Extraction of supported organometallics with various solvents was carried out as about 30 mg of solid were added to 3 mL of solvent. The suspensions were allowed to stand in a drybox, and liquid samples were withdrawn periodically for infrared analysis. All samples were filtered before being placed in the infrared cell (0.202-mm path length).

Solid-state and solution $^1H$ NMR spectra of supported rhenium species were obtained with a spectrometer operated at a frequency of 56.41 MHz for the proton resonance. An extract of the surface species was prepared by bringing 40 mg of solid in contact with 0.4 mL of methanol-$d_4$ (distilled from magnesium turnings under $N_2$) for 0.5 h. A silica blank was also characterized. The magnet had an external deuterium lock to minimize field drift (<0.2 ppm). The solution and solid-state spectra were analyzed by coaddition of 50 and 1000 transients, respectively, followed by Fourier transformation.

Electronic absorption spectra of $[Re(CO)_3OH]_4$ in THF and of THF extracts of supported carbonyls were recorded with a Cary 219 spectrophotometer. UV-visible spectra of the solids were measured with a diffuse reflectance sphere (Model 40513); the cell path length was 1 mm. For the quantitative analysis of the extracts, 10 standards were run at $\lambda_{max}$; a linear regression coefficient of 0.99 was obtained.

The rhenium contents of the solids were evaluated with X-ray fluorescence spectroscopy by using a Phillips automated X-ray spectrometer (PW 1410/80) equipped with an XRG-3100 generator. Separately, solid samples were analyzed for Re by Schwarzkopf Microanalytical Laboratories, Woodside, NY, the results confirming those determined by X-ray fluorescence.

**Catalytic Metathesis of Propene.** The catalytic reaction experiments were carried out with solid samples of supported rhenium in a microflow reactor interfaced to a gas chromatograph (GC) (Antek 300). The flow system allowed monitoring of the propene and helium fed to a Pyrex reactor enclosed in a Lindberg furnace. The propene was Matheson CP grade (99.0%); propane (0.388%) was the sole impurity detected by GC. All gases flowed through traps to remove traces of oxygen (activated Cu) or water (Zeolite 5A). The reactor temperature was controlled with a Thermoelectric (Model 3813011128) proportional controller. At the beginning of each catalysis experiment, the reactor was loaded under nitrogen with 50–100 mg of catalyst powder dispersed between two layers of glass wool. The reactor was placed in the flow system (~1 min exposure to air) and purged with helium (0.25 $cm^3/h$) at 25 °C. The catalyst was then brought to temperature in flowing He. In one set of experiments, sample I (Table II) was heated to 150 °C within 5 min, the propene was then introduced at 0.15 $cm^3/h$, and the He flow was reduced to 0.10 $cm^3/h$ to maintain a constant contact time. The catalyst was then treated with alternating periods of propene + He and He until steady state was attained, as indicated by the on-line product analysis.

A second set of experiments was performed with sample II (Table II), which was simply sample I pretreated at 250 °C in flowing He at 0.25 $cm^3/h$ for 12 h. The temperature was then reduced to 150 °C and the reactant introduced. This set of experiments was also conducted with alternating propene + He and He feed. Omitting the periods of He flow resulted in a more rapid deactivation of the catalyst. Raising the reaction temperature also increased the deactivation rate.

During a catalysis experiment, the reactor effluent stream was periodically analyzed by GC. The product samples were separated in 3.18 mm × 10 m Supelco SP1700 column with a pressure drop of 7.8 atm. at 25 °C. The GC was equipped with a flame ionization detector; the response was calibrated for $C_1$–$C_6$ hydrocarbons. Products were identified by their retention times. To obtain reaction rates directly, differential conversions of propene (<1%) were measured.

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**Registry No.** $[Re(CO)_3OH]_4$, 56553-73-2; $[H_4Re_4(CO)_{12}]$, 60146-15-8.

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# Isolation of Ionic Products in the Reaction of $CO_2$ with (Tetrahydroborato)copper(I) Complexes: Synthesis and Reactions of $[(biL)(Ph_3P)_2Cu][HB(O_2CH)_3]$ and $[(biL)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (biL = 1,10-Phenanthroline, 3,4,7,8-Tetramethyl-1,10-phenanthroline)

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Carbon dioxide reacts with the (tetrahydroborato)copper(I) complexes $(biL)(Ph_3P)Cu(BH_4)$ (biL = 1,10-phenanthroline (phen) (**1**), 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) (**2**)) in the presence of free triphenylphosphine. In nonprotic solvents the stable crystalline complexes of formula $[(biL)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (biL = phen (**3**)) and $[(biL)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (biL = phen (**4a**), TMP (**4b**)) can be isolated. The related reactions of **1** with $^{13}CO_2$ give the corresponding $^{13}C$-labeled products; the reaction of $(TMP)(Ph_3P)Cu(BD_4)$ with $CO_2$ leads to the deuterated derivatives. In protic solvents, $CO_2$ reacts with **1** or **2**, allowing the isolation of the covalent formato complexes $(biL)(Ph_3P)Cu(O_2CH)$ (biL = phen (**5a**), TMP (**5b**)). These can be also obtained by heating **3**, **4a**, and **4b** in ethanol, suggesting that these ionic formato–hydroborato species probably act as intermediates in the reducing property of $BH_4$ toward carbon dioxide. The reactions of **4b** with $HBF_4$ and $NaBPh_4$ give the ionic derivatives $[(TMP)(Ph_3P)_2Cu](BF_4)$ and $[(TMP)(Ph_3P)_2Cu](BPh_4)$. Complexes **3** and **4a** have been confirmed to undergo a reversible interconversion. Infrared and multinuclear magnetic resonance data ($^1H$, $^{11}B$, and $^{13}C$) strongly support the presence of the $[HB(O_2CH)_3]^-$ and $[H_2B(O_2CH)_2]^-$ anions in the complexes **3**, **4a**, and **4b**. In particular their $^{11}B$ NMR spectra substantiate the existence of the BH and $BH_2$ groups in these ionic products.

## Introduction

Covalent metal tetrahydroborato complexes have received increasing attention in recent years. An excellent comprehensive review of this topic has been published in 1977, including a discussion of reasons for the interest in these compounds.[1] Despite the large number of known tetrahydroborato complexes,[2-5] only a few papers have been published dealing with their reactivity. The facile reduction of carbon dioxide and other $CO_2$-like hetercallenes by copper(I) tetrahydroborato complexes containing only tertiary phosphines as ligands has been reported.[6] In all

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0020-1669/85/1324-3920$01.50/0

**Table I.** Infrared and $^{11}B$ NMR Data of $[HB(O_2CH)_3]^-$ and $[H_2B(O_2CH)_2]^-$ Anions

| | signif IR abs, $cm^{-1}$ [a] | | | | | $^{11}B$ NMR[b] | |
|---|---|---|---|---|---|---|---|
| compd | $\nu$(C=O) | $\nu$(C—O) | $\nu(BH_t)$ | $\delta(BH_2)$ | $\nu$(CH) | $\delta$ | $J$(B,H), Hz |
| $[(phen)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (**3**) | 1699 vs | 1220 s | 2410 w | | 2869 w | 3.55 (d) | 129 |
| $[(TMP)(Ph_3P)_2Cu][HB(O_2CH)_3]$ | 1687 vs | *c* | *c* | | *c* | 3.55 (d) | 129 |
| $[(phen)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (**4a**) | 1685 vs | 1264 ms | 2360 ms, 2335 ms | 1140 s | 2845 w | 1.20 (t) | 112 |
| $[(TMP)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (**4b**) | 1700 vs | 1245 ms | 2360 w, 2335 w | 1140 s | 2860 w | 1.20 (t) | 112 |
| $[(TMP)(Ph_3P)_2Cu][D_2B(O_2CD)_2]$ | 1664 vs | 1235 s | 1774 w[d] | 865 s[e] | 2125 w[f] | | |
| $(phen)(Ph_3P)Cu(O_2CH)$ (**5a**) | 1605 s | 1335 s | | | 2740 w | | |
| $(TMP)(Ph_3P)Cu(O_2CH)$ (**5b**) | 1600 s | 1320 s | | | 2740 w | | |
| $(TMP)(Ph_3P)Cu(O_2CD)$ | 1595 s | 1300 s | | | 2040 w[f] | | |

[a] Solid samples prepared as described in the Experimental Section: s = strong; m = medium; w = weak; v = very. [b] $CD_3CN$ solution, chemical shifts given in relative to $Et_2O{\cdot}BF_3$: d = doublet; t = triplet. [c] Not revealed because this complex is obtained mixed with **4b** (see text). [d] $\nu(BD_t)$. [e] $\delta(BD_2)$. [f] $\nu$(CD).

such cases, unidentate or chelating formate derivatives have been obtained from these reactions, regardless of the binding mode of the tetrahydroborato group.

In this paper we report on the synthesis of the new tetrahydroborato copper(I) complex $(TMP)(Ph_3P)Cu(BH_4)$ (**2**) (TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline) and on the reactions of this derivative and of the previously known $(phen)(Ph_3P)Cu(BH_4)$ (**1**)[7] with carbon dioxide in nonprotic solvents. These reactions lead to the isolation of two types of complexes, i.e. $[(phen)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (**3**) and $[(biL)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (biL = 1,10-phenanthroline (**4a**), 3,4,7,8-tetramethyl-1,10-phenanthroline (**4b**)). When the reactions with $CO_2$ of the tetrahydroborato complexes described here are carried out in protic solvents, the formate derivatives $(biL)(Ph_3P)Cu(O_2CH)$ are obtained.

The chemical properties of **3** and **4** have been investigated in order to verify their role as intermediates for understanding the detailed manner in which $BH_4^-$ acts as a reducing agent.

## Results and Discussion

The previously known **1**[7] and the new 3,4,7,8-tetramethyl-1,10-phenanthroline analogue **2** react with carbon dioxide to give different products depending on the experimental conditions. In $CH_2Cl_2$ solution and at −50 °C, **1** reacts with $CO_2$ in the presence of free triphenylphosphine according to eq 1. The analytical and

$$1 + 3CO_2 + PPh_3 \xrightarrow{CH_2Cl_2,\ -50\ °C} \underset{\mathbf{3}}{[(phen)(Ph_3P)_2Cu][HB(O_2CH)_3]} \quad (1)$$

spectral data for **3** support the above formulation (see Experimental Section and Table I). Conductivity measurements confirm the 1:1 ionic nature for this complex. If reaction 1 is carried out in the absence of free $PPh_3$, a quite different pathway is observed, but we were not able to isolate analytically pure products.

The reaction of $CO_2$ with sodium borohydride has been reported about 25 years ago,[8] including a product formulated as $Na[HB(O_2CH)_3]$. This was obtained by carrying out the reaction at −196 °C, and its formulation was based exclusively by analyzing the products derived from its reaction with mineral acids; no spectroscopic data of the compound were given.

We have found that **1** reacts with $CO_2$, in the presence of $PPh_3$ and at 45 °C, according to eq 2. Elemental analyses and spectral

$$1 + 2CO_2 + PPh_3 \xrightarrow{CH_2Cl_2,\ 45\ °C} \underset{\mathbf{4a}}{[(phen)(Ph_3P)_2Cu][H_2B(O_2CH)_2]} \quad (2)$$

data support the formulation given to **4a**. The reaction of $CO_2$ with $NaBH_4$ mentioned above[8] does not lead to the isolation of the sodium analogue of **4a**. Reactions 1 and 2 have also been tried with the new tetrahydroborato complex **2**. This was obtained from $(Ph_3P)_2Cu(BH_4)$ and 3,4,7,8-tetramethyl-1,10-phenanthroline in toluene (see Experimental Section). On the basis of its spectroscopic properties, we attribute to this tetrahydroborato complex the same mode of attachment of the $BH_4$ group to the copper center as is present in **1**.[7] The structure of a complex with an identical formulation has recently been reported to contain a bidentate $BH_4$ group, with a five-coordinate copper(I) center.[9] The IR spectrum of the material used for the X-ray investigation,[9] however, is quite different from that which we observe for our product. We cannot now rationalize the origin of these differences, and we are currently investigating the structures of the two tetrahydroborato derivatives.

The reaction of **2** with $CO_2$ allowed us to obtain a pure product only when the experimental conditions described in eq 2 were followed. In this case a complex that was analyzed as $[(TMP)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (**4b**) is isolated. When **2** is reacted with carbon dioxide at −50 °C in $CH_2Cl_2$ in the presence of free $PPh_3$, a mixture containing **4b** and another product is obtained. The byproduct appears to be the tris(formato)hydroborato complex $[(TMP)(Ph_3P)_2Cu][HB(O_2CH)_3]$ on the basis of its spectroscopic properties (Table I).

**Reversible Conversion of 3 into 4a.** Complexes **3** and **4a** undergo a reversible interconversion under varying experimental conditions (eq 3). In fact, when the monohydroborato derivative **3** is refluxed

$$3 \xrightleftharpoons[CH_2Cl_2,\ -50\ °C]{CH_2Cl_2,\ 45\ °C} 4a + CO_2 \quad (3)$$

in a $CH_2Cl_2$ solution, **4a** is obtained as the only product. On the other hand, **3** can be isolated by bubbling $CO_2$ through a $CH_2Cl_2$ solution of **4a** maintained at −50 °C. As has been already pointed out, we did not succeed in preparing $[(TMP)(Ph_3P)_2Cu][HB(O_2CH)_3]$ as a pure product, a mixture containing **4b** always being obtained. If this mixture is refluxed in a $CH_2Cl_2$ solution, **4b** can be isolated in a pure form. Any attempts to convert **4b** quantitatively into $[(TMP)(Ph_3P)_2Cu][HB(O_2CH)_3]$ failed; a mixture of the two complexes was always obtained.

**Reactions of 1 and 2 with $CO_2$ in Protic Medium.** When the reactions between the tetrahydroborato complexes **1** or **2** and $CO_2$ are carried out in ethanol, quite different products were obtained (eq 4). The presence of free triphenylphosphine was shown to

$$1 \text{ or } 2 + CO_2 \xrightarrow[\text{room temp}]{PPh_3} \underset{\mathbf{5a}\text{ or }\mathbf{5b}}{(biL)(Ph_3P)Cu(O_2CH)} \quad (4)$$

biL = phen (**5a**), TMP (**5b**)

be essential for the isolation of the formato complexes **5**. The possibility that $PPh_3$ could form an adduct with the $BH_3$ residue was ruled out by the absence of $Ph_3P{\cdot}BH_3$ in the mother liquors of the reaction. The gas phase of reaction 4 was further investigated, and the presence of ethyl borate ester was confirmed.

**Role of $PPh_3$ in Reactions 1, 2, and 4.** In order to understand the mechanism by which complexes **3**, **4**, and **5** are formed, we note that, in the presence of free $PPh_3$, the tetrahydroborato complexes **1** and **2** readily give rise to the ionic form A (eq 5).

$$(biL)(Ph_3P)Cu(BH_4) \xrightarrow{PPh_3} \underset{\mathrm{A}}{[(biL)(Ph_3P)_2Cu]^+[BH_4^-]} \quad (5)$$

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This behavior is confirmed by conductivity measurements (see Experimental Section) that show that the addition of triphenylphosphine to $CH_3CN$ solutions of the tetrahydroborato complexes **1** and **2** causes an increase of molar conductivity. In particular, in the case of complex **2**, a value close to that reported for 1:1 electrolytes was found.[10] Ionic structures of type A are well-known only for a number of alkali-metal tetrahydroborates.[11]

Reaction 5 suggests that in reactions 1 and 2 $CO_2$ reacts directly with the $BH_4^-$ anion derived from the dissociated species through an insertion reaction into the B–H bond. The analogous reactions of $CO_2$ with the tetradeuterioborate complex $(TMP)(Ph_3P)Cu(BD_4)$ supports this hypothesis (see discussion of IR spectra, below).

The fact that free $PPh_3$ is essential also in reaction 4, from which formato complexes have been obtained, suggests that the formation of these derivatives proceeds via the intermediate reaction of $CO_2$ with the free $BH_4^-$ to give the anions $[HB(O_2CH)_3]^-$ and $[H_2B(O_2CH)_2]^-$. From these anions the $HCO_2^-$ species is then formed and transferred to the metal center, with the concomitant displacing of the phosphine ligand. This mechanism seemed to receive further support by the transformation reaction of complexes **3** and **4** into the covalent formato compounds **5** when heated at 45 °C in ethanol (eq 6). The formato derivatives **5** were isolated as the only products of this reaction. In the mother liquor the presence of free triphenylphosphine was detected. The gas phase of reaction 6 was shown to contain hydrogen, ethyl borate ester, and carbon dioxide.

$$3 \text{ or } 4 \xrightarrow{\text{ethanol } 45\ ^\circ\text{C}} 5 \tag{6}$$

**Reaction of $[(TMP)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (4b) with $HBF_4$ (a) or with $NaBPh_4$ (b).** Reaction a leads to the ionic derivative $[(TMP)(Ph_3P)_2Cu](BF_4)$, whose nature was confirmed by means of analytical, spectroscopic, and conductivity measurement data. In the evolved gas the presence of hydrogen and carbon dioxide was verified. Reaction b was attempted with the aim of isolating the anion $[H_2B(O_2CH)_2]^-$ as its sodium salt. A 1:1 ionic derivative, $[(TMP)(Ph_3P)_2Cu](BPh_4)$, was obtained, but we did not succeed in isolating the sodium dihydroborato salt as the other reaction product, analogous to prior experience in the direct reaction of $CO_2$ with $NaBH_4$.[8] In one case sodium formate was observed, probably because of the facile transformation of the intermediate $Na[H_2B(O_2CH)_2]$ into HCOONa.

**Infrared and NMR Spectra.** The IR and NMR spectra of the complexes described here are reported in Table I. Spectroscopic data, i.e. IR and $^1H$, $^{11}B$, and $^{13}C$ NMR, strongly support the presence of the anions $[HB(O_2CH)_3]^-$ and $[H_2B(O_2CH)_2]^-$ in the complexes **3** and **4**, respectively. The stretching frequencies $\nu(C{=}O)$ and $\nu(C{-}O)$ of the formato groups bound to the boron atom are closely similar to those reported for formic esters,[12] rather than those of ionic formates.[13] Moreover, the IR spectra of **3**, **4a**, and **4b** showed absorptions due to the $\nu(CH)$ and $\nu(BH_t)$ stretches. The compounds **4a** and **4b** showed in their IR spectra a band at 1140 cm$^{-1}$ (Table I), which can be attributed to the deformation $\delta(BH_2)$.[14] All these absorptions were absent in the IR spectrum of $[(TMP)(Ph_3P)_2Cu](BF_4)$, obtained by reacting **4b** with $HBF_4$, confirming that they are originated by the anion.

In order to confirm previous assignments for the $\nu(CH)$, $\nu(BH_t)$, and $\delta(BH_2)$ modes, we prepared $[(TMP)(Ph_3P)_2Cu][D_2B(O_2CD)_2]$ by reacting $(TMP)(Ph_3P)Cu(BD_4)$ with $CO_2$ in refluxing $CH_2Cl_2$ in the presence of free $PPh_3$. The above absorptions were shown to lie at frequencies lower than those observed in the IR spectrum of **4b** ($\nu(D)/\nu(H) \simeq 0.75$). These isotopic shifts are in agreement with those reported in the literature for (tetradeuterioborato)copper(I) complexes.[15] The IR spectra of complexes **5a** and **5b** strongly support the presence of an unidentate formato ligand in these derivatives (Table I). In fact, $\nu(C{=}O)$ and $\nu(C{-}O)$ are close to the values observed in $(triphos)Cu(O_2CH)$,[6a] in which the presence of the monodentate formato group was confirmed by an X-ray structure determination. Moreover, the IR spectra of **5a** and **5b** showed the $\nu(CH)$ at 2740 cm$^{-1}$. This absorption occurred at 2040 cm$^{-1}$ in the spectrum of $(TMP)(Ph_3P)Cu(O_2CD)$, obtained from $(TMP)(Ph_3P)Cu(BD_4)$ and $CO_2$ in ethanol.

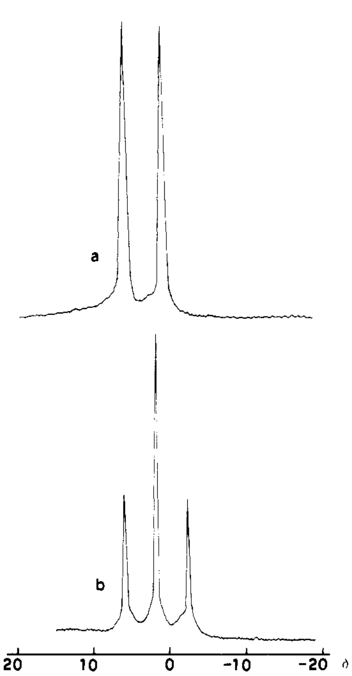

Figure 1. $^{11}B$ NMR spectra ($CD_3CN$ solution, room temperature) of (a) $[(phen)(Ph_3P)_2Cu][HB(O_2CH)_3]$ (**3**) and of (b) $[(phen)(Ph_3P)_2Cu][H_2B(O_2CH)_2]$ (**4a**). Chemical shifts are relative to $Et_2O{\cdot}BF_3$. The $^{11}B$ NMR spectrum of **4b** is identical with that of **4a**.

The $^1H$ NMR spectra of complexes **3** and **4** showed a signal at $\delta = 8.5$, which we assign to the proton resonance of the formate groups bound to the boron atom. This signal is obviously absent in the $^1H$ NMR spectra of the deuterated complex $[(TMP)(Ph_3P)_2Cu][D_2B(O_2CD)_2]$ and in that of $[(TMP)(Ph_3P)_2Cu](BF_4)$. In all the boron-containing complexes here reported, no signals due to BH, $BH_2$, or $BH_4$ hydrogens were observed. This is due to line broadening by the $^{10}B$ and $^{11}B$ quadrupole moments.[1] The $^{11}B$ NMR spectra of the complexes **3** and **4a**,**b** (Table I, Figure 1) substantiate the presence of the BH and $BH_2$ groups, respectively. In fact, compound **3** showed a 1:1 doublet due to $^{11}B$–H coupling (Figure 1a), while for the complexes **4a** and **4b** a 1:2:1 triplet at $\delta = 1.20$ was observed (Figure 1b).

The $^{13}C$ NMR spectra of the complexes $[(phen)(Ph_3P)_2Cu][HB(O_2{}^{13}CH)_3]$ and $[(phen)(Ph_3P)_2Cu][H_2B(O_2{}^{13}CH)_2]$, prepared by using $^{13}CO_2$, showed signals that exhibit the pattern expected for coupling with either the hydrogens of the formato group or the hydrogens bound to boron. In particular the $^{13}C$ NMR spectrum of $[(phen)(Ph_3P)_2Cu][HB(O_2{}^{13}CH)_3]$ ($CD_3CN$ solution) showed a singlet ($^{13}C\{^1H\}$ double resonance) at $\delta = 164.45$ (relative to $Me_4Si$ as standard), which is split into a doublet of doublets by coupling with the proton directly bonded to the carbon atom ($^1J(H,C) = 209$ Hz) and with the proton bonded to the boron atom ($^3J(H,C) = 7$ Hz). The $^{13}C$ NMR spectrum of the complex $[(phen)(Ph_3P)_2Cu][H_2B(O_2{}^{13}CH)_2]$ showed a singlet signal at $\delta = 167.68$. This is split into a doublet of 1:2:1 triplets by coupling with protons ($^1J(H,C) = 203$ Hz and $^3J(H,C) = 8$ Hz). For the formato derivatives **5**, the NMR data are not reliable for their low stability in solution.

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## Experimental Section

**General Techniques.** Infrared spectra were taken on a Nicolet MX-1 FT-IR spectrometer. $^1H$, $^{11}B$, and $^{13}C$ NMR spectra were obtained from a Bruker VP-80 multinuclear spectrometer. Chemical shifts are given relative to $Me_4Si$ ($^1H$, $^{13}C$) and to $BF_3{\cdot}O(C_2H_5)_2$ ($^{11}B$). IR spectra were recorded on solid samples prepared by evaporating their $CH_2Cl_2$ solutions, spread on a NaCl disk, with a nitrogen stream. Conductivity of the complex solutions was measured with an Ōrion Research Type 101-A instrument. Elemental analyses (C, H, N) were carried out in the Analytical Laboratories of Milan University. Oxygen and boron analyses were performed by Pascher's Analytical Laboratories (Bonn).

**Materials.** Cupric sulfate (99.5%), Carlo Erba), triphenylphosphine (Merck), 1,10-phenanthroline (Merck), 3,4,7,8-tetramethyl-1,10-phenanthroline (Ega Chemie), sodium borohydride (Merck), sodium borodeuteride (>99 atoms % D, Fluka), and $^{13}CO_2$ (90 atom % $^{13}C$, MSD Isotopes) were obtained commercially. Technical grade $CO_2$ was passed through a bubbler containing concentrated sulfuric acid and successively through a trap filled with dry molecular sieves. Solvents were distilled before use.

**$(Ph_3P)_2Cu(BH_4)$** was prepared as reported in the literature.[16]

**$(Ph_3P)_2Cu(BD_4)$** was prepared analogously from $NaBD_4$.

**(phen)$(Ph_3P)Cu(BH_4)$ (1)** was obtained as already described,[7] with use of toluene as the reaction medium. Its IR spectrum showed only one strong absorption in the 2000–2400-cm$^{-1}$ region (2330 cm$^{-1}$) assignable to $\nu(BH_t)$ and a medium-weak band at 1140 cm$^{-1}$ due to $\delta(BH_2)$. These IR data are quite different from those reported by Green and co-workers[9] (see text). **1** showed in its $^{11}B$ NMR spectrum ($CD_2Cl_2$ solution) a 1:4:6:4:1 quintet centered at −40.1 ppm ($J$(B,H) = 76.5 Hz). This signal showed broadening when the temperature was lowered.

**(TMP)$(Ph_3P)Cu(BH_4)$ (2).** To a toluene suspension (25 mL) of 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) (1.7 mmol) was added $(Ph_3P)_2Cu(BH_4)$ (1.51 mmol) under a nitrogen atmosphere with stirring. After 2 h the orange crystalline material was filtered, washed with toluene and *n*-hexane, and dried under vacuum: $C_{34}H_{35}PN_2BCu$; mp 150 °C dec. Anal. Calcd: C, 70.77; H, 6.07; N, 4.86; B, 1.91. Found: C, 70.21; H, 5.98; N, 4.65; B, 1.78. Its IR spectrum showed a strong band at 2385 cm$^{-1}$ due to $\nu(BH_t)$ and a shoulder at 1095 cm$^{-1}$, which we assign to $\delta(BH_2)$. The $^{11}B$ NMR spectrum ($CD_2Cl_2$ solution) showed a 1:4:6:4:1 quintet centered at −41.6 ppm ($J$(B,H) = 81.4 Hz). Also for this tetrahydroborato complex, the lowering of the temperature causes a broadening of the signal.

**(TMP)$(Ph_3P)Cu(BD_4)$.** This compound was prepared by the same procedure as the corresponding proton-containing complex, but with $NaBD_4$ being used. Its IR spectrum showed two medium-strong bands at 1753 and 1710 cm$^{-1}$, which can be attributed to terminal B–D stretchings.

**[(phen)$(Ph_3P)_2Cu$][$HB(O_2CH)_3$] (3).** $CO_2$ was bubbled through a $CH_2Cl_2$ solution (20 mL) of triphenylphosphine (2.88 mmol), maintained at −50 °C, to which 0.48 mmol of **1** was added. The resulting yellow solution was stirred for 2 h while $CO_2$ was bubbled through. The temperature was allowed to rise at 0 °C and $CH_2Cl_2$ removed by continuing $CO_2$ bubbling. The yellow residue was treated with diethyl ether (30 mL) under a $CO_2$ atmosphere and at −30 °C. The yellow crystalline product **3** was filtered off, washed with diethyl ether, and dried at atmospheric pressure. It can be stored at 0 °C with no apparent decomposition: $C_{51}H_{42}P_2O_6N_2BCu$; mp 98 °C dec. Anal. Calcd: C, 66.92; H, 4.59; N, 3.06; O, 10.05. Found: C, 65.83; H, 4.63; N, 3.02; O, 9.85. $\Lambda_m$ in acetonitrile: 119 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ mol/L).

**[(phen)$(Ph_3P)_2Cu$][$H_2B(O_2CH)_2$] (4a).** $CO_2$ was bubbled through a $CH_2Cl_2$ solution (25 mL) of triphenylphosphine (3.1 mmol), maintained at 40 °C, to which 0.52 mmol of **1** was added. The yellow solution was refluxed for 2 h under a $CO_2$ atmosphere. The solvent was removed by slow nitrogen bubbling through the solution. To the yellow residue was added diethyl ether (25 mL) and the suspension refluxed for 30 min and filtered. The yellow crystalline product **4a** was washed with diethyl ether and dried under vacuum: $C_{50}H_{42}P_2O_4N_2BCu$; mp 123 °C. Anal. Calcd: C, 68.93; H, 4.83; N, 3.22; O, 7.35. Found: C, 68.97; H, 4.87; N, 3.03; O, 7.17. $\Lambda_m$ in acetonitrile: 132.4 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ mol/L).

**[(TMP)$(Ph_3P)_2Cu$][$H_2B(O_2CH)_2$] (4b).** This complex was obtained as described for **4a**: $C_{54}H_{50}P_2O_4N_2BCu$; mp 144 °C. Anal. Calcd: C, 69.94; H, 5.40; N, 3.02; O, 6.91; B, 1.19. Found: C, 69.47; H, 5.27; N, 3.18; O, 6.73; B, 1.15. $\Lambda_m$ in acetonitrile: 113.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ mol/L).

**[(phen)$(Ph_3P)_2Cu$][$HB(O_2{}^{13}CH)_3$] and [(phen)$(Ph_3P)_2Cu$][$H_2B(O_2{}^{13}CH)_2$].** The reactions leading to these $^{13}C$-labeled complexes were carried out as reported above for **3** and **4a**, respectively.

**[(TMP)$(Ph_3P)_2Cu$][$D_2B(O_2CD)_2$].** This derivative was prepared by reacting (TMP)$(Ph_3P)Cu(BD_4)$ with $CO_2$ under the experimental conditions used for **4a**.

**(phen)$(Ph_3P)Cu(O_2CH)$ (5a).** Through a $PPh_3$ (0.76 mmol) ethanol solution (10 mL) was bubbled $CO_2$, and 0.19 mmol of **1** was added. Gas evolution was noted, and a yellow solution formed. This was stirred for 2 h while $CO_2$ was bubbled through and then evaporated to dryness. The yellow residue was treated several times with diethyl ether, filtered off, and dried under vacuum: $C_{31}H_{24}PO_2N_2Cu$; mp 165 °C dec. Anal. Calcd: C, 67.58; H, 4.36; N, 5.09; O, 5.81. Found: C, 67.32; H, 4.48; N, 5.18; O, 5.77. The same formato complex **5a** can be obtained from **3** or **4a** by heating at 45 °C for 3 h in ethanol. The presence of hydrogen and ethyl borate ester in the gas phase was confirmed.

**(TMP)$(Ph_3P)Cu(O_2CH)$ (5b).** This derivative was prepared by reacting **2** with $CO_2$ under the experimental conditions used for **5a**. It can be also obtained (a) by heating **4b** at 45 °C for 3 h in ethanol and (b) by reacting $(Ph_3P)_3Cu(O_2CH)$[6b] with TMP in ethanol: $C_{35}H_{32}PO_2N_2Cu$; mp 162 °C dec. Anal. Calcd: C, 69.25; H, 5.28; N, 4.62; O, 5.28. Found: C, 69.25; H, 5.32; N, 4.55; O, 4.97.

**(TMP)$(Ph_3P)Cu(O_2CD)$.** This complex was prepared by reacting (TMP)$(Ph_3P)Cu(BD_4)$ with $CO_2$ in ethanol, as described for **5b**.

**Reaction of 4a with $CO_2$.** $CO_2$ was bubbled through $CH_2Cl_2$ (15 mL) at −50 °C, and **4a** (0.095 mmol) was added with stirring. After 2 h the solution was worked up as described for **3**. The yellow product was proved to be the tris(formato)hydroborato complex **3** (analytical and spectroscopic evidence).

**Decarboxylation of 3.** $CH_2Cl_2$ was degassed with dinitrogen, and **3** was added with stirring. The yellow solution was refluxed for 2.5 h and then evaporated to dryness. The yellow residue was treated with diethyl ether and filtered. It was confirmed to be the bis(formato)dihydroborato derivative **4a** by means of analytical and spectroscopic data.

**Reaction of 4b with $HBF_4$.** To a diethyl ether suspension (6 mL) of **4b** (0.054 mmol) was added four drops of an aqueous solution of $HBF_4$ (40%) under a nitrogen atmosphere with stirring. Gas was evolved; it was recognized to be a mixture of $H_2$ and $CO_2$ by gas-chromatography techniques. The insoluble pale yellow compound, [(TMP)$(Ph_3P)_2Cu$]($BF_4$), was recovered by filtration, washed with diethyl ether, and dried under vacuum: $C_{52}H_{46}P_2N_2F_4BCu$; mp 216 °C. Anal. Calcd: C, 68.53; H, 5.05; N, 3.07. Found: C, 68.18; H, 4.86; N, 2.98. $\Lambda_m$ in acetonitrile: 109.4 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ mol/L). Its IR spectrum showed the expected absorptions due to the ligands and to the $BF_4$ anion.

**Anion-Exchange Reaction between 4b and $NaBPh_4$.** To an acetone solution (8 mL) of **4b** (0.22 mmol) was added $NaBPh_4$ (0.44 mmol), dissolved in the minimum amount of acetone, under nitrogen with stirring. After 1 h an off-white insoluble product was filtered off, and the solution was evaporated to dryness. The yellow residue was treated with ethanol, filtered, washed with water and ethanol, and dried under vacuum: $C_{76}H_{66}P_2N_2BCu$; mp 160 °C dec. Anal. Calcd: C, 79.82; H, 5.78; N, 2.45. Found: C, 79.66; H, 5.78; N, 2.41. $\Lambda_m$ in acetonitrile: 90.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ ($10^{-3}$ mol/L). Attempts to determine the fate of the anion $[H_2B(O_2CH)_2]^-$ were unsuccessful. In only one case was sodium formate proved to be the scarce insoluble white product of the above reaction.

**Conductivity Measurements on 1 and 2 in the Presence of Triphenylphosphine.** The conductivities of $CH_3CN$ solutions containing **1** or **2**, in the absence or in the presence of $PPh_3$, were measured. The tetrahydroborato complexes in solutions of $10^{-3}$ M concentration gave the following values: 54.2 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **1** and 62.04 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **2**. Triphenylphosphine ($PPh_3$:Cu = 5:1) was added, and the molar conductivity was again measured. The following values were obtained: 89.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **1** and 127.8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **2**.

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