

# A Trigonal Planar $\mu_3$ -Fluorido Coinage Metal Complex from a Dicationic (Diphosphinomethane)copper(I) Dimer: Syntheses, Structures, and Bonding<sup>‡</sup>

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The triflate and hexafluorophosphate salts of  $[\text{Cu}_2(\mu\text{-dtbpm})_2]^{2+}$  ( $\mathbf{1}^{2+}$ ) [dtbpm = bis(di-*tert*-butylphosphino)methane,  $\text{tBu}_2\text{PCH}_2\text{P}^t\text{Bu}_2$ ] and of  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}$  ( $\mathbf{2}^{2+}$ ) were synthesized and characterized. Coordination of solvent or counterions to  $\mathbf{1}^{2+}$  is observed neither in solution nor in the solid state. The two copper(I) centers in  $\mathbf{1}^{2+}$  indicate weak  $d^{10}\text{--}d^{10}$  closed-shell interactions.  $\mathbf{1}^{2+}$  reacts slowly with  $\text{PF}_6^-$  anions in acetone or KF in  $\text{CH}_2\text{Cl}_2$  to yield the  $\mu_3$ -fluorido complex  $\mathbf{2}^{2+}$  with idealized  $D_3$  symmetry, containing a trigonal planar  $\text{Cu}_3\text{F}$  core, as shown by single-crystal X-ray diffraction. Distinct structural differences are observed compared to monocationic bicapped, trinuclear copper(I) dppm halide complexes [dppm = bis(diphenylphosphino)methane,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ]. The average Cu–Cu, Cu–F, and Cu–P distances and the P–Cu–P' angle in  $\mathbf{2}^{2+}$  are 3.85, 2.22, and 2.28 Å and  $144.3^\circ$ , respectively. The  $\text{P}_2\text{Cu}$  units are twisted out of the  $\text{Cu}_3\text{F}$  plane by an average angle of  $18.4^\circ$ . DFT calculations (BPW91/LANL2DZ) for the model  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dhpm})_3]^{2+}$  (dhpm = diphosphinomethane,  $\text{H}_2\text{PCH}_2\text{PH}_2$ ) are used to explain the formation, structure, and bonding pattern of  $\mathbf{2}^{2+}$ .

## Introduction

Attractive interactions between  $d^{10}$  closed shell coinage metal atoms or ions have found much experimental<sup>1–4</sup> and theoretical<sup>3–6</sup> attention. Diphosphinomethane ligands are well-known to support the formation of dinuclear eight-membered ring systems with intramolecular, transannular metal–metal interactions. We have been employing the crowded bis(di-*tert*-butylphosphino)methane ligand (dtbpm)<sup>7</sup> in late transition metal chemistry, and so far its chelating  $\kappa^2\text{P}$  coordination mode was utilized.<sup>8</sup> We have also reported the formation of the neutral, dinuclear  $d^{10}\text{--}d^{10}$  species  $[\text{Pt}_2(\mu\text{-dtbpm})_2]$  by reductive elimination of neopentane from the cis neopentyl hydrido complex  $[\text{Pt}(\text{CH}_2\text{tBu})(\text{H})(\text{dtbpm-}\kappa^2\text{P})]$  in the absence of reactive substrates.<sup>8c</sup> The synthesis, structure, and reactivity of an analogous dinuclear dicationic Cu(I) complex  $\mathbf{1}^{2+}$  are described here.

Cu(I)  $\text{ML}_2$ , Ag(I)  $\text{ML}_2$ , and Au(I)  $\text{ML}$   $d^{10}$  fragments, isolobal to  $\text{H}^+$ , support high coordination numbers and rare coordination geometries for main group elements boron,<sup>9</sup> carbon,<sup>10</sup> nitrogen,<sup>11</sup> oxygen,<sup>12</sup> fluorine,<sup>13</sup> sulfur,<sup>14</sup> chlorine,<sup>15</sup> arsenic,<sup>11b</sup> selenium,<sup>14a,16</sup> bromine,<sup>17</sup> tellurium,<sup>14a,18</sup> and iodine.<sup>19</sup> Recent studies of Samuelson et al.<sup>20</sup> describe the geometries of monocationic bicapped trinuclear copper(I) complexes  $[\text{Cu}_3(\mu_3\text{-X})(\mu\text{-dppm})_3]^+$  (X = acetylide or halide except fluoride) [dppm = bis(diphenylphosphino)methane,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ] as established by X-ray diffraction and rationalize the structural differences by ab initio model calculations for naked tricopper dihalide monocations.

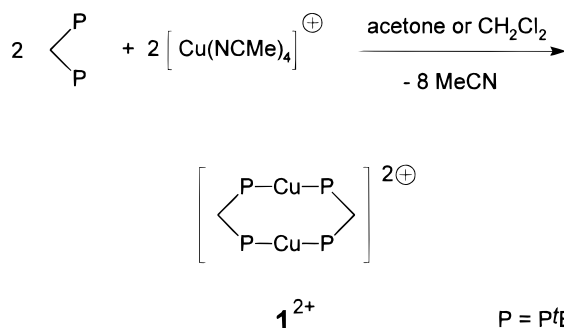
We report here the synthesis of the first dicationic trinuclear copper(I) dtbpm fluorido complex  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}$  ( $\mathbf{2}^{2+}$ )

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<sup>‡</sup> Dedicated to Prof. P. v. R. Schleyer on the occasion of his 70th birthday.

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## Scheme 1



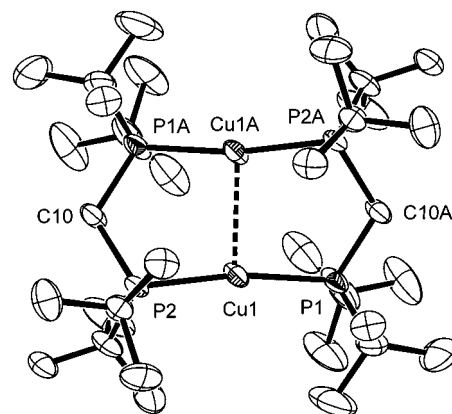
with a  $\mu_3$ -fluorido ligand at the center of a Cu<sub>3</sub> core. One EHMO and DFT study<sup>21</sup> of [Cu<sub>3</sub>( $\mu_3$ -OH)(PH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> (C<sub>3v</sub> restriction), using local exchange-correlation potentials, and one ab initio model study<sup>20a</sup> for tricopper halide cations have been published. We have performed DFT (BPW91) geometry optimizations and vibrational analyses for various conformers of the complex [Cu<sub>3</sub>( $\mu_3$ -F)( $\mu$ -dtbpm)<sub>3</sub>]<sup>2+</sup> as a model of **2<sup>2+</sup>** to gain deeper insight into bonding and structural patterns of the novel copper(I) fluorido complex.

## Results and Discussion

**The [Cu<sub>2</sub>( $\mu$ -dtbpm)<sub>2</sub>]<sup>2+</sup> Cation **1<sup>2+</sup>**.** According to Scheme 1, the reaction of [Cu(NCMe)<sub>4</sub>]<sup>+</sup> X<sup>-</sup> (X<sup>-</sup> = [O<sub>3</sub>SCF<sub>3</sub>]<sup>-</sup> or [PF<sub>6</sub>]<sup>-</sup>) with 1 equiv of dtbpm in acetone or dichloromethane at ambient temperature yields the dinuclear dicationic copper(I) complex [Cu<sub>2</sub>( $\mu$ -dtbpm)<sub>2</sub>]<sup>2+</sup> (**1<sup>2+</sup>**).

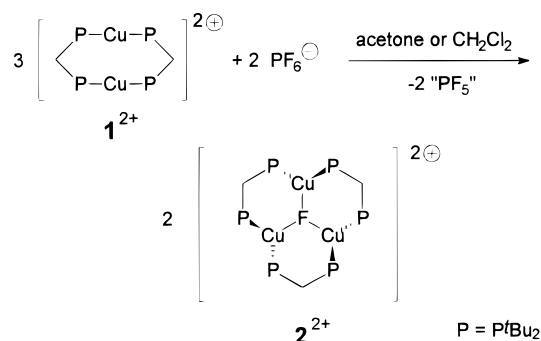
The sterically crowded and electron-rich ligand dtbpm is essential for the formation of this low-coordinate copper(I) species. Trialkylphosphines such as tribenzylphosphine or sterically demanding arylphosphines such as trimesitylphosphine are reported to stabilize two-coordinate copper(I) cations.<sup>22</sup> No coordination of acetonitrile to **1<sup>2+</sup>** could be detected by <sup>1</sup>H NMR spectroscopy, in contrast to the case of [Cu<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>(NCMe)<sub>4</sub>]<sup>2+</sup> with tetracoordinate copper centers.<sup>23</sup> Oxyanions are reported to coordinate to the [Cu<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>]<sup>2+</sup> fragment, too.<sup>20b</sup> Cation **1<sup>2+</sup>** exhibits identical <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts in [D<sub>6</sub>]acetone and CD<sub>2</sub>Cl<sub>2</sub> and in the presence of acetonitrile. Replacing hexafluorophosphate by triflate as a counterion has no observable spectroscopic effect. Consistently neither counterion nor solvent coordination was found in the X-ray crystal structure of [Cu<sub>2</sub>( $\mu$ -dtbpm)<sub>2</sub>]<sup>2+</sup>[(O<sub>3</sub>SCF<sub>3</sub>)<sup>-</sup>]<sub>2</sub> (Figure 1). The Cu–Cu distance of 2.7309(6) Å in **1<sup>2+</sup>** is in accordance with a weak intramolecular d<sup>10</sup>–d<sup>10</sup> closed-shell attraction,<sup>1,5,6</sup> although the ligand environment certainly has a predominant influence on the intramolecular Cu–Cu distance (Table 2).<sup>3</sup>

**The [Cu<sub>3</sub>( $\mu_3$ -F)( $\mu$ -dtbpm)<sub>3</sub>]<sup>2+</sup> Cation **2<sup>2+</sup>**.** From a concentrated solution of (**1<sup>2+</sup>**)[(PF<sub>6</sub>)<sup>-</sup>]<sub>2</sub> in acetone, single crystals of [Cu<sub>3</sub>( $\mu_3$ -F)( $\mu$ -dtbpm)<sub>3</sub>]<sup>2+</sup>[(PF<sub>6</sub>)<sup>-</sup>]<sub>2</sub>, (**2<sup>2+</sup>**)[(PF<sub>6</sub>)<sup>-</sup>]<sub>2</sub>, suitable for X-ray diffraction were obtained after standing at room temperature for 12 h. The formation of the trinuclear ion is observable by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Scheme 2). A similar abstraction of F<sup>-</sup> from BF<sub>4</sub><sup>-</sup> by Cu(I) tris(pyrazolyl) complexes was



**Figure 1.** ORTEP plot of (**1<sup>2+</sup>**)[(O<sub>3</sub>SCF<sub>3</sub>)<sup>-</sup>]<sub>2</sub>. H atoms and counterions have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The cation has crystallographic C<sub>2</sub> symmetry.

## Scheme 2



reported by Thompson et al.,<sup>24</sup> leading to one of the very few copper(I) fluorido complexes described in the literature.<sup>13b,24,25</sup> In fact, BF<sub>4</sub><sup>-</sup> in the presence of nitrogen-containing heterocycles or amines is an often used fluoride source for the preparation of transition metal fluorido complexes.<sup>26,27</sup>

Salts of **2<sup>2+</sup>** can be alternatively prepared in good yield by reacting **1<sup>2+</sup>** with a slurry of KF in dichloromethane. The absence of traces of water is essential to avoid the formation of a so far unidentified side product.<sup>28</sup> Biphasic reaction conditions employing KF in water and [(**1<sup>2+</sup>**)(PF<sub>6</sub>)<sup>-</sup>]<sub>2</sub> in dichloromethane yielded (**2<sup>2+</sup>**)[(PF<sub>6</sub>)<sup>-</sup>]<sub>2</sub> and the byproduct in a ratio of 1:1. Attempts of Samuelson et al. to synthesize a trinuclear, bicapped copper(I) dppm fluorido complex e.g. by employing an aqueous solution of KF under biphasic reaction conditions<sup>20a</sup> led to a trinuclear monocapped  $\mu_3$ -hydroxo complex already described in the literature.<sup>12a</sup> The possibility of getting access to a trinuclear copper(I) fluorido complex like **2<sup>2+</sup>** upon treatment of [Cu<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>(NCMe)<sub>4</sub>]<sup>2+</sup> with suspended KF in aprotic solvents has not been tested yet.<sup>20a</sup> One reason for the facile formation of **2<sup>2+</sup>** may be the absence of acetonitrile ligands in **1<sup>2+</sup>**. The binding energy of acetonitrile to copper(I), unlike for [Cu<sub>2</sub>( $\mu$ -dppm)<sub>2</sub>(NCMe)<sub>4</sub>]<sup>2+</sup>, therefore is of no relevance in our

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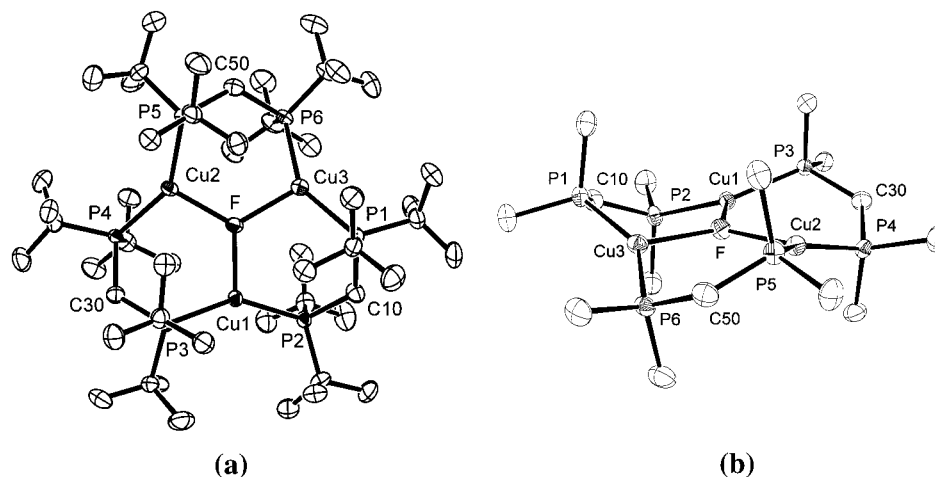
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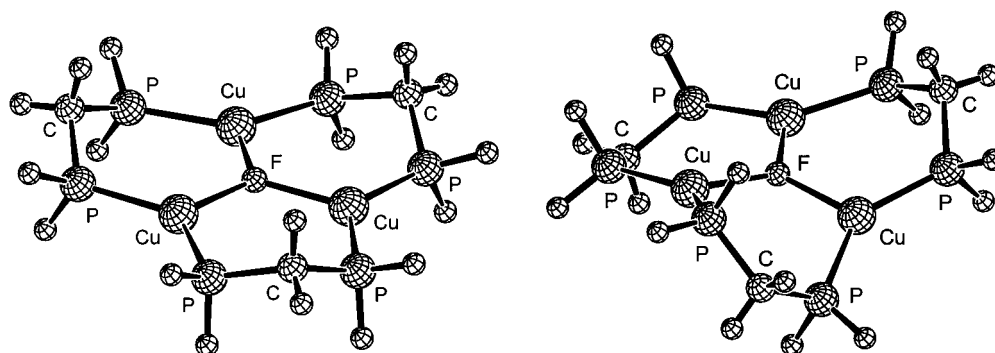
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(28) We assume the side product to be a trinuclear copper(I) dtbpm hydroxo or oxo complex. <sup>31</sup>P{<sup>1</sup>H} NMR (121.50 MHz, [D<sub>6</sub>]acetone, 298 K):  $\delta$  = 31.2 (s)



**Figure 2.** ORTEP plot of  $(2^+)[(PF_6)^-]_2$ : top view (a); side view (b). H atoms and  $PF_6^-$  counterions [and methyl carbon atoms of the *tert*-butyl groups in (b)] have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 3.** Schakal plot of the  $C_{3v}$ -symmetrical local minimum  $3a^{2+}$  (left) and of the  $C_2$ -symmetrical local minimum  $3b^{2+}$  (right) of  $[Cu_3(\mu_3-F)-(\mu-dhpm)_3]^{2+}$ .

system. In the solid state, the  $\mu_3$ -fluorido complex  $2^{2+}$  is slightly distorted from  $D_3$  symmetry (Figure 2, Table 3).  $^{19}F\{^1H\}$  and  $^{31}P\{^1H\}$  NMR spectra underline the equivalence of the six phosphorus nuclei in solution. The dicationic trinuclear copper complex  $2^{2+}$  is the first molecular system in which a fluoride anion is coordinated in such a highly symmetrical trigonal planar fashion.<sup>29</sup> This type of coordination geometry of a fluoride anion, however, is well-known from e.g. rutile type solids such as  $MgF_2$ ,  $ZnF_2$ , or  $FeF_2$ . The average Cu–Cu distance of 3.85 Å in the trinuclear complex  $2^{2+}$  is remarkably larger than the corresponding distance of 2.73 Å in the dinuclear system  $1^{2+}$ . This contrasts the situation for dppm systems, where Cu–Cu distances in dinuclear complexes are larger than the corresponding distances in trinuclear species. The Cu–Cu distances in  $2^{2+}$  are distinctly longer than in the trinuclear dppm copper(I) complexes previously described in the literature.<sup>20</sup>

**DFT Calculations.** Obviously, there are distinct differences between dppm and dtbpm with respect to their metal complexation behavior. Since dtbpm is a more electron donating ligand than dppm, a dicationic trinuclear copper(I) complex is more stabilized than a monocationic bicapped structure as found with dppm. Additionally, steric strain is highly important in dtbpm chemistry. To get more insight into the basic electronic structure

of  $2^{2+}$ , dhpm (dhpm = diphosphinomethane,  $H_2PCH_2PH_2$ ) was used as a simplified model for dtbpm in density functional theory calculations. BPW91 geometry optimizations for  $[Cu_3(\mu_3-F)-(\mu-dhpm)_3]^{2+}$  ( $3^{2+}$ ) were carried out in order to rationalize the formation and electronic structure of the dicationic trinuclear dtbpm copper(I) complex  $2^{2+}$  with its central fluoro ligand and to find out about the role of the steric demand of the 12 *tert*-butyl groups by comparison to the minimum energy structures of the sterically uncongested model  $3^{2+}$ . Two minima and two second-order saddle points were found, revealing relevant features of the structural energy surface of  $3^{2+}$ .

A local minimum,  $3a^{2+}$ , which we consider to be the global minimum for model  $3^{2+}$ , resulted from an unrestricted geometry optimization (NIMAG = 0). It deviates only very slightly from  $C_{3v}$  symmetry. If true  $C_{3v}$  symmetry is imposed, a second-order saddle point with two negative frequencies of  $-3.7\text{ cm}^{-1}$  and  $-10.1\text{ cm}^{-1}$  is obtained, and this geometry is only 0.3 kJ/mol less stable than the minimum structure  $3a^{2+}$  (Figure 3).

A second local minimum of  $3^{2+}$  (NIMAG = 0) is the  $C_2$ -symmetrical conformer  $3b^{2+}$ . This structure was found 5.7 kJ/mol above  $3a^{2+}$ .

A structure close to the experimental geometry of real  $2^{2+}$  with nearby  $D_3$  symmetry and with two negative frequencies of  $-11.6$  and  $-12.7\text{ cm}^{-1}$  is another second-order saddle point,  $3c^{2+}$ , on the energy surface. The deviations from strict  $D_3$  symmetry do not exceed 0.02 Å for bond lengths and 2.1° for bond angles, however. This structure, shown in Figure 4, is 20.9 kJ/mol less stable than the lowest energy local minimum  $3a^{2+}$ .

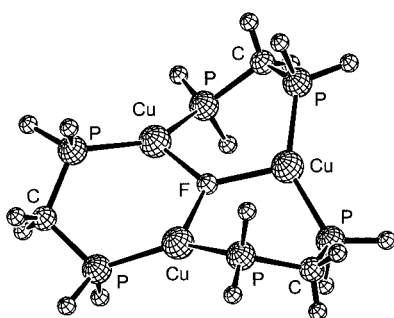
The Cu–Cu distance of 3.85 Å and the Cu–F distance of 2.22 Å of  $2^{2+}$  are considerably longer than the calculated

(29) Cesium triorganofluorometalates with  $Cs_2FGa$  or  $Cs_2FIn$  fragments having angular sums of or close to  $360^\circ$  and angles between  $93.6(1)^\circ$  and  $156.4(3)^\circ$  have been reported: Werner, B.; Kräuter, T.; Neumüller, B. *Organometallics* **1996**, *15*, 3746. A planar  $In_2FMg$  fragment in an organoindium magnesium fluoride cluster displays angles between  $106.2(1)$  and  $141.9(1)^\circ$ : Neumüller, B.; Gahlmann, F. *Z. Anorg. Allg. Chem.* **1993**, *619*, 718. An almost planar  $Fe_3F$  fragment has been reported in ref 27.

**Table 1.** Crystallographic Data for  $[\text{Cu}_2(\mu\text{-dtbpm})_2]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ ,  $(\text{I}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$ ,  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{PF}_6)^-]_2$ ,  $(\text{2}^{2+})[(\text{PF}_6)^-]_2$ , and  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ ,  $(\text{2}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$ 

	$(\text{1}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$	$(\text{2}^{2+})[(\text{PF}_6)^-]_2$	$(\text{2}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$
chem formula	$\text{C}_{44}\text{H}_{66}\text{Cu}_2\text{F}_6\text{O}_8\text{P}_4\text{S}_2$	$\text{C}_{63}\text{H}_{132}\text{Cu}_3\text{F}_{13}\text{O}_3\text{P}_8$	$\text{C}_{62}\text{H}_{132}\text{Cu}_3\text{F}_7\text{O}_9\text{P}_6\text{S}_2$
fw	1182.29	1623.06	1595.24
space group	<i>Fdd2</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	20.2467(1)	12.2534(1)	21.9548(4)
<i>b</i> , Å	41.7750(4)	26.2696(2)	16.7994(1)
<i>c</i> , Å	13.6175(2)	25.2484(2)	23.0086(4)
$\beta$ , deg		90.813(1)	109.6540(10)
<i>V</i> , Å <sup>3</sup>	11 517.8(2)	8126.4(1)	7991.8(2)
<i>Z</i>	8	4	4
<i>T</i> , K	200(2)	200(2)	200(2)
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.36	1.33	1.33
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	9.9	10.0	10.3
reflcs collcd	21 193	59 163	58 874
unique reflcs [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4763	13 888	13 789
no. of params	310	884	967
$\text{R1}^a$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.030	0.072	0.072
$\text{wR2}^b$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.073	0.186	0.167

<sup>a</sup>  $\text{R1} = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $\text{wR2} = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

**Figure 4.** Schakal plot of the nearby  $D_3$ -symmetrical second-order saddle point  $3\text{e}^{2+}$  of  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dhpm})_3]^{2+}$ , corresponding to the X-ray structure of  $2^{2+}$ .**Table 2.** Selected Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) of  $[\text{Cu}_2(\mu\text{-dtbpm})_2]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ ,  $(\text{1}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$ 

Bond Distances			
Cu1–P1	2.2352(8)	P1–C10A	1.857(2)
Cu1–P2	2.2355(7)	P2–C10	1.861(3)
Cu1–Cu1A	2.7309(6)		
Bond Angles			
P1–Cu1–P2	170.35(3)	C10–P2–Cu1	113.35(8)
C10A–P1–Cu1	115.33(9)	P1A–C10–P2	117.55(14)
Dihedral Angles			
Cu1–P1–C10A–P2A	–9.2(2)	P1–Cu1–Cu1A–P2A	–17.79(3)
P1–C10A–P2A–Cu1A	–7.5(2)		

distances of  $3\text{a}-\text{c}^{2+}$  (see Table 4). Higher levels of theory might help to narrow this gap between experiment and theory, but certainly, the steric repulsion of the 12 *tert*-butyl groups in the real complex influences the interatomic distances of the  $\text{Cu}_3\text{F}$  core. Beyond that, the Thorpe–Ingold effect of the two geminal  $\text{P}'\text{Bu}_2$  groups of each  $\text{PCP}'$  unit seems to be the reason for the  $\text{P}-\text{C}-\text{P}'$  angles of  $2^{2+}$  being enlarged by more than  $11^\circ$  compared to the computed conformers of  $3^{2+}$ .

From experimental structure determinations, bending of the diphosphinomethylene groups out of the coordination plane is a typical phenomenon in dinuclear and trinuclear dppm copper(I) complexes.<sup>20</sup> In  $2^{2+}$ , the *tert*-butyl groups prevent the  $\text{CH}_2$  groups from bending out of the respective  $\text{FP}_2$  planes because of their considerable 1,3-repulsion.

Overall, our attempts to localize the global minimum structure (Table 5) for the model system  $3^{2+}$  without the *tert*-butyl substituents inevitably lead to more than one local minimum with somewhat different conformations of the trinuclear fluoride

**Table 3.** Selected Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) of  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{PF}_6)^-]_2$ ,  $(\text{2}^{2+})[(\text{PF}_6)^-]_2$ 

Bond Distances			
Cu1–F1	2.189(3)	Cu1–Cu2	3.818(1)
Cu1–P2	2.2852(19)	Cu1–Cu3	3.836(1)
Cu1–P3	2.2860(17)	Cu2–Cu3	3.868(1)
Cu2–F1	2.213(3)	P1–C10	1.858(6)
Cu2–P4	2.280(2)	P2–C10	1.866(6)
Cu2–P5	2.2772(17)	P3–C30	1.855(6)
Cu3–F1	2.251(3)	P4–C30	1.858(6)
Cu3–P1	2.2890(19)	P5–C50	1.859(6)
Cu3–P6	2.282(2)	P6–C50	1.864(7)
Bond Angles			
F1–Cu1–P2	107.71(10)	P1–C10–P2	124.3(3)
F1–Cu1–P3	107.94(9)	C30–P3–Cu1	118.4(2)
P2–Cu1–P3	144.35(8)	C30–P4–Cu2	118.0(2)
F1–Cu2–P5	107.97(9)	P3–C30–P4	124.9(3)
F1–Cu2–P4	108.57(10)	C50–P5–Cu2	118.7(2)
P5–Cu2–P4	143.46(8)	C50–P6–Cu3	117.7(2)
F1–Cu3–P1	107.31(10)	P5–C50–P6	125.1(3)
F1–Cu3–P6	107.73(9)	Cu1–F1–Cu2	120.33(14)
P6–Cu3–P1	144.95(8)	Cu1–F1–Cu3	119.55(14)
C10–P1–Cu3	117.5(2)	Cu2–F1–Cu3	120.13(13)
C10–P2–Cu1	118.2(2)		
Dihedral Angles			
P3–Cu1–F1–Cu2	–19.21(17)	P6–Cu3–F1–Cu2	–19.81(17)
P2–Cu1–F1–Cu3	–19.08(17)	P5–Cu2–F1–Cu2	–16.90(17)
P1–Cu3–F1–Cu1	–19.17(17)	P4–Cu2–F1–Cu1	–16.76(18)

centered array. These local minima as well as close-by second-order saddle points all lie within an energy range of less than 21 kJ/mol, showing a very flexible skeleton of the trinuclear dication. We did not make efforts to locate any transition structure connecting the minima on the conformational energy surface. There is no significant differentiation between the bonding and electronic structures of the various conformers, and we use the data obtained for the nearby  $D_3$  geometry  $3\text{e}^{2+}$  for the following discussion, because it is structurally closest to  $2^{2+}$ .

**Covalency versus Electrostatic Interactions.** Density functional theory calculations for the model  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dhpm})_3]^{2+}$  ( $3^{2+}$ ) yield a Mulliken charge of  $-0.51$  on the fluoride center for structure  $3\text{e}^{2+}$ . The copper atoms as well as the  $\text{PH}_2$  groups carry a positive charge of 0.29 and 0.36, respectively. Despite the well-known limitations of Mulliken charges, it is clear that electrostatic interactions between  $\text{F}^-$  and the three  $\text{CuP}_2^+$  fragments should be essential for the structure of the  $\text{Cu}_3\text{F}$  core of  $2^{2+}$ . The individual  $\text{Cu}-\text{F}$  distances vary between 2.189(3)



**Table 4.** Selected Average Bond Distances, Angles, and Dihedral Angles of  $(2^{2+})[(PF_6)^-]_2$ ,  $(2^{2+})[(O_3SCF_3)^-]_2$ ,  $3a^{2+}$ , and  $3c^{2+}$ 

	$(2^{2+})[(PF_6)^-]_2$	$(2^{2+})[(O_3SCF_3)^-]_2$	$3a^{2+}$ : near $C_{3v}$	$3c^{2+}$ : near $D_3$
Cu—Cu' (Å)	3.841	3.857	3.642	3.661
Cu—F (Å)	2.218	2.227	2.104	2.114
Cu—P (Å)	2.283	2.277	2.342	2.336
Cu—F—Cu' (deg)	120.0	120.0	119.9	120.0
F—Cu—P (deg)	107.9	107.8	114.9	107.1
P—Cu—P' (deg)	144.3	144.3	131.5	145.8
P—C—P' (deg)	124.8	125.7	112.1	113.1
C—P—Cu (deg)	118.1	118.0	126.0	120.0
P—Cu—F—Cu' (deg)	18.5	18.3	2.2	21.1

**Table 5.** Symmetries and Energies of the Conformers  $3a-c^{2+}$ 

	$3a^{2+}$		$3b^{2+}$		$3c^{2+}$	
	local minimum	second-order saddle point	local minimum	second-order saddle point	local minimum	second-order saddle point
symmetry	$C_1$	$C_{3v}$	$C_2$	near $D_3$		
energy (au)	-582.383 778	-582.383 671	-582.381 626	-582.375 834		
rel energy (kJ/mol)	0	0.3	5.7	20.9		

and 2.251(3) Å in  $(2^{2+})[(PF_6)^-]_2$  and between 2.184(3) and 2.309(4) Å in  $(2^{2+})[(O_3SCF_3)^-]_2$ , probably caused by packing effects, respectively. This observed range of Cu—F distances in  $2^{2+}$  is in accordance with mainly electrostatic interactions between copper and the fluorido ligand, since covalent bonds typically feature narrower bandwidths of interatomic distances. Accordingly, several frequencies below  $100\text{ cm}^{-1}$  distorting the  $Cu_3F$  core are observed in the vibrational analyses of all computed conformers of the model complex  $3^{2+}$ .

In analogy to  $D_{3h}$  “compact polar dianions”  $[MY_3]^{2-}$  ( $M = \text{Li, Na, K; Y = F, Cl}$ ) or  $[\text{Si}(\text{C}_2)_3]^{2-}$ , which were investigated by high-level quantum chemical methods by Cederbaum et al.,<sup>30,31</sup> the  $D_3$ -symmetrical  $P_6Cu_3F$  core of  $2^{2+}$  can be regarded as a “compact polar dication”. Its stability can be understood in terms of Cederbaum’s ionic model, which was utilized to predict and explain the metastable character of ionic species  $[MY_3]^{2-}$  in the gas phase,<sup>30a</sup> and the line of reasoning for dianionic systems<sup>31</sup> can be transferred to the dicationic copper(I) fluorido complex  $2^{2+}$ . Its high symmetry leads to a uniform distribution of two positive charges over three electropositive  $CuP_2$  fragments. The difference in electronegativity between fluorine and copper causes accumulation of negative charge at the central position, leading in turn to strong electrostatic attraction between fluorine and copper. As a consequence, a capping fluorido ligand would be driven into the center of the  $Cu_3$  core by the resulting dipole moment of a capped trinuclear dication. Cu—Cu distances are larger in the case of capping chloride ions than in the case of the larger bromide both in real bicapped trinuclear dppm copper(I) complexes and in computed tricopper dihalide cation model complexes.<sup>20a</sup> Samuelson et al. proposed the participation of vacant copper 4s orbitals in copper halide bonding to explain this effect, since the induced Cu—Cu bonding interaction should be greater in  $Cu_3Br_2^+$ , leading to a shorter Cu—Cu distance. Evidently, however, electrostatic forces increase with decreasing covalent interactions in the copper halide series, leading to greater repulsion of the more positively charged copper atoms in the case of capping chlorides compared to the case of capping bromides. Therefore, there is no intrinsic contradiction between geometrical expectations derived from the “electrostatic” and the “covalent” point of view.

**Structural Features of Trinuclear Copper(I) Diphosphinomethane Complexes.** Previously described trinuclear copper-

(I) dppm halide, acetylide, or hydroxide complexes are either dicationic monocapped or monocationic bicapped. Hydroxo and acetylido ligands obviously cannot function as centered ligands in a trigonal planar  $Cu_3$  core of a dicationic trinuclear copper(I) diphosphinomethane complex, and lead to capped complexes.<sup>12a,32</sup> The hydrogen atom of  $OH^-$  or the methyne group of  $C_2H^-$  only permit the formation of a distorted tetrahedral coordination environment around the  $\mu_3$ -oxygen or carbon atom. Monocapped trinuclear diphosphinomethane copper(I) halide complexes are unknown, in line with electrostatic arguments predicting either monocationic bicapped or dicationic trigonal planar  $Cu_3$  halide cores at least for the very electronegative fluorine. The fluorido ligand is obviously small enough to fit into the central cavity of a triatomic copper(I) unit, and the trigonal planar coordination pattern is in perfect accordance with electrostatic arguments.

$NH_3$ , isoelectronic to  $H_3O^+$  and to the unknown  $H_3F^{2+}$ , electronically related to  $Cu_3F^{2+}$ , possesses a  $C_{3v}$  structure which can be interpreted as a consequence of a second-order Jahn—Teller distortion.<sup>33</sup> Such an electronic effect as well as cuprophilic interactions, leading to a fluorido position above the  $Cu_3$  plane, seem to be of no importance in  $2^{2+}$ . In an ab initio study,  $H_3F^{2+}$  was shown to possess a metastable  $D_{3h}$  minimum 464 kJ/mol above the ion-plus-ion dissociation products.<sup>34</sup>

**Structural Consequences of *tert*-Butyl Substitution.** The steric demand of the 12 *tert*-butyl groups of  $2^{2+}$  favors a geometry with extensive twisting of the PCP' units. Thus the  $\mu_3$ -fluorido complex  $2^{2+}$  with its idealized  $D_3$  symmetry is less crowded than it would be in  $3a^{2+}$  with 12 eclipsed *tert*-butyl groups or in a monocationic bicapped structure with local  $D_{3h}$  symmetry of the  $P_6Cu_3F_2$  core. Moreover, the average P—Cu—P' angle of  $144.3^\circ$  in  $2^{2+}$  lies between the angle of  $180^\circ$  of an unperturbed  $d^{10}$ - $ML_2$   $CuP_2^+$  fragment and the angle of  $120^\circ$  for a  $d^{10}$ - $ML_3$  fragment. This corresponds to very low covalent  $\sigma$ -donor capability of each cationic  $Cu_2F^+$  ligand toward the opposite  $P_2Cu^+$  fragment.

The idealized  $D_3$ -symmetrical and therefore chiral cation  $2^{2+}$  possesses six axial and six equatorial *tert*-butyl groups (Figure 2). At ambient temperature in solution, the methyl groups are found to be isochronous in the  $^{13}C\{^1H\}$  NMR spectrum,

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indicating that they have already coalesced. The quaternary carbon atoms, however, are diastereotopic on the NMR time scale at 300 K, corresponding to a  $\Delta G^\ddagger$  for exchange larger than 60 kJ/mol.  $^{13}\text{C}$  NMR spectra were recorded at different magnetic fields to ensure the existence of two singlets and to exclude the possibility of a doublet caused by  $^1\text{J}(\text{P},\text{C})$  coupling. The minimum  $\Delta G^\ddagger$  value of 60 kJ/mol can be deduced from the fact that for a lower  $\Delta G^\ddagger$  the signals of the quaternary carbons would have already coalesced below room temperature.

The degenerate interconversion of  $2^{2+}$  with its enantiomer contrasts the computed energetic situation of the corresponding conformer  $3\mathbf{a}^{2+}$  and second-order saddle point  $3\mathbf{c}^{2+}$  of the dtpm model complex. Whereas the local minimum  $3\mathbf{a}^{2+}$  (nearby  $C_{3v}$ ) is 20.9 kJ/mol more stable than  $3\mathbf{c}^{2+}$  (nearby  $D_3$ ), experimentally observed  $2^{2+}$  adopts a structure very similar to that of  $3\mathbf{c}^{2+}$ .  $2^{2+}$  has to be more than 60 kJ/mol more stable than any hypothetical experimental transition state, which would be structurally related to  $3\mathbf{a}^{2+}$ . The role of steric hindrance of the *tert*-butyl groups in  $2^{2+}$  for the racemization barrier is obvious, regardless whether a real mechanism would involve a planar  $\text{P}_6\text{Cu}_3\text{F}$  core or even the cleavage of a Cu–P bond. The stabilizing effect of the *tert*-butyl groups for the  $D_3$ -type structure of the copper(I) dtpm fluorido complex  $2^{2+}$  compared to a hypothetical  $D_{3h}$  geometry of the  $\text{P}_6\text{Cu}_3\text{F}$  core with eclipsed *tert*-butyl groups is estimated to be at least 80 kJ/mol.

## Summary

The electron-rich and sterically crowded ligand dtpm favors low coordination numbers in copper(I) complexes, as can be seen in  $[\text{Cu}_2(\mu\text{-dtpm})_2]^{2+}$  ( $1^{2+}$ ) and  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtpm})_3]^{2+}$  ( $2^{2+}$ ). Electrostatic interactions seem to be decisive for the trigonal planar shape of the  $\text{Cu}_3\text{F}$  core of the latter. DFT calculations show the unsubstituted model complex  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtpm})_3]^{2+}$  ( $3^{2+}$ ) to be extremely flexible. Steric repulsion of the 12 *tert*-butyl groups in  $2^{2+}$  forces the molecular skeleton to be twisted in a  $D_3$ -symmetrical fashion.

## Experimental Procedures

**Computational Details.** For the density functional theory calculations the BPW91 method (Becke's exchange<sup>35</sup> and the Perdew–Wang gradient-corrected correlation<sup>36</sup> functionals) within the Gaussian 98 program<sup>37</sup> were used. The BPW91 functionals were successfully employed earlier in theoretical Cu(I) complex chemistry.<sup>3</sup> The geometry of  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtpm})_3]^{2+}$  was optimized without symmetry restriction with the LANL2DZ basis set.<sup>38</sup> An additional D95+(d) basis set<sup>38a</sup> was used for fluorine in all calculations to deal with a possible

second-order Jahn–Teller distortion and with the negative partial charge on the central fluorido ligand. The Cu–F distances increased by 0.02 Å compared to the pure LANL2DZ basis set. Mulliken charges have to be considered as semiquantitative, since they depend on method and basis set to a certain degree. The calculations were carried out on HP C200 and HP J210 workstations.

**Instrumentation.**  $^1\text{H}$  NMR,  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $^{19}\text{F}\{^1\text{H}\}$  NMR, and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker DRX 300 or a Bruker DRX 500. Chemical shifts were calibrated to  $[\text{D}_5]\text{acetone}$  ( $\delta = 2.04$ ) or  $\text{CDCl}_2$  ( $\delta = 5.32$ ) as internal reference for  $^1\text{H}$  NMR spectra,  $[\text{D}_6]\text{acetone}$  ( $\delta = 29.30, 206.3$ ) as internal reference for  $^{13}\text{C}$  NMR spectra, *o*- $\text{C}_6\text{H}_4\text{F}_2$  ( $\delta = -139$ ) as external reference for  $^{19}\text{F}$  NMR spectra, and 85%  $\text{H}_3\text{PO}_4$  ( $\delta = 0.0$ ) as external reference for  $^{31}\text{P}$  NMR spectra. Infrared spectra were measured on a Bruker Equinox 55. Elemental analyses were performed in the Microanalytical Laboratory of the Chemical Institute of the University of Heidelberg. Mass spectra were recorded on a JEOL JMS 700.

**Materials and Methods.**  $\text{Et}_2\text{O}$  was dried with sodium benzophenone ketyl,  $\text{CH}_2\text{Cl}_2$  with  $\text{P}_4\text{O}_{10}$ , and acetone with  $\text{K}_2\text{CO}_3$  under argon, respectively. The solvents were distilled under an argon atmosphere prior to use.  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  was purchased from Aldrich and used as received.  $[\text{Cu}(\text{NCMe})_4]\text{-OTf}$  was prepared from  $\text{Cu}_2\text{O}$  and  $\text{Me}_3\text{SiOTf}$  in MeCN similar to a literature procedure.<sup>39</sup> KF was dried by heating with a heat gun at  $10^{-3}$  mbar and  $>200$  °C for several minutes. All reactions were carried out in an atmosphere of dried and oxygen-free argon (99.998%) using standard Schlenk and vacuum line techniques.

**Syntheses.**  $[\text{Cu}_2(\mu\text{-dtpm})_2]^{2+}[(\text{PF}_6)^-]_2$ , ( $1^{2+}$ )[ $(\text{PF}_6)^-$ ] $_2$ , 126 mg of  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  (338  $\mu\text{mol}$ ) and 101 mg of dtpm (332  $\mu\text{mol}$ ) were dissolved in 20 mL of  $\text{CH}_2\text{Cl}_2$ , stirred for 30 min, and filtered over Celite. The solution was reduced to 5 mL in vacuo. After addition of 5 mL of  $\text{Et}_2\text{O}$ , crystallization at  $-25$  °C, washing with three portions of 1 mL  $\text{Et}_2\text{O}$ , and drying at  $10^{-3}$  mbar for 5 h, 132 mg of colorless ( $1^{2+}$ )[ $(\text{PF}_6)^-$ ] $_2$  (129  $\mu\text{mol}$ , 77.5%) was obtained. Mp (dec): 305 °C. Anal. Calcd: C, 39.81; H, 7.47. Found: C, 39.44; H, 7.43.  $^1\text{H}$  NMR (300.13 MHz,  $[\text{D}_6]\text{acetone}$ , 300 K):  $\delta = 2.79$  (“quint”,  $^{2+4}\text{J}(\text{P},\text{H}) = 5$  Hz, 4H;  $\text{PCH}_2\text{P}$ ), 1.63 (“quin”,  $^{3+5}\text{J}(\text{P},\text{H}) = 4$  Hz, 72H;  $\text{P}^i\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.50 MHz,  $[\text{D}_6]\text{acetone}$ , 300 K):  $\delta = 56.9$  (s, dtpm),  $-143.7$  (sept,  $^1\text{J}(\text{P},\text{F}) = 708$  Hz,  $\text{PF}_6^-$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $[\text{D}_6]\text{acetone}$ , 297 K):  $\delta = 37.9$  (“quin”;  $^{1+3}\text{J}(\text{P},\text{C}) = 5$  Hz,  $\text{PCCH}_3$ ), 30.7 (“t”,  $^{2+4}\text{J}(\text{P},\text{C}) = 1$  Hz,  $\text{PCCH}_3$ ), 10.2 (“quin”,  $^{1+3}\text{J}(\text{P},\text{C}) = 7$  Hz,  $\text{PCH}_2\text{P}$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2955 (m + sh), 1475 (m), 1406 (w), 1398 (w), 1375 (m), 1177 (m), 1021 (w), 937 (w), 840 (vs + sh), 757 (w), 740 (w), 688 (m), 558 (s), 488 (m).

$[\text{Cu}_2(\mu\text{-dtpm})_2]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ , ( $1^{2+}$ )[ $(\text{OTf})^-$ ] $_2$  can be prepared according to the hexafluorophosphate complex salt. Mp (dec): 225–226 °C. Anal. Calcd: C, 41.81; H, 7.41; P, 11.98; S, 6.20. Found: C, 41.55; H, 7.52; P, 11.96; S, 6.23.  $^1\text{H}$  NMR (300.13 MHz,  $[\text{D}_6]\text{acetone}$ , 300 K):  $\delta = 2.84$  (“quin”,  $^{2+4}\text{J}(\text{P},\text{H}) = 5$  Hz, 4H;  $\text{PCH}_2\text{P}$ ), 1.64 (“quint”,  $^{3+5}\text{J}(\text{P},\text{H}) = 4$  Hz, 72H;  $\text{P}^i\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.50 MHz,  $[\text{D}_6]\text{acetone}$ , 298 K):  $\delta = 56.8$  (s, dtpm). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2950 (m + sh), 1475 (m), 1398 (w), 1374 (m), 1280 (vs), 1222 (m), 1148 (vs, sh), 1030 (s), 936 (w), 810 (m), 754 (w), 688 (m), 637 (m), 572 (m), 517 (m), 491 (w). FAB-MS (*m*-nitrobenzyl alcohol):  $m/z$  (%) = 883.2 (0.3) [ $\text{M}^{2+} + \text{OTf}^-$ ], 687.4 (100) [ $\text{M}^{2+} - \text{Cu}^+ + \text{O}$ ], 671.4 (34) [ $\text{M}^{2+} - \text{Cu}^+$ ].

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$[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2, (\mathbf{2}^{2+})[(\text{OTf})^-]_2$ . 295 mg of  $(\mathbf{1}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$  (285  $\mu\text{mol}$ ) and 465 mg of powdered KF (8.00 mmol) were dissolved or suspended in 30 mL of  $\text{CH}_2\text{-Cl}_2$  stirred for 86 h. The suspension was filtered over Celite, the solution was reduced to 5 mL in vacuo, 10 mL of  $\text{Et}_2\text{O}$  was added, and a colorless solid crystallized at  $-25^\circ\text{C}$ . After washing with  $\text{Et}_2\text{O}$ , solvent was removed at  $110^\circ\text{C}$  ( $10^{-3}$  mbar) to afford 236 mg of  $(\mathbf{2}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$  (166  $\mu\text{mol}$ , 87%). Mp (dec):  $264^\circ\text{C}$ . Anal. Calcd: C, 44.80; H, 8.09. Found: C, 44.34; H, 8.15.  $^1\text{H}$  NMR (300.13 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 2.13$  (br s, 6H;  $\text{PCH}_2\text{P}$ ), 1.54 (m, 108H;  $\text{P}^t\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.50 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 29.9$  (d,  $^2J(\text{P},\text{F}) = 35$  Hz, dtbpm).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 36.7$  (s;  $\text{PCCH}_3$ ), 36.0 (s,  $\text{PCCH}_3$ ), 30.6 (s,  $\text{PCCH}_3$ ), 12.5 (s,  $\text{PCH}_2\text{P}$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2968 (m), 2902 (m), 2870 (m), 1472 (m), 1396 (m), 1371 (m), 1268 (vs), 1222 (m), 1147 (s), 1032 (s), 939 (w), 811 (m), 752 (w), 737 (m), 704 (m), 675 (m), 638 (s), 572 (w), 517 (w), 484 (w), 446 (w).

$[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{PF}_6)^-]_2, (\mathbf{2}^{2+})[(\text{PF}_6)^-]_2$ . can be prepared according to the triflate complex salt. Mp (dec):  $284^\circ\text{C}$ .  $^1\text{H}$  NMR (300.13 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 2.12$  (br s, 6H;  $\text{PCH}_2\text{P}$ ), 1.52 (m,  $^1J(\text{C},\text{H}) = 128$  Hz, 108H;  $\text{P}^t\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.50 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 29.5$  (d,  $^2J(\text{P},\text{F}) = 35$  Hz, dtbpm),  $-143.5$  (sept,  $^1J(\text{P},\text{F}) = 708$  Hz,  $\text{PF}_6^-$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.47 MHz,  $[\text{D}_6]$ acetone, 300 K):  $\delta = 36.7$  (br s;  $\text{PCCH}_3$ ), 36.0 (br s,  $\text{PCCH}_3$ ), 30.6 (br s,  $\text{PCCH}_3$ ), 12.5 (br s,  $\text{PCH}_2\text{P}$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.4 MHz,  $[\text{D}_6]$ acetone, 298 K):  $\delta = -67$  (d,  $^1J(\text{P},\text{F}) = 708$  Hz, 12F,  $\text{PF}_6^-$ ),  $-186$  (sept,  $^2J(\text{P},\text{F}) = 35$  Hz, 1F,  $\text{Cu}_3\text{F}$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2970 (s), 2903 (m), 2871 (m), 1472 (s), 1396 (m), 1371 (s), 1262 (w), 1177 (m), 1095 (w), 1019 (w), 939 (w), 840 (vs + sh), 737 (w), 703 (m), 675 (m), 583 (w), 558 (s), 483 (w), 445 (w). FAB-MS (*m*-nitrobenzyl alcohol):  $m/z$  (%) = 1248.6 (2)  $[(\text{dtbpm})_3\text{Cu}_3\text{PF}_6^+]$ , 753.4 (56)  $[(\text{dtbpm})_2\text{Cu}_2\text{F}^+]$ , 677.3 (19)  $[(\text{dtbpm})_2\text{Cu}_2 - ^t\text{Bu}]$ , 671.5 (70)  $[(\text{dtbpm})_2\text{Cu}^+]$ , 449.2 (48)  $[(\text{dtbpm})\text{PF}_6^+]$ , 154.1 (100) [matrix +  $\text{H}^+$ ].

**X-ray Data Collection, Structure Solution, and Refinement. General Methods.** A Bruker (Siemens) Smart-CCD

diffractometer was used. An empirical absorption correction was applied using SADABS<sup>40</sup> on the basis of the Laue symmetry of the reciprocal space. The structures were solved by direct methods and refined against  $F^2$  with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.03) software package.<sup>41</sup>

$[\text{Cu}_2(\mu\text{-dtbpm})_2]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2, (\mathbf{1}^{2+})[(\text{OTf})^-]_2$ . Single crystals were obtained by overlaying a saturated solution of  $(\mathbf{1}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$  in acetone with  $\text{Et}_2\text{O}$  and slow interdiffusion of the solvents at 278 K.

$[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{PF}_6)^-]_2, (\mathbf{2}^{2+})[(\text{PF}_6)^-]_2$ . Single crystals were obtained from a concentrated solution of  $(\mathbf{1}^{2+})[(\text{PF}_6)^-]_2$  in acetone after standing at room temperature for 12 h. About 8% of  $\mathbf{2}^{2+}$  are rotated from the main orientation by  $60^\circ$ . Cu and P atoms from the minor orientation were taken into account with restricted geometry.

$[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2, (\mathbf{2}^{2+})[(\text{OTf})^-]_2$ . Single crystals were obtained by covering a solution of  $(\mathbf{2}^{2+})[(\text{O}_3\text{SCF}_3)^-]_2$  in acetone with  $\text{Et}_2\text{O}$  and slow interdiffusion of the solvents at 278 K. About 4% of  $\mathbf{2}^{2+}$  are rotated from the main orientation by  $60^\circ$ . The Cu atoms of the less populated orientation were taken into account with restricted geometry. The triflate anions are completely disordered.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structures of  $[\text{Cu}_2(\mu\text{-dtbpm})_2]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ ,  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{PF}_6)^-]_2$ , and  $[\text{Cu}_3(\mu_3\text{-F})(\mu\text{-dtbpm})_3]^{2+}[(\text{O}_3\text{SCF}_3)^-]_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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