Table II. Comparison of Nmr, Ir, and Equilibrium Data

L	$\tau(^1H)^c$	$^2J(PH),^c$ Hz	$\nu(CO)$- $(A_1),^d$ cm^{-1}	$K(CH_3OH$ at $0°),^c$ M^{-1}
dppe	22.9	5.5	2067	410
P(OEt)$_3$	24.4	26.5	2076	33
1	23.3^a	34^a	2082^a	$(4.4)^b$
P(OCH$_2$CH$_2$Cl)$_3$	23.9	28	2084	1.2
2a, 2b	23.7^a	41^a	2087	$(0.6)^b$
P(OCH$_2$CCl$_3$)$_3$	e	e	2092	<0.1

^{a} This work; all other data from ref 13 and C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2953 (1970). ^{b} Interpolated from ref 13. ^{c} Data on HNiL$_4^+$ complexes. ^{d} Data on Ni(CO)$_3$L complexes. ^{e} Not observed.

tional to the basicity of the coordinated ligands. Indeed Table II clearly indicates that as the basicity of the ligand decreases, $^2J(PH)$ increases. This difference in basicity must be directly related to the differing basicities of the ligands attached to the nickel atom. As noted by Shriver,[14] the more electron donating the ligand, the more basic the metal. The relative basicities of a series of ligands can be deduced by comparing the change in carbonyl stretching frequency as the ligand is varied. Table II lists the carbonyl stretching frequencies of the A_1 mode in the corresponding Ni(CO)$_3$L series as the P donor is changed.[15] The trend in basicities is reasonably consistent with the trend deduced from $^2J(PH)$ values.

From an extensive spectrophotometric study of the protonation of acyclic nickel phosphites, Tolman[13] deduced an

empirical relation between log K (the equilibrium constant for the protonation reaction 2, measured at 0° in CH$_3$OH) and the frequency of the A_1 mode in the corresponding Ni-(CO)$_3$L complex. Using the observed frequency for this mode we have interpolated K values for the protonation of the Ni(1)$_4$, Ni(2a)$_4$, and Ni(2b)$_4$ complexes and they are listed in Table II. The fact that K for the monocyclic complex is almost one order of magnitude greater than that of the bicyclic derivatives accords with the ready observation of the monocyclic phosphite nickel hydride and the difficulty in detecting the bicyclic phosphite nickel hydride.

Finally, we note that both the protonation behavior and the infrared data suggest the basicity order for unsubstituted phosphites is acyclic $\geqslant$ monocyclic > bicyclic. This sequence has recently been suggested by one of us[16] where it was rationalized in terms of changes in hybridization at the phosphite oxygen stemming from molecular constraint.

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Displacement Reactions on Donor–Haloalanes. Some Novel Four-Coordinate Chelated Aminedihydroaluminum(1+) Salts

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Iodide salts of two novel four-coordinate aluminum cations N,N,N',N'-tetramethylethylenediaminedihydroaluminum(1+) and sparteinedihydroaluminum(1+) have been prepared by nucleophilic displacement reactions on trimethylamine–iodoalane and characterized by infrared absorption and conductivity measurements. Trimethylamine–bromoiodoalane has been prepared along with N,N,N',N'-tetramethylethylenediamine complexes of AlH$_2$Br and AlHBr$_2$. The reaction with the monobromoalane yields the bromide salt of the chelated aluminum(1+) ion, while with the dibromoalane, the product appears to be a molecular complex containing five-coordinate aluminum.

Introduction

The preparation and characterization of electrolytes containing four-coordinate boron cations of the type LL'BH$_2^+$ where L and L' denote neutral electron-donor molecules have been described,[1-4] and although numerous four-coordinate aluminum salts have been prepared,[5-7] analogous dihydro

L$_2$AlH$_2^+$ species have not been reported. We have employed a method similar to one utilized in the synthesis of dihydroboron cations,[8,9] involving the reaction of trimethylamine-iodoalane with the bidentate nitrogen bases N,N,N',N'-tetramethylethylenediamine (TMED) and sparteine to prepare, *via* nucleophilic displacement of iodide ion and transamination, salts containing the corresponding chelated aminedihydroaluminum(1+) ions. Reactions of TMED with (CH$_3$)$_3$N· AlH$_2$Br and (CH$_3$)$_3$N·AlHBr$_2$, respectively, lead to a species which in solution appears to correspond to the bromide salt of the TMED-AlH$_2^+$ ion and to a chelated complex which may contain five-coordinate aluminum.

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Experimental Section

Due to the susceptibility of the aluminum–hydrogen linkage toward hydrolysis, rigorous procedures were necessary for purification of solvents and reagents particularly with regard to exclusion of moisture. All aluminum hydride compounds were handled in a glove box under dry N_2. Freshly distilled benzene was stored over Linde 5A molecular sieve. Anhydrous diethyl ether (Et_2O) was distilled twice from $LiAlH_4$. Hexamethylphosphoric triamide (HMPT) was distilled from CaH_2 and subjected to repeated distillation from sodium (bp 70° (15 mm)) to give material of specific conductivity, κ, of 5.5 × 10^{-8} ohm^{-1} cm^{-1}. After distillation from CaH_2, acetonitrile was passed through a column of 5A molecular sieve and redistilled, bp 81–82°, κ = 1.3 × 10^{-7} ohm^{-1} cm^{-1}. The TMED was distilled from CaH_2, bp 113–115° (749 mm). Sparteine was obtained by neutralization of sparteine sulfate with NaOH, extracted with Et_2O, dried over CaH_2, and distilled, bp 78–92° (0.013 mm).

Analyses of C, H, and N were obtained from Galbraith Laboratories, Knoxville, Tenn., or by M-H-W Laboratories, Garden City, Mich. Hydridic hydrogen was determined by measurement of H_2 evolved upon hydrolysis in dilute aqueous hydrochloric acid. The hydrolysates were used for gravimetric determination of aluminum utilizing 8-hydroxyquinoline.[10] Halide was determined by the Volhard method or, in the case of I$^-$, by oxidation with Br_2 followed by titration with $Na_2S_2O_3$.[11]

Infrared spectra were obtained on Perkin-Elmer PE 237 and Beckman IR-10 spectrometers calibrated with polystyrene film and by using Nujol mulls of samples of ground solids. Conductivity measurements were made in a Freas-type cell with a Fluke Model 710B impedance bridge. A small, linear increase in impedance with time was always observed and impedance at time of mixing was obtained by extrapolation.

Trimethylamine–Haloalanes. Trimethylamine–alane, prepared by the method of Ruff,[12] was converted to the mono- and dibromoalane derivatives by a previously reported procedure using $HgBr_2$.[13] The monoiodolane adduct was similarly prepared by a modification of this method utilizing HgI_2. In contrast to the reported action of $HgCl_2$ and $HgBr_2$ on $(CH_3)_3N \cdot AlH_3$, the reaction with HgI_2 gave approximately an equimolar mixture of $(CH_3)_3N \cdot AlH_2I$ and $(CH_3)_3N \cdot AlI_3$ with no isolable diiodo derivative. The monoiodo- and monobromoalane adducts of trimethylamine were employed in preparation of the aluminum(1+) salts (described below), and $(CH_3)_3N \cdot AlH_2I$ was utilized for the preparation of the mixed haloalane adduct $(CH_3)_3N \cdot AlHBrI$ as follows. A total of 3.54 g (9.83 mmol) of $HgBr_2$ was added to 3.91 g (18.2 mmol) of $(CH_3)_3N \cdot AlH_2I$ in 75 ml of dry Et_2O at $-20°$. After separation of the mercury by filtration, the Et_2O was removed by evaporation and the residue subjected to sublimation *in vacuo*; yield 3.43 g (64% theory); mp 25–26°. *Anal.* Calcd for $C_3H_9N \cdot AlHBrI$ (mol wt 293.9): C, 12.26; H, 3.43; N, 4.77. Found: C, 12.36; H, 3.51; N, 4.84.

Diamine Substitution in Trimethylamine–Haloalanes. A solution of $(CH_3)_3N \cdot AlH_2I$ (3.28 g, 15.3 mmol) in 100 ml of benzene was treated with a solution of 1.77 g (15.2 mmol) of TMED in 25 ml of benzene with stirring under dry N_2 at 25°. A fine white precipitate was collected by filtration, washed with benzene, and dried *in vacuo*; yield 3.68 g (89% theory); mp 225° dec. *Anal.* Calcd for $C_6H_{16}N_2 \cdot AlH_2I$ (mol wt 272.1): C, 26.5; H, 6.67; N, 10.3; Al, 9.92; I, 46.6. Found: C, 25.4; H, 6.42; N, 9.98; Al, 9.58; I, 49.0.

By a similar procedure, 5.52 g (71% theory) of sparteinedihydroaluminum(1+) iodide was prepared from 4.65 g of sparteine and 4.28 g of $(CH_3)_3N \cdot AlH_2I$ in 100 ml of benzene; mp 202°; dec pt 222°. *Anal.* Calcd for $C_{15}H_{26}N_2 \cdot AlH_2I$ (mol wt 390.3): C, 46.6; H, 7.23; H (hydridic), 0.52; N, 7.18; Al, 6.91. Found: C, 45.3; H, 7.11; H (hydridic), 0.47; N, 7.08; Al, 7.14.

Transamination of $(CH_3)_3N \cdot AlH_2Br$ involved the slow addition of 3.73 g (32.1 mmol) of TMED to 5.20 g (31.0 mmol) of $(CH_3)_3N \cdot AlH_2Br$ in 75 ml of benzene at 25°. Initially, two liquid phases were formed with the dense phase solidifying upon continued addition of the diamine. The mixture was boiled under reflux for 12 hr and cooled following which the solid was collected (white crystals), washed with benzene, and dried *in vacuo*; yield 4.68 g (67% theory); mp 146°. *Anal.* Calcd for $C_6H_{16}N_2 \cdot AlH_2Br$ (mol wt 225.1): C, 32.0; H, 8.06; N, 12.4. Found: C, 30.6; H, 7.82; N, 11.9.

A comparable procedure employing 3.94 g (15.9 mmol) of $(CH_3)_3$-

N·AlHBr$_2$ and 1.82 g (15.7 mmol) of TMED gave 2.0 g (42% theory) of crystalline solid, mp 175°, dec pt 205°. *Anal.* Calcd for C_6H_{16}-$N_2 \cdot AlHBr_2$ (mol wt 304.0): C, 23.7; H, 5.64; N, 9.21; Al, 8.88; Br, 52.6. Found: C, 19.2; H, 5.83; N, 7.80; Al, 8.77; Br, 54.0.

Results and Discussion

The addition of TMED or sparteine, which has been described recently as a coordinating ligand for magnesium[14] in organometallic compounds and copper(II) chloride,[15] to a solution of $(CH_3)_3N \cdot AlH_2I$ in benzene forms aluminum(1+) salts as depicted in (1) where L–L denotes the diamine. Char-

$$\text{L–L} + (CH_3)_3NAlH_2I \rightarrow \left[\begin{array}{c} L \quad H \\ \backslash \quad / \\ Al \\ / \quad \backslash \\ L \quad H \end{array}\right]^+ + I^- + (CH_3)_3N \quad (1)$$

acterization of the products as 1:1 electrolytes is based on their infrared spectra and conductivity measurements.
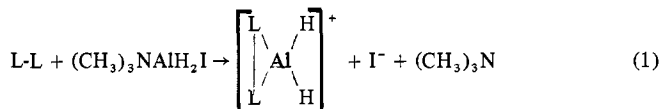
The positions of the strong absorption bands attributable to Al–H stretching vibrations in the infrared spectra of numerous donor adducts of hydride derivatives of aluminum have been interpreted in terms of the coordination number of aluminum, the electronic character of the donor ligand(s), and the electronegativity of the other substituents bound to aluminum.[16-20] Thus, through a series $L \cdot AlH_3$, $L \cdot AlH_2X$, $L \cdot AlHX_2$ ($L = (CH_3)_3N$, $(C_2H_5)_3N$,[21] Et_2O;[22] X = halogen) the positions of the ν_{Al-H} bands move to higher wave numbers by about 40–50 cm^{-1} upon successive substitution of halide ion for hydride in the coordination sphere of aluminum. This is presumably due to hydride being more tightly bound at an aluminum center at which electron density has been diminished by the more electron-withdrawing halide ion. A smaller effect is observed in the bis-donor adduct series $L_2 \cdot AlH_3$, $L_2 \cdot AlH_2X$, $L_2 \cdot AlHX_2$ ($L = (CH_3)_3N$,[19] tetrahydrofuran;[21] X = halogen) where aluminum presumably exists in five-coordination and absorption occurs at much lower energies; *e.g.*, ν_{Al-H} in $[(CH_3)_3N]_2 \cdot AlH_3$ is found at 1709 cm^{-1} as opposed to 1792 cm^{-1} for $(CH_3)_3N \cdot AlH_3$.[23] Chelate–AlH$_3$ spectra have been reported to be very similar to that of $[(CH_3)_3$-N]$_2 \cdot AlH_3$.[17,18,24]

The products of reaction of $(CH_3)_3N \cdot AlH_2I$ with TMED and sparteine exhibit strong absorption attributed to ν_{Al-H} with bands centered at 1890 and 1880 cm^{-1}, respectively. The relatively high frequency of such bands supports the contention that these products contain aluminum in four- (as opposed to five-) coordination. Their positions, which are comparable to those of bands attributed to ν_{Al-H} in various donor–AlHX$_2$ (X = halogen) adducts, suggest an environment of low electron density at the central metal atom, consistent with the supposition that the products are cationic

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Table I. Conductance of Chelated
Aminedihydroaluminum(1+) Salts at 25°

	Λ, cm^2 equiv^{-1} ohm^{-1}	$10^2C^{1/2}$, $M^{1/2}$	Λ, cm^2 equiv^{-1} ohm^{-1}	$10^2C^{1/2}$, $M^{1/2}$
(TMED)AlH$_2^+$I$^-$	20.1	3.58	14.8	8.25
in HMPT	18.2	4.98	16.1	8.44
	17.1	5.98	16.0	9.01
	16.2	6.25	16.2	10.4
	17.0	7.55		
(TMED)AlH$_2^+$Br$^-$	18.6	4.3	17.0	9.3
in HMPT	15.5	4.6	17.0	9.6
	18.2	5.5	14.7	12.7
	18.2	5.9	15.3	13.2
	16.1	6.6		
(sparteine)AlH$_2^+$I$^-$	125.2	3.66	119.1	13.5
in MeCN	130.6	6.01	109.2	16.7
	130.9	7.21		

(L-L)AlH$_2^+$ species. This is further supported by conductance measurements (Table I), wherein values of Λ are in the range reported for other 1:1 electrolytes in hexamethylphosphoric triamide[25] and acetonitrile,[26] respectively.

The observation of absorption, attributed to ν_{Al-H}, in TMED·AlHBr$_2$ at 1735 cm^{-1} suggests this to be a molecular complex with bonding similar to that of TMED·AlH$_3$.[17,18,24] Its low solubility in both solvents employed for conductivity measurements precluded an examination of its electrical conductance in solution.

The TMED·AlH$_2$Br complex exhibited absorption ν_{Al-H} at 1820 cm^{-1}, which is a frequency intermediate between that found for the dibromo analog and those of the cationic four-coordinate aluminum(1+) ions. In hexamethylphosphoric triamide, however, its electrical conductance is similar to that of TMED·AlH$_2$I, and, thus, in solution it appears to exist as the bromide salt of (TMED)AlH$_2^+$.

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Although (CH$_3$)$_3$N·AlHI$_2$ was not synthesized, the mixed haloalane adduct (CH$_3$)N·AlHBrI was prepared and utilized as a substrate in reaction with TMED. The resultant white solid product exhibited strong absorptions at 1893 and 1942 cm^{-1} but was thought to be a mixture of species and its characterization was not completed. Such absorption is in the region expected for cationic aluminum in four-coordination. In a purely speculative sense, the higher frequency band may suggest a divalent cation of the type TMED[(CH$_3$)$_3$-N]AlH^{2+}. A selectivity of different halide ions to serve as leaving groups in nucleophilic displacement reactions has been reported for the formation of analogous chelated boron(n+) ions from the reaction of diamines with trimethylamine-haloboranes with iodide being more susceptible to displacement than bromide.[27] Similar selectivity may prevail in displacement from corresponding alane adducts.

As yet we have not explored the effect of the size of the bidentate amine on the rates of hydride oxidation or selectivity of these aluminum ions as reducing agents. As expected from the known relative reactivities of many hydrides of aluminum and boron, however, the aluminum salts hydrolyze with oxidation of hydridic hydrogen more readily than analogous boron(1+) salts such as (TMED)BH$_2^+$I$^-$. They are hygroscopic and evolve hydrogen rapidly on exposure to hydroxylic solvents.

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Vapor Pressure of Samarium Diiodide and Mass Spectra of Vapors over Samarium Diiodide and Thulium Triiodide

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Mass spectrometric measurements show that SmI$_2$(l) and TmI$_3$(c) vaporize congruently in the Knudsen cell range as the monomolecular species. The second-law enthalpy of sublimation for SmI$_2$(l) is $\Delta H_S°_{298}$ = 69.5 ± 2.0 kcal/mol. The enthalpies of atomization for SmI$_2$(g) and TmI$_3$(g) are 171 ± 5 and 228 ± 5 kcal/mol, respectively. The enthalpies of formation of SmI$_2$(c) and of TmI$_3$(c) are $\Delta H_f°_{298}$ $\geqslant$ −141.0 ± 5 and −164.7 ± 5 kcal/mol, respectively.

Introduction

We earlier determined the vapor pressures over all of the stable lanthanide triiodides,[1,2] as well as that over SmI$_3$.[3] The mass spectra of the vapors over all of the triiodides, ex-

cept that of TmI$_3$, also were determined.[4] These measurements showed that the lanthanide triiodides vaporize congruently as the monomeric LnI$_3$ in the Knudsen cell range, where Ln is the lanthanide. Recently, the vapor pressure and mass spectra of EuI$_2$(l) were reported by Hariharan and Eick.[5] These workers showed that EuI$_2$ also vaporizes congruently as the monomeric diiodide. Comparison of the

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