Volume 18
Number 3
March 1979

Inorganic Chemistry

Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

Transition-Metal–(Carboxylato)trihydroborate Complexes: Copper and Silver Triphenylphosphine Complexes of $H_3BCO_2R^-$ ($R = H, CH_3, C_2H_5$)

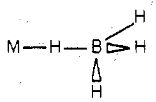
JERRY C. BOMMER and KAREN W. MORSE*[1]

Received July 25, 1978

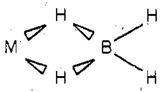
The synthesis and characterization of some copper and silver triphenylphosphine complexes of the (carboxylato)trihydroborate derivatives $H_3BCO_2R^-$ ($R = H, CH_3, C_2H_5$) are reported. Isolated are stable crystalline complexes of composition $(Ph_3P)_nMH_3BCO_2R$ ($n = 2, 3$; $M = Cu$, $R = C_2H_5, CH_3, H$; $M = Ag$, $R = C_2H_5, H$). Results of spectral (IR, NMR), osmometric, and conductivity studies are discussed in terms of the molecular structures of the complexes; possible factors influencing the bidentate or monodentate mode of coordination by the anion are set forth.

Introduction

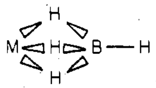
Covalent metal tetrahydroborate complexes have in recent years been a topic of considerable interest. A recent review has explored and analyzed developments in the field of covalent transition-metal, lanthanide, and actinide BH_4^- complexes.[2] This review quite clearly illustrates that of the four different bonding modes (I–IV) that tetrahydroborate can conceivably adopt, the only one which has not received extensive attention is the monodentate mode (I). Holah reports the possibility of monodentate BH_4^- complexes for a cobalt complex and a series of ruthenium complexes.[3] A monodentate BH_4^- copper complex has been reported.[4,5]



I



II



III

$M^+BH_4^-$

IV

M–H–B bonding modes analogous to I–IV might be expected for other B–H-containing anions. Examples when M is Cu are $[Cu(B_3H_8)(PPh_3)_2]$,[6] $[(Cu(PPh_3)_2)_2(B_{10}H_{10})]\cdot CCl_3H$,[7] and $[(Ph_3P)_2Cu(NCBH_3)]_2$.[8] Several other stable anions do exist which possess the ability to show M–H–B bonding modes; they are (carboxylato)trihydroborate ($H_3BCO_2^{2-}$),[9,10] (alkoxycarbonyl)trihydroborates ($H_3BCO_2R^-$, $R = CH_3, C_2H_5$) and (carboxy)trihydroborate ($H_3BCO_2H^-$).[10,12] Cu(I) and Ag(I) complexes of (ethoxycarbonyl)trihydroborate have been reported in a previous communication.[13]

Since the factors which influence the formation and relative stabilities of the bonding modes of I vs. II remained somewhat nebulous, we have undertaken a study which might help clarify such factors. Our investigation resulted in characterization of singly and doubly bridged complexes of BH_4^- and $H_3BCO_2R^-$,[4,5,14] demonstration of the conditions necessary for coordination, factors which influence the mode of coordination, and a comparative investigation of the bonding in the new and established modes of coordination. These points as related to Cu(I) and Ag(I) complexes of (carboxylato)trihydroborate derivatives $H_3BCO_2R^-$ ($R = H, CH_3, C_2H_5$) will be dealt with in this paper; others will be presented in subsequent papers.

Experimental Section

General Techniques. Infrared spectra were taken on a Beckman IR-20A. ^1H NMR spectra were obtained from a Varian XL-100, A-60, or EM-360 spectrometer. Chemical shifts were based upon internal references (Me_4Si or known solvent). Low-temperature spectra were obtained from the XL-100 system with the temperature control device calibrated using an independent thermocouple placed within the NMR tube situated in the probe. 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. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., unless indicated otherwise.

Materials. Diborane,[15] borane carbonyl,[10] potassium (carboxylato)trihydroborate,[10] and potassium (ethoxycarbonyl)trihydroborate[11] were prepared by previously published procedures. It was necessary to purify the technical grade CO (Matheson) by passing it through two successive 1-m bubblers containing 6 N aqueous sodium hydroxide and one 30-cm bubbler held at −78 °C containing a saturated ethanolic sodium hydroxide solution. The borane carbonyl used for the potassium (carboxylato)trihydroborate was separated from the CO and B_2H_6 before being bubbled through dry (200 proof is sufficient) ethanolic KOH.

Cuprous chloride (92.9%, Baker), potassium borohydride (Alfa Inorganics), silver nitrate (Baker, reagent grade), triphenylphosphine (Baker), potassium hydroxide (Mallinckrodt, analytical grade), and the solvents chloroform (Baker), ethanol (Commercial Solvent Corp., 200 proof), ethyl ether (absolute, Mallinckrodt), hydrofluoric acid (Baker, analytical grade), methylene dichloride (Baker, reagent grade), and pentane (Baker, practical grade) were obtained commercially. The chemicals were used without further purification unless otherwise specified.

Tetrahydroborate Complexes. $(Ph_3P)_2CuBH_4$ and $(Ph_3P)_2AgBH_4$ were prepared using the same procedure as Cariati and Naldini.[16]

(Ethoxycarbonyl)trihydroborate Complexes ($H_3BCO_2C_2H_5^-$ Complexes). The (ethoxycarbonyl)trihydroborate complexes were prepared using a similar procedure as that used for the tetrahydroborates, but with some modification in the purification of the products.[6,16-18] $(Ph_3P)_3CuCl$,[17] 0.886 g (1 mmol), was dissolved in

25 mL of chloroform and combined with 0.139 g (1.1 mmol) of $KH_3BCOOC_2H_5$ dissolved in 10 mL of absolute ethanol. ($AgNO_3$, 0.17 g (1 mmol), and 2.5 g (9.5 mmol) of Ph_3P in 20 mL of chloroform were stirred until all of the $AgNO_3$ had dissolved. Added to this was 0.139 g (1.1 mmol) of $KH_3BCOOC_2H_5$ dissolved in 10 mL of absolute methanol.) The mixture was stirred for 0.5 h in a tightly stoppered container with no sign of gas evolution or color change to indicate reduction. The mixture was then filtered, and the solvent was removed from the filtrate by flash evaporation to dryness. Five milliliters of methylene dichloride was added to the resulting solid, and the extracted mixture was filtered again. Dry hexane (10–15 mL) was added slowly to the filtrate while agitating until precipitation was initiated as indicated by sustained cloudiness. The solution was then cooled without further hexane addition to approximately −20 °C for several hours during which time white crystals separated from the solution. These crystals were isolated by filtration, washed with hexane (pentane for the silver complex), and dried under high vacuum at ambient temperature. Additional complex could be recovered by addition of hexane to the mother liquor (until precipitation was again initiated) and cooling to −20 °C. Analytically and spectrally satisfactory results were obtained without further recrystallization. It was necessary to use methylene dichloride with an alkane as the precipitating agent rather than ethanol which was used for the tetrahydroborate complex because the (ethoxycarbonyl)trihydroborate complexes appear to be significantly more soluble in a chloroform–ethanol mixture than the corresponding tetrahydroborates.[14] The latter solvent system leads to unsatisfactory yields. The substitution of hexane for ethanol as the precipitating agent necessitates the extraction with methylene dichloride to separate the complex from the salts (KCl and $K_2H_3BCO_2$) which otherwise would be coprecipitated along with the complex by hexane. The use of reasonably dry solvents is important since hydrolysis of the (ethoxycarbonyl)trihydroborate complexes in solution seems to occur at a fairly substantial rate at ambient temperatures (see the section dealing with the reactivity of (ethoxycarbonyl)trihydroborate complexes). This could lead to the (carboxy)trihydroborate complex as an impurity if care is not taken to exclude the majority of the water or if the purification procedures are not carried out expeditiously. Any recrystallization of the silver salt must be carried out in the presence of at least a threefold excess of phosphine to prevent reduction of the silver. Satisfactory analytical results were obtained without further purification of the product.

$C_{39}H_{38}P_2O_2BCu$: mp 112–114 °C; percent yield, 83.5% based on $(Ph_3P)_3CuCl$; equivalent conductance (Λ_e) in nitromethane (0.001 M) 19.2 Ω^{-1} cm^2 equiv^{-1}. Anal. Calcd: C, 69.42; H, 5.64; P, 9.18. Found: C, 69.66; H, 5.66; P, 9.16 (Chemalytics, Inc., Tempe, Ariz.).

$C_{57}H_{53}P_3O_2BAg$: mp 115–117 °C dec; percent yield, 90% based on $AgNO_3$. Anal. Calcd: C, 69.74; H, 5.44; P, 9.47; Ag, 10.98. Found: C, 69.75, H, 5.54; P, 9.66; Ag, 9.95.

[Trihydro(methoxycarbonyl)borato]bis(triphenylphosphine)copper(I) ($H_3BCO_2CH_3^-$ Complexes). $(Ph_3P)_3CuCl$, 0.866 g (1 mmol), and Ph_3P, 0.20 g (0.8 mmol), were combined in 10 mL of methylene dichloride; 0.15 g (1.1 mmol) of $K_2H_3BCO_2$ dissolved in 5 mL of absolute methanol was added and the solution was stirred for 24 h in a tightly stoppered container. The mixture was filtered and flash evaporated to dryness. Four milliliters of methylene dichloride was added, and the insoluble material was filtered out. Ten to fifteen milliliters of dry pentane was added slowly, and the solution was cooled to approximately −20 °C for several hours. The white crystalline material was filtered, washed with pentane, and dried under high vacuum. Methylene dichloride was used for this reaction instead of chloroform in order to avoid possible competition for the ester site by the ethanol used to stabilize the chloroform. Qualitative chloride tests of the complex proved to be negative, and analytical results were satisfactory without further recrystallization of the complex. $C_{38}H_{36}P_2O_2BCu$: mp 113–115 °C dec.; percent yield, 83.3% based on $(Ph_3P)_3CuCl$. Anal. Calcd: C, 69.04; H, 5.49; B, 1.64; Cu, 9.67. Found: C, 68.87, H, 5.46; B, 1.58; Cu, 9.36.

[(Carboxy)trihydroborato]bis(triphenylphosphine)copper(I), [$(Ph_3P)_2CuH_3BCOOH$]. The complex resulted from the reaction of $Ca(H_3BCOOH)_2$ with $(Ph_3P)_4CuF$. A modification of the procedure reported by Cotton and Goodgame[19] was utilized for the preparation of $(Ph_3P)_4CuF$. $CuF_2{\cdot}2H_2O$, 0.688 g (5 mmol) (prepared from $Cu(OH)_2$ and HF), and Ph_3P, 6.56 g (25 mmol), were dissolved in 30 mL of absolute methanol. When the solution had changed from blue to colorless, it was flash evaporated to dryness, and the solid was redissolved in 30 mL of choroform. Ninety milliliters of hexane was added to precipitate the product, which was filtered, washed with hexane, and dried under high vacuum. The white crystals have an equivalent conductance of 79 Ω^{-1} for a 10^{-3} M solution in nitromethane, which is in the range of 1 to 1 electrolytes with tetrakis(triphenylphosphine)copper(I) cations.[19] The conductivity along with its solubility in methanol indicates the product is likely the tetrakis complex $(Ph_3P)_4CuF$ in which the fluoride does not occupy a coordination site on the copper.

A solution of CaH_3BCO_2 was prepared by passing an aqueous solution of $K_2H_3BCO_2$ through a 20-cm Dowex 50 cation-exchange column charged with Ca^{2+}. The resulting solution was titrated with very dilute HF until the pH reached 9.0.[10] The volume of the solution was then reduced to several milliliters by flash evaporation and could be diluted to the appropriate volume for the next step of the reaction.

Three milliequivalents of $Ca(H_3BCOOH)_2$ in 8 mL of H_2O was stirred with 0.226 g (0.2 mmol) of $(Ph_3P)_4CuF$ and 0.052 g (0.2 mmol) of Ph_3P in 2 mL of methylene dichloride for 15 min. The CH_2Cl_2 solution was then separated and discarded. This step removes the (ethoxycarbonyl)trihydroborate impurity which is present in small amounts in potassium (carboxylato)trihydroborate and apparently complexes to the Cu preferentially. $(Ph_3P)_4CuF$, 2.26 g (2 mmol), and Ph_3P, 9.524 g (2 mmol), in 10 mL of methylene dichloride were added to the aqueous (carboxylato)trihydroborate solution, and the solution was stirred vigorously for 0.5 h. The methylene dichloride solution was decanted and filtered and then flash evaporated to a 5 mL volume. Hexane (10–15 mL) was then added to the point of incipient precipitation. The solution was cooled to −20 °C for several hours during which time crystallization took place. The very small, slightly yellowed crystals were isolated by filtration, washed with hexane, and dried under high vacuum. $C_{37}H_{34}P_2O_2BCu$: mp 133–135 °C dec; percent yield, 80% based on $(Ph_3P)_4CuF$; equivalent conductance (Λ_e) in nitromethane (0.001 M) 22.8 Ω^{-1} cm^2 equiv^{-1}. Anal. Calcd: C, 68.69; H, 5.26; B, 1.67; P, 9.58. Found: C, 68.45; H, 5.32; B, 1.52; P, 9.30.

[(Carboxy)trihydroborato]tris(triphenylphosphine)silver(I), [$(Ph_3P)_3CuH_3BCOOH$]. AgF, 0.28 g (2.2 mmol), and Ph_3P, 2.89 (11 mmol), were combined in 33 mL of methylene dichloride, and the solution was stirred for approximately 2 h until all of the AgF had dissolved. A 10 mL aqueous solution of 3 mequiv of $Ca(H_3BCOOH)_2$ was prepared as described in the preparation of [(carboxy)trihydroborato]bis(triphenylphosphine)copper(I). A 3-mL aliquot of the silver fluoride triphenylphosphine complex (0.2 mmol) with 0.262 g (1 mmol) of Ph_3P added was combined with the aqueous (carboxy)trihydroborate solution and stirred for 15 min. The organic phase was discarded to remove the (ethoxycarbonyl)trihydroborate impurities. The volume of the rest of the silver fluoride complex solution was reduced to a 10 mL volume and along with 2.1 g (9 mmol) of Ph_3P was then added to the calcium (carboxy)trihydroborate solution, and the mixture was stirred for 0.5 h. The organic layer was decanted and filtered. Hexane (20–30 mL) was added to the solution until incipient precipitation, and then the solution was cooled to approximately −20 °C for several hours while crystallization continued. The slightly gray solid was filtered, washed with hexane, and dried under high vacuum. More complex could be isolated by adding more hexane to the filtrate until precipitation began and then cooling further. $C_{55}H_{49}P_3O_2BAg$: percent yield, 85% based on $(Ph_3P)_4CuF$. Anal. Calcd: C, 69.27; H, 5.18; B, 1.13; Ag, 11.31. Found: C, 68.93; H, 5.10; B, 1.28; Ag, 10.69.

Results and Discussion

The new copper and silver complexes of the (carboxylato)trihydroborate derivatives involve coordination of the boron moiety to the metal in either a unidentate (I) or bidentate mode (II) where in the (I) and (II) designation one of the terminal hydrogens attached to the boron may be considered to be X, where X = $COOC_2H_5$, $COOCH_3$, COOH, or H. The metal also is surrounded by two or three triphenylphosphine ligands.

Triphenylphosphine and substituted triarylphosphines are the only ligands which had previously been found to stabilize copper and silver tetrahydroborate complexes.[18] The syntheses of the copper and silver (ethoxycarbonyl)trihydroborate complexes were very similar to previous syntheses for tetrahydroborate complexes[6,16,18,19] and generally involved allowing a solution of the potassium (alkoxycarbonyl)trihydroborate

Table I. Infrared Absorptions Resulting from BH_4^- and (Alkoxycarbonyl)- and (Carboxy)trihydroborates (Complexed and Free)

	absorption range (cm^{-1})					
compd	2500–2200	2200–1900	1700–1500	1500–1300	1300–1000	⩽1000
$K^+H_3BCO_2C_2H_5^-$ (KBr)	2320 s BH str		1630 s C=O str	1450 w CH_2 sciss 1380 w CH bend sym	1220 m B–C–O 1190 m BH_3 def 1110 s BH_3 + COC 1030 m asym	905 m B–C str
KBH_4 (KBr)[a]	2260 vs				1110 vs	
$(Ph_3P)_2CuH_3BCO_2C_2H_5$ (KBr)	2410 s BH_t str 2340 w	2030 s BH_b str	1660 s C=O str		1135 s 1055 vs	990 m ?
$(Ph_3P)_2CuBH_4$ (KBr)[a,b]	2395 s 2340 sh BH_t str	1985 s 1935 s BH_b str		1370 m bridge str	1135 s BH_2 def	
$(Ph_3P)_2CuH_3BCO_2C_2H_5$[c]	2380 s BH_t str	2030 s BH_b str	1655 s C=O str		1145 s	
$(Ph_3P)_2CuH_3BCO_2CH_3$	2400 s BH_t str 2340 w	2040 s BH_b str	1665 s C=O str		1135 s 1055 s	990 m 785 w
$(Ph_3P)_2CuH_3BCO_2H$	2410 s BH_t str 2330 w	2030 s BH_b str	1660 s 1635 s C=O str	1300 s, br	1135 s 1055 vs	785 w
$(Ph_3P)_3AgH_3BCO_2C_2H_5$[c]	2350 sh 2290 s BH_t str	2080 s, br BH_b str	1640 vs C=O str		1140–1150 s 1050 vs	820 w
$(Ph_3P)_3AgH_3BCO_2H$[d]	2330 s BH_t str	2100 s BH_b str	1660 s C=O str		1230 m 1130 m s 1050 vs	770 w ?

[a] Included for comparison. [b] Our spectrum; comparative values available in ref 16–18. [c] $CHCl_3$ solution, concentrated. [d] Neat solid.

Table II. Chemical Shift Data[a] for Non-Borane Hydrogens in (Alkoxycarbonyl)- and (Carboxy)trihydroborate Complexes

	H_3BCO_2R absorptions			neutral ligand absorptions		
compd	CH_3	CH_2	OH	Ph	CH_3	CH_2
$K^+H_3BCO_2C_2H_5^-$	1.07	3.79				
$(Ph_3P)_2CuH_3BCO_2C_2H_5$	0.89	3.58		7.3		
$(Ph_3P)_3AgH_3BCO_2C_2H_5$	0.94	3.84		7.3		
$(Ph_3P)_2CuH_3BCO_2CH_3$	3.13			7.3		
$(Ph_3P)_2CuH_3BCO_2H$			3.14	7.3		
$(Ph_3P)_3AgH_3BCO_2H$			3.20	7.3		

[a] Values in ppm downfield from Me_4Si. Complexes dissolved in $CDCl_3$; $K^+H_3BCO_2C_2H_5^-$ dissolved in Me_2SO-d_6.

to react with a solution of the tris(phosphine)copper halide or the bis(phosphine)silver nitrate. Alternative syntheses were utilized in preparing the trihydro(methoxycarbonyl)borato complex and the (carboxy)trihydroborato complex.

Elemental analysis supports bidentate coordination by $H_3BCO_2C_2H_5^-$ in the solid-state copper complexes and unidentate coordination in the solid-state silver complexes (maintaining the four-coordinate pseudotetrahedral configuration expected with Cu(I) and Ag(I) complexes of this type[2,17,20]). The unidentate mode of coordination to silver had not been reported previous to our communication.[12] Infrared absorptions attributable to the complexed anions are tabulated in Table I. Since Nujol mulls or neat samples gave the same results as KBr, usually only the KBr results are reported. Absorptions due to the neutral ligands are not included. Pertinent proton NMR data for the complexes excluding borane hydrogen proton data appear in Table II. Conductivity of copper and silver complexes in acetonitrile is presented in Table III, and Table IV lists molecular weight (osmometric) data for complexes in $CHCl_3$ at 37 °C.

Infrared Spectra. Infrared spectral data also support the assigned formulation for the compounds. As noted in Table I, the strongest B–H stretching absorption for KBH_4 occurs at approximately 2260 cm^{-1} and at approximately 2320 cm^{-1} for potassium (ethoxycarbonyl)trihydroborate. This difference may be attributed to the lower negative charge on the B–H hydrogens of the (ethoxycarbonyl)trihydroborate due to the inductive effects of the ester group. Similar electronic effects are observed in the copper complexes, the terminal B–H stretching frequency for the copper (ethoxycarbonyl)trihydroborate complex being slightly higher than the corresponding tetrahydroborate complex, which is included in the table for comparison. The bridging B–H stretching frequency is also significantly higher in the (ethoxycarbonyl)trihydro-

Table III. Conductivity of Copper and Silver Complexes in Acetonitrile

complex	concn, M × 10^3	(concn)$^{1/2}$	concn of added ligand, M	specific conductance[a]	equivalent conductance[b]
$(Ph_3P)_2CuH_3BCO_2C_2H_5$	3.60	0.060		1.82×10^{-4}	50.6
	1.80	0.0424		1.18×10^{-4}	65.6
	0.720	0.0268		6.22×10^{-5}	86.3
	0.180	0.0134		2.12×10^{-5}	117.7
	1.80	0.0424	3.80×10^{-3}	1.30×10^{-4}	72.2
	0.720	0.0268	3.80×10^{-3}	6.41×10^{-5}	89.0
	0.360	0.01897	3.80×10^{-3}	3.96×10^{-5}	110.0
	0.180	0.0134	3.80×10^{-3}	2.23×10^{-5}	123.9
$(Ph_3P)_3AgH_3BCO_2C_2H_5$	1.80	0.0424		9.13×10^{-5}	50.7
	0.720	0.0268		4.30×10^{-5}	59.8
	0.360	0.01897		2.50×10^{-5}	69.4
	0.180	0.0134		1.30×10^{-5}	72.3
	1.80	0.0424	3.80×10^{-3}	1.19×10^{-4}	75.6
	0.720	0.0268	3.80×10^{-3}	7.26×10^{-5}	100.8
	0.360	0.01897	3.80×10^{-3}	3.94×10^{-5}	109.4
	0.180	0.0134	3.80×10^{-3}	2.23×10^{-5}	123.8
$(Ph_3P)_3AgBH_4$[c]	0.40	0.020	9.5×10^{-3}	8.04×10^{-6}	20.1
	0.20	0.0141	6.7×10^{-3}	5.70×10^{-6}	28.5

[a] In Ω^{-1}. [b] In Ω^{-1} cm^2 equiv^{-1}. [c] Included for comparison.

borate complex than in the tetrahydroborate complex. The separation between terminal and bridging stretching frequencies is somewhat smaller for the copper (ethoxycarbonyl)trihydroborate than for the tetrahydroborate complex which suggests that the covalent interaction of the (ethoxycarbonyl)trihydroborate with the metal may be weaker if the separation is primarily a function of redistribution of electron density. Marks et al.[21] have pointed out that the frequency difference between B–H$_t$ and B–H$_b$ vibrations should decrease as the B–H force constants become more equal and covalent interaction with the metal weakens.

The infrared spectra of $(Ph_3P)_2CuH_3BCO_2CH_3$ and $(Ph_3P)_2CuH_3BCO_2H$ are very similar to that of the corresponding (ethoxycarbonyl)trihydroborate complex. In the trihydro(methoxycarbonyl)borate complex a sharp peak at 2940 cm^{-1} due to the asymmetric CH_3 stretch distinguishes it from the ethyl derivative. In the (carboxy)trihydroborate complex, the absorptions due to the ethyl group are replaced by weak absorptions in the 3300–3400-cm^{-1} region which are assigned to the O–H stretching mode.

Coordination through the carbonyl group of the CO_2R group is also a possibility, but any coordination through this group would have the effect of lowering the C=O stretching frequency[22] which occurs at 1630 cm^{-1} for the free (ethoxycarbonyl)trihydroborate anion. Upon complexation, however, an increase of approximately 30 cm^{-1} is observed for all of the (carboxylato)trihydroborate derivative complexes, indicating no direct interaction between the carbonyl oxygen and the metal. The increase in frequency is a logical consequence of the inductive effect as a result of complexation to a positive center through the hydrogens of the borane group. Other absorptions due to the (ethoxycarbonyl)trihydroborate group have been assigned with some degree of certainty and are consistent with those of the free anion.[13] One of the absorptions assigned to the symmetrical B–H$_b$ stretching modes in tetrahydroborate complexes[16-18,20] is not found in the (alkoxycarbonyl)- and (carboxy)trihydroborate complexes presumably because of the lower symmetry of the latter. Peaks due to bridge stretching modes (1500–1300 cm^{-}1) and B–H deformation (1300–1000 cm^{-1}) for most of the (alkoxycarbonyl)- and (carboxy)trihydroborate complexes could not be assigned because of conflicting phosphine ligand absorptions and other absorptions due to the (alkoxycarbonyl)- and (carboxy)trihydroborate ligands.

The carbonyl absorption for the (carboxy)trihydroborate complex is unique in that in $CHCl_3$ a single absorption occurs at 1655 cm^{-1}, whereas a doublet occurs in the solid state (both KBr and neat samples) with peaks at 1660 and 1635 cm^{-1}. The two peaks are equal in intensity, suggesting that the solid state consists of an equivalent mixture of hydrogen-bonded and non-hydrogen-bonded complex. This could be accomplished through complex pairing with an orientation favoring hydrogen bonding through one OH group or could be due to crystal effects although this seems less likely since other similar phosphine–(carboxy)trihydroborate and (ethoxycarbonyl)trihydroborate complexes do not exhibit this effect.[14]

The infrared spectrum of the silver complex (formulated as tris(phosphine) or monodentate M–H–B) in the solid state strongly supports coordination to the silver through the hydrogens of the borane group as both terminal and bridging B–H stretching modes are observed. The positioning and separation of these two absorptions are somewhat unusual as compared to bidentate tetrahydroborate[16-18,20] and bidentate (carboxylato)trihydroborate derivative complexes. Both peaks are broad with no clear indication of splitting. The terminal stretch at 2340 cm^{-1} is noticeably lower and the bridging stretch higher than for comparable bidentates which may indicate an overall increase in the ionic character of the co-

Table IV. Molecular Weight (Osmometric) Data for Complexes in Chloroform at 37 °C

complex	d, g/mL	[free L added]	M_{calcd}[a]	M_{obsd}[b]	M_{obsd}/M_{calcd}	[L]	$[L_2M\cdot\cdot]$[c]	$[L_3M\cdot\cdot]$[d]	K_{dissoc},[e] %	fw[f]	mol wt[g]	% dissoc of L[h]
$(Ph_3P)_3AgBH_4$[i]	0.0262	0.0735	0.0288	0.0575	2.0	0.1023	0.0288	0	100	909.6	647	100
$(Ph_3P)_3AgH_3BCO_2C_2H_5$	0.0290	0.1144	0.0296	0.0506	1.71	0.1354	0.0210	0.0086	0.33	981.7	573	71
	0.0200	0.1023	0.0204	0.0362	1.77	0.1181	0.0158	0.0046	0.41	981.7	553	77
	0.0283	0.0735	0.0288	0.0511	1.78	0.0958	0.0223	0.0065	0.33	981.7	554	78
	0.050	0	0.0510	0.0958	1.88	0.0448	0.0448	0.0062	0.32	981.7	522	88
$(Ph_3P)_3AgH_3BCO_2H$	0.0275	0.0735	0.0288	0.0465	1.62	0.0912	0.0177	0.0111	0.15	953.6	592	62
	0.0275	0.0570	0.0288	0.0465	1.62	0.0747	0.0177	0.0111	0.12	953.6	580	62
	0.0275	0.040	0.0288	0.0490	1.70	0.0602	0.0202	0.0086	0.14	953.6	561	70
$(Ph_3P)_2CuBH_4$	0.0372		0.0617	0.0643	1.04					602.9	578[j]	
$(Ph_3P)_2CuH_3BCO_2C_2H_5$	0.0416		0.0617	0.0648	1.05					674.7	643	
$(Ph_3P)_2CuH_3BCO_2CH_3$	0.0408		0.0617	0.0651	1.05					661.0	626	
$(Ph_3P)_2CuH_3BCO_2H$	0.0210		0.0325	0.0388	1.19					646.9	541	

[a] The concentration of complex added based upon the theoretical formula weight and the amount added. [b] The observed molarity based upon vapor pressure osmometer readings. [c] $M_{obsd} - M_{calcd}$. [d] $M_{calcd} - [L_2M\cdot\cdot]$. [e] $[L][L_2M\cdot\cdot]/[L_3M\cdot\cdot]$. [f] Formula weight based upon stoichiometry shown. [g] Molecular weight calculated from osmometric data. [h] $([L_2M\cdot\cdot]/M_{calcd}) \times 100$. [i] Actually $(Ph_3P)_2AgBH_4 + Ph_3P$. [j] Done by Cariati and Naldini with the same molecular weight obtained.[16]

ordinate metal–hydrogen bond.[21] This hypothesis is in line with the observed lower solubility in organic solvents of the singly bridging (triphenylphosphine)silver complexes compared with their bidentate copper counterpart. This was particularly observed in preparation of NMR samples since insufficient samples of the silver compounds could be dissolved to obtain ^{11}B NMR easily. One must be careful, however, in unequivocally concluding that the individual metal–hydrogen interaction is any more or less covalent in one mode of coordination than the other based upon these data alone. The position of the bridge B–H stretch is largely dependent upon the electron density in the B–H bonding orbital and upon electron density in any ligand–metal orbital which may have B–H antibonding character. The relative contribution to these two orbitals for the bidentate and unidentate modes is difficult to assess. Although the absorption in the 1120–1130-cm^{-1} region might be construed to be supportive of the singly bridging (ethoxycarbonyl)trihydroborate in analogy to the BH_4^- modes,[20] no assignments were made because of interfering peaks from (ethoxycarbonyl)trihydroborate.

The infrared spectrum of the silver (carboxy)trihydroborate complex is very similar to its silver (ethoxycarbonyl)trihydroborate complex counterpart except for the ethyl absorptions. Unlike the copper (carboxy)trihydroborate complex, the silver complex exhibits a singlet at the expected position in the carbonyl region, indicating hydrogen bonding is not a significant factor in the solid-state structure. This may be due to different steric constraints placed upon the complex by coordination of the third bulky triphenylphosphine group.

NMR Spectra. The proton NMR spectra of the complexes show the presence of the aromatic multiplet ($\delta \sim 7.3$) due to the triphenylphosphine groups. The borane hydrogens are not observed under normal operating conditions. This is a result of partial decoupling of the boron from the hydrogens by quadrupole-induced ^{11}B and ^{10}B relaxation. The fact that "thermal" decoupling[23] between the nuclei occurs at temperatures well above those at which decoupling might be expected for the free anion is further evidence of covalent interaction between the metal and the (alkoxycarbonyl)- and (carboxy)trihydroborate (the nature of the cation in ionic species seems to have little effect upon the "thermal" decoupling of the tetrahydroborate anion[23]). Fluxional behavior renders all of the borane hydrogens equivalent on the NMR time scale and thus only limited structural information may be obtained. Thermal decoupling is observed upon lowering the temperature with the result being the appearance of a single peak. (See Figure 1a for an example). No indication of a slowing of the fluxional B–H hydrogens can be detected with the decrease in temperature. Solubility precluded temperature studies low enough to observe signal collapse.

The ^{11}B NMR spectra of the complexes substantiates the presence of the BH_3 moiety by the presence of a 1:3:3:1 quartet. Different degrees of broadening occur depending on the complex and the effectiveness of thermal decoupling for the various complexes.

The differentiating features of the proton spectra for the complexes are as follows. With (ethoxycarbonyl)trihydroborate complexes the triplet and quartet assignable to the CH_3 and CH_2 groups, respectively, are present in their expected regions. The trihydro(methoxycarbonyl)borate complex displays a sharp singlet assignable to the methyl protons whereas the sharp singlet in the (carboxy)trihydroborate complexes is due to the hydroxyl hydrogen. The hydroxyl hydrogen resonates in the same region as the hydroxyl hydrogen of alcohols in $CDCl_3$ and much further upfield than that of acids, to which they are structurally much more closely related. This high-field absorption (hydrogen bonding would move the absorptions to lower field) along with the infrared carbonyl absorption which is very similar to those for the (ethoxycarbonyl)trihydroborate complexes support the absence of extensive inter- or intramolecular hydrogen bonding in chloroform solution even at high concentrations.

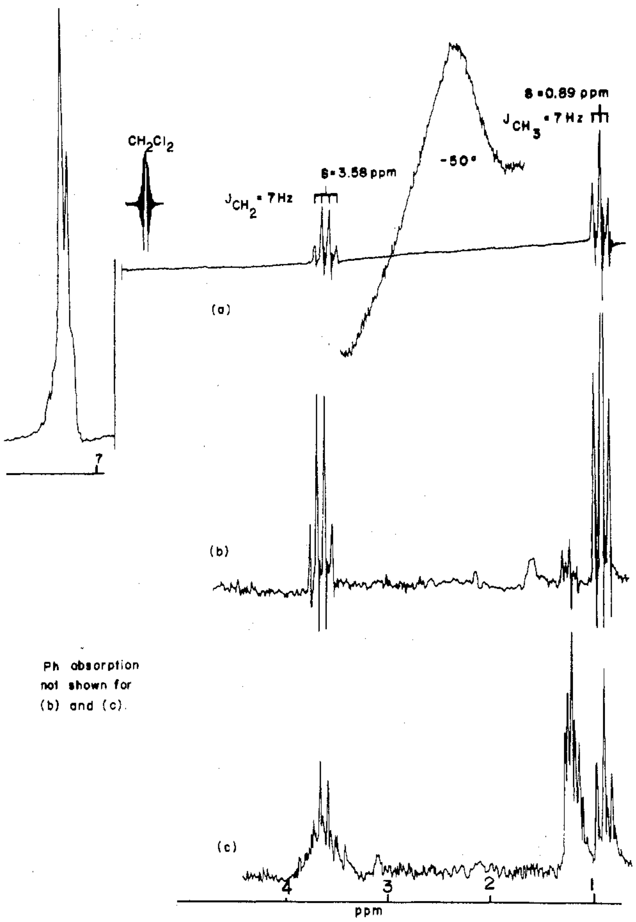


Figure 1. 100.1-MHz ^1H NMR spectra of $(Ph_3P)_2CuH_3BCOOC_2H_5$: (a) in $CDCl_3$ (dried) at ambient temperature (B–H hydrogens at low temperature (−50 °C)), (b) upon initial dissolution in $CDCl_3$ (not dried) at ambient temperature, (c) after 14 h in $CDCl_3$ at ambient temperature.

A complicated situation surfaced in the ^1H NMR studies of the ethyl group in complexed (ethoxycarbonyl)trihydroborate. In the ^1H NMR spectrum of the noncomplexed $H_3BCOOC_2H_5^-$ in $Me_2SO\text{-}d_6$ the methyl absorption occurs at δ 1.07 and the methylene absorption at δ 3.79 (Table III). The chemical shift of the methylene group upon bidentate complexation in the (triphenylphosphine)copper complex changes oppositely (toward higher field) to what would be expected based upon direct electron-withdrawing inductive effects normally accompanying coordination to a positive center [free ligand, δ_{CH_2} 3.79; complexed ligand, δ_{CH_2} 3.58]; e.g., the electron density on these hydrogens would be expected to decrease upon complexation and absorption of the CH_2 hydrogens of the complexed anion would be expected to occur at lower field values.

Anisotropic shielding by the carbonyl π system does not account for the observed values since such differences would also be observed in the trihydro(methoxycarbonyl)borate complex and would result in a much larger change in carbonyl stretching frequency than is observed. Anisotropic shielding of the anionic ligand by the phenyl groups does not account for the opposite shifts of the CH_2 protons for the singly bridged complex compared to those of the doubly bridged complex. The average CH_2–Ph distance is certainly comparable in the two cases.

Models show the least amount of steric interaction between

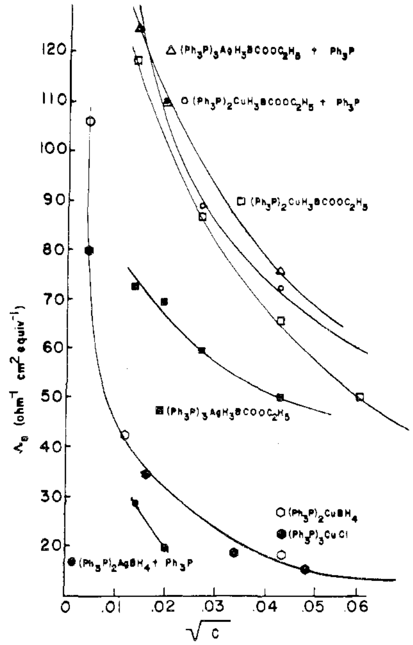


Figure 2. Plots of equivalent conductance (Λ_e) against the square root of concentration for related copper and silver complexes in acetonitrile solution.

the ethyl group and the phenyl groups in the complex $(Ph_3P)_2CuH_3BCO_2C_2H_5$ if the ethyl group is oriented such that the methylene protons occupy the highly shielding portion of the induced magnetic field about the carbonyl. If the lowest energy state for the complex is that particular orientation, the anomalous NMR results for the complex are explained. Phosphite ligands provide considerably less crowding than phosphine ligands according to Tolman's cone angles[50] and models. Consequently, the barrier to rotation out of the highly shielding position for the ethyl group should be lower. In fact, the resulting chemical shifts for the C_2H_5 protons in corresponding phenyl phosphite complexes[14] are very similar to that of the free (ethoxycarbonyl)trihydroborate ligand as perhaps the anisotropic effect is fortuitously attenuated to the point where it nearly balances the expected classical inductive effect.

The chemical shifts of the ethyl groups for the complexes in which the dominant complex form exists as the tris(phosphine) singly hydrogen bridging species in solution are more representative of the expected inductive effects of coordination. Models illustrate that in the monodentate H–B coordination mode excessive steric interaction between the phosphine ligands and the ethyl group occurs without requiring a preferred orientation while still maintaining rotational freedom about the other bonds. It would appear, then, that the change observed in the methylene shift upon monodentate coordination is due to inductive effects alone.

Conductivity Data. Since the equivalent conductance is a function of the extent of ionic dissociation by a species in solution, it is also substantially dependent upon the degree of covalent interaction between the cation and anion. Although not a great deal of information may be obtained from conductivity studies, we felt they were justified since conductivities on similar complexes have been reported[24] and thus comparison of results and trends would be possible.

The equivalent conductances of the copper(I) and silver(I) (ethoxycarbonyl)trihydroborate complexes in acetonitrile over a range of concentrations are listed in Table III; Figure 2 compares equivalent conductances for new and previously characterized cuprous and silver complexes.[24] General conclusions may be drawn from these values. If, as seems likely, solvation differences are relatively unimportant, it is apparent from the larger values of the $H_3BCOOC_2H_5^-$ complexes compared to those of the BH_4^- complexes at comparable concentrations that the (ethoxycarbonyl)trihydroborate ion is less strongly coordinated to the metals than is tetrahydroborate. This is consistent with the lower charge density present on the (ethoxycarbonyl)trihydroborate borane hydrogens and with the infrared and osmometry (dissociation) data.

Equivalent conductance is increased substantially by addition of excess phosphine ligand to a complex. The tris–bis complex equilibrium (see next section) is shifted by addition of excess phosphine, and increased concentration of tris(phosphine) monodentate species occurs for which the conductivity is higher. (This increase in conductivity has been shown to be true for diphenylmethylphosphine bis–tris complexes.[14]) In fact, even for those complexes which crystallize with the bidentate mode of anion coordination an increase in conductivity is observed upon addition of excess phosphine, thereby suggesting formation of some tris complex.

Neutral Ligand Dissociation. Many transition-metal–phosphine complexes are characterized by extensive dissociation of phosphine ligands in solution.[25-28] Studies by Tolman et al. on dissociation of nickel(0)–phosphine complexes[27] as well as studies by Lippard and Mayerle[25] on copper(I)–halide–phosphine complexes indicate the extent of dissociation can be primarily a function of the steric properties of the phosphine ligands. Studies on our triphenylphosphine complexes reflect dependence of dissociation on both steric and electronic properties.

The results of some vapor-pressure osmometry studies of various copper and silver complexes of BH_4^- and substituted (carboxylato)trihydroborates in chloroform at 37 °C appear in Table IV. K_{dissoc} for the tris(phosphine) complexes is defined similarly to the dissociation constant used by Tolman[27] for Ni(0) complexes; i.e., $K_{dissoc} = [L][L_2MH_2BH_2]/[L_3MHBH_3]$. The magnitude of the constant is therefore proportional to the degree of dissociation of the tris complex to give the bis complex.

Examination of the data in Table IV shows that the difference between the observed molecular weight and the calculated formula weight for each of the bis(phosphine) complexes is small compared to the differences for tris(phosphine) complexes. This implies that compared to the tris(phosphine) complexes the degree of phosphine ligand dissociation of the bis(phosphine) complexes to give tridentate BH_3 is small as is the combination of the bis(phosphine) complexes with a free phosphine ligand to give the tris(phosphine) complexes. The former is easily rationalized in terms of the presumed inability of the (alkoxycarbonyl)- and (carboxy)trihydroborate or borohydride anion to effectively occupy the coordination site vacated by the phosphine in the bis complexes due to geometric constraints of tridentate BH_3 on the pseudotetrahedral copper. The latter may be rationalized by the high steric requirements dictated when three triphenylphosphines surround the copper ion which is small compared to the silver ion.

From the osmometric studies (Table IV) K_{dissoc} for (triphenylphosphine)silver complexes varies significantly as a function of the coordinated anions with the dissociation decreasing in the order $BH_4^- > H_3BCOOC_2H_5^- > H_3BCOOH^-$. A similar effect is observed for the tris(phosphine)copper(I) halides:[25] dissociation decreases in the order Cl > Br > I with the differences most pronounced for $(Ph_3P)_3CuX$ complexes. Thus it appears that for complexes in which the metal–phosphine bond strengths are significantly affected by steric repulsions as in the tris(phosphine) complexes, small differences in the coordinating anion also have a large effect upon the phosphine–metal interaction. This could be viewed as the result of perturbations of the metal complexing orbitals by the anion. It has been noted that flow of electron density from filled ligand molecular orbitals with considerable B–H bonding character into molecular orbitals with considerable metal–ligand bonding character is considered general for all covalent tetrahydroborate complexes.[29] Depending upon the extent of interaction of the metal with the anion, the shape and directional characteristics of the remaining metal bonding orbitals will be affected. The stronger the interaction between the hydroborate and the metal, the greater the possibility exists that the remaining metal bonding orbitals will change. It can also be argued that the more sterically restricted ligands are unable to physically adjust to maximize their bonding to the metal without encountering undue strain energy. The bond between the metal and the sterically crowded ligands is, therefore, much more susceptible to perturbations by the anion than in less restricted systems. The differences in phosphine dissociation of the BH_4^-, $H_3BCOOC_2H_5^-$, and H_3BCOOH^- complexes of silver can then be rationally tied to the charge density on the hydroborate or borane portion of the anion. Since the tetrahydroborate has the higher charge density, as illustrated by IR and conductivity data already presented and by boron and proton NMR chemical shifts of the free anion compared to that of free (ethoxycarbonyl)trihydroborate (Table II and ref 14), it will interact more strongly with the metal and thus affect the phosphine dissociation to a greater extent.

The somewhat higher phosphine dissociation in the (ethoxycarbonyl)trihydroborate complex compared to that in the (carboxy)trihydroborate complex is then expected based on the greater electron-releasing inductive effect of the ethyl group compared to that of hydrogen. Using similar arguments, we may also explain the dissociation trends of the halide complexes in terms of the electron density at the halide and its effect upon the other metal bonding orbitals. Thus, interaction of the metal and Cl, which has higher electron density than Br, results in greater perturbation of the metal orbitals, thereby affecting the dissociation to a greater extent.

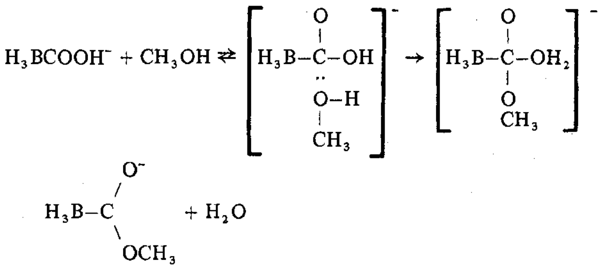
Synthesis of Complexes. Although most of the complexes could be synthesized by published techniques,[16] alternate preparations for some of the complexes are available.

The trihydro(methoxycarbonyl)borate complex was prepared during an attempt to prepare (triphenylphosphine)cuprous complexes of the (carboxylato)trihydroborate anion ($H_3BCO_2^{2-}$). An unexpected reaction took place in a methanol–chloroform reaction mixture of potassium (carboxylato)trihydroborate and chlorotris(triphenylphosphine)copper(I):

$$H_3BCO_2^- + CH_3OH + (Ph_3P)_3CuCl \rightarrow (Ph_3P)_2CuH_3BCOOCH_3 + Cl^- + OH^- + Ph_3P$$

From studies involving the (carboxy)trihydroborate[9,10] and (ethoxycarbonyl)trihydroborate[30] eq 1–3 seem to be a likely mechanism[31] for complex formation. Complex formation removes the equilibrium product, allowing the reaction to go to completion.

$$H_3BCO_2^{2-} + CH_3OH \rightleftarrows H_3BCOOH^- + CH_3O^- \quad (1)$$



$$\mathrm{H_3BCOOH^- + CH_3OH} \rightleftarrows \left[\begin{array}{c} \mathrm{O} \\ | \\ \mathrm{H_3B{-}C{-}OH} \\ \cdot\cdot \\ \mathrm{O{-}H} \\ | \\ \mathrm{CH_3}\end{array}\right]^- \rightarrow \left[\begin{array}{c} \mathrm{O} \\ | \\ \mathrm{H_3B{-}C{-}OH_2} \\ | \\ \mathrm{O} \\ \mathrm{CH_3}\end{array}\right]^- \rightarrow$$

$$\mathrm{H_3B{-}C}\begin{array}{l}\mathrm{/\,O^-} \\ \mathrm{\backslash\,OCH_3}\end{array} + \mathrm{H_2O} \quad (2)$$

$$(Ph_3P)_3CuCl + H_3BCOOCH_3 \rightleftarrows (Ph_3P)_2CuH_3BCOOCH_3 + Ph_3P + Cl^- \quad (3)$$

Substitution of water for methanol under analogous conditions did not result in formation of any isolatable (carboxy)trihydroborate complex. In order to encourage metathesis, which includes ion transport across a phase boundary, along with possible complexation by the (carboxylato)trihydroborate, a system was devised using calcium (carboxylato)trihydroborate and fluorotetrakis(triphenylphosphine)copper(I). It was anticipated that the high lattice energy of the calcium fluoride would provide the necessary driving force for the biphasic reaction (4) to proceed. The water–chloroform mixture of the

$$2(Ph_3P)_4Cu^+F^- + CaH_3BCO_2 \rightarrow (Ph_3P)_xCuH_3BCO_2Cu(Ph_3P)_x + CaF_2\downarrow \quad (4)$$

two reactants resulted in immediate formation of a new complex, as evidenced by the appearance of calcium fluoride precipitate. Somewhat unexpectedly the product was not the (carboxylato)trihydroborate complex indicated in (4) but a (carboxy)trihydroborate complex (eq 5). We had previously

$$2(Ph_3P)_4Cu^+F^- + 2CaH_3BCO_2 + 2H_2O \rightarrow 2(Ph_3P)_2CuH_3BCOOH + CaF_2 + Ca(OH)_2 + 4Ph_3P \quad (5)$$

attempted to prepare the (carboxy)trihydroborate complex by titrating an aqueous solution of potassium (carboxylato)trihydroborate to its first equivalence point and then mixing it with a chloroform solution of $(Ph_3P)_3CuCl$, with negative results. Perhaps this reaction would be successful with a different solvent system which would aid in removal of one of the products. Attempts to use the calcium fluoride method in Me_2SO and DMF to eliminate the possibility of formation of the (carboxy)trihydroborate species resulted in incomplete reactions and inconclusive results. The (carboxy)trihydroborate complex can also be prepared using $Ca(H_3BCOOH)_2$[9,10] in place of CaH_3BCO_2. The corresponding [(carboxy)trihydroborato]tris(triphenylphosphine)silver(I) complex is available from the reaction of $(Ph_3P)_4AgF$ and $Ca(H_3BCOOH)_2$ in a water–chloroform mixture.

Preparation and characterization of the (carboxy)trihydroborate complexes provided the key to understanding what had been puzzling solution behavior exhibited by the (ethoxycarbonyl)trihydroborate complexes. A proton NMR spectrum taken immediately after dissolving $(Ph_3P)_3CuH_3BCO_2C_2H_5$ in deuterated chloroform (Figure 1b) shows a large triplet at δ 0.89 (Table II) due to the methyl group and a very small triplet of previously unknown origin at slightly lower field (δ 1.17). A spectrum of the same sample taken after a few minutes shows a relative increase in the size of the small triplet with respect to the large triplet. The same phenomenon, although less conspicuous because of overlapping peaks, occurs with the methylene quartets. After a period of several hours at ambient temperature, the downfield triplet had become larger than the upfield triplet (Figure 1c), indicating the predominance of new species in the solution. Various attempts to explain this phenomenon were made such as dimerization, dissociations, and reaction with chloroform. The lack of changes in the solution infrared spectrum corresponding to the changes observed in the proton NMR spectrum, however, did not support any of these explanations.

It was determined that the one product responsible for the downfield triplet was ethanol as indicated by its volatility, the chemical shift of the newly formed triplet and quartet, and the absorption of the substance by 4-Å molecular sieves. The determination of this product and the success in preparation of the (carboxy)trihydroborate complexes led to a more detailed reexamination of the proton NMR's of the copper (ethoxycarbonyl)trihydroborate complex. If water is present in the sample of this complex, a small broad peak occurs at

δ 1.60. This peak disappeared as the ethyl peaks of C_2H_5OH and a small somewhat broad peak appeared (δ 3.14). That the latter peak is characteristic of the $(Ph_3P)_2CuH_3BCO_2H$ complex suggests that the overall reaction sequence is simply the hydrolysis of eq 6. This reaction may actually be an equilibrium although, under the described condition, it appears to proceed substantially to the right.

$$(Ph_3P)_2CuH_3BCOOC_2H_5 + H_2O \rightarrow (Ph_3P)_2CuH_3BCOOH + C_2H_5OH \quad (6)$$

Acknowledgment. Gratefully acknowledged are the support of Research Corp., Utah State University Division of University Research, an NSF Fellowship (J.C.B.), and the Eloise Gerry Fellowship Fund of Sigma Delta Epsilon, Graduate Women in Science (K.W.M.).

Registry No. $(Ph_3P)_3AgBH_4$, 68630-67-1; $(Ph_8P)_3AgH_3BCO_2C_2H_5$, 68630-68-2; $(Ph_3P)_3AgH_3BCO_2H$, 68630-69-3; $(Ph_3P)_2CuBH_4$, 16903-61-0; $(Ph_3P)_2CuH_3BCO_2C_2H_5$, 53395-65-6; $(Ph_3P)_2CuH_3BCO_2CH_3$, 68630-70-6; $(Ph_3P)_2CuH_3BCO_2H$, 68630-71-7; $K^+H_3BCO_2C_2H_5^-$, 33752-75-9; $(Ph_3P)_3CuCl$, 15709-76-9; $(Ph_3P)_4CuF$, 68630-72-8.

References and Notes

(1) Eloise Gerry Fellow, 1977–1978.
(2) T. J. Marks and J. R. Kolb, *Chem. Rev.*, **77**, 263 (1977).
(3) D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Can. J. Chem.*, **52**, 2990 (1974).
(4) J. C. Bommer and K. W. Morse, *J. Chem. Soc., Chem. Commun.*, 137 (1977); ref 5.
(5) J. L. Atwood, R. D. Rogers, C. Kutal, and P. A. Grutsch, *J. Chem. Soc., Chem. Commun.*, 593 (1977).
(6) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969), and references therein.
(7) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
(8) K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 69 (1974).
(9) L. H. Malone, Ph.D. Thesis, University of Michigan, 1964.
(10) L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).
(11) L. J. Malone, *Inorg. Chem.*, **7**, 1039 (1968).
(12) M. R. Manley, B.S. in Chemistry Thesis, Saint Louis University, 1969.
(13) J. C. Bommer and K. W. Morse, *J. Am. Chem. Soc.*, **96**, 6222 (1974).
(14) J. C. Bommer, Doctoral Thesis, Utah State University, 1977.
(15) G. F. Freegard and L. H. Lang, *Chem. Ind. (London)*, **11**, 471 (1965).
(16) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
(17) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).
(18) J. M. Davidson, *Chem. Ind. (London)*, 2021 (1964).
(19) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960).
(20) S. J. Lippard and K. M. Melmed, *J. Am. Chem. Soc.*, **89**, 3920 (1967); *Inorg. Chem.*, **6**, 2223 (1967).
(21) T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, **11**, 2540 (1972).
(22) M. F. Lappert, *J. Chem. Soc.*, 817 (1961).
(23) H. Beall, C. H. Bushweller, W. J. Kewkett, and M. Grace, *J. Am. Chem. Soc.*, **92**, 3484 (1970).
(24) S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, **11**, 6 (1972).
(25) S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, **11**, 753 (1972).
(26) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(27) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Am. Chem. Soc.*, **96**, 53 (1974).
(28) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *Inorg. Chem.*, **9**, 2447 (1970).
(29) T. J. Marks and W. J. Kennelly, *J. Am. Chem. Soc.*, **97**, 1439 (1975).
(30) B. D. Hoewe, L. J. Malone, and R. M. Manley, *Inorg. Chem.*, **10**, 931 (1971).
(31) The authors thank a referee for the suggestion that step two is a viable step in this mechanism.

Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Trifluoromethylthio and Trifluoromethylseleno Derivatives of Germane and Digermane[1]

RUPERT D. HOLMES-SMITH and STEPHEN R. STOBART*

Received July 28, 1978

Reactions of halogenogermanes with $Hg(ECF_3)_2$ (E = S or Se) provide a route to the compounds GeH_3ECF_3 and $GeH_2(ECF_3)_2$. The latter in particular exhibit unusual thermal stability in comparison with related derivatives, as do the digermanes $Ge_2H_5ECF_3$ prepared by reaction of the mercury(II) salts in diethyl ether with digermanyl iodide in situ at −63 °C. IR, Raman, mass spectrometric, and ^1H and ^{19}F NMR data are reported and discussed for the new compounds.

Introduction

Questionable thermal stability has continued to be associated with derivatives of germane embodying germanium–chalcogen bonds since the classic difficulties encountered in isolating digermyl oxide,[2] a congener of dimethyl ether. While it has been reported that $O(GeH_3)_2$ and also methoxygermane, GeH_3OMe, undergo decomposition at 0 °C, sulfur- and selenium-containing analogues appear to be less thermally labile:[3] digermyl selenide[4] is said[5] to be unchanged after 6 days in the liquid phase at ambient temperature, although under similar conditions yellowing of a range of methylseleno species related to $Me_3GeSeMe$ has been noted.[6]

Our conclusion that the instability of digermyl oxide may have been overestimated[7] has provided a basis for a continuing interest in this area. In the present paper we report the synthesis of (trifluoromethylthio)germane and its selenium analogue GeH_3ECF_3 (E = S or Se) in which it might be anticipated that the strong electron-withdrawing character of the CF_3 group might effect spectroscopic properties and chemical stability.

Germylene dihalides, GeH_2X_2 (X = F, Cl, Br, or I), decompose much more readily than the corresponding germyl halides GeH_3X, and efforts to produce the disubstituted derivatives GeH_2Y_2 in which Y is a pseudohalogeno group bound through the nitrogen atom have met with failure.[8] By contrast we have been able to isolate the compounds $GeH_2(ECF_3)_2$ (E = S or Se); these are the first examples of well-characterized germylenedichalcogeno derivatives, although $(GeH_3Se)_2GeH_2$ has been tentatively identified[8] as a condensation product between SeH_2 and $Se(GeH_3)_2$.

Little is known about the substitution chemistry of digermane[2,9] and of the very restricted range of compounds Ge_2H_5Y (Y = F, Cl, Br or I,[10] Me or Et,[11] or $Mn(CO)_5$[12]); those in which Y is an electron-withdrawing center, the halides, exhibit the lowest thermal stability decomposing rapidly at ambient temperature.[10] We have found that at low temperature Ge_2H_5I can be converted in high yield to give the products $Ge_2H_5ECF_3$ (E = S or Se), novel examples of digermane derivatives incorporating germanium–chalcogen bonds which possess good thermal stability.

Experimental Section

Details of relevant manipulative techniques and the synthesis of germane and of halogenogermanes have been given previously.[2,7] Digermane[13] was iodinated at −63 °C as described[10] by Mackay and Roebuck. Samples of the trifluoromethylthio salts of silver(I) and mercury(II) were obtained according to literature preparations.[14,15] New compounds were fully characterized using spectroscopic methods (vide infra).

0020-1669/79/1318-0538\$01.00/0 © 1979 American Chemical Society