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REGULAR ARTICLE

Copper formal oxidation states above +1 in organometallic chemistry: the possibility of synthesizing cyclopentadienylcopper chlorides by oxidative addition reactions

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Abstract Although organometallic compounds of Cu(I) have been known for some time, including cyclopentadienyl derivatives of the type CpCuL (Cp = η^5-cyclopentadienyl ligand; L = phosphine or CO), organometallic compounds of copper in higher formal oxidation states are essentially unknown except for a few alkylcopper(III) and allylcopper(III) derivatives, only stable at very low temperatures. Theoretical studies on the cyclopentadienyl derivatives $Cp_2Cu_2Cl_n$ ($n = 1, 2, 3$) indicate a preference for structures with terminal Cp rings and bridging Cl atoms up to a maximum of two of the latter. However, $Cp_2Cu_2Cl_n$ ($n = 1, 2, 3$) structures with bridging Cp rings are found at only slightly higher energies. The lowest energy doublet mixed Cu(II/III) oxidation state $Cp_2Cu_2Cl_3$ structure with a single bridging Cl atom can be formally derived from the lowest energy doublet Cu(I/II) mixed oxidation state Cp_2Cu_2Cl structure by oxidative addition of Cl_2.

Keywords Copper · Cyclopentadienyl · Oxidative addition reactions · Density functional theory

1 Introduction

The landmark discovery of the sandwich compound ferrocene [1, 2], (η^5-$C_5H_5)_2$Fe, in 1951 was followed shortly by the synthesis of similar sandwich compounds of the other first-row transition metals from vanadium to nickel, inclusive. However, an analogous copper sandwich compound (η^5-$C_5H_5)_2$Cu still has not been synthesized, even though ferrocene has now been known for nearly 60 years. This suggests that the formal copper(II) oxidation state, although the most common copper oxidation state in "classical" inorganic chemistry, is too strongly oxidizing to be compatible with Cp rings in a sandwich compound (Cp = η^5-cyclopentadienyl).

The copper(I) oxidation state appears to be more compatible than copper(II) with cyclopentadienyl ligands. The first such compound was $(C_5H_5)Cu(PEt_3)$, which was reported in 1956 by Piper and Wilkinson [3] as the product of the reaction of Cu_2O with triethylphosphine and cyclopentadiene. Initial studies relating to the structure of $(C_5H_5)Cu(PEt_3)$ suggested a monohapto η^1-C_5H_5 ring, even though that would give the copper atom only a 14-electron configuration. However, a 1970 structure determination by X-ray diffraction [4, 5] showed that the C_5H_5 ring in $(C_5H_5)Cu(PEt_3)$ is a pentahapto ligand, thereby giving the copper atom the favored 18-electron configuration.

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Another interesting CpCuL derivative is the carbonyl (L = CO), which, like CpCu(PEt$_3$) discussed above, has the favored 18-electron configuration. Thus, CpCuCO fits into the series of stable cyclopentadienyl metal carbonyls of the first-row transition metals and is isoelectronic with CpNiNO, another molecule synthesized in the early days of cyclopentadienyl metal chemistry [6]. In this connection, unsubstituted (η^5-C$_5$H$_5$)CuCO was synthesized by Cotton and Marks [7] in 1970 by the reaction of CuCl with TlCp in the presence of CO. However, unlike the very stable (η^5-C$_5$H$_5$)NiNO, the copper derivative (η^5-C$_5$H$_5$)CuCO was found to be so unstable that it could only be kept in pentane solution at temperatures below 0 °C. Complete substitution of the hydrogen atoms in (η^5-C$_5$H$_5$)CuCO with methyl groups to give (η^5-Me$_5$C$_5$)CuCO did not improve significantly the stability [8]. Introduction of significantly bulkier alkyl groups onto the cyclopentadienyl ring was required to improve significantly the stability of CpCuCO derivatives. Thus, (η^5-iPr$_4$C$_5$H)CuCO was found to be sufficiently stable to be isolated as a dark brown liquid, which gave reasonable elemental analyses [9]. Homoleptic copper carbonyls are not stable compounds at ambient conditions but have been studied theoretically [10].

All of these CpCuL derivatives have copper in the +1 formal oxidation state. A question of general interest is whether CpCu derivatives can be prepared with the copper atom in a higher formal oxidation state, with +2 and +3 oxidation states being possibilities. The d^9 Cu(II) is the common oxidation state of copper in aqueous solution. The d^8 Cu(III), although an unusual oxidation state for copper in normal inorganic compounds, is isoelectronic with the well-known d^8 Ni(II). Furthermore, formally Cu(III) organometallics such as the allyl derivatives [11] (η^3-C$_3$H$_5$)CuMe$_2$ and [(η^3-C$_3$H$_5$)CuMe$_3$]$^-$ and the homoleptic tetramethylcuprate(III), [12] CuMe$_4^-$, can be generated at temperatures around −100 °C. However, they are thermally unstable and decompose far below room temperature.

A question of interest is whether CpCuX$_n$ derivatives with copper in formal oxidation states above +1 can be synthesized by performing oxidative addition reactions on CpCuL (L = CO, R$_3$P, etc.). We have explored such possibilities theoretically considering the chlorides Cp$_2$Cu$_2$Cl, Cp$_2$Cu$_2$Cl$_2$, and Cp$_2$Cu$_2$Cl$_3$ with copper in the average formal oxidation states of +1.5, +2, and +2.5, respectively, as possible products from such oxidative addition reactions. Such systems could provide novel examples of copper–copper bonding. In this connection, McKee and collaborators [13] reported an example of a Cu–Cu bond of length 2.448 Å in a structurally characterized dicopper cryptate complex with the copper in an average oxidation state of +1.5. The chloride ligand was chosen for the current research since copper(II) chloride, CuCl$_2$, is stable and a commonly used starting material for the synthesis of other copper compounds. Furthermore, oxidative additions of Cl$_2$ or other chlorinating agent on the copper(I) derivatives CpCuL present likely synthetic routes to such cyclopentadienyl copper chlorides.

2 Theoretical methods

The theoretical studies reported in this paper were performed using the unsubstituted η^5-C$_5$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.

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [14–22]. Two DFT methods were used in this study. The first functional is the B3LYP model, which is a hybrid HF-DFT method using Becke's three-parameter exchange functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional [23, 24]. The other approach is the BP86 method, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional method (P86) [25, 26]. All computations were performed using double-ζ plus polarization (DZP) basis sets. For carbon, the DZP basis set used here adds one set of pure spherical harmonic d functions (with orbital exponent $\alpha_d(\mathrm{C}) = 0.75$) to the Huzinaga–Dunning standard contracted DZ sets and is designated (9s5p1d/4s2p1d) [27, 28]. For chlorine, the DZP basis set used here adds one set of pure spherical harmonic d functions (with orbital exponent $\alpha_d(\mathrm{Cl}) = 0.75$) to the Huzinaga–Dunning–Hay standard contracted DZ sets and is designated (12s8p1d/6s4p1d) [27, 28]. For hydrogen, a set of p polarization functions ($\alpha_p(\mathrm{H}) = 0.75$) is added to the Huzinaga–Dunning DZ sets. For Cu, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses Wachters' primitive set [29] augmented by two sets of p functions and one set of d functions, and contracted following Hood et al. [30].

The geometries of all of the 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 [31]. The fine grid (75, 302) was the default for evaluating integrals numerically [32]. The finer grid (120, 974) was used for more precise resolution of the small imaginary vibrational frequencies. The tight (10^{-8} hartree) designation was the default for the self-consistent field (SCF) convergence.

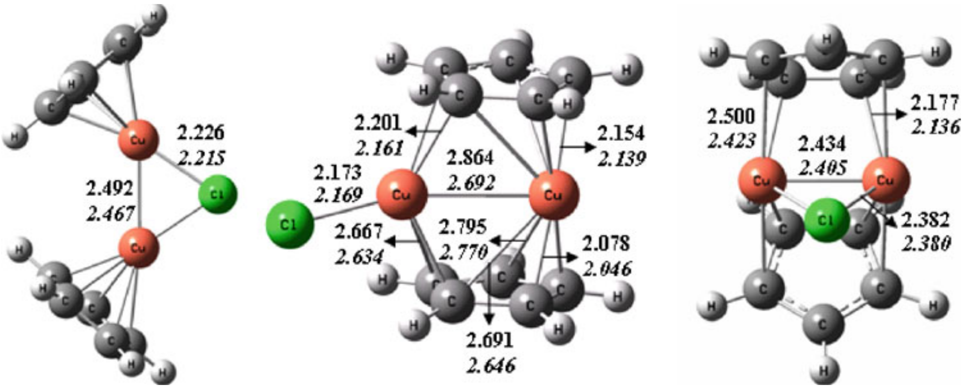
Since there is no wave function per se in the DFT method, the evaluation of the expectation value of $\mathbf{S}^2$ is problematic. The most realistic and practical method is to evaluate $\langle S^2 \rangle$ using the single determinant constructed from the appropriate DFT orbitals. When DFT methods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

The structures for $Cp_2Cu_2Cl_n$ ($n = 1, 2, 3$) are depicted in Figs. 1, 2, 3, 4, 5. They are labeled by the number of Cl atoms, order of relative energies, and spin state (singlets, doublets, triplets, and quartets designated as **S**, **D**, **T**, and **Q**, respectively). For example, the quartet energetically lowest-lying structure of $Cp_2Cu_2Cl_3$ is called **3Cl-1Q**. The upper and lower bond distances in the figures were determined by the B3LYP and BP86 methods, respectively.

3 Results

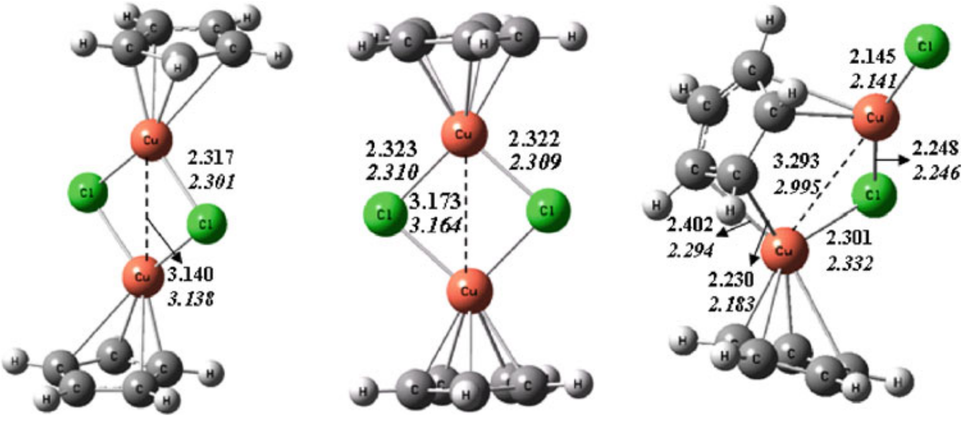
3.1 Cp_2Cu_2Cl

There are the following two general types of structures for $Cp_2Cu_2Cl_n$ derivatives ($n = 1, 2, 3$): (1) coaxial structures, in which each Cp ring is bonded only to a single metal atom so that the C_5 axes of the Cp rings are approximately collinear with the Cu–Cu bond; and (2) perpendicular structures, in which each Cp ring bridges both metal atoms so that the Cu–Cu axis is approximately perpendicular to the C_5 axes of the Cp rings. For Cp_2Cu_2Cl with the copper atoms in an average formal oxidation state of +1.5, there are three possible structures (Fig. 1; Table 1). All three structures are doublet structures with negligible spin contamination, i.e., with $\langle S^2 \rangle$ close to the ideal value of 0.75 (Table 1).



1Cl-1D (**C_2**) **1Cl-2D** (**C_s**) **1Cl-3D** (**C_{2v}**)

Fig. 1 The three doublet stationary points of Cp_2Cu_2Cl. The distances are given in Å. The upper distances (*bold face*) were obtained by the B3LYP method, while the lower numbers (*italics*) by BP86. The subsequent figures have the same arrangement



2Cl-1T (**C_{2h}**) **2Cl-2T** (**C_2**) **2Cl-3T** (**C_1**)

Fig. 2 The three triplet $Cp_2Cu_2Cl_2$ structures

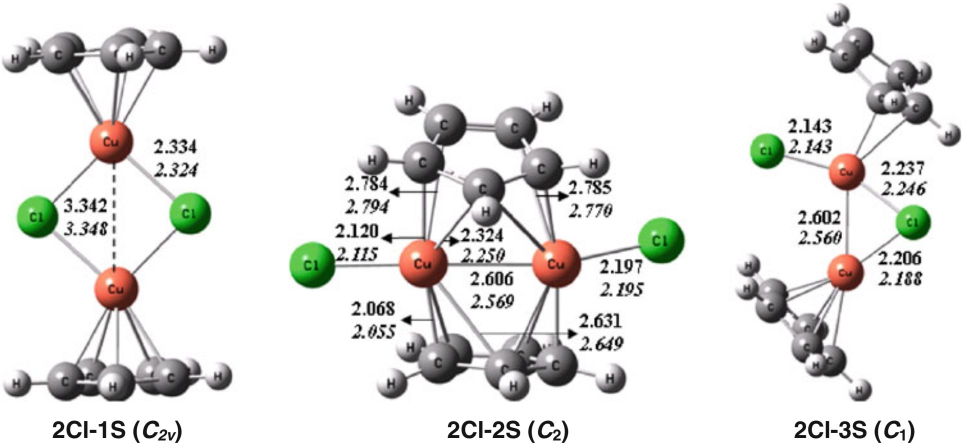


Fig. 3 The three singlet $Cp_2Cu_2Cl_2$ structures

2Cl-1S (C_{2v}) **2Cl-2S** (C_2) **2Cl-3S** (C_1)

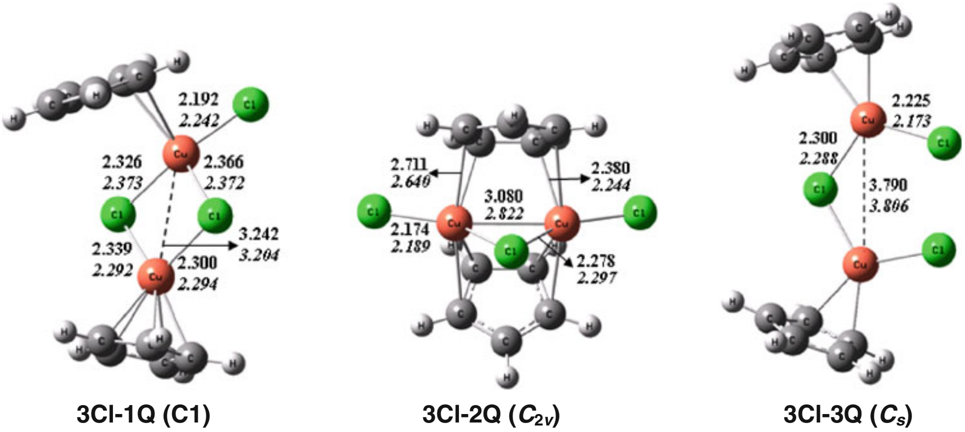


Fig. 4 The three quartet stationary points of $Cp_2Cu_2Cl_3$

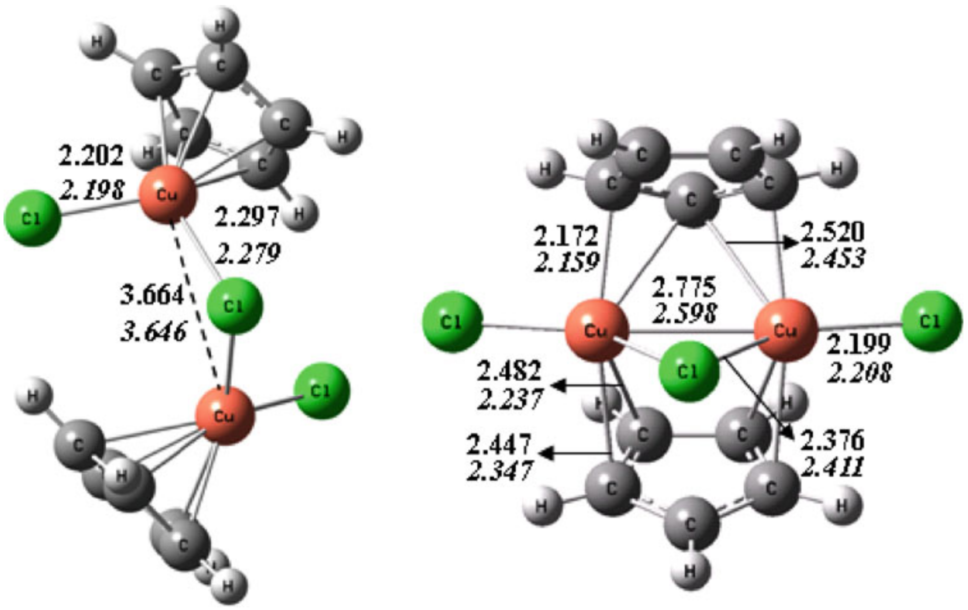
3Cl-1Q (C1) **3Cl-2Q** (C_{2v}) **3Cl-3Q** (C_s)

The global minimum of Cp_2Cu_2Cl, **1Cl-1D**, is a C_2 structure with a bridging Cl ligand and terminal Cp ligands (Fig. 1; Table 1). The Cu–Cl distances to the bridging Cl ligand are 2.226 Å (B3LYP) or 2.215 Å (BP86). Each Cu atom is bonded to a η^5-C_5H_5 ring with all Cu–C distances less than 2.4 Å (Table S1). The Cu–Cu distance is predicted to be 2.492 Å (B3LYP) or 2.467 Å (BP86), which is very close to the experimental Cu–Cu single bond distance of 2.448 Å in a binuclear copper cryptate derivative [13] with the same average copper formal oxidation state of +1.5 as in **1Cl-1D**. A formal Cu–Cu single bond in **1Cl-1D** gives one copper atom the favored 18-electron configuration but the other copper atom a 19-electron configuration. However, the copper atoms are equivalent in **1Cl-1D** by a Mulliken spin density on each copper atom of 0.15 (B3LYP) or 0.17 (BP86). Thus, ~30% of the unpaired electron density in **1Cl-1D** is delocalized over the two copper atoms.

The next Cp_2Cu_2Cl structure **1Cl-2D** (Fig. 1; Table 1) is a C_s structure with two bridging Cp ligands and a terminal Cl ligand. Structure **1Cl-2D** lies 6.9 kcal/mol (B3LYP) or 5.4 kcal/mol (BP86) above the global minimum **1Cl-1D**. Structure **1Cl-2D** has all real harmonic frequencies by BP86, but a small imaginary frequency (32*i* cm^{-1}) by B3LYP, which is not removed using the finer (120, 974) integration grid. The Cu–Cl distance to the terminal Cl ligand is 2.173 Å (B3LYP) or 2.169 Å (BP86). The copper atom bearing the Cl atom is bonded to four carbon atoms of the two Cp rings (two carbon atoms from each ring), while the other copper atom is bonded to eight carbon atoms of the two Cp rings (four carbon atoms from each ring). The Cu–Cu distance in **1Cl-2D** is 2.864 Å (B3LYP) or 2.692 Å (BP86), which is also a Cu–Cu single bond, although ~0.2 Å longer than that in **1Cl-1D**. For **1Cl-2D**, the Mulliken spin density is 0.2 on the "left" copper atom (bearing the terminal Cl ligand) and very small (<0.08) on the "right" copper atom (not bonded to the terminal Cl ligand).

A third doublet Cp_2Cu_2Cl structure, namely **1Cl-3D** (Fig. 1; Table 1), is a C_{2v} structure with a bridging Cl ligand

Fig. 5 The two doublet stationary points of $Cp_2Cu_2Cl_3$



3Cl-1D (*C_2*) **3Cl-2D (*C_s*)**

Table 1 Total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimg), Cu–Cu bond distances (Å), and spin expectation values $\langle S^2 \rangle$ for the Cp_2Cu_2Cl structures

	1Cl-1D (C_2)	1Cl-2D (C_s)	1Cl-3D (C_{2v})
B3LYP			
E	−4,128.46607	−4,128.45501	−4,128.44659
ΔE	0.0	6.9	12.2
Nimg	0	1(32*i*)	0
Cu–Cu	2.492	2.864	2.434
$\langle S^2 \rangle$	0.76	0.76	0.76
BP86			
E	−4,128.94088	−4,128.93227	−4,128.92165
ΔE	0.0	5.4	12.1
Nimg	0	0	0
Cu–Cu	2.467	2.692	2.405
$\langle S^2 \rangle$	0.75	0.75	0.76

Table 2 Total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), number of imaginary vibrational frequencies (Nimg), Cu–Cu bond distance (Å), and spin contamination $\langle S^2 \rangle$ for the triplet $Cp_2Cu_2Cl_2$ structures

	2Cl-1T (C_{2h})	2Cl-2T (C_2)	2Cl-3T (C_1)
B3LYP			
E	−4,588.69648	−4,588.69544	−4,588.67511
ΔE	0.0	0.6	13.4
Nimg	0	0	0
Cu–Cu	3.140	3.173	3.293
$\langle S^2 \rangle$	2.04	2.01	2.02
BP86			
E	−4,589.19231	−4,589.19149	−4,589.17824
ΔE	0.0	0.5	8.8
Nimg	0	0	0
Cu–Cu	3.138	3.164	2.995
$\langle S^2 \rangle$	2.02	2.01	2.00

as well as bridging Cp rings. Structure **1Cl-3D** is predicted to lie 12.2 kcal/mol (B3LYP) or 12.1 kcal/mol (BP86) above the global minimum **1Cl-1D**. The Cu–Cl distances to the bridging Cl ligand are 2.382 Å (B3LYP) or 2.380 Å (BP86). In **1Cl-3D**, each copper atom is bonded to four carbon atoms of the two Cp rings (two C atoms in each ring). The Cu–Cu distance is 2.434 Å (B3LYP) or 2.405 Å (BP86), which is close to the Cu–Cu distance in the global minimum **1Cl-1D**. Similar to **1Cl-1D**, the spin density of each copper atom in **1Cl-3D** is 0.11 (B3LYP) or 0.12 (BP86).

3.2 $Cp_2Cu_2Cl_2$

Six energetically low-lying structures were found for $Cp_2Cu_2Cl_2$ (Figs. 2 and 3; Tables 2 and 3), including three triplet and three singlet structures. The $Cp_2Cu_2Cl_2$ global minimum **2Cl-1T** (Fig. 2; Table 2) is predicted to be a triplet C_{2h} structure with all real vibrational frequencies. Structure **2Cl-1T** has two bridging Cl ligands and terminal Cp rings. The spin contamination in **2Cl-1T** is negligible with $\langle S^2 \rangle = 2.04$ (B3LYP) or $\langle S^2 \rangle = 2.02$ (BP86). The

Table 3 Total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimg), and Cu–Cu bond distances (Å) for the singlet $Cp_2Cu_2Cl_2$ structures

	2Cl-1S (C_{2v})	2Cl-2S (C_2)	2Cl-3S (C_1)
B3LYP			
E	−4,588.66419	−4,588.66383	−4,588.65129
ΔE	20.3	20.5	28.4
Nimg	0	0	0
Cu–Cu	3.342	2.606	2.602
BP86			
E	−4,589.18340	−4,589.18080	−4,589.16541
ΔE	5.6	7.2	16.9
Nimg	0	0	0
Cu–Cu	3.348	2.569	2.560

Cu–Cl distances to the two bridging Cl ligands are 2.317 Å (B3LYP) or 2.301 Å (BP86). Each Cp ring can be considered to be tetrahapto (η^4-C_5H_5), with two bonding Cu–C distances of ~2.1 Å, two bonding Cu–C distances of ~2.7 Å, and one non-bonding Cu–C distance of ~3.1 Å. The long Cu–Cu distance in **2Cl-1T** of 3.140 Å (B3LYP) or 3.138 Å (BP86) suggests that there is no direct copper–copper interaction for this structure with two three-electron donor bridging μ-Cl ligands. This allows each copper atom in **2Cl-1T** to achieve the favored 18-electron configuration. The triplet spin state arises formally from an unpaired electron on the carbon atom of each η^4-C_5H_5 ring not bonded to a copper atom.

The $Cp_2Cu_2Cl_2$ structure **2Cl-2T** is a C_2 coaxial structure geometrically similar to **2Cl-1T** (Fig. 2; Tables 2 and S2). However, each Cp ring is a terminal pentahapto ligand with all five Cu–C distances less than ~2.3 Å. Structure **2Cl-2T** lies only 0.6 kcal/mol (B3LYP) or 0.5 kcal/mol (BP86) above **2Cl-1T**, indicating that these structures are essentially degenerate in energy. Structure **2Cl-2T** is a genuine minimum with very small spin contamination, $\langle S^2 \rangle = 2.01$ (B3LYP and BP86). The Cu–Cu distance in **2Cl-2T** is 3.173 Å (B3LYP) or 3.164 Å (BP86), which is close to that in **2Cl-1T** and suggests the lack of a Cu–Cu bond. With 2 three-electron donor bridging Cl ligands, both copper atoms in **2Cl-2T** have the 19-electron configuration consistent for a binuclear triplet. The Mulliken spin density on each copper atom in **2Cl-2T** is 0.33 (B3LYP) or 0.31 (BP86).

A third triplet $Cp_2Cu_2Cl_2$ structure **2Cl-3T** (Fig. 2; Table 2) lies 13.4 kcal/mol (B3LYP) or 8.8 kcal/mol (BP86) above **2Cl-1T** with very small spin contamination, $\langle S^2 \rangle = 2.02$ (B3LYP) or 2.00 (BP86). Structure **2Cl-3T** has a fascinating geometry with one tetrahapto (η^4-C_5H_5) terminal Cp ring and a different tetrahapto (η^2,η^2-C_5H_5) bridging Cp ring, as well as one semibridging and one terminal Cl ligand (Table S2). The Cu–Cl distance to the terminal Cl ligand is 2.145 Å (B3LYP) or 2.141 Å (BP86), and the Cu–Cl distances for the semibridging Cl ligand are 2.248 and 2.301 Å (B3LYP) or 2.246 and 2.332 Å (BP86). The Cu–Cu distance in **2Cl-3T** is predicted to be quite long at 3.293 Å (B3LYP) or 2.995 Å (BP86), suggesting the absence of a formal copper–copper bond in **2Cl-3T**. Each copper atom in **2Cl-3T** has the favored 18-electron configuration if the three-electron donor semibridging Cl ligand donates two electrons to the "upper" Cu atom (bearing the terminal Cl ligand) and one electron to the "lower" Cu atom, which has no other directly bonded Cl ligands. The unpaired electrons in the triplet **2Cl-3T** arise from the tetrahapto Cp rings.

Three singlet $Cp_2Cu_2Cl_2$ structures were found, namely a doubly bridged structure, a singly bridged structure, and an unbridged structure. The lowest energy singlet $Cp_2Cu_2Cl_2$ structure **2Cl-1S** (Fig. 3; Table 3) is a C_{2v} coaxial structure lying 20.3 kcal/mol (B3LYP) or 5.6 kcal/mol (BP86) above **2Cl-1T**. This discrepancy between the B3LYP and BP86 results is not surprising, since Reiher et al. have found that B3LYP always favors the high-spin state and BP86 favors the low-spin state for a series of the Fe(II)–S complexes [33]. The $Cp_2Cu_2Cl_2$ structure **2Cl-1S** is geometrically similar to **2Cl-2T** with two bridging Cl ligands and two terminal pentahapto (η^5-C_5H_5) rings with a ring–Cu–Cu angle of ~170°. The Cu–Cl distances to the two bridging Cl ligands are 2.334 Å (B3LYP) or 2.324 Å (BP86). The Cu–Cu distance in **2Cl-1S** is 3.342 Å (B3LYP) or 3.348 Å (BP86), indicating the lack of a direct copper–copper bond.

The second singlet $Cp_2Cu_2Cl_2$ structure **2Cl-2S** is a C_2 structure with two bridging Cp ligands and two terminal Cl ligands (Fig. 3; Table 3). Structure **2Cl-2S** is predicted to lie 20.5 kcal/mol (B3LYP) or 7.2 kcal/mol (BP86) in energy above the triplet $Cp_2Cu_2Cl_2$ global minimum **2Cl-1T**. Each copper atom in **2Cl-2S** is bonded to six carbon atoms of the two Cp rings (three C atoms in each ring). However, each copper atom obtains only five electrons since one carbon in each ring shared by both Cu atoms. The Cu–Cu distance, 2.606 Å (B3LYP) or 2.569 Å (BP86), is found to be shorter than that in the just described coaxial structure **2Cl-1S** and can be interpreted as the Cu–Cu single bond required to give both copper atoms the favored 18-electron configuration with 2 one-electron donor terminal Cl ligands.

Another singlet $Cp_2Cu_2Cl_2$ structure **2Cl-3S** has one bridging Cl ligand, one terminal Cl ligand, and two terminal Cp rings (Fig. 3; Table 3). Structure **2Cl-3S** has all real vibrational frequencies and is a relatively high-energy structure, predicted to lie 28.4 kcal/mol (B3LYP) or 16.9 kcal/mol (BP86) above **2Cl-1T**. The "upper" copper atom in **2Cl-3S** is bonded to a portion of one Cp ring (η^2-C_5H_5), but the "lower" copper atom is bonded to all five carbon atoms of the other Cp ring (η^5-C_5H_5). The Cu–Cu distance in **2Cl-3S**, namely 2.602 Å (B3LYP) or 2.560 Å (BP86), is close to that in **2Cl-2S**, corresponding to the Cu–Cu single bond.

3.3 $Cp_2Cu_2Cl_3$

Three quartet and two doublet structures were found for $Cp_2Cu_2Cl_3$ (Figs. 4 and 5; Tables 4 and 5). All five structures have very small spin contamination. Among these $Cp_2Cu_2Cl_3$ structures, **3Cl-2Q** and **3Cl-2D** have two bridging Cp ligands, whereas the other structures have two terminal Cp ligands. As expected, the B3LYP method favors the higher spin states, while the BP86 method favors the lower spin states [33].

Table 4 Total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimg), Cu–Cu bond distances (Å), and spin expectation values $\langle S^2 \rangle$ for the quartet $Cp_2Cu_2Cl_3$ structures

	3Cl-1Q (C_1)	3Cl-2Q (C_{2v})	3Cl-3Q (C_s)
B3LYP			
E	−5,048.87162	−5,048.85543	−5,048.85700
ΔE	0.0	10.2	9.2
Nimg	0	1(240*i*)	0
Cu–Cu	3.242	3.080	3.790
$\langle S^2 \rangle$	3.77	3.77	3.79
BP86			
E	−5,049.40213	−5,049.39581	−5,049.39439
ΔE	0.0	4.0	4.9
Nimg	0	0	0
Cu–Cu	3.204	2.822	3.806
$\langle S^2 \rangle$	3.76	3.76	3.76

Table 5 Total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimg), Cu–Cu bond distances (Å), and spin expectation values $\langle S^2 \rangle$ for the doublet $Cp_2Cu_2Cl_3$ structures

	3Cl-1D (C_2)	3Cl-2D (C_s)
B3LYP		
E	−5,048.86624	−5,048.84809
ΔE	3.4	14.8
Nimg	0	1(13*i*)
Cu–Cu	3.664	2.775
$\langle S^2 \rangle$	0.81	0.76
BP86		
E	−5,049.41062	−5,049.40382
ΔE	−5.3	−1.1
Nimg	0	1(16*i*)
Cu–Cu	3.646	2.598
$\langle S^2 \rangle$	0.77	0.75

The global minimum $Cp_2Cu_2Cl_3$ structure is the quartet **3Cl-1Q**, which has two bridging Cl ligands, one terminal Cl ligand and two terminal Cp rings (Fig. 4; Table 4). The "upper" copper atom is bonded to only two carbon atoms (B3LYP) of one Cp ring (η^2-C_5H_5), while the "lower" copper atom is bonded to all five carbons of the other Cp ring (η^5-C_5H_5). For the terminal Cl ligand in **3Cl-1Q**, the Cu–Cl distance is 2.192 Å (B3LYP) or 2.242 Å (BP86). For one of the bridging Cl ligands, the Cu–Cl distances are 2.326 and 2.339 Å (B3LYP) or 2.373 and 2.292 Å (BP86). For the other bridging Cl ligand, the Cu–Cl distances are 2.300 and 2.366 Å (B3LYP) or 2.294 and 2.372 Å (BP86). The Cu–Cu distance in **3Cl-1Q** is 3.242 Å (B3LYP) or 3.204 Å (BP86), indicating no direct chemical interaction between the two Cu atoms.

The C_{2v} perpendicular quartet $Cp_2Cu_2Cl_3$ structure **3Cl-2Q** (Fig. 4; Table 4) with one bridging and two terminal Cl ligands is predicted to lie 10.2 kcal/mol (B3LYP) or 4.0 kcal/mol (BP86) above **3Cl-1Q**. In **3Cl-2Q**, each copper atom is bonded to four carbon atoms of the two Cp rings (Table S4). The Cu–Cl distances to the bridging Cl ligand are 2.278 Å (B3LYP) or 2.297 Å (BP86), and the Cu–Cl distances to the terminal Cl ligands are 2.174 Å (B3LYP) or 2.189 Å (BP86). The Cu–Cu distance in **3Cl-2Q** is 3.080 Å (B3LYP) or 2.822 Å (BP86). The BP86 method predicts **3Cl-2Q** to be a genuine minimum. However, the B3LYP method predicts a significant imaginary vibrational frequency of 240*i* cm^{-1} for **3Cl-2Q**. Following the corresponding normal mode leads to a C_1 structure (**3Cl-2Q-1**, shown in the Supporting Information). This C_1 structure has lower energy than the C_{2v} one by 2.3 kcal/mol and has a slightly longer Cu–Cu distance (3.15 Å).

The other $Cp_2Cu_2Cl_3$ quartet structure **3Cl-3Q** is a C_s structure with one bridging Cl ligand and two terminal Cl ligands (Fig. 4; Table 4). Structure **3Cl-3Q** lies 9.2 kcal/mol (B3LYP) or 4.9 kcal/mol (BP86) above **3Cl-1Q**. In **3Cl-3Q**, each Cp ring is a terminal dihapto ligand by the B3LYP method, but a trihapto ligand by the BP86 method (see Table S4). The Cu–Cl distances to the bridging Cl ligand are 2.300 Å (B3LYP) or 2.288 Å (BP86), and the Cu–Cl distances for the terminal Cl ligands are 2.225 Å (B3LYP) or 2.173 Å (BP86). The Cu–Cu distance in **3Cl-3Q** is 3.790 Å (B3LYP) or 3.806 Å (BP86), clearly indicating the absence of a direct bond.

The C_2 doublet $Cp_2Cu_2Cl_3$ structure **3Cl-1D** has one bridging Cl ligand and two terminal Cl ligands (Fig. 5; Table 5). The B3LYP method predicts structure **3Cl-2D** to lie 3.4 kcal/mol *above* **3Cl-1Q**. However, the BP86

Table 6 Dissociation energies (kcal/mol) for the $Cp_2Cu_2Cl_n$ derivatives

	B3LYP	BP86
$Cp_2Cu_2Cl_3$ (**3Cl-1Q**) → $Cp_2Cu_2Cl_2$ (**2Cl-1T**) + 1/2 Cl_2	4.2	11.6
$Cp_2Cu_2Cl_2$ (**2Cl-1T**) → Cp_2Cu_2Cl (**1Cl-1D**) + 1/2 Cl_2	38.6	32.4
Cp_2Cu_2Cl (**1Cl-1D**) → Cp_2Cu_2 + 1/2 Cl_2	29.9	31.6
Cp_2Cu_2Cl (**1Cl-1D**) → CpCuCl + CpCu	41.8	49.6
$Cp_2Cu_2Cl_2$ (**2Cl-1T**) → 2 CpCuCl	29.6	27.0
$2Cp_2Cu_2Cl_2$ (**2Cl-1T**) → $Cp_2Cu_2Cl_3$ (**3Cl-1Q**) + Cp_2Cu_2Cl (**1Cl-1D**)	34.7	26.1

method predicts structure **3Cl-2D** to lie 5.3 kcal/mol *below* **3Cl-1Q**. This is another example of the tendency of the B3LYP method to favor higher spin states relative to the BP86 method [33]. In **3Cl-1D**, the Cu–Cl distances to the bridging Cl ligands are 2.297 Å (B3LYP) or 2.279 Å (BP86), and the Cu–Cl distances to the terminal Cl ligands are 2.202 Å (B3LYP) or 2.198 Å (BP86). The Cu…Cu distance for **3Cl-1D** is very long, namely 3.664 Å by B3LYP or 3.646 Å by BP86, indicating the absence of a chemical bond between the two copper atoms.

The other doublet structure for $Cp_2Cu_2Cl_3$, namely **3Cl-2D** (Fig. 5; Table 5), is a C_s perpendicular dimetallocene structure with one bridging and two terminal Cl ligands. Structure **3Cl-2D** lies 14.8 kcal/mol *above* the **3Cl-1Q** global minimum by the B3LYP method but 1.1 kcal/mol *below* the **3Cl-1Q** global minimum by the BP86 method. This again is an indication of the tendency of the B3LYP method to favor high-spin structures [33]. Structure **3Cl-2D** has a very small imaginary vibrational frequency ($13i$ cm^{-1} by B3LYP or $16i$ cm^{-1} by BP86). In **3Cl-2D**, each copper atom is bonded to four carbon atoms of each Cp ring. The Cu–Cl distances to the bridging Cl ligand are 2.376 Å (B3LYP) or 2.411 Å (BP86), and those to the terminal Cl ligands are 2.199 Å (B3LYP) or 2.208 Å (BP86). The Cu–Cu distance in **3Cl-2D** is 2.775 Å (B3LYP) or 2.598 Å (BP86) corresponding to a formal Cu–Cu single bond.

3.4 Dissociation energies

Table 6 shows the dissociation energies for the reactions $Cp_2Cu_2Cl_n \rightarrow Cp_2Cu_2Cl_{n-1} + 1/2\ Cl_2$ based on the lowest energy structures. The dissociation energy for the loss of one Cl atom from $Cp_2Cu_2Cl_3$ (**3Cl-1Q**) is predicted to be only 4.2 kcal/mol (B3LYP) or 11.6 kcal/mol (BP86), whereas those of $Cp_2Cu_2Cl_2$ (**2Cl-1T**) or Cp_2Cu_2Cl (**1Cl-1D**) are larger than 29 kcal/mol. This indicates that $Cp_2Cu_2Cl_2$ and Cp_2Cu_2Cl are more favorable energetically than $Cp_2Cu_2Cl_3$ with respect to extrusion of a chlorine atom. This is consistent with the relative instability of copper oxidation states above +2 in most coordination environments [11, 12].

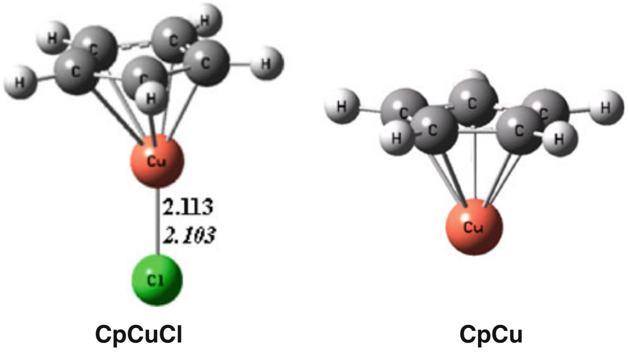


Fig. 6 Optimized CpCuCl and CpCu fragments at the same level of theory

The dissociation energies of the binuclear derivatives $Cp_2Cu_2Cl_2$ (**2Cl-1T**) and Cp_2Cu_2Cl (**1Cl-1D**) into mononuclear fragments are also reported (Table 6). In order to obtain these energetic data, the structures of the mononuclear CpCuCl and CpCu were optimized by the same DFT methods (Fig. 6). As shown in Table 6, the predicted energies of 29.6 kcal/mol (B3LYP) or 27.0 kcal/mol (BP86) for the dissociation from $Cp_2Cu_2Cl_2$ to give CpCuCl indicate that the global minimum **2Cl-1T** of $Cp_2Cu_2Cl_2$ (Fig. 2) is favorable with respect to dissociation into mononuclear fragments. The dissociation energy of Cp_2Cu_2Cl (**1Cl-1D**) into CpCuCl and CpCu is even higher, at 41.8 kcal/mol (B3LYP) or 49.6 kcal/mol (BP86). This can be a consequence of the direct Cu–Cu bond in **1Cl-1D**. In addition, the disproportionation reaction, $2Cp_2Cu_2Cl_2$ (**2Cl-1T**) → $Cp_2Cu_2Cl_3$ (**3Cl-1Q**) + Cp_2Cu_2Cl (**1Cl-1D**), is predicted to be endothermic by 34.7 kcal/mol (B3LYP) or 26.1 kcal/mol (BP86). Thus, $Cp_2Cu_2Cl_2$ appears to be stable with respect to this disproportionation reaction.

4 Discussion

In general, the lowest energy $Cp_2Cu_2Cl_n$ structures ($n = 1$, 2, 3) have terminal Cp rings. The ring–Cu–Cu angles fall in a wide range from 108 to 177°. The chlorine atoms appear to prefer bridging versus terminal positions, up to a maximum of two bridges.

The monochloride, Cp_2Cu_2Cl, is formally a mixed oxidation state derivative with one Cu(II) atom and one Cu(I) atom. The Cp_2Cu_2Cl global minimum **1Cl-1D** (Fig. 1; Table 1) has a Cu–Cu distance of ∼2.5 Å, which should be interpreted as a formal single bond. This Cu–Cu distance is close to the 2.448 Å Cu–Cu distance found by McKee and collaborators [13] in a dicopper cryptate complex with the same average copper oxidation state of +1.5 as in Cp_2Cu_2Cl. The bridging chlorine atom in **1Cl-1D** (considered as a neutral ligand) is formally a two-electron donor to one copper atom and a one-electron donor to the other copper atom. This gives one copper atom the favorable 18-electron configuration, but the other copper atom a 19-electron configuration. Formally, the copper atoms in **1Cl-1D** are non-equivalent, and the unpaired electron would be expected to be on the copper atom with the 19-electron configuration. However, the two copper atoms are equivalent by the C_2 symmetry of **1Cl-1D** and have equivalent Mulliken spin densities of 0.15 (B3LYP) or 0.17 (BP86) on each copper atom. Thus, structure **1Cl-1D** can be considered as a resonance hybrid between the two equivalent structures where one of the copper atoms has an 18-electron configuration and the other copper atom has a 19-electron configuration.

The dichloride $Cp_2Cu_2Cl_2$ is formally a complex of the d^9 Cu(II) with a single unpaired electron per copper atom. Thus, the lowest energy $Cp_2Cu_2Cl_2$ structure with two Cu(II) atoms is expected to be a triplet spin state. Indeed, singlet $Cp_2Cu_2Cl_2$ structures lie consistently at higher energies than corresponding triplet $Cp_2Cu_2Cl_2$ structures by either the B3LYP or the BP86 method.

The two lowest energy $Cp_2Cu_2Cl_2$ structures, namely **2Cl-1T** and **2Cl-2T**, are triplet structures with terminal Cp rings in which the two chlorine atoms bridge the copper atoms with non-bonding Cu…Cu distances of ∼3.1 Å (Fig. 2; Table 2). These two structures differ in energy by less than 1 kcal/mol by either method, indicating that they are essentially degenerate. In **2Cl-1T**, each Cp ring is a tetrahapto ligand so that each copper atom has the favored 18-electron configuration. The unpaired electrons in **2C-1T**, at least formally, lie on the single carbon on each Cp ring not within bonding distance of a copper atom. The $Cp_2Cu_2Cl_2$ structure **2Cl-2T** differs from **2Cl-1T**, by having pentahapto Cp rings thereby giving each copper atom a 19-electron configuration. In **2C-2T**, the unpaired electrons thus formally lie on the copper atoms.

Formally, the trichloride $Cp_2Cu_2Cl_3$ is a mixed valence compound [34] with one Cu(II) atom and one Cu(III) atom. Low-energy doublet and quartet $Cp_2Cu_2Cl_3$ structures are found. The B3LYP method predicts slightly lower energies for the quartet structures, whereas the BP86 method predicts slightly lower energies for the doublet structures. This is in accord with previous observation [33] of the tendency of the B3LYP method to favor higher spin states relative to the BP86 method.

The lowest energy quartet $Cp_2Cu_2Cl_3$ structure **3Cl-1Q** (Fig. 4; Table 4) is an unsymmetrical structure with two bridging chlorine atoms and one terminal chlorine atom. The Cp ring bonded to the copper atom bearing the terminal chlorine is only a dihapto ligand, implying that one of the unpaired electrons in **3Cl-1Q** lies on the three carbon atoms of the Cp ring that are not within bonding distance of this copper atom. This dihapto Cp ring can be considered as an analog of an olefin ligand. The midpoint of the two carbons of this Cp ring bonded to the copper atom forms approximately square planar coordination with the two bridging chlorine atoms and the terminal chlorine atom. The other Cp ring in **3Cl-1Q** is a normal pentahapto ligand.

The lowest energy doublet $Cp_2Cu_2Cl_3$ structure **3Cl-1D** (Fig. 5; Table 5) is very different from the quartet structure **3Cl-1Q**. Thus, structure **3Cl-1D** has C_2 symmetry with the copper atoms equivalent by symmetry. Each copper atom bears one terminal chlorine atom, with the third chlorine atom bridging the two copper atoms. The long Cu…Cu distance of ∼3.6 Å indicates the lack of a direct copper–copper bond. Formally, the $Cp_2Cu_2Cl_3$ structure **3Cl-1D** can be derived by oxidative addition of Cl_2 to the Cp_2Cu_2Cl structure **1Cl-1D** to form two new Cu–Cl bonds to terminal chlorine atoms with concurrent rupture of the Cu–Cu bond (Fig. 7).

Some fairly low-energy $Cp_2Cu_2Cl_n$ structures are found in which one or both Cp rings bridge the copper atoms. For Cp_2Cu_2Cl (Fig. 1), such structures are found both with a terminal Cl atom (**1Cl-2D**) and with a bridging Cl atom (**1Cl-3D**). The Cu–Cu distances are bonding distances in both structures. However, the Cu–Cu distance in the Cp_2Cu_2Cl structure with a terminal Cl atom (**1Cl-2D**) is significantly longer (by 0.3–0.4 Å) than the Cu–Cu distance in the Cp_2Cu_2Cl structure with a bridging Cl atom (**1Cl-3D**). This is an example of the shortening of metal–metal bonds by adding bridging groups. For $Cp_2Cu_2Cl_2$, a symmetrical C_2 singlet structure **2Cl-2S** is found with two bridging Cp rings and two terminal Cl atoms (Fig. 3). However, in addition, an unsymmetrical $Cp_2Cu_2Cl_2$ triplet structure **2Cl-3T** is found (Fig. 2) with one bridging and one terminal Cp ring as well as one bridging and one terminal Cl atom. For $Cp_2Cu_2Cl_3$, both quartet and doublet

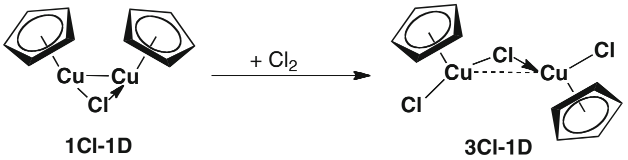


Fig. 7 Formation of $Cp_2Cu_2Cl_3$ (*3Cl-1D*) by oxidative addition of Cl_2 to Cp_2Cu_2Cl (*1Cl-1D*)

structures with two bridging Cp rings are found with one bridging chlorine atom and two terminal chlorine atoms, namely **3Cl-2Q** (Fig. 4) and **3Cl-2D** (Fig. 5), respectively. It thus appears that for $Cp_2Cu_2Cl_n$ structures with bridging Cp rings, terminal chlorine atoms are generally preferred over bridging chlorine atoms up to a maximum of one terminal chlorine atom per copper atom.

None of the structures predicted in this paper has yet been realized experimentally. However, oxidative addition of chlorine or chlorinating agents such as SO_2Cl_2 or $SbCl_5$ to CpCuL derivatives (L = CO, R_3P, RNC, etc.) provide possible synthetic approaches. The experimental observation of copper(III) organometallic derivatives, albeit at low temperatures [11, 12], suggests that copper–carbon bonds are not necessarily incompatible with copper oxidation states above +1. However, the stability of the lowest energy $Cp_2Cu_2Cl_2$ copper(II) structure **2Cl-1T** toward disproportionation into $Cp_2Cp_2Cl + Cp_2Cu_2Cl_3$ by 34.7 kcal/mol (B3LYP) or 26.1 kcal/mol (BP86) combined with the relatively low energy required for chlorine loss from $Cp_2Cu_2Cl_3$ to give $Cp_2Cu_2Cl_2$ (Table 6) suggests that such oxidative addition reactions might stop at the $Cp_2Cu_2Cl_2$ copper(II) stage. Thus, it is unclear whether the mixed Cu(II/III) oxidation state derivative $Cp_2Cu_2Cl_3$ is experimentally realizable. In any case, the stability of the resulting products with average copper oxidation states of +1.5, +2, and +2.5 toward redox reactions involving elimination of the Cp ring might be influenced significantly by the ring substituents. A suitably substituted cyclopentadienyl ligand because of its pentahapto coordination might be a more favorable organic ligand for higher copper oxidation states than the methyl and η^3-allyl ligands in the copper(III) complexes stable only at low temperatures.

5 Supporting information

Tables S1-S5: Copper-carbon (cyclopentadienyl) distances for the 14 structures of $Cp_2Cu_2Cl_n$ (n = 1, 2, 3) using the B3LYP and BP86 methods; Tables S6-S9: The Mulliken spin densities for the $Cp_2Cu_2Cl_n$ (n = 1, 2, 3) structures using B3LYP and BP86 methods; Tables S10-S14: The theoretical harmonic vibrational frequencies for the 14 structures of $Cp_2Cu_2Cl_n$ (n = 1, 2, 3) using the BP86 method; Tables S15-S28: Theoretical Cartesian coordinates for the 14 structures of $Cp_2Cu_2Cl_n$ (n = 1, 2, 3) using the B3LYP methods.

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