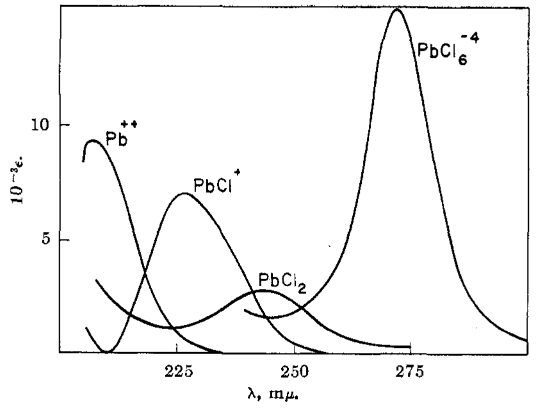

Figure 2.—Absorption spectra deduced for various $PbCl_n^{2-n}$ species. Pb^{+2} and $PbCl_6^{-4}$ spectra were measured directly. Spectra of $PbCl^+$ and $PbCl_2$ were calculated using K_1 and K_2 values obtained in this study.

spectrum of Pb(II) continues to change as [HCl] is increased above 4 *M*. An isosbestic point for the two species of highest *n* is observed only after reaching 6 *M* HCl. A limiting spectrum is observed between 10 and 11 *M* HCl which we attribute to $PbCl_6^{-4}$ by analogy with observations on $BiCl_n^{3-n}$ spectra.[1] This species is formed in significant concentrations only when $[Cl^-] > 4.0$ so only an upper limit can be given to its formation constant. The measured spectra for Pb^{+2} and $PbCl_6^{-4}$ are shown in Figure 2 together with those calculated for $PbCl^+$ and $PbCl_2$ using the constants given above. Knowledge concerning equilibria involving $PbCl_3^-$ is too scanty to permit calculation of $PbCl_4^{-2}$ and $PbCl_3^-$ spectra.

In summary, Pb^{+2} forms weaker complexes with Cl^- than Bi^{+3} while showing a similar preference for even numbers of ligands. Ultraviolet absorption bands are shifted to shorter wave lengths for the +2 central ion consistent with their characterization as ligand-to-metal charge-transfer bands. Although $SnCl_n^{2-n}$ and $PbCl_2^{2-n}$ complexes are of comparable strength up to $n = 4$, Sn(II) complexes do not exhibit the sharp charge-transfer band in the ultraviolet and give no evidence of forming a complex with $n > 4$.

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CONTRIBUTION FROM THE THIOKOL CHEMICAL CORPORATION, REACTION MOTORS DIVISION, DENVILLE, NEW JERSEY

The Chemistry of Alane. VII.[1] Trialkylamine Phenylalanes

BY ROBERT EHRLICH, CHARLES B. PARISEK, AND GEORGE RICE

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The extensive literature on organoaluminum compounds contains no methods for the preparation of aryl-substituted alanes of the type $ArAlH_2 \cdot NR_3$.[2] Recently, Peters and co-workers[3] have prepared trimethylamine complexes of ethyl- and methylalanes ($RAlH_2 \cdot N(CH_3)_3$, where R is CH_3 or C_2H_5).

We wish to report the synthesis of the trimethylamine and triethylamine complexes of phenylalane by an additional method (eq. 1), suitable for the preparation of any substituted alane and originally reported by Wittig[4] for the preparation of triphenylaluminum.

$$nRLi + Cl_nAlH_{3-n} \cdot NR'_3 \longrightarrow nLiCl + R_nAlH_{3-n} \cdot NR'_3; \quad n = 1, 2, 3 \quad (1)$$

Reaction in benzene of triethylamine chloroalane with an equimolar quantity of phenyllithium resulted in the nearly quantitative precipitation of LiCl. Freeze drying the benzene filtrate yielded $C_6H_5AlH_2 \cdot N(C_2H_5)_3$ (I) as a pale yellow liquid. Similarly, the reaction of triethylamine dichloroalane with two equivalents of C_6H_5Li gave a pale yellow liquid, $(C_6H_5)_2AlH \cdot N(C_2H_5)_3$ (II). The synthesis was repeated with $ClAlH_2 \cdot N(CH_3)_3$ to give $C_6H_5AlH_2 \cdot N(CH_3)_3$ (III), also a yellow, viscous liquid, which decomposed rapidly above 50°. Also prepared by this method were $CH_3AlH_2 \cdot N(CH_3)_3$, identical in physical properties and infrared spectrum with the compound reported by Peters,[3] and n-$C_4H_9AlH_2 \cdot N(CH_3)_3$, the infrared spectrum of which resembled that of $C_2H_5AlH_2 \cdot N(CH_3)_3$[3] (Al–H absorption at 1750 cm.$^{-1}$).

The infrared spectra of I, II, and III were remarkably similar with the exception of the Al–H absorption, which occurred at 1770 cm.$^{-1}$ for I, 1780 cm.$^{-1}$ for II, and 1772 cm.$^{-1}$ for III, and they showed the characteristic absorptions of the tertiary amine as well as those of a monosubstituted aromatic ring in the 840–720 cm.$^{-1}$ region.

The molecular weight determinations in benzene showed degrees of association of 1.16 and 1.31 for I and II, respectively. The determinations were performed at concentrations of 0.05 *M*, and the effect of concentration on apparent molecular weight was not examined. It is interesting to note that the degree of association of the series $(C_2H_5)_3N \cdot AlH_3$, $(C_2H_5)_3N \cdot AlH_2(C_6H_5)$, and $(C_2H_5)_3N \cdot AlH(C_6H_5)_2$ increased as the substitution on aluminum increased (1.05,[5] 1.16, and 1.31, respectively) in spite of the fact that there is an increase in the number of bulky groups surrounding the aluminum. At the same time, the diphenyl derivative is more stable than the monophenylalane. This difference in stability may be related to the inherent tendency for disproportionation in monosubstituted alanes.

Surprisingly enough, the corresponding $(CH_3)_3N$

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[1] Paper VI: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, to be published.

[2] J. R. Surtees, *Chem. Ind.* (London), 1260 (1964), has reported the synthesis of $(C_6H_5)AlH_2$ but he was unable to prepare the trimethylamine complex by the addition of $N(CH_3)_3$ to the alane.

[3] F. M. Peters, B. Bartocha, and A. J. Bilbo, *Can. J. Chem.*, **41**, 1050 (1963).

[4] G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

[5] J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960), found a value of 1.10 for $(C_2H_5)_3N \cdot AlH_3$.

complex of $C_6H_5AlH_2$ (III) was considerably less stable than the $(C_2H_5)_3N$ compound (I), decomposing slowly even at room temperature and rapidly above 50°. When III was allowed to stand at room temperature, a white solid began to deposit after 1 day, the quantity of the solid slowly increasing with time. The solid had an Al:N:active H ratio of 1:0.77:1.36, which approaches the ratios for the sesquialane, $(C_6H_5)_3Al_2H_3 \cdot N(CH_3)_3$, or for a mixture of $(C_6H_5)_2AlH$ and $C_6H_5AlH_2 \cdot N(CH_3)_3$ (1:0.5:1.5). Such a product, or mixture of products, could result from a disproportionation of $C_6H_5AlH_2 \cdot N(CH_3)_3$. The observed instability of III may arise from the greater volatility of $(CH_3)_3N$ which shifts the equilibrium of eq. 2 to the right and results in disproportionation of the uncomplexed $C_6H_5AlH_2$.

$$C_6H_5AlH_2 \cdot NR_3 \rightleftharpoons C_6H_5AlH_2 + NR_3 \qquad (2)$$

Experimental

All reagents were handled and all filtrations were performed in a nitrogen-atmosphere vacuum drybox, and all reactions were conducted under dry nitrogen. The trialkylamine chloroalane derivatives were prepared by the method of Ruff.[6] Benzene was purified and dried by refluxing over $LiAlH_4$, distilling, and storing over $LiAlH_4$. Commercially available organolithium compounds were used as received. Quantitative hydrolyses were performed on a Toepler pump system, and both condensable and noncondensable products were collected. The former were separated and identified by standard v.p.c. methods and the latter were identified by their mass spectra. Molecular weights were determined cryoscopically in benzene at 0.05 *M* concentrations. Results are accurate to approximately ±1%.

Preparation of $C_6H_5AlH_2 \cdot N(C_2H_5)_3$ (I).—To a solution of 0.10 mole of $ClAlH_2 \cdot N(C_2H_5)_3$ in 100 ml. of benzene was added, dropwise at room temperature, 0.10 mole of C_6H_5Li in benzene–ether solution. The precipitation of LiCl was immediate and the chloride-free filtrate was freeze dried to produce 20.1 g. (97.1% of theory) of a pale yellow, slightly viscous liquid. It decomposed without boiling below 80° at 0.01 mm. pressure.

Anal. Calcd. for $C_{12}H_{22}AlN$: C, 69.53; H, 10.70; Al, 13.02; N, 6.75; active H, 0.97; mol. wt., 207; Al:N:active H, 1:1:2; C_6H_6:$N(C_2H_5)_3$, 1:1. Found: C, 69.67; H, 9.95; Al, 12.72; N, 6.40; active H, 0.92; mol. wt., 241; Al:N:active H, 1:1.05:1.90; C_6H_6:$N(C_2H_5)_3$, 1:1.1.

Preparation of $(C_6H_5)_2AlH \cdot N(C_2H_5)_3$ (II).—To a solution of 0.10 mole of $Cl_2AlH \cdot N(C_2H_5)_3$ in 100 ml. of benzene was added 0.20 mole of C_6H_5Li as in the preparation of I. The yield of pale yellow, slightly viscous liquid was 27.2 g. (96.1% of theory). It decomposed without boiling below 80° at 0.1 μ pressure.

Anal. Calcd. for $C_{18}H_{26}AlN$: C, 76.28; H, 9.26; Al, 9.52; N, 4.95; active H, 0.36; mol. wt., 283, Al:N:active H, 1:1:1; C_6H_6:$N(C_2H_5)_3$, 2:1. Found: C, 75.77; H, 9.68; Al, 8.98; N, 5.67; active H, 0.33; mol. wt., 370; Al:N:active H, 1:0.83:0.92; C_6H_6:$N(C_2H_5)_3$, 2:0.95.

Preparation of $C_6H_5AlH_2 \cdot N(CH_3)_3$ (III).—The preparation of I was repeated with $ClAlH_2 \cdot N(CH_3)_3$ to produce 15.9 g. of yellow, viscous liquid (96.4% of theory) which decomposed slowly at room temperature and rapidly above 50°.

Anal. Calcd. for $C_9H_{16}AlN$: Al, 16.33; N, 8.48; active H, 1.22; Al:N:active H, 1:1:2. Found: Al, 15.47; N, 8.08; active H, 1.21; Al:N:active H, 1:1:2.1.

Acknowledgment.—We wish to acknowledge the assistance of Raymond N. Storey in the determination and interpretation of the infrared spectra.

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[6] J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).

CONTRIBUTION FROM THE U. S. ARMY NATICK
LABORATORIES, NATICK, MASSACHUSETTS

The Synthesis of a New Series of Zinc Compounds

BY GÜNTER RUDOLPH[1] AND MALCOLM C. HENRY

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In a recent communication[2] we reported the existence of a compound $Zn_2(CH_3CO_2)(C_5H_7O_2)_3$ formed either by (a) the thermal decomposition of bis(acetylacetonato)zinc(II) hydrate or (b) heating zinc acetate with acetylacetone. We have now found a superior synthetic route and have applied it to the preparation of a homologous series of compounds having the generalized formula $Zn_2(RCO_2)(C_5H_7O_2)_3$ where R = CH_3, C_2H_5, $C(CH_3){=}CH_2$, C_6H_5, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, and *p*-BrC_6H_4 (Table I).

The general route to these compounds is *via* the reaction of anhydrous bis(acetylacetonato)zinc(II) with the calculated amount of an organic acid according to the equation

$$2Zn(C_5H_7O_2)_2 + RCOOH \longrightarrow Zn_2(RCO_2)(C_5H_7O_2)_3 + C_5H_8O_2$$

These white crystalline compounds are only slightly soluble in organic solvents at ambient temperatures. They are, however, soluble in chloroform. The acetate and methacrylate derivatives are sufficiently soluble in benzene to conduct molecular weight measurements. Polar solvents generally decompose these new compounds.

It is interesting to note that the molecular weights obtained in chloroform are not in agreement with the calculated formula weight. The two derivatives sufficiently soluble in benzene, however, gave molecular weights in agreement with theoretical. The acetate derivative described earlier[2] has been determined at varying concentrations in chloroform. The experimentally found molecular weight does not vary with concentration (7.17 g./l., mol. wt. found 346; 4.51 g./l., mol. wt. found 348; 19.66 g./l., mol. wt. found 386; 6.45 g./l., mol. wt. found 319).

Attempts to prepare similar compounds with other fatty acids higher than propionic acid were unsuccessful.

We assume that the three acetylacetonate groups of these compounds are attached to one zinc atom, leading to a structure with hexacoordinated zinc such as $Zn(RCO_2)[Zn(C_5H_7O_2)_3]$. This salt-like structure could account for the poor solubility in organic solvents and the anomalous molecular weights obtained in chloroform. The existence of the $[Zn(C_5H_7O_2)_3]^-$ anion, and its low stability in ionizing solvents, has been noted previously.[3]

In this connection sodium tris(acetylacetonato)zincate(II) was prepared by combining methanol

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[1] National Academy of Sciences—National Research Council Visiting Scientist, U. S. Army Natick Laboratories, Natick, Mass.

[2] G. Rudolph and M. C. Henry, *Inorg. Chem.*, **3**, 1317 (1964).

[3] F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc. N.S. Wales*, **90**, 29, 141 (1956).