

Are formal oxidation states above one viable in cyclopentadienylcopper cyanides?

Congzhi Wang · Xiuhui Zhang · Qian-shu Li ·
Yaoming Xie · R. Bruce King · Henry F. Schaefer III

Received: 20 July 2011 / Accepted: 20 September 2011 / Published online: 12 October 2011
© Springer-Verlag 2011

Abstract Recent experiments have led to the discovery of the thermally unstable organocopper compounds $(\eta^3\text{-C}_3\text{H}_5)\text{CuMe}_2$, $[(\eta^3\text{-C}_3\text{H}_5)\text{CuMe}_3]^-$, and CuMe_4^- in which the copper atom is in the +3 formal oxidation state. In a quest for more stable organocopper compounds with copper in formal oxidation states above one, the binuclear cyclopentadienylcopper cyanides $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$; $n=1, 2, 3$) have been studied using density functional theory (DFT). The lowest energy structures are found to have terminal Cp rings and bridging cyanide ligands up to a maximum of two bridges. Higher-energy $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ ($n=1, 2, 3$) structures are found with bridging Cp rings. The $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ derivatives, with the copper atoms in an average +2.5 oxidation state, are clearly thermodynamically disfavored with respect to cyanogen loss. However, $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ and

$\text{Cp}_2\text{Cu}_2(\text{CN})$, with the copper atoms in the average oxidation states +1.5 and +2, respectively, are predicted to have marginal viability. The prospects for the copper(II) derivative $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ contrast with that of the “simple” $\text{Cu}(\text{CN})_2$, which is shown both experimentally and theoretically to be unstable with respect to cyanogen loss to give CuCN .

Keywords Copper · Cyclopentadienylcopper cyanide · Oxidation states · Density functional theory

Introduction

An important recent development in the organometallic chemistry of copper is the discovery of organocopper derivatives with copper in the formal +3 oxidation state. In this connection the formally Cu(III) organometallics such as the allyl derivatives [1] $(\eta^3\text{-C}_3\text{H}_5)\text{CuMe}_2$ and $[(\eta^3\text{-C}_3\text{H}_5)\text{CuMe}_3]^-$ and the homoleptic tetramethylcuprate(III), CuMe_4^- [2], can be generated at temperatures around -100°C . However, they are thermally unstable and decompose far below room temperature.

Other than these very unstable Cu(III) organometallics, the organometallic chemistry of copper has been limited to organocopper compounds with copper in the formal Cu(I) oxidation state [3]. However, the existence of these very unstable methylcopper(III) derivatives suggests that more stable Cu(II) and Cu(III) organometallics might be obtainable using a suitable choice of organometallic ligands. Many of the most stable such organocopper derivatives contain cyclopentadienyl ligands. A question of interest is whether cyclopentadienylcopper derivatives can be synthesized in which the copper atom has a formal oxidation state higher than Cu(I). This paper explores theoretically the possibility of using a combination of cyclopentadienyl and cyanide

Electronic supplementary material The online version of this article (doi:10.1007/s00894-011-1251-9) contains supplementary material, which is available to authorized users.

C. Wang · X. Zhang (✉)
Key Laboratory of Cluster Science, Ministry of Education of
China, Department of Chemistry, Beijing Institute of Technology,
Beijing 100081, Peoples Republic of China
e-mail: zhangxiuhui@bit.edu.cn

Q.-s. Li
Institute of Chemical Physics, Beijing Institute of Technology,
Beijing 100081, Peoples Republic of China

Q.-s. Li
Center for Computational Quantum Chemistry, School of
Chemistry and Environment, South China Normal University,
Guangzhou 510631, Peoples Republic of China

Y. Xie · R. B. King (✉) · H. F. Schaefer III
Department of Chemistry and Center for Computational
Chemistry, University of Georgia,
Athens, GA 30606, USA
e-mail: rbking@chem.uga.edu

ligands to prepare organometallics having copper in formal oxidation states above +1.

The cyanide ligand was chosen for this study since it is a versatile strong field ligand. In this connection metal cyanide complexes have attracted great attention in recent years owing to their potential use as ion exchange materials [4], catalysts [5], and molecular magnets [6, 7]. In these complexes the cyanide ion (CN^-), isoelectronic with the carbonyl (CO) ligand, can act either as a terminal or bridging ligand (Fig. 1) [8].

A neutral cyanide ligand bridging a pair of metal atoms only through the carbon atom (b in Fig. 1) donates a single electron to the pair of metal atoms, analogous to a normal two-electron donor bridging carbonyl group. However, a neutral cyanide ligand can also function as a three-electron donor η^2 - μ -CN bridging moiety with the cyanide group bonded to one metal atom through the usual M–C σ -bond and to the other metal atom through a π -bond from the cyanide group (c in Fig. 1). Structures d and e are alternative versions of three-electron donor η^2 - μ -CN bridging cyanide groups with and without metal-metal bonds, respectively. Linear bridging cyanide groups (e in Fig. 1) are found in polymeric metal cyanide complexes such as Prussian Blue [9–11].

Copper cyanide complexes are of particular interest because of their relationship to magnetic [12], photoluminescent [12], and superconducting [13, 14] materials. Organocopper complexes are also of interest because of their use in organic synthesis [15] and the characterization of organocopper complexes [16–18].

The first reported organocopper(I) compound containing both cyclopentadienyl and cyanide ligands was the thermally unstable and air-sensitive methyl isocyanide complex CpCuCNCH_3 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), reported in 1970 by Cotton and Marks [19] as the product of the reaction of $[\text{CH}_3\text{NCCuI}]_4$ with $\text{C}_5\text{H}_5\text{I}$. The infrared spectrum of CpCuCNCH_3 exhibits a $\nu(\text{CN})$ frequency of 2190 cm^{-1} , which is distinctly higher than that for the free CH_3NC (2158 cm^{-1}), indicating weak π -bonding to the cyanide group. The complex CpCuCNCH_3 is closely related to the likewise thermally unstable carbonyl derivative CpCuCO [16], synthesized by the reaction of CuCl with TiCp in the presence of CO. Both CpCuCNCH_3 and CpCuCO have the favored 18-electron configuration and are isoelectronic with the much more stable CpNiNO , which was synthesized in the early days of cyclopentadienyl metal chemistry [20].

The permethylated derivative $(\eta^5\text{-Me}_5\text{C}_5)\text{CuCO}$, like CpCuCO , is also unstable at room temperature. However, the sterically hindered tetraisopropyl derivative $(\eta^5\text{-C}_5\text{HR}_4)\text{CuCO}$ ($\text{R}=\text{CHMe}_2$) is much more stable and can be stored at room temperature [21]. In addition, the *tert*-butyl isocyanide derivative CpCuCNBu^t is more stable than CpCuCNCH_3 and can remain unchanged for at least one month at room temperature under nitrogen [22].

All of these known cyclopentadienylcopper compounds have copper in the +1 formal oxidation state. However, it is well-known that in aqueous solution the d^9 Cu(II) is the common oxidation state of copper. However, Cu(II) is easily reduced to Cu(I) by cyanide in aqueous solution [23], implying that the Cu(I) oxidation state is more compatible than Cu(II) in the presence of cyanide. However, some stable Cu(II) cyanide complexes have been synthesized, e.g., $[\text{Cu}_2([\text{14}]\text{4,11-diene-N}_4)_2\text{CN}](\text{ClO}_4)_3$ ($[\text{14}]\text{4,11-diene-N}_4=5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11diene}$) [24] and $[\text{Cu}^{\text{II}}(\text{dipn})][\text{Cu}^{\text{II}}(\text{CN})_4]$ ($\text{dipn}=\text{dipropylentriamine}$) [25].

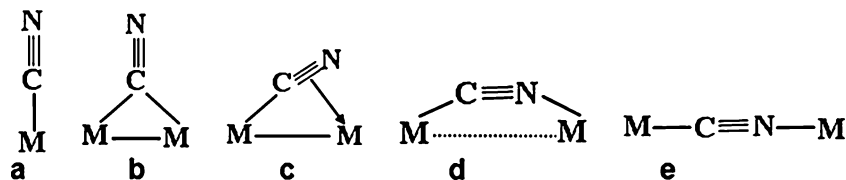
A question of some importance is whether cyclopentadienylcopper cyanides having copper in formal oxidation states above +1 are viable. This paper describes a density functional theory (DFT) study on the organocopper cyanides $\text{Cp}_2\text{Cu}_2(\text{CN})$, $\text{Cp}_2\text{Cu}_2(\text{CN})_2$, and $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ having copper in the average formal oxidation states of +1.5, +2, and +2.5, respectively, in order to provide information on the equilibrium geometries and the relative stabilities of these complexes.

The theoretical studies reported in this paper were performed using the unsubstituted $\eta^5\text{-C}_5\text{H}_5$ ligand in order to simplify the optimizations in this exploratory research. However, the properties of the known CpCuCO derivatives discussed above suggest that highly substituted Cp rings might be required to realize experimentally the chemistry predicted from this theoretical study.

Theoretical methods

Since Cu(I) and Cu(II) complexes can be considered as highly-correlated systems with significant electron clustering, electron correlation effects are particularly important [3]. In this paper, electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computa-

Fig. 1 Terminal and bridging bonding modes for the cyanide ligand



tional tool, especially for organometallic compounds [26–41]. Two DFT methods were used in this study. The first functional is B3LYP, a hybrid HF-DFT method combining Becke's three-parameter functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional [42, 43]. This approach has been shown very reliable for the study of Cu(I) and Cu(II) complexes [3]. The other approach is the BP86 method, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional method (P86) [44, 45], and the BP86 method usually provides better vibrational frequencies [46, 47].

All computations were performed using double- ζ plus polarization (DZP) basis sets. For carbon and cyanogen, the DZP basis set used here adds one set of pure spherical harmonic d functions (with orbital exponents $\alpha_d(\text{C})=0.75$ and $\alpha_d(\text{N})=0.80$) to the Huzinaga-Dunning standard contracted DZ sets and is designated (9s5p1d/4s2p1d) [48–50]. For hydrogen, a set of p polarization functions ($\alpha_p(\text{H})=0.75$) is added to the Huzinaga-Dunning DZ sets. For Cu, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses Wachters' primitive set [51] augmented by two sets of p functions and one set of d functions and contracted following Hood, Pitzer and Schaefer [52].

The geometries of all structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were evaluated analytically as well. All of the computations were carried out with the Gaussian 03 program [53]. The fine grid (75, 302) was the default for evaluating integrals numerically [54]. The finer grid (120, 974) [54] was used for more precise resolution of the imaginary vibrational frequencies. The tight designation was the default for the self-consistent field (SCF) convergence. Unless otherwise indicated, the reported structures do not have any imaginary vibrational frequencies.

Since there is no wave function *per se* in the DFT method, the evaluation of the expectation value of S^2 is problematic. The most realistic and practical method evaluates $\langle S^2 \rangle$ using the single determinant wave function constructed from the appropriate DFT orbitals. When DFT methods for open-shell systems perform poorly, one very often observes serious spin contamination in the sense defined here.

The structures for $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ ($n=1, 2, 3$) are depicted in Figs. 2, 3, 4, and 5. They are labeled by the number of CN groups, order of relative energies, and spin state (singlets, doublets, triplets and quartets designated as S, D, T and Q, respectively). For example, the lowest-lying triplet structure of $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ is called 2CN-1T. The upper and lower bond distances in the Figs. were determined by the B3LYP and BP86 methods, respectively.

Results

$\text{Cp}_2\text{Cu}_2(\text{CN})$

Three structures were found for $\text{Cp}_2\text{Cu}_2(\text{CN})$ in which the copper atoms have an average formal oxidation state of +1.5 (Fig. 2 and Table 1). All three structures are electronic doublet states with negligible spin contamination, i.e., with $\langle S^2 \rangle$ close to the ideal value of 0.75 (Table 1). The global minimum for $\text{Cp}_2\text{Cu}_2(\text{CN})$, namely 1CN-1D, has one bridging cyanide ligand and two terminal Cp ligands (Fig. 2 and Table 1). The predicted Cu-C distances to the bridging cyanide ligand are 1.870 Å and 2.074 Å (B3LYP) or 1.847 Å and 2.030 Å (BP86). The Cu-N distance to this bridging cyanide ligand is very short, namely 2.144 Å (B3LYP) or 2.146 Å (BP86), and the C-N distance is relatively long (1.189 Å by B3LYP or 1.207 Å by BP86), indicating a three-electron donor $\eta^2\text{-}\mu\text{-CN}$ group (c in Fig. 1). The low $\nu(\text{CN})$ frequency of 1CN-1D at 1981 cm^{-1} (BP86) can be assigned to this $\eta^2\text{-}\mu\text{-CN}$ group. The Cu-Cu

Fig. 2 The three doublet $\text{Cp}_2\text{Cu}_2(\text{CN})$ structures

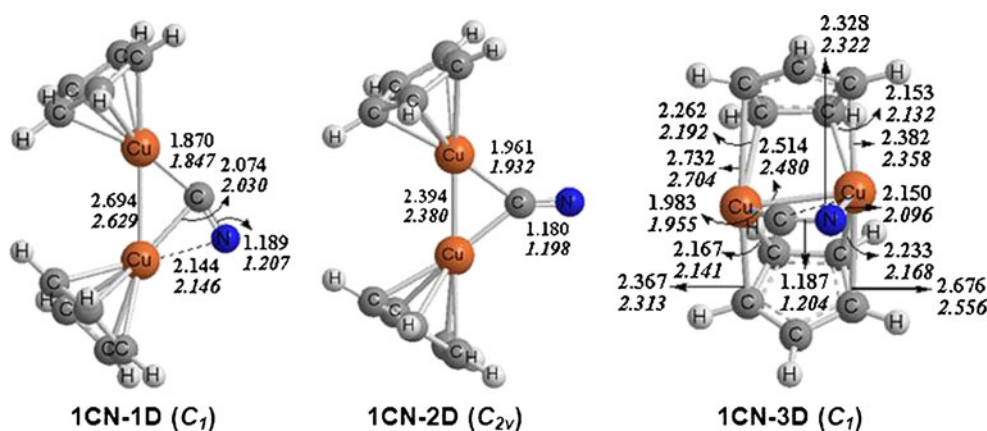
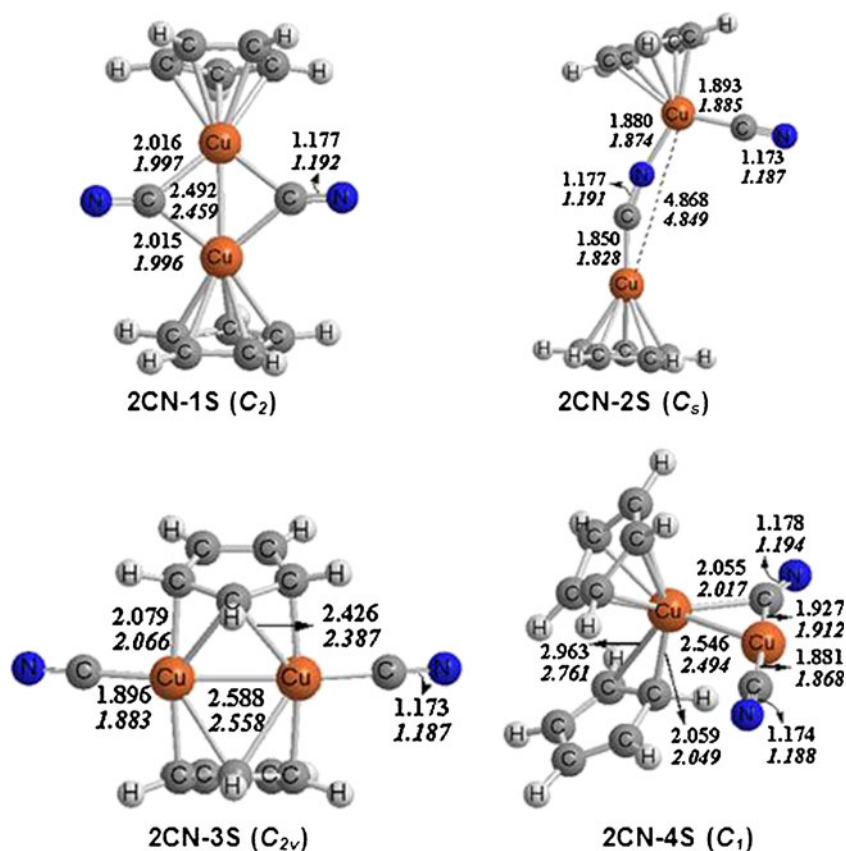


Fig. 3 The four singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structures



distance of 2.694 Å (B3LYP) or 2.629 Å (BP86) can correspond to a formal Cu–Cu single bond. However, this presumed Cu–Cu single bond is ~ 0.2 Å longer than the experimental Cu–Cu single bond distance (2.448 Å) in a binuclear copper cryptate derivative [55] having the same average copper formal oxidation state of +1.5 as **1CN-1D**. A formal Cu–Cu single bond in **1CN-1D** gives one copper atom an 18-electron configuration but the other copper atom a 19-electron configuration, with a three-electron donor bridging cyanide ligand.

The $\text{Cp}_2\text{Cu}_2(\text{CN})$ structure **1CN-2D** is a C_{2v} structure with a symmetrically bridging cyanide ligand and terminal Cp ligands (Fig. 2 and Table 1). Structure **1CN-2D** lies 1.9 kcal mol $^{-1}$ (B3LYP) or 1.1 kcal mol $^{-1}$ (BP86) above the global minimum **1CN-1D**. Structure **1CN-2D** has all real vibrational frequencies by BP86, but an imaginary frequency (43i cm $^{-1}$) by B3LYP. In **1CN-2D**, the bridging cyanide ligand is coordinated through the C atom to the Cu–Cu bond. Thus one sees a μ -CN structure with a Cu_2C three-center two-electron bond to the two copper atoms and the

Fig. 4 The two triplet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structures

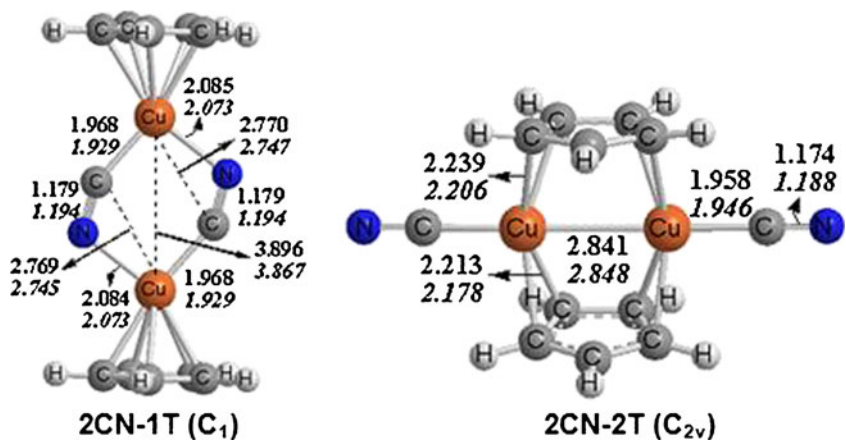
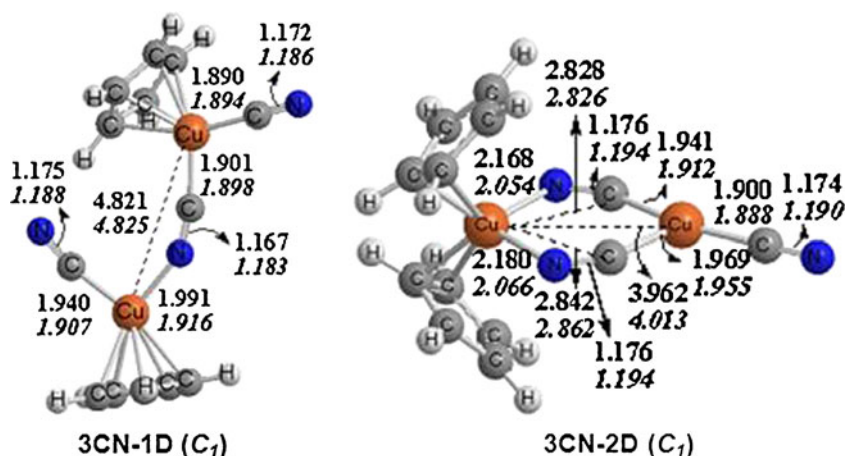


Fig. 5 The two doublet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structures

carbon atom (b in Fig. 1). Such a bridging cyanide, considered as a neutral ligand, donates a single electron to the Cu_2 system. The corresponding $\nu(\text{CN})$ frequency of 2017 cm^{-1} (BP86) for the one-electron donor cyanide ligand in **1CN-2D** is larger than the $\nu(\text{CN})$ frequency for the three-electron donor cyanide ligand in **1CN-1D**. The Cu-C distances in **1CN-2D** are 1.961 \AA (B3LYP) or 1.932 \AA (BP86). The Cu-Cu distance of 2.394 \AA (B3LYP) or 2.380 \AA (BP86), is close to the experimental Cu-Cu single bond distance (2.448 \AA) in the binuclear copper cryptate derivative [55]. The cyanide bridged Cu-Cu single bond gives one copper atom in **1CN-2D** the favored 18-electron configuration but the other copper atom only a 17-electron configuration, consistent with the doublet spin state.

A third doublet $\text{Cp}_2\text{Cu}_2(\text{CN})$ structure, namely **1CN-3D** (Fig. 2 and Table 1), is a C_1 structure with bridging Cp rings as well as a three-electron donor $\eta^2\text{-}\mu\text{-CN}$ bridging cyanide ligand similar to that in **1CN-1D**. Structure **1CN-3D** has all real vibrational frequencies and lies $14.0\text{ kcal mol}^{-1}$ (B3LYP) or $15.1\text{ kcal mol}^{-1}$ (BP86) above the global minimum **1CN-1D**. In **1CN-3D**, each copper atom is bonded to four carbon atoms of the two Cp rings

(two carbon atoms in each ring). The Cu-C distances to the bridging cyanide ligand are predicted to be 1.983 \AA and 2.328 \AA (B3LYP) or 1.955 \AA and 2.322 \AA (BP86). The three-electron donor cyanide ligand in **1CN-3D** is characterized by a short Cu-N distance of 2.150 \AA (B3LYP) or 2.096 \AA (BP86) as well as a relatively long C-N distance of 1.187 \AA (B3LYP) or 1.204 \AA (BP86), indicating a relatively low C-N bond order for the cyanide ligand. The theoretical vibrational frequency $\nu(\text{CN})$ of **1CN-3D** at 1977 cm^{-1} (BP86) corresponds to this bridging cyanide ligand. The predicted Cu-Cu distance of 2.514 \AA (B3LYP) or 2.480 \AA (BP86) in **1CN-3D** is consistent with the Cu-Cu single bond required to give one copper atom the favored 18-electron configuration and the other copper atom a 17-electron configuration, consistent with a binuclear doublet.

$\text{Cp}_2\text{Cu}_2(\text{CN})_2$

Six energetically low-lying structures were found for $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (Figs. 3 and 4 and Tables 2 and 3), including four singlet and two triplet structures. As expected, the B3LYP method favors the higher spin states, while the BP86 method favors the lower spin states [56].

Table 1 Total energies after zero point energy (ZPE) corrections (E_{ZPE} , in Hartree), relative energies (ΔE , in kcal mol^{-1}), numbers of imaginary vibrational frequencies (Nimag), Cu-Cu bond distances (\AA), and spin contamination $\langle S^2 \rangle$ for each of the doublet stationary points of $\text{Cp}_2\text{Cu}_2(\text{CN})$

		$\text{Cp}_2\text{Cu}_2(\text{CN})$ (1CN-1D) (C_1)	$\text{Cp}_2\text{Cu}_2(\text{CN})$ (1CN-2D) (C_{2v})	$\text{Cp}_2\text{Cu}_2(\text{CN})$ (1CN-3D) (C_1)
B3LYP	E_{ZPE}	-3760.915286	-3760.912182	-3760.89295
	ΔE	0.0	1.9	14.0
	Nimag	0	1(43i)	0
	Cu-Cu	2.694	2.394	2.514
	$\langle S^2 \rangle$	0.76	0.76	0.76
BP86	E_{ZPE}	-3761.370216	-3761.368401	-3761.34619
	ΔE	0.0	1.1	15.1
	Nimag	0	0	0
	Cu-Cu	2.629	2.380	2.480
	$\langle S^2 \rangle$	0.75	0.75	0.76

Table 2 Total energies after ZPE corrections (E_{ZPE} , in Hartree), relative energies (ΔE , in kcal mol⁻¹), numbers of imaginary vibrational frequencies (Nimag), Cu-Cu bond distances (Å), and spin contamination $\langle S^2 \rangle$ for each of the singlet stationary points of $\text{Cp}_2\text{Cu}_2(\text{CN})_2$

		$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-1S) (C_2)	$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-2S) (C_s)	$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-3S) (C_{2v})	$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-4S) (C_1)
B3LYP	E_{ZPE}	-3853.733747	-3853.733747	-3853.733747	-3853.733747
	ΔE	0.0	0.2	5.8	7.3
	Nimag	0	1(17i) ^a	0	0
	Cu-Cu	2.492	4.868	2.588	2.546
	$\langle S^2 \rangle$	0.00	0.00	0.00	0.00
BP86	E_{ZPE}	-3854.20819	-3854.20819	-3854.20819	-3854.20819
	ΔE	0.0	3.4	10.1	18.0
	Nimag	0	2(22i, 9i) ^a	0	0
	Cu-Cu	2.459	4.849	2.558	2.494
	$\langle S^2 \rangle$	0.00	0.00	0.00	0.00

^a When the finer grid (Grid=120, 974) was used, the imaginary vibrational frequencies disappeared

The $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ global minimum is the singlet coaxial structure **2CN-1S**, which is predicted to be a C_2 structure with two symmetrically bridging cyanide ligands and two terminal Cp rings (Fig. 3 and Table 2). In **2CN-1S**, each of the bridging cyanide ligands is coordinated through the C atom to the two copper atoms. These bridging cyanide ligands are predicted to exhibit $\nu(\text{CN})$ frequencies at 2065 and 2072 cm⁻¹ (BP86). The Cu-C distances to the two bridging cyanide ligands are 2.015 Å and 2.016 Å (B3LYP) or 1.996 Å and 1.997 Å (BP86). The Cu-Cu distance in **2CN-1S** is 2.492 Å (B3LYP) or 2.459 Å (BP86), which is consistent with the Cu-Cu single bond required to give both copper atoms the favored 18-electron configuration for a binuclear singlet with two one-electron donor bridging cyanide ligands.

The C_s singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-2S** lies 0.2 kcal mol⁻¹ (B3LYP) or 3.4 kcal mol⁻¹ (BP86) above **2CN-1S** (Fig. 3 and Table 2). Structure **2CN-2S** has a small imaginary frequency (17i cm⁻¹) by B3LYP, but two small imaginary frequencies (22i and 9i cm⁻¹) by BP86. All of

Table 3 Total energies after ZPE corrections (E_{ZPE} , in Hartree), relative energies (ΔE , in kcal mol⁻¹), numbers of imaginary vibrational frequencies (Nimag), Cu-Cu bond distance (Å), and spin contamination $\langle S^2 \rangle$ for the two triplet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structures

		$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-1T) (C_1)	$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (2CN-2T) (C_{2v})
B3LYP	E_{ZPE}	-3853.749406	-3853.695024
	ΔE	-9.8	24.3
	Nimag	0	0
	Cu-Cu	3.896	2.841
	$\langle S^2 \rangle$	2.02	2.02
BP86	E_{ZPE}	-3854.195504	-3854.15943
	ΔE	8.0	30.6
	Nimag	0	0
	Cu-Cu	3.867	2.848
	$\langle S^2 \rangle$	2.01	2.00

these small imaginary frequencies become real when a finer (120, 974) integration grid is used, which indicates that these small imaginary frequencies arise from numerical integration error. One of the cyanide ligands in **2CN-2S** is a bridging ligand whereas the other is a terminal ligand. The Cu-N-C bond angle to the bridging cyanide ligand is nearly linear at 177.8° (B3LYP) or 176.9° (BP86). The Cu-C-N bond angle to the bridging cyanide ligand is slightly bent at 163.9° (B3LYP) or 162.6° (BP86). The terminal cyanide ligand in **2CN-2S** exhibits a $\nu(\text{CN})$ frequency at 2140 cm⁻¹ (BP86), which is larger than the $\nu(\text{CN})$ frequency of the bridging cyanide ligand (2084 cm⁻¹), but close to the experimentally reported $\nu(\text{CN})$ frequencies for the bridging cyanide ligands in $[\text{Cu}_2([\text{14}]\text{4,1 l-diene-N}_4)_2\text{CN}]\text{Cl}_3$ and $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ (2130 cm⁻¹ and 2140 cm⁻¹, respectively) [24]. The Cu-C distance to the bridging cyanide ligand in **2CN-2S** is 1.850 Å (B3LYP) or 1.828 Å (BP86), and that to the terminal cyanide ligand is 1.893 Å (B3LYP) or 1.885 Å (BP86). The Cu-N distance to the bridging cyanide ligand is predicted to be 1.880 Å (B3LYP) or 1.874 Å (BP86). The neutral bridging cyanide ligand in **2CN-2S** can be considered a donor of a total of three electrons to the Cu_2 unit, namely one electron through the Cu-C bond to one copper atom and two electrons through the Cu-N bond to the other copper atom (d in Fig. 1). The Cu-Cu distance in **2CN-2S** is very long at 4.868 Å (B3LYP) or 4.849 Å (BP86), indicating the absence of any Cu-Cu bond. Each copper atom in **2CN-2S** can be considered to have the favorable 18-electron configuration, provided that the copper atom bearing the terminal cyanide group has a formal positive charge and the other copper atom a formal negative charge.

The next singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-3S** is a perpendicular C_{2v} structure with two bridging Cp ligands and two terminal cyanide ligands (Fig. 3 and Table 2). Structure **2CN-3S** has all real vibrational frequencies and lies 5.8 kcal mol⁻¹ (B3LYP) or 10.1 kcal mol⁻¹ (BP86) above **2CN-1S**. The $\nu(\text{CN})$ frequencies for the terminal

cyanide ligands are predicted to occur at 2137 and 2138 cm^{-1} (BP86). The Cu-C distances to the terminal cyanide ligands in **2CN-3S** are 1.896 Å (B3LYP) or 1.883 Å (BP86). The Cu-Cu distance is 2.588 Å (B3LYP) or 2.558 Å (BP86), corresponding to the Cu-Cu single bond required to give each copper atom the favored 18-electron configuration with two one-electron donor terminal cyanide ligands and assuming that the five π -electrons from each bridging Cp ring are divided equally between the two copper atoms.

The last singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-4S** (Fig. 3 and Table 2) is a C_1 structure lying 7.3 kcal mol^{-1} (B3LYP) or 18.0 kcal mol^{-1} (BP86) above **2CN-1S**. One of the cyanide ligands in **2CN-4S** is a bridging ligand whereas the other is a terminal ligand. Structure **2CN-4S** has a fascinating geometry since one copper atom is bonded to two terminal Cp ligands whereas the other copper atom is bonded only to the two cyanide ligands. One of the terminal Cp ligands in **2CN-4S** is pentahapto whereas the other terminal Cp ligand is a dihapto ligand. The Cu-C distances to the bridging cyanide ligand are 1.927 and 2.055 Å (B3LYP) or 1.912 and 2.017 Å (BP86), whereas the Cu-C distance to the terminal cyanide ligand is 1.881 Å (B3LYP) or 1.868 Å (BP86). The bridging and terminal cyanide ligands exhibit $\nu(\text{CN})$ frequencies at 2059 and 2135 cm^{-1} (BP86), respectively. The Cu-Cu distance in **2CN-4S** is 2.546 Å (B3LYP) or 2.494 Å (BP86), suggesting a formal single bond.

The two triplet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structures, namely **2CN-1T** and **2CN-2T**, both have all real vibrational frequencies and negligible spin contamination as indicated by $\langle S^2 \rangle$ values close to the ideal 2.00 (Fig. 4 and Table 3). The lowest energy of these triplet structures, namely **2CN-1T**, has two terminal Cp rings and two three-electron donor η^2 - μ -CN bridging cyanide ligands. The B3LYP method predicts structure **2CN-1T** to lie 9.8 kcal mol^{-1} below **2CN-1S**. However, the BP86 method predicts structure **2CN-1T** to lie 8.0 kcal mol^{-1} above **2CN-1S**. This is another example of the tendency of the B3LYP method to favor higher spin states relative to the BP86 method [56]. Realistically, this triplet state is likely to be nearly degenerate with the lowest singlet. The Cu-C distances to one of the bridging cyanide ligands in **2CN-1T** are 1.968 Å and 2.769 Å (B3LYP) or 1.929 Å and 2.745 Å (BP86), whereas the Cu-C distances to the other bridging cyanide ligand are 1.968 Å and 2.770 Å (B3LYP) or 1.929 Å and 2.747 Å (BP86). The two η^2 - μ -CN groups in **2CN-1T** have the expected short Cu-N distances of 2.084 Å and 2.085 Å (B3LYP) or both 2.073 Å (BP86), the expected relatively long C-N distances of 1.179 Å (B3LYP) or 1.194 Å (BP86), and exhibit the expected low $\nu(\text{CN})$ frequencies of 2050 and 2057 cm^{-1} (BP86). The Cu-Cu distance for **2CN-1T** is very long, namely 3.896 Å by B3LYP or

3.867 Å by BP86, indicating the absence of a direct copper-copper bond. This gives each copper atom a 19-electron configuration, corresponding to a binuclear triplet.

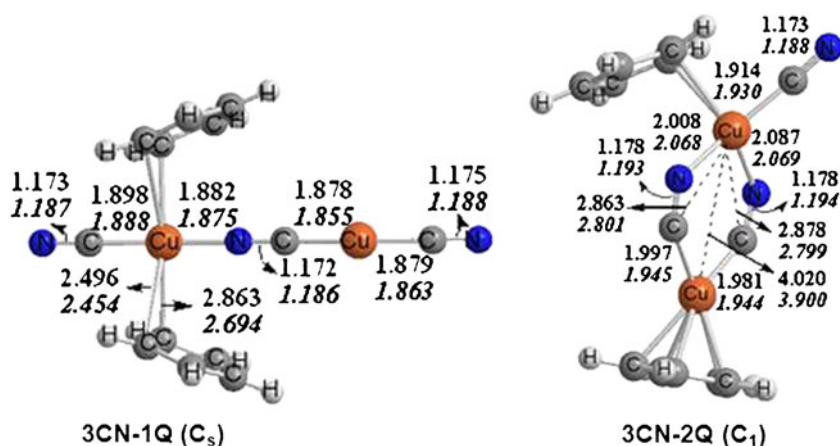
The other triplet structure for $\text{Cp}_2\text{Cu}_2(\text{CN})_2$, namely **2CN-2T**, lies at the relatively high energy of 24.3 kcal mol^{-1} (B3LYP) or 30.6 kcal mol^{-1} (BP86) above **2CN-1S**. Structure **2CN-2T** is a C_{2v} perpendicular dimetalloocene structure with two terminal cyanide ligands and thus is geometrically similar to **2CN-3S**. In **2CN-2T**, each copper atom is bonded to four carbon atoms of the two Cp rings. The terminal cyanide ligands have Cu-C distances of 1.958 Å (B3LYP) or 1.946 Å (BP86) and exhibit $\nu(\text{CN})$ frequencies at 2122 and 2123 cm^{-1} (BP86). These $\nu(\text{CN})$ frequencies are very close to the experimentally reported $\nu(\text{CN})$ frequencies for the terminal cyanide ligands in $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2] \cdot 2(\text{CH}_3\text{CN}) \cdot 2(\text{C}_6\text{H}_6)$ (2079 cm^{-1} and 2094 cm^{-1}) and $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2] \cdot 2(\text{H}_2\text{O}) \cdot 2(\text{C}_6\text{H}_6)$ (2108 cm^{-1}) [57]. The Cu-Cu distance in **2CN-2T** is 2.841 Å (B3LYP) or 2.848 Å (BP86). This can be interpreted as the formal Cu-Cu single bond required to give each copper atom the 17-electron configuration for a binuclear triplet with two one-electron donor terminal cyanide ligands.

$\text{Cp}_2\text{Cu}_2(\text{CN})_3$

Finally, we turn to the copper dimers with three CN groups. Thus, optimizations have been carried out on doublet and quartet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structures, in which the three cyanide ligands are either bridging or terminal. (Figs. 5 and 6 and Tables 4 and 5). All of the doublet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structures have three-electron donor bridging η^2 - μ -CN cyanide ligands.

The global minimum $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structure is the doublet **3CN-1D** with one η^2 - μ -CN bridging cyanide ligand, two terminal cyanide ligands, and two terminal Cp rings (Fig. 5 and Table 4). Structure **3CN-1D** has negligible spin contamination with $\langle S^2 \rangle = 0.76$ (B3LYP) or 0.75 (BP86) and has all real vibrational frequencies. The Cu-C and Cu-N distances to the bridging cyanide ligand in **3CN-1D** are 1.901 and 1.991 Å (B3LYP) or 1.898 and 1.916 Å (BP86), respectively. The corresponding $\nu(\text{CN})$ frequency to the bridging cyanide ligand is predicted to be 2152 cm^{-1} (BP86), which is slightly higher than the $\nu(\text{CN})$ frequencies of the two terminal cyanide ligands (2141 and 2126 cm^{-1}). The bond angles of Cu-C-N and Cu-N-C to this bridging cyanide ligand are 167.3° (B3LYP) or 166.3° (BP86) and 153.0° (B3LYP) or 159.3° (BP86). The Cu-C distances to the terminal cyanide ligands are 1.890 and 1.940 Å (B3LYP) or 1.894 and 1.907 Å (BP86), respectively. The Cu-Cu distance in **3CN-1D** is 4.821 Å by B3LYP or 4.825 Å by BP86, indicating no direct chemical interaction

Fig. 6 The two quartet stationary points of $\text{Cp}_2\text{Cu}_2(\text{CN})_3$



between the two Cu atoms. One of the copper atoms in **3CN-1D** has an 18-electron configuration but the other copper atom has a 19-electron configuration, consistent with the doublet spin multiplicity.

Another doublet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structure **3CN-2D** has one copper atom bonded to a portion of each Cp ring and the second copper atom bonded only to cyanide ligands (Fig. 5 and Table 4). Structure **3CN-2D** has two three-electron donor bridging $\eta^2\text{-}\mu\text{-CN}$ cyanide ligands and one terminal cyanide ligand, and lies at the relatively high energy of 22.0 kcal mol⁻¹ (B3LYP) or 32.0 kcal mol⁻¹ (BP86) above the global minimum **3CN-1D**. Structure **3CN-2D** is found to be problematic, having serious spin contamination with the spin expectation value $\langle S^2 \rangle = 1.75$ (B3LYP) or 1.24 (BP86), which is much higher than the ideal 0.75. For the bridging cyanide ligands, the longer Cu-C distances are 2.828 Å and 2.842 Å (B3LYP) or 2.826 Å and 2.862 Å (BP86), and the shorter ones are 1.941 Å and 1.969 Å (B3LYP) or 1.912 Å and 1.955 Å (BP86). Again

there are very short Cu-N distances, namely 2.168 Å and 2.180 Å (B3LYP) or 2.054 Å and 2.066 Å (BP86), indicating that both bridging cyanide ligands are three-electron donor $\eta^2\text{-}\mu\text{-CN}$ groups, consistent with their low $\nu(\text{CN})$ frequencies of 2032 and 2040 cm⁻¹ (BP86). The $\nu(\text{CN})$ frequency of the terminal cyanide ligand in **3CN-2D** is predicted to be significantly higher at 2108 cm⁻¹ (BP86), very close to the experimentally reported $\nu(\text{CN})$ frequencies for the terminal cyanide ligands in $[\textit{n}\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2] \cdot 2(\text{CH}_3\text{CN}) \cdot 2(\text{C}_6\text{H}_6)$ (2079 cm⁻¹ and 2094 cm⁻¹) and $[\textit{n}\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2] \cdot 2(\text{H}_2\text{O}) \cdot 2(\text{C}_6\text{H}_6)$ (2108 cm⁻¹) [57]. The long Cu-Cu distance in **3CN-2D** of 3.962 Å (B3LYP) or 4.013 Å (BP86) clearly indicates the absence of a direct Cu-Cu bond.

Two quartet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structures were found (Fig. 6 and Table 5), all with very small spin contamination (Table 5). The lowest energy of these quartet $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structures, namely **3CN-1Q**, is a C_s structure with one bridging and two terminal cyanide ligands. Structure **3CN-**

Table 4 Total energies after ZPE corrections (E_{ZPE} , in Hartree), relative energies (ΔE , in kcal mol⁻¹), numbers of imaginary vibrational frequencies (Nimag), Cu-Cu bond distance (Å), and spin contamination $\langle S^2 \rangle$ for each of the doublet stationary points of $\text{Cp}_2\text{Cu}_2(\text{CN})_3$

		$\text{Cp}_2\text{Cu}_2(\text{CN})_3$ (3CN-1D) (C_1)	$\text{Cp}_2\text{Cu}_2(\text{CN})_3$ (3CN-2D) (C_1)
B3LYP	E_{ZPE}	-3946.559983	-3946.524981
	ΔE	0.0	22.0
	Nimag	0	0
	Cu-Cu	4.821	3.962
	$\langle S^2 \rangle$	0.76	1.75
BP86	E_{ZPE}	-3947.027201	-3946.976183
	ΔE	0.0	32.0
	Nimag	0	0
	Cu-Cu	4.825	4.013
	$\langle S^2 \rangle$	0.75	1.24

Table 5 Total energies after ZPE corrections (E_{ZPE} , in Hartree), relative energies (ΔE , in kcal mol⁻¹), numbers of imaginary vibrational frequencies (Nimag), Cu-Cu bond distance (Å), and spin contamination $\langle S^2 \rangle$ for each of the quartet stationary points of $\text{Cp}_2\text{Cu}_2(\text{CN})_3$

		$\text{Cp}_2\text{Cu}_2(\text{CN})_3$ (3CN-1Q) (C_s)	$\text{Cp}_2\text{Cu}_2(\text{CN})_3$ (3CN-2Q) (C_1)
B3LYP	E_{ZPE}	-3946.559983	-3946.559983
	ΔE	13.2	16.1
	Nimag	0	0
	Cu-Cu	—	4.020
	$\langle S^2 \rangle$	3.78	3.77
BP86	E_{ZPE}	-3947.027201	-3947.027201
	ΔE	30.7	25.3
	Nimag	0	0
	Cu-Cu	—	3.900
	$\langle S^2 \rangle$	3.76	3.76

1Q has all real vibrational frequencies and lies 13.2 kcal mol⁻¹ (B3LYP) or 30.7 kcal mol⁻¹ (BP86) above **3CN-1D**. Structure **3CN-1Q**, like **3CN-2D**, is an interesting structure in which one copper atom is bonded to a portion of the two Cp rings (η^2 -C₅H₅ by B3LYP or η^4 -C₅H₅ by BP86) and the other copper atom is only bonded to the cyanide ligands. In addition, in **3CN-1Q**, the Cu-C-N and Cu-N-C bond angles to this bridging cyanide ligand are essentially linear, namely 179.5° and 178.8° by B3LYP or 178.8° and 178.5° by BP86. This bridging cyanide ligand exhibits a ν (CN) frequency at 2120 cm⁻¹, which is very close to the experimentally reported ν (CN) frequencies for the bridging cyanide ligands in [Cu₂([14]4,1 l-diene-N₄)₂CN]Cl₃ and [Cu₂(tren)₂-(CN)₂](BPh₄)₂ (2130 cm⁻¹ and 2140 cm⁻¹) [24]. Moreover, the ν (CN) frequencies for the bridging cyanide ligand are nearly equal to the frequencies for the terminal cyanide ligands, namely 2124 and 2131 cm⁻¹ (BP86). The Cu-C and Cu-N distances to the bridging cyanide ligand are 1.878 and 1.882 Å (B3LYP) or 1.855 and 1.875 Å (BP86), and the Cu-C distances to the terminal cyanide ligands are 1.879 and 1.898 Å (B3LYP) or 1.863 and 1.888 Å (BP86).

The other quartet Cp₂Cu₂(CN)₃ structure **3CN-2Q** has two three-electron donor bridging η^2 - μ -CN cyanide ligands, one terminal cyanide ligand, and two terminal Cp rings (Fig. 6 and Table 5). Structure **3CN-2Q** is predicted to lie 16.1 kcal mol⁻¹ (B3LYP) or 25.3 kcal mol⁻¹ (BP86) above **3CN-1D**. In **3CN-2Q**, the “upper” copper atom is bonded to a portion of one Cp ring (η^2 -C₅H₅ by B3LYP or η^4 -C₅H₅ by BP86), but the “lower” copper atom is bonded to all five carbon atoms of the other Cp ring (η^5 -C₅H₅). The longer Cu-C distances to the bridging cyanide ligands are 2.863 Å and 2.878 Å (B3LYP) or 2.801 Å and 2.799 Å (BP86), and the shorter ones are 1.981 Å and 1.997 Å (B3LYP) or 1.944 Å and 1.945 Å (BP86). Both three-electron donor cyanide ligands are characterized by short Cu-N distances of 2.008 Å and 2.087 Å (B3LYP) or 2.068 Å and 2.069 Å (BP86), relatively long C-N distances of 1.178 Å (B3LYP) or 1.193 Å and 1.194 Å (BP86), and low ν (CN) frequencies of 2042 and 2056 cm⁻¹ (BP86). The ν (CN) frequency for the terminal cyanide ligand is at

2123 cm⁻¹ (BP86), which is very close to the experimentally reported ν (CN) frequencies for the terminal cyanide ligands in [*n*-Bu₄N]₂[Mo₂^{II,III}(CN)₆(dppm)₂] · 2(CH₃CN) · 2(C₆H₆) (2079 cm⁻¹ and 2094 cm⁻¹) and [*n*-Bu₄N]₂[Mo₂^{II,III}(CN)₆(dppm)₂] · 2(H₂O) · 2(C₆H₆) (2108 cm⁻¹) [57]. The Cu-C distance to the terminal cyanide ligand is 1.914 Å (B3LYP) or 1.930 Å (BP86). The Cu-Cu distance in **3CN-2Q** is 4.020 Å (B3LYP) or 3.900 Å (BP86), indicating the lack of a direct copper-copper bond.

Dissociation energies

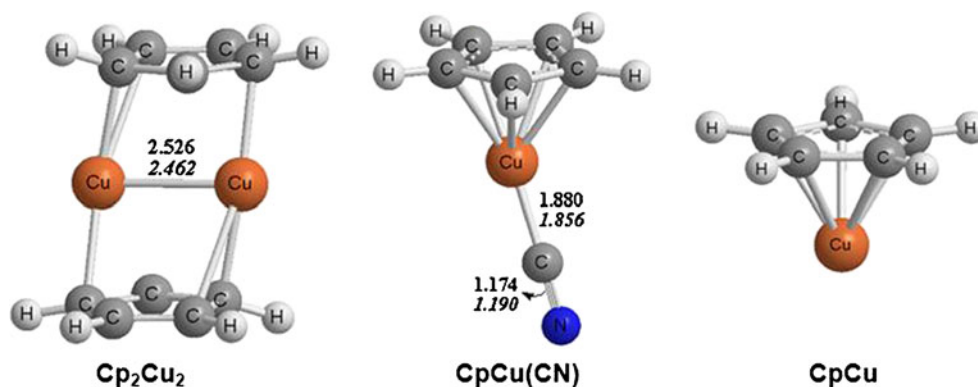
Table 6 lists the dissociation energies for the reactions Cp₂Cu₂(CN)_{*n*} → Cp₂Cu₂(CN)_{*n-1*} + 1/2 (CN)₂ considering the lowest energy structures. Such dissociation of Cp₂Cu₂(CN)₃ is predicted to be exothermic by -10.1 kcal mol⁻¹ (B3LYP) or -6.5 kcal mol⁻¹ (BP86). This suggests that Cp₂Cu₂(CN)₃ is likely to be a thermodynamically disfavored molecule. This is consistent with the observed relative instability of copper oxidation states above +2 in most coordination environments [23]. However, the dissociation energies for Cp₂Cu₂(CN)₂ and Cp₂Cu₂(CN) are slightly endothermic from 2 to 7 kcal mol⁻¹ suggesting that Cp₂Cu₂(CN)₂ and Cp₂Cu₂(CN) are marginally viable with respect to cyanide loss. This suggests that both Cp₂Cu₂(CN)₂ and Cp₂Cu₂(CN) might be stable enough to be observed at low temperatures. For comparison, the dissociation of Cu(CN)₂ into CuCN + 1/2 (CN)₂ at -15.7 kcal mol⁻¹ (B3LYP) or -11.8 kcal mol⁻¹ (BP86) is predicted to be more exothermic than that of either Cp₂Cu₂(CN)₃ or Cp₂Cu₂(CN)₂. This suggests that coordination of the Cp ligand to copper in formal oxidation states above +1 stabilizes Cu-CN bonds, providing a chance to obtain isolable copper cyanide complexes in higher oxidation state.

The dissociation energies of the binuclear derivatives, Cp₂Cu₂(CN)₂ and Cp₂Cu₂(CN), into mononuclear fragments are also reported (Table 6). In order to obtain these energetic data, the structures of the mononuclear CpCu(CN) and CpCu were optimized by the same DFT methods (Fig. 7). The large predicted energies of 29.4 kcal mol⁻¹ (B3LYP) or 36.5 kcal mol⁻¹ (BP86) for the dissociation of

Table 6 Dissociation energies (kcal mol⁻¹) including zero-point vibrational energy (ZPVE) corrections for the Cp₂Cu₂(CN)_{*n*} derivatives

	B3LYP	BP86
Cp ₂ Cu ₂ (CN) ₃ (3CN-1D) → Cp ₂ Cu ₂ (CN) ₂ (2CN-1T/2CN-1S) + 1/2 (CN) ₂	-10.1	-6.5
Cp ₂ Cu ₂ (CN) ₂ (2CN-1T/2CN-1S) → Cp ₂ Cu ₂ (CN) (1CN-1D) + 1/2 (CN) ₂	4.7	5.4
Cp ₂ Cu ₂ (CN) (1CN-1D) → Cp ₂ Cu ₂ + 1/2 (CN) ₂	2.1	6.2
Cp ₂ Cu ₂ (CN) ₂ (2CN-1T/2CN-1S) → 2CpCu(CN)	29.4	36.5
Cp ₂ Cu ₂ (CN) (1CN-1D) → CpCu(CN) + CpCu	44.3	54.6
2Cp ₂ Cu ₂ (CN) ₂ (2CN-1T/2CN-1S) → Cp ₂ Cu ₂ (CN) ₃ (3CN-1D) + Cp ₂ Cu ₂ (CN) (1CN-1D)	14.8	11.9
Cu(CN) ₂ → CuCN + 1/2 (CN) ₂	-15.7	-11.8

Fig. 7 Optimized Cp_2Cu_2 , $\text{CpCu}(\text{CN})$ and CpCu fragments at the same level of theory



$\text{Cp}_2\text{Cu}_2(\text{CN})_2$ into two $\text{CpCu}(\text{CN})$ fragments indicate that the $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ global minimum **2CN-1S** or **2CN-1T** is viable with respect to dissociation into mononuclear fragments. The energy for the dissociation of $\text{Cp}_2\text{Cu}_2(\text{CN})$ into $\text{CpCu}(\text{CN}) + \text{CpCu}$ is even higher at $44.3 \text{ kcal mol}^{-1}$ (B3LYP) or $54.6 \text{ kcal mol}^{-1}$ (BP86). Furthermore, the disproportionation of $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ (**2CN-1T/2CN-1S**) into $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ (**3CN-1D**) + $\text{Cp}_2\text{Cu}_2(\text{CN})$ (**1CN-1D**), is predicted to be endothermic by $14.8 \text{ kcal mol}^{-1}$ (B3LYP) or $11.9 \text{ kcal mol}^{-1}$ (BP86), suggesting at least marginal viability for $\text{Cp}_2\text{Cu}_2(\text{CN})_2$.

Discussion

The lowest energy structures of $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ ($n=1, 2, 3$) generally have terminal Cp rings, and bridging cyanide ligands up to a maximum of two bridges. The monocyanide $\text{Cp}_2\text{Cu}_2(\text{CN})$ with one Cu(II) atom and one Cu(I) atom is formally a mixed oxidation state derivative with an average copper formal oxidation state of +1.5. The Cu-Cu distance in the $\text{Cp}_2\text{Cu}_2(\text{CN})$ global minimum structure **1CN-1D** is $\sim 0.2 \text{ \AA}$ longer than the experimental Cu-Cu single bond distance [55] in a binuclear dicopper cryptate complex with the same average copper oxidation state of +1.5 as in $\text{Cp}_2\text{Cu}_2(\text{CN})$. However, it can still be interpreted as a formal single bond. The neutral bridging cyanide ligand in **1CN-1D** is formally a two-electron donor to the copper atom, being within bonding distance to both the carbon and nitrogen and a one-electron donor to the other copper atom, which is within conventional bonding distance of only the carbon atom. This gives one copper atom the favored 18-electron configuration and the other copper a 19-electron configuration.

The dicyanide, $\text{Cp}_2\text{Cu}_2(\text{CN})_2$, is formally a complex of d^9 Cu(II) with a single unpaired electron per copper atom. Therefore, the lowest energy $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure with two Cu(II) atoms is expected to be a triplet spin state. However, low energy $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structures are found in both the singlet and triplet spin states. The B3LYP method

predicts lower energies for the triplet structures, while the BP86 method predicts lower energies for the singlet structures. This is consistent with previous observation [56] of the tendency of the B3LYP method to favor higher spin states relative to the BP86 method.

The lowest energy singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-1S** (Fig. 3 and Table 2) is a C_2 structure with two bridging cyanide ligands and two terminal Cp rings. The predicted Cu-Cu distance in **2CN-1S** of $\sim 2.48 \text{ \AA}$ can be interpreted as a formal single bond, thereby giving both copper atoms the favored 18-electron configuration.

The lowest energy triplet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-1T** (Fig. 4 and Table 3) is an unsymmetrical structure with two bridging cyanide ligands and two terminal Cp rings. This structure is very different from the singlet structure **2CN-1S**. The bridging cyanide ligands donate two electrons to one copper atom through a dative $\text{N} \rightarrow \text{Cu}$ bond and a single electron to the other copper atom through a $\text{Cu}-\text{C}$ covalent bond. This type of three-electron donor bridging cyanide ligand is different from the $\eta^2-\mu\text{-CN}$ ligand in the $\text{Cp}_2\text{Cu}_2(\text{CN})$ structure **1CN-1D**, where the cyanide carbon is within bonding distance of both copper atoms. The long Cu-Cu distance in **2CN-1T** of $\sim 3.9 \text{ \AA}$ indicates the lack of a direct copper-copper bond. This gives each copper atom a 19-electron configuration consistent with a binuclear triplet structure.

The tricyanide $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ with one Cu(II) atom and one Cu(III) atom is formally a mixed valence compound with an average copper oxidation state of +2.5 [58]. The global minimum $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ structure is the doublet **3CN-1D** with one bridging cyanide ligand, two terminal cyanide ligands, two terminal Cp rings, and a long non-bonding $\text{Cu} \cdots \text{Cu}$ distance of $\sim 4.8 \text{ \AA}$. This structure is predicted to be thermodynamically unstable toward cyanogen loss to give $\text{Cp}_2\text{Cu}_2(\text{CN})_2$.

Some fairly low energy $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ structures are also found having one or two bridging Cp rings. Such a $\text{Cp}_2\text{Cu}_2(\text{CN})$ structure (**1CN-3D**) has a three-electron donor bridging cyanide ligand, which is characterized by a short Cu-N distance and a relatively long C-N distance. The

$\nu(\text{CN})$ frequency in **1CN-3D** of 1977 cm^{-1} (BP86) corresponds to the bridging cyanide ligand. The predicted Cu-Cu distance of $\sim 2.5\text{ \AA}$ in **1CN-3D** corresponds to a Cu-Cu single bond, thereby giving one copper atom the favored 18-electron configuration and the other copper atom a 17-electron configuration for a doublet spin state structure. For $\text{Cp}_2\text{Cu}_2(\text{CN})_2$, both singlet and triplet perpendicular structures, namely **2CN-3S** and **2CN-2T**, respectively, were found having two bridging Cp rings and two terminal cyanide ligands (Figs. 3 and 4). In addition, an unsymmetrical singlet $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ structure **2CN-4S** was found with both Cp rings bonded to one copper atom as terminal ligands and only cyanide ligands bonded to the second copper atom. For $\text{Cp}_2\text{Cu}_2(\text{CN})_3$, both doublet (**3CN-2D**) and quartet (**3CN-1Q**) structures are found with one copper atom bonded to a portion of the two Cp rings and only cyanide ligands bonded to the second copper atom. Structure **3CN-2D** has two three-electron donor bridging $\eta^2\text{-}\mu\text{-CN}$ cyanide ligands and one terminal cyanide ligand, while structure **3CN-1Q** has one bridging and two terminal cyanide ligands.

A study of the energetics of cyanogen dissociation $\text{Cp}_2\text{Cu}_2(\text{CN})_n \rightarrow \text{Cp}_2\text{Cu}_2(\text{CN})_{n-1} + \frac{1}{2}(\text{CN})_2$ (Table 6) suggests that $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ is likely to be a thermodynamically disfavored molecule, while $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ and $\text{Cp}_2\text{Cu}_2(\text{CN})$ are marginally viable. The energies for dissociation of any of the binuclear $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ species into mononuclear fragments is clearly very large (29 to 55 kcal mol^{-1}). The dicyanide $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ is predicted to be viable by $\sim 12\text{ kcal mol}^{-1}$ with respect to disproportionation into $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ and $\text{Cp}_2\text{Cu}_2(\text{CN})$.

Conclusions

The lowest energy structures of the binuclear cyclopentadienylcopper cyanides $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$; $n=1, 2, 3$) are predicted to have terminal Cp rings and bridging cyanide ligands up to a maximum of two bridges, while higher-energy $\text{Cp}_2\text{Cu}_2(\text{CN})_n$ structures are found with bridging Cp rings. The $\text{Cp}_2\text{Cu}_2(\text{CN})$ and $\text{Cp}_2\text{Cu}_2(\text{CN})_2$ derivatives, having average copper oxidation states of +1.5 and +2, respectively, are predicted to have marginal viability. However, with respect to cyanogen loss, the $\text{Cp}_2\text{Cu}_2(\text{CN})_3$ derivative, in which the copper atoms have an average oxidation state +2.5, is likely to be thermodynamically disfavored.

Acknowledgments We are indebted to the Chinese National Natural Science Foundation (20903010 and 20873045), Research Fund for the Doctoral Program of Higher Education (200800071019), China Postdoctoral Science Foundation funded project in China as well as the U. S. National Science Foundation (Grants CHE-1054286 and CHE-0716718) for support of this research.

References

- Bartholomew ER, Bertz SH, Cope SK, Murphy MD, Ogle CA (2008) *J Am Chem Soc* 130:11244–11245
- Bartholomew ER, Bertz SH, Cope SK, Murphy MD, Ogle CA, Thomas AA (2010) *Chem Commun* 46:1253–1254
- Gv K, Jastrzebski JTBH, Lamsabhi AM, Yáñez M, Salpin JY, Tortajada J (2009) In: Rappoport Z, Marek I (eds) *The chemistry of organocopper compounds*. Wiley, Chichester, pp 23–346
- Bennett MV, Shores MP, Beauvais LG, Long JR (2000) *J Am Chem Soc* 122:6664–6668
- Kuyper J, Boxhoorn G (1987) *J Catal* 105:163–174
- Miller J (2001) S, Manson JL. *Acc Chem Res* 34:563–570
- Beauvais LG, Long JR (2002) *J Am Chem Soc* 124:12096–12097
- Dunbar KR, Heintz RA (1997) *Prog Inorg Chem* 45:283–391
- Ohba M, Fukita N, Okawa H (1997) *J Chem Soc Dalton Trans* 1733–1737
- Richardson GN, Brand U, Vahrenkamp H (1999) *Inorg Chem* 38:3070–3079
- Zhu N, Vahrenkamp H (1997) *Chem Ber* 130:1241–1252
- Colacio E, Kivekas R, Lloret F, Sunberg M, Suarez-Varela J, Bardaji M, Laguna A (2002) *Inorg Chem* 41:5141–5149
- Komatsu T, Nakamura T, Matsukawa N, Yamochi H, Saito G, Ito H, Ishiguro T, Kusunoki M, Sakaguchi K (1991) *Solid State Commun* 80:843–847
- Drozдова O, Saito G, Yamochi H, Ookubo K, Yakushi K, Uruichi M, Ouahab L (2001) *Inorg Chem* 40:3265–3266
- Fanta PE (1964) *Chem Rev* 64:613–632
- Cotton FA, Marks T (1969) *J Am Chem Soc* 91:7281–7285
- Cotton FA, Takats J (1970) *J Am Chem Soc* 92:2353–2358
- Whitesides GM, Fleming JS (1967) *J Am Chem Soc* 89:2855–2859
- Cotton FA, Marks TJ (1970) *J Am Chem Soc* 92:5114–5117
- Piper TS, Wilkinson G (1956) *J Inorg Nucl Chem* 1:165–174
- Akbayeva DN, Scherer OJ (2001) *Z Anorg Allgem Chem* 627:1429–1430
- Saegusa T, Ito Y, Tomita S (1971) *J Am Chem Soc* 93:5656–5661
- Cotton FA, Wilkinson G, Murillo CA, Bochmann M (1999) *Advanced inorganic chemistry*. Wiley, New York, Ch 17H
- Duggan DM, Jungst RG, Mann KR, Stucky GD, Hendrickson DN (1974) *J Am Chem Soc* 96:3443–3450
- Zhan SZ, Li W, Wang JG, Liang AQ, Deng YF (2007) *J Organomet Chem* 692:3568–3573
- Ehlers AW, Frenking G (1994) *J Am Chem Soc* 116:1514–1520
- Delley B, Wrinn M, Lüthi HP (1994) *J Chem Phys* 100:5785–5791
- Li J, Schreckenbach G, Ziegler T (1995) *J Am Chem Soc* 117:486–494
- Jonas V, Thiel W (1995) *J Chem Phys* 102:8474–8484
- Barckholtz TA, Bursten BE (1998) *J Am Chem Soc* 120:1926–1927
- Jemmis ED, Giju KT (1998) *J Am Chem Soc* 120:6952–6964
- Niu S, Hall MB (2000) *Chem Rev* 100:353–406
- Cotton FA, Gruhn NE, Gu J, Huang P, Lichtenberger DL, Murillo C, van Dorn LO, Wilkinson CC (2002) *Science* 298:1971–1974
- Macchi P, Sironi A (2003) *Coord Chem Rev* 238:383–412
- Borowski T, Georgiev V, Siegbahn PEM (2005) *J Am Chem Soc* 127:17303–17314
- Ziegler T, Autschbach J (2005) *Chem Rev* 105:2695–2722
- Mota AJ, Dedieu A, Bour C, Suffert J (2005) *J Am Chem Soc* 127:7171–7182
- Bühl M, Kabrede H (2006) *J Chem Theor Comput* 2:1282–1290
- Brynda M, Gagliardi L, Widmark PO, Power PP, Roos BO (2006) *Angew Chem Int Edn* 45:3804–3807
- Zhao Y, Truhlar DG (2006) *J Chem Phys* 124:224105

41. Strickland NS, Harvey JN (2007) *J Phys Chem B* 111:841–852
42. Becke AD (1993) *J Chem Phys* 98:5648–5652
43. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
44. Becke AD (1988) *Phys Rev A* 38:3098–3100
45. Perdew JP (1986) *Phys Rev B* 33:8822–8824
46. Feng X, Gu J, Xie Y, King RB, Schaefer HF (2007) *J Chem Theor Comput* 3:1580–1587
47. Zhao S, Wang W, Li Z, Liu ZP, Fan K, Xie Y, Schaefer HF (2006) *J Chem Phys* 124:184102
48. Dunning TH (1970) *J Chem Phys* 53:2823–2833
49. Dunning TH, Hay PJ (1977) In: Schaefer HF (ed) *Methods of electronic structure theory*. Plenum, New York, pp 1–27
50. Huzinaga S (1965) *J Chem Phys* 42:1293–1302
51. Wachters AJH (1970) *J Chem Phys* 52:1033–1036
52. Hood DM, Pitzer RM, Schaefer HF (1979) *J Chem Phys* 71:705–812
53. Frisch MJ et al. (2004) *Gaussian 03, Revision C 02*. Gaussian Inc, Wallingford, CT (see Supporting Information for details)
54. Papas BN, Schaefer HF (2006) *J Mol Struct THEOCHEM* 768:175–181
55. Al-Obaidi A, Baranovic G, Coyle J, Coates CG, McGarvey JJ, McKee V, Nelson J (1998) *Inorg Chem* 37:3567–3574
56. Reiher M, Salomon O, Hess BA (2001) *Theor Chem Acc* 107:48–55
57. Szalay PS, Dunbar KR (2000) *Inorg Chem Commun* 3:49–51
58. Richardson DE, Taube H (1984) *Coord Chem Rev* 60:107–129