

INSERTION REACTIONS OF CARBON DISULFIDE INTO CARBON—COPPER BONDS OF AROMATIC ORGANOCOPPER(I) COMPOUNDS AND OF THEIR COMPLEXES WITH TRIPHENYLPHOSPHINE AND BIS(DIPHENYLPHOSPHINO) ETHANE

A. CAMUS, N. MARSICH and G. NARDIN

Istituto di Chimica dell'Università di Trieste, 34127 Trieste (Italy)

(Received October 11th, 1979)

Summary

Aromatic organocopper compounds (phenyl-, *m*-, *p*-tolyl-, *o*-anisyl-copper) react with CS₂ to give unstable copper compounds, except for *o*-tolylcopper, from which polymeric *o*-TCSSCu (*o*-T = *o*-tolyl) and another derivative, probably [*o*-TCSSCu₂]_{*n*}, were obtained. Tritylperoxide is the main by-product in the reaction with phenyl copper. Arylcopper(I) complexes with triphenylphosphine and diphos undergo insertion reaction of CS₂ to form the corresponding dithiocarboxylate complexes ArCSSCu(PPh₃)₂ and (ArCSSCu)_{*m*}-(diphos)_{*n*} (*m* = 1, *n* = 1; *m* = 2, *n* = 3). These afford almost pure ArCSSCH₃ by reaction with CH₃I. The crystal structure of PhCSSCu(PPh₃)₂ has been determined.

Introduction

In recent years insertions of carbon disulfide into transition metal—carbon bonds have attracted considerable attention. Examples of this type of reaction with compounds of various metals are known [1], and the reactions involving alkylcopper complexes having tertiary phosphine ligands were investigated recently [2]. We had several times noted that carbon disulfide reacts with organocopper compounds [3–4], but had not established the nature of the products. In the light of work of Miyashita and Yamamoto [2] we have reexamined the reactions between CS₂ and some complexed and uncomplexed organocopper compounds of the aromatic series.

Results and discussion

The compounds examined were (i) phenyl-, (ii) *o*-, *m*-, *p*-tolyl-copper (denoted by *o*-, *m*-, or *p*-T); and (iii) *o*-anisyl copper (denoted by *o*-A) *, and

* Phenylethynylcopper was found to be unreactive.

some of their complexes with triphenylphosphine and bis(diphenylphosphino)ethane (diphos). Except for *o*-tolyl copper, insertion of CS₂ gives unstable intermediates, while the phosphine derivatives give stable dithiocarboxylate complexes.

Reactions between ArCu and CS₂

The reaction between PhCu and carbon disulfide at 0°C gives a brown solution, and during a few hours a brown-black solid separates as the solution fades to yellow. The precipitate is an amorphous powder which cannot be crystallized. It contains approximately one phenyl group and four sulfur atoms for every six copper atoms. The amounts of organic substance remains almost constant even on varying drastically the conditions used in washing the solid. The mother liquor contains only organic products: viz., traces of benzene, about 14% of diphenyl, and other high boiling compounds. When the mother liquors are handled in the air the main product is tritylperoxide, but all attempts to detect trityl radicals in the solution failed.

The corresponding peroxide is also a minor by-product in the reaction of *m*-TCu *. *p*-TCu and *o*-ACu give as by-products yellow oils, diarenes, and minor amounts of high molecular weight compounds, involving at least 12 and 4 Ar groups, respectively.

Completely different results were obtained in the reaction of *o*-TCu. In this case Ar and copper mainly remain together in the same molecule, and from the precipitate two definite products can be isolated. The first is the expected *o*-TCSSCu, for which its insolubility suggests a polymeric nature. The second is probably [*o*-TCSSCu₂]_{*n*} (*n* = about 5 in CHCl₃). The two products give very similar IR spectra, though with broader bands for the second compound. In comparison with *o*-TCu, new bands, attributed in order to $\nu(\text{CSS})$ asym, $\nu(\text{CSS})$ sym, and $\nu(\text{CSS})$ appear at about 1000vs, 900ms and 640m cm⁻¹.

No copper compounds of definite composition were isolated from the reaction with *o*-ACu.

Reactions between ArCu and CS₂ in the presence of tertiary phosphines

With triphenylphosphine PhCu gives complexes of the type (PhCu)_{*n*}PPh₃ (*n* = 2, 3) [5]. These complexes react violently with CS₂ even at 0°C, giving as the main product PhCSSCu(PPh₃)₂, an insoluble black residue, and a significant amount of diphenyl. Probably, in accord with the following equation,



the insertion of CS₂ initially gives some PhCu, which then reacts as noted above with the excess of CS₂, to give a product which partly decomposes owing to the sudden increase of the temperature. PhCSSCu(PPh₃)₂ is in fact obtained readily and in better yield by mixing the reagents in inverse order and different ratios, as described in the experimental section. The same technique was used for the

* The structural characteristics of the peroxides isolated suggest that the corresponding organo-copper compounds must contain preferential groupings of three copper atoms (see also the formation of (PhCu)₃PPh₃ complex [5]. A trimeric structure was recently found for the *m*-TAG, in which bridging aryl groups are present, as in organocopper compounds [6]. However the same authors report that *m*-TCu is a tetramer.

reactions between triphenylphosphine and the other organocopper compounds. Deep coloured air-stable crystals of $\text{ArCSSCu}(\text{PPh}_3)_2$ were isolated in all cases. Starting from a 1 : 1 ratio of $[\text{ArCu}]/[\text{PPh}_3]$ there was also evidence of formation of complexes with only one phosphine, but they were not obtained pure. Upon crystallization they disproportionate, with formation of $\text{ArCSSCu}(\text{PPh}_3)_2$ (isolated) and probably ArCSSCu , which in turn decomposes. Formation of complexes with a $\text{Cu} : \text{P} = 1$ ratio is not surprising, since derivatives of this stoichiometry have been isolated in the alkyl [7], alkoxide [8], alkylthio and arylthio [9] series.

The reaction with diphos gives selectively ArCSSCu -diphos complexes, and these were also produced when the preformed isolated complexes $(\text{ArCu})_2(\text{diphos})_3$ [10] were treated with CS_2 . A derivative of 2 : 3 stoichiometry, which is favoured in the reactions with aliphatic organocopper compounds [2], was formed only from *o*-TCu. This complex, upon recrystallization from hot solvents also disproportionates to the 1 : 1 derivative. Refluxing in CS_2 does not give $[\text{CuPPH}_2(\text{CS}_2)\text{diphos}]$ as it does for $(\text{alkylCu})_2(\text{diphos})_3$ complexes, the 1 : 1 complex again being formed. A product of the above formula and having NMR and IR spectra corresponding to those * of Yamamoto's compounds [2], was, however, obtained by dissolving the well known $[\text{PPh}_2\text{Cu}(\text{diphos}) \cdot \text{C}_6\text{H}_6]$ [11] in CS_2 . Comparison of its IR spectrum with that of $[\text{PPh}_2\text{Cu}(\text{diphos})]$ reveals new frequencies due to the introduction of CS_2 as a multishoulder broad m band in the $1030\text{--}950\text{ cm}^{-1}$ range (maxima at about 1018 and 998 cm^{-1}) and a broad m band at 504 cm^{-1} . These values leave some doubt about the mode of bonding of CS_2 in the complex. The IR data which most nearly approach them are those reported by Butler and Fenster [12] for a bridging CS_2 , but the latter data differ from those for the few other known complexes of this type [13]. $[\text{PPh}_2\text{Cu}(\text{CS}_2)\text{diphos}]$ is an electrolyte in dichloroethane, but its solubility is too low to permit reliable measurements of conductivity or molecular weight.

Table 1 lists the analytical data and some physical properties of the isolated dithiocarboxylate complexes. Reactions of $\text{ArCSSCu}(\text{PPh}_3)_2$ (I) and ArCSSCu -diphos (II) complexes with methyl iodide afford ArCSSCH_3 in almost quantitative yield. At the same time Cu(I)diphos complexes are formed from II, whereas mixtures of complexes with phosphonium moieties are obtained from the species I.

Complexes I are not electrolytes. The low solubility of the diphos derivatives restricted the measurements to the *o*-substituted compounds. Only $(\text{o-TCSSCu})_2(\text{diphos})_3$ showed detectable conductivity ($\leq 16\text{ mhos cm}^2\text{ mol}^{-1}$) in dichloroethane.

Molecular weight measurements were limited to triphenylphosphine derivatives because of the limited solubilities. Values corresponding to the theoretical ones were obtained only for the $\text{ArCSSCu}(\text{PPh}_3)_2$ complexes with *o*-substituted aryls in toluene; the other compounds are partially dissociated, and the dissociation is larger in CHCl_3 . In contrast, in complexes with a $\text{Cu} : \text{P}$ ratio = 1 oligomeric species are present.

The IR spectra show absorption bands of m or ms intensities in the 1030--

* Kindly furnished by those authors.

TABLE 1

ANALYTICAL DATA FOR COPPER(I) DITHIOCARBOXYLATES

Formula	Colour	m.p. (°C)	Analysis found (calc.)(%)			
			C	H	Cu	P
PhCSSCu(PPh ₃) ₂	Brown-black	184—187 dec.	70.2 (69.66)	4.62 (4.76)	8.55 (8.57)	8.7 (8.36)
<i>o</i> -TCSSCu.PPh ₃	Brown	171—172	63.7 (63.33)	4.38 (4.50)	12.38 (12.89)	6.5 (6.28)
<i>o</i> -TCSSCu(PPh ₃) ₂	Minium-red	200—201	69.7 (69.96)	4.86 (4.94)	8.29 (8.41)	
<i>o</i> -TCSSCu(PPh ₃) ₂ · toluene	Violet-red	201—202	71.9 (72.27)	5.15 (5.35)	7.43 (7.49)	7.1 (7.31)
<i>m</i> -TCSSCu(PPh ₃) ₂	Green-brown	195—196	69.5 (69.96)	4.95 (4.94)	8.29 (8.41)	
<i>p</i> -TCSSCu(PPh ₃) ₂	Olive green-red (dicroic)	161—162	69.8 (69.96)	4.77 (4.94)	8.44 (8.41)	8.5 (8.20)
<i>o</i> -ACSSCu · PPh ₃	Red-brown	159—161	61.4 (61.34)	4.70 (4.36)	11.94 (12.48)	
<i>o</i> -ACSSCu(PPh ₃) ₂	Deep brick-red	186—188	68.2 (68.51)	4.87 (4.84)	8.04 (8.24)	
<i>o</i> -ACSSCu(PPh ₃) ₂ · toluene	Orange-red	186—187	71.0 (70.9)	4.98 (5.25)	7.43 (7.17)	tol. 10.1 (10.6)
PhCSSCudiphos	Olive-green	213—216 dec.	64.5 (64.42)	4.71 (4.75)	10.25 (10.33)	
<i>o</i> -TCSSCudiphos	Orange-red	234 dec.	64.9 (64.89)	4.94 (4.97)	10.21 (10.10)	9.9 (9.85)
(<i>o</i> -TCSSCu) ₂ (diphos) ₃ ^a	Pale orange	213—217	68.3 (68.13)	5.22 (5.23)	7.63 (7.67)	
(<i>o</i> -TCSSCu) ₂ (diphos) ₃ · CH ₂ Cl ₂	Orange	210—212	62.8 (63.11)	5.16 (4.97)	6.78 (6.96)	
<i>m</i> -TCSSCudiphos	Light olive green	225—227	65.2 (64.89)	4.94 (4.97)	10.21 (10.10)	9.9 (9.85)
<i>p</i> -TCSSCudiphos	Brown-green	240—244 dec.	65.4 (64.89)	4.83 (4.97)	9.97 (10.0)	10.1 (9.85)
<i>o</i> -ACSSCudiphos	Pink	250—253 dec.	62.9 (63.28)	4.91 (4.84)	9.57 (9.85)	9.5 (9.60)
[CuPPh ₂ CS ₂ diphos] _n	Orange-brown	176—178	65.0 (64.76)	4.47 (4.74)	8.63 (8.79)	12.8 (12.85)

T = tolyl, A = anisyl. ^a In hot solvents disproportionates to *o*-TCSSCudiphos.

TABLE 2

IR DATA FOR COPPER(I) DITHIOCARBOXYLATES

Ar	ArCSS(PPh ₃) ₂		ArCSSCudiphos	
	$\nu(\text{CSS})$ asym (cm ⁻¹)	$\nu(\text{CSS})$ sym (cm ⁻¹)	$\nu(\text{CSS})$ asym (cm ⁻¹)	$\nu(\text{CSS})$ sym (cm ⁻¹)
Ph	1010, 990	924	996	925
<i>o</i> -T	1009	926	1004	927
<i>m</i> -T	1022	985	1026	986
<i>p</i> -T	1011	925	1010	926
<i>o</i> -A	1013	926	1014	927

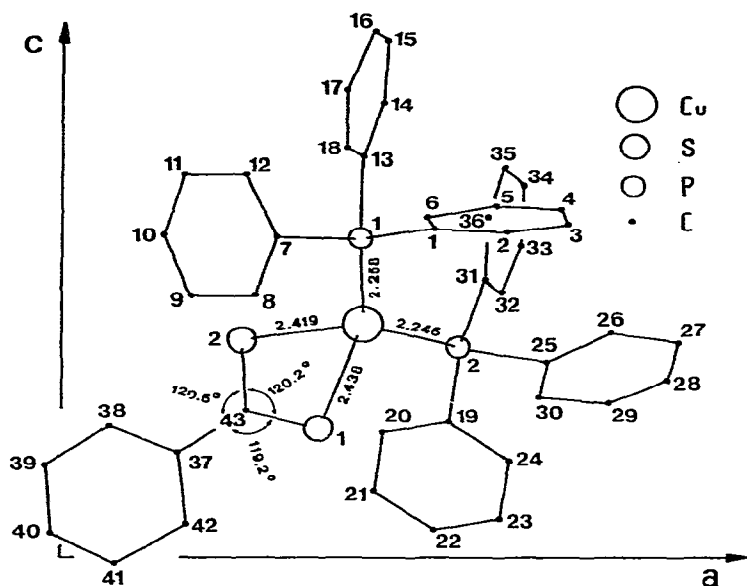


Fig. 1. The *o*-TCSSCu(PPh₃)₂ molecule viewed along the crystallographic *b* axis.

995 cm⁻¹ region (superposed to phenyl modes) and at about 925 cm⁻¹ (higher frequency for the *m*-tolyl derivatives, Table 2). Compared with the (*o*-TCu)₂-(diphos)₃ the corresponding dithiocarboxylate shows a weakening of the two medium intensity bands at 1207 and 1162 cm⁻¹, while new bands appear at 1025 and 903 cm⁻¹. The rest of the spectrum is essentially unchanged.

The frequencies reported in Table 2 for the $\nu(\text{CSS})$ stretchings in I and II differ markedly from those found for alkyl complexes of the same type [2], but are in agreement with those of aromatic dithiocarboxylates of other metals [14].

The dithiocarboxylato group is bonded to copper as a bidentate ligand, as proved by the X-ray structure of PhCSSCu(PPh₃) (Fig. 1). The crystals consist of monomeric units, resulting from insertion of CS₂ into the copper-phenyl bond. The coordination around the copper atom is tetrahedral with a large distortion, as observed for the related complexes C₂H₅SCSSCu(PPh₃)₂ [15] and CH₃OCSSCu(PPh₃)₂ [16]. The two sulfur atoms are symmetrically coordinated to the copper (Cu-S(1) 2.438(3); Cu-S(2) 2.419(3) Å). The Cu-P distances (2.258(3); 2.246(3) Å) fall in the 2.24–2.28 Å range characteristic of the presence of two copper-phosphorus bonds on the same metal atom [17]. Finally, after insertion of carbon disulfide, the C(43) carbon atom appears to be sp² hybridized. The sum of the angles around it is 360°, showing the coplanarity of S(1)S(2)C(43)C(37) atoms.

Experimental

All reactions were carried out under dry nitrogen. Solvents were carefully dried and distilled under nitrogen immediately before use. Carbon disulfide was

TABLE 3
ANALYTICAL DATA FOR COPPER CONTAINING PRODUCTS

	Run	Analysis (%)			
		C	H	Cu	S
PhCu	1	11.2	0.78	63.49	20.15
	2	13.3	1.07	63.50	20.95
	3	12.2	0.60	63.57	18.91
<i>m</i> -TCu	1	13.7	1.04	58.16	26.7
	2	14.3	1.04	58.09	21.54
<i>p</i> -TCu	1	14.2	1.10	61.85	19.30
	2	14.3	1.13	61.75	20.85

of reagent grade quality and was dried over CaH_2 . The organocopper compounds and complexes were prepared by published methods [5,10,18]. $[\text{PPh}_2\text{-Cudiphos} \cdot \text{Toluene}]_2$ was prepared by reaction in toluene between PhCu or *p*-TCu and diphos in 1 : 2 ratio *.

Reactions of organocopper compounds with CS_2

CS_2 (20 ml) was distilled at -50°C into a vessel containing 1 g of the organocopper compound as a solid or suspended in toluene (30 ml). Increase of the temperature to 0°C gave a deep brown solution, from which a brown-black solid slowly precipitated. Different preparations of PhCu showed dramatic difference of solubility, as often observed previously, probably because of varying degree of polymerization of the compound, which also affects the purity [19] and reactivity [20]. Complete formation of the precipitates from the *o*-substituted compounds required several days.

The black solids were filtered off at room temperature, washed with CS_2 until the washings were colourless, and dried in vacuo. Their composition appears to be rather variable, but this is due mainly to uncertainty in the sulfur determinations, which for this kind of compound are not reproducible and probably low. Illustrative analytical data for phenyl, *m*-T-, and *p*-T-copper derivatives are listed in Table 3.

Pyrolysis at 200°C of the residue of the PhCu reaction gave benzoic acid along with some unidentified liquid products **. The corresponding acid was also isolated from *p*-TCu. About 1 g of *o*-TCu was dissolved in CS_2 (30 ml) and $[\text{o-TCSSCu}]_n$.

temperature raised to 0°C . The turbid solution was then filtered and the deep red filtrate was kept for two days at room temperature, during which it slowly become brown violet and a gelatinous solid of the same colour sepa-

* Our experiments confirm the mechanism of reaction proposed by van Koten et al. which differ from that suggested by other authors [11]. ArH is present in quantitative amount in the mother liquors (GLC), and the other main by-product is diphenylvinyl phosphine. Under the same conditions *o*-TCu gave mainly the $(\text{o-TCu})_2(\text{diphos})_3$ complex.

** Trityl peroxide, which is the most likely impurity if the organic entity does not remain bonded to copper, does not form benzoic acid under these conditions even in the presence of copper oxides.

rated. This was filtered off, washed repeatedly with CS_2 until the washings were almost colourless, and dried in vacuo, m.p. 195°C (dec.). Found: C, 41.2; H, 3.0; Cu, 27.65; S, 27.1; $\text{C}_8\text{H}_7\text{CuS}_2$ calcd.: C, 41.62; H, 3.06; Cu, 27.53; S, 27.78%.

The compound is practically insoluble in common solvents, and its solubility in CS_2 is very slight.

$[\text{o-TCSSCu}_2]_n$. The filtrate from the above reaction was evaporated to dryness and the residue dissolved in toluene. The solution was filtered, and pentane was added to give a brown-black solid. This was filtered off, washed repeatedly with pentane, and dried in vacuo. m.p.: gradual decomposition starting at 150°C . The compound is moderately soluble in toluene, benzene, $\text{CH}_2\text{-Cl}_2$ and CHCl_3 as well as in CS_2 . Attempts to recrystallize it gave a product with increased Cu/S ratio. Found: C, 32.0; H, 2.30; Cu, 41.41; S, 22.3; $\text{C}_8\text{H}_7\text{Cu}_2\text{S}_2$ calcd.: C, 32.64; H, 2.40; Cu, 43.17; S, 21.78%. M.W., 1505 (calcd. 294.3) (2.5% w/w in CHCl_3).

It is to be noted that in different samples the sum of C, H, Cu and S was always $\leq 98\%$, what may indicate contamination by oxygen, and in particular that the copper content is always rather low, while the sulphur content is high. These results may indicate presence of significant amounts of *o*-TCSSCu.

Treatment of the mother liquors

Tritylperoxide. Upon bubbling air into the yellow mother liquor obtained from the reaction between PhCu and CS_2 , the solution rapidly absorbed oxygen and the colour faded and white crystals separated. These were filtered off, washed repeatedly with acetone, and dried in vacuo. Yield 50%. Needles from hot benzene + EtOH; m.p. $189\text{--}190^\circ\text{C}$ (lit. $187\text{--}188$) [21]. Their IR spectrum is in satisfactory agreement with the data reported by Tanaka [22] (bands at 647 and 633 cm^{-1} (ms and not w) band at 720 cm^{-1} not present). Triphenylcarbinol was obtained by decomposition in conc. H_2SO_4 , as described by this author.

Found: C, 88.1; H, 5.83; O, 6.10; $\text{C}_{38}\text{H}_{30}\text{O}_2$ calcd.: C, 88.00; H, 5.83; O, 6.17%. M.W. 517 (X ray), 535 (in toluene) (calcd. 518.6).

Tri(m-tolyl)methylperoxide. The mother liquor was evaporated to dryness. The orange oil was extracted with pentane and the residue (20%) recrystallized from hot n-hexane and charcoal: white crystals, m.p. $164\text{--}165^\circ\text{C}$ (lit. $158\text{--}159^\circ\text{C}$ [23]). Found: C, 87.8; H, 6.96; O, 5.28, $\text{C}_{44}\text{H}_{42}\text{O}_2$ calcd.: C, 87.66; H, 7.03; O, 5.31%.

Preparation of the complexes

$\text{ArCSSCu}(\text{PPh}_3)_2$ (I). About 0.5 g of the organocopper compound were suspended in toluene at -50°C . (20 ml) containing a few ml of CS_2 . The mixture was warmed to 0°C and solid PPh_3 ($[\text{PPh}_3]/[\text{ArCu}] = 2$) was immediately added with stirring. The solution lightened in colour and a microcrystalline solid began to form after $1/2\text{--}1$ h. After 2 h the mixture was warmed to room temperature and stirring continued for some hours. The precipitate was filtered off, washed repeatedly with toluene and, dried in vacuo.

The complexes can be recrystallized from hot toluene or CH_2Cl_2 -ether.

Structure of $\text{PhCSSCu}(\text{PPh}_3)_2$. Crystal data: $\text{C}_{43}\text{H}_{35}\text{CuP}_2\text{S}_2$, M.W. 741.3,

orthorhombic, space group $P2_12_12_1$ (from systematic absences), a 20.280(7), b 16.779(6), c 11.229(6) Å, U 3821.0 Å³, $z = 4$, D_{obs} 1.27 g/cm³, D_{calc} 1.29 g/cm³, $\mu(\text{Mo-K}\alpha)$ 8.12 cm⁻¹, $F_{000} = 1344$.

The lattice parameters were deduced from precession photographs, taken with Mo-K α radiation and refined with an on-line single-crystal Siemens diffractometer, using 19 carefully centered reflections.

Intensity measurements: An elongated prismatic crystal of approximately 0.34 × 0.23 × 0.80 mm was mounted on a Siemens automatic diffractometer, with the axis [001] along the spindle axis. Intensity data were collected using the Mo-Zirconium filtered radiation (λ 0.71069 Å) and the $\theta \rightarrow 2\theta$ scan technique in the range $3.5 < \theta < 27^\circ$. A total of 5595 reflections were collected, of which 2304, having $I > 3\sigma(I)$ were considered observed and corrected for the Lorentz polarization factor. No correction for absorption was applied ($\mu r = 0.23$).

Structure determination and refinement: The positional parameters of the copper atom in the asymmetric unit were obtained from a Patterson map, and then used to phase the initial structure factor calculation. Fourier syntheses established the positions of the remaining atoms. An isotropic, block-diagonal matrix least-squares refinement reduced the agreement index R to 0.077. The final anisotropic, block diagonal matrix least squares refinement was performed with isotropic temperature factors for carbon atoms, so that R was reduced to 0.057. The X-Ray 70 set of programs was employed for the calculations. Fractional coordinates and thermal parameters are reported in Table 4, with the estimated standard deviations in parentheses. Bond lengths and angles of interest are listed in Table 5. Atomic scattering factors were calculated according to ref. 24*.

ArCSSCu diphos (II). The complexes were prepared in the same way as I. The changes of colour of the solutions caused by the addition of the phosphine were more marked and the precipitation of the complexes faster. The *o*-derivatives can be recrystallized from hot toluene or CH₂Cl₂-ether, and the phenyl-derivative from pyridine-ether.

Reactions between I and II with CH₃I. An excess of CH₃I was added with stirring in the dark to complex I or II suspended in CS₂. The reaction was almost immediate with the (*o*-TCSSCu)₂(diphos)₃ compound, but slow (some hours) with the other complexes. The solutions turned red, whereas the solids became light brown (PPh₃ derivatives) or white (diphos derivatives). The suspensions were filtered and the solids repeatedly washed with CS₂. The same product, namely the CuI diphos complex [25], was obtained from all the (ArCS₂Cu)_n(diphos)_m complexes ($n = 1, m = 1$; $n = 2, m = 3$), while slightly different crude solids were obtained from the PPh₃ series. Products similar to the latter can be formed by mixing CuI and PPh₃ in 1 : 2 ratio in CS₂ or also in benzene in the presence of an excess of CH₃I. Hence the reaction is not specific for complexes I or for CS₂, but arises from formation of phosphonium derivatives. The mother liquors were evaporated to dryness, and the residue was extracted with pentane. The extract was filtered and evaporated, to leave a deep coloured oil (Ar = Ph, deep red; Ar = *m*-T, blood red; Ar = *p*-T, brilliant

* A list of the observed and calculated structure factors can be obtained from the authors on request.

TABLE 4

FRACTIONAL CO-ORDINATES ($\times 10^{-4}$) AND TEMPERATURE FACTORS, ^a WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES^c

	X	Y	Z	B		
Cu	2696(1)	2444(1)	4175(1)	a		
S(1)	2310(2)	2966(2)	2273(2)	a		
S(2)	1606(2)	1895(2)	3862(2)	a		
P(1)	2661(1)	3320(1)	5701(2)	a		
P(2)	3550(1)	1628(1)	3810(2)	a		
C(1)	3324(5)	4033(6)	5804(11)	4.3(2)		
C(2)	3985(6)	3747(7)	5702(12)	4.6(2)		
C(3)	4510(7)	4244(8)	5789(14)	6.0(3)		
C(4)	4425(8)	5055(9)	6088(15)	7.1(4)		
C(5)	3807(9)	5315(10)	6244(17)	8.0(4)		
C(6)	3215(8)	4841(9)	6098(16)	7.1(4)		
C(7)	1928(6)	3964(6)	5771(12)	4.5(2)		
C(8)	1659(6)	4227(8)	4717(12)	5.3(3)		
C(9)	1127(9)	4759(11)	4667(17)	8.1(4)		
C(10)	901(9)	4983(10)	5713(18)	8.3(4)		
C(11)	1100(9)	4701(11)	6862(17)	8.3(4)		
C(12)	1641(8)	4179(9)	6936(15)	7.4(4)		
C(13)	2678(6)	2857(6)	7170(9)	3.6(2)		
C(14)	3000(6)	3191(8)	8166(12)	5.0(3)		
C(15)	3010(7)	2762(8)	9253(15)	6.8(3)		
C(16)	2734(9)	2012(10)	9350(16)	7.8(4)		
C(17)	2402(8)	1678(9)	8372(13)	6.8(3)		
C(18)	2378(7)	2090(8)	7263(12)	5.4(3)		
C(19)	3475(5)	1018(5)	2474(9)	3.1(2)		
C(20)	2872(5)	673(7)	2249(10)	4.1(2)		
C(21)	2777(7)	153(8)	1245(13)	5.6(3)		
C(22)	3344(7)	13(8)	491(13)	5.8(3)		
C(23)	3916(8)	314(9)	730(16)	6.8(3)		
C(24)	4005(6)	851(7)	1741(11)	4.7(2)		
C(25)	4309(5)	2187(6)	3562(9)	3.2(2)		
C(26)	4906(6)	1961(7)	4041(11)	4.6(2)		
C(27)	5459(7)	2427(9)	3857(13)	6.0(3)		
C(28)	5401(7)	3144(8)	3231(13)	5.7(3)		
C(29)	4855(7)	3352(8)	2768(12)	5.5(3)		
C(30)	4267(7)	2907(8)	2917(13)	5.4(3)		
C(31)	3771(5)	905(6)	4966(10)	3.6(2)		
C(32)	3926(6)	102(7)	4708(11)	4.2(2)		
C(33)	4108(7)	-411(8)	5642(13)	5.4(3)		
C(34)	4098(9)	-144(9)	6833(16)	7.3(4)		
C(35)	3962(8)	643(9)	7096(15)	6.9(4)		
C(36)	3794(6)	1168(7)	6175(12)	5.2(3)		
C(37)	1023(5)	2507(7)	1832(9)	3.9(2)		
C(38)	417(7)	2391(8)	2342(12)	5.3(3)		
C(39)	-147(9)	2470(10)	1616(15)	7.8(4)		
C(40)	-78(8)	2591(10)	379(14)	7.4(4)		
C(41)	507(8)	268(9)	-115(14)	6.4(4)		
C(42)	1098(6)	2641(7)	609(12)	5.2(3)		
C(43)	1626(5)	2444(6)	2627(9)	3.4(2)		
	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cu	3.4(1)	3.3(1)	2.9(1)	0.6(1)	-0.2(1)	-0.4(1)
S(1)	4.0(1)	4.5(1)	3.5(1)	0.1(1)	0.2(1)	0.6(1)
S(2)	3.9(1)	3.8(1)	3.5(1)	0.9(1)	-0.2(1)	0.5(1)
P(1)	3.5(1)	3.2(1)	3.5(1)	0.2(1)	0.2(1)	-0.6(1)
P(2)	3.1(1)	2.9(1)	2.8(1)	0.4(1)	-0.1(1)	-0.1(1)

^a Anisotropic temperature factors are in the form:

$$[\exp -\frac{1}{2}(h^2 B_{11} a^{*2} + k^2 B_{22} b^{*2} + l^2 B_{33} + 2hk B_{12} ab^* + 2hl B_{13} a^* c^* + 2kl B_{23} b^* c^*)]$$

TABLE 5
INTRAMOLECULAR BOND DISTANCES AND ANGLES OF INTEREST

Bond distances (Å)					
Cu—S(1)	2.438(3)	C(7)—C(12)	1.47(2)	C(25)—C(30)	1.41(2)
Cu—S(2)	2.419(3)	C(8)—C(9)	1.40(2)	C(26)—C(27)	1.38(2)
Cu—P(1)	2.258(2)	C(9)—C(10)	1.32(3)	C(27)—C(28)	1.40(2)
Cu—P(2)	2.246(3)	C(10)—C(11)	1.43(3)	C(28)—C(29)	1.27(2)
P(1)—C(1)	1.80(1)	C(11)—C(12)	1.42(2)	C(29)—C(30)	1.42(2)
P(1)—C(7)	1.84(1)	C(13)—C(14)	1.41(2)	C(31)—C(32)	1.41(2)
P(1)—C(13)	1.82(1)	C(13)—C(18)	1.43(2)	C(31)—C(36)	1.43(2)
P(2)—C(19)	1.82(1)	C(14)—C(15)	1.42(2)	C(32)—C(33)	1.41(2)
P(2)—C(25)	1.82(1)	C(15)—C(16)	1.38(2)	C(33)—C(34)	1.41(2)
P(2)—C(31)	1.83(1)	C(16)—C(17)	1.41(2)	C(34)—C(35)	1.38(2)
S(1)—C(43)	1.69(1)	C(17)—C(18)	1.43(2)	C(35)—C(36)	1.40(2)
S(2)—C(43)	1.67(1)	C(19)—C(20)	1.38(1)	C(37)—C(38)	1.37(2)
C(1)—C(2)	1.43(2)	C(19)—C(24)	1.38(2)	C(37)—C(42)	1.40(2)
C(1)—C(6)	1.41(2)	C(20)—C(21)	1.44(2)	C(37)—C(43)	1.52(2)
C(2)—C(3)	1.36(2)	C(21)—C(22)	1.45(2)	C(38)—C(39)	1.41(2)
C(3)—C(4)	1.41(2)	C(22)—C(23)	1.29(2)	C(39)—C(40)	1.41(2)
C(4)—C(5)	1.34(2)	C(23)—C(24)	1.46(2)	C(40)—C(41)	1.32(2)
C(5)—C(6)	1.45(2)	C(25)—C(26)	1.38(2)	C(41)—C(42)	1.45(2)
C(7)—C(8)	1.38(2)				
Bond angles (°)					
S(1)—Cu—S(2)	73.5(1)	C(1)—P(1)—C(13)	102.1(5)		
P(1)—Cu—P(2)	124.0(1)	C(7)—P(1)—C(13)	103.1(6)		
S(1)—Cu—P(1)	114.9(1)	Cu—P(2)—C(19)	115.4(3)		
S(1)—Cu—P(2)	107.8(1)	Cu—P(2)—C(25)	111.4(3)		
S(2)—Cu—P(1)	109.2(1)	Cu—P(2)—C(31)	117.6(4)		
S(2)—Cu—P(2)	116.5(1)	C(19)—P(2)—C(25)	103.5(5)		
Cu—S(1)—C(43)	82.6(4)	C(19)—P(2)—C(31)	103.4(4)		
Cu—S(2)—C(43)	83.6(4)	C(25)—P(2)—C(31)	104.0(5)		
Cu—P(1)—C(1)	117.2(4)	S(1)—C(43)—S(2)	120.2(6)		
Cu—P(1)—C(7)	116.1(4)	S(1)—C(43)—C(37)	119.2(7)		
Cu—P(1)—C(13)	114.1(3)	S(2)—C(43)—S(37)	120.6(8)		
C(1)—P(1)—C(7)	102.1(5)				

red; Ar = *o*-T, orange red; Ar = *o*-A, orange red). All the products gave IR and NMR spectra in agreement with the formulation ArCS_2CH_3 and were $\geq 97\%$ pure (GLC).

$[\text{PPh}_2\text{Cu}(\text{CS}_2)\text{diphos}]_n$. 2.5 ml of CS_2 were added to a suspension of $[\text{PPh}_2\text{Cudiphos}]_2$ (1 g) in 30 ml of toluene. The orange brown solution was filtered, and the product was precipitated by standing overnight or by addition of ether.

Acknowledgements

This research was supported by CNR (Rome). We thank Dr. S. Daolio (Laboratorio di polarografia ed elettrochimica preparativa, CNR Padua) for some of the mass spectral measurements. Microanalyses were carried out by Dr. R. Mosca.

References

- 1 P.V. Yaneff, *Coord. Chem. Rev.*, 23 (1977) 183.
- 2 A. Miyashita and A. Yamamoto, *J. Organometal. Chem.*, 113 (1976) 187.
- 3 G. Costa, A. Camus and E. Pauluzzi, *Gazz. Chim. It. (Rome)*, 86 (1956) 997.
- 4 A. Camus, N. Marsich, G. Nardin and L. Randaccio, *J. Organometal. Chem.*, 60 (1973) C39.
- 5 G. Costa, A. Camus, N. Marsich and L. Gatti, *J. Organometal. Chem.*, 8 (1967) 339.
- 6 H.K. Hofstee, J. Boersma and G.J.M. Van der Kerk, *J. Organometal. Chem.*, 168 (1978) 241.
- 7 A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Japan*, 50 (1977) 1102.
- 8 M. Kubota and A. Yamamoto, *Bull. Chem. Soc. Japan*, 51 (1978) 2909.
- 9 M. Kubota and A. Yamamoto, *Bull. Chem. Soc. Japan*, 51 (1978) 3622.
- 10 A. Camus and N. Marsich, *J. Organometal. Chem.*, 21 (1970) 249.
- 11 G. van Koten and J.G. Noltes, *J. Chem. Soc. Chem. Commun.*, (1972) 452; G. van Koten, J.G. Noltes and A.L. Spek, *J. Organometal. Chem.*, 159 (1978) 441; T. Greiser and E. Weiss, *Chem. Ber.*, 111 (1978) 516.
- 12 I.S. Butler and A.C. Fenster, *J. Organometal. Chem.*, 66 (1974) 161.
- 13 C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, *Inorg. Chim. Acta*, 35 (1979) L375 and references therein.
- 14 T. Roberie and J. Selbin, *J. Coord. Chem.*, 9 (1979) 89 and references therein.
- 15 A. Avdeef and J.P. Fackler, *J. Coord. Chem.*, 4 (1975) 211.
- 16 G. Ciani, L. Manassero, L. Naldini and M. Sansoni, *Proceeding Yugoslav Centre of Crystallography*, Suppl. to vol. 11 (1976) A6.
- 17 A. Camus, N. Marsich, G. Nardin and L. Randaccio, *J. Chem. Soc. Dalton*, (1975) 2560.
- 18 A. Camus and N. Marsich, *J. Organometal. Chem.*, 14 (1968) 441.
- 19 A.J. Leusink, G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 56 (1973) 379.
- 20 A. Camus and N. Marsich, *J. Organometal. Chem.*, 46 (1972) 385.
- 21 L.H. Slaugh and J.H. Raley, *Tetrahedron*, 20 (1964) 1005.
- 22 J. Tanaka, *J. Org. Chem.*, 26 (1961) 4203.
- 23 J.H. Brown and C.S. Marvel, *J. Amer. Chem. Soc.*, 59 (1937) 1175.
- 24 F.H. Moore, *Acta Cryst.*, 16 (1963) 1169.
- 25 N. Marsich, A. Camus and E. Cebulec, *J. Inorg. Nucl. Chem.*, 34 (1972) 933.