932 *Inorg. Chem.* **1985**, *24*, 932-939

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica
dei Composti di Coordinazione del CNR, Florence, Italy

Reactivity of Copper(I) Tetrahydroborates toward CS_2 and SCNPh. Structures of $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$, $(PPh_3)_2Cu(S_2COEt)$, and $(PPh_3)_2Cu(S_2CNHPh)\cdot CHCl_3$

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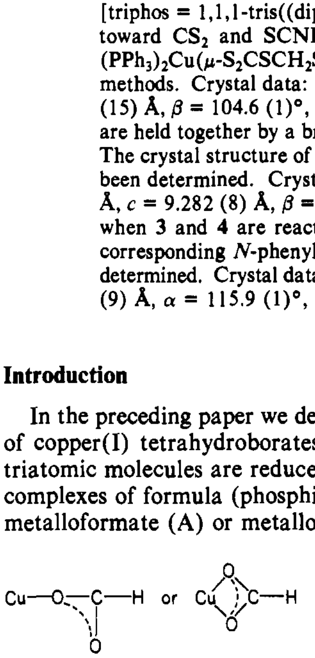
Received March 21, 1984

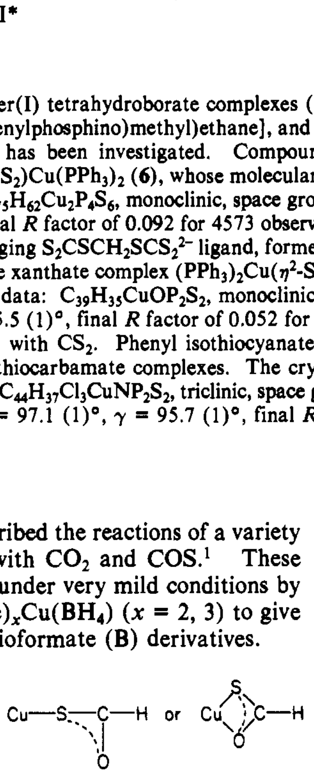
The reactivity of the copper(I) tetrahydroborate complexes $(PPh_3)_2Cu(BH_4)$ (**1**), $(PCy_3)_2Cu(BH_4)$ (**2**), (triphos)Cu(BH_4) (**3**) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane], and $(np_3)Cu(BH_4)$ (**4**) [np_3 = tris(2-(diphenylphosphino)ethyl)amine] toward CS_2 and SCNPh has been investigated. Compound **1** reacts with CS_2 to give the dinuclear copper(I) complex $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$ (**6**), whose molecular structure has been established by single-crystal X-ray diffraction methods. Crystal data: $C_{75}H_{62}Cu_2P_4S_6$, monoclinic, space group $C2/c$, $Z = 8$, $a = 53.573$ (30) Å, $b = 12.759$ (9) Å, $c = 22.856$ (15) Å, $\beta = 104.6$ (1)°, final R factor of 0.092 for 4573 observed reflections. In the dimeric molecule, two $(PPh_3)_2Cu$ fragments are held together by a bridging $S_2CSCH_2SCS_2^{2-}$ ligand, formed from a double head-to-tail condensation of three CS_2 molecules. The crystal structure of the xanthate complex $(PPh_3)_2Cu(\eta^2\text{-}S_2COEt)$ (**7**) obtained by the solvolysis of **6** in CH_2Cl_2/ethanol has been determined. Crystal data: $C_{39}H_{35}CuOP_2S_2$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 20.299$ (14) Å, $b = 18.636$ (12) Å, $c = 9.282$ (8) Å, $\beta = 95.5$ (1)°, final R factor of 0.052 for 2660 observed reflections. Dithioformate complexes are obtained when **3** and **4** are reacted with CS_2. Phenyl isothiocyanate reacts with the present copper(I) tetrahydroborates to give the corresponding *N*-phenyldithiocarbamate complexes. The crystal structure of $(PPh_3)_2Cu(\eta^2\text{-}S_2CNHPh)\cdot CHCl_3$ (**10**) has been determined. Crystal data: $C_{44}H_{37}Cl_3CuNP_2S_2$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 14.772$ (11) Å, $b = 13.105$ (11) Å, $c = 12.332$ (9) Å, $\alpha = 115.9$ (1)°, $\beta = 97.1$ (1)°, $\gamma = 95.7$ (1)°, final R factor of 0.070 for 3635 observed reflections.

Introduction

In the preceding paper we described the reactions of a variety of copper(I) tetrahydroborates with CO_2 and COS.[1] These triatomic molecules are reduced under very mild conditions by complexes of formula (phosphine)$_x$Cu(BH_4) (x = 2, 3) to give metalloformate (A) or metallothioformate (B) derivatives.



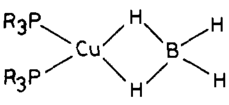
A



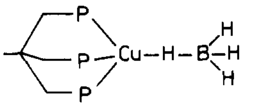
B

The bonding mode of the BH_4^- ligand, i.e. unidentate or bidentate, has been found to play an active role in determining the rate of the reactions.

In this paper we report the reactions of the tetrahydroborate complexes $(PPh_3)_2Cu(\eta^2\text{-}BH_4)$[2] (**1**), $(PCy_3)_2Cu(\eta^2\text{-}BH_4)$[1] (**2**), (triphos)Cu(η^1-BH_4)[3] (**3**) [triphos = 1,1,1-tris(diphenylphosphino)methyl)ethane], and $(np_3)Cu(\eta^1\text{-}BH_4)$[1] (**4**) [$np_3$ = tris(2-(diphenylphosphino)ethyl)amine] with the heteroallene molecules CS_2 and SCNPh.



1, R = Ph
2, R = Cy



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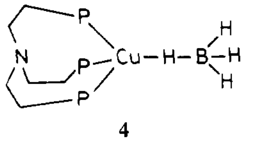

4

A preliminary account has been given of some of the results described in this paper.[4]

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. KS_2CH[5] and the compounds $(PPh_3)_2Cu(BH_4)$,[2] $(PCy_3)_2Cu(BH_4)$,[1] (triphos)Cu(BH_4),[3] $(np_3)Cu(BH_4)$,[1] and $(PPh_3)_3Cu(ClO_4)$[6] were prepared according to published procedures. The solid complexes were collected on a sintered-glass frit, washed first with ethanol and then with petroleum ether, and finally dried in a stream of nitrogen. All the complexes were recrystallized from CH_2Cl_2/ethanol except where stated otherwise. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr plates. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian CFT 20 spectrometer. Peak positions are relative to Me_4Si and H_3PO_4, with downfield values reported as positive.

$(PPh_3)_2Cu(S_2CH)$ (5). A solution of $(PPh_3)_3Cu(ClO_4)$ (1 mmol) in CH_2Cl_2 (30 mL) was mixed with KS_2CH (1 mmol) dissolved in ethanol (20 mL). On concentration, yellow crystals formed; yield 90%. Anal. Calcd for $C_{37}H_{31}CuP_2S_2$: C, 66.80; H, 4.69; Cu, 9.55; S, 9.63. Found: C, 66.63; H, 4.67; Cu, 9.49; S, 9.55.

$(PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2$ (6). A large excess of CS_2 was added to a CH_2Cl_2 solution (30 mL) of **1** (1 mmol) at room temperature. The color changed from colorless to yellow-orange. Addition of ethanol (30 mL) followed by slow evaporation of the solvent gave well-shaped yellow crystals in 80% yield. Anal. Calcd for $C_{75}H_{62}Cu_2P_4S_6$: C, 64.04; H, 4.44, Cu, 9.03; S, 13.67. Found: C, 63.81; H, 4.41; Cu, 8.97; S, 13.56. Recrystallization of **6** in CH_2Cl_2/*n*-heptane gave yellow crystals of **5** in 50% yield. Whereas when a 1:2 mixture of CH_2Cl_2/ethanol was used for the recrystallization, crystals of **5** in 25% yield were obtained as first fraction on partial evaporation of the solvent. Further reduction of the volume led to the precipitation of a second fraction characterized as **$(PPh_3)_2Cu(S_2COEt)$ (7)**, yield 20%. Anal. Calcd for $C_{39}H_{35}CuOP_2S_2$: C, 66.04; H, 4.97; Cu, 8.96; S, 9.04. Found: C, 66.12; H, 4.91; Cu, 8.89; S, 8.99.

(triphos)Cu(S_2CH) (8). A mixture of CS_2 and **3** (1 mmol) in CH_2Cl_2 (30 mL) was allowed to react for 2 h. On addition of ethanol (20 mL) to the resulting yellow solution and concentration, yellow crystals precipitated; yield 80%. Anal. Calcd for $C_{42}H_{40}CuP_3S_2$: C, 65.91; H, 5.26; Cu, 8.30; S, 8.37. Found: C, 65.94; H, 5.31; Cu, 8.24; S, 8.33.

$(np_3)Cu(S_2CH)$ (9). The above reported procedure was successfully used for this synthesis except for substitution of **4** for **3**; yield 70%. Anal.

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Calcd for $C_{43}H_{43}CuNP_3S_2$: C, 65.01; H, 5.45; Cu, 7.99; N, 1.76; S, 8.07. Found: C, 65.06; H, 5.47; Cu, 7.92; N, 1.70; S, 8.03.

$(PPh_3)_2Cu(S_2CNHPh)\cdot CHCl_3$ (10). Neat SCNPh (3 mmol) was pipetted into a solution of **1** (1 mmol) in CH_2Cl_2 (30 mL), and the resulting mixture was allowed to react for 2 h. Addition of ethanol and partial evaporation of the solvent gave yellow crystals in 80% yield. Anal. Calcd for $C_{44}H_{37}Cl_3CuNP_2S_2$: C, 60.35; H, 4.26; Cu, 7.26; N, 1.60; S, 7.32. Found: C, 60.21; H, 4.21; Cu, 7.26; N, 1.62; S, 7.28.

Similar procedures were used to prepare the following dithiocarbamate complexes except for substitution of **2**–**4** for **1**, respectively.

$(PCy_3)_2Cu(S_2CNHPh)$ (11): yield 75%. Anal. Calcd for $C_{43}H_{72}CuNP_2S_2$: C, 65.15; H, 9.15; Cu, 8.01; N, 1.76. Found: C, 65.18; H, 9.13; Cu, 7.96; N, 1.71.

(triphos)Cu(S_2CNHPh) (12): yield 75%. Anal. Calcd for $C_{48}H_{45}CuNP_3S_2$: C, 67.31; H, 5.29; Cu, 7.41; N, 1.63; S, 7.48. Found: C, 67.23; H, 5.34; Cu, 7.34; N, 1.72; S, 7.39.

$(np_3)Cu(S_2CNHPh)$ (13): yield 60%. Anal. Calcd for $C_{49}H_{48}CuN_2P_3S_2$: C, 66.46; H, 5.46; Cu, 7.17; N, 3.16; S, 7.24. Found: C, 66.34; H, 5.49; Cu, 7.09; N, 3.14; S, 7.19.

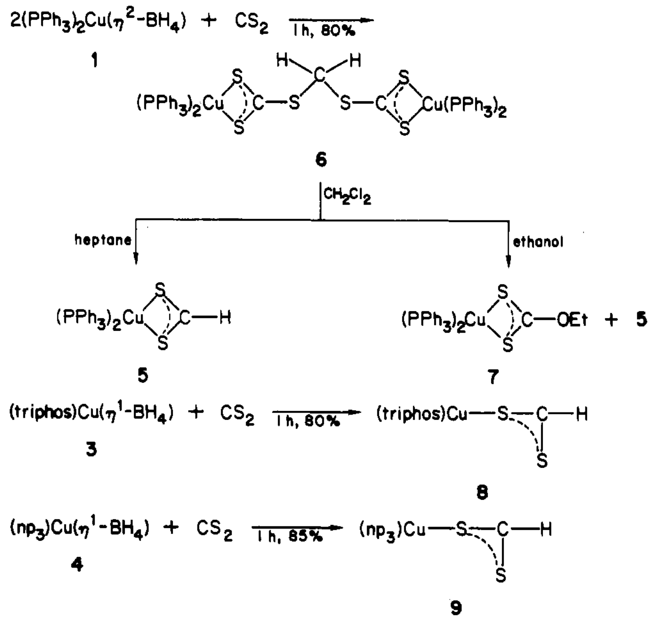
Crystal Data and Data Collection Details. The intensity data of compounds **6**, **7**, and **10** were collected at room temperature on a Philips PW 1100 automatic diffractometer. Cell constants of the three compounds were determined from a least-squares refinement of the setting angles of 25 carefully centered reflections. Table I reports details of crystal data and data collection for the three compounds. The intensity data were processed as elsewhere described,[7] and the standard deviations of the intensity $\sigma(I)$ were calculated[8] by using for the instability factor p the value of 0.03 for all the three compounds. The observed intensities were corrected for Lorentz–polarization effects, and an absorption correction was applied to compounds **6** and **10**. The absorption correction on compound **7** was considered unnecessary, an empirical estimation of the effect of absorption showing the largest change in intensities within 3%.

Solution and Refinement of the Structures. All the calculations were carried out by using the SHELX76 crystallographic system on a SEL 32/70 computer.[9] Atomic scattering factors for non-hydrogen atoms were taken from ref 10, while those for hydrogen atoms were taken from ref 11. An anomalous dispersion correction (real and imaginary part) was applied in the F_c calculations for all the compounds.[12] Full-matrix least-squares refinements were performed, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $1/\sigma^2(F_o)$. Residual R and weighted residual R_w were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

$(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$. The structure was solved by the heavy-atom method; a three-dimensional Patterson map yielded the positions of the two copper atoms. From successive Fourier syntheses all the non-hydrogen atoms were located. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry, their carbon atoms being assigned independent isotropic temperature factors. Hydrogen atoms, introduced in their calculated positions, were not refined. Copper, phosphorus, and sulfur atoms were assigned anisotropic thermal parameters. The structure was refined to R and R_w factors of 0.092. The rather high value of the discrepancy indices could be explained by taking into account some disorder detected in the region of a few phenyl rings. Final positional parameters are reported in Table II.

$(PPh_3)_2Cu(S_2COEt)$. A Patterson map revealed the position of the copper atom. All the non-hydrogen atoms were located and refined, by assigning anisotropic thermal parameters to copper, to phosphorus, and to the atoms of the S_2CO fragment. During the refinement phenyl rings were treated as rigid bodies with idealized geometry and independent isotropic temperature factors. From a ΔF Fourier map some disorder in the region of the ethylenic chain was detected; thus, the terminal carbon atom was split into two positions with population parameters of 0.5. The hydrogen atoms belonging to the disordered methyl group were not introduced; the other hydrogen atoms were introduced in their calculated positions, but not refined. The refinement converged at R and R_w factors of 0.052 and 0.050, respectively. Table III gives the final positional parameters.

Scheme I



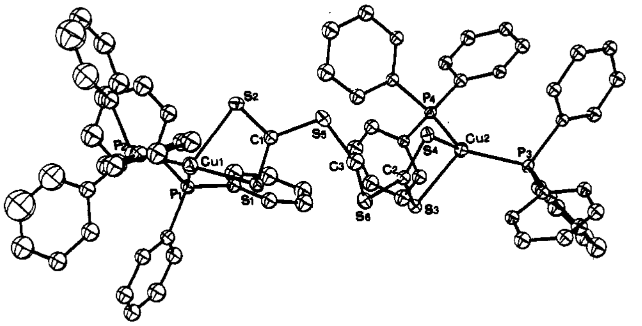


Figure 1. Perspective view of the complex molecule $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$; ORTEP drawing with 30% probability ellipsoids.

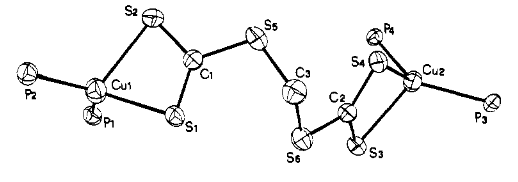


Figure 2. Inner skeleton of the complex molecule $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$; ORTEP drawing with 30% probability ellipsoids.

$(PPh_3)_2Cu(S_2CNHPh)\cdot CHCl_3$. Patterson and Fourier synthesis led to location of all the non-hydrogen atoms. The phenyl rings were refined as rigid bodies with idealized geometry and individual isotropic temperature factors. The copper, phosphorus, sulfur, and chlorine atoms were attributed anisotropic thermal vibrations. Hydrogen atoms were introduced in their calculated positions, but not refined. The detection of the chlorine atoms of the chloroform solvent molecule showed some difficulty, owing to the disordered distribution of the electron densities around the carbon atom of the chloroform. Finally, two differently oriented models were introduced, having population parameters of 0.4 and 0.6, respectively. The refinement converged to R and R_w of 0.070 and 0.072, respectively. Table IV reports final positional parameters.

Results and Discussion

The results of the synthetic work described in this paper are summarized in Schemes I and II. IR and ^{1}H NMR data are listed in Table V.

Reactions of Copper(I) Tetrahydroborates. (a) With CS_2. Reaction of **1** with a large excess of CS_2 produces yellow crystals. By analogy with the reactions of **1** with the related heteroallene molecules CO_2 and COS, which give formate and thioformate complexes,[1] the formation of the corresponding dithioformate

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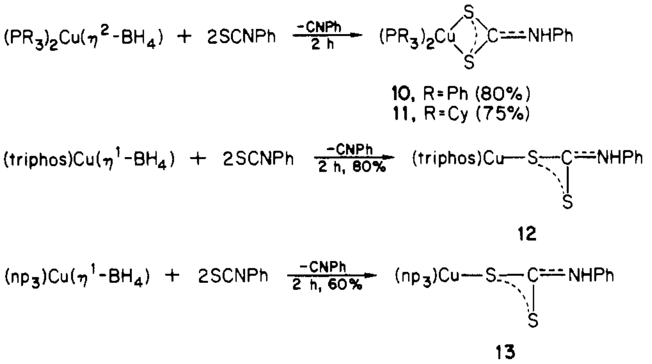
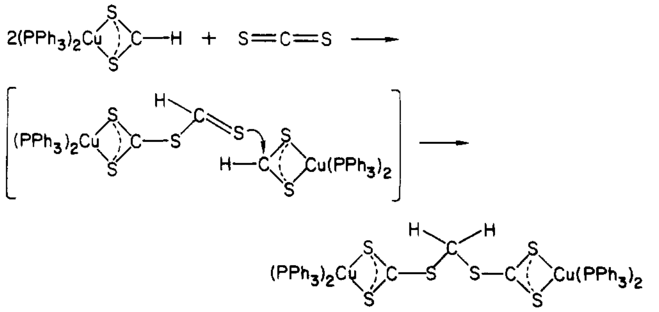
Table I. Crystal Data and Data Collection Details

	6	7	10
mol formula	$C_{75}H_{62}Cu_2P_4S_6$	$C_{39}H_{35}CuOP_2S_2$	$C_{44}H_{37}Cl_3CuNP_2S_2$
mol wt	1406.7	709.3	874.7
a, Å	53.573 (30)	20.299 (14)	14.772 (11)
b, Å	12.759 (9)	18.636 (12)	13.105 (11)
c, Å	22.856 (15)	9.282 (8)	12.332 (9)
α, deg			115.9 (1)
β, deg	104.6 (1)	95.5 (1)	97.1 (1)
γ, deg			95.7 (1)
d_{calcd}, g cm^{-3}	1.236	1.348	1.385
V, Å^3	15119.1	3495.1	2099.4
Z	8	4	2
space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$
color	yellow	yellow	yellow
habit	parallelepiped	parallelepiped	prism
dimens, mm	0.425 × 0.330 × 0.075	0.250 × 0.225 × 0.150	0.462 × 0.125 × 0.025
linear abs coeff, cm^{-1}	33.16 (Cu Kα)	8.59 (Mo Kα)	9.15 (Mo Kα)
transmissn factors	0.78–0.35		0.96–0.74
radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα (0.7107)	Mo Kα (0.7107)
monochromator	graphite crystal	graphite crystal	graphite crystal
method	ω–2θ	ω–2θ	ω–2θ
scan speed, deg/s	0.10	0.08	0.07
scan width, deg	0.70 + 0.30 tan θ	0.70 + 0.30 tan θ	0.70 + 0.30 tan θ
bkgd time	half the scan time	half the scan time	half the scan time
stds	3 every 120 min	3 every 120 min	3 every 120 min
max dev stds, %	±5	±2	±1
2θ limits, deg	$5 \leq 2\theta \leq 100$	$5 \leq 2\theta \leq 45$	$5 \leq 2\theta \leq 50$
data colled	±*h*, +*k*, +*l*	±*h*, +*k*, +*l*	±*h*, ±*k*, +*l*
no. of total data	8463	5041	7398
no. of data used	4573 ($I \geq 4\sigma(I)$)	2660 ($I \geq 3\sigma(I)$)	3635 ($I \geq 3\sigma(I)$)
final no. of variables	266	150	162

Scheme II



Scheme III



derivative was expected. Indeed, this yellow compound exhibits two infrared bands at 1010 and 880 cm^{-1} that could be positively assigned to $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$ of the dithioformate group.[13] Conversely, the absence of the typical ν(HCS) vibration and elemental analytical data indicating a 1:3 copper–sulfur ratio raised doubts about the presence of dithioformate moieties in the molecule. The formation of the expected $\eta^2\text{-}S_2CH$ complex could be then definitively ruled out by comparing the spectroscopic properties of the present compound with those of an authentic specimen of $(PPh_3)_2Cu(\eta^2\text{-}S_2CH)$ (**5**) obtained by reacting $(PPh_3)_3Cu(ClO_4)$ with KS_2CH. Owing to the low stability in solution even under an inert atmosphere (vide infra), any other characterization of the yellow product is precluded. On the contrary it is very stable in the solid state, and since its crystals are suitable for an X-ray analysis a complete structure determination was carried out.

The molecular structure consists of dimeric complex molecules $(PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2$, whose perspective view is shown in Figure 1. Figure 2 shows the skeleton of the molecule. Selected bond distances and angles are given in Table VI.

In the complex two $(PPh_3)_2Cu$ units are held together by a bridging $S_2CSCH_2SCS_2^{2-}$ ligand. Each metal atom is tetrahedrally coordinated by the phosphorus atoms of two phosphine ligands and by the two sulfur atoms of one S_2C fragment. The distortion from the idealized tetrahedral geometry is mainly attributed to the short bite of the S_2C– fragment (S–Cu–S = 73.5 (2), 73.6 (2)°), the other L–M–L angles ranging from 101.6 (2) to 131.6 (2)°. The values of the bond distances as well as of the bond angles in the coordination polyhedra fall in the range of values reported for some monomeric copper(I) complexes, where the copper atom is surrounded by the same P_2S_2 donor atom set.[14]

As concerns the $S_2CSCH_2SCS_2^{2-}$ ligand, the different hybridization state of the central carbon atom with respect to the terminal ones is reflected in the C–S bond distances as well as in the S–C–S bond angles. Indeed, as is to be expected, the C–S bond in the terminal CS_2 groups are shorter than those in the central one; also the values of S–C–S bond angles, averaging 120° for terminal carbon atoms and 113.6 (10)° for the central one, are in agreement with sp^2 and sp^3 hybridization states of the carbon atoms.

Mechanistically, the formation of the unprecedented $S_2CSCH_2SCS_2^{2-}$ ligand might be expected to occur through a double hydrogenation of CS_2 by two $(PPh_3)_2Cu(BH_4)$ units to give the methanedithiolate group $H_2CS_2^{2-}$, followed by nucleophilic attack by the sulfur atoms of the latter species on the carbon atom of two CS_2 molecules. This pathway was suggested by the re-

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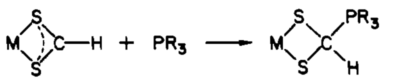
Table II. Final Positional Parameters ($\times 10^4$) for $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$

atom	*x*	*y*	*z*
Cu1	677 (1)	893 (2)	4725 (1)
Cu2	1899 (1)	−3388 (2)	7203 (1)
P1	574 (1)	−698 (4)	4279 (2)
P2	502 (1)	2442 (4)	4360 (2)
P3	2088 (1)	−3838 (4)	8167 (2)
P4	1986 (1)	−3843 (4)	6320 (2)
S1	852 (1)	726 (4)	5801 (2)
S2	1153 (1)	906 (4)	4899 (2)
S3	1428 (1)	−3282 (4)	6989 (2)
S4	1790 (1)	−1520 (4)	7137 (2)
S5	1428 (1)	399 (4)	6123 (2)
S6	1217 (1)	−1191 (4)	6852 (2)
C1	1130 (3)	697 (13)	5617 (7)
C2	1491 (3)	−1961 (13)	6993 (7)
C3	1347 (4)	116 (15)	6821 (8)
C11	775 (3)	−1820 (11)	4575 (4)
C21	841 (3)	−2590 (11)	4206 (4)
C31	979 (3)	−3472 (11)	4465 (4)
C41	1053 (3)	−3584 (11)	5092 (4)
C51	987 (3)	−2815 (11)	5460 (4)
C61	848 (3)	−1933 (11)	5202 (4)
C12	246 (2)	−1200 (9)	4208 (6)
C22	182 (2)	−2250 (9)	4082 (6)
C32	−73 (2)	−2583 (9)	4004 (6)
C42	−263 (2)	−1865 (9)	4053 (6)
C52	−199 (2)	−815 (9)	4179 (6)
C62	55 (2)	−483 (9)	4257 (6)
C13	596 (2)	−630 (12)	3501 (6)
C23	842 (2)	−474 (12)	3411 (6)
C33	871 (2)	−295 (12)	2830 (6)
C43	655 (2)	−274 (12)	2339 (6)
C53	410 (2)	−431 (12)	2428 (6)
C63	380 (2)	−609 (12)	3009 (6)
C14	657 (3)	2965 (10)	3809 (7)
C24	772 (3)	2254 (10)	3493 (7)
C34	892 (3)	2614 (10)	3056 (7)
C44	899 (3)	3684 (10)	2937 (7)
C54	784 (3)	4395 (10)	3253 (7)
C64	663 (3)	4036 (10)	3689 (7)
C15	527 (2)	3520 (9)	4899 (6)
C25	739 (2)	3516 (9)	5400 (6)
C35	769 (2)	4315 (9)	5829 (6)
C45	587 (2)	5117 (9)	5756 (6)
C55	375 (2)	5121 (9)	5255 (6)
C65	345 (2)	4322 (9)	4826 (6)
C16	157 (3)	2411 (11)	3981 (5)
C26	−19 (3)	2281 (11)	4336 (5)
C36	−281 (3)	2179 (11)	4062 (5)
C46	−369 (3)	2208 (11)	3433 (5)
C56	−194 (3)	2338 (11)	3079 (5)
C66	69 (3)	2440 (11)	3352 (5)
C17	1984 (2)	−3115 (9)	8761 (5)
C27	2150 (2)	−2980 (9)	9334 (5)
C37	2066 (2)	−2435 (9)	9778 (5)
C47	1817 (2)	−2023 (9)	9649 (5)
C57	1651 (2)	−2157 (9)	9075 (5)
C67	1735 (2)	−2703 (9)	8631 (5)
C18	2439 (2)	−3620 (7)	8365 (5)
C28	2619 (2)	−4415 (7)	8566 (5)
C38	2882 (2)	−4195 (7)	8691 (5)
C48	2965 (2)	−3180 (7)	8616 (5)
C58	2786 (2)	−2384 (7)	8416 (5)
C68	2522 (2)	−2605 (7)	8290 (5)
C19	2056 (2)	−5223 (9)	8358 (5)
C29	2022 (2)	−5536 (9)	8917 (5)
C39	2017 (2)	−6600 (9)	9056 (5)
C49	2048 (2)	−7350 (9)	8635 (5)
C59	2082 (2)	−7037 (9)	8076 (5)
C69	2086 (2)	−5974 (9)	7937 (5)
C110	2298 (2)	−4447 (9)	6331 (4)
C210	2347 (2)	−4909 (9)	5818 (4)
C310	2591 (2)	−5312 (9)	5840 (4)
C410	2786 (2)	−5255 (9)	6375 (4)
C510	2737 (2)	−4793 (9)	6887 (4)
C610	2493 (2)	−4389 (9)	6866 (4)
C111	1754 (2)	−4749 (10)	5867 (4)
C211	1646 (2)	−5493 (10)	6178 (4)
C311	1480 (2)	−6258 (10)	5859 (4)
C411	1423 (2)	−6280 (10)	5229 (4)
C511	1531 (2)	−5537 (10)	4918 (4)
C611	1696 (2)	−4771 (10)	5237 (4)
C112	1970 (2)	−2732 (9)	5806 (5)
C212	2189 (2)	−2330 (9)	5660 (5)
C312	2167 (2)	−1468 (9)	5275 (5)
C412	1927 (2)	−1008 (9)	5036 (5)
C512	1708 (2)	−1410 (9)	5182 (5)
C612	1729 (2)	−2272 (9)	5567 (5)

actions of the hydride complexes $H_2Os_3(CO)_9L$ (L = CO, PMe_2Ph) with CS_2 reported by Adams.[15] Two hydride complex molecules have been found, in fact, to react with CS_2, forming the bridging $H_2CS_2^{2-}$ ligand. However, such an attractive mechanism seems to be ruled out by the reaction of the dithioformate complex **5** with an excess of CS_2, yielding almost quantitatively **6** (eq 1). A reasonable mechanism for the formation of **6** could be, thus, one involving the preliminary formation of the dithioformate complex **5**. This in turn undergoes nucleophilic attack by CS_2 on the dithioformate carbon atom, followed by transfer of hydrogen to carbon of the attacking CS_2 molecule. An identical process operated by the second sulfur of the -SC(H)S grouping then leads to the formation of **6** (Scheme III). Support to the latter pathway is provided by the well-established electrophilic character of the carbon atom of coordinated dithioformate, which has been found to undergo attack by nucleophiles like tertiary phosphines (eq 2).[16] Indeed, the carbon atom of a variety of 1,1-dithio acid ligands is an electrophilic center, susceptible to attack by nucleophiles, which either add to the dithio ligand or replace the primary substituent on the carbon atom.[17]

$$2(PPh_3)_2Cu(S_2CH) + CS_2 \rightarrow (PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2 \quad (1)$$



(2)

When **6** is dissolved in CH_2Cl_2, the color of the solution changes from bright yellow to red-orange within 1–2 h. Addition of heptane or ethanol causes the precipitation of a red powder that can be separated by decantation, leaving a pale yellow solution. On slow evaporation of the heptane/CH_2Cl_2 solution crystals of the dithioformate complex **5** are obtained, whereas the ethanol-/CH_2Cl_2 solution affords both the xanthate complex $(PPh_3)_2Cu(S_2COEt)$ (**7**)[18] and **5**. Attempts to identify the sulfur-containing red powder were unsuccessful. Compound **7** is stable both in the solid state and in solution. The infrared absorption are congruous with those of other xanthate complexes.[19] The ^1H NMR spectrum in $CDCl_3$ at 293 K contains a quartet at δ 4.41 and a triplet at δ 1.35 (intensity ratio 2:3) assigned to the ethoxy protons of the $EtOCS_2^-$ ligand.

The molecular structure of **7** consists of monomolecular units of $(PPh_3)_2Cu(S_2COEt)$, whose perspective view is shown in Figure 3. Selected bond distances and angles are reported in Table VII. In the complex molecule the copper atom is tetrahedrally coordinated by the phosphorus atoms of the phosphine ligands and

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Table III. Final Positional Parameters ($\times 10^4$) for $(PPh_3)_2Cu(S_2COEt)$

atom	*x*	*y*	*z*
Cu	5284 (1)	2948 (1)	6512 (1)
S1	4774 (1)	3217 (1)	8683 (2)
S2	4178 (1)	3400 (1)	5688 (2)
P1	5178 (1)	1755 (1)	6076 (2)
P2	6131 (1)	3656 (1)	6038 (2)
O	3535 (3)	3395 (3)	8073 (6)
C	4115 (4)	3341 (4)	7500 (8)
C1	2932 (5)	3494 (5)	7061 (11)
C2	2379 (8)	3656 (10)	8138 (20)
C2′	2386 (13)	3197 (15)	7607 (31)
C11	4371 (3)	1364 (3)	6327 (4)
C21	3986 (3)	1003 (3)	5231 (4)
C31	3366 (3)	735 (3)	5488 (4)
C41	3132 (3)	828 (3)	6839 (4)
C51	3517 (3)	1190 (3)	7935 (4)
C61	4137 (3)	1458 (3)	7679 (4)
C12	5744 (2)	1159 (2)	7158 (5)
C22	5567 (2)	462 (2)	7509 (5)
C32	6012 (2)	33 (2)	8366 (5)
C42	6633 (2)	302 (2)	8871 (5)
C52	6809 (2)	999 (2)	8520 (5)
C62	6365 (2)	1427 (2)	7663 (5)
C13	5293 (2)	1535 (2)	4208 (5)
C23	4970 (2)	1975 (2)	3148 (5)
C33	5034 (2)	1843 (2)	1689 (5)
C43	5420 (2)	1270 (2)	1289 (5)
C53	5743 (2)	830 (2)	2349 (5)
C63	5680 (2)	963 (2)	3809 (5)
C14	6155 (2)	4523 (3)	6943 (5)
C24	5551 (2)	4839 (3)	7178 (5)
C34	5541 (2)	5491 (3)	7916 (5)
C44	6133 (2)	5826 (3)	8419 (5)
C54	6736 (2)	5509 (3)	8184 (5)
C64	6747 (2)	4858 (3)	7446 (5)
C15	6178 (2)	3871 (2)	4129 (5)
C25	6236 (2)	4573 (2)	3635 (5)
C35	6244 (2)	4707 (2)	2158 (5)
C45	6194 (2)	4139 (2)	1175 (5)
C55	6136 (2)	3437 (2)	1670 (5)
C65	6128 (2)	3303 (2)	3147 (5)
C16	6946 (3)	3280 (3)	6625 (4)
C26	7399 (3)	3083 (3)	5656 (4)
C36	7989 (3)	2744 (3)	6162 (4)
C46	8127 (3)	2603 (3)	7636 (4)
C56	7674 (3)	2800 (3)	8604 (4)
C66	7084 (3)	3139 (3)	8099 (4)

Table IV. Final Positional Parameters ($\times 10^4$) for $(PPh_3)_2Cu(S_2CNHPh)\cdot CHCl_3$

atom	*x*	*y*	*z*
Cu	2131 (1)	3809 (1)	3385 (1)
P1	1439 (2)	4261 (2)	1948 (2)
P2	1711 (2)	2227 (2)	3606 (2)
S1	3795 (2)	4232 (2)	3655 (2)
S2	2590 (2)	5684 (2)	5136 (2)
Cl1	4245 (6)	1986 (6)	599 (7)
Cl2	5937 (7)	3032 (15)	611 (13)
Cl3	4496 (8)	4106 (8)	356 (7)
Cl11	3877 (8)	2674 (18)	184 (11)
Cl22	5408 (24)	4253 (30)	1428 (36)
Cl33	5819 (22)	2572 (32)	621 (25)
N	4352 (5)	6413 (7)	5074 (7)
C	3629 (6)	5552 (7)	4713 (8)
C1	4880 (11)	3224 (14)	1072 (14)
C11	1908 (3)	5653 (5)	2063 (5)
C21	1370 (3)	6492 (5)	2147 (5)
C31	1781 (3)	7548 (5)	2260 (5)
C41	2730 (3)	7765 (5)	2290 (5)
C51	3268 (3)	6926 (5)	2207 (5)
C61	2857 (3)	5870 (5)	2093 (5)
C12	1401 (4)	3275 (5)	352 (5)
C22	1481 (4)	2136 (5)	57 (5)
C32	1438 (4)	1340 (5)	−1163 (5)
C42	1315 (4)	1683 (5)	−2087 (5)
C52	1235 (4)	2822 (5)	−1791 (5)
C62	1278 (4)	3618 (5)	−572 (5)
C13	235 (3)	4386 (4)	2071 (4)
C23	48 (3)	5003 (4)	3245 (4)
C33	−864 (3)	5092 (4)	3408 (4)
C43	−1589 (3)	4564 (4)	2397 (4)
C53	−1402 (3)	3946 (4)	1223 (4)
C63	−490 (3)	3857 (4)	1060 (4)
C14	2458 (4)	2082 (4)	4802 (5)
C24	2549 (4)	1019 (4)	4767 (5)
C34	3090 (4)	972 (4)	5750 (5)
C44	3540 (4)	1988 (4)	6768 (5)
C54	3449 (4)	3051 (4)	6804 (5)
C64	2908 (4)	3098 (4)	5821 (5)
C15	540 (4)	1967 (5)	3895 (5)
C25	−160 (4)	2305 (5)	3324 (5)
C35	−1058 (4)	2191 (5)	3549 (5)
C45	−1255 (4)	1740 (5)	4346 (5)
C55	−554 (4)	1401 (5)	4917 (5)
C65	343 (4)	1515 (5)	4691 (5)
C16	1791 (3)	925 (5)	2249 (5)
C26	2660 (3)	810 (5)	1920 (5)
C36	2746 (3)	−100 (5)	816 (5)
C46	1966 (3)	−895 (5)	41 (5)
C56	1097 (3)	−779 (5)	370 (5)
C66	1010 (3)	131 (5)	1474 (5)
C17	4427 (5)	7613 (7)	5902 (6)
C27	5043 (5)	8353 (7)	5688 (6)
C37	5199 (5)	9535 (7)	6462 (6)
C47	4740 (5)	9977 (7)	7450 (6)
C57	4124 (5)	9237 (7)	7664 (6)
C67	3968 (5)	8054 (7)	6889 (6)

by the sulfur atoms of the $EtOCS_2^-$ group. The geometry of the complex is very distorted, the distortion from the idealized geometry being mainly due to the short bite of the S_2C- fragment, the value of the S1–Cu–S2 bond angle reaching the value of 74.6° (range of the other angles 102.3 (1)–127.1 (1)°). As previously reported for other copper(I) complexes,[14] the distortion is not restricted to the bond angles but also appears in bond distances. Indeed, while the Cu–P bond distances, very similar each to other, are in excellent agreement with those reported for other copper(I) complexes containing the same donor set, the Cu–S bond distances (2.404 (2), 2.451 (2) Å) are not equivalent. A similar unsymmetrical arrangement around the metal atom is not surprising: it has been observed in other monomeric copper(I) complexes[14] and in dimeric silver(I) complex[20] and tentatively rationalized on the basis of the well-known tendency of copper(I) or silver(I) to be three- as well as four-coordinated.[14] On the other hand, also in the dimeric copper(I) complex **6** a similar difference in the Cu–S bond distances is observed, relative to one coordination sphere.

Even though at present not understood, the solvolysis of **6** is interesting since it involves only a part of the bridging ligand, whereas the $(PPh_3)_2CuS_2C$ fragments remain intact during the process. Whether the formation of the dithioformate ligand occurs through the abstraction of hydrogen from CH_2Cl_2, heptane, or ethanol is an unresolved problem. As for the xanthate complex, ethanol is surely the source of the ethoxy group.

The obtainment of **6** by reacting **5** with CS_2 and its solvolysis in CH_2Cl_2/heptane or CH_2Cl_2/ethanol solutions may help to rationalize the formation of the ethyl carbonate complex (triphos)Cu(O_2COEt). The latter compound has been obtained by treating a CH_2Cl_2 solution of (triphos)Cu(O_2CH) with COS and ehtanol (eq 3).[1] Carbonyl sulfide could, in fact, react with the

$$\text{(triphos)Cu(O}_2\text{CH)} + \text{COS} \xrightarrow{\text{EtOH}} \text{(triphos)Cu(O}_2\text{COEt)} \tag{3}$$

formate group similarly to CS_2 with the dithioformate group. Even though not isolated, we may suppose the formation of an unstable metal species capable of yielding the ethyl carbonate complex in the presence of ethanol. The assumption of the electrophilic nature of the formate carbon atom seems to be plausible by considering

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Table V. IR and ^{1}H NMR Data for Compounds 5–13

	IR, cm^{-1}					^{1}H NMR^a	
	ν(NH)	ν(CN)	ν(HCS)	$\nu(CS_2)_{asym}$	$\nu(CS_2)_{sym}$	δ(CH)	δ(NH)
$(PPh_3)_2Cu(S_2CH)$ (**5**)			1235	960	820	11.27	
$(PPh_3)_2Cu(S_2CSCH_2SCS_2)Cu(PPh_3)_2$ (**6**)				1010	880		
$(PPh_3)_2Cu(S_2COEt)^b$ (**7**)				1150	1045		
(triphos)Cu(S_2CH) (**8**)			1245	1012	810	11.26	
$(np_3)Cu(S_2CH)$ (**9**)			1235	985		*c*	
$(PPh_3)_2Cu(S_2CNHPh){\cdot}CHCl_3$ (**10**)	3185	1510 1315		1000			9.05
$(PCy_3)_2Cu(S_2CNHPh)$ (**11**)	3200	1510 1315		1000			8.99
(triphos)Cu(S_2CNHPh) (**12**)	*d*	1500 1315		1000			9.19
$(np_3)Cu(S_2CNHPh)$ (**13**)	*d*	1505		1110			9.15

^{a} $CDCl_3$ solutions. ^{b} ν(CO) = 1195 cm^{-1}. ^{c} Due to low concentration this peak was not observed. ^{d} Not observed.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $(PPh_3)_2Cu(\mu\text{-}S_2CSCH_2SCS_2)Cu(PPh_3)_2$

	Distances		
Cu1–P1	2.276 (6)	S1–C1	1.647 (16)
Cu1–P2	2.254 (6)	S2–C1	1.697 (16)
Cu1–S1	2.411 (5)	S3–C2	1.718 (17)
Cu1–S2	2.479 (5)	S4–C2	1.652 (16)
Cu2–P3	2.254 (4)	S5–C1	1.759 (16)
Cu2–P4	2.262 (5)	S5–C3	1.791 (18)
Cu2–S3	2.448 (5)	S6–C2	1.725 (16)
Cu2–S4	2.449 (5)	S6–C3	1.815 (19)
	Angles		
P1–Cu1–P2	125.8 (2)	Cu1–S1–C1	83.5 (6)
P1–Cu1–S1	111.4 (2)	Cu1–S2–C1	80.4 (5)
P1–Cu1–S2	101.6 (2)	Cu2–S3–C2	82.1 (6)
P2–Cu1–S1	118.3 (2)	Cu2–S4–C2	83.4 (6)
P2–Cu1–S2	111.6 (2)	C1–S5–C3	104.3 (8)
S1–Cu1–S2	73.5 (2)	C2–S6–C3	102.5 (9)
P3–Cu2–P4	131.6 (2)	S1–C1–S2	122.2 (9)
P3–Cu2–S3	113.4 (2)	S1–C1–S5	124.4 (9)
P3–Cu2–S4	110.5 (2)	S2–C1–S5	113.3 (9)
P4–Cu2–S3	105.7 (2)	S3–C2–S4	120.9 (10)
P4–Cu2–S4	107.1 (2)	S3–C2–S6	113.7 (9)
S3–Cu2–S4	73.6 (2)	S4–C2–S6	125.3 (10)
		S5–C3–S6	113.6 (10)

Table VII. Selected Bond Distances (Å) and Angles (deg) for $(PPh_3)_2Cu(S_2COEt)$

	Distances		
Cu–P1	2.265 (2)	S2–C	1.702 (7)
Cu–P2	2.245 (2)	O–C	1.341 (8)
Cu–S1	2.404 (2)	O–C1	1.482 (11)
Cu–S2	2.451 (2)	C1–C2	1.601 (20)
S1–C	1.664 (7)	C1–C2′	1.377 (26)
	Angles		
P1–Cu–P2	127.1 (1)	Cu–S1–C	81.9 (3)
P1–Cu–S1	108.3 (1)	Cu–S2–C	79.8 (3)
P1–Cu–S2	102.3 (1)	S1–C–S2	122.0 (5)
P2–Cu–S1	116.1 (1)	S1–C–O	115.4 (6)
P2–Cu–S2	115.7 (1)	S2–C–O	122.6 (6)
S1–Cu–S2	74.6 (1)	C–O–C1	117.5 (7)
		O–C1–C2	102.3 (9)
		O–C1–C2′	111.2 (14)

that oxygen is more electronegative than sulfur.

The tricyclohexylphosphine complex **2** reacts with CS_2 to give a yellow orange solution. All our attempts to isolate a solid product from the reaction mixture, however, met without success.

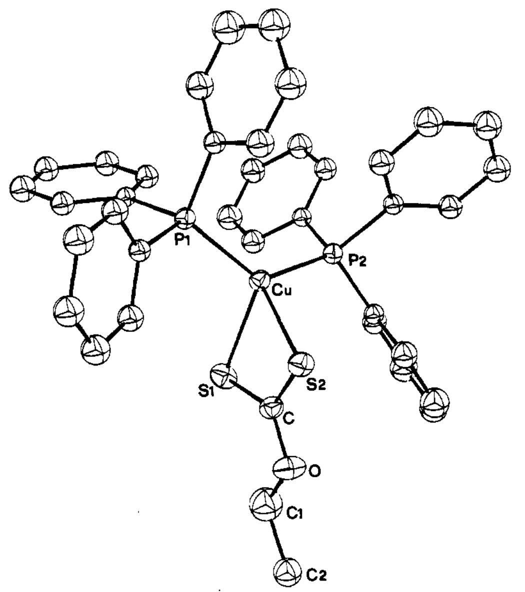
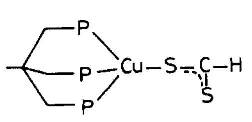
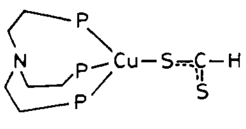


Figure 3. Perspective view of the complex molecule $(PPh_3)_2Cu(S_2COEt)$; ORTEP drawing with 30% probability ellipsoids.

The η^1-BH_4 complexes **3** and **4** react with CS_2 to give the dithioformate derivatives (triphos)Cu(S_2CH) (**8**) and $(np_3)Cu(S_2CH)$ (**9**), respectively. The infrared spectra of both compounds are congruous with those of other dithioformate species, showing the typical ν(HCS) and $\nu(CS_2)_{asym}$ frequencies[13,21] (Table V). Compound **9** exhibits an additional band at 2800 cm^{-1} indicative of the uncoordination of the nitrogen atom of np_3.[22] The ^{1}H NMR spectrum of **8** contains a resonance at δ 11.26 attributable to the dithioformate proton.[21] Due to its low solubility this band is not observed for **9**. The $^{31}P\{^1H\}$ NMR spectrum of **8** in $CDCl_3$ consists of a unique broad resonance at 25.54 ppm. Compounds **8** and **9** have infrared and ^{1}H NMR spectra identical with those of authentic samples prepared by reacting (triphos)Cu(ClO_4)[23] or $(np_3)CuBPh_4$[24] with KS_2CH. On the basis of all of these data, it is reasonable to assign unidentate binding of the dithioformate ligand in both complexes.



8



9

As in the case of the formate ligand in the analogous complexes $(PPh_3)_2Cu(O_2CH)$, (triphos)Cu(O_2CH), and $(np_3)Cu(O_2CH)$,[1] the bonding mode of the dithioformate group, i.e. bidentate in **5** and unidentate in **8** and **9**, poorly affects its infrared vibrations, which furthermore do not differ much from those of the free S_2CH^- ion (ν(HCS) = 1252 cm^{-1}, $\nu(CS_2)_{asym}$ = 982 cm^{-1}).[13] This means that the internal electronic distribution in the bound dithioformate group remains nearly the same as that in the free ion.

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Scheme IV

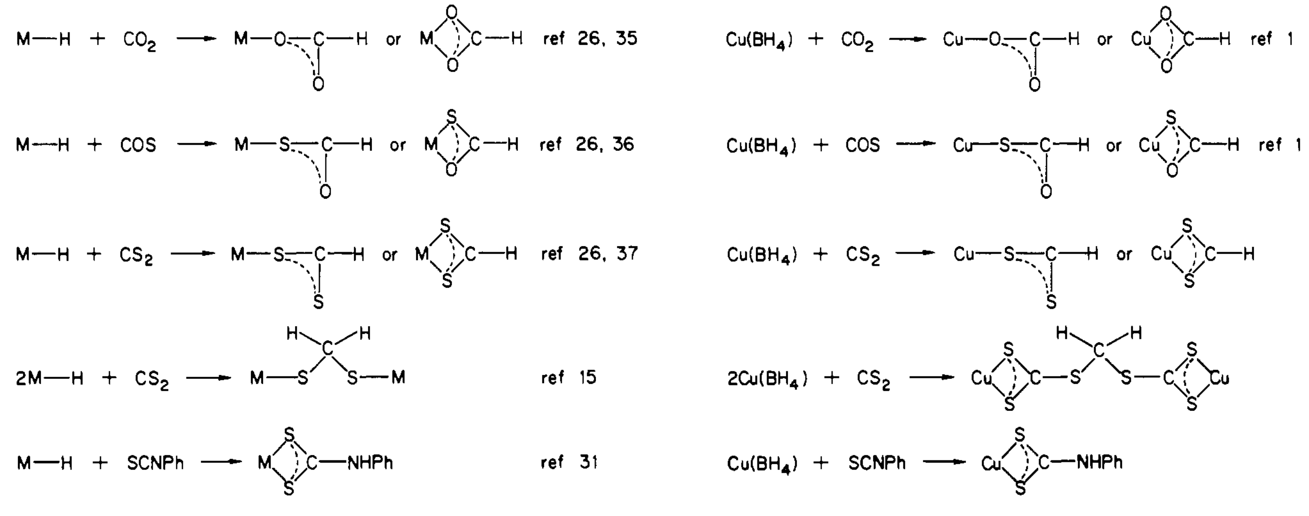

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $(PPh_3)_2Cu(S_2CNHPh){\cdot}CHCl_3$

	Distances		
Cu-P1	2.264 (2)	S1-C	1.716 (9)
Cu-P2	2.244 (2)	S2-C	1.683 (9)
Cu-S1	2.414 (3)	N-C	1.347 (10)
Cu-S2	2.414 (2)	N-C17	1.435 (10)
	Angles		
P1-Cu-P2	126.6 (1)	Cu-S1-C	82.1 (3)
P1-Cu-S1	110.7 (1)	Cu-S2-C	82.7 (3)
P1-Cu-S2	101.4 (1)	S1-C-S2	118.8 (5)
P2-Cu-S1	110.2 (1)	S1-C-N	115.0 (7)
P2-Cu-S2	121.5 (1)	S2-C-N	126.0 (7)
S1-Cu-S2	74.6 (1)	C-N-C17	129.0 (7)

A fact likely due to the low electrophilicity of the phosphine-copper(I) fragments.[1,25,26]

In conclusion, each (phosphine)copper(I) tetrahydroborate complex molecule supplies only a single hydride ion during the reactions with CS_2, dithioformate being the intermediate or final product of the reduction of CS_2. This is in contrast to $NaBH_4$, which reacts with CS_2 to give thioformaldehyde (eq 5).[27]

$$NaBH_4 + 2CS_2 \rightarrow NaBS_2 + 2H_2C{=}S \qquad (4)$$

(b) With SCNPh. Compounds **1** and **2** react with SCNPh, producing yellow solutions from which crystals of formulas $(PPh_3)_2Cu(S_2CNHPh){\cdot}CHCl_3$ (**10**) and $(PCy_3)_2Cu(S_2CNHPh)$ (**11**) are obtained, respectively. Both compounds are air stable both in the solid state and in solution. The IR spectra show almost identical absorption in the ν(NH), $\nu(\mathrm{C}\overset{\ldots}{-}\mathrm{N})$, and $\nu(CS_2)$ regions.[19,28] Reinforced phenyl vibrations appear at ca. 1580 and 1480 cm^{-1}. The ^1H NMR spectra exhibit resonances at δ 9.05 and 8.99 for **10** and **11**, respectively. All of these data are suggestive of the presence of the dithiocarbamate ligand $PhHNCS_2^-$ in both complexes. However, the comparison of the spectroscopic evidence with that recorded in the literature for other dithiocarbamate complexes did not clarify the bonding mode of the anion in this instance, and a single-crystal X-ray diffraction study was undertaken. The molecular structure of compound **10** consists of monomeric units of $(PPh_3)_2Cu(S_2CNHPh)$, with chloroform solvent molecules interspersed in the lattice. Figure 4 gives a perspective view of the complex molecule, whose selected bond distances and angles are reported in Table VIII.

In the complex molecule the copper atom displays the same distorted tetrahedral geometry, which has been described more than once for copper(I) complexes, having the metal surrounded by two tertiary phosphines and by the sulfur atoms of one S_2C-fragment. All the bond distances as well as the bond angles in the coordination sphere are well in the range of values reported for **6** and **7** and for other (phosphine)copper(I) complexes with 1,1-dithio ligands.[14]

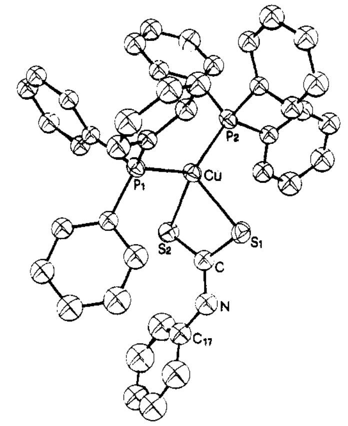

Figure 4. Perspective view of the complex molecule $(PPh_3)_2Cu(S_2CNHPh)$; ORTEP drawing with 30% probability ellipsoids.

As concerns the $PhHNCS_2^-$ ligand, the geometry of the S_2CN fragment is planar within 0.02 Å, while the phenyl ring forms an angle of 29.4° with the remainder of the ligand in order to minimize the contact between S2 and H67 (2.63 Å), H67 being an ortho proton of the dithiocarbamate phenyl group. The dimensions of the *N*-phenyldithiocarbamate ligand are consistent with those reported for a variety of transition-metal dithiocarbamate complexes.[29]

It is noteworthy that the CuS_2CN fragment is not planar, the dihedral angle between the CuS1S2 and S1S2C planes being 15.7°.

Finally, the Cu-S bond distances in these complexes deserve some comment. We have noticed in the title compounds and in previously reported similar tetrahedral Cu(I) complexes[14,30] that the arrangement of the sulfur atoms around the metal atom, surrounded by a P_2S_2 donor set, can be symmetrical, i.e. with two Cu-S bond distances equivalent, or unsymmetrical, with the two Cu-S distances significantly different. Beside the above-mentioned tendency of copper(I) to be three- as well as four-coordinated, packing effects are also probably operative, the difference in energy

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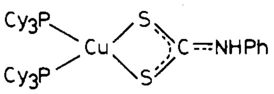
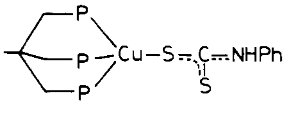
between the two configurations being likely very small. Support of this point of view is provided by the simultaneous presence in **6** of two coordination polyhedra showing symmetrical and unsymmetrical arrangement of the sulfur ligands.

On the basis of the preceding structural analysis, a structure where the copper atom is tetrahedrally coordinated by two tricyclohexylphosphine groups and by the sulfur atoms of the $PhHNCS_2^-$ ligand can be positively assigned to **11**.

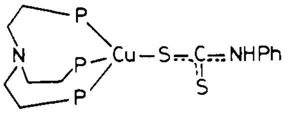


11

Dithiocarbamate complexes are obtained also when phenyl isothiocyanate is reacted with the η^1-BH_4 complexes **3** and **4**. Though the spectroscopic data concerning the *N*-phenyldithiocarbamate group are similar to those found for the η^2-S_2CNHPh complexes **10** and **11**, we believe that the dithiocarbamate ligand is unidentate in (triphos)Cu(S_2CNHPh) (**12**) and (np_3)Cu(S_2CNHPh) (**13**). This assumption is based on the structures of the corresponding formate, thioformate, and dithioformate complexes formed by (triphos)Cu and (np_3)Cu fragments.[1]



12



13

The formation of *N*-phenyldithiocarbamate complexes by reaction of the present copper(I) tetrahydroborates (eq 5) with

$$LCu(Bh_4) + 2SCNPh \rightarrow LCu(S_2CNHPh) + CNPh \quad (5)$$

$$[(PMe_3)_3PdH]BPh_4 + 2SCNMe \rightarrow [(PMe_3)_2Pd(S_2CNHMe)]BPh_4 + CNMe \quad (6)$$

SCNPh closely parallels that of the *N*-methyldithiocarbamate complex $[(PMe_3)_2Pd(S_2CNHMe)]BPh_4$ reported by Werner (eq 6).[31] Both of the above reactions represent unusual reactivity patterns of organo isothiocyanates, which usually insert into M–H bonds to give thioformamides.[32]

Conclusions

The number of metal tetrahydroborates that could find useful applications in the selective reduction of organic functional groups[33] is now increased by five units, namely $(PCy_3)_2Cu(BH_4)$, (triphos)Cu(BH_4), $(PMePh_2)_3Cu(BH_4)$,[1] (np_3)Cu(BH_4), and (etp_3)Cu(BH_4).[1] These complexes supply only a single hydride ion during the reduction, and their reducing capability seems to be influenced by the bonding mode of the BH_4^- ligand.[1]

The use of copper(I) tetrahydroborates in organometallic chemistry seems to be very promising as attested by the reactions reported in this present paper and in the preceding one. The diminished reducing capability of the coordinated BH_4^- group compared to that of the free ligand and the presence of (phosphine)copper fragments in the reaction mixture could lead in fact to the formation and stabilization of unusual chemical species.

The ease of making, handling, storing, and using (phosphine)copper(I) tetrahydroborate complexes represents a favorable feature of these reagents; conversely, their high molecular weight constitutes an unavoidable disadvantage.

Finally, we note the close analogies existing in the chemistry of metal hydrides and copper(I) tetrahydroborates, at least in their reactivity toward heteroallene molecules. Such analogies, which are reported in Scheme IV, lead to the conclusion that copper(I) tetrahydroborates could apparently function as substitutes for copper hydrides, very rare compounds, indeed limited to a few polynuclear species.[34]

Acknowledgment. This work was supported by a grant from the CNR program Chimica Fine e Secondaria. Thanks are due to F. Cecconi and G. Scapacci for technical assistance.

Registry No. **1**, 16903-61-0; **2**, 88637-65-4; **3**, 82678-89-5; **4**, 94500-07-9; **5**, 88927-05-3; **6**, 88279-91-8; **7**, 25263-83-6; **8**, 86322-44-3; **9**, 94517-75-6; **10**, 94517-76-7; **11**, 88622-22-4; **12**, 94500-08-0; **13**, 94500-09-1; $(PPh_3)_3Cu(ClO_4)$, 34010-81-6; CS_2, 75-15-0; SCNPh, 103-72-0; $HS_2CSCH_2SCS_2H$, 94500-10-4.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes for $(PPh_3)_2Cu(\mu$-$S_2CSCH_2SCS_2)Cu(PPh_3)_2$, $(PPh_3)_2Cu(S_2COEt)$, and $(PPh_3)_2Cu(S_2CNHPh)\cdot CHCl_3$ (68 pages). Ordering information is given on any current masthead page.

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The Creutz–Taube Complex Revisited: Polarized Optical Spectroscopy

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Received May 9, 1984

Attention is focused on the absorption and LD and MCD spectroscopy of the mixed-valence Creutz–Taube complex ion. The material is studied in a range of environments including solid solutions in PVA foils, microdispersed crystals in pressed KCl disks, and pure crystalline salts. These studies reveal a structure not shown in existing solution spectra as well as providing polarization information. Of particular interest is the strong polarization of the well-known "intervalence" transition near 6400 cm^{-1} as well as a broad and weaker absorption around 4000 cm^{-1} showing a large negative MCD. Evidence for vibronic coupling is presented.

Introduction

The strong polarization of the absorption region near 6400 cm^{-1} in the decaammine(μ-pyrazine-*N*,*N'*)diruthenium(5+) (C–T) mixed-valence ion was established only recently.[1] In this paper we fully describe these measurements as well as present further absorption experiments and magnetic circular dichroism (MCD)

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