Synthesis and Characterization of Triangulo Copper(I) Complexes Containing Mono- and Bicapping Systems of Asymmetric μ_3-η^1-Acetylide Ligands: Molecular Structures of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$, and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ [dppm = Bis(diphenylphosphino)methane]

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Alkynyl-bridged trinuclear copper(I) complexes containing the triangulo framework $Cu_3(\mu\text{-dppm})_3$ [dppm = bis(diphenylphosphino)methane] have been prepared. Complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$ (R = Ph (1), ^{t}Bu (2), CH_2OCH_3 (3)) are obtained by treating $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ with $LiC{\equiv}CR$ in a molar ratio of 3:2. The treatment of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ with $HC{\equiv}CR$/KOH in CH_2Cl_2/MeOH (molar ratio 3:4) yields the complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppm})_3][BF_4]$ (R = Ph (4), ^{t}Bu (5), CH_2OCH_3 (6)). The reaction of $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$ with $LiC{\equiv}CR$ (1:1.5 molar ratio) in THF affords the double-bridged chloride–alkynyl complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (R = Ph (7), ^{t}Bu (8), CH_2OCH_3 (9)) which are also formed from dichloromethane solutions of 4–6 containing traces of acid. Complex 4 has also been directly obtained by treatment of $[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][BF_4]$ with an excess of $LiC{\equiv}CPh$. Crystal structures of the complexes 1 (CH_2Cl_2 solvate) (space group $P2_1/c$, $Z = 4$, $a = 25.02(1)$ Å, $b = 13.752(1)$ Å, $c = 24.207(1)$ Å, $\beta = 93.375(4)°$, $R = 0.080$), 4 (space group $P2_1/c$, $Z = 4$, $a = 14.61(6)$ Å, $b = 21.863(6)$ Å, $c = 26.67(1)$ Å, $\beta = 102.8(1)°$, $R = 0.077$), and 7 (space group $P\bar{1}$, $Z = 2$, $a = 14.55(7)$ Å, $b = 14.691(4)$ Å, $c = 21.08(2)$ Å, $\alpha = 72.27(4)°$, $\beta = 71.29(4)°$, $\gamma = 68.72(8)°$, $R = 0.105$) have been determined by X-ray diffraction methods. The structure determinations show that each cationic complex consists of an isosceles triangle of copper atoms with a dppm ligand bridging each edge to form a roughly planar $[Cu_3P_6]$ core. These triangulo copper(I) complexes contain mono- and bicapping systems of μ_3-η^1-acetylide ligands in which each phenylethynyl ligand is C-bonded to the three copper atoms, showing an asymmetric μ_3-η^1 bridging mode with the copper to carbon distances significantly different.

Transition metal alkynyl complexes have been widely studied, both experimentally and theoretically, in the last decade.[1] The interest mainly stems from two chemical aspects: (a) the versatile reactivity of the coordinated acetylide groups[2] which have been used in many complexes for the synthesis of other organometallic species; (b) the ability of the acetylide groups to bond to transition metals, forming a large number of mono- and polynuclear complexes which display an unusual variety of bonding modes.[3]

Acetylides are typical multisite bridging ligands in carbonyl cluster derivatives. Their capacity to bind to polymetallic frameworks probably shows, as do the carbonyl groups, a tendency to maximize the electronic back-donation expected for strong π-acceptor ligands. The simultaneous metal–acetylide σ and π bonding modes are now well documented by many structural studies carried out on a large number of homo- and heteropolynuclear derivatives, usually containing metal–metal bonds. Although most of the examples involve electron-rich transition metals, only a few of them contain group 11 metal atoms. Thus, alkynyl derivatives containing heterometallic moieties such as Ru_3–Cu,[4] Cu_4–Ir_2,[5] Mn_2–Cu,[6] Cu_7–Ag_6,[7] Cu_2–Au_3,[8] Ag–Ru_3,[9] Ag_2–Rh,[10] Ag_2–Au_2,[11] Pt_2–Ag_4,[12a]

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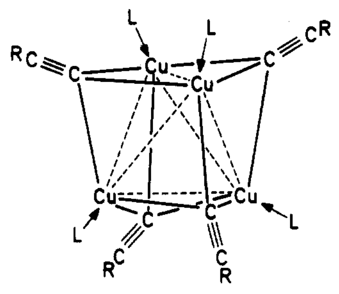
Pt_2–Ag_2,[12b] Au_2–Pt,[13] Au–Pt_2,[14] Pt–Au_7,[15] Os_3–Au,[16] and Au_2Fe_2Ir[17] have been described and structurally characterized.

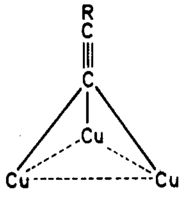
Alkynyl homopolynuclear complexes $[M(C{\equiv}CR)]_n$ (M = Cu, Ag, Au) have been known for a long time[18] but have received less attention probably due to their insolubility which precludes, in many cases, their structural studies.[19] They have been used as starting materials for the preparation of the aforementioned heterometallic derivatives but are not useful precursors for homometallic complexes. In general the polymeric structure can be broken down with donor ligands,[20] forming complexes of the type $[M(C{\equiv}CR)L_n]$, from which only their stoichiometries are known in most cases but not their nuclearity.[21,22]

The lack of general methods for the synthesis of copper alkynyl derivatives and their low solubility have limited the availability of these types of complexes and hence their related structural information. At present, only the following derivatives have been described and structurally characterized: (i) $[Cu_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(PMe_3)_4]$, prepared by the reaction of the polymer $[Cu(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)]_n$ with PMe_3;[23] (ii) a mixed aryl/alkynyl derivative $[Cu_6(C_6H_4NMe_2\text{-}2)_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}C_6H_4Me\text{-}4)_2]$,[24] prepared by aryl/arylacetylide exchange reactions between polymeric [2-(dimethylamino)phenyl]copper(I) and 4-tolylacetylene;[24d] (iii) the hexanuclear thiophenolato/alkynyl complex $[Cu_3(\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]_2$ formed unexpectedly from the equimolar reaction of $[Cu\{SC_6H_4(CH_2NMe_2)\text{-}2\}]_3$ and $LiC{\equiv}C^tBu$;[25] (iv) the tetranuclear cationic complex $[Cu_4L_2(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)]^{3+}$ (L = $C_{18}H_{20}N_4O_2$, macrocyclic ligand) obtained from the reaction of the dinuclear copper(II) complex $[Cu_2(\mu\text{-}OH)_2(L)]^{2+}$ with $PhC{\equiv}CH$ in refluxing CH_3CN/CH_3OH;[26] and (v) a tetrameric phosphino complex, namely $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(PPh_3)]_4$, obtained by treatment of $[Cu(BH_4)(PPh_3)_2]$ with $PhC{\equiv}CH$ and KOH.[27] We have also reported[28] similar complexes $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(L\text{-}L)]_4$ (I) (see Chart I) (L-L = 2-(diphenylphosphino)pyridine (Ph_2Ppy), R = ^{t}Bu, Ph; L-L = bis(diphenylphosphino)methane (dppm), R = Ph) which have been prepared by the treatment of $[Cu_2(\mu\text{-}L\text{-}L)_2(MeCN)_2]^{2+}$ with $RC{\equiv}CH$ and KOH (eq 1). These syntheses represent a systematic method for the preparation of polynuclear alkynylcopper(I) complexes.

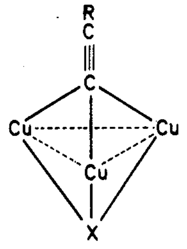
Chart I



(I)



(II)



(III) X = Cl, C≡CR

$$2[Cu_2(\mu\text{-}L\text{-}L)_2(MeCN)_2]^{2+} + 4HC{\equiv}CR + 4OH^- \rightarrow [Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(L\text{-}L)]_4 + 4MeCN + 4H_2O \quad (1)$$

L-L = Ph_2Ppy (P-bonded); R = Ph, ^{t}Bu; L-L = dppm-*P*; R = Ph

In continuation of our work, we extended this methodology of synthesis using different molar ratios of the reactants. In particular, we were interested in finding out whether the copper:acetylide ratios greater than 1, i.e. $[Cu_2(\mu\text{-}L\text{-}L)_2(MeCN)_2]^{2+}$:$HC{\equiv}CR$ molar ratios greater

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Table I. Molar Conductance,[a] IR, and NMR[b] Data for the New Complexes

	^{1}H (δ)	^{31}P{^{1}H} (δ)	Δ_M	ν(C≡C)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$ (**1**)	3.15 (m, 3H, P_2CH_a), 3.55 (m, 3H, P_2CH_b), 6.86–7.23 (m, 60H, PPh_2), 7.53–7.68 (m, 5H, Ph)	−7.7 (s)	172	
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)(\mu\text{-dppm})_3][BF_4]_2$ (**2**)	1.43 (s, 9H, $(CH_3)_3C$), 3.17 (m, 3H, P_2CH_a), 3.68 (m, 3H, P_2CH_b), 6.9–7.3 (m, 60H, PPh_2)	−8.8 (s)	184	1980 (vw)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CCH_2OCH_3)(\mu\text{-dppm})_3][BF_4]_2$ (**3**)	3.10 (m, 3H, P_2CH_a), 3.26 (m, 3H, P_2CH_b), 3.62 (s, 3H, CH_3O), 4.34 (s, 2H, CH_2O), 6.8–7.11 (m, 60H, PPh_2)	−9.4 (s)	162	2038 (w)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$ (**4**)	3.07 (s, br, 6H, P_2CH_2), 6.79–7.18 (m, 60H, PPh_2), 7.50–7.55 (m, 10H, Ph)	−5.3 (s)	130	2027 (w)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2(\mu\text{-dppm})_3][BF_4]$ (**5**)	1.49 (s, 9H, $(CH_3)_3C$), 3.00 (m, 6H, P_2CH_2), 6.84–7.10 (m, 60H, PPh_2)	−8.0 (s)	138	2018 (vw)
$[Cu_3(\mu_3\text{–}\eta^1\text{-}C{\equiv}CCH_2OCH_3)_2(\mu\text{-dppm})_3][BF_4]$ (**6**)	3.15 (m, 6H, P_2CH_2), 3.63 (s, 6H, CH_3O),[c] 4.31 (s, 4H, CH_2O), 6.88–7.12 (m, 60H, PPh_2)	−6.2 (s)[c]	142	2039 (vw)
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (**7**)	3.15 (m, 6H, P_2CH_2), 6.7–7.2 (m, 60H, PPh_2), 7.3–7.6 (m, 5H, Ph)	−9.0 (s)	140	
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (**8**)	1.34 (s, 9H, $(CH_3)_3C$), 3.08 (m, 3H, P_2CH_a), 3.20 (m, 3H, P_2CH_b), 6.77–7.10 (m, 60H, PPh_2)	−10.6 (s)	117	
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CCH_2OCH_3)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (**9**)	3.25 (m, 6H, P_2CH_2), 3.61 (s, 3H, CH_3O),[c] 4.28 (s, 2H, CH_2O), 6.92–7.10 (m, 60H, PPh_2)	−9.6 (s)[c]	142	2027 (vw)

[a] In acetone solution at 20 °C (Ω^{-1} cm^2 mol^{-1}). [b] Proton (300 MHz) and ^{31}P{^{1}H} NMR (79.54 MHz); chemical shifts (δ) in ppm measured in $CDCl_3$ at room temperature. [c] ^{1}H and ^{31}P{^{1}H} in CD_2Cl_2.

than 1:2 (refer to eq 1), would lead to the formation of novel cationic copper–acetylide complexes. This paper deals with the reactions of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ with LiC≡CR (molar ratio 3:2) and HC≡CR/KOH (molar ratio 3:4) (R = Ph, ^{t}Bu, CH_2OCH_3). Under these conditions, the tetranuclear copper(I) complexes I (see Chart I) are not obtained, but instead novel cationic trinuclear derivatives $[Cu_3(C{\equiv}CR)_{3-n}(\mu\text{-dppm})_3][BF_4]_n$ (n = 1, 2) have been isolated. The molecular structures of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$, and the mixed phenylacetylide–chloride $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ have been established by single-crystal X-ray diffraction studies, showing triangulo copper(I) arrangements II and III (see Chart I) with unprecedented mono- and bicapping systems of asymmetric μ_3-η^1-acetylide ligands. Part of these results were preliminarily communicated.[29]

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. Infrared spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 1720-X FT spectrometer using KBr pellets. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Conductivities of acetone solutions in ca. 5×10^{-4} mol dm^{-3} were measured with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker AC300 at 300 MHz (^{1}H) or 121.5 MHz (^{31}P) using $SiMe_4$ or 85% H_3PO_4 as standards. The complexes $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$[30] and $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$[31] were prepared as previously described. Conductivity, infrared, and NMR spectral data for all the new alkynyl complexes are collected in Table I.

Synthesis of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$. R = Ph (1), ^{t}Bu (2), CH_2OCH_3 (3). General Procedure. To a solution of 0.5 mmol of LiC≡CR in THF (40 mL) (prepared in situ by treating the corresponding alkyne with 1.90 M ^{n}BuLi at −20 °C) was added at room temperature $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (0.75 mmol; 0.86 g). The mixture was stirred at room temperature and evaporated to dryness giving a solid residue which was extracted with dichloromethane (30 mL). The addition of diethyl ether (30 mL) to the concentrated solution led to the precipitation of a white solid which was washed with diethyl ether (3 × 10 mL) and vacuum dried. Analytically pure samples were obtained by recrystallization from THF/hexane. Reaction times, yields (%), and analytical data follow. (1) 24 h; 82. Anal. Calcd for $C_{83}H_{71}B_2Cu_3F_8P_6$: C, 61.6; H, 4.4. Found: C, 61.5; H, 4.5. (2) 7 h; 76. Calcd for $C_{81}H_{75}B_2Cu_3F_8P_6$: C, 60.9; H, 4.7. Found: C, 60.3; H, 5.25. (3) 20 h; 80. Calcd for $C_{79}H_{71}B_2Cu_3F_8OP_6$: C, 59.8; H, 4.5. Found: C, 61.7; H, 4.9. IR spectra (KBr), ν(C≡C) and ν(B—F) (cm^{-1}): (1) absent, 1056 (s, br); (2) 1980 (vw), 1055 (s, br); (3) 2038 (w), 1055 (s, br).

Synthesis of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppm})_3][BF_4]$. R = Ph (4), ^{t}Bu (5), CH_2OCH_3 (6). (a) General Procedure. A solution of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (0.5 mmol; 0.575 g) in CH_2Cl_2/MeOH (3:1, 60 mL) was treated with HC≡CR (0.67 mmol) and an excess of KOH, and the mixture was stirred at room temperature. After evaporating to dryness, the resulting solid residue was extracted with CH_2Cl_2 (3 × 5 mL) and the solution partially concentrated. The addition of hexane (30 mL) gave by precipitation the corresponding complexes as cream (**5** and **6**) or yellowish (**4**) solids which were recrystallized from THF/hexane. Reaction times, yields (%), and analytical data follow. (4) 24 h; 90. Anal. Calcd for $C_{91}H_{76}BCu_3F_4P_6$: C, 67.0; H, 4.7. Found: C, 66.85; H, 4.8. (5) 20 h; 85. Calcd for $C_{87}H_{84}BCu_3F_4P_6$: C, 65.6; H, 5.3. Found: C, 65.0; H, 5.5. (6) 20 h; 75. Calcd for $C_{83}H_{76}BCu_3F_4O_2P_6$: C, 63.6; H, 4.85. Found: C, 63.0; H, 5.0. IR spectra (KBr), ν(C≡C) and ν(B—F) (cm^{-1}): (4), 2027 (w), 1056 (s, br); (5) 2018 (vw), 1057 (s, br); (6) 2038 (w), 1050 (s, br).

(b) Direct Synthesis of 4. A mixture of LiC≡CPh (2.5 mmol) and $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ (0.5 mmol; 1.25 g) in THF (40 mL) was stirred at room temperature for 24 h. The resulting solution was evaporated to dryness to give a solid residue which was washed with Et_2O (5 × 50 mL) and extracted with THF. The addition of hexane to the partially evaporated THF solution yielded **4** by precipitation as a yellowish solid (yield: 77%).

Synthesis of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$. R = Ph (7), ^{t}Bu (8), CH_2OCH_3 (9). (a) General Procedure. To a solution of LiC≡CR (R = Ph, ^{t}Bu, 3 mmol; R = CH_2OCH_3, 1.5 mmol) in THF (40 mL) (prepared in situ by treating the corresponding alkyne with 1.90 M ^{n}BuLi at −20 °C) was added at room temperature $[Cu_2(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ (1 mol; 1.50 g). The mixture was stirred at room temperature and evaporated to dryness giving a solid residue which was washed with diethyl ether (3 × 30 mL). The resulting solid was extracted with THF (3 × 15 mL) and the solution partially concentrated. The addition of diethyl ether (30 mL) led to the precipitation of a yellowish solid which was washed with diethyl ether (3 × 10 mL) and vacuum

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Table II. Crystallographic Data for Complexes 1, 4, and 7

	1	4	7
(a) Crystal Parameters			
formula	$C_{83}H_{71}B_2Cu_3F_8P_6\cdot CH_2Cl_2$	$C_{91}H_{76}BCu_3F_4P_6$	$C_{83}H_{71}BClCu_3F_4P_6$
fw	1703.5	1632.9	1567.2
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	25.02(1)	14.613(1)	14.55(7)
b, Å	13.752(1)	21.863(1)	14.691(4)
c, Å	24.207(1)	26.672(1)	21.08(2)
α, deg			72.27(4)
β, deg	93.375(4)	102.8(1)	71.29(4)
γ, deg			68.72(8)
V, Å^3	8315(3)	8307(2)	3887(21)
Z	4	4	2
d_{calcd}, g·cm^{-3}	1.36	1.31	1.34
F_{000}	3480	3368	1610
μ(Mo Kα), cm^{-1}	9.99	9.28	10.22
cryst size, mm	0.50 × 0.50 × 0.10	0.30 × 0.20 × 0.13	0.40 × 0.40 × 0.20
(b) Data Collection			
temp, K	293	293	293
2θ range, deg	50	50	46
data collcd	$+h,+k,\pm l$	$\pm h,+k,+l$	$+h,\pm k,\pm l$
no. of collcd rflcns	15 666	12 486	14 758
no. of unique rflcns	14 616	11 440	13 666
no. of obsd rflcns	5751 ($I > 3\sigma(I)$)	4814 ($I > 3\sigma(I)$)	8121 ($I > 3\sigma(I)$)
(c) Refinement			
R^a	0.080	0.077	0.105
weight	unit weight	unit weight	unit weight
no. of variables	865	910	785
$\Delta(\rho)$, e Å^{-3}	1.50	0.76	1.15

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$.

dried. Reaction times, yields (%), and analytical data follow. (7) 24 h; 80. Anal. Calcd for $C_{83}H_{71}BCu_3ClF_4P_6$: C, 63.7; H, 4.5. Found: C, 63.7; H, 4.9. (8) 15 h; 71. Calcd for $C_{81}H_{75}BCu_3ClF_4P_6$: C, 62.9; H, 4.85. Found: C, 63.0; H, 5.3. (9) 21 h; 75. Calcd for $C_{79}H_{71}BCu_3ClF_4OP_6$: C, 61.8; H, 4.7. Found: C, 61.9; H, 4.5. IR spectra (KBr), ν(C≡C) and ν(B—F) (cm^{-1}): (7) absent, 1049 (s, br); (8) absent, 1049 (s, br); (9) 2027 (vw), 1060 (s, br).

(b) A solution of complex 4, 5, or 6 in CH_2Cl_2 (containing traces of HCl) was stirred at room temperature for 2 h. The addition of hexane to the concentrated solution led to the precipitation of solids which were identified as complexes 7–9 by comparison of the spectroscopic data with those of original samples.

X-ray Diffraction Studies of 1, 4, and 7. Data collection, crystal, and refinement parameters are collected in Table II. Diffraction measurements were made on a Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters were obtained from a least-squares fit of 25 reflections (20° < θ < 25°). Data were collected with the ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s/reflection. Three standard reflections were monitored at every 3600 s. In the reduction of data, profile analysis[32,33] drift and Lorentz and polarization corrections were performed; an empirical absorption correction (DIFABS) was applied.[34] The structures were solved by using SHELXS86[35] and expanded by using DIRDIF.[36] The structures were refined by least squares using a local version of the program SHELX76.[37] During the refinement of the structure of 7 the ΔF maps showed a partial occupancy with molecules of $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ (ca. 30%) probably arising by the cleavage of the copper–alkynyl bond during the crystallization of 7 (CH_2Cl_2–Et_2O). The structure was refined by assuming this fact as a statistical crystallographic disorder.

All non-hydrogen atoms were anisotropically refined except those of the phenylacetylide group in 7; that was refined as a rigid group with a common thermal parameter. All hydrogen atoms were located at the ideal positions and were refined riding on their parents atoms. Geometrical calculations were made with PARST.[38] All calculations were made on a MicroVAX 3300 at the Centro de Cálculo Científico of the University of Oviedo.

Results and Discussion

Synthesis and Characterization of $[Cu_3(C{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$ (1–3), $[Cu_3(C{\equiv}CR)_2(\mu\text{-dppm})_3][BF_4]$ (4–6), and $[Cu_3(C{\equiv}CR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (7–9) (R = Ph, ^{t}Bu, CH_2OCH_3). We have found that the binuclear copper(I) complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ is a useful precursor for novel bi- and tetranuclear copper(I) complexes. Thus, their reactions with bidentate anionic nucleophiles such as acetate, pyrazolate, pyridin-2-olate, or triazenide yield cationic $[Cu_2(\mu\text{-dppm})_2(\mu\text{-L-L})][BF_4]$ and neutral $[Cu_2(\mu\text{-dppm})(\mu\text{-L-L})_2]$ binuclear copper(I) complexes.[39] Similarly, the treatment with HC≡CPh/KOH (1:2 molar ratio) yields the tetranuclear complex $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(dppm\text{-}P)]_4$ where dppm is acting as a monodentate ligand.[28] Since we were interested in extending the series of the scarcely known copper(I) acetylides, we explored the reactions by using different molar ratios of the reactants with the aim of preparing cationic derivatives. Synthesis and transformations of the novel complexes are summarized in Scheme I.

A mixture in THF of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ and LiC≡CR (prepared "in situ" from HC≡CR and ^{n}BuLi), in a molar ratio of 3:2, reacts to give a solution from which trinuclear cationic complexes 1–3 can be isolated as tetrafluoroborate salts (Scheme I, eq *ii*). By using an excess of the lithium salt, the reactions lead to the formation of similar trinuclear bis(acetylide) complexes 4–6 which can also be obtained stepwise from the mono(acetylide) derivatives 1–3 (Scheme I, eq *iv*). However, complexes 4–6 are obtained in better yields by two direct routes: (a) treatment of the precursor complex with the alkyne and an excess of KOH, in a mixture of CH_2Cl_2/MeOH (Scheme I, eq *iii*); (b) alkynyl substitution of two chloride groups in the dichloride complex $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ (Scheme I, eq *v*). In the latter case a large excess of lithium salt is required to have better yields; otherwise, if molar ratios of ca. 1:1.5 or 1:3 are used, mixed chloride/acetylide trinuclear complexes 7–9 are obtained in good yields (Scheme I, eq *vii*). Alternatively, these complexes are also isolated after recrystallization of bis(acetylide) complexes 4–6 with CH_2Cl_2 containing traces of HCl, probably via cleavage of one copper–carbon bond by the acid (Scheme I, eq *vi*).

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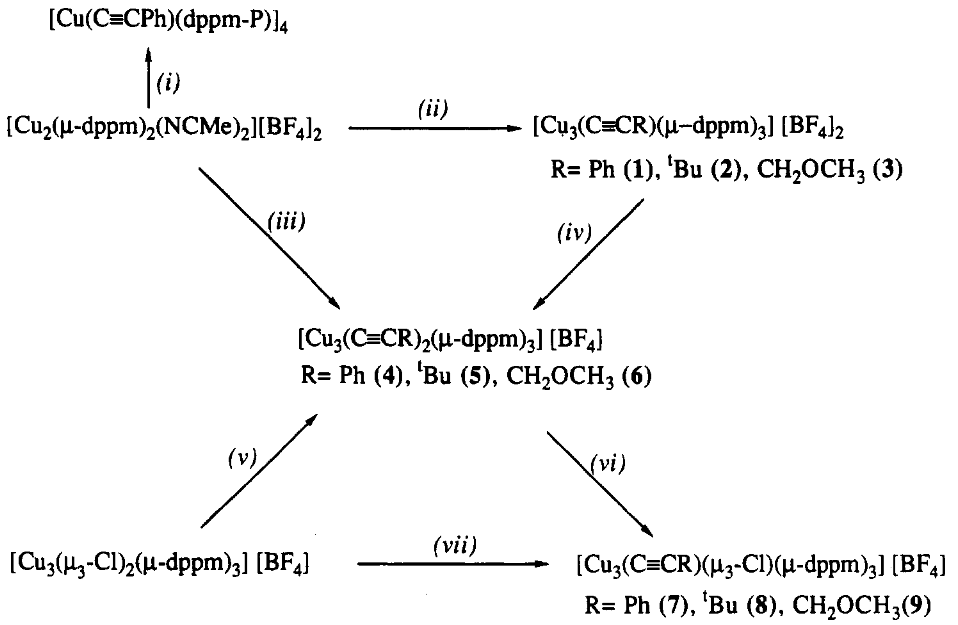
Scheme I[a]



[a] (*i*) Reference (28): +HC≡CR (molar ratio 1/2) in the presence of KOH (excess). CH_2Cl_2/MeOH. (*ii*) +LiC≡CR (molar ratio 3:2). THF. (*iii*) +HC≡CR (molar ratio 3:4) + KOH (excess). CH_2Cl_2/MeOH. (*iv*) +LiC≡CR. THF. (*v*) +LiC≡CR (excess). (*vi*) +CH_2Cl_2 + H^+ (traces). (*vii*) +LiC≡CR. THF.

The complexes are air stable in the solid state and have been characterized by elemental analysis, conductance measurements, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The conductivity and selected spectroscopic data are given in Table I. In addition, the structures of complexes 1, 4, and 7 have been determined by X-ray diffraction methods (see below).

Conductivity data (in Me_2CO) show that 1–3 and 4–9 behave as typical 2/1 and 1/1 electrolytes, respectively. The IR spectra (KBr) exhibit the expected ν(B—F) broad and strong absorptions as well as those characteristic for dppm and ν(C≡C), though the latter are very weak and not observed for 1, 7, and 8 (see Experimental Section). The $^{31}P\{^1H\}$ NMR spectra at room temperature exhibit a single resonance (Table I), showing that all phosphorus atoms in each molecule are chemically equivalent. The chemical shifts, −5.3 to −9.4 ppm, are in the range of those exhibited by other dinuclear copper(I) complexes bridged by dppm ligands,[30,39–41] indicating the bridging coordination mode of the diphosphine. The room temperature ^1H NMR spectra exhibit aromatic, methylene (CH_2P_2) and R signals of the ligands and alkynyl groups (Table I) in accord with the trinuclear nature of the complexes. Significantly, the spectra of the bis(acetylide) complexes 4–6 show methylene resonances (CH_2P_2) at δ ca. 3.1 ppm as a triplet (or nonresolved multiplet), indicating an effective equivalence of the CH_2P_2 protons. The corresponding resonances in the spectra of the mono(acetylide) complexes 1–3 and 8 appear as two unresolved multiplets (observed as one multiplet for 7 and 9) typical of the ABX_2 or $AA'XX'$ spin systems due to the inequivalence of the corresponding protons $Cu_2P_2CH_AH_B$. These spectroscopic data are consistent with a triangular arrangement of the copper atoms bridged by three dppm ligands so that the metal and the phosphorus atoms are lying approximately in a plane. Thus, the presence on each side of the triangle of two capping acetylide ligands defines in the complexes 4–6 a formal plane of symmetry containing the Cu_2P_2C frameworks, giving rise to the typical A_2X_2 spin system for the methylene protons observed in the ^1H NMR spectra. It is also in accordance with the inequivalence of the corresponding methylene protons in mono(acetylide) complexes 1–3 and the mixed chloride–acetylide complexes 7–9 in which there is no plane of symmtry (see II and III in Chart I).

Solid State Structures of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-}dppm)_3][BF_4]_2$ (1), $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-}dppm)_3][BF_4]$ (4), and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-}Cl)(\mu\text{-}dppm)_3][BF_4]$ (7). The structures of complexes 1, 4, and 7 have been determined by single crystal X-ray diffraction (see Table II and Experimental Section). The crystal structure determinations revealed that 1 (CH_2Cl_2 solvate) and 4 crystallize in a monoclinic cell containing four unique discrete molecules whereas 7 crystallizes in a triclinic cell which contains two discrete molecules. However, each of these two molecules is a randomly distributed mixture of ca. 70% 7 and the rest are molecules of the known isomorphous complex $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3][BF_4]$.[31,44] This fact may be treated as a statistical crystallographic disorder, and this model was assumed during the refinement.

The complete molecular structures are shown in Figures 1–3. Selected bond and interatomic distances and bond angles are listed in Table III. The structure determinations show that each cationic complex consists of an isosceles

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(43) A similar bonding description has been proposed for the 3c–2e copper–aryl–copper bridge by van Koten et al., see for instance: van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283 and references therein.

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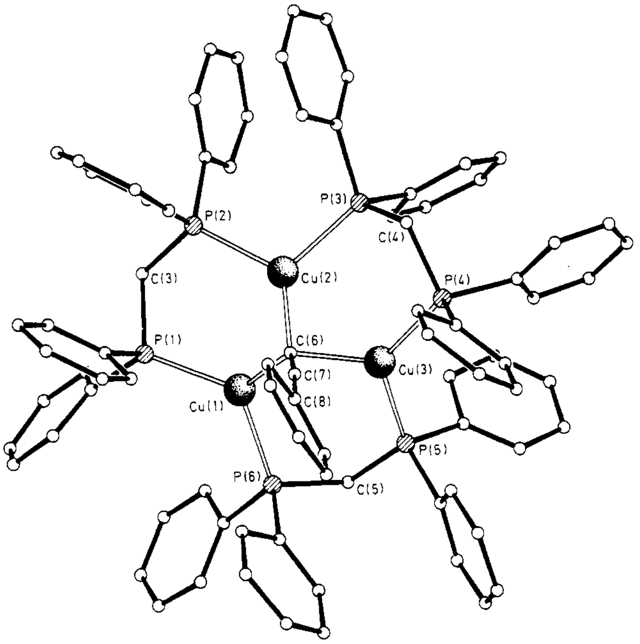

Figure 1. View of the structure of 1 in which for clarity the carbon atoms of the phenyl rings are not labeled.

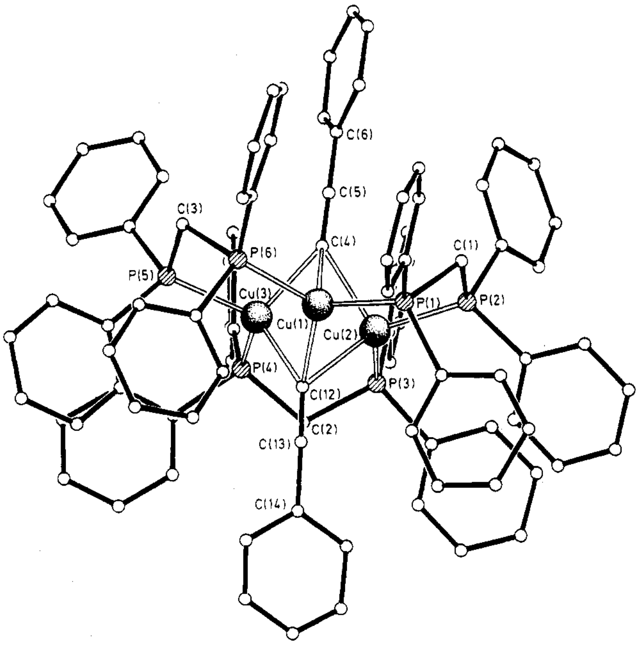

Figure 2. View of the structure of 4 in which for clarity the carbon atoms of the phenyl rings are not labeled.

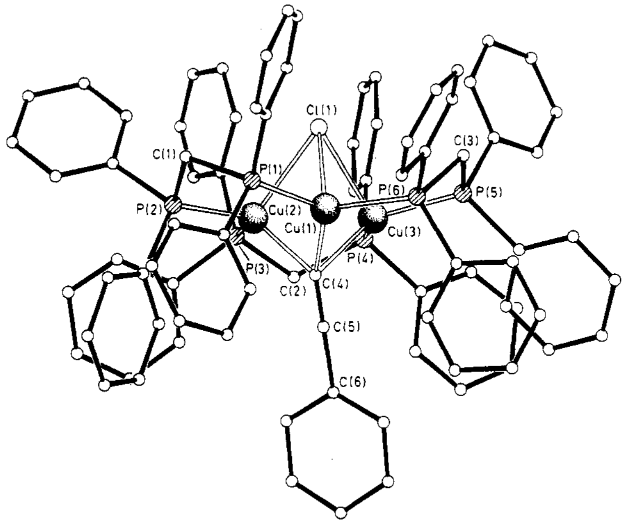

Figure 3. View of the structure of 7 in which the μ_3-η^1-C≡CPh ligand is shown in the arrangement with occupancy factor 0.7. The chloride ligand (occupancy factor of 0.3) is not shown. For clarity the carbon atoms of the phenyl rings are not labeled.

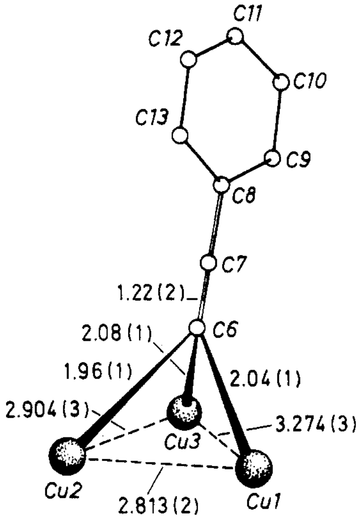

Figure 4. Skeletal view of complex 1 illustrating the asymmetry of the Cu$_3$(μ_3-η^1-C≡CPh) core with Cu—C, Cu—Cu, and C≡C distances. Cu—C7 interatomic distances (Å): Cu1, 2.91(2); Cu2, 2.99(2); Cu3, 2.58(1).

triangle of copper atoms with a dppm ligand bridging each edge to form a roughly planar [Cu$_3$P$_6$] core. The deviations of the P atoms from the Cu$_3$ plane are collected in Table IV. The Cu—P distances, in the range 2.254(5)–2.292(5) Å, are similar to those shown by homologous polynuclear copper(I) complexes (Table V) and shorter than the estimated value of 2.45 Å for a single covalent bond. The Cu$_2$P$_2$C rings adopt envelope conformations with the methylene carbon atoms on the flap, one of them folded toward one of the faces of the triangle, and the other two folded away from it. This seems to be the typical disposition of the three bridging dppm ligands in analogous *triangulo*-M$_3$ clusters (M = Ni, Pd, Pt).[42] In all complexes each phenylethynyl ligand is C-bonded to the three copper atoms, showing an asymmetric μ_3-η^1 bridging mode with the copper to carbon distances significantly different. The linearity of each phenylacetylide group (176(2)–178(2)°) and the C≡C distances (1.21(2)–1.22(2) Å) (Table III) are consistent with typical metal–acetylide σ-bonding and, hence, show electron deficient bonding systems (4c–2e for 1 and 5c–4e for 4). This is shown in more detail for the monocapped 1 and bicapped 4 trigonal complexes in Figures 4 and 5, respectively.

Table V collects structural data of several alkynyl polynuclear copper(I) complexes including for comparison other trinuclear copper(I) derivatives also bearing three dppm bridging ligands. The Cu$_3$—C bond lengths (average) are 2.03(1) (1), 2.21(2) (for C4) and 2.19(2) (for C12) (4), and 2.17(2) Å (7). The shorter Cu—C bond lengths in 1 are comparable to those of μ_2-η^1-bonded alkynyl groups (see Table V) while the values in the last two complexes may be compared with those found in the tetranuclear complexes [Cu(μ_3-η^1-C≡CPh)(Ph$_2$Ppy-*P*)]$_4$[28] and [Cu(μ_3-η^1-C≡CPh)(PPh$_3$)]$_4$[27] (2.1708(8) and 2.185(4) Å, respectively) where the alkynyl groups are also bridging three copper atoms of the triangular skeletal faces. The Cu—Cu

Table III. Selected Bond and Interatomic Distances (Å) and Bond Angles (deg) for Complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$ (1), $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$ (4), and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (7)

Complex 1			
Distances			
Cu(1)–Cu(2)	2.813(2)	Cu(1)–C(6)	2.04(1)
Cu(1)–Cu(3)	3.274(3)	Cu(2)–C(6)	1.96(1)
Cu(2)–Cu(3)	2.904(3)	Cu(3)–C(6)	2.08(1)
Cu(1)–P(6)	2.257(4)	Cu(1)–P(1)	2.263(4)
Cu(2)–P(2)	2.270(4)	Cu(2)–P(3)	2.279(4)
Cu(3)–P(4)	2.275(4)	Cu(3)–P(5)	2.260(4)
C(6)–C(7)	1.22(2)		
Angles			
Cu(1)–C(6)–C(7)	125(1)	Cu(3)–C(6)–C(7)	100(1)
Cu(2)–C(6)–C(7)	138(1)	C(6)–C(7)–C(8)	176(2)
Complex 4			
Distances			
Cu(1)–Cu(2)	2.570(3)	Cu(1)–C(4)	2.34(2)
Cu(1)–Cu(3)	2.598(3)	Cu(2)–C(4)	2.17(2)
Cu(2)–Cu(3)	2.615(3)	Cu(3)–C(4)	2.12(2)
Cu(1)–C(12)	2.06(2)	Cu(2)–C(12)	2.33(2)
Cu(3)–C(12)	2.19(2)	Cu(1)–P(1)	2.292(5)
Cu(1)–P(6)	2.269(5)	Cu(2)–P(2)	2.286(5)
Cu(2)–P(3)	2.277(6)	Cu(3)–P(4)	2.265(5)
Cu(3)–P(5)	2.286(5)	C(4)–C(5)	1.21(2)
C(12)–C(13)	1.21(2)		
Angles			
Cu(1)–C(4)–C(5)	140(2)	Cu(2)–C(4)–C(5)	135(2)
Cu(3)–C(4)–C(5)	138(2)	Cu(1)–C(12)–C(13)	146(2)
Cu(2)–C(12)–C(13)	126(2)	Cu(3)–C(12)–C(13)	136(2)
C(4)–C(5)–C(6)	177(2)	C(12)–C(13)–C(14)	178(2)
Complex 7			
Distances			
Cu(1)–Cu(2)	2.803(3)	Cu(1)–Cu(3)	2.871(3)
Cu(2)–Cu(3)	2.785(3)	Cu(1)–C(4)	1.98(2)
Cu(2)–C(4)	2.18(2)	Cu(3)–C(4)	2.34(2)
Cu(1)–P(6)	2.288(4)	Cu(1)–P(1)	2.280(5)
Cu(2)–P(2)	2.255(4)	Cu(2)–P(3)	2.254(5)
Cu(3)–P(4)	2.256(5)	Cu(3)–P(5)	2.266(5)
Cu(1)–Cl(1)	2.568(4)	Cu(1)–Cl(2)	2.586(4)
Cu(1)–Cl(3)	2.535(4)	C(4)–C(5)	1.22
Angles			
Cu(1)–C(4)–C(5)	151(1)	Cu(2)–C(4)–C(5)	124(1)
Cu(3)–C(4)–C(5)	107(1)	C(4)–C(5)–C(6)	179

Table IV. Deviations of the Phosphorus Atoms from the Cu_3 Core (Å) in Complexes 1, 4, and 7

Complex 1		
P(1) –0.088(4)	P(2) 0.177(4)	P(3) 0.494(4)
P(4) –0.549(4)	P(5) 1.117(4)	P(6) 0.446(4)
Complex 4		
P(1) 0.051(5)	P(2) 0.683(5)	P(3) –0.747(5)
P(4) –0.776(5)	P(5) 0.497(5)	P(6) 0.562(5)
Complex 7		
P(1) –0.538(6)	P(2) –0.223(5)	P(3) 0.223(6)
P(4) 0.296(6)	P(5) –0.466(6)	P(6) –0.168(5)

distances, although shorter than metallic copper are consistent with nonbonding interactions (cf. 1, 2.997(3); 4, 2.594(3); 7, 2.819(3) Å (average)). It is interesting to note that the monocapped alkynyl complex 1 shows among the three complexes the larger Cu—Cu distances but the shortest Cu—C. Apparently, the presence of one additional chloride or acetylide bridging ligand to form a bicapped system leads to the shortening of the copper—copper distances while the copper—carbon bond lengths are increased.

Although the rationalization of the electron deficient copper–alkynyl bonding as 4c–2e and 5c–4e systems requires theoretical calculations, a description based on a simple molecular orbital model, such as that shown in Chart II, may be suggested.[43] Thus, the copper–carbon and copper–copper distances seem to reflect that the bonding combinations between the copper orbitals and that of the bridging ligands are more localized at the metallic system in the bicapped Cu_3–C_2 or Cu_3–(C)Cl systems than in the monocapped Cu_3C core. In contrast, the analogous capped trinuclear complexes $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][Cl]$[44] and $[Cu_3(\mu_3\text{-}OH)(\mu\text{-dppm})_3][BF_4]_2$[41] show the largest Cu–Cu distances (3.210(3) and 3.189(2) Å (average), respectively), probably revealing the different electronic influence due to the presence of the chloride or hydroxide bridging ligands.[45] The influence of the electronic properties of the μ_3-η^1 ligands in the bicapped complexes 4 and 7 on the Cu–Cu distances is also apparent (*d*(Cu–Cu): (7) 2.819(3) vs (4) 2.594(3) Å (average)).

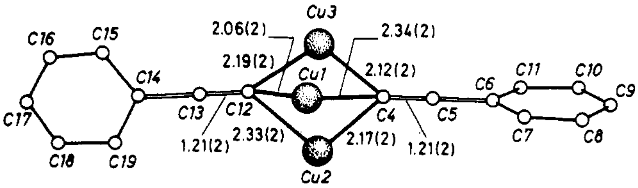

Figure 5. View of the $Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2$ core in complex 4 with Cu—C and C≡C bond distances (Å). Cu—Cu interatomic distances (Å): Cu1—Cu2, 2.70(3); Cu1—Cu3, 2.598(3); Cu2—Cu3, 2.615(3).

As expected for the qualitative bonding model described above, the Cu–Cu distances in these μ_3-η^1 electron deficient systems are larger than those found in other polynuclear copper(I) complexes bearing 3c–2e systems of alkynyl (see Table V) or other organyl μ_2-η^1 bridging groups.[46]

An interesting structural feature is the significant asymmetry of the skeletal cores Cu_3—C, Cu_3—C_2, and Cu_3—(Cl)C (see Figures 4 and 5). When the structural parameters of the cores in 1 and 4 are compared, the following features are evident: (i) The longest difference between the intermetallic Cu—Cu distances in complex 1 (0.461 Å; Cu(1),Cu(3)—Cu(1),Cu(2)) is larger than that found in complex 4 (0.045 Å; Cu(2),Cu(3)—Cu(1),Cu(2)), indicating that the triangular arrangement is more asymmetric in 1. (ii) In contrast, the opposite is found for the differences between Cu—C distances, being smaller (0.12 Å; Cu(3),C(6)—Cu(2),C(6)) in 1 and larger (0.28 Å; Cu(1),C(4)—Cu(1),C(12)) in 4, so that in the latter complex the asymmetry is mainly located in the bicapping system. (iii) A remarkable difference is observed in the acetylide orientations with respect to the trimetallic plane; the Cu—C≡C angles are in the range 100(1)–138(1) and 126(2)–146(2)° for 1 and 4, respectively. (iv) As a consequence of the latter consideration, the C≡C—C linkages

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(45) The Cu–Cu distances in benzoate- or bromide-bridged systems are also larger than those bridged by organyl groups, e.g. $[Cu_3(\mu_2\text{-}\eta^1\text{-}C_6H_2Me_3\text{-}2,4,6)(\mu\text{-}O_2CC_6H_5)_2]$: Cu–Cu (benzoato-bridged), 2.888 (2) Å; Cu–Cu (mesityl-bridged), 2.421(2) Å. Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *Organometallics* **1989**, *10*, 2293.

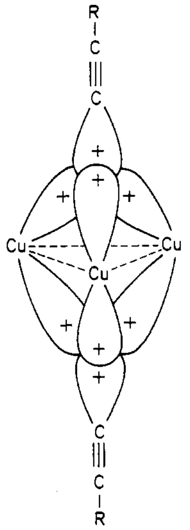
(46) For aryl groups, see for instance: (a) $[Cu_3(\mu_2\text{-}\eta^1\text{-}C_6H_2Me_3\text{-}2,4,6)(\mu\text{-}O_2CC_6H_5)_2]$ Cu–Cu 2.421(2) Å; Cu–C 1.957 (6) Å. (See ref 45.) (b) $[Cu(\mu_2\text{-}\eta^1\text{-}C_6H_2Me_3\text{-}2,4,6)]_5$ Cu–Cu: 2.437(8)–2.469(9) Å; Cu–C: 1.96(2)–2.06(2) Å. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156. (c) $[Cu_4(\mu_2\text{-}\eta^1\text{-}C_6H_2Me_3\text{-}2,4,6)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ Cu–Cu, 2.431(1) and 2.464(1) Å; Cu–C, 1.981(8)–2.064(8) Å. Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten G. *J. Am. Chem. Soc.* **1990**, *112*, 5895. Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, 114, 3400. (d) For alkyl groups, see for instance: $[Cu(CH_2SiMe_3)]_4$ Cu–Cu, 2.417 Å; Cu–C, 2.02 Å. Jarvis, J. A. J; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999.

Table V. Selected Atomic and Bond Distances (Å) of Several Relevant Alkynylcopper(I) and Related Complexes

complex	Cu—P	Cu···Cu X-bridged	Cu···Cu alkynyl-bridged	Cu—C	ref
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$	2.257(4)–2.279(4)		2.813(3)–3.274(3)	1.96(1)–2.08(1)	*e*
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$	2.265(5)–2.292(5)		2.570(3)–2.615(3)	2.06(2)–2.34(2)	*e*
$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$	2.254(5)–2.288(4)	2.785(3)–2.871(3)[a]		1.98(2)–2.34(2)	*e*
$[Cu_3(\mu_3\text{-Cl})_2(\mu\text{-dppm})_3][Cl]$	2.257(4)[c]	3.175(4)–3.281(3)[a]			44
$[Cu_3(\mu_3\text{-OH})(\mu\text{-dppm})_3][BF_4]_2$	2.226(3)–2.244(3)	3.120(2)–3.322(2)[b]			41
$[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(Ph_2Ppy\text{-}P)]_4$	2.220(2)–2.241(2)		2.525(1)–2.686(1)	2.053(8)–2.345(8)	28
$[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(PPh_3)]_4$	2.221(1)–2.234(1)		2.523(1)–2.676(1)	2.072(4)–2.380(4)	27
$[Cu_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(PMe_3)_4]$	2.222(5)–2.238(5)		2.450(3)[d]	1.957(16)–2.223(17)[d]	23
$[Cu_3(C{\equiv}C^tBu)\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2]_2$			2.458(2)–2.587(2)	1.96(1)–2.13(1)	25
$[Cu_6(\mu_2\text{-}\eta^1\text{-}C{\equiv}CC_6H_4Me\text{-}4)_2(C_6H_4NMe_2\text{-}2)_4]$			2.474(4)	1.984(2)–2.130(6)	24

[a] X = Cl. [b] X = OH. [c] Average. [d] μ_2-η^1 bridge. [e] This paper.

Chart II



in both complexes are not perpendicular to the trimetallic plane (69.2(4)° and 82.5(6), 82.4(5)° in 1 and 4, respectively), giving rise to a bent disposition of the acetylide groups with respect to the metallic plane.

Reasons for the occurrence and the structural differences of the mono- and bicapping systems of one or two asymmetric μ_3-η^1-acetylide ligands are difficult to discern. It could be proposed that, probably due to the presence of different anionic ligands and the steric crowding (as a consequence of the phenyl groups), neither electronic nor steric effects can be discarded. Presumably, the presence of the three "small bite" dppm bridging ligands could enforce the irregular arrangement of the Cu_3 triangle but apparently there does not exist any localized electronic effect to induce the observed asymmetry in the copper–acetylide triple bridge of each complex.

Finally, the structure of complex 1 deserves a further comment. As has been discussed above, the acetylide group shows a remarkable bent orientation which notably reduces the formal distance of the acetylene Cβ atom (C(7)) to the Cu_3 plane (Figure 4). In fact, the shortest Cu—C distance found in 1 (Cu(3)—C(7), 2.58(1) Å), although substantially longer than the length of the Cu—C_α(acetylide) σ bonds, is too short to be considered a nonbonding contact. This distance is comparable with those found in $[N^nBu_4][Au_3Cu_2(C_2Ph)_6]$ (Cu—C_β, 2.35–2.65(3) Å)[47] and even shorter than the value found in $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C^tBu)]_2$ (Cu—C_β, 2.84(1) Å), in which an asymmetric σ–π interaction is proposed for the copper–acetylide bonding.[25] Nevertheless it is yet longer than the values of Cu—acetylide "side-on" symmetrical bonding, e.g. $[Cu(C{\equiv}CPh)(PMe_3)]_4$ (Cu—C_α,C_β, 2.06–2.09 Å),[23] $[Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2]$ (Cu—C_α,C_β, 1.99(7) and 2.19(4) Å),[5] $[Mn_2Cu(C{\equiv}C^tBu)_2(CO)_6(dppe)_2][PF_6]$ (Cu—C_α,C_β, 2.08(1)–2.09(1) Å).[6] Since the alkynyl bending and the C≡C bond lengthening typical of η^2 interactions are not observed, we consider that complex 1 is better described as an asymmetric case of a μ_3-η^1 acetylide bonding mode.

Conclusions

In this work we have developed efficient syntheses of novel cationic trinuclear copper(I) complexes containing asymmetric μ_3-η^1-acetylide groups. These complexes consist of *triangulo*-Cu_3 frameworks stabilized by three bridging dppm ligands which appear to be appropriate supports for mono- and bicapping systems of μ_3-η^1 acetylide groups. These peculiar complexes are structurally related to similar *triangulo*-$M_3(\mu\text{-P-P})_3$ clusters, namely $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (M = Pd, Pt),[42a–c] $[Ni_3(\mu_3\text{-CO})(\mu\text{-dmpm})_3]^{2+}$,[42d] and $[M_3(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (M = Ni, Pd, Pt),[42e,f] with triply bridging carbonyl ligands. We and others had previously reported[27,28] tetranuclear copper(I) complexes exhibiting the unprecedented μ_3-η^1 coordination mode of the acetylide groups which is well-known in the coordination chemistry of carbon monoxide. The new Cu_3 complexes here described offer an unusual opportunity to show simultaneously examples of bonding modes and structural analogies between metal acetylide and carbonyl complexes.

Finally, it is apparent that the qualitative molecular orbital description of these electron deficient copper–alkynyl bonding systems does not account for the observed asymmetry of the cores and further theoretical calculations should be undertaken.

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Supplementary Material Available: Figures with complete atom labeling and tables of atomic coordinates, thermal parameters, bond distances and angles, torsion angles, and angles between least-squares planes (57 pages). Ordering information is given on any current masthead page.

OM920803Y

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[47] Abu-Salah, O. M.; Al-Ohaly, A. A. R.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1985**, 1502.