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Reactions of CO_2 with Tetrahydroborato Copper(I) Complexes in Moist Solvents: Synthesis and Reactions of $[(phen)_2Cu][(HO)_3B(O_2CH)]$ and $(phen)(Ph_3P)Cu(O_2COH)$ (phen = 1,10-phenanthroline)

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Abstract

Carbon dioxide reacts with the tetrahydroborato copper(I) complex, $(phen)(Ph_3P)Cu(BH_4)$ (phen = 1,10-phenanthroline) (**1**) in moist tetrahydrofuran and in the presence of free phen affording the ionic derivative $[(phen)_2Cu][(HO)_3B(O_2CH)]$ (**3**). The same complex **3** can be obtained from **1** and aqueous formic acid in the presence of phen; from the new tetrahydroborato copper(I) complex, $(phen)_2Cu(BH_4)$ (**2**), and aqueous formic acid; and from **2** with CO_2 in moist tetrahydrofuran.

The reaction of $(phen)(Ph_3P)Cu(BH_4)$ (**1**) with CO_2 in moist methanol gives the bicarbonato derivative, $(phen)(Ph_3P)Cu(O_2COH)$ (**4**). The action of alcohols, ROH, on **3** causes the formation of the ionic formato complex $[(phen)_2Cu](O_2CH)$ (**5**), the boron atom being eliminated as the alkyl boric ester, $(RO)_3B$. Complex **3** reacts with an alcoholic triphenylphosphine solution giving the already reported covalent formato derivative, $(phen)(Ph_3P)Cu(O_2CH)$. The reaction of **3** with $PhCH_2Br$ gives the benzyl formic ester HCO_2CH_2Ph. The reactivity of **4** toward neutral ligands such as phen and CyNC has been investigated, the ionic bicarbonato derivatives, $[(phen)_2Cu](HCO_3)$ (**8**) and $[(phen)(CyNC)_2Cu](HCO_3)$ (**9**), being obtained respectively.

Introduction

The reduction reaction of carbon dioxide by copper(I) tetrahydroborato complexes containing tertiary phosphines as ligands has already been reported [1]. In all such cases, unidentate or chelating formato derivatives have been obtained from these reactions, regardless of the binding mode of the tetrahydroborato group. In a previous paper [2], we described the reactions of the tetrahydroborato copper(I) complexes, $(biL)(Ph_3P)Cu(BH_4)$ (biL = 1,10-phenanthroline, phen; or 3,4,7,8-tetramethyl-1,10-phenanthroline, TMP), with CO_2 in the presence of free triphenylphosphine in non-protic and in protic solvents. In a non-protic medium, ionic complexes of formula $[(biL)(Ph_3P)_2Cu][H_xB(O_2CH)_y]$ ($x = 1, y = 3$, biL = phen; $x = 2, y = 2$, biL = phen, TMP) have been isolated. CO_2 reacts with **1** or with $(TMP)(Ph_3P)Cu(BH_4)$ in protic solvents, allowing the isolation of the covalent formato complexes $(biL)(Ph_3P)Cu(O_2CH)$.

We have now observed that if water is present in these reaction media, quite different products are obtained. When **1** is reacted with CO_2 in moist THF, the boron-containing complex, $[(phen)_2Cu][(HO)_3B(O_2CH)]$ (**3**), was isolated, while the reaction between **1** and CO_2 in moist MeOH allowed the formation of the bicarbonato–copper(I) derivative $(phen)(Ph_3P)Cu(O_2COH)$ (**4**).

The reactivity of **3** and **4** has also been investigated and the significant results are reported here. In particular, benzyl formate, HCO_2CH_2Ph, was readily obtained by reacting **3** with $PhCH_2Br$ in the presence of free PPh_3.

Results and Discussion

The results of the reactions described here are reported in Schemes 1 and 2.

$(phen)(Ph_3P)Cu(BH_4)$ (**1**) reacts with CO_2 in moist THF and in the presence of free phen according to eqn. (1):

$$\mathbf{1} + CO_2 + \text{phen} \xrightarrow{THF/H_2O} \underset{\mathbf{3}}{[(phen)_2Cu][(HO)_3B(O_2CH)]} \quad (1)$$

The analytical and IR data for **3** support the above formulation (see 'Experimental' and Table I). Its scarce solubility in the common organic solvents prevented further spectroscopic investigations. Indeed, complex **3** seems to be soluble in alcohols, but, as it will be reported later, this fact is related to a reaction between **3** and ROH (Scheme 2). Compound **3** can be alternatively obtained by (Scheme 1): (i) reaction of **1** with formic acid; (ii) reaction of the novel tetrahydroborato copper(I) complex $(phen)_2Cu(BH_4)$ (**2**) with formic acid; (iii) reaction of 2

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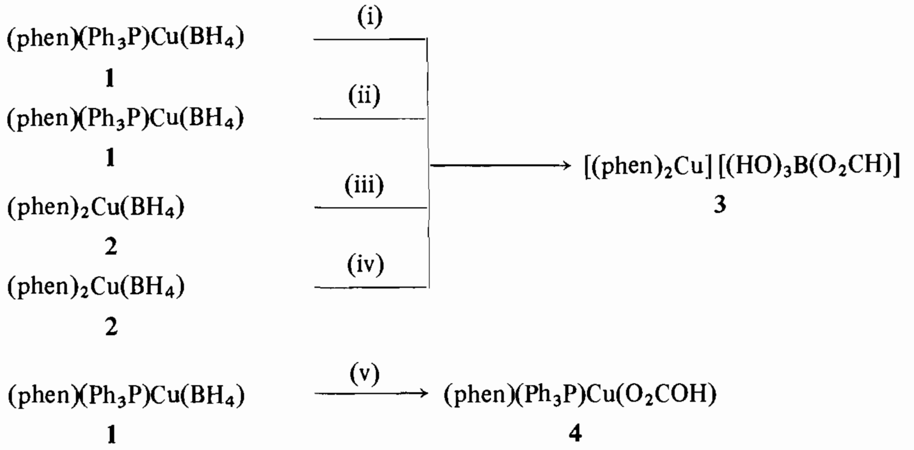
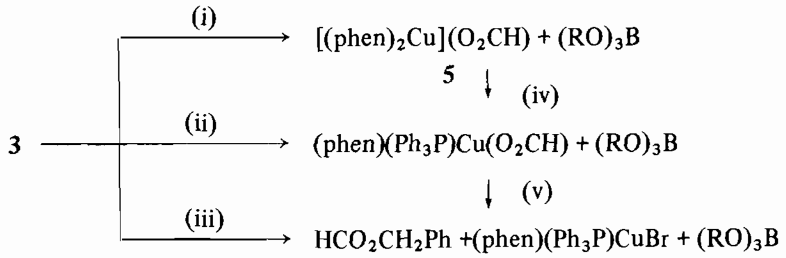


Scheme 1. (i) phen, CO_2, THF(H_2O); (ii) $HCOOH_{aq}$, phen, THF; (iii) CO_2, THF(H_2O); (iv) $HCOOH_{aq}$, THF; (v) CO_2, MeOH-(H_2O).



Scheme 2. (i) ROH (R = Me, Et); (ii) PPh_3, ROH; (iii) $PhCH_2Br$, PPh_3, ROH; (iv) PPh_3; (v) $PhCH_2Br$.

with CO_2. In all cases the presence of water is necessary.

The IR spectrum of complex **3** shows values of the stretching frequencies ν(C=O) and ν(C–O) of the formato group close to those of ionic formates [3]. In the 3100–3600 cm^{-1} region a broad absorption is present, probably due to hydrogen bonds between the OH groups and the formato anion. The values of the ν(C=O) and ν(C–O) stretchings are quite different with respect to those reported for the complex $[(phen)(Ph_3P)_2Cu][HB(O_2CH)_3]$ [2]. Even if the relatively small ν(C=O)–ν(C–O) separation in the spectrum of complex **3** is unexpected for an unidentate coordination of the carboxylato group [4], we believe that in compound **3** the formato ion is uni-coordinated to the boron atom. The unusual stretching frequencies of the carboxylato group in complex **3** are reasonably explained by the involvement of the uncoordinated carboxylate oxygen in hydrogen bonding as was shown for other carboxylato complexes [5].

The tetrahydroborato complex **2** was obtained from **1** and anhydrous 1,10-phenanthroline in THF. Its BH_4 stretching vibrations are consistent with the presence of an unidentate tetrahydroborato moiety [6]. In fact, significant absorptions at 2395, 1975 and 1140 cm^{-1} are present; these can be attributed to $\nu(B{-}H_t)$, $\nu(B{-}H_b)$ and to the BH_3 deformation respectively. Tetrahydroborato copper(I) complexes having a monodentate BH_4 group have already been reported [1], but they proved to be all four-coordinated, while in the present case a penta-coordination is the most probable, as phen does not behave as a monodentate N-donor ligand. In view of this, complex **2** appears to be the first example of a tetrahydroborato compound containing an unidentate BH_4 group attached to a five-coordinated copper(I) center.

The mechanism by which complex **3** is formed from **1** has been investigated. We believe that, in the presence of free phen, the tetrahydroborato complex **1** gives rise in solution to the ionic species, $[(phen)_2Cu]^+(BH_4^-)$. This behaviour is confirmed by conductivity measurements that show that the addition of phen to CH_3CN solutions of **1** causes a gradual increase of molar conductivity which reaches the value expected for an 1:1 electrolyte [7], when the phen:Cu ratio is 20. The role of phen in reaction (1) parallels the results already reported for the action of PPh_3 on the same complex **1** [2]. The formation of the above reported ionic form of complex **2**, suggests that in reaction (1) CO_2 could react directly with the BH_4^- anion through an insertion reaction into a B–H bond. This view, which has been already proposed by us [2], is now supported by the observation that tetrabutylammonium tetraborohydride, $NBu_4(BH_4)$, itself reacts with CO_2. In fact the IR spectrum of a CH_2Cl_2 solution of $NBu_4(BH)_4$ through which CO_2 has been bubbled for 15 min, showed significant absorptions at 2350, 1680 and 1140 cm^{-1}. These values are close to those reported for $[(phen)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ [2] obtained by reacting **1** with CO_2 in CH_2Cl_2 solution in the presence of free PPh_3. These facts seem to suggest that the species $(NBu_4)[H_2B(O_2CH)_2]$ could be formed in the above experiment. Unfortunately, we were unable to isolate this compound. Moreover, $NBu_4(BH_4)$ was reacted with CO_2 also in the same experimental conditions as described for reaction (1). Hydrogen was evolved. After 10 min $[(phen)_2Cu]BPh_4$ was added and the insoluble violet compound **3** was formed. This reaction seems to suggest that the intermediate anion $[H_3B(O_2CH)]^-$ is the first species formed in moist THF; its subsequent hydrolisis leads to $[(HO)_3B(O_2CH)]^-$, which is the anion of complex **3**. This view is further supported by the formation of the related $[(phen)_2Cu][(HO)_3B(O_2CD)]$ by reacting $(phen)(Ph_3P)Cu(BD_4)$ with CO_2 in moist THF in the presence of phen. Moreover, the reaction of $(phen)(Ph_3P)Cu(BD_4)$ with CO_2 and D_2O in the presence of phen in THF, leads to the isolation of $[(phen)_2Cu][(DO)_3B(O_2CD)]$.

The reaction of $(phen)_2Cu(BH_4)$ **2** with CO_2 in moist THF was also investigated (Scheme 1) and the results compared with those obtained from the corresponding reaction carried out in moist methanol (see later). We observed that the action of water on a THF suspension of **2** causes the formation of an insoluble violet compound with concomitant hydrogen evolution. Repeated elemental analyses of this material seem to indicate a formulation as a tetrahydroxoborato–copper(I) complex, $(phen)Cu[B(OH)_4]$. Its ^1H and ^{11}B NMR spectra in CD_3OD were registered. No signals due to the OH hydrogens were detected, while the signal due to ^{11}B appears at 9.5 ppm (relative to $Et_2O\cdot BF_3$). Its IR spectrum does not contain significant bands other than broad absorptions in the 3100–3600 cm^{-1} region, which are assignable to the stretching vibrations of the OH groups bound to boron. The hydrogens of the $[B(OH)_4]^-$ anion did not exchange when it was treated with D_2O.

The reaction of this violet compound with CO_2 in dry methanol, which will be described later, strongly supports the above formulation. We did not observe any reaction when CO_2 was bubbled through a THF suspension of this compound. This fact seems to support the view that, in the preparation of **3** from **2** and CO_2 in moist THF, the reaction of CO_2 with **2** is faster than the reaction of H_2O with the same complex **2**, presumably leading to the formation of the above cited anion $[H_3B(O_2CH)]^-$. The action of water on this anion gives place to the anion of complex **3**, as suggested above. Moreover, by reacting the violet material described above with formic acid in the presence of phen, complex **3** is obtained.

When the reaction between $(phen)(Ph_3P)Cu(BH_4)$ (**1**) and CO_2 was carried out in moist methanol, complex **4**, $(phen)(Ph_3P)Cu(O_2COH)$, was isolated (Scheme 1). In the gas phase of this reaction the presence of hydrogen and methyl boric ester was confirmed. The same complex **4** has also been obtained by reacting the above mentioned violet material with CO_2 in dry methanol in the presence of triphenylphosphine. The presence of methyl boric ester in the gas phase was again verified. This reaction, as previously suggested, strongly supports the formulation of the violet compound as $(phen)Cu[B(OH)_4]$. Finally, by reacting this material with methanol at 50 °C under a nitrogen atmosphere, the formation of $(MeO)_3B$ and of a red solution was observed. The action of CO_2 and PPh_3 on this solution afforded again the bicarbonato derivative **4**. In view of these results, the intermediate formation of a mono-hydroxo–copper(I) complex (red solution), which inserts CO_2 into the Cu–OH bond leading to **4** becomes plausible. Attempts are being made to isolate and characterize this hydroxo species, which presumably is not a monomer.

Elemental analyses, spectroscopic data and its chemical behaviour support the formulation of **4** as a bicarbonato–copper(I) derivative (see 'Experimental' and Table I). Its ^1H NMR spectrum was registered but no OH resonance in CD_3OD was observed probably because the signal is masked by the phenyl resonances of the triphenylphosphine. The IR spectrum of compound **4** shows two strong bands at 1650 and 1635 cm^{-1}. The first band, according to the literature [8], should indicate the presence of a $ROCO_2^-$ group bonded to the copper atom in an unidentate fashion. The second band should indicate the presence of a bicarbonato ion unidentate bonded to the copper atom [8a]. Chemical evidences and analytical data, exclude the presence in compound **4** of an alkyl carbonato group. On the other hand, for compound $[HOCO_2Cu(Ph_3P)_2]_n$ two strong ν(C=O) stretching bands at 1610 and 1640 cm^{-1} have been found [8c]. The presence of these absorptions was explained suggesting that in its structure two different types of bicarbonato ions are present, one unidentate and the other bidentate which interact with each other by means of hydrogen bonds. It seems reasonable to suppose the presence in compound **4** of two different undidentate bicarbonato ions which show in the solid state different hydrogen bonds. The presence of hydrogen bonds seems to be proved by the position of ν(OH) stretch-

TABLE I. Infrared Data

Compound		Significant IR absorptions, nujol (cm^{-1})[a]
$(phen)_2Cu(BH_4)$	**2**	2395(vs) $\nu(B–H_t)$, 1975(s) $\nu(B–H_b)$, 1140(m) BH_3 def.
$[(phen)_2Cu][(HO)_3B(O_2CH)]$[b]	3	2740(w) ν(CH), 1590(vs) ν(C=O), 1380(vs) ν(C–O)
$(phen)(Ph_3P)Cu(O_2COH)$[c]	**4**	1650(s), 1635(s) ν(C=O), 1400(vs) δ(OHO), 1395(sh) ν(C–O)
$[(phen)_2Cu](O_2CH)$	**5**	2650(w) ν(CH), 1600(vs) ν(C=O), 1350(m) ν(C–O)
$(phen)(Ph_3P)Cu(S_2COMe)$	**6**	1173(vs) ν_{as}(C–O–C), 1082(sh) ν_s(C–O–C), 1040(vs) ν(C=S)
$(Ph_3P)_2Cu(S_2COMe)$	7	1195(vs) ν_{as}(C–O–C), 1145(vs) ν_s(C–O–C), 1040(vs) ν(C=S)
$[(phen)_2Cu](HCO_3)$	**8**	1630(s) ν(C=O), 1380(s) ν(C–O), 1000(w, br) ν(C=O) + δ(OHO)
$[(phen)(CyNC)_2Cu](HCO_3)$	9	2190(s), 2170(vs) ν(CN), 1615(vs) ν(C=O), 1380(vs) ν(C–O), 1000(w, br) ν(C=O) + δ(OHO)
$[(phen)(CyNC)_2Cu](BPh_4)$	**10**	2180(s), 2160(vs) ν(CN)

[a] The IR spectra of complexes **4**, **8** and **9** were registered as kelef oil mulls in the range 4000–1300 cm^{-1} and as nujol mulls in the range 1300–600 cm^{-1}. [b] In the 3600–3100 cm^{-1} region a broad absorption is present (ν(OH)). [c] For ν(OH) stretchings in complex **4**, see text.

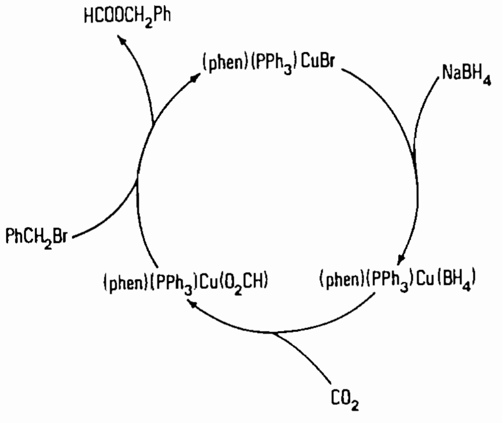
ing vibrations. These appear as two weak sharp bands at 2675 and 2630 cm^{-1}, besides one broad weak band at about 3000 cm^{-1}. These bands are not present in the IR spectra of PPh_3 and of phen; they can be assigned to ν(OH) stretching vibrations of hydrogen-bonded hydroxylic groups [9].

Reactivity of Complexes 3 and 4

Complex **3** reacts with alcohols giving the ionic formato complex **5**, $[(phen)_2Cu](O_2CH)$, the concomitant formation of the alkyl boric ester $(RO)_3B$ (R = Me, Et) being verified (Scheme 2). The formulation of compound **5** is supported by analytical, spectroscopic data and conductivity measurements (see 'Experimental' and Table I). The same complex **5** was obtained by reacting the already reported covalent formato complex $(phen)(Ph_3P)Cu(O_2CH)$ with phen in THF [2]. This alternative route leading to **5** confirms the absence of the starting boron atom when **5** is obtained from **3**. Its IR spectrum shows the ν(C=O) and ν(C–O) stretching frequencies at 1600 and 1350 cm^{-1} respectively and they are consistent with the presence in **5** of an ionic formato group. The ν(CH) absorption of the O_2CH group lies at 2650 cm^{-1}.

When PPh_3 is present in the alcoholic medium, **3** reacts giving place to $(phen)(Ph_3P)Cu(O_2CH)$ [2] in quantitative yields (Scheme 2). The reaction of **3** with benzyl bromide is noteworthy. In fact the benzyl formic ester, HCO_2CH_2Ph, is readily formed (Scheme 2). We observed that the presence of free PPh_3 was essential for the formation of the ester. The possibility that PPh_3 could intermediately form the covalent formato complex, $(phen)(Ph_3P)Cu(O_2CH)$, which should be the true reactive species towards $PhCH_2Br$, was confirmed by directly reacting the covalent formato derivative with benzyl bromide (Scheme 2). The benzyl formic ester was readily obtained even in the absence of free triphenylphosphine. As $(phen)(Ph_3P)CuBr$, which is one of the products of the reaction of **3** with $PhCH_2Br$, gives the corresponding tetrahydroborato derivative **1** when reacted with $NaBH_4$, one could plan the following catalytic cycle, which should allow the achievement of the net overall reaction shown in eqn. (2):

$$NaBH_4 + CO_2 + PhCH_2Br \longrightarrow HCO_2CH_2Ph + NaBr + \tfrac{1}{2}(BH_3)_2 \qquad (2)$$



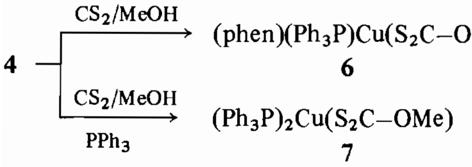
However reaction (2), carried out in ethanol in the presence of catalytic amounts of $(phen)(Ph_3P)CuBr$, always gave HCO_2Na, benzyl bromide being recovered unchanged.

A peculiar behaviour was verified for the bicarbonato complex **4** when dissolved in methanol. Conductivity measurements showed that **4** is partially dissociated when in methanol solution, eqn. (3):

$$\underset{\textbf{4}}{(phen)(Ph_3P)Cu(O_2COH)} \longrightarrow [(phen)(Ph_3P)Cu]^+ + HCO_3^- \qquad (3)$$

Molecular weight measurements, carried out in methanol, confirmed this fact, values always lower than that of the undissociated species being obtained.

Carbon disulphide reacts with **4** according to eqn. (4):



$$\mathbf{4} \xrightarrow{CS_2/MeOH} (phen)(Ph_3P)Cu(S_2C{-}OMe)\ \mathbf{6}$$
$$\mathbf{4} \xrightarrow[PPh_3]{CS_2/MeOH} (Ph_3P)_2Cu(S_2C{-}OMe)\ \mathbf{7} \qquad (4)$$

From reactions (4) the well known complexes **6** and **7**, which contain the *O*-methyl-dithiocarbonate (xanthate) anion, $MeOCS_2^-$, were obtained (see 'Experimental' and Table I) [10].

The bicarbonato complex **4** readily reacts with 1,10-phenanthroline giving place to the ionic derivative $[(phen)_2Cu](HCO_3)$ (**8**), PPh_3 being displaced. An ionic bicarbonato derivative, $[(phen)(CyNC)_2Cu](HCO_3)$ (**9**) is also obtained in the reaction of **4** with CyNC. The IR spectra of compounds **8** and **9** show ν(C=O) stretching vibrations at 1630 and 1615 cm^{-1} respectively. For both complexes we suggest that the bicarbonato group acts as a non-coordinated anion. In fact ν(C=O) stretching vibrations values similar to ours have been found in the IR spectra of $NaHCO_3$ [11a] and of $KHCO_3$ [11b]. It is probable that these two different values for the ν(C=O) frequencies depend on different hydrogen bonds between the bicarbonato groups in the crystal. The bands due to the CyNC ligands in complex **9** appear at 2190 and 2170 cm^{-1}. These C–N stretching frequencies are in the expected range being the isocyanide molecules coordinated to an acidic center, and they are higher with respect to non-ionic copper(I) complexes having the same ligand [12].

By the anion exchange reaction of **9** with $NaBPh_4$, $[(phen)(CyNC)_2Cu](BPh_4)$ (**10**) was isolated. Its IR spectrum showed the C–N stretching arising from the two CyNC ligands at 2180 and 2160 cm^{-1}.

Experimental

All the reactions and manipulations were performed under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen immediately before use. $(phen)(Ph_3P)Cu(BH_4)$ (**1**) was prepared as reported in the literature [2]. IR spectra were recorded on a Nicolet MX-1 FT-IR spectrometer as kelef oil mulls in the range 4000–1300 cm^{-1} and as nujol mulls in the range 1300–600 cm^{-1}. Conductivity of the complex solutions was measured with an Orion Research Type 101-A instrument. Elemental analyses (C, H, N) were carried out in the Analytical Laboratory of Milan University. Oxygen and boron analyses were performed by Pascher's Analytical Laboratories (Bonn).

$(phen)_2Cu(BH_4)$ (2)

$(phen)(Ph_3P)Cu(BH_4)$ (**1**) (0.19 mmol) is dissolved in the minimum amount of THF and to the orange solution anhydrous phen (1.16 mmol) is added. After a few minutes an insoluble pale yellow product formed. It was filtered off, washed with diethyl ether and dried under vacuum. $C_{24}H_{20}N_4BCu$; melting point (m.p.) 155 °C dec. *Anal.* Calc.: C, 65.68; H, 4.56; N, 12.77; B, 2.5. Found: C, 65.42; H, 4.31; N, 12.63; B, 2.54%. The ^{11}B NMR spectrum (CD_2Cl_2 solution) showed a 1:4:6:4:1 quintet centered at −42.4 ppm (J(B, H) = 81.5 Hz). The lowering of the temperature causes a broadening of the signal.

$[(phen)_2Cu][(HO)_3B(O_2CH)]$ (3)

Method A. CO_2 was bubbled through a THF solution (10 ml) of phen (0.22 mmol) containing water (3 drops), and **1** (0.19 mmol) was added. Hydrogen was evolved while an insoluble violet compound formed. After 30 min the violet material was filtered off, washed with THF, diethyl ether and dried under vacuum.

Method B. To a THF solution (10 ml) of phen (0.24 mmol), **1** (0.2 mmol) and aqueous formic acid (3 drops) were added. A violet product formed. It was recovered as described in method A.

Method C. CO_2 was bubbled through THF (10 ml) containing water (3 drops), and **2** (0.25 mmol) was added. The orange suspension turned into an insoluble violet product which was recovered as above described.

Method D. To a THF suspension (10 ml) of **2** (0.31 mmol) aqueous formic acid (3 drops) was added. A fast reaction takes place while hydrogen is evolved. After 30 min the insoluble violet product was recovered as already described. $C_{25}H_{20}O_5N_4BCu$; m.p. 177 °C dec. *Anal.* Calc.: C, 56.55; H, 3.77; N, 10.55; O, 15.08; B, 2.07. Found: C, 56.04; H, 3.81; N, 10.50; O, 14.73; B, 1.97%. Λ_M in acetonitrile: 139.6 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol/l).

$(phen)(Ph_3P)Cu(O_2COH)$ (4)

Method A. To a MeOH solution (20 ml) of PPh_3 (0.23 mmol) containing water (3 drops), **1** was added. Hydrogen evolution was verified while a red solution was obtained. After 10 min CO_2 was bubbled and the temperature raised up to 50 °C, and the colour turned to yellow. A further gas evolution was noted: it was confirmed to be the boric ester $(MeO)_3B$. The yellow solution was evaporated to dryness and the residue treated with diethyl ether. The yellow product was filtered off, washed with diethyl ether and dried under vacuum.

Method B. To a suspension of **2** (0.23 mmol) in THF (4 ml), water (3 drops) is added. Hydrogen was evolved and an insoluble violet compound formed. After 15 min it was filtered off, washed with THF, diethyl ether and dried under vacuum. The plausible formulation of this compound as (phen)Cu[B(OH)$_4$] has been discussed in the text. A methanol solution of the violet product here obtained was heated to 55 °C and a red solution formed while the gas phase was confirmed to contain (MeO)$_3$B. CO$_2$ was bubbled and PPh$_3$ added. From the yellow solution compound **4** was recovered as described above. $C_{31}H_{24}PO_3N_2Cu$; m.p. 155 °C dec. *Anal.* Calc.: C, 65.66; H, 4.23; N, 4.94; O, 8.47. Found: C, 65.44; H, 4.23; N, 4.87; O, 8.32%. Molecular weight measurements carried out in a methanol solution gave always values (*ca.* 400) lower than the calculated value (566.5).

[(phen)$_2$Cu](O$_2$CH) (5)

Method A. A methanol solution (10 ml) of **3** (0.094 mmol) was stirred for 30 min and a deep red solution was obtained. This was evaporated to dryness and the residue treated with diethyl ether. The insoluble violet product **5** was filtered off, washed with diethyl ether and dried under vacuum. Ethanol instead of methanol can be used.

Method B. To a THF solution (15 ml) of phen (0.91 mmol), (phen)(Ph$_3$P)Cu(O$_2$CH)^2 (0.18 mmol) was added. The formation of a violet suspension was readily observed. After 2 h it was filtered off, washed with THF and diethyl ether, and dried under vacuum. $C_{25}H_{17}O_2N_4Cu$; m.p. 120 °C dec. *Anal.* Calc.: C, 64.03; H, 3.62; N, 11.95; O, 6.83. Found: C, 64.22; H, 3.74; N, 11.81; O, 6.90%. Λ_M in methanol: 88 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol/l).

(phen)(Ph$_3$P)Cu(S$_2$COMe) (6)

To a methanol suspension (10 ml) of **4** (0.088 mmol), carbon disulphide (1 ml) was added. A yellow–orange solution formed from which a pale orange product precipitated. It was filtered off, washed with methanol and diethyl ether, and dried under vacuum. $C_{32}H_{26}ON_2S_2Cu$; m.p. 169 °C. *Anal.* Calc.: C, 62.69; H, 4.24; N, 4.57; O, 2.61. Found: C, 62.83; H, 4.25; N, 4.51; O, 2.65%.

(Ph$_3$P)$_2$Cu(S$_2$COMe) (7)

This pale yellow complex was obtained as described for **6** but in the presence of PPh$_3$ (molar ratio PPh$_3$:**4** = 3:1). $C_{38}H_{33}P_2OS_2Cu$; m.p. 194 °C. *Anal.* Calc.: C, 65.66; H, 4.75; O, 2.30. Found: C, 66.13; H, 4.70; O, 2.26%.

[(phen)$_2$Cu](HCO$_3$) (8)

To a THF solution (20 ml) of phen (0.52 mmol), **4** (0.17 mmol) was added. After 2 h the insoluble violet product was filtered off, washed with THF and diethyl ether, and dried under vacuum. $C_{25}H_{17}O_3N_4Cu$; m.p. 190 °C dec. *Anal.* Calc.: C, 61.91; H, 3.50; N, 11.55; O, 9.90. Found: C, 61.70; H, 3.33; N, 11.39; O, 9.78% Λ_M in methanol: 110 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol/l).

[(phen)(CyNC)$_2$Cu](HCO$_3$) (9)

To a methanol solution (20 ml) of CyNC (1 ml), **4** (0.18 mmol) was added. A fast reaction takes place and a pale yellow solution formed. After 1 h the solution was evaporated to dryness and the residue treated with diethyl ether. The insoluble pale yellow product was filtered off, washed several times with diethyl ether and dried under vacuum. $C_{27}H_{31}O_3N_4Cu$; m.p. 106 °C dec. *Anal.* Calc.: C, 62.0; H, 5.93; N, 10.71; O, 9.18. Found: C, 61.44; H, 6.06; N, 10.02; O, 10.15%. Λ_M in methanol: 98 Ω^{-1} cm^2 mol^{-1} (10^{-3} mol/l). Complex **9** showed to be highly hygroscopic.

[(phen)(CyNC)$_2$Cu](BPh$_4$) (10)

To a methanol solution (10 ml) of **9** (0.18 mmol), NaBPh$_4$ (0.39 mmol), dissolved in the minimum amount of MeOH, was added. After 30 min the insoluble yellow product was filtered off, washed with methanol and dried under vacuum. $C_{50}H_{50}N_4BCu$; m.p. 142 °C. *Anal.* Calc.: C, 76.87; H, 6.40; N, 7.17. Found: C, 76.56; H, 6.26; N, 7.05%.

Action of CO$_2$ on a CH$_2$Cl$_2$ Solution of NBu$_4$(BH$_4$)

Carbon dioxide was bubbled through CH$_2$Cl$_2$ (10 ml) containing NBu$_4$(BH$_4$) (0.25 mmmol). After 15 min the IR spectrum of the solution was registered. It showed the presence of significant bands at 2370(s), 1680(s), 1240(m) and 1140(s) cm^{-1}, which we tentatively assign to ν(BH$_t$), ν(C=O), ν(C–O) and δ(BH$_2$) respectively, arising from the anion [H$_2$B(O$_2$CH)$_2$]$^-$ formed. These absorptions are close to those found for the already reported [(phen)(Ph$_3$P)$_2$Cu][H$_2$B(O$_2$CH)$_2$] [2].

Reaction of NBu$_4$(BH$_4$) with CO$_2$ in Moist THF

CO$_2$ was bubbled through THF (15 ml) containing water (3 drops), and NBu$_4$(BH$_4$) (0.39 mmol) was added. A ready reaction takes place while hydrogen was evolved. After 10 min [(phen)$_2$Cu](BPh$_4$) (0.31 mmol) was added and an insoluble violet compound rapidly formed. The suspension was stirred for 1 h and filtered off. The violet product was washed with THF and diethyl ether and dried under vacuum. The IR spectrum of this material was identical to that of complex **3**.

Reactions of CO$_2$ with (phen)(Ph$_3$P)Cu(BD$_4$) [2]

These reactions were carried out by using the experimental conditions described for the preparation of **3** from (phen)(Ph$_3$P)Cu(BH$_4$). When H$_2$O was used, the complex [(phen)$_2$Cu][(HO)$_3$B(O$_2$CD)] was isolated. In its IR spectrum the stretching ν(CD) appears at 2080 cm^{-1} while the ν(C=O), ν(C–O) and ν(OH) absorptions were shown to be practically unchanged with respect to those found for **3**. When D$_2$O was used instead of H$_2$O, [(phen)$_2$Cu][(DO)$_3$B(O$_2$CD)] was isolated. Its IR spectrum showed ν(CD) and ν(OD) at 2080 and 2300 cm^{-1} respectively, while the ν(C=O) and ν(C–O) resulted unchanged with respect to the values found for **3**.

Conductivity Measurements on 1 in the Presence of phen

The conductivity of CH_3CN solutions containing **1**, in the absence or in the presence of 1,10-phenanthroline, were measured. The tetrahydroborato complex **1** in a solution 10^{-3} M concentration gave the values of 54.2 Ω^{-1} cm^2 mol^{-1}. 1,10-phenanthroline (phen:Cu = 20:1) was added, and the molar conductivity was again measured. The value was now 120 Ω^{-1} cm^2 mol^{-1}.

Reactivity of 3 with PPh_3 in Alcoholic Medium

To a methanol solution (10 ml) of PPh_3 (0.28 mmol), **3** (0.094 mmol) was added. A fast reaction takes place and a yellow solution formed, $(MeO)_3B$ being evolved. After 2 h the solution was evaporated to dryness and the residue treated with diethyl ether. The yellow insoluble product was verified to be (phen)(Ph_3P)Cu(O_2CH) by its elemental analysis and its IR spectrum.

Reactivity of 3 with $PhCH_2Br$ and PPh_3 in Alcoholic Medium

To a methanol solution (15 ml) of PPh_3 (0.28 mmol), $PhCH_2Br$ (5 drops) and **3** (0.094 mmol) were added. A fast reaction takes place and a yellow solution formed with concomitant evolution of $(MeO)_3B$. After 2 h the solution was evaporated to dryness and the residue treated with diethyl ether. The insoluble yellow product was recognised to be (phen)(Ph_3P)CuBr by its elemental analysis and its IR spectrum. The mother liquor was verified to contain HCO_2CH_2Ph by gas chromatographic techniques.

Reaction of 5 with PPh_3

To a CH_2Cl_2 solution (10 ml) of PPh_3 (0.32 mmol), **5** (0.11 mmol) was added. After 1 h the yellow solution was evaporated to dryness and the residue treated several times with diethyl ether. The insoluble yellow compound was confirmed to be (phen)(Ph_3P)Cu(O_2CH).

Reaction of (phen)(Ph_3P)Cu(O_2CH) with $PhCH_2Br$

To degassed CH_2Cl_2 (8 ml), (phen)(Ph_3P)Cu(O_2-CH) (0.091 mmol) and $PhCH_2Br$ (7 drops) were added. After 2 h the yellow solution was evaporated to dryness and the residue treated with diethyl ether. The yellow insoluble product was confirmed to be (phen)(Ph_3P)CuBr while in the ether phase the presence of HCO_2CH_2Ph was verified by gas chromatographic techniques.

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