rotated with respect to the other, resulting in a dihedral angle of 55.6 (6)° between the planes of the Cp ligands. The C(7)-C(8) distance is 1.18 (3) Å, short compared to the C≡C distance in unbound acetylene and the C≡C distances in the Chatt type acetylene complexes.[9] The structure of the similar dirhenium complex $(CO)_5ReC{\equiv}CRe(CO)_5$ has recently been reported.[9c] The C≡C distance is again slightly longer than that in 4.

Since **1a** is a relatively weak nuclophile compared with the substituted anion **1b**, it is therefore not surprising that CH_2Br_2 or CH_2Cl_2 would not react with **1a**. The reaction of **1b** with CH_2I_2 directly produces $Cp(CO)_2[P(OMe)_3]WI$ and **6b**. No ketene intermediate was observed. The reaction of **1b** with CH_2Br_2 or with CH_2Cl_2 gives a ketene intermediate, which is then converted to $Cp(CO)_2[P(OMe)_3]WX$ (X = Br, Cl) and **6b** at room temperature, but at a slower rate. The halide anion may play an important role in such a transformation. Preliminary results indicate that the reaction of **5** with **1b** in CD_3CN directly produces $Cp(CO)[P(OMe)_3]W(\mu\text{-}COCH_2)(\mu\text{-}CO)W(CO)_2Cp$. The CO insertion takes place at the substituted metal center. The decomposition products, which contain mostly $Cp(CO)_3WCH_3$ and $Cp(CO)_2[P(OMe)_3]WI$, provide further evidence that CO insertion takes place at the substituted site.

With the tungsten metal, we have demonstrated facile C-C bond formation of the dinuclear methylene complex with no other supporting ligand. The unprecedented transformation of ketene to acetylene may provide another mechanism to account for the deoxygenation of CO in the Fischer-Tropsch synthesis. Further work is in progress, and detailed studies on the formation of methyl complexes and chemical reactivity of the ketene complexes will be the subject of future reports.

Acknowledgment. This research has been supported by the National Science Council (NSC) of the Republic of China.

Supplementary Material Available: Details of the structural determination for complex 4, including tables of data collection parameters, temperature factor expressions, positional parameters, and intramolecular distances and angles, and a table of spectroscopic data for complexes **2b**, **3a**,**b**, **4**, and **5** (7 pages); a table of observed and calculated structure factors for **4** (11 pages). Ordering information is given on any current masthead page.

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$[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-}Ph_2PCH_2PPh_2)_3][BF_4]$, a Triangulo Copper(I) Complex with an Unprecedented Bicapping System of Two Asymmetric $\mu_3\text{-}\eta^1$-Acetylide Ligands

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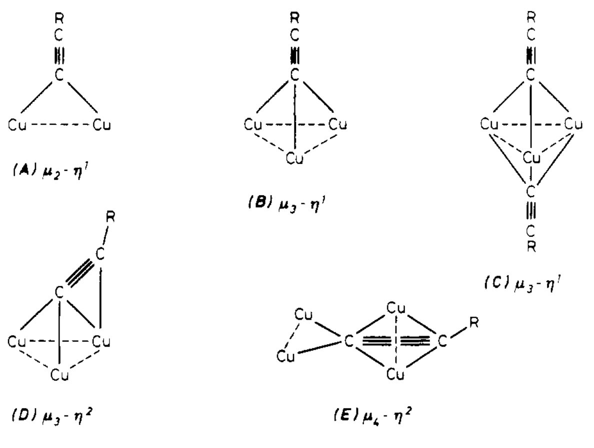
Summary: The synthesis and characterization of $[Cu_3(C{\equiv}CPh)_2(Ph_2PCH_2PPh_2)_3][BF_4]$ (**1**), the first cationic trinuclear copper(I) complex bicapped by two bridging σ-bonded phenylacetylide groups, is described. An X-ray single-crystal structure determination shows that the two linear phenylacetylide groups are bonded in a $\mu_3\text{-}\eta^1$ fashion, representing an unprecedented structure in organocopper(I) chemistry. The electronically deficient bonding can be formally described as a five-center-four-electron system.

Chart I



The chemistry of organocopper derivatives is of increasing interest due to their wide and selective applications in organic chemistry.[1] Much of the work done has been devoted specifically to synthetic studies through low or higher order mixed cuprates,[2] i.e. $[R_TRCuLi]$, $[R_TRCu(CN)Li_2]$. However, the formulas only reflect the ratio of the copper salt to the organolithium reagent and the active species or their molecular structures are scarcely known.[3] At present, there are only a small number of structurally characterized organocopper derivatives, most

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of which are polynuclear or highly aggregated mono- or binuclear species with the polyhedral metallic structure generally held together by bridging aryl groups.[3a] Recent representative examples[4] are $[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$,[4a] $Li_3Cu_2Ph_5(SMe_2)_4$,[4b] and $[\{Li(OEt)_2\}(CuPh_2)]_2$.[4c] The bonding in the copper–aryl–copper bridge can be represented by a three-center–two-electron copper–carbon bond in symmetrical bridges, i.e. $[Cu_5(2,4,6\text{-}Me_3C_6H_2)_5]$,[5a] or by a two-center–two-electron bonding interaction in the asymmetrical bridges,[3b,5b] such as $[Cu_4(2,4,6\text{-}{}^iPr_3C_6H_2)_4]$.[5c]

While much work has been focused on aryl and alkyl groups, alkynyl derivatives have received little attention, probably due to their insolubility which precludes in many cases structural studies. Acetylides can bind to copper frameworks in polynuclear complexes[6] by adopting any of the limiting structures shown in Chart I.

Only a few examples of the types A, B, D, and E have been described:[7] $[Cu_6(C_6H_4NMe_2\text{-}2)_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}CR)_2]$ (R = C_6H_5,[7a] $C_6H_4Me\text{-}2$[7b]), type A; the polymer $[Cu(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)]_n$, type D;[7c] $[Cu_4(\mu_2\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(PMe_3)_4]$, types A and D.[7d] Recently, van Koten et al. described[7e] the crystal structure of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}CBu^t)]$ and proposed an asymmetric bridging μ_3-η^2-*tert*-butylacetylide group. Nevertheless, the expected alkynyl bending and the C≡C bond lengthening typical of η^2 interactions, as shown by the aforementioned examples, are not observed (177° and 1.22 Å). So far, a unique example of a μ^4-η^2 bonding type (E) is known,[7f] namely, the atypical tetranuclear cationic complex $[Cu_4L_2(C{\equiv}CPh)]^{3+}$ (L = macrocyclic ligand).

We report here the first example of a cationic trinuclear copper(I) complex, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3][BF_4]$ (dppm = $Ph_2PCH_2PPh_2$) (**1**), asymmetrically bicapped by two phenylacetylide groups which are bonded in a linear μ^3-η^1 fashion (C).[7g] Recently, we have also prepared[8a] a related trinuclear complex, $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$ (**2**), of the type B. This result, together with the work described here, strongly suggests the special ability of the bridging dppm ligand to stabilize *triangulo*-Cu_3 frameworks, which can be used as an appropriate support of linear bridging alkynyl groups in organocopper chemistry.

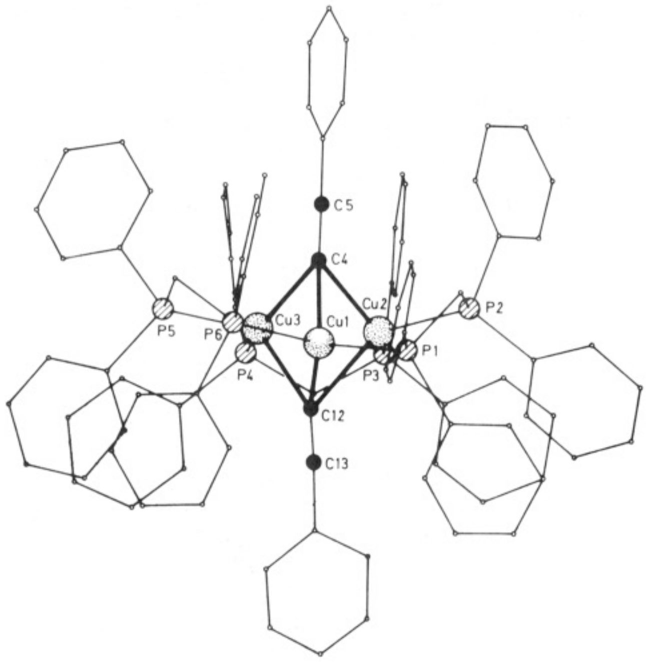

Figure 1. PLUTO drawing of the cation of **1** with main bond lengths (Å) and angles (deg): Cu1–Cu2, 2.570 (3); Cu1–Cu3, 2.598 (3); Cu2–Cu3, 2.615 (3); Cu1–C4, 2.34 (2); Cu1–C12, 2.06 (2); Cu2–C4, 2.17 (2); Cu2–C12, 2.33 (2); Cu3–C4, 2.12 (2); Cu3–C12, 2.19 (2); C4–C5, 1.21 (2); C12–C13, 1.21 (2); Cu1–C4–C5, 139.6 (16); Cu2–C4–C5, 134.8 (14); Cu3–C4–C5, 137.6 (15); Cu1–C12–C13, 145.8 (18); Cu2–C12–C13, 125.9 (15); Cu3–C12–C13, 135.8 (17).

The binuclear copper(I) complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (**3**)[8b] reacts with bidentate nucleophiles and acetylides to give bi-,[8c] tri-,[8a] and tetranuclear[8d] complexes. The reaction of **3** with HC≡CPh (molar ratio 3:4) in the presence of an excess of KOH in CH_2Cl_2/MeOH gives complex **1** quantitatively, which is isolated as a yellowish air-stable solid.[9]

Conductivity data (in Me_2CO) show that **1** behaves as a 1/1 electrolyte. The IR spectrum (KBr) reveals a strong and broad ν(B—F) band at 1056 cm^{-1} and a weak ν(C≡C) absorption at 2027 cm^{-1}. The ^{1}H NMR spectrum of **1** shows a methylene resonance as a nonresolved multiplet, indicating an effective equivalence of the CH_2P_2 protons. This is consistent with the existence of a formal plane of symmetry containing each Cu_2P_2C moiety arising from the presence of the two μ_3-η_1-C≡CPh ligands on each side of the Cu_3 triangle. It is also in accordance with the inequivalence of the corresponding protons $Cu_2P_2CH_AH_B$ in the related complex **2**, where there is no plane of symmetry and a typical ABX_2 spin system is observed in the ^{1}H NMR spectrum.[8a] The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a singlet resonance at δ −4.39 ppm, also indicating

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(9) Under anaerobic and anhydrous conditions, a solution of complex **3** (0.5 mmol) in CH_2Cl_2/MeOH (3:1; 60 mL) was treated with HC≡CPh (0.67 mmol) and an excess of KOH and stirred at room temperature for 24 h. After evaporation to dryness, the resulting solid residue was extracted with CH_2Cl_2 (3 × 5 mL) and the solution partially concentrated. The addition of hexane gave by precipitation complex **1** as a yellowish solid. Anal. Calcd for $C_{91}H_{76}BCu_3F_4P_6$: C, 66.99; H, 4.66. Found: C, 66.85; H, 4.78. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.2 (m, 70 H, C_6H_5), 3.35 (m, 6 H, CH_2P_2). $^{31}P\{^1H\}$ NMR (121.5 MHz): δ −4.39. Complex **3** can be prepared in lower yields by the reaction of **2** with an excess of LiC≡CPh (molar ratio 1:3) in THF or, alternatively, by treating $[Cu_3(\mu\text{-dppm})_3(\mu\text{-}Cl)_2][BF_4]$ with an excess of LiC≡CPh.

the chemical equivalence of the phosphorus atoms. The crystal structure of 1 was determined by X-ray diffraction.[10] A drawing with the main bond distances and angles is shown in Figure 1.

The cationic complex consists of an isosceles triangle "cluster" of copper atoms (Cu–Cu distances 2.594 (3) Å (average)) with a dppm ligand bridging each edge to form a roughly planar $[Cu_3P_6]^+$ core (the deviations of the P atoms from the Cu3 plane are as follows: P1, 0.051 (5); P2, 0.683 (5); P3, −0.747 (5); P4, −0.776 (5); P5, 0.497 (5); P6, 0.562 (5) Å). The most remarkable feature is the presence of two triply bridging phenylacetylide groups, forming an unprecedented bicapped trigonal organocopper(I) derivative. The bridging mode of the alkynyl groups is highly asymmetric, as illustrated by the different bond lengths of Cu–C (2.063 (18)–2.342 (17) Å) or bond angles between the alkynyl groups and each copper atom (125.9 (15)–145.8 (18)°; see Figure 1). The intersection angle between the two bonding lines of the phenylacetylide groups, C(4)–C(5)–C(6) and C(12)–C(13)–C(14), is 166.6 (14)°. The linearity of each phenylacetylide group (bond angles of 177.3 (23) and 178.4 (21)°) and the C≡C distances (1.214 (24) and 1.209 (24) Å) are consistent with typical metal–acetylide σ bonding, and hence, the complex shows a five-center–four-electron bonding system, a very uncommon case in organocopper chemistry.

Another relevant feature concerning the Cu–Cu and Cu–C distances should be mentioned. Although the copper–copper distances (2.594 (3) Å (average)) are consistent with nonbonding interactions,[11] they are shorter than those found in **2** (cf. 2.997 (3) Å (average)).[8a] In contrast, the Cu_3–C distances are significantly larger (2.211 (16) Å for C4 and 2.195 (19) Å for C12 (average); cf. **2**, 2.027 (14) Å (average)). This seems to suggest that the bonding combination between the copper orbitals and the two sp orbitals is more localized at the metallic system in the Cu_3C_2 core (type C) than in the analogous Cu_3C (type B). As expected, the Cu–Cu and Cu–C bond lengths are larger than those found[7b] in the case of the three-center–two-electron alkynyl-bridged μ_2-η^1 system (type A; Cu–C, 1.984 (7)–2.130 (6) Å; Cu–Cu, 2.474 (4) Å).

A solution of complex 1 in CH_2Cl_2 (containing traces of HCl) gives the mixed-bridge derivative $[Cu_3(\mu_3\text{-}Cl)(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]$ (**4**) with a triply bridging chlorine.[12] These peculiar bicapping phenylacetylide and phenylacetylide–chloride systems, found in 1 and **4**, respectively, are structurally and electronically related to similar *triangulo*-M_3 (dppm) clusters (M = Ni, Pd, Pt) with triply bridging carbonyl or methyl isocyanide ligands.[13,14] Therefore, the new Cu_3 complexes bridged by dppm ligands offer an unusual opportunity to compare structures and reactivity between formally metal d^{10} clusters, which may be of interest in elucidating the role of catalytic amounts of Pd(0) phosphine complexes in the copper(I)-mediated couplings of acetylenes.[15]

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Supplementary Material Available: Listings of positional parameters for non-hydrogen atoms, bond lengths and angles, anisotropic temperature factors, positional parameters of hydrogen atoms, and torsion angles (23 pages). Ordering information is given on any current masthead page.

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[10] Crystals of the complex were obtained by slow diffusion of Et_2O into a THF solution of 1. Crystal data for 1: $C_{91}H_{76}BCu_3F_4P_6$, M_r = 1632.9, monoclinic, space group $P2_1/c$, a = 14.613 (1) Å, b = 21.863 (1) Å, c = 26.672 (1) Å, β = 102.86 (1)°, V = 8307.4 (1) Å^3, Z = 4, ρ_{calcd} = 1.31 g/cm^3, T = 293 K; crystal dimensions 0.30 × 0.20 × 0.13 mm^3; Mo Kα radiation (λ = 0.71073 Å), graphite monochromated; 12486 reflections measured on an Enraf-Nonius CAD4 (ω–2θ scan technique), range $0 < \theta < 25°$ and $-16 \le h \le 15, 0 \le k \le 23, 0 \le l \le 29$; 11440 unique reflections (R_{int} = 0.042, averaging some double measured) and 4813 observed ($I > 3\sigma(I)$). Semiempirical and empirical absorption corrections were applied; μ = 9.28 cm^{-1}. The structure was solved by Patterson interpretation (SHELXS 86) and anisotropically refined (SHELX 76) to a final R = 0.077 (910 parameters and unit weights); maximum shift/error 0.28, ρ_{max} = 0.76 e/Å^3.

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[12] Pale yellow solid, Δ_M(acetone) = 140 Ω^{-1} cm^2 mol^{-1}. IR (KBr): ν(B—F) = 1055 (s, br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.15 (m, 6 H, CH_2P_2), 6.7–7.2 (m, 60 H, Ph_2P), 7.3–7.6 (m, 5 H, PhC≡C). $^{31}P\{^1H\}$ NMR: δ −8.98. Anal. Calcd for $C_{83}H_{71}BCu_3ClF_4P_6\cdot{}^1/_2CH_2Cl_2$: C, 62.12; H, 4.45. Found: C, 61.94; H, 4.63. The structure has been confirmed by an X-ray crystallographic determination: Garcia-Granda, S.; Aguirre, A. Personal communication.

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Thermal and Photochemical Decarbonylation of $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$

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Summary: $(MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (**1**) undergoes thermolysis at 60 °C in THF to produce $(MeC_5H_4)_2Nb({=}O)CH_2SiMe_3$ (**2**). The structure of **2** has been confirmed by X-ray diffraction. The **1** → **2** conversion is promoted photochemically, occurring at −20 °C within minutes upon UV irradiation.

Despite expanding interest in transition-metal-mediated chemical[1] and electrochemical[2] transformations of carbon dioxide, the reactivity of *coordinated* CO_2 remains largely unexplored.[3] In this context we reported recently the first

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