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Preliminary communication

FACILE REDUCTION OF CARBON DIOXIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE BY COPPER(I) BOROHYDRIDE. X-RAY CRYSTAL STRUCTURE OF THE COMPLEX [(triphos)Cu(O_2CH)]

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Summary

The copper(I)-borohydride complex [(triphos)Cu(BH_4)] reacts with CO_2, CS_2, and COS under very mild conditions to give formate, dithioformate, or thioformate copper(I) complexes, respectively. A complete X-ray crystal structure determination has been carried out on the formate complex [(triphos)Cu(O_2CH)].

Metal hydrides have been found to play an important role in reactions which effect the reduction of CO_2 and related molecules such as COS, and CS_2 [1]. These reactions have recently received attention because of their possible relevance to the catalysis of the water gas shift reactions, and more generally, because they are a source of information on synthesis gas catalysts [2].

Despite the wide utilization of copper compounds in several of the catalytically active systems [3], very scanty information is available on the ability of copper hydrides to activate C(1) molecules [4]. This is undoubtedly due to the difficulty of isolating stable copper hydrides, so far limited to $[HCuPR_3]_6$ [5,6]. By contrast tetrahydroborate complexes of copper(I) containing phosphine ligands can be easily synthesized [6], and some of them have been successfully employed as selective reducing agents for organic synthesis [7].

We have recently synthesized the copper(I) complex [(triphos)Cu(BH_4)] (1) (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane), which has been found to contain a unidentate borohydride group [8], and we now describe the reactions of complex 1 with CO_2, CS_2, and COS.

Carbon dioxide reacts at room temperature with a methylene chloride solution of 1, to give the complex [(triphos)Cu(O_2CH)] (2), which can be isolated

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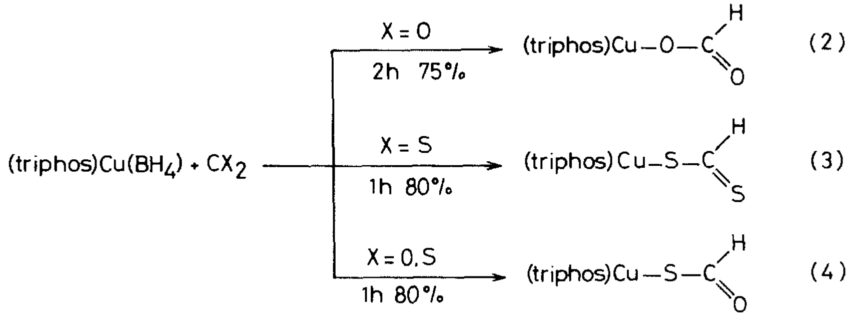
TABLE 1

SPECTRAL DATA FOR 2, 3, AND 4

Compound	IR[a]				^{1}H NMR	^{13}C NMR
	ν(CO)	ν(CO··Cu)	ν(CS)	ν(CS··Cu)	δ(H(X$_2$CH))	δ(C(X$_2$CH))
2	1620	1320			9.01[b]	168.4[b]
3			1012	810	11.26[c]	[d]
4	1625, 1570			805	12.44[c]	201.3[b]

[a] Samples mulled in Nujol. [b] CD_2Cl_2 solution. [c] $CDCl_3$ solution. [d] Due to low concentration this peak was not observed.



Scheme 1

as white crystals. The dithioformate and thioformate analogues 3 and 4 can be obtained by similar procedures starting from carbon disulfide or carbonyl sulfide.

The reaction conditions and yields are summarized in Scheme 1; IR spectral data, and ^{1}H and ^{13}C NMR data at 293 K are listed in Table 1.

The molecular structure of 2 has been determined by X-ray diffraction methods. The crystals, which are isomorphous with compound 1, are orthorhombic, space group $Pn2_1a$ with a 20.901(8), b 17.136(6), c 10.162(4) Å and $Z = 4$. Data collection was carried out on a Philips computer controlled PW 1100 diffractometer using the ω—2ϑ scan technique and graphite monochromated radiation Mo-K_α within $2\vartheta \leqslant 50°$. An absorption correction (μ(Mo-K_α) 7.64 cm^{-1}) giving transmission factors ranging from 0.93 to 0.71 was applied. On account of the isomoprhism of 1 and 2 the final parameters of 1 [8] were used as starting parameters. The formate hydrogen atom located from a difference Fourier map ($\text{sen}\,\vartheta/\lambda < 0.3$ Å^{-1}) was successfully refined. Full matrix least-squares refinements converged at R and R_w factors values of 0.055 and 0.054 for the 2267 reflections having $I \geqslant 3\sigma(I)$. The absolute configuration of the structure was determined by applying the anomalous dispersion correction.

The molecular structure consists of monomolecular (triphos)Cu(O_2CH) units. The copper atom is coordinated by the three phosphorus atoms of the triphos ligand and by an oxygen atom of the formate group acting as monodentate ligand. The geometry is distorted tetrahedral, the oxygen atom being displaced from the pseudo threefold axis defined by the P_3Cu fragment as evidenced by the values of the P—Cu—O angles, which range from 111.2(3) to 130.0(2)°. A perspective view of the molecule is shown in Fig. 1.

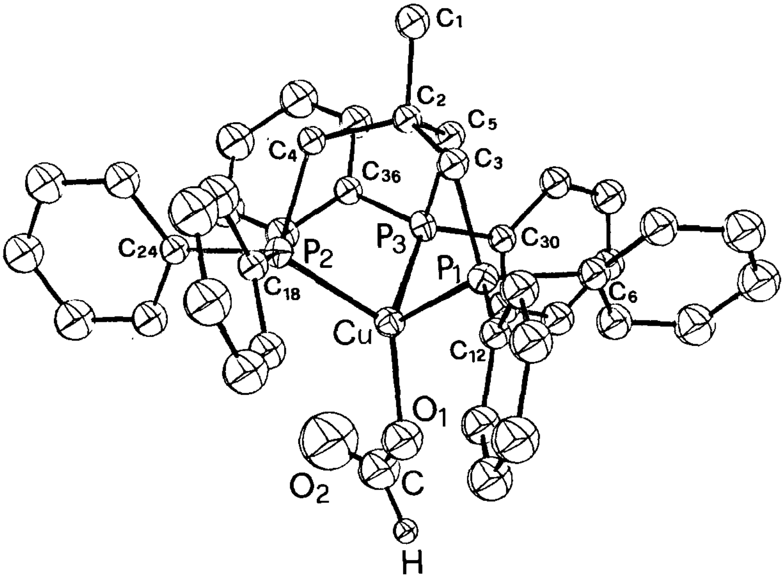


Fig. 1. Perspective view of the molecule of the comples (triphos)Cu(O_2CH). ORTEP drawing with 30% probability ellipsoids. For the sake of clarity the hydrogen atom was assigned an arbitrary temperature factor. Important bond distances and angles: Cu—P(1) 2.287(2), Cu—P(2) 2.274(3), Cu—P(3) 2.288(3), Cu—O(1) 2.015(9), C—O(1) 1.158(14), C—O(2) 1.196(17), C—H 1.17(17) Å, P(1)—Cu—P(2) 93.6(1), P(1)—Cu—P(3) 95.0(1), P(2)—Cu—P(3) 96.0(1), P(1)—Cu—O(1) 111.2(3), P(2)—Cu—O(1) 130.0(2), P(3)—Cu—O(1) 122.6(2), O(1)—C—O(2) 123.5(17), O(1)—C—H 110(8), O(2)—C—H 126(8)°.

Infrared and NMR spectral comparisons of **2** with the products arising from CS_2 and COS reactions with **1** suggest unidentate binding of the dithioformate or thioformate ligands to the copper atom through the sulfur atom [1a,9]. The dithioformate derivative has infrared and ^1H NMR spectra identical with those of an authentic sample prepared by treating potassium dithioformate with [(triphos)$CuClO_4$] [10].

Complex **2** does not undergo decarbonylation when a stream of argon is passed through a methylene chloride solution at room temperature. Decarbonylation of metal formates, which is regarded as a common feature of this type of compound, has been suggested to proceed via β-elimination of the hydrogen atom to the metal center followed by formation of a metal hydride species [1a]. This mechanism requires a vacant coordination site on the metal. The well known rigidity of the triphos ligand, as well as the ascertained low propensity of copper to form hydrides may be responsible for the high stability of **2**.

The unusual features of the reactions reported in this paper are the mild conditions required to activate CO_2, CS_2, and COS and the excellent yields obtained. This may be ascribed to use of copper as the central atom, as well as to the presence of tetrahydroborate as ligand. Which of these factors play the dominant role in the activation of C(1) molecules is currently under investigation. Special attention will be directed toward η^2- and η^3-borohydride complexes, since different binding modes of a ligand are often accompanied by different reactivity pathways.

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