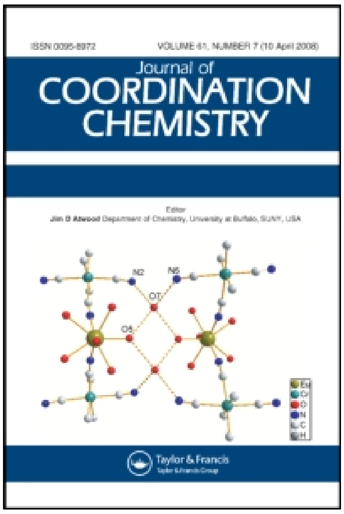

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Direct electrosynthesis of cyano copper(I) complexes: X-ray crystal structure of (cyano-*C*)(2,2'-bipyridine-*N*,*N'*)(triphenylphosphane)copper(I)

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DIRECT ELECTROSYNTHESIS OF CYANO COPPER(I) COMPLEXES: X-RAY CRYSTAL STRUCTURE OF (CYANO-*C*)(2,2′-BIPYRIDINE-*N*,*N*′)(TRIPHENYLPHOSPHANE)COPPER(I)

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Electrosyntheses of cyano copper(I) complexes were carried out by galvanostatic dissolution of copper metal into an acetonitrile solution of malononitrile, used as starting material. Electrochemical reductive cleavage of malononitrile occurs, at the cathode, leading to the formation of cyanide. In the presence of different donors the complexes $[Cu(CN)(PPh_3)_2]\cdot CH_3CN$ (**1**) and $[Cu(CN)(bipy)(PPh_3)]$ (**2**) are obtained. The compounds were characterized analytically and the molecular structure of **2** was determined by single-crystal X-ray analysis. Crystals are triclinic and consist of monomeric molecules in which the copper atom has distorted tetrahedral geometry.

Keywords: Electrosynthesis; Cyanide; Copper(I); Malononitrile; X-ray crystal structure; Mononuclear complex

INTRODUCTION

Organocopper compounds are now among the most frequently used reagents in synthetic organic chemistry [1,2], and constitute a key class of organometallic reagents with numerous applications [3,4]. As the properties of organocopper compounds have become gradually apparent, many new synthetic methods have been discovered [1–6]. In most cases, many reaction steps are involved before obtaining the desired compounds. Electrochemical routes represent one of the most direct and highly reliable methods for obtaining organocopper compounds starting from metallic copper. Recently, we reported the electrochemical syntheses of copper nitrile complexes by potentiostatic dissolution of a copper anode and cathodic reduction of malononitrile in a one-step reaction [7]. As a result, all compounds proved to be ionic binuclear Cu(I)

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complexes in which the copper atoms were bridged by a cyano group. As part of a more extensive investigation of this work, two neutral mononuclear cyano copper(I) complexes have been synthesized by galvanostatic dissolution of a copper anode. In this article we report the synthesis and X-ray crystal structure determination of [Cu(CN)(bipy)(PPh_3)].

EXPERIMENTAL

Electrosynthesis

The electrochemical rig consists of a glass cell (approx. 250 cm^3) with four cross-sectional openings. The copper anode (23 cm^2) and the platinum cathode (23 cm^2) were held by an open-top cap equipped with a joint. Side arms allow the introduction of electrolyte and a supply of argon. A magnetic stirring system was also used. All operations were performed under an argon atmosphere. Acetonitrile (Merck), malononitrile (Acros Organics), triphenylphosphane (Merck) and 2,2′-bipyridine (Gliwice Polska) were of reagent grade and used as received. Tetrabutylammoniumtetrafluoroborate (Fluka) was dried under vacuum. Experiments were carried out at room temperature and at a constant current density of 4.2 mA cm^{-2} with a PG 285 potentiostat/galvanostat (HEKA Electronics).

(Cyano-C)bis(triphenylphosphane)copper(I)-acetonitrile [Cu(CN)(PPh$_3$)$_2$]·CH$_3$CN (1)

Electrosynthesis of [Cu(CN)(PPh_3)$_2$]·CH_3CN has been achieved in an undivided electrochemical cell by the galvanostatic dissolution of copper metal and cathodic reduction of malonodinitrile (0.896 g, 13.56 mmol) in 70 cm^3 of acetonitrile in the presence of 2.256 g (8.60 mmol) of triphenylphosphane and 2.305 g (7.00 mmol) of Bu_4NBF_4 used as supporting electrolyte. Once the reaction was started, hydrogen gas began to evolve. After few minutes an insoluble white compound became visible. Electrolysis was stopped after 160 min and the white product was filtered off, washed with acetonitrile and diethylether and dried under vacuum. Yield: 56.2% (2.449 g, 2.8 mmol) based on copper dissolution. Anal. Calcd. for $C_{39}H_{33}N_2P_2Cu$ (%): C, 71.49; H, 5.03; N, 4.68. Found: C, 70.42; H, 5.03; N, 4.68. ESI-MS: m/z 196.947 $[Cu(CN)(PPh_2)]^+$, 587.111 $[Cu(PPh_3)_2]^+$, 849.212 $[Cu(PPh_3)_3]^+$.

(Cyano-C)(2,2′-bipyridine-N,N′)(triphenylphosphane)copper(I) [Cu(CN)(bipy)(PPh$_3$)] (2)

To a solution containing [Cu(CN)(PPh_3)$_2$]·CH_3CN (0.549 g, 1.08 mmol) in acetonitrile (10 cm^3) was added 2,2′-bipyridine (bipy) (0.469 g, 3 mmol). Yellow single crystals suitable for X-ray characterization were collected after a few days at 0°C. m.p.: 180–185°C.

X-ray Crystal Structure Analysis

Intensity data for [Cu(CN)(bipy)(PPh_3)] were collected at 220 K with an STOE-IPDS diffractometer with Mo Kα radiation (0.71073 Å, graphite monochromator). A summary

TABLE I Crystal data and experimental details of the structure determination of [Cu(CN)(bipy)(PPh_3)]

Empirical formula	$C_{29}H_{23}CuN_3P$
Formula weight ($g\,mol^{-1}$)	508.01
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.062(2)
b (Å)	9.194(2)
c (Å)	15.705(4)
α (°)	89.93(3)
β (°)	92.05(3)
γ (°)	114.09(3)
Volume (Å^3)	1193(5)
Z	2
Calculated density ($g\,cm^{-3}$)	1.413
μ (Mo Kα) (mm^{-1})	0.862
F(000)	524
Crystal size (mm)	0.42 × 0.30 × 0.30
θ range for data collection (°)	2.46 to 25.93
Limiting indices h, k, l	−11/11, −11/11, −19/19
Reflections collected/unique	9233/4254 [R(int) = 0.04]
Data/restraints/parameters	4254/0/399
$R1/wR2$ (all data)	0.0353/0.0840
$R1/wR2$ [$I > 2\sigma(I)$]	0.0304/0.0880
$\Delta\rho$ (min/max) (e Å^{-3})	−0.463/0.469

of crystal data along with further details of structure determination and refinement is given in Table I. Calculations and drawings were done using the programs SHELXS-97 [8] and SHELXL-97 [9]. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-216300. Copies of the data can be obtained free of charge on application to The Director, CCDC,12 Union Road, Cambridge CB2 1EZ, UK (fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Direct anodic dissolution of copper metal and cathodic reduction of malononitrile proved to be a simple and efficient one-step route to copper(I) cyanide mixed ligand complexes which usually are obtained by conventional methods only after many reaction steps [10–14]. The electrochemical cell for this system could be presented as follows: $Pt_{(-)}/CH_3CN + CH_2(CN)_2 + PPh_3 + [(C_4H_9)_4N][BF_4]/Cu_{(+)}$.

The electrochemical efficiency was found to be close to $1\,mol\,F^{-1}$. Taking into account our previous results it is important to mention that the electrochemical reduction of nitrile compounds occurs in most cases with release of cyanide as a byproduct [7,15,16]. Thus an electrochemical reductive cleavage of malononitrile takes place at the cathode and reactions in the electrochemical cell could be described as follows.

Cathode:

$$NC{-}CH_2{-}CN + e^- \longrightarrow [NC{-}CH{-}CN]^- + H^\bullet \qquad (1)$$

$$\mathrm{NC{-}CH_2{-}CN} + \mathrm{e^-} \longrightarrow {}^{\bullet}\mathrm{CH_2CN} + \mathrm{CN^-} \qquad (2)$$

$$\mathrm{H^{\bullet}} + {}^{\bullet}\mathrm{CH_2CN} \longrightarrow \mathrm{CH_3CN} \qquad (3)$$

Anode:

$$\mathrm{CN^-} + \mathrm{Cu} \xrightarrow{\mathrm{2PPh_3/CH_3CN}} \mathrm{e^-} + [\mathrm{Cu(CN)(PPh_3)_2}]\cdot\mathrm{CH_3CN}\ (\mathbf{1}) \qquad (4)$$

The polymeric structure $\{[\mathrm{Cu(CN)(PPh_3)_2}]\cdot\mathrm{CH_3CN}\}_n$ has been characterized by ^{1}H and ^{31}P NMR, IR spectroscopy, ESI-MS and elemental analysis. The IR spectrum (in KBr) exhibited several bands which are diagnostic for the presence of cyanide and triphenylphosphane ligands. Bands characteristic of νCN were observed at 2187 m and 2104 vs cm^{-1}. Zhao *et al.* [10] found a strong peak, νCN, at 2106 cm^{-1} for hexanuclear $[\mathrm{Cu(CN)(PPh_3)}]_6$ obtained by a chemical route. The ^{31}P NMR spectrum showed two singlets at 24.721 and −2.830 ppm. The latter could be due to free $\mathrm{PPh_3}$. In the ^{1}H NMR spectrum, the aromatic protons occurred between 7.2 and 7.8 ppm. Positive-ion electrospray mass spectra in THF/$\mathrm{CH_3CN}$ showed a number of peaks and the most abundant ion, $[\mathrm{Cu(PPh_3)_2}]^+$, appeared at *m*/*z* 587.111.

Reaction of $\{[\mathrm{Cu(CN)(PPh_3)_2}]\cdot\mathrm{CH_3CN}\}_n$ with 2,2′-bipyridine leads to a substituted neutral mononuclear copper(I) complex, as shown below.

$$[\mathrm{Cu(CN)(PPh_3)_3}] + \mathrm{bipy} \xrightarrow{-2\mathrm{PPh_3}} [\mathrm{Cu(CN)(bipy)(PPh_3)}]\ (\mathbf{2}) \qquad (5)$$

The IR spectrum of $[\mathrm{Cu(CN)(bipy)(PPh_3)}]$ showed a strong peak at 2173 cm^{-1} that can be assigned to C≡N stretching for the copper bound cyanide ion. The νC≡N band in solid cuprous cyanide occurs at 2172 cm^{-1}. Singh and Dikshit [11] synthesized $[\mathrm{Cu(CN)(bipy)(PPh_3)}]$ by classical routes and found a small red shift of νC≡N (*ca* $\Delta = 13\,\mathrm{cm^{-1}}$). A single-crystal X-ray analysis was performed to determine the composition of the product of reaction (5).

Crystal Structure of [Cu(CN)(bipy)(PPh$_3$)] (2)

The structure of **2** consists of monomeric $[\mathrm{Cu(CN)(bipy)(PPh_3)}]$ units as shown in Fig. 1. Selected geometrical parameters are compiled in Table II. The copper atom is coordinated by the carbon atom of the cyano group, by the phosphorus atom of $\mathrm{PPh_3}$ and chelated by two nitrogen atoms of the 2,2′-bipyridine ligand. The distorted tetrahedral coordination environment about the copper is consistent with oxidation state +1. The deviation arises from the geometrical constraints imposed by the bond angle N2–Cu–N3 of 78.59(7)° which differs significantly from the ideal value. The N2–Cu–P and N3–Cu–P angles of 112.29(5)° and 105.43(6)° compared to 114.93(8)° and 112.89(8)° for the C1–Cu–N3 and C1–Cu–N2 and 123.66(6)° for C1–Cu–P angles reflect the steric bulk of $\mathrm{PPh_3}$ and bipy ligands compared to the cyano group. The cyano group is almost linear (Cu–C1–N1 174.81(2)°).

The Cu–P distance is in good agreement with the average value of 2.25(4) Å (see Table II) established for Cu$^{\mathrm{I}}$–$\mathrm{PPh_3}$ complexes [7,15–20]. The N1–C1 bond length of

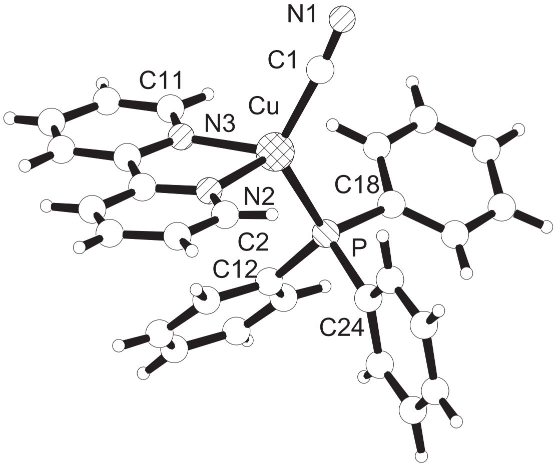

FIGURE 1 Molecular structure of [Cu(CN)(bipy)(PPh3)] with selected atomic labelling.

TABLE II Selected bond lengths (Å) and angles (°) for the complex

Cu–C1	1.936(2)	N1–C1–Cu	174.81(2)
Cu–N2	2.0975(2)	C1–Cu–P	123.66(6)
Cu–N3	2.0944(2)	N2–Cu–P	112.29(5)
Cu–P	2.2384(8)	N3–Cu–P	105.43(6)
C1–N1	1.142(3)	N2–Cu–N3	78.59(7)
N2–C2	1.343(3)	C1–Cu–N2	112.89(8)
N3–C3	1.342(3)	C1–Cu–N3	114.93(8)
P–C12	1.840(2)		
P–C18	1.830(2)		
P–C24	1.824(2)		

1.142(3) Å is close to that expected for a CN triple bond [21] and the Cu–C1 bond distance of 1.936(2) Å is in good agreement with literature data [21].

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