process may thus occur as indicated in eq 6 and 7.

$$\underset{\text{LS}}{\text{FeL}^6(\text{An})_2{}^{2+}} \rightleftarrows \underset{\text{HS}}{\text{FeL}^6(\text{An})_2{}^{2+}} \quad K,\ \text{rapid} \tag{6}$$

$$\underset{\text{HS}}{\text{FeL}^6(\text{An})_2{}^{2+}} + 2\text{MeIm} \rightarrow \underset{\text{LS}}{\text{FeL}^6(\text{MeIm})_2{}^{2+}} \quad \text{rapid} \tag{7}$$

Examination of the temperature dependence of the NMR spectrum of an acetone solution of $FeL^6(An)_2^{2+}$ should allow detection of the high-spin component. At (presumably) higher temperatures, the concentration of high-spin component should increase, giving rise to substantial isotropic shifts in the resonances of the ligand protons. We currently lack facilities for performing these experiments, so the explanation must remain speculative at the present time.

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Registry No. $[FeL^5(An)_2](PF_6)_2$, 57139-48-7; $FeL^6(An)_2(BF_4)_2$, 62637-62-1; An, 75-05-8; MeIm, 616-47-7.

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Phosphite Complexes of Copper(I) Containing Chloride, Tetrahydroborate, and (Ethoxycarbonyl)trihydroborate

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Complexes have been studied of the type $[(RO)_3P]_yCuX$, where $y = 2$ or 3, $R = CH_3$ or C_2H_5, and $X = Cl$, BH_4, or $H_3BCOOC_2H_5$. Characterization has been by elemental analysis, IR, molecular weight, and NMR data. The hydroborate complexes show bidentate coordination to the copper. In contrast to the case of phosphine and phosphite BH_4^- complexes, both IR and NMR spectra show that at room temperature reaction of excess phosphite ligand with $[(RO)_3P]_2CuH_3BCOOC_2H_5$, $R = CH_3$ or C_2H_5, results first in a tris(phosphite) complex and ultimately in complete replacement of the (ethoxycarbonyl)trihydroborate.

Introduction

It is well-known that the tetrahydroborate ion (BH_4^-) and its derivatives have been studied for a variety of reasons in organic and inorganic chemistry. Organic chemistry has provided a wealth of information regarding their use as selective reducing agents in both organic and organometallic synthesis.[1] Inorganic chemists have studied the covalent coordination complexes of BH_4^- and have found them to be of theoretical and practical interest. Theoretical interest arises from the variety of M–H–B bonding modes and the fluxional behavior exhibited by the hydroborate moiety,[2,3] whereas practical interest results from selective reducing behavior, which has recently been reported.[4]

Extensive studies on arylphosphine–copper complexes of tetrahydroborate and substituted tetrahydroborates have shown that arylphosphine and substituted arylphosphine ligands influence the mode and strength of attachment of the hydroborate to the metal.[2,3] In contrast, alkylphosphines and arylarsines and -stibines fail to stabilize copper with respect to reduction by tetrahydroborate.[5] The effect of phosphites as ligands in tetrahydroborate complexes is relatively unexplored. A few phosphite complexes of first-row transition metals with halides or perchlorate have been reported, e.g. $[(RO)_3P{\cdot}CuX]_3$ and $[(RO)_3P{\cdot}AgX]_3$[6-9] and $[(RO)_3P(RO)_3P{\cdot}CuX]_3$, $[(PhO)_3P]_2{\cdot}CuX$, and $[(EtO)_3P]_4CuClO_4$.[8-10] In addition, monomeric tetrakis(trialkyl and triaryl phosphite)nickel(0) complexes have been prepared by Tolman.[11] However, the only report of monomeric (phosphite)copper complexes containing hydroborate and comparable to those obtained with phosphine ligands has been from our work.[3a,d] We wish to report the preparation and characterization of new phosphite complexes of copper(I): $[(RO)_3P]_3CuCl$ ($R = C_2H_5$, CH_3) and $[(RO)_3P]_2CuBH_3R'$ ($R = C_2H_5$, CH_3; $R' = H$, $COOC_2H_5$). The relative ease of replacement of the hydroborate by the phosphite at room temperature is a characteristic that differentiates these complexes from their phosphine counterparts, and this will also be discussed.

Experimental Section

General Techniques. Infrared spectra were taken on a Beckman IR-20A spectrometer. ^1H NMR spectra were obtained with a Varian XL-100, A-60, and EM-360 or JEOL 90Q spectrometer. Chemical shifts were based upon internal references (Me_4Si, (^1H), $BF_3{\cdot}OEt_2$ (^{11}B), 85% H_3PO_4 (^{31}P), or known solvent). Vapor pressure osmometry was performed on a Mechrolab, Inc., Model 301A osmometer at 37 °C with chloroform solvent. Conductivity of the complex solutions was measured with a General Radio Co. Type 1608-A impedance bridge and a submersible conductivity cell with cylindrical plates and a cell constant of 1.1626 cm^{-1}. Spectral grade acetonitrile and nitromethane were used for the conductance measurements. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Percent yields in the synthesis of the complexes were comparable to triphenylphosphine complexes[3b] and ranged from 70 to 80%.

Materials. Diborane,[12] borane carbonyl,[3b,13] and potassium (ethoxycarbonyl)trihydroborate[14] were prepared by previously published

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Table I. Results of Osmometric Studies on Copper(I) Complexes

complex	c, g/mL	M_{calcd} = [Cu], M	M_{obsd}, M	$N^{a,d}$	fw	mol wt (obsd)
$[(EtO)_3P]_3CuCl$	0.0299	0.0500	0.0585	1.17	597.4	511
$[(MeO)_3P]_3CuCl$	0.0235	0.0500	0.060	1.20	471.2	392
$(MePh_2P)_3CuCl^b$		0.0505	0.0565	1.12		
$(Ph_3P)_3CuCl^b$		0.0500	0.0925	1.85		
$[(EtO)_3P]_2CuBH_4$	0.0254	0.0618	0.0632	1.02	410.7	402
$[(MeO)_3P]_2CuBH_4$	0.0163	0.0500	0.0510	1.02	326.5	320
$[(EtO)_3P]_2CuH_3BCO_2C_2H_5$	0.0251	0.0520	0.0580	1.11	482.8	433
$[(MeO)_3P]_2CuH_3BCO_2CH_2H_5$	0.0163	0.0409	0.0420	1.03	398.6	388
$(MePh_2P)_3CuBH_4{}^c$	0.0199	0.0288	0.0538	1.87	678.9	370
$(MePh_2P)_3CuH_3BCO_2C_2H_5{}^c$	0.0221	0.0295	0.3090	1.33	751.1	566

[a] $M_{obsd}/M_{calcd} = M_{obsd}/[Cu]$. [b] Reference 15; included for comparison. [c] Reference 3c; included for comparison. [d] Values for $K_d = [L_2CuCl][L]/[L_3CuCl]$: $[(EtO)_3P]_3CuCl$, 0.0017; $[(MeO)_3P]_3CuCl$, 0.0025; $(MePh_2P)_3CuCl$, 0.0008; $(Ph_3P)_3CuCl$, 0.24. This is assuming that no association takes place to give species such as $(L_2CuX)_2$ or $L_3Cu_2X_2$ as described by Lippard.[15] We believe this to be the case on the basis of evidence obtained in our laboratory. These data will be presented in a later paper.

Table II. Infrared Absorptions Assigned to BH_n Moieties of (Tetrahydroborato)- and [(Ethoxycarbonyl)trihydroborato]copper–Phosphite Complexes

compd	abs ranges, cm^{-1} [c]					
	2500–2200	2200–1900	1700–1500	1500–1300	1300–1000	1000...
$[(EtO)_3P]_2CuBH_4$ (neat)	2380 s 2350 sh (BH_t str) 2260 w[a]	1990 s 1930 s (BH_b str)			1135 s (BH_2 def)	
$[(MeO)_3P]_2CuBH_4{}^{2d}$ (neat)	2380 s 2345 sh (BH_t str) 2260 w[a]	1995 s 1935 s (BH_b str)		1390 m (bridge str)	1135 s (BH_2 def)	
$[(MeO)_3P]_2CuBD_4$		1805, 1740 s (ν_H/ν_D = 1.34; BD_t str)	1685 m (ν_H/ν_D = 1.33)	BD_b str obscured	*b*	BD_2 def obscured
$[(MeO)_3P]_3CuBD_4$ (neat; large excess of ligand)			1750 s, br (ν_H/ν_D = 1.34; BD_t str)	1520 m, br (ν_H/ν_D = 1.35; BD_b str)	*b*	BD_3 def obscured
$[(MeO)_3P]_2CuH_3BCOOC_2H_5$ (KBr; neat liquid)	2360 s, br (BH_t str)	2050 s (BH_b str)	1665 s (C=O)		1150–1000 (obscured)	700–800 (obscured)
$[(EtO)_3P]_2CuH_3BCOOC_2H_5$ (neat liquid)	2400 s, br (BH_t str)	2055 s (BH_b str)	1660 s (C=O str)		1125 m–s?	700–800 (obscured)
$[(MeO)_3P]_4CuH_3BCOOC_2H_5$ (liquid)	2270 s, br		1645 s (C=O str)			
$[(EtO)_3P]_4CuH_3BCOOC_2H_5$ (liquid)	2260 s, br		1650 s (C=O str)		1240 m	
$[(PhO)_3P]_2CuH_3BCOOC_2H_5$ ($CHCl_3$ solution)	2410 s	2020 s	1655 s (C=O str)			
included for comparison						
$(MePh_2P)_3CuBH_4{}^{3c}$	2335 sh 2315 s	2045 s			1060 s	
$(Ph_3P)_2CuBH_4{}^{3c}$	2395 s 2340 sh	1985 s 1935 s	1370 m		1135 s	
$(Ph_3P)_2CuH_3BCO_2C_2H_5{}^{3b}$	2380 s	2030 s	1655 s (C=O str)		1145 s	
$(MePh_2P)_3CuH_3BCO_2C_2H_5{}^{3c}$	2330 s	2090 s	1660 s (C=O str)		1130–1140 s	

[a] Weak peaks at this frequency have been assigned to an overtone of a BH_2 deformation. [b] Region obscured by neutral ligand peaks. [c] vs = very strong, s = strong, m = medium, w = weak, str = stretch, def = deformation, H_t = terminal H, H_b = bridging H.

procedures. All other chemicals were obtained commercially and used without further purification. Molecular weight data on complexes are presented in Table I.

Preparation of Complexes. Chlorotris(triethyl phosphite)copper(I). CuCl (2.46 g, 24.8 mmol) and $(C_2H_5O)_3P$ (6.4 mL, 37.2 mmol) were combined in 100 mL of chloroform, and the mixture was stirred for 5 h. The solution was filtered, and the chloroform was removed by flash evaporation. The complex and excess ligand were dissolved in 30 mL of commercial absolute ethyl ether and cooled to −78 °C overnight to give crystals. These were filtered off and washed with 15 mL of cold (−78 °C) absolute ether, and any excess solvent was removed under high vacuum. The product was a white, needlelike crystalline material: yield 65%; mp 57–58 °C. Anal. Calcd for $C_{18}H_{45}O_9P_3CuCl$: C, 36.14; H, 7.53; Cu, 10.63; Cl, 5.93. Found: C, 36.31; H, 7.32; Cu, 10.84; Cl, 5.84. Equivalent conductance (Λ_e) in nitromethane (0.000 95 g/mL): 40.7 Ω^{-1} cm^2 $equiv^{-1}$. NMR ($CDCl_3$): ^1H $\delta(CH_3)$ 1.28 (t, J = 7.1 Hz), $\delta(CH_2)$ 4.1 (complex multiplet); ^{31}P δ +121.4 (s, br).

Chlorotris(trimethyl phosphite)copper(I). CuCl (2.48 g, 25.1 mmol) and $(CH_3O)_3P$ (4 mL, 33.6 mmol) were combined in 100 mL of chloroform, and the mixture was stirred for 3 days. The solution was filtered and the volume reduced to 10 mL. Hexane (100 mL) was added, and the solution was cooled to −78 °C. The hexane solution was decanted from the clear oil, and the remaining hexane and excess phosphite ligand were removed under high vacuum at 70 °C. The product was a clear, only slightly viscous liquid, yield 40%. Anal. Calcd for $C_9H_{27}O_9P_3CuCl$: C, 22.92; H, 5.73; Cu, 13.48. Found: C, 22.70; H, 5.63; Cu, 13.65. Equivalent conductance (Λ_e) in nitromethane (0.001 05 g/mL): 30.0 Ω^{-1} cm^2 $equiv^{-1}$. NMR ($CDCl_3$): ^1H $\delta(CH_3)$ 3.71 (d, J_{HP} = 10 Hz); ^{31}P δ + 125.5 (s, br).

(Tetrahydroborato)bis(triethyl phosphite)copper(I) and (Tetrahydroborato)bis(trimethyl phosphite)copper(I). The literature procedure reported[3a] for the methyl phosphite complex was used for the ethyl phosphite complex except that no methylene dichloride was used in the purification process. Repeated washing of the product with

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(14) Malone, L. J. *Inorg. Chem.* **1968**, *7*, 1039.

pentane should be avoided as very poor analyses were obtained, and molecular weight data on samples treated in this way were inconsistent with data obtained on the pure product. Anal. Calcd for $C_{12}H_{34}P_2O_6BCu$: C, 35.09; H, 8.34; B, 2.63; Cu, 15.47. Found: C, 35.89; H, 8.59; B, 2.85; Cu, 15.04. NMR (2:1 CH_2CHCl/CH_2CHF): ^1H $\delta(BH)$ +0.65 (q, $J_{BH} = 82$ Hz), $\delta(CH_3)$ 1.26 (t, $J_{HCH} = 7$ Hz), $\delta(CH_2)$ 4.02 (quintet, $J_{HH} \sim J_{HP} = 8$ Hz); ^{11}B δ 29.1 (quintet, $J_{BH} = 80$ Hz). Analysis for $(CH_3O)_3P$ complexes: see ref 13. NMR (2:1 CH_2CHCl/CH_2CHF): ^1H $\delta(BH)$ +0.69 (q, $J_{BH} = 82$ Hz), $\delta(CH_3)$ 3.64 (d, $J_{HP} = 11$ Hz); ^{11}B δ −30.4 (quintet, $J_{BH} = 80$ Hz). IR data: see Table II.

[(Ethoxycarbonyl)trihydroborato]bis(triethyl phosphite)copper(I) and [(Ethoxycarbonyl)trihydroborato]bis(trimethyl phosphite)copper(I). The complexes were made by the same procedure as the tetrahydroborate complexes except that the procedure of removal of solvent and addition of pentane followed by filtering off the solid had to be repeated several times. Moreover, the oil was washed several times with 10–15 mL of pentane. Anal. Calcd for $C_{15}H_{38}P_2O_3BCu$: C, 37.32; H, 7.93; B, 2.25; Cu, 13.16. Found: C, 38.16; H, 8.14; B, 2.40; Cu, 12.70. Molecular weight data: see Table I. NMR ($CDCl_3$): ^1H $\delta(BH)$ estimated +0.88 (only one peak not obscured); ethoxycarbonyl $\delta(CH_3)$ 1.08 (t, $J = 7.0$ Hz), $\delta(CH_2)$ 3.78 (q, overlaps with CH_2 on phosphite, $J = 7.0$ Hz); ethyl phosphite $\delta(CH_3)$ 1.26 (t, $J = 7.0$ Hz), $\delta(CH_2)$ 4.04 (complex multiplet, overlaps with CH_2 on ethoxycarbonyl, $J_{HH} \sim J_{HP} = 7$ Hz). Anal. Calcd for $C_9H_{26}P_2BCu$: C, 27.12; H, 6.58; B, 2.71; Cu, 15.94. Found: C, 27.14; H, 6.72; B, 2.86; Cu, 15.60. NMR ($CDCl_3$): ^1H $\delta(BH)$ 1.02 ($J_{BH} = 73$ Hz, estd); ethoxycarbonyl $\delta(CH_2)$ 3.83 (q, $J = 7$ Hz), $\delta(CH_3)$ 1.12 (t, $J = 7$ Hz); methyl phosphite $\delta(CH_3)$ 3.52 (d, $J = 11$ Hz). IR data: see Table II.

Results

A. Chloride Complexes. Treatment of copper(I) chloride with triethyl phosphite in chloroform yields, upon purification, a new crystalline complex designated as $[(EtO)_3P]_3CuCl$ from analysis and molecular weight data in chloroform. The degree of dissociation is indicated by $N = 1.17$ (Table I). This value is consistent with osmometric results of analogous (phosphine)copper(I) halide complexes for which steric interactions are not dominant.[15] The value also suggests, by comparison to the halide complexes, that the only species of importance in solution at the designated concentrations is the one having a ligand:copper ratio of 3:1.[15] The conductivity of $[(C_2H_5O)_3P]_3CuCl$ in nitromethane is in the range expected for a weak electrolyte. Both conductivity and osmometric data exclude an ionic tetrakis(phosphite) formulation.

Chlorotris(trimethyl phosphite)copper(I) was obtained similarly to the triethyl phosphite complex as a slightly viscous liquid at ambient temperatures. Conductivity in nitromethane is very similar to the tris(triethyl phosphite)copper complex, indicating that it is also a weak electrolyte. Molecular weight data indicate practically the same degree of ligand dissociation in chloroform as the triethyl phosphite complex (Table I). This result, reasonable because of the very similar steric and electronic properties shared by the two ligands, is consistent with a tris(trimethyl phosphite) structure.

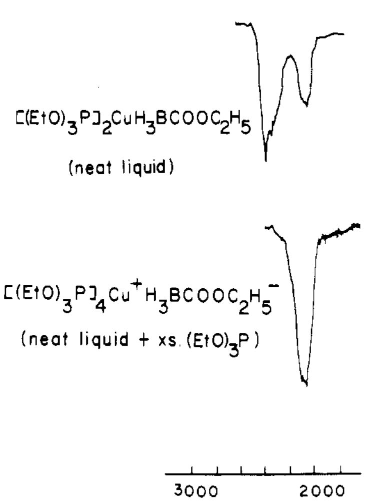

Figure 1. Infrared spectrum of (a) $[(EtO)_3P]_2CuH_3BCOOC_2H_5$ (neat liquid) and (b) $[(EtO)_3P]_4Cu^+H_3BCOOC_2H_5^-$ (neat liquid + excess $(EtO)_3P$) in the B–H absorption region.

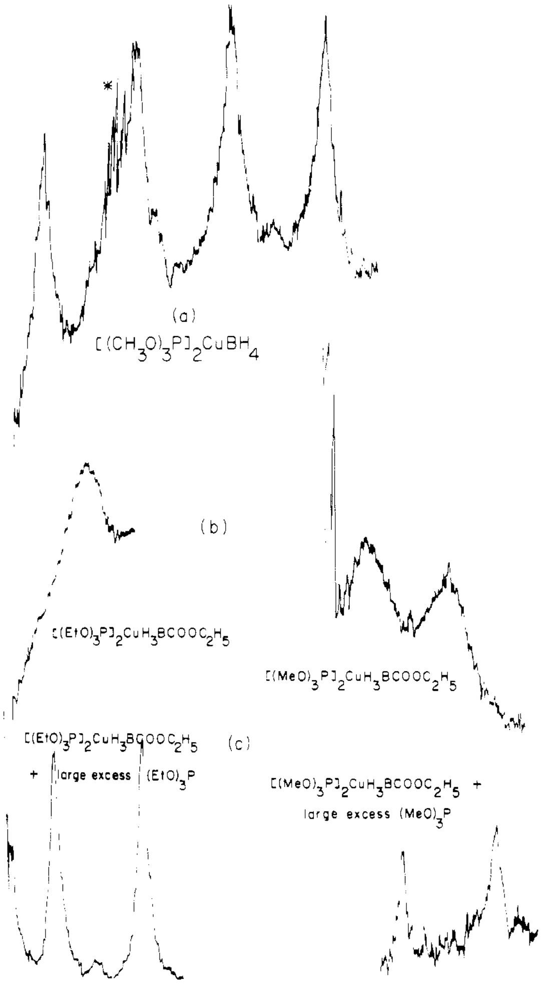

Figure 2. Ambient-temperature 100.1-MHz ^1H NMR spectra in $DCCl_3$ of borane hydrogens: (a) $[(MeO)_3P]_2CuBH_4$ (* = impurity in solvent); (b) $[(EtO)_3P]_2CuH_3BCOOC_2H_5$ in CH_2Cl_2 and $[(MeO)_3P]_2CuH_3BCOOC_2H_5$ in $CDCl_3$ + benzene; (c) complex + excess ligand ($(EtO)_3P$ complex in CH_2Cl_2; $(MeO)_3P$ complex in 2:1 CH_2CHCl/CH_2CHF).

The molecular weight data for the complex obtained by reacting an excess of triphenyl phosphite (35.5 mmol) with copper(I) chloride (20 mmol) correspond closely with the value obtained by Arbuzov and Zorastrova[9] for the complex that they characterized as $[(PhO)_3P]_2CuCl$. Further characterization was not attempted when we discovered that the complex was not useful in preparing stable tetrahydroborate– and (ethoxycarbonyl)trihydroborate–copper(I) or –silver(I) complexes. Although the stable complex $[(PhO)_3P]_2CuB_3H_8$ has been reported,[16] treatment of solutions of the above chloro complex with the tetrahydroborate anion results in immediate reduction of the copper as evidenced by the appearance of a dark precipitate. Treatment of the chloro complex with (ethoxycarbonyl)trihydroborate results in what is assumed to be a bis(phosphite) complex since the infrared spectrum of the neat crude oily product (Table II) shows B–H and carbonyl stretching frequencies very close to those for [(ethoxycarbonyl)trihydroborato]bis(triphenylphosphine)copper(I).

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[15] Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 753.

[16] Bushweller, C. H.; Beall, H.; Bewkett, W. J. *Inorg. Chem.* **1976**, *15*, 1739.

Further characterization of the former complex was not pursued since attempts to purify it or isolate it in a crystalline state led to decomposition, as evidenced by gas evolution and precipitation of a dark material.

B. Hydroborate Complexes. Reaction of $[(RO)_3P]_3CuCl$ (R = Et, Me) with sodium tetrahydroborate, according to the method of Cariati and Naldini,[17] resulted in the formation of clear viscous liquids of composition $[(RO)_3P]_2CuBH_4$. Extreme care must be taken in the purification process since what appear to be ligand-deficient species (based on analyses and molecular weight data) are obtained with excessive washings with pentane.

Both complexes are monomeric in $CHCl_3$ solution (Table I), and elemental analysis and the IR spectra are consistent with the presence of bidentate tetrahydroborate. Pertinent features supporting bidentate coordination rather than monodentate coordination are the position and number of peaks in the B–H terminal and bridging stretching region, which are analogous to those found in the well-known monomeric $(Ph_3P)_2CuBH_4$[3b,5,17,18] (Table II). The latter compound contains a bidentate hydroborate and displays B–H stretching modes different from those of $(MePh_2P)_3CuBH_4$,[3c,e] which contain a monodentate hydroborate. Also, notably absent in the phosphite complexes is a strong absorption conspicuous in singly bridged hydroborates found around 1060 cm^{-1} and assignable to a BH_3 deformation.[2,3c,e] In addition, $[(MeO)_3P]_2CuBD_4$ was prepared and its IR spectrum (Table II) supports the assignment of both the B–H$_t$ and B–H$_b$ absorptions with the B–D$_t$ doublet resolved in the deuterated complex. $\nu_H{:}\nu_D = 1.34$ and 1.32 for terminal and bridging absorptions, respectively. Both values are comparable to values obtained in other deuteration studies.[3c] It should be noted that, unless *extreme* precautions are taken to remove any excess ligand from the hydroborate complexes, the B–H stretching bands are broad and the separation between them is less, depending upon the degree of purity, than that for the pure bidentate complex. Such results, analogous to those for the tris(methyldiphenylphosphine) complexes,[3c,e] indicate the presence of a sizable proportion of the tris(phosphite) complex with single hydrogen bridging.

The ^1H NMR spectrum of the borane hydrogens of the tetrahydroborate complexes at ambient temperature consists of four distinct, although somewhat broad, peaks of equal intensity (Figure 2a). The ^1H NMR spectra for different BH_4 phosphine and phosphite complexes show the quartet in various stages of collapse to a singlet. Each spectrum is dependent upon the complex and the temperature.[3] The chemical shifts for the borane hydrogens in the ethyl phosphite and methyl phosphite complexes are almost the same under identical conditions. This is consistent with the very similar steric and electronic properties of the two ligands.

Reaction of (ethoxycarbonyl)trihydroborate ($H_3BCO_2C_2H_5^-$) with the complex $[(RO)_3P]_3CuCl$ (R = Me, Et) also results in coordination through the B–H hydrogens. In each instance, purification of the product yields a clear viscous oil. The analytical data correspond well with the formulations $[(EtO)_3P]_2CuH_3BCOOC_2H_5$ and $[(MeO)_3P]_2CuH_3BCOOC_2H_5$. The infrared spectra of the pure complexes (Table II, Figure 1a) show B–H stretching frequencies that are comparable to those of the corresponding bidentate triphenylphosphine complex (Table II). A bidentate hydroborate formulation is thus supported. In the case of the methyl phosphite the BH$_t$ stretching frequency is somewhat lower than expected, possibly due to some tris complex as a contaminant. A lower value for the B–H$_t$ frequency is expected in a singly bridged hydroborate (see Table II for example), and frequency assignments for both doubly and singly bridged hydroborates have been made in mixtures of the two complexes.[2c,e] Addition at room temperature of an additional 1 equiv of triethyl phosphite (based on the amount of copper present) to the presumed mixture of the triethyl phosphite complexes results in a mixture in which the B–H terminal and bridging stretching modes in the infrared spectrum are substantially weakened. This is accompanied by the appearance of the strong B–H stretching band of the free or noncoordinated (ethoxycarbonyl)trihydroborate anion. Addition of still more phosphite results in complete disappearance of B–H terminal and bridging bands of the coordinated borane and the appearance of a very strong B–H stretching band (Figure 1b) of the noncoordinated (ethoxycarbonyl)trihydroborate anion as is represented by the reaction

$$[(EtO)_3P]_2CuH_3BCO_2C_2H_5 + \text{excess } (EtO)_3P \rightarrow [(EtO)_3P]_4Cu^+H_3BCOOC_2H_5^-$$

This replacement occurs at room temperature, and this is in direct contrast to the BH_4^- complexes, which require excess ligand and a lowering of the temperature for the same phenomenon to be observed.[3d]

The ^1H NMR data also support the formation of the ionic complex upon addition of excess phosphite. The pure (ethoxycarbonyl)trihydroborate complexes $[(EtO)_3P]_2CuH_3BCOOC_2H_5$ and $[(MeO)_3P]_2CuH_3BCOOC_2H_5$ have borane proton resonances assigned as broadened quartets at ambient temperature ($W_{1/2} \sim 30$ Hz). So that these borane proton resonances could be observed, high field power and signal amplitude had to be used. As a result, only the farthest upfield resonance for the triethyl phosphite complex and the two upfield resonances of the trimethyl phosphite complex are discernible (Figure 2b). The remaining members of the quartet are masked by the very intense absorptions assigned to the CH_3 protons of the ethyl group on the (ethoxycarbonyl)trihydroborate and, in the case of the ethyl phosphite complex, by the CH_3 proton absorptions of $(EtO)_3P$. (At the high field power and signal amplitude required, Me_4Si interferes substantially with the borane resonances. To circumvent this, we first obtained the chemical shift of the methylene protons in a sample containing Me_4Si. The borane proton chemical shift could then be calculated in the Me_4Si free sample by comparison of the borane resonances to the methylene proton absorption.) Addition of excess phosphite results in the predominance of the ionic complex $[(RO)_3P]_4Cu^+H_3BCOOC_2H_5^-$ ($R = C_2H_5, CH_3$) even at ambient temperature since the somewhat broadened members of quartet, which are visible, become quite sharp ($W_{1/2}$ comparable to $KH_3BCOOC_2H_5$) and shift upfield considerably toward the value for the noncomplexed anion (0.72 ppm) (Figure 2c). The shift and sharpening are sufficiently great in the ethyl phosphite complex that two members of the quartet are observed.

Discussion

A. Chloride Complexes. The dissociation of the halide complexes warrants more extensive discussion. Among the tris(phosphine)[15] and -(phosphite)copper(I) chloride complexes, an apparent anomaly exists in comparing the experimental results with those expected on the basis of steric properties and the results reported on work with nickel(0) complexes.[19] The dissociation constants for the NiL_4 complexes follow the trend expected on the basis of steric properties as represented in terms of Tolman's cone angles (shown in parentheses):[19] PPh_3 (145°) > $PMePh_2$ (136°) > $P(OEt)_3$ (109°). (The cone angle of a ligand has been defined as being the angle needed to

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encompass complete rotation of the ligand, the angle apex being the metal atom.)[19] The dissociation constant for L = $P(OMe)_3$ was not reported. For the chlorocuprous complexes (L_3CuCl) the values for the extent of dissociation, N, (Table I) reflect the following trend (cone angles are given for each ligand[19]): PPh_3 (145°) > $P(OMe)_3$ (107°) > $P(OEt)_3$ (109°) > $PMePh_2$ (136°). These trends clearly indicate that, contrary to results obtained with Ni(0) complexes, steric considerations are not always the dominant factor when considering dissociation of copper(I) chloro complexes. Steric interaction is reasonably the dominant factor in the ligand dissociation when triphenylphosphine is the ligand. This assumption is supported by the studies of Lippard and Mayerle[15] which showed that ligand dissociation was greatly affected for the complexes L_3CuX upon going from triphenylphosphine to methyldiphenylphosphine but not significantly changed by substitution of dimethylphenylphosphine for methyldiphenylphosphine. Since methyldiphenylphosphine is significantly bulkier (θ = 136°) than triethyl phosphite (θ = 109°), an explanation other than one using steric interaction is needed to rationalize the larger dissociation for the ethyl phosphite compared to the methyldiphenylphosphine complexes.

The difference between the dissociation of methyldiphenylphosphine and the phosphite complexes could be considered in terms of the π-acid character of the ligands. A ligand that is a stronger π acid would exhibit less dissociation. Although studies have suggested that the coordination of copper to phosphine and chlorides involves little or no metal to ligand π back-bonding,[20,21] the possibility of importance for back-bonding in Cu(I) complexes of phosphites has been suggested.[16,22] Since phosphites are generally considered to be better π acids than phosphines, the predicted trend in dissociation of the complexes would be methyldiphenylphosphine > phosphites. Our results for methyldiphenylphosphine and phosphites show that differing π acidity cannot be the dominant factor in the observed dissociation pattern since the observed trend in dissociation of the complexes is phosphites > methyldiphenylphosphine.

The difference between the dissociation of the methyldiphenylphosphine and that of the phosphite complexes could also be considered by using Weaver and Parry's argument, which describes the basicity of amines and phosphines in terms of a polarization model.[23] According to this model, the base strength of the phosphine would be a function of the ability of electrons to move into position for bonding under the influence of the polarizing field of the metal. Under conditions of a weak field, as one would expect with copper, the original distribution of the electrons in the molecular ground state may be the important factor in determining basicity. The greater dissociation of the phosphite complexes relative to that of the methyldiphenylphosphine complex is then attributable to the stronger electron-withdrawing properties of the alkoxy groups. This results in a tightening of the charge cloud about the phosphorus, rendering it less susceptible to polarization by the metal than the phosphorus in the phosphine. Thus, a weaker interaction of the copper(I) with the phosphite occurs compared to that with the phosphine, and the measured dissociation is larger for the phosphite.

The instability of the [(ethoxycarbonyl)trihydroborato]bis(triphenyl phosphite) complex compared to the analogous triphenylphosphine complexes may then not be too surprising in view of the much lower basicity of triphenyl phosphite compared to that of triphenylphosphine. The triphenyl phosphite ligands should leave the copper with a higher net positive charge than would the phosphine ligands, and therefore the copper should be more vulnerable to electron transfer from a reducing agent.

B. Hydroborate Complexes. Studies on the IR and ^1H NMR spectra of (phosphine)- and (phosphite)copper hydroborate complexes have shown that in the presence of excess ligand various dissociative equilibria are present in solution depending on the temperature.[3d] The fact that the (ethoxycarbonyl)trihydroborate is completely replaceable by a phosphite even at ambient temperature contrasts sharply with the behavior of either the phosphine or phosphite tetrahydroborate complexes. The latter complexes require a reduction in temperature to allow the substitution to manifest itself and be observed in the NMR and IR spectra.[3d] This difference in behavior indicates that the trialkyl phosphites are relatively good ligands toward copper(I) compared to the (ethoxycarbonyl)trihydroborate anion since they can fairly readily break the M–H–B attachment when this weaker trihydroborate ligand is present. The ability to control the form of the complex at ambient temperature simply by changing the phosphite ligand concentration suggests an interesting possibility. If the complexed hydroborate were to display differing reducing capability toward organic functional groups depending upon its mode of complexation, different selective reducing agents might be generated in situ simply by varying the amount of phosphite ligand present.

Another difference between phosphine and phosphite complexes is found in the ^1H NMR. The chemical shifts for the ethyl group on the (ethoxycarbonyl)trihydroborate differ markedly for the two types of complexes. In phosphite complexes they are very similar to those of the free (ethoxycarbonyl)trihydroborate ligand. In the phosphine bidentate complexes the chemical shift of the methylene group moved toward higher field, i.e., in a directly opposite to what would be expected on the basis of direct electron-withdrawing inductive effects normally accompanying coordination to a positive center.[3b] The explanation offered was that the methylene protons occupy the highly shielding portion of the induced magnetic field about the carbonyl. Phosphite ligands, on the other hand, provide considerably less crowding than phosphine ligand according to Tolman's cone angles[19] and models. With the barrier to rotation out of the highly shielding position for the ethyl group having been lowered, it is possible that the anisotropic effect is fortuitiously attenuated to the point where it nearly balances the expected classical inductive effect.

In summary, we have shown that, although the phosphite complexes are somewhat similar to their phosphine analogues, important differences do exist. An additional significant property of the phosphite complexes is their extreme solubility in chlorinated hydrocarbons, and even slight solubility in normal alkanes. This solubility makes them a more facile species to study and increases their potential for use in synthetic applications.

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Registry No. $[(EtO)_3P]_3CuCl$, 84040-95-9; $[(MeO)_3P]_3CuCl$, 67784-65-0; $[(EtO)_3P]_2CuBH_4$, 76986-52-2; $[(MeO)_3P]_2CuBH_4$, 67784-66-1; $[(EtO)_3P]_2CuH_3BCO_2C_2H_5$, 76986-69-1; $[(MeO)_3P]_2CuH_3BCO_2C_2H_5$, 76986-71-5; $[(EtO)_3P]_4CuH_3BCOOC_2H_5$, 84049-89-8; $[(PhO)_3P]_2CuH_3BCOOC_2H_5$, 84040-96-0.

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