may be construed to occur *primarily* for steric reasons, as a position cis to the nitrosyl will be sterically less congested than the trans position.

Acknowledgments. Support from the National Science Foundation (Grant No. CHE82-06117 to R.A.W.) is gratefully acknowledged. We also acknowledge support from the Monsanto Fund and the Chemical Instrumentation Program (Grant No. CHE82-04994) for providing funds for the upgrading of our X-ray crystallographic facilities.

Supplementary Material Available: Details of the structure solution and full tables of the experimental details (Table S1), atomic parameters (Table S2), anisotropic thermal parameters (Table S3), bond distances and bond angles (Table S4), and observed and calculated structure factors for the crystal structure of $[Cr(NO)(CNCMe_3)_3(dppm)]PF_6$ (60 pages). Ordering information is given on any current masthead page.

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 CO_2 and COS. Structure of (triphos)$Cu(\eta^1\text{-}O_2CH)$

CLAUDIO BIANCHINI,* CARLO A. GHILARDI, ANDREA MELI, STEFANO MIDOLLINI,
and ANNABELLA ORLANDINI

Received March 21, 1984

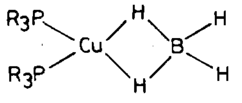
The novel tetrahydroborate complexes $(PCy_3)_2Cu(BH_4)$, $(np_3)Cu(BH_4)$ [np_3 = tris(2-(diphenylphosphino)ethyl)amine] and $(etp_3)Cu(BH_4)$ [etp_3 = 1,1,1-tris((diphenylphosphino)ethyl)ethane] have been synthesized and characterized. The reactivity of these compounds and of other copper(I) tetrahydroborates, $(PPh_3)_2Cu(BH_4)$, (triphos)$Cu(BH_4)$ [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane], and $(PMePh_2)_3Cu(BH_4)$, toward CO_2 and COS have been investigated. The latter triatomic molecules are reduced under very mild conditions to give metalloformate or metallothioformate derivatives. The bonding mode of the BH_4^- ligand, i.e. unidentate or bidentate, has been found to influence the rate of the reactions. The reactivity of the formate complex (triphos)$Cu(O_2CH)$ has been investigated in some detail. The latter compound has been studied by X-ray analysis. Crystal data: orthorhombic, space group $Pn2_1a$, a = 20.901 (8) Å, b = 17.136 (6) Å, c = 10.162 (4) Å, Z = 4, R, R_w = 0.055, 0.054 for 2267 reflections having $I \geq 3\sigma(I)$. The bonding mode of the formate group was shown to be through one oxygen atom.

Introduction

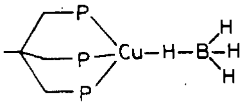
Organic chemists largely use alkali-metal tetrahydroborates to effect the reduction of a plethora of compounds such as ketones or aldehydes to alcohols. At the same time, the tetrahydroborate ion plays an important role in both coordination and organometallic chemistry. Its coordinative properties make the BH_4^- group one of the most versatile ligands, being able to coordinate a metal in a uni-, bi-, or tridentate fashion.[1-10] Bridging BH_4 groups have been also reported.[11] The use of tetrahydroborates as sources of hydridic hydrogen atoms is widely exploited by organometallic chemists in a variety of reactions. These include (i) synthesis of hydrido metal complexes;[12] (ii) attack by hydride from BH_4^- on an electrophilic center;[13] and (iii) reduction of a coordinated species.[14] In addition there is considerable experimental evidence indicative of the action of tetrahydroborates as effective catalysts for polymerization, oligomerization, and hydrogenation of olefins.[1]

In 1978 Sorrell[15] and Fleet[16] reported that the BH_4 moiety in the complex $(PPh_3)_2Cu(\eta^2\text{-}BH_4)$ (**1**) is deactivated to the extent that it only reduces carboxylic acid chlorides to aldehydes. This is in contrast to the case of $NaBH_4$, which results in further reduction to the alcohol. Since then, the exploitation of **1** as a selective reducing agent in organic chemistry has received increasing attention[17] as attested by the presence of **1** in the recent catalogs of the principal chemical suppliers.[18]

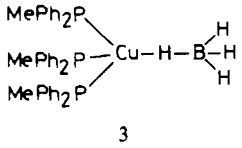
Here and in the following paper of this issue we contrast the reactivities of the related heteroallene molecules CO_2, COS, CS_2, and SCNPh toward a variety of copper(I) tetrahydroborate complexes with phosphine coligands. These include known compounds such as $(PPh_3)_2Cu(BH_4)$ (**1**),[19] (triphos)$Cu(BH_4)$[6] (**2**) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane], and $(PMePh_2)_3Cu(BH_4)$ (**3**)[20] and novel compounds such as (np_3)-



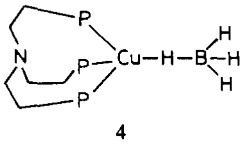
1, R = Ph
6, R = Cy



2



3



4

---

(1) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263 and references therein.
(2) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1 and references therein.
(3) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558.
(4) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165.
(5) Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1967**, *6*, 2223.
(6) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096.
(7) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1983**, 206.
(8) Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961.
(9) Corey, E. J.; Cooper, N. J.; Canning, W. M.; Lipscomb, W. N.; Koetzle, T. F. *Inorg. Chem.* **1982**, *21*, 192.
(10) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1982**, *231*, C78.
(11) Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1308.
(12) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405.
(13) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 141. Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2419.
(14) Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1978**, *173*, C9.
(15) Sorrell, T. N.; Spillane, R. J. *Tetrahedron Lett.* **1978**, 2473.
(16) Fleet, G. W. J.; Fuller, C. J.; Harding, P. J. C. *Tetrahedron Lett.* **1978**, 1437.
(17) Kano, S.; Shibuya, S.; Ebata, T. *J. Heterocycl. Chem.* **1981**, *18*, 1239. Kametani, T.; Huang, S. P.; Nakayama, A.; Honda, T. *J. Org. Chem.* **1982**, *47*, 2328.
(18) See: Fluka Catalog 14, 1984/1985, p 184, item 15251.
(19) Cariati, F.; Naldini, L. *Gazz. Chim. Ital.* **1965**, *95*, 3.

0020-1669/85/1324-0924$01.50/0

Cu(BH_4) (**4**) [np_3 = tris(2-(diphenylphosphino)ethyl)amine], (etp_3)Cu(BH_4) (**5**) [etp_3 = 1,1,1-tris((diphenylphosphino)ethyl)ethane], and (PCy_3)$_2$Cu(BH_4) (**6**).

It seemed to us that it would be interesting to probe the reactivity of the above heteroallene molecules toward copper(I) tetrahydroborate complexes for at least three reasons: (i) There is an increasing interest in the chemistry of CO_2 and related molecules. In particular, the reduction is an essential requisite for the utilization of CO_2 as a source of carbon in current laboratory and industrial practices. (ii) The complexed BH_4 group as reducing agent is deactivated with respect to the free species. Consequently, unusual reactivities toward heterocumulenes are expected. (iii) The presence in the reaction mixture of coordinatively unsaturated metal fragments could be particularly suitable for the stabilization of eventual unstable species through the coordination to the metal.

A preliminary account has been given of some of the results described in this paper.[21]

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. The compounds (np_3)CuCl and (etp_3)CuCl were prepared by the method described for the preparation of (PPh_3)$_3$CuCl.[22] The compounds (PPh_3)$_3$Cu(ClO_4),[23] (PCy_3)$_2$Cu(ClO_4),[24] (PPh_3)$_2$Cu(BH_4),[19] (triphos)Cu(BH_4),[25] and ($PMePh_2$)$_3$Cu(BH_4)[26] 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 are white and were recrystallized from CH_2Cl_2 and ethanol. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr plates. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian CFT 20 spectrometer. Proton and carbon-13 chemical shifts are relative to Me_4Si, whereas phosphorus-31 chemical shifts are relative to H_3PO_4. All positive chemical shifts are downfield. Conductivity measurements were made on a WTW Model LBR/B conductivity bridge.

(np_3)Cu(BH_4) (4). $NaBH_4$ (1.3 mmol) dissolved in ethanol (30 mL) was added at room temperature to a magnetically stirred solution of (np_3)CuCl (1 mmol) in CH_2Cl_2 (30 mL). After 1 h, filtration of the resulting colorless solution (to remove NaCl) followed by partial evaporation of the solvent from the filtrate afforded a crystalline precipitate in almost quantitative yield. Anal. Calcd for $C_{42}H_{46}BCuNP_3$: C, 68.90; H, 6.33; Cu, 8.67; N, 1.91. Found: C, 68.75; H, 6.35; Cu, 8.59; N, 1.84.

(etp_3)Cu(BH_4) (5) was prepared as above starting from (etp_3)CuCl; yield 80%. Anal. Calcd for $C_{44}H_{49}BCuP_3$: C, 70.92; H, 6.62; Cu, 8.52. Found: C, 70.79; H, 6.65; Cu, 8.46.

(PCy_3)$_2$Cu(BH_4) (6). This complex was synthesized by the same procedure as for **4**, but the perchlorate (PCy_3)$_2$Cu(ClO_4) was used in place of the chloride derivative; yield 90%. Anal. Calcd for $C_{36}H_{70}BCuP_2$: C, 67.63; H, 11.03; Cu, 9.94; P, 9.69. Found: C, 67.52; H, 10.94; Cu, 9.91; P, 9.74.

(PPh_3)$_2$Cu(O_2CH) (7). CO_2 was bubbled at room temperature into a solution of **1** (1 mmol) in CH_2Cl_2 (60 mL) for 24 h. Addition of ethanol (30 mL) under CO_2 atmosphere and partial evaporation of the solvent produced crystals in 70% yield. Anal. Calcd for $C_{37}H_{31}CuO_2P_2$: C, 70.18; H, 4.93; Cu, 10.03; P, 9.78. Found: C, 70.05; H, 4.89; Cu, 9.94; P, 9.82.

(PPh_3)$_3$Cu(O_2CH) (8). CO_2 was bubbled at room temperature into a mixture of **1** (1 mmol) and PPh_3 (1 mmol) in CH_2Cl_2 (50 mL) for 12 h. Treating the resulting solution as above allowed crystals in 70% yield to be obtained. Anal. Calcd for $C_{55}H_{46}CuO_2P_3$: C, 73.77; H, 5.17; Cu, 7.09; P, 10.37. Found: C, 73.66; H, 5.11; Cu, 6.98; P, 10.41.

[(PPh_3)$_3$Cu(O_2CH)Cu(PPh_3)$_3$]ClO_4 (9). Method A. CO_2 was bubbled into a mixture of **1** (1 mmol), PPh_3 (1 mmol), and NBu_4ClO_4 (0.7 mmol) in CH_2Cl_2 (60 mL) for 1 h at room temperature. The resulting solution was treated as described above to give crystals in 80% yield.

Method B. (PPh_3)$_3$Cu(ClO_4) (1 mmol) dissolved in CH_2Cl_2 (20 mL) was added to a CH_2Cl_2 solution (10 mL) of **8**. After 1 h, the resulting mixture was concentrated and ethanol was added to give **9**. Anal. Calcd for $C_{109}H_{91}ClCu_2O_6P_6$: C, 70.94; H, 4.97; Cu, 6.88; P, 10.07. Found: C, 70.81; H, 4.97; Cu, 6.83; P, 10.18.

(PCy_3)$_2$Cu(O_2CH) (10). The method reported above for **7** was used for this preparation except for substitution of **6** for **1**; yield 65%. Anal. Calcd for $C_{37}H_{67}CuO_2P_2$: C, 66.38; H, 10.08; Cu, 9.49; P, 9.25. Found: C, 66.33; H, 10.04; Cu, 9.47; P, 9.31.

(triphos)Cu(O_2CH) (11). CO_2 was bubbled into a CH_2Cl_2 solution (30 mL) of **2** (1 mmol) for 2 h. Addition of ethanol (30 mL) under CO_2 atmosphere followed by concentration gave well-shaped crystals in 75% yield. Anal. Calcd for $C_{42}H_{40}CuO_2P_3$: C, 68.79; H, 5.49; Cu, 8.66. Found: C, 68.71, H, 5.51; Cu, 8.63.

($PMePh_2$)$_3$Cu(O_2CH) (12). An analogous procedure to the one reported above using **3** instead of **2** was successful for this synthesis; yield 85%. Anal. Calcd for $C_{40}H_{40}CuO_2P_3$: C, 67.74; H, 5.68; Cu, 8.95; P, 13.10. Found: C, 67.65; H, 5.71; Cu, 8.86; P, 13.03.

(np_3)Cu(O_2CH) (13). After CO_2 was bubbled through a THF solution (30 mL) of **4** (1 mmol), white crystals of **13** began to deposit after ca. 4 h; yield 75%. Anal. Calcd for $C_{43}H_{43}CuNO_2P_3$: C, 67.75; H, 5.68; Cu, 8.33; N, 1.83. Found: C, 67.69; H, 5.71; Cu, 8.28; N, 1.75.

(etp_3)Cu(O_2CH) (14). This compound was prepared as solid material by a similar procedure as for **7** starting from **5**; yield 60%. Anal. Calcd for $C_{45}H_{46}CuO_2P_3$: C, 69.71; H, 5.98; Cu, 8.19. Found: C, 69.57; H, 6.04; Cu, 8.15.

(PPh_3)$_2$Cu(SOCH) (15). Method A. COS was bubbled into a solution of **1** (1 mmol) in CH_2Cl_2 (30 mL) for 30 min. Addition of ethanol (30 mL) and partial evaporation of the solvent gave crystals in 75% yield.

Method B. A mixture of CS_2 (10 mL) and **7** (1 mmol) in CH_2Cl_2 (30 mL) was allowed to react for 3 h. Addition of ethanol (30 mL) and partial evaporation of the solvent gave **15**, yield 50%. Anal. Calcd for $C_{37}H_{31}CuOP_2S$: C, 68.45; H, 4.81; Cu, 9.78; S, 4.93. Found: C, 68.41; H, 4.73; Cu, 9.76; S, 4.91.

(PCy_3)$_2$Cu(SOCH) (16). Method A reported above for **15** was successfully used for this preparation, substituting **6** for **1**; yield 65%. Anal. Calcd for $C_{37}H_{67}CuOP_2S$: C, 64.82; H, 9.85; Cu, 9.26; S, 4.67. Found: C, 64.79; H, 9.81; Cu, 9.25; S, 4.64.

(triphos)Cu(SOCH) (17). Method A. COS was bubbled into a solution of **2** (1 mmol) in CH_2Cl_2 (30 mL) for 1 h. The addition of an equal volume of ethanol followed by slow removal of solvent produced a crystalline product, yield 80%.

Method B. A solution of **11** (1 mmol) in CH_2Cl_2 (30 mL) was treated with an excess of CS_2 for 3 h. Upon treatment of the resulting solution as above was obtained **17** in 70% yield. Anal. Calcd for $C_{42}H_{40}CuOP_3S$: C, 67.32; H, 5.38; Cu, 8.48; S, 4.27. Found: C, 67.35; H, 5.35; Cu, 8.41; S, 4.23.

(np_3)Cu(SOCH) (18). An analogous procedure to that described for **17** (method A) using **4** instead of **2** was successful for this synthesis; yield 80%. Anal. Calcd for $C_{43}H_{43}CuNOP_3S$: C, 66.35; H, 5.56; Cu, 8.16; N, 1.80; S, 4.11. Found: C, 66.29; H, 5.53; Cu, 8.13; N, 1.71; S, 4.06.

(triphos)Cu(O_2COEt) (19). After COS was bubbled into a CH_2Cl_2 solution (30 mL) of **11** (1 mmol), the color changed from colorless to yellow. Nitrogen was then bubbled through the reaction mixture until all of the unreacted COS was eliminated. By addition of ethanol (30 mL), the solution became almost colorless. Slow evaporation of the solvent afforded white crystals in 40% yield. Anal. Calcd for $C_{44}H_{44}CuO_3P_3$: C, 67.98; H, 5.70; Cu, 8.17; O, 6.17. Found: C, 67.91; H, 5.74; Cu, 8.15; O, 6.12.

Collection and Reduction of X-ray Intensity Data. A well-formed crystal, delimited by the faces 100, 010, 001, and the centrosymmetric ones, was selected for X-ray investigation and mounted along the crystallographic *b* axis on a Philips PW 1100 automatic diffractometer. The crystals belong to the orthorhombic system, with extinctions $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$, characteristic of the $Pn2_1a$ space group. The cell dimensions were determined by least-squares refinement of the angular settings of 20 carefully centered reflections. Crystal data and data collection details are given in Table I. Intensities were rescaled, and after correction for backgrounds, the standard deviations of the intensities $\sigma(I)$ were calculated as already described, by using the value of 0.03 for the instability factor p.[27] Intensity data were corrected for Lorentz-polarization effects and for absorption. Atomic scattering factors for non-hydrogen atoms were taken from ref 28 and those for hydrogen atoms from ref 29. Both the $\Delta f'$ and $\Delta f''$ components of

---

(20) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19*, 587.

(21) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *248*, C13; Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *255*, C27.

(22) Jardine, F. H.; Rule, L.; Vohra, G. *J. Chem. Soc., Dalton Trans.* **1970**, 238.

(23) Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325.

(24) Restivo, R. J.; Costin, A.; Ferguson, G.; Carty, A. J. *Can. J. Chem.* **1975**, *53*, 1949.

(25) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768.

(26) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19*, 587.

(27) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 1979.

(28) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

Table I. Crystal Data and Data Collection Details

formula	$C_{42}H_{40}CuO_2P_3$
mol wt	733.25
a, Å	20.901 (8)
b, Å	17.136 (6)
c, Å	10.162 (4)
d_{calcd}, g cm^{-3}	1.338
V, Å^3	3639.6
Z	4
space group	$Pn2_1a$
color	white
habit	parallelepiped
dimens, mm	0.375 × 0.225 × 0.050
linear abs coeff, cm^{-1}	7.64
transmissn factors	0.93–0.71
radiation, λ(Mo Kα), Å	0.7107
monochromator	graphite crystal
method	ω–2θ scan technique
scan speed, deg/s	0.07
scan width, deg	$0.80 + 0.69 \tan\theta$
bkgd time	half the scan time
stds	3 every 120 min
max dev stds, %	±1
2θ limits, deg	$5 \leqslant 2\theta \leqslant 50$
data collcd	$+h,+k,+l$
no. of total data	3622
no. of data ($I \geqslant 3\sigma(I)$)	2267
final no. of variables	147

anomalous dispersion were included for all non-hydrogen atoms.[30]

Solution and Refinement of the Structure. All the calculations were performed by using the SHELX-76 crystallographic system on a SEL 32/77 computer.[31] On the assumption that the compound is isomorphous with (triphos)Cu(BH_4)[6] the final parameters of this structure were used as starting parameters of the present complex. A Δ Fourier synthesis, calculated on the basis of the metal and of the triphos ligand coordinates, revealed the positions of the formate group. By using anisotropic thermal parameters for copper and phosphorus atoms, full-matrix least-squares refinement was carried out. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w was set at $1/\sigma(F_o)^2$. The phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms, introduced in their geometrical positions, were not refined. Only the formate hydrogen atom, located from a difference Fourier map ($(\sin\theta)/\lambda \leqslant 0.3$ Å^{-1}) was successfully refined. Owing to the polar space group $Pn2_1a$, the polar axis direction was determined. Refinements of the x, y, z structure and of the inverted $x, \bar{y}, z$, gave R and R_w values of 0.058, 0.057 and 0.055, 0.054, respectively. An analysis of the standard deviations confirmed that the $x, \bar{y}, z$ structure was the correct one. Final positional parameters are reported in Table II.

Results and Discussion

The complexes **1**–**6** have been prepared by reaction of an excess of sodium tetrahydroborate with the corresponding copper(I) chloride (**1**–**5**) or perchlorate (**6**). The mode of attachment of the tetrahedral BH_4^- ligand in the novel compounds **4**–**6** has been assigned by means of IR spectroscopy.[1] Pertinent features supporting the mode of tetrahydroborate bonding are the position and number of peaks in the B–H terminal and bridging stretching regions. BH_3 and BH_2 deformation frequencies are also diagnostic of the bonding mode of BH_4^-. Infrared absorptions assigned to B–H_n moieties in compounds **1**–**6** are given in Table III.

The data are consistent with the presence of unidentate tetrahydroborate in **4**. The spectrum of the latter complex shows also a band at 2830 cm^{-1}, which is typical of np_3 complexes where the tripodal ligand acts as tridentate, the nitrogen atom being not coordinated to the metal.[32]

The IR spectrum of **6**, even though strongly indicative of the presence of a double-hydrogen bridge attachment of the BH_4^- moiety, however, does not completely rule out the unidentate bonding mode. This ambiguity stems also from the tendency of the $(PCy_3)_2Cu$ fragment to form three-coordinate complexes.[24] To clarify the stereochemistry around the copper atom, we are presently trying to prepare crystals of **6** suitable for an X-ray structural analysis.

Table II. Final Positional Parameters[a] (×10^4)

atom	x	y	z
Cu	612 (1)	1320	−720 (1)
P1	−449 (1)	1273 (2)	−1269 (2)
P2	594 (1)	137 (2)	293 (2)
P3	967 (1)	870 (2)	−2710 (2)
O1	853 (4)	2377 (5)	−8 (8)
C	1369 (7)	2617 (9)	88 (14)
O2	1835 (7)	2211 (10)	87 (14)
C1	−340 (4)	−989 (6)	−2866 (10)
C2	−47 (4)	−248 (5)	−2204 (9)
C3	−620 (4)	233 (5)	−1688 (9)
C4	392 (4)	−545 (5)	−1070 (8)
C5	338 (4)	201 (5)	−3259 (8)
C6	−708 (3)	1827 (4)	−2706 (7)
C7	−1290 (3)	1697 (4)	−3340 (7)
C8	−1481 (3)	2182 (4)	−4370 (7)
C9	−1089 (3)	2799 (4)	−4765 (7)
C10	−507 (3)	2929 (4)	−4131 (7)
C11	−316 (3)	2444 (4)	−3102 (7)
C12	−1068 (3)	1550 (3)	−95 (6)
C13	−1672 (3)	1206 (3)	−49 (6)
C14	−2122 (3)	1462 (3)	867 (6)
C15	−1968 (3)	2064 (3)	1737 (6)
C16	−1364 (3)	2408 (3)	1691 (6)
C17	−914 (3)	2152 (3)	775 (6)
C18	−43 (3)	−27 (3)	1507 (6)
C19	−342 (3)	−745 (3)	1703 (6)
C20	−811 (3)	−822 (3)	2672 (6)
C21	−979 (3)	−182 (3)	3445 (6)
C22	−680 (3)	537 (3)	3248 (6)
C23	−212 (3)	614 (3)	2279 (6)
C24	1268 (3)	−359 (4)	1087 (6)
C25	1327 (3)	−1169 (4)	1119 (6)
C26	1852 (3)	−1513 (4)	1738 (6)
C27	2318 (3)	−1046 (4)	2325 (6)
C28	2260 (3)	−235 (4)	2292 (6)
C29	1735 (3)	108 (4)	1673 (6)
C30	1111 (3)	1515 (3)	−4111 (6)
C31	901 (3)	1354 (3)	−5386 (6)
C32	1047 (3)	1866 (3)	−6411 (6)
C33	1402 (3)	2539 (3)	−6160 (6)
C34	1611 (3)	2700 (3)	−4885 (6)
C35	1465 (3)	2188 (3)	−3861 (6)
C36	1689 (3)	266 (4)	−2760 (5)
C37	1826 (3)	−228 (4)	−3813 (5)
C38	2371 (3)	−698 (4)	−3780 (5)
C39	2779 (3)	−673 (4)	−2694 (5)
C40	2642 (3)	−178 (4)	−1641 (5)
C41	2097 (3)	291 (4)	−1674 (5)
H1[b]	136 (7)	329 (10)	30 (15)

[a] The y coordinate of the Cu atom was chosen in accordance with the isomorphous (triphos)Cu(BH_4) complex. [b] The hydrogen atom coordinates are multiplied by 10^3.

As for **5**, our structural conclusions are even more puzzling than those reached for **6**. The infrared data, in fact, do not allow us to discriminate unambiguously between η^2- or η^1-BH_4 bonding modes. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ is too poorly resolved even at low temperatures to given any structural information. It is noteworthy that the etp_3 ligand has been found so far unable to coordinate to one metal atom in a tridentate fashion.[33] Thus, since molecular weight measurements have excluded the formation of polynuclear species, **5** can be assigned in the solid state either structure A or structure B.

Compounds **1**–**6** are air-stable both in the solid state and in solution. They are soluble in halogenated solvents.

The great stability of these tetrahydroborate complexes with respect to processes 1 and 2 is likely due both to the basicity and

---

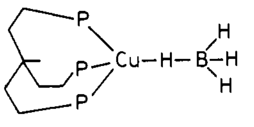
(29) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

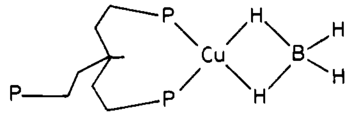
(31) Sheldrick, G. M. "System of Computing Programs"; University of Cambridge: Cambridge, 1976 (adapted by Dr. C. Mealli).

(32) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834.

(33) Cecconi, F.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chim. Acta* **1980**, *42*, 59.



A



B

$$Cu^+BH_4^- \rightarrow Cu + BH_3 + {}^1/_2H_2 \quad (1)$$

$$Cu^+BH_4^- \rightarrow Cu^+H^- + BH_3 \quad (2)$$

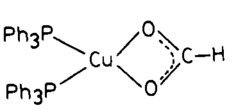
to the bulkiness of the phosphine coligands. In particular, basic ligands decrease the oxidative tendency of the metal ion, whereas ligands such as the present tripodal phosphines may impede process 2 by saturating and immobilizing the copper coordination sphere.[1] In this context, the bulkiness of the coligands seems to be a requisite of critical importance in determining the stability of BH_4^- complexes since alkylphosphines, even though more basic than arylphosphines, fail to stabilize copper with respect to reduction by tetrahydroborate.[34]

Reactions of Copper(I) Tetrahydroborates. (a) With CO_2. Schemes I and II illustrate the reactions performed and the results obtained; IR and ^1H NMR data are listed in Table IV.

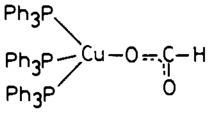
Depending on the reaction conditions, the three different formate complexes $(PPh_3)_2Cu(O_2CH)$ (**7**), $(PPh_3)_3Cu(O_2CH)$ (**8**), and $[(PPh_3)_6Cu_2(O_2CH)]ClO_4$ (**9**) are formed by reacting CO_2 with $(PPh_3)_2Cu(\eta^2\text{-}BH_4)$ (**1**). Compound **7** is obtained by bubbling CO_2 into a solution of **1** for at least 24 h, whereas **8** is obtained when 1 equiv of PPh_3 is added to the reaction mixture. The transformation of the tetrahydroborate **1** into the unidentate formate **8** is completed within 12 h. Finally, the addition of PPh_3 together with NBu_4ClO_4 gives crystals of the bridging formate complex **9**. In the latter case the reaction is much faster, being completed within 1 h.

Both compounds **7** and **8** have been previously synthesized by reducing copper(II) formates with PPh_3.[35] An X-ray analysis has been also carried out on **7**.[36] Sneeden et al. have reported an indirect route to **7**,[37] which involves the reaction of CO_2 with the hexameric copper hydride $[HCuPPh_3]_6$. In the same paper the authors reported that on reaction of **1** with CO_2 a formate is formed, as evidenced by the fact that the treatment of the reaction mixture with MeI affords HCOOMe. However, no formula for this formate was proposed.

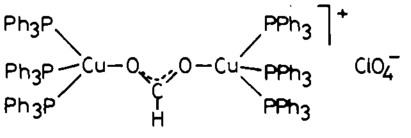
Compounds **7** and **8**, thus, can be easily identified by comparing their chemical and physical properties with those of authentic specimens. A similar identification is not at hand for the unprecedented complex **9**.



7



8



9

This is soluble in 1,2-dichloroethane where it behaves as a 1:1 electrolyte (molar conductance in 10^{-3} M solution: 77 Ω^{-1} cm^2 mol^{-1}). The IR spectrum exhibits the typical absorptions of ClO_4^- counteranion (for the other important vibrations see Table IV).

Table III. Infrared Absorption Assigned to B–H$_n$ Moieties in Copper(I) Tetrahydroborate Complexes[a]

	abs range, cm^{-1}			
compd	2500–2200	2200–1900	1500–1300	1300–1000
$(PPh_3)_2Cu(BH_4)$[e]	2395 s 2340 sh BH$_t$ str	1985 s 1935 s BH$_b$ str	1370 m bridge str	1135 s BH$_2$ def
(triphos)Cu(BH$_4$)[f]	2360 sh 2300 s BH$_t$ str	1980 s, br BH$_b$ str		
$(PMePh_2)_3Cu(BH_4)$[e]	2335 sh 2315 s BH$_t$ str	2045 s BH$_b$ str		1060 s BH$_3$ def
$(np_3)Cu(BH_4)$[g]	2310 s BH$_t$ str	2060 s BH$_b$ str		1060 s BH$_3$ def
$(etp_3)Cu(BH_4)$[g]	2375 s BH$_t$ str	2000 s BH$_b$ str 1950 m, br[c]		1130 s[d]
$(PCy_3)_2Cu(BH_4)$[g]	2360 s 2260 m[b] BH$_t$ str	2015 s 1960 s BH$_b$ str	1370 m, br bridge str	1140 s BH$_2$ def

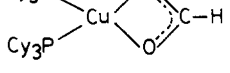
[a] Key: s, strong; m, medium; sh, shoulder; str, stretch; def, deformation; H$_t$, terminal H; H$_b$, bridging H. [b] Weak peaks at this frequency have been also assigned to an overtone of a BH$_2$ deformation. [c] This band could be assigned both to BH$_b$ stretch and to MH$_b$ stretch. [d] This band could be assigned both to BH$_3$ deformation and to BH$_2$ deformation. [e] Reference 20. [f] Reference 25. [g] This work.

The molecular structure of **9** has been established by a preliminary X-ray analysis.[38] In the complex cation, a formate ion is found to hold together two $(PPh_3)_3Cu$ fragments. Both copper atoms are thus tetracoordinated in a distorted tetrahedral geometry. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at −60 °C, consisting of an unique resonance at −1.01 ppm, confirms the equivalence of the two $(PPh_3)_3Cu$ moieties. Metal complexes containing bridging formate ligand are extremely rare, being indeed limited to $(\mu\text{-}H)(\mu\text{-}O_2CH)Os_3(CO)_{10}$,[39] and $[N(PPh_3)_2][(\mu\text{-}O_2CH)Ru_3(CO)_{10}]$.[40] Further support of structure **9** is given by the synthesis of **9** through the reaction of **8** with the complex $(PPh_3)_3Cu(ClO_4)$ in (3). Implicitly, eq 3 confirms also the unidentate bonding mode of the formate in **8**.

$$(PPh_3)_3Cu(\eta^1\text{-}O_2CH) + (PPh_3)_3Cu(ClO_4) \rightarrow [(PPh_3)_3Cu(\mu\text{-}O_2CH)Cu(PPh_3)]ClO_4 \quad (3)$$

The infrared spectra of **7**–**9** in the $\nu(CO_2)$ region are congruous with those of other formate species,[35] consisting of a strong antisymmetric $\nu(CO_2)$ vibration at ca. 1600 cm^{-1} and a weaker symmetrical $\nu(CO_2)$ vibration at ca. 1350 cm^{-1}. In bidentate and bridging formate complexes $\nu(CO_2)_{asym}$ is slightly lower than that in unidentate species, whereas the opposite is observed for $\nu(CO_2)_{sym}$. Conversely, the proton resonances of the formate ligand do not vary significantly with the bonding mode of the HCO_2^- group.

The reaction of CO_2 with **6** closely parallels that of the triphenylphosphine analogue **1**, affording white crystals analyzing as $(PCy_3)_2Cu(O_2CH)$ (**10**). The presence of a η^2-bonded formate ligand is more likely than that of the unidentate attachment. The infrared vibrations $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ are, in fact, more congruous with the bidentate bonding mode of the HCO_2^- ligand.



10

---

(34) Lippard, S. J.; Ucko, D. A. *Inorg. Chem.* **1968**, *7*, 1051.

(35) Hammond, B.; Jardine, F. J.; Vohra, A. G. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1017.

(36) Marsich, N.; Camus, A.; Nardin, G. *J. Organomet. Chem.* **1982**, *239*, 429.

(37) Beguin, B.; Denise, B.; Sneeden, R. P. A. *J. Organomet. Chem.* **1981**, *208*, C18.

(38) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A., unpublished results.

(39) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295.

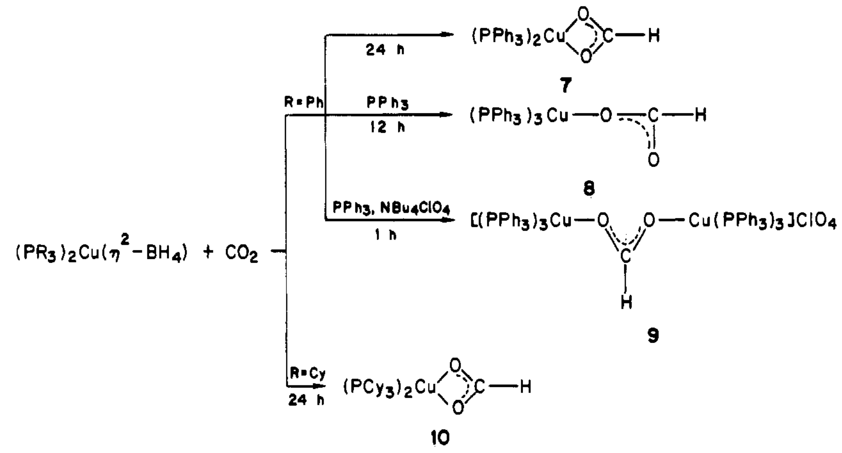
(40) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285.

Table IV. IR and ^{1}H NMR Data for Formate and Thioformate Complexes

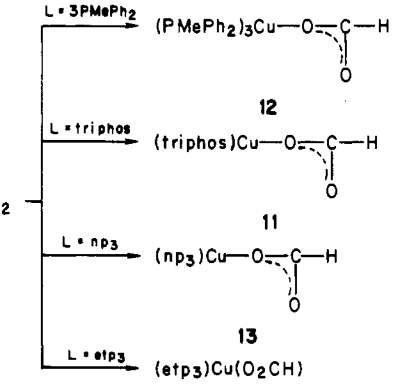
compd	IR, cm^{-1} ν(CO)	ν(CO···Cu)	ν(CS···Cu)	ν(CH)	^{1}H NMR^a δ(CH)
$(PPh_3)_2Cu(O_2CH)$	1585	1350		2810	8.55
$(PPh_3)_3Cu(O_2CH)$	1610	1340		2780 2690	9.00
$[(PPh_3)_3Cu(O_2CH)Cu(PPh_3)_3]ClO_4$	1585	1360		2790 2700	8.55
$(PCy_3)_2Cu(O_2CH)$	1600	1330		2780	8.60
(triphos)$Cu(O_2CH)$	1620	1320		2755 2660	9.01^b
$(PMePh_2)_3Cu(O_2CH)$	1620	1330		2790 2695	8.70
$(np_3)Cu(O_2CH)$	1610	1320		2780	*c*
$(etp_3)Cu(O_2CH)$	1585	1350		*d*	8.54
$(PPh_3)_2Cu(SOCH)$	1632 1580	1340	800	2800 2770	10.12
$(PCy_3)_2Cu(SOCH)$	1630 1580	1350	805	2800 2760	10.76
(triphos)Cu(SOCH)	1625 1570		805	2755 2660	12.44^b
$(np_3)Cu(SOCH)$	1635 1570			2760	

^{a} $CDCl_3$ solutions. ^{b} CD_2Cl_2 solutions. ^{c} Due to low concentration this peak was not observed. ^{d} Not observed.

Scheme I



Scheme II



White crystals of the complex (triphos)$Cu(O_2CH)$ (**11**) are obtained when CO_2 is bubbled for 2 h into a CH_2Cl solution of **2**. The IR absorptions in the $\nu(CO_2)$ region are indicative of the presence of an unidentate formate ligand. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at -60 °C does not show any resonance attributable to free phosphinic groups, thus providing evidence that all of the three arms of triphos are linked to the copper atom.

A single-crystal X-ray diffraction study has completely clarified the bonding mode of the formate ion in **11**. The molecular structure consists of mononuclear (triphos)$Cu(O_2CH)$ molecules. A perspective view of the complex molecule is shown in Figure 1. Selected bond distances and angles are reported in Table V.

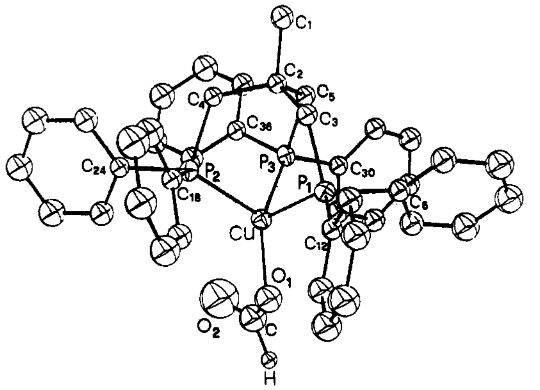


Figure 1. Perspective view of the complex molecule (triphos)$Cu(O_2CH)$; ORTEP drawing with 30% probability ellipsoids. For the sake of clarity the hydrogen atom was assigned an arbitrary temperature factor.

The metal atom is coordinated by the three phosphorus atoms of the triphos ligand and by an oxygen atom of the formate group, which acts as monodentate ligand. The coordination geometry is distorted tetrahedral, the oxygen atom being displaced from the pseudo-3-fold axis defined by the P_3Cu fragment, as evidenced by the values of the P-Cu-O angles, ranging from 111.2 (3) to 130.0 (2)°.

The Cu-P bond distances (average 2.283 (4) Å) as well as the P-Cu-P angles (average 94.8 (7)°) are in good agreement with

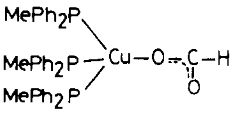
Table V. Selected Bond Distances (Å) and Angles (deg)

	Distances		
Cu-P1	2.287 (2)	P3-C5	1.831 (9)
Cu-P2	2.274 (3)	P3-C30	1.827 (6)
Cu-P3	2.288 (3)	P3-C36	1.831 (7)
Cu-O1	2.015 (9)	C-O1	1.158 (14)
P1-C3	1.867 (9)	C-O2	1.196 (17)
P1-C6	1.824 (7)	C-H	1.17 (17)
P1-C12	1.823 (7)	C1-C2	1.561 (13)
P2-C4	1.861 (8)	C2-C3	1.547 (12)
P2-C18	1.836 (7)	C2-C4	1.558 (11)
P2-C24	1.833 (7)	C2-C5	1.546 (11)
	Angles		
P1-Cu-P2	93.6 (1)	Cu-P2-C24	126.9 (2)
P1-Cu-P3	95.0 (1)	C4-P2-C18	103.9 (3)
P2-Cu-P3	96.0 (1)	C4-P2-C24	102.2 (3)
P1-Cu-O1	111.2 (3)	C18-P2-C24	101.0 (3)
P2-Cu-O1	130.0 (2)	Cu-P3-C5	104.3 (3)
P3-Cu-O1	122.6 (2)	Cu-P3-C30	122.6 (2)
Cu-P1-C3	106.0 (3)	Cu-P3-C36	118.9 (2)
Cu-P1-C6	117.7 (2)	C5-P3-C30	105.0 (3)
Cu-P1-C12	121.3 (2)	C5-P3-C36	103.2 (4)
C3-P1-C6	104.9 (4)	C30-P3-C36	100.6 (3)
C3-P1-C12	105.1 (3)	Cu-O1-C	125.6 (11)
C6-P1-C12	100.3 (3)	O1-C-O2	123.5 (17)
Cu-P2-C4	103.1 (3)	O1-C-H	110 (8)
Cu-P2-C18	116.9 (2)	O2-C-H	126 (8)

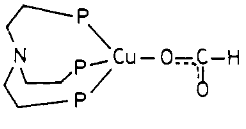
the corresponding values reported for the (triphos)Cu(BH_4) complex.[6] In the latter compound the triphos ligand and the unidentate borohydride ligand determine a very similar coordination geometry around the copper atom.

Concerning the formate ligand, the values of the C–O1 and C–O2 bond distances, 1.158 (14) and 1.196 (17) Å, respectively, seem in contrast with the conventional formulation of Cu—O1—C and C═O2. As it has been already observed for acetate, and thioformate ligands displaying a similar nonconventional binding configuration,[41,42] the geometry of these groups in low-valent metal complexes is mainly determined by the electron density at the metal center. When the carboxylate group is bound to an acceptor of very low electrophilicity such as copper(I) its internal electron distribution can remain the same as in the free anion, with the consequence of two C–O bonds approximately equal in length. Within this context it is noteworthy that the value of the Cu–O bond distance of 2.015 (9) Å is somewhat larger than the sum of covalent radii (1.90 Å). On the basis of these considerations, it is possible to rationalize some features of the infrared spectra of the present formate and dithioformate complexes (vide infra). The vibrations of the complexed formate group are surprisingly similar to those of the free ion (1567, 1366 cm^{-1})[35] (a similar comparison cannot be done for the thioformate group since the free ligand is unstable). Furthermore, the bonding mode of formate and thioformate ligands, i.e. unidentate or bidentate, poorly affects the infrared absorptions of these groups. Both of these facts are indicative of the negligible alteration of the internal electronic distribution of HCO_2^- and $HCOS^-$ upon coordination to a metal of very low electrophilicity such as copper(I).

Unidentate formates are also formed when solutions of the η^1-BH_4 complexes **3** and **4** are allowed to react with CO_2. These compounds have formulas $(PMePh_2)_3Cu(O_2CH)$ (**12**) and $(np_3)Cu(O_2CH)$ (**13**), respectively. Their structures have been assigned on the basis of spectroscopic data, which agree very well with those of the triphos derivative. The np_3 complex shows the typical band at 2830 cm^{-1} indicative of the uncoordination of the nitrogen atom.

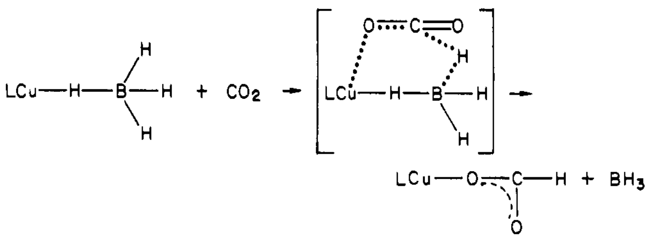


12

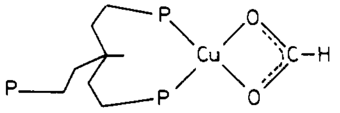


13

Scheme III



On the contrary, the formate ion is very probably bidentate in the complex $(etp_3)Cu(O_2CH)$ (**14**) obtained by reaction of **5** with CO_2. The low $\nu(CO_2)_{asym}$ vibration (1585 cm^{-1}) and the reported scarce propensity of the etp_3 ligand to share its three phosphorus atoms with one metal atom[33] suggest the bidentate structure. Although poorly resolved, the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at –60 °C, showing two resonances at 14.20 and –22 ppm, provides further support of structural formulation **14**.



14

A perusal of the synthetic procedures reported in the Experimental Section for all of these formate complexes reveals that there is a connection between the bonding mode of the BH_4^- ligand and the rate of the reaction with CO_2. In particular, the reactions of η^1-BH_4 complexes are remarkably faster than those of η^2 complexes. Accordingly, the rate of the reaction with CO_2 could be adopted as a diagnostic tool for discriminating between unidentate and bidentate attachments of tetrahydroborate. In this light, the suggested bidentate bonding mode of BH_4^- in **5** and **6** receives further support.

When once realized that the mode of attachment of the tetrahydroborate to the metal influences the reactivity of BH_4^- complexes toward CO_2, it is possible to rationalize the reaction leading to **8**. Since the addition of PPh_3 to a solution of **1** has also the effect of increasing the rate of reduction of CO_2, the formation of the tris(phosphine) formate complex **8** very likely involves the preliminary formation in solution of $(PPh_3)_3Cu(\eta^1$-$BH_4)$ rather than the attack by PPh_3 on preformed $(PPh_3)_2Cu(\eta^2$-$O_2CH)$. The formation of the μ-O_2CH dimer **9** may be, then, rationalized in terms of nucleophilic attack by the uncoordinated oxygen of **8** on a $(PPh_3)_3Cu$ moiety.

The present connection between the bonding mode of BH_4^- and the reactivity of its copper(I) complexes as reducing agents toward CO_2 may help to elucidate an interesting class of reactions, namely the reduction of acid chlorides to aldehydes by **1** (eq 4).[15,16,43,44]

$$(PPh_3)_2Cu(BH_4) + RCOCl \rightarrow \tfrac{1}{2}[(PPh_3)_2CuCl]_2 + RCHO + BH_3 \quad (4)$$

It has been reported that the rate of reduction of the acid chloride with **1** is increased in the presence of an excess of PPh_3; in several cases, the yield of aldehyde is also increased.[43,44] The role of PPh_3 has been explained on the basis of a possible nucleophilic catalysis involving an intermediate acyl phosphonium salt.

In light of our results, we suggest that PPh_3 may be also important for the formation of a more reactive η^1-BH_4 intermediate (eq 5).

$$(PPh_3)_2Cu(\eta^2\text{-}BH_4) + PPh_3 \rightarrow [(PPh_3)_3Cu(\eta^1\text{-}BH_4)] + RCOCl \rightarrow (PPh_3)_3CuCl + RCHO + BH_3 \quad (5)$$

---

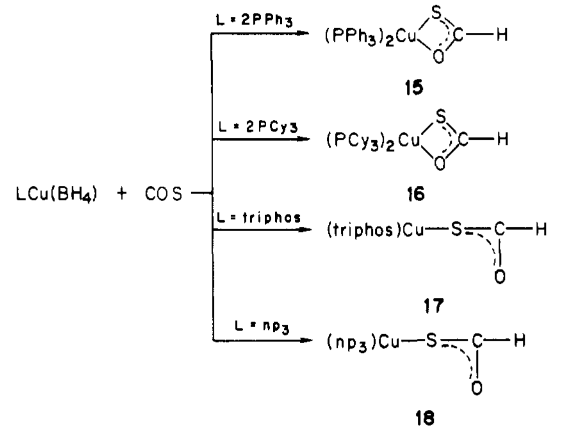
(41) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudoroski, R. *Inorg. Chem.* **1982**, *21*, 1656. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 1287.

(42) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

(43) Fleet, G. W. J.; Harding, P. J. C. *Tetrahedron Lett.* **1979**, 975.

(44) Sorrell, T. N.; Pearlman, P. S. *J. Org. Chem.* **1980**, *45*, 3449.

Scheme IV



In the absence of kinetic measurements as well as of intermediates, it should be hazardous to propose a detailed mechanism for the reduction of CO_2 to HCO_2^- by copper(I) tetrahydroborates. However, by analogy with the proposed mechanisms for some organic reductive reactions of $LiAlH_4$ and alkali-metal tetrahydroborates,[45] a reasonable pathway could be that shown in Scheme III. Such a mechanism may well account for the lower reactivity of η^2-BH_4 complexes, the cleavage of two Cu–H bonds being required to liberate borane.

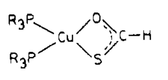
Methanol has not been detected as a byproduct of the reaction of copper(I) tetrahydroborate complexes with CO_2. This in contrast to $LiBH_4$, which has been found to reduce CO_2 to formate (yield 73%) and methanol (yield 13%) in ether solution according to eq 6 and 7.[46]

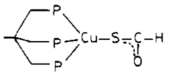
$$LiBH_4 + CO_2 \rightarrow LiO_2CH + {}^1/{}_2B_2H_6 \qquad (6)$$

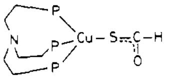
$$3LiBH_4 + 4CO_2 \rightarrow LiB(OCH_3)_4 + 2LiBO_2 \qquad (7)$$

(b) With COS. Scheme IV illustrates the reactions performed and the results obtained; IR and ^{1}H NMR data are listed in Table IV.

Thioformate complexes are obtained when COS is reacted with the present copper(I) tetrahydroborates. In particular, the η^2-S,O-bonded thioformates $(PPh_3)_2Cu(\eta^2$-SOCH) (**15**) and $(PCy_3)_2Cu(\eta^2$-SOCH) (**16**) are obtained from the η^2-BH_4 complexes **1** and **6**, whereas the η^1-S-bonded thioformates (triphos)Cu(η^1-SOCH) (**17**) and $(np_3)Cu(\eta^1$-SOCH) (**18**) are obtained from the η^1-BH_4 complexes **2** and **4**.


15, R = Ph
16, R = Cy

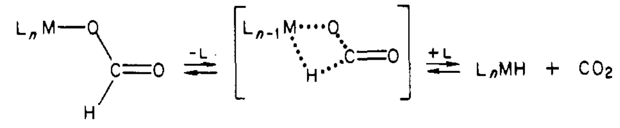

17


18

The processes involving COS as a substrate to give thioformate derivatives take place much more readily than those involving CO_2. This observation is probably due to copper–sulfur bond formation, a process more favorable than copper–oxygen bond formation.

The infrared spectra of **15**–**18** in the ν(CO) region exhibit two strong absorptions at 1625–1635 and 1570–1580 cm^{-1}. Compounds **15** and **16** show additional bands at 1340 and 1350 cm^{-1}, respectively, which can be assigned to ν(CO···Cu). Comparisons with the ν(CO) vibrations of the η^1-SC(O)H complex anion $[Cr(CO)_5SC(O)H]^-$, for which an X-ray structure is available,[42] are precluded since the infrared data for the thioformate group are not reported by the authors. A thioformate ligand has been also suggested to exist in the complex $[Ru(OSCH)(PMe_2Ph)_4]PF_6$ obtained by reaction of $[RuH(PMe_2Ph)_5]PF_6$ with COS.[47] Infrared absorptions at 1480 and 1380 cm^{-1} have been assigned to a bidentate thioformate group. The presence of two bands of almost comparable intensity in the ν(CO) region in compounds **15**–**18** is not yet explained. However, it is noteworthy that metal complexes with the dithiocarbonate ligand S_2CO^{2-} show two infrared bands in the ν(CO) region at ca. 1700 and 1600 cm^{-1}.[48] The higher energy band has been attributed to Fermi resonance between the carbon–oxygen stretching mode and the first overtone band of the carbon–sulfur asymmetric stretching mode.[49]

Scheme V



It is interesting to note that the positions of the two ν(CO) frequencies in **15**–**18** do not vary significantly with the bonding mode of the $HCOS^-$ group. This can likely be due to the above-cited low electrophilicity of copper(I).[41]

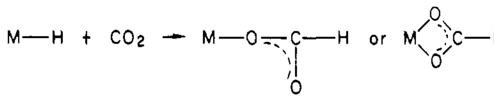
The np_3 complex presents the typical infrared band at 2830 cm^{-1}.

The ^{1}H and ^{13}C NMR data are in excellent agreement with those reported for the complex anion $[Cr(CO)_5SC(O)H]^-$.[42] The resonance of the thioformate proton, in fact, is shifted downfield with respect to that of the formate proton. Indeed, a progressive downfield shift of the HCX_2^- proton absorption is found in order of substituents HCO_2 [δ(CH) $\sim$ 8.5] < HCOS [δ(CH) $\sim$ 10.5] < HCS_2 [δ(CH) $\sim$ 11.26].

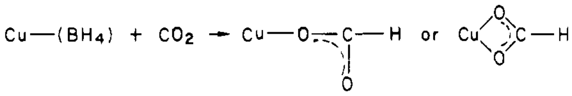
The ^{13}C NMR spectrum in CD_2Cl_2 of **17** shows a signal at 201.3 ppm due to the thiocarboxylic group, which agrees well with the value of 198.8 ppm found for the same carbon in $[Cr(CO)_5SC(O)H]^-$.

Interesting structural information is obtained by analyzing the values of the ^{13}C resonances of the carboxylic and thiocarboxylic groups in **11** and **17**, respectively. Since $\delta(C{=}S) = 1.45[\delta(C{=}O)] - 46.5$ ppm,[50] $\delta(C{=}O)$ observed in **11** at 168.4 ppm gives a calculated $\delta(C{=}S)$ value of 197.7 ppm, in fairly nice agreement with its observed value of 201.3 ppm. This suggests a partial double bond between carbon and sulfur in the thioformate group even though the ligand is linked to the metal through sulfur. Indeed, the C–S bond length in $[Cr(CO)_5SC(O)H]^-$ is quite close to that reported for partial C–S double-bond character.[42]

Reactivity of Copper Formates. Considerable interest is being shown in the chemistry of metal formates.[40,51] These compounds could be, in fact, key intermediates in a number of catalytic reactions of carbon oxides (Fisher–Tropsch synthesis,[52] water gas shift reaction).[53] In particular, the reduction of CO_2 to HCO_2^- by transition-metal hydrides can be considered as a crucial step in the homogeneous catalytic reduction of CO_2 (eq 8).[54] It therefore seemed that it would be interesting to investigate the


(8)

$$M{-}H + CO_2 \rightarrow M{-}O{-}C(=O){-}H \text{ or } M(\eta^2\text{-}O_2CH) \qquad (8)$$


(9)

$$Cu{-}(BH_4) + CO_2 \rightarrow Cu{-}O{-}C(=O){-}H \text{ or } Cu(\eta^2\text{-}O_2CH) \qquad (9)$$

---

(45) Hajos, A. "Komplexe Hydride"; VEB Deutscher Verlag der Wissenschaften: Berlin, 1968.

(46) Bun, J. G., Jr.; Brown, W. G.; Heller, H. E. *J. Am. Chem. Soc.* **1950**, *72*, 2560.

(47) Ashworth, T. V.; Nolte, M.; Singleton, E. *J. Organomet. Chem.* **1976**, *121*, C57.

(48) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4166 and references therein.

(49) Burke, M. J.; Fackler, J. P. *Inorg. Chem.* **1972**, *11*, 2744.

(50) Kalinowski, H. O.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 90.

(51) Slegeir, A. R.; Sapienza, R. S.; Rayford, R.; Lam L. *Organometallics* **1982**, *1*, 1728 and references therein.

(52) Storch, H.; Golmubic, N.; Anderson, R. B. "The Fischer-Tropsch and Related Syntheses"; Wiley: New York, 1951.

(53) Rubene, N. A.; Davydon, A. A.; Krauslov, A. V.; Ursheva, N. V.; Smolyaninov, S. I. *Kinet. Katal.* **1976**, *17*, 465.

reactivity of the present copper formates (eq 9). Some reactions of the η^2-formate complex **7** have been already reported by Sneeden et al.[37] The formate group in this compound is neither reduced nor transformed into organic formate by H_2, protic solvents, or hydride donor or acceptors. Instead, these reagents cause extensive decomposition to CO_2 and Cu(0). The treatment of **7** with $NaBH_4$ regenerates **1**. Indeed, we have observed that the metathetical reaction with BH_4^- is a common feature of all of the formates **7–14**.

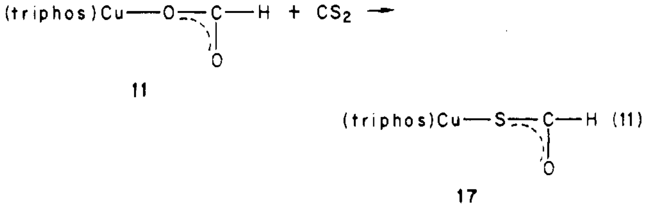
The reactivity of the η^1-formate complex **11** has been particularly investigated. This compound does not undergo decarboxylation when a stream of argon or nitrogen is passed through its solutions at room temperature. Decarboxylation of metal formates, which is regarded as a common feature of this type of compound,[42,55] has been suggested to proceed via β elimination of the hydrogen atom to the metal center, followed by formation of a metal hydride species (Scheme V). This mechanism requires a vacant coordination site on the metal. The relative 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 **11**.

Another interesting feature of formate complexes is to exchange CO_2 with CS_2 or COS, as recently reported by Darensbourg and Rokicki (eq 10).[42] With the aim of obtaining similar exchange reactions, we have reacted **11** with CS_2 and COS.

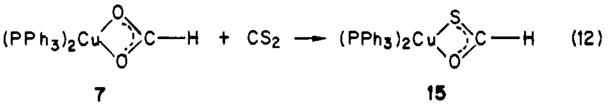
$$M(CO)_5O_2CH^- + CSX \rightarrow M(CO)_5SCXH^- + CO_2 \qquad (10)$$

$$M = Cr, Mo, W; X = O, S$$

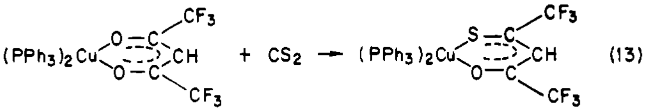
A methylene chloride solution of **11** reacts with CS_2 to give crystals, which by comparison with an authentic specimen, have been identified as the thioformate complex **17** (eq 11). Current studies are under way to rationalize the mechanism of reaction 11. This could be important to gain insight into the reactivity of the formate ligand. The exchange of one oxygen atom of the HCO_2^- group for sulfur seems to be, in fact, characteristic of copper formates, and in general of copper(I) complexes with oxygen ligands, as evidenced by the following experimental results. The η^2-formate complex **7** reacts with CS_2 to give the corresponding thioformate derivative **15** (eq 12). Analogously, the (trifluoromethyl)acetylacetonate complex $(PPh_3)_2Cu(acacCF_3)$ has been found to react with CS_2 undergoing the exchange of one oxygen of the ligand (eq 13).[23]



11 **17** (11)

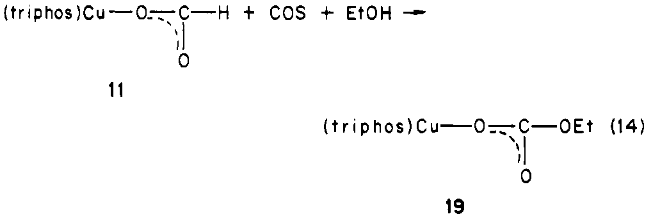


7 **15** (12)



(13)

Another interesting conversion of the formate group is observed when **11** is reacted with COS in the presence of ethanol (eq 14).



11 **19** (14)

White crystals of the complex (triphos)Cu(O_2COEt) (**19**) are obtained. The presence of the ethyl carbonate ligand has been unambiguously ascertained by means of analytical and spectroscopic data. The IR spectrum shows the disappearance of the C–H stretching frequency, whereas two new strong bands appear at 1640 and 1085 cm^{-1}, which are assigned to $\nu(CO_2)_{asym}$ and ν(CO) of an alkyl carbonate group, respectively.[54] $\nu(CO_2)_{sym}$, a vibration usually at ca. 1300 cm^{-1}, is not observed. The positions of these absorptions as well as their intensities are strongly indicative of the presence of an unidentate carbonate monoalkyl ligand. Almost identical bands (1640, 1090 cm^{-1}) in fact have been found for the η^1-O_2COMe complex $PtH(O_2COMe)(PCy_3)_2$.[56] The ^1H NMR spectrum in $CDCl_3$ contains a quartet at δ 4.21 and a triplet at δ 1.28 (intensity ratio 2:3), which are typical of the ethoxy protons of carbonic esters.[57]

At present, the role played by COS in reaction 14 remains to be elucidated. Indeed, COS seems to be of critical importance in the process under way since **11** has been found to be stable in CH_2Cl_2/ethanol solutions at least for reasonable times (10 h). Nevertheless, the transformation of formate to ethyl carbonate is interesting (note that the overall process assisted by copper(I) species is $CO_2 \rightarrow HCO_2^- \rightarrow EtOCO_2^-$) and deserves a more detailed mechanistic investigation. This could help to rationalize the formation of alkyl carbonate complexes from metal hydrides, CO_2, and alcohols, for which either attack of alcohol on the formate group of CO_2 insertion into M–OR bonds have been hypothesized.[57]

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**, 82678-89-5; **3**, 63371-86-8; **4**, 94500-07-9; **5**, 94518-23-7; **6**, 88637-65-4; **7**, 32335-51-6; **8**, 32335-50-5; **9**, 88622-18-8; **10**, 88637-68-7; **11**, 86322-43-2; **12**, 94518-24-8; **13**, 94518-25-9; **14**, 94518-26-0; **15**, 88622-19-9; **16**, 88622-20-2; **17**, 86322-45-4; **18**, 94518-27-1; **19**, 94518-28-2; (np_3)CuCl, 94518-29-3; (etp_3)CuCl, 94518-30-6; $(PCy_3)_2Cu(ClO_4)$, 31168-45-3; $(PPh_3)_2Cu(ClO_4)$, 34010-81-6; CO_2, 124-38-9; CS_2, 75-15-0; ethanol, 64-17-5; formate, 71-47-6.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

---

[54] Sneeden, R. P. A. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 225.

[55] Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1982**, *234*, C5.

[56] Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35.

[57] Yamamoto, T.; Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 680. Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 204.