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Reactivity of CS_2 and $Et_3P{\cdot}CS_2$ toward Copper(I)–Phosphine Complexes. X-ray Crystal Structure of the Complex $[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$

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Carbon disulfide reacts with the complexes $(PEt_3)_3CuBPh_4$ (**1**) and $(PPh_3)_3CuBPh_4$ (**2**), affording $[(PEt_3)_2Cu(S_2CPEt_3)]BPh_4$ (**3**) and $(PPh_3)_2Cu(S_2CPh)$ (**4**), respectively. Compound **3** is formed by CS_2 insertion into a copper–phosphorus bond; **4** is formed by copper-assisted phenylation of CS_2 by BPh_4^-. The phosphoniodithiocarboxylate complexes **3** and $[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$ (**5**) are obtained by addition of the zwitterion $Et_3P{\cdot}CS_2$ to **1** and **2**, respectively. The X-ray structure of **5** is reported. Pathways to the formation of **3** and **4** are proposed.

Recent reports describe the preparation of metal complexes involving zwitterionic phosphoniodithiocarboxylate groups, $R_3P{\cdot}CS_2$ (R = Me, Et, Cy, Ph), as ligands. These complexes can be synthesized by two different preparative routes: (i) the reaction of CS_2 with metal–phosphine complexes;[1–4] (ii) the addition of preformed $R_3P{\cdot}CS_2$ (R = Et, Cy) to metal complexes.[4–9] The CS_2 reactions have been suggested to proceed via two different mechanisms: the direct insertion of CS_2 into a metal–phosphorus bond or the dissociation of a phosphine from the complex, followed by the formation of the ligand $R_3P{\cdot}CS_2$.[4]

Much remains to be explored in $R_3P{\cdot}CS_2$ complexes, including a wider range of transition metals, kinetics, and theoretical studies of the bonding.

The present paper concerns the reactions of CS_2 and $Et_3P{\cdot}CS_2$ with the copper(I) complexes $(PEt_3)_3CuBPh_4$ (**1**) and $(PPh_3)_3CuBPh_4$ (**2**); as a result, the complexes $[(PEt_3)_2Cu(S_2CPEt_3)]BPh_4$ (**3**), $(PPh_3)_2Cu(S_2CPh)$ (**4**), and $[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$ (**5**) have been isolated.

Here, we report in detail all the reactions performed (Scheme I), the chemical and physical properties of the products, and the complete X-ray structural determination of **5**.

Experimental Section

All the reactions and manipulations were routinely performed under a nitrogen atmosphere. All materials and solvents were of reagent grade quality and were used without further purification. The compounds $(PEt_3)_3CuBPh_4$,[10] $(PPh_3)_3CuClO_4$,[11] $(PPh_3)_3CuBPh_4$,[10] and Et_3PCS_2[12] were prepared as previously described. The complexes were collected on a sintered-glass frit, washed first with 1:1 *n*-butyl alcohol/*n*-butyl ether and then with petroleum ether, and finally dried in a stream of nitrogen. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr plates. ^1H and ^{31}P NMR spectra of CD_2Cl_2 solutions were recorded at 293 K with a Varian CFT 20 spectrometer. Peak positions are relative to tetramethylsilane and phosphoric acid, with downfield values reported as positive. Conductivity measurements were made on a WTW Model LBR/B conductance bridge.

Scheme I

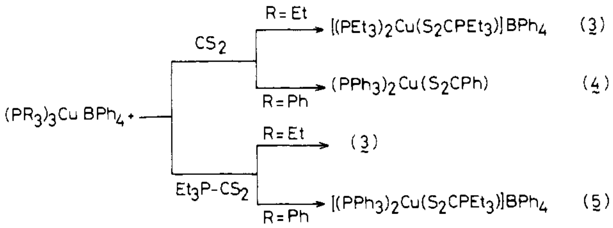

Table I. Crystal Data and Collection Details

mol formula	$C_{67}H_{65}BCuP_3S_2$	diffractometer	Philips PW 1100
mol wt	1101.67		
a, Å	17.168 (7)	monochromator	flat graphite crystal
b, Å	31.284 (12)		
c, Å	11.542 (5)	method	ω–2ϑ scan technique
β, deg	107.16 (4)		
d_{calcd}, g cm^{-3}	1.235	scan speed, deg/s	0.08
V, Å^3	5923.06	scan width, deg	$0.8 + 0.3 \tan \vartheta$
space group	$P2_1/n$	bkgd	half the scan time
Z	4		
abs coeff (μ(Mo Kα)), cm^{-1}	5.54	stds	3 every 120′
		max dev of std	±2%
		2ϑ limits, deg	$5 \leqslant 2\vartheta \leqslant 45$
		no. of total data	8363
		no. of data with $I \geqslant 3\sigma(I)$	4000
		final no. of variables	224

$[(PEt_3)_2Cu(S_2CPEt_3)]BPh_4$ (3). Method A. Carbon disulfide (10 mL) was added to a solution of $(PEt_3)_3CuBPh_4$ (0.5 mmol) in 10 mL of acetone, and the mixture was left standing at room temperature for 2 h. A 1:1 mixture of *n*-butyl alcohol and *n*-butyl ether (20 mL) was then added to the resulting solution. On slow evaporation of the solvent, orange-brown crystals were obtained; yield 65%.

Method B. Et_3PCS_2 (0.6 mmol) in 10 mL of CH_2Cl_2 was added to a solution of $(PEt_3)_3CuBPh_4$ (0.5 mmol) in 10 mL of acetone. After addition of a 1:1 mixture of *n*-butyl alcohol and *n*-butyl ether (20 mL) and slow concentration, crystals precipitated; yield 70%. Anal. Calcd for $C_{43}H_{65}BCuP_3S_2$: C, 63.49; H, 8.05; Cu, 7.81; S, 7.88. Found: C, 63.63; H, 8.25; Cu, 7.75; S, 7.82.

$(PPh_3)_2Cu(S_2CPh)$ (4). Method A. Carbon disulfide (15 mL) was added to $(PPh_3)_3CuBPh_4$ (0.5 mmol) dissolved in 40 mL of a 1:3 mixture of CH_2Cl_2 and acetone, and then the reaction mixture was refluxed for 1 h. On addition of *n*-butyl ether (20 mL) and slow concentration, red-brown crystals were separated; yield 70%. After distillation of the mother liquor at reduced pressure, a white crystalline sublimate was obtained at 70 °C (0.5 torr). This air-sensitive product was identified by elemental analysis and infrared spectra as triphenylboron.[13]

Method B. CS_2 (20 mL) was added to a solution of $(PPh_3)_3CuClO_4$ (0.5 mmol) in 20 mL of CH_2Cl_2. $NaBPh_4$ (1 mmol) in 10 mL of acetone was then added to the resulting orange solution. The reaction

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Table II. Positional and Thermal Parameters[a]

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
Cu	2359 (1)	391 (1)	2671 (1)	anis	C44	3517 (4)	547 (2)	−1668 (6)	85 (4)
P1	1565 (1)	226 (1)	3856 (2)	anis	C54	2980 (4)	747 (2)	−1138 (6)	81 (3)
P2	2984 (1)	−43 (1)	1678 (2)	anis	C64	2833 (4)	569 (2)	−115 (6)	66 (3)
P3	2500 (2)	1870 (1)	2536 (3)	anis	C15	3990 (4)	−184 (2)	2655 (6)	52 (3)
S1	3182 (2)	1015 (1)	3412 (3)	anis	C25	4188 (4)	−589 (2)	3167 (6)	70 (3)
S2	1567 (2)	1062 (1)	1618 (3)	anis	C35	4971 (4)	−670 (2)	3927 (6)	92 (4)
B	6249 (7)	2176 (3)	2747 (11)	53 (3)	C45	5557 (4)	−346 (2)	4174 (6)	79 (3)
C	2392 (5)	1290 (3)	2539 (8)	55 (3)	C55	5359 (4)	58 (2)	3662 (6)	82 (3)
C1	3166 (13)	2038 (7)	3991 (19)	62 (7)	C65	4575 (4)	139 (2)	2903 (6)	67 (3)
C1′	2752 (13)	2053 (7)	4194 (19)	61 (7)	C16	2478 (4)	−543 (2)	1126 (5)	48 (3)
C2	3363 (14)	2536 (7)	4029 (21)	77 (7)	C26	1700 (4)	−598 (2)	1250 (5)	67 (3)
C2′	2880 (15)	2564 (7)	4282 (22)	89 (8)	C36	1250 (4)	−963 (2)	786 (5)	97 (4)
C3	1531 (7)	2123 (3)	1840 (10)	85 (4)	C46	1578 (4)	−1273 (2)	197 (5)	94 (4)
C4	815 (15)	2066 (7)	2300 (24)	79 (8)	C56	2355 (4)	−1218 (2)	72 (5)	89 (4)
C4′	1111 (16)	2137 (8)	2949 (25)	89 (9)	C66	2805 (4)	−853 (2)	537 (5)	79 (3)
C5	3227 (9)	2002 (5)	1717 (15)	131 (6)	C17	5587 (3)	2588 (2)	2502 (5)	51 (3)
C6	3008 (15)	1877 (8)	571 (23)	81 (8)	C27	5699 (3)	2903 (2)	3392 (5)	73 (3)
C6′	3484 (16)	1734 (8)	946 (25)	86 (8)	C37	5151 (3)	3243 (2)	3232 (5)	90 (4)
C11	1983 (3)	−123 (2)	5117 (6)	45 (2)	C47	4491 (3)	3268 (2)	2183 (5)	81 (3)
C21	1759 (3)	−94 (2)	6182 (6)	63 (3)	C57	4380 (3)	2953 (2)	1293 (5)	72 (3)
C31	2050 (3)	−394 (2)	7105 (6)	82 (3)	C67	4927 (3)	2613 (2)	1453 (5)	57 (3)
C41	2565 (3)	−722 (2)	6962 (6)	80 (3)	C18	6300 (3)	1994 (2)	4150 (6)	54 (3)
C51	2788 (3)	−750 (2)	5896 (6)	77 (3)	C28	7044 (3)	1878 (2)	4970 (6)	59 (3)
C61	2497 (3)	−451 (2)	4974 (6)	62 (3)	C38	7072 (3)	1730 (2)	6121 (6)	75 (3)
C12	1255 (3)	702 (2)	4517 (5)	53 (3)	C48	6355 (3)	1697 (2)	6452 (6)	76 (3)
C22	455 (3)	852 (2)	4188 (5)	74 (3)	C58	5611 (3)	1813 (2)	5632 (6)	86 (4)
C32	275 (3)	1240 (2)	4649 (5)	87 (4)	C68	5583 (3)	1962 (2)	4481 (6)	84 (4)
C42	896 (3)	1477 (2)	5439 (5)	89 (4)	C19	5894 (4)	1800 (2)	1696 (7)	55 (3)
C52	1697 (3)	1327 (2)	5769 (5)	88 (4)	C29	5921 (4)	1895 (2)	528 (7)	81 (3)
C62	1876 (3)	939 (2)	5308 (5)	69 (3)	C39	5594 (4)	1610 (2)	−419 (7)	97 (4)
C13	623 (4)	−39 (2)	3018 (6)	47 (2)	C49	5239 (4)	1229 (2)	−199 (7)	92 (4)
C23	178 (4)	130 (2)	1900 (6)	77 (3)	C59	5211 (4)	1134 (2)	969 (7)	87 (4)
C33	−503 (4)	−88 (2)	1181 (6)	94 (4)	C69	5539 (4)	1419 (2)	1916 (7)	74 (3)
C43	−739 (4)	−474 (2)	1580 (6)	87 (4)	C110	7168 (4)	2323 (2)	2682 (6)	59 (3)
C53	−294 (4)	−642 (2)	2698 (6)	77 (3)	C210	7406 (4)	2750 (2)	2726 (6)	79 (3)
C63	387 (4)	−425 (2)	3417 (6)	62 (3)	C310	8197 (4)	2855 (2)	2733 (6)	98 (4)
C14	3222 (4)	190 (2)	378 (6)	50 (3)	C410	8750 (4)	2532 (2)	2696 (6)	91 (4)
C24	3759 (4)	−10 (2)	−152 (6)	84 (3)	C510	8512 (4)	2105 (2)	2652 (6)	85 (4)
C34	3906 (4)	169 (2)	−1175 (6)	90 (4)	C610	7721 (4)	2000 (2)	2645 (6)	76 (3)

[a] Coordinates multiplied by 10^4; temperature factors, by 10^3. Atoms C1, C1′, C2, C2′, C4, C4′, C6, and C6′ are assigned a population parameter of 0.5.

mixture was refluxed for 1 h. On addition of *n*-butyl ether (20 mL) and slow concentration, red-brown crystals of **4** precipitated, yield 75%. Anal. Calcd for $C_{43}H_{35}CuP_2S_2$: C, 69.66; H, 4.75; Cu, 8.57. Found: C, 69.54; H, 4.82; Cu, 8.45.

$[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$ (5). Solid Et_3PCS_2 (0.5 mmol) was added to a CH_2Cl_2 solution (30 mL) of $(PPh_3)_3CuBPh_4$ (0.5 mmol). On addition of a 1:1 mixture of *n*-butyl alcohol and *n*-butyl ether (20 mL) and slow concentration, orange-brown crystals were formed; yield 50%. Anal. Calcd for $C_{67}H_{65}BCuP_3S_2$: C, 73.04; H, 5.94; Cu, 5.76. Found: C, 72.97; H, 5.91; Cu, 5.71.

Collection and Reduction of X-ray Intensity Data. The crystal used for the structure analysis was an orange-brown irregular prism of approximate dimensions 0.40 × 0.30 × 0.15 mm. A total of 22 reflections were carefully centered on a Philips PW 1100 automatic diffractometer (λ(Mo Kα) = 0.7107 Å) to determine the unit cell parameters by least-squares refinement of the setting angles. Systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ were consistent with the space group $P2_1/n$ with $Z = 4$. Details of the data collection are given in Table I. The intensities I as well as the standard deviations $\sigma(I)$ were calculated as described elsewhere,[14] by using the value of 0.03 for the instability factor p. The raw intensity data were corrected for Lorentz–polarization effects but not for absorption (μ(Mo kα) = 5.54 cm^{-1}). Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[15] and those for hydrogen atoms from Stewart et al.[16] Both the $\Delta f'$ and the $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[17]

Solution and Refinement of the Structure. All the calculations were carried out on a SEL 32/70 computer by using the SHELX76 crystallographic system of programs.[18] The refinement was based on F_o, the function minimizing being $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The position of the copper atom was determined from a three-dimensional Patterson function. All the other atoms were located from successive Fourier maps. The refinement was performed by full-matrix least-squares techniques, with anisotropic temperature factors assigned to copper, phosphorus, and sulfur atoms. Phenyl rings were refined as rigid bodies with idealized geometry, their carbon atoms being assigned independent isotropic temperature factors. Hydrogen atoms were introduced in their calculated positions but were not refined. A final ΔF Fourier map showed no particular feature with the exception of some residual electronic density in the regions of the ethylenic chains. Thus, the carbon atoms affected by disorder were split into two separate components, with population parameters of 0.5. The refinement converged to R and R_w factors of 0.073 and 0.070, respectively. Final thermal and positional parameters are reported in Table II and in Table III, given in the supplementary material.

Results

An acetone solution of the complex $(PEt_3)_3CuBPh_4$ (**1**) reacts at room temperature with CS_2, producing an orange-brown solution from which crystals of empirical formula $[(PEt_3)_2Cu(S_2CPEt_3)]BPh_4$ (**3**) are obtained in good yield. Alternatively, this complex can be synthesized by adding the red zwitterion $Et_3P{\cdot}CS_2$ to an acetone solution of **1**.

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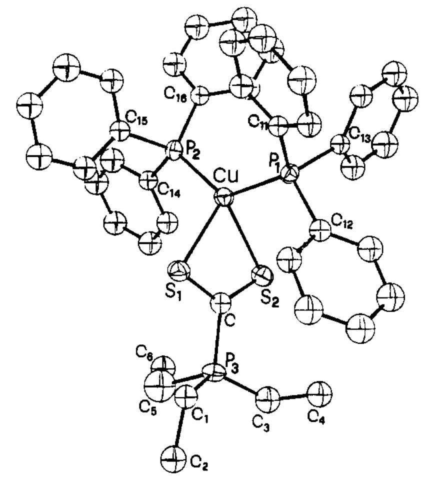

Figure 1. Perspective view of the complex cation $[(PPh_3)_2Cu(S_2CPEt_3)]^+$ (ORTEP drawing with 30% probability ellipsoids).

Compound 3 is air stable in the solid state and soluble in chlorinated solvents, acetone, and nitroethane, in which it behaves as a 1:1 electrolyte (molar conductance in 10^{-3} M nitroethane solution: 43 $cm^2\ \Omega^{-1}\ mol^{-1}$).

IR spectra of phosphoniodithiocarboxylate complexes usually exhibit bands in the regions 1050–950 and 800–700 cm^{-1}, which are attributed to $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$, respectively.[6,19] These regions, however, are often masked by vibrations associated with alkyl- and arylphosphines. For this reason, $\nu(CS_2)_{sym}$ is not apparently observed in the IR spectrum of 3, which however exhibits a broad and intense absorption at 1040 cm^{-1}, assigned to $\nu(CS_2)_{asym}$. The broadness of this band is probably due to $C-CH_3$ rocking at 1030 cm^{-1},[20] a vibration observed also in the spectrum of the starting product 1.

The $^{31}P\{^1H\}$ NMR spectrum of 3 at 293 K shows a sharp resonance at 32.11 ppm due to the phosphorus atom of the phosphoniodithiocarboxylate group and a resonance at −6.21 ppm due to the triethylphosphine groups. The latter resonance is considerably broadened by quadrupole relaxation of the copper nucleus. On the basis of all of these data, it is therefore reasonable to assign a structure to 3, where the copper atom is tetracoordinated by two phosphorus atoms of two PEt_3 molecules and by the two sulfur atoms of the $Et_3P{\cdot}CS_2$ group in a tetrahedral environment.

Decisive support to the tetrahedral geometry proposed for 3 is provided by the X-ray crystal structure determination of the complex $[(PPh_3)_2Cu(S_2CPEt_3)]BPh_4$ (5).

Compound 5 is air stable in the solid state and soluble in chlorinated solvents, acetone, and nitroethane, in which it behaves as a 1:1 electrolyte (molar conductance in 10^{-3} M nitroethane solution: 46 $cm^2\ \Omega^{-1}\ mol^{-1}$). The IR spectrum is identical with that of 3, except in the regions where the triphenylphosphine group absorbs. The $^{31}P\{^1H\}$ NMR spectrum of 5 shows a broad resonance at −1.24 ppm and a sharp resonance at 32.57 ppm, consistent with the presence of two PPh_3 groups linked to the copper atom and one PEt_3 group of $Et_3P{\cdot}CS_2$, respectively.

The crystal and molecular structure consists of monomeric complex cations $[(PPh_3)_2Cu(S_2CPEt_3)]^+$ and tetraphenylborate anions. Figure 1 shows a perspective view of the complex cation, whose selected bond distances and angles are reported in Table IV. The copper atom is four-coordinated by two triphenylphosphine groups and by the two sulfur atoms of the zwitterionic ligand in tetrahedral environment. The geometry of this compound is very distorted; besides the S1–Cu–S2 angle whose value of 71.5 (1)° is imposed by the bidentate ligand requirement, the other angles range from 98.1 (1) to 129.6 (1)°. A look at these values shows that the P1–Cu–P2 angle, 129.6 (1)°, is rather large compared with the value of 125.6 (1)° in complex 4, where the copper atom is coordinated by an identical donor atom set in a tetrahedral environment[21] (see Figure 2). Moreover, the P1–Cu–S2 angle, 98.1 (1)°, is surprisingly small with respect to the other P–Cu–S angles ranging from 110.6 (1) to 120.8 (1)°. These distortions also appear in the bond distances: indeed, while the Cu–P distances are equivalent and very close to those reported for the complex 4, the Cu–S bond distances are quite different. The Cu–S1 bond of 2.416 (3) Å is in excellent agreement with the average value found in 4 (2.410 (2) Å), while the Cu–S2 bond is significantly larger, reaching the value 2.600 (3) Å. A similar difference between the Cu–S bond distances found in the copper(I) thioxanthate complex $(PPh_3)_2Cu(EtSXant)$ (2.379 (3) and 2.493 (3) Å),[22] was attributed to the tendency of copper(I) to be three- as well as four-coordinated; that is, the 1,1-dithio ligand may occupy one coordination site of a pseudotrigonal geometry. On the other hand, in spite of the bending of a phosphine group (P1) toward S2, packing effects are probably not determinant. An examination of the contact distances shows that, although there are some short intermolecular distances that are nonexistent in 4, these values seem inadequate to explain such striking distortion. With respect to the bond distances and angles within the phosphoniodithiocarboxylate ligand, while the C–S bond distances agree very well with those reported in a variety of $R_3P{\cdot}CS_2$ complexes[1,4,6,7] and in the free zwitterion,[23] the value of the S–C–S angle is somewhat smaller than that found in the free ligand and somewaht larger than those reported in complexes where the zwitterionic ligand acts as bidentate.

Table IV. Selected Bond Distances (Å) and Angles (deg)

Cu-P1	2.257 (3)	P3-C	1.822 (9)
Cu-P2	2.243 (3)	S1-C	1.670 (9)
Cu-S1	2.416 (3)	S2-C	1.660 (9)
Cu-S2	2.600 (3)	Cu· · ·C	2.820 (8)
P1-Cu-P2	129.6 (1)	Cu-S1-C	85.2 (3)
P1-Cu-S1	111.4 (1)	Cu-S2-C	79.6 (3)
P1-Cu-S2	98.1 (1)	S1-C-P3	116.6 (5)
P2-Cu-S1	110.6 (1)	S2-C-P3	119.7 (5)
P2-Cu-S2	120.8 (1)	S1-C-S2	123.5 (5)
S1-Cu-S2	71.5 (1)		

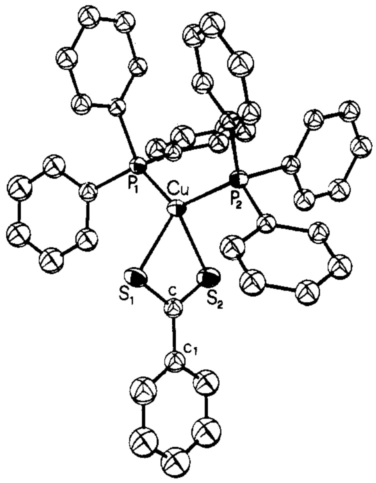

Figure 2. Perspective view of the complex molecule $(PPh_3)_2Cu(S_2CPh)$ (ORTEP drawing with 30% probability ellipsoids).

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CS_2 reacts at reflux temperature with a solution of **2** in methylene chloride/acetone, producing a red-brown solution from which crystals of empirical formula $(PPh_3)_2Cu(S_2CPh)$ (**4**) are obtained in good yield. **4** is fairly air stable both in the solid state and in solution. It is soluble in chlorinated solvents, acetone, and nitroethane, in which it is nonconducting. The IR spectrum exhibits bands at 1015 and 925 cm^{-1}, attributable to $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$ of dithiocarboxylate groups,[24] respectively. The $^{31}P\{^1H\}$ NMR spectrum consists of a unique broad resonance at 0.48 ppm. The ^1H NMR spectrum does not show the resonances associated with the tetraphenylborate group.

A crystal structure determination[21] has shown that **4** is the triclinic form of the polymorphic dithiobenzoate complex $(PPh_3)_2Cu(S_2CPh)$. A brown-black orthorhombic form, synthesized by reaction of CS_2 with CuPh and PPh_3, has been previously described.[24]

Tetraphenylborate has been unambigously confirmed as the source of phenyl groups linked to CS_2 by treatment of a solution of the complex $(PPh_3)_3CuClO_4$ with CS_2. **4** is not obtained unless BPh_4^- anions are added to the reaction mixture. The mode of formation of **4** can therefore be summarized by

$$(PPh_3)_3CuBPh_4 + CS_2 \rightarrow (PPh_3)_2Cu(S_2CPh) + PPh_3 + BPh_3$$

Both BPh_3 and free PPh_3 have been detected in the reaction mixture.

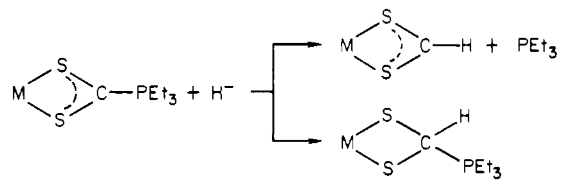
Discussion

CS_2 insertion into metal-phosphorus bonds to give phosphoniodithiocarboxylate complexes may be viewed as occurring either through coordination of CS_2 and subsequent transfer of PR_3 to the carbon atom of CS_2 or through PR_3 dissociation from the complex, followed by formation of the zwitterion $R_3P{\cdot}CS_2$, which could then react with a complex molecule or with a metal-ligand fragment. The factors that could favor either of these mechanisms are still a matter of discussion. In our opinion, a great relevance must be attributed to the nature of the phosphine ligands.

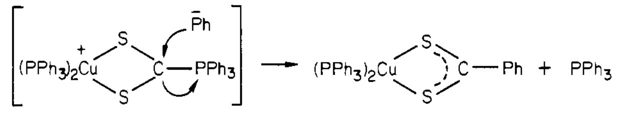
Metal complexes with phosphines (trialkylphosphines and aminophosphines) capable of forming stable CS_2 adducts, $R_3P{\cdot}CS_2$,[25] may follow both mechanisms. Examples of this type are the complexes **3**, $[(PMe_3)_2Pd(S_2CPMe_3)R]BPh_4$ (R = Me, $COCH_3$, Ph),[3] and $[RuH(CO)(S_2CPCy_3)(PCy_3)]BPh_4$.

Metal complexes with triarylphosphines, unreactive toward CS_2, should form phosphoniodithiocarboxylate complexes only through preliminary coordination of CS_2 to the metal. Upon coordination to metals, the carbon atom of CS_2 becomes more electrophilic[6,8] and thus susceptible to attack also by the less basic triarylphosphines. The reaction of CS_2 with the complex $IrCl(CO)(PPh_3)_2$ and PPh_3 to give the complex $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]BPh_4$[1] could follow this pathway, which may be also proposed as a preliminary step in the formation of the dithiobenzoate complex **4**.

Scheme II



A reasonable reaction mechanism for **4** is that including the initial formation of an unstable (triphenylphosphonio)dithiocarboxylate complex, which then undergoes nucleophilic attack by a phenyl group from BPh_4^- on the CS_2 carbon atom, followed by expulsion of PPh_3.



Support for the above reaction pathway is provided by the reactions of other phosphoniodithiocarboxylate complexes, namely $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ (depe = 1,2-bis(diethylphosphino)ethane)[6] and $[(triphos)Co(S_2CPEt_3)](BPh_4)_2$ (triphos = 1,1,1-tris(diphenylphosphino)methyl)ethane),[5,8] with nucleophiles and in particular with the hydride ion. The $-CS_2$ carbon atom of the coordinated $Et_3P{\cdot}CS_2$ ligand is, in fact, electrophilic and susceptible to attack by hydride ion from $NaBH_4$ or from C_2H_5OH. As a result, depending on electronic and steric factors, dithioformate or phosphonium betaine complexes are obtained (Scheme II).

CS_2 is known to react with a variety of nucleophiles forming dithio acids or 1,1-dithiolates;[25] no reaction, however, occurs between CS_2 and BPh_4^- anions.

It is interesting to note that the chemical behavior of BPh_4^- has been demonstrated to parallel closely that of BH_4^-.[26] The analogy between the reactions of BPh_4^- and BH_4^- can be expressed schematically as

$$2BH_4^- \rightarrow B_2H_6 + 2H^- \qquad 2BPh_4^- \rightarrow 2BPh_3 + 2Ph^-$$

The phenylating properties of tetraphenylborate toward metal species have been already ascertained;[26] however, metal-assisted phenyl transfer to CS_2 is an unprecedented reactivity pathway of BPh_4^-.

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Registry No. **1**, 85883-35-8; **2**, 34013-06-4; **3**, 85883-37-0; **4**, 74468-53-4; **5**, 85883-39-2; $(PPh_3)_3CuClO_4$, 34010-81-6; CS_2, 75-15-0; $NaBPh_4$, 143-66-8.

Supplementary Material Available: A listing of the structure factor amplitudes and Table III, giving anisotropic thermal parameters (24 pages). Ordering information is given on any current masthead page.

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