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Novel Copper(I) Complexes Containing 1,1′-Bis(diphenylphosphino)ferrocene (dppf) as a Chelate and Bridging Ligand: Synthesis of Tetrabridged Dicopper(I) Complexes $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}R)_2(\mu\text{-dppf})_2]$ and X-ray Crystal Structure of $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$

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Binuclear copper(I) complexes $[Cu(\kappa^2\text{-}P,P\text{-dppf})(CH_3CN)_2][BF_4]$ **(1)**, $[Cu(\kappa^2\text{-}P,P\text{-dppf})(bipy)][BF_4]$ **(2)** containing the chelating dppf ligand (dppf = 1,1′-bis(diphenylphosphino)ferrocene) have been prepared by substitution reactions of the acetonitrile ligands from the complexes $[Cu(CH_3CN)_4][BF_4]$ and (**1**) with dppf and bipy, respectively. Similarly, the treatment of the complex $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2][BF_4]_2$ with dppf in CH_2Cl_2 at room temperature gives the tetranuclear complex $[Cu_2(\mu\text{-dppm})_2(\kappa^2\text{-}P,P\text{-dppf})_2][BF_4]_2$ (**3**). The analogous bridging chloride tetranuclear complex $[Cu_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**4**) has been also prepared by the addition of dppf to a solution in THF containing an equimolar mixture of CuCl and tetramethylethylenediamine. Complex **4** has been used as a precursor for $\mu\text{-}\eta^1$-alkynyl bridging dicopper(I) complexes containing the framework $[Cu_2(\mu\text{-dppf})_2]$. Complexes $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppf})_2]$ ($R = C_6H_4CH_3\text{-}4$ **(5)**, C_6H_5 **(6)**, CH_2OCH_3 **(7)**, $CH_2CH_2CH_3$ **(8)**, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ **(9)**) are obtained by the treatment of complex **4** with an excess of $LiC{\equiv}CR$ in THF. Complexes **5**−**9** can also be prepared from the reaction of an equimolar mixture of $[Cu(C{\equiv}CR)]_n$ and dppf in toluene at room temperature. The crystal structure of complex **5** has been determined by X-ray diffraction. The crystallographic asymmetric unit consists of three molecules of **5**, all with related stereochemistries at their centers. The complex consists of two copper atoms linked by two bridging dppf ligands and two bridging alkynyl groups in a $\mu\text{-}\eta^1$ bonding arrangement with an almost planar $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2]$ framework. The arylethynyl groups are nearly linear ($C{\equiv}C{-}C$ angles 174(2)−175(2)°), and the $C{\equiv}C$ distances (1.20(2)−1.21(2) Å) are typical for cases of metal−acetylide σ-bonding. Both bridging dppf ligands are twisted from the eclipsed conformation (mean value 77(2)°) and also show a relatively large value of the angle (mean value 56.8(6)°) formed by the projection of the Cp···Cp axis of dppf onto the Cu···Cu axis. This seems to indicate that the molecular core $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2]$ is a sterically demanding system that forces the dppf ligand to adopt a relatively strained conformation.

Introduction

We have recently reported[1a] the systematic synthesis and structural characterization of a series of cationic trinuclear copper(I) alkynyl complexes of the type $[Cu_3(C{\equiv}CR)_n(\mu\text{-dppm})_3][BF_4]_{3-n}$ ($n = 1, 2$) containing a *triangular* Cu_3 arrangement stabilized by three bridging bis(diphenylphosphino)methane (dppm) ligands (**A**).[1b] This metal framework appears to be an appropriate support for the $\mu_3\text{-}\eta^1$-acetylide group (**B**)[1c,d] and bis($\mu_3\text{-}\eta^1$-acetylide) groups (**C**)[1c] as well as for the mixed bridging systems ($\mu_3\text{-}\eta^1$-acetylide)−($\mu_2\text{-}\eta^1$-isocyanide) (**D**)[2]

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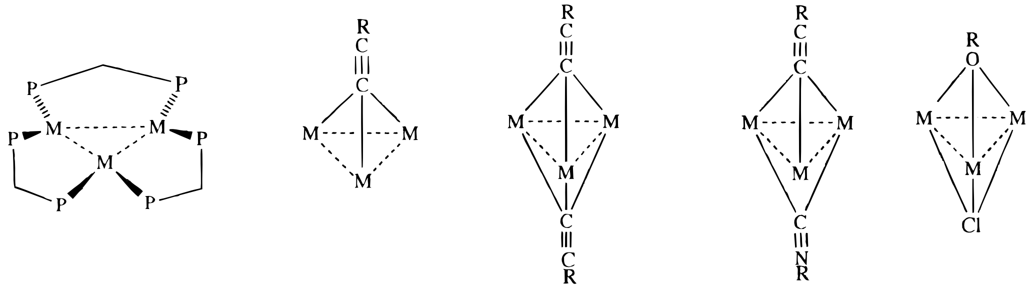
Chart 1



(A) (B) (C) (D) (E)

and (μ_3-η^1-alkoxy)−(μ_3-η^1-chloride) (**E**)[3] (Chart 1). The remarkable ability of the bridging dppm ligand to stabilize *triangular* metallic frameworks $M_3(\mu\text{-dppm})_3$ is evidenced by the isolation of the structurally and electronically related clusters with M = Ni, Pd, Pt, which are also able to support triply bridging carbonyl or isocyanide ligands.[4]

It is well-known that the bidentate ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) shows a versatile coordination ability adapting its steric bite angle to the geometric requirement of the metal through the appropriate ring twisting or tilting. Although the chelating coordination mode is the predominant character of dppf in most metal centers to which it is attached,[5] homo- and heteropolinuclear complexes containing bridging dppf are also known.[6−13] As part of our ongoing work on the chemistry of alkynyl copper(I) complexes, we have investigated the ability of dppf to act as a stabilizing ligand for polynuclear copper(I) systems. Our interest in this stems from the possibility of using these complexes as alternative frameworks for the stabilization of bridging alkynyl groups in a manner similar to that shown by dppm in the aforementioned trinuclear $[Cu_3(\mu\text{-dppm})_3]$ systems.

Here we report the synthesis and characterization of novel copper(I) dppf-containing complexes of the following types: (a) with chelating dppf in binuclear complexes $[Cu(\kappa^2\text{-}P,P\text{-dppf})(CH_3CN)_2][BF_4]$ **(1)**, $[Cu(\kappa^2\text{-}P,P\text{-dppf})(bipy)][BF_4]$ **(2)** and tetranuclear complexes $[Cu_2(\mu\text{-dppm})_2(\kappa^2\text{-}P,P\text{-dppf})_2][BF_4]_2$ **(3)** and $[Cu_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ **(4)**; (b) tetranuclear complexes with bridging dppf $[Cu_2(\mu\text{-}\eta^1\text{-C}{\equiv}CR)_2(\mu\text{-dppf})_2]$ (R = $C_6H_4CH_3$-4 **(5)**, C_6H_5 **(6)**, CH_2OCH_3 **(7)**, $CH_2CH_2CH_3$ **(8)**, $(\eta^5\text{-}C_5H_4)\text{Fe}(\eta^5\text{-}C_5H_5)$ **(9)**) in which the metal centers are also linked by bridging alkynyl groups, forming an unusual mixed tetrabridged system consisting of two μ-η^1−alkynyl groups and two μ-dppf ligands. The bridging coordination mode of the ligands has been confirmed by an X-ray diffraction study of complex **5**.

Results and Discussion

Synthesis of Chelating dppf Complexes (1−4). We have previously reported[14,15] that the reaction of

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Table 1. IR, $^{31}P\{^1H\}$, and ^1H NMR[a] Data for the Complexes 1-9

complex	$\upsilon(N{\equiv}C)$ or $\upsilon(C{\equiv}C)$	$^{31}P\{^1H\}$	^1H
$[Cu(CH_3CN)_2(\kappa^2\text{-}P,P\text{-dppf})]\,[BF_4]$ (**1**)	2303 w, 2276 w	−12.7	2.22 (s,6H,CH_3CN), 4.11 (s,4H,C_5H_4), 4.31 (s,4H,C_5H_4), 7.3−7.6 (m,20H,Ph)
$[Cu(bipy)(\kappa^2\text{-}P,P\text{-dppf})]\,[BF_4]$ (**2**)		−8.9	4.49 (s,4H,C_5H_4), 4.75 (s,4H,C_5H_4), 8.80−7.75 (m,28H,Ph,bipy)
$[Cu_2(\mu\text{-dppm})_2(\kappa^2\text{-}P,P\text{-dppf})_2]\,[BF_4]_2$ (**3**)		−5.90,−6.7	3.45 (m,4H,CH_2P_2), 4.10 (s,8H,C_5H_4), 4.33 (s,8H,C_5H_4), 7.45−6.80 (m,80H, Ph)
$[Cu_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**4**)		−19.7	4.12 (s,8H,C_5H_4), 4.30 (s,8H,C_5H_4), 8.10−6.90 (m,40H,Ph)
$[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$ (**5**)	2036 w	−11.04	2.3 (s,6H,$C_6H_4CH_3$), 3.53 (s,4H,C_5H_4), 3.58 (s,4H,C_5H_4), 3.87 (s,4H,C_5H_4), 6.6−8.0 (m,52H,Ph,C_5H_4)
$[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)_2(\mu\text{-dppf})_2]$ (**6**)	2030 w	−10.31	3.61 (s,4H,C_5H_4), 3.66 (s,4H,C_5H_4), 3.95 (s,4H,C_5H_4), 6.7−8.1 (m,54H,Ph,C_5H_4)
$[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CCH_2OCH_3)_2(\mu\text{-dppf})_2]$ (**7**)	2044 w	−11.99	3.27 (s,6H,CH_3O), 3.84 (s,4H,CH_2O), 3.58 (s,4H,C_5H_4), 3.76 (s,4H,C_5H_4), 3.99 (s,4H,C_5H_4), 6.6−8.0 (m,44H,Ph,C_5H_4)
$[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CCH_2CH_2CH_3)_2(\mu\text{-dppf})_2]$ (**8**)	2046 w	−12.10	0.96 (t,6H,CH_3), 1.46 (m,4H,CH_2), 2.12 (m,4H,CCH_2), 3.58 (s,4H,C_5H_4), 3.66 (s,4H,C_5H_4), 3.93 (s,4H,C_5H_4), 6.6−8.0 (m,44H,Ph,C_5H_4)
$[Cu_2\{(\mu\text{-}\eta^1\text{-}C{\equiv}C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-dppf})_2]$ (**9**)	2033 w	−12.79	4.14 (s,4H,C_5H_4), 3.99 (s,14H,C_5H_5,C_5H_4), 3.95 (s,4H,C_5H_4), 3.75 (s,4H,C_5H_4), 3.60 (s,4H,C_5H_4), 6.6−8.05 (m,44H,PPh,C_5H_4)

[a] Spectra recorded in $CDCl_3$; δ in ppm.

$[Cu(CH_3CN)_4][BF_4]$ and dppm affords in high yield the binuclear copper(I) complex $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2][BF_4]_2$ (**I**). This complex proved to be an efficient precursor for a large series of novel triply bridged binuclear copper(I) complexes containing the moieties $[Cu_2(\mu\text{-dppm})_2(\mu\text{-L}{-}\text{L})]$ and $[Cu_2(\mu\text{-dppm})(\mu\text{-L}{-}\text{L})_2]$. (L−L = 6-methypyridin-2-olate, 3,5-dimethylpyrazolate, 1,3-di-*p*-tolyltriazenide, acetate).[15] Accordingly, we set out to explore similar reactions with dppf hoping to get a good entry point for the preparation of bridging dppf copper(I) complexes. However, the reaction of an equimolar mixture of $[Cu(CH_3CN)_4][BF_4]$ and dppf in CH_2Cl_2 or in CH_3CN, in contrast to the synthesis of complex **I**, leads[16] to the formation of the chelate complex $[Cu(\kappa^2\text{-}P,P\text{-dppf})(CH_3CN)_2][BF_4]$ (**1**), which is isolated, after addition of Et_2O to a concentrated solution, as a yellow solid (80% yield). As expected the remaining coordinated acetonitrile molecules are easily displaced; thus, the reaction of complex **1** with 2,2′-bipyridine (bipy) in Me_2CO leads to a solution from which the complex $[Cu(\kappa^2\text{-}P,P\text{-dppf})(bipy)][BF_4]$ (**2**) was obtained as an insoluble orange solid (80%yield).

In a similar way, the acetonitrile ligands of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2][BF_4]_2$ are also easily substituted by dppf in dichloromethane, leading to the formation of the cationic tetranuclear complex $[Cu_2(\mu\text{-dppm})_2(\kappa^2\text{-}P,P\text{-dppf})_2][BF_4]_2$ (**3**) isolated as a yellow solid (75% yield) after addition of Et_2O to the concentrated solution of the reaction mixture. The analogous bridging chloride complex $[Cu_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**4**) has also been prepared by the addition of dppf to a THF solution containing an equimolar mixture of CuCl and tetramethylethylenediamine (tmeda). Complex **4** is isolated from the reaction mixture as an insoluble yellow solid (72%yield)[17a,b] (eq 1).

$$CuCl + tmeda + dppf \rightarrow [Cu_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2] + tmeda \quad (1)$$

All of the complexes are air stable in the solid state and soluble in chlorinated solvents. They have been characterized by elemental analyses, conductance measurements, and IR and NMR (^1H, and $^{31}P\{^1H\}$) spectroscopy. Selected spectroscopic data are given in Table 1. Conductivity data (in Me_2CO) show that complexes **1** and **2** are 1:1 electrolytes and complex **3** is a 1:2 electrolyte. IR spectra (KBr) exhibit the expected absorptions for the tetrafluoroborate anion as well as those characteristic for dppf and the rest of the ligands (see Experimental Section). In particular, the presence of the coordinated MeCN molecules is evidenced by the appearance of two weak $\nu(C{\equiv}N)$ absorption bands at 2303 and 2276 cm^{-1} and is confirmed by the ^1H NMR spectrum, which shows a single methyl resonance at δ 2.22 ppm. The NMR spectra (^1H and $^{31}P\{^1H\}$) of complexes **1**−**4** reveal the presence of dppf, although no conclusive information can be obtained regarding its coordination mode. Thus, $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ show a single resonance (δ −12.7 (**1**), −8.9 (**2**), and −19.7(**4**) ppm) for dppf, while that of complex **3** appears as two very broad signals (δ −5.9 and −6.7 ppm) probably as a consequence of overlap with the corresponding resonances of the bridging dppm ligands. Although we have not carried out variable-temperature experiments, chemical exchange of dppf and dppm cannot be discarded given the ability of dppf to act as a bridging ligand (see below) and the dissociation processes of dppm shown by the solutions of complex **I** in dichloromethane.[14] An analogous chemical exchange of bridging and chelating dppf has also been described for the complex $[Cu_2(\mu\text{-dppf})(\kappa^2\text{-}P,P\text{-dppf})_2]\,[BF_4]_2$.[8a] The ^1H NMR ($CDCl_3$) spectra of complexes **1**−**4** exhibit, in

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(16) It has been reported previously that the reaction of $[Cu(CH_3CN)_4][BF_4]$ with dppf in a molar ratio of 1:2 leads to the formation of the complex $[Cu_2(\mu\text{-dppf})(\kappa^2\text{-}P,P\text{-dppf})_2][BF_4]_2$. See ref 8a.

(17) (a) The X-ray crystal structure determination confirms the dinuclear nature of this complex: Tiripicchio, A.; Lanfranchi, M.; Unpublished results. (b) The structure is isotypic with that described for $[Cu_2(\kappa^2\text{-}P,P\text{-dppf})_2(\mu\text{-I})_2]$: Neo, S. P.; Zhou, Z.-Y.; Mak, T. C. W.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1994,** 3451.

addition to the aromatic and methylene resonances of the ligands, the typical pair of unresolved multiplets at δ 4.10−4.49 and 4.30−4.75 ppm expected for the A_2B_2 spin system of the η^5-C_5H_4 ring, in accord with the proposed formulations. The structure of complex **4** has been confirmed by an X-ray diffraction study.[17]

Synthesis of Bridging dppf Complexes (5−9). We have previously shown that complex **I** reacts with LiC≡CR to give the complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-dppm})_3][BF_4]_2$ and $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppm})_3][BF_4]$. The structures of these complexes show that the alkynyl groups are able to form electron-deficient bonding systems containing the triply bridging moieties $Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_x$ ($x = 1, 2$) stabilized by the *triangular* framework $Cu_3(\mu\text{-dppm})_3$. This efficient synthetic approach involves the transformation of a dinuclear species into a trinuclear one, likely promoted by the dissociation of dppm in the starting complex **I**. Since the ability of dppf ligands to bridge a wide range of metallic systems may provoke the assembly of similar systems, we have investigated the reactivity of complex **4** with alkynyl groups. Thus, the treatment of a solution of complex **4** in THF with an excess of LiC≡CR (prepared in situ from the reaction of equimolar amounts of HC≡CR and Li^{n}Bu 1.6 M in THF at −20 °C) gives, after workup, complexes **5**−**9** in good yields (70−80%) (eq 2).

$$[Cu_2(\mu\text{-}Cl)_2(\kappa^2\text{-}P,P\text{-dppf})_2] + 2LiC{\equiv}CR \rightarrow [Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-dppf})_2] + 2LiCl \quad (2)$$

(R = $C_6H_4CH_3$-4 **(5)**, C_6H_5 **(6)**, CH_2OCH_3 **(7)**, $CH_2CH_2CH_3$ **(8)**, (η^5-C_5H_4)Fe(η^5-C_5H_5) **(9)**.)

Alternatively, these complexes can also be prepared in similar yields from the reaction of an equimolar mixture of $[Cu(C{\equiv}CR)]_n$ and dppf in toluene at room temperature. All the alkynyl complexes are air stable in the solid state and soluble in chlorinated solvents and THF. They have been characterized by elemental analysis and IR and NMR (^{1}H and ^{31}P{^{1}H}) spectroscopy (details are given in the Experimental Section and Table 1). All the spectroscopic data are in accord with the proposed formulations, but these are not relevant to the question of the coordination mode—bridging or terminal—of the ligands. Thus, although the presence of the alkynyl group is confirmed by the appearance in the IR spectra (KBr) of a weak ν(C≡C) absorption[18] in the range 2046−2030 cm^{-1} and ^{31}P{^{1}H} NMR spectra show a single signal (δ from −11.04 to −12.79 ppm) consistent with the chemical equivalence of the phosphorus atoms, these data do not allow an unambiguous elucidation of the structure. The ^{1}H NMR spectra of complexes **5**−**9** show only three signals (ca. δ 3.55, 3.70, and 3.90 ppm), attributed to the protons of the cyclopentadienyl rings on the dppf ligand. Apparently the remaining signal undergoes the largest shifting to lower field and is masked by the phenyl resonances. This large range of the chemical shifts has been observed in the ^{1}H NMR spectra of a series of related complexes $[Re_2(\mu\text{-}OR)_2(\mu\text{-dppf})(CO)_6]$, and it is attributed to ring current effects from the phenyl groups of the bridging dppf ligand.[19] To ascertain the coordination modes of the alkynyl and dppf ligands and to obtain information on the dppf conformation, provided that a bridging mode is adopted, the structure of complex **5** has been analyzed by X-ray crystallography.

Table 2. Crystallographic Data for Complex 5

empirical formula	$C_{86}H_{70}Cu_2Fe_2P_4$
fw	1466.08
temp	293(2) K
wavelength	0.710 73 Å
cryst syst, space group	monoclinic, *C*2
unit cell dimens	a = 46.713(9) Å, α = 90°
	b = 22.586(5) Å, β = 90.55(3)°
	c = 19.961(4) Å, γ = 90°
volume	21 059(7) Å^3
Z, calcd density	12, 1.387 Mg/m^3
abs coeff	1.140 mm^{-1}
F(000)	9072
cryst size	0.30 × 0.26 × 0.26 mm
θ range for data collection	0.87−24.98°
index ranges	$-55 \le h \le 49$, $0 \le k \le 23$, $0 \le l \le 21$
no. of reflns collected/unique	14759/14291 [*R*(int) = 0.0429]
completeness to 2θ	24.98, 37.5%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	14291/65/1238
goodness-of-fit on F^2	1.043
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0715, wR2 = 0.1790
R indices (all data)	R1 = 0.2073, wR2 = 0.2246
abs structure param	0.55(7)
largest diff peak and hole	0.734 and −0.650 e Å^{-3}

Solid State Structure of $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$ (5). The crystallographic asymmetric unit consists of two molecules at general positions, plus two crystallographically independent half-molecules related to their respective other halves by crystallographic 2-fold axes. All of the molecules are chiral, because of twisting of the dppf ligands (described below). The two complete molecules in the asymmetric unit have opposite hands, as do the two molecules that sit astride crystallographic 2-fold axes. A more detailed description of the asymmetric unit is given in the Experimental Section and in the Supporting Information, as this aspect of the structure is relevant to the correct choice of space group. For now, we will limit the discussion to chemically relevant features of the structure. Although there are conformational differences among the molecules of the asymmetric unit, the chemically important derived parameters, especially the bond distances and angles, are very similar in all four molecules; so the distances and angles of just one of them will be used for the present discussion. General crystallographic parameters are given in Table 2. A view of the molecular structure is shown in Figure 1. Selected bond distances and bond angles are listed in Table 3. The molecule consists of two copper atoms linked by two bridging dppf ligands and two bridging alkynyl groups in a μ-η^1 bonding arrangement. Each copper atom, which displays a distorted tetrahedral geometry (internal angles in the range 99.6(6)−118.9(3)°), is bonded to two phosphorus atoms of the dppf ligands and to the two carbon atoms of the alknyl groups. The Cu−P distances, in the range 2.284(7)−2.317(7) Å, are slightly longer than those shown by other polynuclear copper(I) complexes with dppm[1c] and dppf[8b,d] bridging ligands**.** The two alkynyl ligands, which are C-bonded to the two copper atoms, form an almost planar $Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2$ framework, with Cu−C distances varying over the range 2.136(2)−2.03(2) Å. The arylethynyl groups which are

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[18] Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995,** *38,* 79.

[19] See ref 11d and references therein.

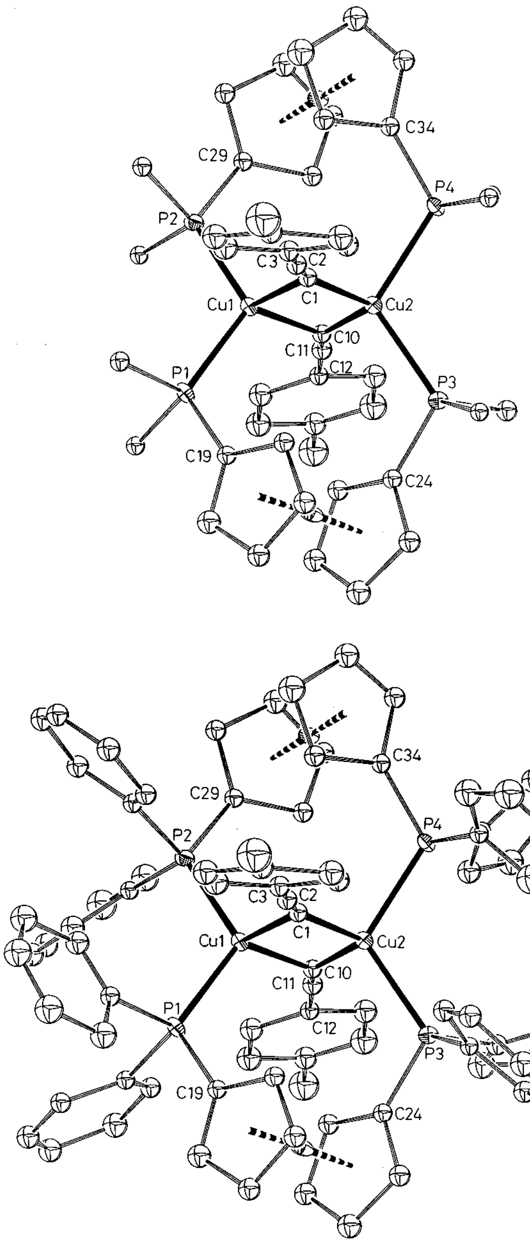

Figure 1. ORTEP views of the structure of the complex $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$ (**5**).

Table 3. Selected Bond and Interatomic Distances (Å) and Bond Angles (deg) for $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$ (5)

	Distances		
Cu(1)−Cu(2)	2.447(4)	Cu(1)−P(1)	2.310(6)
Cu(1)−P(2)	2.284(7)	Cu(2)−P(3)	2.317(7)
Cu(2)−P(4)	2.315(6)	Cu(1)−C(1)	2.136(2)
Cu(1)−C(10)	2.11(2)	Cu(2)−C(1)	2.06(2)
Cu(2)−C(10)	2.03(2)	C(1)−C(2)	1.20(2)
C(10)−C(11)	1.21(2)		
	Angles		
C(10)−Cu(1)−C(1)	104.9(8)	C(10)−Cu(1)−P(2)	99.6(6)
C(1)−Cu(1)−P(2)	116.6(6)	C(10)−Cu(1)−P(1)	116.7(6)
C(1)−Cu(1)−P(1)	100.0(6)	P(2)−Cu(1)−P(1)	118.9(3)
C(10)−Cu(1)−Cu(2)	52.1(6)	C(1)−Cu(1)−Cu(2)	52.8(6)
P(2)−Cu(1)−Cu(2)	120.2(2)	P(1)−Cu(1)−Cu(2)	120.9(2)
C(10)−Cu(2)−C(1)	111.1(8)	C(10)−Cu(2)−P(4)	117.0(6)
C(1)−Cu(2)−P(4)	98.6(6)	C(10)−Cu(2)−P(3)	100.8(6)
C(1)−Cu(2)−P(3)	116.1(6)	P(4)−Cu(2)−P(3)	114.0(3)
C(10)−Cu(2)−Cu(1)	55.4(6)	C(10)−Cu(1)−Cu(2)	55.7(6)
P(4)−Cu(2)−Cu(1)	122.3(2)	P(3)−Cu(2)−Cu(1)	123.7(2)
C(2)−C(1)−Cu(1)	151(2)	C(2)−C(1)−Cu(2)	136.6(19)
Cu(2)−C(1)−Cu(1)	71.5(7)	C(1)−C(2)−C(3)	175(2)
C(11)−C(10)−Cu(2)	149.7(19)	C(11)−C(10)−Cu(1)	137.4(19)
Cu(2)−C(10)−Cu(1)	72.4(7)	C(10)−C(11)−C(12)	174(2)
C(34)−P(4)−Cu(2)	118.2(7)	C(24)−P(3)−Cu(2)	113.7(8)
C(45)−P(1)−Cu(1)	117.0(7)	C(29)−P(2)−C8(1)	119.2(7)

almost linear (C≡C−C angles 174(2)−175(2)°), and the C≡C distances (1.20(2)−1.21(2) Å) (Table 3), are consistent with the presence of metal−acetylide σ-bonding.

Table 4 collects structural data of several alkynyl polynuclear copper(I) complexes including for comparison other dinuclear copper(I) complexes bearing bridging dppf ligands. The Cu_2−C bond lengths in **5** (average 2.08(2) Å) are comparable to those of other μ-η^1-bonded alkynyl groups (see Table 4) and significantly shorter than those found in the μ_3-η^1-coordination modes, i.e., $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)\{P(C_6H_5)_3\}]_4$[20] and $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_5)(\kappa\text{-}P\text{-}(C_6H_5)_2Ppy)]_4$[21] (2.185(4) and 2.1708(8) Å, respectively). The Cu−Cu distance, 2.447(4) Å, may be compared to that found in analogous dicopper(I) μ-η^1-alkynyl-bridged derivatives (see Table 4), and it is significantly shorter than those found in trinuclear complexes containing the moiety $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)_x]$ (x = 1, 2) (distances in the range 2.523(1)−3.274(3) Å)[1c] and metallic copper (2.556 Å).[20] On the whole, the Cu−Cu distances found for **5** are comparable to those found in other polynuclear complexes containing organyl μ-η^1 bridging groups.[27]

The structure of complex **5** also shows the ability of the dppf ligand to adapt its conformation to the steric demands of the dicopper(I) fragment to which it is bonded. It is apparent that the skeletal flexibility of dppf is also able to stabilize the planar system $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2]$. In this respect the following structural features are significant (see Figure 2): (a) the angle ϕ formed by the projection of the Cp···Cp axis of dppf onto the Cu···Cu vector (mean value 56.8(6)°); (b) the angle ω by which the two Cp rings of a given dppf are twisted from the eclipsed position (mean value 77-(2)°); (c) the angle α $C_{ipso(Cp)}$−P−Cu of 117.55(8)° (average). Structural data of analogous dinuclear rhenium

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(27) (a) For aryl groups, see for instance: $[Cu_3(\mu\text{-}\eta^1\text{-}C_6H_2(CH_3)_3\text{-}2,4,6)(m\text{-}O_2CC_6H_5)_2]$, Cu−Cu 2.421(2) Å; Cu−C 1.957(6) Å. Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *Organometallics* **1989,** *10,* 2293. (b) $[Cu(\mu\text{-}\eta^1\text{-}C_6H_2(CH_3)_3\text{-}2,4,6)]_5$, 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) $[Cu_4(\mu\text{-}\eta^1\text{-}C_6H_2(CH_3)_3\text{-}2,4,6)_4(\mu\text{-}SAr)_2(MgSAr)_2]$, 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 Kotten, G. *J. Am. Chem. Soc.* **1990**, *112,* 5895. Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Kotten, G. *J. Am. Chem. Soc.* **1992,** *114,* 3400. (d) For alkyl groups, see for instance: $[Cu(CH_2Si(CH_3)_3)]_4$ Cu−Cu 2.417 Å; Cu−C 2.02 Å. Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. J. Chem. Soc., Dalton Trans.* **1977**, 999. (e) For a recent discussion on metal−metal interactions in copper(I) complexes $[Cu_3(2\text{-}(3(5)\text{-}pz)py)_3]_2{\cdot}2py$, Cu−Cu 2.905(3) Å. Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997,** *119,* 2942.

Table 4. Selected Atomic and Bond Distances (Å) of Several Relevant Alkynyl Copper(I) and Related Complexes

complex	Cu−P	Cu⋯Cu	Cu−C	ref
$[Cu(\mu_3\text{-}\eta^1{-}C{\equiv}CC_6H_5)\{(\kappa\text{-}P)\text{-}(C_6H_5)_2Ppy\}]_4$	2.230(2)	2.605(1)	2.199(8)	21
$[Cu(\mu_3\text{-}\eta^1{-}C{\equiv}CC_6H_5)\{P(C_6H_5)_3\}]_4$	2.227(1)	2.599(1)	2.226(4)	20
$[Cu_4(\mu\text{-}\eta^1{-}C{\equiv}CC_6H_5)_2(\mu_3\text{-}\eta^2{-}C{\equiv}CC_6H_5)_2\{P(CH_3)_3\}_4]$	2.240(5)	2.450(3)[a]	2.090(17)[a]	22
$[Cu_6(\mu\text{-}\eta^1{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2\{C_6H_4N(CH_3)_2\text{-}2\}_4]$		2.474(4)	2.057(6)	23
$[Cu_2(\mu\text{-}\eta^1{-}C{\equiv}C^tBu)_2\{P(C_6H_5)_3\}_2\{P(C_6H_{11})_3\}]$	2.253(3)	2.3892 (14)	2.101(19)	24
$[Cu(\mu\text{-}\eta^1{-}C{\equiv}CC_6H_5)(tmtch)]_2$		2.386(1)	2.018(3)	25
$[Cu_2(\mu\text{-}\eta^1{-}C{\equiv}CC_6H_5)_2\{P(C_6H_5)_2CH_3\}_4]$	2.2816(1)	2.454(1)	2.011(3)	26
$[Cu_2(\mu\text{-}\eta^1{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu{-}dppf)_2]$	2.313(7)	2.447(4)	2.08(2)	*b*
$[Cu_2\ Ru_4\ (\mu_3\text{-}H)_2(\mu{-}dppf)(CO)_{12}]$	2.23(4)	2.528(2)		8d
$[Cu_2\ (\mu{-}dppf)(dppf)_2](ClO_4)_2$	2.264(5)			8b
$[Cu_3(\mu_3\text{-}\eta^1{-}C{\equiv}CC_6H_5)_2(\mu{-}dppm)_3][BF_4]$	2.277(6)	2.594(3)	2.202(2)	1c
$[Cu_3(\mu_3\text{-}\eta^1{-}C{\equiv}CC_6H_5)(\mu_3{-}Cl)\ (\mu{-}dppm)_3][BF_4]$	2.266(5)	2.820(3)	2.344(2)	1c
$[Cu_3(\mu_3\text{-}\eta^1{-}C{\equiv}CC_6H_5)(\mu{-}dppm)_3][BF_4]_2$	2.267(4)	2.997(3)	1.906(1)	1c

[a] $\mu_3\text{-}\eta^1$ bridge. [b] This paper.

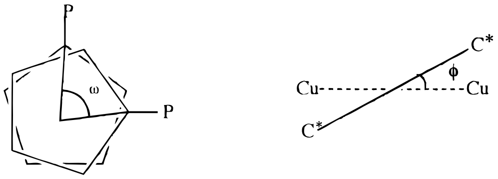

Figure 2.

and silver complexes with bridging dppf are listed in Table 5 for comparison. It is interesting to note that while the angles ω and α in complex **5** can be compared to those of the other complexes, the value of the angle ϕ for **5** is the largest of the set. This seems to indicate that the $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2]$ core in **5** is the most sterically demanding of the systems listed, forcing the dppf ligand to adopt a relatively strained conformation.

Final Remarks

In this work we report novel copper(I) complexes containing dppf of two types: (a) mono- and dicopper complexes $[Cu(\kappa^2\text{-}P,P\text{-}dppf)L_2][BF_4]$ (L = CH_3CN (**1**), bipy (**2**)), $[Cu_2(\mu\text{-}X)_2(\kappa^2\text{-}P,P\text{-}dppf)_2]$ (X = *P*,*P*-dppm (**3**), Cl (**4**)) with dppf chelating ligands, and (b) unprecedented tetrabridged dicopper complexes $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-}dppf)_2]$ (R = $C_6H_4CH_3$-4 **(5)**, C_6H_5 **(6)**, CH_2OCH_3 **(7)**, $CH_2CH_2CH_3$ **(8)**, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ **(9)**) containing two three-center two-electron systems (3c-2e) of two $\mu\text{-}\eta^1$-alkynyl groups forming a typical electron deficient system of 3c-2e. It is interesting to note that the bridging alkynyl complexes are formed through reactions that proceed via transformation of the dppf coordination mode from chelating in the precursor $[Cu_2(\mu\text{-}Cl)_2(\kappa^2\text{-}P,P\text{-}dppf)_2]$ **(4)** to bridging in the resulting novel products $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu_2\text{-}dppf)_2]$ **(5−9)**. This change seems to indicate the ability of the ligand dppf to adapt to the electronic and/or steric requirements of the dicopper(I) fragment $Cu_2(\mu_2\text{-}\eta^1\text{-}C{\equiv}CR)_2$. In this regard the complexes described here show the capacity of dppf ligands to stabilize, for the first time, the doubly bridged system $M_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2$. This represents one further example of the well-known bonding and structural analogies between metal acetylide and carbonyl complexes.

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 PCM_3 conductimeter. NMR spectra were recorded on a Bruker AC300 at 300 MHz (^1H) and 121.5 MHz (^{31}P) using $SiMe_4$ or 85% H_3PO_4 as standards. The complexes of $[Cu(NCCH_3)_4][BF_4]$[28] and $[Cu_2(\mu\text{-}dppm)_2(NCCH_3)_4][BF_4]_2$[14] were prepared as previously described. Infrared and NMR spectral data for all the new complexes are collected in Table 1.

Synthesis of $[Cu(CH_3CN)_2(\kappa^2\text{-}P,P\text{-}dppf)][BF_4]$ (1). dppf (0.554 g, 1 mmol) was added to a solution of $[Cu(NCCH_3)_4][BF_4]$ (0.314 g, 1 mmol) in CH_3CN (30 mL), at room temperature. The mixture was stirred at room temperature for 8 h. The addition of diethyl ether (30 mL) to the concentrated solution led to the precipitation of a yellow solid, which was recrystallized from CH_3CN/diethyl ether. Yield: 80%. Conductivity, Δ_M (Ω^{-1} cm^2 mol^{-1}): 138. IR spectra (KBr), ν(B−F) (cm^{-1}): 1060. Anal. Calcd for $C_{38}N_2H_{44}BCuF_4P_2Fe$: C, 58.03; N, 3.56; H, 4.32. Found: C, 56.33; N, 2.42; H, 4.32.

Synthesis of $[Cu(bipy)(\kappa^2\text{-}P,P\text{-}dppf)][BF_4]$. (2). bipy (0.037 g, 0.25 mmol) was added at room temperature to a solution of $[Cu(CH_3CN)_2(dppf)][BF_4]$ (0.175 g, 0.25 mmol) in acetone (30 mL). The mixture was stirred at room temperature for 8 h. After 2 h the orange precipitate was filtered and washed with diethyl ether (3 × 10 mL) and vacuum-dried. Yield: 80%. Conductivity, Δ_M (Ω^{-1} cm^2 mol^{-1}): 136. IR spectra (KBr), ν(B−F) (cm^{-1}): 1060. Anal. Calcd for $C_{38}N_2H_{36}BCuF_4P_2Fe$: C, 61.37; N, 3.25; H, 4.18. Found: C, 61.21; N, 3.12; H, 3.94.

Synthesis of $[Cu_2(\mu\text{-}dppm)_2(\kappa^2\text{-}P,P\text{-}dppf)_2][BF_4]_2$ (3). $[Cu_2(\mu\text{-}dppm)_2(CH_3CN)_4][BF_4]_2$ (0.0864 g, 0.07 mmol) was added at room temperature to a solution of dppf (0.08 g, 0.14 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 6 h. The addition of diethyl ether (30 mL) to the concentrated solution led to the precipitation of a yellow solid, which was filtered, washed with diethyl ether (3 × 10 mL), and vacuum-dried. Yield: 75%. Conductivity, Δ_M (Ω^{-1} cm^2 mol^{-1}): 207. IR spectra (KBr), ν(B−F) (cm^{-1}): 1066. Anal. Calcd for $C_{118}H_{100}B_2Cu_2F_8P_4Fe_2$: C, 65.05; H, 4.59. Found: C, 64.11; H, 4.59.

Synthesis of $[Cu_2(\mu\text{-}Cl)_2(\kappa^2\text{-}P,P\text{-}dppf)_2]$ (4). dppf (0.5 g, 0.9 mmol) was added at room temperature to a mixture of CuCl (0.089 g, 0.9 mmol) and tmeda (0.136 mL, 0.9 mmol) in THF (30 mL) after 10 min. The solution was stirred at room temperature for 6 h. The yellow precipitate was filtered and washed with diethyl ether (3 × 10 mL) and vacuum-dried. Yield: 72%. Anal. Calcd for $C_{68}H_{56}Cu_2P_4Fe_2Cl_2$: C, 62.50; H, 4.32. Found: C, 61.91; H, 4.46.

Synthesis of $[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CR)_2(\mu\text{-}dppf)_2]$, R = $C_6H_4CH_3$-4 (5), C_6H_5 (6), CH_2OCH_3 (7), $CH_2CH_2CH_3$ (8), (η^5-

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[28] Kubas, G. J. *Inorg. Synth.* **1979,** *119,* 90.

Table 5. Selected Structural Parameters of Several Relevant Complexes Containing the Framework $[M_2(\mu\text{-}X)_2(\mu\text{-dppf})_n]$ ($n = 1$ or 2)

complexes	θ^a (deg)	ω (deg)	ϕ (deg)	α (deg)	ref
$[Re_2(\mu\text{-}OH)_2(\mu\text{-dppf})(CO)_6]$	29.7	86.1	46.1	120.5	11d
$[Re_2(\mu\text{-}OCH_3)_2(\mu\text{-dppf})(CO)_6]$	30.7	85.9	53.5	122.6	11d
$[Re_2(\mu\text{-}OCH_2CH_3)_2(\mu\text{-dppf})(CO)_6]$	26.3	84.0	50.8	123.7	11d
$[Cu_2(\mu\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CH_3\text{-}4)_2(\mu\text{-dppf})_2]$	0.1	77.2	56.8(6)	117.55(8)	*b*
$[Ag_2(\mu\text{-}ONO_2)_2(\mu\text{-dppf})_2]$		89.6	42.3	117.85	5
$[Ag_2(CH_3CO_2)_2(\mu\text{-dppf})_2]$		88.8	42.64	112.85	5

[a] θ is the fold angle of the $\{Re_2O_2\}$ and $\{Cu_2O_2\}$ cores. [b] This paper.

$C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (9). General Procedure. $[Cu_2(\mu\text{-}Cl)_2(dppf)_2]$ (0.1 g, 0.08 mmol) was added at room temperature to a solution of 0.46 mmol of $LiC{\equiv}CR$ in THF (40 mL) (prepared "in situ" by treating the corresponding alkyne with 1.60 M Li^nBu at −20 °C). The mixture was stirred at room temperature for 2 h and evaporated to dryness to give a solid residue, which was extracted with dichloromethane (30 mL). The addition of hexane (30 mL) to the concentrated solution led to the precipitation of cream solids, which were washed with hexane (3 × 10 mL) and vacuum-dried. Analytically pure samples were obtained by recrystallization from dichloromethane/hexane. Yields: 60−70%. Anal. Calcd for $C_{86}H_{70}Cu_2P_4Fe_2$ (**5**): C, 70.49; H, 4.78. Found: C, 69.37; H, 4.81. Calcd for $C_{84}H_{66}Cu_2P_4Fe_2$ (**6**): C, 70.16; H, 4.63. Found: C, 69.21; H, 4.90. Calcd for $C_{76}H_{76}Cu_2O_2P_4Fe_2$ (**7**): C, 66.34; H, 4.98. Found: C, 66.04; H, 4.87. Calcd for $C_{78}H_{70}Cu_2P_4Fe_2$ (**8**): C, 68.38; H, 5.15. Found: C, 67.00; H, 5.00. Calcd for $C_{92}H_{74}Cu_2P_4Fe_4$ (**9**): C, 66.81; H, 4.51. Found: C, 68.30; H, 4.58.

Direct Synthesis of 6. A mixture of dppf (0.443 g, 0.8 mmol) and $[CuC{\equiv}CC_6H_5]_n$ (0.13 g, 0.8 mmol) in toluene (40 mL) was stirred at room temperature for 3 h and filtered. The resulting solution was evaporated to dryness, giving a solid residue, which was extracted with CH_2Cl_2 (15 mL). The addition of hexane to the partially evaporated solution gave by precipitation the corresponding complex as a cream solid. Yield: 70%. Anal. Calcd for $C_{84}H_{66}Cu_2P_4Fe_2$ (**6**): C, 70.16; H, 4.63. Found: C, 69.70; H, 4.57.

X-ray Diffraction Study of 5. Data collection, crystal, and refinement parameters are collected in Table 2. Data were taken from a red crystal of **5** using a Nonius CAD-4 single-crystal diffractometer. The lattice parameters were verified by normal-beam oscillation photography. Accurate values for the unit-cell dimensions were determined from the angular settings of 25 reflections with θ between 10° and 15°. Intensity data were measured using the $\omega-2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.99 and 1.07. Profile analysis was performed for all reflections.[29] Redundant data were averaged ($R_{\text{int}} = \Sigma(I - \langle I\rangle)/\Sigma I = 0.043$), giving a total of 14 291 unique reflections of which 7022 had $I > 2\sigma(I)$. The structure solution began with the successful location of some copper, iron, and phosphorus atoms by direct methods.[30] The remaining atoms were found and refined in the usual alternating sequence of least-squares refinements and difference Fourier maps. Isotropic least-squares refinement using SHELXL-93[31] converged to R1 = 0.087. In the final stages of refinement, anisotropic displacement parameters were used only for the copper, phosphorus, and iron atoms; the remaining non-hydrogen atoms were treated isotropically, because of the size of the calculation. Hydrogen atoms were placed at idealized positions and refined as riding atoms with a common isotropic thermal parameter. Several rings were held to ideal stereochemistries, either by restraints to planarity or by restraints to ideal bond distances, or both. The structure was refined on F^2, and all data were used in the final refinement, which gave the residuals listed in Table 2. In all, 1238 parameters were refined to 14 291 data, for a data-to-parameter ratio of 11.5. The maximum shift to esd ratio in the last, full-matrix least-squares cycle was 0.076. The final difference Fourier map showed no features of chemical interest. As will be discussed below, the Flack parameter refined to a value of 0.55(7).[31] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[32] Geometrical calculations were made with PARST.[33] The figure showing the coordination and the atom-numbering scheme was drawn using the *EUCLID* package.[34] All calculations at the University of Oviedo were done at the Scientific Computer Center and on X-ray Group DEC/AXP computers.

The structure of compound **5** possesses some uncommon features that require further comment. The crystallographic asymmetric unit consists of a total of three molecules of the complex: two whole molecules on general equivalent positions and two independent half-molecules sitting alongside crystallographic 2-fold axes which complete the molecules. We report this structure in space group *C*2, and there are 12 molecules in the unit cell. In the following, we shall refer to the two whole molecules as molecule 1 (containing Cu(1), Cu(2), Fe(1), and Fe(2)) and molecule 2 (which has Cu(3), Cu(4), Fe(3), and Fe(4)). The two molecules sitting on crystallographic 2-fold axes will be referred to as molecule 3 (Cu(5) and Fe(5)) and molecule 4 (Cu(6) and Fe(6)). Each molecule of **5** is chiral, as the two dppf ligands are twisted in the same sense. Molecules 1 and 2 are of opposite handedness, as are molecules 3 and 4. Because of the suggestive aspects of this structure, $Z' = 3$, an acentric group with the same systematic absences as a centric group (*C*2/*m*), and a monoclinic cell with β near 90°, we comment briefly here, and in full detail in the Supporting Information, on the choice of crystal system and space group.

Systematic absences limit the choice of space groups in the monoclinic system to three, namely, *C*2, *Cm*, and *C*2/*m*. Note: there is no systematic absence for a *c*-glide. The successful refinement in space group *C*2 and the absence of important features in the final difference Fourier map mean that the structural model is correct in its general aspects, although the choice of space group could still be erroneous. But specifically, the refinement establishes that each of the molecules in the cell, taken individually, is chiral and cannot possess a crystallographically imposed mirror plane. Considering molecule

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(29) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974,** *A30*, 580. Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978,** *11*, 114.

(30) (a) Calculations for the initial solution of the structure were performed on a Hewlett-Packard 9000 model 715/50 (HP-UX V9.05) and on an AlphaStation 200 4/166 (OpenVMS/Alpha V6.2). (b) Sheldrick, G. M. *SHELXS-86*: FORTRAN program for crystal structure solution; Göttingen University, 1986. (c) Beurskens, P. T.; Admiraall, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF Users's Guide*; Technical report; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1992.

(31) (a) Sheldrick, G. M. *SHELXL93*, Program for crystal structure determination; University of Göttingen, 1993. (b) Flack parameter: Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881. (c) Flack parameter: Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1985**, *A41*, 500−511.

(32) *International Tables for X-ray Crystallography*; Kynoch Press: Byrmingham (Present distributor Kluwer Academic Publishers: Dordrecht), 1974; Vol. IV.

(33) Nardelli, M. *Comput. Chem.* **1983,** *7*, 95.

(34) Spek, A. L. *The Euclid Package.* In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

3, it and one symmetry relative of the same hand are present in the unit cell. If the space group were *Cm*, which has four operators, then molecule 3 would have to sit astride a mirror plane in order to give rise to just two molecules in the cell. The same consideration applies to molecule 4. But since molecules 3 and 4 cannot possess mirror symmetry, space group *Cm* is ruled out. Similarly for *C*2/*m*, molecules 3 and 4 would have to sit on positions of symmetry 2/*m* in order for there to be just two of each in the cell. So space group *C*2/*m* is ruled out.

Since on the whole this structure is racemic, with equal numbers of molecules of each enantiomer, the enantiomorph determination gives the expected result that the Flack parameter refines to a value of about one-half. The *C*2 structure is thus indistinguishable from its enantiomorph and further indistinguishable from a racemic twin.

A fuller description of all of the possible space groups, including the orthorhombic system, along with further twinning possibilities and alternative refinements, is given in the Supporting Information.

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Supporting Information Available: Tables giving all bond lengths and angles, positional and thermal parameters, torsion angles, and least-squares planes for **5**, along with a detailed description of the choice of space group, tests for twinning, and alternative refinements (48 pages). Ordering information is given on any current masthead page.

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