Journal of Organometallic Chemistry, 259 (1983) 367–377
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

COMPLEXATION WITH BIS(DIPHENYLPHOSPHINO)METHANE OF REACTION PRODUCTS BETWEEN ARYLCOPPER(I) COMPOUNDS AND CARBON DISULFIDE

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(Received July 29th, 1983)

Summary

The insertion products $[ArCS_2Cudppm]_2$ and $[(o\text{-}tolylCS_2Cu)_2dppm]_2$ (dppm = bis(diphenylphosphino)methane) were isolated after addition of dppm to CS_2 solutions of arylcopper(I) (Ar = phenyl, *o*-, *m*- and *p*-tolyl). Another series of complexes, tentatively assigned the formula $[Cu_6(dppm)_2Ar_4C_4S_9]$, was also isolated. All the complexes were non electrolytes and were characterized by IR and ^1H and ^{31}P NMR spectra. In addition to the $[ArCS_2Cudppm]_2$ complexes also the related product $[(Cudppm)_4(CS_3)_2]$ was obtained.

Introduction

In recent years the reactions of carbon disulfide with transition metal complexes have been extensively studied [1]. Carbon disulfide is a very versatile ligand, capable of coordinating to almost every transition metal and showing great variety of insertion and disproportionation reactions. With the copper derivatives, however, studies of this kind of reaction have been focussed mainly on alkyl compounds [2]. Recently we have studied the insertion reactions of carbon disulfide into copper–carbon bonds of arylcopper(I) compounds and of their complexes with triphenylphosphine or diphos [3]. With bis(diphenylphosphino)methane (dppm) different behaviour is expected, since this ligand does not usually act as a chelating agent but bridges two copper atoms, and moreover reacts with the above organometallics to give ArH and the trinuclear $[Cu(Ph_2P)_2CH]_3 \cdot 2S$ (S = ether, toluene or similar solvent) [4]. Thus the reaction with carbon disulfide can lead to different products depending upon whether dppm is added after or before the former reagent. In this paper we describe the compounds obtained by addition of dppm to carbon disulfide solutions of arylcopper(I) compounds.

0022-328X/83/$03.00

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Number	Formula	Colour	M.p.	Analysis (found(calcd.)(%))					M.W.(found(calcd.))	W/W (%)	Solvent
				C	H	Cu	P	S			
I	$[PhCS_2Cudppm]_2$	Brown	178–179	63.8	4.75	10.40	10.0	10.8	1177	2.6	DCE
				(63.93)	(4.53)	(10.57)	(10.30)	(10.67)	(1202)		
II	$[o\text{-}TCS_2Cudppm]_2$	Red-violet	214–215	64.5	4.85	10.30	10.1	10.3	1219	1.3	Toluene
				(64.4)	(4.75)	(10.33)	(10.07)	(10.42)	(1230)		
III	$[m\text{-}TCS_2Cudppm]_2$	Green-brown	165–166	64.5	4.83	10.47	9.9		1201	1.9	DCH
IV	$[p\text{-}TCS_2Cudppm]_2$	Green-brown	192–193	64.4	4.55	10.46	9.95		1228	1.9	DCE
VI	$[(o\text{-}TCS_2Cu)_2dppm]_2$	Orange	229–230	57.7	4.37	14.95	7.3	15.1	1091	1.3	DCE
				(58.20)	(4.29)	(15.02)	(7.32)	(15.16)	(1692)		
VII	$[Cu_6(dppm)_2Ph_4C_4S_9]$ [a]	Brown-black	188–190	52.4	3.71	21.19	6.9	16.1	1792	1.0	DCE
				(52.07)	(3.81)	(21.19)	(6.89)	(16.04)	(1799)		
VIII	$[Cu_6(dppm)_2\text{-}o\text{-}T_4C_4S_9]$ [a]	Deep-brown	199–201 [b]	52.5	3.67	20.56	6.8	15.9	1846	2.0	DCE
				(53.20)	(3.92)	(20.59)	(6.69)	(15.59)	(1851)		
IX	$[Cu_6(dppm)_2\text{-}m\text{-}T_4C_4S_9]$ [a]	Brown-black	195–197 [b]	52.4	3.67	20.58	6.8	15.5	1974	1.8	DCE
X	$[Cu_6(dppm)_2\text{-}p\text{-}T_4C_4S_9]$ [a]	Brown-black	201–203	53.4	4.0	20.31	6.7	15.6	2000–2300	1.2	DCE Toluene

[a] The freshly precipitated complexes contained about 1 mol of solvent of crystallization (CH_2Cl_2 or toluene), which could be almost completely eliminated at 100°C in vacuo. [b] After several recrystallizations.

Results

The starting organometallics were phenyl, and *o*-, *m*, or *p*-tolylcopper (denoted respectively by PhCu, *o*, *m*, or *p*-TCu henceforth). Table 1 lists the elemental analyses, molecular weights and some physical properties of the products. All these substances are diamagnetic and non electrolytes in acetone and in dichloroethane (DCE). Some of their characteristic IR frequencies are reported in Table 2, while ^{1}H and ^{31}P NMR data are given in Table 3.

As different dppm/ArCu ratios result in different products they are described under two headings: dppm/ArCu $\geqslant$ 1 and dppm/ArCu $\leqslant$ 0.5.

dppm/ArCu $\geqslant$ 1

With these ratios the reaction gave the $[ArCS_2Cudppm]_2$ complexes (I–IV), formed by insertion of CS_2 into the copper–carbon bond. As expected, owing to the tendency of dppm to form bridged rather than chelated complexes, these compounds were found to be dimeric in solution (Table 1). There is a complete correspondence of their IR spectra with those of the $ArCS_2Cu(PPh_3)_2$ series, the X-ray structure of which is known [3,5]. Therefore the existence of complex absorption peaks in the $\nu(CS_{2asym})$ region (Table 2) cannot reasonably be interpreted as due to different or asymmetrically bound dithiocarboxylato groups [6].

Integrations of ^{1}H NMR spectra of I–IV in $CDCl_3$ are in good agreement with the assigned formulae. Methylene protons resonate at about 3 ppm, giving rise to a broad unresolved signal, like that of the $[CuXdppm]_n$ complexes (X = halide) [7], apart for the slightly higher shielding. The influence of the temperature has been examined in the case of IV, for which the shape of the spectrum changes towards a triplet with increase in temperature. In the phenyl, *m*- and *p*-tolyl derivatives, the protons *ortho* to CS_2 resonate at low fields as a pseudo doublet (splitting ~ 8 Hz) further split (~ 2 Hz) by the *meta* coupling in I, as a pseudo doublet in IV, and as a superimposition of a pseudo singlet and a pseudo doublet in III. These signals resemble those observed for the corresponding protons of benzoic and *m*- and *p*-toluic acids. All the other aromatic protons of III and IV give strong partially overlapping signals with similar patterns for the three compounds. The methyl protons of III and IV have resonances very close to those of free toluene. In II the proton *ortho* to dithiocarboxylate resonates in the δ 6.8–7.5 ppm region, together with all the other aromatic protons. It is usual for *o*-disubstituted benzenes to show

(Continued on p. 372)

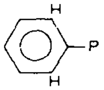
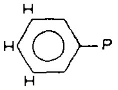
TABLE 2

CHARACTERISTIC IR DATA OF THE COMPLEXES (cm^{-1})

Number	Formula	$\nu(CS_{2asym})$		$\nu(CS_{2sym})$	
I	$[PhCS_2Cudppm]_2$	1215m	1010sh, 997s	923m	476ms
II	$[o\text{-}TCS_2Cudppm]_2$		1034sh, 1013s	926m	473m
III	$[m\text{-}TCS_2Cudppm]_2$	1247m	1025s, 990m	961m	471m
IV	$[p\text{-}TCS_2Cudppm]_2$	1225m	1011s, 975m	926m	470m,br
VI	$[(o\text{-}TCS_2Cu)_2dppm]_2$		1043s, 1025m, 1012ms	935w, 920w	479, 473w
VII	$[Cu_6(dppm)_2Ph_4C_4S_9]$	1200w	990s,br	900mw	470w
VIII	$[Cu_6(dppm)_2\text{-}o\text{-}T_4C_4S_9]$		1010m, 995m	902mw	470w,br
IX	$[Cu_6(dppm)_2\text{-}m\text{-}T_4C_4S_9]$	1240mw	1015m, 985ms	948mw	470w,br
X	$[Cu_6(dppm)_2\text{-}p\text{-}T_4C_4S_9]$	1205w	1005s, 973m	900mw	469w,br

TABLE 3

^{1}H AND ^{31}P NMR DATA [a] (δ, ppm; J, Hz; s, singlet; ps, pseudo singlet; dd, double doublet; pd, pseudo doublet; t, triplet; m, unresolved multiplet; cm, complex multiplet.)

Compound	Solvent	Aryl aromatic protons	dppm phenyl protons	
				
		δ range	δ range	
dppm	$CDCl_3$	–	7.65–7.15 cm	
	C_6D_6	–	7.8–7.35 cm	7.35–7 m
dppmS	$CDCl_3$	–	P(S)8.05–7.55 cm	o to P + m, p to P(S) 7.55–7.05 m
	C_6D_6	–	P(S)8.1–7.6 cm P 7.55–7.2 cm	7.2–6.8 m
$dppmS_2$	$CDCl_3$	–	8.05–7.65 cm	7.55–7.15 m
	C_6D_6	–	8.1–7.75 cm	7.1–6.85 m
I	$CDCl_3$	8.35 m [b], 7.5–6.8 obscured [c]	7.5–6.8 m	
II	$CDCl_3$	7.5–6.8 m		
III	$CDCl_3$	8.15 pd J ~ 7 [b] 8.14 ps 7.45–6.85 obscured [c]	7.45–6.85 m	
IV	$CDCl_3$	8.30 pd J 8.3 [b] 7.45–6.85 obscured [c]	7.45–6.85 m	
VI	$CDCl_3$	7.4–7.2 m	7.7–7.3 cm partially obscured	7.25–7.0m
VII	$CDCl_3$	8.5–7.7 m, 7–6.8 partially obscured	7.7–7.3 m	7.3–7.0 m
VIII	$CDCl_3$	~ 7.35?, 7.05–6.6 partially obscured	7.85–7.4 cm	7.3–7.05 m
IX	$CDCl_3$	8.2–7.7 m, obscured	7.7–7.3 cm	7.3–7.0 m
X	$CDCl_3$	8.3–7.65 m, 7.0–6.5 partially obscured	7.65–7.3 cm	7.25–6.95 m
	C_6D_6	8.65–8.0 m, 6.8–6.4	7.9–7.4 cm	7.0–6.8 m
XI	$CDCl_3$	–	o to P(S) 8.15–7.7 all other 7.7–7.3	

[a] Reported data are from room temperature spectra; chemical shifts for ^{1}H in ppm from Me_4Si; for ^{31}P ($CHCl_3$, solutions, broad band proton decoupled spectra) in ppm from 10% H_3PO_4 in D_2O as external

CH$_3$ protons	P>CH$_2$ protons (P)				δ(P)	J(P,P(S))		δ(P(S))	J(P,P(S))	
δ	δ	^2J(P,H)	^2J(P(S),H)							
–	2.82 t 2.87 t	1.3 1.7			−22.5	–	(< 10)	–	–	–
–	3.36 dd 3.25 dd	10 0.8	12.6 12.4		−28	74	(< 10)	40.5	74	(< 10)
–	4.0 t 3.85 t	14.5 13.5			–	–	–	35.5	–	(< 10)
–	3.15 s			(10)		–		–	–	–
2.5 s	3.1 s			(7)		–		–	–	–
2.38 s	3.12 s			(7)		–		–	–	–
2.33 s	3.10 s			(7)	−12	–	(60)	–	–	–
2.5 s (sharp)	3.25 t	9		(3)		–		–	–	–
–	2.95					–		–	–	–
2.30 (3)	3.2 t	9		(4)		–		–	–	–
2.15 (10)	2.9					–		–	–	–
2.25	2.9				−13	–	(50)	–	–	–
2.0 s (7)	3.0	9		(7)						
–	3.6 dd 4.2 t	8	11 13		−16.5		(200)	47.5 d 40 s	75	(< 15) (< 10)

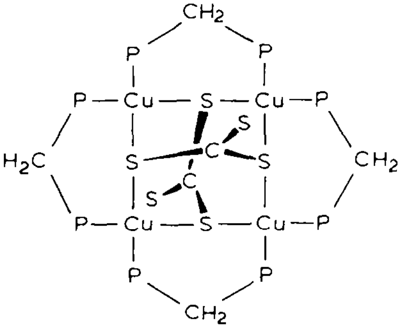
standard without correction for magnetic susceptibility, positive if deshielded; half height widths in Hz (parenthesis). [b] Protons in *ortho* to CS$_2$. [c] Protons in *meta* and *para* to CS$_2$.

deviations from the expected substituent effects, but the above δ values are likely to reflect some structural differences between II and I, III, IV.

The ^{31}P NMR spectrum of IV consists of a single signal. We attribute its considerable width to the phosphorus spin–spin couplings with the quadrupolar ^{63}Cu and ^{65}Cu.

The $[ArCS_2Cudppm]_2$ complexes are very stable and were recovered almost quantitatively after treatment for some hours with a concentrated HCl/benzene mixture (1/4) at room temperature. A small amount of decomposition was indicated, however, by the red colour of the organic layer. Small amounts of $[CuCldppm]_n$ and $Ph_2P(O)CH_2P(S)PPh_2$ were isolated after treatment of the *o*-tolyl derivative [7].

In all these reactions the complex $[(Cudppm)_4(CS_3)_2]$ (V), lacking the aryls, was also formed. Its structure has been determined by an X-ray study [8] and shows the four copper atoms to be in a square arrangement with the dppm bridging along the edges, while the trithiocarbonate anions act as nearly symmetrically bridges between couples of metal atoms, each coordinating through only two sulfur atoms (**1**).



(**1**)

Compound V was the main product obtained from the tetrametric *m*- [9] and *p*-tolyl copper [10], whilst phenyl * and *o*-tolyl copper gave high yields of the dithiocarboxylato derivatives I and II.

dppm / ArCu ≤ 0.5

Only *o*-tolylcopper readily gave the expected 2/1 complex $(o\text{-}TCS_2Cu)_2dppm$ (VI). Evidence of formation of analogous complexes from phenyl and *p*-tolyl copper was obtained, but the very low yields did not allow satisfactory characterization of these products. The presence of three sharp peaks in the $\nu(CS_2)$ region of the IR spectrum suggests that there may be two different types of dithiocarboxylato groups, as in the corresponding dimeric chloride derivative in which the dppm bridges copper atoms alternately bonded to di- and tri-coordinated halide atoms [12]. The observed molecular weight indicates that VI is also probably a dimer in the solid state. The ^1H NMR spectrum agrees well with the assigned formula. The methyl resonance appears as a sharp peak, and the methylene signal is symmetrically split by the adjacent phosphorus atoms, with a coupling constant close to that for the corresponding chloride complex. All the other protons gave partially unresolved

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* Phenylcopper has a polymeric, still undefined structure [11]; *o*-tolylcopper is a hexamer in the solid state and turns slowly into a tetramer in solution [10].

signals in the region δ 7–7.6 ppm, and thus again the proton *ortho* to CS_2 fails to resonate in the expected low field region. Compared to compound II the methyl shows the same shielding, while the methylene and aromatic protons are deshielded.

All the other organocopper compounds gave products (VII, IX, X) of analytical composition $[Cu_6(dppm)_2Ar_4C_4S_9]$ with characteristics very different from those of VI. The corresponding *o*-tolyl derivative (VIII) was also isolated from the mother liquors of VI. After repeated crystallizations molecular weights agreed with the above formula for the phenyl and the *o*-tolyl derivatives, while six different samples of the *p*-tolyl compound always gave higher values both in dichloroethane and toluene, independent of the concentration of the solutions used. The value for the *m*-derivative was also appreciably higher than expected.

The IR spectra of these complexes show patterns not very different from those of the corresponding compounds I–IV, except for medium peaks in the 1250–1210 cm^{-1} region (absent in *o*-tolyl derivative) and at about 470 cm^{-1}, which in this case are significantly weakened and shifted to lower frequencies. The latter absorptions, which are present also in compound V but not in the polymeric $[o\text{-}TCS_2Cu]_n$ and

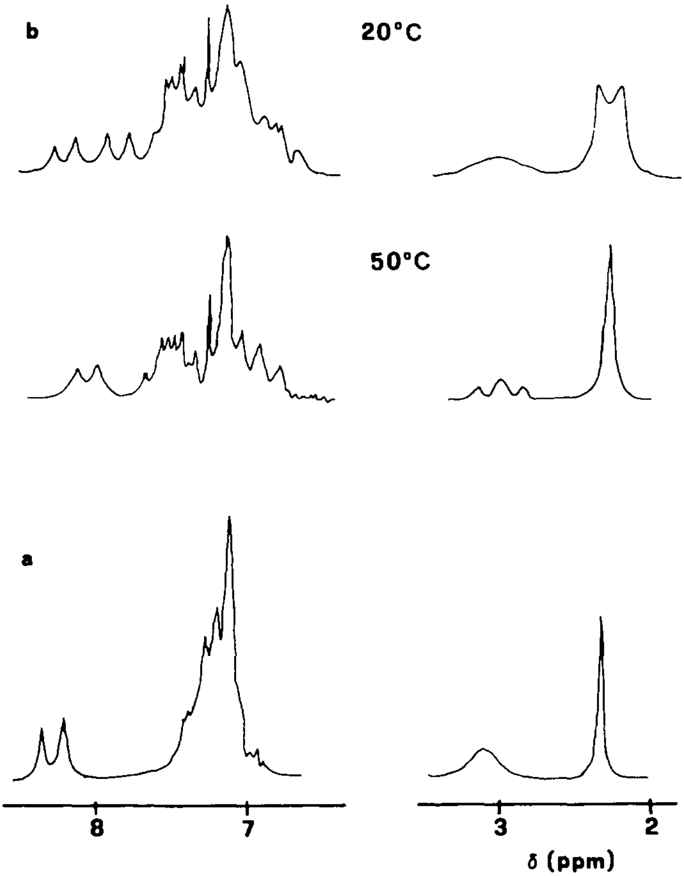

Fig. 1. ^1H NMR spectral patterns from $CDCl_3$ solutions of: (a) $[p\text{-}TCS_2Cudppm]_2$; (b) $[Cu_6(dppm)_2\,p\text{-}T_4C_4S_9]$.

$[o\text{-}TCS_2Cu_2]_n$ [3], are probably due to dppm. The good agreement of the spectrum of $[o\text{-}TCS_2Cu_2]_n$ with that of VIII in the 1100–800 cm^{-1} region excludes the possibility of a CS_2 insertion into the P–Cu bond, as found for other metals [13].

The ^1H NMR spectra agree quantitatively with the proposed formulae. For compounds VII, IX and X, eight protons of phenyl, *m*- and *p*-tolyl are significantly deshielded and give rise to complex patterns. In particular, in *p*-tolyl [Fig. 1] they give rise to two pseudo doublets, and the other eight ring protons of the toluene moieties give distinguishable signals in the high field range of the aromatic region; at higher temperatures the two groups of resonances each coalesce into a pseudo doublet. The methyls give broad signals at room temperature; in X two signals can be distinguished at 20°C, but they coalesce into a single sharp peak with increase in temperature. The methylene protons give a broad triplet slightly deshielded with respect to the free ligand, with a proton phosphorus coupling constant stronger than in the $[ArCS_2Cudppm]_2$ complexes and with line width which decreases with increasing temperature. The phosphine phenyl protons give two groups of signals (Table 3, Fig. 1). The internal shift between these two groups is stronger than in free dppm and in the $[ArCS_2Cudppm]_2$ complexes and the spectral pattern of the free ligand (as observed in benzene), including the complex splitting of *ortho* protons due to phosphorus coupling, is almost completely retained. The ^{31}P NMR spectrum ($Ar = p\text{-}T$) in chloroform consists of a single broad resonance; as for compound IV we attribute the broadening to copper quadrupole relaxation, but cannot exclude simultaneous chemical non equivalence of phosphorus atoms.

The $[Cu_6(dppm)_2Ar_4C_4S_9]$ compounds released H_2S when treated with a concentrated HCl/benzene mixture (1/4) at room temperature. The hydrolysis, however, was not complete in 2 h, and gave red-black products which still contained some Ar groups. Under reflux the phenyl, *m*- and *p*-tolyl complexes afforded small amounts of the same final product $[(CuCl)_2dppmS(dppmS_2)]$ (XI) ($dppmS = Ph_2P(S)CH_2PPh_2$; $dppmS_2 = Ph_2P(S)CH_2P(S)Ph_2$). The new sulfurated ligands were not present initially in solution, but were formed with time, as could be seen by monitoring the reaction by NMR spectroscopy. The formula of XI, was confirmed by synthesis. Its IR spectrum is similar to that of a $[CuCldppmS_2]_2$ sample (m.p. 183°C [14]), but considerably more complicated in the phenyl absorption region, where some peaks are clearly split. Metal-halogen frequencies do not appear above 200 cm^{-1}. The ^1H NMR spectrum (Table 3) shows, as expected, different multiplets for the dppmS and $dppmS_2$ methylenes, the low field complexation shift for the former being slightly stronger [15] but substantially lower than that in $[CuCldppm]_n$ [7]. The aromatic protons give rise to a complex pattern very close to that of an equivalent mixture of dppmS and $dppmS_2$ *, including the splittings due to proton–phosphorus spin–spin couplings. In the ^{31}P NMR spectrum the complexed $dppmS_2$ and dppmS give rise respectively to a singlet and a broad band plus a doublet. Assuming that the exchange of the ligands between coordination sites is slow on the NMR time scale, the phosphorus–phosphorus couplings and relative magnitudes and signs of phosphorus complexation shifts indicate [17] that each ligand binds only one copper atom and that the binding occurs through the sulfur atoms and the unsubstituted phosphorus of dppmS, as shown by the selective

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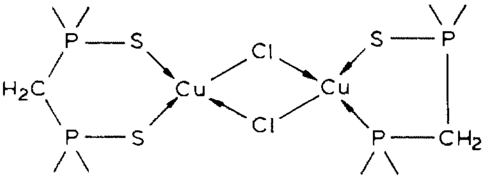
* ^1H and ^{31}P NMR data for the free ligands dppm, dppmS and $dppmS_2$ are also reported in Table 3 and are in good agreement with literature [16].

broadening of the resonance of the phosphorus. The preference of dppmS for binding in chelated fashion via sulfur and phosphino phosphorus to form a five-membered ring is recognised [17]. A possible formulation for the complex is thus **2**.



(**2**)

However the usual strong deshielding for phosphorus directly bound to the metal in five-membered chelated rings [17] does not occur in this case. We were unable to obtain crystals for X-ray studies.

Discussion and conclusions

Like other tertiary phosphines [3], dppm stabilizes the aromatic dithiocarboxylato copper compounds. Stable $[ArCS_2Cudppm]_2$ were obtained, but the $[(Ar(CS_2Cu)_2dppm]_2$ derivative was easily formed only from *o*-tolylcopper. This emphasizes once more the peculiarity of the behaviour of this organocopper compound in the presence of CS_2, in comparison with its *meta*- and *para*-isomers and with the phenyl derivative. *o*-Tolylcopper, is also unique in giving an $[(ArCS_2Cu)_2diphos_3]$ derivative and CS_2 insertion products stable even in the absence of phosphine, and probably owing to the stability of the latter compounds, does not form V. Furthermore, in all the *o*-tolyl derivatives reported in this paper, there is no specially deshielded tolyl proton, in contrast with results for all the other compounds, for which some aryl protons resonate at $\delta > 8.1$ ppm. We hope to interpret its different behaviour with the aid of X-ray diffraction studies, which are in progress.

A valuable aid in structural assignments in these copper-phosphine complexes is provided by the strong and selective broadening of the signals from the phosphorus atom directly bonded to the metal. Due to electric field gradients, the ^{63}Cu and ^{65}Cu relaxation times are such that splittings originated through coupling with copper are not observed, nevertheless a clear evidence for strong direct couplings is still present in the spectra. Furthermore information on phosphorus-copper bonds can be gained from the $^2J(P,H)$ values obtained from the methylene proton signals. In dppm derivatives these coupling constants increase with the increasing electron-withdrawing ability of the atom bound to phosphorus (Table 3, [16,17]). Assuming that also in our complexes the coupling constants reflect the electronic charge in phosphorus, it can be inferred that more donation from the latter is involved in $[Cu_6(dppm)_2Ar_4C_4S_9]$ than in $[ArCS_2Cudppm]_2$ compounds. Also the shielding of the phosphine phenyl protons *ortho* to phosphorus supports this point. However, owing to the versatility of CS_2 in binding to metals [1,18], it is difficult to advance a reliable hypothesis for the structure of compounds VII–X with the data so far available. Difficulties in obtaining suitable crystals seem to preclude X-ray diffractometry. Therefore further chemical reactivity and NMR studies (variable temperature and ^{13}C) are in progress to obtain better mechanistic and structural information about these complexes.

Experimental

General details of experimental procedures were described in [3]. The organocopper compounds were synthesized by published methods [19]. Molecular weights were determined with a Mechrolab Osmometer model 302. IR spectra were recorded as Nujol mulls or in KBr pellets on a Perkin-Elmer 225 Spectrophotometer. ^{1}H NMR spectra were recorded from solutions in 5 mm tubes at 60 MHz on a Jeol JNM-C60 HL Spectrometer in the field sweep-external lock mode and at 80 MHz with a Bruker WP80 equipped with a BNC28 computer with 8K data points; pulses of 90° were used; in the case of FID accumulation 1 min minimum interval between successive pulses was employed; the digital resolution of the FT spectrum was of 0.25 Hz. ^{31}P NMR spectra were obtained at 32.37 MHz, with and without proton broad band decoupling, from chloroform solutions in 10 mm tubes, by the above Bruker instrument equipped with a multinuclear probehead. The deuterium resonance of the 10% H_3PO_4 in D_2O standard solution contained in a 2 mm coaxial tube was used as the locking signal. The spectrometer parameters were: spectral width 10.000 Hz; pulse length 4 μsec; aquisition time 0.409 sec; digital resolution of the transformed spectrum 2.5 Hz. Accumulation of FIDS from about 15.000 pulses was followed by exponential multiplication and FT.

Preparation of the complexes

[ArCS$_2$Cudppm]$_2$ (I–IV). ArCu (6 mmol) was suspended in toluene (30 ml) at 0°C and allowed to react with 5 ml of CS_2 for 15 min. Then dppm (2.0 g, 6 mmol) was added and the muddy red-brown solution filtered. The products, were precipitated by adding ether, then filtered off, washed repeatedly with this solvent, and recrystallized from hot toluene or CH_2Cl_2 plus ether.

[(o-TCS$_2$Cu)$_2$dppm]$_2$ (VI). CS_2 (5 ml) was added to a stirred suspension of 0.77 g (5.0 mmol) of *o*-TCu in 30 ml of ether. After 15 min orange crystals were precipitated by adding 0.84 g (2.5 mmol) of dppm to the clear brown solution. They were filtered off, washed repeatedly with small amounts of toluene and dried in vacuo. Recrystallization was from hot toluene.

[Cu$_6$(dppm)$_2$Ar$_4$C$_4$S$_9$] (VII–X). The preparation was successful when carried out as above, but was better when a larger excess of ArCu was used. Recrystallization was from hot toluene or CH_2Cl_2 plus ether. An ArCu/dppm ratio 3/1 was used for the *o*-tolyl derivative, for which several fractional crystallizations from toluene plus ether (followed through microscopic control) were necessary for isolation of the required complex from VI.

[(CuCl)$_2$dppmS(dppmS$_2$)] (XI). (a) [$Cu_6(dppm)_2Ar_4C_4S_9$] (0.5 g) was heated under reflux with 20 ml of benzene plus 5 ml of concentrated HCl with vigorous stirring. The compound dissolved with release of H_2S and the red-brown solution turned slowly (hours) to pale yellow, while a white powder separated. This was filtered off and washed successively with water, methanol and ether. Recrystallization was from CH_2Cl_2 plus ether (m.p. 231°C). Analysis: Found: C, 56.9; H, 4.22; Cu, 11.99; Cl, 6.5; P, 11.6; M.W: 810 (1.0% w/w, in DCE); Ω^{-1} cm^2 mol^{-1} 22.9 (10^{-3} *M* in DCE at 20°C); $C_{50}H_{44}Cu_2Cl_2P_4S_3$ calcd.: C, 56.50; H, 4.17; Cu, 11.95; Cl, 6.67; P, 11.66%. M.W. 1062.9.

(b) 1.5 mmol of CuCl were added to a solution of 0.75 mmol of dppmS and 0.75 mmol of dppmS$_2$ in CH_2Cl_2 (10 ml). The muddy yellow solution rapidly became colourless. It was filtered and ether was added until a white powder began to precipitate. The m.p., and IR and NMR spectra were identical with those of samples obtained by procedure (a).

Acknowledgments

We are grateful to the Italian MPI for support of this work. We thank dr. E. Cebulec for C, H analyses and M.W. measurements and Mr. P. de Baseggio and Mr. L. Stoppari for assistance in recording the spectra.

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