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Reactions of $Cu_3(dppm)_3(\mu_3-OH)(ClO_4)_2$ (dppm=bis-(diphenylphosphino) methane) with Soft Heterocumulenes

Note

C. Sivasankar, J.K. Bera, M. Nethaji, A.G. Samuelson *

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Malleswaram, Bangalore 560012, India

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Abstract

The reaction of $[Cu_3(dppm)_3(\mu_3-OH)](ClO_4)_2$ (1) with heterocumulenes (X=C=S; X=NPh, NMe and S) has been studied. The μ_3 -OH ligand inserts into PhNCS and MeNCS only in the presence of methanol. Insertion products are formed in accord with earlier observations made with copper(I)–aryloxides. On heating, the insertion products convert to a S bridged cluster $[Cu_4(dppm)_4(\mu_4-S)](ClO_4)_2$ (8), having a tetrameric core. However, in the reaction with CS₂, 1 is converted to 8 even at room temperature in the presence of methanol. On the other hand, the dimeric complex $[Cu_2(dppm)_2(CH_3CN)_4](ClO_4)_2$, reacts with CS₂ to give (diphenylphosphinomethyl)-diphenylphosphine sulfide, Ph₂P–CH₂–P(=S)Ph₂ (dppmS), which forms the complex $[Cu(dppmS)_2]ClO_4$ (9). A single crystal X-ray crystallographic study of 9, the first copper(I) complex of dppmS has been taken up to confirm the mono-oxidation of the dppm ligand and the nuclearity of the complex. Reactions of complex 1 with heterocumulenes and with elemental sulfur, are compared.

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1. Introduction

Late transition metal alkoxides and aryloxides have been the subject of numerous studies in the last two decades [1]. Extensive studies done with heterocumulenes indicate the major reaction pathway to be an insertion of the OR group of M–OR fragment into the more polar double bond of Y=C=X [2]. This is followed by a rearrangement if necessary to form a M– X or M–Y bond or even a chelated complex with both X and Y bonded to M [3,4]. In the recent past, it has come to light that there could be significant differences in the reactivity of late transition metal alkoxides and

E-mail address: ashoka@ipc.iisc.ernet.in (A.G. Samuelson).

aryloxides, especially in their reactions with electrophiles such as SO₂, CO₂, and COS [5]. In contrast with the number of studies on metal alkoxides and aryloxides, the chemistry of metal hydroxides is less explored [6]. In part this is due to the lack of well characterized hydroxy metal complexes. Recent efforts, primarily by Bergman and others, have uncovered routes to several late transition metal hydroxides [7]. Unusual insertion reactions patterns have been observed. For example, with the Ir(I) hydroxo complex studied by Werner, a facile methanol dehydrogenation has been observed instead of simple substitution [8]. In the case of Pt hydroxo complexes, both Wacker type insertion reactions and acid base reactions take place [9] while Pd hydroxo complexes undergo exchange/insertion reactions [10]. A dinuclear tungsten complex has been found to undergo several unusual rearrangements

^{*} Corresponding author. Tel.: +(080)-293-2663/+91-803-942-663; fax: +(080)-360-1552/+91-803-601-552.

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[11]. These studies warrant further investigations of metal hydroxo complexes.

We choose to study copper(I) hydroxo complexes, for interesting reactivity patterns have emerged from the mismatch of a hard donor and the soft metal center Cu(I). Reactions of Cu(I)-aryloxide which has a hard donor coordinated to it reacts with heterocumulenes to give insertion products [3]. These are followed by rearrangements driven by the tendency of Cu(I) to have soft ligands around it [3,4]. Similar reactions or increased reactivity is expected for Cu(I) hydroxides, due to the increased hardness of the ligand. In the light of what has been said of late transition metal hydroxo complexes and as part of our continuing study of the reactivity of the Cu(I)–O bond, we have studied the well-characterized complex $[Cu_3(dppm)_3(\mu_3-OH)](ClO_4)_2$ [16a] with three heterocumulenes PhNCS, MeNCS, CS₂ and for comparison, elemental sulfur. The reactivity of a triply bridging hydroxide ligand is also interesting for another reason. It serves as a model for the reactivity of a hydroxide ligand coordinated to the surface of metal or metal oxide.

2. Results and discussion

2.1. Reactions of the hydroxo complex

The reaction of a soft heterocumulene (HC) with $[Cu_3(dppm)_3(\mu_3-OH)](ClO_4)_2$ (1) leads to complexes of the type [1 HC] in pure dichloromethane. The presence of one equivalent of PhNCS, MeNCS or CS₂ in the products **3**, **4** and **5**, respectively, was inferred from analytical data, NMR and IR spectroscopy. Repeated washing of this product with the solvent did not remove the heterocumulene from the complex. Since no significant changes are observed in the IR stretching frequency of the heterocumulene in the complex, it is assumed that the HC is encapsulated in the complex rather than inserted into the hydroxide ligand.

On the other hand, in a mixture of CH₂Cl₂/CH₃OH, addition of PhNCS to a solution of $[Cu_3(dppm)_3(\mu_3 -$ OH)](ClO₄)₂ immediately results in a color change and a yellow colored solution is formed. The structure of the isolated insertion product 6 has been assigned on the basis of analysis data and the NMR spectra in chloroform. The ³¹P{¹H} NMR value at δ –15.4 ppm is a good indication that the trimeric moiety, Cu₃(dppm)₃, is intact. The ¹H NMR spectrum of the isolated product shows methylene signals at δ 3.25 and 4.13 ppm in a 2:1 ratio. This is caused by the methylene groups oriented in a 2-up and 1-down fashion with respect to the Cu_3P_6 plane. In the presence of a symmetrical cap like a halogen or acetylide, $Cu_3(dppm)_3$ complexes exhibit a single methylene resonance due to rapid flipping of the methylene flap of the Cu-P-CH₂-P-Cu unit [12]. The very bulky nature of the cap in complex 1 leads to much

slower flipping and so the three methylene signals are differentiated. The phenyl protons resonate from δ 6.98–7.34 ppm. A signal at 9.9 ppm for a single proton exchanges with D₂O and has been assigned to the NH proton with a sulfur cap (Scheme 1). An alternative nitrogen-capped species is not likely as it would have a much lower δ value for the –SH group.

Likewise in a mixture of CH_2Cl_2 and CH_3OH , reaction of MeNCS gives a pale yellow colored solution. The NMR and analyses data show the formation of a complex where MeNCS has inserted into the OH group to give $[Cu_3(dppm)_3(\mu_3-SC(O)NHCH_3)]$ (7), analogous to 6. Attempts to recrystallise 7 from acetonitrile solution led to the formation of crystalline $[Cu_2(dppm)_2(CH_3CN)_4]$ - $(ClO_4)_2$ [4] as the major product. The reversible insertion of MeNCS has been documented recently in the case of Cu(I)-aryloxy complexes [3]. Such a ready extrusion of PhNCS was not observed in the case of complex 6.

In the reaction of $[Cu_3(dppm)_3(\mu_3-OH)](ClO_4)_2$ with CS₂, the insertion product analogous to **6** and **7** is not isolated and the product isolated has a sulfide capped cluster. This is surprising since similar adducts have been isolated in the case of CS₂, PhNCS and MeNCS, in the absence of methanol. This result is also completely different from the reactivity patterns exhibited by aryloxide ligands [3] and hence unique to the hydroxide ligand and CS₂. The isolated *S*-capped tetrameric cluster **8** is known in the literature from the reaction of $[Cu_2(dppm)_2(NO_3)_2]$ with Na₂S [13]. This illustrates yet another unique reaction pathway available to Cu(I)-dppm complexes and a heterocumulene.

One possibility for the reactivity difference is that the intermediate complex analogous to 6 and 7 transforms to 8. Complex 7 can indeed be converted to 8 on refluxing in a solution of CH_2Cl_2 and MeOH. On standing at room temperature for several days, 3 or 4 also slowly convert to 8, whereas 5 which contains a volatile heterocumulene does not and reverts to 1 rather than 8.

2.2. Reactions of the dimer 2

The dimeric complex 2 is converted to 1 in the presence of methanol. In the case of PhNCS and MeNCS, the reaction with 2 is slow and so the conversion of 2–1 takes place at a comparable rate leading to products 6 and 7. However the reaction of 2 with CS₂ is faster than its conversion to 1. Addition of CS₂ to a CH₂Cl₂/CH₃OH solution of $[Cu_2(dppm)_2(CH_3CN)_4(ClO_4)_2]$ (2) immediately results in a red color. After work-up, the major product was found to be $[Cu(dppmS)_2]ClO_4$ (9) which could be isolated and has been characterized by elemental analysis, IR and NMR spectroscopy (Scheme 2).

¹H NMR spectra of **9** in CDCl₃ has a single resonance at δ 3.73 ppm due to the methylene protons. The phenyl protons exhibit peaks ranging from δ 7.17 to 7.44 ppm along with multiplets at δ 7.70–





7.78 ppm. The presence of peaks beyond δ 7.6 ppm suggested the oxidation of P(III) of the dppm ligand to P(V). The ³¹P{¹H} NMR spectrum of complex **9** in CDCl₃ exhibits two well-separated signals at δ –9.98 and δ 50.9 ppm. The signal in the high field region is characteristic of P(V) and in particular the (R)Ph₂P=S group [14] coordinated to a metal center. The other signal is typical of a tertiary phosphorus center coordinated to Cu(I) [10,14]. The spectroscopic evidence is clearly indicative of the oxidation of dppm ligand during the course of reaction, although, not sufficient to distinguish between an unsymmetrically oxidised ligand and a mixture of unoxidised and oxidised ligands coordinated to copper.

The molecular structure of the complex was confirmed by a single-crystal X-ray structure determination of **9**. A perspective drawing of the cationic part of **9** with selected atomic numbering scheme is shown in Fig. 1 and the summary of crystallographic information is given in Table 1. The molecular structure consists of the cationic [Cu(dppmS)₂]⁺ unit and an isolated ClO_4^- . Oxidation of one of the phosphorus atoms of the dppm ligand to P=S makes it a good chelating ligand compared to dppm which can only function as a bridging ligand with small metal ions. A mononuclear complex is formed as a result of this transformation. The coordinating environment around the copper is distorted tetrahedral with two sulfur and two phosphorus atoms of two dppmS ligands. The



Fig. 1. ORTEP view of the complex cation of **9** with selected atomic numbering scheme. Phenyl rings of the dppe and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (°) for **9**: Cu(1)-P(1) 2.273(2), Cu(1)-P(3) 2.274(2), Cu(1)-S(2) 2.392(3), Cu(1)-S(1) 2.398(3), S(1)-P(2) 1.975(3), S(2)-P(4) 1.981(3), P(1)-Cu(1)-P(3) 126.88(9), P(1)-Cu(1)-S(2) 112.55(9), P(3)-Cu(1)-S(2) 97.21(8), P(1)-Cu(1)-S(1) 96.43(8), P(3)-Cu(1)-S(1) 115.90(10), S(2)-Cu(1)-S(1) 107.37(11).

Table 1

Summary of crystallographic information for complex 9

Crystal data	Complex 9
Empirical formula	C ₅₀ H ₄₄ ClCuO ₄ P ₄ S ₂
Formula weight	995.84
Crystal system, space group	Triclinic, $P\overline{1}$
a (Å)	11.473(2)
b (Å)	14.048(2)
c (Å)	15.762(3)
α (°)	90.60(2)
β (°)	98.35(2)
γ (°)	107.57(2)
$V(\text{\AA})^3$	2392.1(7)
$\rho_{\rm calc} ({\rm mg/m}^3)$	1.383
Ζ	2
Absolute coefficient (mm^{-1})	0.777
<i>F</i> (000)	1028
Crystal size	0.3×0.3×0.2 mm
Range	1.31–24.97°
Reflections collected/unique	$8868/8408 (R_{int} = 0.0246)$
Data/restraints/parameters	8408/0/559
Goodness-of-fit on F^2	1.084
Final R_1^{a} , wR_2^{b} , $[I > 2\sigma(I)]$	$R_1 = 0.0967, wR_2 = 0.2774$
Final R_1^{a} , wR_2^{b} (all data)	$R_1 = 0.1595, wR_2 = 0.3027$

^a $R_1 = (\Sigma ||F_0| - |F_c||) / (\Sigma |F_0|).$ ^b $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2] / \Sigma [w|F_0|^2)^2]^{1/2}$

P1–Cu1–P3 angle is 126.88(9)°, higher than the ideal tetrahedral value of 109°. The P1–Cu1–S1 and P3–Cu1–S2 angles (96.43(8)° and 97.21(8)°, respectively) are much less than the ideal tetrahedral values but larger than what is observed for the same ligand in Rh, and Hg complexes [14,15]. The copper–phosphorus distances are similar to that found in other Cu(I)-dppm complexes [12]. The Cu1–S2 distance is 2.392(3) Å while Cu1–S1 is 2.398(3) Å. There are no inter or intra molecular S–S interactions in the complex. Carbon atoms of one phenyl ring are considerably disordered and is reflected in the larger *R* factor. There was no improvement even after attempts were made to solve the structure from three independent data sets collected from three different crystals. In spite of these limitations, the structural study provides better understanding of the chemistry of heterocumulenes and their reaction with the $[Cu_3(dppm)_3OH]^{2+}$ cluster (Scheme 2).

Another interesting fact to note is that the addition of excess CS_2 or prolonged reaction times does not lead to oxidation of the second phosphorus center. Although the doubly oxidised ligand is known and has been structurally characterized in the complexed form, only the mono-oxidised product is isolated in this reaction. Such a preference for mono-oxidation on treatment with elemental sulfur, has been reported for other metals [14]. The formation of a stable five-membered chelate ring probably hinders further oxidation. The fate of the second copper(I) ion is not clear in this reaction.

2.3. Reactions of 2 and 1 with elemental S

The transfer of a sulfur atom to the ligand from the heterocumulene suggested the possibility of adding a sulfur atom to the ligand by reaction with elemental sulfur. Reactions with elemental sulfur were carried out under similar reaction conditions but with different results. With the dimeric complex 2, CuS and dppmS₂ were isolated. In this case, the formation of the dppmS complex of copper 9 could not be detected. A similar observation was made when the trimeric complex was treated with sulfur. A plausible explanation for this behavior was obtained by the treatment of $[Cu(dppmS)_2]ClO_4$ with sulfur. Under the reaction conditions, only the free ligand $dppmS_2$ and a brown solid were formed. The brown solid was shown to be a mixture of sulfides of copper from EDAX analysis. The dppmS complex is apparently unstable in the presence of sulfur and converts to CuS.

3. Summary

The reactions carried out here with the hydroxo complex reveals the unique reaction pathways accessible to copper in the presence of the OH group rather than the aryloxy group. The importance of a protic solvent in the reaction of heterocumulenes is also noteworthy. Since alcohols and phenols have been shown to be involved in hydrogen bonding, the presence of these solvents invoke different reactivity pathways. Lastly, the heterocumulenes, especially CS_2 , transfer S in a mild and effective manner.

4. Experimental

4.1. Materials

Dichloromethane, methanol, petroleum ether and *n*-hexane were purified and dried by conventional methods

and distilled under nitrogen. [Cu(CH₃CN)₄]ClO₄ was freshly prepared before use. (Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive.*) Bis(diphenylphosphino)methane, PhNCS and MeNCS were purchased from Aldrich. Carbondisulfide was bought from Spectrochem (India).

4.2. Synthesis

All reactions were carried out in an atmosphere of dried nitrogen using standard Schlenk and vacuum line techniques. $[Cu_3(dppm)_3OH](ClO_4)_2$ [16a] and $[Cu_2(dppm)_2(CH_3CN)_4](ClO_4)_2$ [16b] were prepared using the procedure reported in the literature.

4.3. Preparation of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2 \cdot PhNC-S \cdot 2CH_2Cl_2$ (3)

To a solution of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂, PhNCS 0.084 ml (0.07 mmol) was added at room temperature. The mixture immediately turned yellow and was stirred for 8 h at room temperature. The solvent was removed under reduced pressure resulting in an oily residue. Trituration with *n*-hexane resulted in the precipitation of an yellow product identified as **3**: Yield 79%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.25–3.49 (m, 6H, CH₂), 6.94–7.35 (m, 65H, Ph), 5.31 (4H, CH₂Cl₂). ³¹P{¹H} NMR (400 MHz, CDCl₃, 297 K): δ –14.6 ppm. IR (KBr, cm⁻¹): 1098 (s, br), 620 (m) [ClO₄]; 2065 (br, N=C=S): Anal. Calc. for C₈₄H₇₆Cu₃N₁O₉P₆S₁Cl₆: C, 54.22; H, 4.12; N, 0.75. Found: C, 54.43; H, 4.81; N, 1.08%.

4.4. Preparation of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2$ ·MeNC-S·2CH₂Cl₂ (4)

Following the procedure adopted for obtaining **3**, the reaction of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂ with MeNCS 0.048 ml (0.07 mmol) gave compound **4**: Yield 76%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.2–3.51 (m, 6H, CH₂, 3H, CH₃), 6.94–7.26 (m, 60H, Ph), 5.31 (4H, CH₂Cl₂). ³¹P{^H} NMR (400 MHz, CDCl₃, 297 K): δ –14.2 ppm. IR (KBr, cm⁻¹): 1092 (s, br), 623 (m) [ClO₄]: 2055 (br, N=C=S): Anal. Calc. for C₇₉H₇₄Cu₃N₁O₉P₆S₁Cl₆: C, 52.63; H, 4.08; N, 0.78. Found: C, 51.48; H, 4.75; N, 1.53%.

4.5. Preparation of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2$ ·C-S₂·CH₂Cl₂ (5)

To a solution of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2$ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂, CS₂ 0.042 ml (0.07 mmol) was added at room temperature the mixture turned red immediately and was stirred for 8 h at room temperature. The solvent was removed under reduced

pressure resulting in a red solid. It was redissolved in minimum amount of CH₂Cl₂ and addition of petroleum ether resulted in the precipitation of the product. The precipitate was washed with *n*-hexane to give analytically pure compound **5**: Yield 71%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.30–3.45 (m, 6H, CH₂), 6.94–7.21 (m, 60H, Ph), 5.31 (2H, CH₂Cl₂). IR (KBr, cm⁻¹): 1097 (s, br), 623 (m) [ClO₄]; 1125 (C=S): Anal. Calc. for C₇₇H₆₉Cu₃O₉P₆S₂Cl₄: C, 53.85; H, 4.05. Found: C, 53.35; H, 4.73%.

4.6. Preparation of $[Cu_3(dppm)_3(SC(O)NHPh)]$ - $(ClO_4)_2$ (6)

Following procedure used for preparing **3**, a solution of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ (0.3 g, 0.023 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), PhNCS 0.084 ml (0.07 mmol) were reacted at room temperature. The yellow product was identified as **6**: Yield 75%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 4.32 (s, 2H, CH₂), 3.1–3.2 (m, 4H, CH₂), 6.94–7.34 (m, 65H, Ph), 10.4 (br, 1H, NH). ³¹P{¹H} NMR (400 MHz, CDCl₃, 297 K): δ –14.2 ppm. IR (KBr, cm⁻¹): 1092 (s, br), 624 (m) [ClO₄]; 510 (C–S); 1450 (C–N); 1550 (C=O); 3325 (b, N–H): Anal. Calc. for C₈₂H₇₂Cu₃N₁O₉P₆S₁Cl₂: C, 58.19; H, 4.29; N, 0.83. Found: C, 57.78; H, 4.72; N, 0.69%.

4.7. Preparation of $[Cu_3(dppm)_3(SC(O)NHMe)]$ - $(ClO_4)_2 \cdot CH_2Cl_2 \cdot CH_3OH$ (7)

To a solution of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), MeNCS 0.048 ml (0.07 mmol) was added at room temperature. Following the procedure reported for **3**, gave a yellow product 7: Yield 73%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.26–3.50 (m, 6H, CH₂), 6.95–7.31 (m, 60H, Ph), 7.81 (br, 1H, NH). 5.30 (2H, CH₂Cl₂), 3.49 (3H, CH₃OH). ³¹P{¹H} NMR (400 MHz, CDCl₃, 297 K): δ –13.9 ppm. IR (KBr, cm⁻¹): 1092 (s, br), 623 (m) [ClO₄]; 507 (C–S); 1450 (C–N); 1625 (C=O); 3250 (b, N–H): Anal. Calc. for C₇₉H₇₆Cu₃-N₁O₁₀P₆S₁Cl₄: C, 53.91; H, 4.18; N, 0.79. Found: C, 53.71; H, 4.59; N, 1.71%.

4.8. Reaction of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2$ with CS_2 (8)

To a solution of $[Cu_3(dppm)_3OH]$ $(ClO_4)_2$ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), CS₂ 0.042 ml (0.07 mmol) was added at room temperature and the yellow mixture stirred for 8 h at room temperature. The solvent was removed under reduced pressure to give a yellow solid. The solid was redissolved in a minimum amount of CH₂Cl₂ and addition of petroleum ether resulted in the precipitation of the product. which was washed with *n*-hexane to give pure **8**

[Cu₄(dppm)₄S] (ClO₄)₂: Yield 85%; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.21 (s, 4H, CH₂), 3.36 (s, 4H, CH₂), 6.91–7.19 (m, 80H, Ph). Anal. Calc. for C₁₀₀H₈₈Cu₄ O₈P₈S₁Cl₂: C, 59.38; H, 4.38. Found: C, 59.28; H, 4.43%.

4.9. Reaction of $[Cu_2(dppm)_2(CH_3CN)_4]$ $(ClO_4)_2$ with *PhNCS*

To a solution of $[Cu_2(dppm)_2(CH_3CN)_4]$ (ClO₄)₂ 0.15 g (0.117 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), PhNCS 0.042 ml (0.351 mmol) was added at room temperature. The mixture immediately turned yellow and was stirred for 8 h at room temperature. The solvent was removed under reduced pressure resulting in an oily residue identified as **6** from spectroscopic data. Trituration with *n*-hexane resulted in the precipitation of **6** in 78% yield.

4.10. Reaction of $[Cu_2(dppm)_2(CH_3CN)_4]$ $(ClO_4)_2$ with MeNCS

To a solution of $[Cu_2(dppm)_2(CH_3CN)_4]$ (ClO₄)₂ 0.15 g (0.117 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), MeNCS 0.024 ml (0.07 mmol) was added at room temperature. On stirring for 10 min, the reaction mixture turned light yellow and was further stirred for 8h at room temperature. The solvent was removed under reduced pressure resulting in an oily residue. Trituration with *n*-hexane resulted in the precipitation of 7 as an yellow solid (Yield 72%).

4.11. Reaction of $[Cu_2(dppm)_2(CH_3CN)_4]$ $(ClO_4)_2$ with CS₂ to give $[Cu_4(dppm)_4S](ClO_4)_2$ (8)

To a solution of $[Cu_2(dppm)_2(CH_3CN)_4]$ (ClO₄)₂ 0.15 g (0.117 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), CS₂ 0.021 ml (0.07 mmol) was added at room temperature. On stirring for 10 min, the reaction mixture turned light yellow and was further stirred for 8 h at room temperature. The solvent was removed under reduced pressure to give compound **9** [Cu(dppmS)₂] ClO₄: Yield 43.5% with respect to copper; ¹H NMR (200 MHz, CDCl₃, 297 K): δ 3.73 (m, 4H, CH₂), 7.15–7.47 (m, 32H, Ph), 7.67–7.76 (8H, Ph); Anal. Calc. for C₅₀H₅₄CuO₄P₄S₂Cl: C, 60.30; H, 4.45. Found: C, 60.39; H, 4.57%. CCDC 217020.

4.12. Reaction of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ with S₈

To a solution of $[Cu_3(dppm)_3OH]$ (ClO₄)₂ 0.3 g (0.023 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), S₈ 0.024 mg (0.092 mmol) was added at room temperature and the mixture turned yellow. After stirring for 8 h at room temperature, a brown solid precipitated out and a colorless solution remained. The brown solid was

removed by filtration, this contains 50.13% of copper, 39.38% of sulfur and 10.47% of chloride by EDAX analysis, the solvent from the filtrate removed under reduced pressure resulting in a white solid $7(C_{25}H_{22}P_2S_2)$; yield 92%: ¹H NMR (200 MHz, CDCl₃, 297 K): δ 4.23 (2H, CH₂), 7.26–7.39 (m, 16H, Ph), 7.62–7.69 (4H, Ph): IR (KBr, cm⁻¹): 610 (s, P=S).

4.13. Reaction of $[Cu_2(dppm)_2(CH_3CN)_4]$ $(ClO_4)_2$ with S_8

To a solution of $[Cu_2(dppm)_2(CH_3CN)_4]$ (ClO₄)₂ 0.15 g (0.117 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), S₈ 0.120 g (0.468 mmol) was added at room temperature. After stirring for a period of 8 h at room temperature, a brown solid precipitated out leaving behind a colorless solution. The brown solid was removed by filtration, the filtrate was concentrated and dried under reduced pressure to give compound **10**; (73% yield).

4.14. Reaction of $[Cu(dppmS)_2]$ ClO₄ with S₈

To a solution of $[Cu(dppmS)_2] ClO_4$: 0.1 g (0.1 mmol) in 20 ml of CH₂Cl₂ and CH₃OH (1:1), S₈ 0.102 g (0.4 mmol) was added and after a period of stirring for 8 h at room temperature, a brown solid was precipitated leaving a colorless solution. The brown solid was removed by filtration, the solvent was removed from the filtrate under reduced pressure to give compound **10**; (94% yield).

4.15. X-ray structure determination

Crystals of complex 9 suitable for diffraction studies were glued to the tip of glass fibers and transferred to a computer controlled Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromatized Mo Ka radiation. The intensity data were collected and corrected for Lorentz, polarization and absorption effects using DI-FABS. The positions of the heavy atoms were determined by Patterson methods using SHELXS-86 [17]. The remaining atoms were located from difference Fourier analysis using SHELXTL-97 [18]. Carbon atoms C2, C3, C11 and C12 on the phenyl ring attached to P1 showed positional disorder and so they were assigned sharing occupancy and refined isotropically using constraints. H atoms attached to these carbons could neither be located nor fixed. Hydrogen atoms were included in the final stage of the refinement on calculated positions bonded to their carrier atoms. All crystallographic computations were performed using the WINGX package [19].

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Appendix A. Supplementary material

Crystallographic data (excluding structural factors) for the structural analysis of 9, has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 217020. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.05.026.

References

- (a) J. Robin Fulton, A.W. Holland, D.J. Fox, R.G. Bergman, Acc. Chem. Res. 35 (2002) 44;
 - (b) J.P. Collman, R. Boulatov, Inorg. Chem. 40 (2001) 560;
 - (c) M.H. Chisholm, R.E. Davidson, J.C. Huffman, K.B. Quinlan, J. Am. Chem. Soc. 123 (2001) 9652;
 - (d) Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T. Koizumi, H. Yamazaki, Y. Wakatsuki, J. Am. Chem. Soc. 122 (2000) 10533;
 (e) D.S. Glueck, L.J. Newman Winslow, R.G. Bergman, Organometallics 10 (1991) 1462;
 - (f) H.E. Bryndza, W. Tam, Chem. Rev. 88 (1988) 1163;
 - (g) D.J. Darensbourg, K.M. Sancher, J.H. Reibenspies, Inorg. Chem. 27 (1988) 3269;
 - (h) H.E. Bryndza, Organometallics 4 (1985) 406;
 - (i) T.J. McNeese, T.E. Mueller, D.A. Wierda, D.J. Darensbourg, T.J. Delord, Inorg. Chem. 24 (1985) 3465.
- [2] (a) M.A. Lockwood, P.E. Fanwick, I.P. Rothwell, Organometallics 16 (1997) 3574;

(b) D.J. Darensbourg, B.L. Mueller, J.H. Reibenspies, C.J. Bischoff, Inorg. Chem. 29 (1990) 1789;

(c) D.J. Darensbourg, K.M. Sanchez, J.H. Reibenspies, A.L. Rheingold, J. Am. Chem. Soc. 111 (1989) 7094;

- (d) R.A. Michelin, G. Strukul, N. Bresciani-Pahor, E. Zangrando, L. Randaccio, Inorg. Chim. Acta. 184 (1984) 229;
- (e) M.H. Chisholm, F.A. Cotton, M.W. Extine, W.W. Reichert, J. Am. Chem. Soc. 100 (1978) 1727.
- [3] (a) N. Narasimhamurthy, A.G. Samuelson, H. Manohar, J. Chem. Soc., Chem. Commun. (1989) 1803;

(b) C. Wycliff, A.G. Samuelson, M. Nethaji, Inorg. Chem. 35 (1996) 5427.

- [4] S.P. Abraham, N. Narasimhamurthy, M. Nethaji, A.G. Samuelson, Inorg. Chem. 32 (1993) 1739.
- [5] R.D. Simpson, R.G. Bergman, Angew. Chem. Int. Ed. 31 (1992) 220.
- [6] (a) J.C.M. Ritter, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 2580;

(b) J.C.M. Ritter, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 6826;

- (c) R.W. Hay, N. Govan, Polyhedron 14 (1996) 2381.
- [7] R.G. Bergman, Polyhedron 22 (1995) 322.
- [8] K. Ilg, W. Werner, Organometallics 20 (2001) 3782.
- [9] (a) I. Torresan, R.A. Michelin, A. Marsella, A. Zanardo, F. Pinna, G. Strukul, Organometallics 10 (1991) 623;
 (b) T.G. Appleton, M.A. Bennett, J. Organomet. Chem. 55 (1973) C88.
- [10] S. Ganguly, J.T. Mague, D.M. Roundhill, Inorg. Chem. 31 (1992) 3831.
- [11] (a) T.A. Budzichowski, M.H. Chisholm, K. Folting, J.C. Huffman, W.E. Streib, J. Am. Chem. Soc. 117 (1995) 7428;
 (b) D.J. Darensbourg, M.L. Jones, L.M. Monica, J.H. Reibenspies, Inorg. Chem. 32 (1993) 4675.
- [12] (a) J.K. Bera, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1998;
 (b) J.K. Bera, M. Nethaji, A.G. Samuelson, Inorg. Chem. 38 (1999) 218.
- [13] (a) W.-W.V. Yam, W.-K. Lee, T.-F. Lai, J. Chem. Soc., Chem. Commun. (1993) 1571;

(b) V.W. Yam, K.K.W. Lo, Inorg. Chem. 19 (1997) 209.

- [14] (a) M. Lusser, P. Peringer, Inorg. Chem. Acta 127 (1987) 151;
 (b) G. Pilloni, B. Longato, G. Bandoli, B. Corain, J. Chem. Soc., Dalton Trans. (1997) 819.
- [15] M. Valderrama, R. Contreras, M. Bascunan, S. Alegra, Polyhedron 14 (1995) 2239.
- [16] (a) D. Ho, R. Bau, Inorg. Chem. 22 (1983) 4079;
 (b) J. Diez, M.P. Gamasa, J. Gimeno, A. Tiripicchio, M.T. Camellini, J. Chem. Soc., Dalton Trans. (1987) 1275.
- [17] G.M. Sheldrick, SHELXS-86: A Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1986.
- [18] G.M. Sheldrick, SHELXL-97: A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [19] WINGX (1.63.02), An Integrated System of Windows Program for the Solution, Refinement, and Analysis of Single Crystal X-Ray Diffraction.