Pergamon

Polyhedron Vol. 14, No. 6, pp. 741–745, 1995
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0277–5387/95 $9.50+0.00

0277–5387(94)00307–6

SYNTHESIS AND CHARACTERIZATION OF NOVEL TRIANGULAR COPPER(I) COMPLEXES CONTAINING THE TRINUCLEAR MOIETY $Cu_3(\mu\text{-dppm})_3$ (dppm = BIS(DIPHENYLPHOSPHINO)METHANE) AND TRIPLY BRIDGING ALKOXIDE AND THIOLATE LIGANDS

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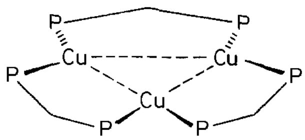
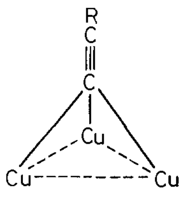
(*Received* 13 *May* 1994; *accepted* 29 *July* 1994)

Abstract—The novel cationic trinuclear alkoxide copper(I) complexes of the type $[Cu_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BF_4]$ (R = 2,4,6-$^tBu_3C_6H_2$, 2,6-$^tBu_2C_6H_3$, 2,6-$^tBu_2$-*p*-MeC_6H_2, *p*-MeC_6H_4) and $[Cu_3(\mu_3\text{-}XR)_2(\mu\text{-dppm})_3][BF_4]$ (R = *p*-MeC_6H_4; X = O, S) have been obtained by reaction of $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-dppm})_3][BF_4]$ with the sodium derivative of the corresponding alcohol or thiol. A high yield method for the synthesis of the trinuclear copper(I) precursor complex, based on the reaction of $[Cu_2(\mu\text{-AcO})(\mu\text{-dppm})_2][BF_4]$ and Me_3SiCl, is also described. IR, ^1H and $^{31}P\{^1H\}$ NMR data are discussed.

We have recently reported[1] a series of cationic trinuclear copper(I) complexes containing a triangular Cu_3 arrangement stabilized by three bridging bis(diphenylphosphino)methane (dppm) ligands (**A**). This framework appears to be appropriate support for the μ_3-η^1-acetylide group (**B**) and bis(μ_3-η^1-acetylide) or μ_3-η^1-acetylide, μ_3-chloride groups (**C**).

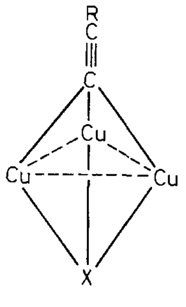


(A)



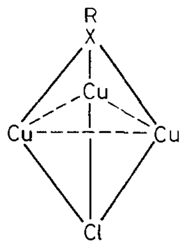
(B)

Since these $Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)$ moieties are formally electron deficient systems (4c-2e), it is evident that the skeletal framework $Cu_3(\mu\text{-dppm})_3$ can be



X = Cl, C≡CR

(C)



X = O, S

(D)

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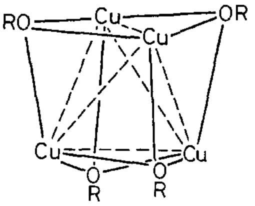
appropriate template entities for the coordination of conventional triply bridging (μ_3) ligands. It is well known that alkoxide ligands exhibit this type of coordination in a number of "cubane-like" copper(I) complexes, including the structurally



characterized tetranuclear derivatives $[Cu(O^tBu)]_4$,[2] $[Cu(O^tBu)(CO)]_4$[3] and $[Cu(OCH^tBu_2)]_4$,[4] which show similar skeletal faces to those found in the above mentioned trinuclear copper(I) complexes.[5] Here we report the synthesis and characterization of novel cationic trinuclear copper(I) complexes of the type $[Cu_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}dppm)_3][BF_4]$ (R = $2,4,6\text{-}{}^tBu_3C_6H_2$, $2,6\text{-}{}^tBu_2C_6H_3$, $2,6\text{-}{}^tBu_2\text{-}p\text{-}MeC_6H_2$, $p\text{-}MeC_6H_4$) and $[Cu_3(\mu_3\text{-}XR)_2(\mu\text{-}dppm)_3][BF_4]$ (R = $p\text{-}MeC_6H_4$; X = O, S), showing the structural analogies between the acetylide and alkoxide or thiolate groups to act as μ_3 bridging ligands (**D**). They have been prepared from the trinuclear complex $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3]^+$ by the metathesis of one or two triply bridging chloride ligands with alkoxide or thiolate anions. Table 1 lists the novel complexes synthesized along with NMR spectroscopic and molar conductance data. A novel high yield method for the preparation of the known precursor complex $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3]^+$ is also described.

RESULTS AND DISCUSSION

Synthesis of $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3][BF_4]$

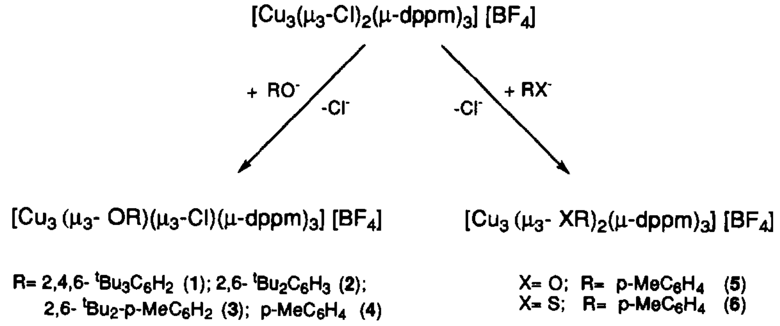
This complex (chloride salt) has been synthesized previously[6] by the direct reaction of copper(I) chloride with dppm. The crystal structure has also been described.[7] However, this method usually affords impure samples since other stoichiometries are often competitive, leading to the formation of complexes with different Cu : P ratios, i.e. 2 :1, 3 : 2, 4 : 3 and 2 : 3. Therefore, we sought an alternative, more efficient synthetic procedure starting from the dinuclear copper(I) complex $[Cu_2(\mu\text{-}AcO)(\mu\text{-}dppm)_2][BF_4]$[8] previously prepared by us. We expected Me_3SiCl to act as the source of chloride anions, while the oxophilic nature of the Me_3Si moiety should lead to the abstraction of the bridging acetate group.[9] Thus, the treatment of a THF solution of the copper complex with Me_3SiCl in 3 : 4 molar ratio leads [eq. (1)]

$$3[Cu_2(\mu\text{-}AcO)(\mu\text{-}dppm)_2][BF_4]+4Me_3SiCl \rightarrow 2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3][BF_4] + 3Me_3Si(OAc)+Me_3SiFBF_3 \quad (1)$$

to a colourless solution from which the desired cationic complex can be obtained (yield 80%). The conductivity in acetone solution is typical of a 1 : 1 electrolyte and the spectroscopic data (${}^{31}P\{{}^1H\}$ and ${}^1H$ NMR) (see Experimental section) are consistent with the bridging coordination mode of the dppm ligands in the $Cu_3(\mu\text{-}dppm)_3$ triangular core.

Synthesis of the alkoxide (**1–5**) *and thiolate* (**6**) *complexes*

Treatment of a solution of $[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3][BF_4]$ in THF at room temperature with an excess of the sodium derivative (prepared *in situ* from the free alcohol and sodium hydride in THF; Scheme 1) gave a solution from which the trinuclear cationic complexes (**1–4**) were isolated in good yields (80–90%). Even though a great excess of the derivative was used (molar ratio *ca* 1 : 4) the reactions only led to the selective formation of the monosubstituted complexes (**1–3**). Nevertheless, cationic disubstituted complexes (**5** and **6**) were obtained (Scheme 1) by using a 1 : 4 molar ratio of



Scheme 1.

the precursor complex to the alkoxide or thiolate ligand. All attempts to obtain the corresponding mixed μ_3-chloride–μ_3-thiolate derivatives by using an equimolar ratio of the reactants have failed, giving instead unresolved mixtures of complexes.

All the complexes are air-stable yellow solids and soluble in THF, benzene and diethyl ether, but the solutions must be handled rigorously under nitrogen otherwise they are readily oxidized by air. Rapid decomposition processes are observed when solvents with traces of acid are used. All the complexes have been characterized by elemental analysis, conductance measurements in solution and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Table 1).

Conductance values of the cationic complexes in acetone show they are 1 : 1 electrolytes. IR spectra (KBr pellets) exhibit the expected ν(B–F) absorptions as well as those characteristic for the bridging ligands (see Experimental section for details). In particular, the spectra show medium bands at *ca* 1000 cm^{-1} which may be assigned to the ν(R–O) absorptions,[10] although in some cases they appear close to those of dppm and BF_4^- and therefore the assignments must be considered tentative. ^{1}H NMR spectra in C_6D_6 at room temperature show resonances which are characteristic of aromatic and methylene (P_2CH_2) protons, along with singlet signals assigned to the corresponding Me and ^{t}Bu groups of the alkoxide or thiolate ligands.

The ^{1}H NMR spectra of the mixed chloride–alkoxide complexes (**1**–**4**) exhibit methylene resonances (P_2CH_2) at δ *ca* 3.2–3.3 ppm as one or two unresolved multiplets showing the ABX_2 spin system expected for the two sets of chemically inequivalent protons $Cu_2P_2CH_aH_b$. These resonances are typical for the unsymmetrical bicapped $Cu_3(\mu_3\text{-dppm})_3$ framework such as those contained in the μ_3-acetylide complexes $[Cu_3(\mu_3\text{-}\eta^1\text{-C{\equiv}CR})(\mu\text{-dppm})_3][BF_4]_2$ and $[Cu_3(\mu_3\text{-}\eta^1\text{-C{\equiv}CR})(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (R = Ph, ^{t}Bu, CH_2OCH_3).[1c] The corresponding resonances in the spectra of the bis (alkoxide) and bis(thiolate) complexes (**5** and **6**) appear as a triplet (or unresolved multiplet), indicating an effective equivalence of the P_2CH_2 protons (A_2X_2 spin system). These spectroscopic data are consistent with a triangular arrangement of the copper atoms bridged by three dppm ligands lying approximately in a formal plane of symmetry due to the presence on each side of the triangle of one alkoxide or thiolate bridging ligand.

The ^{31}P{^{1}H} NMR spectra at room temperature show a single resonance at δ −13.64 to −15.38 ppm (Table 1), showing that all phosphorus atoms in each molecule are chemically equivalent, which is also in accordance with the trinuclear nature of the complexes. These chemical shifts can be com-

Table 1. NMR spectroscopic[a] and molar conductance[b] data for the novel complexes

Compound	^{1}H (δ)	^{31}P{^{1}H} (δ)	Λ_M
$[Cu_3\{\mu_3\text{-O}(2,4,6\text{-}^tBu_3C_6H_2)\}(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (**1**)	1.36 (s, 9H, ^{t}Bu), 1.44 (s, 18H, ^{t}Bu), 3.26 (m, 3H, P_2CH_a), 3.34 (m, 3H, P_2CH_b), 6.74–7.40 (m, 62H, PPh_2, C_6H_2)	−15.36	143
$[Cu_3\{\mu_3\text{-O}(2,6\text{-}^tBu_2C_6H_3)\}(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (**2**)	1.44 (s, 18H, ^{t}Bu), 3.20 (m, 6H, $P_2CH_aH_b$), 6.84–7.80 (m, 63H, PPh_2, C_6H_3)	−15.38	130
$[Cu_3\{\mu_3\text{-O}(2,6\text{-}^tBu_2\text{-}p\text{-MeC}_6H_2)\}(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (**3**)	1.48 (s, 18H, ^{t}Bu), 2.30 (s, 3H, Me), 3.30 (m, 3H, P_2CH_a), 3.43 (m, 3H, P_2CH_b), 6.61–7.47 (m, 62H, PPh_2, C_6H_2)	−15.38	106
$[Cu_3\{\mu_3\text{-O}(p\text{-MeC}_6H_4)\}(\mu_3\text{-Cl})(\mu\text{-dppm})_3][BF_4]$ (**4**)	2.24 (s, 3H, Me), 3.30 (m, 6H, $P_2CH_aH_b$), 6.72–7.50 (m, 64H, PPh_2, C_6H_4)	−14.93	105
$[Cu_3\{\mu_3\text{-O}(p\text{-MeC}_6H_4)\}_2(\mu\text{-dppm})_3][BF_4]$ (**5**)	2.30 (s, 6H, Me), 3.35 (m, 6H, P_2CH_2), 6.77–7.72 (m, 68H, PPh_2, C_6H_4)	−13.64	112
$[Cu_3\{\mu_3\text{-S}(p\text{-MeC}_6H_4)\}_2(\mu\text{-dppm})_3][BF_4]$ (**6**)	2.06 (s, 6H, Me), 2.98 (m, 6H, P_2CH_2), 6.55–7.72 (m, 68H, PPh_2, C_6H_4)	−14.34	120

[a] ^{1}H (300 MHz) and ^{31}P{^{1}H}NMR (79.54 MHz); chemical shifts (δ) in ppm measured in C_6D_6.

[b] In acetone solution (5×10^{-4} M) at room temperature (Ω^{-1} cm^2 mol^{-1}).

pared with that shown by the precursor complex $[\mathrm{Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$ (δ -14.00 ppm).

In summary, novel cationic trinuclear copper(I) complexes containing metallic triangular arrangements with bicapping systems of the type μ_3-alkoxide–μ_3-chloride, μ_3-bis(*p*-methylphenoxide) and μ_3-bis(*p*-methylthiophenoxide) are described. It is shown that the triangular framework $\mathrm{Cu_3(\mu\text{-}dppm)_3}$ is an appropriate support for the μ_3 coordination mode of alkoxide and thiolate ligands.

EXPERIMENTAL

Measurements

IR spectra were recorded (4000–400 cm^{-1}) on a Perkin–Elmer 1720-X FT spectrometer using KBr pellets. The carbon and hydrogen analyses were carried out with a Perkin–Elmer 240-B microanalyser. 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 instrument at 300 MHz (^{1}H) and 121.5 MHz (^{31}P) using $\mathrm{SiMe_4}$ or 85% $\mathrm{H_3PO_4}$ as standards. Conductivity and NMR spectroscopic data for all the new complexes are collected in Table 1.

Synthesis

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. 2,4,6-$^t\mathrm{Bu_3C_6H_2OH}$, 2,6-$^t\mathrm{Bu_2C_6H_3OH}$, 2,6-$^t\mathrm{Bu_2}$-*p*-$\mathrm{MeC_6H_2OH}$, *p*-$\mathrm{MeC_6H_4OH}$ and *p*-Me $\mathrm{C_6H_4SH}$ were purchased from Aldrich and used as received. The complex $[\mathrm{Cu_2(\mu\text{-}AcO)(\mu\text{-}dppm)_2}]$ $[\mathrm{BF_4}]$ were prepared as described in the literature.[8]

Preparation of $[\mathrm{Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$

To a solution of $[\mathrm{Cu_2(\mu\text{-}AcO)(\mu\text{-}dppm)_2}][\mathrm{BF_4}]$ (0.564 g, 0.5 mmol) in THF (40 cm^3) was added at room temperature $\mathrm{Me_3SiCl}$ (1.5 mmol). The mixture was stirred at room temperature (12 h) and evaporated to dryness giving a solid which was extracted with dichloromethane (30 cm^3). The addition of diethyl ether (30 cm^3) to the concentrated solution led to the precipitation of a white solid which was washed with diethyl ether (3×10 cm^3) and vacuum dried (yield: 80%). Conductivity value, analytical and spectroscopic data are as follows: 135 Ω^{-1} cm^2 mol^{-1}. Found: C, 59.5; H, 4.6. Calc. for $\mathrm{C_{75}H_{66}BCu_3Cl_2F_4P_6}$: C, 60.0; H, 4.4%. ^{1}H ($\mathrm{CDCl_3}$) δ: 3.20 (m, 6H, $\mathrm{P_2CH_2}$), 6.93–7.26 (m, 60H, $\mathrm{PPh_2}$) ppm. ^{31}P $\{^1\mathrm{H}\}$($\mathrm{CDCl_3}$) δ: -14.00 ppm. IR spectrum (KBr, cm^{-1}): 3054 (m), 1964 (w), 1895 (w), 1811 (w), 1586 (m), 1573 (w), 1483 (s), 1436 (s), 1358 (m), 1331 (m), 1279 (w), 1188 (m), 1159 (m), 1061 (s, br), 999 (s), 848 (w), 778 (s), 738 (s), 718 (s), 693 (s), 617 (w), 515 (s), 483 (s), 442 (s).

Preparation of the complexes $[\mathrm{Cu_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$[R = 2,4,6-$^t\mathrm{Bu_3C_6H_2}$ (**1**), 2,6-$^t\mathrm{Bu_2C_6H_3}$ (**2**), 2,6-$^t\mathrm{Bu_2}$-*p*-$\mathrm{MeC_6H_2}$ (**3**), *p*-$\mathrm{MeC_6H_4}$ (**4**)]

To a solution of $[\mathrm{Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$ (0.375 g, 0.25 mmol) in THF (40 cm^3) was added at room temperature the sodium alkoxide (0.5 mmol) in THF (10 cm^3) (prepared *in situ* by treatment of a solution of the alcohol in THF with NaH and filtering the resulting suspension after 30 min of stirring). The mixture was stirred for 12 h at room temperature. Concentration of the resulting solution and addition of hexane (30 cm^3) led to the precipitation of a yellow solid which was recrystallized from THF–hexane and vacuum dried. Yields (%) and analytical data. Compound **1** (85%). Found: C, 64.2; H, 6.2. Calc. for $\mathrm{C_{93}H_{95}BCu_3ClOF_4P_6}$: C, 64.7; H, 5.5%. Compound **2** (90%). Found: C, 63.1; H, 5.6. Calc. for $\mathrm{C_{89}H_{87}BCu_3ClOF_4P_6}$: C, 64.0; H, 5.2%. Compound **3** (87%). Found: C, 64.7; H, 5.7. Calc. for $\mathrm{C_{84}H_{87}BCu_3ClOF_4P_6}$: C, 64.2; H, 5.3%. Compound **4** (90%). Found: C, 60.8; H, 4.5. Calc. for $\mathrm{C_{82}H_{73}BCu_3ClF_4P_6}$: C, 62.6; H, 4.6%. IR (KBr, cm^{-1}): **1** 3051 (w), 3003 (m), 1483 (m), 1435 (s), 1361 (w), 1296 (w), 1098 (m), 1027 (m), 738 (s), 693 (s), 516 (m), 483 (m); **2** 3070 (w), 2967 (w), 1484 (m), 1435 (s), 1390 (w), 1371 (w), 1097 (m), 1047 (w), 738 (s), 693 (s), 516 (m), 508 (m), 484 (m); **3** 3051 (w), 2955 (w), 1483 (m), 1434 (s), 1364 (w), 1094 (s), 999 (m), 883 (w), 777 (m), 737 (s), 718 (m), 692 (s), 517 (m), 482 (w); **4** 3051 (w), 3004 (m), 1495 (m), 1483 (m), 1435 (s), 1385 (w), 1361 (w), 1252 (m), 1099 (m), 1056 (m), 1027 (m), 999 (m), 824 (w), 775 (m), 738 (s), 717 (m), 692 (s), 516 (m), 482 (m), 441 (w).

Preparation of the complexes $[\mathrm{Cu_3(\mu_3\text{-}XR)_2(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$ [R = *p*-$\mathrm{MeC_6H_4}$; X = O (**5**), S (**6**)]

A mixture of $[\mathrm{Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppm)_3}][\mathrm{BF_4}]$ (0.375 g, 0.25 mmol) in THF (40 cm^3) and the sodium salt of *p*-$\mathrm{MeC_6H_4XH}$ (X = O, S) (1 mmol; prepared *in situ* as described above) was stirred at room temperature for 12 h. The addition of hexane (30 cm^3) to the concentrated solution led to the precipitation of a yellow solid which was recrystallized from THF-hexane and vacuum dried. Yields (%) and analytical data. Compound **5** (80%). Found: C, 64.9, H, 4.9. Calc. for $\mathrm{C_{89}H_{80}BCu_3O_2F_4P_6}$: C, 65.0;

H, 4.9%. Compound **6** (85%). Found: C, 62.3; H, 5.0. Calc. for $C_{89}H_{80}BCu_3S_2F_4P_6$: C, 63.7; H, 4.8%. IR. (KBr, cm^{-1}): **5** 3051 (w), 1495 (s), 1483 (m), 1434 (s), 1362 (w), 1308 (w), 1253 (m), 1182 (w), 1100 (m), 1000 (m), 824 (m), 775 (m), 738 (s), 717 (m), 693 (s), 517 (m), 482 (m), 440 (w); **6** 3052 (w), 1483 (m), 1435 (s), 1400 (m), 1309 (w), 1277 (w), 1187 (w), 1152 (w), 1098 (s), 1085 (s), 1055 (s), 999 (m), 718 (m), 692 (s), 516 (m), 473 (m).

Acknowledgement—We thank the Dirección General de Investigación Científica y Técnica (DGICYT) for financial support (Project PB90-384).

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