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Preparation, Distorted Step Structure, and Topological Analysis of $(\mu_3\text{-SPh})_2(\mu\text{-SPh})_2(\text{CuPPh}_3)_4(\text{tol})_2$ (tol = Toluene)

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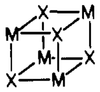
Received August 28, 1984

Pale yellow $Cu_4(SPh)_4(PPh_3)_4$, crystallized as the toluene solvate from solutions of CuSPh plus 1–1.5 equiv of PPh_3, possesses a "step" structure $(\mu_3\text{-SPh})_2(\mu\text{-SPh})_2(\text{CuPPh}_3)_4$ in which two copper atoms are trigonally coordinated and two are pseudotetrahedrally coordinated. The step is extended over that which occurs in $X_4Cu_4(PPh_3)_4$ (X = Br, I) by an outward folding of the outer Cu_2S_2 quadrilateral about the S- -S diagonal. There is no steric crowding of phenyl groups on the surface of the molecule. It is probable that this compound does not adopt the cubanoid structure of $(\mu_3\text{-X})_4Cu_4(PPh_3)_4$ (X = Cl, Br) because there is insufficient space for the SPh substituents. Relationships with other $(SR)_mM_m(PPh_3)_n$ aggregates are described. Crystal data: triclinic, $P\bar{1}$, $a = 12.716$ (7) Å, $b = 13.292$ (6) Å, $c = 14.695$ (11) Å, $\alpha = 75.46$ (4)°, $\beta = 84.10$ (4)°, $\gamma = 84.16$ (4)°, $Z = 2$ $(\times Cu_2(SPh)_2(PPh_3)_2(\text{tol}))$, Cu K$\alpha$, 4036 observed $(I > 3\sigma(I))$ data, $R = 0.044$.

Introduction

The structurally nonmolecular compound CuSPh (**1**) has been converted by reaction with PPh_3 to the structurally molecular compounds $(\mu\text{-SPh})_2Cu_2(PPh_3)_4$ (**2**)[1] and $(\mu\text{-SPh})_3Cu_3(PPh_3)_4$ (**3**)[2] in which the number of metal atoms increases as the phosphine/metal ratio decreases from 2 to 1.33. We now report the formation and molecular structure of the homologous compound with a PPh_3/Cu ratio of 1, viz. $Cu_4(SPh)_4(PPh_3)_4$ (**4**).

Complexes in the established class $X_4M_4(PR_3)_4$, analogous to **4** but with monatomic ligands X, usually adopt the cubanoid structure I comprised of intersecting M_4 and X_4 tetrahedra of



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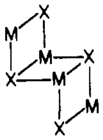

II

variable dimensions but invariant T_d symmetry. The X_4 size is determined by the X- -X van der Waals separation, and the M_4 and P_4 tetrahedra then adjust along the threefold axes according to the M–X and M–P bond distances.[3] When large X and small M reduce the size of the M_4 and P_4 tetrahedra to the point where intramolecular interference occurs between PR_3 ligands, the alternative "step" (or "chair") structure II with more widely separated PR_3 ligands is adopted. This occurs in $Br_4Cu_4(PPh_3)_4$ (**5**)[4,5] and $I_4Cu_4(PPh_3)_4$ (**6**).[6] On the basis of core-atom size, **4** is comparable with $Cl_4Cu_4(PPh_3)_4$ (**7**),[7,8] which has the cubanoid structure I, but in fact the structure of **4** is an elongated version of the step structure II.

Experimental Section

Table I. Details of Diffraction Analysis of $Cu_4(SPh)_4(PPh_3)_4(\text{tol})_2$

formula, fw	$Cu_2S_2P_2C_{55}H_{48}$, 962.2
cryst faces	{100}, {091}, {3,2,19}, {011}
space group	$P\bar{1}$, confirmed by successful structure soln
a, Å	12.716 (7)
b, Å	13.292 (6)
c, Å	14.695 (11)
α, deg	75.46 (4)
β, deg	84.10 (4)
γ, deg	84.16 (4)
V, Å^3	2384 (2)
temp, °C	21 (1)
Z	2
d_{calcd}, g cm^{-3}	1.34
radiation; λ, Å	Cu Kα; 1.5418 (unmonochromated)
μ, cm^{-1}	27.96
cryst dimens, mm	0.13 × 0.11 × 0.08
max, mean, and min transmission coeff	0.83, 0.79, 0.72
scan mode	$\theta/2\theta$
$2\theta_{\max}$, deg	110
data recorded	$-h,\pm k,\pm l$
no. of intens measmts	6007
std intens decay	1–0.97
wts used in refinement	$1/\sigma^2(F_o)$ derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$
criterion for obsd reflcn	$I/\sigma(I) > 3$
no. of indep obsd reflcns	4036
no. of reflcns (m) and variables (n) in final refinement	4036, 221
$R(F)$	0.044
$R_w(F)$	0.056
s	1.60

$Cu_4(SPh)_4(PPh_3)_4(\text{tol})_2$ (4). CuSPh[1] (3.0 g, 17 mmol) was added in small portions with stirring to a solution of PPh_3 (4.6 g, 17 mmol) in toluene (50 mL) under nitrogen. The mixture was stirred at room temperature for 30 min, and then the temperature was raised to 50 °C during 30 min. After separation of a small amount of bright yellow powder by filtration, the solution was diluted with propanol (100 mL) and held at 0 °C. Very pale yellow crystals (1.2 g; mp 171–173 °C) of the product were collected after 2 h, and a further crop (4.6 g; mp 165–169 °C) was collected after 4 days. Recrystallization was from warm toluene/propanol; mp 171–173 °C. Anal. Calcd for $C_{110}H_{96}Cu_4S_4P_4$: C, 68.66; H, 5.03. Found: C, 68.31; H, 5.21. Polycrystalline diffraction pattern (*d*/Å, intensity): 14.07 m, 12.81 vs, 10.94 vs, 9.80 s, 8.81 vs, 8.61 m, 7.06 w, 6.45 w, 6.03 w, 5.84 vw, 5.52 vw, 5.43 w, 5.37 w, 5.053 w, 4.809 w, 4.685 w, 4.538 m, 4.437 m, 4.312 s, 4.207 m, 4.142 m, 4.068 m, 3.890 w, 3.798 w, 3.651 m, 3.552 vw, 3.418 w, 3.346 m, 3.223 m, 3.126 m. This compound was also obtained by crystallization of **2** (0.5 g) from warm toluene (10 mL) by addition of propanol (15 mL).

4 gives a colorless solution in acetonitrile but a yellow solution in acetone, carbon tetrachloride, or warm toluene. There is slight decomposition to a yellow powder on refluxing in toluene. The compound is slightly soluble in 2-propanol and insoluble in methanol, ethanol, and petroleum ether.

Crystallography. The procedures for collection of diffraction data (using an Enraf-Nonius CAD4 diffractometer) and for data reduction and correction for absorption have been described.[1] Numerical details of the crystallographic analysis, including the final least-squares refinement, are contained in Table I. Structure solution was by direct methods (MULTAN80). Structure refinement minimized the function $\sum w(F_o - F_c)^2$

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0020-1669/85/1324-2547$01.50/0

Table II. Atomic Coordinates[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu1	0.4296 (1)	0.5900 (1)	−0.0797 (1)	C231	0.1569 (3)	0.6461 (2)	−0.0579 (3)
Cu2	0.3961 (1)	0.4181 (1)	0.2094 (1)	C331	0.0497 (3)	0.6442 (3)	−0.0698 (3)
S1	0.3800 (1)	0.4458 (1)	0.0495 (1)	C431	−0.0136 (2)	0.7374 (4)	−0.0953 (3)
S2	0.5635 (1)	0.4561 (1)	0.2230 (1)	C531	0.0305 (3)	0.8326 (3)	−0.1089 (3)
P1	0.3422 (1)	0.7363 (1)	−0.0539 (1)	C631	0.1377 (3)	0.8346 (2)	−0.0970 (3)
P2	0.2649 (1)	0.3683 (1)	0.3179 (1)	C112	0.1367 (2)	0.4413 (3)	0.2992 (3)
C11	0.3304 (2)	0.3358 (2)	0.0260 (2)	C212	0.1182 (3)	0.5006 (3)	0.2086 (2)
C21	0.3429 (3)	0.2385 (3)	0.0892 (2)	C312	0.0192 (3)	0.5540 (3)	0.1908 (2)
C31	0.3056 (3)	0.1514 (2)	0.0700 (3)	C412	−0.0614 (3)	0.5481 (3)	0.2637 (3)
C41	0.2557 (3)	0.1616 (3)	−0.0126 (3)	C512	−0.0429 (3)	0.4887 (4)	0.3543 (3)
C51	0.2432 (3)	0.2590 (3)	−0.0758 (2)	C612	0.0561 (3)	0.4353 (3)	0.3720 (2)
C61	0.2806 (3)	0.3461 (2)	−0.0566 (2)	C122	0.2878 (3)	0.3763 (3)	0.4361 (2)
C12	0.6272 (3)	0.3560 (3)	0.3090 (2)	C222	0.3304 (3)	0.4668 (3)	0.4425 (2)
C22	0.5699 (2)	0.2961 (3)	0.3864 (3)	C322	0.3516 (4)	0.4791 (3)	0.5303 (3)
C32	0.6227 (3)	0.2179 (3)	0.4521 (2)	C422	0.3303 (3)	0.4009 (4)	0.6116 (2)
C42	0.7328 (3)	0.1997 (3)	0.4405 (3)	C522	0.2878 (4)	0.3104 (3)	0.6052 (2)
C52	0.7900 (2)	0.2596 (3)	0.3631 (3)	C622	0.2665 (3)	0.2981 (3)	0.5174 (3)
C62	0.7372 (3)	0.3377 (3)	0.2974 (2)	C132	0.2367 (3)	0.2338 (2)	0.3304 (3)
C111	0.3814 (3)	0.2615 (2)	−0.1277 (2)	C232	0.1378 (3)	0.2079 (3)	0.3141 (3)
C211	0.4138 (4)	0.9399 (3)	−0.0914 (2)	C332	0.1212 (3)	0.1042 (3)	0.3198 (3)
C311	0.4424 (4)	1.0335 (3)	−0.1523 (3)	C432	0.2034 (4)	0.0263 (2)	0.3419 (3)
C411	0.4387 (4)	1.0489 (3)	−0.2496 (3)	C532	0.3023 (3)	0.0523 (3)	0.3583 (3)
C511	0.4063 (4)	0.9705 (3)	−0.2858 (2)	C632	0.3189 (3)	0.1560 (3)	0.3525 (3)
C611	0.3777 (4)	0.8769 (3)	−0.2249 (3)	C1T	0.0314 (4)	0.7774 (4)	0.3758 (4)
C121	0.3411 (3)	0.7528 (3)	0.0654 (2)	C2T	−0.0086 (4)	0.8364 (5)	0.4397 (4)
C221	0.4209 (3)	0.6982 (3)	0.1211 (3)	C3T	−0.0839 (5)	0.9202 (4)	0.4131 (5)
C321	0.4243 (3)	0.7099 (3)	0.2125 (3)	C4T	−0.1191 (4)	0.9449 (4)	0.3226 (6)
C421	0.3479 (4)	0.7760 (4)	0.2484 (2)	C5T	−0.0789 (6)	0.8858 (6)	0.2587 (4)
C521	0.2680 (3)	0.8306 (4)	0.1927 (3)	C6T	−0.0037 (6)	0.8021 (5)	0.2853 (4)
C621	0.2646 (3)	0.8189 (3)	0.1012 (3)	C7T	0.1053 (8)	0.6951 (8)	0.4019 (8)
C131	0.2009 (2)	0.7413 (3)	−0.0715 (3)				

[a] Non-hydrogen atoms.

and incorporated rigid-body least-squares techniques. All aromatic rings were refined as rigid groups of fixed regular hexagonal geometry, while the external C–C bond of the toluene molecule was allowed to vary. The thermal motion of the toluene molecule was parameterized with the TLX model[9] with the center of libration on the methyl carbon atom, while the thermal motions of the ligand phenyl rings were parameterized with the TL model.[9] All atoms except the methyl hydrogen atoms were included. On completion of the refinement, *R* was 0.044 for 4036 independent observed reflections, and the difference map contained only two peaks between 0.3 and 0.7 e Å^{-3}, both near the lattice toluene. Scattering factors, including real and imaginary anomalous scattering by Cu, S, and P, were from ref 10. No extinction correction was included.

The labeling of the Cu, S, and P atoms is shown in Figure 1. Thiolate ligand atoms are C*mn* (m = 1–6; n = 1, 2) and phosphine ring atoms are C*rst* (r = 1–6; s = 1–3; t = 1, 2); the toluene atoms are labeled C*p*T (p = 1–7). Atomic coordinates are listed in Table II. A complete tabulation of parameters and structure factors is deposited.[11]

Results

Formation and Solution Behavior. Very pale yellow crystals of $Cu_4(SPh)_4(PPh_3)_4(tol)_2$ (**4**) are readily obtained by treatment of CuSPh with 1 equiv of PPh_3 in toluene and crystallization with propanol. **4** is also obtained in diminished yield in similar reactions with PPh_3/CuSPh = 1.2 or 1.5, but when this ratio is 2, $Cu_2(SPh)_2(PPh_3)_4$ (**2**) is formed. Recrystallization of **2** from toluene/propanol yields **4**. The formation of the complex $Cu_4(SPh)_4(PPh_3)_4$ is dependent on the presence of toluene, which occurs in the crystals of **4**: reactions of CuSPh with 1 equiv of PPh_3 in chloroform yield **2** and/or **3**, while reactions in acetone have given uncharacterized mixtures.

Molecular Structure. The molecular structure of **4**, with the connectivity of the step arrangement II, has an exact center of symmetry but no additional virtual symmetry. There are two triply bridging (μ_3-X, S1) and doubly bridging (μ-X, S2) ligands and metal atoms with tetrahedral (M^{tet}, Cu1) and trigonal (M^{trig}, Cu2) coordination. The central rhomb $M^{tet}{}_2(\mu_3\text{-X})_2$ is planar, but the outer quadrilaterals $M^{tet}M^{trig}(\mu_3\text{-X})(\mu\text{-X})$ are folded. Important bonding dimensions are given in Table III, together with the comparable dimensions of **5** and **6**. The bond lengths and angles are not abnormal, and the lengths are dependent on the coordination numbers of both the copper and the sulfur atoms in the usual fashion: [Cu^{tet}–(μ_3-S) = 2.417, 2.484 Å] > [Cu^{tet}–(μ-S) = 2.328 Å] ≈ [Cu^{trig}–(μ_3-S) = 2.313] > [Cu^{trig}–(μ-S) = 2.278 Å]. The Cu^{trig} coordination is planar to within 0.01 Å, and the angles at Cu^{tet} range from 92.0 (in the central rhomb) to 119.1 and 123.1° (Ph_3P–Cu–SPh).

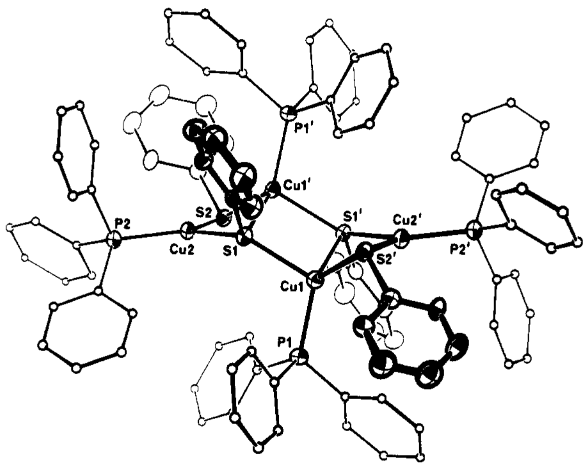

Figure 1. Centrosymmetric molecular structure of $(\mu_3\text{-SPh})_2(\mu\text{-SPh})_2(CuPPh_3)_4$ in **4**.

The substantial difference between **4** and the halide-bridged step molecules **5** and **6** is the position of Cu^{trig} further from the center of the molecule in **4**. This extension occurs principally by a relocation of Cu^{trig}: the Cu^{trig} coordination plane flaps around the (μ_3-S)- -(μ-S) diagonal of the outer quadrilateral, away from the central region of the molecule and in the direction that tends to flatten the whole molecule, as shown in **8**. Comparison of the (μ_3-X)–Cu^{tet}–(μ-X) angles reveals that the μ-S atom in **4** is

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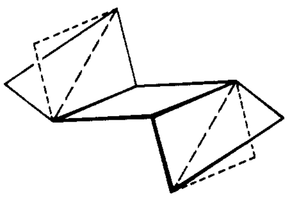
(9) Pawley, G. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1970**, *A26*, 289.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(11) See paragraph at end of paper regarding supplementary material.



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displaced only slightly from the μ-X position in **5** and **6**. The extent of the flap folding of the Cu^{trig} coordination planes can be seen in the dihedral angles at the (μ-X)- -(μ_3-X) diagonal of the outer quadrilateral (142.3° in **4**; 168.7 and 167.3° in **5** and **6**).[12] An alternative expression of this unique feature of **4** occurs in the increased value of the Cu^{trig}–(μ_3-X)–Cu^{tet} angle: 130.1° in **4** vs. 107.2 and 108.3° in **5** and **6**. The elongation of molecule **4**, and the increased separation of the PPh_3 ligands on the Cu^{trig} atoms, is shown by the dimensions in Table IV; while the intramolecular P^{tet}- -P^{tet} separations 7.02, 7.16, and 7.24 Å in **4**, **5**, and **6** reflect the increasing size of X, the P^{trig}- -P^{trig} separation in **4**, 10.57 Å, exceeds the separations in **5** (10.29 Å[13]) and **6** (10.56 Å[13]).

The component of **4** that is absent from **5** and **6** is the substituent on the bridging ligands. The doubly bridging thiolate has pyramidal stereochemistry at sulfur, the angle between the S2–C12 bond and the Cu1′–S2–Cu2 plane being 63.3 (1)°, but the inverted configuration at S2 is not possible as it would incur interference with the PPh_3 ligand at P1′. At the triply bridging thiolate the stereochemistry is irregular, with the α-carbon atom and the two copper atoms almost coplanar with the sulfur atom: the S1–C11 bond is inclined at only 4.0 (2)° to the Cu2–S1–Cu1 plane. The S1–C11 bond is symmetrically inclined (the two Cu–S1–C11 angles are 110°) at 64.8 (1)° to the Cu1′–S1–Cu2 plane, and in this respect it is almost identical with that in the doubly bridging thiolate. The stereochemistry at the triply bridging thiolate approaches the extreme found in $\text{Ag}_6(\text{SC}_6\text{H}_4\text{Cl})_6(\text{PPh}_3)_5$, where the sulfur atoms are outside their Ag_3C coordination polyhedra.[14]

Over the surface of the molecule there are no abnormally short distances between substituents of different ligands. Figure 1 shows that two Ph groups on P1 oppose two Ph groups on P2, while over the outer quadrilateral four Ph groups (one each from S1, S2, P1′, and P2) are contiguous. In this latter region the shortest interphenyl ring contacts are HC22- -HC632 = 2.46 Å and C62- -C231′ = 3.60 Å. There is only one other intramolecular H- -H distance less than 2.8 Å, namely HC61- -HC231 = 2.61 Å.

Discussion

In a survey investigation Reichle[15] has reported the conversion of a compound "$(\text{PPh}_3)_2\text{CuSPh}$" to "$\text{Cu}_2(\text{SPh})_2(\text{PPh}_3)_2$" by heating the solid at 116 °C (0.01 mmHg) for 48 h. The product (mp 155–180 °C) was partially characterized by C, H, S analysis and by measurement of molecular weight in chloroform solution, which yielded the dicopper formulation. It is conceivable that Reichle's solid was $\text{Cu}_4(\text{SPh})_4(\text{PPh}_3)_4$ but not the toluene solvate **4** reported here. It is also possible that **4** dissociates in chloroform solution. Figure 1 shows that the structure of **4** is composed of two $\text{Ph}_3\text{PCu}(\mu\text{-SPh})_2\text{CuPPh}_3$ moieties (**9**) linked by two Cu–S bonds, providing a facile mechanism for dissociation. Not being subject to the steric crowding of **2**, **9** is expected to contain pyramidally bridging sulfur atoms.

Table III. Molecular Dimensions for **4**, with Comparative Dimensions for **5** and **6**

atoms	dist, Å	type	dist, Å 5	 6
Cu1- -Cu2′	2.782 (1)	M^{tet}- -M^{trig}	2.991 (2)	2.835 (3)
Cu1- -Cu2	4.289 (1)	M^{tet}- -M^{trig}	3.987 (2)	4.295 (3)
Cu1- -Cu1′	3.404 (2)	M^{tet}- -$\text{M}^{\text{tet}'}$	3.448 (3)	3.404 (4)
Cu1–S1	2.418 (2)	M^{tet}–(μ_3-X)	2.525 (2)	2.707 (2)
Cu1–S1′	2.482 (2)	M^{tet}–(μ_3-X)′	2.664 (2)	2.728 (2)
Cu1–S2′	2.327 (2)	M^{tet}–(μ-X)	2.477 (3)	2.620 (2)
Cu2–S1	2.313 (2)	M^{trig}–(μ_3-X)	2.430 (2)	2.591 (2)
Cu2–S2	2.277 (2)	M^{trig}–(μ-X)	2.377 (2)	2.527 (2)
Cu1–P1	2.238 (2)	M^{tet}–P^{tet}	2.207 (3)	2.242 (4)
Cu2–P2	2.217 (2)	M^{trig}–P^{trig}	2.194 (4)	2.228 (5)
S1- -S2	3.665 (2)	(μ_3-X)- -(μ-X)	3.957 (2)	4.384 (2)
S1- -S1′	3.526 (3)	(μ_3-X)- -(μ_3-X)′	3.880 (3)	4.238 (2)
S1- -S2′	3.902 (2)	(μ_3-X)- -(μ-X)′	3.897 (2)	4.204 (2)
S1–C11	1.772 (3)			
S2–C12	1.780 (3)			

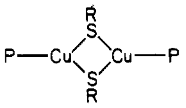
atoms	angle, deg	type	angle, deg 5	 6
S1–Cu1–P1	108.4 (1)	(μ_3-X)–Cu^{tet}–P^{tet}	119.1 (1)	112.9 (1)
S1–Cu1–S1′	92.0 (1)	(μ_3-X)–Cu^{tet}–(μ_3-X)′	96.8 (1)	102.5 (1)
S1–Cu1–S2′	110.6 (1)	(μ_3-X)–Cu^{tet}–(μ-X)	102.3 (1)	104.2 (1)
P1–Cu1–S1′	119.1 (1)	(μ_3-X)′–Cu^{tet}–P^{tet}	114.9 (1)	114.5 (1)
P1–Cu1–S2′	123.1 (1)	(μ-X)–Cu^{tet}–P^{tet}	118.7 (1)	112.0 (1)
S2′–Cu1–S1′	99.2 (1)	(μ-X)–Cu^{tet}–(μ_3-X)′	100.6 (1)	110.1 (1)
S1–Cu2–S2	106.0 (1)	(μ_3-X)–Cu^{trig}–(μ-X)	110.8 (1)	117.9 (1)
S1–Cu2–P2	123.0 (1)	(μ_3-X)–Cu^{trig}–P^{trig}	119.0 (1)	114.2 (1)
S2–Cu2–P2	131.0 (1)	(μ-X)–Cu^{trig}–P^{trig}	128.8 (1)	127.5 (1)
Cu1–S1–Cu2	130.1 (1)	M^{tet}–(μ_3-X)–M^{trig}	107.2 (1)	108.3 (1)
Cu1–S1–Cu1′	88.0 (1)	M^{tet}–(μ_3-X)–$\text{M}^{\text{tet}'}$	83.2 (1)	77.6 (1)
Cu2–S1–Cu1′	70.8 (1)	M^{trig}–(μ_3-X)–$\text{M}^{\text{tet}'}$	71.1 (1)	64.3 (1)
Cu2–S2–Cu1′	74.3 (1)	M^{trig}–(μ-X)–$\text{M}^{\text{tet}'}$	76.0 (1)	66.8 (1)
Cu1–S1–C11	119.8 (1)			
Cu2–S1–C11	110.0 (1)			
Cu1′–S1–C11	110.7 (1)			
Cu2–S2–C12	110.9 (1)			
Cu1′–S2–C12	111.1 (1)			

Table IV. Molecular Extension Distances (Å)

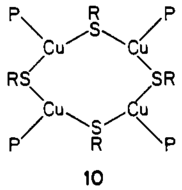
	P^{tet}- -$\text{P}^{\text{tet}'}$	P^{trig}- -$\text{P}^{\text{trig}'}$	P^{trig}- -P^{tet}	P^{trig}- -$\text{P}^{\text{tet}'}$
4	7.02	10.57	6.42	6.27
5	7.24	10.29[a]	6.58	5.98
6	7.16	10.56[a]	6.44	6.31

[a] The values published[6] for these distances are erroneous.

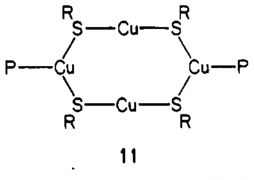
We note that if the longest Cu–S bond (Cu1–S1 = 2.484 Å) is secondary and dissociable, **4** opens to an eight-membered cycle $(\mu\text{-SPh})_4(\text{CuPPh}_3)_4$ (**10**) with trigonal coordination at each metal atom. There is precedent for a cycle of this size in the analogous compound $(\mu\text{-}S\text{-}t\text{-Bu})_4\text{Cu}_4(\text{PPh}_3)_2$ (**11**)[16] with two- and three-coordinate copper: **10** is intermediate between **11** and **3** (with three- and four-coordinate copper).



9



10



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An evident question is whether the thiolate substituents of **4** could be accommodated in a cubanoid structure $(\mu_3\text{-SPh})_4\text{Cu}_4(\text{PPh}_3)_4$ (I) as occurs in **7** with donor atoms of the same size. In **7** there is staggered conformation about the Cu–P bonds; i.e., the Cl–Cu–P–C torsional angles are close to 180°. Consequently six phenyl groups are arrayed symmetrically around the threefold

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[12] The rms displacements of atoms from the least-squares plane for the four atoms in the outer quadrilateral are 0.24 Å in **4**, 0.07 Å in **5**, and 0.08 Å in **8**.

[13] The values published[6] for these distances are erroneous.

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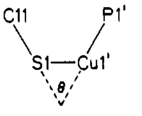
[15] Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325.

[16] Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L., submitted for publication.

axes of I; the SPh ligands of cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ would be collinear with these axes and therefore positioned within the cone of six Ph groups connected as $PhS\text{-}Cu\text{-}(\text{-}P\text{-}Ph_2)_3$. Connections of this type occur in **4**, along Ph-S1-Cu1′-P1′. Therefore the structural unit, including phenyl rings, sufficient for construction of cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ is present in **4**. The critical dimensional property is the angle θ shown in **12**: in the cubanoid structure this angle between threefold axes is 70.5°, while in **4** it is ca. 59° (S1-Cu1′-P1′ = 119.0°, C11-S1-Cu1′ = 119.8°). In 7, Cl-Cu-P angles average 122°. From this we conclude that SPh- -Ph_2P contacts in the cubanoid $(\mu_3\text{-SPh})_4Cu_4(PPh_3)_4$ would be slightly shorter than in **4**, and this may be the reason for the adoption of the step structure II.



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Acknowledgments. We thank the Australian Research Grants Scheme for financial support and D. C. Craig for collection of the diffraction data.

Registry No. 4, 96705-31-6.

Supplementary Material Available: A tabulation of all atomic coordinates and thermal parameters and a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Triply Bonded Dirhenium(II) Complexes $Re_2Cl_4(\mu\text{-}Ph_2PCH_2PPh_2)_2$ and $\alpha\text{-}Re_2Cl_4(Me_2P(CH_2)_2PMe_2)$

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Received November 20, 1984

The complexes $Re_2Cl_4(LL)_2$, where LL are the bidentate ligands $Ph_2PCH_2PPh_2$ (dppm) (**1**) and $Me_2P(CH_2)_2PMe_2$ (dmpe) (**2**), which both possess the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ and thus formally a metal-metal triple bond, have been structurally characterized by X-ray crystallography. $Re_2Cl_4(dppm)_2$ (**1**): $Re_2Cl_4P_4C_{50}H_{44}$; monoclinic, $P2_1/n$; a = 11.647 (3) Å, b = 12.849 (4) Å, c = 38.691 (9) Å, β = 85.96 (2)°, V = 5776 (43) Å^3, Z = 4. The molecule has two dppm molecules spanning the Re-Re bond. The two fused five-membered rings assume twist-boat conformations, leading to a completely staggered arrangement of the substituents on the two rhenium atoms. The average Cl-Re-Re-Cl torsion angle is 56 [1]°, and the Re-Re bond length is 2.234 (3) Å. $Re_2Cl_4(dmpe)_2{\cdot}CH_3OH$ (**2**) was isolated and crystallized as the α isomer, viz., with the dmpe ligands chelating. The crystallographic parameters are as follows: $Re_2Cl_4P_4OC_{13}H_{36}$; orthorhombic, *Ccma* (nonstandard setting of *Cmca*); a = 11.595 (2) Å, b = 14.475 (2) Å, c = 14.925 (2) Å, V = 2505 (1) Å, Z = 4. The dimetallic unit has a Re-Re bond length of 2.264 (1) Å and an eclipsed conformation with the geminal chlorides in a cis configuration. The five-membered chelate rings have envelope conformations.

Introduction

The reaction of the dimeric rhenium(III) halo complexes $Re_2X_8{}^{4-}$ with bidentate phosphines (LL) affords complexes of the type $Re_2X_6(LL)_2$, $Re_2X_5(LL)_2$, and $Re_2X_4(LL)_2$, many of which have been previously described.[2-4] The extent of reduction is dependent upon the nature of the Re^{III} starting material, the diphosphine ligands, and the reaction conditions.

We describe here the preparation and structural characterization, by X-ray crystallography, of two Re(II)-Re(II) dimers, $Re_2Cl_4(dppm)_2$ (**1**) and $Re_2Cl_4(dmpe)_2$ (**2**). Both have the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$, viz., a formal metal-metal triple bond, and thus no electronically imposed barrier to rotation about the metal-metal bond.

$Re_2Cl_4(dppm)_2$ (**1**) was prepared several years ago, and an interesting and intensive reaction chemistry has since developed.[3,5-7] Furthermore, the complex constitutes a member of the series $Re_2Cl_4(dppm)_2$, $Re_2Cl_5(dppm)_2$, and $Re_2Cl_6(dppm)_2$, which are formally related to one another by one-electron oxidation and concomitant gain of Cl^-. With the successful growth of single crystals, after many earlier frustrations, we were now able to complete the structural investigation of this series.

When bis(phosphines) with a two-carbon linkage are involved, the reduction process is known to provide two major configurational isomers: the α (chelating) and the β (bridging) forms. Our present results corroborate previous findings that the isolation of the α or β isomer depends on whether the reaction proceeds under kinetic or thermodynamic control.[8] It appears that the α form is in all instances the primary product, which will eventually isomerize to the more stable β form.

Experimental Section

Preparation of $Re_2Cl_4(dppm)_2$ (1). Samples of $Re_2Cl_4(dppm)_2$ were obtained by a slight modification of the existing literature preparation.[3] A mixture of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.674 g, 0.682 mmol) and dppm (1.4 g, 3.6 mmol) was added to 30 mL of *reagent grade* methanol and refluxed for 0.5 h. The resulting purple solid was filtered off and washed with copious amounts of diethyl ether to remove any unreacted dppm. The excess dppm can be recovered unchanged from the ether washings by addition of methanol and chilling to 0 °C. The purple complex was obtained in a sufficiently pure state by this process to avoid the necessity

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