

An oscillating  $C_2^{2-}$  unit inside a copper rectangle†Wing-Yin Lo,<sup>ab</sup> Chi-Ho Lam,<sup>ab</sup> Wendy Kit-Mai Fung,<sup>ab</sup> Hong-Zhe Sun,<sup>b</sup> Vivian Wing-Wah Yam,<sup>\*ab</sup> David Balcells,<sup>c</sup> Feliu Maseras<sup>c</sup> and Odile Eisenstein<sup>\*d</sup><sup>a</sup> Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China. E-mail: wwyam@hku.hk<sup>b</sup> Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China<sup>c</sup> Unitat de Química Física, Edifici Cn, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain<sup>d</sup> LSDSMS, UMR 5636, Université Montpellier 2, 34095 Montpellier, France.

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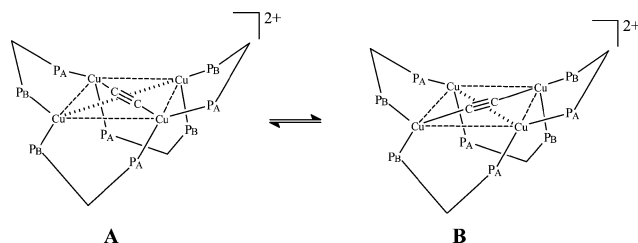
$[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$  has been shown by  $^{31}P$  and  $^1H$  NMR studies to undergo two fluxional processes in solution, the oscillation of the  $C\equiv C^{2-}$  unit inside the copper rectangle and the flipping of the diphosphines, and this has been supported by DFT(B3LYP) calculations.

The chemistry of transition metal acetylide complexes has attracted wide interest and has been studied both experimentally and theoretically.<sup>1</sup> It is noted that the acetylide ligands in transition metal complexes may not only show a wide diversity of bonding modes but also a variety of fluxional behavior.<sup>2–9</sup> A commonly observed fluxionality is the  $\sigma, \pi$ -interchange of the  $\mu-\eta^1, \eta^2$ -acetylide ligand, with examples found in polynuclear complexes of iron, ruthenium, osmium and rhenium.<sup>1, c, 2–7</sup>

We recently reported the synthesis, structure, luminescence and excited-state redox properties of a tetranuclear copper(II) acetylide complex,  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)](BF_4)_2$ .<sup>10</sup> We now report the first observation of two fluxional processes occurring in this complex which has been revealed by variable temperature  $^1H$  and  $^{31}P$  NMR experiments. As shown in Scheme 1, the complex (structure A) shows a  $C\equiv C^{2-}$  unit that bridges the four copper atoms in both  $\eta^1$  and  $\eta^2$  bonding modes. The phosphorus atoms  $P_A$  and  $P_B$  coordinated to the different sets of copper atoms are in a different environment and should exhibit different chemical shifts in the  $^{31}P\{-^1H\}$  NMR spectrum. However, only one sharp  $^{31}P$  NMR signal due to the dppm ligands was observed in acetone- $d_6$  at room temperature at  $\delta -10.4$  ppm. It is likely that a fluxional process occurs in the complex, which causes an exchange of the  $P_A$  and  $P_B$  environment. Upon cooling the sample, the  $^{31}P$  NMR signal becomes broader and finally resolved into two sharp peaks, one at  $\delta -9.6$  ppm and one at  $\delta -12.3$  ppm at 182 K, corresponding to the two phosphorus environments. A fluxional process that may account for such an observation is proposed in Scheme 1, in which the rate of interchange of bonding modes between the  $C\equiv C^{2-}$  unit at the two  $Cu_2$  units from  $\eta^1$  to  $\eta^2$  and *vice versa* is fast on the NMR timescale, and hence only a time-averaged  $^{31}P$

resonance is observed. The signal at  $\delta -9.6$  ppm is tentatively assigned to the phosphorus atoms with  $\pi$ -bonding to the  $C\equiv C^{2-}$  unit, while the more upfield  $^{31}P$  signal at  $\delta -12.3$  ppm is assigned to the phosphorus atoms attached to the copper with the  $C\equiv C^{2-}$  unit  $\sigma$ -bonded to it. Variable temperature  $^1H$  NMR experiments of  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$  in dichloro-methane- $d_2$  indicated the presence of a second fluxional process. At room temperature, a time-averaged methylene proton signal was observed at  $\delta 3.5$  ppm. On cooling the sample, the  $^1H$  NMR signal becomes broader and finally resolved into two sharp peaks at  $\delta 3.4$  and  $3.6$  ppm at 193 K. The signals at  $\delta 3.4$  and  $3.6$  ppm are tentatively assigned as the axial and equatorial methylene protons of the dppm ligands respectively. An exchange of the axial and equatorial protons on the dppm ligand is likely to be a result of an up-down flipping process of the dppm ligands, as is commonly found in other dppm bridged metal complexes.<sup>11</sup> Using the gNMR simulation program,<sup>12</sup> the exchange rate constants (*k*) at different temperatures were determined. According to the Eyring equation, a  $\Delta G^\ddagger$  value of *ca.* 38 kJ mol<sup>-1</sup> for the oscillatory process was obtained for  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$  from the variable temperature  $^{31}P$  NMR studies, which is slightly lower than the  $\Delta G^\ddagger$  values of 43.1 and 43.9 kJ mol<sup>-1</sup> reported for  $\sigma, \pi$ -acetylide exchange in the respective  $Fe_2(CO)_6(\mu_2-\eta_2-C\equiv C-^iPr)(\mu-PPH_2)_2$  and  $(\mu-H)Re_2(\mu_2-\eta^2-C\equiv CH)(CO)_6(\mu-dppm)$  complexes.<sup>3</sup> A  $\Delta G^\ddagger$  value of *ca.* 47 kJ mol<sup>-1</sup> was obtained from the variable temperature  $^1H$  NMR experiments for the dppm flipping process of  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$ . Similar  $\Delta G^\ddagger$  values have been estimated for the dppm flipping processes in  $[(RC\equiv C)Pt(\mu-C\equiv CR)(\mu-dppm)_2W(CO)_3]$  (R = Ph, Tol or Me).<sup>11</sup>

The  $^{13}C$  NMR spectrum of the  $^{13}C$ -enriched  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-^{13}C\equiv^{13}C-)]^{2+}$  at room temperature exhibits a nine-peak signal with intensity ratios of *ca.* 1:8:28:56:70:56:28:8:1 at  $\delta 149.4$  ppm, similar to that obtained by simulation, corresponding to the resonance of the two acetylenic carbon atoms. The acetylenic carbons have a two bond coupling,  $^2J$ , with two  $P_A$  atoms and three bond coupling,  $^3J$ , with the other six phosphorus atoms. On cooling the sample to 213 K, the  $^{13}C$  NMR signal of the  $C_2^{2-}$  unit starts to fuse together and become a broad signal at 181 K. Attempts to study the NMR behaviour at lower temperatures were unsuccessful as a result of the reduced solubility of the complex and the freezing of the deuterated solvent. It is noteworthy that the coplanar arrangement of the four copper atoms in  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$  is suggestive of the absence of strong  $\pi$  bonding between the  $C\equiv C^{2-}$  unit and the copper atoms since best overlap of the two  $\pi$  orbitals of the acetylide ligand with the four copper atoms would require an orthogonal arrangement of the two  $Cu_2$  units. It is likely that the relatively small activation barrier for the oscillatory fluxional process is a result of the weak  $\pi$  interaction between the  $C\equiv C^{2-}$  unit and the copper atoms.



**Scheme 1** Structural fluxionality of  $[Cu_4(\mu-dppm)_4(\mu_4-\eta^1, \eta^2-C\equiv C-)]^{2+}$  in fluid solution showing a  $\sigma, \pi$ -acetylide exchange.

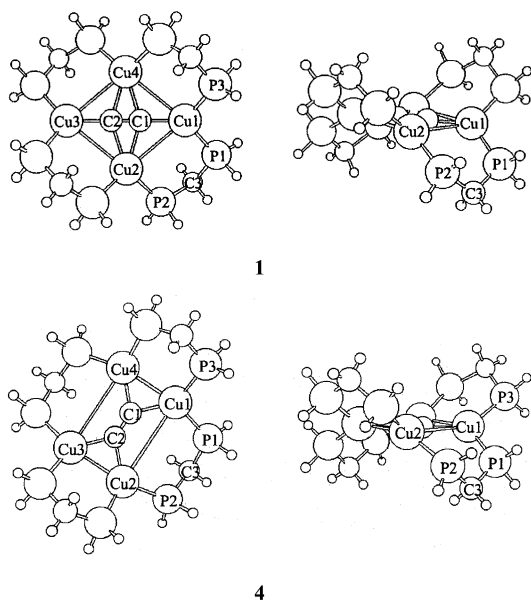
† Electronic supplementary information (ESI) available: NMR spectra and computational details. See <http://www.rsc.org/suppdata/cc/b3/b301842c/>

To further confirm the existence of the two fluxional processes, a DFT(B3LYP) calculation was carried out.† The calculations were performed on a model system where the phenyl substituents on the phosphorus atoms were replaced by hydrogen atoms. A total of five stationary points (**1**–**5**) were located on the potential hypersurface. Selected geometrical parameters are collected in Table 1. The most stable species, **1**, has a calculated geometry which closely resembles that of the experimental structure. Structures **2**–**4** describe the oscillatory movement of the C<sub>2</sub> fragment within the tetracopper unit. Transition state **4** is the highest energy structure on the path. The free energy of **4** is 32.9 kJ mol<sup>-1</sup> which is not far from the experimentally determined ΔG<sup>‡</sup> value of 38 kJ mol<sup>-1</sup>, especially taking into account the fact that our model replaces the experimental phenyl groups by hydrogens, confirming the existence of a low energy fluxional process involving this type of transformation. On the path from **1** to **4**, the system goes first through a transition state **2** and an intermediate **3**. These two species are close in energy, around 23 kJ mol<sup>-1</sup> above **1**. The gradual change from **1** to **4** can be observed in a variety of parameters, like the lengthening of Cu(1)–C(1), the shortening of Cu(4)–C(1) and the closing of the Cu(1)–C(1)–C(2) and Cu(1)–C(1)–Cu(4) angles. The oscillatory process therefore follows a path **1** → **2** → **3** → **4** → **3'** → **2'** → **1'**, where **1'**, **2'** and **3'** are enantiomeric forms of **1**, **2** and **3**. The last stationary structure **5**, which is not on the previous path, is a transition state

**Table 1** Selected optimized (B3LYP) geometrical parameters (Å and °) and relative energy values (ΔE/kJ mol<sup>-1</sup>) for the five stationary points (TS for transition state). Experimental data for [Cu<sub>4</sub>(μ-dppm)<sub>4</sub>(μ<sub>4</sub>-η<sup>1</sup>,η<sup>2</sup>-C≡C<sup>-</sup>)<sub>2</sub>]<sup>2+</sup>; are given for comparison. See Fig. 1 for atom labels<sup>a</sup>

	<b>1</b> (exp)	<b>1</b>	<b>2</b> (TS)	<b>3</b>	<b>4</b> (TS)	<b>5</b> (TS)
ΔE		0	23 <sup>a</sup>	23 <sup>a</sup>	32.9	18.7
Cu(1)–C(2)	1.255	1.277	1.266	1.262	1.261	1.282
Cu(1)–C(1)	1.913	1.934	1.949	1.977	1.992	1.940
Cu(4)–C(1)	2.131	2.211	2.057	2.008	1.992	2.208
Cu(1)–Cu(2)	3.245	3.336	3.917	4.159	4.157	3.403
Cu(1)–Cu(4)	3.264	3.333	2.911	2.738	2.723	3.424
Cu(1)–C(1)–C(2)	178	180	161	146	137	170
Cu(1)–C(1)–Cu(4)	108	107	93	87	86	111
P(1)–Cu(1)–Cu(2)–Cu(4)	132	148	147	149	149	169
P(3)–Cu(1)–Cu(4)–Cu(2)	131	147	158	159	149	169

<sup>a</sup> The energy values for **2** and **3** cannot be significantly separated with the calculation methods used.



**Fig. 1** Two views of the optimized B3LYP geometries for **1** and **4**.

for the 'flipping' movement of the four dppm groups. The transition vector corresponds to a movement by which the two pairs of diphosphines exchange their positions above and below the tetracopper unit. The movement of the phosphines with respect to the coppers can be followed by inspecting the P(1)–Cu(1)–Cu(2)–Cu(4) and P(3)–Cu(1)–Cu(4)–Cu(2) dihedral angles (Table 1). It can be seen that while these two dihedral angles, especially the first one, are largely unchanged in the oscillatory movement from **1** to **4**, they increase their values up to 169° in structure **5**, already close to the value of 180° associated to the inversion around the Cu centre. The free energy of **5** is ca. 19 kJ mol<sup>-1</sup> which is significantly smaller than the experimental finding of 47 kJ mol<sup>-1</sup>. However, this discrepancy is explainable because of the presence of the eight bulkier phenyl substituents in the real system. The bulk of the phenyls is likely to have more effect in the diphosphine flipping than in the C–C oscillation process.

The tetranuclear copper cluster has two independent fluxional processes with similar activation energies. The fluxional process of the C<sub>2</sub><sup>2-</sup> unit with the copper rectangle modifies the shape of the cage but does not influence the supporting dppm ligands for which a flipping motion has been located.

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## Notes and references

† The Gaussian98 program was used. Geometry optimizations were performed without any geometry constraints with basis set I: LANL2DZ for Cu, P; 6-31G for acetylide; STO-3G for phosphine substituents. Energetics were evaluated with basis set II: LANL2DZ for Cu, P (with extra d shell on P); 6-31G(d) for acetylide; 6-31G for phosphine substituents. Thermal, zero-point and entropic corrections were evaluated with basis set I.

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