CH_3COCH_3)(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co)]_n[PF_6]_n$ (23 mg, 33%). Anal. Calcd for $C_{25}H_{25}AgCoF_6NO_4P_2$: C, 40.24; H, 3.38; N, 1.88. Found: C, 40.68; H, 3.66; N, 1.68. ^1H NMR (400 MHz, CD_3COCD_3): δ 5.77 (s, 5H, C_5H_5), 6.09 (s, 2H, C_5H_4), 6.27 (s, 2H, C_5H_4), 7.56–7.66 (m, 10H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (160 MHz, CD_3COCD_3): δ −144.84 (quintet, $J_{P\text{–}F} = 711.0$ Hz, PF_6), −4.62 ppm. IR (KBr pellet, cm^{-1}): 3116w, 1482w, 1434m, 1387w, 1308w, 1281w, 1099w, 1030w, 839vs, 697m, 558m.

2.5. *Crystallographic analysis*

Crystals of **2** and **3** were grown by layering hexane on an acetone solution at room temperature. The crystalline samples were glued to a glass fiber and mounted on a Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Diffraction measurements were made at room temperature. An absorption correction by SADABS was applied to the intensity data. The structures were solved by the Patterson method. The remaining non-hydrogen atoms were determined from successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogens were generated geometrically and refined with isotropic thermal parameters. Structures were refined on F^2 by full-matrix least-square methods using SHELXTL-97 [25]. The crystallographic data of **2** and **3** are summarized in table 1. Selected bond lengths (Å), bond angles (°), and hydrogen-bonding interactions (Å) for complexes **2** and **3** are listed in table 2.

Table 1. Crystal data and structure refinement for **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{88}H_{78}Br_5Co_4Cu_4F_{18}OP_7$	$C_{25}H_{25}AgCoF_6NO_4P_2$
Formula weight	2599.72	746.2
Temperature (K)	292(2)	292(2)
Crystal system	Tetrahedral	Monoclinic
Space group	*P4/n*	*P2(1)*
Unit cell dimensions (Å, °)		
a	22.5991(14)	10.9026(13)
b	22.5991(14)	8.6234(10)
c	9.8737(13)	15.3722(18)
α	90	90
β	90	99.968(2)
γ	90	90
Volume (Å^3), Z	5042.7(8), 2	1423.4(3), 2
Calculated density ($g\,cm^{-3}$)	1.712	1.741
Absorption coefficient (mm^{-1})	1.454	3.635
$R_1(F_o)$[a]	0.1033	0.0488
$wR_2(F_o)$[b]	0.2575	0.1144

[a] $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$. [b] $wR_2 = \Sigma[\omega(F_o^2 - F_c^2)2]/\Sigma[\omega(F_o^2)]^{1/2}$.

Table 2. Selected bond lengths (Å), hydrogen-bonding interactions (Å), and bond angles (°) for **2** and **3**.

Complex **2**			
Br(1)–Cu(1)	2.627(15)	Br(2)–Cu(1)	2.466(2)
Br(2)–Cu(1a)	2.441(2)	Cu(1)–P(1)	2.190(3)
C(1)–P(1)	1.830(10)	C(11)–P(1)	1.830(3)
C(17)–P(1)	1.837(8)		
Cu(1a)–Br(1)–Cu(1)	76.47(7)	Cu(1a)–Br(1)–Cu(1c)	122.14(7)
Cu(1)–Br(2)–Cu(1a)	83.01(6)	P(1)–Cu(1)–Br(2)	114.37(14)
Br(2c)–Cu(1)–Br(2)	106.50(7)	P(1)–Cu(1)–Br(1)	114.69(8)
Br(2c)–Cu(1)–Br(1)	99.70(7)	Br(2)–Cu(1)–Br(1)	99.06(7)
Complex **3**			
Ag(1)–O(1)	2.559(4)	Ag(1)–P(1)	2.393(10)
Ag(1)–O(4)	2.331(5)	P(1)–C(5)	1.813(4)
P(1)–C(11)	1.817(4)	P(1)–C(17)	1.825(4)
N(1)–O(4)	1.203(7)	N(1)–O(2)	1.200(8)
N(1)–O(3)	1.189(7)		
C(12)–H(12)···O(2a)	2.52	C(14)–H(14)···F(5)	2.53
C(1)–H(1)···O(1)	2.44	C(3)–H(3)···F(3)	2.48
C(8)–H(8)···F(1)	2.39	C(10)–H(10)···O(3)	2.58
O(4)–Ag(1)–P(1)	140.08(18)	O(4)–Ag(1)–O(1)	81.82(18)
P(1)–Ag(1)–O(1)	97.64(11)	C(5)–P(1)–C(11)	101.98(18)
C(5)–P(1)–Ag(1)	115.69(13)	O(3)–N(1)–O(2)	117.5(7)
N(1)–O(4)–Ag(1)	115.6(4)		

3. Results and discussion

3.1. *Synthesis*

Treatment of CuBr with $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ in CH_2Cl_2 afforded $\{Cu_4Br_5[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]_4\}[PF_6]_3$ (**2**) as an air-stable red crystalline solid in 19% yield. However, treatment of $AgNO_3$ with $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ in CH_2Cl_2 afforded a yellow solid $\{Ag(NO_3)(CH_3COCH_3)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co)]\}_n[PF_6]_n$ (**3**) in 33% yield (scheme 1).

3.2. *Spectroscopy*

The ^1H NMR spectra of **2** show singlets at 5.96 and 5.98 ppm for their substituted Cp rings, and a singlet at 5.74 ppm for the unsubstituted Cp rings. The two singlets for the substituted Cp rings of **2** are downfield from those of **3**, suggesting a stronger electron-withdrawing influence by silver. The ^{31}P NMR spectrum of **2** shows one singlet at higher field than that of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$, implying that $[Cu_4Br_5]$ pushes electron density toward $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$. Phosphorus in $[PF_6]^-$ of **2** and **3** appear as one quintet at *ca* −145 ppm, similar to other compounds containing $[PF_6]^-$ [17, 19].

IR spectra of **2** and **3** show absorption bonds resulting from skeletal vibrations of the Cp rings at 1099 cm^{-1} and a strong band at *ca* 838 cm^{-1} for C–H wagging of the Cp [26]. For **3**, the characteristic band $\nu_s(NO_2)$ for NO_3^- appears at 1281 cm^{-1}.

3.3. *Crystal structures*

X-ray structural determinations were carried out on **2** and **3**. The molecular structure of **2** is shown in figure 1. Details about the data collection, solution, and refinement are

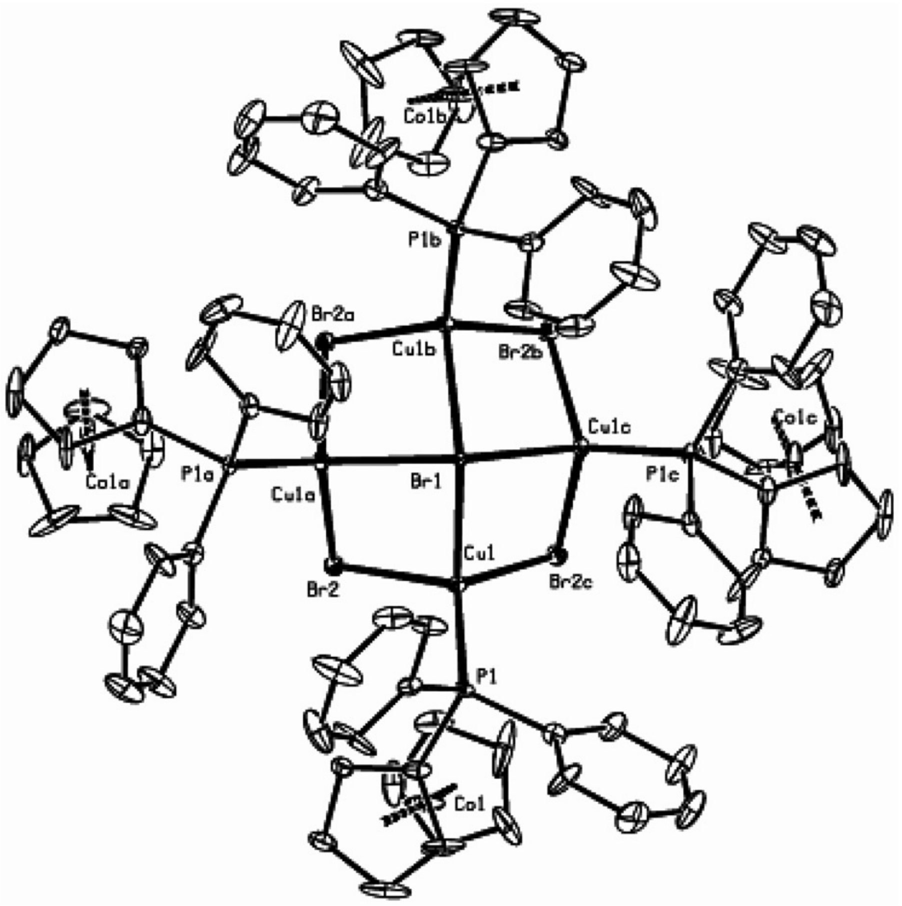


Figure 1. ORTEP diagram of **2**; H atoms, solvent molecule, and PF_6^- are omitted for clarity.

summarized in table 1 and selected bond lengths and angles are provided in table 2. Complex **2** contains a $[Cu_4(\mu\text{-}Br)_4(\mu_4\text{-}Br)]$ core (figure 2) and four $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ units linked by Cu–P bonds of 2.189(3) Å. The structure of the $[Cu_4(\mu\text{-}Br)_4(\mu_4\text{-}Br)]$ core is similar to that reported for several related compounds $\{[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]\}_n$ [27], $[C_5H_5NH][(PhCH_2CH_2CHC_6H_2O_2PPh)_4Cu_4Br_5]$ [28], $[C_5H_5NH][(PhCH_2CH_2CHC_6H_2O_2PPh)_4Ag_4Cl_5]$ [29], $[C_5H_5NH][(PhCH_2CH_2CHC_6H_2O_2PPh)_4Cu_4Cl_5]$ [30], and $[C_5H_5NH][(^iBuCHC_6H_2O_2PPh)_4Ag_4Cl_5]$ [31]. The central $Cu_4(\mu_4\text{-}Br)$ is square pyramidal C_{4v} symmetry with the μ_4-Br atom located at the apex and the four Cu atoms defining the basal plane. The μ_4-Br and the four μ-Br atoms are displaced 1.270 and 1.430 Å, respectively, in opposite directions from this plane. The eight atoms of $Cu_4(\mu\text{-}Br)_4$ exhibit a crown shape and a tetrahedral ligand arrangement is observed about each copper. As expected, the Cu–μ_4-Br distance of 2.627(2) Å is substantially longer than the Cu–μ-Br distance of 2.443(3) Å. The four μ-Br–Cu–μ-Br angles are 106.5(1)°, whereas the four μ-Br–Cu–μ_4-Br are smaller by *ca* 7°.

Crystals of **3** were grown by a layering hexane on the acetone solution at room temperature; acetone also coordinates to silver. The crystal structure of **3** is

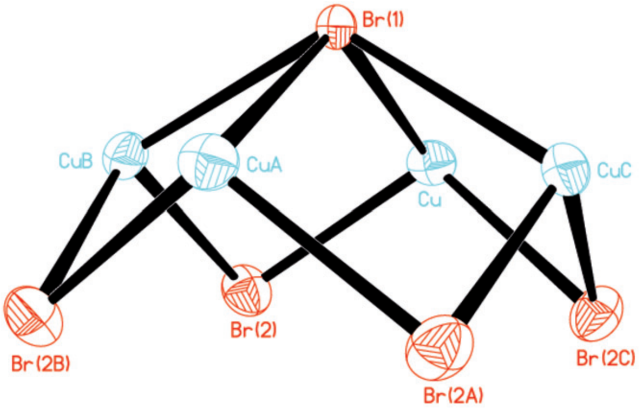


Figure 2. Molecular structure of the $[Cu_4Br_5]^-$ core in **2**.

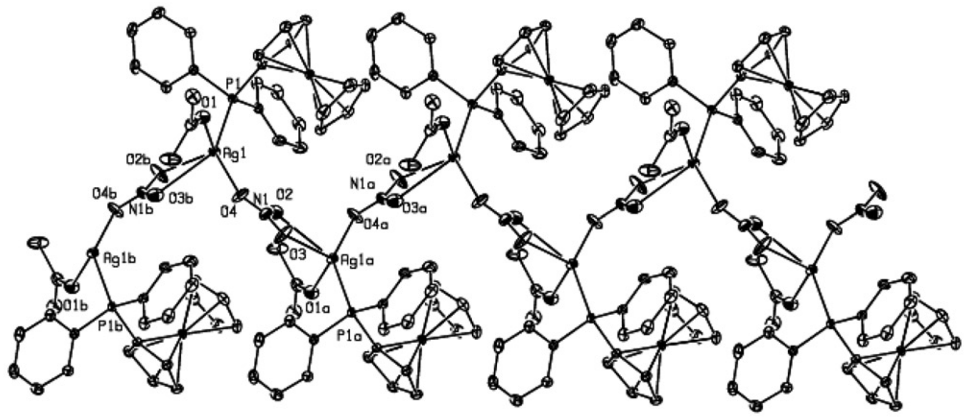


Figure 3. 1-D chain of the polymeric cation of **3**; H atoms and PF_6^- are omitted for clarity.

composed of $\{Ag(NO_3)(CH_3COCH_3)[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]\}[PF_6]$ moieties, depicted in figure 3. The silver and nitrate form an infinite, 1-D zigzag chain (figure 4), interlinked by bridging nitrate. All three oxygens of each nitrate participate in metal coordination. One binds monodentate to one silver and the other two chelate to a different silver. The phosphorus of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ coordinates monodentate to silver, as does O of acetone, with the four Ag–O bond distances in the range 2.331–2.664 Å. As a result, silver is five-coordinate with bond angles in the range of 45.2(2)° (O(2b)–Ag(1)–O(3b)) (figure 3) to 140.09(15)° (O(4)–Ag(1)–P(1)). The polymer containing Ag^+ and NO_3^- was also reported by Erxleben [32], which is a macrocyclic polymeric cation. Oxygens of nitrate form hydrogen bonds (C···O, 3.0–4.0 Å) [33], one with hydrogen on benzene (C(12)···O(2a), 3.265 Å), and another with hydrogen on Cp (C(10)···O(3), 3.485 Å). The O of acetone also forms hydrogen bonds with H on Cp (C(1)···O(1), 3.264 Å) (figure 5).

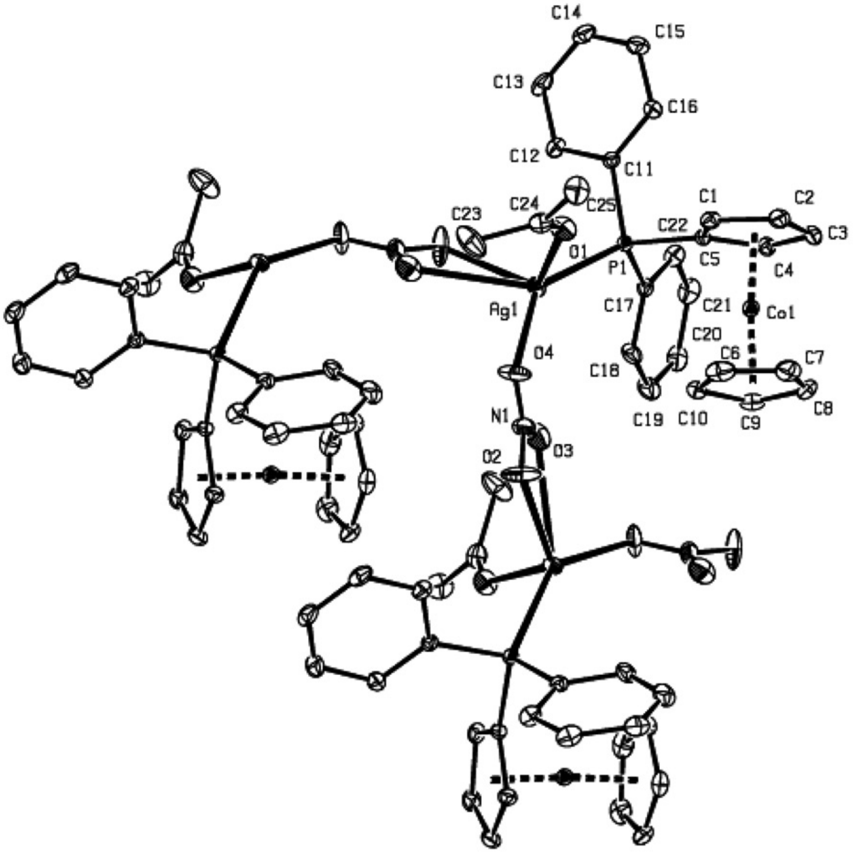


Figure 4. ORTEP diagram of the polymeric cation of **3**; H atoms and PF_6^- are omitted for clarity.

3.4. *Electrochemical studies*

Although some electrochemical studies on complexes containing $[(\eta^5\text{-}C_5H_4PPh_2)_2Co]$ ligand have been performed [20, 23], no such studies on $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$-containing complexes have been reported. Table 3 compares the cyclic voltammetric responses of **2** and **3** with that of free $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ in acetonitrile at 20°C. Complex **2** displays irreversible reduction at about 0.3 V positive to that of free $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$; this result is not consistent with the ^{31}P NMR spectrum, clearly the $[Cu_4Br_5]$ core of **2** decomposes in this electrochemical process. Complex **3** displays quasi-reversible reduction, shifted by about 0.1 V toward more positive potential values with respect to the corresponding processes of free $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$. Such electrochemical behavior implies that the coordinated $[AgNO_3]$ fragment draws electron density from $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$.

4. Conclusions

We have synthesized the first $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ complexes of Cu and Ag. Structures of **2** and **3** have been confirmed by X-ray diffraction crystallography as well

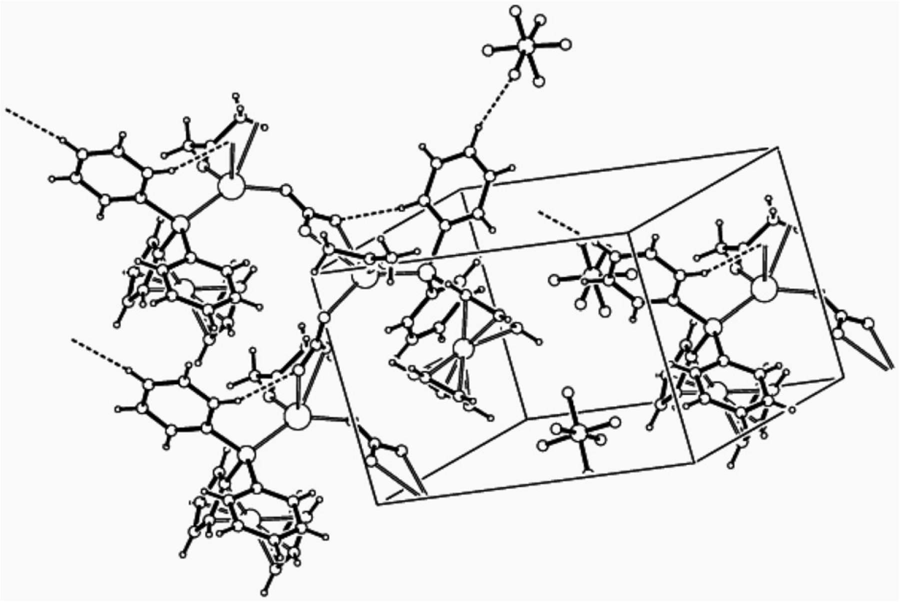
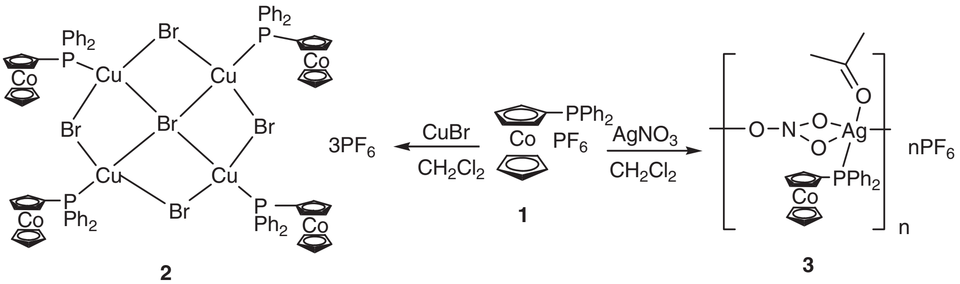


Figure 5. Hydrogen-bonding interactions in **3**.

Table 3. Formal electrode potentials for redox changes exhibited by **1**, **2**, and **3** in acetonitrile at 20°C ($100\,mV\,s^{-1}$).

	E_{pa} (III/II) (V)	E_{pc}(III/II) (V)	$E_{1/2}$(III/II) (V)	E (III/II) (V)
1	−1.118	−1.346	−1.232	0.228
2		−1.069		
3	−0.996	−1.241	−1.119	0.245



Scheme 1. Reactions of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co][PF_6]$ (**1**) with CuBr and $AgNO_3$.

as characterized by elemental analysis and various spectroscopic methods. Complex **2** contains the $[Cu_4(\mu\text{-}Br)_4(\mu_4\text{-}Br)]$ core, complex **3** is a 1-D-coordination zigzag polymer, and the Ag atom is five-coordinate. Through comparison of ^{31}P NMR spectra of **2** and **3** with $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$, the chemical shift of

P of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ in **2** at higher field than that of free $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ $(\Delta\delta = \delta(^{31}P_{\text{complex 2}}) - \delta(^{31}P_{\text{free ligand}}) = -5.82\,\text{ppm})$, whereas P of $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ in **3** is much more deshielded than that of free $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_5)Co]$ $(\Delta\delta = \delta(^{31}P_{\text{complex 3}}) - \delta(^{31}P_{\text{free ligand}}) = 16.84\,\text{ppm})$. Electro chemical studies show that **2** and **3** both display reduction at positive potentials to free $[(\eta^5\text{-}C_5H_4PPh_2)(\tilde{n}^5\text{-}C_5H_5)Co]$.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC numbers 653826 (**2**) and 653827 (**3**). Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.com.ac.uk or www:http://www.ccdc.com.ac.uk).

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