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Preliminary communication

REACTIVITY OF THE TETRAHYDROBORATE COPPER(I) COMPLEXES $[(PR_3)_2Cu(\eta^2\text{-}BH_4)]$ (R = Ph, Cy) TOWARD CO_2, COS, AND SCNPh

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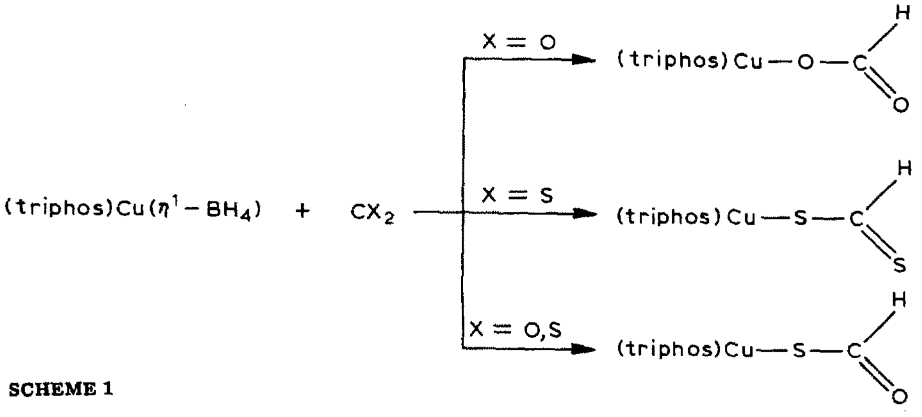
Summary

CO_2, COS, and SCNPh react under very mild conditions with the copper(I)-tetrahydroborate complexes $[(PR_3)_2Cu(\eta^2\text{-}BH_4)]$ (R = Ph, Cy); CO_2 and COS give the complexes $[(PR_3)_2Cu(\eta^2\text{-}O_2CH)]$ and $[(PR_3)_2Cu(\eta^2\text{-}OSCH)]$ respectively, whereas SCNPh gives the η^2-dithiocarbamate complexes $[(PR_3)_2Cu(\eta^2\text{-}S_2CNHPh)]$. Addition of PPh_3 under CO_2 to solutions of $[(PPh_3)_2Cu(\eta^2\text{-}BH_4)]$ gives $[(PPh_3)_3Cu(\eta^1\text{-}O_2CH)]$ while addition of PPh_3 and NBu_4ClO_4 under CO_2 gives $[(PPh_3)_3Cu(\mu\text{-}O_2CH)Cu(PPh_3)_3]ClO_4$.

We recently reported the facile reduction of CO_2, COS, and CS_2 by the complex $[(triphos)Cu(\eta^1\text{-}BH_4)]$ [triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane] to give metalloformate derivatives [1] (Scheme 1). These reactions are of interest for various reasons: (i) the copper(I)-tetrahydroborate complexes parallel metal hydrides in their reactivity towards CO_2 and related molecules



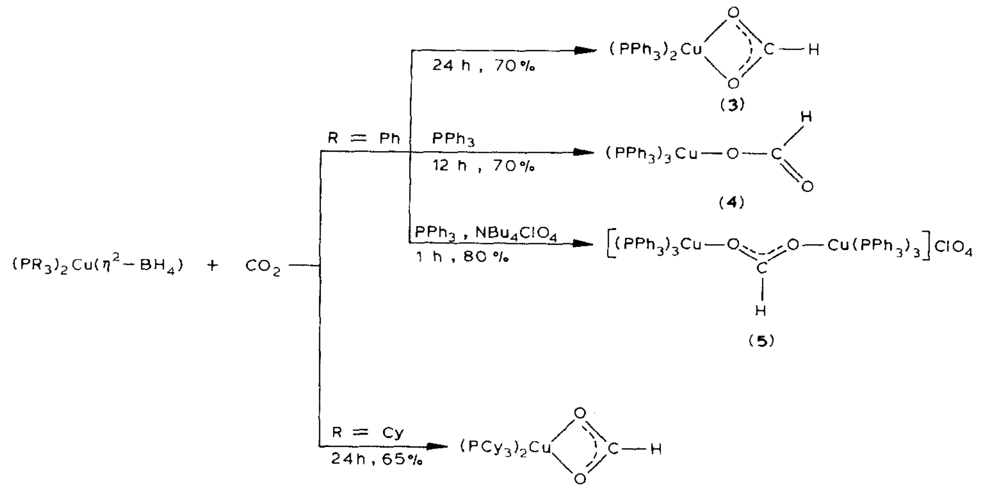
SCHEME 1

[2], and so could function as substitutes for copper hydrides, so far used only with a very few polynuclear species; (ii) metal formates have been suggested to be intermediates in a number of catalysis-related reactions, e.g., Fischer—Tropsch Synthesis, and the water gas shift reaction [3]; (iii) copper(I)-tetrahydroborate complexes could possibly be employed as selective reducing agents not only for organic synthesis [4] but also for organometallic synthesis.

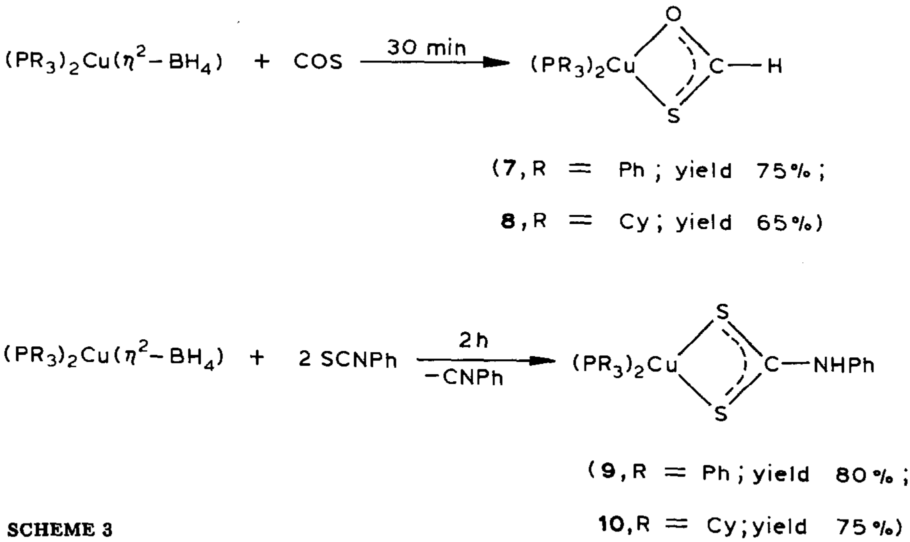
In an effort to more fully explore these reactions as well as to extend their applicability, we are investigating the reactivity of different types of copper(I)-tetrahydroborate complexes toward heteroallenes of formula X=C=Y (X, Y = O, S, CR, NR_2). We now report the reactions of the complexes $[(PPh_3)_2Cu(\eta^2\text{-}BH_4)]$ (1) [5] and $[(PCy_3)_2Cu(\eta^2\text{-}BH_4)]$ (2) with CO_2, COS, and SCNPh. Schemes 2 and 3 illustrate the reactions performed and the results obtained; IR spectral data and ^1H NMR data are listed in Table 1.

On bubbling CO_2 into a methylene chloride/ethanol solution of **1**, white crystals of the complex $[(PPh_3)_2Cu(\eta^2\text{-}O_2CH)]$ (**3**) are formed. Identification of this product was based on spectroscopic, X-ray, and analytical data (the complex is identifical with an authentic specimen previously prepared [6a] and characterized by an X-ray study [6b]). Sneeden et al. have recently treated the hexameric copper hydride $[HCuPPh_3]_6$ with CO_2 to give **3** [7]. They also reported that on reaction of **1** with CO_2 a formate is formed, as evidenced by the fact that treatment of the reaction mixture with MeI affords HCOOMe. However, the authors do not suggest a formula for this formate.

Addition of 1 equiv. of PPh_3 under an atmosphere of CO_2 to the reaction mixture leading to **3** results in the formation of the monodentate formate complex $[(PPh_3)_3Cu(\eta^1\text{-}O_2CH)]$ (**4**) [6a]. Addition of PPh_3 together with NBu_4ClO_4 instead gives white crystals of the complex $[(PPh_3)_3Cu(\mu\text{-}O_2CH)Cu(PPh_3)_3]ClO_4$ (**5**). Preliminary results of an X-ray structural analysis of **5** have been shown that in the complex cation two $(PPh_3)_3Cu$ moieties are held together by a bridging formate group.



SCHEME 2



SCHEME 3

TABLE 1

INFRARED AND ^{1}H NMR DATA FOR COMPOUNDS 3—10

	IR^a				^{1}H NMR^b	
Compound	ν(CO)	ν(CO···Cu)	ν(CS···Cu)	other	δ(X$_2$CH)	δ(NH)
3	1585	1350			8.55	
4	1610	1340			9.00	
5	1585	1360			8.55	
6	1600	1330			8.60	
7	1632 1580	1340	800		10.12	
8	1630 1580	1350	805		10.76	
9				3185 ν(NH) 1510, 1315 ν(CN) 1000 ν(CS)		9.05
10				3200 ν(NH) 1510, 1315 ν(CN) 1000 ν(CS)		8.99

^{a}KBr plates, samples mulled in Nujol. ^{b}CDCl$_3$ solutions at 293 K.

It is noteworthy that addition of NaBH$_4$ in ethanol to methylene chloride solutions of 3, 4, or 5 quantitatively regenerates the tetrahydroborate complex 1 together with sodium formate.

The novel η^2-BH$_4$ complex 2 was synthesized by treatment of a methylene chloride solution of [(PCy$_3$)$_2$Cu(ClO$_4$)] with NaBH$_4$ (ν(BH$_t$) 2360, 2260 cm^{-1}, ν(BH$_b$) 2015, 1910 cm^{-1}). Bubbling of CO$_2$ into a methylene chloride/ethanol solution of 2 gave white crystals of the formate complex [(PCy$_3$)$_2$Cu(η^2-O$_2$CH)] (6).

Both compounds 1 and 2 react in methylene chloride with COS to give white crystals of [(PPh$_3$)$_2$Cu(η^2-OSCH)] (7), and [(PCy$_3$)$_2$Cu(η^2-OSCH) (8), respectively. Carbonyl sulfide insertion into M—H bonds to give metallothioformate complexes is extremely rare, being limited to $[(CO)_5MSCO(H)]^-$ (M = Cr, Mo, W) [2], and to the above reported triphos complex. To our knowledge, this is the first example of an η^2-O,S bonded thioformate ligand.

Organoisothiocyanates can react with metal hydrides to give either thioformamide [8] or dithiocarbamate complexes [9]. We have found that SNCPh reacts with methylene chloride solutions of 1 or 2 to give the η^2-dithiocarbamate complexes $[(PPh_3)Cu(\eta^2\text{-}S_2CNHPh)]$ (9), and $[(PCy_3)Cu(\eta^2\text{-}S_2CNHPh)]$ (**10**), as yellow crystals, further confirming that phosphine-BH_4 copper(I) complexes can mimic metal hydrides in reactions with heteroallenes.

Current studies are underway to investigate both the reaction mechanisms and the reactivity of the formate complexes. Preliminary studies have shown that the η^2-O_2CH complex 3 reacts with CS_2 to give the η^2-thioformate complex 7.

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